NBO 6.0 Program Manual

Natural Bond Orbital Analysis Programs

compiled and edited by

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NBO6 Website: http://www.chem.wisc.edu/~nbo6

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PREFACE: HOW TO USE THIS MANUAL

The NBO6 Manual consists of three major divisions:

Section A ("Getting Started") contains introductory and one-time information for the novice user – what the program does, new program functionality, program installation, and a brief tutorial on sample output.

Section B ("NBO User's Guide") is for the experienced user who has an installed program and general familiarity with standard default NBO output. This section documents the many keywords that can be used to alter and extend standard NBO job options, with examples of the resulting output. Section B is mandatory for users who wish to use the program to its full potential. This section describes keyword-controllable capabilities of the basic NBO modules (Sec. B.1-B.6) and *GenNBO* stand-alone program (Sec. B.7), as well as NBO-based supplemental modules (Sec. B.8 *et seq.*).

Section C ("NBO Programmer's Guide") is for accomplished programmers who are interested in program logic and detailed source code. This section describes the relationship of the source code subprograms to published algorithms, providing documentation at the level of individual program parameters, common blocks, functions, and subroutines. This in turn serves as a bridge to the micro-documentation included as comment statements within the source code. Section C also provides guidelines for constructing interface routines to attach the NBO6 to new electronic structure packages.

The Appendices provide information on specific NBO versions (for Gaussian, GAMESS,...), with details of installation and sample input files for individual electronic structure systems.

The NBO website <http://www.chem.wisc.edu/~nbo6> provides additional tutorials, sample input and output for main program keywords, and explanatory background and bibliographic material to supplement this Manual.

A quick-reference index to NBO keywords and keylists discussed in this manual is presented in Table 1 below. The table lists default (in [brackets]) and optional keywords, indicating whether additional parameters must be provided (Parms? Y = yes; N = no; opt. = optional) with a brief summary of the keyword result and the page number of the Manual for further reference.

Table 1: NBO Keyword/Keylist Quick Summary

Keyword	Parms?	Keyword Description	Page
Main Program Options			
[BEND]	opt.	Hybrid directionality and "bond-bending" analysis	A-26
CMO	opt.	Bonding character of canonical molecular orbitals	B-144
DIPOLE	opt.	Dipole moment analysis	B-34
[E2PERT]	opt.	2nd-order perturbative estimates of NBO interactions	A-27
MATRIX	Y	General operator and transformation matrix	B-193
NBBP	opt.	Natural bond-bond polarizability indices	B-104
NBCP	N	Natural bond critical point analysis	B-172
[NBO]	N	Natural bond orbital compositions	A-21
[NBOSUM]	N	NBO summary table	A-22
NCE	N	Natural coulomb electrostatics analysis	B-183
NCS	opt.	Natural chemical shielding analysis	B-148
NCU	opt.	Natural cluster unit analysis	B-186
NEDA	opt.	Natural energy decomposition analysis	B-113
NJC	opt.	Natural J-coupling analysis	B-157
NLMO	N	Natural localized molecular orbital compositions	B-32
[NPA]	N	Natural population analysis	A-18
NRT	N	Natural resonance theory analysis	B-80
PROP	Y	General 1e property analysis	B-190
STERIC	opt.	Natural steric analysis	B-108
Control Options			
AOINFO	N	Write AO basis information to LFN 31	B-14
ARCHIVE	opt.	Write ARCHIVE (FILE47) for stand-alone GenNBO input	B-68

Section A: GETTING STARTED

A.1 INTRODUCTION TO THE NBO 6.0 PROGRAM

A.1.1 What Does the NBO Program Do?

The NBO program performs the analysis of a many-electron molecular wavefunction in terms of localized electron-pair bonding units. The program carries out the determination of natural atomic orbitals (NAOs), natural hybrid orbitals (NHOs), natural bond orbitals (NBOs), and natural localized molecular orbitals (NLMOs), and uses these to perform natural population analysis (NPA), NBO energetic (deletions) analysis, and other tasks pertaining to localized analysis of wavefunction properties, including natural resonance theory (NRT) and natural chemical shielding (NCS) analysis. This section provides a brief introduction to NBO algorithms and nomenclature.

The NBO method makes use of only the first-order reduced density matrix of the wavefunction, and hence is applicable to wavefunctions of general mathematical form. In the open-shell case, the analysis is performed in terms of "different NBOs for different spins," based on distinct density matrices for α and β spin. [Note, however, that electronic structure packages may not provide the spin density matrices for certain types of open-shell wavefunctions (e.g., MCSCF or CASSCF wavefunctions calculated by the GUGA formalism). In this case NBO analysis can only be applied in the "maximum spin-paired" (MSPNBO) formulation.]

NBO analysis is based on a method for optimally transforming a given wavefunction into localized form, corresponding to the one-center ("lone pair") and two-center ("bond") elements of the chemist's Lewis structure picture. The NBOs are obtained as local block eigenfunctions of the density matrix, and are hence "natural" in the sense of Löwdin, having optimal convergence properties for describing the electron density. The set of high-occupancy NBOs, each taken doubly occupied, is said to represent the "natural Lewis structure" (NLS) of the molecule. Delocalization effects appear as weak departures from this idealized localized picture. (For transition metals, a normal-valent Lewis-like structure conforms to a dodectet rule, rather than the normal octet rule for main-group elements.)

The various natural localized sets can be considered to result from a sequence of transformations of the input atomic orbital basis set $\{\chi_i\}$,

$$\text{input basis AOs} \rightarrow \text{NAOs} \rightarrow \text{NHOs} \rightarrow \text{NBOs} \rightarrow \text{NLMOs}$$
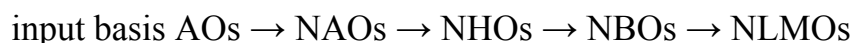
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[Note that the restriction to starting AOs is not intrinsic. If the wavefunction were not calculated in an atom-centered basis, one could first compute wavefunctions for the individual atoms (in the actual basis set and geometry of the molecular calculation) and select the most highly occupied natural orbitals as the starting "atomic orbitals" for that atom. Indeed, NBOs have now been obtained for a variety of systems in the framework of plane-wave and related grid-type descriptions; see B. Dunnington and J. R. Schmidt, "Generalization of Natural Bond Orbital Analysis to Periodic Systems: Applications to Solids and Surfaces via Plane-Wave Density Functional Theory," *J. Chem. Theor. Comp.* **8**, 1902 (2012); L. P. Lee, D. J. Cole, M. C. Payne, and C.-K. Skylaris, "Natural Bond Orbital Analysis in Linear-Scaling Density Functional Theory Calculations" <http://www2.tcm.phy.cam.ac.uk/onetep/Focus/ BiologicalApplications>. However, because atom-centered basis functions are the nearly universal choice for molecular calculations, the NBO6 program makes no provision for this step.]

Each natural localized set forms a complete orthonormal set of one-electron functions for expanding the delocalized molecular orbitals (MOs) or forming matrix representations of one-electron operators. The overlap of associated "pre-orthogonal" NAOs (PNAOs), lacking only the interatomic orthogonalization step of the NAO procedure, can be used to estimate the strength of orbital interactions in the usual way, based on Mulliken-type approximations.

The optimal condensation of occupancy in the natural localized orbitals leads to partitioning into high- and low-occupancy orbital types (reduction in dimensionality of the orbitals having significant occupancy), as reflected in the orbital labelling. The small set of most highly-occupied NAOs, having a close correspondence with the effective minimal basis set of semi-empirical quantum chemistry, is referred to as the "natural minimal basis" (NMB) set. The NMB (core + valence) functions are distinguished from the weakly occupied "Rydberg" (extra-valence-shell) functions that complete the span of the NAO space, but typically make little contribution to molecular properties. Similarly in the NBO space, the highly occupied NBOs of the natural Lewis structure (NLS) can be distinguished from the "non-Lewis" antibond and Rydberg orbitals that complete the span of the NBO space. Each pair of valence hybrids h_A, h_B in the NHO basis give rise to a bond (σ_{AB}) and antibond (σ^*_{AB}) in the NBO basis,

$$\sigma_{AB} = c_A h_A + c_B h_B$$

$$\sigma^*_{AB} = c_B h_A - c_A h_B$$

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the former a Lewis (L, occupied) and the latter a non-Lewis (NL, unoccupied) orbital. The antibonds (valence shell non-Lewis orbitals) typically play the primary role in departures (delocalization) from the idealized Lewis structure.

The NBO program also makes extensive provision for energetic analysis of NBO interactions, based on the availability of a 1-electron effective energy operator (Fock or Kohn-Sham matrix) for the system. [As noted above, the construction of NAOs and NBOs is wholly independent of any such energy operator (or geometry) information.] Estimates of energy effects are based on second-order perturbation theory, or on the effect of deleting certain orbitals or matrix elements and recalculating the total energy. NBO energetic analysis is dependent on the host electronic structure system (ESS) to which the NBO program is attached, as described in the Appendix. Analysis of a DFT calculation is performed analogously to a Hartree-Fock calculation, but uses Kohn-Sham orbitals that incorporate important effects of a correlated electronic distribution that are displayed in details of the NAOs, NBOs, and their occupancies.

NBO 6.0 includes NBO-based supplementary modules for performing natural resonance theory (NRT) analysis, natural bond-bond polarizability (NBBP) evaluation, natural steric analysis, natural energy decomposition analysis (NEDA), and natural bond critical point (NBCP) analysis. New features of *NBO 6.0* include modules for analyzing NMR chemical shielding tensors and J-coupling constants as well as improved localized description of canonical MO composition. The supplementary modules build on and extend the capabilities of core NBO analysis, and are described separately in Sections B.8 *et seq.*

NBO 6.0 comes installed in a number of leading ESS packages, and one should follow the instructions provided with the ESS on how to run NBO. The NBO program can also be obtained as a binary or source code distribution that, in principle, can be attached to any ESS of the user's choice. In addition, specific interface routines are provided that facilitate the attachment to a number of popular *ab initio* packages (Gaussian, GAMESS, Molpro).

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A.1.2 Input and Output

From the user's point of view, <u>input</u> to the NBO portion of an ESS/NBO program consists simply of one or more keywords enclosed in NBO *keylists* in the ESS input file. The main NBO keylist (the $NBO keylist) is of the form:

```
$NBO ...(keywords)... $END
```

Simple examples of such $NBO keylists are

```
$NBO  dipole  nrt  $END

$NBO  file=myjob  archive  naonbo  ncs=0.05  $END
```

Note that keylists are always delimited with $-prefixed identifiers: an identifier such as $NBO to open the keylist and $END to terminate it. Keylist delimiters and keywords are case-insensitive, and the keylist can extend across multiple lines, e.g.

```
$nbo
  file=/home/me/nbo6/myjob
  ARCHIVE
  naonbo
  ncs=0.05 <csa>
$end
```

Other keylist identifiers include $CORE, $CHOOSE, $NRTSTR, and $DEL. Keylists cannot be nested, and each new keylist must begin on a new line. The NBO program reads the keywords of each keylist to set various job options, then interrogates the ESS program for information concerning the wavefunction to perform the requested tasks.

Common abbreviations used in naming keywords are:

S   Overlap matrix
DM   Density matrix
F   Fock or Kohn-Sham matrix
K   Kinetic energy matrix
V   1-electron potential energy (nuclear-electron attraction) matrix
DI   Dipole matrix
NPA   Natural population analysis
NAO   Natural atomic orbital
NHO   Natural hybrid orbital
NBO   Natural bond orbital
NLMO   Natural localized molecular orbital

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PNAO   pre-orthogonal NAO (omit interatomic orthogonalization)
PNHO   pre-orthogonal NHO (formed from PNAOs)
PNBO   pre-orthogonal NBO (formed from PNAOs)
PNLMO   pre-orthogonal NLMO (formed from PNAOs)

The general form of NBO keylists and the specific functions associated with each keyword are detailed in the User's Guide, Section B. The particular way of including NBO keylists in the input file for each ESS is detailed in the appropriate section of the Appendix.

Principal <u>output</u> from the NBO program consists of the tables and summaries describing the results of NBO analysis, generally written to the ESS output file. Sample default NBO output is described in Section A.3, and sample output for many NBO keyword options is presented in Sec. B.6 and the individual sections for NBO supplementary modules (Sec. B.8 *et seq*).

The NBO program writes transformation matrices and other data to disk files. Two particularly noteworthy files are the NBO direct-access file (FILE48) that the program uses to store intermediate results during a calculation, and the archive file (FILE47) that, written on request, can be used with the stand-alone *GenNBO* program to repeat NBO analysis without running the ESS program to recalculate the wavefunction. Details of FILE47 and FILE48 are given in Section B.7 and the Programmer's Guide, Section C.

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A.1.3 General Capabilities and Restrictions

Principal capabilities of the NBO program are:

(1) Natural population, natural bond orbital, and natural localized molecular orbital analysis of densities from SCF, Moller-Plesset, MCSCF, CI, coupled cluster, and density functional calculations;

(2) For HF/DFT methods only, energetic analysis of the wavefunction in terms of the interactions (Fock or Kohn-Sham matrix elements) between NBOs;

(3) Localized analysis of molecular dipole moments in terms of NLMO and NBO bond moments and their interactions;

(4) Additional analyses provided by NBO-based supplemental modules (Sec. B.8 *et seq.*), including natural resonance theory, natural steric analysis, bond-bond polarizability indices, natural chemical shielding analysis, natural J-coupling analysis, and natural energy decomposition analysis. New features of *NBO 6.0* are summarized in Sec. A.1.5.

Most NBO storage is allocated dynamically to conform to the minimum required for the molecular system under study. However, certain NBO common blocks of fixed dimensionality are used for storage. These are currently dimensioned to accommodate up to 200 atoms and 2000 basis functions. Section C.3 describes how these restrictions can be altered. The program is not set up to handle complex wavefunctions, but can treat any real RHF, ROHF, UHF, MCSCF (including GVB), CI, CC, or Moller-Plesset-type wavefunction (i.e., any form of wavefunction for which the requisite density matrices are available) for ground or excited states of general open- or closed-shell molecules. Effective core potentials ("pseudopotentials") can be handled, including complete neglect of core electrons as assumed in semi-empirical treatments. The atomic orbital basis functions (including Cartesian *spdfg* and spherical *spdfghi* functions in angular symmetry) may be of general Slater-type, contracted Gaussian-type, or other general composition, including the "effective" orthonormal valence-shell AOs of semi-empirical treatments. AO basis functions are assumed to be normalized, but in general non-orthogonal. Linear dependence is handled by discarding subshells of offending functions.

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A.1.4 References and Relationship to Previous Versions

The *NBO 6.0* program should be cited as follows:

NBO 6.0. E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, C. R. Landis, and F. Weinhold, Theoretical Chemistry Institute, University of Wisconsin, Madison (2012).

NBO 6.0 is an extension of previous versions of the NBO method:

(1) "Version 1.0," the semi-empirical version incorporated in program *BONDO* and distributed through the Quantum Chemistry Program Exchange [F. Weinhold, *Quantum Chemistry Program Exchange No. 408* (1980)];

(2) "Version 2.0," the first *ab initio* implementation, designed for interfacing with Gaussian-82 and distributed through QCPE [A. E. Reed and F. Weinhold, *QCPE Bull.* **5**, 141 (1985)];

(3) Version 3.0, the general-purpose *ab initio* implementation developed for distribution through QCPE, and soon incorporated (as "Version 3.1") into commercial Gaussian distributions [E. D. Glendening, A. E. Reed, J. E. Carpenter, and F. Weinhold, *QCPE Bull.* **10**, 58 (1990)];

(4) Version 4.0, the subsequent UW/TCI version (under copyright of the University of Wisconsin, Madison) that added NRT, STERIC, NEDA, and other capabilities [*NBO 4.0.* E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, and F. Weinhold, Theoretical Chemistry Institute, University of Wisconsin, Madison (1996)];

(5) Version 5.0, the long-running UW/TCI version that maintained link-ready connectivity to leading ESS host systems and added CMO, NCS, NJC, 3CHB, and other capabilities [*NBO 5.0.* E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, and F. Weinhold (Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, 2001)].

NBO 6.0 should be considered to supercede those versions, as well as interim revisions and extensions of *NBO 5.0*, such as *NBO 5.X, NBO 5.G,* and *NBO 5.9*.

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Principal contributors (1975-2012) to the conceptual development of the NBO methods contained in this program are

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F. Weinhold	

Others who contributed to program development or technical implementation of individual program segments include S. Baker, J. K. Blair, S. H. Feldgus, T. C. Farrar, J. L. Markley, J. Michl, A. V. Nemukhin, A. Streitwieser, W. M. Westler, and H. E. Zimmerman. Many other colleagues and co-workers have provided useful comments and suggestions that are reflected in the final version of the program, and for which we are grateful.

References to the development and applications of principal NAO/NBO/NLMO methods include:

Natural Bond Orbitals:

J. P. Foster and F. Weinhold, *J. Am. Chem. Soc.* **102**, 7211-7218 (1980)

Natural Atomic Orbitals and Natural Population Analysis:

A. E. Reed and F. Weinhold, *J. Chem. Phys.* **78**, 4066-4073 (1983)

A. E. Reed, R. B. Weinstock, and F. Weinhold, *J. Chem. Phys.* **83**, 735-746 (1985)

Natural Localized Molecular Orbitals:

A. E. Reed and F. Weinhold, *J. Chem. Phys.* **83**, 1736-1740 (1985)

Open-Shell NBO:

J. E. Carpenter and F. Weinhold, *J. Molec. Struct. (Theochem)* **169**, 41-62 (1988)

Comprehensive Review Articles:

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A. E. Reed, L. A. Curtiss, and F. Weinhold, *Chem. Rev.* **88**, 899-926 (1988)

F. Weinhold, "Natural Bond Orbital Methods," In, *Encyclopedia of Computational Chemistry* P. v.R. Schleyer, N. L. Allinger, T. Clark, J. Gasteiger, P. A. Kollman, H. F. Schaefer III, P. R. Schreiner (Eds.), (John Wiley & Sons, Chichester, UK, 1998), Vol. 3, pp. 1792-1811

E. D. Glendening, C. R. Landis and F. Weinhold, "Natural Bond Orbital Methods," *WIREs Comp. Mol. Sci.* **2**, 1-42 (2012)

F. Weinhold, "Natural bond orbital analysis: A critical overview of relationships to alternative bonding perspectives," *J. Comput. Chem.* (2012).

Books:

F. Weinhold and C. R. Landis, *Valency and Bonding: A Natural Bond Orbital Donor-Acceptor Perspective* (Cambridge U. Press, 2004), 760pp.

F. Weinhold and C. R. Landis, *Discovering Chemistry with Natural Bond Orbitals* (Wiley-VCH, 2012), 319pp.

Leading references for NBO-based supplementary modules are included in Sections B.8 *et seq.* Further background and bibliographic materials can be found on the NBO website: <http://www.chem.wisc.edu/~nbo6/biblio.htm>

A.1 INTRODUCTION TO THE NBO 6.0 PROGRAM

A.1.5. What's New in NBO 6.0?

NBO 6.0 introduces deep structural, algorithmic, and notational changes from previous versions of the NBO program, as well as a variety of new analysis modules (described below) that add to the power and versatility of general NBO analysis technology. We describe in turn the leading changes of each type:

Structural Programming Changes

NBO 6.0 inaugurates a fundamentally new programming model for interacting with a host electronic structure system (ESS). For suitable "NBO6-compatible" ESS host programs <http://www.chem.wisc.edu/~nbo6/affil.htm>), *NBO 6.0* is provided as a binary executable (nbo6.exe) that cooperates interactively with the host ESS program through a direct message-passing protocol, *without* linking into an integrated binary (as required in previous ESS/NBO5 implementations).

Practically speaking, the new-style unlinked ESS/NBO6 has both similar capabilities and similar "look and feel" as older linked ESS/NBO5 versions – including $DEL-deletions, NEDA, NCS, NJC, CAS/NBO, and other interactive options. However, such two-way interactivity is now achieved at "arms length" by a binary-to-binary communication protocol that avoids technical, commercial, and legal complications of older linked versions.

NBO 6.0 is still provided in source code form. The source can be used to generate the stand-alone *GenNBO* program (gennbo.exe) that accepts input from NBO archive (FILE47) files, as produced by many current ESS programs. One can also generate binaries (message-passing nbo6.exe) for alternative OS/hardware configurations or NBO6-compatible ESS host systems. *NBO 6.0* source cannot be used to create old-style linked ESS/NBO binaries.

Algorithmic Changes

NBO 6.0 introduces important algorithmic improvements that will scarcely be noticable in applications to common chemical species, but significantly improve the consistency, generality, and reliability of NBO analysis for more exotic excited-state and multi-center species. These improvements also underlie new analysis options and notational conventions to be described below.

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(1) In former versions of the sequential search for one- and two-center NBOs, a simple "depletion" procedure was used to (approximately) remove 1c contributions from the NAO density matrix prior to 2c search, with small errors subsequently removed by symmetric orthogonalization. Depletion has now been replaced by strict orthogonal projection (annihilation) to insure rigorous orthonormality at each step of the multi-center search sequence.

(2) In former versions of the search for high-occupancy NBOs, the "pair" occupancy threshold was decremented over a coarse grid (1.90, 1.80,...,1.50) that sometimes allowed a superior natural Lewis structure to be skipped over in strongly delocalized systems. The revised *NBO 6.0* search uses a more sophisticated threshold decrement algorithm to thoroughly explore possible NLS bonding patterns. Compared to the older algorithm, this corresponds to a finer grid search and insures, at the theorem level, that the optimal NLS has been found, The newer algorithm is usually more efficient as well.

Notational and Organizational Output Changes

Two principal changes in the notation and organization of NBO output will be evident to the experienced NBO user:

(1) In former NBO output, a star(*)-label (such as BD*, LP*, RY*, 3C*) was conventionally taken to identity NL-type "excited" NBOs of low occupancy, which provide small delocalization corrections to the highly occupied "unstarred" L-type NBOs of the formal NLS configuration. However, a star-label is also conventionally used to identify out-of-phase ("antibonding") *symmetry* of a 2-center orbital about an inversion center or reflection plane, or an analogous more highly-noded phase pattern of a multi-center orbital. The ambiguities of using "*" to connote both "excitation" and "out-of-phase symmetry" are consistent with common chemical usage, and present no apparent difficulties for conventional 2-center NLS bonding patterns of ground state species. However, such ambiguities lead to increasing conflicts for the exotic multi-center bonding scenarios of excited-state or metallic species, mandating more restricted usage of star-labels in *NBO 6.0*.

Gross inconsistencies arise whenever an out-of-phase "BD*" orbital is found to be of *higher* occupancy than the corresponding in-phase "BD" orbital, thereby forcing *reversal* of the usual assignments of L vs. NL labels. In such cases, earlier NBO versions printed a warning message ("apparent excited-state configuration encountered...") and reassigned "BD" vs. "BD*" labels according to phase-pattern rather than occupancy order. This leads to superficially large NL-density and (often) to grossly sub-optimal NBOs and NLS assignments.

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Although rare for ground-state species, such cases become increasingly common in excited states.

NBO 6.0 avoids these notational conflicts by more clearly distinguishing L-type and NL-type NBOs in separated output sections, removing any presumed association with "*" labels. Instead, the "*" label is reserved primarily for the more traditional chemical association with out-of-phase ("antibonding") character of 2c/2e ("BD*" type) or 3c/2e ("3C*" type) NBOs, and secondarily for the distinctive "LP*" (unfilled valence-shell nonbonding) NBOs of hypovalent species (following usage established in previous NBO program versions). For common ground-state species, these notational changes have practically no perceptible effect. However, a more comprehensive perspective that includes excited-state and far-from-equilibrium species makes the need for such changes increasingly apparent.

(2) In *NBO 6.0* output, the ordering of NBOs is now altered to reflect the actual multi-center search priority for L-type NBOs (1c < 2c < 3c) and prioritized occupancy ordering for NL-type NBOs. As a result, the 1c core ("CR") and lone pair ("LP") NBOs appear first, followed by 2c bonds ("BD") [and, if needed, 3c bonds ("3C")] in the L-listing, while the formally empty 1c valence orbitals (LP*), 2c valence antibonds (BD*) [and, if needed, 3-center NL orbitals (3Cn and 3C*)] now precede the residual 1c Rydberg-type (RY) NBOs in the NL-listing. As mentioned above, the clear delineation of Lewis and non-Lewis sections of NBO output also departs from older format.

New Analysis Features and Options

NBO 6.0 includes major new capabilities related to multi-center bonding, supramolecular aggregation, and L/NL decomposition of electrostatic and other properties, as well as extensions and improvements of established NBO analysis tools. Principal new NBO features include:

(1) *Automatic Three-Center Bond Search.* If the initial 1c/2c search leaves unassigned NL-density exceeding the current occupancy threshold, the NBO search automatically extends to 3-center NBOs. The former "3CBOND" keyword is therefore deprecated, and hypovalent 3c/2e τ-bonds of borane-type species are now recognized without user intervention. The corresponding "3CHB" keyword for Pimentel-Rundle-Coulson-type 3c/4e interactions is also deprecated, and such strong 2-resonance "hyperbonds" are now automatically recognized by the program.

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(2) *Natural Coulomb Electrostatics Analysis (NCE Keyword).* NPA atomic charges for the idealized NLS and actual molecular charge distribution are combined with interatomic distances to distinguish the classical-type (L) and resonance-type (NL) contributions to apparent "Coulomb electrostatics."

(3) *Natural Cluster Unit Analysis (NCU Keyword).* A general measure of interaction strength (τ_{NCU}) is continuously varied to obtain the intrinsic "units" or "building blocks" that are characteristic of aggregation in each range of interatomic interactions, from the strong forces of chemical bonding to the weak forces of London dispersion.

(4) *General 1-Electron Property Analysis (PROP Keyword).* A template is provided for NBO analysis of *any* 1e property whose AO matrix elements are provided by the host ESS program.

(5) *General 1-Electron Property Matrix (MATRIX Keyword).* A template is provided for transforming the matrix elements of *any* available 1e property to localized (NAO/NHO/NBO/NLMO) or delocalized (MO) basis form.

(6) *"Local NRT" Options*. New provision is made for constraining NRT weighting to selected sub-units (resonance units) of the overall system, thus allowing a "divide and conquer" strategy for overcoming convergence difficulties of multiple resonating groups. Other algorithmic improvements now allow efficient NRT description of many previously intractable species.

Despite these changes and extensions, *NBO 6.0* was designed to be compatible with earlier versions as nearly as possible. Experienced NBO users should find that familiar features run practically unchanged, providing the framework for a smooth and intuitive migration to new keywords and features.

A.2 INSTALLING THE NBO PROGRAM

[*NBO 6.0* comes installed in a number of leading ESS packages. Users of these packages may ignore this section.]

The NBO program is distributed in electronic download or CD form, either as binary executables or source code. Installation instructions differ in these cases. In either case, the final NBO6 binary executables are intended to communicate interactively with a chosen NBO6-compatible host electronic structure system (ESS) or with the *GenNBO* program that takes its input from an archive (.47) file.

Windows Binary Executable Distribution

The Windows distribution includes NBO6 executables for 32- and 64-bit environments (nbo6.i4.exe and nbo6.i8.exe), the *GenNBO* executable (gennbo.i4.exe and gennbo.i8.exe), sample archive files (with .gen extension), and a batch script (gennbo.bat) for executing sample calculations. Instructions for installing and testing these executables are provided with the distribution.

Linux Binary Executable Distribution

Convenient binary executable distribution is available for Linux operating systems, including cygwin for Windows and Mac OS-X. (Installation for other Unix-based operating systems may require the source distribution described below.) The Linux binary distribution includes NBO6 executables for 32- and 64-bit environments (nbo6.i4.exe and nbo6.i8.exe), the *GenNBO* executable (gennbo.i4.exe and gennbo.i8.exe), sample archive files (with .gen extension), and a batch script (gennbo) for executing sample calculations. Instructions for installing and testing these executables are provided with the distribution.

Source Code Distribution

The source distribution consists of the master NBO source code, GNU makefiles, and utility routines for building 32- and 64-bit executables, including the NBO6 executables (nbo6.i4.exe and nbo6.i8.exe) and *GenNBO* executables (gennbo.i4.exe and gennbo.i8.exe) GNU, Portland Group, and Intel Fortran compilers are fully supported by the distribution. Other compilers may successfully build executables too, but are not currently supported by the NBO development team. Consult the "Frequently Asked Questions" link of the NBO6 website <http://www.chem.wisc.edu/~nbo6/faq.htm> or contact the

A.2 INSTALLING THE NBO PROGRAM

authors if you encounter undue difficulties when building the NBO executables.

Note that installation of the NBO programs into your host ESS system generally does not affect the way your system processes standard input files. The only change involves the reading of NBO keylists (if detected in your input file), performance of the NBO tasks requested in the keylist, and return of control to the ESS program in the state in which the NBO call was encountered (unless special checkpointing commands were performed; Sec. B.12).

If you are interfacing *NBO 6.0* to a new ESS package (not currently supported by the source code distribution), see Section C.13 for guidance on how to create interface routines so that NBO can acquire the necessary information from the ESS. Alternatively, see Section B.7 for a description of the input file to *GenNBO,* the stand-alone version of the NBO program.

A.3 TUTORIAL EXAMPLE FOR METHYLAMINE

A.3.1 Running the Example

This section provides an introductory quick-start tutorial on running a simple NBO job and interpreting the output. The example chosen is that of methylamine (CH_3NH_2) in Pople-Gordon idealized geometry, treated at the *ab initio* RHF/3-21G level. This simple split-valence basis set consists of 28 AOs (nine each on C and N, two on each H), extended by 13 AOs beyond the minimal basis level.
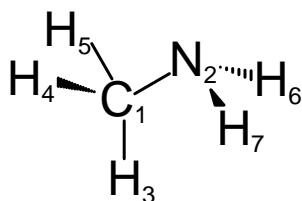
Input files to run this job (or its nearest equivalent) with each ESS are given in the Appendix. In most cases, you can modify the standard ESS input file to produce NBO output by simply including the line

```
$NBO   $END
```

at the end of the file. This is an empty NBO keylist, specifying that NBO analysis should be carried out at the *default* level. Alternatively, *GenNBO* can be run with the FILE47 archive file (ch3nh2.gen) provided with the binary and source distributions to produce the NBO output described here.

Default NBO output produced by this example is shown below, just as it appears in your output file. The start of the NBO section is marked by a standard header, citation, job title, and storage info:

A.3 TUTORIAL EXAMPLE FOR METHYLAMINE

```
********************************* NBO 6.0 *********************************
           N A T U R A L   A T O M I C   O R B I T A L   A N D
        N A T U R A L   B O N D   O R B I T A L   A N A L Y S I S
******************************* DEV0001 *********************************
 (c) Copyright 1996-2012 Board of Regents of the University of Wisconsin System
     on behalf of the Theoretical Chemistry Institute.  All rights reserved.

        Cite this program as:

        NBO 6.0.  E. D. Glendening, J. K. Badenhoop, A. E. Reed,
        J. E. Carpenter, J. A. Bohmann, C. M. Morales, C. R. Landis,
        and F. Weinhold (Theoretical Chemistry Institute, University
        of Wisconsin, Madison, WI, 2012); http://nbo6.chem.wisc.edu/

Filename set to ch3nh2

Job title:  Methylamine...RHF/3-21G//Pople-Gordon standard geometry
```

The NBO banner reports the program version (NBO 6.0) and serial number ("DEV0001" in this case). The latter is associated with the license that was purchased from the University of Wisconsin.

NBO output is formatted to maximum 80-character width for convenient display on a computer terminal or printed page. The NBO heading echoes any requested keywords (none for the present default case). The filename that is reported ("ch3nh2" in this case) is used to open named files, such as the FILE48 direct-access file (ch3nh2.48) and FILE47 archive file (ch3nh2.47). (The latter is only produced when the user adds the ARCHIVE keyword to the $NBO keylist.)

A.3 TUTORIAL EXAMPLE FOR METHYLAMINE

A.3.2 Natural Population Analysis

The next four NBO output segments summarize the results of natural population analysis (NPA). The first segment is the main NAO table, as shown below:

```
NATURAL POPULATIONS:   Natural atomic orbital occupancies

 NAO Atom No lang    Type(AO)    Occupancy      Energy
 ----------------------------------------------------------
   1    C   1   s     Cor( 1s)    1.99901     -11.04148
   2    C   1   s     Val( 2s)    1.09144      -0.28255
   3    C   1   s     Ryd( 3s)    0.00067       1.95637
   4    C   1   px    Val( 2p)    0.88696      -0.01597
   5    C   1   px    Ryd( 3p)    0.00142       0.93152
   6    C   1   py    Val( 2p)    1.21481      -0.07285
   7    C   1   py    Ryd( 3p)    0.00063       1.02989
   8    C   1   pz    Val( 2p)    1.24537      -0.08879
   9    C   1   pz    Ryd( 3p)    0.00056       1.01733

  10    N   2   s     Cor( 1s)    1.99953     -15.25896
  11    N   2   s     Val( 2s)    1.42760      -0.71766
  12    N   2   s     Ryd( 3s)    0.00017       2.76139
  13    N   2   px    Val( 2p)    1.29291      -0.18361
  14    N   2   px    Ryd( 3p)    0.00116       1.56628
  15    N   2   py    Val( 2p)    1.82116      -0.33490
  16    N   2   py    Ryd( 3p)    0.00186       1.48617
  17    N   2   pz    Val( 2p)    1.35158      -0.19162
  18    N   2   pz    Ryd( 3p)    0.00068       1.59367

  19    H   3   s     Val( 1s)    0.81422       0.13249
  20    H   3   s     Ryd( 2s)    0.00175       0.95053

  21    H   4   s     Val( 1s)    0.78179       0.15344
  22    H   4   s     Ryd( 2s)    0.00096       0.94536

  23    H   5   s     Val( 1s)    0.78179       0.15344
  24    H   5   s     Ryd( 2s)    0.00096       0.94536

  25    H   6   s     Val( 1s)    0.63929       0.20519
  26    H   6   s     Ryd( 2s)    0.00123       0.99956

  27    H   7   s     Val( 1s)    0.63929       0.20519
  28    H   7   s     Ryd( 2s)    0.00123       0.99956
```

For each of the 28 NAO functions, this table lists the atom to which NAO is attached (in the numbering scheme of the ESS program), the angular momentum type "lang" (s, p_x, etc., in the coordinate system of the ESS program), the orbital type (whether core, valence, or Rydberg, and a conventional hydrogenic-type label), the orbital occupancy (number of electrons, or "natural population" of the orbital), and the orbital energy (in the favored units of the ESS program, in this case atomic units: 1 a.u. = 627.51 kcal/mol). [For example, NAO 4 (the highest energy C orbital of the NMB set) is the valence shell $2p_x$ orbital on carbon, occupied by 0.8870 electrons, whereas NAO 5 is a Rydberg $3p_x$ orbital with only 0.0014 electrons.] Note that the occupancies of the Rydberg (Ryd) NAOs are typically much lower than

those of the core (Cor) and valence (Val) NAOs of the natural minimum basis (NMB) set, reflecting the dominant role of the NMB orbitals in describing molecular properties.

The principal quantum numbers for the NAO labels ($1s$, $2s$, $3s$, etc.) are assigned on the basis of the energy order if a Fock matrix is available, or on the basis of occupancy otherwise. A message is printed warning of a "population inversion" if the occupancy and energy ordering do not coincide (of interest, but usually not of concern).

The next segment is an atomic summary showing the natural atomic charges (nuclear charge minus summed natural populations of NAOs on the atom) and total core, valence, and Rydberg populations on each atom:

```
Summary of Natural Population Analysis:

                                  Natural Population
                  Natural    ------------------------------------------
 Atom No          Charge        Core      Valence     Rydberg      Total
---------------------------------------------------------------------------
   C   1         -0.44086     1.99901     4.43857     0.00328     6.44086
   N   2         -0.89664     1.99953     5.89326     0.00386     7.89664
   H   3          0.18403     0.00000     0.81422     0.00175     0.81597
   H   4          0.21726     0.00000     0.78179     0.00096     0.78274
   H   5          0.21726     0.00000     0.78179     0.00096     0.78274
   H   6          0.35948     0.00000     0.63929     0.00123     0.64052
   H   7          0.35948     0.00000     0.63929     0.00123     0.64052
===========================================================================
* Total *         0.00000     3.99853    13.98820     0.01327    18.00000
```

This table succinctly describes the molecular charge distribution in terms of NPA charges. [For example, the carbon atom of methylamine is assigned a net NPA charge of −0.441 at this level; note also the slightly less positive charge on H(3) than on the other two methyl hydrogens: +0.184 vs. +0.217.]

Next follows a summary of the NMB and NRB populations for the composite system, summed over atoms:

```
                          Natural Population
      ---------------------------------------------------------
       Core                    3.99853 ( 99.9633% of    4)
       Valence                13.98820 ( 99.9157% of   14)
       Natural Minimal Basis  17.98673 ( 99.9263% of   18)
       Natural Rydberg Basis   0.01327 (  0.0737% of   18)
      ---------------------------------------------------------
```

A.3 TUTORIAL EXAMPLE FOR METHYLAMINE

This exhibits the high percentage contribution (typically, > 99%) of the NMB set to the molecular charge distribution. [In the present case, for example, the 13 Rydberg orbitals of the NRB set contribute only 0.07% of the electron density, whereas the 15 NMB functions account for 99.93% of the total.]

Finally, the natural populations are summarized as an effective valence electron configuration ("natural electron configuration") for each atom:

```
   Atom No           Natural Electron Configuration
 ----------------------------------------------------------------
   C   1         [core]2s( 1.09)2p( 3.35)
   N   2         [core]2s( 1.43)2p( 4.47)
   H   3               1s( 0.81)
   H   4               1s( 0.78)
   H   5               1s( 0.78)
   H   6               1s( 0.64)
   H   7               1s( 0.64)
```

Although the occupancies of the atomic orbitals are non-integer in the molecular environment, the effective atomic configurations can be related to idealized atomic states in "promoted" configurations. [For example, the carbon atom in the above table is most nearly described by an idealized $1s^2 2s^1 2p^3$ electron configuration.]

A.3 TUTORIAL EXAMPLE FOR METHYLAMINE

A.3.3 Natural Bond Orbital Analysis

The next segments of the output summarize the results of NBO analysis. The first segment reports on details of the search for an NBO natural Lewis structure:

```
NATURAL BOND ORBITAL ANALYSIS:

                          Occupancies      Lewis Structure   Low   High
           Max   Occ    -------------------  ----------------  occ   occ
  Cycle  Ctr  Thresh   Lewis    non-Lewis   CR  BD  nC  LP   (L)   (NL)
  ===============================================================================
    1     2    1.90    17.95101  0.04899     2   6   0   1    0     0
  -------------------------------------------------------------------------------

Structure accepted: No low occupancy Lewis orbitals
```

Normally, there is but one cycle of the NBO search. The table summarizes a variety of information for each cycle: the occupancy threshold for a "good" pair in the NBO search; the total populations of Lewis and non-Lewis NBOs; the number of core (CR), 2-center bond (BD), 3-center bond (3C), and lone pair (LP) NBOs in the natural Lewis structure; and the number of low-occupancy Lewis (L) and "high-occupancy" ($> 0.1e$) non-Lewis (NL) orbitals. The Lewis structure is accepted if all orbitals of the formal Lewis structure exceed the occupancy threshold (default, 1.90 electrons).

Next follows a more detailed breakdown of the Lewis and non-Lewis occupancies into core, valence, and Rydberg shell contributions:

```
    ------------------------------------------------------
     Core                     3.99853 ( 99.963% of    4)
     Valence Lewis           13.95248 ( 99.661% of   14)
    ==================       ============================
     Total Lewis             17.95101 ( 99.728% of   18)
    ------------------------------------------------------
     Valence non-Lewis        0.03928 (  0.218% of   18)
     Rydberg non-Lewis        0.00971 (  0.054% of   18)
    ==================       ============================
     Total non-Lewis          0.04899 (  0.272% of   18)
    ------------------------------------------------------
```

This shows the general quality of the natural Lewis structure description in terms of the percentage of the total electron density (e.g., in the above case, about 99.7%). The table also exhibits the relatively important role of the valence non-Lewis orbitals (i.e., the six valence antibonds, NBOs 23-28) relative to the extra-valence orbitals (the 13 Rydberg NBOs 10-22) in the slight departures from a localized Lewis structure model.

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Next follows the main listing of NBOs, displaying the form and occupancy of
the complete set of NBOs that span the input AO space:

```
   (Occupancy)   Bond orbital / Coefficients / Hybrids
----------------- Lewis -------------------------------------------------
  1. (1.99901) CR ( 1) C  1          s(100.00%)
                                      1.0000  0.0000  0.0000  0.0000  0.0000
                                      0.0000  0.0000  0.0000  0.0000
  2. (1.99953) CR ( 1) N  2          s(100.00%)
                                      1.0000  0.0000  0.0000  0.0000  0.0000
                                      0.0000  0.0000  0.0000  0.0000
  3. (1.97845) LP ( 1) N  2          s( 18.17%)p 4.50( 81.83%)
                                     -0.0000  0.4263  0.0002 -0.2719  0.0033
                                     -0.8626  0.0162 -0.0000 -0.0000
  4. (1.99849) BD ( 1) C  1- N  2
              ( 40.06%)   0.6330* C  1 s( 21.58%)p 3.63( 78.42%)
                                      0.0000  0.4640  0.0235 -0.8837 -0.0293
                                     -0.0481 -0.0099 -0.0000  0.0000
              ( 59.94%)   0.7742* N  2 s( 30.68%)p 2.26( 69.32%)
                                      0.0000  0.5539 -0.0011  0.8324 -0.0000
                                      0.0112 -0.0100 -0.0000 -0.0000
  5. (1.99863) BD ( 1) C  1- H  3
              ( 59.72%)   0.7728* C  1 s( 25.93%)p 2.86( 74.07%)
                                      0.0000  0.5091 -0.0068  0.2216  0.0101
                                      0.8316 -0.0051 -0.0000  0.0000
              ( 40.28%)   0.6347* H  3 s(100.00%)
                                      1.0000  0.0029
  6. (1.99402) BD ( 1) C  1- H  4
              ( 61.03%)   0.7812* C  1 s( 26.27%)p 2.81( 73.73%)
                                      0.0000  0.5125 -0.0037  0.2902  0.0020
                                     -0.3912  0.0017  0.7070 -0.0104
              ( 38.97%)   0.6243* H  4 s(100.00%)
                                      1.0000  0.0008
  7. (1.99402) BD ( 1) C  1- H  5
              ( 61.03%)   0.7812* C  1 s( 26.27%)p 2.81( 73.73%)
                                      0.0000  0.5125 -0.0037  0.2902  0.0020
                                     -0.3912  0.0017 -0.7070  0.0104
              ( 38.97%)   0.6243* H  5 s(100.00%)
                                      1.0000  0.0008
  8. (1.99443) BD ( 1) N  2- H  6
              ( 68.09%)   0.8252* N  2 s( 25.56%)p 2.91( 74.44%)
                                      0.0000  0.5055  0.0006 -0.3413 -0.0177
                                      0.3572 -0.0062 -0.7070 -0.0093
              ( 31.91%)   0.5649* H  6 s(100.00%)
                                      1.0000  0.0020
  9. (1.99443) BD ( 1) N  2- H  7
              ( 68.09%)   0.8252* N  2 s( 25.56%)p 2.91( 74.44%)
                                      0.0000  0.5055  0.0006 -0.3413 -0.0177
                                      0.3572 -0.0062  0.7070  0.0093
              ( 31.91%)   0.5649* H  7 s(100.00%)
                                      1.0000  0.0020
---------------- non-Lewis ----------------------------------------------
 10. (0.00011) BD*( 1) C  1- N  2
              ( 59.94%)   0.7742* C  1 s( 21.58%)p 3.63( 78.42%)
                                      0.0000  0.4640  0.0235 -0.8837 -0.0293
                                     -0.0481 -0.0099 -0.0000  0.0000
              ( 40.06%)  -0.6330* N  2 s( 30.68%)p 2.26( 69.32%)
                                      0.0000  0.5539 -0.0011  0.8324 -0.0000
                                      0.0112 -0.0100 -0.0000 -0.0000
 11. (0.01533) BD*( 1) C  1- H  3
              ( 40.28%)   0.6347* C  1 s( 25.93%)p 2.86( 74.07%)
                                     -0.0000 -0.5091  0.0068 -0.2216 -0.0101
                                     -0.8316  0.0051  0.0000 -0.0000
              ( 59.72%)  -0.7728* H  3 s(100.00%)
                                     -1.0000 -0.0029
 12. (0.00765) BD*( 1) C  1- H  4
              ( 38.97%)   0.6243* C  1 s( 26.27%)p 2.81( 73.73%)
```

```
                                       -0.0000 -0.5125  0.0037 -0.2902 -0.0020
                                        0.3912 -0.0017 -0.7070  0.0104
              ( 61.03%)  -0.7812* H  4 s(100.00%)
                                       -1.0000 -0.0008
 13. (0.00765) BD*( 1) C  1- H  5
              ( 38.97%)   0.6243* C  1 s( 26.27%)p 2.81( 73.73%)
                                       -0.0000 -0.5125  0.0037 -0.2902 -0.0020
                                        0.3912 -0.0017  0.7070 -0.0104
              ( 61.03%)  -0.7812* H  5 s(100.00%)
                                       -1.0000 -0.0008
 14. (0.00427) BD*( 1) N  2- H  6
              ( 31.91%)   0.5649* N  2 s( 25.56%)p 2.91( 74.44%)
                                       -0.0000 -0.5055 -0.0006  0.3413  0.0177
                                       -0.3572  0.0062  0.7070  0.0093
              ( 68.09%)  -0.8252* H  6 s(100.00%)
                                       -1.0000 -0.0020
 15. (0.00427) BD*( 1) N  2- H  7
              ( 31.91%)   0.5649* N  2 s( 25.56%)p 2.91( 74.44%)
                                       -0.0000 -0.5055 -0.0006  0.3413  0.0177
                                       -0.3572  0.0062 -0.7070 -0.0093
              ( 68.09%)  -0.8252* H  7 s(100.00%)
                                       -1.0000 -0.0020
 16. (0.00104) RY ( 1) C  1           s(  1.51%)p65.10( 98.49%)
                                       -0.0000 -0.0089  0.1227  0.0308 -0.7574
                                        0.0035 -0.6405 -0.0000  0.0000
 17. (0.00032) RY ( 2) C  1           s(  0.00%)p 1.00(100.00%)
                                        0.0000 -0.0000  0.0000 -0.0000 -0.0000
                                        0.0000  0.0000  0.0147  0.9999
 18. (0.00022) RY ( 3) C  1           s( 57.82%)p 0.73( 42.18%)
                                        0.0000 -0.0019  0.7604  0.0239 -0.3421
                                        0.0085  0.5514 -0.0000 -0.0000
 19. (0.00002) RY ( 4) C  1           s( 40.61%)p 1.46( 59.39%)
 20. (0.00114) RY ( 1) N  2           s(  1.61%)p60.93( 98.39%)
                                       -0.0000 -0.0061  0.1269 -0.0073 -0.0754
                                       -0.0195 -0.9888  0.0000  0.0000
 21. (0.00042) RY ( 2) N  2           s(  0.00%)p 1.00(100.00%)
                                        0.0000 -0.0000 -0.0000  0.0000  0.0000
                                       -0.0000  0.0000 -0.0131  0.9999
 22. (0.00039) RY ( 3) N  2           s( 33.53%)p 1.98( 66.47%)
                                        0.0000  0.0135  0.5789 -0.0082  0.8151
                                        0.0127  0.0118  0.0000  0.0000
 23. (0.00002) RY ( 4) N  2           s( 64.88%)p 0.54( 35.12%)
 24. (0.00176) RY ( 1) H  3           s(100.00%)
                                       -0.0029  1.0000
 25. (0.00096) RY ( 1) H  4           s(100.00%)
                                       -0.0008  1.0000
 26. (0.00096) RY ( 1) H  5           s(100.00%)
                                       -0.0008  1.0000
 27. (0.00123) RY ( 1) H  6           s(100.00%)
                                       -0.0020  1.0000
 28. (0.00123) RY ( 1) H  7           s(100.00%)
                                       -0.0020  1.0000
```

For each NBO (1-28), the first line of printout shows the occupancy (between 0 and 2.0000 electrons) and unique label of the NBO. This label gives the type ("CR" for 1-center core pair, "LP" for 1-center valence lone pair, "BD" for 2-center bond, "BD*" for 2-center antibond, and "RY" for 1-center Rydberg, the unstarred and starred labels corresponding to Lewis and non-Lewis NBOs, respectively), a serial number (1, 2,... if there is a single, double,... bond between the pair of atoms), and the atom(s) to which the NBO is affixed. [For example, the first 2-center NBO in the sample output, NBO 4, is the bond (with 1.9985 electrons) between carbon (atom 1) and nitrogen (atom 2), the σ_{CN}

bond.] The next lines summarize the natural atomic hybrids h_A of which the NBO is composed, giving the percentage $(100|c_A|^2)$ of the NBO on each hybrid (in parentheses), the polarization coefficient c_A, the atom label, and a hybrid label showing the sp^λ composition (percentage s-character, p-character, etc.) of each h_A. [For example, the σ_{CN} NBO is formed from an $sp^{3.63}$ hybrid (78.4% p-character) on carbon interacting with an $sp^{2.26}$ hybrid (69.3% p-character) on nitrogen,

$$\sigma_{CN} = 0.633(sp^{3.63})_C + 0.774(sp^{2.26})_N$$

corresponding roughly to the qualitative concept of interacting sp^3 hybrids (75% p-character) and the higher electronegativity (larger polarization coefficient) of N.] Below each NHO label is the set of coefficients that specify how the NHO is written explicitly as a linear combination of NAOs on the atom. The order of NAO coefficients follows the numbering of the NAO tables. [For example, in the first NBO entry, the carbon hybrid h_C of the σ_{CN} bond has largest coefficients for the 2nd and 4th NAOs, corresponding to the approximate description

$$h_C \cong -0.464(2s)_C - 0.884(2p_x)_C$$

in terms of the valence NAOs of the carbon atom.] In the CH_3NH_2 example, the NBO search finds the C-N bond (NBO 4), three C-H bonds (NBOs 5, 6, 7), two N-H bonds (NBOs 8, 9), N lone pair (NBO 3), and C and N core pairs (NBOs 1, 2) of the expected Lewis structure. NBOs 10-28 represent the residual non-Lewis NBOs of low occupancy, led by the valence antibonds (BD*, NBOs 10-15) that are usually of principal chemical interest. In this example, it is interesting to note the slight asymmetry of the three σ_{CH} NBOs, and the slightly higher occupancy (0.0153 $vs.$ 0.0077 electrons) in the σ^*_{C1H3} antibond (NBO 11) lying $anti$ to the nitrogen lone pair.

[Note that the ordering of NBOs differs slightly from that in earlier NBO program versions, with "Lewis" (L-type; highly occupied) and "non-Lewis" NBOs (NL-type; unoccupied in the formal NLS) more clearly identified in program output. The present ordering always places L before NL, with 1-center (1c; CR, LP) preceding 2-center bonds (2c; BD) and 3-center NBOs in the L-type listing, and with 2c valence antibonds (BD*) or 3-center (3C*) NBOs preceding residual 1c extra-valent Rydberg (RY) NBOs in the NL-type listing. The current ordering of NBOs therefore conforms more closely to the usual priorities of chemical interest, with valence lone pairs (LP) near the top of L-type listing and valence antibonds (BD*) topping the NL-type listing order,

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followed by the long list of residual RY-type NBOs (required for completeness of the orthonormal NBO set) that are normally of negligible chemical interest.]

A.3 TUTORIAL EXAMPLE FOR METHYLAMINE

A.3.4 NHO Directional Analysis

The next segment of output summarizes the angular properties of the natural hybrid orbitals:

```
NHO DIRECTIONALITY AND BOND BENDING (deviations from line of nuclear centers)

        [Thresholds for printing:  angular deviation  >  1.0 degree]
                                        p-character  > 25.0%
                                   orbital occupancy >  0.10e

                      Line of Centers        Hybrid 1               Hybrid 2
                      ---------------    -------------------    ------------------
           NBO          Theta   Phi      Theta   Phi    Dev     Theta   Phi    Dev
     ==============================================================================
      3. LP ( 1) N  2      --     --      90.0  252.4   --       --     --     --
      4. BD ( 1) C  1- N  2   90.0  183.2   --     --    --      90.0    0.1    3.2
      8. BD ( 1) N  2- H  6  145.0  127.8  145.0  135.6   4.5     --     --     --
      9. BD ( 1) N  2- H  7   35.0  127.8   35.0  135.6   4.5     --     --     --
```

The "direction" of an sp^λ hybrid is specified in terms of the polar (θ) and azimuthal (φ) angles (in the ESS coordinate system) of the vector describing its *p*-component. For more general $sp^\lambda d^\mu$ hybrids the hybrid direction is determined numerically to correspond to maximum angular amplitude. The program compares the hybrid direction with the direction of the line of centers between the two nuclei to determine the bending of the bond, expressed as the deviation angle ("Dev," in degrees) between these two directions. For example, in the CH_3NH_2 case shown above, the nitrogen hybrid of the σ_{CN} bond (NBO 4) is bent away from the line of C-N centers by 3.2°, whereas the carbon NHO is approximately aligned with the C-N axis (within the 1.0° threshold for printing). The N hybrids of the N-H bonds (NBOs 8, 9) are bent even further (4.5°). The information in this table is often useful in anticipating the direction of geometry changes resulting from geometry optimization (i.e., the likely reduction in pyramidalization of the -NH_2 group in order to relieve the ~4° nitrogen bond bendings found in the idealized tetrahedral Pople-Gordon geometry).

A.3 TUTORIAL EXAMPLE FOR METHYLAMINE

A.3.5 Perturbation Theory Energy Analysis

The next segment summarizes the second-order perturbative estimates of donor-acceptor (bond-antibond) interactions in the NBO basis:

```
SECOND ORDER PERTURBATION THEORY ANALYSIS OF FOCK MATRIX IN NBO BASIS

    Threshold for printing:   0.50 kcal/mol
                                                   E(2) E(NL)-E(L) F(L,NL)
       Donor (L) NBO              Acceptor (NL) NBO      kcal/mol   a.u.    a.u.
   =============================================================================

within unit  1
   1. CR ( 1) C  1           22. RY ( 3) N  2              0.61   13.11    0.080
   1. CR ( 1) C  1           24. RY ( 1) H  3              1.40   11.99    0.116
   1. CR ( 1) C  1           25. RY ( 1) H  4              1.55   11.99    0.122
   1. CR ( 1) C  1           26. RY ( 1) H  5              1.55   11.99    0.122
   2. CR ( 1) N  2           16. RY ( 1) C  1              1.51   16.23    0.140
   2. CR ( 1) N  2           18. RY ( 3) C  1              0.82   16.79    0.105
   2. CR ( 1) N  2           27. RY ( 1) H  6              0.61   16.26    0.089
   2. CR ( 1) N  2           28. RY ( 1) H  7              0.61   16.26    0.089
   3. LP ( 1) N  2           11. BD*( 1) C  1- H  3        7.92    1.13    0.085
   3. LP ( 1) N  2           12. BD*( 1) C  1- H  4        1.45    1.14    0.036
   3. LP ( 1) N  2           13. BD*( 1) C  1- H  5        1.45    1.14    0.036
   5. BD ( 1) C  1- H  3     20. RY ( 1) N  2              0.82    2.18    0.038
   6. BD ( 1) C  1- H  4     13. BD*( 1) C  1- H  5        0.52    1.39    0.024
   6. BD ( 1) C  1- H  4     14. BD*( 1) N  2- H  6        3.02    1.37    0.057
   7. BD ( 1) C  1- H  5     12. BD*( 1) C  1- H  4        0.52    1.39    0.024
   7. BD ( 1) C  1- H  5     15. BD*( 1) N  2- H  7        3.02    1.37    0.057
   8. BD ( 1) N  2- H  6     12. BD*( 1) C  1- H  4        2.86    1.51    0.059
   8. BD ( 1) N  2- H  6     16. RY ( 1) C  1              0.54    1.78    0.028
   9. BD ( 1) N  2- H  7     13. BD*( 1) C  1- H  5        2.86    1.51    0.059
   9. BD ( 1) N  2- H  7     16. RY ( 1) C  1              0.54    1.78    0.028
```

This is carried out by examining all possible interactions between "filled" (donor, L) Lewis-type NBOs and "unfilled" (acceptor, NL) non-Lewis-type NBOs, and estimating their energetic importance by 2nd-order perturbation theory. Since these interactions lead to loss of occupancy from the localized NBOs of the idealized Lewis structure into the empty non-Lewis orbitals (and thus, to departures from the idealized Lewis structure description), they are referred to as "delocalization" corrections to the zeroth-order natural Lewis structure. For each donor NBO (*i*) and acceptor NBO (*j*), the donor-acceptor stabilization energy *E(2)* associated with $i \rightarrow j$ delocalization is estimated as

$$E(2) = \Delta E_{ij}^{(2)} = q_i \, F(i,j)^2/(\varepsilon_j - \varepsilon_i)$$

where q_i is the donor orbital occupancy (2 for closed-shell, 1 for open-shell), ε_i, ε_j are diagonal elements (orbital energies), and *F(i,j)* is the off-diagonal NBO Fock matrix element. [In the example above, the $n_N \rightarrow \sigma^*_{CH}$ interaction between the nitrogen lone pair (NBO 3) and the antiperiplanar C_1-H_3 antibond

(NBO 11) is seen to give the strongest stabilization, 7.92 kcal/mol.] As the heading indicates, entries are included in this table only when the interaction energy exceeds a default threshold of 0.5 kcal/mol.

A.3 TUTORIAL EXAMPLE FOR METHYLAMINE

A.3.6 NBO Summary

Next appears a condensed summary of the principal NBOs, showing the occupancy, orbital energy, and the qualitative pattern of delocalization interactions associated with each:

```
NATURAL BOND ORBITALS (Summary):

                                                 Principal Delocalizations
            NBO               Occupancy   Energy  (geminal,vicinal,remote)
===============================================================================
Molecular unit  1  (CH5N)
------ Lewis -------------------------------------
   1. CR ( 1) C  1            1.99901   -11.04148  25(v),26(v),24(v),22(v)
   2. CR ( 1) N  2            1.99953   -15.25896  16(v),18(v),27(v),28(v)
   3. LP ( 1) N  2            1.97845    -0.44752  11(v),12(v),13(v)
   4. BD ( 1) C  1- N  2      1.99849    -0.89737
   5. BD ( 1) C  1- H  3      1.99863    -0.69256  20(v)
   6. BD ( 1) C  1- H  4      1.99402    -0.68912  14(v),13(g)
   7. BD ( 1) C  1- H  5      1.99402    -0.68912  15(v),12(g)
   8. BD ( 1) N  2- H  6      1.99443    -0.80927  12(v),16(v)
   9. BD ( 1) N  2- H  7      1.99443    -0.80927  13(v),16(v)
------ non-Lewis ----------------------------------
  10. BD*( 1) C  1- N  2      0.00011     0.57010
  11. BD*( 1) C  1- H  3      0.01533     0.68699
  12. BD*( 1) C  1- H  4      0.00765     0.69611
  13. BD*( 1) C  1- H  5      0.00765     0.69611
  14. BD*( 1) N  2- H  6      0.00427     0.68044
  15. BD*( 1) N  2- H  7      0.00427     0.68044
  16. RY ( 1) C  1            0.00104     0.97087
  17. RY ( 2) C  1            0.00032     1.02058
  18. RY ( 3) C  1            0.00022     1.52988
  19. RY ( 4) C  1            0.00002     1.40784
  20. RY ( 1) N  2            0.00114     1.48818
  21. RY ( 2) N  2            0.00042     1.59197
  22. RY ( 3) N  2            0.00039     2.06927
  23. RY ( 4) N  2            0.00002     2.25600
  24. RY ( 1) H  3            0.00176     0.94849
  25. RY ( 1) H  4            0.00096     0.94477
  26. RY ( 1) H  5            0.00096     0.94477
  27. RY ( 1) H  6            0.00123     0.99809
  28. RY ( 1) H  7            0.00123     0.99809
            --------------------------------
               Total Lewis   17.95101  ( 99.7278%)
           Valence non-Lewis  0.03928  (  0.2182%)
           Rydberg non-Lewis  0.00971  (  0.0539%)
            --------------------------------
               Total unit  1  18.00000  (100.0000%)
               Charge unit  1   0.00000

Maximum scratch memory used by NBO was 32668 words
```

This table allows one to quickly identify the principal delocalizing acceptor orbitals associated with each donor NBO, and their topological relationship to this NBO, i.e., whether attached to the same atom (geminal, "g"), to an adjacent bonded atom (vicinal, "v"), or to a more remote ("r") site. These acceptor NBOs will generally correspond to the principal "delocalization tails" of the NLMO associated with the parent donor NBO. [For example, in the table

above, the N lone pair (NBO 3) is seen to be the lowest-occupancy (1.9874 electrons) and highest-energy (−0.4475 a.u.) Lewis NBO, and to be primarily delocalized into antibonds 11, 12, 13 (the vicinal σ^*_{CH} NBOs). The summary at the bottom of the table shows that the Lewis NBOs 1-9 describe about 99.7% of the total electron density, with the remaining non-Lewis density found primarily in the valence-shell antibonds (0.0393 electrons, mostly in NBO 11).]

NBO output concludes by reporting the maximum amount of scratch memory used during the calculation.

Section B: NBO USER'S GUIDE

B.1 INTRODUCTION TO THE NBO USER'S GUIDE AND NBO KEYLISTS

Section B constitutes the general user's guide to the NBO program. It assumes that the user has an installed electronic structure system (ESS) with attached NBO program, a general idea of what the NBO method is about, and some acquaintance with standard NBO terminology and output data. If you are completely inexperienced in these areas, read Section A ("Getting Started") for the necessary background to this Section. The NBO User's Guide describes core NBO options (Sec. B.1-B.6), the GenNBO program (Sec. B.7), and the NBO-based supplementary modules (Sec. B.8 *et seq.*).

The NBO User's Guide describes how to use the NBO program by modifying your input file to the ESS program to get some NBO output. The modification consists of adding a list of *keywords* in a prescribed *keylist* format. Four main keylist ($KEY) types are recognized ($NBO, $CORE, $CHOOSE, and $DEL), and these will be described in turn in Sections B.2-B.5. Other keylists are specific to GenNBO or NBO-based supplementary modules, described in subsequent sections. Some of the details of inserting NBO keylists into the input file depend on the details of your ESS method, and are described in the appropriate Appendix for the ESS. However, the general form of NBO keylists and the meaning and function of each keyword are identical for all versions (insofar as the option is meaningful for the ESS), and are described herein.

The four keylist types have common rules of syntax: Keylist delimiters are identified by a "$" prefix. Each keylist begins with the parent keylist name (e.g., "$NBO"), followed by any number of keywords, and ended with the word "$END"; for example,

```
    $NBO   keyword-1   keyword-2   . . .    $END      !comment
```

The keylist is "free format," with keywords separated by commas or any number of spaces. An NBO option is activated by simply including its keyword in the appropriate keylist. The order of keywords in the principal $NBO keylist does not matter, but multiple keylists must be given in the order (1) $NBO, (2) $CORE, (3) $CHOOSE, (4) $DEL of presentation in Sections B.2-B.5. Keywords may be typed in upper or lower case. A keylist can be continued to any number of lines, but all the entries of a keylist must appear in a distinct set of lines, starting with the $KEY delimiter on the first line and ending with the closing $END on the last line (i.e., no two $KEY lists should

share parts of the same line). As the above example indicates, any line in the keylist input may terminate with an exclamation point (!) followed by 'comment' of your choice; the "!" is considered to terminate the line, and the trailing 'comment' is ignored by the program.

Recognized $NBO keylist entries are echoed near the top of NBO output, and unrecognized entries are flagged above the NBO banner.

B.2 THE $NBO KEYLIST

B.2.1 Overview of $NBO keywords

The $NBO keylist is the principal means of specifying NBO job options and controlling output, and must precede any other keylist ($CORE, $CHOOSE, or $DEL) in your input file. Basic keywords that can appear in a $NBO keylist are grouped as follows (other "semi-documented" keywords are described in Sec. B.2.7, and keywords of NBO supplemental programs are described in Sec. B.8 *et seq.*):

Job Control Keywords:

NPA	NBOSUM	NOBOND	SKIPBO
NBO	MSPNBO	3CBOND	NLMO

Job Threshold Keywords:

BEND	E2PERT	DIPOLE

Matrix Output Keywords:

AONAO	AONHO	AONBO	AONLMO	AOMO
AOPAO	AOPNAO	AOPNHO	AOPNBO	AOPNLMO
NAONHO	NAONBO	NAONLMO	NAOMO	NHONBO
NHONLMO	NHOMO	NBONLMO	NBOMO	NLMOMO
DIAO	DINAO	DINHO	DINBO	DINLMO
DIMO	DMAO	DMNAO	DMNHO	DMNBO
DMNLMO	DMMO	DMPNAO	FAO	FNAO
FPNHO	FNHO	FPNBO	FNBO	FNLMO
FMO	KAO	KNAO	KNHO	KNBO
KNLMO	KMO	VAO	VNAO	VNHO
VNBO	VNLMO	VMO	SAO	SPAO
SPNAO	SPNHO	SPNBO	SPNLMO	

Other Output Control Keywords:

FILE	DETAIL	BNDIDX	AOINFO
PLOT	ARCHIVE	NBODAF	DIST

Print Level Control:

PRINT=n

B.2 THE $NBO KEYLIST

Keywords are first listed and described according to these formal groupings in
Sections B.2.2-B.2.6. Section B.6 illustrates the effect of commonly used
$NBO keywords (as well as other keylists) on the successive stages of
NAO/NBO/NLMO transformation and subsequent energy or dipole analysis,
with sample output for these keyword options.

Some keywords of the $NBO keylist require (or allow) numerical values or
other parameters to specify their exact function. In this case, the numerical
value or parameter must immediately follow the keyword after an equal sign
(=) or any number of blank spaces. Examples:

```
    E2PERT=2.5    NBOMO W25
```

(The equal sign is recommended, and will be used in the remaining examples.)

B.2 THE $NBO KEYLIST

B.2.2 Job Control Keywords

The keywords in this group activate or deactivate basic tasks to be performed by the NBO programs, or change the way the NBO search is conducted. Each keyword is described in terms of the option it activates (together with an indication of where the option is useful):

KEYWORD	*OPTION DESCRIPTION*
NPA	Request Natural Population Analysis and printing of NPA summary tables (Section A.3.2). This keyword also activates calculation of NAOs, except for semi-empirical ESS methods.
NBO	Request calculation of NBOs and printing of the main NBO table (Section A.3.3).
NBOSUM	Request printing of the NBO summary table (Section A.3.6). This combines elements of the NBO table and 2nd-order perturbation theory analysis table (see below) in a convenient form for recognizing the principal delocalization patterns.
MSPNBO	Request "maximum spin-paired" NBOs from the spin-averaged density matrix (rather than the separate density matrices for α and β spin), as suggested by Michl and coworkers [*J. Am. Chem. Soc.* **114**, 10631 (1992)]. This has no effect for closed-shell systems, but gives an alternative (somewhat less accurate) description of open-shell systems. MSPNBO is useful when the ESS provides no spin information (e.g., GUGA algorithm).
NOBOND	Request that no bonds (2-center NBOs) are to be formed in the NBO procedure (Section B.6.7). The resulting NBOs will then simply be 1-center atomic hybrids. (Useful for highly ionic species.)
3CBOND	Request search for 3-center, 2-electron bonds (Section B.6.8; for 3-center, 4-electron hyperbonds, see Sec. B.16.). The normal default is to search for only 1- and 2-center NBOs. (Useful for diborane and other electron-deficient `bridged' species.)
SKIPBO	Skip the computation of NBOs, i.e., only determine NAOs and perform natural population analysis. (Useful when only NPA is desired.)
NLMO	Compute and print out the summary table of Natural Localized Molecular Orbitals (Section B.6.2). NLMOs are similar to Boys or Edmiston-Ruedenberg LMOs, but more efficiently calculated. (Useful for `semi-localized' description of an SCF or correlated wavefunction, and activated automatically by NLMO-related keywords such as DIPOLE, STERIC, NCS, NJC.)

B.2 THE $NBO KEYLIST

Note that the SKIPBO keyword has higher precedence than other keywords in this list, so that keywords with which it is implicitly in conflict (e.g., NBO, 3CBOND, NLMO) will be ignored if SKIPBO is included in the $NBO keylist.

B.2.3 Job Threshold Keywords

The keywords in this group also activate new tasks to be performed by the NBO program, but these keywords may be modified by one or more parameters (thresholds) that control the precise action to be taken. (In each case the keywords may also be used without parameters, accepting the default values [in brackets].)

KEYWORD	parameter(s)	OPTION DESCRIPTION
BEND	ang, pct, occ	Request the NHO Directional Analysis table (Section A.3.4). The three parameters [and default values] have the following significance: ang [1.0] = threshold angular deviation for printing pct [25] = threshold percentage p/d-character for printing occ [0.1] = threshold NBO occupancy for printing Parameter values may be separated by a space or a comma; for example: BEND=2,10,1.9 This example specifies that the bond-bending table should only include entries for angular deviations of at least 2 (ang), hybrids of at least 10% p/d-character (pct), and NBOs of occupancy at least 1.9 electrons (occ).
E2PERT	eval	Request the Perturbation Theory Energy Analysis table (Section A.3.5), where eval [0.5] = threshold energy (in kcal/mol) for printing Entries will be printed for NBO donor-acceptor interaction energies that exceed the `eval' threshold; for example: E2PERT=5.0 This example would print only interactions of at least 5 kcal/mol (i.e., only the single entry for the 8.13 kcal/mol $n_N \rightarrow \sigma^*_{CH}$ interaction in the output of Section A.3.5).
DIPOLE	dval	Request the Molecular Dipole Moment Analysis table (Section B.6.3), where

		dval [0.02] = threshold dipole moment (Debye) for printing The program will carry out a decomposition of the total molecular dipole moment in terms of localized NLMO and NBO contributions, including all terms whose contribution (in vector norm) exceeds the 'dval' threshold, e.g., `DIPOLE=0.1` This example prints out dipole contributions of all NBOs (and their delocalization interactions) of magnitude ≥ 0.1 D.

Both the BEND and E2PERT keywords are activated by default at the standard PRINT level option (see Section B.2.6). Note that the DIPOLE keyword leads to an analysis in terms of both NBOs and NLMOs, so that the NLMO keyword (Section B.2.2) is automatically activated in this case.

B.2 THE $NBO KEYLIST

B.2.4 Matrix Output Keywords

The keywords in this group activate the printing of various matrices to the output file, or their writing to (or reading from) external disk files. The large number of keywords in this group provide great flexibility in printing out the details of the successive transformations,

input AOs → (PNAOs) → NAOs → NHOs → NBOs → NLMOs → canonical MOs

or the matrices of various operators in the natural localized basis sets. This ordered sequence of transformations forms the basis for naming the keywords.

Keyword Names

The keyword for printing the matrix for a particular basis transformation, IN → OUT, is constructed by concatenating the acronymns for the two sets (in generic form "INOUT"). For example, the transformation AO → NBO is keyed as "AONBO", while that from NBOs to NLMOs is correspondingly "NBONLMO". The transformations are always specified in the ordered sequence shown above (i.e., "AONBO" is allowed, but "NBOAO" is an unrecognized `backward' keyword). Keywords are recognized for *all possible* transformations from the input AOs to other sets (NAO, NHO, NBO, NLMO, MO, or "pure" PAO, or the pre-orthogonal PNAO, PNHO, PNBO, PNLMO sets) in the overall sequence leading to canonical MOs, i.e.,

$$\textit{AO basis: } \text{AONAO AONHO AONBO AONLMO AOMO}$$
$$\text{AOPNAO AOPNHO AOPNBO AOPNLMO AOPAO}$$

and from each of the orthonormal natural localized sets to sets lying to the right in the sequence, i.e.,

NAO basis: NAONHO   NAONBO   NAONLMO NAOMO
NHO basis: NHONBO   NHONLMO NHOMO
NBO basis: NBONLMO NBOMO
NLMO basis: NLMOMO

The matrix $T_{IN,OUT}$ for a specified IN → OUT transform has rows labelled by the IN set and columns labelled by the OUT set.

One can also print out the matrix representations of the Fock or Kohn-Sham matrix (F), kinetic energy matrix (K), 1-e potential energy matrix (V), density matrix (DM), or dipole moment matrix (DI) in the AO or MO set or any of the

B.2 THE $NBO KEYLIST

natural localized sets (NAO, NHO, NBO, or NLMO). The corresponding
keyword is constructed by concatenating the abbreviation for the operator (M)
with that for the set (SET) (in generic form "MSET"). For example, to print the
Fock matrix (F) in the NBO set, use the keyword "FNBO," and to print the
dipole matrix in the NLMO basis, use "DINLMO." (For the dipole matrix
keywords, all three vector components will be printed.) One can also print out
elements of the overlap matrix (S) in the input AO or "pure" PAO bases or any
of the `pre-orthogonal' sets (PNAO, PNHO, PNBO, or PNLMO), using, e.g.,
"SPNAO" for the overlap matrix in the PNAO basis. The Fock operator is also
provided in PNHO and PNBO sets (FPNHO, FPNBO) and the density matrix
in the PNAO basis (DMPNAO). The list of allowed keywords for operator
matrices is:

energy matrices FAO	FNAO	FNHO	FNBO	FNLMO	FMO
FMO	FPNHO	FPNBO			
KAO	KNAO	KNHO	KNBO	KNLMO	KMO
VAO	VNAO	VNHO	VNBO	VNLMO	VMO

density matrix DMAO	DMNAO	DMNHO	DMNBO	DMNLMO	DMMO
DMPNAO					

dipole matrix DIAO	DINAO	DINHO	DINBO	DINLMO	DIMO

overlap matrix SAO	SPNAO	SPNHO	SPNBO	SPNLMO	SPAO

Other desired transformations can be readily obtained from the keyword
transformations by matrix multiplication.

Keyword Parameters

Each generic matrix keyword ("MATKEY") can include a parameter that
specifies the output operation to be performed on the matrix. The allowed
MATKEY parameters are of two types (three for AONAO, NAONBO; see
below):

MATKEY=P[c] (print out the matrix in the standard output file, 'c' columns)

MATKEY=W[n] (write out the matrix to disk file *n*)

The first (P[c]) parameter is used to control output to the standard output file.
When the MATKEY keyword is inserted in the $NBO keylist with no
parameters, the matrix is by default printed (in its entirety) in the standard

output file. Thus, "MATKEY=P" would be equivalent to "MATKEY", with no parameters. The complete `P[c]' form of the print parameter serves to truncate the printed matrix output to a specified number of columns [c]. For example, to print out only the first 16 columns of the NBO→MO transformation matrix, use the form

```
    NBOMO=P16          (print 16 columns)
```

For certain matrices, one can also restrict printing to only the valence (VAL) or Lewis (LEW) columns with modified `[c]' specifiers. For the transformations to MOs, use the form

```
    MATKEY=PVAL        (print core + valence MO columns only)
```

where "MATKEY" is AOMO, NAOMO, NHOMO, NBOMO, or NLMOMO (only). This will print out only the occupied MOs and the lowest few unoccupied MOs, e.g., the six lowest virtual MOs of the methylamine example (Section A.3), though not necessarily those with predominant valence character. Similarly, for the transformations to NBOs or NLMOs, use the form

```
    MATKEY=PLEW        (print Lewis orbital columns only)
```

where "MATKEY" is AONBO, NHONBO, NAONBO, AONLMO, NAONLMO, NHONLMO, NBONLMO (or AOMO, NAOMO, NHOMO, NBOMO, NLMOMO). This prints out the Lewis NBOs or occupied MOs only, e.g., only the nine occupied NBOs or MOs of the methylamine example. Judicious use of these print parameters keeps printed output within reasonable bounds in calculations with large basis sets.

The second type of MATKEY parameter (W[n]) is used to write the matrix (in its entirety) to a specified disk file [n]. By default, each keyword transformation matrix is associated with a logical file number (LFN) in the range 32-49, as tabulated below:

matrix	default LFN	matrix	default LFN	matrix	default LFN
AOPNAO	32	AOPNBO	36	AOMO	40
AONAO	33	AONBO	37	DMAO	41
AOPNHO	34	AOPNLMO	38	NAONBO	42
AONHO	35	AONLMO	39	others	49

When the "MATKEY=Wn" keyword is inserted in the $NBO keylist with no `n' specifier, the matrix is by default written out (in its entirety) to this LFN.

Thus, "AOPNAO=W" is equivalent to "AOPNAO=W32" for the first entry of the table. Use the "Wn" parameter to direct output to any non-default LFN disk file. For example, the keyword

```
AONBO=W51
```

would write out the AO→NBO transformation to LFN=51 (rather than default LFN=37).

The format of the printed output under the print `P' parameter differs from that written to an external file under the `W' parameter. The `P' output (intended for a human reader) includes an identifying label for each row, and gives the numerical entries to somewhat lesser precision (F8.4 format) than the corresponding `W' output (F15.9 format), which is usually intended as input to another program. Use the "MATKEY=W6" keyword to route the more precise `W' form of the matrix to the standard output file, LFN 6.

For the operator matrices (only), one can also request printing of specific i,j matrix elements, rather than the entire table, by means of a *bracket list*. This is a list of the form $<i_1 j_1/i_2 j_2/.../i_n j_n>$ that follows the main keyword (separated by at least one space). For example, the command

```
FNBO <6 6/7 13/8 14>
```

would print out only the matrix elements $F_{6,6}$, $F_{7,13}$ and $F_{8,14}$ of the NBO Fock matrix.

For the AONAO, NAONBO matrices (only), one can also include a read parameter (R), e.g.,

```
NAONBO=R[n]
```

which causes the matrix to be input to the program from a file (perhaps written with the "AONAO=W" or "NAONBO=W" keyword on a previous run). This parameter has the effect of `freezing' orbitals to a set prescribed in the input file (thus bypassing the NBO optimization of these orbitals for the molecular system). For example, the keyword "NAONBO=R44" would have the effect of freezing the NAO → NBO transformation coefficients to the form specified in LFN 44 (perhaps written with the "NAONBO=W44" keyword in a previous calculation on isolated molecules, and now to be used in a calculation on a molecular complex). Similarly, the keywords "AONAO=R   FILE=C2H4" could be used to force the analysis of an excited state to be carried out in terms

of the NAOs of the ground state stored in file "C2H4.33" (previously written out with the "AONAO=W" keyword).

[A third output option is the *checkpoint* (C) option (of generic form "MATKEY=C"), which allows orbital transformation info to be stored in the ESS checkpoint file (see Sec. B.12).]

B.2 THE $NBO KEYLIST

B.2.5 Other Output Control Keywords

The keywords in this group also help to control the I/O produced by a specified set of job options, and thus supplement the keywords of the previous section. However, the keywords of this section steer the flow of information that is routinely produced by the NBO program (or can be passed through from the ESS program) without materially affecting the actual jobs performed by the NBO program. The options associated with each keyword are tabulated below:

KEYWORD	*OPTION DESCRIPTION*
FILE=name	Specify a job*name* stem for NBO file I/O. For example, "FILE=ch3nh2" could be used for methylamine (leading to a "ch3nh2.47" archive file, etc.). This helps identify NBO output (PLOT files, etc.) from different jobs.
DETAIL	Request additional details of the NBO search. This option (primarily for programming and debugging purposes) records details of the NBO loops over atoms and atom pairs, enroute to the final NBOs.
BNDIDX	Request print-out of the NAO-Wiberg Bond Index array and related valency indices (Section B.6.5). (The Wiberg bond index is routinely used to screen atom pairs for possible bonding in the NBO and NRT searches, but the values are not printed unless the BNDIDX keyword is activated.)
AOINFO	Request writing of information concerning the AO basis set (geometrical positions, orbital exponents, contraction coefficients, etc.) to an external file, LFN 31. This provides minimal information needed by the ORBPLOT orbital contour plotting programs (cf. "PLOT" keyword below.)
PLOT	Request writing of plot files required by orbital contour plotting program *NBOView*. This activates the AOINFO keyword as well as other matrix output keywords (AONBO=W, etc.) needed by *NBOView*.
ARCHIVE=n	Request writing the FILE47 archive file (Sec. B.7) to external disk file LFN = n, or, if "=n" is not present, to the default LFN = 47). This file can serve as the input file to run the GenNBO program in stand-alone mode, to repeat the NBO analysis (possibly with new job options) without repeating the calculation of the wavefunction.
NBODAF=n	Request writing the NBO direct access file (DAF) to external disk file LFN = n, or, if "=n" is not present, to the default LFN = 48.
DIST	Print out an atomic distance table (primarily for convenience in GenNBO

	applications). This keyword is turned on automatically when BNDIDX or NRT are requested under GenNBO.

B.2.6 Print Level Keywords

The keyword "PRINT=n" (*n* = 0-4) can be used to give flexible heirarchical control of all NBO output in terms of a specified print level *n*. This keyword activates groups of keywords in a heirarchical manner, and thus incrementally increases the volume of output, ranging from *no* NBO output (PRINT=0) to a considerable volume of detail (PRINT=4). The keywords associated with each print level are tabulated below [default value, PRINT=2]:

print level	additional output or activated keywords
0	suppress *all* output from the NBO program
1	activate NPA and NBO keywords
[2]	activate BEND, NBOSUM, and E2PERT keywords
3	activate NLMO, DIPOLE, and BNDIDX keywords
4	activate all(!) keywords

For each print level *n*, the NBO output will include items activated by the listed keywords, as well as all items from lower print levels.

When additional keywords are included with a "PRINT=n" keyword in the $NBO keylist, the NBO output includes the additional keyword items as well as those implied by the print level. This can be used to tailor the NBO output to virtually any selection of output items. For example, the keylist

```
    $NBO  PRINT=2  NLMO  FNBO=P  NAOMO=P11  $END
```

would add to the standard methylamine output file of Section A.3 an NLMO summary table, the Fock matrix in the NBO basis, and the transformation coefficients for the first 11 molecular orbitals in terms of NAOs. Similarly, to produce the NPA listing only, one could use either form shown below

```
    $NBO  PRINT=1  SKIPBO  $END
    $NBO  PRINT=0  NPA  $END
```

[There is actually a slight difference between the two examples: The NBOs are determined by default (once the $NBO keylist is encountered), even if all output is suppressed with PRINT=0; in the first example, the keyword SKIPBO bypasses NBO determination, whereas in the second example the NBOs are still determined `in background.']

B.2 THE $NBO KEYLIST

B.2.7 Semi-Documented Additional Keywords

Some additional keywords are listed below (primarily of use to specialists or program developers):

KEYWORD	OPTION DESCRIPTION
THRESH=val	Set the threshold of orbital occupancy desired for bond orbital selection. If this is not included, the default occupancy [1.90] will be used (or values decreasing from 1.90 to 1.50 by 0.10 steps).
PRJTHR=val	Set the projection threshold [default 0.20] to determine if a `new' hybrid orbital has too high overlap with hybrids previously found.
MULAT	Print total gross Mulliken populations by atom.
MULORB	Print gross Mulliken populations, by orbital and atom. (This keyword also activates printing the Mayer-Mulliken bond order and valency indices if BNDIDX is active.)
RPNAO	Revises PAO to PNAO transformation matrix by post-multiplying by T_{Ryd} and T_{red} [A. E. Reed, R. B. Weinstock, and F. Weinhold, J. Chem. Phys. **83**, 735-746 (1985)].
PAOPNAO	Input or output of pure AO (PAO) to pre-NAO (PNAO) transformation. The PAOs are AOs of pure angular momentum symmetry (rather than cartesian gaussians). This keyword can be used with read (`R'), write (`W', default LFN 43) or print (`P') parameters.
BOAO	Print the bond-order matrix (Fock-Dirac density matrix) in the basis set of input AOs. This keyword can be used with write (`W', default LFN 49) or print (`P') parameters.
SVEC	Print the eigenvectors of the overlap matrix in the AO basis.
FIXDM	Massage the input density matrix to remove unphysical occupancies (negative or Pauli-violating values) while preserving integer number of electrons. NBO analysis then begins from a modified density matrix that is "close" to the input density matrix, but is (in principle) N-representable. FIXDM merely camouflages, but does not fundamentally remove, non-physical aspects of certain non-variational densities (e.g., MP2, RhoCI, or CIS density). It should be used with caution.

B.3 THE $CORE LIST

In the Lewis structure picture, the inner core electron pairs are pictured as occupying orbitals having essentially isolated atomic orbital character. In NBO parlance, these core orbitals correspond to 1-center unhybridized NAOs of near-maximum occupancy, which are isolated on each center before the main NBO search begins for localized valence electron pairs. A warning message is printed if the occupancy of a presumed closed-shell core NBO falls below 1.9990 electrons (or 0.9990 in the open-shell case), indicative of a possible core-valence mixing effect of physical significance.

The NBO program contains a table giving the nominal number of core orbitals to be isolated on each type of atom (e.g., $1s$ for first-row atoms Li-Ne, $1s$, $2s$, $2p$ for second-row atoms Na-Ar, etc.). At times, however, it is interesting to examine the effect of allowing core orbitals to mix into the bonding hybrids, or to hybridize (polarize) among themselves. This can be accomplished by including a $CORE keylist to specify the number of core orbitals to be isolated on each atomic center, thus modifying the nominal core table. Unlike other NBO keylists, the $CORE list includes only integers (rather than keywords) to specify the core modifications, but the rules are otherwise similar to those for other keylists. The $CORE list (if included) must follow the $NBO keylist and precede the $CHOOSE or $DEL keylists.

The format of the $CORE modification list is:

first line:	The keyword "$CORE"
next lines:	Pairs of integers, one pair for each center. The first integer indicates the atomic center (in the numbering of the main ESS) and the second is the number of core orbitals to be isolated on that atom. Note that atomic centers not included in the CORE list are assigned default cores.
last line:	The keyword "$END", to indicate the end of core input.

The entire list may also be condensed to a single line, but the word "$CORE" must occur as the first word of the line and "$END" as the last word; that is, the core modification keylist cannot continue on a line that contains other keylist information.

B.3 THE $CORE LIST

The core orbitals are isolated by occupancy, the most occupied NAOs being first selected, and full subshells are isolated at a time. Thus, for example, to select the five orbitals of the $n = 1$ and $n = 2$ shells as core orbitals, it would make no difference to select "3" or "4" (instead of "5"), since all three of these choices would specify a core containing a $1s$, $2s$, and all three $2p$ orbitals. The $CORE modification list is read only once, and applies to both α and β spin manifolds in an open-shell calculation.

An example, appropriate for Ni(1)-C(2)-O(3) with the indicated numbering of atoms, is shown below:

```
$CORE
  1    5
$END
```

This would direct the NBO program to isolate only 5 core orbitals on Nickel (atom 1), rather than the nominal 9 core orbitals. In other words, only $1s$, $2s$, and $2p$ orbitals will be considered as core orbitals in the search for NBOs of NiCO, allowing the $3s$ and $3p$ orbitals to mix with valence NAOs in bond formation. Since the carbon and oxygen atoms were not included in the modification list, the nominal set of core orbitals ($1s$ only) is isolated on each of these atoms.

[The alternative example

```
$CORE   1  0    2  0    3  0    $END
```

(no cores) would allow all NAOs to be included in the NBO search (equivalent to the default treatment in the earliest version of the program).]

B.4 THE $CHOOSE KEYLIST (DIRECTED NBO SEARCH)

A $CHOOSE keylist requests that the NBO search be directed to find a particular Lewis structure (`resonance structure') chosen by the user. (This is useful for testing the accuracy of alternative resonance structure representations of the wavefunction, relative to the optimal Lewis structure returned in a free NBO search.) In the $CHOOSE list, a resonance structure is specified by indicating where lone pairs and bonds (including multiple bonds) are to be found in the molecule. In some cases, the user may wish to specify only the location of bonds, letting the NBO algorithm seek the best location for lone pairs, but it is usually safest to completely specify the resonance structure, both lone pairs and bonds.

The format of the $CHOOSE list is:

first line:	The keyword "$CHOOSE"
next line:	The keyword "ALPHA" (only for open-shell wavefunction)
next lines:	If one-center (`lone') NBOs are to be searched for, type the keyword "LONE" followed by a list of pairs of numbers, the first number of each pair being the atomic center and the second the number of valence lone pairs on that atom. Terminate the list with "END". (Note that only the occupied *valence* lone pairs should be entered, since the number of core orbitals on each center is presumed known.) If two-center (`bond') NBOs are to be searched for, type the keyword "BOND", followed by the list of bond specifiers, and terminated by "END". Each bond specifier is one of the letters "S" single bond "D" double bond "T" triple bond "Q" quadruple bond "P" pentuple bond "H" hextuple bond

	followed by the two atomic centers of the bond (e.g., "D 9 16" for a double bond between atoms 9 and 16).
	If three-center NBOs are to be searched for, type the keyword "3CBOND", followed by the list of 3-c bond specifiers, and terminated by "END". Each 3-c bond specifier is again one of the letters "S" (single), "D" (double), "T" (triple), or "Q" (quadruple), followed by three integers for the three atomic centers (e.g., "S 4 8 10" for a single three-center bond 4-8-10). (Note that the 3CBOND keyword of the $NBO keylist is implicitly activated if 3-c bonds are included in a $CHOOSE list.)
next line:	The word "END" to signal the end of the α spin list.
next line:	The keyword "BETA" (for open-shell wavefunctions)
next lines:	The input for β spin, same format as above. The overall $CHOOSE list should always end with the "$END" keyword.

Two examples will serve to illustrate the $CHOOSE format (each is rather artificial, inasmuch as the specified $CHOOSE structure corresponds to the `normal' structure that would be found by the NBO program):

(1) The closed-shell H-bonded complex FH··CO, with atom numbering F(1)-H(2)··C(3)-O(4), might be specified as

```
$CHOOSE
    LONE   1   3
           3   1
           4   1      END
    BOND   S   1   2
           T   3   4   END
$END
```

This would direct the NBO program to search for three lone pairs on atom F(1), one lone pair on atom C(3), one lone pair on atom O(4), one bond between F(1)-H(2), and three bonds between C(3)-O(4).

(2) The open-shell FH··O_2 complex, with atom numbering F(1)-H(2)··O(3)-O(4), and with the unpaired electrons on O_2 being of α spin, might be specified as

```
$CHOOSE
  ALPHA
    LONE   1   3
           3   3
```

```
               4   3        END
        BOND   S   1   2
               S   3   4    END
     END
     BETA
        LONE   1   3
               3   1
               4   1        END
        BOND   S   1   2
               T   3   4    END
     END
   $END
```

Note that this example incorporates the idea of "different Lewis structures for different spins," with a distinct pattern of localized 1-c (`lone') and 2-c (`bond') functions for α and β spin.

As with other keylists, the $CHOOSE keylist can be condensed to a smaller number of lines, as long as no line is shared with another keylist. The order of keywords within the $CHOOSE keylist should be as shown above (i.e., ALPHA before BETA, LONE before BOND, etc.), but the order of entries within a LONE or BOND list is immaterial. A $CORE keylist (if present) must precede the $CHOOSE list.

B.5 THE $DEL KEYLIST (NBO ENERGETIC ANALYSIS)

B.5.1 Introduction to NBO Energetic Analysis

The fourth and final type of keylist is a deletions ($DEL) keylist, to activate NBO energetic analysis. (NEDA input is also handled by the $DEL keylist, and will be described in Sec. B.11.) Standard NBO energetic analysis is performed by (1) deleting specified elements (or blocks of elements) from the NBO Fock matrix, (2) diagonalizing this new Fock matrix to obtain a new density matrix, and (3) passing this density matrix to the SCF routines for a single pass through the SCF energy evaluator. The difference between this `deletion' energy and the original SCF energy provides a useful measure of the energy contribution of the deleted terms. Since a Fock (or Kohn-Sham) matrix is required, the energetic analysis is performed only for RHF, UHF, and corresponding DFT levels. For deletion type (2), element deletions can optionally be performed on the NAO or NHO Fock matrix.

Input for the NBO energetic analysis is through the $DEL keylist, which specifies the deletions to be performed. Multiple analyses (deletions) can be performed during a single job, with each deletion included in the overall $DEL keylist. The nine distinct types of deletions input are described in Section B.5.2 below.

The deletions keylist begins with the "$DEL" keyword. For the analysis of UHF wavefunctions, the deletions for the α and β spin manifolds must be separately specified (see Section B.5.3). Otherwise, the input for closed shells RHF and UHF is identical. The input is free format and the input for a single deletion can be spread over as many lines as desired. The desired deletions should be listed one after the other. After the last deletion, the word "$END" signals the end of the keylist.

WARNING
If symmetry is used, one must be careful to only do deletions that will preserve the symmetry of the electronic wavefunction!! Otherwise, the energy of the deletion will be incorrect and the variational principle may be violated. (For example, if symmetry is used for ethane, it is permissible to do a "LEWIS" (a.k.a. "NOSTAR") deletion, but not the deletion of a single C-H antibond.) The remedy is not to use symmetry in the SCF calculation.

In describing the deletion types, use is made of the terms "molecular unit" and "chemical fragment." The NBO program looks at the chemical bonding pattern

produced by the bonding NBOs and identifies the groups of atoms that are linked together in distinct "molecular units" (usually synonymous with "molecules" in the chemical sense). The first atom that is not in molecular unit 1 will be in molecular unit 2, and so forth. For example, if the list of atoms is C(1), H(2), F(3), O(4), and bonding NBOs are found between C(1)-O(4) and H(2)-F(3), then molecular unit 1 will be CO and molecular unit 2 will be HF. A "chemical fragment" is taken to be any subset of the atoms, usually (but not necessarily) in the same molecular unit, and usually (but not necessarily) connected by bond NBOs. Typically, a chemical fragment might be specified to be a single atom, the four atoms of a methyl group, or any other `radical' of a molecular unit, identified by giving the atom numbers of which the fragment consists.

B.5 THE $DEL KEYLIST (NBO ENERGETIC ANALYSIS)

B.5.2 The Nine Deletion Types

The keywords and format to specify each of the nine allowed deletion types are described below. Except for type (2), deletions refer to NBOs only.

(1) Deletion of entire orbitals.

This is called for by typing "DELETE", then the number of orbitals to be deleted, then the keyword "ORBITAL" (or "ORBITALS"), then the list of the orbitals to be deleted; for example:

```
DELETE  3  ORBITALS  15  18  29
```

[See also deletion types (4) and (7) for deleting sets of orbitals.]

WARNING
The "single-pass" method of evaluating deletion energies is appropriate only for deletions of *low*-occupancy (non-Lewis) orbitals, for which the loss of self-consistency in the Coulomb and exchange potentials (due to redistribution of the electron density of deleted orbitals) is small compared to the net energy change of deletion. It is fundamentally erroneous to delete *high*-occupancy (Lewis) orbitals by this procedure.

(2) Deletion of specific Fock matrix elements.

This is requested by typing "DELETE", then the number of elements to be deleted, then the keyword "ELEMENT" (or "ELEMENTS"), then the list of the elements to be deleted (each as a pair of integers); for example:

```
DELETE  3  ELEMENTS  1 15  3 19  23 2
```

This example would result in the zeroing of the following NBO Fock matrix elements: (1,15), (15,1), (3,19), (19,3), (23,2), (2,23).

For this deletion type (only), one can also specify deletion of elements from the NAO or NHO Fock matrix by merely including the desired basis preceding "ELEMENT." Thus, the command "DELETE 3 NHO ELEMENTS..." would perform the deletions on the NHO Fock matrix.

(3) Deletion of off-diagonal blocks of the Fock matrix.

Each block is specified by two sets of orbitals, and all Fock matrix elements in common between these two sets are set to zero. This is called for by typing

B.5 THE $DEL KEYLIST (NBO ENERGETIC ANALYSIS)

"ZERO", then the number of off-diagonal blocks to be zeroed, and then, for each block, the following:

(1) the dimensions of the block, separated by the word "BY" (e.g., "6 BY 3" if the first set has 6 orbitals and the second set has 3 orbitals);

(2) the list of orbitals in the first set;

(3) the list of orbitals in the second set.

An example is shown below:

```
ZERO   2   BLOCKS   2   BY   5
                          3   4
                          9   10   11   14   19
                  3   BY   2
                          1   2   7
                       20   24
```

This will set the following Fock matrix elements to zero:

(3,9), (3,10), (3,11), (3,14), (3,19), (9,3), (10,3), (11,3), (14,3), (19,3), (4,9), (4,10), (4,11), (4,14), (4,19), (9,4), (10,4), (11,4), (14,4), (19,4), (1,20), (1,24), (2,20), (2,24), (7,20), (7,24) (20,1), (24,1), (20,2), (24,2), (20,7), (24,7)

[Usually, in studying the total delocalization from one molecular unit to another, it is much easier to use deletion type (8) below. Similarly, in studying the total delocalization from one chemical fragment to another, it is easier to use deletion type (9).]

(4) Deletion of all non-Lewis orbitals.

The non-Lewis NBO orbitals correspond to the "unfilled" (acceptor) orbitals of NBO analysis output, unused in the idealized Lewis structure picture. To delete all these orbitals, simply enter "LEWIS". The result of this deletion is the energy of the idealized NBO natural Lewis structure (NLS), with all Lewis NBOs doubly occupied. Unlike other deletions, in which there is a slight loss of variational self-consistency due to the redistributed occupancy of the deleted orbitals, the result of a "LEWIS" deletion corresponds rigorously to the variational expectation value of the determinant of doubly occupied Lewis NBOs. (For compatibility with previous NBO versions, "NOSTAR" is accepted as a synonym for "LEWIS".)

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(5) Deletion of all vicinal delocalizations.

To delete all Fock matrix elements between Lewis NBOs and the vicinal non-Lewis NBOs, simply enter "NOVIC".

(6) Deletion of all geminal delocalizations.

To delete all Fock matrix elements between Lewis NBOs and the geminal non-Lewis NBOs, simply enter "NOGEM".

(7) Deletion of all non-Lewis orbitals on a particular molecular unit.

Unit-based deletions of non-Lewis orbitals are requested by typing "ULEWIS", then the number of molecular units to be described in idealized Lewis structure limit, then the keyword "UNIT" (or "UNITS"), then the list of units; for example:

```
ULEWIS  2  UNITS  3  4
```

(For compatibility with previous NBO versions, "DESTAR" is also accepted as a synonym for "ULEWIS".)

(8) Zeroing all delocalizations from one molecular unit to another.

This is requested by typing "ZERO", then the number of delocalizations to zero, then the keyword "DELOCALIZATION" (can be abbreviated to "DELOC"), and then, for each delocalization, the word "FROM", the number of the donor unit, the word "TO", and the number of the acceptor unit; for example:

```
ZERO  2  DELOC  FROM 1 TO 2   FROM 2 TO 1
```

The above example would zero *all* intermolecular delocalizations between units 1 and 2 (i.e., both $1 \rightarrow 2$ and $2 \rightarrow 1$). The effect is to remove all Fock matrix elements between high-occupancy (core/lone pair/bond) NBOs of the donor unit to the low-occupancy (antibond/Rydberg) NBOs of the acceptor unit. The donor and acceptor units may be the same.

(9) Zeroing all delocalization from one chemical fragment to another.

This is called for by typing "ZERO", then the number of inter-fragment delocalizations to be zeroed, then the words "ATOM BLOCKS", and then, for each delocalization, the following:

B.5 THE $DEL KEYLIST (NBO ENERGETIC ANALYSIS)

(1) the number of atoms in the two fragments, separated by the word "BY" (e.g., "6 BY 3" if the first fragment has 6 atoms and the second has 3 atoms);

(2) the list of atoms in the first fragment;

(3) the list of atoms in the second fragment.

For example, to zero all delocalizations between the fragments defined by atoms (1,2) and by atoms (3,4,5), the $DEL entries would be

```
ZERO   2   ATOM BLOCKS
          2   BY   3
                    1   2
                    3   4   5
          3   BY   2
                    3   4   5
                    1   2
```

In this example, the first block removes the $(1,2) \rightarrow (3,4,5)$ delocalizations, while the second removes the $(3,4,5) \rightarrow (1,2)$ delocalizations.

For additional examples of $DEL input, see Section B.6.10.

B.5 THE $DEL KEYLIST (NBO ENERGETIC ANALYSIS)

B.5.3 Input for UHF Analysis

Deletions of the alpha and beta Fock matrices can be done independently. The deletions are input as above (Section B.5.2) for RHF closed shell, but they must be specified separately for alpha and beta in the UHF case.

The deletion to be done on the alpha Fock matrix must be preceded by the keyword "ALPHA", and the deletion of the beta Fock matrix must be preceded by the keyword "BETA". (Actually, only the first letter "A" or "B" is searched for by the program.) The ALPHA deletion must precede the BETA deletion. The BETA deletion may be the same as the ALPHA deletion, or different.

NOTE: The types of the α NBOs often differ from those of the β NBOs, so that distinct α, β deletions lists are generally required. For example, O_2 (triplet) has one bond in the α system and three in the β system, if the unpaired electrons are in the α system.

Here are three examples to illustrate UHF open-shell deletions:

Example 1:

```
ALPHA   ZERO  1  DELOC   FROM  1  TO  2
BETA    NOSTAR
```

Example 2:

```
ALPHA   ZERO  1  DELOC   FROM  1  TO  2
BETA    ZERO  0  DELOC
```

Example 3:

```
ALPHA   DELETE  0  ORBITALS
BETA    DELETE  1  ORBITAL  8
```

If no deletion is done, this must be specified using zero (0) with one of the deletion input formats, as shown in Examples 2,3 above.

UHF deletions can also be done with MSPNBOs (Sec. B.2.2) by using the following two-step procedure: (i) compute and store the MSPNBOs in a non-$DEL job; (ii) read in the stored MSPNBOs and use them for the $DEL job. The initial job should include the $NBO keywords "MSPNBO NAONBO=W44" to write the MSPNBO NAO→NBO transformation matrix to an external file LFN 44 (cf. Sec. B.2.4), while the second job should include the $NBO keyword "NAONBO=R44" (but *not* MSPNBO) to read in the stored MSPNBOs from LFN 44 for the deletions.

B.5 THE $DEL KEYLIST (NBO ENERGETIC ANALYSIS)

Caveat for DFT Deletions

Density functional methods are often poorly parameterized to evaluate the energetics of $DEL densities, which by nature differ significantly from "usual" densities. The $DEL-based methods may therefore lead to unrealistic DFT energetics. Extreme caution should be exercised in employing $DEL options with DFT methods.

B.6 NBO ILLUSTRATIONS

B.6.1 Introduction

This section illustrates the output produced by several important keyword options of the NBO keylists ($NBO, $CHOOSE, $DEL, $CORE lists), supplementing the illustrations of Section A.3. Excerpts are provided rather than full output, since, e.g., NPA analysis is unaffected by keywords that modify the NBO search. Keywords of general applicability are illustrated with the methylamine example (RHF/3-21G, Pople-Gordon geometry) of Section A.3, which should be consulted for further information. More specialized keywords and options are illustrated with prototype molecules (benzene, diborane, methyl radical).

Sections B.6.2-B.6.8 illustrate representative examples from the $NBO keyword groups, including NLMO, DIPOLE, BNDIDX, NOBOND, 3CBOND, and matrix output keywords. Section B.6.9 and B.6.10 similarly illustrate the use of the $CHOOSE and $DEL keylists. Section B.6.11 illustrates the output for open-shell UHF cases, emphasizing features associated with the "different Lewis structures for different spins" representation of α and β spin manifolds. Section B.6.12 shows the effect of using effective core potentials for Cu_2, also illustrating aspects of the inclusion of *d* functions.

B.6 NBO ILLUSTRATIONS

B.6.2 NLMO Keyword

When the NLMO keyword is activated, the program computes the NLMOs and prints out three tables summarizing their form. For the RHF/3-21G methylamine example (cf. Section A.3), the principal NLMO table is shown below:

```
NATURAL LOCALIZED MOLECULAR ORBITAL (NLMO) ANALYSIS:

Maximum off-diagonal element of DM in NLMO basis: 0.00000009

Hybridization/Polarization Analysis of NLMOs in NAO Basis:
NLMO/Occupancy/Percent from Parent NBO/ Atomic Hybrid Contributions
-----------------------------------------------------------------------------
  1. (2.00000)  99.9504% CR ( 1) C  1
                        99.951%  C  1 s(100.00%)p 0.00(  0.00%)
                         0.013%  H  3 s(100.00%)
                         0.013%  H  4 s(100.00%)
                         0.013%  H  5 s(100.00%)
  2. (2.00000)  99.9763% CR ( 1) N  2
                         0.010%  C  1 s( 22.45%)p 3.45( 77.55%)
                        99.980%  N  2 s(100.00%)p 0.00(  0.00%)
  3. (2.00000)  98.9222% LP ( 1) N  2
                         0.430%  C  1 s(  1.05%)p93.85( 98.95%)
                        98.922%  N  2 s( 18.13%)p 4.51( 81.87%)
                         0.477%  H  3 s(100.00%)
                         0.083%  H  4 s(100.00%)
                         0.083%  H  5 s(100.00%)
  4. (2.00000)  99.9247% BD ( 1) C  1- N  2
                        40.035%  C  1 s( 21.38%)p 3.68( 78.62%)
                        59.891%  N  2 s( 30.79%)p 2.25( 69.21%)
                         0.016%  H  3 s(100.00%)
                         0.022%  H  6 s(100.00%)
                         0.022%  H  7 s(100.00%)
  5. (2.00000)  99.9313% BD ( 1) C  1- H  3
                        59.681%  C  1 s( 25.55%)p 2.91( 74.45%)
                         0.039%  N  2 s(  2.19%)p44.61( 97.81%)
                        40.253%  H  3 s(100.00%)
  6. (2.00000)  99.7012% BD ( 1) C  1- H  4
                        60.854%  C  1 s( 25.29%)p 2.95( 74.71%)
                         0.092%  N  2 s( 14.19%)p 6.05( 85.81%)
                         0.013%  H  3 s(100.00%)
                        38.856%  H  4 s(100.00%)
                         0.016%  H  5 s(100.00%)
                         0.159%  H  6 s(100.00%)
  7. (2.00000)  99.7012% BD ( 1) C  1- H  5
                        60.854%  C  1 s( 25.29%)p 2.95( 74.71%)
                         0.092%  N  2 s( 14.19%)p 6.05( 85.81%)
                         0.013%  H  3 s(100.00%)
                         0.016%  H  4 s(100.00%)
                        38.856%  H  5 s(100.00%)
                         0.159%  H  7 s(100.00%)
  8. (2.00000)  99.7213% BD ( 1) N  2- H  6
                         0.113%  C  1 s(  5.20%)p18.23( 94.80%)
                        67.905%  N  2 s( 25.76%)p 2.88( 74.24%)
                         0.138%  H  4 s(100.00%)
                         0.014%  H  5 s(100.00%)
                        31.817%  H  6 s(100.00%)
  9. (2.00000)  99.7213% BD ( 1) N  2- H  7
                         0.113%  C  1 s(  5.20%)p18.23( 94.80%)
                        67.905%  N  2 s( 25.76%)p 2.88( 74.24%)
                         0.014%  H  4 s(100.00%)
                         0.138%  H  5 s(100.00%)
                        31.817%  H  7 s(100.00%)
```

For each of the nine occupied NLMOs, the table shows first the NLMO occupancy (necessarily 2.0000 at SCF level, as in the present example), the percentage of the total NLMO composition represented by this parent NBO (usually > 99%), and the label of the `parent' NBO. Below this, there follows an NAO decomposition of the NLMO, showing the percentage of the NLMO on each atom and the hybrid composition ratios (effective sp^λ character and percentage s- and p-character) of the NAOs. For example, NLMO 3 is the most delocalized NLMO of the table, having only about a 98.9% contribution from the localized N(2) parent lone pair NBO, with "delocalization tails" composed primarily of contributions (~0.4% each) from C(1) and H(3), and smaller contributions (~0.09%) from H(4) and H(5). This corresponds to what might have been anticipated from the NBO summary table (Section A.3.6) or perturbation theory energy analysis table (Section A.3.5), which showed that the N(2) lone pair, NBO 3, is principally delocalized onto NBO 11, the vicinal C(1)-H(3) antibond [with lesser delocalizations onto NBOs 12, 13, the C(1)-H(4) and C(1)-H(5) antibonds].

B.6 NBO ILLUSTRATIONS

B.6.3 DIPOLE Keyword

The DIPOLE keyword activates the NBO/NLMO analysis of the molecular dipole moment, as shown below for the example of RHF/3-21G methylamine (cf. Section A.3):

```
DIPOLE MOMENT ANALYSIS:

[Print threshold: Net dipole > 0.02 Debye]

                             NLMO bond dipole           NBO bond dipole
                        ------------------------   ------------------------
           Orbital        x     y     z   Total      x     y     z   Total
  =============================================================================
   1. CR ( 1) C 1        0.00  0.00  0.00  0.00     0.00  0.00  0.00  0.00

   2. CR ( 1) N 2        0.00 -0.01  0.00  0.01     0.00  0.00  0.00  0.00

   3. LP ( 1) N 2        0.76  2.84  0.00  2.94     1.00  2.91  0.00  3.08
                                         deloc  11: -0.16 -0.08  0.00  0.18
                                         deloc  12: -0.03 -0.01  0.01  0.03
                                         deloc  13: -0.03 -0.01 -0.01  0.03
                                         deloc  16: -0.01  0.02  0.00  0.03

   4. BD ( 1) C 1- N 2   0.76  0.06  0.00  0.76     0.76  0.08  0.00  0.76

   5. BD ( 1) C 1- H 3  -0.57 -1.88  0.00  1.96    -0.57 -1.88  0.00  1.97
                                         deloc  20: -0.03  0.01  0.00  0.03
                                         deloc  12:  0.01  0.00  0.02  0.02
                                         deloc  13:  0.01  0.00 -0.02  0.02

   6. BD ( 1) C 1- H 4  -0.65  0.79 -1.50  1.81    -0.69  0.81 -1.49  1.83
                                         deloc  14:  0.05  0.00  0.00  0.05
                                         deloc  13:  0.02 -0.03 -0.03  0.04
                                         deloc  11:  0.01  0.02  0.00  0.02

   7. BD ( 1) C 1- H 5  -0.65  0.79  1.50  1.81    -0.69  0.81  1.49  1.83
                                         deloc  15:  0.05  0.00  0.00  0.05
                                         deloc  12:  0.02 -0.03  0.03  0.04
                                         deloc  11:  0.01  0.02  0.00  0.02

   8. BD ( 1) N 2- H 6   0.44 -0.46  0.86  1.07     0.49 -0.47  0.89  1.11
                                         deloc  12: -0.06  0.01 -0.02  0.06

   9. BD ( 1) N 2- H 7   0.44 -0.46 -0.86  1.07     0.49 -0.47 -0.89  1.11
                                         deloc  13: -0.06  0.01  0.02  0.06
                                        -----------------------------------------
        Net dipole moment  0.52  1.66  0.00  1.74     0.79  1.79  0.00  1.96
  Delocalization correction                          -0.26 -0.13  0.00  0.29
                                        -----------------------------------------
      Total dipole moment  0.52  1.66  0.00  1.74     0.52  1.66  0.00  1.74
```

The bottom line of the table shows the individual (x,y,z) vector components (0.52,1.66,0.00) and length (1.74 D) of the total molecular dipole moment, in the coordinate system of the ESS program. This is decomposed in the main body of the table into the individual contributions of "NLMO bond dipoles" (which strictly add to give the net molecule dipole at the SCF level) and "NBO bond dipoles" (which must be added with their off-diagonal `deloc'

B.6 NBO ILLUSTRATIONS

contributions to give the net molecular moment). Each NLMO or NBO bond dipole vector $\boldsymbol{\mu}_{AB}$ is evaluated as

$$\boldsymbol{\mu}_{AB} = \boldsymbol{\mu}_{AB}^{(elec)} + \boldsymbol{\mu}_{AB}^{(nuc)}$$

where $\boldsymbol{\mu}_{AB}^{(elec)} = 2e<\sigma_{AB}|\mathbf{r}|\sigma_{AB}>$ is the electronic dipole expectation value for an electron pair in the σ_{AB} NLMO or NBO, and $\boldsymbol{\mu}_{AB}^{(nuc)}$ is the nuclear contribution of compensating unit positive charges at the positions of nuclei A and B (or both on A for a 1-center NBO). The `deloc' contributions below each NBO bond dipole show the off-diagonal corrections to an additive bond dipole approximation (i.e., the corrections to localized NBO bond dipoles to get the NLMO bond dipoles) to account for the delocalization from parent NBO i onto other (primarily, non-Lewis) NBOs j; in terms of the expansion of an NLMO in the set $\{\sigma_j\}$ of NBOs,

$$\sigma_u^{(NLMO)} = c_{ii}\sigma_i + \sum_j c_{ji}\sigma_j$$

this correction is (for each electron, α or β spin)

$$c_{ji}^2[<\sigma_j|\boldsymbol{\mu}|\sigma_j> - <\sigma_i|\boldsymbol{\mu}|\sigma_i>] + 2\,c_{ii}\,c_{ji}<\sigma_i|\boldsymbol{\mu}|\sigma_j> + \sum_k{}'' c_{ji}\,c_{ki}<\sigma_j|\boldsymbol{\mu}|\sigma_k>$$

where the primes on the summation denote omission of terms k equal to i or j. For example, in the above table the largest individual contribution to $\boldsymbol{\mu}$ is from the nitrogen lone pair, table entry 3, which has an NLMO dipole of 2.94 D or NBO dipole of 3.08 D. The latter has also the largest off-diagonal delocalization correction in the table, a 0.18 D correction due to the $n_N \rightarrow \sigma^*_{CH}$ delocalization into the vicinal C(1)-H(3) antibond, NBO 11. For a post-SCF (correlated) calculation, the dipole table would also include an additional line for the correction due to non-additivity of the NLMO bond dipoles. For an ionic species, there would also be an additional line for the "residual nuclear charge" contribution; here, one must be aware that the dipole moment is calculated with respect to the origin of the cartesian coordinate system chosen by the ESS program (since the dipole moment is origin-dependent in this case).

Note that the amount of detail in the dipole table can be altered by using the "DIPOLE=thr" form of the keyword to alter the threshold dipole (`thr') for printing [default: 0.02 D].

B.6 NBO ILLUSTRATIONS

B.6.4 Matrix Output Keywords

Three simple examples will be given to illustrate the formatting of output for operators or basis set transformation matrices using the matrix output keywords of Section B.2.4. For the RHF/3-21G methylamine example of Section A.3, the keyword "FNHO" would cause the Fock matrix in the NHO basis to be printed out. Shown below is a reproduction of the first eight columns (out of 28) of this output:

```
NHO Fock matrix:

          NHO        1       2       3       4       5       6       7       8
      ---------- ------- ------- ------- ------- ------- ------- ------- -------
   1.  C 1(cr)  -11.0415  0.0481  0.0445 -0.3909 -0.4170 -0.4404 -0.3894 -0.4448
   2.  N 2(cr)    0.0481-15.2590 -0.6352 -0.6146 -0.7039 -0.0060 -0.0248 -0.0133
   3.  N 2(lp)    0.0445 -0.6352 -0.4475 -0.0771 -0.0961  0.1036 -0.0244 -0.0383
   4.  C 1( N 2) -0.3909 -0.6146 -0.0771 -0.0201 -0.7196 -0.0565 -0.0672 -0.0433
   5.  N 2( C 1) -0.4170 -0.7039 -0.0961 -0.7196 -0.3072 -0.0794 -0.0620 -0.0836
   6.  C 1( H 3) -0.4404 -0.0060  0.1036 -0.0565 -0.0794 -0.1401 -0.6760 -0.0642
   7.  H 3( C 1) -0.3894 -0.0248 -0.0244 -0.0672 -0.0620 -0.6760  0.1345 -0.0726
   8.  C 1( H 4) -0.4448 -0.0133 -0.0383 -0.0433 -0.0836 -0.0642 -0.0726 -0.1470
   9.  H 4( C 1) -0.3870 -0.0251  0.0159 -0.0697 -0.0639 -0.0735 -0.0680 -0.6761
  10.  C 1( H 5) -0.4448 -0.0133 -0.0383 -0.0433 -0.0836 -0.0642 -0.0726 -0.0550
  11.  H 5( C 1) -0.3870 -0.0251  0.0159 -0.0697 -0.0639 -0.0735 -0.0680 -0.0746
  12.  N 2( H 6)  0.0387 -0.6791 -0.0981 -0.0935 -0.1495 -0.0247  0.0112  0.0908
  13.  H 6( N 2) -0.0395 -0.4402 -0.0693 -0.1077 -0.0835  0.0006 -0.0233 -0.0108
  14.  N 2( H 7)  0.0387 -0.6791 -0.0981 -0.0935 -0.1495 -0.0247  0.0112 -0.0348
  15.  H 7( N 2) -0.0395 -0.4402 -0.0693 -0.1077 -0.0835  0.0006 -0.0233  0.0016
  16.  C 1(ry)    0.0045  0.1399  0.0217  0.1323 -0.0929 -0.0707  0.0818  0.0014
  17.  C 1(ry)    0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0721
  18.  C 1(ry)   -0.0025  0.1049  0.0203  0.1014 -0.0760  0.0644 -0.0796 -0.0067
  19.  C 1(ry)    0.0030 -0.0297 -0.0025 -0.0276  0.0224 -0.0028  0.0069  0.0673
  20.  N 2(ry)    0.0040  0.0692  0.0026 -0.0160  0.0184  0.0351  0.0167 -0.0179
  21.  N 2(ry)    0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000 -0.0158
  22.  N 2(ry)    0.0799 -0.0572 -0.0015 -0.1798  0.1437  0.0054 -0.0295  0.0035
  23.  N 2(ry)   -0.0257  0.0314  0.0026 -0.0176  0.0131  0.0049 -0.0211  0.0032
  24.  H 3(ry)    0.1157  0.0135 -0.0111 -0.0262  0.0042 -0.2834  0.3498 -0.0237
  25.  H 4(ry)    0.1217  0.0131  0.0106 -0.0240  0.0075 -0.0201  0.0063 -0.2788
  26.  H 5(ry)    0.1217  0.0131  0.0106 -0.0240  0.0075 -0.0201  0.0063 -0.0216
  27.  H 6(ry)    0.0161  0.0889 -0.0026 -0.0119 -0.0182  0.0066 -0.0221 -0.0077
  28.  H 7(ry)    0.0161  0.0889 -0.0026 -0.0119 -0.0182  0.0066 -0.0221  0.0058
```

The NHO labels on each row identify the atom to which the NHO belongs, and (in parentheses) the atom toward which the hybrid is pointed, if a bond hybrid, or a 1-center label (cr, lp, lp*, or ry), if a non-bonded hybrid. Thus, "C 1 (N 2)" (NHO 4) is the bonding hybrid on C(1) directed toward N(2), "N 2(lp)" (NBO 3) is a non-bonded (lone pair) hybrid on N(2), etc. This label allows one to find the precise form of the NHO in the main listing of NBOs. The FNHO matrix shows, for example, that the (4,5) Fock matrix element between the directly interacting NHOs forming the C-N bond NBO is -0.7196 a.u., whereas the (4,12) matrix element, between the C(1) hybrid pointing toward N(2) and the N(2) hybrid pointing toward H(6), is –0.0935 a.u.

B.6 NBO ILLUSTRATIONS

As a second example, the keyword "NBOMO=PVAL" would print out the core
+ valence columns of the NBO → MO transformation, as reproduced below:

```
MOs in the NBO basis:

         NBO        1       2       3       4       5       6       7       8
      ---------- ------- ------- ------- ------- ------- ------- ------- -------
   1.  C 1(cr)     0.0021  0.9931  0.0692  0.0919  0.0000  0.0008  0.0015  0.0000
   2.  N 2(cr)    -0.9935 -0.0019  0.1047 -0.0351  0.0000 -0.0130  0.0023  0.0000
   3.  N 2(lp)    -0.0436 -0.0037 -0.1691  0.1245  0.0000  0.3341  0.1440  0.0000
   4.  C 1- N 2   -0.0658  0.0571 -0.6291 -0.1241  0.0000  0.3063 -0.6894  0.0000
   5.  C 1- H 3   -0.0019  0.0579 -0.2078 -0.4709  0.0000 -0.7782 -0.1175  0.0000
   6.  C 1- H 4   -0.0023  0.0579 -0.1840 -0.4901 -0.3822  0.2409  0.3866 -0.5934
   7.  C 1- H 5   -0.0023  0.0579 -0.1840 -0.4901  0.3822  0.2409  0.3866  0.5934
   8.  N 2- H 6   -0.0570  0.0001 -0.4731  0.3577  0.5931 -0.1873  0.3083 -0.3823
   9.  N 2- H 7   -0.0570  0.0001 -0.4731  0.3577 -0.5931 -0.1873  0.3083  0.3823
  10.  C 1- N 2*  -0.0021  0.0031  0.0022  0.0017  0.0000 -0.0034 -0.0038  0.0000
  11.  C 1- H 3*  -0.0012  0.0023 -0.0054 -0.0018  0.0000  0.0347  0.0131  0.0000
  12.  C 1- H 4*  -0.0009  0.0028 -0.0143 -0.0035  0.0407 -0.0184  0.0063 -0.0148
  13.  C 1- H 5*  -0.0009  0.0028 -0.0143 -0.0035 -0.0407 -0.0184  0.0063  0.0148
  14.  N 2- H 6*   0.0011  0.0050 -0.0048 -0.0181 -0.0179  0.0129  0.0153 -0.0321
  15.  N 2- H 7*   0.0011  0.0050 -0.0048 -0.0181  0.0179  0.0129  0.0153  0.0321
  16.  C 1(ry)     0.0088 -0.0003  0.0112 -0.0088  0.0000 -0.0019 -0.0084  0.0000
  17.  C 1(ry)     0.0000  0.0000  0.0000  0.0000 -0.0106  0.0000  0.0000  0.0069
  18.  C 1(ry)     0.0062  0.0002 -0.0050  0.0035  0.0000 -0.0029  0.0027  0.0000
  19.  C 1(ry)    -0.0020 -0.0003 -0.0003  0.0003  0.0000 -0.0009  0.0002  0.0000
  20.  N 2(ry)     0.0041 -0.0003 -0.0007 -0.0017  0.0000  0.0194  0.0102  0.0000
  21.  N 2(ry)     0.0000  0.0000  0.0000  0.0000 -0.0079  0.0000  0.0000 -0.0122
  22.  N 2(ry)    -0.0035 -0.0060 -0.0040 -0.0104  0.0000 -0.0023  0.0042  0.0000
  23.  N 2(ry)     0.0018  0.0023 -0.0007 -0.0013  0.0000 -0.0006  0.0005  0.0000
  24.  H 3(ry)     0.0008 -0.0094 -0.0104 -0.0143  0.0000  0.0017 -0.0025  0.0000
  25.  H 4(ry)     0.0008 -0.0100 -0.0061 -0.0117 -0.0064  0.0005 -0.0057  0.0097
  26.  H 5(ry)     0.0008 -0.0100 -0.0061 -0.0117  0.0064  0.0005 -0.0057 -0.0097
  27.  H 6(ry)     0.0052 -0.0013 -0.0147  0.0016  0.0030 -0.0018 -0.0100  0.0158
  28.  H 7(ry)     0.0052 -0.0013 -0.0147  0.0016 -0.0030 -0.0018 -0.0100 -0.0158

         NBO        9      10      11      12      13      14      15
      ---------- ------- ------- ------- ------- ------- ------- -------
   1.  C 1(cr)     0.0037 -0.0133  0.0082  0.0000 -0.0009  0.0000  0.0014
   2.  N 2(cr)    -0.0191 -0.0054 -0.0031  0.0000  0.0026  0.0000 -0.0036
   3.  N 2(lp)     0.9005 -0.0148 -0.0063  0.0000 -0.0913  0.0000 -0.0126
   4.  C 1- N 2   -0.1066  0.0145  0.0009  0.0000  0.0056  0.0000 -0.0063
   5.  C 1- H 3    0.3341  0.0044  0.0020  0.0000  0.0009  0.0000 -0.0077
   6.  C 1- H 4   -0.1178 -0.0191 -0.0106 -0.0257  0.0049  0.0274  0.0094
   7.  C 1- H 5   -0.1178 -0.0191 -0.0106  0.0257  0.0049 -0.0274  0.0094
   8.  N 2- H 6   -0.1188 -0.0026  0.0146  0.0295  0.0164  0.0250 -0.0039
   9.  N 2- H 7   -0.1188 -0.0026  0.0146 -0.0295  0.0164 -0.0250 -0.0039
  10.  C 1- N 2*   0.0028  0.2347  0.2571  0.0000 -0.1089  0.0000  0.8057
  11.  C 1- H 3*   0.0791  0.3240 -0.2615  0.0000  0.6693  0.0000  0.1125
  12.  C 1- H 4*  -0.0367  0.2601 -0.3883 -0.4713 -0.2952 -0.3162  0.0485
  13.  C 1- H 5*  -0.0367  0.2601 -0.3883  0.4713 -0.2952  0.3162  0.0485
  14.  N 2- H 6*  -0.0025  0.4317  0.3150  0.3239 -0.0493 -0.4545 -0.2169
  15.  N 2- H 7*  -0.0025  0.4317  0.3150 -0.3239 -0.0493  0.4545 -0.2169
  16.  C 1(ry)    -0.0128 -0.0992 -0.0563  0.0000 -0.0538  0.0000 -0.3304
  17.  C 1(ry)     0.0000  0.0000  0.0000 -0.0851  0.0000 -0.1849  0.0000
  18.  C 1(ry)    -0.0039 -0.0588 -0.0751  0.0000  0.1152  0.0000 -0.1180
  19.  C 1(ry)    -0.0018  0.0942 -0.0177  0.0000 -0.1045  0.0000  0.1524
  20.  N 2(ry)    -0.0085 -0.0229 -0.0068  0.0000  0.0465  0.0000  0.0183
  21.  N 2(ry)     0.0000  0.0000  0.0000 -0.0167  0.0000  0.0867  0.0000
  22.  N 2(ry)     0.0007  0.0393  0.0844  0.0000 -0.0224  0.0000  0.1563
  23.  N 2(ry)     0.0003  0.0611  0.0224  0.0000 -0.0119  0.0000 -0.0588
  24.  H 3(ry)    -0.0217 -0.2491  0.2188  0.0000 -0.4844  0.0000  0.0041
  25.  H 4(ry)     0.0058 -0.1984  0.3215  0.3399  0.2058  0.2121  0.0522
  26.  H 5(ry)     0.0058 -0.1984  0.3215 -0.3399  0.2058 -0.2121  0.0522
  27.  H 6(ry)     0.0026 -0.2845 -0.2161 -0.2283  0.0374  0.3552  0.1716
  28.  H 7(ry)     0.0026 -0.2845 -0.2161  0.2283  0.0374 -0.3552  0.1716
```

B.6 NBO ILLUSTRATIONS

In this transformation matrix, rows correspond to NBOs and columns to MOs (in the ordering used elsewhere in the program), and each basis NBO is further identified with a row label. The print parameter "PVAL" specified that only 15 MOs (the number of core + valence orbitals) should be printed, corresponding to the nine occupied MOs 1-9 and the lowest six virtual MOs 10-15. The matrix allows one to see the composition of each canonical MO in terms of localized bond NBOs. For example, MOs 5 and 8 can be approximately described as

$$\varphi_5 \cong -0.593(\sigma_{N2H6} - \sigma_{N2H7}) + 0.382(\sigma_{C1H4} - \sigma_{C1H5})$$

$$\varphi_8 \cong 0.382(\sigma_{N2H6} - \sigma_{N2H7}) + 0.593(\sigma_{C1H4} - \sigma_{C1H5})$$

whereas φ_6 is primarily the C-H(3) NBO and φ_9 the N lone pair NBO. Note that the CMO keyword (Sec. B.13) presents a more convenient summary of MO composition and bonding character.

As a final example, the keyword "SPNBO <3 11/9 13>" will print out the values of the $S_{3,11} = <n_N|\sigma^*_{CH3}>$ and $S_{9,13} = <\sigma_{NH7}|\sigma^*_{CH5}>$ PNBO overlap integrals as shown below:

```
PNBO overlap matrix:

    2 user-requested elements:
   ---------------------------------------------------
    i    j       matrix(i,j)    label(i)   label(j)
   ---------------------------------------------------
    3   11    0.1658146514E+00  N 2(lp)    C 1- H 3*
    9   13    0.1707604944E+00  N 2- H 7   C 1- H 5*
   ---------------------------------------------------
```

Note that descriptive basis labels are provided for all basis sets except canonical MOs.

B.6.5 BNDIDX Keyword

The BNDIDX keyword activates the printing of several types of non-NRT bond order and valency indices. (For the NRT "natural bond order" and "natural atomic valency," see Sec. B.8.) These alternative indices are based on varying assumptions and formulas. We illustrate these bond order tables for the example of RHF/3-21G methylamine (Section A.3).

The first segment of BNDIDX output shows the Wiberg bond index [the sum of squares of off-diagonal density matrix elements between atoms; K. B. Wiberg, *Tetrahedron* **24**, 1083 (1968)], as formulated in terms of the NAO basis set:

```
Wiberg bond index matrix in the NAO basis:

    Atom    1       2       3       4       5       6       7
    ---- ------  ------  ------  ------  ------  ------  ------
 1.  C  0.0000  0.9959  0.9475  0.9394  0.9394  0.0020  0.0020
 2.  N  0.9959  0.0000  0.0203  0.0052  0.0052  0.8615  0.8615
 3.  H  0.9475  0.0203  0.0000  0.0004  0.0004  0.0002  0.0002
 4.  H  0.9394  0.0052  0.0004  0.0000  0.0009  0.0079  0.0005
 5.  H  0.9394  0.0052  0.0004  0.0009  0.0000  0.0005  0.0079
 6.  H  0.0020  0.8615  0.0002  0.0079  0.0005  0.0000  0.0002
 7.  H  0.0020  0.8615  0.0002  0.0005  0.0079  0.0002  0.0000


Wiberg bond index, Totals by atom:

    Atom    1
    ---- ------
 1.  C  3.8263
 2.  N  2.7496
 3.  H  0.9690
 4.  H  0.9543
 5.  H  0.9543
 6.  H  0.8723
 7.  H  0.8723
```

This index is intrinsically a positive quantity, making no distinction between net bonding or antibonding character of the density matrix elements.

The next segment tabulates the "overlap-weighted NAO bond order," as shown below:

```
Atom-atom overlap-weighted NAO bond order:

    Atom   1       2       3       4       5       6       7
    ---- ------  ------  ------  ------  ------  ------  ------
 1.  C  0.0000  0.7800  0.7619  0.7636  0.7636 -0.0105 -0.0105
 2.  N  0.7800  0.0000 -0.0227 -0.0100 -0.0100  0.6689  0.6689
 3.  H  0.7619 -0.0227  0.0000 -0.0037 -0.0037 -0.0020 -0.0020
```

```
    4.  H  0.7636 -0.0100 -0.0037  0.0000  0.0026  0.0039 -0.0033
    5.  H  0.7636 -0.0100 -0.0037  0.0026  0.0000 -0.0033  0.0039
    6.  H -0.0105  0.6689 -0.0020  0.0039 -0.0033  0.0000 -0.0067
    7.  H -0.0105  0.6689 -0.0020 -0.0033  0.0039 -0.0067  0.0000


Atom-atom overlap-weighted NAO bond order, Totals by atom:

     Atom    1
     ----  ------
  1.  C  3.0480
  2.  N  2.0752
  3.  H  0.7279
  4.  H  0.7531
  5.  H  0.7531
  6.  H  0.6504
  7.  H  0.6504
```

This index corresponds to a sum of off-diagonal NAO density matrix elements
between atoms, each multiplied by the corresponding PNAO overlap integral.

Another type of BNDIDX output appears if the NLMO keyword is included,
summarizing a formal "NLMO/NPA bond order" that can be associated with
each NLMO:

```
Individual LMO bond orders greater than 0.002 in magnitude,
with the overlap between the hybrids in the NLMO given:

Atom I / Atom J / NLMO / Bond Order / Hybrid Overlap /
   1        2       3     0.0086031      0.3051867
   1        2       4     0.8007093      0.7305290
   1        2       8     0.0022555      0.1809076
   1        2       9     0.0022555      0.1809076
   1        3       3    -0.0086031     -0.5768504
   1        3       5     0.8050682      0.7865538
   1        4       6     0.7771169      0.7875814
   1        4       8    -0.0022555     -0.5428010
   1        5       7     0.7771169      0.7875814
   1        5       9    -0.0022555     -0.5428010
   1        6       6    -0.0031742     -0.0925060
   1        6       8     0.0022555      0.0866524
   1        7       7    -0.0031742     -0.0925060
   1        7       9     0.0022555      0.0866524
   2        3       3    -0.0095444     -0.0937818
   2        4       8    -0.0027542     -0.0706654
   2        5       9    -0.0027542     -0.0706654
   2        6       8     0.6363467      0.7283871
   2        7       9     0.6363467      0.7283871
   4        6       6     0.0031742      0.0437116
   4        6       8     0.0027542      0.0407558
   5        7       7     0.0031742      0.0437116
   5        7       9     0.0027542      0.0407558
```

This NLMO bond order is calculated by the method described by A. E. Reed
and P. v.R. Schleyer [*Inorg. Chem.* 27, 3969-3987 (1988); *J. Am. Chem. Soc.*
112, 1434 (1990)], based on the shared occupancies and hybrid overlaps (last
column) of NAOs composing the NLMO. In the above table, for example,

B.6 NBO ILLUSTRATIONS

NLMO 4 occurs only in the second line, contributing a bond of formal order 0.8007 between C(1) and N(2), whereas NLMO 3 (the nitrogen lone pair) contributes a slight strengthening (+0.0086) of the C(1)-N(2) bond, a weakening (-0.0086) of the vicinal C(1)-H(3) bond, and a slight negative bond order (-0.0095) between atoms N(2), H(3).

The NLMO bond order contributions are then summed for each atom pair to give the net NLMO/NPA bond orders shown below:

```
Atom-Atom Net Linear NLMO/NPA Bond Orders:

    Atom    1       2       3       4       5       6       7
    ----  ------  ------  ------  ------  ------  ------  ------
 1.  C    0.0000  0.8171  0.7961  0.7732  0.7732 -0.0013 -0.0013
 2.  N    0.8171  0.0000 -0.0102 -0.0067 -0.0067  0.6342  0.6342
 3.  H    0.7961 -0.0102  0.0000 -0.0020 -0.0020  0.0001  0.0001
 4.  H    0.7732 -0.0067 -0.0020  0.0000  0.0020  0.0062  0.0000
 5.  H    0.7732 -0.0067 -0.0020  0.0020  0.0000  0.0000  0.0062
 6.  H   -0.0013  0.6342  0.0001  0.0062  0.0000  0.0000 -0.0001
 7.  H   -0.0013  0.6342  0.0001  0.0000  0.0062 -0.0001  0.0000
```

For example, the table attributes a formal bond order of 0.8171 to the C(1)-N(2) bond of methylamine, the highest bond order in this molecule. (The higher value for C(1)-H(3) than for the other two CH bonds reflects an unsatisfactory aspect of this method of assessing bond order.)

These non-NRT bond indices are based on different assumptions, with certain advantages and disadvantages. ***Caveat emptor!***

B.6 NBO ILLUSTRATIONS

B.6.6 Strong Delocalization: Benzene

When NBO analysis is performed on a wavefunction that cannot be satisfactorily localized [i.e., in which one or more NBOs of the natural Lewis structure fail to achieve the default threshold occupancy (1.90) for a satisfactory "pair"], the NBO program successively lowers the occupancy threshold and repeats the search. (This formerly involved a coarse grid of 0.1e decrements, but the search now corresponds to an infinitely fine grid, with the search summary reporting only the discrete occupancies corresponding to changes of bonding pattern. For example, when benzene (RHF/STO-3G level, idealized Pople-Gordon geometry) is treated by the NBO program in default mode, one obtains the summary of NBO search cycles shown below.

```
NATURAL BOND ORBITAL ANALYSIS:

                       Occupancies       Lewis Structure    Low   High
           Max   Occ   ------------------ ----------------   occ   occ
 Cycle Ctr  Thresh  Lewis    non-Lewis   CR  BD  nC  LP    (L)   (NL)
 =====================================================================
    1    2   1.90   38.87478   3.12522    6  12   0   3     3     3
    2    2   1.66   40.87478   1.12522    6  15   0   0     0     3
 ---------------------------------------------------------------------
```

The NBO search considers "pair" occupancy thresholds throughout the range from 1.90e to 1.50e. In this case, the best Lewis structure (of lowest overall non-Lewis occupancy, 1.125e) was found at occupancy threshold 1.66e. The NBO program therefore resets the threshold to this value and calculates the set of NBOs corresponding to this "best" Lewis structure, as shown below:

```
    (Occupancy)   Bond orbital / Coefficients / Hybrids
----------------- Lewis -------------------------------------------------
  1. (1.99995) CR ( 1) C  1              s(100.00%)
                                         1.0000  0.0000  0.0000  0.0000  0.0000
  2. (1.99995) CR ( 1) C  2              s(100.00%)
                                         1.0000  0.0000  0.0000  0.0000  0.0000
  3. (1.99995) CR ( 1) C  3              s(100.00%)
                                         1.0000  0.0000  0.0000  0.0000  0.0000
  4. (1.99995) CR ( 1) C  4              s(100.00%)
                                         1.0000  0.0000  0.0000  0.0000  0.0000
  5. (1.99995) CR ( 1) C  5              s(100.00%)
                                         1.0000  0.0000  0.0000  0.0000  0.0000
  6. (1.99995) CR ( 1) C  6              s(100.00%)
                                         1.0000  0.0000  0.0000  0.0000  0.0000
  7. (1.98935) BD ( 1) C  1- C  2
           ( 50.00%)   0.7071* C  1 s( 34.19%)p 1.93( 65.81%)
                                         0.0000  0.5847  0.7071 -0.3977  0.0000
           ( 50.00%)   0.7071* C  2 s( 34.19%)p 1.93( 65.81%)
                                         0.0000  0.5847 -0.6979  0.4135  0.0000
  8. (1.66667) BD ( 2) C  1- C  2
           ( 50.00%)   0.7071* C  1 s(  0.00%)p 1.00(100.00%)
                                         0.0000  0.0000  0.0000  0.0000  1.0000
           ( 50.00%)   0.7071* C  2 s(  0.00%)p 1.00(100.00%)
                                         0.0000  0.0000  0.0000  0.0000  1.0000
  9. (1.98935) BD ( 1) C  1- C  6
           ( 50.00%)   0.7071* C  1 s( 34.19%)p 1.93( 65.81%)
                                         0.0000  0.5847 -0.7071 -0.3977  0.0000
           ( 50.00%)   0.7071* C  6 s( 34.19%)p 1.93( 65.81%)
```

```
                                        0.0000  0.5847  0.6979  0.4135  0.0000
 10. (1.98983) BD ( 1) C  1- H  7
             ( 51.74%)   0.7193* C  1 s( 31.63%)p 2.16( 68.37%)
                                        0.0000  0.5624  0.0000  0.8269  0.0000
             ( 48.26%)   0.6947* H  7 s(100.00%)
                                        1.0000
 11. (1.98935) BD ( 1) C  2- C  3
             ( 50.00%)   0.7071* C  2 s( 34.19%)p 1.93( 65.81%)
                                        0.0000 -0.5847 -0.0092  0.8112  0.0000
             ( 50.00%)   0.7071* C  3 s( 34.19%)p 1.93( 65.81%)
                                        0.0000 -0.5847 -0.0092 -0.8112  0.0000
 12. (1.98983) BD ( 1) C  2- H  8
             ( 51.74%)   0.7193* C  2 s( 31.63%)p 2.16( 68.37%)
                                        0.0000  0.5624  0.7161  0.4134  0.0000
             ( 48.26%)   0.6947* H  8 s(100.00%)
                                        1.0000
 13. (1.98935) BD ( 1) C  3- C  4
             ( 50.00%)   0.7071* C  3 s( 34.19%)p 1.93( 65.81%)
                                        0.0000  0.5847 -0.6979 -0.4135  0.0000
             ( 50.00%)   0.7071* C  4 s( 34.19%)p 1.93( 65.81%)
                                        0.0000  0.5847  0.7071  0.3977  0.0000
 14. (1.66667) BD ( 2) C  3- C  4
             ( 50.00%)   0.7071* C  3 s(  0.00%)p 1.00(100.00%)
                                        0.0000  0.0000  0.0000  0.0000  1.0000
             ( 50.00%)   0.7071* C  4 s(  0.00%)p 1.00(100.00%)
                                        0.0000  0.0000  0.0000  0.0000  1.0000
 15. (1.98983) BD ( 1) C  3- H  9
             ( 51.74%)   0.7193* C  3 s( 31.63%)p 2.16( 68.37%)
                                        0.0000  0.5624  0.7161 -0.4134  0.0000
             ( 48.26%)   0.6947* H  9 s(100.00%)
                                        1.0000
 16. (1.98935) BD ( 1) C  4- C  5
             ( 50.00%)   0.7071* C  4 s( 34.19%)p 1.93( 65.81%)
                                        0.0000  0.5847 -0.7071  0.3977  0.0000
             ( 50.00%)   0.7071* C  5 s( 34.19%)p 1.93( 65.81%)
                                        0.0000  0.5847  0.6979 -0.4135  0.0000
 17. (1.98983) BD ( 1) C  4- H 10
             ( 51.74%)   0.7193* C  4 s( 31.63%)p 2.16( 68.37%)
                                        0.0000  0.5624  0.0000 -0.8269  0.0000
             ( 48.26%)   0.6947* H 10 s(100.00%)
                                        1.0000
 18. (1.98935) BD ( 1) C  5- C  6
             ( 50.00%)   0.7071* C  5 s( 34.19%)p 1.93( 65.81%)
                                        0.0000  0.5847 -0.0092  0.8112  0.0000
             ( 50.00%)   0.7071* C  6 s( 34.19%)p 1.93( 65.81%)
                                        0.0000  0.5847 -0.0092 -0.8112  0.0000
 19. (1.66667) BD ( 2) C  5- C  6
             ( 50.00%)   0.7071* C  5 s(  0.00%)p 1.00(100.00%)
                                        0.0000  0.0000  0.0000  0.0000  1.0000
             ( 50.00%)   0.7071* C  6 s(  0.00%)p 1.00(100.00%)
                                        0.0000  0.0000  0.0000  0.0000  1.0000
 20. (1.98983) BD ( 1) C  5- H 11
             ( 51.74%)   0.7193* C  5 s( 31.63%)p 2.16( 68.37%)
                                        0.0000  0.5624 -0.7161 -0.4134  0.0000
             ( 48.26%)   0.6947* H 11 s(100.00%)
                                        1.0000
 21. (1.98983) BD ( 1) C  6- H 12
             ( 51.74%)   0.7193* C  6 s( 31.63%)p 2.16( 68.37%)
                                        0.0000  0.5624 -0.7161  0.4134  0.0000
             ( 48.26%)   0.6947* H 12 s(100.00%)
                                        1.0000
---------------- non-Lewis ----------------------------------------------------
 22. (0.01071) BD*( 1) C  1- C  2
             ( 50.00%)   0.7071* C  1 s( 34.19%)p 1.93( 65.81%)
                                        0.0000  0.5847  0.7071 -0.3977  0.0000
             ( 50.00%)  -0.7071* C  2 s( 34.19%)p 1.93( 65.81%)
                                        0.0000  0.5847 -0.6979  0.4135  0.0000
 23. (0.33333) BD*( 2) C  1- C  2
             ( 50.00%)   0.7071* C  1 s(  0.00%)p 1.00(100.00%)
                                        0.0000  0.0000  0.0000  0.0000  1.0000
             ( 50.00%)  -0.7071* C  2 s(  0.00%)p 1.00(100.00%)
```

```
                                         0.0000  0.0000  0.0000  0.0000  1.0000
   24. (0.01071) BD*( 1) C  1- C  6
            ( 50.00%)   0.7071* C  1 s( 34.19%)p 1.93( 65.81%)
                                         0.0000  0.5847 -0.7071 -0.3977  0.0000
            ( 50.00%)  -0.7071* C  6 s( 34.19%)p 1.93( 65.81%)
                                         0.0000  0.5847  0.6979  0.4135  0.0000
   25. (0.01016) BD*( 1) C  1- H  7
            ( 48.26%)   0.6947* C  1 s( 31.63%)p 2.16( 68.37%)
                                         0.0000 -0.5624  0.0000 -0.8269  0.0000
            ( 51.74%)  -0.7193* H  7 s(100.00%)
                                        -1.0000
   26. (0.01071) BD*( 1) C  2- C  3
            ( 50.00%)   0.7071* C  2 s( 34.19%)p 1.93( 65.81%)
                                         0.0000 -0.5847 -0.0092  0.8112  0.0000
            ( 50.00%)  -0.7071* C  3 s( 34.19%)p 1.93( 65.81%)
                                         0.0000 -0.5847 -0.0092 -0.8112  0.0000
   27. (0.01016) BD*( 1) C  2- H  8
            ( 48.26%)   0.6947* C  2 s( 31.63%)p 2.16( 68.37%)
                                         0.0000 -0.5624 -0.7161 -0.4134  0.0000
            ( 51.74%)  -0.7193* H  8 s(100.00%)
                                        -1.0000
   28. (0.01071) BD*( 1) C  3- C  4
            ( 50.00%)   0.7071* C  3 s( 34.19%)p 1.93( 65.81%)
                                         0.0000 -0.5847  0.6979  0.4135  0.0000
            ( 50.00%)  -0.7071* C  4 s( 34.19%)p 1.93( 65.81%)
                                         0.0000 -0.5847 -0.7071 -0.3977  0.0000
   29. (0.33333) BD*( 2) C  3- C  4
            ( 50.00%)   0.7071* C  3 s(  0.00%)p 1.00(100.00%)
                                         0.0000  0.0000  0.0000  0.0000 -1.0000
            ( 50.00%)  -0.7071* C  4 s(  0.00%)p 1.00(100.00%)
                                         0.0000  0.0000  0.0000  0.0000 -1.0000
   30. (0.01016) BD*( 1) C  3- H  9
            ( 48.26%)   0.6947* C  3 s( 31.63%)p 2.16( 68.37%)
                                         0.0000 -0.5624 -0.7161  0.4134  0.0000
            ( 51.74%)  -0.7193* H  9 s(100.00%)
                                        -1.0000
   31. (0.01071) BD*( 1) C  4- C  5
            ( 50.00%)   0.7071* C  4 s( 34.19%)p 1.93( 65.81%)
                                         0.0000  0.5847 -0.7071  0.3977  0.0000
            ( 50.00%)  -0.7071* C  5 s( 34.19%)p 1.93( 65.81%)
                                         0.0000  0.5847  0.6979 -0.4135  0.0000
   32. (0.01016) BD*( 1) C  4- H 10
            ( 48.26%)   0.6947* C  4 s( 31.63%)p 2.16( 68.37%)
                                         0.0000 -0.5624  0.0000  0.8269  0.0000
            ( 51.74%)  -0.7193* H 10 s(100.00%)
                                        -1.0000
   33. (0.01071) BD*( 1) C  5- C  6
            ( 50.00%)   0.7071* C  5 s( 34.19%)p 1.93( 65.81%)
                                         0.0000  0.5847 -0.0092  0.8112  0.0000
            ( 50.00%)  -0.7071* C  6 s( 34.19%)p 1.93( 65.81%)
                                         0.0000  0.5847 -0.0092 -0.8112  0.0000
   34. (0.33333) BD*( 2) C  5- C  6
            ( 50.00%)   0.7071* C  5 s(  0.00%)p 1.00(100.00%)
                                         0.0000  0.0000  0.0000  0.0000  1.0000
            ( 50.00%)  -0.7071* C  6 s(  0.00%)p 1.00(100.00%)
                                         0.0000  0.0000  0.0000  0.0000  1.0000
   35. (0.01016) BD*( 1) C  5- H 11
            ( 48.26%)   0.6947* C  5 s( 31.63%)p 2.16( 68.37%)
                                         0.0000 -0.5624  0.7161  0.4134  0.0000
            ( 51.74%)  -0.7193* H 11 s(100.00%)
                                        -1.0000
   36. (0.01016) BD*( 1) C  6- H 12
            ( 48.26%)   0.6947* C  6 s( 31.63%)p 2.16( 68.37%)
                                         0.0000 -0.5624  0.7161 -0.4134  0.0000
            ( 51.74%)  -0.7193* H 12 s(100.00%)
                                        -1.0000
```

B.6 NBO ILLUSTRATIONS

As one can see from this table, the set of NBOs obtained by the program corresponds to one of the two equivalent Kekulé structures, with reasonably well localized σ_{CC} and σ_{CH} NBOs (1.9894 and 1.9898 electrons, respectively), but three severely depleted π_{CC} bonds (1.6667e) and corresponding high occupancy π^*_{CC} antibonds (0.3333e). Other sections of the NBO output (not shown) will similarly exhibit the sharp distinctions between benzene and more typical (non-aromatic) compounds.

In the case of the completely symmetric (D_{6h}) structure, the NBO program "arbitrarily" chooses one of the two equivalent localized Kekulé structures (in this case, the one with pi bonds between carbon atoms 1-2, 3-4, and 5-6), dependent on atom numbering. However, if slight distortions are introduced, the program will recognize that the two Kekulé structures are no longer exactly degenerate, and will return the unique "best" structure (of lowest ρ^*). More subtle aspects of the near-equivalency of aromatic Kekulé structures may be studied by the NRT method of Sec. B.8, avoiding the apparent "discontinuity" of bonding pattern in the main NBO structure that may occur when two closely related aromatic systems are compared.

B.6 NBO ILLUSTRATIONS

B.6.7 NOBOND Keyword

The NOBOND keyword forces the NBO program to analyze the wavefunction in terms of 1-center functions only, thus forcing a description of the bonding in terms of atomic or ionic hybrids. The modifications of NBO output that result from activating this keyword can be illustrated for the HF molecule (RHF/3-21G level). This molecule might be described in terms of a polar covalent H-F bond or in terms of ionic $H^+ F^-$ interactions.

The default NBO analysis of this example is shown below:

```
NATURAL BOND ORBITAL ANALYSIS:

                      Occupancies      Lewis Structure    Low   High
          Max   Occ   ------------------- ----------------- occ   occ
Cycle Ctr  Thresh   Lewis   non-Lewis    CR  BD  nC  LP   (L)   (NL)
==========================================================================
  1    2    1.90    9.99942   0.00058     1   1   0   3    0     0
--------------------------------------------------------------------------

Structure accepted: No low occupancy Lewis orbitals

------------------------------------------------------------
  Core                    1.99993 ( 99.997% of   2)
  Valence Lewis           7.99948 ( 99.994% of   8)
  ================        =============================
  Total Lewis             9.99942 ( 99.994% of  10)
  ------------------------------------------------
  Valence non-Lewis       0.00000 (  0.000% of  10)
  Rydberg non-Lewis       0.00058 (  0.006% of  10)
  ================        =============================
  Total non-Lewis         0.00058 (  0.006% of  10)
------------------------------------------------------------


   (Occupancy)  Bond orbital / Coefficients / Hybrids
----------------- Lewis -------------------------------------------------
  1. (1.99993) CR ( 1) F  1           s(100.00%)
                                        1.0000  0.0000  0.0000  0.0000  0.0000
                                        0.0000  0.0000  0.0000  0.0000
  2. (2.00000) LP ( 1) F  1           s(  0.00%)p 1.00(100.00%)
                                        0.0000  0.0000  0.0000  1.0000 -0.0013
                                        0.0000  0.0000  0.0000  0.0000
  3. (2.00000) LP ( 2) F  1           s(  0.00%)p 1.00(100.00%)
                                        0.0000  0.0000  0.0000  0.0000  0.0000
                                        1.0000 -0.0013  0.0000  0.0000
  4. (1.99948) LP ( 3) F  1           s( 83.71%)p 0.19( 16.29%)
                                        0.0000  0.9149 -0.0052  0.0000  0.0000
                                        0.0000  0.0000  0.4036  0.0062
  5. (2.00000) BD ( 1) F  1- H  2
          ( 75.22%)   0.8673* F  1 s( 16.31%)p 5.13( 83.69%)
                                        0.0000 -0.4036 -0.0158  0.0000  0.0000
                                        0.0000  0.0000  0.9148  0.0001
          ( 24.78%)   0.4978* H  2 s(100.00%)
                                       -1.0000  0.0000
---------------- non-Lewis -------------------------------------------------
  6. (0.00000) BD*( 1) F  1- H  2
          ( 24.78%)   0.4978* F  1 s( 16.31%)p 5.13( 83.69%)
          ( 75.22%)  -0.8673* H  2 s(100.00%)
  7. (0.00002) RY ( 1) F  1           s(  0.00%)p 1.00(100.00%)
  8. (0.00000) RY ( 2) F  1           s( 99.97%)p 0.00(  0.03%)
  9. (0.00000) RY ( 3) F  1           s(  0.00%)p 1.00(100.00%)
```

```
10. (0.00000) RY ( 4) F  1          s(  0.00%)p 1.00(100.00%)
11. (0.00056) RY ( 1) H  2          s(100.00%)
                                      0.0000  1.0000
```

As the output shows, default NBO analysis leads to a polar covalent description of HF. The σ_{HF} bond, NBO 1, is formed from a *p*-rich ($sp^{5.13}$, 83.69% *p*-character) hybrid on F and the 1*s* AO on H, strongly polarized (about 75.22%) toward F. This provides a satisfactory Lewis structure, describing 99.994% of the total electron density.

When the NOBOND keyword is activated to bypass the search for 2-center bonds, the NBO output is modified as shown below:

```
       /NOBOND / : No two-center NBO search

NATURAL BOND ORBITAL ANALYSIS:

                    Occupancies     Lewis Structure    Low    High
         Max   Occ   -----------------  ----------------  occ    occ
 Cycle  Ctr  Thresh  Lewis   non-Lewis   CR  BD  nC  LP   (L)    (NL)
 ===================================================================
   1     1    1.00   9.50379  0.49621    1   0   0   4    0      1
 -------------------------------------------------------------------

Structure accepted: Search for bonds prevented by NOBOND keyword


 ----------------------------------------------------------
  Core                    1.99993 ( 99.997% of   2)
  Valence Lewis           7.50386 ( 93.798% of   8)
 =================         ============================
  Total Lewis             9.50379 ( 95.038% of  10)
 ----------------------------------------------------------
  Valence non-Lewis       0.49563 (  4.956% of  10)
  Rydberg non-Lewis       0.00058 (  0.006% of  10)
 =================         ============================
  Total non-Lewis         0.49621 (  4.962% of  10)
 ----------------------------------------------------------

    (Occupancy)  Bond orbital / Coefficients / Hybrids
 ----------------- Lewis ----------------------------------------------
  1. (1.99993) CR ( 1) F  1          s(100.00%)
                                      1.0000  0.0000  0.0000  0.0000  0.0000
                                      0.0000  0.0000  0.0000  0.0000
  2. (2.00000) LP ( 1) F  1          s(  0.00%)p 1.00(100.00%)
                                      0.0000  0.0000  0.0000  1.0000 -0.0013
                                      0.0000  0.0000  0.0000  0.0000
  3. (2.00000) LP ( 2) F  1          s(  0.00%)p 1.00(100.00%)
                                      0.0000  0.0000  0.0000  0.0000  0.0000
                                      1.0000 -0.0013  0.0000  0.0000
  4. (1.99948) LP ( 3) F  1          s( 83.71%)p 0.19( 16.29%)
                                      0.0000  0.9149 -0.0052  0.0000  0.0000
                                      0.0000  0.0000  0.4036  0.0062
  5. (1.50437) LP ( 4) F  1          s( 16.31%)p 5.13( 83.69%)
                                      0.0000  0.4036  0.0158  0.0000  0.0000
                                      0.0000  0.0000 -0.9148 -0.0001
 ---------------- non-Lewis -------------------------------------------
  6. (0.49563) LP ( 1) H  2          s(100.00%)
                                      1.0000  0.0000
  7. (0.00002) RY ( 1) F  1          s(  0.00%)p 1.00(100.00%)
  8. (0.00000) RY ( 2) F  1          s( 99.97%)p 0.00(  0.03%)
```

B.6 NBO ILLUSTRATIONS

```
  9. (0.00000) RY ( 3) F  1            s(  0.00%)p 1.00(100.00%)
 10. (0.00000) RY ( 4) F  1            s(  0.00%)p 1.00(100.00%)
 11. (0.00056) RY ( 1) H  2            s(100.00%)
                                        0.0000  1.0000
```

In this case, the NBO output indicates a rather poor Lewis structure (4.962% non-Lewis density), with a severely depleted F^- lone pair (NBO 5, the $sp^{5.13}$ hybrid) and significant occupancy (about 0.496e) in the `empty' H^+ $1s$ orbital (NBO 6) of the cation. The NOBOND comparison would therefore indicate the superiority of a polar covalent description in this case.

B.6 NBO ILLUSTRATIONS

B.6.8 Hypovalent Bonding: Diborane

When the standard NBO search of previous NBO program versions is applied to diborane or related electron-deficient compounds, one finds a dramatic failure to represent the electronic distribution in terms of 1- and 2-center (1c/2c) functions only. For example, for B_2H_6 (RHF/3-21G level), the default NBO search of *NBO 5.0* returns a fractured set of 4 units (two BH_2^+ and two H^- fragments), with about 2.14 electrons unaccounted for (13.4% non-Lewis occupancy), symptomatic of severe breakdown of the conventional Lewis structure representation. Only with inclusion of the "3CBOND" keyword was the NBO search extended to 3-center bridge-bonding NBOs that are generally required to describe such species accurately.

In *NBO 6.0*, however, no special 3CBOND keyword is required. Instead, the NBO search is *always* widened to include possible 3-center electron-pair (3c/2e) bonds if the conventional 1c/2c search fails to yield a satisfactory Lewis structure. For diborane, one obtains the NBO output shown below:

```
NATURAL BOND ORBITAL ANALYSIS:

                        Occupancies      Lewis Structure    Low    High
           Max    Occ   -------------------  ----------------   occ    occ
  Cycle  Ctr   Thresh   Lewis    non-Lewis    CR  BD  nC  LP   (L)    (NL)
 ========================================================================
    1     2     1.90   13.86001   2.13999     2   4   0   2     2      4
    2     3     1.90   15.94323   0.05677     2   4   2   0     0      0
 ------------------------------------------------------------------------

 Structure accepted: No low occupancy Lewis orbitals

          1 low occupancy (<1.9990e) core orbital  found on  B 1
          1 low occupancy (<1.9990e) core orbital  found on  B 2


 -------------------------------------------------------------
   Core                      3.99702 ( 99.925% of    4)
   Valence Lewis            11.94621 ( 99.552% of   12)
  =================         ============================
   Total Lewis             15.94323 ( 99.645% of   16)
 -------------------------------------------------------------
   Valence non-Lewis         0.04574 (  0.286% of   16)
   Rydberg non-Lewis         0.01103 (  0.069% of   16)
  =================         ============================
   Total non-Lewis           0.05677 (  0.355% of   16)
 -------------------------------------------------------------


    (Occupancy)   Bond orbital / Coefficients / Hybrids
 ----------------- Lewis ----------------------------------------------
  1. (1.99851) CR ( 1) B  1           s(100.00%)
                                       1.0000  0.0000  0.0000  0.0000  0.0000
                                       0.0000  0.0000  0.0000  0.0000
  2. (1.99851) CR ( 1) B  2           s(100.00%)
                                       1.0000  0.0000  0.0000  0.0000  0.0000
                                       0.0000  0.0000  0.0000  0.0000
  3. (1.99425) BD ( 1) B  1- H  6
```

```
                    ( 48.80%)   0.6986* B  1 s( 31.69%)p 2.16( 68.31%)
                                           0.0000  0.5629 -0.0062  0.4274  0.0221
                                          -0.7067  0.0244  0.0000  0.0000
                    ( 51.20%)   0.7155* H  6 s(100.00%)
                                           1.0000  0.0004
  4. (1.99425) BD ( 1) B  1- H  7
                    ( 48.80%)   0.6986* B  1 s( 31.69%)p 2.16( 68.31%)
                                           0.0000  0.5629 -0.0062  0.4274  0.0221
                                           0.7067 -0.0244  0.0000  0.0000
                    ( 51.20%)   0.7155* H  7 s(100.00%)
                                           1.0000  0.0004
  5. (1.99425) BD ( 1) B  2- H  5
                    ( 48.80%)   0.6986* B  2 s( 31.69%)p 2.16( 68.31%)
                                           0.0000  0.5629 -0.0062 -0.4274 -0.0221
                                           0.7067 -0.0244  0.0000  0.0000
                    ( 51.20%)   0.7155* H  5 s(100.00%)
                                           1.0000  0.0004
  6. (1.99425) BD ( 1) B  2- H  8
                    ( 48.80%)   0.6986* B  2 s( 31.69%)p 2.16( 68.31%)
                                           0.0000  0.5629 -0.0062 -0.4274 -0.0221
                                          -0.7067  0.0244  0.0000  0.0000
                    ( 51.20%)   0.7155* H  8 s(100.00%)
                                           1.0000  0.0004
  7. (1.98461) 3C ( 1) B  1- B  2- H  3
                    ( 26.44%)   0.5142* B  1 s( 18.30%)p 4.46( 81.70%)
                                           0.0000 -0.4276 -0.0124  0.5630 -0.0008
                                           0.0000  0.0000 -0.7067 -0.0246
                    ( 26.44%)   0.5142* B  2 s( 18.30%)p 4.46( 81.70%)
                                           0.0000 -0.4276 -0.0124 -0.5630  0.0008
                                           0.0000  0.0000 -0.7067 -0.0246
                    ( 47.13%)   0.6865* H  3 s(100.00%)
                                          -1.0000 -0.0066
  8. (1.98461) 3C ( 1) B  1- B  2- H  4
                    ( 26.44%)   0.5142* B  1 s( 18.30%)p 4.46( 81.70%)
                                           0.0000 -0.4276 -0.0124  0.5630 -0.0008
                                           0.0000  0.0000  0.7067  0.0246
                    ( 26.44%)   0.5142* B  2 s( 18.30%)p 4.46( 81.70%)
                                           0.0000 -0.4276 -0.0124 -0.5630  0.0008
                                           0.0000  0.0000  0.7067  0.0246
                    ( 47.13%)   0.6865* H  4 s(100.00%)
                                          -1.0000 -0.0066
--------------- non-Lewis -------------------------------------------------
  9. (0.00400) BD*( 1) B  1- H  6
                    ( 51.20%)   0.7155* B  1 s( 31.69%)p 2.16( 68.31%)
                                           0.0000  0.5629 -0.0062  0.4274  0.0221
                                          -0.7067  0.0244  0.0000  0.0000
                    ( 48.80%)  -0.6986* H  6 s(100.00%)
                                           1.0000  0.0004
 10. (0.00400) BD*( 1) B  1- H  7
                    ( 51.20%)   0.7155* B  1 s( 31.69%)p 2.16( 68.31%)
                                           0.0000  0.5629 -0.0062  0.4274  0.0221
                                           0.7067 -0.0244  0.0000  0.0000
                    ( 48.80%)  -0.6986* H  7 s(100.00%)
                                           1.0000  0.0004
 11. (0.00400) BD*( 1) B  2- H  5
                    ( 51.20%)   0.7155* B  2 s( 31.69%)p 2.16( 68.31%)
                                           0.0000  0.5629 -0.0062 -0.4274 -0.0221
                                           0.7067 -0.0244  0.0000  0.0000
                    ( 48.80%)  -0.6986* H  5 s(100.00%)
                                           1.0000  0.0004
 12. (0.00400) BD*( 1) B  2- H  8
                    ( 51.20%)   0.7155* B  2 s( 31.69%)p 2.16( 68.31%)
                                           0.0000  0.5629 -0.0062 -0.4274 -0.0221
                                          -0.7067  0.0244  0.0000  0.0000
                    ( 48.80%)  -0.6986* H  8 s(100.00%)
                                           1.0000  0.0004
 13. (0.01445) 3C*( 1) B  1- B  2- H  3
                    ( 23.56%)   0.4854* B  1 s( 18.30%)p 4.46( 81.70%)
                                           0.0000  0.4276  0.0124 -0.5630  0.0008
                                           0.0000  0.0000  0.7067  0.0246
                    ( 23.56%)   0.4854* B  2 s( 18.30%)p 4.46( 81.70%)
```

```
                                      0.0000  0.4276  0.0124  0.5630 -0.0008
                                      0.0000  0.0000  0.7067  0.0246
            ( 52.87%)   0.7271* H  3 s(100.00%)
                                     -1.0000 -0.0066
 14. (0.01445) 3C*( 1) B  1- B  2- H  4
            ( 23.56%)   0.4854* B  1 s( 18.30%)p 4.46( 81.70%)
                                      0.0000  0.4276  0.0124 -0.5630  0.0008
                                      0.0000  0.0000 -0.7067 -0.0246
            ( 23.56%)   0.4854* B  2 s( 18.30%)p 4.46( 81.70%)
                                      0.0000  0.4276  0.0124  0.5630 -0.0008
                                      0.0000  0.0000 -0.7067 -0.0246
            ( 52.87%)   0.7271* H  4 s(100.00%)
                                     -1.0000 -0.0066
 15. (0.00041) 3Cn( 1) B  1- B  2- H  3
            ( 50.00%)   0.7071* B  1 s( 18.30%)p 4.46( 81.70%)
                                      0.0000 -0.4276 -0.0124  0.5630 -0.0008
                                      0.0000  0.0000 -0.7067 -0.0246
            ( 50.00%)  -0.7071* B  2 s( 18.30%)p 4.46( 81.70%)
                                      0.0000 -0.4276 -0.0124 -0.5630  0.0008
                                      0.0000  0.0000 -0.7067 -0.0246
            (  0.00%)   0.0000* H  3 s(  0.00%)p 0.00(  0.00%)
                                      0.0000  0.0000
 16. (0.00041) 3Cn( 1) B  1- B  2- H  4
            ( 50.00%)   0.7071* B  1 s( 18.30%)p 4.46( 81.70%)
                                      0.0000 -0.4276 -0.0124  0.5630 -0.0008
                                      0.0000  0.0000  0.7067  0.0246
            ( 50.00%)  -0.7071* B  2 s( 18.30%)p 4.46( 81.70%)
                                      0.0000 -0.4276 -0.0124 -0.5630  0.0008
                                      0.0000  0.0000  0.7067  0.0246
            (  0.00%)   0.0000* H  4 s(  0.00%)p 0.00(  0.00%)
                                      0.0000  0.0000
 17. (0.00148) RY ( 1) B  1         s(  0.00%)p 1.00(100.00%)
                                      0.0000  0.0000  0.0000  0.0000  0.0000
                                      0.0345  0.9994  0.0000  0.0000
 18. (0.00081) RY ( 2) B  1         s(  4.04%)p23.76( 95.96%)
                                      0.0000  0.0244  0.1995  0.0215 -0.9794
                                      0.0000  0.0000  0.0000  0.0000
 19. (0.00002) RY ( 3) B  1         s( 95.99%)p 0.04(  4.01%)
 20. (0.00000) RY ( 4) B  1         s(  0.00%)p 1.00(100.00%)
 21. (0.00148) RY ( 1) B  2         s(  0.00%)p 1.00(100.00%)
                                      0.0000  0.0000  0.0000  0.0000  0.0000
                                      0.0345  0.9994  0.0000  0.0000
 22. (0.00081) RY ( 2) B  2         s(  4.04%)p23.76( 95.96%)
                                      0.0000  0.0244  0.1995 -0.0215  0.9794
                                      0.0000  0.0000  0.0000  0.0000
 23. (0.00002) RY ( 3) B  2         s( 95.99%)p 0.04(  4.01%)
 24. (0.00000) RY ( 4) B  2         s(  0.00%)p 1.00(100.00%)
 25. (0.00181) RY ( 1) H  3         s(100.00%)
                                     -0.0066  1.0000
 26. (0.00181) RY ( 1) H  4         s(100.00%)
                                     -0.0066  1.0000
 27. (0.00070) RY ( 1) H  5         s(100.00%)
                                     -0.0004  1.0000
 28. (0.00070) RY ( 1) H  6         s(100.00%)
                                     -0.0004  1.0000
 29. (0.00070) RY ( 1) H  7         s(100.00%)
                                     -0.0004  1.0000
 30. (0.00070) RY ( 1) H  8         s(100.00%)
                                     -0.0004  1.0000
```

The resulting NBO Lewis structure has improved significantly [only 0.057e (0.36%) non-Lewis occupancy]. The structure includes the expected 3-center B-H-B bonds (NBOs 7, 8), each with reasonably high occupancy (1.9846e). Each 3-c bond is composed of *p*-rich ($sp^{4.46}$) boron hybrids and the hydrogen 1*s* NAO, with about 47.13% of the orbital density on the central hydrogen. Note

that each 3-center bond NBO is associated with *two* 3-c non-Lewis NBOs [viz., NBOs 13 ("3C*") and 15 ("3Cn") for the first 3-c bond], which contribute in distinct ways to delocalization interactions. The "3C*" and "3Cn" labels are assigned to the orbital with "greater" and "lesser" 3-center character, respectively, i.e.. "n" has the smaller ("non-bonding") contribution from its least important atomic component).

Of course, the accuracy of *any* standard Lewis structure might be improved slightly by extending the NBO search from 2-center to 3-center bonds, thus allowing greater variational flexibility to maximize occupancy. However, this example illustrates the kind of *qualitative* improvement that signals the need for a truly new type of 3-center "connector" to augment the zeroth-order 1c/2c picture of Lewis structural bonding.

Note that the NBO 3c label may appear to have the wrong connectivity (as in the present case, e.g., where "B 1- B 2- H 3" is written instead of the more reasonable "B 1- H 3- B 2"). This is a consequence of the fact that the NBO algorithms have no inkling of the positions of the atoms in space, and thus of which label is more "reasonable."

B.6 NBO ILLUSTRATIONS

B.6.9 NBO Directed Search ($CHOOSE Keylist)

To illustrate the $CHOOSE keylist for a directed NBO search, we again make use of the methylamine example (Section A.3). The vicinal $n_N \rightarrow \sigma^*_{CH}$ delocalization, to which attention has been repeatedly called in the examples, may be associated, in resonance theory terms, with the "double-bond, no-bond" resonance structure shown below:
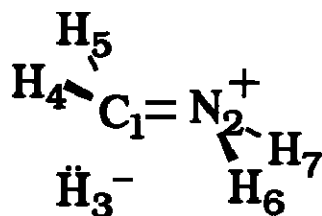
To investigate the suitability of this resonance structure for describing the methylamine wavefunction, we would specify the $CHOOSE keylist (Section B.4) as follows:

```
$CHOOSE                !double-bond, no-bond resonance
   LONE  3  1   END
   BOND  S 1 4  S 1 5  D 1 2  S 2 6  S 2 7   END
$END
```

When this is included in the input file, the NBO program produces the output shown below:

```
NATURAL BOND ORBITAL ANALYSIS:
Reading $CHOOSE keylist

                      Occupancies      Lewis Structure    Low   High
        Max   Occ    -------------------  -----------------  occ   occ
 Cycle  Ctr  Thresh   Lewis   non-Lewis   CR  BD  nC  LP    (L)   (NL)
========================================================================
   1     2    0.71   16.67241  1.32759     2   6   0   1     0     2
------------------------------------------------------------------------

Structure accepted: NBOs selected via the $CHOOSE keylist

 -------------------------------------------------------
  Core                   3.99853 ( 99.963% of    4)
  Valence Lewis         12.67387 ( 90.528% of   14)
 =================     ============================
  Total Lewis           16.67241 ( 92.624% of   18)
 -------------------------------------------------------
  Valence non-Lewis      1.29951 (  7.220% of   18)
  Rydberg non-Lewis      0.02808 (  0.156% of   18)
 =================     ============================
  Total non-Lewis        1.32759 (  7.376% of   18)
 -------------------------------------------------------

    (Occupancy)   Bond orbital / Coefficients / Hybrids
 ----------------- Lewis -------------------------------------------------
  1. (1.99901) CR ( 1) C  1             s(100.00%)
                                     1.0000  0.0000  0.0000  0.0000  0.0000
```

```
                                        0.0000  0.0000  0.0000  0.0000
   2. (1.99953) CR ( 1) N   2           s(100.00%)
                                        1.0000  0.0000  0.0000  0.0000  0.0000
                                        0.0000  0.0000  0.0000  0.0000
   3. (0.81422) LP ( 1) H   3           s(100.00%)
                                        1.0000  0.0000
   4. (1.96987) BD ( 1) C   1- N   2
             (  6.75%)   0.2598* C  1 s(  0.71%)p99.99( 99.29%)
                                        0.0000  0.0822  0.0182  0.5683 -0.0569
                                        0.8142 -0.0612  0.0000  0.0000
             ( 93.25%)   0.9657* N  2 s( 19.87%)p 4.03( 80.13%)
                                        0.0000 -0.4458  0.0000 -0.0427 -0.0067
                                        0.8940 -0.0111  0.0000  0.0000
   5. (1.92744) BD ( 2) C   1- N   2
             ( 39.65%)   0.6297* C  1 s( 39.10%)p 1.56( 60.90%)
                                        0.0000  0.6241  0.0374 -0.6684 -0.0667
                                        0.3945 -0.0469  0.0000  0.0000
             ( 60.35%)   0.7769* N  2 s( 20.55%)p 3.87( 79.45%)
                                        0.0000  0.4534 -0.0012  0.8504 -0.0020
                                        0.2665 -0.0135  0.0000  0.0000
   6. (1.98627) BD ( 1) C   1- H   4
             ( 61.01%)   0.7811* C  1 s( 29.91%)p 2.34( 70.09%)
                                        0.0000  0.5469 -0.0001  0.3391 -0.0075
                                       -0.2929 -0.0075  0.7070 -0.0104
             ( 38.99%)   0.6244* H  4 s(100.00%)
                                        1.0000  0.0008
   7. (1.98627) BD ( 1) C   1- H   5
             ( 61.01%)   0.7811* C  1 s( 29.91%)p 2.34( 70.09%)
                                        0.0000  0.5469 -0.0001  0.3391 -0.0075
                                       -0.2929 -0.0075 -0.7070  0.0104
             ( 38.99%)   0.6244* H  5 s(100.00%)
                                        1.0000  0.0008
   8. (1.99490) BD ( 1) N   2- H   6
             ( 68.36%)   0.8268* N  2 s( 29.77%)p 2.36( 70.23%)
                                        0.0000  0.5456  0.0005 -0.3706 -0.0171
                                        0.2542 -0.0038 -0.7070 -0.0093
             ( 31.64%)   0.5625* H  6 s(100.00%)
                                        1.0000  0.0031
   9. (1.99490) BD ( 1) N   2- H   7
             ( 68.36%)   0.8268* N  2 s( 29.77%)p 2.36( 70.23%)
                                        0.0000  0.5456  0.0005 -0.3706 -0.0171
                                        0.2542 -0.0038  0.7070  0.0093
             ( 31.64%)   0.5625* H  7 s(100.00%)
                                        1.0000  0.0031
--------------- non-Lewis ----------------------------------------------------
  10. (1.02153) BD*( 1) C   1- N   2
             ( 93.25%)   0.9657* C  1 s(  0.71%)p99.99( 99.29%)
                                        0.0000  0.0822  0.0182  0.5683 -0.0569
                                        0.8142 -0.0612  0.0000  0.0000
             (  6.75%)  -0.2598* N  2 s( 19.87%)p 4.03( 80.13%)
                                        0.0000 -0.4458  0.0000 -0.0427 -0.0067
                                        0.8940 -0.0111  0.0000  0.0000
  11. (0.23037) BD*( 2) C   1- N   2
             ( 60.35%)   0.7769* C  1 s( 39.10%)p 1.56( 60.90%)
                                        0.0000  0.6241  0.0374 -0.6684 -0.0667
                                        0.3945 -0.0469  0.0000  0.0000
             ( 39.65%)  -0.6297* N  2 s( 20.55%)p 3.87( 79.45%)
                                        0.0000  0.4534 -0.0012  0.8504 -0.0020
                                        0.2665 -0.0135  0.0000  0.0000
  12. (0.01206) BD*( 1) C   1- H   4
             ( 38.99%)   0.6244* C  1 s( 29.91%)p 2.34( 70.09%)
                                        0.0000 -0.5469  0.0001 -0.3391  0.0075
                                        0.2929  0.0075 -0.7070  0.0104
             ( 61.01%)  -0.7811* H  4 s(100.00%)
                                       -1.0000 -0.0008
  13. (0.01206) BD*( 1) C   1- H   5
             ( 38.99%)   0.6244* C  1 s( 29.91%)p 2.34( 70.09%)
                                        0.0000 -0.5469  0.0001 -0.3391  0.0075
                                        0.2929  0.0075  0.7070 -0.0104
             ( 61.01%)  -0.7811* H  5 s(100.00%)
                                       -1.0000 -0.0008
```

```
 14. (0.01174) BD*( 1) N  2- H  6
              ( 31.64%)   0.5625* N  2 s( 29.77%)p 2.36( 70.23%)
                                        0.0000 -0.5456 -0.0005  0.3706  0.0171
                                       -0.2542  0.0038  0.7070  0.0093
              ( 68.36%)  -0.8268* H  6 s(100.00%)
                                       -1.0000 -0.0031
 15. (0.01174) BD*( 1) N  2- H  7
              ( 31.64%)   0.5625* N  2 s( 29.77%)p 2.36( 70.23%)
                                        0.0000 -0.5456 -0.0005  0.3706  0.0171
                                       -0.2542  0.0038 -0.7070 -0.0093
              ( 68.36%)  -0.8268* H  7 s(100.00%)
                                       -1.0000 -0.0031
 16. (0.01936) RY ( 1) C  1           s( 10.51%)p 8.51( 89.49%)
                                        0.0000 -0.0740  0.3157  0.0052 -0.7444
                                       -0.0985 -0.5753  0.0000  0.0000
 17. (0.00032) RY ( 2) C  1           s(  0.00%)p 1.00(100.00%)
                                        0.0000  0.0000  0.0000  0.0000  0.0000
                                        0.0000  0.0000  0.0147  0.9999
 18. (0.00024) RY ( 3) C  1           s( 58.63%)p 0.71( 41.37%)
                                        0.0000 -0.0010  0.7657  0.0177 -0.1576
                                        0.0064  0.6233  0.0000  0.0000
 19. (0.00003) RY ( 4) C  1           s( 31.23%)p 2.20( 68.77%)
 20. (0.00116) RY ( 1) N  2           s(  1.59%)p62.07( 98.41%)
                                        0.0000 -0.0066  0.1257 -0.0071 -0.0764
                                       -0.0164 -0.9889  0.0000  0.0000
 21. (0.00042) RY ( 2) N  2           s(  0.00%)p 1.00(100.00%)
                                        0.0000  0.0000  0.0000  0.0000  0.0000
                                        0.0000  0.0000 -0.0131  0.9999
 22. (0.00039) RY ( 3) N  2           s( 33.56%)p 1.98( 66.44%)
                                        0.0000  0.0135  0.5791 -0.0082  0.8149
                                        0.0126  0.0104  0.0000  0.0000
 23. (0.00002) RY ( 4) N  2           s( 64.89%)p 0.54( 35.11%)
 24. (0.00175) RY ( 1) H  3           s(100.00%)
                                        0.0000  1.0000
 25. (0.00096) RY ( 1) H  4           s(100.00%)
                                       -0.0008  1.0000
 26. (0.00096) RY ( 1) H  5           s(100.00%)
                                       -0.0008  1.0000
 27. (0.00124) RY ( 1) H  6           s(100.00%)
                                       -0.0031  1.0000
 28. (0.00124) RY ( 1) H  7           s(100.00%)
```

One can see that the $CHOOSE resonance structure is significantly inferior to the principal resonance structure found by the default NBO search in Section A.3. About 1.33e, or 7.4% of the electron density, is found in non-Lewis NBOs of the $CHOOSE structure (compared to 0.05e, or 0.3%, for the principal structure). Particularly defective is the hydride `lone pair' (NBO 3), which has less than half the expected occupancy (0.814e). The C-N π bond (NBO 4) is seen to be more than 93% polarized toward N, indicative of essential lone pair character.

Note that structural elements shared by the two resonance structures (e.g., the two N-H bonds, which are common to both structures) need not have identical forms, since each detail of the NBOs is optimized with respect to the overall structure.

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B.6.10 NBO Energetic Analysis ($DEL Keylist)

The NBO energetic analysis with deletions ($DEL keylist) will be illustrated with two simple examples for RHF/3-21G methylamine (Section A.3).

The first example is the "LEWIS" option (type 4, Section B.5), requesting deletion of all non-Lewis orbitals, and hence leading to the energy of the idealized Natural Lewis Structure (NLS). (In former NBO versions, this option was known as the "NOSTAR" deletion, an alias that is retained for compatibility.) The $DEL keylist in this case is

```
$DEL   LEWIS   $END
```

which leads to the output shown below:

```
LEWIS: Delete all non-Lewis NBOs
Deletion of the following orbitals from the NBO Fock matrix:
  10  11  12  13  14  15  16  17  18  19  20  21  22  23  24  25  26  27  28

Orbital occupancies:

      Orbital                       No deletions  This deletion    Change
    ----------------------------------------------------------------------
     1. CR ( 1) C  1                   1.99900      2.00000       0.00100
     2. CR ( 1) N  2                   1.99953      2.00000       0.00047
     3. LP ( 1) N  2                   1.97795      2.00000       0.02205
     4. BD ( 1) C  1- N  2             1.99856      2.00000       0.00144
     5. BD ( 1) C  1- H  3             1.99861      2.00000       0.00139
     6. BD ( 1) C  1- H  4             1.99401      2.00000       0.00599
     7. BD ( 1) C  1- H  5             1.99401      2.00000       0.00599
     8. BD ( 1) N  2- H  6             1.99441      2.00000       0.00559
     9. BD ( 1) N  2- H  7             1.99441      2.00000       0.00559
    10. BD*( 1) C  1- N  2             0.00012      0.00000      -0.00012
    11. BD*( 1) C  1- H  3             0.01569      0.00000      -0.01569
    12. BD*( 1) C  1- H  4             0.00770      0.00000      -0.00770
    13. BD*( 1) C  1- H  5             0.00770      0.00000      -0.00770
    14. BD*( 1) N  2- H  6             0.00427      0.00000      -0.00427
    15. BD*( 1) N  2- H  7             0.00427      0.00000      -0.00427
    16. RY ( 1) C  1                   0.00105      0.00000      -0.00105
    17. RY ( 2) C  1                   0.00034      0.00000      -0.00034
    18. RY ( 3) C  1                   0.00022      0.00000      -0.00022
    19. RY ( 4) C  1                   0.00002      0.00000      -0.00002
    20. RY ( 1) N  2                   0.00116      0.00000      -0.00116
    21. RY ( 2) N  2                   0.00044      0.00000      -0.00044
    22. RY ( 3) N  2                   0.00038      0.00000      -0.00038
    23. RY ( 4) N  2                   0.00002      0.00000      -0.00002
    24. RY ( 1) H  3                   0.00178      0.00000      -0.00178
    25. RY ( 1) H  4                   0.00096      0.00000      -0.00096
    26. RY ( 1) H  5                   0.00096      0.00000      -0.00096
    27. RY ( 1) H  6                   0.00122      0.00000      -0.00122
    28. RY ( 1) H  7                   0.00122      0.00000      -0.00122

 NEXT STEP:  Evaluate the energy of the new density matrix
             that has been constructed from the deleted NBO
             Fock matrix by doing one SCF cycle.

   ----------------------------------------------------------------------

   Energy of deletion :        -94.618078245
    Total SCF energy :         -94.679444938
                           -------------------
        Energy change :           0.061367 a.u.,          38.508 kcal/mol
```

In the output above, the NBO program first enumerates the 19 NBOs to be deleted by the "LEWIS" request, then gives the complete list of NBOs with their occupancies before ("no deletions") and after ("this deletion") deletions, with the net change for each. For this LEWIS deletion, each of the nine Lewis NBOs (1-9) necessarily gets 2.0000 electrons, and each of the non-Lewis NBOs (10-28) gets occupancy 0.0000. The program than reports the energy (−94.618078 a.u.) obtained from a single pass through the SCF evaluator with the modified density matrix. In this case, deletion of the 19 non-Lewis orbitals led to an energy change of only 0.061367 a.u. (38.5 kcal/mol), less than 0.07% of the total energy.

The next example is a more selective set of deletions between `chemical fragments' (type 9), selected by the $DEL keylist input shown below:

```
$DEL
   ZERO  2  ATOM BLOCKS
             4  BY  3
                 1  3  4  5
                 2  6  7
             3  BY  4
                 2  6  7
                 1  3  4  5
   $END
```

This specifies removal of all delocalizing interactions from Lewis NBOs of the methyl fragment (atoms 1,3,4,5) into non-Lewis NBOs of the amine fragment (atoms 2,6,7), or vice versa. The NBO output for this example is shown below:

```
Zero delocalization from NBOs localized on atoms:
   1    3    4    5
 to NBOs localized on atoms:
   2    6    7
    (NBOs in common to the two groups of atoms left out)
 Zero delocalization from NBOs localized on atoms:
   2    6    7
 to NBOs localized on atoms:
   1    3    4    5
    (NBOs in common to the two groups of atoms left out)
 Deletion of the NBO Fock matrix elements between orbitals:
   1    5    6    7
 and orbitals:
  14   15   20   21   22   23   27   28
 Deletion of the NBO Fock matrix elements between orbitals:
   2    3    8    9
 and orbitals:
  11   12   13   16   17   18   19   24   25   26

 Orbital occupancies:

      Orbital                    No deletions  This deletion    Change
   --------------------------------------------------------------------------
```

```
  1. CR ( 1) C  1                        1.99900       1.99919       0.00019
  2. CR ( 1) N  2                        1.99953       1.99974       0.00021
  3. LP ( 1) N  2                        1.97795       1.99996       0.02201
  4. BD ( 1) C  1- N  2                  1.99856       1.99857       0.00001
  5. BD ( 1) C  1- H  3                  1.99861       1.99938       0.00077
  6. BD ( 1) C  1- H  4                  1.99401       1.99915       0.00513
  7. BD ( 1) C  1- H  5                  1.99401       1.99915       0.00513
  8. BD ( 1) N  2- H  6                  1.99441       1.99979       0.00538
  9. BD ( 1) N  2- H  7                  1.99441       1.99979       0.00538
 10. BD*( 1) C  1- N  2                  0.00012       0.00027       0.00016
 11. BD*( 1) C  1- H  3                  0.01569       0.00026      -0.01543
 12. BD*( 1) C  1- H  4                  0.00770       0.00057      -0.00713
 13. BD*( 1) C  1- H  5                  0.00770       0.00057      -0.00713
 14. BD*( 1) N  2- H  6                  0.00427       0.00009      -0.00418
 15. BD*( 1) N  2- H  7                  0.00427       0.00009      -0.00418
 16. RY ( 1) C  1                        0.00105       0.00016      -0.00090
 17. RY ( 2) C  1                        0.00034       0.00000      -0.00033
 18. RY ( 3) C  1                        0.00022       0.00002      -0.00020
 19. RY ( 4) C  1                        0.00002       0.00002       0.00000
 20. RY ( 1) N  2                        0.00116       0.00004      -0.00112
 21. RY ( 2) N  2                        0.00044       0.00000      -0.00044
 22. RY ( 3) N  2                        0.00038       0.00003      -0.00035
 23. RY ( 4) N  2                        0.00002       0.00001      -0.00001
 24. RY ( 1) H  3                        0.00178       0.00088      -0.00090
 25. RY ( 1) H  4                        0.00096       0.00057      -0.00039
 26. RY ( 1) H  5                        0.00096       0.00057      -0.00039
 27. RY ( 1) H  6                        0.00122       0.00057      -0.00065
 28. RY ( 1) H  7                        0.00122       0.00057      -0.00065


NEXT STEP:  Evaluate the energy of the new density matrix
            that has been constructed from the deleted NBO
            Fock matrix by doing one SCF cycle.

 -------------------------------------------------------------------------

  Energy of deletion :        -94.635054298
    Total SCF energy :        -94.679444938
                          ------------------
       Energy change :          0.044391 a.u.,         27.856 kcal/mol
 -------------------------------------------------------------------------
```

The output first lists the various orbitals and Fock matrix elements affected by this deletion, then the "before" and "after'" occupancies and net changes for each NBO. In this case, one can see that the principal effect of the deletion was increased occupancy (+0.022) of the nitrogen lone pair, NBO 3, and depleted occupancy (−0.015) of the antiperiplanar σ^*_{C1H3} antibond, NBO 11, with somewhat lesser depletion (−0.007) of the other two C-H antibonds. The total energy change (loss of delocalization energy) associated with this deletion was 27.9 kcal/mol.

To further pinpoint the source of this delocalization, one could do more selective deletions of individual orbitals or Fock matrix elements. For example, if one uses deletion type 2 (deletion of a single Fock matrix element, Section B.5.2) to delete the (3,11) element associated with the $n_N \rightarrow \sigma^*_{C1H3}$ interaction, one finds a deletion energy of 7.06 kcal/mol associated with this interaction alone. [This value may be compared with the simple second-order perturbative estimate (7.92 kcal/mol) of the $n_N \rightarrow \sigma^*_{C1H3}$ (3→11) interaction that was noted in Section A.3.5.]

B.6 NBO ILLUSTRATIONS

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B.6.11 Open-Shell UHF Output: Methyl Radical

Open-shell NBO output will be illustrated with the simple example of the planar methyl radical (CH_3), treated at the UHF/6-31G* level ($R_{CH} =$ 1.0736 Å). In the open-shell case, one obtains two separate NPA and NBO listings, one for the α and one for the β spin set, corresponding to the "different Lewis structures for different spins" description. A portion of the NBO output for the α spin manifold is reproduced below:

```
NATURAL BOND ORBITAL ANALYSIS, alpha spin orbitals:

                          Occupancies      Lewis Structure    Low    High
          Max    Occ    ------------------  ----------------   occ    occ
 Cycle    Ctr   Thresh   Lewis    non-Lewis   CR  BD  nC  LP   (L)    (NL)
================================================================================
    1      2    0.95    4.99906   0.00094    1   3   0   1     0       0
--------------------------------------------------------------------------------

Structure accepted: No low occupancy Lewis orbitals


--------------------------------------------------------------
  Core                    0.99984 ( 99.984% of    1)
  Valence Lewis           3.99923 ( 99.981% of    4)
==================      =============================
  Total Lewis            4.99906 ( 99.981% of    5)
--------------------------------------------------------------
  Valence non-Lewis      0.00070 (  0.014% of    5)
  Rydberg non-Lewis      0.00024 (  0.005% of    5)
==================      =============================
  Total non-Lewis        0.00094 (  0.019% of    5)
--------------------------------------------------------------


   (Occupancy)   Bond orbital / Coefficients / Hybrids
----------------- Lewis -------------------------------------------------------
 1. (0.99984) CR ( 1) C  1             s(100.00%)
                                          1.0000  0.0000  0.0000  0.0000  0.0000
                                          0.0000  0.0000  0.0000  0.0000  0.0000
                                          0.0000  0.0000  0.0000  0.0000  0.0000
 2. (1.00000) LP ( 1) C  1             s(  0.00%)p 1.00(100.00%)
                                          0.0000  0.0000  0.0000  0.0000  0.0000
                                          0.0000  0.0000  0.0000  0.9975 -0.0708
                                          0.0000  0.0000  0.0000  0.0000  0.0000
 3. (0.99974) BD ( 1) C  1- H  2
        ( 60.49%)   0.7778* C  1 s( 33.33%)p 2.00( 66.59%)d 0.00(  0.09%)
                                          0.0000  0.5773 -0.0030  0.0000 -0.4078
                                         -0.0120  0.7064  0.0208  0.0000  0.0000
                                         -0.0244  0.0000  0.0000 -0.0141 -0.0090
        ( 39.51%)   0.6286* H  2 s(100.00%)
                                          1.0000  0.0049
 4. (0.99974) BD ( 1) C  1- H  3
        ( 60.49%)   0.7778* C  1 s( 33.33%)p 2.00( 66.59%)d 0.00(  0.09%)
                                          0.0000  0.5773 -0.0030  0.0000 -0.4078
                                         -0.0120 -0.7064 -0.0208  0.0000  0.0000
                                          0.0244  0.0000  0.0000 -0.0141 -0.0090
        ( 39.51%)   0.6286* H  3 s(100.00%)
                                          1.0000  0.0049
 5. (0.99974) BD ( 1) C  1- H  4
        ( 60.49%)   0.7778* C  1 s( 33.33%)p 2.00( 66.59%)d 0.00(  0.09%)
                                          0.0000  0.5773 -0.0030  0.0000  0.8157
                                          0.0241  0.0000  0.0000  0.0000  0.0000
                                          0.0000  0.0000  0.0000  0.0282 -0.0090
        ( 39.51%)   0.6286* H  4 s(100.00%)
```

```
                                   1.0000  0.0049
--------------- non-Lewis --------------------------------------------------
  6. (0.00023) BD*( 1) C  1- H  2
            ( 39.51%)   0.6286* C  1 s( 33.33%)p 2.00( 66.59%)d 0.00(  0.09%)
                                     0.0000 -0.5773  0.0030  0.0000  0.4078
                                     0.0120 -0.7064 -0.0208  0.0000  0.0000
                                     0.0244  0.0000  0.0000  0.0141  0.0090
            ( 60.49%)  -0.7778* H  2 s(100.00%)
                                    -1.0000 -0.0049
  7. (0.00023) BD*( 1) C  1- H  3
            ( 39.51%)   0.6286* C  1 s( 33.33%)p 2.00( 66.59%)d 0.00(  0.09%)
                                     0.0000 -0.5773  0.0030  0.0000  0.4078
                                     0.0120  0.7064  0.0208  0.0000  0.0000
                                    -0.0244  0.0000  0.0000  0.0141  0.0090
            ( 60.49%)  -0.7778* H  3 s(100.00%)
                                    -1.0000 -0.0049
  8. (0.00023) BD*( 1) C  1- H  4
            ( 39.51%)   0.6286* C  1 s( 33.33%)p 2.00( 66.59%)d 0.00(  0.09%)
                                     0.0000 -0.5773  0.0030  0.0000 -0.8157
                                    -0.0241  0.0000  0.0000  0.0000  0.0000
                                     0.0000  0.0000  0.0000 -0.0282  0.0090
            ( 60.49%)  -0.7778* H  4 s(100.00%)
                                    -1.0000 -0.0049
  9. (0.00000) RY ( 1) C  1         s( 17.19%)p 0.00(  0.00%)d 4.82( 82.81%)
 10. (0.00000) RY ( 2) C  1         s( 85.66%)p 0.01(  0.58%)d 0.16( 13.76%)
 11. (0.00000) RY ( 3) C  1         s(  0.00%)p 1.00( 97.18%)d 0.03(  2.82%)
 12. (0.00000) RY ( 4) C  1         s(  0.62%)p99.99( 94.94%)d 7.17(  4.44%)
 13. (0.00000) RY ( 5) C  1         s(  4.96%)p 0.80(  3.95%)d18.36( 91.09%)
 14. (0.00000) RY ( 6) C  1         s(  0.00%)p 0.00(  0.00%)d 1.00(100.00%)
 15. (0.00000) RY ( 7) C  1         s(  0.00%)p 0.00(  0.00%)d 1.00(100.00%)
 16. (0.00000) RY ( 8) C  1         s( 91.59%)p 0.01(  0.65%)d 0.08(  7.76%)
 17. (0.00000) RY ( 9) C  1         s(  0.00%)p 1.00(  2.94%)d33.04( 97.06%)
 18. (0.00000) RY (10) C  1         s(  0.00%)p 1.00(100.00%)d 0.00(  0.00%)
 19. (0.00008) RY ( 1) H  2         s(100.00%)
 20. (0.00008) RY ( 1) H  3         s(100.00%)
 21. (0.00008) RY ( 1) H  4         s(100.00%)
```

As can be seen in the output, the initial NBO spin-orbital occupancy threshold was set at 0.95 (rather than 1.90). The occupancies of L-type spin-NBOs 1-5 are about 1.0000, but other aspects of the output are familiar. Note the slight admixture of d-character (0.09%) in the σ_{CH} bond hybrids (NBOs 4-6), whereas the out-of-plane radical LP ("lone particle") orbital (NBO 2) has pure p-character.

The NBO output for the β (`ionized') spin set then follows:

```
NATURAL BOND ORBITAL ANALYSIS, beta spin orbitals:

                       Occupancies      Lewis Structure    Low   High
        Max   Occ    -------------------  -----------------  occ   occ
 Cycle  Ctr  Thresh   Lewis    non-Lewis   CR  BD  nC  LP   (L)   (NL)
 ===========================================================================
   1     2    0.95   3.99969   0.00031     1   3   0   0     0     0
 ---------------------------------------------------------------------------

Structure accepted: No low occupancy Lewis orbitals

 --------------------------------------------------------
  Core                      0.99985 ( 99.985% of   1)
  Valence Lewis             2.99984 ( 99.995% of   3)
 ==================        ============================
  Total Lewis               3.99969 ( 99.992% of   4)
```

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```
      -------------------------------------------------------
      Valence non-Lewis       0.00008 (  0.002% of   4)
      Rydberg non-Lewis       0.00023 (  0.006% of   4)
      ==================      =============================
      Total non-Lewis         0.00031 (  0.008% of   4)
      -------------------------------------------------------


       (Occupancy)  Bond orbital / Coefficients / Hybrids
   ----------------- Lewis -------------------------------------------------
    1. (0.99985) CR ( 1) C  1           s(100.00%)
                                         1.0000  0.0000  0.0000  0.0000  0.0000
                                         0.0000  0.0000  0.0000  0.0000  0.0000
                                         0.0000  0.0000  0.0000  0.0000  0.0000
    2. (0.99995) BD ( 1) C  1- H  2
             ( 57.47%)   0.7581* C  1 s( 33.27%)p 2.00( 66.59%)d 0.00(  0.14%)
                                         0.0000  0.5768  0.0033  0.0000 -0.4078
                                        -0.0127  0.7063  0.0221  0.0000  0.0000
                                        -0.0244  0.0000  0.0000 -0.0141 -0.0256
             ( 42.53%)   0.6521* H  2 s(100.00%)
                                         1.0000 -0.0041
    3. (0.99995) BD ( 1) C  1- H  3
             ( 57.47%)   0.7581* C  1 s( 33.27%)p 2.00( 66.59%)d 0.00(  0.14%)
                                         0.0000  0.5768  0.0033  0.0000 -0.4078
                                        -0.0127 -0.7063 -0.0221  0.0000  0.0000
                                         0.0244  0.0000  0.0000 -0.0141 -0.0256
             ( 42.53%)   0.6521* H  3 s(100.00%)
                                         1.0000 -0.0041
    4. (0.99995) BD ( 1) C  1- H  4
             ( 57.47%)   0.7581* C  1 s( 33.27%)p 2.00( 66.59%)d 0.00(  0.14%)
                                         0.0000  0.5768  0.0033  0.0000  0.8156
                                         0.0255  0.0000  0.0000  0.0000  0.0000
                                         0.0000  0.0000  0.0000  0.0282 -0.0256
             ( 42.53%)   0.6521* H  4 s(100.00%)
                                         1.0000 -0.0041
   --------------- non-Lewis -----------------------------------------------
    5. (0.00000) LP ( 1) C  1           s(  0.00%)p 1.00(100.00%)d 0.00(  0.00%)
    6. (0.00003) BD*( 1) C  1- H  2
             ( 42.53%)   0.6521* C  1 s( 33.27%)p 2.00( 66.59%)d 0.00(  0.14%)
             ( 57.47%)  -0.7581* H  2 s(100.00%)
    7. (0.00003) BD*( 1) C  1- H  3
             ( 42.53%)   0.6521* C  1 s( 33.27%)p 2.00( 66.59%)d 0.00(  0.14%)
             ( 57.47%)  -0.7581* H  3 s(100.00%)
    8. (0.00003) BD*( 1) C  1- H  4
             ( 42.53%)   0.6521* C  1 s( 33.27%)p 2.00( 66.59%)d 0.00(  0.14%)
             ( 57.47%)  -0.7581* H  4 s(100.00%)
    9. (0.00001) RY ( 1) C  1           s(  5.35%)p 0.00(  0.00%)d17.69( 94.65%)
   10. (0.00000) RY ( 2) C  1           s( 90.24%)p 0.06(  5.72%)d 0.04(  4.05%)
   11. (0.00000) RY ( 3) C  1           s(  0.00%)p 1.00( 91.42%)d 0.09(  8.58%)
   12. (0.00000) RY ( 4) C  1           s(  6.64%)p12.61( 83.70%)d 1.46(  9.66%)
   13. (0.00000) RY ( 5) C  1           s( 72.52%)p 0.00(  0.34%)d 0.37( 27.14%)
   14. (0.00000) RY ( 6) C  1           s(  0.00%)p 0.00(  0.00%)d 1.00(100.00%)
   15. (0.00000) RY ( 7) C  1           s(  0.00%)p 0.00(  0.00%)d 1.00(100.00%)
   16. (0.00000) RY ( 8) C  1           s(  0.00%)p 1.00(100.00%)d 0.00(  0.00%)
   17. (0.00000) RY ( 9) C  1           s(  0.00%)p 1.00(  8.70%)d10.50( 91.30%)
   18. (0.00000) RY (10) C  1           s( 25.46%)p 0.41( 10.37%)d 2.52( 64.18%)
   19. (0.00008) RY ( 1) H  2           s(100.00%)
   20. (0.00008) RY ( 1) H  3           s(100.00%)
   21. (0.00008) RY ( 1) H  4           s(100.00%)
```

The principal difference to be seen is that the radical orbital (NBO 5) is essentially empty in this spin set, and the polarization of the σ_{CH} bonds is somewhat altered (about 57.5% on the C atom in the β set set, *vs.* 60.5% in the α set). [In other cases, the α and β NBO Lewis structures might differ even in the number and location of 1-c (non-bonding) and 2-c (bond) structural

B.6 NBO ILLUSTRATIONS

elements.] Note that the overall quality of the open-shell natural Lewis structure description (> 99.9%) is comparable to that of ordinary closed-shell molecules, and the interpretation of the NBO output follows familiar lines.

WARNING
If you wish to analyze an open-shell wavefunction with an ESS method that produces only the "spinless" (spin-averaged) density matrix, rather than the separate density matrices for α and β spin, you can use the MSPNBO keyword (Sec. B.2.2) to calculate "maximum spin-paired" MSPNBOs rather than "true" NBOs. (NAOs and total populations are identical in NBO and MSPNBO searches, but NHOs, NBOs, and NLMOs are not.) Note the differences!

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B.6.12 Effective Core Potential: Cu₂ Dimer

To illustrate the variations of NBO output associated with use of effective core potentials (ECP) and inclusion of *d* orbitals, we use the example of the copper dimer Cu_2 ($R = 2.2195$ Å, RHF/LANL1DZ level). Because the NBO program communicates directly with the ESS program for details of the ECP, no special keywords are necessary.

Use of an ECP shows up most directly in the NPA portion of the output, shown below:

```
 NATURAL POPULATIONS:  Natural atomic orbital occupancies

  NAO Atom No lang   Type(AO)     Occupancy      Energy
 -------------------------------------------------------
    1    Cu   1   s     Val( 4s)     0.99541     -0.03232
    2    Cu   1   s     Ryd( 5s)     0.00034      1.55373
    3    Cu   1   px    Ryd( 4p)     0.00130      0.16919
    4    Cu   1   px    Ryd( 5p)     0.00000      0.10809
    5    Cu   1   py    Ryd( 4p)     0.00130      0.16919
    6    Cu   1   py    Ryd( 5p)     0.00000      0.10809
    7    Cu   1   pz    Ryd( 4p)     0.00760      1.01137
    8    Cu   1   pz    Ryd( 5p)     0.00020      0.29342
    9    Cu   1   dxy   Val( 3d)     1.99997     -0.46633
   10    Cu   1   dxy   Ryd( 4d)     0.00003      1.04801
   11    Cu   1   dxz   Val( 3d)     1.99870     -0.46849
   12    Cu   1   dxz   Ryd( 4d)     0.00000      1.13602
   13    Cu   1   dyz   Val( 3d)     1.99870     -0.46849
   14    Cu   1   dyz   Ryd( 4d)     0.00000      1.13602
   15    Cu   1   dx2y2 Val( 3d)     1.99997     -0.46633
   16    Cu   1   dx2y2 Ryd( 4d)     0.00003      1.04801
   17    Cu   1   dz2   Val( 3d)     1.99626     -0.46858
   18    Cu   1   dz2   Ryd( 4d)     0.00018      1.65132

   19    Cu   2   s     Val( 4s)     0.99541     -0.03232
   20    Cu   2   s     Ryd( 5s)     0.00034      1.55373
   21    Cu   2   px    Ryd( 4p)     0.00130      0.16919
   22    Cu   2   px    Ryd( 5p)     0.00000      0.10809
   23    Cu   2   py    Ryd( 4p)     0.00130      0.16919
   24    Cu   2   py    Ryd( 5p)     0.00000      0.10809
   25    Cu   2   pz    Ryd( 4p)     0.00760      1.01137
   26    Cu   2   pz    Ryd( 5p)     0.00020      0.29342
   27    Cu   2   dxy   Val( 3d)     1.99997     -0.46633
   28    Cu   2   dxy   Ryd( 4d)     0.00003      1.04801
   29    Cu   2   dxz   Val( 3d)     1.99870     -0.46849
   30    Cu   2   dxz   Ryd( 4d)     0.00000      1.13602
   31    Cu   2   dyz   Val( 3d)     1.99870     -0.46849
   32    Cu   2   dyz   Ryd( 4d)     0.00000      1.13602
   33    Cu   2   dx2y2 Val( 3d)     1.99997     -0.46633
   34    Cu   2   dx2y2 Ryd( 4d)     0.00003      1.04801
   35    Cu   2   dz2   Val( 3d)     1.99626     -0.46858
   36    Cu   2   dz2   Ryd( 4d)     0.00018      1.65132

 [36 electrons found in the effective core potential]
     Population inversion found on atom Cu   1
     Population inversion found on atom Cu   2


  Summary of Natural Population Analysis:

                                Natural Population
                Natural    ------------------------------------------
```

B.6 NBO ILLUSTRATIONS

```
 Atom No    Charge        Core     Valence   Rydberg      Total
------------------------------------------------------------------
  Cu  1    0.00000     18.00000    10.98901    0.01099    29.00000
  Cu  2    0.00000     18.00000    10.98901    0.01099    29.00000
==================================================================
* Total *  0.00000     36.00000    21.97802    0.02198    58.00000

                           Natural Population
------------------------------------------------------------
  Effective Core          36.00000
  Valence                 21.97802 ( 99.9001% of   22)
  Natural Minimal Basis   57.97802 ( 99.9621% of   58)
  Natural Rydberg Basis    0.02198 (  0.0379% of   58)
------------------------------------------------------------

   Atom No        Natural Electron Configuration
--------------------------------------------------------------------------
    Cu  1       [core]4s( 1.00)3d( 9.99)4p( 0.01)
    Cu  2       [core]4s( 1.00)3d( 9.99)4p( 0.01)
```

As noted below the first NPA table, 36 electrons were found in the ECP, so the labels for NAOs in the table begin with the designations 4*s*, 5*s*, etc. of the presumed extra-core electrons. The ECP electrons are duly entered in the NPA tables (labelled as "effective core" in the NPA summary table) as part of the total Lewis occupancy, and are taken into proper account in assigning atomic charges. The NPA output in this case includes a "population inversion" message to indicate that one or more NAO occupancies are not ordered in accordance with the energy order [e.g., NBO 34 has lower energy than NBO 36 (1.04801 a.u. vs. 1.65132 a.u.), but NBO 36 has the higher occupancy (0.00018e vs. 0.00003e), a "population inversion" of negligible physical significance].

The main ECP effect in the NBO portion of the output is the omission of core NBOs, as illustrated below:

```
NATURAL BOND ORBITAL ANALYSIS:

                          Occupancies       Lewis Structure    Low    High
           Max    Occ   -------------------  ----------------   occ    occ
 Cycle Ctr  Thresh   Lewis    non-Lewis   CR  BD  nC  LP   (L)    (NL)
=========================================================================
   1    2    1.90   57.99424   0.00576     0   1   0  10    0      0
-------------------------------------------------------------------------

Structure accepted: No low occupancy Lewis orbitals

  ------------------------------------------------------
  Effective core          36.00000
  Valence Lewis           21.99424 ( 99.974% of  22)
  ==================      ============================
  Total Lewis             57.99424 ( 99.990% of  58)
  ------------------------------------------------------
  Valence non-Lewis        0.00000 (  0.000% of  58)
  Rydberg non-Lewis        0.00576 (  0.010% of  58)
  ==================      ============================
  Total non-Lewis          0.00576 (  0.010% of  58)
  ------------------------------------------------------
```

B.6 NBO ILLUSTRATIONS

```
     (Occupancy)   Bond orbital / Coefficients / Hybrids
----------------- Lewis ------------------------------------------------
   1. (1.99999) LP ( 1)Cu  1            s(  0.00%)p 0.00(  0.00%)d 1.00(100.00%)
                                         0.0000  0.0000  0.0000  0.0000  0.0000
                                         0.0000  0.0000  0.0000  1.0000 -0.0036
                                         0.0000  0.0000  0.0000  0.0000  0.0000
                                         0.0000  0.0000  0.0000
   2. (1.99999) LP ( 2)Cu  1            s(  0.00%)p 0.00(  0.00%)d 1.00(100.00%)
                                         0.0000  0.0000  0.0000  0.0000  0.0000
                                         0.0000  0.0000  0.0000  0.0000  0.0000
                                         0.0000  0.0000  0.0000  0.0000  1.0000
                                        -0.0036  0.0000  0.0000
   3. (1.99966) LP ( 3)Cu  1            s(  0.30%)p 0.05(  0.02%)d99.99( 99.68%)
                                         0.0545 -0.0063  0.0000  0.0000  0.0000
                                         0.0000 -0.0074 -0.0098  0.0000  0.0000
                                         0.0000  0.0000  0.0000  0.0000  0.0000
                                         0.0000 -0.9984 -0.0063
   4. (1.99874) LP ( 4)Cu  1            s(  0.00%)p 0.00(  0.00%)d 1.00(100.00%)
                                         0.0000  0.0000  0.0042  0.0011  0.0000
                                         0.0000  0.0000  0.0000  0.0000  0.0000
                                         1.0000  0.0004  0.0000  0.0000  0.0000
                                         0.0000  0.0000  0.0000
   5. (1.99874) LP ( 5)Cu  1            s(  0.00%)p 0.00(  0.00%)d 1.00(100.00%)
                                         0.0000  0.0000  0.0000  0.0000  0.0042
                                         0.0011  0.0000  0.0000  0.0000  0.0000
                                         0.0000  0.0000  1.0000  0.0004  0.0000
                                         0.0000  0.0000  0.0000
   6. (1.99999) LP ( 1)Cu  2            s(  0.00%)p 0.00(  0.00%)d 1.00(100.00%)
                                         0.0000  0.0000  0.0000  0.0000  0.0000
                                         0.0000  0.0000  0.0000  1.0000 -0.0036
                                         0.0000  0.0000  0.0000  0.0000  0.0000
                                         0.0000  0.0000  0.0000
   7. (1.99999) LP ( 2)Cu  2            s(  0.00%)p 0.00(  0.00%)d 1.00(100.00%)
                                         0.0000  0.0000  0.0000  0.0000  0.0000
                                         0.0000  0.0000  0.0000  0.0000  0.0000
                                         0.0000  0.0000  0.0000  0.0000  1.0000
                                        -0.0036  0.0000  0.0000
   8. (1.99966) LP ( 3)Cu  2            s(  0.30%)p 0.05(  0.02%)d99.99( 99.68%)
                                         0.0545 -0.0063  0.0000  0.0000  0.0000
                                         0.0000  0.0074  0.0098  0.0000  0.0000
                                         0.0000  0.0000  0.0000  0.0000  0.0000
                                         0.0000 -0.9984 -0.0063
   9. (1.99874) LP ( 4)Cu  2            s(  0.00%)p 0.00(  0.00%)d 1.00(100.00%)
                                         0.0000  0.0000 -0.0042 -0.0011  0.0000
                                         0.0000  0.0000  0.0000  0.0000  0.0000
                                         1.0000  0.0004  0.0000  0.0000  0.0000
                                         0.0000  0.0000  0.0000
  10. (1.99874) LP ( 5)Cu  2            s(  0.00%)p 0.00(  0.00%)d 1.00(100.00%)
                                         0.0000  0.0000  0.0000  0.0000 -0.0042
                                        -0.0011  0.0000  0.0000  0.0000  0.0000
                                         0.0000  0.0000  1.0000  0.0004  0.0000
                                         0.0000  0.0000  0.0000
  11. (2.00000) BD ( 1)Cu  1-Cu  2
               ( 50.00%)   0.7071*Cu  1 s( 98.95%)p 0.01(  0.75%)d 0.00(  0.30%)
                                         0.9947  0.0007  0.0000  0.0000  0.0000
                                         0.0000 -0.0865  0.0026  0.0000  0.0000
                                         0.0000  0.0000  0.0000  0.0000  0.0000
                                         0.0000  0.0549  0.0051
               ( 50.00%)   0.7071*Cu  2 s( 98.95%)p 0.01(  0.75%)d 0.00(  0.30%)
                                         0.9947  0.0007  0.0000  0.0000  0.0000
                                         0.0000  0.0865 -0.0026  0.0000  0.0000
                                         0.0000  0.0000  0.0000  0.0000  0.0000
                                         0.0000  0.0549  0.0051
--------------- non-Lewis ----------------------------------------------
  12. (0.00000) BD*( 1)Cu  1-Cu  2
               ( 50.00%)   0.7071*Cu  1 s( 98.95%)p 0.01(  0.75%)d 0.00(  0.30%)
               ( 50.00%)  -0.7071*Cu  2 s( 98.95%)p 0.01(  0.75%)d 0.00(  0.30%)
  13. (0.00126) RY ( 1)Cu  1            s(  0.00%)p 1.00( 99.99%)d 0.00(  0.01%)
                                         0.0000  0.0000  0.9996  0.0258  0.0000
```

```
                                          0.0000   0.0000   0.0000   0.0000   0.0000
                                         -0.0042  -0.0093   0.0000   0.0000   0.0000
                                          0.0000   0.0000   0.0000
 14. (0.00126) RY ( 2)Cu  1              s(  0.00%)p 1.00( 99.99%)d 0.00(  0.01%)
                                          0.0000   0.0000   0.0000   0.0000   0.9996
                                          0.0258   0.0000   0.0000   0.0000   0.0000
                                          0.0000   0.0000  -0.0042  -0.0093   0.0000
                                          0.0000   0.0000   0.0000
 15. (0.00034) RY ( 3)Cu  1              s( 75.24%)p 0.03(  2.18%)d 0.30( 22.59%)
                                         -0.0102   0.8673   0.0000   0.0000   0.0000
                                          0.0000  -0.1383   0.0515   0.0000   0.0000
                                          0.0000   0.0000   0.0000   0.0000   0.0000
                                          0.0000  -0.0026  -0.4753
 16. (0.00001) RY ( 4)Cu  1              s(  0.00%)p 0.00(  0.00%)d 1.00(100.00%)
 17. (0.00001) RY ( 5)Cu  1              s(  0.00%)p 0.00(  0.00%)d 1.00(100.00%)
 18. (0.00000) RY ( 6)Cu  1              s(  0.00%)p 1.00(  0.09%)d99.99( 99.91%)
 19. (0.00000) RY ( 7)Cu  1              s(  0.00%)p 1.00(  0.09%)d99.99( 99.91%)
 20. (0.00000) RY ( 8)Cu  1              s(  0.35%)p99.99( 97.55%)d 6.06(  2.10%)
 21. (0.00000) RY ( 9)Cu  1              s(  0.00%)p 1.00( 99.92%)d 0.00(  0.08%)
 22. (0.00000) RY (10)Cu  1              s(  0.00%)p 1.00( 99.92%)d 0.00(  0.08%)
 23. (0.00000) RY (11)Cu  1              s(  1.45%)p67.18( 97.47%)d 0.74(  1.07%)
 24. (0.00000) RY (12)Cu  1              s( 23.72%)p 0.09(  2.03%)d 3.13( 74.25%)
 25. (0.00126) RY ( 1)Cu  2              s(  0.00%)p 1.00( 99.99%)d 0.00(  0.01%)
                                          0.0000   0.0000   0.9996   0.0258   0.0000
                                          0.0000   0.0000   0.0000   0.0000   0.0000
                                          0.0042   0.0093   0.0000   0.0000   0.0000
                                          0.0000   0.0000   0.0000
 26. (0.00126) RY ( 2)Cu  2              s(  0.00%)p 1.00( 99.99%)d 0.00(  0.01%)
                                          0.0000   0.0000   0.0000   0.0000   0.9996
                                          0.0258   0.0000   0.0000   0.0000   0.0000
                                          0.0000   0.0000   0.0042   0.0093   0.0000
                                          0.0000   0.0000   0.0000
 27. (0.00034) RY ( 3)Cu  2              s( 75.24%)p 0.03(  2.18%)d 0.30( 22.59%)
                                         -0.0102   0.8673   0.0000   0.0000   0.0000
                                          0.0000   0.1383  -0.0515   0.0000   0.0000
                                          0.0000   0.0000   0.0000   0.0000   0.0000
                                          0.0000  -0.0026  -0.4753
 28. (0.00001) RY ( 4)Cu  2              s(  0.00%)p 0.00(  0.00%)d 1.00(100.00%)
 29. (0.00001) RY ( 5)Cu  2              s(  0.00%)p 0.00(  0.00%)d 1.00(100.00%)
 30. (0.00000) RY ( 6)Cu  2              s(  0.00%)p 1.00(  0.09%)d99.99( 99.91%)
 31. (0.00000) RY ( 7)Cu  2              s(  0.00%)p 1.00(  0.09%)d99.99( 99.91%)
 32. (0.00000) RY ( 8)Cu  2              s(  0.35%)p99.99( 97.55%)d 6.06(  2.10%)
 33. (0.00000) RY ( 9)Cu  2              s(  0.00%)p 1.00( 99.92%)d 0.00(  0.08%)
 34. (0.00000) RY (10)Cu  2              s(  0.00%)p 1.00( 99.92%)d 0.00(  0.08%)
 35. (0.00000) RY (11)Cu  2              s(  1.45%)p67.18( 97.47%)d 0.74(  1.07%)
 36. (0.00000) RY (12)Cu  2              s( 23.72%)p 0.09(  2.03%)d 3.13( 74.25%)
```

As the output shows, the NBO tables include reference to only 11 occupied NBOs, rather than the 29 that would appear in a full calculation. Semi-empirical methods that neglect core electrons (AMPAC, etc.) are handled similarly.

The output for the Cu_2 example also illustrates some aspects of the inclusion of d orbitals in the basis set. NBOs 1-5 and 6-10 represent the $3d^8$ subshells on each atom, essentially of pure atomic d character (except for a small admixture of p character in NBOs 3, 8 oriented along the internuclear axis). The σ_{CuCu} bond (NBO 11) contains a very slight admixture (0.3%) of d character, but remaining orbitals of predominant d character (e.g., NBOs 16-19 and 28-31) are of negligible occupancy. Note that the abbreviated "$sp^\lambda d^\mu$" designations can lead to strange variations among hybrids of essentially similar character. For

B.6 NBO ILLUSTRATIONS

example, NBO 3 ("$sp^{0.05}d^{99.99}$") , NBO 17 ("$d^{1.00}$"), and NBO 18 ("$p^{1.00}d^{99.99}$") are all of essentially pure (>99%) d character, but with strikingly different labels depending on whether there is sufficient s or p character (in numerical terms) to express the hybrid ratios in $sp^{\lambda}d^{\mu}$ form. Consult the percentages of s-. p-, and d-character whenever there is doubt about how to interpret a particular $sp^{\lambda}d^{\mu}$ designation.

B.7 FILE47: INPUT FOR THE GenNBO STAND-ALONE NBO PROGRAM

B.7.1 Introduction

The general NBO program, GenNBO, is a stand-alone program which is not directly attached to an ESS program. Rather, information about the wavefunction is provided to the core NBO program by a sequential input file, FILE47, described in this section. [If a "FILE=jobname" keyword is provided in the $NBO keylist (as recommended), this file will actually have a filename of the form "jobname.47", but we refer to the generic "FILE47" in the following.]

Some knowledge of FILE47 is useful even if your NBO program is attached to an ESS package. If requested (see the ARCHIVE keyword, Section B.2.5), the NBO program writes FILE47, a file that summarizes all information pertaining to the computed electronic wavefunction. This file can be subsequently used as standard input to the GenNBO program to repeat the analysis of the wavefunction; simply include the $NBO keylist, and, if desired, the $CORE, $CHOOSE, and $NRTSTR keylists in FILE47 and execute GenNBO. You need never recompute the wavefunction to vary its NBO analysis! In fact, generating the FILE47 input file is a useful way to archive a wavefunction for future use or reference. [Note: the GenNBO program cannot perform the NBO energetic analysis ($DEL keylist) or other options that require access to the formatted two-electron integrals of the parent ESS package.]

If you intend to use the NBO program in conjunction with an ESS package not supported in this distribution (i.e. for which no custom interface is available), you might consider attaching a routine to your ESS program that would write the proper form of FILE47 for input into the GenNBO program. Thus, a two-step process would be required to obtain the NBO analysis of a wavefunction: (i) the initial calculation of the wavefunction with the ESS package, writing FILE47; (ii) the NBO analysis using the GenNBO program with FILE47 as input. [Alternatively, you may decide to attach the NBO program directly to your ESS package by writing your own interface routines. See the Programmer's Guide for direction.]

Section B.7.2 describes and illustrates the overall format of FILE47. Sections B.7.3-B.7.7 detail the entries of the keylists and datalists that compose this file.

B.7 FILE47: INPUT FOR THE GenNBO PROGRAM

B.7.2 Format of the FILE47 Input File

The FILE47 input file is composed of a set of keylists and datalists, each list beginning with a "$" identifier (e.g. "$BASIS") and ending with "$END",

```
    $BASIS  entries  $END
```

Individual lists are used to specify basis set information ($BASIS), density matrix elements ($DENSITY), and so forth. The order of the lists within FILE47 is immaterial. Entries within each datalist are generally free format, and may be continued on as many lines as desired. Entries can be formatted to facilitate the parsing of FILE47 (see FORMAT in B.7.3). An exclamation point (!) on any line terminates input from the line, and may be followed by arbitrary comments. The $GENNBO keylist and the $COORD, $BASIS, $DENSITY, and $OVERLAP datalists are required, but the other datalists ($FOCK, $KINETIC, $NUCLEAR, $LCAOMO, $CONTRACT, $DIPOLE, $C10, $H01, $H11) or the standard NBO keylists ($NBO, $CORE, $CHOOSE) are optional, depending on the requested application. If the $NBO keylist is not present in FILE47, the default NBO analysis is performed.

The entries of each keylist or datalist may be keywords, numerical matrix elements, or other parameters of prescribed form. A sample FILE47 input file for the RHF/3-21G methylamine example of Section A.3 is shown below (with only the first three elements of each datalist):

```
$GENNBO  NATOMS=7  NBAS=28  UPPER  BODM  FORMAT  $END
$NBO  FILE=ch3nh2  $END
$COORD
Methylamine...RHF/3-21G//Pople-Gordon standard geometry
    6    6       0.052902       0.711852       0.000000
    7    7       0.052902      -0.758148       0.000000
    1    1      -0.974760       1.075185       0.000000
    1    1       0.566733       1.075185       0.889981
    1    1       0.566733       1.075185      -0.889981
    1    1      -0.423217      -1.094815      -0.824662
    1    1      -0.423217      -1.094815       0.824662
$END
$BASIS
  CENTER =    1    1    1    1    1    1    1    1    1    2    2    2    2
              2    2    2    2    2    3    3    4    4    5    5    6    6
              7    7
   LABEL =    1    1  101  102  103    1  101  102  103    1    1  101  102
            103    1  101  102  103    1    1    1    1    1    1    1    1
              1    1
$END
$CONTRACT
  NSHELL =   16
    NEXP =   27
   NCOMP =    1    4    4    1    4    4    1    1    1    1    1    1    1
              1    1    1
   NPRIM =    3    2    1    3    2    1    2    1    2    1    2    1    2
              1    2    1
```

B.7 FILE47: INPUT FOR THE GenNBO PROGRAM

```
   NPTR =    1    4    6    7   10   12   13   15   16   18   19   21   22
            24   25   27
    EXP =  0.1722560E+03   0.2591090E+02   0.5533350E+01   0.3664980E+01
           0.7705450E+00   0.1958570E+00   0.2427660E+03   0.3648510E+02
           0.7814490E+01   0.5425220E+01   0.1149150E+01   0.2832050E+00
           0.5447178E+01   0.8245472E+00   0.1831916E+00   0.5447178E+01
           0.8245472E+00   0.1831916E+00   0.5447178E+01   0.8245472E+00
           0.1831916E+00   0.5447178E+01   0.8245472E+00   0.1831916E+00
           0.5447178E+01   0.8245472E+00   0.1831916E+00
     CS =  0.2093132E+01   0.2936751E+01   0.1801737E+01  -0.7473843E+00
           0.7126610E+00   0.2098285E+00   0.2624092E+01   0.3734359E+01
           0.2353454E+01  -0.1047101E+01   0.9685501E+00   0.2766851E+00
           0.3971513E+00   0.5579200E+00   0.1995672E+00   0.3971513E+00
           0.5579200E+00   0.1995672E+00   0.3971513E+00   0.5579200E+00
           0.1995672E+00   0.3971513E+00   0.5579200E+00   0.1995672E+00
           0.3971513E+00   0.5579200E+00   0.1995672E+00
     CP =  0.0000000E+00   0.0000000E+00   0.0000000E+00   0.1709178E+01
           0.8856221E+00   0.1857223E+00   0.0000000E+00   0.0000000E+00
           0.0000000E+00   0.2808586E+01   0.1456735E+01   0.2944871E+00
           0.0000000E+00   0.0000000E+00   0.0000000E+00   0.0000000E+00
           0.0000000E+00   0.0000000E+00   0.0000000E+00   0.0000000E+00
           0.0000000E+00   0.0000000E+00   0.0000000E+00   0.0000000E+00
           0.0000000E+00   0.0000000E+00   0.0000000E+00
$END
$OVERLAP
  0.1000000E+01   0.1914474E+00   0.1000000E+01
$END
$DENSITY
  0.2036321E+01   0.1108528E+00   0.1039318E+00
$END
$FOCK
 -0.1112779E+02  -0.2858979E+01  -0.8956899E+00
$END
$LCAOMO
 -0.5742823E-03  -0.2383551E-02  -0.1730951E-03
$END
$KINETIC
  0.1657897E+02  -0.1435027E+01   0.1357367E+01
$END
$NUCLEAR
 -0.3893233E+02  -0.3169558E+01  -0.1073697E+02
$END
$DIPOLE
  0.5290207E-01   0.1012797E-01   0.5290207E-01
$END
```

The various datalists of FILE47 are described in turn in the following sections, making use of this example for illustration.

B.7 FILE47: INPUT FOR THE GenNBO PROGRAM

B.7.3 $GENNBO Keylist

The $GENNBO keylist (required) contains keywords essential to the proper execution of the NBO program. The following is the list of keywords recognized by this keylist:

KEYWORD	*OPTION DESCRIPTION*
REUSE	Instructs GenNBO to reuse an old NBO direct-access file, FILE48, rather than create a new FILE48 from the wavefunction information contained in the FILE47 datalists. If the REUSE keyword is specified, all keylists and datalists in FILE47 will be ignored except for $NBO, $CORE, $CHOOSE, and $NRTSTR. This keyword preempts all other keywords of the $GENNBO keylist.
SAVE	Instructs GenNBO to save, rather than delete, the NBO direct-access file, FILE48, on program termination.
NATOMS	Number of atoms (required).
NBAS	Number of basis functions (required).
OPEN	Designates an open-shell wavefunction. GenNBO will subsequently read in alpha and beta density, Fock, and MO coefficient matrices.
ORTHO	Indicates that the AO basis set is orthogonal (basis functions are always assumed normalized). If this keyword is specified, GenNBO will not read the $OVERLAP datalist. This keyword is incompatible with $NBO keywords for 'pre-orthogonal' basis sets (e.g. SPNAO, SPNHO, SPNBO, SPNLMO, AOPNAO, AOPNHO, AOPNBO, AOPNLMO, FPNHO, FPNBO, etc.).
UPPER	Indicates that only the upper triangular portions of the overlap, density, Fock, dipole, MO derivative, and Hamiltonian derivative matrices are listed in the their respective datalists. By default, GenNBO assumes that the full matrices are given.
BODM	Indicates that the $DENSITY datalist contains the bond-order matrix ("Fock-Dirac density matrix") rather than the density matrix (i.e., matrix elements of the density operator). [In orthogonal AO basis sets, the bond-order matrix and density matrix are identical, but in nonorthogonal basis sets they must be distinguished.] By default, GenNBO assumes this datalist contains the density matrix elements. If "BODM" is included, the datalist elements are transformed with the AO overlap matrix to produce the true density matrix.

B.7 FILE47: INPUT FOR THE GenNBO PROGRAM

BOHR	Indicates that the atomic coordinates ($COORD) and the dipole integrals ($DIPOLE) are in atomic units, rather than the default angstroms.
EV	Indicates that the Fock matrix elements ($FOCK) have units of electron volts (eV), rather than the default atomic units (Hartrees).
CUBICF	Instructs GenNBO to use the set of seven cubic f-type functions rather than the seven pure f functions (cf. Section B.7.5).
FORMAT	Read formatted (rather than free-formatted) values for the $OVERLAP, $DENSITY, $FOCK, $LCAOMO, $KINETIC, $POTENTIAL, $DIPOLE, $H01, and $H11 datalists. The format is (2x,5e15.7).

The methylamine sample $GENNBO keylist specifies 7 atoms, 28 basis functions, upper triangular matrix input, $DENSITY datalist containing the bond-order matrix, and formatted datalists.

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B.7.4 $COORD Datalist

The $COORD datalist (required, unless REUSE is specified in $GENNBO) contains the job title and information indicating the identity and coordinates of each atom, including missing core electrons or effective core potentials.

The first line following the $COORD identifier is an arbitrary job title of up to 80 characters. Subsequent lines are used to specify the atomic number, the nuclear charge, and the (x,y,z) coordinates of each atom. [For example, atom 1 in the methylamine sample input is a carbon atom (atomic number 6) with nuclear charge 6 and coordinates x = 0.052902, y = 0.711852, z = 0.00000, in angstroms.] Coordinates are assumed to be in angstroms unless the BOHR keyword appears in the $GENNBO keylist, specifying atomic units. The atomic number and nuclear charge are generally identical, but if core electrons are neglected (as in most semi-empirical treatments) or if effective core potentials (ECP) are employed, the nuclear charge will be less than the atomic number by the number of electrons neglected on that particular atom. Thus, for an AMPAC calculation, in which the two $1s$ core electron of a carbon atom are neglected, the line following the job title in the methylamine example would read

```
   6    4       0.052902      0.711852      0.000000
```

where "4" is the effective (valence) nuclear charge of the atom.

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B.7.5 $BASIS Datalist

The $BASIS datalist (required, unless REUSE is specified in $GENNBO) provides essential information about the AO basis functions, specifying the atomic center and the angular symmetry (s, p_x, p_y, p_z, etc.) of each AO. This information is contained in this datalist in two arrays called CENTER and LABEL.

The atomic center for each AO is specified by entering "CENTER=" followed by the serial number of the atom for each AO, separated by commas or spaces. [For example, the entry

```
CENTER = 1,1,1,1,1,1,1,1,1,2,2,2,2,2,2,2,2,2,3,3,4,4,5,5,6,6,7,7
```

of the methylamine sample file indicates that the first 9 AOs (1-9) are centered on atom 1 (the carbon atom), the next nine AOs (10-18) on center 2, and so forth.]

The angular symmetry for each AO is specified by entering "LABEL=" followed by a symmetry label for each AO, separated by commas or spaces. The NBO program handles Cartesian s, p, d, f, and g functions and pure s, p, d, f, g, h, and i functions ($l = 0\text{-}6$). The label for each AO is a 3-digit integer of the form $l*100 + k + m$, where k is 0 (cartesian) or 50 (pure), and m is a particular component of the l-type symmetry (see table below). For s or p AOs, the cartesian and pure l-symmetry sets are identical, so each AO can be labelled in two distinct ways (e.g. either 1 or 51 for an s-type function), but the six cartesian d functions can be transformed to the five pure d functions plus an additional s function, and the ten cartesian f functions can be transformed to the seven pure f functions plus three additional p functions. Two distinct sets of pure f functions are recognized, the "standard" [default] set and the "cubic" set, the latter being used whenever the "CUBICF" keyword is included in the $GENNBO keylist.

The labels associated with each allowed AO function type are tabulated below, where x, y, z refer to the specified cartesian axis system:

Cartesian Sets   Angular Symmetries

Cartesian Sets	Angular Symmetries
s (1)	s
p (101-103)	x, y, z
d (201-206)	xx, xy, xz, yy, yz, zz
f (301-310)	xxx, xxy, xxz, xyy, xyz, xzz, yyy, yyz, yzz, zzz

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g (401-415)	xxxx, xxxy, xxxz, xxyy, xxyz, xxzz, xyyy, xyyz, xyzz, xzzz, yyyy, yyyz, yyzz, yzzz, zzzz

Pure Sets   *Angular Symmetries*

s (51)	s
p (151-153)	x, y, z
d (251-255)	xy, xz, yz, x2-y2, z2
f (351-357) (standard)	0=z(5z2-3r2), c1=x(5z2-r2), s1=y(5z2-r2), c2=z(x2-y2), s2=xyz, c3=x(x2-3y2), s3=y(3x2-y2)
f (351-357) (cubic)	D1=x(5x2-3r2), D2=y(5y2-3r2), D3=z(5z2-3r2), B=xyz, E1=x(z2-y2), E2=y(z2-x2), E3=z(x2-y2)
g (451-459)	0, c1, s1, c2, s2, c3, s3, c4, s4
h (551-561)	0, c1, s1, c2, s2, c3, s3, c4, s4, c5, s5
i (651-663)	0, c1, s1, c2, s2, c3, s3, c4, s4, c5, s5, c6, s6

For example, in the methylamine sample input the first nine entries of the LABEL array,

```
LABEL = 1,1,101,102,103,1,101,102,103,. . .
```

identify the first 9 AOs (of carbon) as being of s, s, p_x, p_y, p_z, s, p_x, p_y, p_z type, respectively.

B.7.6 *$CONTRACT Datalist*

The $CONTRACT datalist (optional) contains additional information about contraction coefficients and orbital exponents of AO basis functions. This information is not used in basic NBO analysis of a wavefunction. However, if the AOINFO or PLOT keyword is specified in the $NBO keylist (See Section B.2.5), the GenNBO writes out this information to an external file (LFN 31) in the proper format for orbital plotting with the *NBOView* program. This information is also required for the NBCP and NJC analyses.

Two integers must be initially given: NSHELL (the number of shells of basis functions) and NEXP (the number of orbital exponents). [In the methylamine example, there are 16 shells of basis functions and 27 orbital exponents.] These integers should precede the remainder of the basis set information of this datalist.

The number of components (basis functions) in each shell is specified in the NCOMP array. The sum of the components for each shell should equal the total number of basis functions. This list of components is a partitioning of the basis function centers and labels (in the $BASIS datalist) into shells. [For example, in the methylamine sample, the NCOMP array

```
NCOMP = 1,4,4,. . .
```

indicates that the first three shells have a total of 9 (i.e. 1+4+4) basis functions. These are the 9 AOs (1-9) discussed previously in the $BASIS datalist.]

The NPRIM array gives the number of primitive gaussian functions of each shell. [For the methylamine example, the first three shells of the AO basis are contractions of

```
NPRIM = 3,2,1,. . .
```

three, two, and one primitives, respectively, corresponding to the conventional "3-21G" basis set designation.]

Pointers for each shell are listed in the NPTR array. These pointers specify the location of the orbital exponents (EXP) and contraction coefficients (CS, CP, CD, CF, etc.) for each shell. [In the sample input file,

```
     NPTR = 1,4,6,. . .
```

the orbital exponents and contraction coefficients for the first three shells begin at elements 1, 4, and 6, respectively.]

EXP, CS, CP, CD, CF, CG, CH, and CI are free format, real arrays containing the orbital exponents, and the *s, p, d, f, g, h,* and *i* contraction coefficients of the AO basis set. NEXP elements should appear in each array, and the arrays of contraction coefficients need only be given in $CONTRACT if there are basis functions of that particular symmetry in the basis set. [For example, the 3-21G basis of the sample methylamine input has *s* and *p* basis functions only. Therefore, the CD, CF, etc. arrays are not necessary.]

The information in the $CONTRACT datalist along with that in the $BASIS datalist is enough to completely determine the AO basis set. [For example, the second shell on the methylamine sample contains 4 basis functions (NCOMP). These are $s, p_x, p_y,$ and p_z orbitals (LABEL), all centered on atom 1 (CENTER), and each basis function is a contraction of two primitive gaussians (NPRIM). From NPTR, EXP, CS, and CP, we find the explicit form of these functions:

$$\varphi_s(\mathbf{r}) \ = -0.747 \ e^{-3.66 \ r2} + 0.713 \ e^{-0.77 \ r2}$$

$$\varphi_{px}(\mathbf{r}) = 1.709 \ x \ e^{-3.66 \ r2} + 0.886 \ x \ e^{-0.77 \ r2}$$

$$\varphi_{py}(\mathbf{r}) = 1.709 \ y \ e^{-3.66 \ r2} + 0.886 \ y \ e^{-0.77 \ r2}$$

$$\varphi_{pz}(\mathbf{r}) = 1.709 \ z \ e^{-3.66 \ r2} + 0.886 \ z \ e^{-0.77 \ r2}$$

where $\mathbf{r} = (x,y,z)$ is measured in bohr units relative to the cartesian coordinates of atom 1.]

B.7 FILE47: INPUT FOR THE GenNBO PROGRAM

B.7.7 Matrix Datalists

The remaining datalists ($OVERLAP, $DENSITY, $FOCK, $LCAOMO, $DIPOLE, $KINETIC, $NUCLEAR, $C10, $H01, $H11) specify various matrix elements possibly used by the NBO analysis. By default, all entries in these datalists are free format, although formatted entries (2x,5e15.7) are expected if the FORMAT keyword is specified in the $GENNBO keylist. Only the upper triangular portions of each symmetric matrix (all matrices except for the MO coefficients and derivatives) should be provided if the UPPER keyword is specified in the $GENNBO keylist. The numbering of the matrix rows and columns must correspond to the ordering of the AOs in the $BASIS datalist. All three matrices of dipole integrals should appear in the $DIPOLE datalist, with x integrals before y before z. Similarly, the three matrices of the $C10 datalist should be ordered x before y before z. The matrices of the $H01 and $H11 datalists are ordered by atom, the (x, y, z) matrices for $H01 and the $(xx, xy, xz, yx, yy, yz, zx, zy, zz)$ matrices for $H11 for atom 1 before those of atom 2, before those of atom 3, and so on. When using formatted matrix input, the first element of each matrix should begin a new line.

Of the matrix datalists, the $DENSITY datalist is always required, and the $OVERLAP datalist is required for all non-orthogonal AO basis sets, but other datalists are optional (unless implicitly required by specified keyword options). Nevertheless, it is good practice to include as many of these datalists in FILE47 as possible for later use with keyword options which require them. The following table lists the leading $NBO keywords that require each datalist to be included in FILE47 (requirements for keywords of the supplementary modules, Sec. B.8 *et seq.*, can be determined by analogy):

Datalist	$NBO Keywords Requiring the Datalist
$OVERLAP	SAO, SPAO, SPNAO, SPNHO, SPNBO, SPNLMO, AOPNAO, AOPNHO, AOPNBO, AOPNLMO
$FOCK	E2PERT, FAO, FNAO, F(P)NHO, F(P)NBO, FNLMO, FMO
$KINETIC	KAO, KNAO, KNHO, KNBO, KNLMO, KMO
$NUCLEAR	VAO, VNAO, VNHO, VNBO, VNLMO, VMO
$LCAOMO	AOMO, NAOMO, NHOMO, NBOMO, NLMOMO
$DIPOLE	DIAO, DINAO, DINHO, DINBO, DINLMO, DIMO, DIPOLE
$CONTRACT	AOINFO, PLOT

B.7 FILE47: INPUT FOR THE GenNBO PROGRAM

For example, in the methylamine sample input, the keyword "NAOMO=PVAL" of the $NBO keylist requires that the $LCAOMO datalist be present (in addition to the $OVERLAP, $DENSITY, and $FOCK datalists used for default PRINT=2 analysis), but the $DIPOLE datalist might have been omitted in this case. Inclusion of the $LCAOMO datalist (in addition to the $FOCK datalist) insures that degenerate MOs will be chosen in a prescribed way for decomposition in terms of other functions.

MO derivatives ($C10) and GIAO Hamiltonian first- ($H01) and second-derivatives ($H11) are only required for natural chemical shielding (NCS) analysis (see Section B.14).

B.8 NATURAL RESONANCE THEORY (NRT)

References: E. D. Glendening and F. Weinhold, *J. Comp. Chem.* **19**, 593-609 (1998); E. D. Glendening and F. Weinhold, *J. Comp. Chem.* **19**, 610-627 (1998); E. D. Glendening, J. K. Badenhoop, and F. Weinhold, *J. Comp. Chem.* **19**, 628-646 (1998).

B.8.1 Introduction: Single- and Multi-Reference NRT Analysis

The natural resonance theory (NRT) module provides an analysis of molecular electron density (correlated or uncorrelated) in terms of resonance structures and weights. It also calculates measures of bond order and valency that are closely related to classical resonance theory concepts.

The NRT algorithm is based on representing the one-electron reduced density operator, Γ, as an optimized "resonance hybrid" of density operators, $\{\Gamma_\alpha\}$,

$$\Gamma \cong \sum_\alpha w_\alpha \Gamma_\alpha$$

where each Γ_α is the reduced density operator corresponding to an idealized resonance structure wavefunction Ψ_α (determinant of doubly occupied NBOs for the chosen Lewis structure). The NRT resonance weights $\{w_\alpha\}$ are constrained to satisfy

$$w_\alpha \geq 0, \sum_\alpha w_\alpha = 1$$

in order to preserve the normalization, hermiticity, and positivity of the true Γ. NRT analysis can be performed on any wavefunction or density functional method that leads to a one-electron density matrix.

Single-reference NRT analysis corresponds to the limiting case of weak delocalization and a single dominant "reference" structure. Starting from the NBOs $\{\sigma_i\}$, $i = 1,2,...,n$, of the reference structure, one seeks to approximate the diagonal NBO occupancies

$$q_i = \langle \sigma_i | \Gamma | \sigma_i \rangle$$

in terms of localized resonance-weighted occupancies,

$$q_i^{(NRT)} = \sum_\alpha w_\alpha \langle \sigma_i | \Gamma_\alpha | \sigma_i \rangle$$

B.8 NATURAL RESONANCE THEORY (NRT)

Given the density operator $\mathbf{\Gamma}$ for the full wavefunction Ψ and the candidate density operators $\{\mathbf{\Gamma}_\alpha\}$ of the NRT expansion, the NRT program will compute the set of resonance weights $\{w_\alpha\}$ that minimize the variational functional

$$d(\underline{w}) = min\{n^{-1} \sum_i (q_i^{(NRT)} - q_i)^2\}^{1/2}$$

Thus, single-reference NRT resonance weights are chosen such that the resonance-weighted NBO occupancies $\{q_i^{(NRT)}\}$ most nearly resemble (in a root-mean-square sense) the exact NBO occupancies $\{q_i\}$ of the full molecular wavefunction.

The effectiveness of the single-reference NRT expansion is assessed by evaluation of the fractional improvement, $f(\underline{w})$,

$$f(\underline{w}) = 1 - d(\underline{w})/d(0)$$

where $d(0)$ is the value of the variational functional for the single term expansion $\{w_1 = 1, w_2 = w_3 = ... = 0\}$. The optimal $f(\underline{w})$ lies in the range

$$0 \le f(\underline{w}) \le 1$$

The limiting case, $f(\underline{w}) = 1$ corresponds to *exact* representation of the occupancies q_i by resonance averaging, whereas the limit $f(\underline{w}) = 0$ corresponds to no improvement over the single term expansion.

Multi-reference NRT analysis is necessary in cases of strong delocalization when two or more resonance structures contribute comparably to the description of the density matrix. In this case the off-diagonal density matrix elements (as well as diagonal populations) must be taken into account.

The initial step of multi-reference NRT is to perform single-reference NRT analysis for each reference manifold r. As described above, this leads to a set of resonance structures (with associated density matrices $\mathbf{\Gamma}_\alpha^{(r)}$ and optimized weights $w_\alpha^{(r)}$) within each reference manifold.

In the second step, the program calculates an optimized set of reference weights $\{W^{(r)}\}$ satisfying

$$W^{(r)} \ge 0, \quad \sum_r W^{(r)} = 1$$

to give the relative weighting of each reference manifold. These weights are chosen to minimize the r.m.s. deviation

B.8 NATURAL RESONANCE THEORY (NRT)

$$D(\underline{W}^{(r)}) = min \ \{n^{-1}\mathrm{Tr}[\boldsymbol{\Gamma} - \textstyle\sum_r W^{(r)} \boldsymbol{\Gamma}^{(r)}]^2 \}^2 \geq 0$$

where "Tr" denotes the matrix trace and the minimization is over all $W^{(r)}$. The density matrices $\boldsymbol{\Gamma}$ for the full wave function and $\boldsymbol{\Gamma}^{(r)}$ for reference structure r are transformed to the basis of valence natural atomic orbitals (or the full NAO set, when valence space truncation fails).

In the final step, the optimized weights $\{W^{(r)}\}$ for each reference manifold are combined with the weightings $\{w_\alpha^{(r)}\}$ within each manifold

$$w_\alpha = \textstyle\sum_r w_\alpha^{(r)} \ W^{(r)}$$

to give the final weighting w_α of each resonance structure α. Structures of high weight ($w_\alpha > w_{max}$ *NRTWGT/100.) are selected as reference structures for subsequent cycles.

Bond Orders and Valencies are evaluated from the final optimized resonance weights $\{w_\alpha\}$. The *natural bond order* is evaluated as

$$b_{AB} = \textstyle\sum_\alpha \ w_\alpha b_{AB}^{(\alpha)}$$

where $b_{AB}^{(\alpha)}$ is the integer number of bonds connecting centers A,B in resonance structure Ψ_α. The program also calculates the ionic ($b_{AB}^{(ion)}$) and covalent ($b_{AB}^{(cov)}$) contributions to bond order

$$b_{AB}^{(ion)} = b_{AB}i_{AB}, \ b_{AB}^{(cov)} = b_{AB}(1 - i_{AB})$$

in terms of the (average) ionic character i_{AB} of each A-B bond,

$$i_{AB} = \textstyle\sum_\alpha \ w_\alpha i_{AB}^{(\alpha)}/b_{AB}$$

where $i_{AB}^{(\alpha)}$ is the ionicity of the A-B bond in the resonance structure Ψ_α, as determined from NBO polarization coefficients c_A, c_B

$$i_{AB}^{(\alpha)} = |(c_A^2 - c_B^2)/(c_A^2 + c_B^2)|$$

(averaged, if necessary, over multiple bonds).

Finally, the program evaluates the *natural atomic valency*

$$V_A = \textstyle\sum_{B \neq A} \ b_{AB}$$

and its electrovalent ($V_A^{(ion)}$) and covalent ($V_A^{(cov)}$) contributions,

B.8 NATURAL RESONANCE THEORY (NRT)

$$V_A^{(ion)} = \sum_{B \neq A} b_{AB}^{(ion)}, \ V_A^{(cov)} = \sum_{B \neq A} b_{AB}^{(cov)}$$

The default NRT program automatically generates candidate resonance structures to be considered in multi-reference resonance averaging, including (i) the main NBO structure, (ii) structures generated by subroutine LEWIS or the 3CHB hyperbond search, or (iii) structures generated from delocalization lists of any of the above. (Note that 3CHB is automatically activated by the NRT keyword.) However, one can override the default reference selection(s) by explicitly designating a chosen set of reference structures through the $NRTSTR keylist (Sec. B.8.3). [By altering the NRTWGT threshold (Sec. B.8.2), one can also effectively control the number of secondary structures to be included.] The $NRTSTR keylist can be used to insure a consistent set of reference structures for NRT comparisons of dissimilar systems. For convenience, the NRT program lists reference structure(s) of each job as a sample $NRTSTR keylist at the end of the output, for possible use in subsequent jobs. Complete $NRTSTR listings for other structures can be forced with the NRTLST keyword (Sec. B.8.2).

The NRT program also provides "local" NRT options to deal with the numerical challenges of increasing numbers of resonating units. These options allow systematic divide/conquer strategies to deal with complex systems beyond the reach of default NRT search.

B.8 NATURAL RESONANCE THEORY (NRT)

B.8.2 NRT Job Control Keywords

NRT analysis is requested by inserting NRT job control keywords in the $NBO keylist of the user's standard input deck.

Below, we list the NRT keywords and the effect that each has on NRT program execution:

KEYWORD	OPTION DESCRIPTION
NRT	Request that the default NRT analysis be performed (using results from 3CHB hyperbond search, automatically activated). The keyword leads to calculation of the NRT resonance weights and the natural bond orders and atomic valencies. Sample output is shown in Section B.8.4.
NRTTHR=*val*	Select the delocalization list threshold (*val*, in kcal/mol) which controls the length of the NRT expansion. The default threshold is 1.0 kcal mol^{-1}. Increasing the NRT threshold shortens the NRT expansion and speeds execution, but may sacrifice detail of the delocalization list (Sec. A.3.5). The value NRTTHR=5 (or 10) will often give adequate accuracy for aromatic systems.
NRTLST=*val*	Request that $NRTSTR structure specifications be written to the output file for all structures with weight > *val*%. For example, the keyword NRTLST=10 would print $NRTSTR specifications for all structures with 10% or greater weight. This is provided primarily as a convenience in preparing $NRTSTR keylist input (Sec. B.8.3) for subsequent runs. The default is to print $NRTSTR specifications for reference structures only.
NRTMEM=*n*	Request that memory be reallocated to prepare for a maximum of *n* reference structures (default 20, maximum 100). This allows a somewhat larger number of reference structures to be treated, but reduces the available storage for secondary structures in each manifold.
NRTDTL	Print additional details of the NRT optimizations and the search for resonance structures, as well as info for structures with weights below 0.1%. This keyword is primarily for debugging and development.
NRTCHG=*val*	Control the maximum formal charges (with respect to net total charge) allowed in candidate structures generated by SR LEWIS. By default, NRTCHG=1. (For a neutral species, the effect of setting NRTCHG=0 is to ignore candidate reference structures with formal

	charge on any atom, whereas that of setting NRTCHG > 1 may be to generate many unrealistic structures that are ultimately rejected.)
NRTFDM	Specify that the full density matrix (rather than the default valence-only submatrix) should be used in multi-reference optimization. (The NRT program automatically switches to this option whenever possible hypervalency is detected, so this keyword is not recommended.)
NRTWGT=*val*	Request an altered threshold (default: 35%) for consideration as a reference structure. (This keyword is primarily for testing and development and is not recommended.)
NRTOPT=*method*	Select alternative method for single-reference variational optimization (not recommended). The following methods may be selected (default [BFGS]): NRTOPT=BFGS Steepest descent, analytic gradients NRTOPT=SA Simulated annealing (SA) method NRTOPT=POWELL Steepest descent, numerical gradients Note that the default BFGS algorithm is automatically replaced by simulated annealing (with a penalty function) whenever numerical indeterminacy is detected, and the numerical POWELL algorithm is generally much less efficient. Therefore, this option is primarily for testing that a unique global minimum has been located.

Note that inserting any one of these keywords in the $NBO keylist automatically invokes the NRT keyword.

In addition to job control keywords listed above, one can also employ NRTCML and NRTMOL keywords to write NRT structural data files for other graphical utilities, as described in Sec. 22.

The main NRT keyword can also be followed by a bracket list to specify a "local" subset of atom numbers to which NRT averaging is restricted

    NRT <atom-1 atom-2 ... atom-n>

For example, "NRT <12 15 18 19> would include only resonance delocalizations involving atoms 12, 15, 18, 19 of a larger system.

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B.8.3 Auxiliary $NRTSTR Keylist Input

The $NRTSTR keylist allows the user to precisely specify the resonance structures that will be chosen as "reference" structures in the NRT analysis. User-selected $NRTSTR structures override the automated methods (subroutine LEWIS, NRTWGT threshold, etc.) for selecting reference structures. This option is useful in assuring that a consistent set of reference structures will be used to compare two NRT expansions. Note that the NRTLST keyword (Sec. B.8.2) is a convenient means to automate preparation of $NRTSTR keylist input for a subsequent run.

$NRTSTR keylist input of NRT reference structures is essentially similar to $CHOOSE input (Sec. B.4). The format of the $NRTSTR keylist is:

first line:	The keylist identifier "$NRTSTR"
next line:	The keyword "STRUCTURE" (only "STR" is necessary) to begin the specification of the first resonance structure.
next lines:	"LONE" and "BOND" specifications of the resonance structure, identical to those of the $CHOOSE keylist. Note that the "3CBOND" specification of the $CHOOSE keylist is incompatible with the $NRTSTR keylist, since the NRT analysis does not support 3-center bonds. Note furthermore that (unlike the $CHOOSE keylist) the $NRTSTR keylist should contain the *complete specification of all valence lone pairs and bonds* for each resonance structure (core orbitals should be neglected); do not assume that the NRT routines will augment a resonance form with lone pairs, as needed. The NRT program determines whether an appropriate number of bonds and lone pairs have been listed in the $NRTSTR keylist, and rejects the resonance structure if this is not the case.
next line:	The word "END" to terminate the specification of the first resonance structure. (Note that there must be a matching "END" for each "STR," "BOND," or "LONE" keyword.)
next lines:	Additional input for other resonance structures, each beginning with the word "STRUCTURE" and terminated by the word "END".
next line:	The keylist terminator "$END".

As with the other keylists of the NBO program, the $NRTSTR keylist can be condensed to a smaller number of lines, as long as no line of this keylist is shared with any other keylist.

B.8 NATURAL RESONANCE THEORY (NRT)

For open-shell wavefunctions, the user should specify separate $NRTSTR keylists for different spins. The alpha spin keylist has the identifier, $NRTSTRA, and the beta, $NRTSTRB. A different number of reference structures can be specified in the $NRTSTRA and $NRTSTRB keylists. Otherwise, the form of these keylists is identical to that described above.

The order in which keylists appear in the input deck is important for some electronic structure packages. Therefore, we recommend that the $NRTSTR keylist follow the $NBO, $CORE, and $CHOOSE keylists and precede the $DEL keylist. Due to a limitation of the NBO program, $CHOOSE and $NRTSTR keylists may not be used simultaneously in the analysis of open-shell wavefunctions.

An example serves to illustrate the $NRTSTR format. The $NRTSTR specification for the leading two resonance structures of allyl anion (**I,II**)
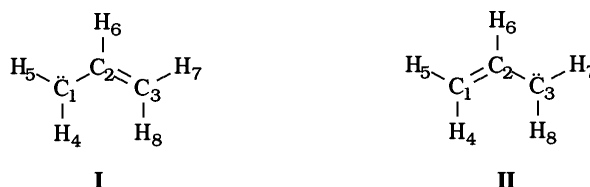
could be given as follows:

```
$NRTSTR
        STR1         ! C1 anion center
           LONE   1 1   END
           BOND   S 1 2   S 1 4   S 1 5   D 2 3   S 2 6   S 3 7   S 3 8   END
        END
        STR2         ! C3 anion center
           LONE   3 1   END
           BOND   D 1 2   S 1 4   S 1 5   S 2 3   S 2 6   S 3 7   S 3 8   END
        END
$END
```

Note that $NRTSTR input can be used to correct defects of the automated NRT analysis if significant structures were initially overlooked.

B.8 NATURAL RESONANCE THEORY (NRT)

B.8.4 NRT Illustrations

We describe output of NRT analysis for two illustrative examples: (i) the closed-shell methylamine molecule (RHF/3-21G level), and (ii) the open-shell allyl radical (UHF/6-31G* level).

B.8.4.1 Methylamine

We first describe the NRT output for RHF/3-21G methylamine (Pople-Gordon bond lengths, tetrahedral bond angles). This default-level output would be obtained by simply including the "NRT" keyword in the usual $NBO keylist portion of the input file.

The first segment of NRT output is shown below:

```
NATURAL RESONANCE THEORY ANALYSIS:

Maximum reference structures :    20
Maximum resonance structures :   300
Memory requirements :      897670 words of  99988579 available

2 candidate reference structure(s) calculated by SR LEWIS
Initial loops searched 2 bonding pattern(s); 1 was retained
Delocalization list threshold set to 0.79 kcal/mol for reference 1
Reference  1:  rho*=0.04899, f(w)=0.85960 converged after  11 iterations

                                            fractional accuracy f(w)
                       non-Lewis      -----------------------------------
  Ref    Wgt      density     d(0)      all NBOs    val+core    valence
 -----------------------------------------------------------------------
   1    1.00000   0.04899   0.00598    0.85960     0.90510     0.91172
```

NRT output begins with a brief summary of the memory requirements. In this example, nearly ten million double precision words were made available to the NRT program, far more than needed to accomodate the maximum 300 resonance structures for methylamine at this basis set level (which in turn is far more than required for the eight resonance structures that were actually generated in the calculation). If insufficient memory is available to complete a calculation, program execution will halt, and the memory allocated by the attached electronic structure package should be increased. (See Sec. C.14 for additional details.)

The variational optimization of the NRT weights converged after 11 BFGS iterations, and the high accuracy of the resulting NRT expansion is evident from the large $f(\underline{w})$ value (85.96%). [Note that this percentage refers to the very small ρ^* "error" of the leading NBO structure (which itself is often less that

B.8 NATURAL RESONANCE THEORY (NRT)

B.8.4 NRT Illustrations

We describe output of NRT analysis for two illustrative examples: (i) the closed-shell methylamine molecule (RHF/3-21G level), and (ii) the open-shell allyl radical (UHF/6-31G* level).

B.8.4.1 Methylamine

We first describe the NRT output for RHF/3-21G methylamine (Pople-Gordon bond lengths, tetrahedral bond angles). This default-level output would be obtained by simply including the "NRT" keyword in the usual $NBO keylist portion of the input file.

The first segment of NRT output is shown below:

```
NATURAL RESONANCE THEORY ANALYSIS:

Maximum reference structures :    20
Maximum resonance structures :   300
Memory requirements :      897670 words of  99988579 available

2 candidate reference structure(s) calculated by SR LEWIS
Initial loops searched 2 bonding pattern(s); 1 was retained
Delocalization list threshold set to 0.79 kcal/mol for reference 1
Reference  1:  rho*=0.04899, f(w)=0.85960 converged after  11 iterations

                                            fractional accuracy f(w)
                       non-Lewis      -----------------------------------
  Ref    Wgt      density     d(0)      all NBOs    val+core    valence
 -----------------------------------------------------------------------
   1    1.00000   0.04899   0.00598    0.85960     0.90510     0.91172
```

NRT output begins with a brief summary of the memory requirements. In this example, nearly ten million double precision words were made available to the NRT program, far more than needed to accomodate the maximum 300 resonance structures for methylamine at this basis set level (which in turn is far more than required for the eight resonance structures that were actually generated in the calculation). If insufficient memory is available to complete a calculation, program execution will halt, and the memory allocated by the attached electronic structure package should be increased. (See Sec. C.14 for additional details.)

The variational optimization of the NRT weights converged after 11 BFGS iterations, and the high accuracy of the resulting NRT expansion is evident from the large $f(\underline{w})$ value (85.96%). [Note that this percentage refers to the very small ρ^* "error" of the leading NBO structure (which itself is often less that

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0.1% of the total electron density), so that the overall accuracy of the NRT expansion is very high indeed.] For each reference structure, the NRT program lists the non-Lewis density ($\rho^* = 0.04899e$) and $d(0)$ value ($0.00598e$). The program also reports the $f(\underline{w})$ value as referred to valence-shell NBOs only (91.17%), or to valence plus core orbitals (90.81%), so that one can judge separate core, valence, and Rydberg contributions by difference.

The next segment of output lists the TOPO matrix of the leading reference structure and prints the table of resonance structures and corresponding resonance weights:

```
TOPO matrix for the leading resonance structure:

     Atom  1   2   3   4   5   6   7
     ----  --- --- --- --- --- --- ---
   1.  C    0   1   1   1   1   0   0
   2.  N    1   1   0   0   0   1   1
   3.  H    1   0   0   0   0   0   0
   4.  H    1   0   0   0   0   0   0
   5.  H    1   0   0   0   0   0   0
   6.  H    0   1   0   0   0   0   0
   7.  H    0   1   0   0   0   0   0

        Resonance
   RS   Weight(%)                    Added(Removed)
   ------------------------------------------------------------------------
   1*      97.90
   2        0.78    C  1- N  2, ( C  1- H  3), ( N  2),  H  3
   3        0.26    C  1- N  2, ( C  1- H  4), ( N  2- H  6),  H  4
   4        0.26    C  1- N  2, ( C  1- H  5), ( N  2- H  7),  H  5
   5        0.26    C  1- N  2, ( C  1- H  4), ( N  2- H  6),  H  6
   6        0.26    C  1- N  2, ( C  1- H  5), ( N  2- H  7),  H  7
   7        0.14    C  1- N  2, ( C  1- H  4), ( N  2),  H  4
   8        0.14    C  1- N  2, ( C  1- H  5), ( N  2),  H  5
   ------------------------------------------------------------------------
          100.00    * Total *                    [* = reference structure]
```

The TOPO matrix shows the number of bonds and lone pairs (lone pairs as diagonal elements, bonds off-diagonal) for the leading reference structure, corresponding to the expected methylamine structure diagram (having dominant 97.90% weighting in this case),

1
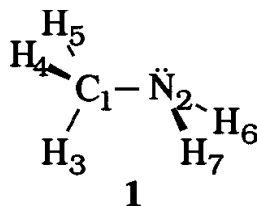
B.8 NATURAL RESONANCE THEORY (NRT)

For this molecule, the NRT program generates seven distinct secondary resonance structures, **2-8**, as shown in the table. In this table, each secondary structure is specified by giving the bonds and lone pairs to be *added* to (or, in parentheses, those to be *removed* from) the reference structure. For example, structure **2** (with resonance weighting 0.78%) is formed from reference structure **1** by adding a bond C_1-N_2, removing a bond C_2-H_3, removing a lone pair on N_2, and adding a lone pair on H_3, to obtain the "double bond-no bond" structure shown below (associated with the $n_N \rightarrow \sigma^*_{CH}$ NBO interaction):

$$
\begin{array}{c}
H \\
H \diagdown \\
\quad C = N^+ \\
H^- \qquad H \diagup H \\
\mathbf{2}
\end{array}
$$
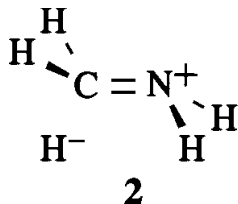
In a similar way, one can determine from the output table that the remaining entries **3-8** have the structures and weightings shown below (with the associated NBO interaction also given for each entry):

	Structure	Weight	Interaction
3.	$H^- $ $H-C=\ddot{N}$ (H, H, H$^+$)	0.26%	$\sigma_{NH} \rightarrow \sigma^*_{CH}$
4.	H^- $H-C=\ddot{N}$ (H, H, H$^+$)	0.26%	$\sigma_{NH} \rightarrow \sigma^*_{CH}$
5.	H^+ $H-C=\ddot{N}$ (H, H, H$^-$)	0.26%	$\sigma_{CH} \rightarrow \sigma^*_{NH}$
6.	H^+ $H-C=\ddot{N}$ (H, H, H$^-$)	0.26%	$\sigma_{CH} \rightarrow \sigma^*_{NH}$
7.	H^- $H-C=N^+$ (H, H, H)	0.14%	$n_N \rightarrow \sigma^*_{CH}$
8.	H^- $H-C=N^+$ (H, H, H)	0.14%	$n_N \rightarrow \sigma^*_{CH}$

The NRT output convention of specifying resonance structures by adding or deleting elements from a reference structure provides a compact general depiction of the bonding pattern for any molecular structure framework. (Additional NRTCML, NRTMOL keyword options to draw resonance structure diagrams are discussed in Sec. 22.)

The next segment of the NRT output gives the table of "natural bond orders," showing the total (t), covalent (c), and ionic (i) bond order contributions for each pair of atoms:

B.8 NATURAL RESONANCE THEORY (NRT)

```
Natural Bond Order:  (total/covalent/ionic)

   Atom       1      2      3      4      5      6      7
   ----    ------ ------ ------ ------ ------ ------ ------
 1.  C   t 0.0000 1.0210 0.9922 0.9934 0.9934 0.0000 0.0000
         c   ---  0.8014 0.7993 0.7743 0.7743 0.0000 0.0000
         i   ---  0.2196 0.1929 0.2191 0.2191 0.0000 0.0000

 2.  N   t 1.0210 0.9894 0.0000 0.0000 0.0000 0.9948 0.9948
         c 0.8014   ---  0.0000 0.0000 0.0000 0.6349 0.6349
         i 0.2196   ---  0.0000 0.0000 0.0000 0.3600 0.3600

 3.  H   t 0.9922 0.0000 0.0078 0.0000 0.0000 0.0000 0.0000
         c 0.7993 0.0000   ---  0.0000 0.0000 0.0000 0.0000
         i 0.1929 0.0000   ---  0.0000 0.0000 0.0000 0.0000

 4.  H   t 0.9934 0.0000 0.0000 0.0040 0.0000 0.0000 0.0000
         c 0.7743 0.0000 0.0000   ---  0.0000 0.0000 0.0000
         i 0.2191 0.0000 0.0000   ---  0.0000 0.0000 0.0000

 5.  H   t 0.9934 0.0000 0.0000 0.0000 0.0040 0.0000 0.0000
         c 0.7743 0.0000 0.0000 0.0000   ---  0.0000 0.0000
         i 0.2191 0.0000 0.0000 0.0000   ---  0.0000 0.0000

 6.  H   t 0.0000 0.9948 0.0000 0.0000 0.0000 0.0026 0.0000
         c 0.0000 0.6349 0.0000 0.0000 0.0000   ---  0.0000
         i 0.0000 0.3600 0.0000 0.0000 0.0000   ---  0.0000

 7.  H   t 0.0000 0.9948 0.0000 0.0000 0.0000 0.0000 0.0026
         c 0.0000 0.6349 0.0000 0.0000 0.0000 0.0000   ---
         i 0.0000 0.3600 0.0000 0.0000 0.0000 0.0000   ---
```

This shows, for example, that the total NRT bond order between C_1 and N_2 is 1.0210 (corresponding to the slight "partial double-bond character" associated with the contributions of structures **2-8**, all of which have formal double bonds), and its covalent (0.8014) and ionic (0.2196) components correspond to about 21.5% ionic character. In addition, one can see that the C_1-H_3 bond order (0.9922) is slightly less than those (0.9934) for C_1-H_4, C_1-H_5 (corresponding to the slightly higher weight of structure **2** among the secondary structures). The latter difference in $b_{CH}^{(N)}$ bond orders, despite the identical Pople-Gordon bond geometries, reflects the greater strength of hyperconjugative $n_N \rightarrow \sigma^*_{CH}$ NBO interactions in antiperiplanar arrangements.

The next table shows the result of summing over bond orders on each atom to obtain the natural atomic valencies:

```
Natural Atomic Valencies:

                     Co-      Electro-
     Atom  Valency  Valency   Valency
     ----  -------  -------   -------
  1.  C    4.0000   3.1493    0.8507
  2.  N    3.0106   2.0711    0.9395
  3.  H    0.9922   0.7993    0.1929
  4.  H    0.9934   0.7743    0.2191
  5.  H    0.9934   0.7743    0.2191
  6.  H    0.9948   0.6349    0.3600
  7.  H    0.9948   0.6349    0.3600
```

This table shows the near-integer total NRT atomic valencies (viz., 4.00 for C, 3.01 for N, etc.) and its decomposition into covalent and electrovalent (ionic) contributions.

The final segment shows the $NRTSTR keylist specification for the single reference structure of methylamine (cf. Sec. B.8.3):
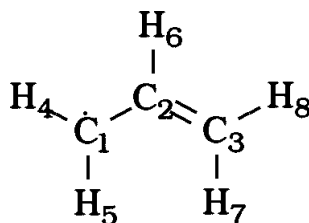
```
$NRTSTR
 STR        ! Wgt = 97.90%
   LONE  2  1  END
   BOND  S  1  2  S  1  3  S  1  4  S  1  5  S  2  6  S  2  7  END
 END
$END
```

This shows the lone pair on N_2 ("LONE 2"), the single bond between atoms C_1 and N_2 ("S 1 2"), and so forth for leading resonance structure **1**.

B.8.4.2 Allyl Radical

We next describe the somewhat more complex example of the allyl radical
(UHF/6-31G* optimized geometry),

to demonstrate the multi-reference NRT treatment of open-shell wavefunctions.
In this case, the NRT analysis is applied separately to the alpha and beta spin
manifolds, resulting in "different resonance structures for different spins."
Indeed, the alpha (majority) spin analysis closely resembles the NRT analysis
of the closed-shell allyl anion, whereas the beta (minority) spin analysis is most
similar to the allyl cation. This example also demonstrates multi-reference NRT
treatment, since the two leading resonance forms for allyl radical are
symmetry-related.

The following is the NRT output for the alpha spin system:

```
NATURAL RESONANCE THEORY ANALYSIS, alpha spin:

Maximum reference structures :     20
Maximum resonance structures :    300
Memory requirements :     1171044 words of    9981841 available

7 candidate reference structure(s) calculated by SR LEWIS
0 candidate reference structure(s) added by hyperbond search (SR HBRES)
Initial loops searched 7 bonding pattern(s); 3 were retained
Delocalization list threshold set to 6.63 kcal/mol for reference 1
Delocalization list threshold set to 6.63 kcal/mol for reference 2
Delocalization list threshold set to 9.28 kcal/mol for reference 3
Reference   1:  rho*=0.17709, f(w)=0.90635 converged after   2 iterations
Reference   2:  rho*=0.17709, f(w)=0.90635 converged after   2 iterations
Reference   3:  rho*=0.31704, f(w)=0.94691 converged after   3 iterations
Multi-ref( 3):  D(W)=0.02487, F(W)=0.26173 converged after 119 iterations
Multi-ref( 2):  D(W)=0.02487, F(W)=0.26175 converged after 204 iterations
```

		non-Lewis		fractional accuracy f(w)		
Ref	Wgt	density	d(0)	all NBOs	val+core	valence
1	0.50000	0.17709	0.02667	0.90635	0.91001	0.91007
2	0.50000	0.17709	0.02667	0.90635	0.91001	0.91007

```
TOPO matrix for the leading resonance structure:

    Atom  1   2   3   4   5   6   7   8
    ----  --- --- --- --- --- --- --- ---
  1. C    1   1   0   1   1   0   0   0
```

```
2.  C   1   0   2   0   0   1   0   0
3.  C   0   2   0   0   0   0   1   1
4.  H   1   0   0   0   0   0   0   0
5.  H   1   0   0   0   0   0   0   0
6.  H   0   1   0   0   0   0   0   0
7.  H   0   0   1   0   0   0   0   0
8.  H   0   0   1   0   0   0   0   0
```

```
        Resonance
  RS   Weight(%)                    Added(Removed)
-------------------------------------------------------------------------
  1*      50.00
  2*      50.00    C  1- C  2, ( C  2- C  3), ( C  1),  C  3
-------------------------------------------------------------------------
         100.00    * Total *                [* = reference structure]
```

Natural Bond Order: (total/covalent/ionic)

```
   Atom      1      2      3      4      5      6      7      8
   ----   ------ ------ ------ ------ ------ ------ ------ ------
 1.  C  t 0.2500 0.7500 0.0000 0.5000 0.5000 0.0000 0.0000 0.0000
        c   ---  0.5656 0.0000 0.3825 0.3854 0.0000 0.0000 0.0000
        i   ---  0.1844 0.0000 0.1175 0.1146 0.0000 0.0000 0.0000

 2.  C  t 0.7500 0.0000 0.7500 0.0000 0.0000 0.5000 0.0000 0.0000
        c 0.5656   ---  0.5656 0.0000 0.0000 0.4055 0.0000 0.0000
        i 0.1844   ---  0.1844 0.0000 0.0000 0.0945 0.0000 0.0000

 3.  C  t 0.0000 0.7500 0.2500 0.0000 0.0000 0.0000 0.5000 0.5000
        c 0.0000 0.5656   ---  0.0000 0.0000 0.0000 0.3854 0.3825
        i 0.0000 0.1844   ---  0.0000 0.0000 0.0000 0.1146 0.1175

 4.  H  t 0.5000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000
        c 0.3825 0.0000 0.0000   ---  0.0000 0.0000 0.0000 0.0000
        i 0.1175 0.0000 0.0000   ---  0.0000 0.0000 0.0000 0.0000

 5.  H  t 0.5000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000
        c 0.3854 0.0000 0.0000 0.0000   ---  0.0000 0.0000 0.0000
        i 0.1146 0.0000 0.0000 0.0000   ---  0.0000 0.0000 0.0000

 6.  H  t 0.0000 0.5000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000
        c 0.0000 0.4055 0.0000 0.0000 0.0000   ---  0.0000 0.0000
        i 0.0000 0.0945 0.0000 0.0000 0.0000   ---  0.0000 0.0000

 7.  H  t 0.0000 0.0000 0.5000 0.0000 0.0000 0.0000 0.0000 0.0000
        c 0.0000 0.0000 0.3854 0.0000 0.0000 0.0000   ---  0.0000
        i 0.0000 0.0000 0.1146 0.0000 0.0000 0.0000   ---  0.0000

 8.  H  t 0.0000 0.0000 0.5000 0.0000 0.0000 0.0000 0.0000 0.0000
        c 0.0000 0.0000 0.3825 0.0000 0.0000 0.0000 0.0000   ---
        i 0.0000 0.0000 0.1175 0.0000 0.0000 0.0000 0.0000   ---
```

Natural Atomic Valencies:

```
                   Co-    Electro-
   Atom  Valency Valency  Valency
   ----  ------- -------  -------
 1.  C    1.7500  1.3335   0.4165
 2.  C    2.0000  1.5367   0.4633
 3.  C    1.7500  1.3335   0.4165
 4.  H    0.5000  0.3825   0.1175
 5.  H    0.5000  0.3854   0.1146
 6.  H    0.5000  0.4055   0.0945
 7.  H    0.5000  0.3854   0.1146
 8.  H    0.5000  0.3825   0.1175
```

```
$NRTSTRA
  STR        ! Wgt = 50.00%
    LONE 1 1 END
```

B.8 NATURAL RESONANCE THEORY (NRT)

```
   BOND S 1 2 S 1 4 S 1 5 D 2 3 S 2 6 S 3 7 S 3 8 END
 END
 STR        ! Wgt = 50.00%
   LONE 3 1 END
   BOND D 1 2 S 1 4 S 1 5 S 2 3 S 2 6 S 3 7 S 3 8 END
 END
$END
```

Notice that the bond order and valency values are roughly half of the expected values, since only alpha spin resonance structures are considered here.

Following is the NRT output for the beta spin system:

```
NATURAL RESONANCE THEORY ANALYSIS, beta spin:

Maximum reference structures :    20
Maximum resonance structures :   300
Memory requirements :     1171044 words of   9981841 available

7 candidate reference structure(s) calculated by SR LEWIS
0 candidate reference structure(s) added by hyperbond search (SR HBRES)
Initial loops searched 7 bonding pattern(s); 3 were retained
Delocalization list threshold set to 6.43 kcal/mol for reference 1
Delocalization list threshold set to 6.43 kcal/mol for reference 2
Delocalization list threshold set to 9.58 kcal/mol for reference 3
Reference   1:  rho*=0.17014, f(w)=0.90528 converged after   3 iterations
Reference   2:  rho*=0.17014, f(w)=0.90528 converged after   3 iterations
Reference   3:  rho*=0.30404, f(w)=0.94552 converged after   2 iterations
Multi-ref( 3):  D(W)=0.02459, F(W)=0.25798 converged after 119 iterations
Multi-ref( 2):  D(W)=0.02459, F(W)=0.25800 converged after 206 iterations

                                           fractional accuracy f(w)
                      non-Lewis     -----------------------------------
  Ref    Wgt         density     d(0)     all NBOs     val+core     valence
-----------------------------------------------------------------------------
   1    0.50000    0.17014    0.02565    0.90528     0.90840     0.90846
   2    0.50000    0.17014    0.02565    0.90528     0.90840     0.90846


TOPO matrix for the leading resonance structure:

    Atom  1   2   3   4   5   6   7   8
    ---- --- --- --- --- --- --- --- ---
  1.  C   0   1   0   1   1   0   0   0
  2.  C   1   0   2   0   0   1   0   0
  3.  C   0   2   0   0   0   0   1   1
  4.  H   1   0   0   0   0   0   0   0
  5.  H   1   0   0   0   0   0   0   0
  6.  H   0   1   0   0   0   0   0   0
  7.  H   0   0   1   0   0   0   0   0
  8.  H   0   0   1   0   0   0   0   0

        Resonance
   RS   Weight(%)                    Added(Removed)
-----------------------------------------------------------------------
   1*      50.00
   2*      50.00    C  1- C  2, ( C  2- C  3)
-----------------------------------------------------------------------
         100.00   * Total *                [* = reference structure]


Natural Bond Order:  (total/covalent/ionic)

    Atom      1      2      3      4      5      6      7      8
    ----   ------ ------ ------ ------ ------ ------ ------ ------
  1.  C  t 0.0000 0.7500 0.0000 0.5000 0.5000 0.0000 0.0000 0.0000
```

```
           c   ---  0.5314 0.0000 0.4238 0.4256 0.0000 0.0000 0.0000
           i   ---  0.2186 0.0000 0.0762 0.0744 0.0000 0.0000 0.0000

  2.  C  t 0.7500 0.0000 0.7500 0.0000 0.0000 0.5000 0.0000 0.0000
         c 0.5314   ---  0.5314 0.0000 0.0000 0.3780 0.0000 0.0000
         i 0.2186   ---  0.2186 0.0000 0.0000 0.1220 0.0000 0.0000

  3.  C  t 0.0000 0.7500 0.0000 0.0000 0.0000 0.0000 0.5000 0.5000
         c 0.0000 0.5314   ---  0.0000 0.0000 0.0000 0.4256 0.4238
         i 0.0000 0.2186   ---  0.0000 0.0000 0.0000 0.0744 0.0762

  4.  H  t 0.5000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000
         c 0.4238 0.0000 0.0000   ---  0.0000 0.0000 0.0000 0.0000
         i 0.0762 0.0000 0.0000   ---  0.0000 0.0000 0.0000 0.0000

  5.  H  t 0.5000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000
         c 0.4256 0.0000 0.0000 0.0000   ---  0.0000 0.0000 0.0000
         i 0.0744 0.0000 0.0000 0.0000   ---  0.0000 0.0000 0.0000

  6.  H  t 0.0000 0.5000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000
         c 0.0000 0.3780 0.0000 0.0000 0.0000   ---  0.0000 0.0000
         i 0.0000 0.1220 0.0000 0.0000 0.0000   ---  0.0000 0.0000

  7.  H  t 0.0000 0.0000 0.5000 0.0000 0.0000 0.0000 0.0000 0.0000
         c 0.0000 0.0000 0.4256 0.0000 0.0000 0.0000   ---  0.0000
         i 0.0000 0.0000 0.0744 0.0000 0.0000 0.0000   ---  0.0000

  8.  H  t 0.0000 0.0000 0.5000 0.0000 0.0000 0.0000 0.0000 0.0000
         c 0.0000 0.0000 0.4238 0.0000 0.0000 0.0000 0.0000   ---
         i 0.0000 0.0000 0.0762 0.0000 0.0000 0.0000 0.0000   ---


Natural Atomic Valencies:

                    Co-     Electro-
     Atom  Valency  Valency Valency
     ----  -------  ------- -------
  1.  C    1.7500   1.3808  0.3692
  2.  C    2.0000   1.4409  0.5591
  3.  C    1.7500   1.3808  0.3692
  4.  H    0.5000   0.4238  0.0762
  5.  H    0.5000   0.4256  0.0744
  6.  H    0.5000   0.3780  0.1220
  7.  H    0.5000   0.4256  0.0744
  8.  H    0.5000   0.4238  0.0762

$NRTSTRB
  STR         ! Wgt = 50.00%
    BOND S 1 2 S 1 4 S 1 5 D 2 3 S 2 6 S 3 7 S 3 8 END
  END
  STR         ! Wgt = 50.00%
    BOND D 1 2 S 1 4 S 1 5 S 2 3 S 2 6 S 3 7 S 3 8 END
  END
$END
```

Finally, we show the composite bond orders and atomic valencies for the sum of alpha and beta spin structures (printed just after the beta valency table, before the $NRTSTRB list):

```
Natural Bond Order (total):

    Atom    1      2      3      4      5      6      7      8
    ---- ------ ------ ------ ------ ------ ------ ------ ------
  1.  C  0.2500 1.5000 0.0000 1.0000 1.0000 0.0000 0.0000 0.0000
  2.  C  1.5000 0.0000 1.5000 0.0000 0.0000 1.0000 0.0000 0.0000
  3.  C  0.0000 1.5000 0.2500 0.0000 0.0000 0.0000 1.0000 1.0000
```

```
4.  H  1.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
5.  H  1.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
6.  H  0.0000  1.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000
7.  H  0.0000  0.0000  1.0000  0.0000  0.0000  0.0000  0.0000  0.0000
8.  H  0.0000  0.0000  1.0000  0.0000  0.0000  0.0000  0.0000  0.0000
```

```
Natural Atomic Valencies (total):

                    Co-     Electro-
    Atom  Valency  Valency  Valency
    ----  -------  -------  -------
1.   C    3.5000   2.7144   0.7856
2.   C    4.0000   2.9776   1.0224
3.   C    3.5000   2.7144   0.7856
4.   H    1.0000   0.8063   0.1937
5.   H    1.0000   0.8110   0.1890
6.   H    1.0000   0.7835   0.2165
7.   H    1.0000   0.8110   0.1890
8.   H    1.0000   0.8063   0.1937
```

B.8 NATURAL RESONANCE THEORY (NRT)

B.8.4.3 Gold Methyl and Gold Methyl Hydride

We finally describe two simple examples of resonance in transition metal species. The selected species are (a) `normal-valent' AuCH$_3$ and (b) `hypervalent' [HAuCH$_3$]$^-$ anion, both of C_s symmetry (B3LYP/LANL2DZ level). These species are representative of (a) a well-localized single Lewis-like resonance structure, and (b) multi-reference delocalization associated with strong 3-center, 4-electron hyperbonding. These species also illustrate the dominance of NRT resonance structures conforming to the "Dodectet Rule" (Rule of 12) for transition metals, analogous to the Octet Rule for main group elements.

(a) Gold Methyl (AuCH$_3$)

For neutral AuCH$_3$, the first segment of NRT output is shown below:

```
NATURAL RESONANCE THEORY ANALYSIS:

Maximum reference structures :    20
Maximum resonance structures :   300
Memory requirements :      846164 words of   9986848 available

2 candidate reference structure(s) calculated by SR LEWIS
Initial loops searched 2 bonding pattern(s); 1 was retained
Delocalization list threshold set to 0.18 kcal/mol for reference 1
Reference   1:  rho*=0.03497, f(w)=0.54229 converged after   8 iterations

                                          fractional accuracy f(w)
                      non-Lewis     -----------------------------------
   Ref     Wgt        density       d(0)     all NBOs     val+core     valence
  -------------------------------------------------------------------------
    1    1.00000     0.03497     0.00330     0.54229     0.58697     0.84358


TOPO matrix for the leading resonance structure:

    Atom  1   2   3   4   5
    ---- --- --- --- --- ---
   1. Au   5   1   0   0   0
   2. C    1   0   1   1   1
   3. H    0   1   0   0   0
   4. H    0   1   0   0   0
   5. H    0   1   0   0   0
```
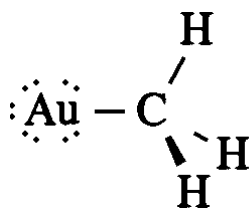
As shown, two candidate reference structures were initially guessed, but the only surviving structure (identical to the NBO structure) corresponds to the Lewis-like diagram

with five lone pairs and one bond pair (12 electrons) around Au and the normal octet arrangement around C. The $\rho^* = 0.03497$ for this structure is very small, corresponding to the high accuracy (99.96%) of the Lewis-like description. The dominance of this structure (98.68%) is reflected in the calculated NRT weightings and bond orders, as shown below:

```
         Resonance
   RS    Weight(%)                      Added(Removed)
 --------------------------------------------------------------------------
   1*       98.68
   2 (2)     0.33    Au  1- C   2, ( C   2- H   3), (Au   1),   H   3
   3 (2)     0.33    Au  1- C   2, ( C   2- H   4), (Au   1),   H   4
   4 (2)     0.33    Au  1- C   2, ( C   2- H   5), (Au   1),   H   5
   5         0.12    (Au  1- C   2), ( C   2- H   3), Au   1,   C   2
   6         0.12    (Au  1- C   2), ( C   2- H   4), Au   1,   C   2
   7         0.12    (Au  1- C   2), ( C   2- H   5), Au   1,   C   2
 --------------------------------------------------------------------------
          100.00    * Total *                  [* = reference structure]

Natural Bond Order:  (total/covalent/ionic)

     Atom       1      2      3      4      5
     ----    ------ ------ ------ ------ ------
  1. Au   t 4.9937 1.0063 0.0000 0.0000 0.0000
          c   ---  0.8425 0.0000 0.0000 0.0000
          i   ---  0.1638 0.0000 0.0000 0.0000

  2.  C   t 1.0063 0.0035 0.9956 0.9956 0.9956
          c 0.8425   ---  0.7629 0.7627 0.7628
          i 0.1638   ---  0.2327 0.2328 0.2328

  3.  H   t 0.0000 0.9956 0.0033 0.0000 0.0000
          c 0.0000 0.7629   ---  0.0000 0.0000
          i 0.0000 0.2327   ---  0.0000 0.0000

  4.  H   t 0.0000 0.9956 0.0000 0.0033 0.0000
          c 0.0000 0.7627 0.0000   ---  0.0000
          i 0.0000 0.2328 0.0000   ---  0.0000

  5.  H   t 0.0000 0.9956 0.0000 0.0000 0.0033
          c 0.0000 0.7628 0.0000 0.0000   ---
          i 0.0000 0.2328 0.0000 0.0000   ---


Natural Atomic Valencies:

                    Co-     Electro-
     Atom  Valency  Valency  Valency
     ----  -------  -------  -------
  1. Au     1.0063   0.8425   0.1638
  2.  C     3.9931   3.1309   0.8621
  3.  H     0.9956   0.7629   0.2327
  4.  H     0.9956   0.7627   0.2328
  5.  H     0.9956   0.7628   0.2328
```
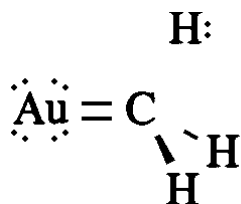
The three weak secondary structures (each with ~0.3% weighting) correspond to $n_{Au} \to \sigma^*_{CH}$ hyperconjugative delocalizations from gold lone pairs into CH antibonds, with formal Lewis-like structure

$$\ddot{A}\ddot{u} = C \overset{H:}{\underset{H}{\diagdown^{`}H}}$$

As shown in the bond order table, these delocalizations lead to slight Au=C double-bond character ($b_{AuC} = 1.006$) and weakening of each CH bond ($b_{CH} \cong 0.996$). The slight asymmetries of these interactions (resulting in slight distortions from ideal C_{3v} symmetry) are due to the greater strength of the unique $d_{xy} \to \sigma^*_{CH}$ interaction for the particular CH bond in the xy plane.

(b) $HAuCH_3^-$

Because Au ($s^2 d^9$) is formally monovalent, we expect that both Au-H and Au-CH_3 are normal-valent (with well-localized NRT descriptions), but the hydride of gold methyl is a 3-center, 4-electron hyperbonded species which can be envisioned as the resonance hybrid

$$H - \ddot{A}\ddot{u}: \quad :CH_3^- \quad \longleftrightarrow \quad H:^- \quad :\ddot{A}\ddot{u} - CH_3$$
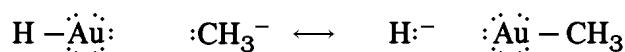
corresponding to strong $n_H \to \sigma^*_{AuC}$ donor-acceptor interaction for the resonance structure on the right, or $n_C \to \sigma^*_{AuH}$ for that on the left. Both the 3CHB search (activated automatically) and other aspects of the preceding NBO analysis strongly suggest this picture of $HAuCH_3^-$. [For the most direct comparisons with $AuCH_3$, we set NRTTHR=1 (kcal/mol) to insure that weak hyperconjugative interactions were treated comparably in the two cases.]

As shown below, the initial LEWIS candidate search is supplemented by the complementary resonance structure from the 3CHB hyperbond search to give the two expected candidate structures, each with comparable ρ^* and resonance weighting,

   1. H-Au CH_3^- ($\rho^*_1 = 0.43537$, $w_1 = 57.30\%$)

   2. H^- Au-CH_3 ($\rho^*_2 = 0.58429$, $w_2 = 41.57\%$)

B.8 NATURAL RESONANCE THEORY (NRT)

in accord with the simple 2-resonance description of the H···Au···C hyperbond:

```
NATURAL RESONANCE THEORY ANALYSIS:

Maximum reference structures :    20
Maximum resonance structures :   300
Memory requirements :       925840 words of   9986381 available

1 candidate reference structure(s) calculated by SR LEWIS
1 candidate reference structure(s) added by hyperbond search (SR HBRES)
Initial loops searched 2 bonding pattern(s); 2 were retained
Delocalization list threshold set to 1.00 kcal/mol for reference 1
Delocalization list threshold set to 1.00 kcal/mol for reference 2
Reference   1:  rho*=0.41803, f(w)=0.93684 converged after  18 iterations
Reference   2:  rho*=0.63643, f(w)=0.93812 converged after   5 iterations
Multi-ref( 2):  D(W)=0.06694, F(W)=0.25280 converged after 220 iterations

                                                fractional accuracy f(w)
                        non-Lewis           -----------------------------------
    Ref    Wgt         density      d(0)       all NBOs    val+core     valence
    ------------------------------------------------------------------------------
     1    0.59775     0.41803    0.08395      0.93684     0.95446     0.95450
     2    0.40225     0.63643    0.13330      0.93812     0.95011     0.95013


TOPO matrix for the leading resonance structure:

     Atom  1   2   3   4   5   6
     ----  --- --- --- --- --- ---
    1. Au    5   0   1   0   0   0
    2.  C    0   1   0   1   1   1
    3.  H    1   0   0   0   0   0
    4.  H    0   1   0   0   0   0
    5.  H    0   1   0   0   0   0
    6.  H    0   1   0   0   0   0

          Resonance
    RS    Weight(%)                      Added(Removed)
    -------------------------------------------------------------------------
    1*      60.54
    2*      38.68    Au  1- C  2, (Au  1- H  3), ( C  2),  H  3
    3        0.20    Au  1- C  2, ( C  2- H  4), (Au  1),  H  4
    4        0.13    Au  1- C  2, ( C  2- H  5), (Au  1),  H  5
    5        0.13    Au  1- C  2, ( C  2- H  6), (Au  1),  H  6
    6        0.11    Au  1- C  2, Au  1- C  2, (Au  1- H  3), ( C  2- H  4),
                     (Au  1), ( C  2),  H  3,  H  4
    7-11     0.20
    -------------------------------------------------------------------------
           100.00   * Total *                  [* = reference structure]
```

As the following bond order table shows, the resulting Au···H, Au···C bond orders ($b_{AuH} = 0.6101$, $b_{AuC} = 0.3977$) are greatly weakened compared to normal-valent single-bonded species. The expected additivity of hyperbonded bond orders

$$b_{AuH} + b_{AuC} \cong 1$$

is seen to be well satisfied at the equilibrium geometry (as well as throughout dissociation to either $H^- + AuCH_3$ or $HAu + CH_3^-$ products):

```
Natural Bond Order:  (total/covalent/ionic)

    Atom       1      2      3      4      5      6
    ----     ------ ------ ------ ------ ------ ------
  1. Au   t 4.9922 0.3977 0.6101 0.0000 0.0000 0.0000
         c   ---   0.1624 0.3792 0.0000 0.0000 0.0000
         i   ---   0.2354 0.2309 0.0000 0.0000 0.0000

  2.  C   t 0.3977 0.6101 0.0000 0.9969 0.9977 0.9977
         c 0.1624   ---   0.0000 0.8067 0.8074 0.8074
         i 0.2354   ---   0.0000 0.1901 0.1903 0.1903

  3.  H   t 0.6101 0.0000 0.3899 0.0000 0.0000 0.0000
         c 0.3792 0.0000   ---   0.0000 0.0000 0.0000
         i 0.2309 0.0000   ---   0.0000 0.0000 0.0000

  4.  H   t 0.0000 0.9969 0.0000 0.0031 0.0000 0.0000
         c 0.0000 0.8067 0.0000   ---   0.0000 0.0000
         i 0.0000 0.1901 0.0000   ---   0.0000 0.0000

  5.  H   t 0.0000 0.9977 0.0000 0.0000 0.0023 0.0000
         c 0.0000 0.8074 0.0000 0.0000   ---   0.0000
         i 0.0000 0.1903 0.0000 0.0000   ---   0.0000

  6.  H   t 0.0000 0.9977 0.0000 0.0000 0.0000 0.0023
         c 0.0000 0.8074 0.0000 0.0000 0.0000   ---
         i 0.0000 0.1903 0.0000 0.0000 0.0000   ---


 Natural Atomic Valencies:

                   Co-    Electro-
    Atom  Valency Valency Valency
    ----  ------- ------- -------
  1. Au   1.0078  0.5416  0.4662
  2.  C   3.3899  2.5838  0.8061
  3.  H   0.6101  0.3792  0.2309
  4.  H   0.9969  0.8067  0.1901
  5.  H   0.9977  0.8074  0.1903
  6.  H   0.9977  0.8074  0.1903

$NRTSTR
  STR         ! Wgt = 60.54%
    LONE 1 5 2 1 END
    BOND S 1 3 S 2 4 S 2 5 S 2 6 END
  END
  STR         ! Wgt = 38.68%
    LONE 1 5 3 1 END
    BOND S 1 2 S 2 4 S 2 5 S 2 6 END
  END
$END
```

As usual, NRT output terminates with the printed $NRTSTR specification for the two leading resonance structures.

B.9. NATURAL BOND-BOND POLARIZABILITY (NBBP)

Reference: H. E. Zimmerman and F. Weinhold, *J. Am. Chem. Soc.* **116**, 1579-1580 (1994); H. E. Zimmerman and F. Weinhold, *J. Org. Chem.* (submitted).

B.9.1 Introduction to NBBP

The "bond-bond polarizability" $\Pi_{rs;tu}$ was originally introduced by Coulson and Longuet-Higgins [C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.* **A191**, 39 (1947); **A192**, 16 (1947)] in the framework of Hückel pi-electron theory, but a full *ab initio* SCF-MO generalization can be given with natural hybrid orbitals (NHOs). In Hückel theory the indices r, s, t, u of $\Pi_{rs;tu}$ refer to atoms connected by pi bonds, *viz.*, pi-bond π_{rs} between atoms r, s and pi-bond π_{tu} between atoms t, u. More generally, these indices refer to bonding natural hybrid orbitals h_r, h_s, h_t, h_u forming occupied NBOs of the natural Lewis structure, *viz.*, NBO b_{rs} between hybrids h_r, h_s and NBO b'_{tu} between hybrids h_t, h_u.

The bond-bond polarizability is formally defined as

$$\Pi_{b;b'} = \Pi_{rs;tu} = \sum_j^{occ} \sum_k^{vir} n_j \, (c_{rj}c_{sk} + c_{rk}c_{sj}) \, (c_{tj}c_{uk} + c_{tk}c_{uj})/(\varepsilon_k - \varepsilon_j)$$

where c_{rj}, c_{rk} denote the coefficients of hybrid h_r in an occupied MO φ_j or virtual MO φ_k, with respective orbital energies ε_j, ε_k and occupied orbital occupancy n_j (= 2 for closed-shell systems). When evaluated in this general NHO-based formulation, $\Pi_{rs;tu}$ is referred to as the "natural bond-bond polarizability" (NBBP) index. For open-shell systems, NBBP indices are calculated separately for alpha and beta spin (with $n_j = 1$), consistent with the NBO "different hybrids for different spins" description.

The matrix elements $\Pi_{rs;tu}$ can be formally related to changes in bond order between hybrids r, s, due to changes in the interaction between hybrids t, u. The NBBP index therefore allows one to analyze how changes in one part of the molecule affect the strength of bonds (or incipient bonds) elsewhere.

Elements of the natural bond-bond polarizability array may be identified by NBO indices ($\Pi_{b;b'}$) or NHO indices ($\Pi_{rs;tu}$) in the NBBP program output. By default, the program calculates $\Pi_{b;b'}$ values for bonding NBOs of the formal Lewis structure. In addition, the user can request values of other $\Pi_{rs;tu}$ elements by listing desired sets of NHO indices in a supplementary "bracket list" to be described below.

B.9. NATURAL BOND-BOND POLARIZABILITY (NBBP)

B.9.2 NBBP Keyword Usage and Sample Output

Basic NBBP analysis is requested by simply including the "NBBP" keyword in the $NBO keylist, as in the example below:

```
$NBO   NBBP   $END
```

This produces an array of $\Pi_{b;b'}$ elements for each pair of occupied NBOs b, b' of the natural Lewis structure. Rows and columns of this array are labelled according to the standard NBO numbering. For the simple case of methylamine (RHF/3-21G level, Pople-Gordon geometry), the output is illustrated below:

```
NBBP: NBO bond-bond polarizability matrix

        NBO        1       2       3       4       5       6       7       8
    ---------- ------- ------- ------- ------- ------- ------- ------- -------
    1.  C 1(cr)    0.0004  0.0000  0.0000  0.0001  0.0002  0.0001  0.0001  0.0000
    2.  N 2(cr)    0.0000  0.0001  0.0000  0.0001  0.0000  0.0000  0.0000  0.0000
    3.  N 2(lp)    0.0000  0.0000  0.0999  0.0004  0.0277  0.0051  0.0051  0.0009
    4.  C 1- N 2   0.0001  0.0001  0.0004  0.0633 -0.0001 -0.0001 -0.0001 -0.0013
    5.  C 1- H 3   0.0002  0.0000  0.0277 -0.0001  0.0755  0.0000  0.0000  0.0004
    6.  C 1- H 4   0.0001  0.0000  0.0051 -0.0001  0.0000  0.0921  0.0012  0.0040
    7.  C 1- H 5   0.0001  0.0000  0.0051 -0.0001  0.0000  0.0012  0.0921  0.0005
    8.  N 2- H 6   0.0000  0.0000  0.0009 -0.0013  0.0004  0.0040  0.0005  0.2102
    9.  N 2- H 7   0.0000  0.0000  0.0009 -0.0013  0.0004  0.0005  0.0040 -0.0014

        NBO        9
    ---------- -------
    1.  C 1(cr)    0.0000
    2.  N 2(cr)    0.0000
    3.  N 2(lp)    0.0009
    4.  C 1- N 2  -0.0013
    5.  C 1- H 3   0.0004
    6.  C 1- H 4   0.0005
    7.  C 1- H 5   0.0040
    8.  N 2- H 6  -0.0014
    9.  N 2- H 7   0.2102
```

In this example, the strongest off-diagonal NBBP element (+0.0277) is that connecting the amine lone pair (NBO 3) with the vicinal antiperiplanar C1-H3 bond (NBO 5), evidence of their strong hyperconjugative coupling. It can also be seen that bond-bond polarizability between CH and NH bonds is stronger for antiperiplanar than gauche orientation (viz., 0.0040 for C1-H4 with N2-H6, vs. 0.0005 for C1-H4 with N2-H7).

In addition, one can request subsidiary $\Pi_{rs;tu} = \Pi(r,s;t,u)$ NBBP values to be computed for an arbitrary list of NHO indices r, s, t, u. This is done by including a *bracket list* of the form $<r\ s\ t\ u/r'\ s'\ t'\ u'/\ldots>$ following the NBBP keyword in the $NBO keylist. For example, to request the additional elements $\Pi(4,5,9,15)$, $\Pi(7,6,8,12)$, and $\Pi(8,9,12,13)$, one could use the $NBO keylist shown below:

B.9. NATURAL BOND-BOND POLARIZABILITY (NBBP)

```
$NBO   NBBP   <4 5 9 15/7 6 8 12/8 9 12 13>   $END
```

The bracket list can also be broken onto multiple lines as illustrated below:

```
$NBO   NBBP
<   4   5   9  15 /
    7   6   8  12 /
    8   9  12  13 >
$END
```

As illustrated, each field of 4 indices (free format, separated by spaces or commas) is separated by slashes (/) from neighboring fields, with the angle bracket delimiters (<, >) separated by at least one space from adjacent keywords.

The keylist above will produce the usual table of $\Pi_{b;b'}$ values for bonding NBOs as well as the supplementary table shown below with $\Pi_{rs;tu}$ values for the requested NHO indices:

```
User-requested Pi(r,s;t,u) NBBP Values:

   NHO indices      uncorrected       sign         "corrected"
  -------------    -----------    -------------    -----------
  r   s   t   u    Pi(r,s;t,u)  F(r,s) F(t,u)    Pi(r,s;t,u)
  -------------    -----------    ------ ------    -----------
  4   5   9  15     -0.001658      -      -         -0.001658
  7   6   8  12      0.000412      -      +         -0.000412
  8   9  12  13      0.004018      -      -          0.004018
```

In this case, the final entry $\Pi(8,9,12,13)$ of the supplementary table corresponds to the 6-8 entry (0.0040) in the main table, since NBO 6 is composed of hybrids 8, 9 and NBO 8 of hybrids 12, 13. Note that user-selected $\Pi_{rs;tu}$ values are printed with somewhat higher numerical precision than those of the main NBBP table.

As the example above shows, the program prints both the "uncorrected" $\Pi_{rs;tu}$ value (as directly calculated for the actual hybrid phases) as well as a "corrected" value, $sgn(F_{rs}F_{tu})\Pi_{rs;tu}$, whose sign is adjusted to correspond to the intuitive choice of phase with *negative* Fock matrix elements F_{rs}, F_{tu}, i.e., with both *r-s* and *t-u* hybrid pairs chosen to have "in-phase overlap." (The sign information given in this table helps to consistently interpret the physical significance of negative $\Pi_{rs;tu}$ values, since the sign of $\Pi_{rs;tu}$ can otherwise be reversed by arbitrarily changing the phases of any of its indexed NHOs.) For example, in the second entry of the sample output, the "corrected" value of $\Pi(7,6;8,12)$ is *negative*, as if the phase of hybrid 7 (or 6) were reversed to give a negative Fock matrix element ("positive overlap") between NHOs 7 and 6.

B.9. NATURAL BOND-BOND POLARIZABILITY (NBBP)

[However, for very small polarizability values, the near-zero Fock matrix elements F_{rs} (weak overlap limit) can become slightly positive even if orbitals r, s are in-phase. In case of doubt one should therefore check the actual orbital overlap with ORBPLOT, or with the explicit value in the SPNHO overlap matrix, to confirm the presumed phase assignments.]

B.10. NATURAL STERIC ANALYSIS

References: J. K. Badenhoop and F. Weinhold, *J. Chem. Phys.* **107**, 5406-5421, 5422-5432 (1997); *Int. J. Quantum Chem.* **72**, 269-280 (1999).

B.10.1 Introduction

Natural steric analysis expresses steric exchange repulsion as the energy difference due to orbital orthogonalization, in accordance with a well-established physical picture of "steric repulsions" [V. W. Weisskopf, *Science* **187**, 605-612 (1975); P. A. Christiansen and W. E. Palke, *J. Chem. Phys.* **67**, 57 (1977)]. The present implementation improves that introduced in NBO 4.0 by systematic replacement of NBOs by NLMOs, thereby incorporating the coupling of steric repulsions with delocalization effects described by the weak "tails" of NLMOs. This replacement leads to negligible numerical changes for well-localized systems (e.g., rare gas interactions), but it significantly improves the description of steric effects in strongly delocalized species.

The overall NBO/NLMO steric exchange energy is expressed as the sum of orbital orthogonalization energy changes, calculated as differences in diagonal Fock matrix elements for nonorthogonal PNLMOs $\{^p\Omega_I\}$ vs. orthogonal NLMOs $(\Omega_I\}$

$$E_x^{NLMO} = \sum_I \left(F_{I,I}^{NLMO} - F_{I,I}^{PNLMO} \right)$$

where $F_{I,I}^{NLMO} = \langle \Omega_I | \mathbf{F} | \Omega_I \rangle$ and $F_{I,I}^{PNLMO} = \langle ^p\Omega_I | \mathbf{F} | ^p\Omega_I \rangle$. The reference zero in this expression refers to the isolated PNLMO limit in which all atoms are separated to infinity. The steric exchange energy includes effects from *all* occupied orbitals and therefore typically contains contributions from covalent (*intra*bond) groups. In order to calculate intermolecular steric energies, one first performs a calculation with the molecular units separated by a large distance (typically at least 8 Å) as the asymptote, then a second one in the desired geometry, and subtracts the two values.

Natural steric analysis also approximates the pairwise steric exchange interaction $E_{I,J}^{pwx}$ between two semi-localized NLMOs *I, J* by using the inverse of a 2 x 2 occupancy-weighted symmetric orthogonalization to obtain two "partial NLMOs" $^{p2}\Omega_I$, $^{p2}\Omega_J$ (labelled "PNLMO/2" orbitals). The steric exchange energy associated with NLMOs *I, J* is calculated as

$$E_{I,J}^{pwx} = \left(F_{I,I}^{NLMO} - F_{I,I}^{PNLMO/2} \right) + \left(F_{J,J}^{NLMO} - F_{J,J}^{PNLMO/2} \right)$$

B.10. NATURAL STERIC ANALYSIS

where $F_{I,I}^{PNLMO/2} = <{}^{p2}\Omega_I|\mathbf{F}|\,{}^{p2}\Omega_I>$, etc. The strength of these pairwise interactions between localized orbitals falls off rapidly with distance, so "steric effects" due to interaction of orbitals in close proximity can be exhibited in a short list of the most important terms.

For the total steric exchange energy, both the individual NLMO bond energy changes and the sum E_x^{NLMO} (overall and by molecular unit) are tabulated. This is followed by a list of the pairwise steric interactions between orbitals on different centers above an energy print threshold which can be specified by the user. The user can also specify pairs of NLMO indices in a supplementary bracket list, described below.

B.10. NATURAL STERIC ANALYSIS

B.10.2 STERIC Keyword Usage and Sample Output

Basic NBO/NLMO steric analysis is requested by simply including the "STERIC" keyword in the $NBO keylist, as in the example below:

```
    $NBO   STERIC   FILE=CH3NH2_He   $END
```

This produces a list of orbital contributions to the overall steric exchange energy and their sum organized by molecular unit, followed by a table of PNLMO overlaps and pairwise steric exchange energies.

Sample output will be shown to illustrate both intra- and intermolecular steric interactions for a simple $CH_3NH_2 \cdots He$ model, where a helium "probe" atom is placed 2.3 Å (in collinear N-H$\cdots$He arrangement) from an amine hydrogen of methylamine (RHF/3-21G, Pople-Gordon geometry). The first segment of output shows the individual NLMO steric exchange energies within each molecular unit, and in total:

```
NBO/NLMO STERIC ANALYSIS:

Occupied NLMO contributions dE(i) (kcal/mol) to total steric exchange energy

NLMOs (i) in unit  1                 dE(i)
   1. CR ( 1) C  1                    75.90
   2. CR ( 1) N  2                   101.45
   3. LP ( 1) N  2                   -18.87
   5. BD ( 1) C  1- N  2             -15.57
   6. BD ( 1) C  1- H  3             -11.22
   7. BD ( 1) C  1- H  5             -13.13
   8. BD ( 1) C  1- H  6             -13.16
   9. BD ( 1) N  2- H  4             -11.06
  10. BD ( 1) N  2- H  7             -11.40

Steric exchange energy, unit 1:    82.95 kcal/mol

NLMOs (i) in unit  2                 dE(i)
   4. LP ( 1)He  8                    0.12

Steric exchange energy, unit 2:     0.12 kcal/mol
-------------------------------------------------
   Total steric exchange energy:    83.07 kcal/mol
-------------------------------------------------
```

As shown, the total steric exchange energy is calculated as +83.07 kcal/mol in this case, arising almost entirely from the CH_3NH_2 unit (82.95 kcal/mol, vs. 0.12 kcal/mol for the He unit). Within CH_3NH_2, the exchange energies are seen to be typically negative for valence NLMOs (*viz.*, −18.87 kcal/mol for the nitrogen lone pair), but strongly positive for core NLMOs (*viz.*, +101.45 kcal/mol for the nitrogen core 1s orbital), leading to the expected net positive (repulsive) contribution of steric exchange interactions.

B.10. NATURAL STERIC ANALYSIS

[To obtain the intermolecular steric exchange energy between CH_3NH_2 and He units, one would repeat the calculation with the two units separated by a large distance (e.g., 12 Å). The total steric exchange energy obtained from this calculation (not shown) is +82.66 kcal/mol, so the steric interaction energy would be estimated as +83.07 − 82.66 = +0.41 kcal/mol for the 2.3 Å separation, similar to the room-temperature kT value characteristic of van der Waals contact distance.]

The next segment of output shows the corresponding estimates of pairwise steric exchange interactions (and associated pre-NLMO overlap integrals) for "disjoint" pairs of NLMOs (i.e., sharing no common atom):

```
Pairwise steric exchange energies dE(i,j) (kcal/mol) and associated
pre-NLMO overlaps S(i,j) for disjoint (no common atoms) interactions
between NLMOs i,j:

         Threshold for printing:     0.50 kcal/mol
         (Intermolecular threshold:  0.05 kcal/mol)
                                                    PNLMO    dE(i,j)
        NLMO (i)                     NLMO (j)        S(i,j)   kcal/mol
 ===============================================================================

within unit  1
   3. LP ( 1) N   2          6. BD ( 1) C   1- H   3      0.1646    10.80
   3. LP ( 1) N   2          7. BD ( 1) C   1- H   5     -0.0770     1.69
   3. LP ( 1) N   2          8. BD ( 1) C   1- H   6      0.0772     1.71
   6. BD ( 1) C   1- H   3   9. BD ( 1) N   2- H   4     -0.0825     1.74
   6. BD ( 1) C   1- H   3  10. BD ( 1) N   2- H   7      0.0826     1.75
   7. BD ( 1) C   1- H   5   9. BD ( 1) N   2- H   4      0.0991     4.05
   7. BD ( 1) C   1- H   5  10. BD ( 1) N   2- H   7      0.0941     2.45
   8. BD ( 1) C   1- H   6   9. BD ( 1) N   2- H   4      0.0937     2.44
   8. BD ( 1) C   1- H   6  10. BD ( 1) N   2- H   7      0.0990     4.02


                                          sum within unit 1:    31.15

between units  1 and  2
   4. LP ( 1)He  8          10. BD ( 1) N   2- H   7     -0.0282     0.29

                                      sum between units 1 and 2:    0.21

within unit  2

                                          sum within unit 2:    0.00

 -------------------------------------------------------------------------------
     Total disjoint NLMO steric exchange energy from pairwise sum:    31.36
 -------------------------------------------------------------------------------
```

As shown, the only appreciable steric interaction between He and CH_3NH_2 (above the default intermolecular printing threshold of 0.05 kcal/mol) is that (+0.29 kcal/mol) with the N_2-H_7 bond pointed directly toward He. The total intermolecular steric exchange interaction estimated from the pairwise sum (+0.21 kcal/mol) differs from the total exchange energy difference calculated above (+0.41 kcal/mol) due to non-pairwise additivity of exchange interactions.

B.10. NATURAL STERIC ANALYSIS

By default, only pairwise steric energies above 0.5 kcal/mol (intramolecular) or 0.05 kcal/mol (intermolecular) are printed. The user can set a different threshold (e.g., 0.4 kcal/mol, with the intermolecular threshold scaled accordingly) by including a real number value after the STERIC keyword, as illustrated below:

```
   $NBO  STERIC=0.4  $END
```

The user can also request specific additional pair interaction energies (*I,J*), (*K,L*),... to be printed by specifying pairs of NLMO indices in brackets (cf Sec. B.9.2),

```
   STERIC <I J/K L/..>
```

As indicated, each field of two indices (free format, separated by spaces or commas) is separated by slashes (/) from neighboring fields, with the entire list enclosed by angle bracket delimiters () separated by at least one space from adjacent keywords. If desired, the bracket list may be broken up onto separate lines (each terminated by a / field delimiter) as shown below:

```
   STERIC <I1 J1/I2 J2/
   I3 J3/I4 J4>
```

An altered printing threshold can also be combined with user-requested bracket input as shown below:

```
   $NBO  STERIC=0.4 <6 4/5 6/6 1> FILE=CH3NH2_He  $END
```

In the case of the $CH_3NH_2\cdots He$ example (2.3 Å), this would lead to the additional output shown below:

```
_____
User-requested steric interactions:
                                                                PNLMO     dE(i,j)
        NLMO (i)                         NLMO (j)               S(i,j)    kcal/mol
  ============================================================================
     6. BD ( 1) C  1- H  3         4. LP ( 1)He  8            -0.0026      0.00
     5. BD ( 1) C  1- N  2         6. BD ( 1) C  1- H  3      -0.1140     15.35
     6. BD ( 1) C  1- H  3         1. CR ( 1) C  1            -0.0421     28.70
  ----------------------------------------------------------------------------
```

As shown, the He probe atom is outside the range in which it has any appreciable steric interaction with the C_1-H_3 bond, but the exchange interactions between NLMOs 5, 6 (the non-disjoint interaction between geminal bonds σ_{CN}, σ_{CH}: +15.35 kcal/mol) or NLMOs 6, 1 (the interaction of bond C_1-H_3 with its own carbon core orbital: +28.70 kcal/mol) are quite significant.

B.11. NEDA: NATURAL ENERGY DECOMPOSITION ANALYSIS

Reference: 1. E. D. Glendening and A. Streitwieser, *J. Chem. Phys.* **100**, 2900 (1994). 2. E. D. Glendening, *J. Am. Chem. Soc.* **118**, 2473 (1996). 3. G. K. Schenter and E. D. Glendening, *J. Phys. Chem.* **100**, 17152 (1996). 4. E. D. Glendening, *J. Phys. Chem.A* **109**, 11936 (2005).

B.11.1 Introduction to NEDA

Natural energy decomposition analysis is an energy partitioning procedure for molecular interactions. Electrical interaction (EL), charge transfer (CT), and core repulsion (CORE) contributions are evaluated for self-consistent field (SCF) wavefunctions. The electrical term

$$EL = ES + POL + SE$$

arises from classical electrostatic (ES) and polarization interactions (POL+SE) that are well described by electrodynamics. SE is the linear response self energy (energy penalty) of polarization. The CORE contribution

$$CORE = EX + DEF - SE$$

results principally from intermolecular exchange interactions (EX) and deformation (DEF), where the latter is the energy cost to distort a fragment wavefunction in the field of all other fragments of the complex. The total interaction energy is then given by

$$\Delta E = EL + CT + CORE$$

A key element of the NEDA approach is the evaluation of perturbed fragment wavefunctions, Ψ_A^{def} one for each of the monomers that comprise the complex. These wavefunctions are constructed from the local block eigenvectors of the NBO Fock matrix. The charge distributions described by the perturbed wavefunctions arise from electric field and quantum mechanical effects experienced by the fragments within the complex. A localized wavefunction, Ψ_{loc}, is then constructed for the complex as an antisymmetrized product of perturbed wavefunctions. NEDA further employs the supermolecule wavefunction, Ψ, and the SCF-converged wavefunctions for the isolated fragments, Ψ_A.

Given these wavefunctions, the interaction energy and its NEDA components are obtained as follows:

B.11. NEDA: NATURAL ENERGY DECOMPOSITION ANALYSIS

$$\Delta E = E(\Psi) - \sum_A E(\Psi_A)$$

$$\mathrm{CT} = E(\Psi) - E(\Psi\mathrm{loc})$$

$$\mathrm{ES} + \mathrm{POL} + \mathrm{EX} = E(\Psi\mathrm{loc}) - \sum_A E(\Psi_A{}^{\mathrm{def}})$$

$$\mathrm{DEF} = \sum_A [E(\Psi_A{}^{\mathrm{def}}) - E(\Psi_A)]$$

Further details of the evaluation of these components are given in the original papers.

NEDA evaluates all energies in the complete basis set of the complex so that ΔE corresponds to the counterpoise-corrected interaction energy of Boys and Bernardi [*Mol. Phys.* **19**, 553 (1970)]. The NEDA program has been generalized to handle complexes consisting of more than two fragments.

NEDA also calculates the dipole moments for the wavefunctions Ψ_A and $\Psi_A{}^{\mathrm{def}}$

$$\mathbf{\mu}_A = \mathbf{\mu}_{\mathrm{nuc}} - \langle \Psi_A{}^{\mathrm{def}}| \mathbf{\mu}_{\mathrm{el}} |\Psi_A{}^{\mathrm{def}}\rangle$$

The difference between these two vector quantities is a measure of the induced dipole for a fragment in the complex. The moments are origin independent, except for charged fragments for which the origin is placed at the center of the fragment mass.

The NEDA program is fully implemented in GAMESS; certain references below assume that GAMESS is the host ESS. Check the latest ESS documentation for whether NEDA is currently available in other ESS/NBO6 combinations.

B.11. NEDA: NATURAL ENERGY DECOMPOSITION ANALYSIS

B.11.2 Running NEDA in the NBO Framework

B.11.2.1 $DEL Input

NEDA is implemented in the energetic (deletions) analysis of the NBO program and is activated by inserting the keyword NEDA in the $DEL keylist. NEDA input is terminated by the word END. Thus, adding the following lines to the GAMESS input deck runs default NEDA.

```
$NBO $END
$DEL NEDA END $END
```

The first line activates the NBO program. In the second line, the word END terminates NEDA input and the $END completes the $DEL keylist. This input is entirely free-format and keylists can span more than one line. The $NBO and $DEL keylist identifiers should, however, be the first words appearing on their respective lines.

By default, NEDA analyzes a wavefunction in terms of the molecular units of the NBO program. These units are determined by the connectivity of the NBOs and are printed in the summary table that appears at the bottom of NBO output (see Section B.11.4.2 for an example). For instance, a calculation of the water dimer gives two molecular units (the two water molecules), and the analysis of the trimer gives three. Default NEDA would therefore analyze these wavefunctions in terms of two and three water molecules, respectively. For most applications, the set of molecular units calculated by NBO will be exactly that desired for NEDA. In these cases, no input beyond that shown above is required. Section B.11.2.2 describes methods for defining alternative sets of molecular units.

Other NBO deletion types, such as `LEWIS' and `DELETE 5 ELEMENTS...' can be placed in the $DEL keylist together with NEDA input, and multiple NEDA evaluations can appear in the keylist (each beginning with NEDA and ending with END). The deletions and NEDA are performed in the order that the keywords are specified in the keylist.

To activate NEDA for UHF wavefunctions, use a $DEL keylist of the form

```
$DEL
    ALPHA NEDA END
    BETA  NEDA END
$END
```

B.11. NEDA: NATURAL ENERGY DECOMPOSITION ANALYSIS

Note that the program halts if the molecular units of the alpha spin system differ from those of beta (use the methods described in B.11.2.2 to define identical alpha and beta spin molecular units).

NEDA can be applied to any RHF or UHF wavefunction calculated by GAMESS, including those evaluated by direct SCF methods and those involving effective core potentials (ECPs). The SOSCF, DIIS, damping, and direct energy minimization (DEM) methods of the GAMESS $SCF group can be employed to control the convergence of the fragment SCF wavefunctions.

Symmetry should be disabled (NOSYM=1 in the GAMESS $CONTRL group) *for all NEDA calculations.*

See Section B.6.10 for more details on the NBO energetic analysis and the $DEL keylist.

B.11. NEDA: NATURAL ENERGY DECOMPOSITION ANALYSIS

B.11.2.2 Defining Fragments

In certain cases, it may be desirable to define a set of molecular fragments other than that calculated by the NBO program. Extended NEDA input, $CHOOSE input, and the NBO keyword NOBOND together offer the user several methods to specify an alternate selection.

Extended NEDA input allows one to combine two or more molecular units of the NBO analysis into a single fragment. For example, suppose that NBO calculates six molecular units, numbered 1 to 6. The following input forces NEDA to treat the wavefunction as a collection of four fragments.

```
$DEL NEDA (1,3) (2,6) (4) (5) END $END
```

In this case, the first fragment consists of molecular units 1 and 3, the second consists of units 2 and 6, the third corresponds to unit 4, and the fourth corresponds to unit 5. The `(4)' and `(5)' are optional, as any molecular unit absent in the NEDA input is treated as a separate fragment.

$CHOOSE input and the NOBOND option can be used to modify the molecular units calculated by the NBO program. For example, consider BH_3NH_3 at its equilibrium geometry. By default, the NBO program calculates a single molecular unit with seven bonds: B1-N2, B1-H3, B1-H4, B1-H5, N2-H6, N2-H7, and N2-H8. To treat this system as an interacting pair of Lewis acid-base molecules BH_3, NH_3, one can use the $CHOOSE input to specify the pattern of bonds for NBO to calculate.

```
$NBO $END
$CHOOSE
        LONE 2 1 END
        BOND S 1 3 S 1 4 S 1 5 S 2 6 S 2 7 S 2 8 END
$END
$DEL NEDA END $END
```

Alternatively, the NOBOND keyword prevents NBO from calculating any bonding functions. Each molecular unit therefore consists of a single atom and extended NEDA input can be used to collect atomic centers into the desired fragments.

```
$NBO NOBOND $END
$DEL NOSTAR (1,3,4,5) (2,6,7,8) END $END
```

Another example of $CHOOSE and NOBOND input is shown in Section B.11.3.3.

B.11. NEDA: NATURAL ENERGY DECOMPOSITION ANALYSIS

Additional information on NOBOND and $CHOOSE is available in Sections B.2.2 and B.6.9.

B.11. NEDA: NATURAL ENERGY DECOMPOSITION ANALYSIS

B.11.3 Sample NEDA Input

B.11.3.1 Water Dimer

The following is a sample GAMESS input deck for the RHF/4-31G calculation of the water dimer.

```
$CONTRL  SCFTYP=RHF  RUNTYP=ENERGY  COORD=HINT  NOSYM=1  $END
$INTGRL  NOPK=1  $END
$BASIS  GBASIS=N31  NGAUSS=4  $END
$NBO  $END
$DEL  NEDA  END  $END
$DATA
Water dimer...(rhf/4-31g//from Umeyama and Morokuma, JACS 99, 1316
(1977))
Cs

Oxygen    8.0   LC   0.0000   0.0000   0.0000  +  O I
Hydrogen  1.0   TCT  0.9560  52.6000  90.0000  +  O I J
Oxygen    8.0   TCT  2.8800 120.0000   0.0000  +  O I J
Hydrogen  1.0   TCT  0.9560 105.2000 180.0000  +  3 O J
Hydrogen  1.0   TCT  0.9560 105.2000   0.0000  +  3 4 O
$END
```

NBO analysis calculates two molecular units based on the connectivity of the bonding NBOs. Default NEDA therefore analyzes the wavefunction in terms of these two monomer fragments.

Additional details of this analysis are shown in Section B.11.4.1.

B.11. NEDA: NATURAL ENERGY DECOMPOSITION ANALYSIS

B.11.3.2 Lithium Chloride Monohydrate

LiCl·H2O (RHF/6-31+G*) demonstrates two applications of NEDA to a complex consisting of more than two fragments.

```
$CONTRL  SCFTYP=RHF  RUNTYP=ENERGY  COORD=ZMT  NOSYM=1  $END
$INTGRL  NOPK=1  $END
$BASIS  GBASIS=N31  NGAUSS=6  NDFUNC=1  $END
$NBO  $END
$DEL  NEDA  END
      NEDA  (1,2) (3) END
$END
$DATA
LiCl..H2O...rhf/6-31g*
C1
LI
CL     1   2.0993427
O      1   1.9020655  2   179.9605863
H      3    .9500458  1   126.3708465  2   178.7919157  0
H      3    .9500473  4   107.2871778  1  -179.9941078  0
$END
```

In this case, NBO analysis calculates three molecular units: (1) lithium cation, (2) chloride, and (3) a water molecule. These units are listed in the NBO summary that is printed at the end of the NBO output, just before the NEDA.

The first application of NEDA (the default `NEDA END') analyzes the wavefunction in terms of these three fragments.

The second application (`NEDA (1,2) (3) END') then treats the system in terms of two fragments, LiCl and a water molecule. Here, the NEDA input stipulates that the first fragment consists of molecular units 1 and 2 and that the second fragment corresponds to molecular unit 3.

See Section B.11.4.2 for additional details.

B.11. NEDA: NATURAL ENERGY DECOMPOSITION ANALYSIS

B.11.3.3 Scandium Hydride/Hydrogen Molecule Transition State

The transition state for reaction of ScH_3 with H_2 closely resembles an interacting pair of ions, ScH_2^+ and H_3^-. However, default NBO analysis calculates three molecular units rather than two: (1) a cation ScH_2^+, (2) a hydrogen molecule, and (3) an anion H^-. Below we show three methods to perform NEDA in terms of the two molecular ions.

The first method employs the results of default NBO analysis. Extended NEDA input defines two fragments, the second (H_3^-) consisting of molecular units 2 and 3.

```
$CONTRL  SCFTYP=RHF  RUNTYP=ENERGY  NOSYM=1  $END
$INTGRL  NOPK=1  $END
$BASIS  GBASIS=MIDI  $END
$NBO  $END
$DEL  NEDA  (1) (2,3) END  $END
$DATA
Scandium hydride + H2...rhf/midi
Cnv 2

SCANDIUM   21.0    .0000000000    .0000000000    .1416928244
HYDROGEN    1.0   1.5303094005    .0000000000   1.0915868204
HYDROGEN    1.0    .0000000000    .0000000000  -1.8080659704
HYDROGEN    1.0    .0000000000   .9871723019   -1.5311962463
$END
```

The second method uses $CHOOSE input to stipulate the pattern of bonds.

```
$NBO $END
$CHOOSE BOND S 1 2 S 1 3 END 3CBOND S 4 5 6 END $END
$DEL NEDA END $END
```

Here, NBO is directed to search for the two, two-center ScH bonds of the ScH_2^+ fragment and one, three-center bond for the H_3^- fragment. Note that the four electrons of the latter unit occupy bonding and non-bonding orbitals.

Substituting these three lines into the input deck listed above will give NEDA results identical to that of the first method. Note however that the NBO output will differ for these two calculations as the $CHOOSE input of the second provides a different Lewis structure description of the wavefunction than calculated by default NBO in the first. See Section B.6.9 for more information on $CHOOSE input.

B.11. NEDA: NATURAL ENERGY DECOMPOSITION ANALYSIS

The third method uses the NOBOND option of the $NBO keylist.

```
$NBO NOBOND $END
$DEL NEDA (1,2,3) (4,5,6) END $END
```

This keyword disables the NBO search for bond functions, and hence, each `molecular unit' consists of a single atom. NEDA input indicates that atoms 1-3 comprise the first fragment, and atoms 4-6 the second.

The following results are obtained in each calculation: $\Delta E = -222.9$, $EL = -240.3$, $CT = -117.8$, and $CORE = 135.2$ (all in kcal/mol).

B.11. NEDA: NATURAL ENERGY DECOMPOSITION ANALYSIS

B.11.3.4 Open-Shell Sodium/Water Complex

The following sample input demonstrates NEDA of the open-shell wavefunction describing the interaction of a water molecule with a sodium atom:

```
$CONTRL  SCFTYP=UHF  RUNTYP=ENERGY  MULT=2  NOSYM=1  $END
$INTGRL  NOPK=1  $END
$BASIS  GBASIS=N31  NGAUSS=6  NDFUNC=1  NPFUNC=1  DIFFSP=.T.  DIFFS=.T.
$END
$NBO  $END
$DEL  ALPHA NEDA END  BETA NEDA END  $END
$DATA
Na..OH2 (rhf/6-31++G**)
Cnv 2

NA         11.0    .0000000000    .0000000000   -.3404656616
O           8.0    .0000000000    .0000000000   2.0240196206
H           1.0    .0000000000    .7627333242   2.5832459068
$END
```

An output excerpt showing the calculated energetics is given below:

```
Natural Energy Decomposition Analysis (Summary):

                                              Component
              Energy(wfn)        Energy(wfn)    (kcal/mol)
-----------------------------------------------------------------------
H2ONa      -237.8815335(scf)  -237.8644181(loc)   CT =    -10.74
                                                  ES =    -24.12
                                                  POL =   -12.23
                                                  EX =     -6.45
1. Na      -161.7882513(def)  -161.8414917(cp)  DEF(SE) =  33.41(   4.48)
2. H2O      -76.0079719(def)   -76.0324201(cp)  DEF(SE) =  15.34(   1.88)
                                                         ---------
                                                  E =     -4.78


Electrical (ES+POL+SE) :     -29.99
  Charge Transfer (CT) :     -10.74
       Core (EX+DEF-SE) :     35.94
                         -----------
 Total Interaction (E) :      -4.78
```

B.11. NEDA: NATURAL ENERGY DECOMPOSITION ANALYSIS

B.11.4 Sample NEDA Output

B.11.4.1 Water Dimer

The following is NEDA output for the default analysis of RHF/4-31G water dimer in the geometry given in Section B.11.3.1.

NEDA begins by calculating a localized wavefunction in which all intermolecular CT effects are deleted. This is accomplished by zeroing all off-diagonal elements of the NBO Fock matrix between orbitals on separate monomer units and diagonalizing to obtain localized MOs for each monomer. This first section of output details the occupancy shifts and energy change that occur upon localization.

```
NEDA: Natural Energy Decomposition Analysis
Deletion of the NBO Fock matrix elements between orbitals:
   1   3   4   7   8  11  12  15  16  17  18  19  20
and orbitals:
   2   5   6   9  10  13  14  21  22  23  24  25  26

Orbital occupancies:

      Orbital                      No deletions  This deletion    Change
-----------------------------------------------------------------------------
   1. CR ( 1) O  1                    1.99982       1.99983       0.00001
   2. CR ( 1) O  4                    1.99979       1.99980       0.00000
   3. LP ( 1) O  1                    1.99920       1.99930       0.00010
   4. LP ( 2) O  1                    1.98029       1.99914       0.01885
   5. LP ( 1) O  4                    1.99994       2.00000       0.00006
   6. LP ( 2) O  4                    1.99922       1.99932       0.00010
   7. BD ( 1) O  1- H  2              1.99912       1.99942       0.00030
   8. BD ( 1) O  1- H  3              1.99912       1.99942       0.00030
   9. BD ( 1) O  4- H  5              1.99960       1.99961       0.00000
  10. BD ( 1) O  4- H  6              1.99919       1.99943       0.00024
  11. BD*( 1) O  1- H  2              0.00032       0.00016      -0.00016
  12. BD*( 1) O  1- H  3              0.00032       0.00016      -0.00016
  13. BD*( 1) O  4- H  5              0.00027       0.00008      -0.00019
  14. BD*( 1) O  4- H  6              0.01827       0.00014      -0.01814
  15. RY ( 1) O  1                    0.00004       0.00001      -0.00003
  16. RY ( 2) O  1                    0.00002       0.00000      -0.00002
  17. RY ( 3) O  1                    0.00001       0.00000      -0.00001
  18. RY ( 4) O  1                    0.00000       0.00001       0.00001
  19. RY ( 1) H  2                    0.00124       0.00127       0.00003
  20. RY ( 1) H  3                    0.00124       0.00127       0.00003
  21. RY ( 1) O  4                    0.00009       0.00000      -0.00009
  22. RY ( 2) O  4                    0.00002       0.00000      -0.00002
  23. RY ( 3) O  4                    0.00001       0.00000       0.00000
  24. RY ( 4) O  4                    0.00000       0.00000       0.00000
  25. RY ( 1) H  5                    0.00127       0.00120      -0.00007
  26. RY ( 1) H  6                    0.00159       0.00042      -0.00117

 NEXT STEP:  Evaluate the energy of the new density matrix
             that has been constructed from the deleted NBO
             Fock matrix by doing one SCF cycle.

 ----------------------------------------------------------------------------

        -------------------------
```

```
                 RHF SCF CALCULATION
              --------------------------
        DENSITY MATRIX CONV=  1.00E-05

ITER EX DEM     TOTAL ENERGY        E CHANGE  DENSITY CHANGE     ORB. GRAD
  1  0  0     -151.8065596360  -151.8065596360   0.061186977   0.000000000

SCF IS UNCONVERGED, TOO MANY ITERATIONS
      TIME TO FORM FOCK OPERATORS=       0.0 SECONDS (       0.0 SEC/ITER)
      TIME TO SOLVE SCF EQUATIONS=       0.0 SECONDS (       0.0 SEC/ITER)

FINAL RHF ENERGY IS        0.0000000000 AFTER   1 ITERATIONS
...... END OF RHF CALCULATION ......
STEP CPU TIME =     0.12 TOTAL CPU TIME =        0.2 (     0.0 MIN)
TOTAL WALL CLOCK TIME=        0.2 SECONDS, CPU UTILIZATION IS  94.74%

----------------------------------------------------------------------------
   Energy of deletion :      -151.806559636
     Total SCF energy :      -151.827680724
                         ------------------
         Energy change :       0.021121 a.u.,        13.254 kcal/mol
----------------------------------------------------------------------------
```

The most significant change in occupancy is found for NBOs 4 and 14, an oxygen lone pair of the electron donor fragment and an OH antibond of the acceptor, respectively. Localizing the wavefunction back-transfers about 0.018 electrons from the antibond to the lone pair, effectively suppressing the leading CT interaction of the dimer. This increases the energy from −151.82768 to −151.80656 a.u., suggesting that CT stabilizes the dimer by 13.254 kcal/mol. The warning that the SCF is unconverged should be neglected at this point in the calculation.

Next, NEDA calculates the energy of the perturbed and variationally optimized wavefunctions for the first fragment (water monomer). The former is evaluated by a single pass through the SCF routines with the localized monomer MOs of the previous step. The latter is then obtained using the usual SCF convergence methods. Both wavefunctions are calculated in the full dimer basis set and at fixed geometry (the monomer geometry in the complex).

```
 --------------
  Fragment  1:
 --------------

...... END OF ONE-ELECTRON INTEGRALS ......
STEP CPU TIME =     0.01 TOTAL CPU TIME =        0.2 (     0.0 MIN)
TOTAL WALL CLOCK TIME=        0.2 SECONDS, CPU UTILIZATION IS  95.00%

              --------------------------
                 RHF SCF CALCULATION
              --------------------------
        DENSITY MATRIX CONV=  1.00E-05

ITER EX DEM     TOTAL ENERGY        E CHANGE  DENSITY CHANGE     ORB. GRAD
  1  0  0      -75.8820038771   -75.8820038771   0.051585286   0.000000000
              ---------------START SECOND ORDER SCF---------------
  2  1  0      -75.9081413953    -0.0261375181   0.018452073   0.009561181
```

```
   3  2  0     -75.9092479375   -0.0011065422   0.009032407   0.003595518
   4  3  0     -75.9094058121   -0.0001578747   0.000764754   0.000898516
   5  4  0     -75.9094124510   -0.0000066389   0.000263894   0.000128113
   6  5  0     -75.9094127399   -0.0000002890   0.000084067   0.000046344
   7  6  0     -75.9094127514   -0.0000000114   0.000018443   0.000008466
   8  7  0     -75.9094127518   -0.0000000005   0.000003845   0.000002277
   9  8  0     -75.9094127518    0.0000000000   0.000001199   0.000000691


             -----------------
             DENSITY CONVERGED
             -----------------
      TIME TO FORM FOCK OPERATORS=        0.0 SECONDS (        0.0 SEC/ITER)
      TIME TO SOLVE SCF EQUATIONS=        0.0 SECONDS (        0.0 SEC/ITER)

 FINAL RHF ENERGY IS      -75.9094127518 AFTER   9 ITERATIONS
 ...... END OF RHF CALCULATION ......
 STEP CPU TIME =     0.02 TOTAL CPU TIME =         0.2 (    0.0 MIN)
 TOTAL WALL CLOCK TIME=        0.2 SECONDS, CPU UTILIZATION IS 100.00%
 ...... END OF ONE-ELECTRON INTEGRALS ......
 STEP CPU TIME =     0.00 TOTAL CPU TIME =         0.2 (    0.0 MIN)
 TOTAL WALL CLOCK TIME=        0.2 SECONDS, CPU UTILIZATION IS 100.00%

 Dipole (def):    2.6394(x),    0.0793(y),    0.0000(z);   2.6406(tot) Debye
 Dipole  (cp):    2.6541(x),   -0.0947(y),    0.0000(z);   2.6557(tot) Debye
 Dipole (ind):   -0.0146(x),    0.1740(y),    0.0000(z);   0.1747(tot) Debye
```

The energy of the perturbed and variationally optimized wavefunctions for this monomer (the electron donor) are −75.88200 and −75.90941 a.u., respectively.

Polarization of the fragment electron distribution is revealed, in part, from the dipole moments of the perturbed (def) and optimized (cp) wavefunctions. The isolated donor molecule has a dipole moment of 2.656 Debye. Its dipole decreases slightly to 2.641 Debye in the presence of the acceptor. The orthogonality required of the two monomer wavefunctions prevents the electron distribution of the donor from significantly penetrating the acceptor.

Note that the `cp' (counterpoise) designation on the dipole moment indicates that these values are calculated for the variationally optimized wavefunction in the full dimer basis set (in the sense that BSSE counterpoise corrections for binding energies are evaluated in the full basis).

The monomer analysis is then repeated for the acceptor unit.

```
 --------------
  Fragment  2:
 --------------

 ...... END OF ONE-ELECTRON INTEGRALS ......
 STEP CPU TIME =     0.00 TOTAL CPU TIME =         0.2 (    0.0 MIN)
 TOTAL WALL CLOCK TIME=        0.2 SECONDS, CPU UTILIZATION IS  95.45%

             --------------------------
                RHF SCF CALCULATION
             --------------------------
       DENSITY MATRIX CONV=  1.00E-05
```

B.11. NEDA: NATURAL ENERGY DECOMPOSITION ANALYSIS

```
ITER EX DEM     TOTAL ENERGY        E CHANGE   DENSITY CHANGE    ORB. GRAD
  1  0  0      -75.8962673806    -75.8962673806   0.016278993   0.000000000
              --------------START SECOND ORDER SCF---------------
  2  1  0      -75.9079696846     -0.0117023040   0.007570847   0.005067234
  3  2  0      -75.9083141028     -0.0003444182   0.005463348   0.001684405
  4  3  0      -75.9083555888     -0.0000414859   0.001012338   0.000672210
  5  4  0      -75.9083571171     -0.0000015284   0.000352290   0.000297195
  6  5  0      -75.9083574089     -0.0000002918   0.000092465   0.000043124
  7  6  0      -75.9083574187     -0.0000000097   0.000014019   0.000006844
  8  7  0      -75.9083574192     -0.0000000005   0.000004722   0.000002775
  9  8  0      -75.9083574192     -0.0000000001   0.000000684   0.000000532


            -----------------
            DENSITY CONVERGED
            -----------------
     TIME TO FORM FOCK OPERATORS=       0.0 SECONDS (       0.0 SEC/ITER)
     TIME TO SOLVE SCF EQUATIONS=       0.0 SECONDS (       0.0 SEC/ITER)

FINAL RHF ENERGY IS      -75.9083574192 AFTER   9 ITERATIONS
...... END OF RHF CALCULATION ......
STEP CPU TIME =     0.01 TOTAL CPU TIME =        0.2 (    0.0 MIN)
TOTAL WALL CLOCK TIME=        0.2 SECONDS, CPU UTILIZATION IS  95.65%
...... END OF ONE-ELECTRON INTEGRALS ......
STEP CPU TIME =     0.00 TOTAL CPU TIME =        0.2 (    0.0 MIN)
TOTAL WALL CLOCK TIME=        0.2 SECONDS, CPU UTILIZATION IS  95.65%

Dipole (def):   -0.8286(x),  -2.6607(y),   0.0000(z);   2.7867(tot) Debye
Dipole  (cp):   -1.0045(x),  -2.3894(y),   0.0000(z);   2.5919(tot) Debye
Dipole (ind):    0.1759(x),  -0.2713(y),   0.0000(z);   0.3234(tot) Debye
```

The induced dipole of the acceptor (0.323 Debye) is sizable as it polarizes away from the donor.

Finally, NEDA writes a summary.

```
Natural Energy Decomposition Analysis (Summary):

                                                   Component
                 Energy(wfn)         Energy(wfn)     (kcal/mol)
-----------------------------------------------------------------------------
H4O2          -151.8276807(scf)  -151.8065596(loc)    CT =   -13.25
                                                      ES =   -12.24
                                                     POL =    -3.89
                                                      EX =    -1.62
1. H2O         -75.8820039(def)   -75.9094128(cp)  DEF(SE) =   17.20(   0.10)
2. H2O         -75.8962674(def)   -75.9083574(cp)  DEF(SE) =    7.59(   1.78)
                                                              ---------
                                                        E =    -6.22



Electrical (ES+POL+SE) :    -14.25
  Charge Transfer (CT) :    -13.25
      Core (EX+DEF-SE) :     21.29
                           -----------
   Total Interaction (E) :    -6.22
```

The energies for each of the calculated wavefunctions are reported together with the NEDA components. The total binding energy (counterpoise corrected) is −6.22 kcal/mol.

B.11. NEDA: NATURAL ENERGY DECOMPOSITION ANALYSIS

B.11.4.2 Lithium Chloride Hydrate

The following sample output is taken from the analysis of LiCl·H$_2$O. The input deck is given in Section B.11.3.2.

The following segment of output is the summary of the NBO analysis that appears just before the NEDA.

```
NATURAL BOND ORBITALS (Summary):

                                              Principal Delocalizations
            NBO              Occupancy   Energy  (geminal,vicinal,remote)
=============================================================================
Molecular unit  1  (Li)
------ Lewis -------------------------------------
   1. CR ( 1)Li  1            1.99953   -2.41595  17(r),18(r)
------ non-Lewis ---------------------------------
  16. LP ( 1)Li  1            0.08610    0.27978
  19. RY ( 1)Li  1            0.01062    0.19772
  20. RY ( 2)Li  1            0.01045    0.20133
  21. RY ( 3)Li  1            0.00360    0.78711
  22. RY ( 4)Li  1            0.00036    0.79469
  23. RY ( 5)Li  1            0.00025    0.89939
  24. RY ( 6)Li  1            0.00020    0.41056
  25. RY ( 7)Li  1            0.00006    1.50512
  26. RY ( 8)Li  1            0.00000    0.23532
  27. RY ( 9)Li  1            0.00000    0.58519
  28. RY (10)Li  1            0.00000    0.27136
  29. RY (11)Li  1            0.00000    0.59539
  30. RY (12)Li  1            0.00000    0.55741
  31. RY (13)Li  1            0.00000    0.59400
            -------------------------------
                 Total Lewis  1.99953  ( 94.7117%)
           Valence non-Lewis  0.08610  (  4.0784%)
           Rydberg non-Lewis  0.02554  (  1.2099%)
            -------------------------------
                Total unit  1  2.11118  (100.0000%)
               Charge unit  1  0.88882

Molecular unit  2  (Cl)
------ Lewis -------------------------------------
   2. CR ( 1)Cl  2            2.00000 -104.24681  16(r)
   3. CR ( 2)Cl  2            2.00000   -7.88598
   4. CR ( 3)Cl  2            1.99999   -7.88599
   5. CR ( 4)Cl  2            1.99998  -10.56907  16(r),21(r)
   6. CR ( 5)Cl  2            1.99997   -7.88629  16(r)
   8. LP ( 1)Cl  2            1.99941   -1.04682  16(r),23(r),21(r)
   9. LP ( 2)Cl  2            1.99057   -0.35653  19(r),24(r)
  10. LP ( 3)Cl  2            1.98955   -0.35633  20(r),28(r),22(r)
  11. LP ( 4)Cl  2            1.93359   -0.55836  16(r),23(r),21(r),25(r)
                                                  42(r),27(r),17(r),18(r)
------ non-Lewis ---------------------------------
  32. RY ( 1)Cl  2            0.00007    1.08215
  33. RY ( 2)Cl  2            0.00005    0.78167
  34. RY ( 3)Cl  2            0.00001    0.78822
  35. RY ( 4)Cl  2            0.00001    0.87323
  36. RY ( 5)Cl  2            0.00000    1.51857
  37. RY ( 6)Cl  2            0.00000    1.33360
  38. RY ( 7)Cl  2            0.00000    1.33464
  39. RY ( 8)Cl  2            0.00000    4.64803
  40. RY ( 9)Cl  2            0.00000    1.27505
  41. RY (10)Cl  2            0.00000    1.27499
            -------------------------------
                 Total Lewis 17.91306  ( 99.9992%)
           Valence non-Lewis  0.00000  (  0.0000%)
```

B.11. NEDA: NATURAL ENERGY DECOMPOSITION ANALYSIS

```
         Rydberg non-Lewis     0.00013  (  0.0008%)
         ----------------------------
             Total unit   2   17.91320  (100.0000%)
             Charge unit  2   -0.91320

Molecular unit  3  (H2O)
------ Lewis -------------------------------------
    7. CR ( 1) O   3                1.99992   -20.50855  16(r)
   12. LP ( 1) O   3                1.99853    -0.61093  19(r)
   13. LP ( 2) O   3                1.97591    -0.96508  16(r),21(r),23(r)
   14. BD ( 1) O   3- H   4         1.99945    -1.08660  16(r),22(r)
   15. BD ( 1) O   3- H   5         1.99945    -1.08659  16(r),22(r)
------ non-Lewis ---------------------------------
   17. BD*( 1) O   3- H   4         0.00027     0.71146
   18. BD*( 1) O   3- H   5         0.00027     0.71146
   42. RY ( 1) O   3                0.00120     1.37432
   43. RY ( 2) O   3                0.00004     1.11917
   44. RY ( 3) O   3                0.00003     1.26642
   45. RY ( 4) O   3                0.00002     1.69517
   46. RY ( 5) O   3                0.00001     2.48812
   47. RY ( 6) O   3                0.00000     3.44228
   48. RY ( 7) O   3                0.00000     1.96764
   49. RY ( 8) O   3                0.00000     1.97655
   50. RY ( 9) O   3                0.00000     2.75660
   51. RY (10) O   3                0.00000     1.91724
   52. RY ( 1) H   4                0.00027     0.62922
   53. RY ( 1) H   5                0.00027     0.62925
         ----------------------------
                Total Lewis     9.97326  ( 99.9763%)
           Valence non-Lewis    0.00054  (  0.0054%)
           Rydberg non-Lewis    0.00183  (  0.0183%)
         ----------------------------
             Total unit   3    9.97563  (100.0000%)
             Charge unit  3    0.02437
```

This segment shows the three molecular units calculated by NBO analysis, a lithium cation (q_{Li} = +0.88882), a chlorine anion (q_{Cl} = −0.91320), and a water molecule (q_{H2O} = +0.02437).

Default NEDA then analyzes the wavefunction in terms of these molecular units.

```
NEDA: Natural Energy Decomposition Analysis
Deletion of the NBO Fock matrix elements between orbitals:
   1  16  19  20  21  22  23  24  25  26  27  28  29  30  31
and orbitals:
   2   3   4   5   6   7   8   9  10  11  12  13  14  15  17  18  32  33  34  35
  36  37  38  39  40  41  42  43  44  45  46  47  48  49  50  51  52  53
Deletion of the NBO Fock matrix elements between orbitals:
   2   3   4   5   6   8   9  10  11  32  33  34  35  36  37  38  39  40  41
and orbitals:
   1   7  12  13  14  15  16  17  18  19  20  21  22  23  24  25  26  27  28  29
  30  31  42  43  44  45  46  47  48  49  50  51  52  53
Deletion of the NBO Fock matrix elements between orbitals:
   7  12  13  14  15  17  18  42  43  44  45  46  47  48  49  50  51  52  53
and orbitals:
   1   2   3   4   5   6   8   9  10  11  16  19  20  21  22  23  24  25  26  27
  28  29  30  31  32  33  34  35  36  37  38  39  40  41

Orbital occupancies:

     Orbital                         No deletions  This deletion    Change
```

B.11. NEDA: NATURAL ENERGY DECOMPOSITION ANALYSIS

```
--------------------------------------------------------------------------
   1. CR ( 1)Li  1                        1.99953      1.99979      0.00026
   2. CR ( 1)Cl  2                        2.00000      2.00000      0.00000
   3. CR ( 2)Cl  2                        2.00000      2.00000      0.00000
   4. CR ( 3)Cl  2                        1.99999      2.00000      0.00001
   5. CR ( 4)Cl  2                        1.99998      2.00000      0.00002
   6. CR ( 5)Cl  2                        1.99997      2.00000      0.00003
   7. CR ( 1) O  3                        1.99992      1.99993      0.00000
   8. LP ( 1)Cl  2                        1.99941      1.99999      0.00057
   9. LP ( 2)Cl  2                        1.99057      1.99996      0.00939
  10. LP ( 3)Cl  2                        1.98955      1.99996      0.01040
  11. LP ( 4)Cl  2                        1.93359      1.99964      0.06605
  12. LP ( 1) O  3                        1.99853      1.99999      0.00147
  13. LP ( 2) O  3                        1.97591      1.99978      0.02387
  14. BD ( 1) O  3- H  4                  1.99945      1.99982      0.00036
  15. BD ( 1) O  3- H  5                  1.99945      1.99982      0.00036
  16. LP ( 1)Li  1                        0.08610      0.00018     -0.08592
  17. BD*( 1) O  3- H  4                  0.00027      0.00005     -0.00022
  18. BD*( 1) O  3- H  5                  0.00027      0.00005     -0.00022
  19. RY ( 1)Li  1                        0.01062      0.00000     -0.01062
  20. RY ( 2)Li  1                        0.01045      0.00000     -0.01045
  21. RY ( 3)Li  1                        0.00360      0.00002     -0.00358
  22. RY ( 4)Li  1                        0.00036      0.00000     -0.00036
  23. RY ( 5)Li  1                        0.00025      0.00000     -0.00024
  24. RY ( 6)Li  1                        0.00020      0.00000     -0.00020
  25. RY ( 7)Li  1                        0.00006      0.00000     -0.00006
  26. RY ( 8)Li  1                        0.00000      0.00000      0.00000
  27. RY ( 9)Li  1                        0.00000      0.00000      0.00000
  28. RY (10)Li  1                        0.00000      0.00000      0.00000
  29. RY (11)Li  1                        0.00000      0.00000      0.00000
  30. RY (12)Li  1                        0.00000      0.00000      0.00000
  31. RY (13)Li  1                        0.00000      0.00000      0.00000
  32. RY ( 1)Cl  2                        0.00007      0.00000     -0.00007
  33. RY ( 2)Cl  2                        0.00005      0.00001     -0.00004
  34. RY ( 3)Cl  2                        0.00001      0.00001      0.00001
  35. RY ( 4)Cl  2                        0.00001      0.00009      0.00008
  36. RY ( 5)Cl  2                        0.00000      0.00029      0.00028
  37. RY ( 6)Cl  2                        0.00000      0.00003      0.00003
  38. RY ( 7)Cl  2                        0.00000      0.00003      0.00003
  39. RY ( 8)Cl  2                        0.00000      0.00000      0.00000
  40. RY ( 9)Cl  2                        0.00000      0.00000      0.00000
  41. RY (10)Cl  2                        0.00000      0.00000      0.00000
  42. RY ( 1) O  3                        0.00120      0.00001     -0.00119
  43. RY ( 2) O  3                        0.00004      0.00001     -0.00004
  44. RY ( 3) O  3                        0.00003      0.00001     -0.00001
  45. RY ( 4) O  3                        0.00002      0.00000     -0.00002
  46. RY ( 5) O  3                        0.00001      0.00001      0.00000
  47. RY ( 6) O  3                        0.00000      0.00001      0.00000
  48. RY ( 7) O  3                        0.00000      0.00000      0.00000
  49. RY ( 8) O  3                        0.00000      0.00000      0.00000
  50. RY ( 9) O  3                        0.00000      0.00000      0.00000
  51. RY (10) O  3                        0.00000      0.00000      0.00000
  52. RY ( 1) H  4                        0.00027      0.00026      0.00000
  53. RY ( 1) H  5                        0.00027      0.00026      0.00000

NEXT STEP:  Evaluate the energy of the new density matrix
            that has been constructed from the deleted NBO
            Fock matrix by doing one SCF cycle.

--------------------------------------------------------------------------

           --------------------------
              RHF SCF CALCULATION
           --------------------------
      DENSITY MATRIX CONV=  1.00E-05

ITER EX DEM     TOTAL ENERGY       E CHANGE   DENSITY CHANGE    ORB. GRAD
  1  0  0     -542.9705153982  -542.9705153982   0.188923472   0.000000000

SCF IS UNCONVERGED, TOO MANY ITERATIONS
     TIME TO FORM FOCK OPERATORS=        0.0 SECONDS (       0.0 SEC/ITER)
```

```
        TIME TO SOLVE SCF EQUATIONS=        0.0 SECONDS (        0.0 SEC/ITER)

FINAL RHF ENERGY IS        0.0000000000 AFTER   1 ITERATIONS
...... END OF RHF CALCULATION ......
STEP CPU TIME =     0.16 TOTAL CPU TIME =        0.4 (    0.0 MIN)
TOTAL WALL CLOCK TIME=        0.4 SECONDS, CPU UTILIZATION IS 100.00%


------------------------------------------------------------------------------
  Energy of deletion :      -542.970515398
    Total SCF energy :      -543.059663886
                          -------------------
        Energy change :        0.089148 a.u.,        55.942 kcal/mol
------------------------------------------------------------------------------



 --------------
  Fragment  1:
 --------------

...... END OF ONE-ELECTRON INTEGRALS ......
STEP CPU TIME =     0.00 TOTAL CPU TIME =        0.4 (    0.0 MIN)
TOTAL WALL CLOCK TIME=        0.4 SECONDS, CPU UTILIZATION IS  97.73%


          -------------------------
               RHF SCF CALCULATION
          -------------------------
     DENSITY MATRIX CONV=  1.00E-05

ITER EX DEM      TOTAL ENERGY        E CHANGE  DENSITY CHANGE    ORB. GRAD
  1  0  0        -7.1981557101   -7.1981557101  0.063419835   0.000000000
          ---------------START SECOND ORDER SCF---------------
  2  1  0        -7.2353149765   -0.0371592664  0.007354720   0.010209216
  3  2  0        -7.2355369468   -0.0002219703  0.001583276   0.001064694
  4  3  0        -7.2355399344   -0.0000029876  0.000070998   0.000033960
  5  4  0        -7.2355399363   -0.0000000019  0.000006107   0.000002908
  6  5  0        -7.2355399363    0.0000000000  0.000000128   0.000000058


          -----------------
            DENSITY CONVERGED
          -----------------
     TIME TO FORM FOCK OPERATORS=        0.1 SECONDS (        0.0 SEC/ITER)
     TIME TO SOLVE SCF EQUATIONS=        0.0 SECONDS (        0.0 SEC/ITER)

FINAL RHF ENERGY IS       -7.2355399363 AFTER   6 ITERATIONS
...... END OF RHF CALCULATION ......
STEP CPU TIME =     0.08 TOTAL CPU TIME =        0.5 (    0.0 MIN)
TOTAL WALL CLOCK TIME=        0.5 SECONDS, CPU UTILIZATION IS  98.08%
...... END OF ONE-ELECTRON INTEGRALS ......
STEP CPU TIME =     0.01 TOTAL CPU TIME =        0.5 (    0.0 MIN)
TOTAL WALL CLOCK TIME=        0.5 SECONDS, CPU UTILIZATION IS 100.00%

Dipole (def):  -0.0120(x),   0.0000(y),   0.0000(z);   0.0120(tot) Debye
Dipole  (cp):   0.0000(x),   0.0000(y),   0.0000(z);   0.0000(tot) Debye
Dipole (ind):  -0.0120(x),   0.0000(y),   0.0000(z);   0.0120(tot) Debye


 --------------
  Fragment  2:
 --------------

...... END OF ONE-ELECTRON INTEGRALS ......
STEP CPU TIME =     0.02 TOTAL CPU TIME =        0.5 (    0.0 MIN)
TOTAL WALL CLOCK TIME=        0.5 SECONDS, CPU UTILIZATION IS 100.00%


          -------------------------
               RHF SCF CALCULATION
          -------------------------
     DENSITY MATRIX CONV=  1.00E-05

ITER EX DEM      TOTAL ENERGY        E CHANGE  DENSITY CHANGE    ORB. GRAD
  1  0  0     -459.4681484003 -459.4681484003  0.198845516   0.000000000
```

```
          --------------START SECOND ORDER SCF--------------
 2  1  0    -459.5286215216   -0.0604731213   0.084729992   0.021549547
 3  2  0    -459.5323460286   -0.0037245070   0.021185451   0.004874568
 4  3  0    -459.5327576218   -0.0004115933   0.005392366   0.000798500
 5  4  0    -459.5327738511   -0.0000162292   0.002043071   0.000215489
 6  5  0    -459.5327755309   -0.0000016799   0.000119962   0.000041488
 7  6  0    -459.5327755441   -0.0000000132   0.000016995   0.000006855
 8  7  0    -459.5327755446   -0.0000000004   0.000004132   0.000001213
 9  8  0    -459.5327755446    0.0000000000   0.000001055   0.000000260

          -----------------
           DENSITY CONVERGED
          -----------------
      TIME TO FORM FOCK OPERATORS=      0.1 SECONDS (      0.0 SEC/ITER)
      TIME TO SOLVE SCF EQUATIONS=      0.0 SECONDS (      0.0 SEC/ITER)

 FINAL RHF ENERGY IS    -459.5327755446 AFTER   9 ITERATIONS
 ...... END OF RHF CALCULATION ......
 STEP CPU TIME =     0.11 TOTAL CPU TIME =       0.6 (    0.0 MIN)
 TOTAL WALL CLOCK TIME=       0.7 SECONDS, CPU UTILIZATION IS  98.48%
 ...... END OF ONE-ELECTRON INTEGRALS ......
 STEP CPU TIME =     0.00 TOTAL CPU TIME =       0.6 (    0.0 MIN)
 TOTAL WALL CLOCK TIME=       0.7 SECONDS, CPU UTILIZATION IS  98.48%

 Dipole (def):    0.0931(x),    0.0000(y),    0.0000(z);   0.0931(tot) Debye
 Dipole  (cp):    0.6545(x),    0.0002(y),    0.0000(z);   0.6545(tot) Debye
 Dipole (ind):   -0.5614(x),   -0.0002(y),    0.0000(z);   0.5614(tot) Debye


 --------------
  Fragment  3:
 --------------

 ...... END OF ONE-ELECTRON INTEGRALS ......
 STEP CPU TIME =     0.02 TOTAL CPU TIME =       0.7 (    0.0 MIN)
 TOTAL WALL CLOCK TIME=       0.7 SECONDS, CPU UTILIZATION IS  98.53%


          -------------------------
               RHF SCF CALCULATION
          -------------------------
      DENSITY MATRIX CONV=  1.00E-05

 ITER EX DEM     TOTAL ENERGY       E CHANGE  DENSITY CHANGE    ORB. GRAD
  1  0  0    -75.9761443122   -75.9761443122   0.063617601   0.000000000
          --------------START SECOND ORDER SCF--------------
  2  1  0    -76.0122509527    -0.0361066405   0.030657633   0.020699453
  3  2  0    -76.0139430266    -0.0016920739   0.010594506   0.007804061
  4  3  0    -76.0142895309    -0.0003465043   0.001346105   0.000625036
  5  4  0    -76.0142941869    -0.0000046559   0.000761013   0.000249417
  6  5  0    -76.0142947559    -0.0000005690   0.000094730   0.000020485
  7  6  0    -76.0142947660    -0.0000000101   0.000034127   0.000007823
  8  7  0    -76.0142947672    -0.0000000012   0.000002560   0.000001624
  9  8  0    -76.0142947672     0.0000000000   0.000000785   0.000000444

          -----------------
           DENSITY CONVERGED
          -----------------
      TIME TO FORM FOCK OPERATORS=      0.1 SECONDS (      0.0 SEC/ITER)
      TIME TO SOLVE SCF EQUATIONS=      0.0 SECONDS (      0.0 SEC/ITER)

 FINAL RHF ENERGY IS     -76.0142947672 AFTER   9 ITERATIONS
 ...... END OF RHF CALCULATION ......
 STEP CPU TIME =     0.11 TOTAL CPU TIME =       0.8 (    0.0 MIN)
 TOTAL WALL CLOCK TIME=       0.8 SECONDS, CPU UTILIZATION IS  97.50%
 ...... END OF ONE-ELECTRON INTEGRALS ......
 STEP CPU TIME =     0.00 TOTAL CPU TIME =       0.8 (    0.0 MIN)
 TOTAL WALL CLOCK TIME=       0.8 SECONDS, CPU UTILIZATION IS  97.50%

 Dipole (def):   -2.6384(x),    0.0016(y),    0.0002(z);   2.6384(tot) Debye
 Dipole  (cp):   -2.2688(x),    0.0014(y),    0.0002(z);   2.2688(tot) Debye
 Dipole (ind):   -0.3696(x),    0.0002(y),    0.0000(z);   0.3696(tot) Debye
```

B.11. NEDA: NATURAL ENERGY DECOMPOSITION ANALYSIS

```
Natural Energy Decomposition Analysis (Summary):

                                             Component
                Energy(wfn)      Energy(wfn)      (kcal/mol)
-----------------------------------------------------------------------
H2OLiCl        -543.0596639(scf)  -542.9705154(loc)   CT =   -55.94
                                                      ES =  -190.03
                                                     POL =   -10.77
                                                      EX =    -5.06
1. Li(+)          -7.1981557(def)    -7.2355399(cp)  DEF(SE) =   23.46(   4.77)
2. Cl(-)        -459.4681484(def)  -459.5327755(cp)  DEF(SE) =   40.55(  -1.96)
3. H2O           -75.9761443(def)   -76.0142948(cp)  DEF(SE) =   23.94(   2.48)
                                                              ---------
                                                       E =  -173.85


Electrical (ES+POL+SE) :    -195.52
  Charge Transfer (CT) :     -55.94
      Core (EX+DEF-SE) :      77.61
                            ------------
 Total Interaction (E) :    -173.85
```

The binding energy in this case (−173.85 kcal/mol) is evaluated relative to the three infinitely separated fragments (of energies −7.23554, −459.53278, and −76.01429 a.u.).

The second application analyzes the wavefunction in terms of two fragments, a LiCl molecule and a water molecule.

```
NEDA: Natural Energy Decomposition Analysis
Deletion of the NBO Fock matrix elements between orbitals:
   1   2   3   4   5   6   8   9  10  11  16  19  20  21  22  23  24  25  26  27
  28  29  30  31  32  33  34  35  36  37  38  39  40  41
and orbitals:
   7  12  13  14  15  17  18  42  43  44  45  46  47  48  49  50  51  52  53

Orbital occupancies:

      Orbital                     No deletions  This deletion   Change
-----------------------------------------------------------------------
    1. CR ( 1)Li  1                 1.99953       1.99996       0.00042
    2. CR ( 1)Cl  2                 2.00000       2.00000       0.00000
    3. CR ( 2)Cl  2                 2.00000       2.00000       0.00000
    4. CR ( 3)Cl  2                 1.99999       1.99999       0.00000
    5. CR ( 4)Cl  2                 1.99998       1.99998       0.00000
    6. CR ( 5)Cl  2                 1.99997       1.99997       0.00000
    7. CR ( 1) O  3                 1.99992       1.99993       0.00000
    8. LP ( 1)Cl  2                 1.99941       1.99966       0.00025
    9. LP ( 2)Cl  2                 1.99057       1.99083       0.00026
   10. LP ( 3)Cl  2                 1.98955       1.99003       0.00047
   11. LP ( 4)Cl  2                 1.93359       1.93483       0.00124
   12. LP ( 1) O  3                 1.99853       1.99999       0.00147
   13. LP ( 2) O  3                 1.97591       1.99978       0.02387
   14. BD ( 1) O  3- H  4           1.99945       1.99982       0.00036
   15. BD ( 1) O  3- H  5           1.99945       1.99982       0.00036
   16. LP ( 1)Li  1                 0.08610       0.06475      -0.02135
   17. BD*( 1) O  3- H  4           0.00027       0.00005      -0.00022
   18. BD*( 1) O  3- H  5           0.00027       0.00005      -0.00022
   19. RY ( 1)Li  1                 0.01062       0.00915      -0.00147
   20. RY ( 2)Li  1                 0.01045       0.00996      -0.00049
   21. RY ( 3)Li  1                 0.00360       0.00050      -0.00310
```

```
 22. RY ( 4)Li  1                    0.00036      0.00002     -0.00034
 23. RY ( 5)Li  1                    0.00025      0.00020     -0.00005
 24. RY ( 6)Li  1                    0.00020      0.00003     -0.00017
 25. RY ( 7)Li  1                    0.00006      0.00011      0.00004
 26. RY ( 8)Li  1                    0.00000      0.00002      0.00001
 27. RY ( 9)Li  1                    0.00000      0.00000      0.00000
 28. RY (10)Li  1                    0.00000      0.00000      0.00000
 29. RY (11)Li  1                    0.00000      0.00000      0.00000
 30. RY (12)Li  1                    0.00000      0.00000      0.00000
 31. RY (13)Li  1                    0.00000      0.00000      0.00000
 32. RY ( 1)Cl  2                    0.00007      0.00002     -0.00005
 33. RY ( 2)Cl  2                    0.00005      0.00000     -0.00005
 34. RY ( 3)Cl  2                    0.00001      0.00000     -0.00001
 35. RY ( 4)Cl  2                    0.00001      0.00000      0.00000
 36. RY ( 5)Cl  2                    0.00000      0.00000      0.00000
 37. RY ( 6)Cl  2                    0.00000      0.00000      0.00000
 38. RY ( 7)Cl  2                    0.00000      0.00000      0.00000
 39. RY ( 8)Cl  2                    0.00000      0.00000      0.00000
 40. RY ( 9)Cl  2                    0.00000      0.00000      0.00000
 41. RY (10)Cl  2                    0.00000      0.00000      0.00000
 42. RY ( 1) O  3                    0.00120      0.00001     -0.00119
 43. RY ( 2) O  3                    0.00004      0.00001     -0.00004
 44. RY ( 3) O  3                    0.00003      0.00001     -0.00001
 45. RY ( 4) O  3                    0.00002      0.00000     -0.00002
 46. RY ( 5) O  3                    0.00001      0.00001      0.00000
 47. RY ( 6) O  3                    0.00000      0.00001      0.00000
 48. RY ( 7) O  3                    0.00000      0.00000      0.00000
 49. RY ( 8) O  3                    0.00000      0.00000      0.00000
 50. RY ( 9) O  3                    0.00000      0.00000      0.00000
 51. RY (10) O  3                    0.00000      0.00000      0.00000
 52. RY ( 1) H  4                    0.00027      0.00026      0.00000
 53. RY ( 1) H  5                    0.00027      0.00026      0.00000

 NEXT STEP:  Evaluate the energy of the new density matrix
             that has been constructed from the deleted NBO
             Fock matrix by doing one SCF cycle.

 ------------------------------------------------------------------------------

             -------------------------
                RHF SCF CALCULATION
             -------------------------
     DENSITY MATRIX CONV=  1.00E-05

 ITER EX DEM    TOTAL ENERGY       E CHANGE  DENSITY CHANGE    ORB. GRAD
  1  0  0    -543.0308278158  -543.0308278158   0.069331501   0.000000000

 SCF IS UNCONVERGED, TOO MANY ITERATIONS
      TIME TO FORM FOCK OPERATORS=       0.0 SECONDS (      0.0 SEC/ITER)
      TIME TO SOLVE SCF EQUATIONS=       0.0 SECONDS (      0.0 SEC/ITER)

 FINAL RHF ENERGY IS       0.0000000000 AFTER   1 ITERATIONS
 ...... END OF RHF CALCULATION ......
 STEP CPU TIME =     0.13 TOTAL CPU TIME =        0.9 (    0.0 MIN)
 TOTAL WALL CLOCK TIME=        0.9 SECONDS, CPU UTILIZATION IS  98.91%

 ------------------------------------------------------------------------------
   Energy of deletion :       -543.030827816
     Total SCF energy :       -543.059663886
                        -------------------
        Energy change :        0.028836 a.u.,         18.095 kcal/mol
 ------------------------------------------------------------------------------


 --------------
  Fragment  1:
 --------------

 ...... END OF ONE-ELECTRON INTEGRALS ......
 STEP CPU TIME =     0.00 TOTAL CPU TIME =        0.9 (    0.0 MIN)
 TOTAL WALL CLOCK TIME=        0.9 SECONDS, CPU UTILIZATION IS  97.85%
```

```
               --------------------------
                    RHF SCF CALCULATION
               --------------------------
          DENSITY MATRIX CONV=  1.00E-05

ITER EX DEM      TOTAL ENERGY       E CHANGE  DENSITY CHANGE    ORB. GRAD
  1  0  0     -466.9938117215  -466.9938117215   0.052107302   0.000000000
              --------------START SECOND ORDER SCF--------------
  2  1  0     -467.0101579240    -0.0163462025   0.011014586   0.006113155
  3  2  0     -467.0103676267    -0.0002097026   0.005174620   0.001151462
  4  3  0     -467.0103786066    -0.0000109799   0.000765976   0.000224984
  5  4  0     -467.0103791555    -0.0000005489   0.000227689   0.000062821
  6  5  0     -467.0103791954    -0.0000000399   0.000051724   0.000009720
  7  6  0     -467.0103791975    -0.0000000021   0.000010094   0.000002825
  8  7  0     -467.0103791977    -0.0000000002   0.000004014   0.000000849
  9  8  0     -467.0103791977     0.0000000000   0.000000619   0.000000118


                -----------------
                 DENSITY CONVERGED
                -----------------
          TIME TO FORM FOCK OPERATORS=       0.1 SECONDS (       0.0 SEC/ITER)
          TIME TO SOLVE SCF EQUATIONS=       0.0 SECONDS (       0.0 SEC/ITER)

FINAL RHF ENERGY IS     -467.0103791977 AFTER   9 ITERATIONS
...... END OF RHF CALCULATION ......
STEP CPU TIME =      0.12 TOTAL CPU TIME =        1.0 (    0.0 MIN)
TOTAL WALL CLOCK TIME=         1.0 SECONDS, CPU UTILIZATION IS  99.04%
...... END OF ONE-ELECTRON INTEGRALS ......
STEP CPU TIME =      0.00 TOTAL CPU TIME =        1.0 (    0.0 MIN)
TOTAL WALL CLOCK TIME=         1.0 SECONDS, CPU UTILIZATION IS  99.04%

Dipole (def):   -8.0598(x),   -0.0025(y),    0.0000(z);    8.0598(tot) Debye
Dipole  (cp):   -7.7165(x),   -0.0024(y),    0.0000(z);    7.7165(tot) Debye
Dipole (ind):   -0.3433(x),   -0.0001(y),    0.0000(z);    0.3433(tot) Debye


       --------------
        Fragment  2:
       --------------

...... END OF ONE-ELECTRON INTEGRALS ......
STEP CPU TIME =      0.02 TOTAL CPU TIME =        1.0 (    0.0 MIN)
TOTAL WALL CLOCK TIME=         1.1 SECONDS, CPU UTILIZATION IS  99.06%

               --------------------------
                    RHF SCF CALCULATION
               --------------------------
          DENSITY MATRIX CONV=  1.00E-05

ITER EX DEM      TOTAL ENERGY       E CHANGE  DENSITY CHANGE    ORB. GRAD
  1  0  0      -75.9761443122   -75.9761443122   0.063617601   0.000000000
              --------------START SECOND ORDER SCF--------------
  2  1  0      -76.0122509527    -0.0361066405   0.030657633   0.020699453
  3  2  0      -76.0139430266    -0.0016920739   0.010594506   0.007804061
  4  3  0      -76.0142895309    -0.0003465043   0.001346105   0.000625036
  5  4  0      -76.0142941869    -0.0000046559   0.000761013   0.000249417
  6  5  0      -76.0142947559    -0.0000005690   0.000094730   0.000020485
  7  6  0      -76.0142947660    -0.0000000101   0.000034127   0.000007823
  8  7  0      -76.0142947672    -0.0000000012   0.000002560   0.000001624
  9  8  0      -76.0142947672     0.0000000000   0.000000785   0.000000444


                -----------------
                 DENSITY CONVERGED
                -----------------
          TIME TO FORM FOCK OPERATORS=       0.1 SECONDS (       0.0 SEC/ITER)
          TIME TO SOLVE SCF EQUATIONS=       0.0 SECONDS (       0.0 SEC/ITER)

FINAL RHF ENERGY IS      -76.0142947672 AFTER   9 ITERATIONS
...... END OF RHF CALCULATION ......
STEP CPU TIME =      0.11 TOTAL CPU TIME =        1.2 (    0.0 MIN)
```

B.11. NEDA: NATURAL ENERGY DECOMPOSITION ANALYSIS

```
TOTAL WALL CLOCK TIME=         1.2 SECONDS, CPU UTILIZATION IS  98.31%
...... END OF ONE-ELECTRON INTEGRALS ......
STEP CPU TIME =     0.00 TOTAL CPU TIME =        1.2 (    0.0 MIN)
TOTAL WALL CLOCK TIME=         1.2 SECONDS, CPU UTILIZATION IS  98.31%


Dipole (def):   -2.6384(x),   0.0016(y),   0.0002(z);   2.6384(tot) Debye
Dipole  (cp):   -2.2688(x),   0.0014(y),   0.0002(z);   2.2688(tot) Debye
Dipole (ind):   -0.3696(x),   0.0002(y),   0.0000(z);   0.3696(tot) Debye


Natural Energy Decomposition Analysis (Summary):

                                                   Component
                 Energy(wfn)        Energy(wfn)     (kcal/mol)
--------------------------------------------------------------------------
H2OLiCl         -543.0596639(scf)  -543.0308278(loc)   CT =   -18.09
                                                       ES =   -27.42
                                                       POL =   -8.69
                                                       EX =   -2.09
1. LiCl         -466.9938117(def)  -467.0103792(cp)  DEF(SE) =   10.40(   2.01)
2. H2O           -75.9761443(def)   -76.0142948(cp)  DEF(SE) =   23.94(   2.35)
                                                              ---------
                                                       E =   -21.96


Electrical (ES+POL+SE) :     -31.75
  Charge Transfer (CT) :     -18.09
      Core (EX+DEF-SE) :      27.89
                         ------------
 Total Interaction (E) :     -21.96
```

This calculation shows that the binding affinity of LiCl for H_2O is only -21.96 kcal/mol.

B.12. CHECKPOINTING OPTIONS

B.12.1 Introduction

It is sometimes desirable to employ NBOs (or a related set of localized orbitals) in procedures that would otherwise employ canonical MOs (CMOs). For example, one may wish to calculate a post-SCF wavefunction in terms of NBOs rather than CMOs, or use graphical utilities to plot NBOs instead of CMOs (e.g., using GaussView with a Gaussian checkpoint file). In these cases, it is convenient to substitute NBOs in the ESS direct-access file (and indirectly, the checkpoint file) where CMOs are usually kept. This operation is called "checkpointing" the NBO set. In effect, checkpointing results in overwriting the CMOs with NBOs (or other localized set), allowing the checkpointed set to serve as feedback to the ESS or initial input for subsequent operations.

One application of NBO checkpointing is to calculate CAS/NBO wavefunctions for localized treatment of electron correlation [A. V. Nemukhin and F. Weinhold, *J. Chem. Phys.* **97**, 1095 (1992)]. Another is to carry out CI in a complete active space of NBOs (CI/NBO), the first step in full CAS/NBO optimization. NBO checkpointing options allow these applications to be performed using either the numbers or labels of NBOs to be included in the active space.

Checkpoint feedback to the host ESS is performed with host-specific drivers (analogous to those in SR FEAOIN) that write to (instead of read from) the host direct-access file. Thus, the implementation and uses of checkpointing options are highly ESS-specific. Checkpointing options are not supported for programs that have no direct-access file.

B.12. CHECKPOINTING OPTIONS

B.12.2 Checkpointing Options

Basic checkpointing is requested by typing a `C' (checkpointing) in place of `P' (printing) or `W' (writing) for selected matrix output keywords (see Sec. B.2.4). Checkpointing is supported for any transformations from AOs to PAO, PNAO, NAO, PNHO, NHO, PNBO, NBO, PNLMO, NLMO, or MO basis sets, hence for the following keywords:

   AOPAO AOPNAO AONAO AOPNHO AONHO

   AOPNBO AONBO AOPNLMO AONLMO AOMO

For example, the input file

```
   $NBO AONBO=C $END
```

will stash the NBOs (in place of CMOs) in the checkpoint file, while the keyword "AONLMO=C" would stash NLMOs, etc. (The keyword "AOMO=C" is superfluous, since this simply rewrites the AO→MO information that is already present in the checkpoint file.) In the following, we use the example of the NBOs as the orbital set to be checkpointed, but analogous considerations apply to the other localized sets.

In its basic form, the checkpointing command

```
   AONBO=C
```

writes NBOs to the checkpoint file in the standard order of appearance in the NBO output file (e.g., with lone pairs and Rydberg orbitals preceding valence antibonds). However, it is also possible to alter the orbital order by occupancy sorting or by an explicit "permutation list" that describes the reordered list by serial numbers of by permuted NBO labels. Each option will be described in turn.

Occupancy sorting. One can automatically sort the NBOs by occupancy with a "checkpoint-sort" command of the form

```
   AONBO=CS
```

This will order the NBOs according to their populations (diagonal density matrix elements), from most highly to least occupied. For example, this command would typically put core orbitals before valence bonds, and valence

B.12. CHECKPOINTING OPTIONS

antibonds before Rydberg orbitals, contrary to the order of the standard NBO listing.

Occupancy sorting typically brings the most important correlating orbitals into the active-space window around the "Fermi level." For present purposes the Fermi level can be described as the dividing line between the highest occupied ($n_{occ} = N_e/2$) and lowest unoccupied ($n_{occ} + 1$) orbital, i.e., that between the least-occupied Lewis NBO (usually, a high-energy lone pair or bond) and the most-occupied non-Lewis NBO (usually, a valence antibond).

<u>Permutations Lists.</u> One can also include an explicit "permutation list" as a file-input bracket following the checkpoint command to specify the desired order:

```
$NBO AONBO=C <permutation list> $END
```

As indicated, the permutation list must be enclosed by left-bracket (<) and right-bracket (>) symbols, and the brackets must be separated by at least one space from surrounding keywords. For open-shell systems one can also provide a special form of AOPNBO spin permutation list that allows pairwise exchanges of orbitals between spin sets, as described below.

B.12. CHECKPOINTING OPTIONS

B.12.3 Checkpoint Permutation Lists

The checkpointing option supports a variety of forms for the permutation list file-input bracket <. . .>.

<u>Permuting by Serial Number.</u> At the simplest level, the permutation list could simply be a list of integers that specifies the permuted order ("n1" is first, "n2" is second, etc.). Orbital numbers not included in the list will be placed after those included. For example, the command

```
AONBO=C <1 2 3 8 5 6 7 4>
```

would interchange orbitals 4 and 8 with respect to the original NBO ordering, but leave other NBOs (including 9, 10,...) in their original positions.

An alternative form of permutation list includes a vertical bar (|) to denote the Fermi level (separation of occupied and unoccupied orbitals). This allows one to permute the orbital ordering by specifying only a few orbitals above and below the Fermi level (e.g., only the few to be included in the active window),

```
<...n2 n1 | m1 m2 ...>
```

Here "n1" identifies the orbital just below the Fermi level, "n2" the next lowest, etc., while "m1" is the first orbital above the Fermi level, "m2" the next highest, etc. This form is most convenient for explicitly specifying the active-space window in CAS procedures.

Orbital numbers not explicitly included in the permutation list are left in their former positions as nearly as possible, or are used to fill in available slots around the specified active window. For example, if one were creating a CAS(5,4) active window, the command

```
AONBO=C <7 8 5 | 10 12>
```

would specify that NBOs 7, 8, and 5 should lie just below the Fermi level, while 10 and 12 should lie just above. If there were originally 15 NBOs with $n_{occ} = 8$, the permuted order would become [active space enclosed in brackets],

```
1 2 3 4 6 [ 7 8 5 | 10 12 ] 9 11 13 14 15
```

However, if the Fermi-level marker (|) were absent, the corresponding command

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```
AONBO=C <7 8 5 10 12>
```

would lead to the permuted order

```
7 8 5 10 12 [ 1 2 3 | 4 6 ] 9 11 13 14 15
```

with the five specified orbitals moved to the beginning of the list, and remaining orbitals occupying remaining positions in serial order.

Permuting by Label. It is also possible to identify each permuted orbital by its generic *label* in the NBO output. Since the precise numbering of NBOs may not be known in advance, this option makes it possible to identify an NBO by its unique chemical *type*, avoiding the indeterminacies of numerical ordering.

The form of each label should be chosen to conform to that in the NBO output [such as "BD(1) C3-H15", "LP(2) N11", "BD*(2) C4-C5", etc.], based on the known atom numbering and the expected Lewis structure. Each label should be separated from adjacent labels by at least one comma or space, as in the following example,

```
AONBO=C <BD(1)C3-H15 , LP(2)N11 | BD*(2)C4-C5>
```

Spaces within each label are ignored (so that, e.g., "BD(1) C 3- H15" and BD(1)C3-H15" are equivalent). Note that "BD(1)" is typically (but not invariably) the sigma bond and "BD(2)" the pi bond of a double-bonded atom pair, so that the above example would correspond to the NBO ordering [$\sigma_{\text{C3-H15}}$ n_{N11} | $\pi^*_{\text{C4-C5}}$] in a standard notation.

As above, inclusion of a Fermi level "|" marker positions the listed orbitals at the top of the Lewis set (left of |) or bottom of the non-Lewis set (right of |), while omission of "|" requests that these orbitals be moved to the beginning of the list.

Spin Permutations for Open Shells

For open-shell systems (only) and AOPNBO checkpointing (only), one can also provide a special form of *spin permutation list* that allows checkpointed spin-orbitals to be exchanged between alpha and beta spin sets. This is useful in creating customized NBO "guess" configurations for spin states that are difficult to calculate by standard SCF convergence methods. For this purpose, PNBOs provide the most transferable orbitals for specifying a generic electronic configuration in localized Lewis-like terms (i.e., fewest perturbations from the original chemical environment).

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Each field of a spin permutation list consists of a pair of NBO indices, each prefixed by `a' (alpha) or `b' beta to denote the spin set. Fields are separated as usual by a slash (/), and the two spin-PNBOs entries of each field are separated by a comma or space. The spin-orbital entries of each field are permuted in pairs, starting with the first field and proceding to the last. For example, the command

```
AOPNBO=C <b8 b9/a9 b8>
```

would first exchange the 8th and 9th PNBOs of the beta set (b8 with b9), then exchange the 8th PNBO of the beta set (formerly b9, now b8) with the 9th PNBO of the alpha set. Note that the ordering of indices within each field is immaterial, but the order of successive fields affects the final orbital ordering (because permutations do not commute).

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B.12.4 Example: CAS/NBO and CI/NBO Calculations

A sample Gaussian 9X input deck to carry out a multiconfigurational CAS/NBO(2,2) calculation on methylamine (3-21G basis) is shown below, where the active space consists of the nitrogen lone pair ("LP(1) N 2", NBO 9 in the output) and the antiperiplanar C-H antibond (σ^*_{C1H3}, "BD*(1) C 1- H 3", NBO 24):

```
%mem=1000000
%chk=ch3nh2
#casscf(2,2)/3-21g pop=nboread density=scf

[z-matrix and variable data]

$NBO AONBO=C $END
```

The $NBO keylist could equivalently be written as

```
$NBO AONBO=C <9 | 24> $END
```

i.e., in terms of NBO serial numbers rather than labels. In this case the first step of the post-SCF procedure gives the 4-term CI/NBO wavefunction consisting of the possible single and double excitations from the amine lone pair into the antibonding C-H_3 orbital.

B.13. CMO: CANONICAL MO ANALYSIS

B.13.1 Introduction

The CMO keyword provides an analysis of canonical (delocalized) MOs in terms of their leading NBO contributions. The CMO analysis tables summarize the composition and bonding nature of each MO in a qualitative abbreviated form, providing a convenient alternative to the NBOMO keyword (Sec. B.2.4) which gives full quantitative detail of the LCNBO-MO expansion.

Each MO φ_i can be expressed in terms of the complete orthonormal set of NBOs $\{\Omega_\alpha\}$ by the equation,

$$\varphi_i = \sum_\alpha \Omega_\alpha t_{\alpha i}$$

The coefficients $t_{\alpha i}$ (elements of the NBOMO transformation matrix) determine the percentage contribution $(100*|t_{\alpha i}|^2)$ of each NBO to the LCNBO-MO expansion of φ_i. Each coefficient $t_{\alpha i}$ can in turn be identified with an NBO Ω_α of bonding $(t_{\alpha i}^{(b)})$, nonbonding $(t_{\alpha i}^{(n)})$, or antibonding $(t_{\alpha i}^{(a)})$ character. By adding the percentage contributions of each NBO type, one obtains a convenient measure of the total bonding (b), nonbonding (n), or antibonding (a) character of each MO. These in turn can be decomposed into the contributions from individual atomic centers, leading to a detailed description of the "atom-atom bonding character" of each MO.

The CMO keyword summarizes the composition and bonding character of the MOs in two tables. The first table lists the leading LCNBO-MO coefficients and NBO labels (in decreasing order of magnitude) for requested MOs, showing only NBO contributions of 5% or greater. The second table summarizes leading (>5%) atom-atom bond characters for each MO, showing the atoms or atom pairs where the nonbonding, bonding, or antibonding character of the MO is most strongly manifested. The latter information can be useful in predicting structural and vibrational changes that result from changing the occupancy of the MO in an ionization process.

B.13. CMO: CANONICAL MO ANALYSIS

B.13.2 CMO Keyword Usage and Sample Output

Basic CMO analysis is requested by including the "CMO" keyword in the $NBO keylist, as in the example below:

```
    $NBO   CMO   $END
```

The first table shows the leading NBO contributions to each MO, as illustrated below for the example of CH_3NH_2 at RHF/3-21G level (selected MOs only):

```
CMO: NBO Analysis of Canonical Molecular Orbitals

Leading (> 5%) NBO Contributions to Molecular Orbitals
=======================================================
 MO   1 (occ): orbital energy = -15.445475 a.u.
              -0.993*[  2]: CR ( 1) N 2(cr)
 MO   2 (occ): orbital energy = -11.182456 a.u.
               0.993*[  1]: CR ( 1) C 1(cr)
 MO   3 (occ): orbital energy =  -1.164751 a.u.
              -0.629*[  4]: BD ( 1) C 1- N 2
              -0.473*[  8]: BD ( 1) N 2- H 6
              -0.473*[  9]: BD ( 1) N 2- H 7
  .
  .
  .
 MO   8 (occ): orbital energy =  -0.517662 a.u.
              -0.593*[  6]: BD ( 1) C 1- H 4
               0.593*[  7]: BD ( 1) C 1- H 5
              -0.382*[  8]: BD ( 1) N 2- H 6
               0.382*[  9]: BD ( 1) N 2- H 7
 MO   9 (occ): orbital energy =  -0.368845 a.u.
               0.900*[  3]: LP ( 1) N 2(lp)
               0.334*[  5]: BD ( 1) C 1- H 3
 MO  10 (vir): orbital energy =   0.265351 a.u.
               0.432*[ 14]: BD*( 1) N 2- H 6*
               0.432*[ 15]: BD*( 1) N 2- H 7*
               0.324*[ 11]: BD*( 1) C 1- H 3*
              -0.284*[ 28]: RY ( 1) H 7(ry)
              -0.284*[ 27]: RY ( 1) H 6(ry)
               0.260*[ 12]: BD*( 1) C 1- H 4*
               0.260*[ 13]: BD*( 1) C 1- H 5*
              -0.249*[ 24]: RY ( 1) H 3(ry)
               0.235*[ 10]: BD*( 1) C 1- N 2*
  .
  .
  .
 MO  28 (vir): orbital energy =   2.843994 a.u.
              -0.723*[ 23]: RY ( 4) N 2(ry)
              -0.651*[ 22]: RY ( 3) N 2(ry)
```

In this example, MO 1 and 2 are both found to be highly localized and transferable, with strong (~99%) contributions from NBO 2 (the nitrogen core orbital) and NBO 1 (the carbon core orbital), respectively. However, MO 3 is a strong admixture of σ_{CN} (NBO 4) and the two σ_{NH} bonds (NBOs 8, 9) with approximate composition

$$\varphi_3 \cong 0.629 \ \sigma_{CN} + 0.473(\sigma_{NH} + \sigma_{NH'})$$

and higher MOs show still more strongly mixed NBO character. The HOMO (MO 9) derives primarily (~81%) from the n_N lone pair (NBO 3), with weaker (11%) contribution from the *anti* σ_{CH} bond (NBO 5). However, the LUMO (MO 10) has significant contributions from at least *nine* NBOs, including three Rydberg orbitals (NBOs 24, 27, 28) from outside the formal valence shell, and hence exhibits little transferability to other molecules.

The table of "atom-atom bonding character" follows (truncated to the same seven MOs as above):

```
          Molecular Orbital Atom-Atom Bonding Character
          ================================================
              bonding          nonbonding        antibonding
    MO        (2c, 3c)          (1c, 1c*)          (2c*, 3c*)
 ------    ---------------     ----------       ---------------
   1(o)                        0.987  N 2
          -----                 -----             -----
          0.011(b)             0.989(n)          0.000(a)  total
 --------------------------------------------------------------
   2(o)                        0.986  C 1
          -----                 -----             -----
          0.013(b)             0.987(n)          0.000(a)  total
 --------------------------------------------------------------
   3(o)   0.396  C 1- N 2
          0.224  N 2- H 7
          0.224  N 2- H 6
          -----                 -----             -----
          0.954(b)             0.045(n)          0.000(a)  total
 --------------------------------------------------------------
    .
    .
    .
 --------------------------------------------------------------
   8(o)   0.352  C 1- H 5
          0.352  C 1- H 4
          0.146  N 2- H 7
          0.146  N 2- H 6
          -----                 -----             -----
          0.997(b)             0.001(n)          0.003(a)  total
 --------------------------------------------------------------
   9(o)   0.112  C 1- H 3     0.811  N 2
          -----                 -----             -----
          0.179(b)             0.812(n)          0.009(a)  total
 --------------------------------------------------------------
  10(v)                        0.081  H 7        0.186  N 2- H 7
                               0.081  H 6        0.186  N 2- H 6
                               0.062  H 3        0.105  C 1- H 3
                                                 0.068  C 1- H 5
                                                 0.068  C 1- H 4
                                                 0.055  C 1- N 2
          -----                 -----             -----
          0.001(b)             0.331(n)          0.668(a)  total
 --------------------------------------------------------------
    .
    .
    .
 --------------------------------------------------------------
  28(v)                        0.946  N 2
          -----                 -----             -----
          0.000(b)             0.993(n)          0.007(a)  total
 --------------------------------------------------------------
          6.000(b)            16.000(n)          6.000(a)  Sum total for MOs
```

B.13. CMO: CANONICAL MO ANALYSIS

This table shows, e.g., that MOs 1, 2 have predominantly (>98%) nonbonding character, whereas MO 3 is predominantly (95.4%) of bonding character, primarily at CN (39.6%) and the two NH bonds (22.4% each). Similarly, the entries for MO 9 suggest that the HOMO is about 81% non-bonding (on N) and only 18% bonding (primarily on the C1-H3 bond). Hence, in the spirit of simple Koopmans-type reasoning, ionization of an electron from the HOMO might be expected to result in only slight bond weakening (primarily at C1-H3), whereas ionization from MO 8 (SOMO) should significantly weaken C1-H4 and C1-H5, as well as (to a lesser extent) both NH bonds.

The "Sum total" shown after the last MO entry reflects that the sum of tabulated MO bond characters must correspond to the total of 6 bond NBOs, 16 nonbonding NBOs (cores, lone pairs, Rydbergs), and 6 antibond NBOs of the full NBO basis.

B.14. NCS: NMR CHEMICAL SHIELDING ANALYSIS

Reference: J. A. Bohmann, F. Weinhold, and T. C. Farrar, *J. Chem. Phys*. **107**, 1173-1184 (1997).

B.14.1 Introduction to Natural Chemical Shielding Analysis

The GIAO (gauge-including atomic orbitals) treatment [R. Ditchfield, *Mol. Phys.* **27**, 789 (1974); K. Wolinski, J. F. Hinton, and P. Pulay, *J. Am. Chem. Soc.* **112**, 8251 (1990)] of nuclear magnetic moments (***m***) in external magnetic fields (***B***) leads to the expression for the anisotropic NMR chemical shielding tensor components $\sigma_{\alpha\beta}$ as a sum of "unperturbed" (u) and "induced" (i) contributions,

(1) $\sigma_{\alpha\beta} = \text{Tr}\{\mathbf{D}^{00}\ \mathbf{h}^{\alpha\beta}\} + \text{Tr}\{\mathbf{D}^{\alpha0}\ \mathbf{h}^{0\beta}\} = \sigma_{\alpha\beta}^{(u)} + \sigma_{\alpha\beta}^{(i)}$

where the matrices $\mathbf{D}^{00}$, $\mathbf{D}^{\alpha0}$, $\mathbf{h}^{0\beta}$, and $\mathbf{h}^{\alpha\beta}$ represent, respectively, the Fock-Dirac density matrix, the density derivative with respect to field component B_α, the derivative of the 1-e Hamiltonian (**h**) with respect to magnetic moment component m_β, and the crossed second derivative of **h** with respect to M_α and m_β, all in the basis of atomic orbitals $\{\chi_p\}$. For the full chemical shielding anisotropy, the tensor indices α, β range over the cartesian components x, y, z, but the simpler isotropic scalar shielding (average diagonal component)

(2) $\sigma_{iso} = {}^1\!/_3 \sum_\alpha \sigma_{\alpha\alpha}$

is usually the quantity of principal chemical interest. The distinction between "unperturbed" (field-free) and "induced" (field-dependent) GIAO contributions is parallel to that between "diamagnetic" and "paramagnetic" terms in Ramsey's non-GIAO theory. In both cases the labels distinguish contributions associated with the unperturbed ground state ($\sigma_{\alpha\beta}^{(u)}$) from those associated with excited states ($\sigma_{\alpha\beta}^{(i)}$).

To carry out localized analysis of $\sigma_{\alpha\beta}$ (or σ_{iso}), we make use of the following transformations that relate the canonical MOs (φ_k^{MO}) to the NLMOs (φ_j^{NLMO}), NBOs (Ω_n) and AOs (χ_p), viz.,

(3a) $\varphi_j^{NLMO} = \sum_n{}^{NBO} a_{nj}\Omega_n$ (NBONLMO)

(3b) $\Omega_n = \sum_q{}^{AO} b_{qn} \chi_q$ (AONBO)

(3c) $\varphi_k^{MO} = \sum_p{}^{AO} c_{pk}\chi_p$ (AOMO)

B.14. NCS: NMR CHEMICAL SHIELDING ANALYSIS

(3d) $\varphi_j^{NLMO} = \sum_q^{AO} d_{qj} \chi_q$ (AONLMO)

(3e) $\varphi_k^{MO} = \sum_j^{NLMO} t_{jk} \varphi_j^{NLMO}$ (NLMOMO)

The program analyzes $\sigma_{\alpha\beta}$ in terms of localized NBO contributions

(4) $\sigma_{\alpha\beta} = \sum_j^L [{}^j\sigma_{\alpha\beta} + \sum_n^{NL} {}^{j \to n}\sigma_{\alpha\beta}\backslash 09<$

where ${}^j\sigma_{\alpha\beta}$ is a Lewis-type (L) contribution from the parent NBO (Ω_j) of φ_j^{NLMO}, and ${}^{j \to n}\sigma_{\alpha\beta}$ is a non-Lewis-type (NL) contribution from the "delocalization tail" Ω_n of this NLMO (the same label serving to identify both the NLMO and its parent NBO). Each ${}^{j \to n}\sigma_{\alpha\beta}$ is therefore the shielding associated with a particular $\Omega_j \to \Omega_n$ donor-acceptor (L → NL) interaction of NBO energetic analysis (Sec. A.3.5), contributing only when conjugative or hyperconjugative delocalization is present. Note that such delocalization occurs in both ground and excited states, so NL contributions of both "unperturbed" and "induced" type are possible.

To evaluate the terms in (4), the program first calculates $\sigma_{\alpha\beta}^{(u)}$ (corresponding to contributions from occupied field-free MOs φ_k^{MO}) from localized contractions of the form

(5) ${}^{j \to n}\sigma_{\alpha\beta}^{(u)} = \mathrm{Tr}\{{}^{j \to n}\mathbf{D}^{00}\mathbf{h}^{\alpha\beta}\}$

where the partial density matrix for localized $j \to n$ NBO interaction is

(6) ${}^{j \to n}\mathbf{D}^{00}{}_{pq} = 2\, a_{nj}\, b_{pn}\, d_{qj}$

This follows from writing the Fock-Dirac density matrix elements $\mathbf{D}^{00}{}_{pq} = 2\sum_k c_{pk}c_{qk}$ in the alternative NLMO form

(7) $\mathbf{D}^{00}{}_{pq} = 2\sum_j^{NLMO} d_{pj}\, d_{qj}$

and using (3a) to write NLMO j in terms of its parent NBO Ω_j and delocalization tail Ω_n.

The program next calculates $\sigma_{\alpha\beta}^{(i)}$ (corresponding to contributions from virtual MOs φ_v^{MO}) from localized contractions of the form

(8) ${}^{j \to n}\sigma_{\alpha\beta}^{(i)} = \mathrm{Tr}\{{}^{j \to n}\mathbf{D}^{\alpha 0}\mathbf{h}^{0\beta}\}$

where the $j \to n$ contribution to the density derivative matrix can be written as

B.14. NCS: NMR CHEMICAL SHIELDING ANALYSIS

(9) $^{j \to n}\mathbf{D}^{\alpha 0}{}_{pq} = 2 \sum_k{}^{occ} t_{jk} \, a_{nj} \, [b_{pn} \, c^{\alpha 0}{}_{qk} - c^{\alpha 0}{}_{pk} \, b_{qn}]$

The coefficients $c^{\alpha 0}{}_{pk}$ describe the field-dependent correction to the field-free LCAO coefficient c_{qk} in the 1st-order perturbative expression

(10) $c_{pk}{}^{(1)}(B_\alpha, m_\beta) = c_{pk} + iB_\alpha \, c^{\alpha 0}{}_{pk} + im_\beta \, c^{0\beta}{}_{pk} + \ldots$

They are evaluated by the formalism of Pulay in the form

(11) $c^{\alpha 0}{}_{pk} = \sum_q{}^{AO} \sum_r{}^{AO} \, c_{rk} \, [^k\mathbf{W}_{pq}(\mathbf{F}^{\alpha 0}{}_{qr} - \varepsilon_k \mathbf{S}^{\alpha 0}{}_{qr}) + \frac{1}{4} \mathbf{D}^{00}{}_{pq} \, \mathbf{S}^{\alpha 0}{}_{qr}]$

where $\mathbf{F}^{\alpha 0}$ and $\mathbf{S}^{\alpha 0}$ are the first-order Fock matrix and overlap matrix derivatives and $^k\mathbf{W}$ is the Ditchfield weighting matrix

(12) $^k\mathbf{W}_{pq} = \sum_v{}^{vir} c_{pv} \, c_{qv}/(\varepsilon_k - \varepsilon_v)$

for MO k with orbital energy ε_k. The final L, NL contributions in (4) are obtained as the sum of unperturbed and induced terms (5), (8).

B.14. NCS: NMR CHEMICAL SHIELDING ANALYSIS

B.14.2 NCS Keyword Usage

The NCS module is currently implemented only for Gaussian versions. To calculate GIAO shieldings and perform NCS analysis, one should include the Gaussian keyword NMR in the Gaussian route card (as shown below), together with chosen NCS options in the $NBO keylist.

Basic natural chemical shielding (NCS) analysis is requested by simply including the NCS keyword in the $NBO keylist. A sample Gaussian input deck for the idealized HF/3-21G calculation of CH_3NH_2 is illustrated below:

```
#HF/3-21G POP=NBOread NMR

CH3NH2

0   1
C        0.053054       0.712391       0.000000
N        0.053054      -0.757609       0.000000
H       -0.977562       1.067260       0.000000
H        0.568362       1.067261       0.892539
H        0.568362       1.067261      -0.892539
H       -0.424433      -1.086433      -0.827032
H       -0.424433      -1.086433       0.827032

$NBO   NCS   $END
```

This calculation produces a table of localized contributions to isotropic chemical shielding constants (σ_{iso}) for each nucleus for which GIAO calculations were performed, showing the Lewis "L" ($^j\sigma_{\alpha\beta}$) and non-Lewis "NL" ($\sum_n {}^{j\rightarrow n}\sigma_{\alpha\beta}$) contributions arising from each occupied NBO j.

One can request additional details of the shielding tensors by appending one or more of the following options to the NCS keyword (separated by commas or spaces):

OPTION	*OPTION DESCRIPTION*
CSA	Request analysis of diagonal tensor components (in the principal shielding axes) and chemical shielding anisotropy (CSA) for each nucleus. The transformation matrix from the molecular cartesian frame to the principal shielding frame of each nucleus is also printed.
XYZ	Request analysis of full chemical shielding tensor in the molecular

	cartesian axes (x,y,z). This automatically sets the CSA option.
U	Request separate analysis of the "unperturbed" (field-free or diamagnetic) contribution $\sigma_{\alpha\beta}^{(u)}$ to chemical shielding.
I	Request separate analysis of the "induced" (field-dependent or paramagnetic) contribution $\sigma_{\alpha\beta}^{(i)}$ to chemical shielding. (Since the total shielding is analyzed by default, this contribution can be determined from the analysis by difference.)
MO	Request analysis of the shielding tensor in terms of canonical MOs (in addition to localized NBO/NLMO analysis), following Ditchfield's original treatment.

For example, a sample $NBO keylist to request NCS analysis including both total and induced anisotropic shielding tensor components in the principal shielding axes is shown below:

```
$NBO  NCS=CSA,I  $END
```

The keywords "NCS=XYZ,I" would request analogous analysis with respect to the molecular cartesian axes (in addition to CSA printout). Note that each NCS option "compounds" the effect of others, so that, e.g., a combination such as "NCS=CSA,XYZ,I,MO" would give ~8 *times* the printout of "NCS=CSA".

Each table produced by NCS analysis includes all $j{\rightarrow}n$ delocalization contributions that exceed the default threshold of 0.1 ppm for printing. This threshold is also the minimum off-diagonal element that characterizes the tensor as "non-symmetric" and leads to full printout of antisymmetric tensor components.

The default printing threshold can be altered as illustrated in the following example,

```
$NBO  NCS=0.02  $END
```

which lowers the threshold to 0.02 ppm. Modified forms of the NCS keyword can be combined, as in the following example,

```
$NBO  NCS=0.5,CSA  $END
```

which requests printing of delocalized anisotropic and isotropic shielding contributions exceeding 0.5 ppm.

B.14. NCS: NMR CHEMICAL SHIELDING ANALYSIS

Note that NCS analysis can be performed by the stand-alone GenNBO program if NCS-related datalists are available in FILE47 as described in Section B.7. When the NMR keyword is included on the Gaussian route card and the ARCHIVE keyword in the $NBO keylist, the NBO program will write these datalists to FILE47, which in turn serves as input for GenNBO. The NCS datalists include the MO derivative coefficients ($C10) and GIAO Hamiltonian first derivatives ($H01) and second derivatives ($H11).

B.14. NCS: NMR CHEMICAL SHIELDING ANALYSIS

B.14.3 NCS Sample Output

Sample default NCS output is shown below for the CH_3NH_2 molecule (RHF/3-21G level, idealized Pople-Gordon geometry):

```
Summary of isotropic NMR chemical shielding
Total Lewis (L) and non-Lewis (NL) contributions: (ppm)

        NBO          C  1    N  2    H  3    H  4    H  5    H  6    H  7
--------------- ------- ------- ------- ------- ------- ------- -------
 1.  C 1(cr)   L   202.40   -0.07    0.15    0.13    0.13   -0.03   -0.03
               NL    0.15    0.00    0.00   -0.01   -0.01    0.00    0.00
 2.  N 2(cr)   L     0.08  238.43    0.05    0.03    0.03    0.07    0.07
               NL    0.00    0.10    0.00    0.00    0.00    0.00    0.00
 3.  N 2(lp)   L    -0.12    6.29   -0.49    0.18    0.18    5.41    5.41
               NL   -0.08    0.75   -0.34   -0.01   -0.01    0.05    0.05
 4.  C 1- N 2  L    -6.50    6.31    0.57    0.49    0.49    2.40    2.40
               NL    0.17   -0.35    0.02    0.08    0.08   -0.09   -0.09
 5.  C 1- H 3  L    -4.29    0.45   26.51    1.85    1.85    0.09    0.09
               NL   -0.59   -0.37    0.06   -0.05   -0.05   -0.01   -0.01
 6.  C 1- H 4  L    -2.68    2.10    2.10   25.73    2.04    0.13    0.21
               NL   -0.23   -1.41   -0.01    0.05    0.03   -0.04   -0.08
 7.  C 1- H 5  L    -2.68    2.10    2.10    2.04   25.73    0.21    0.13
               NL   -0.23   -1.41   -0.01    0.03    0.05   -0.08   -0.04
 8.  N 2- H 6  L     0.06    7.09    0.33    0.28    0.23   22.89    3.37
               NL    0.00    0.17   -0.02   -0.12   -0.01    0.03   -0.04
 9.  N 2- H 7  L     0.06    7.09    0.33    0.23    0.28    3.37   22.89
               NL    0.00    0.17   -0.02   -0.01   -0.12   -0.04    0.03
--------------- ------- ------- ------- ------- ------- ------- -------
       Lewis      186.32  269.80   31.67   30.98   30.98   34.54   34.54
   non-Lewis       -0.82   -2.35   -0.33   -0.02   -0.02   -0.19   -0.19
--------------- ------- ------- ------- ------- ------- ------- -------
       Total      185.50  267.45   31.34   30.95   30.95   34.36   34.36
```

For each NBO j, the table gives the sum of "L" ($^j\sigma_{\alpha\beta}$) and total "NL" ($\sum_n^{NL} {}^{j\rightarrow n}\sigma_{\alpha\beta}$) contributions to σ_{iso}.

An example of the output produced by keyword option "NCS=CSA" is shown below for the H(3) atom of methylamine:

```
Principal components of the tensor (ppm) for atom  H(  3):
This tensor is non-symmetric.  The antisymmetric part will be printed.

                 Principal components    Antisymmetric part
      NBO          11      22      33      12      13      23     CSA     ISO
================================================================================
   1. C 1(cr)     0.00    0.18    0.28    0.00    0.00    0.11    0.18    0.15
   3. N 2(lp)    -1.87   -0.16    0.56    0.00    0.00    0.04    1.57   -0.49
   NL  11. BD*   -0.56   -0.49    0.40    0.00    0.00   -0.14    0.92   -0.22
   NL  16. RY     0.14    0.03   -0.01    0.00    0.00    0.04   -0.09    0.05
   NL  24. RY    -0.15   -0.14   -0.01    0.00    0.00    0.01    0.14   -0.10
   4. C 1- N 2    0.28   -0.83    2.24    0.00    0.00   -0.10    2.51    0.57
   NL  24. RY    -0.11   -0.11    0.02    0.00    0.00    0.05    0.13   -0.07
   5. C 1- H 3   25.62   25.84   28.08    0.00    0.00    0.34    2.34   26.51
   6. C 1- H 4    1.15    3.01    2.15   -0.16    0.83   -0.16    0.07    2.10
   7. C 1- H 5    1.15    3.01    2.15    0.16   -0.83   -0.16    0.07    2.10
   8. N 2- H 6    0.15   -0.09    0.93   -0.18   -0.51    0.23    0.90    0.33
   9. N 2- H 7    0.15   -0.09    0.93    0.18    0.51    0.23    0.90    0.33
--------------------------------------------------------------------------------
       Lewis     26.70   30.94   37.36    0.00    0.00    0.51    8.54   31.67
```

B.14. NCS: NMR CHEMICAL SHIELDING ANALYSIS

```
      non-Lewis    -0.66   -0.66    0.34    0.00    0.00    0.12    1.00   -0.33
 ------------------------------------------------------------------------------
         Total     26.05   30.28   37.70    0.00    0.00    0.63    9.54   31.34
 ------------------------------------------------------------------------------

Cartesian XYZ to principal shielding axes for atom  H (   3):

        1         2         3
 -------------------------------
 X   0.000000  0.730597 -0.682809
 Y   0.000000  0.682809  0.730597
 Z   1.000000  0.000000  0.000000
```

This table displays contributions to the individual tensor components in the principal axes of the nuclear shielding tensor. "ISO" denotes $\sigma_{iso} = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3$, the isotropic shielding, and "CSA" denotes $\sigma_{33} - (\sigma_{11} + \sigma_{22})/2$, the chemical shielding anisotropy (with conventional axis ordering $\sigma_{33} \geq \sigma_{22} \geq \sigma_{11}$). Off-diagonal contributions are displayed ("Antisymmetric Part") only if the magnitude of at least one σ_{ij} exceeds the print threshold. Note that individual NL contributions $^{j \rightarrow n}\sigma_{\alpha\beta}$ (> 0.1 ppm, the default threshold) are printed in this more detailed analysis of the shielding tensor. The printout includes the matrix of direction cosines from the overall cartesian XYZ system (as chosen by the ESS) to the principal shielding axes for each nucleus.

Similarly, the keyword option "NCS=XYZ" leads to the additional output for H(3) shown below:

```
Full Cartesian NMR shielding tensor (ppm) for atom  H(   3):
Lewis (L) and non-Lewis (NL) contributions

   NBO
  L  NL    XX      XY      XZ      YX      YY      YZ      ZX      ZY      ZZ
 =============================================================================
   1.      0.48    0.04    0.00   -0.17   -0.02    0.00    0.00    0.00    0.00
   3.     -0.84   -0.25    0.00   -0.33    1.24    0.00    0.00    0.00   -1.87
     11.    0.01   -0.59    0.00   -0.31   -0.11    0.00    0.00    0.00   -0.56
     12.   -0.04    0.03    0.05   -0.05   -0.01    0.01   -0.01    0.15   -0.06
     13.   -0.04    0.03   -0.05   -0.05   -0.01   -0.01    0.01   -0.15   -0.06
     16.    0.02    0.05    0.00   -0.02    0.00    0.00    0.00    0.00    0.14
     24.   -0.07   -0.06    0.00   -0.07   -0.07    0.00    0.00    0.00   -0.15
   4.      0.46   -1.62    0.00   -1.42    0.95    0.00    0.00    0.00    0.28
     24.   -0.05   -0.01    0.00   -0.11   -0.04    0.00    0.00    0.00   -0.11
   5.     28.98   -0.92    0.00   -1.59   24.94    0.00    0.00    0.00   25.62
   6.      2.35    0.28   -0.61    0.61    2.81   -0.86    0.77   -1.85    1.15
   7.      2.35    0.28    0.61    0.61    2.81    0.86   -0.77    1.85    1.15
   8.      0.03   -0.25    0.03   -0.72    0.81   -0.88   -0.41    0.11    0.15
   9.      0.03   -0.25   -0.03   -0.72    0.81    0.88    0.41   -0.11    0.15
 -----------------------------------------------------------------------------
     L     33.87   -2.69    0.00   -3.71   34.42    0.00    0.00    0.00   26.70
    NL     -0.14   -0.38    0.00   -0.62   -0.19    0.00    0.00    0.00   -0.66
 -----------------------------------------------------------------------------
  Total    33.74   -3.07    0.00   -4.33   34.24    0.00    0.00    0.00   26.05
 -----------------------------------------------------------------------------
```

B.14. NCS: NMR CHEMICAL SHIELDING ANALYSIS

This table displays all tensor elements $\sigma_{\alpha\beta}$ (regardless of magnitude) in the cartesian axis system of the ESS. Due to space limitations, contributing L-type and NL-type NBOs are identified by number only. Note that the fixed printing threshold may lead to slightly different lists of leading NL contributions in the CSA and XYZ tables.

Finally, option "NCS=MO" adds delocalized MO analysis of isotropic shieldings for all nuclei, as shown below:

```
Summary of isotropic NMR chemical shielding
Canonical MO contributions: (ppm)

      MO          C  1    N  2    H  3    H  4    H  5    H  6    H  7
---------------   ------- ------- ------- ------- ------- ------- -------
   1.               0.35  234.43    0.18    0.13    0.13   -0.11   -0.11
   2.             199.51    0.35   -0.13   -0.24   -0.24    0.17    0.17
   3.               5.21   22.08    1.12    1.42    1.42    4.68    4.68
   4.              28.17   12.34    6.12    6.08    6.08    3.76    3.76
   5.              -3.48  -19.03    0.84    3.51    3.51   10.43   10.43
   6.             -12.02   -3.54   17.17    3.09    3.09    2.04    2.04
   7.              -3.81   20.76    3.07    5.30    5.30    4.18    4.18
   8.             -21.05    0.71   -0.44   11.20   11.20    4.33    4.33
   9.              -7.38   -0.65    3.41    0.46    0.46    4.87    4.87
---------------   ------- ------- ------- ------- ------- ------- -------
       Total      185.50  267.45   31.34   30.95   30.95   34.36   34.36
```

The MO contributions of this table are typically much less transferable than corresponding NBO contributions.

B.15. NJC: NATURAL J-COUPLING ANALYSIS

Reference: S. J. Wilkens, W. M. Westler, J. L. Markley, and F. Weinhold, *J. Am. Chem. Soc.* **123**, 12026-12036 (2001).

B.15.1 Introduction to Natural J-Coupling Analysis

The Fermi-contact contribution to scalar J-coupling J[A,B] between magnetic nuclei A,B can be conveniently evaluated in the framework of HF/DFT theory by the finite-field perturbative method [J. A. Pople, J. W. McIver, and N. S. Ostlund, *J. Chem. Phys.* **49**, 2960-2964, 2965-2970 (1968); T. Onak, J. Jaballas, and M. Barfield, *J. Am. Chem. Soc.* **121**, 2850-2856 (1999)]. In this method, a Fermi contact (Dirac delta function) α-spin perturbation $\delta(\mathbf{r}_B)$ with formal perturbative field strength λ_B is added at the position $\mathbf{r}_B$ of nucleus B, and the resulting spin-density distribution $\Delta\rho(\mathbf{r}) = \rho^{(\alpha)}(\mathbf{r}) - \rho^{(\beta)}(\mathbf{r})$ is evaluated at the position $\mathbf{r}_A$ of nucleus A. If $\Delta_B\rho(\mathbf{r}_A)$ denotes the spin density at A induced by perturbation of strength λ_B at B, the J-coupling (Hz) can be evaluated as

(1) $J[A,B] = (16h\mu_b^2 \gamma_A\gamma_B/9) \Delta_B\rho(\mathbf{r}_A) /\lambda_B$

where h is Planck's constant, μ_b is the Bohr magneton, and γ_A, γ_B are nuclear gyromagnetic ratios. The perturbative field strength should be taken sufficiently small (e.g., $\lambda_B = 0.02$ a.u.) that the ratio $\Delta_B\rho/\lambda_B$ is numerically independent of λ_B.

To obtain a localized decomposition of the densities ($\rho^{(\alpha)}$, $\rho^{(\beta)}$) of either spin, one can replace the usual expansion over occupied MOs $\{\varphi_i^{(\sigma)}\}$ by the corresponding expansion over NLMOs $\{\Omega_i^{(\sigma)}\}$

(2) $\rho^{(\sigma)} = \sum_i^{occ} |\Omega_i^{(\sigma)}|^2$, ($\sigma = \alpha, \beta$)

Each semi-localized NLMO Ω_i can in turn be expanded in the complete set of localized NBOs $\{\sigma_j\}$, viz., for α spin,

(3) $\Omega_i^{(\alpha)} = c_{ii}^{(\alpha)}\sigma_i^{(\alpha)} + \sum_{j\neq i}^{NL} c_{ji}^{(\alpha)}\sigma_j^{(\alpha)}$

where the $\{c_{ji}^{(\alpha)}\}$ are elements of the NBO $\rightarrow$ NLMO transformation matrix.

Eqs. (1)-(3) lead to a localized decomposition of J[A,B] into Lewis (L) and non-Lewis (NL) contributions of the form

(4) $J[A,B] = \sum_i^L \{J_i^{(L)}[A,B] + \sum_j^{NL} J_{ji}^{(NL)}[A,B]\}$

analogous to that previously described for the dipole operator (Sec. B.6.3). Each Lewis-type $J_i^{(L)}$ corresponds to the contribution of a completely localized NBO σ_i [i.e., the result of setting $c_{ji} \neq 0$ for all $j \neq i$ in Eq. (3)], whereas $J_{ji}^{(NL)}$ is the contribution of $\sigma_i \rightarrow \sigma_j^*$ interactions in each spin set. Because Eq. (1) expresses J[A,B] unsymmetrically in terms of the perturbation "from B to A," a second evaluation of J[A,B] is performed with the roles of A and B reversed, and each term in Eq. (4) is evaluated as the average of these unsymmetrical contributions in order to restore the physical symmetry of the A,B spin coupling.

The $\sigma_i \rightarrow \sigma_j^*$ interactions can in turn be partitioned into two sets:

Repolarization: Those ("internal") in which σ_j^* is centered on one or both of the *same* atoms as σ_i, viz.,

(4) $\sigma_{AB} \rightarrow \sigma^*_{AB}, r^*_A, r^*_B$ ("internal")
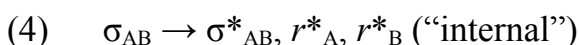
Delocalization: Those ("external") in which σ_i, σ_j^* are centered in *distinct* bonding regions, viz.,

(5) $\sigma_{AB} \rightarrow \sigma^*_{CD}, r^*_C, r^*_D$ ("external")
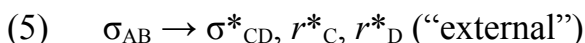
Each J[A,B] can thereby be expressed as a sum of "Lewis," "repolarization," and "delocalization" contributions

(6) $J = J^{(L)} + J^{(repol)} + J^{(deloc)}$

or, in terms of individual NBOs, as

(7) $J = \sum_i^L \{ J_i^{(L)} + J_i^{(repol)} + \sum_j^{NL} J_{ji}^{(deloc)} \}$

Physically, the $J_i^{(L)}$ contributions represent primarily the *steric* (exchange antisymmetry) effects that are present even in the completely localized natural Lewis structure wavefunction, the $J_i^{(repol)}$ contributions describe how the electron pair in each NBO can repolarize (altering the left-right, radial, or angular separation of α and β electrons) in response to the perturbation, and the $J_{ji}^{(deloc)}$ contributions represent the effect of hyperconjugative or conjugative $\sigma_i \rightarrow \sigma_j^*$ delocalizations of "resonance" type (irreducible departures from a single localized Lewis structure). See Wilkens et al. for further discussion.

In each case the gyromagnetic ratios γ_A, γ_B (taken from a standard compilation of NMR properties <www.webelements.com> are chosen to correspond to the

"most important" magnetic isotope, i.e., the isotope of half-integer nuclear spin (I) of greatest natural abundance. J-couplings for other isotopic nuclei can then be obtained by correcting for the change in γ values. For cases where isotopic spin and γ are unknown, the program uses the value $\gamma = 1$ $(x10^7)$, so that calculated J values can be easily rescaled to correct physical units when the proper γ becomes known. (A similar rescaling procedure can be used to correct for possible future revisions of the γ values.) The table below summarizes the selected isotope, nuclear spin, γ value (in units of 10^7 rad $T^{-1}s^{-1}$) and percentage terrestrial abundance for all atoms $Z = 1$-103.

Z	isotope	I	$\gamma(x10^{-7})$	%−abund.
1	^{1}H	1/2	26.7522	99.98
2	^{3}He	1/2	−20.3802	0.00
3	^{7}Li	3/2	10.3977	92.57
4	^{9}Be	3/2	−3.7597	100.00
5	^{11}B	3/2	2.8747	80.10
6	^{13}C	1/2	6.7283	1.10
7	^{15}N	1/2	−2.7126	0.37
8	^{17}O	5/2	−3.6281	0.04
9	^{19}F	1/2	25.1815	100.00
10	^{21}Ne	3/2	−2.1131	0.27
11	^{23}Na	3/2	7.0808	100.00
12	^{25}Mg	5/2	−1.6389	10.05
13	^{27}Al	5/2	6.9763	100.00
14	^{29}Si	1/2	−5.3190	4.67
15	^{31}P	1/2	10.8394	100.00
16	^{33}S	3/2	2.0557	0.75
17	^{35}Cl	3/2	2.6242	75.78
18	^{39}Ar	7/2	1.0000	0.00
19	^{39}K	3/2	1.2501	93.26
20	^{43}Ca	7/2	−1.8031	0.13
21	^{45}Sc	7/2	6.5088	100.00
22	^{47}Ti	5/2	−1.5105	7.30
23	^{51}V	7/2	7.0455	99.75

24	^{53}Cr	3/2	−1.5152	9.50
25	^{55}Mn	5/2	6.6453	100.00
26	^{57}Fe	1/2	0.8681	2.25
27	^{59}Co	7/2	6.3320	100.00
28	^{61}Ni	3/2	−2.3948	1.14
29	^{63}Cu	3/2	7.1118	69.17
30	^{67}Zn	5/2	1.6767	4.12
31	^{69}Ga	3/2	6.4389	60.11
32	^{73}Ge	9/2	−0.9360	7.73
33	^{75}As	3/2	4.5962	100.00
34	^{77}Se	1/2	5.1254	7.63
35	^{79}Br	3/2	6.7256	50.69
36	^{83}Kr	9/2	−1.0331	11.55
37	^{85}Rb	5/2	2.5927	72.17
38	^{87}Sr	9/2	−1.1639	7.00
39	^{89}Y	1/2	−1.3163	100.00
40	^{91}Zr	5/2	−2.4974	11.22
41	^{93}Nb	9/2	6.5674	100.00
42	^{95}Mo	5/2	−1.7880	15.92
43	^{99}Tc	9/2	6.0460	0.00
44	^{101}Ru	5/2	−1.3770	16.98
45	^{103}Rh	1/2	−0.8468	100.00
46	^{105}Pd	5/2	−1.2300	22.33
47	^{107}Ag	1/2	−1.0889	51.84
48	^{111}Cd	1/2	−5.6983	12.80
49	^{115}In	9/2	5.8972	95.70
50	^{119}Sn	1/2	−10.0317	8.59
51	^{121}Sb	5/2	6.4435	57.36
52	^{125}Te	1/2	−8.5108	7.14
53	^{127}I	5/2	5.3896	100.00
54	^{129}Xe	1/2	−7.4521	26.40
55	^{133}Cs	7/2	3.5333	100.00
56	^{137}Ba	3/2	2.9930	11.23
57	^{139}La	7/2	3.8083	99.91
58	^{141}Ce	7/2	1.0000	0.00

59	^{141}Pr	5/2	8.1907	100.00
60	^{143}Nd	7/2	−1.4570	12.18
61	^{147}Pm	7/2	3.6130	0.00
62	^{147}Sm	7/2	−1.1150	15.07
63	^{153}Eu	5/2	2.9369	52.20
64	^{157}Gd	7/2	−1.0769	15.65
65	^{159}Tb	3/2	6.4310	100.00
66	^{163}Dy	7/2	1.2890	24.90
67	^{165}Ho	7/2	5.7100	100.00
68	^{167}Er	7/2	−0.7716	22.95
69	^{169}Tm	1/2	−2.2180	100.00
70	^{173}Yb	5/2	−1.3025	16.12
71	^{175}Lu	7/2	3.0552	97.41
72	^{177}Hf	7/2	1.0860	18.61
73	^{181}Ta	7/2	3.2438	99.99
74	^{183}W	1/2	1.1282	14.28
75	^{187}Re	5/2	6.1057	62.60
76	^{189}Os	3/2	2.1071	16.10
77	^{193}Ir	3/2	0.5227	62.70
78	^{195}Pt	1/2	5.8385	33.80
79	^{197}Au	3/2	0.4731	100.00
80	^{199}Hg	1/2	4.8458	16.87
81	^{205}Tl	1/2	15.6922	70.48
82	^{207}Pb	1/2	5.5805	22.10
83	^{209}Bi	9/2	4.3750	100.00
84	^{209}Po	1/2	7.4000	0.00
85	$^{?}$At	?	1.0000	0.00
86	$^{?}$Rn	?	1.0000	0.00
87	^{223}Fr	?	1.0000	0.00
88	$^{?}$Ra	?	1.0000	0.00
89	^{227}Ac	3/2	3.5000	0.00
90	^{229}Th	5/2	0.4000	0.00
91	^{231}Pa	3/2	3.2100	100.00
92	^{235}U	7/2	−0.5200	0.72
93	^{237}Np	5/2	3.1000	0.00

94	^{239}Pu	1/2	0.9720	0.00
95	^{241}Am	5/2	1.4000	0.00
96	^{247}Cm	9/2	0.2000	0.00
97	^{247}Bk	3/2	1.0000	0.00
98	^{251}Cf	1/2	1.0000	0.00
99	$^{?}$Es	?	1.0000	0.00
100	^{257}Fm	?	1.0000	0.00
101	$^{?}$Md	?	1.0000	0.00
102	^{259}No	?	1.0000	0.00
103	$^{?}$Lr	?	1.0000	0.00

B.15. NJC: NATURAL J-COUPLING ANALYSIS

B.15.2 NJC Keyword Usage and Sample Input

The NJC keyword is currently implemented only for Gaussian host programs. Default natural J-coupling analysis is invoked by simply including the NJC keyword in the $NBO keylist. However, evaluation of all $J_{A,B}$ couplings in a closed-shell molecule of *N* magnetic nuclei requires a separate open-shell Fermi FIELD calculation for each perturbed nucleus. These calculations should be prepared as a chained sequence of "Link1" jobs, each requesting perturbation of a different nucleus *n*, and each having a FILE name of the form JOB_*n* (as well as the NJC keyword) in the $NBO keylist. The NJC output from JOB_*n* will contain the couplings to previously perturbed atoms of the chain (i.e., JOB_1 output contains no couplings, JOB_2 output contains $J_{1,2}$ coupling, JOB_3 output contains $J_{1,3}$ and $J_{2,3}$ couplings, and so forth).

[Note that each JOB_*n* of the chain creates a file "JOB_*n*.njc" that is read by subsequent JOB_*m* links to analyze $J_{n,m}$ coupling. Thus, the individual jobs of the chain can also be run separately, provided the JOB_*n*.njc files from previous runs remain accessible on the default directory.]

The following input deck creates a chain of seven jobs for the example of CH_3NH_2 (7 nuclei), using a field strength of "200" (0.02 a.u.) for each perturbation. The field strength "200" is assumed by NJC and should always be chosen on the Gaussian route card. [If it is necessary to alter this field strength for numerical reasons, one can always use Eq. (1) to re-scale the calculated J value for the actual λ_B employed.] In the present case the J-couplings will be evaluated with gyromagnetic ratios for ^1H, ^{13}C, and ^{15}N nuclei. Note that the "PRINT=0" keyword is included in the $NBO keylist after the first job to suppress repetitive printing of NBO output that differs infinitesimally from that of the first job.

```
%mem=2000000
%chk=ch3nh2
HF/3-21G POP=NBORead field=f(1)200

Methylamine: perturb C1

0    1
C
N    1    1.47
H    1    1.09 2    109.47
H    1    1.09 2    109.47    3    120.   0
H    1    1.09 2    109.47    3    240.   0
H    2    1.01 1    109.47    3     60.   0
H    2    1.01 1    109.47    3    300.   0
```

B.15. NJC: NATURAL J-COUPLING ANALYSIS

```
$NBO FILE=CH3NH2_1 NJC $END

--Link1--
%mem=2000000
%chk=ch3nh2
HF/3-21G POP=NBORead field=f(2)200 guess=read geom=allcheckpoint

$NBO FILE=CH3NH2_2 NJC PRINT=0 $END

--Link1--
    .
    .
    .
--Link1--
%mem=2000000
%chk=ch3nh2
HF/3-21G POP=NBORead field=f(7)200 guess=read geom=allcheckpoint

$NBO FILE=CH3NH2_7 NJC PRINT=0 $END
```

By default, all J-coupling contributions are printed that exceed a printing
threshold of 0.1 Hz. This can be altered by including a chosen print threshold
with the NJC keyword, as illustrated below (e.g., to increase the print threshold
to 0.5 Hz)

```
$NBO FILE=CH3NH2_7 NJC=0.5 $END
```

(Note that NJC table entries are only printed to 0.01 Hz precision, so that
setting the print threshold below 0.01 only results in additional rows and
colums with zero entries.)

B.15.3 NJC Sample Output

A sample of NJC output produced (on the CH3NH2_7 step) for the J[H5,H7] spin coupling in the idealized methylamine example is shown below:

```
J[H5,H7] = 8.35 Hz:   3-J[H5-C1-N2-H7]
   Threshold for printing:    0.10 Hz
                  1.          3.          4.          5.          6.
             | C 1- N 2   C 1- H 4   C 1- H 5   N 2- H 6   N 2- H 7
     ------------------------------------------------------------------
         Lewis |    0.03       -0.06        1.74       -0.08        4.07
         Repol.|    0.00        0.00       -0.08        0.00       -0.08
     ------------------------------------------------------------------
      C 1(ry*) |                                       -0.00 v      0.17 v
      N 2(ry*) |              -0.01 v     -0.28 v
 20. H 5(ry*) |    -0.04 v    -0.03 v                  -0.05 r     -0.25 r
 22. H 7(ry*) |    -0.07 v    -0.05 r     -0.25 r      -0.04 v
 26. C 1- H 5*|     0.08 g     0.08 g                   0.18 v      1.21 v
 28. N 2- H 7*|     0.11 g     0.12 v      1.38 v       0.11 g
        Others|    -0.01       0.00       -0.05        0.00        0.10
(Total deloc.)|    (0.07)     (0.12)      (0.80)       (0.20)      (1.23)
     ------------------------------------------------------------------
         NLMO |     0.10       0.06        2.47        0.12        5.23

                   9.
             | N 2(lp)     Others |    Total
     -------------------------------------------
         Lewis |    0.10       0.03 |     5.84
         Repol.|    0.00       0.00 |    -0.15
     -------------------------------------------
      C 1(ry*) |    0.01 v     0.00 |     0.18
      N 2(ry*) |              -0.01 |    -0.30
 20. H 5(ry*) |   -0.05 r    -0.02 |    -0.44
 22. H 7(ry*) |   -0.11 v    -0.04 |    -0.56
 26. C 1- H 5*|    0.27 v     0.04 |     1.86
 28. N 2- H 7*|    0.09 g     0.07 |     1.88
        Others|   -0.00      -0.01 |     0.04
(Total deloc.)|   (0.20)     (0.05)|    (2.66)
     -------------------------------------------
         NLMO |    0.30       0.08 |     8.35
```

As shown in the output heading, the J[H5,H7] coupling is evaluated as 8.35 Hz, and the coupling pattern is identified as being of "3-J" (^3J, vicinal, through-3-bonds) type, bridged by bonds to C1 and N2. In the chosen geometry (Sec. B.15.2), the H5, H7 protons are in the vicinal antiperiplanar orientation that is expected to favor strong J-coupling, according to the well-known Karplus equation. (In accordance with Karplus-like torsional dependence, the *gauche*-oriented H5, H6 protons have much weaker 4.62 Hz J-coupling in this molecule.) From the final "Total" column, the total Lewis, repolarization, and delocalization contributions to J[H5,H7] can be identified as

$$J^{(L)} = 5.84 \text{ Hz}, \ J^{(repol)} = -0.15 \text{ Hz}, \ J^{(deloc)} = 2.66 \text{ Hz}$$

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The final "NLMO" row gives the total contribution of each NLMO identified in the column heading, showing that the leading contributions are from NLMOs 4 (the C1-H5 NLMO) and 6 (the N2-H7 NLMO),

$$J_4^{(NLMO)} = 2.47 \text{ Hz}, J_6^{(NLMO)} = 5.23 \text{ Hz}$$

with relatively insignificant contributions (< 0.3 Hz) from other NLMOs. The "Lewis" entry at the head of the column gives the corresponding NBO contribution, viz.,

$$J_4^{(NBO)} = 1.74 \text{ Hz}, J_6^{(NBO)} = 4.07 \text{ Hz}$$

the following "Repol." entry gives the (relatively negligible) repolarization correction for the NBO, and the remaining column entries give the $\sigma_i \to \sigma_j{}^*$ delocalization corrections. The two most important such corrections are seen to be

$$J_{4 \to 28} = 1.38 \text{ Hz} (\sigma_{C1H5} \to \sigma^*_{N2H7}), J_{6 \to 26} = 1.21 \text{ Hz} (\sigma_{N2H7} \to \sigma^*_{C1H5})$$

corresponding to the expected strong hyperconjugative interaction in the vicinal *trans*-like relationship between these NBOs. These $J_{4 \to 28}$ and $J_{6 \to 26}$ delocalizations are expected to vary with torsional angle in a Karplus-like manner (showing strong proportionality to the corresponding entries in the table of 2nd-order stabilization energies). This example illustrates how the J-coupling is often dominated by a relatively small number of localized (and transferable) NBO interactions of clear physical origin and distinctive dihedral dependence. In the present case, increasing the print threshold to 0.5 Hz would eliminate all but the few entries listed above, compacting the output table considerably.

As seen in the output table, each delocalization entry is labelled as vicinal (v), geminal (g), or "remote" (r) to identify the through-bonds relationship of the interacting σ_i, $\sigma_j{}^*$ NBOs. The table also shows how multiple Rydberg-type (ry*) orbitals on a single atom are grouped together in a single entry (unnumbered, unless there is only one such ry* orbital in the group). Due to this condensation of ry* contributions, the size of the NJC output table tends to remain relatively constant as the basis set is extended. Note that setting the print threshold NJC=0.0 bypasses condensation and forces printing of table entries for all individual orbitals.

NJC analysis also recognizes and flags J-coupling through hydrogen bonds. In this case the coupling is identified by a label of the form "2h-J[H1-O2:H4],"

where "2h" denotes geminal through-H-bond coupling and the colon (:) denotes the coordinative H-bond.

B.16. 3-CENTER, 4-ELECTRON HYPERBOND SEARCH

Reference: F. Weinhold and C. R. Landis, *Valency and Bonding: A Natural Bond Orbital Donor-Acceptor Perspective* (Cambridge U. Press, London, 2005), Secs 3.E, 4.F

B.16.1 Introduction

The NBO program initiates a subsidiary "3CHB" search for 3-center, 4-electron "hyperbonds" (ω-bonds). As described in the 3-center MO picture [G. C. Pimentel, *J. Chem. Phys.* **19**, 446 (1951); R. E. Rundle, *J. Chem. Phys.* **17**, 671 (1941)] a hyperbonded triad of atoms A, B, C, with strongly interacting valence hybrids h_A, h_B, h_C, can give rise to *two* doubly occupied MOs accommodating four electrons. Such 3-c, 4-e triads are more aptly described in Coulson's picture [C. A. Coulson, *J. Chem. Soc.* **1964**, 1442 (1964)] as a strong resonance hybrid of the two localized Lewis structure representations

(1)   A-B :C $\longleftrightarrow$ A: B-C
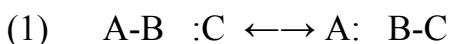
which is denoted in the computer output as A:-B-:C. [In earlier program versions, the "3CHB" keyword (now deprecated) was required to initiate this search.]

In NBO language, each A:-B-:C triad corresponds to strong $n_C \rightarrow \sigma_{AB}*$ delocalization in the A-B :C Lewis structure, or equivalently, strong $n_A \rightarrow \sigma_{BC}*$ delocalization in the alternative A: B-C Lewis structure, leading to nearly equivalent NRT weightings of these structures ($w_{A\text{-}B\,:C} \cong w_{A:\,B\text{-}C}$; cf. Sec. B.8). The 3CHB search attempts to locate such A:-B-:C triads and to identify the participating NHOs and NBOs in the framework of the parent A-B :C Lewis structure. While 3-c, 4-e hyperbonding is a somewhat unusual feature of main-group compounds, it is a ubiquitous feature of transition metal bonding, as illustrated in the W(CO)$_5$ example below.

An estimate of the %A-B vs. %B-C character of the resonance hybrid (1) can be obtained from the approximate inverse relationship to relative occupancies of $\sigma_{AB}*$, $\sigma_{BC}*$ antibond NBOs in the respective Lewis structures, viz.,

(2)   %A-B / %B-C $\cong$ occ($\sigma_{BC}*$) / occ($\sigma_{AB}*$)

The $\sigma_{BC}*$ occupancy can in turn be estimated from the eigenvalues of the 2x2 density matrix in the basis of h_B, h_C NHOs. [Because these NHOs belong to the

"wrong" (A-B :C) resonance structure, the estimates of occ(σ_{BC}*) and %A-B vs. %B-C are only qualitatively correct; however, these approximations allow the hyperbonds to be efficiently recognized and characterized in terms of a *single* parent NBO Lewis structure, bypassing alternative $CHOOSE structures or full NRT search.]

The total occupancy of the A:-B-:C resonance triad (i.e., of the occupied $\omega_{AB:C}$, $\omega_{A:BC}$ hyperbonds, or of the interacting h_A, h_B, h_C valence NHOs) can be estimated by adding the delocalized σ_{AB}* occupancy to the localized n_C, σ_{AB} occupancies of the nominal A-B :C Lewis structure,

(3)   occ(A:-B-:C) $\cong$ occ(n_C) + occ(σ_{AB}) + occ(σ_{AB}*)

With the approximations noted above, the A:-B-:C hyperbonds can be characterized in terms of NHOs (h_A, h_B, h_C) and NBOs (σ_{AB}, n_C) of only the A-B :C parent NBO Lewis structure.

In principle, the resonance hybrid (1) could exhibit a continous range of weightings, and thus continuously variable %A-B vs. %B-C values in (2). By default, the 3CHB search flags as a hyperbond only those (A,B,C) triads in which the apparent %B-C weighting is at least half that of %A-B, i.e.,

(4)   %B-C > 33%

Although this numerical cut-off is rather arbitrary, it corresponds approximately to the limit where A-B :C and A: B-C must both be considered as NRT "reference" structures (Sec. B.8). Threshold (4) therefore corresponds to the onset of pronounced chemical effects that signal a uniquely distinctive "hyperbond" element of the skeletal bonding framework.

B.16. 3-CENTER, 4-ELECTRON HYPERBOND SEARCH

B.16.2 Sample Output

Let us illustrate 3CHB output for the model $W(CO)_5$ transition metal complex with Gaussian input file

---

```
#b3lyp/lanl2dz pop=nboread scf=qc scfcyc=200

W(CO)5, E=-634.4598757

0 1
    W1     .000000     .000000     .244387
    C2     .000000    2.041935     .272300
    O3     .000000    3.221160     .270578
    C4    2.041935     .000000     .272300
    O5    3.221160     .000000     .270578
    C6     .000000     .000000   -1.698425
    O7     .000000     .000000   -2.885976
    C8     .000000   -2.041935     .272300
    O9     .000000   -3.221160     .270578
    C10  -2.041935     .000000     .272300
    O11  -3.221160     .000000     .270578

$nbo file=w_co5 $end
```

---

corresponding to the C_{4v} geometry and atom numbering shown below:
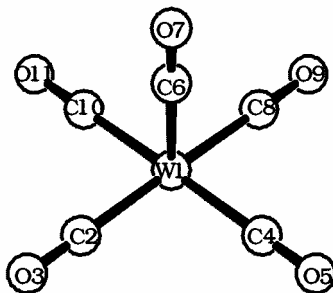
The default NBO search leads to three molecular units $[W(CO)_3 + 2\ CO]$, corresponding to three coordinate covalent W-C bonds (carbon atoms C_2, C_4, C_6) and two detached CO ligands (carbon atoms C_8, C_{10}). The 3CHB search leads to the output shown below:

```
3-Center, 4-Electron A:-B-:C Hyperbonds (A-B :C <=> A: B-C)
          [threshold for detection: 33.3%]

                                      NBOs         3-center hybrids
                                   -------------   ----------------
      Hyperbond A:-B-:C   %A-B/%B-C   occ    BD(A-B) LP(C)  h(A)  h(B)  h(C)
      ------------------  ---------  ------  ------- -----  ----  ----  ----
 1.  C  4:- W  1-: C 10  51.4/48.6  3.9710     25     23     25    26    23
 2.  C  8:- W  1-: C  2  51.4/48.6  3.9709     27     18     29    30    18
```

As shown in the output, two hyperbonds (C_4:-W_1-:C_{10} and C_2:-W_1-:C_8) were discovered, each with occupancy $3.971e$ and essentially equivalent weighting of C: W-C and C-W :C resonance forms. [The slight deviation from the actual 50/50 mixture is due to the slight bias of the NHOs and NBOs toward their own parent Lewis structure.] For the first hyperbond, the NBOs 25 (σ_{CW}) and 23 (n_C) are composed of NHOs 25, 26 and 23, which have approximate hybrid compositions

$$(sp^{0.5})_{C4}\text{-}(sd^{2.0})_{W1}\text{-}(sp^{0.5})_{C10}$$
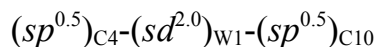
As also found in other segments of the NBO analysis, the low occupancy of n_C ($1.56e$), high occupancy of σ_{WC}* ($0.45e$), and large estimated n_C-σ_{WC}* 2nd-order interaction energy (274 kcal/mol) are all consistent with strong C:-W-:C hyperbond character.

B.17. NBCP: NATURAL BOND CRITICAL POINT ANALYSIS

Reference: F. Weinhold, *J. Comput. Chem.* (2012)

B.17.1 Introduction to Natural Bond Critical Point Analysis

The bond path (BP) and bond critical point (BCP) concepts are associated with topological analysis of electron density $\rho(\mathbf{r})$, as formulated in the "quantum theory of atoms in molecules" (QTAIM) theory of Bader and coworkers [R. F. W. Bader, *Atoms in Molecules: A Quantum Theory* (Oxford U. Press, London, 1990)]. In this approach, the gradient vector ($\nabla\rho(\mathbf{r})$) and Laplacian ($\nabla^2\rho(\mathbf{r})$) of $\rho(\mathbf{r})$ provide topological "curvature" descriptors of density at each spatial position $\mathbf{r}$, allowing one to locate the nuclear peaks $\mathbf{r}_A$, $\mathbf{r}_B$ and connecting ridge lines that may lead to a continuous "bond path" $BP_{AB}(\mathbf{r})$ between atoms A and B. In general, $BP_{AB}(\mathbf{r})$ is expected to descend steeply from each nucleus toward the unique intermediate stationary point BCP_{AB} that satisfies the characteristic "critical point" requirements of $(3,-1)$ saddle-type topology: (i) vanishing gradient, $\nabla\rho(\mathbf{r})|_{BCP} = 0$, and (ii) proper curvature characteristics (one positive and two negative eigenvalues) of the Hessian matrix $(\mathbf{H})_{ij} = (\partial^2\rho/\partial\mathbf{r}_i\partial\mathbf{r}_j)_{BCP}$, $(i, j = 1\text{-}3)$.

Because both gradient and Laplacian are linear operators, their action on $\rho(\mathbf{r})$ can be decomposed unambiguously into distinct orbital contributions. In terms of delocalized MOs $\{\varphi_i\}$, semi-localized NLMOs $\{^{sl}\Omega_i\}$, localized NBOs $\{\Omega_i\}$, or atomic NAOs $\{\Theta_i^{(A)}\}$, $\rho(\mathbf{r})$ can be equivalently decomposed as

(1a) $\rho(\mathbf{r}) = \sum_i n_i^{(MO)} |\varphi_i(\mathbf{r})|^2$

(1b) $\rho(\mathbf{r}) = \sum_i n_i^{(NLMO)} |^{sl}\Omega_i(\mathbf{r})|^2$

(1c) $\rho(\mathbf{r}) = \sum_i n_i^{(NBO)} |\Omega_i(\mathbf{r})|^2 + \sum_{j\neq i} (\gamma^{(NBO)})_{ij}\Omega_i(\mathbf{r})\Omega_j(\mathbf{r})$

(1d) $\rho(\mathbf{r}) = \sum_i n_i^{(NAO)} |\Theta_i^{(A)}(\mathbf{r})|^2 + \sum_{j\neq i} (\gamma^{(NAO)})_{ij}\Theta_i^{(A)}(\mathbf{r})\Theta_j^{(A)}(\mathbf{r})$

where each diagonal MO or NLMO orbital occupancy $n_i^{(MO)} = n_i^{(NLMO)} = 1$ or 2 for open- or closed-shell species, respectively, and $(\gamma^{(basis)})_{ij}$ denotes an off-diagonal coupling element of the 1-particle density matrix in the non-diagonal NBO or NAO basis.

The conventional BP_{AB} and BCP_{AB} descriptors, as determined from total density $\rho(\mathbf{r})$, can be compared with the corresponding "natural" bond path

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(NBP_{AB}) and bond critical point ($NBCP_{AB}$) as obtained from the *partial* density $\rho_{AB}^{(NAO)}(\mathbf{r})$ of contributions from idealized "natural atoms" A and B,

(2) $\quad \rho_{AB}^{(NAO)}(\mathbf{r}) = \rho_A^{(NAO)}(\mathbf{r}) + \rho_B^{(NAO)}(\mathbf{r})$

Consistency (or inconsistency) between BCP and NBCP properties can then be taken as a measure of how accurately the NAO-based formulation of "natural atoms in molecules" (NAIM) leads to topological features that are consistent with those actually found in the total electron density.

Each NAIM-based "natural atomic density" $\rho_A^{(NAO)}(\mathbf{r})$ in Eq. (2) arises from the NAOs $\{\Theta_i^{(A)}\}$ of a particular atom A,

(3) $\quad \rho_A^{(NAO)}(\mathbf{r}) = \sum_i n_i^{(NAO)} |\Theta_i^{(A)}(\mathbf{r})|^2 + \sum_{j\neq i} (\gamma^{(NAO)})_{ij}\Theta_i^{(A)}(\mathbf{r})\Theta_j^{(A)}(\mathbf{r})$

Consistent with general NPA properties, the integrated $\rho_A^{(NAO)}(\mathbf{r})$ densities (total NPA populations) for each atom sum properly to the total number of electrons (N) of the system,

(4) $\quad N = \int\rho(\mathbf{r})\,d\mathbf{r} = \sum_A \int\rho_A^{(NAO)}(\mathbf{r})\,d\mathbf{r}$

The NAIM-based partitioning (4) of total electron density therefore serves as a useful alternative to the virial-based spatial partitioning that underlies the conventional QTAIM definition of "atoms in molecules".

Numerical evaluation of the idealized $NBCP_{AB}$ from idealized $\rho_{AB}^{(NAO)}(\mathbf{r})$ proceeds in exact analogy to corresponding evaluation of conventional BCP_{AB} from total $\rho(\mathbf{r})$. The differences (if any) between BCP_{AB} vs. $NBCP_{AB}$ location, density, and Laplacian density give a quantitative measure of deviations from a simple picture of localized natural atom contributions, reflecting "spill-over" density from atomic centers other than A and B. Such BCP vs. NBCP differences are tabulated for each atom pair in the first section of NBCP output to illustrate the high accuracy of the alternative NAIM-based topological model of electron density.

In the second section of NBCP output, the electron density and Laplacian density at each BCP are analyzed in terms of individual orbital contributions (1a-c) of NBO, NLMO, or MO type. In the simplest NAIM picture, each BCP arises essentially from a *single* localized NBO or NLMO, or if multiply bonded, from the summed bond-type NBO/NLMO contributions between the same two atoms. Absolute and percentage differences of BCP properties from the idealized NAIM limit provide an alternative measure of resonance or spill-

over effects (strictly absent in corresponding NBCP descriptors) that may strongly affect the chemical interpretation of BCP descriptors. If MO-based analysis of BCP properties is selected, one may also employ the results of CMO analysis (Sec. B.13) to anticipate how a *single* dominant NBO/NLMO contribution may be portrayed as a confusing mixture of delocalized contributions in conventional MO framework.

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B.17.2 NBCP Keyword Usage

The NBCP keyword is implemented for all ESS host programs and stand-alone GenNBO configurations.

Basic NBCP analysis is requested by simply including the "NBCP" keyword in the $NBO keylist. A sample Gaussian input deck to request default NBCP analysis for formamide (B3LYP/6-311++G** level) is shown below:

```
#b3lyp/6-311++g** pop=nboread

Formamide...b3lyp/6-311++g**

0 1
N    -0.938183    -0.566210     0.000000
C     0.000000     0.419629     0.000000
O     1.197940     0.237612     0.000000
H    -0.643765    -1.531541     0.000000
H    -1.922100    -0.353445     0.000000
H    -0.450374     1.429785     0.000000

$nbo file=h2ncho nbcp $end
```

This produces the basic table comparing conventional BCP and localized NBCP topological descriptors, as well as a second table showing individual NBO contributions to each BCP. The NAIM description makes no provision for spatial dissection of $\rho(\mathbf{r})$ into the virial-based "atomic basins" of QTAIM theory, nor is it restricted to equilibrium geometries in which the virial theorem is satisfied.

[It should be noted that computed entries of NBCP output tables are obtained by finite-difference rather than analytic differentiation procedures. Particularly for the case of Laplacian density, the numerical accuracy may not extend to the apparent precision (±0.0001e) of printed output, which attempts to display the small BCP vs. NBCP differences near the limits of machine accuracy.]

The basic NBCP keyword can be modified to specify alternative NLMO-based ("NBCP=NLMO") or MO-based ("NBCP=MO") analysis of BCP properties in the second table. In orbital-type density expansions based on NBOs, the non-diagonal coupling terms are gathered with neglected small diagonal terms as "others" in tabulated decompositions.

One can also append a bracket list of selected atom pairs to be specified for analysis of BCP/NBCP features, using a command of the form

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```
NBCP[=basis] ⟨IA1 IB1/IA2 IB2/.../IAn IBn⟩
```

to bypass the exhaustive search over all possible atom pairs of a large molecule. For example, the modified $NBO keylist

```
$nbo file=h2ncho nbcp=nlmo ⟨1 2/1 3/2 3⟩ $end
```

would request NLMO-based analysis of only the non-hydride (atoms 1-3: C, N, O) BCP features in the formamide example above.

Detailed information pertaining to the searches for BCP_{AB} and BP_{AB} descriptors is written to the output file on request ("NBCP=DETAIL").

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B.17.3 Additional NBCP_BP and NBCP_PT Keyword Options

One can also request additional details of bond-path coordinates by including the "NBCP_BP" keyword. This prints a summary of computed bond path coordinates and atomic composition to an external ".50" file. This keyword can also be used in the optional form "NBCP_BP[=nstep]" to alter the granularity of computed bond paths by specifying a chosen NSTEP parameter that determines the number of path-segments from A to B (default NSTEP=100). Thus, to specify more coarse-grained (faster) path searches of 20 steps between atoms, one could employ the keylist shown below:

```
$nbo file=h2ncho nbcp nbcp_bp=20 $end
```

A complete set of bond path coordinates for successful BCP searches will be found in the output file "h2ncho.50" (or corresponding name specified by the FILE keyword). Cartesian coordinates of each point on the A-B bond path are shown together with the NAIM-based percentage of density contributed by the atom at each terminus.

One can also employ the "NBCP_PT" keyword to analyze the density at arbitrary points of interest, as specified in bracket-list format. The general form of command is

```
NBCP_PT[=ibas] <x1 y1 z1/x2 y2 z2/.../xn yn zn>
```

where *ibas* = [NBO], NLMO, or MO is the basis set in which the density-point is analyzed. For example, to analyze the density at cartesian points (0.461, 0.115, 1.0) and (–0.680, 0.070, 1.0) in terms of NLMO contributions, the command would be

```
NBCP_PT=NLMO <-0.3454 0.0552 1.0/0.4098 0.3504 1.0>
```

In this manner, one can analyze the electron density at ring or cage critical points (RCP, CCP) or other points of interest that are not located by the NBCP program itself.

B.17. NBCP: NATURAL BOND CRITICAL POINT ANALYSIS

B.17.4 NBCP Sample Output

The first table of default NBCP output is shown below for the formamide input file of the previous section:

```
NATURAL BOND CRITICAL POINT (NBCP) ANALYSIS

[Topological (3,-1) bond critical points:
   BCP (total density); NBCP (NAO atomic densities)]

   Atoms           Rho    Lapl.    Laplacian curvatures       Coordinates
----------       ------- -------  ---------------------   ---------------------
N  1- C  2  BCP    0.3160 -0.8804  0.4236 -0.6219 -0.6821  -0.3454  0.0552  0.0000
            NBCP   0.3174 -0.6773  0.4670 -0.5328 -0.6115  -0.3659  0.0372  0.0000
                                                    [|R(BCP)-R(NBCP)|=  0.0273]
N  1- H  4  BCP    0.3372 -1.6447  0.8714 -1.2257 -1.2904  -0.7222 -1.2778  0.0000
            NBCP   0.3374 -1.5774  0.8786 -1.2184 -1.2376  -0.7212 -1.2759  0.0000
                                                    [|R(BCP)-R(NBCP)|=  0.0022]
N  1- H  5  BCP    0.3397 -1.6391  0.8779 -1.2239 -1.2930  -1.6608 -0.4087  0.0000
            NBCP   0.3399 -1.5958  0.8720 -1.2212 -1.2466  -1.6610 -0.4076  0.0000
                                                    [|R(BCP)-R(NBCP)|=  0.0011]
C  2- O  3  BCP    0.4124 -0.2192  1.8569 -1.0049 -1.0711   0.4098  0.3504  0.0000
            NBCP   0.4204 -0.1654  1.7289 -0.8546 -1.0396   0.4213  0.3461  0.0000
                                                    [|R(BCP)-R(NBCP)|=  0.0123]
C  2- H  6  BCP    0.2773 -0.9467  0.5480 -0.7382 -0.7565  -0.2965  1.0719  0.0000
            NBCP   0.2746 -0.8296  0.6229 -0.7220 -0.7305  -0.3000  1.0788  0.0000
                                                    [|R(BCP)-R(NBCP)|=  0.0078]
```

For each listed pair of atoms in the first column, the successive columns describe the density ("Rho"), Laplacian density ("Lapl."), the three Hessian eigenvalues ("Laplacian curvatures"), and the Cartesian position vector ("Coordinates") for the listed BCP and/or NBCP, with the spatial separation ("|R(BCP)-R(NBCP)|", in Å) listed below. As seen in the table, the five atom pairs exhibit BCP features that are generally in close proximity to an idealized NBCP (within 0.01-0.03Å in all cases). The BCP and NBCP are also found to have similar density (within 2% in all cases), and the corresponding Laplacian densities are also of similar magnitude and sign (but with significantly larger differences, ranging up to ca. 35%). Such close agreement of total $\rho(\mathbf{r}_{BCP})$ and idealized $\rho(\mathbf{r}_{NBCP})$ densities is rather typical, suggesting why NAO/NBO descriptors are often highly correlated with measures of chemical bonding interactions inferred from topological BCP densities (although corresponding correlations with Lagrangian densities are significantly weaker).

In the second portion of default NBCP output, the five BCP features are analyzed in terms of individual NBO contributions, as shown below:

```
NBO-based contributions to   5 bond critical points

BCP  1.  N  1- C  2: ( -0.3454,  0.0552,  0.0000)
-------------------------------------------------
  NBO   1.  N 1(cr)  : Rho = 0.0006 (  0.2%), LaplRho = -0.0026
  NBO   2.  C 2(cr)  : Rho = 0.0007 (  0.2%), LaplRho =  0.2428
  NBO   6.  O 3(lp)  : Rho = 0.0027 (  0.8%), LaplRho = -0.0220
```

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```
   NBO    7.   N 1- C 2 : Rho = 0.3033 ( 96.0%), LaplRho = -1.6882
   NBO    8.   N 1- H 4 : Rho = 0.0038 (  1.2%), LaplRho = -0.0312
   NBO    9.   N 1- H 5 : Rho = 0.0043 (  1.3%), LaplRho = -0.0344
   NBO   12.   C 2- H 6 : Rho = 0.0003 (  0.1%), LaplRho =  0.1373
   NBO   13.   N 1- C 2*: Rho = 0.0084 (  2.7%), LaplRho = -0.0185
   NBO   36.   C 2(ry)  : Rho = 0.0004 (  0.1%), LaplRho = -0.0008
   NBO   37.   C 2(ry)  : Rho = 0.0014 (  0.4%), LaplRho = -0.0226
                 [others =-0.0099 ( -3.1%)               0.5598]
                     total 0.3160                       -0.8804

 BCP  2.  N  1- H  4: ( -0.7222, -1.2778,  0.0000)
 -------------------------------------------------
   NBO    1.   N 1(cr)  : Rho = 0.0006 (  0.2%), LaplRho = -0.0041
   NBO    8.   N 1- H 4 : Rho = 0.3352 ( 99.4%), LaplRho = -1.8261
   NBO    9.   N 1- H 5 : Rho = 0.0005 (  0.1%), LaplRho =  0.0302
   NBO   12.   C 2- H 6 : Rho = 0.0002 (  0.1%), LaplRho =  0.0031
   NBO   14.   N 1- H 4*: Rho = 0.0006 (  0.2%), LaplRho =  0.0218
   NBO   70.   H 4(ry)  : Rho = 0.0001 (  0.0%), LaplRho =  0.0005
                 [others = 0.0000 (  0.0%)               0.1300]
                     total 0.3372                       -1.6447

 BCP  3.  N  1- H  5: ( -1.6608, -0.4087,  0.0000)
 -------------------------------------------------
   NBO    1.   N 1(cr)  : Rho = 0.0006 (  0.2%), LaplRho = -0.0043
   NBO    8.   N 1- H 4 : Rho = 0.0004 (  0.1%), LaplRho =  0.0335
   NBO    9.   N 1- H 5 : Rho = 0.3378 ( 99.4%), LaplRho = -1.8298
   NBO   11.   C 2- O 3 : Rho = 0.0001 (  0.0%), LaplRho =  0.0005
   NBO   12.   C 2- H 6 : Rho = 0.0002 (  0.1%), LaplRho =  0.0003
   NBO   15.   N 1- H 5*: Rho = 0.0004 (  0.1%), LaplRho =  0.0152
                 [others = 0.0003 (  0.1%)               0.1455]
                     total 0.3397                       -1.6391

 BCP  4.  C  2- O  3: (  0.4098,  0.3504,  0.0000)
 -------------------------------------------------
   NBO    2.   C 2(cr)  : Rho = 0.0107 (  2.6%), LaplRho =  1.6384
   NBO    3.   O 3(cr)  : Rho = 0.0006 (  0.2%), LaplRho = -0.0010
   NBO    5.   O 3(lp)  : Rho = 0.0175 (  4.2%), LaplRho = -0.2193
   NBO    7.   N 1- C 2 : Rho = 0.0002 (  0.0%), LaplRho =  0.1634
   NBO    8.   N 1- H 4 : Rho = 0.0010 (  0.2%), LaplRho = -0.0036
   NBO    9.   N 1- H 5 : Rho = 0.0012 (  0.3%), LaplRho = -0.0121
   NBO   11.   C 2- O 3 : Rho = 0.3674 ( 89.1%), LaplRho = -2.7680
   NBO   12.   C 2- H 6 : Rho = 0.0018 (  0.4%), LaplRho =  0.2205
   NBO   13.   N 1- C 2*: Rho = 0.0003 (  0.1%), LaplRho =  0.0285
   NBO   17.   C 2- O 3*: Rho = 0.0012 (  0.3%), LaplRho = -0.0120
   NBO   18.   C 2- H 6*: Rho = 0.0003 (  0.1%), LaplRho =  0.0222
   NBO   36.   C 2(ry)  : Rho = 0.0017 (  0.4%), LaplRho =  0.0019
   NBO   37.   C 2(ry)  : Rho = 0.0002 (  0.0%), LaplRho =  0.0007
                 [others = 0.0082 (  2.0%)               0.7212]
                     total 0.4124                       -0.2192

 BCP  5.  C  2- H  6: ( -0.2965,  1.0719,  0.0000)
 -------------------------------------------------
   NBO    2.   C 2(cr)  : Rho = 0.0003 (  0.1%), LaplRho = -0.0037
   NBO    6.   O 3(lp)  : Rho = 0.0009 (  0.3%), LaplRho = -0.0016
   NBO    8.   N 1- H 4 : Rho = 0.0001 (  0.0%), LaplRho =  0.0019
   NBO    9.   N 1- H 5 : Rho = 0.0003 (  0.1%), LaplRho =  0.0005
   NBO   12.   C 2- H 6 : Rho = 0.2736 ( 98.7%), LaplRho = -1.0297
                 [others = 0.0020 (  0.7%)               0.0859]
                     total 0.2773                       -0.9467
```

For each BCP, the table displays an exhaustive list of all orbitals contributing at least 0.0001e to $\rho(\mathbf{r}_{NBCP})$. Nevertheless, the table shows that the hydride BCP densities derive ca. 99% from the *single* NBO that is "expected" to link the atoms in elementary Lewis structure representation. The resonance-delocalized C-N (BCP 1) and C-O (BCP 4) BCP densities exhibit somewhat weaker contributions from the dominant "parent" NBOs (96% and 89%, respectively).

However, both the reduced percentages and the unusually large NBO contributions from off-diagonal couplings (included in "others") are characteristic signatures of the important *resonance* delocalization in these bonds, as expected on chemical grounds.

For comparison, we show the corresponding NLMO-based decompositions (as obtained from "NBCP=NLMO" keyword):

```
NLMO-based contributions to   5 bond critical points

BCP  1.  N  1- C  2: ( -0.3454,  0.0552,  0.0000)
-------------------------------------------------
 NLMO   1.  N 1(cr)  : Rho = 0.0009 (  0.3%), LaplRho = -0.0056
 NLMO   2.  C 2(cr)  : Rho = 0.0007 (  0.2%), LaplRho =  0.2481
 NLMO   7.  N 1- C 2 : Rho = 0.3054 ( 96.6%), LaplRho = -1.7121
 NLMO   8.  N 1- H 4 : Rho = 0.0042 (  1.3%), LaplRho = -0.0147
 NLMO   9.  N 1- H 5 : Rho = 0.0045 (  1.4%), LaplRho = -0.0189
 NLMO  11.  C 2- O 3 : Rho = 0.0003 (  0.1%), LaplRho =  0.0697
               [others = 0.0001 (  0.0%)            0.5530]
                  total 0.3160                     -0.8804

BCP  2.  N  1- H  4: ( -0.7222, -1.2778,  0.0000)
-------------------------------------------------
 NLMO   1.  N 1(cr)  : Rho = 0.0009 (  0.3%), LaplRho = -0.0084
 NLMO   8.  N 1- H 4 : Rho = 0.3347 ( 99.3%), LaplRho = -1.8245
 NLMO   9.  N 1- H 5 : Rho = 0.0007 (  0.2%), LaplRho =  0.0329
 NLMO  12.  C 2- H 6 : Rho = 0.0007 (  0.2%), LaplRho = -0.0024
               [others = 0.0001 (  0.0%)            0.1577]
                  total 0.3372                     -1.6447

BCP  3.  N  1- H  5: ( -1.6608, -0.4087,  0.0000)
-------------------------------------------------
 NLMO   1.  N 1(cr)  : Rho = 0.0009 (  0.3%), LaplRho = -0.0087
 NLMO   6.  O 3(lp)  : Rho = 0.0004 (  0.1%), LaplRho =  0.0015
 NLMO   8.  N 1- H 4 : Rho = 0.0006 (  0.2%), LaplRho =  0.0374
 NLMO   9.  N 1- H 5 : Rho = 0.3373 ( 99.3%), LaplRho = -1.8288
 NLMO  11.  C 2- O 3 : Rho = 0.0002 (  0.1%), LaplRho = -0.0008
 NLMO  12.  C 2- H 6 : Rho = 0.0003 (  0.1%), LaplRho = -0.0027
               [others = 0.0000 (  0.0%)            0.1630]
                  total 0.3397                     -1.6391

BCP  4.  C  2- O  3: (  0.4098,  0.3504,  0.0000)
-------------------------------------------------
 NLMO   2.  C 2(cr)  : Rho = 0.0103 (  2.5%), LaplRho =  1.6420
 NLMO   3.  O 3(cr)  : Rho = 0.0011 (  0.3%), LaplRho = -0.0066
 NLMO   5.  O 3(lp)  : Rho = 0.0284 (  6.9%), LaplRho = -0.3477
 NLMO   7.  N 1- C 2 : Rho = 0.0007 (  0.2%), LaplRho =  0.1461
 NLMO  11.  C 2- O 3 : Rho = 0.3697 ( 89.6%), LaplRho = -2.7716
 NLMO  12.  C 2- H 6 : Rho = 0.0021 (  0.5%), LaplRho =  0.1951
               [others = 0.0001 (  0.0%)            0.9234]
                  total 0.4124                     -0.2192

BCP  5.  C  2- H  6: ( -0.2965,  1.0719,  0.0000)
-------------------------------------------------
 NLMO   2.  C 2(cr)  : Rho = 0.0004 (  0.1%), LaplRho = -0.0043
 NLMO   6.  O 3(lp)  : Rho = 0.0009 (  0.3%), LaplRho =  0.0151
 NLMO   9.  N 1- H 5 : Rho = 0.0003 (  0.1%), LaplRho = -0.0020
 NLMO  12.  C 2- H 6 : Rho = 0.2756 ( 99.4%), LaplRho = -1.0525
               [others = 0.0001 (  0.0%)            0.0970]
                  total 0.2773                     -0.9467
```

For NLMOs (as for MOs), the individual orbital contributions are strictly non-negative and additive, with no off-diagonal couplings to complicate orbital

analysis of $\rho(\mathbf{r}_{BCP})$. Note that the Laplacian density $\nabla^2\rho(\mathbf{r}_{BCP})$ ("LaplRho") is much more sensitive than $\rho(\mathbf{r}_{BCP})$ to distracting spill-over contributions from nearby NBOs or NLMOs of little chemical interest [see, e.g., the large contribution of the C core orbital to $\nabla^2\rho(\mathbf{r}_{BCP})$ in BCP 4]. These results are typical of strong correlations that are generally found between NBO and $\rho(\mathbf{r}_{BCP})$ density descriptors, as well as the weaker NBO correlations with $\nabla^2\rho(\mathbf{r}_{BCP})$ Laplacian descriptors. In the latter context, NBCP output can be helpful in identifying the sources of unexpected variability in Laplacian $\nabla^2\rho(\mathbf{r}_{BCP})$ values, which carry the "image" of the parent NBO in less clear-cut form.

Next, we show sample output from the "NBCP_BP=20" command for the NC bond path (atoms 1, 2), as printed to the "h2ncho.50" file:

```
Atoms   1   2 (nstep =   20)
step lambda      x         y         z        rho       %-a       %-b     %-other
  0  0.000 (  -0.9382,  -0.5662,   0.0000) 193.8621e, 99.79%,   0.11%,   0.10%
  1  0.089 (  -0.8541,  -0.4781,   0.0000)   9.0332e, 99.43%,   0.05%,   0.52%
  2  0.135 (  -0.8113,  -0.4332,   0.0000)   2.2687e, 98.23%,   0.85%,   0.92%
  3  0.181 (  -0.7685,  -0.3884,   0.0000)   0.9204e, 96.65%,   2.33%,   1.02%
  4  0.226 (  -0.7257,  -0.3436,   0.0000)   0.6406e, 96.61%,   2.62%,   0.78%
  5  0.272 (  -0.6828,  -0.2988,   0.0000)   0.5532e, 97.52%,   1.92%,   0.56%
  6  0.317 (  -0.6399,  -0.2540,   0.0000)   0.4971e, 98.35%,   1.20%,   0.44%
  7  0.363 (  -0.5970,  -0.2092,   0.0000)   0.4469e, 97.88%,   1.73%,   0.39%
  8  0.408 (  -0.5542,  -0.1644,   0.0000)   0.4027e, 93.65%,   5.94%,   0.41%
  9  0.454 (  -0.5114,  -0.1196,   0.0000)   0.3674e, 81.61%,  17.83%,   0.56%
 10  0.500 (  -0.4685,  -0.0747,   0.0000)   0.3421e, 59.54%,  39.59%,   0.87%
 11  0.545 (  -0.4258,  -0.0298,   0.0000)   0.3262e, 33.87%,  64.90%,   1.23%
 12  0.591 (  -0.3831,   0.0152,   0.0000)   0.3180e, 15.07%,  83.44%,   1.49%
 13  0.631 (  -0.3454,   0.0552,   0.0000)   0.3158e,  6.41%,  91.96%,   1.63%
 14  0.677 (  -0.3030,   0.1005,   0.0000)   0.3197e,  2.66%,  95.59%,   1.75%
 15  0.722 (  -0.2606,   0.1457,   0.0000)   0.3402e,  1.83%,  96.25%,   1.91%
 16  0.768 (  -0.2181,   0.1908,   0.0000)   0.4223e,  1.68%,  96.25%,   2.08%
 17  0.814 (  -0.1747,   0.2365,   0.0000)   0.7628e,  1.01%,  97.09%,   1.90%
 18  0.860 (  -0.1320,   0.2814,   0.0000)   2.1223e,  0.24%,  98.52%,   1.23%
 19  0.905 (  -0.0892,   0.3262,   0.0000)   7.4001e,  0.01%,  99.36%,   0.63%
 20  1.000 (   0.0000,   0.4196,   0.0000) 119.7618e,  0.10%,  99.82%,   0.08%
```

Each step of the bond path is shown with the associated fractional progress parameter ("lambda"), cartesian coordinates (x,y,z), and the NAO-based percentage contribution from each "natural atom" (terminal atoms A. B or "others") along the path. As seen, the N-C BCP is at step 13 ($\lambda_{BCP} = 0.631$), with 6.41% contribution from NAOs on N, 91.96% from those on C, and 1.63% from other atoms. The calculated λ_{BCP} is in sensible agreement with the "Perrin estimate" that can be directly inferred from the σ_{CN} NBO polarization coefficients ($c_C = 0.6158$, $c_N = 0.7879$), viz.,

$$\lambda_{BCP} \approx |c_N|^2/(|c_C|^2 + |c_N|^2) = 0.621$$

in accordance with the expected dominant contribution of the single σ_{CN} NBCP.

B.17. NBCP: NATURAL BOND CRITICAL POINT ANALYSIS

Finally, we show sample output from the illustrative NBCP_PT command for two density points, as given in the previous section. The chosen points, (-0.3454, 0.0552, 1.0) and (0.4098, 0.3504, 1.0), correspond to the NC and CO BCPs, respectively, but are placed 1.0Å above the molecular xy plane to sample possible π-type as well as σ-type contributions to electron density.

```
NLMO-based contributions to   2 density points

 Density point  1: ( -0.3454,  0.0552,  1.0000)
     ---------------------------------------------
                             Rho                GradRho            LaplRho
                       --------------    ----------------------    -------
    NLMO    4.  N 1(lp)  : 0.0125 ( 46.8%)  -0.0085 -0.0070 -0.0186   0.0141
    NLMO    7.  N 1- C 2 : 0.0082 ( 31.0%)  -0.0030 -0.0032 -0.0238   0.0448
    NLMO   10.  C 2- O 3 : 0.0050 ( 18.7%)   0.0082  0.0052 -0.0079   0.0144
    NLMO   11.  C 2- O 3 : 0.0002 (  0.6%)   0.0009  0.0001 -0.0003   0.0040
    NLMO   12.  C 2- H 6 : 0.0005 (  1.8%)  -0.0001  0.0024 -0.0006   0.0075
               [others = 0.0003 (  1.0%)    0.0007  0.0003 -0.0007  -1.0313]
                     total 0.0266          -0.0018 -0.0022 -0.0521  -0.9464

 Density point  2: (  0.4098,  0.3504,  1.0000)
     ---------------------------------------------
                             Rho                GradRho            LaplRho
                       --------------    ----------------------    -------
    NLMO    4.  N 1(lp)  : 0.0007 (  2.5%)  -0.0032 -0.0006 -0.0009   0.0080
    NLMO    5.  O 3(lp)  : 0.0002 (  0.6%)  -0.0008  0.0001 -0.0008   0.0033
    NLMO    7.  N 1- C 2 : 0.0004 (  1.3%)  -0.0014 -0.0010 -0.0008   0.0058
    NLMO   10.  C 2- O 3 : 0.0206 ( 71.5%)   0.0032  0.0005 -0.0361   0.0194
    NLMO   11.  C 2- O 3 : 0.0061 ( 21.3%)   0.0033 -0.0004 -0.0195   0.0406
    NLMO   12.  C 2- H 6 : 0.0007 (  2.4%)  -0.0017  0.0022 -0.0010   0.0075
               [others = 0.0001 (  0.5%)   -0.0002 -0.0004 -0.0003  -1.0309]
                     total 0.0288          -0.0008  0.0005 -0.0593  -0.9464
```

In this example, the two spatial points are found to have distinctly non-zero values of the $\nabla\rho(\mathbf{r})$ ("GradRho") gradient vector , but quite similar values of $\rho(\mathbf{r})$ ("Rho": 0.0266 vs. 0.0288) and Laplacian $\nabla^2\rho(\mathbf{r})$ ("LaplRho": both -0.9464). As expected, the second point draws largest $\rho(\mathbf{r})$ contribution from π_{CO} (NLMO 10) and the first point from n_N (NLMO 4), consistent with the strong amide resonance delocalization that is expected to spread appreciable π-character into the NC bonding region.

B.18. NCE: NATURAL COULOMB ELECTROSTATICS ANALYSIS

Reference: F. Weinhold and C. R. Landis, *Discovering Chemistry with Natural Bond Orbitals* (Wiley-VCH, Hoboken NJ, 2012), p. 145ff.

B.18.1 Introduction to Natural Coulombic Energy Analysis

A simplified picture of long-range electrostatic interactions can be based on the concept of effective atomic point charges Q_A that interact according to the classical law of Coulomb electrostatics,

(1) $E_{Coulomb} = \Sigma_{A,B} \, Q_A \, Q_B / R_{AB}$

where R_{AB} is the interatomic distance between nuclei A, B. The classical Coulomb formula (1) is highly questionable in the short-range domain of quantal exchange interactions. Nevertheless, Eq. (1) may provide a useful estimate of "electrostatic effects" when R_{AB} separations sufficiently exceed the sum of atomic van der Waals radii. When Eq. (1) is evaluated with *natural* atomic charges, the formula defines what may be called the "Natural Coulomb Electrostatics" (E_{NCE}) potential energy for the species and geometry in question.

The "NCE" keyword provides the simple NPA-based evaluation of Coulomb electrostatic potential energy E_{NCE}. The variations of E_{NCE} with respect to geometry changes thereby provide simple estimates of "electrostatic" contributions to intra- or intermolecular interaction energy, which may be compared with independent estimates of "steric" and "donor-acceptor" contributions. Such simplified estimates complement the more sophisticated dissection of interaction energy in "energy decomposition analysis" methods such as NEDA.

An issue in such energy decompositions is the *coupling* between localized Lewis (L) and delocalized non-Lewis (NL) contributions to perceived "classical type" electrostatic or steric components. For E_{NCE}, one can quantitatively assess such L/NL coupling by comparing the actual NPA charge Q_A with that ($Q_A^{(L)}$) for the ideally localized "natural Lewis structure" (NLS), in which each L-type NBO is constrained to exact double-occupancy. In this manner, one can separate the L-type charge distribution of an idealized Lewis structural model from the NL-type "charge transfer" delocalizations of non-classical origin. The NCE analysis module displays such L/NL contributions to E_{NCE} for each atom pair, providing a direct estimate of non-classical CT corrections to Coulomb electrostatics.

B.18. NCE: NATURAL COULOMB ELECTROSTATICS ANALYSIS

The NL-induced charge shifts are often found to be leading contributors to chemically important "electrostatic effects", providing an important quantal correction to quasi-classical interpretation of total E_{NCE}. For open shells, an additional spin-charge NCE table shows the distinct α-NCE and β-NCE contributions of each spin set, again emphasizing the limitations of naive classical interpretations.

B.18.2 NCE Keyword Usage and Sample Output

The NCE keyword is implemented for all ESS host programs and stand-alone GenNBO configurations.

NCE analysis is requested by simply including the "NCE" keyword in the $NBO keylist. A sample Gaussian input deck to request NCE analysis for formamide (RHF/3-21G level) is shown below:

```
#RHF/3-21G POP=NBORead

Formamide

0 1
H       -1.913380      -0.349570       0.000000
H       -0.655700      -1.514100       0.000000
N       -0.940200      -0.557500       0.000000
C        0.000000       0.415950       0.000000
O        1.198300       0.232820       0.000000
H       -0.435920       1.407901       0.000000

$NBO nce $END
```

This produces the first NCE output table comparing L and NL contributions to total NPA charge for each atom:

```
NATURAL COULOMB ELECTROSTATICS (NCE):

  Lewis(L) and non-Lewis(NL) contributions to NPA atomic charge
  and Coulomb potential energy

                      atomic charge
                 ----------------------------
   atom   unit       L        NL       total
   ----   ----    --------  --------  --------
   H  1     1      0.41730  -0.00287   0.41443
   H  2     1      0.42685  -0.00681   0.42004
   N  3     1     -1.12743   0.18029  -0.94714
   C  4     1      0.81557  -0.21133   0.60423
   O  5     1     -0.70603   0.06755  -0.63848
   H  6     1      0.17375  -0.02683   0.14691
 -------------------------------------------
 Total unit  1     0.00000   0.00000   0.00000
 -------------------------------------------
 Total species    0.00000   0.00000   0.00000
```

The second output table then evaluates L and NL contributions to total Coulomb potential energy $E_{Coulomb}$ both within and between units:

B.18. NCE: NATURAL COULOMB ELECTROSTATICS ANALYSIS

```
                  NCE Potential Energy (au)
                  ---------------------------
        unit  unit     L        NL       total
        ----  ----  --------  --------  --------
 within  1           -0.79462   0.21469  -0.57993
-----------------------------------------------
              Total  -0.79462   0.21469  -0.57993
```

B.19. NCU: NATURAL CLUSTER UNIT ANALYSIS

B.19.1 Introduction to Natural Cluster Unit Analysis

For conceptual purposes, one often envisions the sequential aggregation of particulate matter into ever-larger "building blocks" of macroscopic phases, viz.,

(1)   (elementary particles →) atoms → molecules
         → supramolecular clusters → ... → "condensation"

From a chemistry perspective (assuming existence of nuclei and electrons), the focal step in (1) is formation of molecules from atoms, under the influence of quantum mechanical exchange-type forces. From a biochemical perspective, the focus is on H-bonding and other supramolecular clustering processes (often attributed to so-called "noncovalent forces") that are active in the domain of near-ambient terrestrial conditions. From a materials perspective, attention focuses on higher-order clustering processes that lead finally to the aggregated liquid and solid phases of the macroscopic world. Advances in each domain can be associated with successful identification and characterization of fundamental "units" or "building blocks" that underlie steps of sequence (1).

To address the broader aspects of sequence (1), we can envision a formal interaction parameter τ_{NCU} that varies *continuously* from the weakest interatomic forces (i.e., those characteristic of London dispersion and long-range Casimir-Polder interactions) to the powerful exchange-type forces of chemical bonding. Each range of τ_{NCU} values leads to characteristic "natural cluster units" (NCUs) that are intrinsic building blocks of that range. The NCU module determines the numerical τ_{NCU} transition values and associated NCU building blocks that characterize a chosen system of nuclei and electrons in specified nuclear geometry.

Mathematically, the τ_{NCU} interaction parameter can be expressed as the strength (matrix norm) of off-diagonal couplings between atomic blocks of the NAO density matrix, viz.,

(2) $\tau_{NCU}(A,B) = Tr\{D_A{}^*D_B\}^{1/2}$

where "Tr" denotes matrix trace and D_A, D_B are respective density matrix blocks for atoms A, B. Alternatively, the $\tau_{NCU}(A,B)$ value can be related to the square-root of the NAO-based Wiberg bond index (Sec. 6.5), which represents

B.19. NCU: NATURAL CLUSTER UNIT ANALYSIS

a type of "bond order" between atoms A, B. Conceptually, the τ_{NCU} coupling-strength parameter can also be pictured as an "effective temperature" that leads to complete atomic dissociation at sufficiently high values, or complete condensation at sufficiently low values, but with distinctive alternative NCU cluster patterns at characteristic τ_{NCU} transition values.

For a given interaction strength τ_{NCU}, each pair of atoms A, B is considered to form a connective "link" if and only if

$$(3) \quad \tau_{NCU} \leq \tau_{NCU}(A,B)$$

Each contiguously linked network of atoms identifies a distinct NCU for the chosen τ_{NCU} value, analogous to the usual identification of NBO-linked networks as "molecular units." In the appropriate range of τ_{CU} values, the NCU assignments will agree with NBO-based molecular unit assignments. However, alternative NCU patterns are generally found in other τ_{NCU} ranges.

For a chosen input system of nuclei and electrons, the NCU module displays the list of distinct τ_{NCU} transition values and associated NCU clustering patterns for all possible interaction strengths, $0 \leq \tau_{NCU} \leq 1$. As shown in Eq. (2), NCU analysis depends only NAO-based definitions of underlying constituent atoms, with no other dependence on NBO-based description of intramolecular or intermolecular interactions. Nevertheless, subsequent NBO analysis of individual NCU species and their mutual interactions may further illuminate the composite system initially selected for NCU study.

B.19. NCU: NATURAL CLUSTER UNIT ANALYSIS

B.19.2 NCU Sample Output

A simple illustration of NCU analysis can be given for the model water dimer (RHF/4-31G level), with Gaussian input file:

```
#RHF/4-31G POP=NBORead

Water dimer

0  1
O        0.699995      -1.217080       0.000000
H        1.280646      -1.217080      -0.759460
H        1.280646      -1.217080       0.759460
O       -0.740005       1.277073       0.000000
H       -1.664288       1.032867       0.000000
H       -0.262005       0.449153       0.000000

$NBO ncu $END
```

Corresponding output from the NCU module is shown below:

```
Natural Cluster Unit (NCU) Analysis:

 NCU        Unit        Unit
 thr       formula     charge  Atom list
----- --------------- ------ ------------------------------------------------
1.000  1. O           -0.924  O1
       2. H            0.477  H2
       3. H            0.477  H3
       4. O           -0.952  O4
       5. H            0.447  H5
       6. H            0.474  H6
----- --------------- ------ ------------------------------------------------
0.890  1. O           -0.924  O1
       2. H            0.477  H2
       3. H            0.477  H3
       4. HO          -0.505  O4,H5
       5. H            0.474  H6
----- --------------- ------ ------------------------------------------------
0.870  1. H2O          0.031  O1,H2,H3
       2. HO          -0.505  O4,H5
       3. H            0.474  H6
----- --------------- ------ ------------------------------------------------
0.850  1. H2O          0.031  O1,H2,H3
       2. H2O         -0.031  O4,H5,H6
----- --------------- ------ ------------------------------------------------
0.210  1. H4O2         0.000  O1,H2,H3,O4,H5,H6
----- --------------- ------ ------------------------------------------------
```

In this case, five distinct τ_{NCU} transition values and associated NCU aggregation regimes were found, with atomic constitution and net charge shown for each NCU unit. For $\tau_{NCU} = 0.210$ (and below), the full water dimer aggregate is found as the single NCU, with zero net charge. Up to $\tau_{NCU} =$

0.850, the NCU units are the usual monomer "molecular units" found in default NBO analysis, with the expected charge transfer (± 0.031) on each unit. At higher τ_{NCU} values up to 0.870, the bridging H_6 and residual O_4H_5 of the former Lewis acid (acceptor) monomer are recognized as a distinct NCU "ion pair" (with respective charges $+0.474$, -0.505). Further breakup of the remaining $O_1H_2H_3$ monomer leads to five NCU fragments (up to $\tau_{NCU} = 0.890$) and thereafter to final breakup of anionic O_4H_5 into mononuclear fragments (up to final $\tau_{NCU} = 1.000$).

B.20. PROP: GENERAL 1e PROPERTY ANALYSIS

Reference: Cf. DIPOLE analysis (Sec. B.6.3).

The PROP (property) keyword provides a powerful tool to perform NBO analysis of *any* 1e property that is available from the host ESS program (or input .47 file). Familiar examples of 1e properties include

- kinetic energy (PROP=KINETIC)
- nuclear-electron attraction (PROP=V)
- Fock or Kohn-Sham operator (PROP=F),
- dipole moment (PROP=DIPOLE)
- electron density (PROP=DM)

or any other property that depends solely on electron density. The above list includes properties that are generally computed by all host ESS programs and included in the .47 file, but many additional properties may be available from individual ESS hosts. If your ESS can calculate a property, the PROP keyword can perform its NBO analysis.

As indicated by examples given above, the PROP keyword must include an identifying label (id_label) of the chosen property

```
PROP=id_label
```

(e.g., PROP=KINETIC). The proper "id_label" is matched to .47 file input (e.g., $KINETIC keylist) or provided by the host ESS program through ESS/NBO message-passing protocol. Consult the ESS program documentation for available properties and labels from each host.

For any chosen property, the format of PROP output resembles that of DIPOLE or NJC output. The overall expectation value of the property is expressed as a sum of Lewis (L) and non-Lewis (NL) contributions, with subsidiary correlation correction for post-SCF methods.

The PROP keyword can be illustrated for the kinetic energy operator (PROP=KINETIC) of formamide (RHF/3-21G level), with input file

```
#RHF/3-21G POP=NBORead

RHF/3-21G for formamide (H2NCHO)

0 1
```

B.20. PROP: GENERAL 1e PROPERTY ANALYSIS

```
   H   -1.91338      -0.34957       0.00000
   H   -0.65570      -1.51410       0.00000
   N   -0.94020      -0.55750       0.00000
   C    0.00000       0.41595       0.00000
   O    1.19830       0.23282       0.00000
   H   -0.43592       1.40790       0.00000
```

```
$NBO prop=kinetic $END
```

The corresponding PROP output segment is shown below:

```
PROPerty Analysis for P = K   (all values in a.u.)

                 Lewis(L)                Non-Lewis(NL)      L + NL
        ================================ ======================= =========
            NBO              P(NBO)   NL   P(NL)  (%-NL)   P(NLMO)   e-corr
--------------------------------------------------------------------------
 1. CR ( 1) N  1             22.8091  24   0.0214 (  0.1)  22.8453   0.0000
                                      13   0.0208 (  0.1)
                                      22   0.0156 (  0.1)
                                     rem  -0.0216 ( -0.1)
 2. CR ( 1) C  2             16.4799  17  -0.0105 ( -0.1)  16.4996   0.0000
                                      25  -0.0103 ( -0.1)
                                      13   0.0084 (  0.1)
                                     rem   0.0322 (  0.2)
 3. CR ( 1) O  3             30.4278  23   0.0432 (  0.1)  30.4976   0.0000
                                      29   0.0181 (  0.1)
                                      17  -0.0166 ( -0.1)
                                     rem   0.0250 (  0.1)
 4. LP ( 1) N  1              1.7328  16  -0.1434 ( -8.3)   1.5892   0.0000
                                      28  -0.0049 ( -0.3)
                                      26   0.0046 (  0.3)
                                     rem   0.0000 (  0.0)
 5. LP ( 1) O  3              1.9631  23  -0.0549 ( -2.8)   1.8970   0.0000
                                      24  -0.0050 ( -0.3)
                                      14  -0.0025 ( -0.1)
                                     rem  -0.0037 ( -0.2)
 6. LP ( 2) O  3              2.5600  13  -0.1009 ( -3.9)   2.2837   0.0000
                                      18  -0.0999 ( -3.9)
                                      24  -0.0474 ( -1.9)
                                     rem  -0.0282 ( -1.1)
 7. BD ( 1) N  1- C  2        1.3642  27  -0.0018 ( -0.1)   1.3588   0.0000
                                      18  -0.0013 ( -0.1)
                                      14  -0.0010 ( -0.1)
                                     rem  -0.0014 ( -0.1)
 8. BD ( 1) N  1- H  5        1.2331  18  -0.0081 ( -0.7)   1.2178   0.0000
                                      17  -0.0072 ( -0.6)
                                      13  -0.0041 ( -0.3)
                                     rem   0.0042 (  0.3)
 9. BD ( 1) N  1- H  6        1.2267  17  -0.0102 ( -0.8)   1.2125   0.0000
                                      13  -0.0034 ( -0.3)
                                      24   0.0028 (  0.2)
                                     rem  -0.0034 ( -0.3)
10. BD ( 1) C  2- O  3        1.7983  20  -0.0047 ( -0.3)   1.7936   0.0000
                                     rem   0.0000 (  0.0)
11. BD ( 2) C  2- O  3        1.6619  15  -0.0031 ( -0.2)   1.6585   0.0000
                                     rem  -0.0003 (  0.0)
12. BD ( 1) C  2- H  4        0.9525  14  -0.0075 ( -0.8)   0.9381   0.0000
                                      27  -0.0042 ( -0.4)
                                      19  -0.0035 ( -0.4)
                                     rem   0.0008 (  0.1)
                            ----------------------------------------------------
             * Sum *        84.2095      -0.4218 ( -0.5)  83.7917   0.0000
                                                         -------------------
                                              * Total *  83.7917
```

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As expected, the total kinetic energy (83.7917 a.u.) is dominated by well-localized CR (core) NBOs 1-3, with relatively small NL corrections (ca. 79 kcal/mol, 0.1%, acting to increase K.E.) .   However, the resonance-type NL effects act to significantly *reduce* K.E. in valence NBOs, particularly for the lone pairs on oxygen [NBOs 6 (ca. 173 kcal/mol, 11%) and 4 (ca. 41 kcal/mol, 3%)] and nitrogen [NBO 4 (ca. 90 kcal/mol, 9%)]. The final column shows (unsurprisingly) that each electron correlation "e-corr" contribution vanishes in RHF level.

B.21. MATRIX: GENERAL MATRIX OPERATOR AND TRANSFORMATION OUTPUT

Reference: Sec. B.2.4, "Matrix Output Keywords"

The MATRIX keyword provides a powerful utility for obtaining general matrix elements of one or more chosen operators (*OP*) or basis set (*BAS*) transformations of interest. General MATRIX keyword input supplements and extends the "old-style" specific matrix output keywords listed in Sec. B.2.4, offering a vitually unlimited set of new output options as enabled by ESS hosts.

As in Sec. B.2.4, matrix output may refer to an **operator matrix** [the matrix representation of an operator (*OP*) in a chosen basis (*BAS*)] or a **transformation matrix** [transforming one basis (*BAS1*) to another (*BAS2*)] The particular choice of matrix is specified by the entries of a bracket list that follows the MATRIX keyword.

To specify a chosen **operator matrix** for a chosen operator *OP* in a chosen basis *BAS*, the input form is

<div align="center">MATRIX <*OP*/*BAS*></div>

For example, "MATRIX <FOCK/NBO>" specifies the Fock (or Kohn-Sham) matrix in the NBO basis, and "MATRIX <KINETIC/PNLMO>" specifies the kinetic energy matrix in the PNLMO basis.

To specify a chosen **transformation matrix** from one basis (*BAS1*) to another (*BAS2*), the input form is

<div align="center">MATRIX <*BAS1*/*BAS2*></div>

For example, "MATRIX <AO/MO>" specifies the LCAO-MO transformation from basis AOs to MOs, whereas "MATRIX <NAO/NLMO>" specifies the LCNAO-NLMO transformation from NAOs to NLMOs.

In the above commands the chosen *BAS* name may be chosen from any of the twelve recognized basis sets:

<div align="center">*BAS*: AO, PAO, PNAO, NAO, PNHO, NHO, PNBO, NBO, PNLMO, NLMO, MO, NO</div>

B.21. MATRIX: GENERAL MATRIX OUTPUT

The chosen *OP* name may be chosen from *any* 1e operator included in the input archive (.47) file, such as

- "DM" or "Density" (density operator),
- "S" or "Overlap" (unit operator),
- "F" or "Fock" (Fock/Kohn-Sham operator),
- "K" or "Kinetic" (kinetic energy operator),
- "V" or "Nuclear" (nuclear-electronic potential),
- "DI" or "Dipole" (electric dipole moment)

In addition, the SD (spin-density) operator is available for all open-shell NBO options.

Alternatively, *OP* might be any operator provided to NBO from the host ESS program through general ESS/NBO message-passing protocol. Check the ESS User Manual for valid *OP* options available in your host ESS program. Symbolic names or abbreviations for *OP* or *BAS* entries are generally case-insensitive.

A single MATRIX keyword may be followed by multiple (up to 25) bracket lists for different matrices, such as

MATRIX <S/PNBO> <DIPOLE/NLMO> <NAO/NO>

Old-style keywords such as SPNBO or DINLMO are still recognized for popular options, but many new possibilities become available in NBO 6. Note however that additional keyword parameters as provided for old-style matrix output keywords (see Sec. B.2.4) are unrecognized by MATRIX.

The sample Gaussian input file below illustrates requests for the Fock matrix in the NBO basis ("matrix <fock/nbo>") and the AO → NAO transformation matrix ("matrix <ao/nao>") for formamide.

```
#rhf/3-21g pop=nboread

RHF/3-21G for formamide (H2NCHO)

0 1
  H    -1.91338      -0.34957      0.00000
  H    -0.65570      -1.51410      0.00000
  N    -0.94020      -0.55750      0.00000
  C     0.00000       0.41595      0.00000
  O     1.19830       0.23282      0.00000
  H    -0.43592       1.40790      0.00000

$nbo matrix <fock/nbo> <ao/nao> $end
```

B.21. MATRIX: GENERAL MATRIX OUTPUT

In each case, the output format is identical to that for the respective old-style keywords FNBO, AONAO (which are still recognized in NBO 6).

B.21. MATRIX: GENERAL MATRIX OUTPUT

B.22. STRUCTURAL AND GRAPHICAL OUTPUT KEYWORDS

Reference: Sec. B.2.4, "Matrix Output Keywords"

The NBO program offers additional keywords to write details of molecular structure and bonding in alternative file formats that serve as input to popular "molecular editor" and "cheminfomatics" utilities. Graphical utilities are particularly useful for representing the 2D/3D structural geometry and bonding properties of resonance structures, providing a visualizable alternative to the $NRTSTR keylists of Sec. B.8.3. However, non-graphical utilities can also convert such keyword output to a variety of ESS input file formats, derive a proper IUPAC name, or make other use of the information.

Two keywords (NRTCML and NRTMOL) are specifically tied to NRT usage and will prompt NRT analysis to be performed (if not already specified in the $NBO keylist). A third keyword (XMOL) is for more generic graphical depiction of structural geometry, including animation along a vibrational or chemical reaction coordinate. We describe brief details of each keyword and some aspects of their applicability in turn:

NRTCML

This keyword produces a valid CML (chemical markup language) format file that can be used as input to the widely used *ChemDraw* program (see <www.cambridgesoft.com>) to produce journal-quality illustrations of chemical bonding formulas.
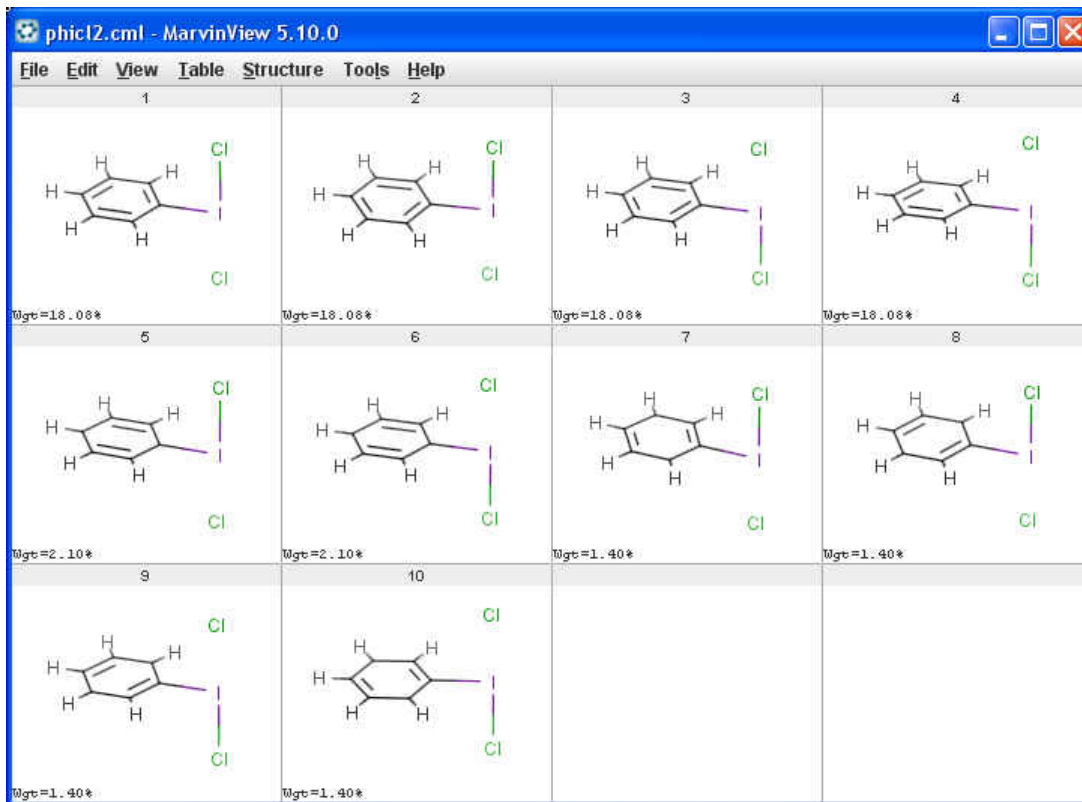
NRTMOL

This keyword produces a valid MDL (Molfile) format file for advanced cheminformatics applications (see <www.accelrys.com>). The Molfile can in turn be used as input to *OpenBabel* (see <openbabel.sourceforge.net>) to convert to a wide variety of alternative formats, including the SMILES structural specification. The Molfile also provides input to *MarvinView* applets (see <www.chemaxon.com/products/marvin>) that provide effective displays of groups of resonance structures.

XMOL

This keyword produces a valid input file for the *XMOL* viewer, a freeware program for displaying simple static or animated molecular structure diagrams that is available on many platforms.

B.21. MATRIX: GENERAL MATRIX OUTPUT

The illustration below shows sample NRTDRAW output for $C_6H_5ICl_2$.