

# *Natural Bond Orbital*

## *Analysis Programs*

### ***NBO 5.0*** ***Program Manual***

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# **NBO 5.0 Program Manual**

## ***Natural Bond Orbital Analysis Programs***

compiled and edited by

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## **APPENDIX: Specific ESS Versions**

*Gaussian Version*

*GAMESS Version*

*Mopac/Ampac Version*

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## **PREFACE: HOW TO USE THIS MANUAL**

The NBO manual consists of three major divisions:

Section A ("General Introduction and Installation") contains general introductory and one-time information for the novice user: what the program does, initial installation, "quick start" sample input data, 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 the 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 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 driver routines to attach the NBO programs 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.

A quick-reference index to NBO keywords and keylists discussed in this manual is presented in Table 1 below. The table lists [default] and optional keywords, indicating whether additional parameters must be provided (Parms?

Y = yes; N = no; O = optional), with brief summary of the keyword result and the page number of the manual for further reference.

**Table 1: NBO Keyword/Keylist Quick Summary**

<b>Keyword</b>	<b>Parms?</b>	<b>Keyword Description</b>	<b>Page</b>
<i>Main Program Options</i>			
[BEND]	O	Hybrid directionality and ``bond-bending" analysis	A-20
CMO	O	Bonding character of canonical molecular orbitals	B-133
DIPOLE	O	Dipole moment analysis	B-24
[E2PERT]	O	2nd-order perturbative estimates of NBO interactions	A-21
NBBP	O	Natural bond-bond polarizability indices	B-97
[NBO]	N	Natural bond orbital compositions	A-16
[NBOSUM]	N	NBO summary table	A-22
NCS	O	Natural chemical shielding analysis	B-138
NEDA	O	Natural energy decomposition analysis	B-104
NJC	O	Natural J-coupling analysis	B-147
NLMO	N	Natural localized molecular orbital compositions	B-22
[NPA]	N	Natural population analysis	A-13
NRT	N	Natural resonance theory analysis	B-72
STERIC	O	Natural steric analysis	B-100
3CHB	N	3-c, 4-e hyperbond search	B-154
<i>Control Options</i>			
AOINFO	N	Write AO basis information to LFN 31	B-9
ARCHIVE	O	Write ARCHIVE (FILE47) for stand-alone GENNBO input	B-62
BNDIDX	N	NAO-Wiberg Bond Index and related valency indices	B-29
BOAO	O	Fock-Dirac density matrix (``Bond order matrix")	B-11

DETAIL	N	Additional details of NBO search	B-9
DIST	N	Atomic distance table	B-9
FILE	Y	Specify filestem for PLOT files and other I/O	B-9
FIXDM	N	Correct unphysical occupancies of input density matrix	B-11
LFNPR	Y	Set logical file number (LFN) for NBO program output	B-9
MSPNBO	N	Maximum Spin-Paired NBOs (spin-averaged density matrix)	B-3
MULAT	N	Gross Mulliken populations, by atom	B-11
MULORB	N	Gross Mulliken populations, by orbital and atom	B-11
NBODAF	O	Write NBO direct access file (DAF) to disk	B-9
NOBOND	N	1-center atomic hybrids (no 2-c NBO search)	B-37
NRTCHG	Y	Alter maximum formal charge for candidate NRT structures	B-75
NRTDTL	N	Additional details of NRT search	B-75
NRTFDM	N	Use full density matrix for multi-reference NRT	B-75
NRTLST	Y	Print leading \$NRTSTR structure specifications	B-75
NRTMEM	Y	Specify maximum number of NRT reference structures	B-75
NRTOPT	Y	Specify alternative NRT optimization method	B-76
NRTTHR	Y	Specify delocalization threshold for NRT search	B-75
NRTWGT	Y	Alter weighting threshold for NRT reference structure	B-75
PAOPNAO	O	Read/write ``pure" AO to PNAO transformation	B-11
PLOT	N	Write files for orbital plotting	B-9
PRINT	Y	Heirarchical print control of NBO output	B-10
PRJTHR	Y	Alter projection threshold for NHO search	B-11
RPNAO	N	Revised ``pure" AO (PAO) to PNAO transformation	B-11
SKIPBO	N	Skip NBO search (NPA only for PRINT=1)	B-3

SPARTAN	N	Write Spartan-type archive file	B-11
3CBOND	N	Search for 3-center NBOs	B-3
THRESH	Y	Alter default occupancy for NBO search	B-11

*Operator Matrix  
Output: Basis  
AO, (P)NAO,  
(P)NBO,  
(P)NLMO, MO*

DI	O	Output dipole moment matrix (DIAO, DINAO, etc.)	B-6
DM	O	Output density matrix (DMAO, DMNAO, etc.)	B-6
F	O	Output Fock matrix (FAO, FNAO, etc.)	B-6
K	O	Output kinetic energy matrix (KAO, KNAO, etc.)	B-6
S	O	Output overlap matrix (SAO, SPNAO, SPNBO, SPNLMO)	B-6
V	O	Output 1-e (N-e attraction) potential matrix (VAO, VNAO, etc.)	B-6

*Transformation  
Matrix Output:  
Basis AO,  
(P)NAO,  
(P)NBO,  
(P)NLMO, MO*

AONAO	O	Output AO to NAO transformation	B-6
AOPNAO	O	Output AO to PNAO transformation	B-6
AONBO	O	Output AO to NBO transformation	B-6
AOPNBO	O	Output AO to PNBO transformation	B-6
AONLMO	O	Output AO to NLMO transformation	B-6
AOPNLMO	O	Output AO to PNLMO transformation	B-6
AOMO	O	Output AO to MO (LCAO-MO) transformation	B-6
NAONHO	O	Output NAO to NHO transformation	B-6
NAONBO	O	Output NAO to NBO transformation	B-6
NAONLMO	O	Output NAO to NLMO transformation	B-6

NAOMO	O	Output NAO to MO transformation	B-6
NHONBO	O	Output NHO to NBO transformation	B-6
NHONLMO	O	Output NHO to NLMO transformation	B-6
NHOMO	O	Output NHO to MO transformation	B-6
NBONLMO	O	Output NBO to NLMO transformation	B-6
NBOMO	O	Output NBO to MO transformation	B-6
NLMOMO	O	Output NLMO to MO transformation	B-6

*Auxiliary Keylists*

\$CHOOSE	Y	Specify alternative Lewis structure for NBO search	B-14
\$SCORE	Y	Modify default NBO core table	B-12
\$DEL	Y	Delete selected NBOs, interactions, or blocks of interactions	B-16
\$NRTSTR	Y	Specify reference structures for NRT analysis	B-77

*Auxiliary Keylists  
(Only in FILE47  
Input for  
GENNBO)*

\$BASIS	Y	Atomic centers and angular symmetries of AOs	B-67
\$CONTRACT	Y	Contraction coefficients and orbital exponents of AOs	B-69
\$COORD	Y	Job title, atoms, Cartesian coordinates	B-66
\$DENSITY	Y	Density matrix in AO basis	B-71
\$DIPOLE	Y	Dipole matrix in AO basis	B-71
\$FOCK	Y	Fock matrix in AO basis	B-71
\$GENNBO	Y	Specify calculation model size, type and units	B-65
\$KINETIC	Y	Kinetic energy matrix in AO basis	B-71
\$LCAOMO	Y	Canonical MOs in AO basis	B-71
\$NUCLEAR	Y	Nuclear-electron attraction matrix in AO basis	B-71
\$OVERLAP	Y	Overlap matrix in AO basis	B-71

# Section A: GENERAL INTRODUCTION AND INSTALLATION

## A.1 INTRODUCTION TO THE NBO 5.0 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 analysis, and other tasks pertaining to localized analysis of wavefunction properties, including natural resonance theory (NRT) analysis. 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  $\alpha$  and  $\beta$  spin. [Note, however, that some electronic structure packages do 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.] This section provides a brief introduction to NBO algorithms and nomenclature.

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 one-electron 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" 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 dodecet 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  $\{\chi_i\}$ ,



[Note that the restriction to starting AOs is not intrinsic, for if the wavefunction were not calculated in an atom-centered basis, it would first be necessary to compute a wavefunction for each isolated atom (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; because atom-centered basis functions are the nearly universal choice for molecular calculations, the current NBO program makes no provision for this hypothetical 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.

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 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 ( $\sigma_{AB}$ ) and antibond ( $\sigma^*_{AB}$ ) in the NBO basis,

$$\begin{aligned}\sigma_{AB} &= c_A h_A + c_B h_B \\ \sigma^*_{AB} &= c_B h_A - c_A h_B\end{aligned}$$

the former a Lewis (L) and the latter a non-Lewis (NL) 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 actual formation of NAOs and NBOs is wholly independent of any such information about molecular energetics (or geometry).] 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 energy analysis is dependent on the specific 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 the Kohn-Sham orbitals incorporate important effects of a correlated electronic distribution that are displayed in details of the NAOs, NBOs and their occupancies.

NBO 5.0 also includes NBO-based supplementary modules for performing natural resonance theory (NRT) analysis, natural bond-bond polarizability (NBBP) evaluation, NBO-based steric analysis, and natural energy decomposition analysis (NEDA). New features of NBO 5.0 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 5.0 comes installed in a number of leading electronic structure system (ESS) packages, and one should follow the instructions provided with the ESS on how to run NBO. However, the NBO program is also provided as a set of routines that can be attached to an electronic structure system of the user's choice. In addition, specific driver routines are provided that facilitate the attachment to other popular *ab initio* and semi-empirical packages (GAUSSIAN-9X, GAMESS, AMPAC, MOPAC). These versions are described in the Appendix.

### A.1.2 Input and Output

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

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

usually separated by a blank line from the last line of the ESS input file. Simple examples of such \$NBO keylists are

```
$NBO dipole nrt $END
```

```
$NBO file=myjob plot naobo ncs=0.05 $END
```

Note that keylists are always delimited with  $\$$ -prefixed symbols: an identifier \$NAME symbol to open the keylist and \$END to end it. The keylist delimiters and keywords are case-insensitive, and the keylist can be continued on multiple lines, e.g.

```
$nbo  
file=myjob  
PLOT  
naobo  
ncs=0.05  
$end
```

but each new keylist must begin on a new line. In effect, the NBO program reads these keywords to set various job options, then interrogates the ESS program for additional information concerning the wavefunction to perform the requested task.

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.

The principal output from the NBO program consists of the tables and summaries describing the results of NBO analysis, included in the ESS output file. Sample default NBO output is described in Section A.2.4, 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*).

If requested, the NBO program may also write out transformation matrices or other data to disk files. The NBO program also creates or updates two files, the direct-access file (FILE48) and the archive file (FILE47) that can be used to repeat NBO analysis with different options, without running the ESS program to recalculate the wavefunction. Necessary details of these files are given in Section B.7 and the Programmer's Guide, Section C.

### *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 SCF, MCSCF, CI, and Moller-Plesset wavefunctions or density functional treatments (main subroutine: NBO);

2. For HF/DFT methods only, energetic analysis of the wavefunction in terms of the interactions (Fock matrix elements) between NBOs (main subroutine: NBOEAN);
3. Localized analysis of molecular dipole moment in terms of NLMO and NBO bond moments and their interactions (main subroutine: DIPANL).
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, and natural energy decomposition analysis. New features of NBO 5.0 are summarized in Sec. A.1.5.

A highly transportable subset of standard FORTRAN 77 is employed, with no special vendor compiler extensions. Common abbreviations used in naming variables and keywords (as well as program symbols) are:

S	overlap matrix
DM	density matrix (or D)
F	Fock or Kohn-Sham matrix
K	kinetic energy matrix
V	1-electron potential energy (nuclear-electron attraction) matrix
DI	dipole matrix (or DXYZ, or DX, DY, DZ)
NPA	Natural Population Analysis
NAO	Natural Atomic Orbital
NHO	Natural Hybrid Orbital
NBO	Natural Bond Orbital
NLMO	Natural Localized Molecular Orbital
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)

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 integer 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, 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 (up to g orbitals 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.

#### *A.1.4 References and Relationship to Previous Versions*

The NBO 5.0 program should be cited as follows:

*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 (2001).

NBO 5.0 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 [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)].

NBO 5.0 should be considered to supercede those versions, as well as interim revisions and extensions such as NBO 4.M (the "large memory" version of NBO 4.0).

Principal contributors (1975-2001) to the conceptual development of the NBO methods contained in this program are

T. K. Brunck	J. P. Foster
A. B. Rives	A. E. Reed
R. B. Weinstock	J. E. Carpenter
E. D. Glendening	J. K. Badenhop
J. A. Bohmann	S. J. Wilkens
C. M. Morales	C. R. Landis
F. Weinhold	

Others who contributed to the conceptual development of individual program segments include 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 provided useful comments and suggestions that are reflected in the final version of the program, and for which we are grateful.

Principal references to the development and applications of 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); J. E. Carpenter, *Ph. D. Thesis*, University of Wisconsin, Madison, 1987.

Comprehensive Review Article:

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.

### Other Review Articles:

A. E. Reed, L. A. Curtiss, and F. Weinhold, *Chem. Rev.* **88**, 899-926 (1988); F. Weinhold and J. E. Carpenter, in, R. Naaman and Z. Vager (eds.), "The Structure of Small Molecules and Ions," (Plenum, New York, 1988), pp. 227-236.

### Book:

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

### Overview of NBO 5.0 Program and NBO Transition Metal Extensions

F. Weinhold and C. R. Landis, "Natural Bond Orbitals and Extensions of Localized Bonding Concepts," *Chem. Educ. Res. Pract. Eur.* **2**, 91-104 (2001).

Leading references for NBO-based supplementary modules are included in the appropriate Sections B.8 *et seq.*.

#### *A.1.5. What's New in NBO 5.0?*

NBO 5.0 includes major new capabilities, particularly related to magnetic properties and transition metal bonding, as well as extensions and improvements of established NBO analysis tools. Principal new NBO features include:

1. *Canonical Molecular Orbital (CMO) Analysis*. This module provides a capsule description of the NBO composition of each canonical molecular orbital (occupied and virtual) as well as the percentage "bonding", "non-bonding", or "antibonding" character of each CMO; see Sec. B.13.
2. *Natural Chemical Shielding (NCS) Analysis*. This module provides a localized NBO-based analysis of diamagnetic and paramagnetic contributions to chemical shielding tensors calculated by the GIAO method; see Sec. B.14.
3. *Natural J-Coupling (NJC) Analysis*. This module provides a localized NBO-based analysis of the scalar J-coupling (spin-spin coupling) calculated by finite-field Fermi contact method; see Sec. B.15.
4. *3-Center, 4-Electron Hyperbond (3CHB) Search*. This module detects and tabulates strongly interacting "hyperbond" triads, corresponding to strong A:

B-C  $\longleftrightarrow$  A-B :C resonance interactions (Pimentel-Rundle 3-c, 4-e bonding); see Sec. B.16. Hyperbonded triads, although somewhat unusual in main-group bonding, are found to be a ubiquitous motif in transition metal bonding.

5. *Additional Keywords.* The new FIXDM keyword corrects unphysical (negative or Pauli-violating) occupancies of an input density matrix that is corrupted by numerical errors or poorly converged perturbative corrections, allowing completion of many analysis tasks that were previously aborted with fatal numerical inconsistencies; see Sec. B.2.7. New keywords are also provided to print eigenvectors of the overlap matrix (SEV), write a Spartan-style archive file (SPARTAN), print the density matrix in the PNAO basis (DMPNAO), or print the table of inter-hybrid valence angles around all skeletal atoms (BEND).

6. *Larger Systems.* The entire program has been configured and formatted to allow easy re-dimensioning up to 999 atoms and 9999 basis functions [default: 200 atoms, 2000 basis functions]; see discussion of MAXATM, MAXORB parameters, Sec. C.3. This may lead to small changes in the usual output format, designed to preserve the resemblance to previous versions and remain within standard 80-character format for convenient screen and page display. In tightly formatted output, atom numbers above 99 are represented by a 2-character "extended digit" code, with first character A-Z denoting numbers 10-35, a-z denoting 36-61, and remaining printable ASCII symbols denoting 62-99 (for example, "A1" denotes 101 and "z3" denotes 613).

NBO 5.0 also provides extensions and improvements of program options introduced in earlier versions:

1. *Basis Linear Dependence.* NBO 5.0 reduces the dimensionality of the NAO basis as necessary to remove linearly dependent components of the input AO basis set, thus avoiding insidious effects of basis set linear dependency. The dimensional reduction for linear dependency is usually consistent with corresponding measures taken by the host program (e.g., Gaussian or GAMESS), but NBO 5.0 detects and defeats linear dependency even if the host ESS does not. (When dimensional reduction occurs, NBO 5.0 determines canonical MOs independently, so the description of degenerate MOs may differ somewhat from that of the host ESS.)

2. *NRT Improvements.* NBO 5.0 corrects a bug in the original NBO 4.0 implementation of the NRT algorithm [S. H. Feldgus et al., *J. Comp. Chem.* **21**, 411 (2000)]. Numerous changes in the NRT module improve the generation of

initial Lewis-like structures for transition metals and remove other numerical problems.

3. *NLMO Improvement.* The NLMO routines are now able to handle cases of non-Lewis orbitals with higher occupancy than Lewis orbitals, which formerly led to a halt. With the additional help provided by the FIXDM keyword (see above), NLMOs can now be successfully determined for a large fraction of the cases that failed in previous NBO versions (Sec. B.6.2). For platforms of lower numerical precision, NLMO automatically adjusts numerical thresholds until the program can continue.

4. *STERIC Improvement.* NBO steric analysis has been extended to include higher-order coupling effects between steric interactions and non-Lewis delocalizations. The extension consists of systematically replacing NBOs by NLMOs (and PNBOs by PNLMOs, etc.), in order to automatically incorporate resonance effects associated with the weak "delocalization tails" of the NLMOs. This leads to practically no numerical change when the system is well localized (e.g., rare gas interactions), but gives considerably improved description of steric effects in delocalized organic and organometallic species (Sec. B.10).

5. *Checkpointing Options.* New checkpointing options are provided for open-shell calculations, allowing different checkpointed orbital lists for different spins. These options allow one to store specific localized PNBO electronic configurations (ground or excited) in the checkpoint file for post-SCF calculations or improved GUESS in SCF calculations (Sec. B.12).

6. *New Matrix Output Options.* For all operator matrices, NBO 5.0 now allows the user to select a small number of specific matrix elements for printing, rather than the entire matrix. An input bracket list of user-requested elements guides the order of matrix elements and labels to be printed (Sec. B.2.4).

7. *Transition Metal Hybrid Directionality.* The hybrid directionality and bond bending table now describes a much broader range of hybrid types, including the *d*-rich bonding hybrids of transition metals. The explicit BEND keyword now augments the standard bond-bending table with tables of inter-hybrid valence angles around skeletal atoms (Sec. B.2.3).

8. *Other Improvements.* A bug in the NBBP module has been corrected that sometimes caused other input keywords to be swallowed. The FEAOIN subroutine and keyword has been corrected to handle *g*-orbital input for correlation-consistent cc-pVnZ basis sets. The job-options control routine

(JOB OPT) has been rewritten to facilitate compilation. A bug in the open-shell implementation of the \$CHOOSE keylist (to specify different Lewis structures for different spins) has been corrected.

Despite these changes and extensions, NBO 5.0 was designed to be compatible with v. 4.0 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 5.0 comes installed in a number of leading ESS packages. Users of these packages may ignore this section.]

The NBO programs may be provided on floppy diskette or other medium. The distribution medium contains the master NBO source code (file NBO\_50.SRC) and the Fortran ``enabler" program (file enable.f). For floppy diskette distribution, the source program is divided into segments NBO\_50A.SRC, NBO\_50B.SRC. If you received diskettes or CD in a PC-DOS format for transfer to a unix or linux system, be sure to use ftp (file transfer protocol) or other file-conversion utility to restore the proper EOL (end-of-line) characters for a unix-based environment.

In overview, the installation procedure involves the following steps (the details of each step being dependent on your operating system):

1. *Enabling the NBO routines.* Copy the contents of the distribution medium onto your system. The source program file(s) must keep the capitalized name (e.g., ``NBO\_50.SRC", all capital letters). Using your system Fortran 77 compiler, compile and link the appropriate enabler program to create the executable. For example, the Unix command to create an executable ``enable" on the IBM RISC/6000 is

```
xlf -o enable enable.f &
```

while the VMS commands to create ENABLE.EXE are

```
FOR ENABLE.F  
LINK ENABLE
```

Now, run the ENABLE program (type ``enable" for Unix/Linus or DOS; or ``RUN ENABLE" on a VMS system). (If using the bash environment, you may need to type "./enable" to avoid conflict with the built-in "enable" bash shell command.)

## Answer the prompts

```
Environment to enable (1-4)?  
NBO program version to enable (1-5)?
```

by selecting from the available offerings. Each ESS package is associated with a 3-letter identifier (e.g., ``G98" for Gaussian 98, ``GMS" for GAMESS, ``AM1" for MOPAC or AMPAC). The ENABLE program will create a file *XXXNBO.FOR* (VMS, DOS) or *xxxnbo.f* (Unix) that incorporates the appropriate drivers for your ESS. Gaussian 9X (*g98nbo.f*) and GAMESS (*gmsnbo.f*) users should immediately consult the installation instructions in the Appendix.

If you are creating *GENNBO.FOR*, the stand-alone program is now ready to compile and link. The default memory allocated by the program is 2 megawords (``MEMORY = 2000000"). Edit the file to adjust this parameter according to memory resources available or needed.

2. *Compiling the NBO routines.* Using your system Fortran 77 compiler, compile the NBO Fortran file to an object code file, e.g.

```
xlf -c xxxnbo.f &
```

which creates *xxxnbo.o*. [Compiler errors (if any) should be fixed before proceeding. Please notify the authors if you encounter undue difficulties in this step.] Note that G9X (*g98nbo.f*) and GAMESS (*gmsnbo.f*) files *cannot* be compiled directly, but must be incorporated in the script procedure as described in the Appendix.

3. *Modifying the ESS routines.* In general, the ESS source Fortran code must be modified to call the NBO routines near the point where the ESS performs Mulliken Population Analysis or evaluates properties of the final wavefunction. The modification generally consists of inserting a single statement (viz., ``CALL RUNNBO") in one subroutine of your ESS system. See the appropriate Appendix of this Manual for detailed information on exactly how to modify the ESS code for your chosen system.

4. *Rebuilding the integrated ESS/NBO program.* Re-compile your modified ESS programs and link the resulting object file(s) [say, *ess.o* (Unix) or *ESS.OBJ* (VMS)] with the *XXXnbo.o* or *XXXNBO.OBJ* file to form the final executable *.EXE* file. In general, this step will closely follow the initial installation procedure for your ESS, with the exception that the NBO object file

must be included in the link statement (or deposited in one of the libraries accessed by the linker, etc.).

Note that installation of the NBO programs into your ESS system generally does not affect the way your system processes standard input files. The only change involves enabling the reading of NBO keylists (if detected in your input file), performance of the tasks requested in the keylist, and return of control to the parent 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 the NBO programs to a new ESS package (not represented in the driver routines provided with this distribution), see Section C.13 for guidance on how to create drivers for your ESS to provide the necessary information. 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 ( $\text{CH}_3\text{NH}_2$ ) 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.

The 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:

---

\*\*\*\*\* NBO 5.0  
 \*\*\*\*\*  
 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  
 \*\*\*\*\*  
 \*\*\*\*\*

(c) Copyright 1996-2001 Board of Regents of the University of Wisconsin System  
 on behalf of the Theoretical Chemistry Institute. All Rights Reserved.

Cite this program as:

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)

/FILE / : Set to ch3nh2

Analyzing the SCF density

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

Storage needed:            2562 in NPA,            3278 in NBO (            2000000 available)

---

Note that all NBO output is formatted to a maximum 80-character width for convenient display on a computer terminal. The NBO heading echoes any requested keywords (none for the present default case) and shows an estimate of the memory requirements (in double precision words) for the separate steps of the NBO process, compared to the total allocated memory available through your ESS process. Increase the memory allocated to your ESS process if the estimated NBO requests exceed the available storage. *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)	1.99900	-11.04204
2	C	1	s	Val( 2s)	1.09039	-0.28194
3	C	1	s	Ryd( 3s)	0.00068	1.95499
4	C	1	px	Val( 2p)	1.21709	-0.07391
5	C	1	px	Ryd( 3p)	0.00056	1.03024
6	C	1	py	Val( 2p)	0.88595	-0.01462
7	C	1	py	Ryd( 3p)	0.00149	0.93116
8	C	1	pz	Val( 2p)	1.24518	-0.08869
9	C	1	pz	Ryd( 3p)	0.00057	1.01794

10	N	2	s	Cor( 1s)	1.99953	-15.25957
11	N	2	s	Val( 2s)	1.42622	-0.71714
12	N	2	s	Ryd( 3s)	0.00016	2.75765
13	N	2	px	Val( 2p)	1.80521	-0.32969
14	N	2	px	Ryd( 3p)	0.00181	1.49139
15	N	2	py	Val( 2p)	1.31017	-0.18930
16	N	2	py	Ryd( 3p)	0.00118	1.56322
17	N	2	pz	Val( 2p)	1.35221	-0.19183
18	N	2	pz	Ryd( 3p)	0.00070	1.59488
19	H	3	s	Val( 1s)	0.81444	0.13285
20	H	3	s	Ryd( 2s)	0.00177	0.95061
21	H	4	s	Val( 1s)	0.78189	0.15351
22	H	4	s	Ryd( 2s)	0.00096	0.94520
23	H	5	s	Val( 1s)	0.78189	0.15351
24	H	5	s	Ryd( 2s)	0.00096	0.94520
25	H	6	s	Val( 1s)	0.63877	0.20572
26	H	6	s	Ryd( 2s)	0.00122	0.99883
27	H	7	s	Val( 1s)	0.63877	0.20572
28	H	7	s	Ryd( 2s)	0.00122	0.99883

---

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. = 627.5 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 0.8909 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) plus 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:

Atom No	Natural Charge	Natural Population			
		Core	Valence	Rydberg	Total
C 1	-0.44092	1.99900	4.43861	0.00331	6.44092
N 2	-0.89718	1.99953	5.89381	0.00384	7.89718
H 3	0.18378	0.00000	0.81444	0.00177	0.81622
H 4	0.21715	0.00000	0.78189	0.00096	0.78285
H 5	0.21715	0.00000	0.78189	0.00096	0.78285
H 6	0.36001	0.00000	0.63877	0.00122	0.63999
H 7	0.36001	0.00000	0.63877	0.00122	0.63999
* Total *	0.00000	3.99853	13.98820	0.01328	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 ( 99.9632% of 4)
Valence	13.98820 ( 99.9157% of 14)
Natural Minimal Basis	17.98672 ( 99.9262% of 18)
Natural Rydberg Basis	0.01328 ( 0.0738% of 18)

---

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  $1s^22s^12p^3$  electron configuration.]

### 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:

Cycle Dev	Occ. Thresh.	Occupancies		Lewis Structure				Low	High
		Lewis	Non-Lewis	CR	BD	3C	LP	occ (L)	occ (NL)
1 (1) 0.02	1.90	17.95048	0.04952	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; the number of low-occupancy Lewis (L) and "high-occupancy" ( $> 0.1e$ ) non-Lewis (NL) orbitals; and the maximum deviation ('Dev') of any formal bond order from a nominal estimate (NAO

Wiberg bond index) for the structure. [If the latter exceeds 0.1, additional NBO searches are initiated (indicated by the parenthesized number under `Cycle') for alternative Lewis structures.] 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:

---

1 low occupancy (

---

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. (In this case, the table also includes a warning about a carbon core orbital with slightly less than double occupancy.)

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
-----			
1. (1.99858)	BD ( 1) C 1- N 2		
( 40.07%)	0.6330*	C 1 s( 21.71%)p 3.61( 78.29%)	0.0003 0.4653 0.0238 -0.0046
0.0083			-0.8843 -0.0300 0.0000 0.0000
	( 59.93%)	0.7742* N 2 s( 30.87%)p 2.24( 69.13%)	0.0001 0.5556 -0.0010 0.0339
0.0098			0.8307 -0.0005 0.0000 0.0000
2. (1.99860)	BD ( 1) C 1- H 3		
( 59.72%)	0.7728*	C 1 s( 25.78%)p 2.88( 74.22%)	0.0002 0.5077 -0.0069 -0.8177
0.0055			0.2709 0.0093 0.0000 0.0000
	( 40.28%)	0.6347* H 3 s(100.00%)	1.0000 0.0030
3. (1.99399)	BD ( 1) C 1- H 4		
( 61.02%)	0.7812*	C 1 s( 26.28%)p 2.80( 73.72%)	

				0.0001	0.5127	-0.0038	0.4069
-0.0016				0.2675	0.0016	0.7070	-0.0103
	( 38.98%)	0.6243*	H 4 s	(100.00%)			
				1.0000	0.0008		
	4. (1.99399)	BD ( 1) C 1-	H 5				
	( 61.02%)	0.7812*	C 1 s	( 26.28%)	p 2.80	( 73.72%)	
				0.0001	0.5127	-0.0038	0.4069
-0.0016				0.2675	0.0016	-0.7070	0.0103
	( 38.98%)	0.6243*	H 5 s	(100.00%)			
				1.0000	0.0008		
	5. (1.99442)	BD ( 1) N 2-	H 6				
	( 68.12%)	0.8253*	N 2 s	( 25.61%)	p 2.90	( 74.39%)	
				0.0000	0.5060	0.0005	-0.3728
0.0053				-0.3234	-0.0177	-0.7070	-0.0093
	( 31.88%)	0.5646*	H 6 s	(100.00%)			
				1.0000	0.0020		
	6. (1.99442)	BD ( 1) N 2-	H 7				
	( 68.12%)	0.8253*	N 2 s	( 25.61%)	p 2.90	( 74.39%)	
				0.0000	0.5060	0.0005	-0.3728
0.0053				-0.3234	-0.0177	0.7070	0.0093
	( 31.88%)	0.5646*	H 7 s	(100.00%)			
				1.0000	0.0020		
	7. (1.99900)	CR ( 1) C 1		s(100.00%)	p 0.00	( 0.00%)	
				1.0000	-0.0003	0.0000	0.0001
0.0000				0.0002	0.0000	0.0000	0.0000
	8. (1.99953)	CR ( 1) N 2		s(100.00%)	p 0.00	( 0.00%)	
				1.0000	-0.0001	0.0000	0.0000
0.0000				-0.0001	0.0000	0.0000	0.0000
	9. (1.97795)	LP ( 1) N 2		s( 17.88%)	p 4.59	( 82.12%)	
				0.0000	0.4229	0.0001	0.8487
-0.0159				-0.3173	0.0042	0.0000	0.0000
	10. (0.00105)	RY*( 1) C 1		s( 1.55%)	p63.33	( 98.45%)	
				0.0000	-0.0095	0.1243	-0.0016
0.6002				0.0308	-0.7894	0.0000	0.0000
	11. (0.00034)	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	0.0146	0.9999
	12. (0.00022)	RY*( 3) C 1		s( 56.56%)	p 0.77	( 43.44%)	
				0.0000	-0.0023	0.7520	-0.0071
-0.5763				0.0245	-0.3188	0.0000	0.0000
	13. (0.00002)	RY*( 4) C 1		s( 41.83%)	p 1.39	( 58.17%)	
	14. (0.00116)	RY*( 1) N 2		s( 1.51%)	p65.19	( 98.49%)	
				0.0000	-0.0062	0.1228	0.0191
0.9836				-0.0082	-0.1300	0.0000	0.0000
	15. (0.00044)	RY*( 2) N 2		s( 0.00%)	p 1.00	(100.00%)	

			0.0000	0.0000	0.0000	0.0000
0.0000						
	16.	(0.00038)	RY*( 3)	N 2		
			0.0000	0.0000	-0.0132	0.9999
			s( 33.39%)	p 1.99	( 66.61%)	
			0.0000	0.0133	0.5777	-0.0129
0.0359						
	17.	(0.00002)	RY*( 4)	N 2		
			-0.0075	0.8152	0.0000	0.0000
			s( 65.13%)	p 0.54	( 34.87%)	
	18.	(0.00178)	RY*( 1)	H 3		
			s(100.00%)			
			-0.0030	1.0000		
	19.	(0.00096)	RY*( 1)	H 4		
			s(100.00%)			
			-0.0008	1.0000		
	20.	(0.00096)	RY*( 1)	H 5		
			s(100.00%)			
			-0.0008	1.0000		
	21.	(0.00122)	RY*( 1)	H 6		
			s(100.00%)			
			-0.0020	1.0000		
	22.	(0.00122)	RY*( 1)	H 7		
			s(100.00%)			
			-0.0020	1.0000		
	23.	(0.00016)	BD*( 1)	C 1- N 2		
		( 59.93%)	0.7742*	C 1	s( 21.71%)	p 3.61( 78.29%)
					0.0003	0.4653 0.0238 -0.0046
0.0083						
		( 40.07%)	-0.6330*	N 2	s( 30.87%)	p 2.24( 69.13%)
					0.0001	0.5556 -0.0010 0.0339
0.0098						
			0.8307	-0.0005	0.0000	0.0000
	24.	(0.01568)	BD*( 1)	C 1- H 3		
		( 40.28%)	0.6347*	C 1	s( 25.78%)	p 2.88( 74.22%)
					-0.0002	-0.5077 0.0069 0.8177
-0.0055						
		( 59.72%)	-0.7728*	H 3	s(100.00%)	
					-1.0000	-0.0030
	25.	(0.00770)	BD*( 1)	C 1- H 4		
		( 38.98%)	0.6243*	C 1	s( 26.28%)	p 2.80( 73.72%)
					-0.0001	-0.5127 0.0038 -0.4069
0.0016						
		( 61.02%)	-0.7812*	H 4	s(100.00%)	
					-1.0000	-0.0008
	26.	(0.00770)	BD*( 1)	C 1- H 5		
		( 38.98%)	0.6243*	C 1	s( 26.28%)	p 2.80( 73.72%)
					-0.0001	-0.5127 0.0038 -0.4069
0.0016						
		( 61.02%)	-0.7812*	H 5	s(100.00%)	
					-1.0000	-0.0008
	27.	(0.00427)	BD*( 1)	N 2- H 6		
		( 31.88%)	0.5646*	N 2	s( 25.61%)	p 2.90( 74.39%)
					0.0000	-0.5060 -0.0005 0.3728
-0.0053						
		( 68.12%)	-0.8253*	H 6	s(100.00%)	
					-1.0000	-0.0020
	28.	(0.00427)	BD*( 1)	N 2- H 7		
		( 31.88%)	0.5646*	N 2	s( 25.61%)	p 2.90( 74.39%)

```

-0.0053
0.0000 -0.5060 -0.0005 0.3728
0.3234 0.0177 -0.7070 -0.0093
( 68.12%) -0.8253* H 7 s(100.00%)
-1.0000 -0.0020

```

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 ("BD" for 2-center bond, "CR" for 1-center core pair, "LP" for 1-center valence lone pair, "RY\*" for 1-center Rydberg, and "BD\*" for 2-center antibond, 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 NBO in the sample output is the 2-center bond (with 1.99858 electrons) between carbon (atom 1) and nitrogen (atom 2), the  $\sigma_{\text{CN}}$  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  $sp^\lambda$  composition (percentage  $s$ -character,  $p$ -character, etc.) of each  $h_A$ . [For example, the  $\sigma_{\text{CN}}$  NBO is formed from an  $sp^{3.61}$  hybrid (78.3%  $p$ -character) on carbon interacting with an  $sp^{2.24}$  hybrid (69.1%  $p$ -character) on nitrogen,

$$\sigma_{\text{CN}} = 0.633(sp^{3.61})_{\text{C}} + 0.774(sp^{2.24})_{\text{N}}$$

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  $h_{\text{C}}$  of the  $\sigma_{\text{CN}}$  bond has largest coefficients for the 2<sup>nd</sup> and 4<sup>th</sup> NAOs, corresponding to the approximate description

$$h_{\text{C}} \cong -0.4653(2s)_{\text{C}} - 0.8808(2p_x)_{\text{C}}$$

in terms of the valence NAOs of the carbon atom.] In the  $\text{CH}_3\text{NH}_2$  example, the NBO search finds the C-N bond (NBO 1), three C-H bonds (NBOs 2, 3, 4), two N-H bonds (NBOs 5, 6), N lone pair (NBO 9), and C and N core pairs (NBOs 7, 8) of the expected Lewis structure. NBOs 10-28 represent the residual non-Lewis NBOs of low occupancy. In this example, it is also interesting to note the slight asymmetry of the three  $\sigma_{\text{CH}}$  NBOs, and the slightly higher occupancy

(0.0157 vs. 0.0077 electrons) in the  $\sigma^*_{\text{C1H3}}$  antibond (NBO 24) lying *trans* to the nitrogen lone pair.

### 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- or d-character > 25.0%  
 orbital occupancy > 0.10e

Hybrid 2		Line of Centers		Hybrid 1					
Phi	Dev	Theta	Phi	Theta	Phi	Dev	Theta		
1.	BD ( 1)	C 1-	N 2	90.0	270.0	--	--	--	90.0
87.0	3.0								
3.	BD ( 1)	C 1-	H 4	35.3	35.3	34.9	33.6	1.0	--
--	--								--
4.	BD ( 1)	C 1-	H 5	144.7	35.3	145.1	33.6	1.0	--
--	--								--
5.	BD ( 1)	N 2-	H 6	144.7	215.3	145.0	222.9	4.4	--
--	--								--
6.	BD ( 1)	N 2-	H 7	35.3	215.3	35.0	222.9	4.4	--
--	--								--
9.	LP ( 1)	N 2		--	--	90.0	159.4	--	--
--	--								--

---

The "direction" of an  $sp^{\lambda}$  hybrid is specified in terms of the polar ( $\theta$ ) and azimuthal ( $\phi$ ) 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  $\text{CH}_3\text{NH}_2$  case shown above, the nitrogen NHO of the  $\sigma_{\text{CN}}$  bond (NBO 1) is bent away from the line of C-N centers by 3.0, whereas the carbon NHO is approximately aligned with the C-N axis (within the 1.0 threshold for printing). The N-H bonds (NBOs 5, 6) are bent even further (4.4). The information in

this table is often useful in anticipating the direction of geometry changes resulting from geometry optimization (viz., likely reduced pyramidalization of the -NH<sub>2</sub> group to relieve the ~4 nitrogen bond bendings found in the tetrahedral Pople-Gordon geometry).

### 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(i) a.u.	F(i,j) Donor NBO (i)	Acceptor NBO (j)	E(2) kcal/mol	E(j)- a.u.
=====				
within unit 1				
0.038	2. BD ( 1) C 1- H 3	14. RY*( 1) N 2	0.84	2.18
0.024	3. BD ( 1) C 1- H 4	26. BD*( 1) C 1- H 5	0.52	1.39
0.057	3. BD ( 1) C 1- H 4	27. BD*( 1) N 2- H 6	3.03	1.37
0.024	4. BD ( 1) C 1- H 5	25. BD*( 1) C 1- H 4	0.52	1.39
0.057	4. BD ( 1) C 1- H 5	28. BD*( 1) N 2- H 7	3.03	1.37
0.028	5. BD ( 1) N 2- H 6	10. RY*( 1) C 1	0.56	1.78
0.059	5. BD ( 1) N 2- H 6	25. BD*( 1) C 1- H 4	2.85	1.51
0.028	6. BD ( 1) N 2- H 7	10. RY*( 1) C 1	0.56	1.78
0.059	6. BD ( 1) N 2- H 7	26. BD*( 1) C 1- H 5	2.85	1.51
0.080	7. CR ( 1) C 1	16. RY*( 3) N 2	0.61	13.11
0.116	7. CR ( 1) C 1	18. RY*( 1) H 3	1.40	11.99
0.122	7. CR ( 1) C 1	19. RY*( 1) H 4	1.55	11.99
0.122	7. CR ( 1) C 1	20. RY*( 1) H 5	1.55	11.99
0.140	8. CR ( 1) N 2	10. RY*( 1) C 1	1.51	16.23
0.106	8. CR ( 1) N 2	12. RY*( 3) C 1	0.84	16.77

8. CR ( 1) N 2 0.089	21. RY*( 1) H 6	0.61	16.26
8. CR ( 1) N 2 0.089	22. RY*( 1) H 7	0.61	16.26
9. LP ( 1) N 2 0.086	24. BD*( 1) C 1- H 3	8.13	1.13
9. LP ( 1) N 2 0.037	25. BD*( 1) C 1- H 4	1.46	1.14
9. LP ( 1) N 2 0.037	26. BD*( 1) C 1- H 5	1.46	1.14

This is carried out by examining all possible interactions between "filled" (donor) Lewis-type NBOs and "empty" (acceptor) non-Lewis 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 stabilization energy  $E(2)$  associated with delocalization ("2e-stabilization")  $i \rightarrow j$  is estimated as

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

where  $q_i$  is the donor orbital occupancy,  $\epsilon_i$ ,  $\epsilon_j$  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 8) and the antiperiplanar  $C_1-H_3$  antibond (NBO 24) is seen to give the strongest stabilization, 8.13 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.3.6 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):

Delocalizations	Principal	
NBO	Occupancy	Energy
(geminal, vicinal, remote)		
=====		
=====		

Molecular unit 1 (CH5N)				
1.	BD ( 1) C 1- N 2	1.99858	-0.89915	
2.	BD ( 1) C 1- H 3	1.99860	-0.69187	14 (v)
3.	BD ( 1) C 1- H 4	1.99399	-0.68897	27 (v) , 26 (g)
4.	BD ( 1) C 1- H 5	1.99399	-0.68897	28 (v) , 25 (g)
5.	BD ( 1) N 2- H 6	1.99442	-0.80949	25 (v) , 10 (v)
6.	BD ( 1) N 2- H 7	1.99442	-0.80949	26 (v) , 10 (v)
7.	CR ( 1) C 1	1.99900	-11.04151	
19 (v) , 20 (v) , 18 (v) , 16 (v)				
8.	CR ( 1) N 2	1.99953	-15.25935	
10 (v) , 12 (v) , 21 (v) , 22 (v)				
9.	LP ( 1) N 2	1.97795	-0.44606	24 (v) , 25 (v) , 26 (v)
10.	RY* ( 1) C 1	0.00105	0.97103	
11.	RY* ( 2) C 1	0.00034	1.02114	
12.	RY* ( 3) C 1	0.00022	1.51443	
13.	RY* ( 4) C 1	0.00002	1.42177	
14.	RY* ( 1) N 2	0.00116	1.48799	
15.	RY* ( 2) N 2	0.00044	1.59319	
16.	RY* ( 3) N 2	0.00038	2.06473	
17.	RY* ( 4) N 2	0.00002	2.25916	
18.	RY* ( 1) H 3	0.00178	0.94854	
19.	RY* ( 1) H 4	0.00096	0.94462	
20.	RY* ( 1) H 5	0.00096	0.94462	
21.	RY* ( 1) H 6	0.00122	0.99735	
22.	RY* ( 1) H 7	0.00122	0.99735	
23.	BD* ( 1) C 1- N 2	0.00016	0.56992	
24.	BD* ( 1) C 1- H 3	0.01568	0.68732	
25.	BD* ( 1) C 1- H 4	0.00770	0.69635	
26.	BD* ( 1) C 1- H 5	0.00770	0.69635	
27.	BD* ( 1) N 2- H 6	0.00427	0.68084	
28.	BD* ( 1) N 2- H 7	0.00427	0.68084	
-----				
	Total Lewis	17.95048	( 99.7249%)	
	Valence non-Lewis	0.03977	( 0.2209%)	
	Rydberg non-Lewis	0.00975	( 0.0542%)	
-----				
	Total unit 1	18.00000	(100.0000%)	
	Charge unit 1	0.00000		

---

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 nitrogen lone pair (NBO 9) is seen to be the lowest-occupancy (1.97795 electrons) and highest-energy (-0.44592 a.u.) Lewis NBO, and to be primarily delocalized into antibonds 24, 25, 26 (the vicinal  $\sigma^*_{\text{CH}}$  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 (particularly, NBO 24).]

---

---

## 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 (General Introduction and Installation) for the necessary background to this Section. The NBO User's Guide describes core NBO options (Sec. B.1-B.6), the GENNBO keylist (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, \$SCORE, \$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) \$SCORE, (3) \$CHOOSE, (4) \$DEL of presentation in Sections B.2-B.5. Keywords may be typed in upper or lower case, and will be echoed near the top of the NBO output. A \$KEY list can be continued to any number of lines, but

all the entries of a \$KEY list must appear in a distinct set of lines, starting with the \$KEY name 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          LFNPR          DETAIL          BNDIDX          AOINFO  
 PLOT          ARCHIVE          NBODAF          DIST

*Print Level Control:*

PRINT=n

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 \$KEY lists) 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    LFNPR 16    NBOMO=W25

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

*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):

<i>KEYWORD</i>	<i>OPTION DESCRIPTION</i>
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 $\alpha$ and $\beta$ spin), as suggested by Michl and coworkers [ <i>J. Am. Chem. Soc.</i> <b>114</b> , 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.)

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

		<p>following significance:</p> <p>ang [1.0] = threshold angular deviation for printing</p> <p>pct [25] = threshold percentage <i>p/d</i>-character for printing</p> <p>occ [0.1] = threshold NBO occupancy for printing</p> <p>Parameter values may be separated by a space or a comma; for example:</p> <pre>BEND=2, 10, 1.9</pre> <p>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% <i>p/d</i>-character (pct), and NBOs of occupancy at least 1.9 electrons (occ).</p>
E2PERT	eval	<p>Request the Perturbation Theory Energy Analysis table (Section A.3.5), where</p> <p>eval [0.5] = threshold energy (in kcal/mol) for printing</p> <p>Entries will be printed for NBO donor-acceptor interaction energies that exceed the 'eval' threshold; for example:</p> <pre>E2PERT=5.0</pre> <p>This example would print only interactions of at least 5 kcal/mol (i.e., only the single entry for the 8.13 kcal/mol <math>n_N \rightarrow \sigma^*_{CH}</math> interaction in the output of Section A.3.5).</p>
DIPOLE	dval	<p>Request the Molecular Dipole Moment Analysis table (Section B.6.3), where</p> <p>dval [0.02] = threshold dipole moment (Debye) for printing</p> <p>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; for example:</p> <pre>DIPOLE=0.1</pre> <p>This example would print out dipole contributions of all NBOs (and their delocalization interactions) of magnitude <math>\geq 0.1</math> D.</p>

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.2.4 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  $\rightarrow$  (PNAOs)  $\rightarrow$  NAOs  $\rightarrow$  NHOs  $\rightarrow$  NBOs  $\rightarrow$  NLMOs  $\rightarrow$  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  $\rightarrow$  OUT, is constructed by concatenating the acronymms for the two sets (in generic form ``INOOUT"). For example, the transformation AO  $\rightarrow$  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.,

*AO basis:* AONAO AONHO AONBO AONLMO AOMO  
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  $IN \rightarrow OUT$  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 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:

<i>energy matrices</i>	FAO	FNAO	FNHO	FNBO	FNLMO	FMO
	FMO	FPNHO	FPNBO			
	KAO	KNAO	KNHO	KNBO	KNLMO	KMO
	VAO	VNAO	VNHO	VNBO	VNLMO	VMO
<i>density matrix</i>	DMAO	DMNAO	DMNHO	DMNBO	DMNLMO	DMMO
	DMPNAO					
<i>dipole matrix</i>	DIAO	DINAO	DINHO	DINBO	DINLMO	DIMO
<i>overlap matrix</i>	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:

<i>matrix</i>	<i>default</i> LFN	<i>matrix</i>	<i>default</i> LFN	<i>matrix</i>	<i>default</i> 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  $\langle i_1 j_1 / i_2 j_2 / \dots / i_n j_n \rangle$  that follows the main keyword (separated by at least one space). For example, the command

```
FNBO
```

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.2.5 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 <i>jobname</i> 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.
LFNPR=n	Set the logical file number (LFN) for NBO program output. The default LFN is $n = 6$ , the usual LFN for output from the ESS program. This option can be used to steer the NBO section of the job output to a desired file.
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 <i>NBOView</i> . This activates the AOINFO keyword as well as other matrix output keywords (AONBO=W, etc.) needed by <i>NBOView</i> .
ARCHIVE=n	Request writing the FILE47 archive file (Sec. B.7) to external disk file LFN = <i>n</i> , 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 = <i>n</i> , 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 <i>all</i> 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.2.7 Semi-Documented Additional Keywords

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

<i>KEYWORD</i>	<i>OPTION DESCRIPTION</i>
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 $\mathbf{T}_{\text{Ryd}}$ and $\mathbf{T}_{\text{red}}$ [A. E. Reed, R. B. Weinstock, and F. Weinhold, J. Chem. Phys. <b>83</b> , 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.

SEV	Print the eigenvectors of the overlap matrix in the AO basis.
SPARTAN	Print a Spartan-style archive file.
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 \$SCORE 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 \$SCORE 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 \$SCORE list includes only integers (rather than keywords) to specify the core modifications, but the rules are otherwise similar to those for other keylists. The \$SCORE list (if included) must follow the \$NBO keylist and precede the \$CHOOSE or \$DEL keylists.

The format of the \$SCORE modification list is:

first line:	The keyword ``\$SCORE"
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 ``\$SCORE" 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.

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 \$SCORE modification list is read only once, and applies to both  $\alpha$  and  $\beta$  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:

```
$SCORE
  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

```
$SCORE  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:	<p>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 <i>valence</i> lone pairs should be entered, since the number of core orbitals on each center is presumed known.)</p> <p>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</p> <p>``S" single bond</p> <p>``D" double bond</p> <p>``T" triple bond</p> <p>``Q" quadruple bond</p> <p>followed by the two atomic centers of the bond (e.g., ``D 9 16" for a double bond between atoms 9 and 16).</p> <p>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</p>

	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 $\alpha$ spin list.
next line:	The keyword ``BETA" (for open-shell wavefunctions)
next lines:	The input for $\beta$ 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  $\text{FH} \cdots \text{CO}$ , with atom numbering F(1)-H(2)  $\cdots$  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  $\text{FH} \cdots \text{O}_2$  complex, with atom numbering F(1)-H(2)  $\cdots$  O(3)-O(4), and with the unpaired electrons on  $\text{O}_2$  being of  $\alpha$  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  $\alpha$  and  $\beta$  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  $\alpha$  and  $\beta$  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!! If this is not done, the energy of the deletion will be incorrect because the assumption is made in evaluating the energy that the original symmetry still exists, and the variational principle may be violated. (For example, if symmetry is used for ethane, it is permissible to do 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.5.2 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 called for 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 "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 Rydberg and antibond orbitals.

The Rydberg and antibond orbitals are the non-Lewis NBO orbitals that have stars in their labels (RY\*, BD\*) in the NBO analysis output. To delete all these orbitals, simply enter ``NOSTAR". The result of this deletion is the energy of the idealized NBO natural Lewis structure, 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 ``NOSTAR" deletion corresponds rigorously to the variational expectation value of the determinant of doubly occupied Lewis NBOs).

#### (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 starred (antibond/Rydberg) orbitals on a particular molecular unit.

This is called for by typing ``DESTAR", then the number of molecular units to be destarred, then the keyword ``UNIT" (or ``UNITS"), then the list of units; for example:

DESTAR 2 UNITS 3 4

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

This is called for 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:

- (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.5.3 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  $\alpha$  NBOs often differ from those of the  $\beta$  NBOs, so that distinct  $\alpha$ ,  $\beta$  deletions lists are generally required. For example, O<sub>2</sub> (triplet) has one bond in the  $\alpha$  system and three in the  $\beta$  system, if the unpaired electrons are in the  $\alpha$  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.5.4 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  $\alpha$  and  $\beta$  spin manifolds. Section B.6.12 shows the effect of using effective core potentials for Cu<sub>2</sub>, also illustrating aspects of the inclusion of *d* functions.

#### *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: 0.00000

Hybridization/Polarization Analysis of NLMOs in NAO Basis:  
 NLMO/Occupancy/Percent from Parent NBO/ Atomic Hybrid Contributions

---

-----

1.	(2.00000)	99.9290%	BD ( 1) C 1- N 2
			40.039% C 1 s( 21.54%)p 3.64( 78.46%)
			59.891% N 2 s( 30.98%)p 2.23( 69.02%)
			0.015% H 3 s(100.00%)
			0.021% H 6 s(100.00%)
			0.021% H 7 s(100.00%)
2.	(2.00000)	99.9301%	BD ( 1) C 1- H 3
			59.675% C 1 s( 25.44%)p 2.93( 74.56%)
			0.040% N 2 s( 1.99%)p49.22( 98.01%)
			40.258% H 3 s(100.00%)
3.	(2.00000)	99.6996%	BD ( 1) C 1- H 4
			60.848% C 1 s( 25.25%)p 2.96( 74.75%)
			0.093% N 2 s( 13.08%)p 6.65( 86.92%)
			0.014% H 3 s(100.00%)
			38.861% H 4 s(100.00%)
			0.017% H 5 s(100.00%)
			0.158% H 6 s(100.00%)
4.	(2.00000)	99.6996%	BD ( 1) C 1- H 5
			60.848% C 1 s( 25.25%)p 2.96( 74.75%)
			0.093% N 2 s( 13.08%)p 6.65( 86.92%)
			0.014% H 3 s(100.00%)
			0.017% H 4 s(100.00%)
			38.861% H 5 s(100.00%)
			0.158% H 7 s(100.00%)
5.	(2.00000)	99.7206%	BD ( 1) N 2- H 6
			0.113% C 1 s( 5.15%)p18.41( 94.85%)
			67.929% N 2 s( 25.82%)p 2.87( 74.18%)
			0.137% H 4 s(100.00%)
			0.014% H 5 s(100.00%)
			31.793% H 6 s(100.00%)
6.	(2.00000)	99.7206%	BD ( 1) N 2- H 7
			0.113% C 1 s( 5.15%)p18.41( 94.85%)
			67.929% N 2 s( 25.82%)p 2.87( 74.18%)
			0.014% H 4 s(100.00%)
			0.137% H 5 s(100.00%)
			31.793% H 7 s(100.00%)
7.	(2.00000)	99.9499%	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%)
8.	(2.00000)	99.9763%	CR ( 1) N 2
			0.010% C 1 s( 22.30%)p 3.48( 77.70%)
			99.980% N 2 s(100.00%)p 0.00( 0.00%)
9.	(2.00000)	98.8972%	LP ( 1) N 2
			0.440% C 1 s( 1.05%)p94.15( 98.95%)
			98.897% N 2 s( 17.85%)p 4.60( 82.15%)
			0.489% H 3 s(100.00%)
			0.085% H 4 s(100.00%)
			0.085% H 5 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  $sp^\lambda$  character and percentage  $s$ - and  $p$ -character) of the NAOs. For example, NLMO 9 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 9, is principally delocalized onto NBO 24, the vicinal C(1)-H(3) antibond [with lesser delocalizations onto NBOs 25, 26, the C(1)-H(4) and C(1)-H(5) antibonds].

### 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]

dipole	Orbital	NLMO bond dipole				NBO bond		
		x	y	z	Total	x	y	z
----- Total								
=====								
0.77	1. BD ( 1) C 1- N 2	-0.76	-0.08	0.00	0.76	-0.76	-0.09	0.00
1.97	2. BD ( 1) C 1- H 3	0.49	1.90	0.00	1.96	0.50	1.90	0.00
0.03					deloc 14:	0.03	-0.01	0.00
0.02					deloc 25:	-0.01	0.00	0.02
0.02					deloc 26:	-0.01	0.00	-0.02



The bottom line of the table shows the individual (x,y,z) vector components (-0.45,-1.67,0.00) and length (1.73 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' contributions to give the net molecular moment). Each NLMO or NBO bond dipole vector  $\mu_{AB}$  is evaluated as

$$\mu_{AB} = \mu_{AB}^{(elec)} + \mu_{AB}^{(nuc)}$$

where  $\mu_{AB}^{(elec)} = 2e\langle\sigma_{AB}|\mathbf{r}|\sigma_{AB}\rangle$  is the electronic dipole expectation value for an electron pair in the  $\sigma_{AB}$  NLMO or NBO, and  $\mu_{AB}^{(nuc)}$  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,  $\alpha$  or  $\beta$  spin)

$$c_{ji}^2 [ \langle\sigma_j|\mu|\sigma_j\rangle - \langle\sigma_i|\mu|\sigma_i\rangle ] + 2 c_{ii} c_{ji} \langle\sigma_i|\mu|\sigma_j\rangle + \sum_k' c_{ji} c_{ki} \langle\sigma_j|\mu|\sigma_k\rangle$$

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  $\mu$  is from the nitrogen lone pair, table entry 9, which has an NLMO dipole of 2.91 Debye or NBO dipole of 3.06. 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 24. 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.6.4 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.	C1 ( N2 )	-0.0208	-0.7203	-0.0571	-0.0665	0.0438	0.0672	0.0438
		0.0672						
2.	N2 ( C1 )	-0.7203	-0.3083	-0.0773	-0.0627	0.0835	0.0646	0.0835
		0.0646						
3.	C1 ( H3 )	-0.0571	-0.0773	-0.1394	-0.6758	0.0638	0.0746	0.0638
		0.0746						
4.	H3 ( C1 )	-0.0665	-0.0627	-0.6758	0.1349	0.0740	0.0672	0.0740
		0.0672						
5.	C1 ( H4 )	0.0438	0.0835	0.0638	0.0740	-0.1466	-0.6761	-0.0548
		-0.0759						
6.	H4 ( C1 )	0.0672	0.0646	0.0746	0.0672	-0.6761	0.1541	-0.0759
		-0.0697						
7.	C1 ( H5 )	0.0438	0.0835	0.0638	0.0740	-0.0548	-0.0759	-0.1466
		-0.6761						
8.	H5 ( C1 )	0.0672	0.0646	0.0746	0.0672	-0.0759	-0.0697	-0.6761
		0.1541						
9.	N2 ( H6 )	0.0926	0.1499	0.0240	-0.0113	0.0912	-0.0078	-0.0349
		0.0134						
10.	H6 ( N2 )	0.1083	0.0826	-0.0010	0.0232	-0.0118	-0.0242	0.0017
		-0.0224						
11.	N2 ( H7 )	0.0926	0.1499	0.0240	-0.0113	-0.0349	0.0134	0.0912
		-0.0078						
12.	H7 ( N2 )	0.1083	0.0826	-0.0010	0.0232	0.0017	-0.0224	-0.0118
		-0.0242						
13.	C1 (cr)	0.3962	0.4168	0.4400	0.3893	-0.4447	-0.3869	-0.4447
		-0.3869						
14.	N2 (cr)	0.6147	0.7083	0.0039	0.0249	-0.0130	-0.0251	-0.0130
		-0.0251						
15.	N2 (lp)	0.0762	0.0955	-0.1043	0.0254	-0.0386	0.0160	-0.0386
		0.0160						

16.	C1 (ry*)	-0.1320	0.0924	0.0705	-0.0815	0.0022	-0.0037	0.0022
		-0.0037						
17.	C1 (ry*)	0.0000	0.0000	0.0000	0.0000	0.0719	-0.0910	-0.0719
		0.0910						
18.	C1 (ry*)	-0.1023	0.0764	-0.0643	0.0795	-0.0074	0.0105	-0.0074
		0.0105						
19.	C1 (ry*)	0.0266	-0.0213	0.0019	-0.0057	0.0667	-0.0788	0.0667
		-0.0788						
20.	N2 (ry*)	0.0151	-0.0177	-0.0351	-0.0172	-0.0179	-0.0146	-0.0179
		-0.0146						
21.	N2 (ry*)	0.0000	0.0000	0.0000	0.0000	-0.0158	-0.0249	0.0158
		0.0249						
22.	N2 (ry*)	0.1799	-0.1440	-0.0064	0.0295	0.0038	-0.0289	0.0038
		-0.0289						
23.	N2 (ry*)	0.0183	-0.0136	-0.0051	0.0213	0.0032	-0.0095	0.0032
		-0.0095						
24.	H3 (ry*)	0.0253	-0.0038	0.2834	-0.3497	-0.0248	0.0047	-0.0248
		0.0047						
25.	H4 (ry*)	0.0223	-0.0071	0.0211	-0.0068	-0.2789	0.3553	-0.0227
		0.0069						
26.	H5 (ry*)	0.0223	-0.0071	0.0211	-0.0068	-0.0227	0.0069	-0.2789
		0.3553						
27.	H6 (ry*)	0.0124	0.0172	-0.0067	0.0219	-0.0080	0.0097	0.0057
		-0.0222						
28.	H7 (ry*)	0.0124	0.0172	-0.0067	0.0219	0.0057	-0.0222	-0.0080
		0.0097						

---

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 1) is the bonding hybrid on C(1) directed toward N(2), ``N 2(lp)" (NBO 15) 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 (1,2) Fock matrix element between the directly interacting NHOs forming the C-N bond NBO is -0.7203 a.u., whereas the (1,9) matrix element, between the C(1) hybrid pointing toward N(2) and the N(2) hybrid pointing toward H(6), is 0.0926 a.u.

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



	NBO	9	10	11	12	13	14	15
1.	C1 - N2	0.1062	-0.0143	0.0006	0.0000	0.0049	0.0000	-0.0061
2.	C1 - H3	-0.3343	-0.0044	0.0015	0.0000	0.0007	0.0000	-0.0080
3.	C1 - H4	-0.1186	-0.0186	0.0103	0.0258	-0.0048	-0.0272	-0.0104
4.	C1 - H5	-0.1186	-0.0186	0.0103	-0.0258	-0.0048	0.0272	-0.0104
5.	N2 - H6	-0.1167	-0.0024	-0.0145	-0.0293	-0.0162	-0.0253	0.0040
6.	N2 - H7	-0.1167	-0.0024	-0.0145	0.0293	-0.0162	0.0253	0.0040
7.	C1 (cr)	0.0037	-0.0134	-0.0082	0.0000	0.0008	0.0000	-0.0008
8.	N2 (cr)	-0.0189	-0.0055	0.0030	0.0000	-0.0026	0.0000	0.0035
9.	N2 (lp)	0.9007	-0.0144	0.0055	0.0000	0.0925	0.0000	0.0130
10.	C1 (ry*)	-0.0128	-0.0993	0.0553	0.0000	0.0536	0.0000	0.3301
11.	C1 (ry*)	0.0000	0.0000	0.0000	0.0836	0.0000	0.1845	0.0000
12.	C1 (ry*)	-0.0039	-0.0612	0.0748	0.0000	-0.1160	0.0000	0.1213
13.	C1 (ry*)	-0.0018	0.0936	0.0192	0.0000	0.1022	0.0000	-0.1516
14.	N2 (ry*)	-0.0086	-0.0232	0.0071	0.0000	-0.0461	0.0000	-0.0178
15.	N2 (ry*)	0.0000	0.0000	0.0000	0.0176	0.0000	-0.0856	0.0000
16.	N2 (ry*)	0.0006	0.0395	-0.0836	0.0000	0.0221	0.0000	-0.1565
17.	N2 (ry*)	0.0003	0.0614	-0.0222	0.0000	0.0114	0.0000	0.0584
18.	H3 (ry*)	-0.0218	-0.2483	-0.2232	0.0000	0.4827	0.0000	0.0001
19.	H4 (ry*)	0.0060	-0.1973	-0.3224	-0.3372	-0.2069	-0.2151	-0.0483
20.	H5 (ry*)	0.0060	-0.1973	-0.3224	0.3372	-0.2069	0.2151	-0.0483
21.	H6 (ry*)	0.0027	-0.2869	0.2132	0.2297	-0.0372	-0.3543	-0.1737
22.	H7 (ry*)	0.0027	-0.2869	0.2132	-0.2297	-0.0372	0.3543	-0.1737
23.	C1 - N2 *	-0.0031	-0.2357	0.2598	0.0000	-0.1096	0.0000	0.8051
24.	C1 - H3 *	-0.0799	-0.3214	-0.2654	0.0000	0.6687	0.0000	0.1133
25.	C1 - H4 *	-0.0369	0.2559	0.3890	0.4699	0.2968	0.3193	-0.0477
26.	C1 - H5 *	-0.0369	0.2559	0.3890	-0.4699	0.2968	-0.3193	-0.0477
27.	N2 - H6 *	-0.0031	0.4339	-0.3112	-0.3280	0.0474	0.4519	0.2168
28.	N2 - H7 *	-0.0031	0.4339	-0.3112	0.3280	0.0474	-0.4519	0.2168

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

$$\varphi_5 \cong -0.594(\sigma_{N_2H_6} - \sigma_{N_2H_7}) + 0.381(\sigma_{C_1H_4} - \sigma_{C_1H_5})$$

$$\varphi_8 \cong 0.381(\sigma_{N_2H_6} - \sigma_{N_2H_7}) + 0.594(\sigma_{C_1H_4} - \sigma_{C_1H_5})$$

whereas  $\varphi_6$  is primarily the C-H(3) NBO and  $\varphi_9$  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 " will print out the values of the  $S_{9,24} = \langle n_N | \sigma_{CH_3}^* \rangle$  and  $S_{6,26} = \langle \sigma_{NH_7} | \sigma_{CH_5}^* \rangle$  PNBO overlap integrals as shown below:

---

PNBO overlap matrix:

```
  2 user-requested elements:
-----
   i   j   matrix(i,j)   label(i)   label(j)
-----
   9  24   0.1681451485D+00  N 2(lp)   C 1- H 3*
   6  26   0.1703815205D+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	0.9964	0.9472	0.9394	0.9394	0.0020	0.0020
2. N	0.9964	0.0000	0.0208	0.0052	0.0052	0.8611	0.8611
3. H	0.9472	0.0208	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	0.8611	0.0002	0.0079	0.0005	0.0000	0.0003
7. H	0.0020	0.8611	0.0002	0.0005	0.0079	0.0003	0.0000

Wiberg bond index, Totals by atom:

Atom	1
1. C	3.8265
2. N	2.7499
3. H	0.9691

4. H 0.9544  
5. H 0.9544  
6. H 0.8720  
7. H 0.8720

---

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	0.7815	0.7614	0.7633	0.7633	-0.0103	-0.0103
2.	N	0.7815	0.0000	-0.0225	-0.0097	-0.0097	0.6688	0.6688
3.	H	0.7614	-0.0225	0.0000	-0.0039	-0.0039	-0.0019	-0.0019
4.	H	0.7633	-0.0097	-0.0039	0.0000	0.0024	0.0038	-0.0032
5.	H	0.7633	-0.0097	-0.0039	0.0024	0.0000	-0.0032	0.0038
6.	H	-0.0103	0.6688	-0.0019	0.0038	-0.0032	0.0000	-0.0069
7.	H	-0.0103	0.6688	-0.0019	-0.0032	0.0038	-0.0069	0.0000

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

	Atom	1
1.	C	3.0488
2.	N	2.0772
3.	H	0.7273
4.	H	0.7527
5.	H	0.7527
6.	H	0.6503
7.	H	0.6503

---

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	1	0.8007741	0.7314361
1	2	5	0.0022694	0.1796696
1	2	6	0.0022694	0.1796696
1	2	9	0.0088061	0.3053730
1	3	2	0.8051647	0.7862263
1	3	9	-0.0088061	-0.5762575
1	4	3	0.7772179	0.7874312
1	4	5	-0.0022694	-0.5396947
1	5	4	0.7772179	0.7874312
1	5	6	-0.0022694	-0.5396947
1	6	3	-0.0031652	-0.0920524
1	6	5	0.0022694	0.0852070
1	7	4	-0.0031652	-0.0920524
1	7	6	0.0022694	0.0852070
2	3	9	-0.0097841	-0.0930204
2	4	5	-0.0027437	-0.0701717
2	5	6	-0.0027437	-0.0701717
2	6	5	0.6358512	0.7286061
2	7	6	0.6358512	0.7286061
4	6	3	0.0031652	0.0429202
4	6	5	0.0027437	0.0399352
5	7	4	0.0031652	0.0429202
5	7	6	0.0027437	0.0399352

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, NLMO 1 occurs only in the first line, contributing a bond of formal order 0.801 between C(1) and N(2), whereas NLMO 9 (the nitrogen lone pair) contributes a slight strengthening (+0.0088) of the C(1)-N(2) bond, a weakening (-0.0088) of the vicinal C(1)-H(3) bond, and a slight negative bond order (-0.0098) 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	0.8174	0.7960	0.7732	0.7732	-0.0013	-0.0013
2. N	0.8174	0.0000	-0.0104	-0.0030	-0.0030	0.6337	0.6337
3. H	0.7960	-0.0104	0.0000	-0.0020	-0.0020	0.0001	0.0001
4. H	0.7732	-0.0030	-0.0020	0.0000	0.0020	0.0062	0.0000
5. H	0.7732	-0.0030	-0.0020	0.0020	0.0000	0.0000	0.0062
6. H	-0.0013	0.6337	0.0001	0.0062	0.0000	0.0000	-0.0001
7. H	-0.0013	0.6337	0.0001	0.0000	0.0062	-0.0001	0.0000

For example, the table attributes a formal bond order of 0.8174 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, and each has certain advantages and disadvantages. *Caveat emptor!*

### 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 alters the occupancy threshold downward by 0.1e and repeats the search. (This formerly required the RESONANCE keyword, but now occurs automatically.) 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 the NBO search cycles shown below:

---

NATURAL BOND ORBITAL ANALYSIS:

Cycle Dev	Occ. Thresh.	Occupancies		Lewis Structure				Low	High
		Lewis	Non-Lewis	CR	BD	3C	LP	occ (L)	occ (NL)
1 (1) 0.44	1.90	38.87476	3.12524	6	12	0	3	3	3
2 (2) 0.44	1.90	38.87476	3.12524	6	12	0	3	3	3
3 (1) 0.44	1.80	38.87476	3.12524	6	12	0	3	3	3
4 (2) 0.44	1.80	38.87476	3.12524	6	12	0	3	3	3
5 (1) 0.44	1.70	38.87476	3.12524	6	12	0	3	3	3
6 (2) 0.44	1.70	38.87476	3.12524	6	12	0	3	3	3
7 (1) 0.44	1.60	40.87476	1.12524	6	15	0	0	0	3
8 (2) 0.44	1.60	40.87476	1.12524	6	15	0	0	0	3
9 (1) 0.44	1.50	40.87476	1.12524	6	15	0	0	0	3

10(2)	1.50	40.87476	1.12524	6	15	0	0	0	3
0.44									
11(1)	1.60	40.87476	1.12524	6	15	0	0	0	3
0.44									

-----

-----

As this table shows, the occupancy threshold was successively lowered from 1.90 to 1.50 by 0.1e for each cycle, and the NBO search repeated. In this case, the best Lewis structure (lowest overall non-Lewis occupancy, 1.12524e) was found in cycle 7, with occupancy threshold 1.60e. 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
-----			
1. (1.98940)	BD ( 1) C 1- C 2		
0.0000	( 50.00%)	0.7071* C 1 s( 34.23%)p 1.92( 65.77%)	0.0000 0.5851 -0.8109 0.0097
0.0000	( 50.00%)	0.7071* C 2 s( 34.23%)p 1.92( 65.77%)	0.0000 0.5851 0.8109 0.0097
2. (1.98940)	BD ( 1) C 1- C 6		
0.0000	( 50.00%)	0.7071* C 1 s( 34.23%)p 1.92( 65.77%)	0.0000 0.5851 0.4138 -0.6974
0.0000	( 50.00%)	0.7071* C 6 s( 34.23%)p 1.92( 65.77%)	0.0000 0.5851 -0.3971 0.7071
3. (1.66667)	BD ( 2) C 1- C 6		
1.0000	( 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 6 s( 0.00%)p 1.00(100.00%)	0.0000 0.0000 0.0000 0.0000
4. (1.98977)	BD ( 1) C 1- H 7		
0.0000	( 51.73%)	0.7193* C 1 s( 31.53%)p 2.17( 68.47%)	0.0000 0.5615 0.4137 0.7166
0.0000	( 48.27%)	0.6947* H 7 s(100.00%)	1.0000
5. (1.98940)	BD ( 1) C 2- C 3		
0.0000	( 50.00%)	0.7071* C 2 s( 34.23%)p 1.92( 65.77%)	0.0000 0.5851 -0.4138 -0.6974
0.0000	( 50.00%)	0.7071* C 3 s( 34.23%)p 1.92( 65.77%)	0.0000 0.5851 0.3971 0.7071
6. (1.66667)	BD ( 2) C 2- C 3		
	( 50.00%)	0.7071* C 2 s( 0.00%)p 1.00(100.00%)	

1.0000				0.0000	0.0000	0.0000	0.0000
	( 50.00%)	0.7071*	C 3 s	( 0.00%)	p 1.00	(100.00%)	
				0.0000	0.0000	0.0000	0.0000
1.0000							
7. (1.98977)	BD ( 1) C 2-	H 8					
	( 51.73%)	0.7193*	C 2 s	( 31.53%)	p 2.17	( 68.47%)	
				0.0000	0.5615	-0.4137	0.7166
0.0000							
	( 48.27%)	0.6947*	H 8 s	(100.00%)			
				1.0000			
8. (1.98940)	BD ( 1) C 3-	C 4					
	( 50.00%)	0.7071*	C 3 s	( 34.23%)	p 1.92	( 65.77%)	
				0.0000	0.5851	0.3971	-0.7071
0.0000							
	( 50.00%)	0.7071*	C 4 s	( 34.23%)	p 1.92	( 65.77%)	
				0.0000	0.5851	-0.4138	0.6974
0.0000							
9. (1.98977)	BD ( 1) C 3-	H 9					
	( 51.73%)	0.7193*	C 3 s	( 31.53%)	p 2.17	( 68.47%)	
				0.0000	0.5615	-0.8275	0.0000
0.0000							
	( 48.27%)	0.6947*	H 9 s	(100.00%)			
				1.0000			
10. (1.66667)	BD ( 2) C 4-	C 5					
	( 50.00%)	0.7071*	C 4 s	( 0.00%)	p 1.00	(100.00%)	
				0.0000	0.0000	0.0000	0.0000
1.0000							
	( 50.00%)	0.7071*	C 5 s	( 0.00%)	p 1.00	(100.00%)	
				0.0000	0.0000	0.0000	0.0000
1.0000							
11. (1.98940)	BD ( 1) C 4-	C 5					
	( 50.00%)	0.7071*	C 4 s	( 34.23%)	p 1.92	( 65.77%)	
				0.0000	0.5851	0.8109	-0.0097
0.0000							
	( 50.00%)	0.7071*	C 5 s	( 34.23%)	p 1.92	( 65.77%)	
				0.0000	0.5851	-0.8109	-0.0097
0.0000							
12. (1.98977)	BD ( 1) C 4-	H10					
	( 51.73%)	0.7193*	C 4 s	( 31.53%)	p 2.17	( 68.47%)	
				0.0000	0.5615	-0.4137	-0.7166
0.0000							
	( 48.27%)	0.6947*	H10 s	(100.00%)			
				1.0000			
13. (1.98940)	BD ( 1) C 5-	C 6					
	( 50.00%)	0.7071*	C 5 s	( 34.23%)	p 1.92	( 65.77%)	
				0.0000	0.5851	0.4138	0.6974
0.0000							
	( 50.00%)	0.7071*	C 6 s	( 34.23%)	p 1.92	( 65.77%)	
				0.0000	0.5851	-0.3971	-0.7071
0.0000							
14. (1.98977)	BD ( 1) C 5-	H11					
	( 51.73%)	0.7193*	C 5 s	( 31.53%)	p 2.17	( 68.47%)	
				0.0000	0.5615	0.4137	-0.7166
0.0000							
	( 48.27%)	0.6947*	H11 s	(100.00%)			
				1.0000			



0.0000				0.0000	0.5851	0.3971	0.7071
27. (0.33333)	BD*( 2) C 2- C 3	( 50.00%)	0.7071*	C 2 s( 0.00%)p 1.00(100.00%)	0.0000	0.0000	0.0000
1.0000		( 50.00%)	-0.7071*	C 3 s( 0.00%)p 1.00(100.00%)	0.0000	0.0000	0.0000
1.0000					0.0000	0.0000	0.0000
28. (0.01011)	BD*( 1) C 2- H 8	( 48.27%)	0.6947*	C 2 s( 31.53%)p 2.17( 68.47%)	0.0000	-0.5615	0.4137
0.0000		( 51.73%)	-0.7193*	H 8 s(100.00%)			-0.7166
							-1.0000
29. (0.01077)	BD*( 1) C 3- C 4	( 50.00%)	0.7071*	C 3 s( 34.23%)p 1.92( 65.77%)	0.0000	0.5851	0.3971
0.0000		( 50.00%)	-0.7071*	C 4 s( 34.23%)p 1.92( 65.77%)	0.0000	0.5851	-0.7071
					0.0000	0.5851	-0.4138
0.0000							0.6974
30. (0.01011)	BD*( 1) C 3- H 9	( 48.27%)	0.6947*	C 3 s( 31.53%)p 2.17( 68.47%)	0.0000	-0.5615	0.8275
0.0000		( 51.73%)	-0.7193*	H 9 s(100.00%)			0.0000
							-1.0000
31. (0.33333)	BD*( 2) C 4- C 5	( 50.00%)	0.7071*	C 4 s( 0.00%)p 1.00(100.00%)	0.0000	0.0000	0.0000
1.0000		( 50.00%)	-0.7071*	C 5 s( 0.00%)p 1.00(100.00%)	0.0000	0.0000	0.0000
					0.0000	0.0000	0.0000
1.0000							0.0000
32. (0.01077)	BD*( 1) C 4- C 5	( 50.00%)	0.7071*	C 4 s( 34.23%)p 1.92( 65.77%)	0.0000	0.5851	0.8109
0.0000		( 50.00%)	-0.7071*	C 5 s( 34.23%)p 1.92( 65.77%)	0.0000	0.5851	-0.0097
					0.0000	0.5851	-0.8109
0.0000							-0.0097
33. (0.01011)	BD*( 1) C 4- H10	( 48.27%)	0.6947*	C 4 s( 31.53%)p 2.17( 68.47%)	0.0000	-0.5615	0.4137
0.0000		( 51.73%)	-0.7193*	H10 s(100.00%)			0.7166
							-1.0000
34. (0.01077)	BD*( 1) C 5- C 6	( 50.00%)	0.7071*	C 5 s( 34.23%)p 1.92( 65.77%)	0.0000	0.5851	0.4138
0.0000		( 50.00%)	-0.7071*	C 6 s( 34.23%)p 1.92( 65.77%)	0.0000	0.5851	0.6974
					0.0000	0.5851	0.4138
0.0000							0.6974
					0.0000	0.5851	-0.3971
0.0000							-0.7071
35. (0.01011)	BD*( 1) C 5- H11	( 48.27%)	0.6947*	C 5 s( 31.53%)p 2.17( 68.47%)			

```

0.0000          0.0000 -0.5615 -0.4137  0.7166
          ( 51.73%) -0.7193* H11 s(100.00%)
          -1.0000
36. (0.01011) BD*( 1) C 6- H12
          ( 48.27%)  0.6947* C 6 s( 31.53%)p 2.17( 68.47%)
          0.0000 -0.5615 -0.8275  0.0000
0.0000
          ( 51.73%) -0.7193* H12 s(100.00%)
          -1.0000

```

---

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  $\sigma_{CC}$  and  $\sigma_{CH}$  NBOs (1.98940 and 1.98977 electrons, respectively), but three severely depleted  $\pi_{CC}$  bonds (1.66667e) and corresponding high occupancy  $\pi^*_{CC}$  antibonds (0.33333e). 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 2-3, 4-5, and 1-6), 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  $\rho^*$ ). 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.6.7 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//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
-------------	-----------------	-----	------

Cycle Dev	Occ. Thresh.	Lewis	Non-Lewis	CR	BD	3C	LP	occ (L)	occ (NL)
1(1) 0.00	1.90	9.99942	0.00058	1	1	0	3	0	0

Structure accepted: No low occupancy Lewis orbitals

Core	1.99994 ( 99.997% of 2)
Valence Lewis	7.99948 ( 99.994% of 8)
<b>Total Lewis</b>	<b>9.99942 ( 99.994% of 10)</b>
Valence non-Lewis	0.00000 ( 0.000% of 10)
Rydberg non-Lewis	0.00058 ( 0.006% of 10)
<b>Total non-Lewis</b>	<b>0.00058 ( 0.006% of 10)</b>

(Occupancy) Bond orbital/ Coefficients/ Hybrids

1. (2.00000) BD ( 1) F 1- H 2 ( 75.22%) 0.8673* F 1 s( 16.31%)p 5.13( 83.69%) 0.0000 0.0000 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
2. (1.99994) 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
3. (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
4. (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
5. (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
6. (0.00002) RY*( 1) F 1 s( 0.00%)p 1.00(100.00%)
7. (0.00000) RY*( 2) F 1 s( 0.00%)p 1.00(100.00%)
8. (0.00000) RY*( 3) F 1 s( 0.00%)p 1.00(100.00%)
9. (0.00000) RY*( 4) F 1 s( 99.97%)p 0.00( 0.03%)
10. (0.00056) RY*( 1) H 2 s(100.00%) 0.0000 1.0000

```

11. (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%)

```

As the output shows, default NBO analysis leads to a polar covalent description of HF. The  $\sigma_{\text{HF}}$  bond, NBO 1, is formed from a  $p$ -rich ( $sp^{5.13}$ ) hybrid on F and the  $1s$  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:

Cycle Dev	Occ. Thresh.	Occupancies		Lewis Structure				Low	High
		Lewis	Non-Lewis	CR	BD	3C	LP	occ (L)	occ (NL)
1(1) 0.75	1.00	9.50378	0.49622	1	0	0	4	0	1

Structure accepted: Search for bonds prevented by NOBOND keyword

Core	1.99993 ( 99.997% of 2)
Valence Lewis	7.50385 ( 93.798% of 8)
<b>Total Lewis</b>	<b>9.50378 ( 95.038% of 10)</b>
Valence non-Lewis	0.49564 ( 4.956% of 10)
Rydberg non-Lewis	0.00058 ( 0.006% of 10)
<b>Total non-Lewis</b>	<b>0.49622 ( 4.962% of 10)</b>

(Occupancy)	Bond orbital/	Coefficients/	Hybrids
1. (1.99993)	CR ( 1) F 1	s(100.00%)p 0.00( 0.00%)	1.0000 0.0000 0.0000 0.0000
0.0000		0.0000 0.0000 0.0001 0.0000	
2. (2.00000)	LP ( 1) F 1	s( 0.00%)p 1.00(100.00%)	

0.0013	0.0000	0.0000	0.0000	1.0000	-
3. (2.00000) LP ( 2) F 1	0.0000	0.0000	0.0000	0.0000	
	s( 0.00%)p 1.00(100.00%)				
0.0000	0.0000	0.0000	0.0000	0.0000	
4. (1.99948) LP ( 3) F 1	1.0000	-0.0013	0.0000	0.0000	
	s( 83.71%)p 0.19( 16.29%)				
0.0000	0.0000	0.9149	-0.0052	0.0000	
5. (1.50436) LP ( 4) F 1	0.0000	0.0000	-0.4036	-0.0062	
	s( 16.31%)p 5.13( 83.69%)				
0.0000	-0.0001	0.4036	0.0158	0.0000	
6. (0.49564) LP*( 1) H 2	0.0000	0.0000	0.9148	0.0001	
	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( 0.00%)p 1.00(100.00%)				
9. (0.00000) RY*( 3) F 1	s( 0.00%)p 1.00(100.00%)				
10. (0.00000) RY*( 4) F 1	s( 99.97%)p 0.00( 0.03%)				
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<sup>-</sup> lone pair (NBO 5, the  $sp^{5.13}$  hybrid) and significant occupancy (about 0.496e) in the 'empty' H<sup>+</sup> 1s orbital (NBO 6) of the cation. The NOBOND comparison would therefore indicate the superiority of a polar covalent description in this case.

### B.6.8 3CBOND Keyword: Diborane

When the default NBO analysis is applied to diborane or related electron-deficient compounds, there is a dramatic failure to represent the electronic distribution in terms of 1- and 2-center functions only. For example, for B<sub>2</sub>H<sub>6</sub> at the RHF/3-21G//RHF/3-21G level, the default NBO search returns a fractured set of 4 units (two BH<sub>2</sub><sup>+</sup> and two H<sup>-</sup> fragments), with about 2.13 electrons unaccounted for (~15% non-Lewis occupancy), symptomatic of general breakdown of the conventional Lewis structure representation.

However, when the NBO search is extended to 3-center bonds by activating the 3CBOND keyword, one obtains the NBO output shown below:

---

```

/3CBOND / : Search for 3-center bonds
NATURAL BOND ORBITAL ANALYSIS:

```

Cycle Dev	Occ. Thresh.	Occupancies		Lewis Structure				Low	High
		Lewis	Non-Lewis	CR	BD	3C	LP	occ (L)	occ (NL)
1 (1) 0.15	1.90	15.94335	0.05665	2	4	2	0	0	0
2 (2) 0.15	1.90	15.94335	0.05665	2	4	2	0	0	0

Structure accepted: No low occupancy Lewis orbitals

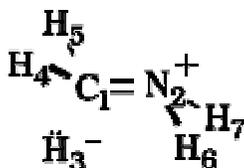
WARNING: 1 low occupancy (

The resulting NBO Lewis structure has improved significantly [only 0.057e (0.35%) non-Lewis occupancy]. The structure includes the expected 3-center B-H-B bonds (NBOs 1, 2), each with reasonably high occupancy (1.9847e). Each 3-c bond is composed of *p*-rich ( $sp^{4.55}$ ) boron hybrids and the hydrogen 1s NAO, with about 47.14% of the orbital density on the central hydrogen. Note that each 3-center bond NBO is associated with *two* 3-c antibond NBOs (viz., NBOs 23, 24 for the first 3-c bond, NBO 1), which contribute in distinct ways to delocalization interactions. Of course, the accuracy of *any* molecular Lewis structure might be improved slightly by extending the NBO search to 3-center bonds (thus allowing greater variational flexibility to maximize occupancy), but this example illustrates the kind of *qualitative* improvement that indicates when 3-center bonds are needed in the zeroth-order picture of the bonding.

Note that the NBO 3-c label may frequently 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.6.9 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:

Cycle	Occ. Thresh.	Occupancies		Lewis Structure				Low	High
		Lewis	Non-Lewis	CR	BD	3C	LP	occ (L)	occ (NL)
1 (1)	1.90	16.66741	1.33259	2	6	0	1	1	2
Dev	0.95								

Structure accepted: NBOs selected via the \$CHOOSE keylist

WARNING: 1 low occupancy (

---

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 1.333e, 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 9), which has less than half the expected occupancy (0.81453e). The C-N  $\pi$  bond (NBO 1) is seen to be more than 92% 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.

### 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 ``NOSTAR" 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. The \$DEL keylist in this case is

```
$DEL NOSTAR $END
```

This leads to the output shown below:

---

```
NOSTAR: Delete all Rydberg/antibond 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
```

Occupations of bond orbitals:

Orbital	No deletions	This deletion	Change
1. BD ( 1) C 1- N 2	1.99858	2.00000	0.00142
2. BD ( 1) C 1- H 3	1.99860	2.00000	0.00140
3. BD ( 1) C 1- H 4	1.99399	2.00000	0.00601
4. BD ( 1) C 1- H 5	1.99399	2.00000	0.00601
5. BD ( 1) N 2- H 6	1.99442	2.00000	0.00558
6. BD ( 1) N 2- H 7	1.99442	2.00000	0.00558
7. CR ( 1) C 1	1.99900	2.00000	0.00100
8. CR ( 1) N 2	1.99953	2.00000	0.00047
9. LP ( 1) N 2	1.97795	2.00000	0.02205
10. RY*( 1) C 1	0.00105	0.00000	-0.00105
11. RY*( 2) C 1	0.00034	0.00000	-0.00034
12. RY*( 3) C 1	0.00022	0.00000	-0.00022
13. RY*( 4) C 1	0.00002	0.00000	-0.00002
14. RY*( 1) N 2	0.00116	0.00000	-0.00116
15. RY*( 2) N 2	0.00044	0.00000	-0.00044
16. RY*( 3) N 2	0.00038	0.00000	-0.00038
17. RY*( 4) N 2	0.00002	0.00000	-0.00002
18. RY*( 1) H 3	0.00178	0.00000	-0.00178
19. RY*( 1) H 4	0.00096	0.00000	-0.00096
20. RY*( 1) H 5	0.00096	0.00000	-0.00096
21. RY*( 1) H 6	0.00122	0.00000	-0.00122
22. RY*( 1) H 7	0.00122	0.00000	-0.00122
23. BD*( 1) C 1- N 2	0.00016	0.00000	-0.00016
24. BD*( 1) C 1- H 3	0.01569	0.00000	-0.01569
25. BD*( 1) C 1- H 4	0.00769	0.00000	-0.00769
26. BD*( 1) C 1- H 5	0.00769	0.00000	-0.00769
27. BD*( 1) N 2- H 6	0.00426	0.00000	-0.00426
28. BD*( 1) N 2- H 7	0.00426	0.00000	-0.00426

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 :          -94.618081014  
Total SCF energy   :          -94.679444944  
-----  
Energy change     :          0.061364 a.u.,          38.506 kcal/mol
```

In the output above, the NBO program first enumerates the 19 NBOs to be deleted by the ``NOSTAR" 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 NOSTAR 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 then reports the energy (-94.618081 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 0.061364 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:

2 3 4 7

and orbitals:

14 15 16 17 21 22 27 28

Deletion of the NBO Fock matrix elements between orbitals:

5 6 8 9

and orbitals:

10 11 12 13 18 19 20 24 25 26

Occupations of bond orbitals:

Orbital	No deletions	This deletion	Change
1. BD ( 1) C 1- N 2	1.99858	1.99860	0.00002
2. BD ( 1) C 1- H 3	1.99860	1.99937	0.00077
3. BD ( 1) C 1- H 4	1.99399	1.99911	0.00512
4. BD ( 1) C 1- H 5	1.99399	1.99911	0.00512
5. BD ( 1) N 2- H 6	1.99442	1.99979	0.00537
6. BD ( 1) N 2- H 7	1.99442	1.99979	0.00537
7. CR ( 1) C 1	1.99900	1.99919	0.00019
8. CR ( 1) N 2	1.99953	1.99974	0.00021
9. LP ( 1) N 2	1.97795	1.99996	0.02201
10. RY*( 1) C 1	0.00105	0.00016	-0.00090
11. RY*( 2) C 1	0.00034	0.00000	-0.00033
12. RY*( 3) C 1	0.00022	0.00002	-0.00020
13. RY*( 4) C 1	0.00002	0.00002	0.00000
14. RY*( 1) N 2	0.00116	0.00004	-0.00112
15. RY*( 2) N 2	0.00044	0.00000	-0.00044
16. RY*( 3) N 2	0.00038	0.00003	-0.00035
17. RY*( 4) N 2	0.00002	0.00001	-0.00001
18. RY*( 1) H 3	0.00178	0.00088	-0.00090
19. RY*( 1) H 4	0.00096	0.00057	-0.00038
20. RY*( 1) H 5	0.00096	0.00057	-0.00038
21. RY*( 1) H 6	0.00122	0.00057	-0.00065
22. RY*( 1) H 7	0.00122	0.00057	-0.00065
23. BD*( 1) C 1- N 2	0.00016	0.00034	0.00018
24. BD*( 1) C 1- H 3	0.01569	0.00027	-0.01542
25. BD*( 1) C 1- H 4	0.00769	0.00055	-0.00714
26. BD*( 1) C 1- H 5	0.00769	0.00055	-0.00714
27. BD*( 1) N 2- H 6	0.00426	0.00009	-0.00417
28. BD*( 1) N 2- H 7	0.00426	0.00009	-0.00417

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 :	-94.635029232	
Total SCF energy :	-94.679444944	
Energy change :	0.044416 a.u.,	27.871 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 9, and depleted occupancy (-0.015) of the antiperiplanar  $\sigma^*_{\text{C1H3}}$  antibond, NBO 24, 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 (9,24) element associated with the  $n_{\text{N}} \rightarrow \sigma^*_{\text{C1H3}}$  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 (8.13 kcal/mol) of the  $n_{\text{N}} \rightarrow \sigma^*_{\text{C1H3}}$  (9 $\rightarrow$ 24) interaction that was noted in Section A.3.5.]

### 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 ( $\text{CH}_3$ ), treated at the UHF/6-31G\* level ( $R_{\text{CH}} = 1.0736 \text{ \AA}$ ). In the open-shell case, one obtains two separate NPA and NBO listings, one for the  $\alpha$  and one for the  $\beta$  spin set, corresponding to the "different Lewis structures for different spins" description. A portion of the NBO output for the  $\alpha$  spin manifold is reproduced below:

---

NATURAL BOND ORBITAL ANALYSIS, alpha spin orbitals:

Cycle	Occ. Thresh.	Occupancies		Lewis Structure				Low	High
		Lewis	Non-Lewis	CR	BD	3C	LP	occ (L)	occ (NL)
Dev									
1 (1)	0.90	4.99903	0.00097	1	3	0	1	0	0

Structure accepted: No low occupancy Lewis orbitals

---

Core	0.99984 ( 99.984% of	1)
Valence Lewis	3.99919 ( 99.980% of	4)
Total Lewis	4.99903 ( 99.981% of	5)

---

Valence non-Lewis	0.00081 ( 0.016% of 5)
Rydberg non-Lewis	0.00016 ( 0.003% of 5)
=====	
Total non-Lewis	0.00097 ( 0.019% of 5)

```

-----
(Occupancy)  Bond orbital/ Coefficients/ Hybrids
-----
1. (0.99973) BD ( 1) C 1- H 2
   ( 61.14%)  0.7819* C 1 s( 33.33%)p 2.00( 66.51%)d 0.00(
0.16%)
                                0.0000  0.5772 -0.0070  0.0000 -
0.4076
                                -0.0110  0.7060  0.0191  0.0000
0.0000
                                -0.0338  0.0000  0.0000 -0.0195 -
0.0090
                                ( 38.86%)  0.6233* H 2 s(100.00%)
                                1.0000  0.0080
2. (0.99973) BD ( 1) C 1- H 3
   ( 61.14%)  0.7819* C 1 s( 33.33%)p 2.00( 66.51%)d 0.00(
0.16%)
                                0.0000  0.5772 -0.0070  0.0000 -
0.4076
                                -0.0110 -0.7060 -0.0191  0.0000
0.0000
                                0.0338  0.0000  0.0000 -0.0195 -
0.0090
                                ( 38.86%)  0.6233* H 3 s(100.00%)
                                1.0000  0.0080
3. (0.99973) BD ( 1) C 1- H 4
   ( 61.14%)  0.7819* C 1 s( 33.33%)p 2.00( 66.51%)d 0.00(
0.16%)
                                0.0000  0.5772 -0.0070  0.0000
0.8153
                                0.0221  0.0000  0.0000  0.0000
0.0000
                                0.0000  0.0000  0.0000  0.0391 -
0.0090
                                ( 38.86%)  0.6233* H 4 s(100.00%)
                                1.0000  0.0080
4. (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
5. (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  0.9978 -
0.0668
                                0.0000  0.0000  0.0000  0.0000
0.0000

```

6.	(0.00000)	RY*( 1)	C 1	s(100.00%)p 0.00( 0.00%)d 0.00(
	0.00%)			
7.	(0.00000)	RY*( 2)	C 1	s(100.00%)
8.	(0.00000)	RY*( 3)	C 1	s( 0.00%)p 1.00(100.00%)d 0.00(
	0.00%)			
9.	(0.00000)	RY*( 4)	C 1	s( 0.00%)p 1.00(100.00%)d 0.00(
	0.00%)			
10.	(0.00000)	RY*( 5)	C 1	s( 0.00%)p 1.00(100.00%)
11.	(0.00000)	RY*( 6)	C 1	s( 0.00%)p 1.00( 0.23%)d99.99(
	99.77%)			
12.	(0.00000)	RY*( 7)	C 1	s( 0.00%)p 0.00( 0.00%)d
	1.00(100.00%)			
13.	(0.00000)	RY*( 8)	C 1	s( 0.00%)p 0.00( 0.00%)d
	1.00(100.00%)			
14.	(0.00000)	RY*( 9)	C 1	s( 0.00%)p 1.00( 0.23%)d99.99(
	99.77%)			
15.	(0.00000)	RY*(10)	C 1	s( 0.02%)p 0.00( 0.00%)d99.99(
	99.98%)			
16.	(0.00005)	RY*( 1)	H 2	s(100.00%)
17.	(0.00005)	RY*( 1)	H 3	s(100.00%)
18.	(0.00005)	RY*( 1)	H 4	s(100.00%)
19.	(0.00027)	BD*( 1)	C 1- H 2	
	( 38.86%)	0.6233*	C 1	s( 33.33%)p 2.00( 66.51%)d 0.00(
	0.16%)			
				0.0000 -0.5772 0.0070 0.0000
	0.4076			0.0110 -0.7060 -0.0191 0.0000
	0.0000			0.0338 0.0000 0.0000 0.0195
	0.0090			
		( 61.14%)	-0.7819*	H 2 s(100.00%)
				-1.0000 -0.0080
20.	(0.00027)	BD*( 1)	C 1- H 3	
	( 38.86%)	0.6233*	C 1	s( 33.33%)p 2.00( 66.51%)d 0.00(
	0.16%)			
				0.0000 -0.5772 0.0070 0.0000
	0.4076			0.0110 0.7060 0.0191 0.0000
	0.0000			-0.0338 0.0000 0.0000 0.0195
	0.0090			
		( 61.14%)	-0.7819*	H 3 s(100.00%)
				-1.0000 -0.0080
21.	(0.00027)	BD*( 1)	C 1- H 4	
	( 38.86%)	0.6233*	C 1	s( 33.33%)p 2.00( 66.51%)d 0.00(
	0.16%)			
				0.0000 -0.5772 0.0070 0.0000 -
	0.8153			-0.0221 0.0000 0.0000 0.0000
	0.0000			0.0000 0.0000 0.0000 -0.0391
	0.0090			
		( 61.14%)	-0.7819*	H 4 s(100.00%)
				-1.0000 -0.0080

---

As can be seen in the output, the NBO spin-orbital occupancy threshold was set at 0.90 (rather than 1.90), and the occupancies of  $\alpha$  Lewis spin-NBOs (1-5) are about 1.0000, but other aspects of the output are familiar. Note the slight admixture of  $d$ -character (0.16%) in the  $\sigma_{\text{CH}}$  bond hybrids (NBOs 1-3), whereas the out-of-plane radical non-bonded orbital (NBO 5) has pure  $p$ -character.

The NBO output for the  $\beta$  ('ionized') spin set then follows:

---

NATURAL BOND ORBITAL ANALYSIS, beta spin orbitals:

Cycle Dev	Occ. Thresh.	Occupancies		Lewis Structure				Low occ (L)	High occ (NL)
		Lewis	Non-Lewis	CR	BD	3C	LP		
1 (1) 0.00	0.90	3.99981	0.00019	1	3	0	0	0	

Structure accepted: No low occupancy Lewis orbitals

Core	0.99985 ( 99.985% of 1)
Valence Lewis	2.99996 ( 99.999% of 3)
<b>Total Lewis</b>	<b>3.99981 ( 99.995% of 4)</b>
Valence non-Lewis	0.00002 ( 0.000% of 4)
Rydberg non-Lewis	0.00017 ( 0.004% of 4)
<b>Total non-Lewis</b>	<b>0.00019 ( 0.005% of 4)</b>

(Occupancy)	Bond orbital/	Coefficients/	Hybrids
1. (0.99999)	BD ( 1) C 1- H 2	( 55.80%) 0.7470* C 1 s( 33.21%)p 2.00( 66.51%)d 0.01( 0.28%)	0.0000 0.5762 0.0080 0.0000 - 0.4076 -0.0125 0.7059 0.0217 0.0000 0.0000 -0.0345 0.0000 0.0000 -0.0199 - 0.0350
	( 44.20%)	0.6649* H 2 s(100.00%)	1.0000 -0.0069
2. (0.99999)	BD ( 1) C 1- H 3		

( 55.80%) 0.7470\* C 1 s( 33.21%)p 2.00( 66.51%)d 0.01( 0.28%)  
 0.0000 0.5762 0.0080 0.0000 -  
 0.4076 -0.0125 -0.7059 -0.0217 0.0000  
 0.0000 0.0345 0.0000 0.0000 -0.0199 -  
 0.0350  
 ( 44.20%) 0.6649\* H 3 s(100.00%)  
 1.0000 -0.0069  
 3. (0.99999) BD ( 1) C 1- H 4  
 ( 55.80%) 0.7470\* C 1 s( 33.21%)p 2.00( 66.51%)d 0.01( 0.28%)  
 0.0000 0.5762 0.0080 0.0000  
 0.8151 0.0251 0.0000 0.0000 0.0000  
 0.0000 0.0000 0.0000 0.0000 0.0399 -  
 0.0350  
 ( 44.20%) 0.6649\* H 4 s(100.00%)  
 1.0000 -0.0069  
 4. (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  
 5. (0.00002) LP\*( 1) C 1 s( 10.35%)p 0.00( 0.00%)d 8.66( 89.65%)  
 6. (0.00000) RY\*( 1) C 1 s( 98.99%)p 0.00( 0.00%)d 0.01( 1.01%)  
 7. (0.00000) RY\*( 2) C 1 s( 0.00%)p 1.00(100.00%)d 0.00( 0.00%)  
 8. (0.00000) RY\*( 3) C 1 s( 0.00%)p 1.00(100.00%)d 0.00( 0.00%)  
 9. (0.00000) RY\*( 4) C 1 s( 0.00%)p 1.00(100.00%)  
 10. (0.00000) RY\*( 5) C 1 s( 0.00%)p 1.00(100.00%)  
 11. (0.00000) RY\*( 6) C 1 s( 0.00%)p 1.00( 0.24%)d99.99( 99.76%)  
 12. (0.00000) RY\*( 7) C 1 s( 0.00%)p 0.00( 0.00%)d 1.00(100.00%)  
 13. (0.00000) RY\*( 8) C 1 s( 0.00%)p 0.00( 0.00%)d 1.00(100.00%)  
 14. (0.00000) RY\*( 9) C 1 s( 0.00%)p 1.00( 0.24%)d99.99( 99.76%)  
 15. (0.00000) RY\*(10) C 1 s( 91.02%)p 0.00( 0.00%)d 0.10( 8.98%)  
 16. (0.00006) RY\*( 1) H 2 s(100.00%)  
 17. (0.00006) RY\*( 1) H 3 s(100.00%)  
 18. (0.00006) RY\*( 1) H 4 s(100.00%)  
 19. (0.00000) BD\*( 1) C 1- H 2  
 ( 44.20%) 0.6649\* C 1 s( 33.21%)p 2.00( 66.51%)d 0.01( 0.28%)  
 ( 55.80%) -0.7470\* H 2 s(100.00%)  
 20. (0.00000) BD\*( 1) C 1- H 3

```

( 44.20%) 0.6649* C 1 s( 33.21%)p 2.00( 66.51%)d 0.01(
0.28%)
( 55.80%) -0.7470* H 3 s(100.00%)
21. (0.00000) BD*( 1) C 1- H 4
( 44.20%) 0.6649* C 1 s( 33.21%)p 2.00( 66.51%)d 0.01(
0.28%)
( 55.80%) -0.7470* 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  $\sigma_{\text{CH}}$  bonds is somewhat altered (about 55.8% on the C atom in the  $\beta$  set set, vs. 61.1% in the  $\alpha$  set). [In other cases, the  $\alpha$  and  $\beta$  NBO Lewis structures might differ even in the number and location of 1-c (non-bonding) and 2-c (bond) structural 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  $\alpha$  and  $\beta$  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!

#### *B.6.12 Effective Core Potential: Cu<sub>2</sub> Dimer*

To illustrate some of 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<sub>2</sub> ( $R = 2.2195 \text{ \AA}$ ), treated at the RHF level with a Hay-Wadt ECP and valence DZ basis (RHF/LANL1DZ), carried out with the GAUSSIAN-88 system. (The wavefunction returned by GAUSSIAN-88 in this case corresponds to an excited state configuration of Cu<sub>2</sub>.) Since the NBO program communicates directly with the ESS program for details about 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	lang	Type(AO)	Occupancy	Energy
-----					

1	Cu	1	s	Val( 4s)	0.94240	-0.26321
2	Cu	1	s	Ryd( 5s)	0.00019	0.92165
3	Cu	1	px	Ryd( 4p)	0.99604	-0.06989
4	Cu	1	px	Ryd( 5p)	0.00001	0.09916
5	Cu	1	py	Ryd( 4p)	0.99604	-0.06989
6	Cu	1	py	Ryd( 5p)	0.00001	0.09916
7	Cu	1	pz	Ryd( 5p)	0.05481	1.09062
8	Cu	1	pz	Ryd( 4p)	0.00062	0.52821
9	Cu	1	dxy	Val( 3d)	0.00000	-0.36077
10	Cu	1	dxy	Ryd( 4d)	0.00000	0.72280
11	Cu	1	dxz	Val( 3d)	1.99997	-1.29316
12	Cu	1	dxz	Ryd( 4d)	0.00398	0.75681
13	Cu	1	dyz	Val( 3d)	1.99997	-1.29316
14	Cu	1	dyz	Ryd( 4d)	0.00398	0.75681
15	Cu	1	dx2y2	Val( 3d)	1.99939	-1.38791
16	Cu	1	dx2y2	Ryd( 4d)	0.00061	0.67825
17	Cu	1	dz2	Val( 3d)	1.99890	-1.26114
18	Cu	1	dz2	Ryd( 4d)	0.00308	1.16392
19	Cu	2	s	Val( 4s)	0.94240	-0.26321
20	Cu	2	s	Ryd( 5s)	0.00019	0.92165
21	Cu	2	px	Ryd( 4p)	0.99604	-0.06989
22	Cu	2	px	Ryd( 5p)	0.00001	0.09916
23	Cu	2	py	Ryd( 4p)	0.99604	-0.06989
24	Cu	2	py	Ryd( 5p)	0.00001	0.09916
25	Cu	2	pz	Ryd( 5p)	0.05481	1.09062
26	Cu	2	pz	Ryd( 4p)	0.00062	0.52821
27	Cu	2	dxy	Val( 3d)	0.00000	-0.36077
28	Cu	2	dxy	Ryd( 4d)	0.00000	0.72280
29	Cu	2	dxz	Val( 3d)	1.99997	-1.29316
30	Cu	2	dxz	Ryd( 4d)	0.00398	0.75681
31	Cu	2	dyz	Val( 3d)	1.99997	-1.29316
32	Cu	2	dyz	Ryd( 4d)	0.00398	0.75681
33	Cu	2	dx2y2	Val( 3d)	1.99939	-1.38791
34	Cu	2	dx2y2	Ryd( 4d)	0.00061	0.67825
35	Cu	2	dz2	Val( 3d)	1.99890	-1.26114
36	Cu	2	dz2	Ryd( 4d)	0.00308	1.16392

[ 36 electrons found in the effective core potential]

WARNING: Population inversion found on atom Cu 1  
Population inversion found on atom Cu 2

Summary of Natural Population Analysis:

Atom	Natural Charge	Natural Population			
		Core	Valence	Rydberg	Total
Cu 1	0.00000	18.00000	8.94064	2.05936	29.00000
Cu 2	0.00000	18.00000	8.94064	2.05936	29.00000
* Total *	0.00000	36.00000	17.88127	4.11873	58.00000

Natural Population

```

Effective Core          36.00000
Valence                17.88127 ( 81.2785% of 22)
Natural Minimal Basis  53.88127 ( 92.8987% of 58)
Natural Rydberg Basis   4.11873 (  7.1013% of 58)

```

---

```

Atom          Natural Electron Configuration
-----
Cu  1      [core]4s( 0.94)3d( 8.00)4p( 1.99)4d( 0.01)5p( 0.05)
Cu  2      [core]4s( 0.94)3d( 8.00)4p( 1.99)4d( 0.01)5p( 0.05)

```

---

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 4s, 5s, 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 warn that one or more NAO occupancies are not ordered in accordance with the energy order [e.g., the 3d<sub>xy</sub> orbital (NAO 9) is unoccupied in this excited configuration, although its energy lies below the occupied 4s, 4p<sub>y</sub>, 4p<sub>z</sub> levels.]

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

---

NATURAL BOND ORBITAL ANALYSIS:

Cycle	Occ. Thresh.	Occupancies		Lewis Structure				Low	High
		Lewis	Non-Lewis	CR	BD	3C	LP	occ (L)	occ (NL)
Dev									
1(1)	1.90	57.99970	0.00030	0	3	0	8	0	0

Structure accepted: No low occupancy Lewis orbitals

```

Effective Core          36.00000
Valence Lewis          21.99970 ( 99.999% of 22)
-----
Total Lewis            57.99970 ( 99.999% of 58)
-----
Valence non-Lewis      0.00000 (  0.000% of 58)
Rydberg non-Lewis      0.00030 (  0.001% of 58)

```



	( 50.00%)	0.7071*	Cu 2	s( 0.00%)	p 1.00( 99.60%)	d 0.00(	
0.40%)							
							0.0000 0.0000 0.0000 0.0000
0.9980							
							0.0029 0.0000 0.0000 0.0000
0.0000							
							0.0000 0.0000 0.0035 0.0630
0.0000							
							0.0000 0.0000 0.0000
4. (2.00000) 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 0.0000
0.0000							
0.9998							
							-0.0175 0.0000 0.0000
5. (2.00000) 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
0.0037							
							-0.0010 0.0000 0.0000 0.0000
0.0000							
							0.0000 0.0000 1.0000 0.0026
0.0000							
							0.0000 0.0000 0.0000
6. (2.00000) LP ( 3)Cu 1				s( 0.00%)	p 0.00( 0.00%)	d	
1.00(100.00%)							
							0.0000 0.0000 0.0037 -0.0010
0.0000							
							0.0000 0.0000 0.0000 0.0000
0.0000							
							1.0000 0.0026 0.0000 0.0000
0.0000							
							0.0000 0.0000 0.0000
7. (1.99985) LP ( 4)Cu 1				s( 0.06%)	p 0.02( 0.00%)	d99.99(	
99.94%)							
							0.0231 0.0070 0.0000 0.0000
0.0000							
							0.0000 -0.0030 -0.0008 0.0000
0.0000							
							0.0000 0.0000 0.0000 0.0000
0.0000							
							0.0000 -0.9996 -0.0115
8. (2.00000) 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 0.0000
0.0000							
							0.0000 0.0000 0.0000 0.0000
0.9998							
							-0.0175 0.0000 0.0000
9. (2.00000) LP ( 2)Cu 2				s( 0.00%)	p 0.00( 0.00%)	d	
1.00(100.00%)							

0.0037	0.0000	0.0000	0.0000	0.0000	-
0.0000	0.0010	0.0000	0.0000	0.0000	
0.0000	0.0000	0.0000	1.0000	0.0026	
10. (2.00000) LP ( 3)Cu 2	0.0000	0.0000	0.0000		
1.00 (100.00%)	s( 0.00%)p 0.00( 0.00%)d				
0.0000	0.0000	0.0000	-0.0037	0.0010	
0.0000	0.0000	0.0000	0.0000	0.0000	
0.0000	1.0000	0.0026	0.0000	0.0000	
0.0000	0.0000	0.0000	0.0000		
11. (1.99985) LP ( 4)Cu 2	s( 0.06%)p 0.02( 0.00%)d99.99(				
99.94%)	0.0231	0.0070	0.0000	0.0000	
0.0000	0.0000	0.0030	0.0008	0.0000	
0.0000	0.0000	0.0000	0.0000	0.0000	
0.0000	0.0000	0.0000	0.0000	0.0000	
12. (0.00015) RY*( 1)Cu 1	0.0000	-0.9996	-0.0115		
3.85%)	s( 63.84%)p 0.51( 32.31%)d 0.06(				
0.0000	-0.1106	0.7913	0.0000	0.0000	
0.0000	0.0000	-0.4699	0.3199	0.0000	
0.0000	0.0000	0.0000	0.0000	0.0000	
13. (0.00000) RY*( 2)Cu 1	0.0000	0.0064	-0.1962		
0.00%)	s( 0.00%)p 1.00(100.00%)d 0.00(				
14. (0.00000) RY*( 3)Cu 1	s( 0.00%)p 1.00(100.00%)d 0.00(				
0.00%)					
15. (0.00000) RY*( 4)Cu 1	s( 31.12%)p 2.21( 68.87%)d 0.00(				
0.00%)					
16. (0.00000) RY*( 5)Cu 1	s( 7.79%)p11.84( 92.21%)d 0.00(				
0.00%)					
17. (0.00000) RY*( 6)Cu 1	s( 0.00%)p 0.00( 0.00%)d				
1.00 (100.00%)					
18. (0.00000) RY*( 7)Cu 1	s( 0.00%)p 0.00( 0.00%)d				
1.00 (100.00%)					
19. (0.00000) RY*( 8)Cu 1	s( 0.00%)p 1.00( 0.40%)d99.99(				
99.60%)					
20. (0.00000) RY*( 9)Cu 1	s( 0.00%)p 1.00( 0.40%)d99.99(				
99.60%)					
21. (0.00000) RY*(10)Cu 1	s( 0.00%)p 0.00( 0.00%)d				
1.00 (100.00%)					
22. (0.00000) RY*(11)Cu 1	s( 3.06%)p 0.35( 1.07%)d31.35(				
95.87%)					
23. (0.00015) RY*( 1)Cu 2	s( 63.84%)p 0.51( 32.31%)d 0.06(				
3.85%)					

0.0000		-0.1106	0.7913	0.0000	0.0000
0.0000		0.0000	0.4699	-0.3199	0.0000
0.0000		0.0000	0.0000	0.0000	0.0000
0.0000		0.0000	0.0064	-0.1962	
24. (0.00000)	RY*( 2)Cu 2	s( 0.00%)	p 1.00(100.00%)	d 0.00(	0.00%)
25. (0.00000)	RY*( 3)Cu 2	s( 0.00%)	p 1.00(100.00%)	d 0.00(	0.00%)
26. (0.00000)	RY*( 4)Cu 2	s( 31.12%)	p 2.21( 68.87%)	d 0.00(	0.00%)
27. (0.00000)	RY*( 5)Cu 2	s( 7.79%)	p11.84( 92.21%)	d 0.00(	0.00%)
28. (0.00000)	RY*( 6)Cu 2	s( 0.00%)	p 0.00( 0.00%)	d	
29. (0.00000)	RY*( 7)Cu 2	s( 0.00%)	p 0.00( 0.00%)	d	
30. (0.00000)	RY*( 8)Cu 2	s( 0.00%)	p 1.00( 0.40%)	d99.99(	99.60%)
31. (0.00000)	RY*( 9)Cu 2	s( 0.00%)	p 1.00( 0.40%)	d99.99(	99.60%)
32. (0.00000)	RY*(10)Cu 2	s( 0.00%)	p 0.00( 0.00%)	d	
33. (0.00000)	RY*(11)Cu 2	s( 3.06%)	p 0.35( 1.07%)	d31.35(	95.87%)
34. (0.00000)	BD*( 1)Cu 1-Cu 2	( 50.00%)	0.7071*Cu 1	s( 94.13%)	p 0.06( 5.54%)
0.33%)		( 50.00%)	-0.7071*Cu 2	s( 94.13%)	p 0.06( 5.54%)
0.33%)				d 0.00(	
35. (0.00000)	BD*( 2)Cu 1-Cu 2	( 50.00%)	0.7071*Cu 1	s( 0.00%)	p 1.00( 99.60%)
0.40%)		( 50.00%)	-0.7071*Cu 2	s( 0.00%)	p 1.00( 99.60%)
0.40%)				d 0.00(	
36. (0.00000)	BD*( 3)Cu 1-Cu 2	( 50.00%)	0.7071*Cu 1	s( 0.00%)	p 1.00( 99.60%)
0.40%)		( 50.00%)	-0.7071*Cu 2	s( 0.00%)	p 1.00( 99.60%)
0.40%)				d 0.00(	

Natural Bond Orbitals (Summary):

Delocalizations		Principal	
NBO	Occupancy	Energy	
(geminal, vicinal, remote)			
=====			
=====			
Molecular unit 1 (Cu2)			
1. BD ( 1)Cu 1-Cu 2	2.00000	-0.53276	
2. BD ( 2)Cu 1-Cu 2	2.00000	-0.21503	

3.	BD ( 3)Cu 1-Cu 2	2.00000	-0.21503
4.	LP ( 1)Cu 1	2.00000	-1.38854
5.	LP ( 2)Cu 1	2.00000	-1.29317
6.	LP ( 3)Cu 1	2.00000	-1.29317
7.	LP ( 4)Cu 1	1.99985	-1.26133
8.	LP ( 1)Cu 2	2.00000	-1.38854
9.	LP ( 2)Cu 2	2.00000	-1.29317
10.	LP ( 3)Cu 2	2.00000	-1.29317
11.	LP ( 4)Cu 2	1.99985	-1.26133
12.	RY*( 1)Cu 1	0.00015	0.70166
13.	RY*( 2)Cu 1	0.00000	0.09932
14.	RY*( 3)Cu 1	0.00000	0.09932
15.	RY*( 4)Cu 1	0.00000	1.09217
16.	RY*( 5)Cu 1	0.00000	0.44430
17.	RY*( 6)Cu 1	0.00000	-0.36077
18.	RY*( 7)Cu 1	0.00000	0.72280
19.	RY*( 8)Cu 1	0.00000	0.75266
20.	RY*( 9)Cu 1	0.00000	0.75266
21.	RY*(10)Cu 1	0.00000	0.67888
22.	RY*(11)Cu 1	0.00000	1.26372
23.	RY*( 1)Cu 2	0.00015	0.70166
24.	RY*( 2)Cu 2	0.00000	0.09932
25.	RY*( 3)Cu 2	0.00000	0.09932
26.	RY*( 4)Cu 2	0.00000	1.09217
27.	RY*( 5)Cu 2	0.00000	0.44430
28.	RY*( 6)Cu 2	0.00000	-0.36077
29.	RY*( 7)Cu 2	0.00000	0.72280
30.	RY*( 8)Cu 2	0.00000	0.75266
31.	RY*( 9)Cu 2	0.00000	0.75266
32.	RY*(10)Cu 2	0.00000	0.67888
33.	RY*(11)Cu 2	0.00000	1.26372
34.	BD*( 1)Cu 1-Cu 2	0.00000	0.41179
35.	BD*( 2)Cu 1-Cu 2	0.00000	0.08327
36.	BD*( 3)Cu 1-Cu 2	0.00000	0.08327
-----			
	Total Lewis	57.99970	( 99.9995%)
	Valence non-Lewis	0.00000	( 0.0000%)
	Rydberg non-Lewis	0.00030	( 0.0005%)
-----			
	Total unit 1	58.00000	(100.0000%)
	Charge unit 1	0.00000	

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<sub>2</sub> example also illustrates some aspects of the inclusion of *d* orbitals in the basis set. NBOs 4-7 and 8-11 represent the 3*d*<sup>8</sup> subshells on each atom, essentially of pure atomic *d* character (except for a small admixture of *p* character in NBOs 7, 11). Both the σ<sub>CuCu</sub> bond (NBO 1) and the two π<sub>CuCu</sub> bonds (NBOs 2, 3) have very slight admixtures (< 0.4%) of *d* character. The

remaining orbitals of predominant  $d$  character (NBOs 17-22 and 28-33) are of negligible occupancy. Note that the abbreviated `` $sp^\lambda d^\mu$ '' designations can lead to strange variations among hybrids of essentially similar character; thus, NBO 20 ( $p^{1.0}d^{99.9}$ ), NBO 21 ( $d^{1.0}$ ), and NBO 22 ( $s^{3.1}p^{0.4}d^{31.4}$ ) are all of nearly pure ( $> 95\%$ )  $d$  character, the difference in labelling stemming from 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 routines by a sequential input file, FILE47, described in this section. [If a ``FILE=jobname'' keyword is provided (as recommended), this file will actually have a filename of the form ``jobname.47'', but we refer to the generic ``FILE47'' in the following. The ``FILE=jobname'' entry is automatically echoed in the \$NBO keylist of FILE47.]

Some knowledge of FILE47 is useful even if your NBO program is attached to an ESS package. If requested (see the ARCHIVE option, Section B.2.5), the NBO program writes out FILE47 which summarizes all information pertaining to the computed electronic wavefunction. This file can be subsequently used as input to the GENNBO program (reassigned as LFN 5) to repeat the analysis of this wavefunction; simply include the \$NBO, \$SCORE, and \$CHOOSE 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 one- and 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 drivers are provided), you might consider attaching a routine to your ESS program which 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 driver routines. See the Programmer's Guide, Section C.13, 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.7.2 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. 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) 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 $END
$NBO NAOMO=PVAL FILE=ch3nh2 $END
$COORD
*** CH3NH2
   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 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 1
$END
$CONTRACT
  NSHELL = 16
  NEXP = 27
  NCOMP = 1 4 4 1 4 4 1 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
  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
0.0000000E+00
          0.0000000E+00 0.0000000E+00 0.0000000E+00

```

```

$END
$OVERLAP      ! Overlap matrix elements in the AO basis
  0.1000000E+01  0.1914474E+00  0.1000000E+01
$END
$DENSITY      ! Bond-order matrix elements in the AO basis
  0.2036322E+01  0.1108524E+00  0.1039309E+00
$END
$FOCK         ! Fock matrix elements in the AO basis
  -0.1112778E+02 -0.2858975E+01 -0.8957029E+00
$END
$LCAOMO       ! AO to MO transformation matrix
  -0.5742837E-03 -0.2383571E-02 -0.1731177E-03
$END
$KINETIC      ! Kinetic energy matrix in the AO basis
  0.1657897E+02 -0.1435027E+01  0.1357367E+01
$END
$NUCLEAR      ! Nuclear-electron (1-electron potential) matrix in AO
basis
  -0.3893233E+02 -0.3169558E+01 -0.1073697E+02
$END
$DIPOLE       ! Dipole matrix in AO basis (x,y,z)
  0.5290206E-01  0.1012796E-01  0.5290206E-01
$END

```

---

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

### 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:

<i>KEYWORD</i>	<i>OPTION DESCRIPTION</i>
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. Therefore, if the REUSE keyword is specified, all datalists in FILE47 will be ignored, but the \$NBO, \$SCORE, and \$CHOOSE keylists will still be recognized. This keyword preempts all other keywords of the \$GENNBO keylist.
NATOMS	Number of atoms in the molecule (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 (SPNAO, SPNHO, SPNBO, SPNLMO, AOPNAO, AOPNHO, AOPNBO, AOPNLMO, FPNHO, FPNBO).
UPPER	Indicates that only the upper triangular portions of the overlap, density, Fock, and dipole 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.
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 <i>f</i> -type functions rather than the ten Cartesian or seven pure <i>f</i> functions (cf. Section B.7.5).

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

#### 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, 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 ! Carbon
```

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

### 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 two arrays in this datalist 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  $s, p, d, f$ , or  $g$  ( $^{\circ} = 0-4$ ) basis AOs, of either cartesian or pure angular symmetry types. The label for each AO is a 3-digit integer of the form  $^{\circ} * 100 + k + m$ , where  $k$  is 0 (cartesian) or 50 (pure), and  $m$  is a particular component of the  $^{\circ}$ -type symmetry (see table below). For  $s$  or  $p$  AOs, the cartesian and pure  $^{\circ}$ -symmetry sets are identical, so each AO can be labelled in two distinct ways, 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:

<i>label</i>	<i>AO type</i>	<i>label</i>	<i>AO type</i>	<i>label</i>	<i>AO type</i>
<u>Pure <math>s, p</math> sets:</u>		<u>Cartesian <math>f</math> set:</u>		<u>Pure <math>f</math> "cubic" set:</u>	
1 (51)	$s$	301	$f_{xxx}$	351	$f(D1): x(5x^2-3r^2)$
101 (151)	$p_x$	302	$f_{xxy}$	352	$f(D2): y(5y^2-3r^2)$
102 (152)	$p_y$	303	$f_{xxz}$	353	$f(D3): z(5z^2-3r^2)$
103 (153)	$p_z$	304	$f_{xyy}$	354	$f(B): xyz$
		305	$f_{xyz}$	355	$f(E1): x(z^2-y^2)$
		306	$f_{xzz}$	356	$f(E2): y(z^2-x^2)$
<u>Cartesian <math>d</math> set:</u>		307	$f_{yyy}$	357	$f(E3): z(x^2-y^2)$
201	$d_{xx}$	308	$f_{yyz}$		
202	$d_{xy}$	309	$f_{yzz}$		
203	$d_{xz}$	310	$f_{zzz}$		
204	$d_{yy}$				
205	$d_{yz}$				
206	$d_{zz}$				
		<u>Pure <math>f</math> "standard" set:</u>			
<u>Pure <math>d</math> set:</u>		351	$f(0): z(5z^2-3r^2)$		
251	$d_{xy}$	352	$f(c1): x(5z^2-r^2)$		
252	$d_{xz}$	353	$f(s1): y(5z^2-r^2)$		
253	$d_{yz}$	354	$f(c2): z(x^2-y^2)$		
254	$d_{x^2-y^2}$	355	$f(s2): xyz$		
255	$d_{z^2} = d_{3z^2-r^2}$	356	$f(c3): x(x^2-3y^2)$		
		357	$f(s3): y(3x^2-y^2)$		

Cartesian  $g$  functions are labelled in obvious analogy (401 =  $g_{xxxx}$ , 402 =  $g_{xxyy}$ , . . ., 415 =  $g_{zzzz}$ ).

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 the contraction coefficients and orbital exponents of AO basis functions. This information is not used in the 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 driver routines write out this information to an external file (LFN 31) in the proper format for orbital plotting with the ORBPLOT program. Omit the \$CONTRACT datalist if you do not intend to make orbital plots.

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) 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, and CF are free format, real arrays containing the orbital exponents, and the s, p, d, and f contraction coefficients of the AO basis set. NEXP elements should appear in each array, and the arrays of contraction coefficients need only appear if there are basis functions of that particular symmetry in the basis set. [For example, the 3-21G basis of the sample methylamine input only has *s* and *p* basis functions. Therefore, the CD and CF 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<sub>x</sub>*, *p<sub>y</sub>*, and *p<sub>z</sub>* 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:

$$\phi_s(\mathbf{r}) = -0.747 e^{-3.66 r^2} + 0.713 e^{-0.77 r^2}$$

$$\phi_{px}(\mathbf{r}) = 1.709 x e^{-3.66 r^2} + 0.886 x e^{-0.77 r^2}$$

$$\phi_{py}(\mathbf{r}) = 1.709 y e^{-3.66 r^2} + 0.886 y e^{-0.77 r^2}$$

$$\phi_{pz}(\mathbf{r}) = 1.709 z e^{-3.66 r^2} + 0.886 z e^{-0.77 r^2}$$

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

### B.7.7 Matrix Datalists

The remaining datalists (\$OVERLAP, \$DENSITY, \$FOCK, \$LCAOMO, \$DIPOLE, \$KINETIC, \$NUCLEAR) specify various matrix elements possibly used by the NBO analysis. All entries in these datalists are free format, with entries separated by commas or spaces. Only the upper triangular portions of each symmetric matrix (overlap, density, Fock, dipole) 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, all *x* integrals before *y* before *z*.

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):

<i>Datalist</i>	<i>\$NBO Keywords Requiring the Datalist</i>
\$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

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.

## **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,  $\Gamma$ , as an optimized "resonance hybrid" of density operators,  $\{\Gamma_\alpha\}$ ,

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

where each  $\Gamma_\alpha$  is the reduced density operator corresponding to an idealized resonance structure wavefunction  $\Psi_\alpha$  (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  $\Gamma$ . 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  $\{\sigma_i\}$ ,  $i = 1, 2, \dots, n$ , 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,

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

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

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

Thus, single-reference NRT resonance weights are chosen such that the resonance-weighted NBO occupancies  $\{q_i^{(\text{NRT})}\}$  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  $\{w_1 = 1, w_2 = w_3 = \dots = 0\}$ . The optimal  $f(\underline{w})$  lies in the range

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

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  $\Gamma_\alpha^{(r)}$  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

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

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

$$D(\underline{W}^{(r)}) = \min \{n^{-1} \text{Tr}[\mathbf{I} - \sum_r W^{(r)} \mathbf{I}^{(r)}]^2\} \geq 0$$

where "Tr" denotes the matrix trace and the minimization is over all  $W^{(r)}$ . The density matrices  $\mathbf{I}$  for the full wave function and  $\mathbf{I}^{(r)}$  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

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

to give the final weighting  $w_\alpha$  of each resonance structure  $\alpha$ . Structures of high weight ( $w_\alpha > w_{\max} * \text{NRTWGT}/100.$ ) 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

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

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

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

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

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

where  $i_{AB}^{(\alpha)}$  is the ionicity of the A-B bond in the resonance structure  $\Psi_\alpha$ , 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*

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

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

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

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). Note that the default NRT program now generates satisfactory initial guesses of reference structures for most transition metal species (as well as main group elements), so the need for user-supplied \$NRTSTR input is considerably reduced compared to the earlier NBO 4.0 implementation.

### 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= <i>val</i>	Select the delocalization list threshold ( <i>val</i> , in kcal/mol) which controls the length of the NRT expansion. The default threshold is 1.0 kcal mol <sup>-1</sup> . 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= <i>val</i>	Request that \$NRTSTR structure specifications be written to the output file for all structures with weight > <i>val</i> %. 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= <i>n</i>	Request that memory be reallocated to prepare for a maximum of <i>n</i> 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.
<i>NRTCHG=val</i>	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.)
<i>NRTFDM</i>	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.)
<i>NRTWGT=val</i>	Request an altered threshold (default: 35%) for consideration as a reference structure. (This keyword is primarily for testing and development and is not recommended.)
<i>NRTOPT=method</i>	<p>Select alternative method for single-reference variational optimization (not recommended). The following methods may be selected (default [BFGS]):</p> <p>NRTOPT=BFGS      Steepest descent, analytic gradients  NRTOPT=SA        Simulated annealing (SA) method  NRTOPT=POWELL   Steepest descent, numerical gradients</p> <p>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.</p>

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

### *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 <i>complete specification of all valence lone pairs and bonds</i> 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.

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.8.4 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 : 411  
Memory requirements : 980442 words of 981903 available

2 candidate reference structures calculated by SR LEWIS  
Reference 1:  $\rho^*=0.04952$ ,  $f(w)=0.86158$  converged after 11 iterations

non-Lewis				fractional accuracy $f(w)$	
Ref	Wgt	density	$d(0)$	all NBOs	val+core
1	1.00000	0.04952	0.00609	0.86158	0.90660

-----  
0.91317

---

NRT output begins with a brief summary of the memory requirements. In this example, nearly one million double precision words were available to the NRT program, sufficient to accommodate 411 resonance structures for methylamine at this basis set level (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  $f(w)$  value (86.157%). [Note that this percentage refers to the very small  $\rho^*$  "error" of the leading NBO structure (which itself is often less than 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 ( $\rho^* = 0.04952e$ ) and  $d(0)$  value ( $0.00609e$ ). The program also reports the  $f(w)$  value as referred to valence-shell NBOs only (91.317%), or to valence plus core orbitals (90.660%), 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:

---

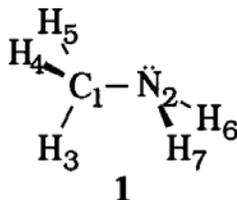
TOPO matrix for the leading resonance structure:

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

RS	Resonance Weight (%)	Added (Removed)
1*	97.88	
2	0.80	C 1- N 2, ( C 1- H 3), ( N 2), H 3
3	0.26	C 1- N 2, ( C 1- H 5), ( N 2- H 7), H 5
4	0.26	C 1- N 2, ( C 1- H 4), ( N 2- H 6), H 4
5	0.26	C 1- N 2, ( C 1- H 5), ( N 2- H 7), H 7
6	0.26	C 1- N 2, ( C 1- H 4), ( N 2- H 6), H 6
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]

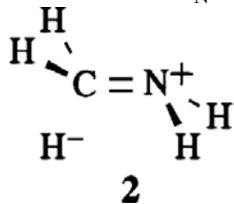
---

The TOPO matrix shows the number of bonds and lone pairs (lone pairs on diagonal, bonds elsewhere) for the leading reference structure, corresponding in this case to the classical methylamine structure,



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 0.80%) is formed from reference structure **1** by adding a bond C<sub>1</sub>-N<sub>2</sub>, removing a bond C<sub>2</sub>-H<sub>3</sub>, removing a lone pair on N<sub>2</sub>, and adding a lone pair on H<sub>3</sub>, to obtain the "double bond-no bond" structure shown below (associated with the  $n_{\text{N}} \rightarrow \sigma^*_{\text{CH}}$  NBO interaction):



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):

	<i>Structure</i>	<i>Weight</i>	<i>Interaction</i>
3.		0.26%	$\sigma_{\text{NH}} \rightarrow \sigma_{\text{CH}}^*$
4.		0.26%	$\sigma_{\text{NH}} \rightarrow \sigma_{\text{CH}}^*$
5.		0.26%	$\sigma_{\text{CH}} \rightarrow \sigma_{\text{NH}}^*$
6.		0.26%	$\sigma_{\text{CH}} \rightarrow \sigma_{\text{NH}}^*$
7.		0.14%	$n_{\text{N}} \rightarrow \sigma_{\text{CH}}^*$
8.		0.14%	$n_{\text{N}} \rightarrow \sigma_{\text{CH}}^*$

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.

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:

Natural Bond Order: (total/covalent/ionic)

Atom		1	2	3	4	5	6	7
1. C	t	0.0000	1.0212	0.9920	0.9934	0.9934	0.0000	0.0000
	c	---	0.8014	0.7992	0.7744	0.7744	0.0000	0.0000
	i	---	0.2198	0.1927	0.2190	0.2190	0.0000	0.0000
2. N	t	1.0212	0.9891	0.0000	0.0000	0.0000	0.9948	0.9948
	c	0.8014	---	0.0000	0.0000	0.0000	0.6344	0.6344
	i	0.2198	---	0.0000	0.0000	0.0000	0.3605	0.3605
3. H	t	0.9920	0.0000	0.0080	0.0000	0.0000	0.0000	0.0000
	c	0.7992	0.0000	---	0.0000	0.0000	0.0000	0.0000
	i	0.1927	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	0.7744	0.0000	0.0000	---	0.0000	0.0000	0.0000
	i	0.2190	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	0.7744	0.0000	0.0000	0.0000	---	0.0000	0.0000
	i	0.2190	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	0.6344	0.0000	0.0000	0.0000	---	0.0000
	i	0.0000	0.3605	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	0.6344	0.0000	0.0000	0.0000	0.0000	---
	i	0.0000	0.3605	0.0000	0.0000	0.0000	0.0000	---

This shows, for example, that the total NRT bond order between C<sub>1</sub> and N<sub>2</sub> is 1.0212 (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 (0.2198) components correspond to about 21.52% ionic character. In addition, one can see that the C<sub>1</sub>-H<sub>3</sub> bond order (0.9920) is slightly less than those (0.9934) for C<sub>1</sub>-H<sub>4</sub>, C<sub>1</sub>-H<sub>5</sub> (corresponding to the slightly higher weight of structure **2** among the secondary structures). The latter difference in  $b_{\text{CH}}^{(N)}$  bond orders, despite the identical Pople-Gordon bond geometries, reflects the greater strength of hyperconjugative  $n_{\text{N}} \rightarrow \sigma_{\text{CH}}^*$  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:

Atom	Valency	Co-Valency	Electro-Valency
1. C	4.0000	3.1495	0.8505
2. N	3.0109	2.0701	0.9407
3. H	0.9920	0.7992	0.1927
4. H	0.9934	0.7744	0.2190
5. H	0.9934	0.7744	0.2190
6. H	0.9948	0.6344	0.3605
7. H	0.9948	0.6344	0.3605

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):

```

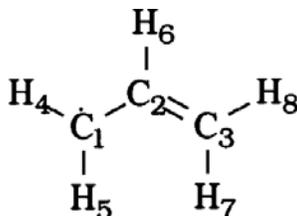
$NRTSTR
STR          ! Wgt = 97.88%
  LONE 2 1 END
  BOND S 1 2 S 1 3 S 1 4 S 1 5 S 2 6 S 2 7 END
END
$END

```

This shows the lone pair on N<sub>2</sub> ("LONE 2"), the single bond between atoms C<sub>1</sub> and N<sub>2</sub> ("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 : 250  
 Memory requirements : 717398 words of 719078 available

7 candidate reference structures calculated by SR LEWIS  
 Structure 3 is ionic. CONDENS will delete it.  
 Reference 1: rho\*=0.17716, f(w)=0.96545 converged after 22 iterations  
 Reference 2: rho\*=0.17716, f(w)=0.96545 converged after 22 iterations  
 Reference 3: rho\*=0.31713, ionic; deleted  
 Multi-ref( 2): D(W)=0.02446, F(W)=0.29289 converged after 202 iterations

Ref	Wgt	density	d(0)	fractional accuracy f(w)	
				all NBOs	val+core
1	0.50000	0.17716	0.02668	0.96545	0.97726
0.97749					
2	0.50000	0.17716	0.02668	0.96545	0.97726
0.97749					

TOPO matrix for the leading resonance structure:

Atom	1	2	3	4	5	6	7	8
1. C	0	2	0	1	1	0	0	0
2. C	2	0	1	0	0	1	0	0
3. C	0	1	1	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*	48.50	
2*	48.50	( C 1- C 2), C 2- C 3, C 1, ( C 3)
3	0.20	( C 1- C 2), ( C 1- C 2), C 2- C 3, C 2- C 3, ( C 3- H 7), C 1, C 1, ( C 3)
4	0.20	( C 1- H 5), C 1
5	0.20	C 1- C 2, ( C 1- H 5), ( C 2- C 3), C 3
6	0.20	( C 1- C 2), C 2- C 3, ( C 3- H 7), C 1
7	0.19	( C 1- H 4), C 2- C 3, ( C 2- H 6), C 1, ( C 3), H
4		
8	0.19	C 1- C 2, ( C 1- H 4), ( C 2- H 6), H 4
9	0.19	C 2- C 3, ( C 2- H 6), ( C 3- H 8), H 8
10	0.19	( C 1- C 2), C 2- C 3, C 2- C 3, ( C 2- H 6), ( C 3- H 8), C 1, ( C 3), H 8
11	0.19	( C 1- H 4), C 2- C 3, ( C 2- H 6), C 1, ( C 3), H
6		
12	0.19	C 1- C 2, ( C 1- H 4), ( C 2- H 6), H 6
13	0.19	( C 1- C 2), C 2- C 3, C 2- C 3, ( C 2- H 6), ( C 3- H 8), C 1, ( C 3), H 6
14	0.19	C 2- C 3, ( C 2- H 6), ( C 3- H 8), H 6
15	0.10	( C 1- C 2), C 2- C 3, ( C 3- H 7), H 7
16	0.10	( C 1- H 5), C 1, ( C 3), H 5
17	0.10	( C 1- C 2), ( C 1- C 2), C 2- C 3, C 2- C 3, ( C 3- H 7), C 1, ( C 3), H 7
18	0.10	C 1- C 2, ( C 1- H 5), ( C 2- C 3), H 5
19-26	0.24	
-----		
	100.00	* Total * [* = reference structure]

Natural Bond Order: (total/covalent/ionic)

Atom	1	2	3	4	5	6	7	8
1. C	t 0.2524	0.7528	0.0000	0.4962	0.4970	0.0000	0.0000	0.0000
	c ---	0.5617	0.0000	0.3824	0.3802	0.0000	0.0000	0.0000
	i ---	0.1911	0.0000	0.1137	0.1168	0.0000	0.0000	0.0000
2. C	t 0.7528	0.0012	0.7528	0.0000	0.0000	0.4920	0.0000	0.0000
	c 0.5617	---	0.5617	0.0000	0.0000	0.3992	0.0000	0.0000
	i 0.1911	---	0.1911	0.0000	0.0000	0.0927	0.0000	0.0000
3. C	t 0.0000	0.7528	0.2524	0.0000	0.0000	0.0000	0.4970	0.4962
	c 0.0000	0.5617	---	0.0000	0.0000	0.0000	0.3802	0.3824
	i 0.0000	0.1911	---	0.0000	0.0000	0.0000	0.1168	0.1137
4. H	t 0.4962	0.0000	0.0000	0.0019	0.0000	0.0000	0.0000	0.0000
	c 0.3824	0.0000	0.0000	---	0.0000	0.0000	0.0000	0.0000
	i 0.1137	0.0000	0.0000	---	0.0000	0.0000	0.0000	0.0000
5. H	t 0.4970	0.0000	0.0000	0.0000	0.0010	0.0000	0.0000	0.0000
	c 0.3802	0.0000	0.0000	0.0000	---	0.0000	0.0000	0.0000
	i 0.1168	0.0000	0.0000	0.0000	---	0.0000	0.0000	0.0000

```

6.  H  t  0.0000  0.4920  0.0000  0.0000  0.0000  0.0041  0.0000  0.0000
    c  0.0000  0.3992  0.0000  0.0000  0.0000  ---  0.0000  0.0000
    i  0.0000  0.0927  0.0000  0.0000  0.0000  ---  0.0000  0.0000

7.  H  t  0.0000  0.0000  0.4970  0.0000  0.0000  0.0000  0.0010  0.0000
    c  0.0000  0.0000  0.3802  0.0000  0.0000  0.0000  ---  0.0000
    i  0.0000  0.0000  0.1168  0.0000  0.0000  0.0000  ---  0.0000

8.  H  t  0.0000  0.0000  0.4962  0.0000  0.0000  0.0000  0.0000  0.0019
    c  0.0000  0.0000  0.3824  0.0000  0.0000  0.0000  0.0000  ---
    i  0.0000  0.0000  0.1137  0.0000  0.0000  0.0000  0.0000  ---

```

Natural Atomic Valencies:

Atom	Valency	Co-Valency	Electro-Valency
1. C	1.7459	1.3243	0.4216
2. C	1.9976	1.5227	0.4749
3. C	1.7459	1.3243	0.4216
4. H	0.4962	0.3824	0.1137
5. H	0.4970	0.3802	0.1168
6. H	0.4920	0.3992	0.0927
7. H	0.4970	0.3802	0.1168
8. H	0.4962	0.3824	0.1137

\$NRTSTRA

```

STR          ! Wgt = 48.50%
  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
STR          ! Wgt = 48.50%
  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
$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 :   250
Memory requirements :    717398 words of    719078 available

```

7 candidate reference structures calculated by SR LEWIS  
 Structure 3 is ionic. CONDENS will delete it.  
 Reference 1: rho\*=0.17029, f(w)=0.96935 converged after 149 iterations  
 Reference 2: rho\*=0.17029, f(w)=0.96935 converged after 149 iterations  
 Reference 3: rho\*=0.30426, ionic; deleted  
 Multi-ref( 2): D(W)=0.02407, F(W)=0.29289 converged after 202 iterations

Ref	Wgt	non-Lewis density	d(0)	fractional accuracy f(w)	
				all NBOs	val+core
1	0.50000	0.17029	0.02566	0.96935	0.98115
2	0.50000	0.17029	0.02566	0.96935	0.98115

TOPO matrix for the leading resonance structure:

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

RS	Resonance Weight(%)	Added (Removed)
1*	48.50	
2*	48.50	( C 1- C 2), C 2- C 3
3	0.20	( C 1- H 4), C 2- C 3, ( C 2- H 6), H 4
4	0.20	( C 1- C 2), C 2- C 3, C 2- C 3, ( C 2- H 6), ( C 3- H 8), H 8
5	0.20	C 1- C 2, ( C 1- H 4), ( C 2- H 6), H 4
6	0.20	C 2- C 3, ( C 2- H 6), ( C 3- H 8), H 8
7	0.19	C 1- C 2, ( C 1- H 4), ( C 2- H 6), H 6
8	0.19	( C 1- H 4), C 2- C 3, ( C 2- H 6), H 6
9	0.19	( C 1- C 2), C 2- C 3, C 2- C 3, ( C 2- H 6), ( C 3- H 8), H 6
10	0.19	C 2- C 3, ( C 2- H 6), ( C 3- H 8), H 6
11	0.12	C 1- C 2, ( C 1- H 5), ( C 2- C 3), H 5
12	0.12	( C 1- H 5), H 5
13	0.12	( C 1- C 2), C 2- C 3, ( C 3- H 7), H 7

```

14      0.12   ( C 1- C 2), ( C 1- C 2), C 2- C 3, C 2- C 3,
          ( C 3- H 7), H 7
15      0.10   ( C 1- C 2), ( C 1- C 2), ( C 1- H 5), C 2- C 3, C
1,
          C 2
16      0.10   ( C 1- C 2), ( C 1- H 5), C 1, C 2
17      0.10   ( C 2- C 3), ( C 3- H 7), C 2, C 3
18      0.10   ( C 1- C 2), ( C 3- H 7), C 2, C 3
19-29   0.55

```

```

-----
-----
100.00  * Total *                [* = reference structure]

```

Natural Bond Order: (total/covalent/ionic)

Atom		1	2	3	4	5	6	7	8
1. C	t	0.0024	0.7516	0.0000	0.4961	0.4970	0.0000	0.0000	0.0000
	c	---	0.5277	0.0000	0.4224	0.4213	0.0000	0.0000	0.0000
	i	---	0.2239	0.0000	0.0737	0.0757	0.0000	0.0000	0.0000
2. C	t	0.7516	0.0033	0.7516	0.0000	0.0000	0.4922	0.0000	0.0000
	c	0.5277	---	0.5277	0.0000	0.0000	0.3720	0.0000	0.0000
	i	0.2239	---	0.2239	0.0000	0.0000	0.1202	0.0000	0.0000
3. C	t	0.0000	0.7516	0.0024	0.0000	0.0000	0.0000	0.4970	0.4961
	c	0.0000	0.5277	---	0.0000	0.0000	0.0000	0.4213	0.4224
	i	0.0000	0.2239	---	0.0000	0.0000	0.0000	0.0757	0.0737
4. H	t	0.4961	0.0000	0.0000	0.0020	0.0000	0.0000	0.0000	0.0000
	c	0.4224	0.0000	0.0000	---	0.0000	0.0000	0.0000	0.0000
	i	0.0737	0.0000	0.0000	---	0.0000	0.0000	0.0000	0.0000
5. H	t	0.4970	0.0000	0.0000	0.0000	0.0012	0.0000	0.0000	0.0000
	c	0.4213	0.0000	0.0000	0.0000	---	0.0000	0.0000	0.0000
	i	0.0757	0.0000	0.0000	0.0000	---	0.0000	0.0000	0.0000
6. H	t	0.0000	0.4922	0.0000	0.0000	0.0000	0.0037	0.0000	0.0000
	c	0.0000	0.3720	0.0000	0.0000	0.0000	---	0.0000	0.0000
	i	0.0000	0.1202	0.0000	0.0000	0.0000	---	0.0000	0.0000
7. H	t	0.0000	0.0000	0.4970	0.0000	0.0000	0.0000	0.0012	0.0000
	c	0.0000	0.0000	0.4213	0.0000	0.0000	0.0000	---	0.0000
	i	0.0000	0.0000	0.0757	0.0000	0.0000	0.0000	---	0.0000
8. H	t	0.0000	0.0000	0.4961	0.0000	0.0000	0.0000	0.0000	0.0020
	c	0.0000	0.0000	0.4224	0.0000	0.0000	0.0000	0.0000	---
	i	0.0000	0.0000	0.0737	0.0000	0.0000	0.0000	0.0000	---

Natural Atomic Valencies:

Atom	Valency	Co-Valency	Electro-Valency
------	---------	------------	-----------------

	---	-----	-----	-----
1.	C	1.7448	1.3715	0.3732
2.	C	1.9955	1.4275	0.5680
3.	C	1.7447	1.3715	0.3732
4.	H	0.4961	0.4224	0.0737
5.	H	0.4970	0.4213	0.0757
6.	H	0.4922	0.3720	0.1202
7.	H	0.4970	0.4213	0.0757
8.	H	0.4961	0.4224	0.0737

\$NRTSTRB

```

STR          ! Wgt = 48.50%
  BOND D 1 2 S 1 4 S 1 5 S 2 3 S 2 6 S 3 7 S 3 8 END
END
STR          ! Wgt = 48.50%
  BOND S 1 2 S 1 4 S 1 5 D 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	0.2548	1.5044	0.0000	0.9923	0.9940	0.0000	0.0000	0.0000
2.	C	1.5044	0.0045	1.5044	0.0000	0.0000	0.9842	0.0000	0.0000
3.	C	0.0000	1.5044	0.2548	0.0000	0.0000	0.0000	0.9940	0.9923
4.	H	0.9923	0.0000	0.0000	0.0040	0.0000	0.0000	0.0000	0.0000
5.	H	0.9940	0.0000	0.0000	0.0000	0.0023	0.0000	0.0000	0.0000
6.	H	0.0000	0.9842	0.0000	0.0000	0.0000	0.0079	0.0000	0.0000
7.	H	0.0000	0.0000	0.9940	0.0000	0.0000	0.0000	0.0023	0.0000
8.	H	0.0000	0.0000	0.9923	0.0000	0.0000	0.0000	0.0000	0.0040

Natural Atomic Valencies (total):

Atom	Valency	Co-Valency	Electro-Valency	
---	-----	-----	-----	
1.	C	3.4907	2.6958	0.7948
2.	C	3.9931	2.9502	1.0429
3.	C	3.4907	2.6958	0.7948
4.	H	0.9923	0.8049	0.1874
5.	H	0.9940	0.8015	0.1925
6.	H	0.9842	0.7713	0.2129
7.	H	0.9940	0.8015	0.1925
8.	H	0.9923	0.8049	0.1874

---

### 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<sub>3</sub> and (b) 'hypervalent' [HAuCH<sub>3</sub>]<sup>-</sup> anion, both of C<sub>s</sub> symmetry (B3LYP/LACV3P 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<sub>3</sub>)

For neutral AuCH<sub>3</sub>, the first segment of NRT output is shown below:

---

NATURAL RESONANCE THEORY ANALYSIS:

Maximum reference structures : 20  
Maximum resonance structures : 1468  
Memory requirements : 9924044 words of 9927103 available

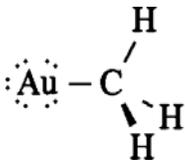
2 candidate reference structure(s) calculated by SR LEWIS  
Total of 2 candidate reference structures.  
Initial loops searched 2 bonding pattern(s); all but 1 were discarded  
Reference 1: rho\*=0.04013, f(w)=0.33026 converged after 2 iterations

		non-Lewis		fractional accuracy f(w)	
Ref	Wgt	density	d(0)	all NBOs	val+core
-----					
valence					
-----					
1	1.00000	0.04013	0.00246	0.33026	0.34541
0.42003					

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  $\rho^* = 0.04013$  for this structure is very small, corresponding to the high accuracy (99.96%) of the Lewis-like description. The dominance of this structure (>99%) is reflected in the calculated NRT weightings and bond orders, as shown below:

RS	Resonance Weight (%)	Added (Removed)
1*	99.10	
2	0.39	Au 1- C 2, ( C 2- H 5), (Au 1), H 5
3	0.26	Au 1- C 2, ( C 2- H 3), (Au 1), H 3
4	0.26	Au 1- C 2, ( C 2- H 4), (Au 1), H 4
100.00		* Total *

[\* = reference structure]

Natural Bond Order: (total/covalent/ionic)

Atom	1	2	3	4	5
1. Au	t 4.9910	1.0090	0.0000	0.0000	0.0000
	c ---	0.8818	0.0000	0.0000	0.0000
	i ---	0.1272	0.0000	0.0000	0.0000
2. C	t 1.0090	0.0000	0.9974	0.9974	0.9961
	c 0.8818	---	0.7947	0.7948	0.7937
	i 0.1272	---	0.2027	0.2027	0.2024
3. H	t 0.0000	0.9974	0.0026	0.0000	0.0000
	c 0.0000	0.7947	---	0.0000	0.0000
	i 0.0000	0.2027	---	0.0000	0.0000
4. H	t 0.0000	0.9974	0.0000	0.0026	0.0000
	c 0.0000	0.7948	0.0000	---	0.0000
	i 0.0000	0.2027	0.0000	---	0.0000

```

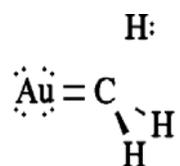
5.  H  t  0.0000  0.9961  0.0000  0.0000  0.0039
    c  0.0000  0.7937  0.0000  0.0000  ---
    i  0.0000  0.2024  0.0000  0.0000  ---

```

Natural Atomic Valencies:

Atom	Valency	Co-Valency	Electro-Valency
1. Au	1.0090	0.8818	0.1272
2. C	4.0000	3.2650	0.7350
3. H	0.9974	0.7947	0.2027
4. H	0.9974	0.7948	0.2027
5. H	0.9961	0.7937	0.2024

The three weak secondary structures (each with  $\sim 0.3\%$  weighting) correspond to  $n_{\text{Au}} \rightarrow \sigma_{\text{CH}}^*$  hyperconjugative delocalizations from gold lone pairs into CH antibonds, with formal Lewis-like structure



As shown in the bond order table, these delocalizations lead to slight Au=C double-bond character ( $b_{\text{AuC}} = 1.009$ ) and weakening of each CH bond ( $b_{\text{CH}} \cong 0.997$ ). The slight asymmetries of these interactions (resulting in slight distortions from ideal  $C_{3v}$  symmetry) are due to the greater strength of the unique  $d_{xy} \rightarrow \sigma_{\text{CH}}^*$  interaction for the particular CH bond in the  $xy$  plane.

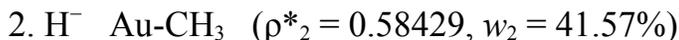
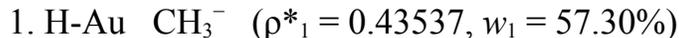
(b)  $\text{HAuCH}_3^-$

Because Au ( $s^2d^9$ ) is formally monovalent, we expect that both Au-H and Au-CH<sub>3</sub> 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



corresponding to strong  $n_{\text{H}} \rightarrow \sigma_{\text{AuC}}^*$  donor-acceptor interaction for the resonance structure on the right, or  $n_{\text{C}} \rightarrow \sigma_{\text{AuH}}^*$  for that on the left. Both the 3CHB search (activated automatically by the NRT keyword) and other aspects of the preceding NBO analysis strongly suggest this picture of  $\text{HAuCH}_3^-$ .

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  $\rho^*$  and resonance weighting,



in accord with the simple 2-resonance description of the H<sup>-</sup>Au<sup>+</sup>C hyperbond:

NATURAL RESONANCE THEORY ANALYSIS:

Maximum reference structures : 20  
 Maximum resonance structures : 1428  
 Memory requirements : 9916529 words of 9926242 available

1 candidate reference structure(s) calculated by SR LEWIS  
 1 candidate reference structure(s) added by hyperbond search (SR HBRES)

Total of 2 candidate reference structures.

Initial loops searched 2 bonding pattern(s); all but 2 were discarded

Reference 1:  $\rho^*=0.43537$ ,  $f(w)=0.95234$  converged after 288 iterations

Reference 2:  $\rho^*=0.58429$ ,  $f(w)=0.95719$  converged after 308 iterations

Multi-ref( 2):  $D(W)=0.06680$ ,  $F(W)=0.26720$  converged after 210 iterations

Ref	Wgt	density	d(0)	fractional accuracy f(w)	
				all NBOs	val+core
1	0.57035	0.43537	0.05740	0.95234	0.96183
2	0.42965	0.58429	0.07940	0.95719	0.96344

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

RS	Resonance Weight (%)	Added (Removed)
1*	57.30	
2*	41.57	Au 1- C 2, (Au 1- H 3), ( C 2), H 3
3	0.19	(Au 1- H 3), C 2- H 3, Au 1, ( C 2)
4	0.17	Au 1- C 2, Au 1- C 2, (Au 1- H 3), ( C 2- H 4), (Au 1), ( C 2), H 3, H 4
5	0.16	Au 1- H 4, ( C 2- H 4), (Au 1), C 2
6	0.12	Au 1- C 2, Au 1- C 2, (Au 1- H 3), ( C 2- H 6), (Au 1), ( C 2), H 3, H 6
7	0.12	Au 1- C 2, Au 1- C 2, (Au 1- H 3), ( C 2- H 5), (Au 1), ( C 2), H 3, H 5
8	0.11	Au 1- H 5, ( C 2- H 5), (Au 1), C 2
9	0.11	Au 1- H 6, ( C 2- H 6), (Au 1), C 2
10-15	0.16	
100.00		* Total *

[\* = reference structure]

As the following bond order table shows, the resulting Au<sup>+</sup>H, Au<sup>+</sup>C bond orders ( $b_{\text{AuH}} = 0.5784$ ,  $b_{\text{AuC}} = 0.4254$ ) are greatly weakened compared to normal-valent single-bonded species. The expected additivity of hyperbonded bond orders

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

is seen to be well satisfied at the equilibrium geometry (as well as throughout dissociation to either  $\text{H}^- + \text{AuCH}_3$  or  $\text{HAu} + \text{CH}_3^-$  products):

Natural Bond Order: (total/covalent/ionic)

Atom		1	2	3	4	5	6
1. Au	t	4.9924	0.4254	0.5784	0.0016	0.0011	0.0011
	c	---	0.1795	0.3272	0.0000	0.0000	0.0000
	i	---	0.2459	0.2512	0.0016	0.0011	0.0011
2. C	t	0.4254	0.5822	0.0019	0.9959	0.9973	0.9973
	c	0.1795	---	0.0002	0.8237	0.8248	0.8248
	i	0.2459	---	0.0017	0.1722	0.1725	0.1725
3. H	t	0.5784	0.0019	0.4197	0.0000	0.0000	0.0000

```

c 0.3272 0.0002 --- 0.0000 0.0000 0.0000
i 0.2512 0.0017 --- 0.0000 0.0000 0.0000

4. H t 0.0016 0.9959 0.0000 0.0025 0.0000 0.0000
c 0.0000 0.8237 0.0000 --- 0.0000 0.0000
i 0.0016 0.1722 0.0000 --- 0.0000 0.0000

5. H t 0.0011 0.9973 0.0000 0.0000 0.0016 0.0000
c 0.0000 0.8248 0.0000 0.0000 --- 0.0000
i 0.0011 0.1725 0.0000 0.0000 --- 0.0000

6. H t 0.0011 0.9973 0.0000 0.0000 0.0000 0.0016
c 0.0000 0.8248 0.0000 0.0000 0.0000 ---
i 0.0011 0.1725 0.0000 0.0000 0.0000 ---

```

Natural Atomic Valencies:

Atom	Valency	Co-Valency	Electro-Valency
1. Au	1.0076	0.5067	0.5009
2. C	3.4178	2.6530	0.7648
3. H	0.5803	0.3273	0.2529
4. H	0.9975	0.8237	0.1738
5. H	0.9984	0.8248	0.1736
6. H	0.9984	0.8248	0.1736

```

$NRTSTR
STR          ! Wgt = 57.30%
  LONE 1 5 2 1 END
  BOND S 1 3 S 2 4 S 2 5 S 2 6 END
END
STR          ! Wgt = 41.57%
  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).

### *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  $\pi_{rs}$  between atoms  $r, s$  and pi-bond  $\pi_{tu}$  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

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

where  $c_{rj}, c_{rk}$  denote the coefficients of hybrid  $h_r$  in an occupied MO  $\phi_j$  or virtual MO  $\phi_k$ , with respective orbital energies  $\epsilon_j, \epsilon_k$  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.9.2 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 FILE=CH3NH2 $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- N 2	0.0631	0.0000	-0.0001	-0.0001	-0.0013	-0.0013	0.0001
2.	C 1- H 3	0.0000	0.0758	0.0000	0.0000	0.0004	0.0004	0.0002
3.	C 1- H 4	-0.0001	0.0000	0.0922	0.0012	0.0041	0.0005	0.0001
4.	C 1- H 5	-0.0001	0.0000	0.0012	0.0922	0.0005	0.0041	0.0001
5.	N 2- H 6	-0.0013	0.0004	0.0041	0.0005	0.2107	-0.0014	0.0000
6.	N 2- H 7	-0.0013	0.0004	0.0005	0.0041	-0.0014	0.2107	0.0000
7.	C 1(cr)	0.0001	0.0002	0.0001	0.0001	0.0000	0.0000	0.0004
8.	N 2(cr)	0.0001	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
9.	N 2(lp)	0.0003	0.0284	0.0052	0.0052	0.0008	0.0008	0.0000
	NBO	9						
1.	C 1- N 2	0.0003						
2.	C 1- H 3	0.0284						
3.	C 1- H 4	0.0052						
4.	C 1- H 5	0.0052						
5.	N 2- H 6	0.0008						
6.	N 2- H 7	0.0008						
7.	C 1(cr)	0.0000						
8.	N 2(cr)	0.0000						
9.	N 2(lp)	0.1023						

---

In this example, the strongest off-diagonal NBBP element (+0.0284) is that connecting the amine lone pair (NBO 9) with the vicinal antiperiplanar C1-H3 bond (NBO 2), 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., 0.0041 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  $\langle r\ s\ t\ u/r'\ s'\ t'\ u' / \dots \rangle$  following the NBBP keyword in the \$NBO keylist. For example, to request the additional elements  $\Pi(1,2;6,12)$ ,  $\Pi(4,3;5,9)$ , and  $\Pi(3,4;9,10)$ , one could use the \$NBO keylist shown below:

```
$NBO NBBP FILE=CH3NH2 $END
```

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

```
$NBO NBBP
< 1 2 6 12 /
  4 3 5 9 /
  3 4 9 10 >
FILE=CH3NH2 $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	$\Pi(r,s;t,u)$	$F(r,s)$	$F(t,u)$	$\Pi(r,s;t,u)$
1	2	6	12	-0.001617	-	-	-0.001617
4	3	5	9	0.000426	-	+	-0.000426
3	4	9	10	0.000395	-	-	0.000395

---

In this case, the final entry  $\Pi(3,4;9,10)$  of the supplementary table corresponds to the 2-5 entry (0.0040) in the main table, since NBO 2 is composed of hybrids 3, 4 and NBO 5 of hybrids 9, 10. 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,  $\text{sgn}(F_{rs}F_{tu})\Pi_{rs;tu}$ , 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  $\Pi(4,3;5,9)$  is *negative*, as if the phase of hybrid 5 (or 9) were reversed to give a negative Fock matrix element ("positive overlap") between NHOs 5 and 9.

[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. Badenhop 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 [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 ( $\Omega_i$ )

$$E_x^{\text{NLMO}} = \sum_i (F_{i,i}^{\text{NLMO}} - F_{i,i}^{\text{PNLMO}})$$

where  $F_{I,I}^{\text{NLMO}} = \langle \Omega_i | \mathbf{F} | \Omega_i \rangle$  and  $F_{I,I}^{\text{PNLMO}} = \langle {}^p\Omega_i | \mathbf{F} | {}^p\Omega_i \rangle$ . 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 (*intrabond*) 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  $E_{I,J}^{\text{pwx}}$  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"  ${}^{p^2}\Omega_i, {}^{p^2}\Omega_j$  (labelled "PNLMO/2" orbitals). The steric exchange energy associated with NLMOs  $I, J$  is calculated as

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

where  $F_{I,I}^{\text{PNLMO/2}} = \langle {}^{p^2}\Omega_i | \mathbf{F} | {}^{p^2}\Omega_i \rangle$ , 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  $E_x^{\text{NLMO}}$  (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.10.2 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<sub>3</sub>NH<sub>2</sub>...He model, where a helium "probe" atom is placed 2.3 Å (in collinear N-H...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. BD ( 1) C 1- N 2		-12.40
2. BD ( 1) C 1- H 3		-12.78
3. BD ( 1) C 1- H 4		-15.36
4. BD ( 1) C 1- H 5		-15.39
5. BD ( 1) N 2- H 6		-11.17
6. BD ( 1) N 2- H 7		-11.58
7. CR ( 1) C 1		82.22
8. CR ( 1) N 2		108.73
9. LP ( 1) N 2		-20.37
Steric exchange energy, unit 1:		91.88 kcal/mol
NLMOs (i) in unit	2	dE(i)
10. LP ( 1) He 8		0.15
Steric exchange energy, unit 2:		0.15 kcal/mol
-----		
Total steric exchange energy:		92.03 kcal/mol
-----		

---

As shown, the total steric exchange energy is calculated as +92.03 kcal/mol in this case, arising almost entirely from the CH<sub>3</sub>NH<sub>2</sub> unit (91.88 kcal/mol, vs. 0.15 kcal/mol for the He unit). Within CH<sub>3</sub>NH<sub>2</sub>, the exchange energies are seen to be typically negative for valence NLMOs (*viz.*, -20.37 kcal/mol for the nitrogen lone pair), but strongly positive for core NLMOs (*viz.*, +108.73 kcal/mol for the nitrogen core 1s orbital), leading to the expected net positive (repulsive) contribution of steric exchange interactions.

[To obtain the intermolecular steric exchange energy between CH<sub>3</sub>NH<sub>2</sub> 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 +91.47 kcal/mol, so the steric interaction energy would be estimated as +92.03 - 91.47 = +0.56 kcal/mol for the 2.3 Å separation, roughly equal 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)

$dE(i,j)$	NLMO (i)	NLMO (j)	PNLMO	
kcal/mol			$S(i,j)$	
=====				
within unit 1				
2. BD (1) C 1- H 3		5. BD (1) N 2- H 6	0.0814	1.82
2. BD (1) C 1- H 3		6. BD (1) N 2- H 7	-0.0815	1.83
2. BD (1) C 1- H 3		9. LP (1) N 2	-0.1678	13.79
3. BD (1) C 1- H 4		5. BD (1) N 2- H 6	-0.1013	5.26
3. BD (1) C 1- H 4		6. BD (1) N 2- H 7	-0.0942	2.75
3. BD (1) C 1- H 4		9. LP (1) N 2	0.0759	1.93
4. BD (1) C 1- H 5		5. BD (1) N 2- H 6	0.0938	2.73
4. BD (1) C 1- H 5		6. BD (1) N 2- H 7	0.1013	5.23
4. BD (1) C 1- H 5		9. LP (1) N 2	0.0761	1.94
		sum within unit 1:		37.87
between units 1 and 2				
6. BD (1) N 2- H 7		10. LP (1) He 8	-0.0268	0.31
		sum between units 1 and 2:		0.24
within unit 2				
		sum within unit 2:		0.00
-----				
Total disjoint NLMO steric exchange energy from pairwise sum:				38.11
-----				

As shown, the only appreciable steric interaction between He and  $\text{CH}_3\text{NH}_2$  (above the default intermolecular printing threshold of 0.05 kcal/mol) is that (+0.31 kcal/mol) with the  $\text{N}_2\text{-H}_7$  bond pointed directly toward He. The total intermolecular steric exchange interaction estimated from the pairwise sum (+0.24 kcal/mol) differs from the total exchange energy difference calculated above (+0.56 kcal/mol) due to non-pairwise additivity of exchange interactions.

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
```

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
```

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

```
$NBO STERIC=0.4 FILE=CH3NH2_He $END
```

In the case of the  $\text{CH}_3\text{NH}_2\cdots\text{He}$  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			
=====			
=			
2. BD ( 1) C 1- H 3	10. LP ( 1) He 8	0.0019	0.00
1. BD ( 1) C 1- N 2	2. BD ( 1) C 1- H 3	0.1150	19.11
2. BD ( 1) C 1- H 3	7. CR ( 1) C 1	0.0409	30.15

As shown, the He probe atom is outside the range in which it has any appreciable steric interaction with the  $\text{C}_1\text{-H}_3$  bond, but the exchange interactions between NLMOs 1, 2 (the non-disjoint interaction between

geminal bonds  $\sigma_{\text{CN}}$ ,  $\sigma_{\text{CH}}$ : +19.11 kcal/mol) or NLMOs 2, 7 (the interaction of bond  $\text{C}_1\text{-H}_3$  with its own carbon core orbital: +30.15 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).

### *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

$$\text{EL} = \text{ES} + \text{POL} + \text{SE}$$

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

$$\text{CORE} = \text{EX} + \text{DEF} - \text{SE}$$

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

$$\Delta E = \text{EL} + \text{CT} + \text{CORE}$$

A key element of the NEDA approach is the evaluation of perturbed fragment wavefunctions,  $\Psi_{\text{A}}^{\text{def}}$  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,  $\Psi_{\text{loc}}$ , is then constructed for the complex as an antisymmetrized product of perturbed wavefunctions. NEDA further employs the supermolecule wavefunction,  $\Psi$ , and the SCF-converged wavefunctions for the isolated fragments,  $\Psi_{\text{A}}$ .

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

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

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

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

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

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  $\Delta E$  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  $\Psi_A$  and  $\Psi_A^{def}$

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

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 the GAMESS and NWCHEM versions; certain references below assume that GAMESS is the host ESS. The NEDA program is partially implemented in GAUSSIAN, allowing evaluation of only the CT component. NEDA is not implemented in MOPAC/AMPAC versions.

### *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 'NOSTAR' 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
```

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 and PK-transformed integrals should be disabled (NOSYM=1 in the GAMESS \$CONTRL group, and NOPK=1 in the \$INTGRL group) for all NEDA calculations.*

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

### 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  $\text{BH}_3\text{NH}_3$  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  $\text{BH}_3$ ,  $\text{NH}_3$ , 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.

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

### *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.11.3.2 Lithium Chloride Monohydrate*

LiCl·H<sub>2</sub>O (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.11.3.3 Scandium Hydride/Hydrogen Molecule Transition State*

The transition state for reaction of ScH<sub>3</sub> with H<sub>2</sub> closely resembles an interacting pair of ions, ScH<sub>2</sub><sup>+</sup> and H<sub>3</sub><sup>-</sup>. However, default NBO analysis calculates three molecular units rather than two: (1) a cation ScH<sub>2</sub><sup>+</sup>, (2) a hydrogen molecule, and (3) an anion H<sup>-</sup>. 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<sub>3</sub><sup>-</sup>) 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<sub>2</sub><sup>+</sup> fragment and one, three-center bond for the H<sub>3</sub><sup>-</sup> 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.

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.11.3.4 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):

	Energy (wfn)	Energy (wfn)	Component (kcal/mol)
-----			
H2ONa	-237.8685424 (scf)	-237.8473541 (loc)	CT = -13.30
			ES = -24.56
			POL = -13.63
			EX = -6.13
1. Na 5.21)	-161.7801659 (def)	-161.8414889 (cp)	DEF (SE) = 38.48 (
2. H2O 1.85)	-75.9965680 (def)	-76.0193088 (cp)	DEF (SE) = 14.27 (
			-----
			E = -4.86

Electrical (ES+POL+SE) :	-31.13
Charge Transfer (CT) :	-13.30
Core (EX+DEF-SE) :	39.57
	-----
Total Interaction (E) :	-4.86

---

### 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 2 5 7 8 11 12 13 14 15 16 23 24  
 and orbitals:  
 3 4 6 9 10 17 18 19 20 21 22 25 26

Orbital occupancies:

Orbital	No deletions	This deletion	Change
1. BD ( 1) O 1- H 2	1.99912	1.99942	.00030
2. BD ( 1) O 1- H 3	1.99912	1.99942	.00030
3. BD ( 1) O 4- H 5	1.99961	1.99961	.00000
4. BD ( 1) O 4- H 6	1.99918	1.99942	.00024
5. CR ( 1) O 1	1.99982	1.99983	.00001
6. CR ( 1) O 4	1.99979	1.99980	.00000
7. LP ( 1) O 1	1.99920	1.99930	.00010
8. LP ( 2) O 1	1.98029	1.99914	.01885
9. LP ( 1) O 4	1.99994	2.00000	.00006
10. LP ( 2) O 4	1.99922	1.99932	.00010
11. RY*( 1) O 1	.00004	.00001	-.00003
12. RY*( 2) O 1	.00001	.00000	.00000
13. RY*( 3) O 1	.00002	.00000	-.00002
14. RY*( 4) O 1	.00000	.00001	.00000
15. RY*( 1) H 2	.00124	.00127	.00003
16. RY*( 1) H 3	.00124	.00127	.00003
17. RY*( 1) O 4	.00009	.00000	-.00009
18. RY*( 2) O 4	.00002	.00000	-.00002
19. RY*( 3) O 4	.00002	.00001	-.00001
20. RY*( 4) O 4	.00000	.00000	.00000
21. RY*( 1) H 5	.00127	.00120	-.00007
22. RY*( 1) H 6	.00159	.00042	-.00117
23. BD*( 1) O 1- H 2	.00032	.00016	-.00016
24. BD*( 1) O 1- H 3	.00032	.00016	-.00016
25. BD*( 1) O 4- H 5	.00027	.00009	-.00019
26. BD*( 1) O 4- H 6	.01827	.00013	-.01814

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.

---

```
ITER EX DEM  TOTAL ENERGY      E CHANGE  DENSITY CHANGE      ORB. GRAD
  1  0  0  -151.806559619  -151.806559619    .061186980    .000000000
```

SCF IS UNCONVERGED, TOO MANY ITERATIONS

```
  TIME TO FORM FOCK OPERATORS=      .0 SECONDS (      .0
SEC/ITER)
```

```
  TIME TO SOLVE SCF EQUATIONS=      .0 SECONDS (      .0
SEC/ITER)
```

FINAL ENERGY IS .0000000000 AFTER 1 ITERATIONS

..... END OF RHF CALCULATION .....

```
STEP CPU TIME =      .15 TOTAL CPU TIME =      .4 (      .0 MIN)
```

```
TOTAL WALL CLOCK TIME=      .7 SECONDS, CPU UTILIZATION IS  61.76%
```

```
-----
-----
Energy of deletion :      -151.806559619
Total SCF energy   :      -151.827680721
-----
Energy change     :      .021121 a.u.,      13.254 kcal/mol
-----
-----
```

The most significant change in occupancy is found for NBOs 8 and 26, 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 =      .00 TOTAL CPU TIME =      .4 (      .0 MIN)
```

```
TOTAL WALL CLOCK TIME=      .7 SECONDS, CPU UTILIZATION IS  60.87%
```

```
ITER EX DEM  TOTAL ENERGY      E CHANGE  DENSITY CHANGE      ORB. GRAD
```

```

1  0  0  -75.882003865  -75.882003865  .051585272  .000000000
-----START SECOND ORDER SCF-----
2  1  0  -75.908141392  -.026137526  .018452090  .009561187
3  2  0  -75.909247934  -.001106543  .009032409  .003595523
4  3  0  -75.909405809  -.000157875  .000764753  .000898516
5  4  0  -75.909412448  -.000006639  .000263894  .000128113
6  5  0  -75.909412737  -.000000289  .000084067  .000046344
7  6  0  -75.909412748  -.000000011  .000018443  .000008466
8  7  0  -75.909412749  .000000000  .000003845  .000002277
9  8  0  -75.909412749  .000000000  .000001199  .000000691

-----
DENSITY CONVERGED
-----

TIME TO FORM FOCK OPERATORS=          .1 SECONDS (          .0
SEC/ITER)
TIME TO SOLVE SCF EQUATIONS=          .0 SECONDS (          .0
SEC/ITER)

FINAL ENERGY IS      -75.9094127490 AFTER      9 ITERATIONS
..... END OF RHF CALCULATION .....
STEP CPU TIME =          .10 TOTAL CPU TIME =          .5 (          .0 MIN)
TOTAL WALL CLOCK TIME=          .8 SECONDS, CPU UTILIZATION IS  65.82%

Dipole (def):      2.6394(x),      .0793(y),      .0000(z);      2.6406(tot)
Debye
Dipole (cp):      2.6541(x),      -.0947(y),      .0000(z);      2.6558(tot)
Debye
Dipole (ind):      -.0146(x),      .1740(y),      .0000(z);      .1747(tot)
Debye
..... END OF ONE-ELECTRON INTEGRALS .....
STEP CPU TIME =          .00 TOTAL CPU TIME =          .5 (          .0 MIN)
TOTAL WALL CLOCK TIME=          .8 SECONDS, CPU UTILIZATION IS  65.82%

```

---

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 = .01 TOTAL CPU TIME = .5 ( .0 MIN)  
TOTAL WALL CLOCK TIME= .8 SECONDS, CPU UTILIZATION IS 66.25%

ITER	EX	DEM	TOTAL ENERGY	E CHANGE	DENSITY CHANGE	ORB. GRAD
1	0	0	-75.896267359	-75.896267359	.016278998	.000000000
-----START SECOND ORDER SCF-----						
2	1	0	-75.907969678	-.011702319	.007570846	.005067237
3	2	0	-75.908314096	-.000344419	.005463349	.001684406
4	3	0	-75.908355582	-.000041486	.001012339	.000672211
5	4	0	-75.908357111	-.000001528	.000352291	.000297196
6	5	0	-75.908357403	-.000000292	.000092465	.000043124
7	6	0	-75.908357412	-.000000010	.000014019	.000006844
8	7	0	-75.908357413	-.000000001	.000004722	.000002775
9	8	0	-75.908357413	.000000000	.000000684	.000000532

-----  
DENSITY CONVERGED  
-----

TIME TO FORM FOCK OPERATORS= .1 SECONDS ( .0  
SEC/ITER)  
TIME TO SOLVE SCF EQUATIONS= .0 SECONDS ( .0  
SEC/ITER)

FINAL ENERGY IS -75.9083574128 AFTER 9 ITERATIONS  
..... END OF RHF CALCULATION .....  
STEP CPU TIME = .10 TOTAL CPU TIME = .6 ( .0 MIN)  
TOTAL WALL CLOCK TIME= .9 SECONDS, CPU UTILIZATION IS 70.79%

Dipole (def): -.8286(x), -2.6607(y), .0000(z); 2.7867(tot)  
Debye  
Dipole (cp): -1.0045(x), -2.3894(y), .0000(z); 2.5919(tot)  
Debye  
Dipole (ind): .1759(x), -.2713(y), .0000(z); .3234(tot)  
Debye

..... END OF ONE-ELECTRON INTEGRALS .....  
STEP CPU TIME = .00 TOTAL CPU TIME = .6 ( .0 MIN)  
TOTAL WALL CLOCK TIME= .9 SECONDS, CPU UTILIZATION IS 70.00%

---

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):

	Energy (wfn)	Energy (wfn)	Component (kcal/mol)
-----			
H4O2	-151.8276807 (scf)	-151.8065596 (loc)	CT = -13.25 ES = -12.24 POL = -3.89 EX = -1.62
1. H2O .10)	-75.8820039 (def)	-75.9094127 (cp)	DEF (SE) = 17.20 (
2. H2O 1.78)	-75.8962674 (def)	-75.9083574 (cp)	DEF (SE) = 7.59 (
			----- 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.11.4.2 Lithium Chloride Hydrate

The following sample output is taken from the analysis of  $\text{LiCl}\cdot\text{H}_2\text{O}$ . 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):

Delocalizations NBO (geminal, vicinal, remote)	Occupancy	Energy	Principal
=====			
Molecular unit 1 (Li)			
3. CR ( 1)Li 1	1.99953	-2.41595	52 (r) , 53 (r)
16. LP* ( 1)Li 1	.08610	.27978	
17. RY* ( 1)Li 1	.01062	.19772	
18. RY* ( 2)Li 1	.01045	.20133	
19. RY* ( 3)Li 1	.00360	.78711	
20. RY* ( 4)Li 1	.00036	.79469	
21. RY* ( 5)Li 1	.00025	.89939	

22.	RY*( 6)Li	1	.00020	.41055	
23.	RY*( 7)Li	1	.00006	1.50513	
24.	RY*( 8)Li	1	.00000	.58517	
25.	RY*( 9)Li	1	.00000	.27135	
26.	RY*(10)Li	1	.00000	.55742	
27.	RY*(11)Li	1	.00000	.59400	
28.	RY*(12)Li	1	.00000	.22692	
29.	RY*(13)Li	1	.00000	.60382	

---

Total Lewis	1.99953	( 94.7117%)
Valence non-Lewis	.08610	( 4.0784%)
Rydberg non-Lewis	.02554	( 1.2099%)

---

Total unit	1	2.11118	(100.0000%)
Charge unit	1	.88882	

Molecular unit 2 (Cl)

4.	CR ( 1)Cl	2	2.00000	-104.24680	16(r)
5.	CR ( 2)Cl	2	1.99998	-10.56909	16(r),19(r)
6.	CR ( 3)Cl	2	1.99997	-7.88635	16(r)
7.	CR ( 4)Cl	2	1.99999	-7.88597	
8.	CR ( 5)Cl	2	2.00000	-7.88595	
10.	LP ( 1)Cl	2	1.99941	-1.04678	16(r),21(r),19(r)
11.	LP ( 2)Cl	2	1.99057	-.35655	17(r),22(r)
12.	LP ( 3)Cl	2	1.98955	-.35636	18(r),25(r),20(r)
13.	LP ( 4)Cl	2	1.93359	-.55831	

16(r),21(r),19(r),23(r)

40(r),24(r),52(r),53(r)

30.	RY*( 1)Cl	2	.00007	1.08215	
31.	RY*( 2)Cl	2	.00005	.78167	
32.	RY*( 3)Cl	2	.00000	.95058	
33.	RY*( 4)Cl	2	.00001	.78867	
34.	RY*( 5)Cl	2	.00000	4.59389	
35.	RY*( 6)Cl	2	.00000	1.33304	
36.	RY*( 7)Cl	2	.00000	1.33464	
37.	RY*( 8)Cl	2	.00000	1.27499	
38.	RY*( 9)Cl	2	.00000	1.44150	
39.	RY*(10)Cl	2	.00000	1.32900	

---

Total Lewis	17.91306	( 99.9992%)
Valence non-Lewis	.00000	( .0000%)
Rydberg non-Lewis	.00013	( .0008%)

---

Total unit	2	17.91320	(100.0000%)
Charge unit	2	-.91320	

Molecular unit 3 (H2O)

1.	BD ( 1) O 3- H 4		1.99945	-1.08671	16(r),20(r)
2.	BD ( 1) O 3- H 5		1.99945	-1.08670	16(r),20(r)
9.	CR ( 1) O 3		1.99992	-20.50862	16(r)
14.	LP ( 1) O 3		1.99853	-.61093	17(r)
15.	LP ( 2) O 3		1.97591	-.96478	16(r),19(r),21(r)
40.	RY*( 1) O 3		.00120	1.37432	
41.	RY*( 2) O 3		.00004	1.11917	
42.	RY*( 3) O 3		.00003	1.26642	
43.	RY*( 4) O 3		.00000	3.78877	

44.	RY*( 5) O 3	.00001	1.53517
45.	RY*( 6) O 3	.00001	2.30288
46.	RY*( 7) O 3	.00000	1.97655
47.	RY*( 8) O 3	.00000	1.91724
48.	RY*( 9) O 3	.00001	1.96639
49.	RY*(10) O 3	.00000	2.75660
50.	RY*( 1) H 4	.00027	.62921
51.	RY*( 1) H 5	.00027	.62925
52.	BD*( 1) O 3- H 4	.00027	.71147
53.	BD*( 1) O 3- H 5	.00027	.71146

---

Total Lewis	9.97326	( 99.9763%)
Valence non-Lewis	.00054	( .0054%)
Rydberg non-Lewis	.00183	( .0183%)

---

Total unit	3	9.97563	(100.0000%)
Charge unit	3	.02437	

---

This segment shows the three molecular units calculated by NBO analysis, a lithium cation ( $q_{Li} = +0.88883$ ), a chlorine anion ( $q_{Cl} = -0.91318$ ), and a water molecule ( $q_{H2O} = +0.02439$ ).

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:

3 16 17 18 19 20 21 22 23 24 25 26 27 28 29  
and orbitals:

1 2 4 5 6 7 8 9 10 11 12 13 14 15 30 31 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:

4 5 6 7 8 10 11 12 13 30 31 32 33 34 35 36 37  
38 39

and orbitals:

1 2 3 9 14 15 16 17 18 19 20 21 22 23 24 25 26  
27 28 29  
40 41 42 43 44 45 46 47 48 49 50 51 52 53

Deletion of the NBO Fock matrix elements between orbitals:

1 2 9 14 15 40 41 42 43 44 45 46 47 48 49 50 51  
52 53

and orbitals:

3 4 5 6 7 8 10 11 12 13 16 17 18 19 20 21 22  
23 24 25  
26 27 28 29 30 31 32 33 34 35 36 37 38 39

Orbital occupancies:

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

1.	BD ( 1) O 3- H 4	1.99945	1.99982	.00036
2.	BD ( 1) O 3- H 5	1.99945	1.99982	.00036
3.	CR ( 1) Li 1	1.99953	1.99979	.00026
4.	CR ( 1) Cl 2	2.00000	2.00000	.00000
5.	CR ( 2) Cl 2	1.99998	2.00000	.00002
6.	CR ( 3) Cl 2	1.99997	2.00000	.00003
7.	CR ( 4) Cl 2	1.99999	2.00000	.00001
8.	CR ( 5) Cl 2	2.00000	2.00000	.00000
9.	CR ( 1) O 3	1.99992	1.99993	.00000
10.	LP ( 1) Cl 2	1.99941	1.99999	.00057
11.	LP ( 2) Cl 2	1.99057	1.99996	.00939
12.	LP ( 3) Cl 2	1.98955	1.99996	.01040
13.	LP ( 4) Cl 2	1.93359	1.99964	.06605
14.	LP ( 1) O 3	1.99853	1.99999	.00147
15.	LP ( 2) O 3	1.97591	1.99978	.02387
16.	LP*( 1) Li 1	.08610	.00018	-.08592
17.	RY*( 1) Li 1	.01062	.00000	-.01062
18.	RY*( 2) Li 1	.01045	.00000	-.01045
19.	RY*( 3) Li 1	.00360	.00002	-.00358
20.	RY*( 4) Li 1	.00036	.00000	-.00036
21.	RY*( 5) Li 1	.00025	.00000	-.00024
22.	RY*( 6) Li 1	.00020	.00000	-.00020
23.	RY*( 7) Li 1	.00006	.00000	-.00006
24.	RY*( 8) Li 1	.00000	.00000	.00000
25.	RY*( 9) Li 1	.00000	.00000	.00000
26.	RY*(10) Li 1	.00000	.00000	.00000
27.	RY*(11) Li 1	.00000	.00000	.00000
28.	RY*(12) Li 1	.00000	.00000	.00000
29.	RY*(13) Li 1	.00000	.00000	.00000
30.	RY*( 1) Cl 2	.00007	.00000	-.00007
31.	RY*( 2) Cl 2	.00005	.00001	-.00004
32.	RY*( 3) Cl 2	.00000	.00004	.00003
33.	RY*( 4) Cl 2	.00001	.00001	.00001
34.	RY*( 5) Cl 2	.00000	.00003	.00003
35.	RY*( 6) Cl 2	.00000	.00003	.00003
36.	RY*( 7) Cl 2	.00000	.00003	.00003
37.	RY*( 8) Cl 2	.00000	.00000	.00000
38.	RY*( 9) Cl 2	.00000	.00023	.00023
39.	RY*(10) Cl 2	.00000	.00008	.00007
40.	RY*( 1) O 3	.00120	.00001	-.00119
41.	RY*( 2) O 3	.00004	.00001	-.00004
42.	RY*( 3) O 3	.00003	.00001	-.00001
43.	RY*( 4) O 3	.00000	.00001	.00000
44.	RY*( 5) O 3	.00001	.00000	-.00001
45.	RY*( 6) O 3	.00001	.00001	.00000
46.	RY*( 7) O 3	.00000	.00000	.00000
47.	RY*( 8) O 3	.00000	.00000	.00000
48.	RY*( 9) O 3	.00001	.00000	.00000
49.	RY*(10) O 3	.00000	.00000	.00000
50.	RY*( 1) H 4	.00027	.00026	.00000
51.	RY*( 1) H 5	.00027	.00026	.00000
52.	BD*( 1) O 3- H 4	.00027	.00005	-.00022
53.	BD*( 1) O 3- H 5	.00027	.00005	-.00022

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.

```
-----  
-----  
ITER EX DEM  TOTAL ENERGY      E CHANGE  DENSITY CHANGE  ORB. GRAD  
  1  0  0  -542.970515395  -542.970515395   .188923448   .000000000
```

SCF IS UNCONVERGED, TOO MANY ITERATIONS

```
TIME TO FORM FOCK OPERATORS=      .1 SECONDS (      .1  
SEC/ITER)  
TIME TO SOLVE SCF EQUATIONS=      .0 SECONDS (      .0  
SEC/ITER)
```

```
FINAL ENERGY IS      .0000000000 AFTER      1 ITERATIONS  
..... END OF RHF CALCULATION .....  
STEP CPU TIME =      .61 TOTAL CPU TIME =      3.6 (      .1 MIN)  
TOTAL WALL CLOCK TIME=      3.6 SECONDS, CPU UTILIZATION IS  99.16%
```

```
-----  
-----  
Energy of deletion :      -542.970515395  
Total SCF energy :      -543.059663903  
-----  
Energy change :      .089149 a.u.,      55.942 kcal/mol  
-----  
-----
```

Fragment 1:

```
-----  
-----  
..... END OF ONE-ELECTRON INTEGRALS .....  
STEP CPU TIME =      .02 TOTAL CPU TIME =      3.6 (      .1 MIN)  
TOTAL WALL CLOCK TIME=      3.6 SECONDS, CPU UTILIZATION IS  99.17%
```

```
ITER EX DEM  TOTAL ENERGY      E CHANGE  DENSITY CHANGE  ORB. GRAD  
  1  0  0  -7.198155704  -7.198155704   .063419837   .000000000  
-----START SECOND ORDER SCF-----  
  2  1  0  -7.235314976  -.037159272   .007354720   .010209216  
  3  2  0  -7.235536947  -.000221970   .001583276   .001064694  
  4  3  0  -7.235539934  -.000002988   .000070998   .000033960  
  5  4  0  -7.235539936  -.000000002   .000006107   .000002908  
  6  5  0  -7.235539936   .000000000   .000000128   .000000058
```

DENSITY CONVERGED

```
-----  
-----  
TIME TO FORM FOCK OPERATORS=      .7 SECONDS (      .1  
SEC/ITER)  
TIME TO SOLVE SCF EQUATIONS=      .0 SECONDS (      .0  
SEC/ITER)
```

```
FINAL ENERGY IS      -7.2355399363 AFTER      6 ITERATIONS  
..... END OF RHF CALCULATION .....  
-----
```

STEP CPU TIME = .74 TOTAL CPU TIME = 4.3 ( .1 MIN)  
TOTAL WALL CLOCK TIME= 4.4 SECONDS, CPU UTILIZATION IS 99.31%

Dipole (def): -.0120(x), .0000(y), .0000(z); .0120(tot)  
Debye  
Dipole (cp): .0000(x), .0000(y), .0000(z); .0000(tot)  
Debye  
Dipole (ind): -.0120(x), .0000(y), .0000(z); .0120(tot)  
Debye

..... END OF ONE-ELECTRON INTEGRALS .....

STEP CPU TIME = .01 TOTAL CPU TIME = 4.3 ( .1 MIN)  
TOTAL WALL CLOCK TIME= 4.4 SECONDS, CPU UTILIZATION IS 99.31%

-----  
Fragment 2:  
-----

..... END OF ONE-ELECTRON INTEGRALS .....

STEP CPU TIME = .02 TOTAL CPU TIME = 4.3 ( .1 MIN)  
TOTAL WALL CLOCK TIME= 4.4 SECONDS, CPU UTILIZATION IS 99.32%

ITER	EX	DEM	TOTAL ENERGY	E CHANGE	DENSITY CHANGE	ORB. GRAD
1	0	0	-459.468148379	-459.468148379	.198845489	.000000000
-----START SECOND ORDER SCF-----						
2	1	0	-459.528621522	-.060473143	.084729977	.021549541
3	2	0	-459.532346029	-.003724507	.021185451	.004874568
4	3	0	-459.532757622	-.000411593	.005392364	.000798499
5	4	0	-459.532773851	-.000016229	.002043071	.000215489
6	5	0	-459.532775531	-.000001680	.000119962	.000041488
7	6	0	-459.532775544	-.000000013	.000016995	.000006855
8	7	0	-459.532775545	.000000000	.000004132	.000001213
9	8	0	-459.532775545	.000000000	.000001055	.000000260

-----  
DENSITY CONVERGED  
-----

TIME TO FORM FOCK OPERATORS= 1.0 SECONDS ( .1  
SEC/ITER)

TIME TO SOLVE SCF EQUATIONS= .0 SECONDS ( .0  
SEC/ITER)

FINAL ENERGY IS -459.5327755446 AFTER 9 ITERATIONS

..... END OF RHF CALCULATION .....

STEP CPU TIME = 1.10 TOTAL CPU TIME = 5.4 ( .1 MIN)  
TOTAL WALL CLOCK TIME= 5.5 SECONDS, CPU UTILIZATION IS 99.63%

Dipole (def): .0931(x), .0000(y), .0000(z); .0931(tot)  
Debye  
Dipole (cp): .6545(x), .0002(y), .0000(z); .6545(tot)  
Debye  
Dipole (ind): -.5614(x), -.0002(y), .0000(z); .5614(tot)  
Debye

..... END OF ONE-ELECTRON INTEGRALS .....

STEP CPU TIME = .01 TOTAL CPU TIME = 5.5 ( .1 MIN)  
TOTAL WALL CLOCK TIME= 5.5 SECONDS, CPU UTILIZATION IS 99.45%

-----  
Fragment 3:  
-----

..... END OF ONE-ELECTRON INTEGRALS .....

STEP CPU TIME = .02 TOTAL CPU TIME = 5.5 ( .1 MIN)  
TOTAL WALL CLOCK TIME= 5.5 SECONDS, CPU UTILIZATION IS 99.64%

ITER	EX	DEM	TOTAL ENERGY	E CHANGE	DENSITY CHANGE	ORB. GRAD
1	0	0	-75.976144307	-75.976144307	.063617604	.000000000
-----START SECOND ORDER SCF-----						
2	1	0	-76.012250953	-.036106646	.030657630	.020699451
3	2	0	-76.013943027	-.001692074	.010594505	.007804060
4	3	0	-76.014289531	-.000346504	.001346105	.000625036
5	4	0	-76.014294187	-.000004656	.000761013	.000249417
6	5	0	-76.014294756	-.000000569	.000094731	.000020485
7	6	0	-76.014294766	-.000000010	.000034127	.000007823
8	7	0	-76.014294767	-.000000001	.000002560	.000001624
9	8	0	-76.014294767	.000000000	.000000785	.000000444

-----  
DENSITY CONVERGED  
-----

TIME TO FORM FOCK OPERATORS= 1.0 SECONDS ( .1  
SEC/ITER)  
TIME TO SOLVE SCF EQUATIONS= .1 SECONDS ( .0  
SEC/ITER)

FINAL ENERGY IS -76.0142947674 AFTER 9 ITERATIONS

..... END OF RHF CALCULATION .....

STEP CPU TIME = 1.08 TOTAL CPU TIME = 6.6 ( .1 MIN)  
TOTAL WALL CLOCK TIME= 6.6 SECONDS, CPU UTILIZATION IS 99.39%

Dipole (def): -2.6384(x), .0016(y), .0002(z); 2.6384(tot)  
Debye  
Dipole (cp): -2.2688(x), .0014(y), .0002(z); 2.2688(tot)  
Debye  
Dipole (ind): -.3696(x), .0002(y), .0000(z); .3696(tot)  
Debye

..... END OF ONE-ELECTRON INTEGRALS .....

STEP CPU TIME = .02 TOTAL CPU TIME = 6.6 ( .1 MIN)  
TOTAL WALL CLOCK TIME= 6.6 SECONDS, CPU UTILIZATION IS 99.55%

Natural Energy Decomposition Analysis (Summary):

	Energy (wfn)	Energy (wfn)	Component (kcal/mol)
H2OLiCl	-543.0596639 (scf)	-542.9705154 (loc)	CT = -55.94 ES = -190.03 POL = -10.77 EX = -5.06
1. Li (+) 4.77)	-7.1981557 (def)	-7.2355399 (cp)	DEF (SE) = 23.46 (

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:

3 4 5 6 7 8 10 11 12 13 16 17 18 19 20 21 22  
 23 24 25  
 26 27 28 29 30 31 32 33 34 35 36 37 38 39  
 and orbitals:  
 1 2 9 14 15 40 41 42 43 44 45 46 47 48 49 50 51  
 52 53

Orbital occupancies:

Orbital	No deletions	This deletion	Change
1. BD ( 1) O 3- H 4	1.99945	1.99982	.00036
2. BD ( 1) O 3- H 5	1.99945	1.99982	.00036
3. CR ( 1) Li 1	1.99953	1.99996	.00042
4. CR ( 1) Cl 2	2.00000	2.00000	.00000
5. CR ( 2) Cl 2	1.99998	1.99998	.00000
6. CR ( 3) Cl 2	1.99997	1.99997	.00000
7. CR ( 4) Cl 2	1.99999	1.99999	.00000
8. CR ( 5) Cl 2	2.00000	2.00000	.00000
9. CR ( 1) O 3	1.99992	1.99993	.00000
10. LP ( 1) Cl 2	1.99941	1.99966	.00025
11. LP ( 2) Cl 2	1.99057	1.99083	.00026
12. LP ( 3) Cl 2	1.98955	1.99003	.00047
13. LP ( 4) Cl 2	1.93359	1.93483	.00124
14. LP ( 1) O 3	1.99853	1.99999	.00147
15. LP ( 2) O 3	1.97591	1.99978	.02387
16. LP* ( 1) Li 1	.08610	.06475	-.02135
17. RY* ( 1) Li 1	.01062	.00915	-.00147

18.	RY*( 2)Li 1	.01045	.00996	-.00049
19.	RY*( 3)Li 1	.00360	.00050	-.00310
20.	RY*( 4)Li 1	.00036	.00002	-.00034
21.	RY*( 5)Li 1	.00025	.00020	-.00005
22.	RY*( 6)Li 1	.00020	.00003	-.00017
23.	RY*( 7)Li 1	.00006	.00011	.00004
24.	RY*( 8)Li 1	.00000	.00000	.00000
25.	RY*( 9)Li 1	.00000	.00000	.00000
26.	RY*(10)Li 1	.00000	.00000	.00000
27.	RY*(11)Li 1	.00000	.00000	.00000
28.	RY*(12)Li 1	.00000	.00002	.00001
29.	RY*(13)Li 1	.00000	.00000	.00000
30.	RY*( 1)Cl 2	.00007	.00002	-.00005
31.	RY*( 2)Cl 2	.00005	.00000	-.00005
32.	RY*( 3)Cl 2	.00000	.00000	.00000
33.	RY*( 4)Cl 2	.00001	.00000	-.00001
34.	RY*( 5)Cl 2	.00000	.00000	.00000
35.	RY*( 6)Cl 2	.00000	.00000	.00000
36.	RY*( 7)Cl 2	.00000	.00000	.00000
37.	RY*( 8)Cl 2	.00000	.00000	.00000
38.	RY*( 9)Cl 2	.00000	.00000	.00000
39.	RY*(10)Cl 2	.00000	.00000	.00000
40.	RY*( 1) O 3	.00120	.00001	-.00119
41.	RY*( 2) O 3	.00004	.00001	-.00004
42.	RY*( 3) O 3	.00003	.00001	-.00001
43.	RY*( 4) O 3	.00000	.00001	.00000
44.	RY*( 5) O 3	.00001	.00000	-.00001
45.	RY*( 6) O 3	.00001	.00001	.00000
46.	RY*( 7) O 3	.00000	.00000	.00000
47.	RY*( 8) O 3	.00000	.00000	.00000
48.	RY*( 9) O 3	.00001	.00000	.00000
49.	RY*(10) O 3	.00000	.00000	.00000
50.	RY*( 1) H 4	.00027	.00026	.00000
51.	RY*( 1) H 5	.00027	.00026	.00000
52.	BD*( 1) O 3- H 4	.00027	.00005	-.00022
53.	BD*( 1) O 3- H 5	.00027	.00005	-.00022

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.

-----  
-----

ITER	EX	DEM	TOTAL ENERGY	E CHANGE	DENSITY CHANGE	ORB. GRAD
1	0	0	-543.030827809	-543.030827809	.069331507	.000000000

SCF IS UNCONVERGED, TOO MANY ITERATIONS

TIME TO FORM FOCK OPERATORS= .1 SECONDS ( .1  
SEC/ITER)

TIME TO SOLVE SCF EQUATIONS= .0 SECONDS ( .0  
SEC/ITER)

FINAL ENERGY IS .0000000000 AFTER 1 ITERATIONS

..... END OF RHF CALCULATION .....

STEP CPU TIME = .65 TOTAL CPU TIME = 7.2 ( .1 MIN)

TOTAL WALL CLOCK TIME= 7.3 SECONDS, CPU UTILIZATION IS 99.45%

```

-----
Energy of deletion :      -543.030827809
Total SCF energy :      -543.059663903
-----
Energy change :          .028836 a.u.,      18.095 kcal/mol
-----

```

```

-----
Fragment 1:
-----

```

```

..... END OF ONE-ELECTRON INTEGRALS .....
STEP CPU TIME =      .02 TOTAL CPU TIME =      7.3 (      .1 MIN)
TOTAL WALL CLOCK TIME=      7.3 SECONDS, CPU UTILIZATION IS  99.59%

```

ITER	EX	DEM	TOTAL ENERGY	E CHANGE	DENSITY CHANGE	ORB. GRAD
1	0	0	-466.993811707	-466.993811707	.052107301	.000000000
-----START SECOND ORDER SCF-----						
2	1	0	-467.010157929	-.016346221	.011014584	.006113155
3	2	0	-467.010367631	-.000209703	.005174620	.001151462
4	3	0	-467.010378611	-.000010980	.000765975	.000224984
5	4	0	-467.010379160	-.000000549	.000227689	.000062821
6	5	0	-467.010379200	-.000000040	.000051724	.000009720
7	6	0	-467.010379202	-.000000002	.000010094	.000002825
8	7	0	-467.010379202	.000000000	.000004014	.000000849
9	8	0	-467.010379202	.000000000	.000000619	.000000118

```

-----
DENSITY CONVERGED
-----

```

```

TIME TO FORM FOCK OPERATORS=      1.0 SECONDS (      .1
SEC/ITER)
TIME TO SOLVE SCF EQUATIONS=      .1 SECONDS (      .0
SEC/ITER)

```

```

FINAL ENERGY IS      -467.0103792022 AFTER      9 ITERATIONS
..... END OF RHF CALCULATION .....
STEP CPU TIME =      1.08 TOTAL CPU TIME =      8.3 (      .1 MIN)
TOTAL WALL CLOCK TIME=      8.4 SECONDS, CPU UTILIZATION IS  99.52%

```

```

Dipole (def):  -8.0598(x),  -.0025(y),  .0000(z);  8.0598(tot)
Debye
Dipole (cp):   -7.7165(x),  -.0024(y),  .0000(z);  7.7165(tot)
Debye
Dipole (ind):  -.3433(x),  -.0001(y),  .0000(z);  .3433(tot)
Debye

```

```

..... END OF ONE-ELECTRON INTEGRALS .....
STEP CPU TIME =      .01 TOTAL CPU TIME =      8.3 (      .1 MIN)
TOTAL WALL CLOCK TIME=      8.4 SECONDS, CPU UTILIZATION IS  99.40%

```

```

-----
Fragment 2:
-----

```

..... END OF ONE-ELECTRON INTEGRALS .....

STEP CPU TIME = .02 TOTAL CPU TIME = 8.4 ( .1 MIN)  
TOTAL WALL CLOCK TIME= 8.4 SECONDS, CPU UTILIZATION IS 99.52%

ITER	EX	DEM	TOTAL ENERGY	E CHANGE	DENSITY CHANGE	ORB. GRAD
1	0	0	-75.976144307	-75.976144307	.063617604	.000000000
-----START SECOND ORDER SCF-----						
2	1	0	-76.012250953	-.036106646	.030657630	.020699451
3	2	0	-76.013943027	-.001692074	.010594505	.007804060
4	3	0	-76.014289531	-.000346504	.001346105	.000625036
5	4	0	-76.014294187	-.000004656	.000761013	.000249417
6	5	0	-76.014294756	-.000000569	.000094731	.000020485
7	6	0	-76.014294766	-.000000010	.000034127	.000007823
8	7	0	-76.014294767	-.000000001	.000002560	.000001624
9	8	0	-76.014294767	.000000000	.000000785	.000000444

-----  
DENSITY CONVERGED  
-----

TIME TO FORM FOCK OPERATORS= 1.0 SECONDS ( .1  
SEC/ITER)  
TIME TO SOLVE SCF EQUATIONS= .0 SECONDS ( .0  
SEC/ITER)

FINAL ENERGY IS -76.0142947674 AFTER 9 ITERATIONS

..... END OF RHF CALCULATION .....

STEP CPU TIME = 1.09 TOTAL CPU TIME = 9.5 ( .2 MIN)  
TOTAL WALL CLOCK TIME= 9.5 SECONDS, CPU UTILIZATION IS 99.58%

Dipole (def): -2.6384(x), .0016(y), .0002(z); 2.6384(tot)  
Debye  
Dipole (cp): -2.2688(x), .0014(y), .0002(z); 2.2688(tot)  
Debye  
Dipole (ind): -.3696(x), .0002(y), .0000(z); .3696(tot)  
Debye

..... END OF ONE-ELECTRON INTEGRALS .....

STEP CPU TIME = .01 TOTAL CPU TIME = 9.5 ( .2 MIN)  
TOTAL WALL CLOCK TIME= 9.5 SECONDS, CPU UTILIZATION IS 99.58%

Natural Energy Decomposition Analysis (Summary):

	Energy (wfn)	Energy (wfn)	Component (kcal/mol)
H2OLiCl	-543.0596639 (scf)	-543.0308278 (loc)	CT = -18.09 ES = -27.42 POL = -8.69 EX = -2.09
1. LiCl 2.01)	-466.9938117 (def)	-467.0103792 (cp)	DEF (SE) = 10.40 (
2. H2O 2.35)	-75.9761443 (def)	-76.0142948 (cp)	DEF (SE) = 23.94 (

$$E = -21.96$$

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<sub>2</sub>O 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 (such as MOPAC or AMPAC) that have no direct-access file.

### *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 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 ( $n_{\text{occ}} = N_e/2$ ) and lowest unoccupied ( $n_{\text{occ}} + 1$ ) 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).

Permutations Lists. 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 $END
```

As indicated, the permutation list must be enclosed by left-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.12.3 Checkpoint Permutation Lists*

The checkpointing option supports a variety of forms for the permutation list file-input bracket .

Permuting by Serial Number. 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
```

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. 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),

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
```

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  $n_{\text{occ}} = 8$ , 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

```
AONBO=C
```

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
```

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 [ $\sigma_{\text{C3-H15}}$   $n_{\text{N11}}$  |  $\pi^*_{\text{C4-C5}}$ ] 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).

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 proceeding to the last. For example, the command

```
AOPNBO=C
```

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).

#### *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 ( $\sigma^*_{\text{C1H3}}$ , "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 \$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<sub>3</sub> 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  $\varphi_i$  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  $\varphi_i$ . Each coefficient  $t_{\alpha i}$  can in turn be identified with an NBO  $\Omega_\alpha$  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.13.2 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 FILE=CH3NH2 $END
```

The first table shows the leading NBO contributions to each MO, as illustrated below for the example of CH<sub>3</sub>NH<sub>2</sub> 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 = -15.445850 a.u.
          0.993*[ 8]: CR ( 1) N 2(cr)
MO   2 (occ): orbital energy = -11.182857 a.u.
          0.993*[ 7]: CR ( 1) C 1(cr)
MO   3 (occ): orbital energy = -1.164070 a.u.
          0.629*[ 1]: BD ( 1) C 1- N 2
          0.474*[ 6]: BD ( 1) N 2- H 7
          0.474*[ 5]: BD ( 1) N 2- H 6
.
.
MO   8 (occ): orbital energy = -0.517129 a.u.
          -0.594*[ 4]: BD ( 1) C 1- H 5
           0.594*[ 3]: BD ( 1) C 1- H 4
          -0.381*[ 6]: BD ( 1) N 2- H 7
           0.381*[ 5]: BD ( 1) N 2- H 6
MO   9 (occ): orbital energy = -0.368736 a.u.
          0.901*[ 9]: LP ( 1) N 2(lp)
          0.334*[ 2]: BD ( 1) C 1- H 3
MO  10 (vir): orbital energy =  0.266307 a.u.
          0.434*[ 28]: BD*( 1) N 2- H 7*
          0.434*[ 27]: BD*( 1) N 2- H 6*
          0.322*[ 24]: BD*( 1) C 1- H 3*
          -0.287*[ 21]: RY*( 1) H 6(ry*)
          -0.287*[ 22]: RY*( 1) H 7(ry*)
          0.256*[ 26]: BD*( 1) C 1- H 5*
          0.256*[ 25]: BD*( 1) C 1- H 4*
          -0.248*[ 18]: RY*( 1) H 3(ry*)
          0.236*[ 23]: BD*( 1) C 1- N 2*
.
.
MO  28 (vir): orbital energy =  2.839449 a.u.
          0.725*[ 17]: RY*( 4) N 2(ry*)
```

$$0.649^*[16]: RY^*(3) N 2(ry^*)$$

In this example, MO 1 and 2 are both found to be highly localized and transferable, with strong (~99%) contributions from NBO 8 (the nitrogen core orbital) and NBO 7 (the carbon core orbital), respectively. However, MO 3 is a strong admixture of  $\sigma_{CN}$  (NBO 1) and the two  $\sigma_{NH}$  bonds (NBOs 5,6) with approximate composition

$$\varphi_3 \cong 0.629 \sigma_{CN} + 0.474(\sigma_{NH} + \sigma_{NH'})$$

and higher MOs show still more strongly mixed NBO character. The HOMO (MO 9) derives primarily (~81%) from the  $n_N$  lone pair (NBO 9), with weaker (11%) contribution from  $\sigma_{CH}$  (NBO 2). However, the LUMO (MO 10) has significant contributions from at least *nine* NBOs, including two Rydberg orbitals (NBOs 21, 22) 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				
MO	bonding (2c, 3c)	nonbonding (1c, 1c*)	antibonding (2c*, 3c*)	
1 (o)		0.987 N 2		
	$\overline{0.011}$ (b)	$\overline{0.989}$ (n)	$\overline{0.000}$ (a)	total
2 (o)		0.986 C 1		
	$\overline{0.013}$ (b)	$\overline{0.987}$ (n)	$\overline{0.000}$ (a)	total
3 (o)	0.395 C 1- N 2 0.225 N 2- H 7 0.225 N 2- H 6			
	$\overline{0.955}$ (b)	$\overline{0.045}$ (n)	$\overline{0.000}$ (a)	total
.				
.				
.				
8 (o)	0.353 C 1- H 5 0.353 C 1- H 4 0.146 N 2- H 7 0.146 N 2- H 6			

	$\overline{0.997}$ (b)		$\overline{0.001}$ (n)		$\overline{0.003}$ (a)	total
9 (o)	0.112	C 1- H 3	0.811	N 2		
	$\overline{0.178}$ (b)		$\overline{0.812}$ (n)		$\overline{0.009}$ (a)	total
10 (v)			0.082	H 7	0.188	N 2- H 7
			0.082	H 6	0.188	N 2- H 6
			0.062	H 3	0.103	C 1- H 3
					0.065	C 1- H 5
					0.065	C 1- H 4
					0.056	C 1- N 2
	$\overline{0.001}$ (b)		$\overline{0.333}$ (n)		$\overline{0.666}$ (a)	total
.						
.						
.						
28 (v)			0.947	N 2		
	$\overline{0.000}$ (b)		$\overline{0.993}$ (n)		$\overline{0.007}$ (a)	total
	6.000 (b)		16.000 (n)		6.000 (a)	Sum total for MOs

This table shows, e.g., that MOs 1, 2 have predominantly (>98%) nonbonding character, whereas MO 3 is predominantly (>95%) of bonding character, primarily at CN (40%) and the two NH bonds (22% each). Similarly, the entries for MO 9 suggest that the HOMO is about 81% non-bonding (on N) and only 18% bonding (on the C1-H3 bond). Hence, ionization of an electron from the HOMO should 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.

#### 14. NCS: NMR CHEMICAL SHIELDING ANALYSIS

Reference: J. A. Bohmann, F. Weinhold, and T. C. Farrar, *J. Chem. Phys.* **107**, 1173-1184 (1997).

##### *B14.1 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 ( $\rightarrow m$ ) in external magnetic fields ( $\rightarrow B$ ) 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,

$$(1) \quad \sigma_{\alpha\beta} = \text{Tr}\{\mathbf{D}^{00} \mathbf{h}^{\alpha\beta}\} + \text{Tr}\{\mathbf{D}^{\alpha 0} \mathbf{h}^{0\beta}\} = \sigma_{\alpha\beta}^{(u)} + \sigma_{\alpha\beta}^{(i)}$$

where the matrices  $\mathbf{D}^{00}$ ,  $\mathbf{D}^{\alpha 0}$ ,  $\mathbf{h}^{0\beta}$ , and  $\mathbf{h}^{\alpha\beta}$  represent, respectively, the Fock-Dirac density matrix, the density derivative with respect to field component  $B_\alpha$ , the derivative of the 1-e Hamiltonian ( $\mathbf{h}$ ) with respect to magnetic moment component  $m_\beta$ , and the crossed second derivative of  $\mathbf{h}$  with respect to  $M_\alpha$  and  $m_\beta$ , all in the basis of atomic orbitals  $\{\chi_p\}$ . For the full chemical shielding anisotropy, the tensor indices  $\alpha, \beta$  range over the cartesian components  $x, y, z$ , but the simpler isotropic scalar shielding (average diagonal component)

$$(2) \quad \sigma_{\text{iso}} = 1/3 \sum_{\alpha} \sigma_{\alpha\alpha}$$

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  $\sigma_{\text{iso}}$ ), we make use of the following transformations that relate the canonical MOs ( $\varphi_k^{\text{MO}}$ ) to the NLMOs ( $\varphi_j^{\text{NLMO}}$ ), NBOs ( $\Omega_n$ ) and AOs ( $\chi_p$ ), viz.,

$$(3a) \quad \varphi_j^{\text{NLMO}} = \sum_n^{\text{NBO}} a_{nj} \Omega_n \quad (\text{NBONLMO})$$

$$(3b) \quad \Omega_n = \sum_q^{\text{AO}} b_{qn} \chi_q \quad (\text{AONBO})$$

$$(3c) \quad \varphi_k^{\text{MO}} = \sum_p^{\text{AO}} c_{pk} \chi_p \quad (\text{AOMO})$$

$$(3d) \quad \varphi_j^{\text{NLMO}} = \sum_q^{\text{AO}} d_{qj} \chi_q \quad (\text{AONLMO})$$

$$(3e) \quad \varphi_k^{\text{MO}} = \sum_j^{\text{NLMO}} t_{jk} \varphi_j^{\text{NLMO}} \quad (\text{NLMOMO})$$

The program analyzes  $\sigma_{\alpha\beta}$  in terms of localized NBO contributions

$$(4) \quad \sigma_{\alpha\beta} = \sum_j^L [^j\sigma_{\alpha\beta} + \sum_n^{NL} {}^{j \rightarrow n}\sigma_{\alpha\beta}]$$

where  $^j\sigma_{\alpha\beta}$  is a Lewis-type (L) contribution from the parent NBO ( $\Omega_j$ ) of  $\varphi_j^{NLMO}$ , and  ${}^{j \rightarrow n}\sigma_{\alpha\beta}$  is a non-Lewis-type (NL) contribution from the "delocalization tail"  $\Omega_n$  of this NLMO (the same label serving to identify both the NLMO and its parent NBO). Each  ${}^{j \rightarrow n}\sigma_{\alpha\beta}$  is therefore the shielding associated with a particular  $\Omega_j \rightarrow \Omega_n$  donor-acceptor (L  $\rightarrow$  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  $\varphi_k^{MO}$ ) from localized contractions of the form

$$(5) \quad {}^{j \rightarrow n}\sigma_{\alpha\beta}^{(u)} = \text{Tr} \{ {}^{j \rightarrow n}\mathbf{D}^{00} \mathbf{h}^{\alpha\beta} \}$$

where the partial density matrix for localized  $j \rightarrow n$  NBO interaction is

$$(6) \quad {}^{j \rightarrow n}\mathbf{D}_{pq}^{00} = 2 a_{nj} b_{pn} d_{qj}$$

This follows from writing the Fock-Dirac density matrix elements  $\mathbf{D}_{pq}^{00} = 2 \sum_k c_{pk} c_{qk}$  in the alternative NLMO form

$$(7) \quad \mathbf{D}_{pq}^{00} = 2 \sum_j^{NLMO} d_{pj} d_{qj}$$

and using (3a) to write NLMO  $j$  in terms of its parent NBO  $\Omega_j$  and delocalization tail  $\Omega_n$ .

The program next calculates  $\sigma_{\alpha\beta}^{(i)}$  (corresponding to contributions from virtual MOs  $\varphi_v^{MO}$ ) from localized contractions of the form

$$(8) \quad {}^{j \rightarrow n}\sigma_{\alpha\beta}^{(i)} = \text{Tr} \{ {}^{j \rightarrow n}\mathbf{D}^{\alpha 0} \mathbf{h}^{0\beta} \}$$

where the  $j \rightarrow n$  contribution to the density derivative matrix can be written as

$$(9) \quad {}^{j \rightarrow n}\mathbf{D}_{pq}^{\alpha 0} = 2 \sum_k^{\text{occ}} t_{jk} a_{nj} [b_{pn} c_{qk}^{\alpha 0} - c_{pk}^{\alpha 0} b_{qn}]$$

The coefficients  $c_{pk}^{\alpha 0}$  describe the field-dependent correction to the field-free LCAO coefficient  $c_{qk}$  in the 1st-order perturbative expression

$$(10) \quad c_{pk}^{(1)}(B_\alpha, m_\beta) = c_{pk} + iB_\alpha c_{pk}^{\alpha 0} + im_\beta c_{pk}^{0\beta} + \dots$$

They are evaluated by the formalism of Pulay in the form

$$(11) \quad c_{pk}^{\alpha 0} = \sum_q^{AO} \sum_r^{AO} c_{rk} [{}^k\mathbf{W}_{pq}(\mathbf{F}_{qr}^{\alpha 0} - \varepsilon_k \mathbf{S}_{qr}^{\alpha 0}) + 1/4 \mathbf{D}_{pq}^{00} \mathbf{S}_{qr}^{\alpha 0}]$$

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

$$(12) \quad {}^k\mathbf{W}_{pq} = \sum_v^{\text{vir}} c_{pv} c_{qv} / (\varepsilon_k - \varepsilon_v)$$

for MO  $k$  with orbital energy  $\varepsilon_k$ . The final L, NL contributions in (4) are obtained as the sum of unperturbed and induced terms (5), (8).

### B.14.2 NCS Keyword Usage

The NCS module is currently implemented only for Gaussian 9X versions. To calculate GIAO shieldings and perform NCS analysis, one should include the Gaussian keyword NMR and the IOP(10/46=1) parameter in the Gaussian route card, 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<sub>3</sub>NH<sub>2</sub> is illustrated below:

---

```

%mem=4000000
#HF/3-21G POP=NBOrad NMR IOP(10/46=1)

CH3NH2

  0  1
  6   1.0900000    0.0000000    0.0000000
  7   1.5800000    1.3859293    0.0000000
  1   1.4533333   -0.5138309   -0.8899814
  1   0.0000000    0.0000000    0.0000000
  1   1.4533335   -0.5138310    0.8899813
  1   2.5900002    1.3859293   -0.0000001
  1   1.2433335    1.8620479   -0.8246616

$NBO FILE=ch3nh2 NCS $END

```

---

This produces a table of localized contributions to isotropic chemical shielding constants ( $\sigma_{\text{iso}}$ ) 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 including a *bracket list* (Sec. B.9.2) immediately following the NCS keyword that contains one or more of the following keywords (separated by commas or spaces):

KEYWORD	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 keyword 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 <u>analysis by difference</u> .)
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 < I CSA > $END
```

The keywords "NCS < I XYZ >" would request analogous analysis with respect to the molecular cartesian axes (in addition to CSA printout). Note that each NCS bracket list entry "compounds" the effect of others, so that, e.g., a combination such as "NCS < I XYZ MO >" would give ~8 *times* the printout of "NCS".

Each table produced by NCS analysis includes all  $j \rightarrow n$  delocalization contributions that exceed the default threshold for printing, 0.1 ppm. 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 $END
```

which requests printing of delocalized anisotropic and isotropic shielding contributions exceeding 0.5 ppm.

### B.14.3 NCS Sample Output

Sample default NCS output is shown below for the CH<sub>3</sub>NH<sub>2</sub> molecule (RHF/3-21G level, idealized Pople-Gordon geometry):

---

```
Natural NMR Chemical Shielding Tensor Analysis
NCS Tensor analysis is using      8624 words
Threshold for printing:      .10 ppm
```

```
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- N 2	L	-6.30	6.51	.65	.51	.51	2.47	2.47
	NL	-.08	-.47	-.06	.07	.07	-.15	-.15
2. C 1- H 3	L	-4.38	.43	26.60	1.84	1.84	.08	.08
	NL	-.44	-.32	-.01	-.04	-.04	.01	.01
3. C 1- H 4	L	-2.68	2.18	2.16	25.86	2.06	.13	.25
	NL	-.16	-1.48	-.07	-.07	.02	-.04	-.11
4. C 1- H 5	L	-2.69	2.17	2.15	2.06	25.86	.25	.13
	NL	-.16	-1.47	-.07	.01	-.08	-.11	-.03
5. N 2- H 6	L	.10	7.24	.34	.34	.23	22.82	3.35
	NL	-.02	.12	-.03	-.16	.00	.08	-.03
6. N 2- H 7	L	.11	7.33	.35	.24	.34	3.41	22.88
	NL	-.03	.03	-.03	.00	-.16	-.09	.02
7. C 1(cr)	L	202.23	-.05	.17	.14	.14	-.02	-.02
	NL	.32	-.02	-.02	-.01	-.01	-.01	-.01
8. N 2(cr)	L	.13	238.42	.07	.04	.04	.04	.04
	NL	-.05	.11	-.01	-.01	-.01	.02	.02
9. N 2(lp)	L	-.34	6.30	-.47	.10	.10	5.31	5.31
	NL	.16	.95	-.33	.07	.07	.17	.17
-----		-----						
	Lewis	186.18	270.53	32.01	31.13	31.13	34.49	34.49
	non-Lewis	-.46	-2.55	-.62	-.14	-.14	-.12	-.12
-----		-----						
	Total	185.72	267.97	31.39	30.99	30.99	34.38	34.38



```

-----
-----
Lewis      27.26   31.43   37.34     .00     .00     .54     8.00
32.01
non-Lewis  -1.14   -1.15     .42     .00     .00     .09     1.57
-.62
-----
-----
Total      26.13   30.27   37.77     .00     .00     .63     9.57
31.39
-----
-----

```

Cartesian XYZ to principal shielding axes: atom H( 3)

```

      1      2      3
-----
X   .000000   .729704  -.683763
Y   .000000   .683763   .729704
Z   1.000000   .000000   .000000

```

This table displays contributions to the individual tensor components in the principal axes of the nuclear shielding tensor. ``ISO" denotes  $\sigma_{\text{iso}} = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3$ , 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  $\sigma_{ij}$  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 " leads to the additional output for H(3) shown below:

Full cartesian NMR shielding tensor (ppm) for atom H( 3):

```

NBO      Lewis (L) and non-Lewis (NL) contributions
-----
L  NL      XX      XY      XZ      YX      YY      YZ      ZX      ZY
ZZ
=====
1.      .53   -1.55   .00   -1.39   1.04   .00   .00   .00
.38
18.     -.13   -.06   .00   -.18   -.10   .00   .00   .00
-.23
21.     .10    .08    .05   -.02   -.02   -.06   -.03   -.03
.08

```

2.	29.08	-1.00	.00	-1.67	24.97	.00	.00	.00
25.74								
14.	-.12	-.03	.00	-.03	-.17	.00	.00	.00
-.25								
19.	.02	.06	-.08	.03	.14	-.02	-.06	-.05
.13								
20.	.01	.09	.08	.03	.14	.02	.06	.05
.13								
3.	2.41	.32	-.62	.59	2.90	-.85	.75	-1.84
1.16								
18.	-.08	-.03	.05	.04	-.18	-.01	.11	-.03
-.16								
26.	.04	-.12	.02	.03	.05	.03	.05	-.09
.00								
4.	2.41	.33	.62	.59	2.89	.85	-.75	1.84
1.16								
18.	-.08	-.04	-.05	.04	-.18	.01	-.11	.03
-.16								
19.	-.06	.13	-.03	-.03	-.01	.01	.04	-.05
.00								
25.	.06	-.17	-.02	.03	.06	-.03	-.05	.09
-.01								
5.	.07	-.22	.06	-.71	.78	-.88	-.39	.11
.17								
6.	.08	-.22	-.06	-.73	.79	.88	.39	-.11
.17								
7.	.49	.01	.00	-.16	.01	.00	.00	.00
.02								
9.	-.84	-.08	.00	-.04	1.03	.00	.00	.00
-1.61								
10.	.05	.07	.00	-.05	.03	.00	.00	.00
.18								
18.	-.19	-.07	.00	-.12	-.15	.00	.00	.00
-.29								
24.	.12	-.67	.00	-.46	.18	.00	.00	.00
-.59								
25.	-.03	-.01	.09	-.07	-.01	.03	-.01	.14
-.09								
26.	-.04	.01	-.09	-.07	-.01	-.03	.01	-.14
-.09								
-----								
L	34.30	-2.42	.00	-3.50	34.47	.00	.00	.00
27.26								
NL	-.52	-.69	.00	-.87	-.21	.00	.00	.00
-1.14								
-----								
Total	33.78	-3.11	.00	-4.37	34.26	.00	.00	.00
26.13								
-----								

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 and tables.

Finally, option ``NCS '' 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.	.35	234.43	.18	.13	.13	-.11	-.11
2.	199.51	.35	-.13	-.24	-.24	.17	.17
3.	5.19	22.23	1.12	1.42	1.42	4.69	4.69
4.	28.33	12.26	6.11	6.08	6.08	3.74	3.74
5.	-3.52	-19.19	.82	3.49	3.49	10.44	10.44
6.	-11.52	-3.19	16.99	2.95	2.95	2.19	2.19
7.	-4.33	20.38	3.21	5.43	5.43	4.04	4.04
8.	-20.93	.80	-.41	11.25	11.25	4.34	4.34
9.	-7.35	-.11	3.49	.48	.48	4.89	4.89
Total	185.72	267.97	31.39	30.99	30.99	34.38	34.38

---

The MO contributions of this table are typically much less transferable than corresponding NBO contributions.

## B.15. NJC: NATURAL J-COUPPLING 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)  $\alpha$ -spin perturbation  $\delta(\mathbf{r}_B)$  with formal perturbative field strength  $\lambda_B$  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  $\lambda_B$  at B, the J-coupling (Hz) can be evaluated as

$$(1) \quad J[A,B] = (16h\mu_b^2 \gamma_A\gamma_B/9) \Delta_B\rho(\mathbf{r}_A) / \lambda_B$$

where  $h$  is Planck's constant,  $\mu_b$  is the Bohr magneton, and  $\gamma_A, \gamma_B$  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  $\lambda_B$ .

To obtain a localized decomposition of the densities ( $\rho^{(\alpha)}, \rho^{(\beta)}$ ) of either spin, one can replace the usual expansion over occupied MOs  $\{\phi_i^{(\sigma)}\}$  by the corresponding expansion over NLMOs  $\{\Omega_i^{(\sigma)}\}$

$$(2) \quad \rho^{(\sigma)} = \sum_i^{\text{occ}} |\Omega_i^{(\sigma)}|^2, \quad (\sigma = \alpha, \beta)$$

Each semi-localized NLMO  $\Omega_i$  can in turn be expanded in the complete set of localized NBOs  $\{\sigma_j\}$ , viz., for  $\alpha$  spin,

$$(3) \quad \Omega_i^{(\alpha)} = c_{ii}^{(\alpha)}\sigma_i^{(\alpha)} + \sum_j^{\text{NL}} c_{ji}^{(\alpha)}\sigma_j^{(\alpha)}$$

where the  $\{c_{ji}^{(\alpha)}\}$  are elements of the NBO→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

$$(4) \quad J[A,B] = \sum_i^{\text{L}} \{J_i^{(\text{L})}[A,B] + \sum_j^{\text{NL}} J_{ji}^{(\text{NL})}[A,B]\}$$

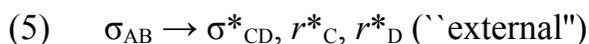
analogous to that previously described for the dipole operator (Sec. B.6.3). Each Lewis-type  $J_i^{(\text{L})}$  corresponds to the contribution of a completely localized NBO  $\sigma_i$  [i.e., the result of setting  $c_{ji} \neq 0$  for all  $j \neq i$  in Eq. (3)], whereas  $J_{ji}^{(\text{NL})}$  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  $\sigma_j^*$  is centered on one or both of the *same* atoms as  $\sigma_i$ , viz.,

$$(4) \quad \sigma_{AB} \rightarrow \sigma_{AB}^*, r_{A}^*, r_{B}^* \text{ ("internal")}$$

*Delocalization*: Those ("external") in which  $\sigma_i, \sigma_j^*$  are centered in *distinct* bonding regions, viz.,



Each  $J[A,B]$  can thereby be expressed as a sum of "Lewis," "repolarization," and "delocalization" contributions

$$(6) \quad J = J^{(L)} + J^{(\text{repol})} + J^{(\text{deloc})}$$

or, in terms of individual NBOs, as

$$(7) \quad J = \sum_i^L \{J_i^{(L)} + J_i^{(\text{repol})} + \sum_{j_i}^{\text{NL}} J_{ji}^{(\text{deloc})}\}$$

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  $J_i^{(\text{repol})}$  contributions describe how the electron pair in each NBO can repolarize (altering the left-right, radial, or angular separation of  $\alpha$  and  $\beta$  electrons) in response to the perturbation, and the  $J_{ji}^{(\text{deloc})}$  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  $\gamma_A, \gamma_B$  (taken from a standard compilation of NMR properties ([www.webelements.com](http://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  $\gamma$  values. For cases where isotopic spin and  $\gamma$  are unknown, the program uses the value  $\gamma = 1$  ( $\times 10^7$ ), so that calculated J values can be easily rescaled to correct physical units when the proper  $\gamma$  becomes known. (A similar rescaling procedure can be used to correct for revisions of the  $\gamma$  values tabulated in Ref. 3.) The table below summarizes the selected isotope, nuclear spin,  $\gamma$  value (in units of  $10^7 \text{ rad T}^{-1}\text{s}^{-1}$ ) and percentage terrestrial abundance for all atoms  $Z = 1-103$ .

Z	isotope	I	$\gamma(\times 10^{-7})$	%-abund.
1	<sup>1</sup> H	1/2	26.7522	99.98
2	<sup>3</sup> He	1/2	-20.3802	0.00
3	<sup>7</sup> Li	3/2	10.3977	92.57

4	<sup>9</sup> Be	3/2	-3.7597	100.00
5	<sup>11</sup> B	3/2	2.8747	80.10
6	<sup>13</sup> C	1/2	6.7283	1.10
7	<sup>15</sup> N	1/2	-2.7126	0.37
8	<sup>17</sup> O	5/2	-3.6281	0.04
9	<sup>19</sup> F	1/2	25.1815	100.00
10	<sup>21</sup> Ne	3/2	-2.1131	0.27
11	<sup>23</sup> Na	3/2	7.0808	100.00
12	<sup>25</sup> Mg	5/2	-1.6389	10.05
13	<sup>27</sup> Al	5/2	6.9763	100.00
14	<sup>29</sup> Si	1/2	-5.3190	4.67
15	<sup>31</sup> P	1/2	10.8394	100.00
16	<sup>33</sup> S	3/2	2.0557	0.75
17	<sup>35</sup> Cl	3/2	2.6242	75.78
18	<sup>39</sup> Ar	7/2	1.0000	0.00
19	<sup>39</sup> K	3/2	1.2501	93.26
20	<sup>43</sup> Ca	7/2	-1.8031	0.13
21	<sup>45</sup> Sc	7/2	6.5088	100.00
22	<sup>47</sup> Ti	5/2	-1.5105	7.30
23	<sup>51</sup> V	7/2	7.0455	99.75
24	<sup>53</sup> Cr	3/2	-1.5152	9.50
25	<sup>55</sup> Mn	5/2	6.6453	100.00
26	<sup>57</sup> Fe	1/2	0.8681	2.25
27	<sup>59</sup> Co	7/2	6.3320	100.00
28	<sup>61</sup> Ni	3/2	-2.3948	1.14
29	<sup>63</sup> Cu	3/2	7.1118	69.17
30	<sup>67</sup> Zn	5/2	1.6767	4.12
31	<sup>69</sup> Ga	3/2	6.4389	60.11
32	<sup>73</sup> Ge	9/2	-0.9360	7.73
33	<sup>75</sup> As	3/2	4.5962	100.00
34	<sup>77</sup> Se	1/2	5.1254	7.63
35	<sup>79</sup> Br	3/2	6.7256	50.69
36	<sup>83</sup> Kr	9/2	-1.0331	11.55
37	<sup>85</sup> Rb	5/2	2.5927	72.17
38	<sup>87</sup> Sr	9/2	-1.1639	7.00

39	<sup>89</sup> Y	1/2	-1.3163	100.00
40	<sup>91</sup> Zr	5/2	-2.4974	11.22
41	<sup>93</sup> Nb	9/2	6.5674	100.00
42	<sup>95</sup> Mo	5/2	-1.7880	15.92
43	<sup>99</sup> Tc	9/2	6.0460	0.00
44	<sup>101</sup> Ru	5/2	-1.3770	16.98
45	<sup>103</sup> Rh	1/2	-0.8468	100.00
46	<sup>105</sup> Pd	5/2	-1.2300	22.33
47	<sup>107</sup> Ag	1/2	-1.0889	51.84
48	<sup>111</sup> Cd	1/2	-5.6983	12.80
49	<sup>115</sup> In	9/2	5.8972	95.70
50	<sup>119</sup> Sn	1/2	-10.0317	8.59
51	<sup>121</sup> Sb	5/2	6.4435	57.36
52	<sup>125</sup> Te	1/2	-8.5108	7.14
53	<sup>127</sup> I	5/2	5.3896	100.00
54	<sup>129</sup> Xe	1/2	-7.4521	26.40
55	<sup>133</sup> Cs	7/2	3.5333	100.00
56	<sup>137</sup> Ba	3/2	2.9930	11.23
57	<sup>139</sup> La	7/2	3.8083	99.91
58	<sup>141</sup> Ce	7/2	1.0000	0.00
59	<sup>141</sup> Pr	5/2	8.1907	100.00
60	<sup>143</sup> Nd	7/2	-1.4570	12.18
61	<sup>147</sup> Pm	7/2	3.6130	0.00
62	<sup>147</sup> Sm	7/2	-1.1150	15.07
63	<sup>153</sup> Eu	5/2	2.9369	52.20
64	<sup>157</sup> Gd	7/2	-1.0769	15.65
65	<sup>159</sup> Tb	3/2	6.4310	100.00
66	<sup>163</sup> Dy	7/2	1.2890	24.90
67	<sup>165</sup> Ho	7/2	5.7100	100.00
68	<sup>167</sup> Er	7/2	-0.7716	22.95
69	<sup>169</sup> Tm	1/2	-2.2180	100.00
70	<sup>173</sup> Yb	5/2	-1.3025	16.12
71	<sup>175</sup> Lu	7/2	3.0552	97.41
72	<sup>177</sup> Hf	7/2	1.0860	18.61
73	<sup>181</sup> Ta	7/2	3.2438	99.99

74	<sup>183</sup> W	1/2	1.1282	14.28
75	<sup>187</sup> Re	5/2	6.1057	62.60
76	<sup>189</sup> Os	3/2	2.1071	16.10
77	<sup>193</sup> Ir	3/2	0.5227	62.70
78	<sup>195</sup> Pt	1/2	5.8385	33.80
79	<sup>197</sup> Au	3/2	0.4731	100.00
80	<sup>199</sup> Hg	1/2	4.8458	16.87
81	<sup>205</sup> Tl	1/2	15.6922	70.48
82	<sup>207</sup> Pb	1/2	5.5805	22.10
83	<sup>209</sup> Bi	9/2	4.3750	100.00
84	<sup>209</sup> Po	1/2	7.4000	0.00
85	?At	?	1.0000	0.00
86	?Rn	?	1.0000	0.00
87	<sup>223</sup> Fr	?	1.0000	0.00
88	?Ra	?	1.0000	0.00
89	<sup>227</sup> Ac	3/2	3.5000	0.00
90	<sup>229</sup> Th	5/2	0.4000	0.00
91	<sup>231</sup> Pa	3/2	3.2100	100.00
92	<sup>235</sup> U	7/2	-0.5200	0.72
93	<sup>237</sup> Np	5/2	3.1000	0.00
94	<sup>239</sup> Pu	1/2	0.9720	0.00
95	<sup>241</sup> Am	5/2	1.4000	0.00
96	<sup>247</sup> Cm	9/2	0.2000	0.00
97	<sup>247</sup> Bk	3/2	1.0000	0.00
98	<sup>251</sup> Cf	1/2	1.0000	0.00
99	?Es	?	1.0000	0.00
100	<sup>257</sup> Fm	?	1.0000	0.00
101	?Md	?	1.0000	0.00
102	<sup>259</sup> No	?	1.0000	0.00
103	?Lr	?	1.0000	0.00

---

### *B.15.2 NJC Keyword Usage and Sample Input*

The NJC keyword is currently implemented only for Gaussian 9X. 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  $\text{CH}_3\text{NH}_2$  (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  $\lambda_B$  employed.] In the present case the  $J$ -couplings will be evaluated with gyromagnetic ratios for  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{15}\text{N}$  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

$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 columns 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" (<sup>3</sup>J, 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

$$J^{(L)} = 5.84 \text{ Hz}, J^{(\text{repol})} = -0.15 \text{ Hz}, J^{(\text{deloc})} = 2.66 \text{ Hz}$$

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),

$$J_4^{(\text{NLMO})} = 2.47 \text{ Hz}, J_6^{(\text{NLMO})} = 5.23 \text{ Hz}$$

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.,

$$J_4^{(\text{NBO})} = 1.74 \text{ Hz}, J_6^{(\text{NBO})} = 4.07 \text{ Hz}$$

the following ``Repol." entry gives the (relatively negligible) repolarization correction for the NBO, and the remaining column entries give the  $\sigma_i \rightarrow \sigma_j^*$  delocalization corrections. The two most important such corrections are seen to be

$$J_{4\rightarrow 28} = 1.38 \text{ Hz } (\sigma_{\text{C1H5}} \rightarrow \sigma_{\text{N2H7}}^*), J_{6\rightarrow 26} = 1.21 \text{ Hz } (\sigma_{\text{N2H7}} \rightarrow \sigma_{\text{C1H5}}^*)$$

corresponding to the expected strong hyperconjugative interaction in the vicinal *trans*-like relationship between these NBOs. These  $J_{4\rightarrow 28}$  and  $J_{6\rightarrow 26}$  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  $\sigma_i$ ,  $\sigma_j^*$  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  $\text{NJC}=0.0$  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. 3CHB: 3-CENTER, 4-ELECTRON HYPERBOND SEARCH**

Reference: F. Weinhold and C. R. Landis, "Valency and Bonding: A Natural Bond Orbital Donor-Acceptor Perspective," Sections 3.E, 4.F

### *B.16.1 Introduction*

The 3CHB keyword initiates the search for 3-center, 4-electron "hyperbonds" ( $\omega$ -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



which is denoted in the computer output as A:-B-:C.

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 ( $w_{\text{A-B:}C} \cong w_{\text{A: B-C}}$ ; 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 relatively rare feature of main-group compounds, it is found to be a fairly ubiquitous feature in transition metal species, as in the  $\text{W}(\text{CO})_5$  example described 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.,

$$(2) \quad \% \text{A-B} / \% \text{B-C} \cong \text{occ}(\sigma_{BC}^*) / \text{occ}(\sigma_{AB}^*)$$

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  $\text{occ}(\sigma_{BC}^*)$  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  $\omega_{\text{A-B:}C}$ ,  $\omega_{\text{A: B-C}}$  hyperbonds, or of the interacting  $h_A$ ,  $h_B$ ,  $h_C$  valence NHOs) can be estimated by adding the delocalized  $\sigma_{AB}^*$  occupancy to the localized  $n_C$ ,  $\sigma_{AB}$  occupancies of the nominal A-B :C Lewis structure,

$$(3) \quad \text{occ}(\text{A:-B-:C}) \cong \text{occ}(n_C) + \text{occ}(\sigma_{AB}) + \text{occ}(\sigma_{AB}^*)$$

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 ( $\sigma_{AB}$ ,  $n_C$ ) of only the A-B :C parent NBO Lewis structure.

In principle, the resonance hybrid (1) could exhibit a continuous range of weightings, and thus continuously variable %A-B vs. %B-C values in (2). By default, the 3CHB keyword 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.,

$$(4) \quad \%B-C > 33\%$$

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 qualitatively new and important feature of the bonding.

### B.16.1 Sample Output

Let us illustrate 3CHB output for the model  $W(CO)_5$  transition metal complex with G9X input file

---

```
%mem=6000000
%chk=w_co5
#b3lyp/lanl2dz pop=nboread scf=qc scfcyc=200

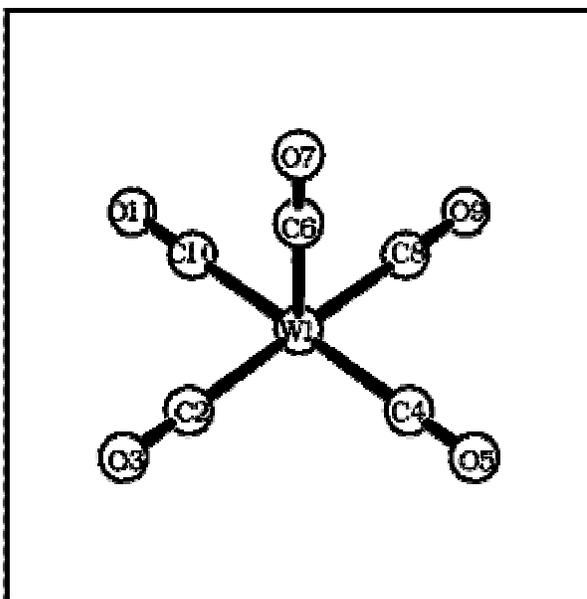
W(CO)5, E=-634.4598757

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 3chb $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<sub>2</sub>, C<sub>4</sub>, C<sub>6</sub>) and two detached CO ligands (carbon atoms C<sub>8</sub>, C<sub>10</sub>). The 3CHB search leads to the output shown below:

---

3-Center, 4-Electron A:-B-:C Hyperbonds (A-B :C  $\rightleftharpoons$  A: B-C)  
 [threshold for detection: 33.3%]

hybrids			NBOs		3-center		
-----			-----		-----		
h(C)	Hyperbond A:-B-:C	%A-B/%B-C	OCC.	BD(A-B)	LP(C)	h(A)	h(B)
-----	-----	-----	-----	-----	-----	-----	-----
1.	C 2:- W 1-: C 8	51.4/48.6	3.9642	1	39	1	2
57							
2.	C 4:- W 1-: C 10	51.4/48.6	3.9642	2	41	3	4
59							

---

As shown in the output, two hyperbonds (C<sub>2</sub>:-W<sub>1</sub>-:C<sub>8</sub> and C<sub>4</sub>:-W<sub>1</sub>-:C<sub>10</sub>) were discovered, each with occupancy 3.9642e 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 1 ( $\sigma_{CW}$ ) and 39 ( $n_C$ ) are composed of NHOs 1, 2, and 57, which have approximate hybrid compositions

$$(sp^{0.5})_{C2}-(sd^{2.0})_{W1}-(sp^{0.5})_{C8}$$

As also found in other segments of the NBO analysis, the low occupancy of  $n_C$  (1.56e), high occupancy of  $\sigma_{WC}^*$  (0.45e), and large estimated  $n_C$ - $\sigma_{WC}^*$  2nd-order interaction energy (270 kcal/mol) are all consistent with strong C:-W-:C hyperbond character.

---

---

## Section C: NBO PROGRAMMER'S GUIDE

### C.1 INTRODUCTION

Section C constitutes the programmer's guide to the NBO.SRC program. It assumes that the user has a thorough familiarity with Fortran programming and the operations of the NBO program (Sections A and B) as well as some familiarity with published algorithms for NAO/NBO/NLMO determination. This section is intended for the accomplished programmer who wishes to inquire into the details of the NBO numerical methods and find the specific source code associated with individual steps of the published NAO/NBO/NLMO algorithms or segments of NBO output.

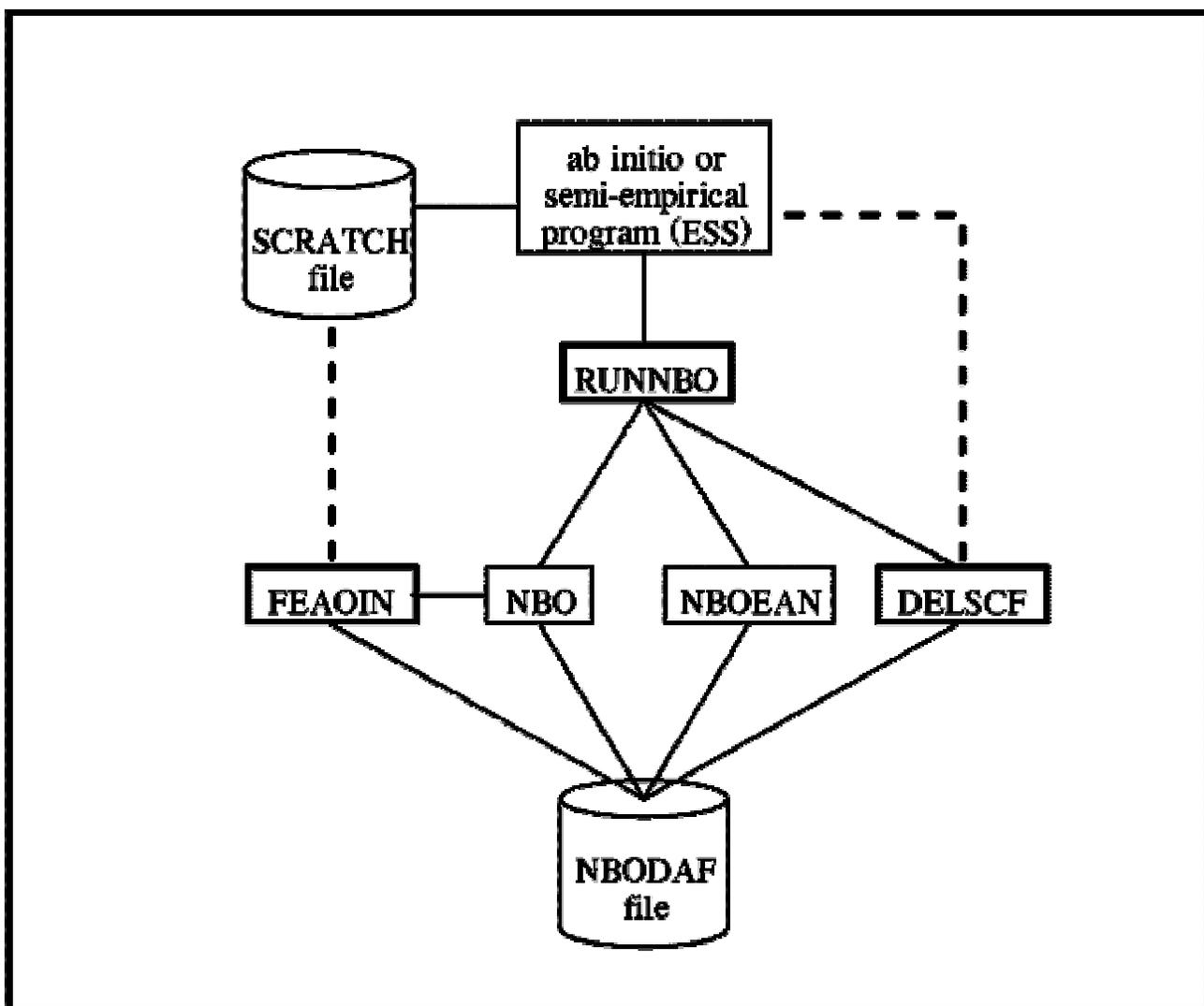
The NBO.SRC program consists of more than 50,000 lines, of which almost 15,000 are comment lines (about as long as this manual!). These comment statements provide the definitive documentation of the steps within each subroutine or function, and should be consulted on questions pertaining to individual subprograms.

This Programmer's Guide describes global aspects of program organization and data structure. Individual subprograms (about 300 in number) are described in capsule form to indicate the relationship to program tasks and the association with specific segments of NBO output. The capsule descriptions include mention [in brackets] of numerical thresholds or possible dependencies on machine precision that are of particular concern to the programmer. The abbreviations ``SR" for subroutine and ``FN" for function are used throughout this section.

The overall logical structure of the NBO program and its attachment to an electronic structure system (ESS) are illustrated in the block diagram, Fig. 1. This figure illustrates how the ESS and its scratch files (in the upper part of the diagram) communicate through the interface routines RUNNBO, FEAOIN, and

DELSCF with the main NBO modules and associated direct access file (in the lower part). The main NBO program is represented by modules labelled ``NBO" and ``NBOEAN." Each module consists of subroutines and functions that perform the required tasks of NBO formation and energetic analysis, respectively. These two modules communicate with the direct-access disk file NBODAF (LFN 48, labelled ``FILE48" elsewhere in this manual) that is created and maintained by the NBO routines.

The NBO program blocks communicate with the attached ESS through three system-dependent driver subroutines (RUNNBO, FEAOIN, DELSCF). The purpose of these drivers is to load needed information about the wavefunction and various matrices into the FILE48 direct access file and NBO common blocks. Although the ESS is usually thought of as driving the NBO program, from the point of view of the NBO program the ESS is merely a ``device" that provides initial input (e.g., a density matrix and label information) or other feedback (a calculated energy value) upon request. Each such ESS device therefore requires special drivers to make this feedback possible, as described in Secs. C.11 and C.13.



**Figure 1:** Schematic diagram depicting flow of information between the electronic structure system (ESS) and the NBO program, and the communication lines connecting these programs to the ESS scratch file (called the "dictionary file," "read-write file," etc., in various systems) and the NBO direct access file (NBODAF). Heavier box borders mark the ESS-specific driver routines (RUNNBO, FEAOIN, DELSCF) that directly interface the ESS program. The heavy dashed lines denote calls from the NBO program backward to the ESS program for information needed to carry out its tasks. Otherwise, the sequential flow of program control is generally from top to bottom and from left to right in the diagram.

## C.2 OVERVIEW OF NBO SOURCE PROGRAM GROUPS

The core of the NBO.SRC program is organized into seven principal groups of routines (I-VII), described in Sections C.5-C.11, respectively. Routines of the NBO-based supplemental modules are separately described in Sections C.14 *et seq.*

The principal groups are shown below:

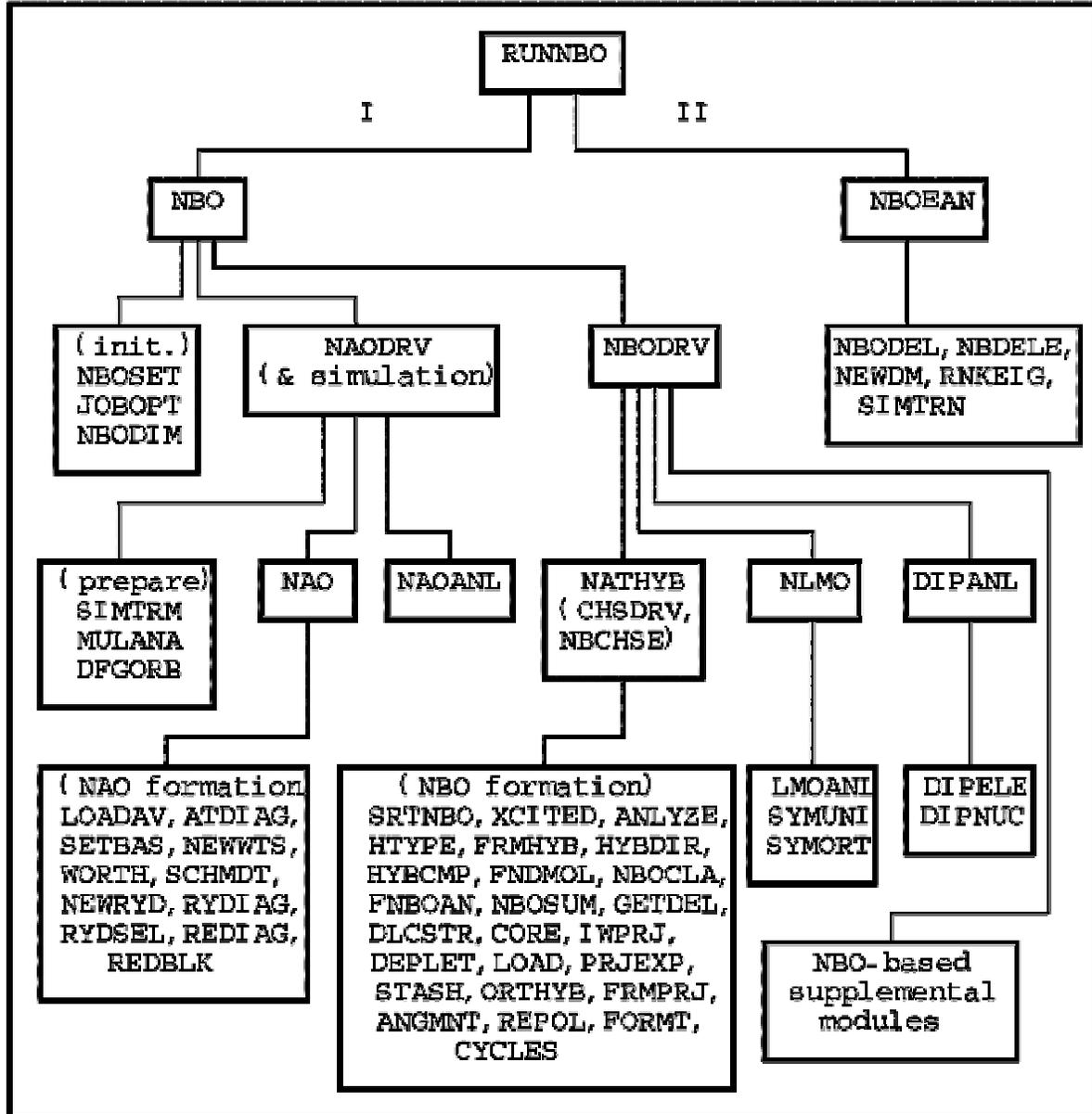
Groupdescription	no.	Section
I.NAO/NBO/NLMO routines	61	C.5
II.Energy analysis routines	6	C.6
III.Direct access file (DAF) routines	41	C.7
IV.Free format input routines	7	C.8
V.Other I/O routines	27	C.9
VI.General utility routines	31	C.10
VII.System-dependent routines	(3)	C.11

The routines of Groups I, II are associated with the two main tasks of the NBO program: (1) NAO/NBO/NLMO formation, and (2) NBO energetic analysis. Group II routines generally require Fock matrix information, and thus are restricted to HF and DFT methods, whereas Group I are applicable to general wavefunctions. Each of these groups is controlled by a master subroutine (NBO and NBOEAN, respectively) of highest precedence, which in turn calls routines of secondary precedence (such as NAODRV, NBODRV, etc.) to control the task. Routines are generally clustered together under the subroutine of next higher precedence, and within each cluster, the order of routines generally corresponds to the chronological sequence in which the routines are called in execution.

The remaining Groups III-VI 'serve' various routines of Groups I-II, and are ordered more loosely by function, or alphabetically. Groups I-VI are system-independent, whereas Group VII contains the special drivers (RUNNBO, FEAOIN, DELSCF) for individual ESS programs, whose generic function is described in Section C.11. Further information on the ESS-specific forms of the Group VII driver routines is given in the Appendix.

A general overview of the subprograms of Groups I and II is shown in the accompanying flow chart, indicating the logical relationship of the routines to be discussed in Sections C.5, C.6. The sequence of execution is generally from top to bottom and from left to right, with subprograms of equal precedence shown at an equal vertical level.

## NBO Flow Chart for Group I, II Subprograms



### C.3 LABELLED COMMON BLOCKS

The NBO programs contain labelled COMMON blocks to control information flow between subprograms (other than through explicit argument lists). Each COMMON block name begins with ``NB'' to minimize possible conflicts with a linked ESS program.

The COMMON blocks can be divided into six `primary' and remaining `secondary' blocks, with regard to claim on the programmer's attention. The

`primary' COMMON blocks 1-6 (/NBINFO/, /NBFLAG/, /NBOPT/, /NBAO/, /NBATOM/, and /NBIO/) contain variables that must be set by the ESS-specific driver routine FEAOIN, or by an equivalent interface provided by the programmer. The remaining `secondary' blocks 7-19 are for internal communication only, and are ordinarily of lesser concern.

The dimensions of COMMON block arrays are fixed by PARAMETER declarations of the form

```
PARAMETER (MAXATM = 200, MAXBAS = 2000)
```

where MAXATM and MAXBAS are, respectively, the maximum allowed numbers of atoms and basis functions. These program limits can be adjusted to any values up to MAXATM = 999 or MAXBAS = 9999. (Larger values may result in format overflows in orbital labels throughout the output.)

All entries of a given COMMON block are generally of the same numeric type (INTEGER, LOGICAL, etc.), as specified below. The names (dummy), and meaning of variables in each primary COMMON block 1-6 are described briefly, with an asterisk (\*) marking the items that must be passed from the external ESS program via driver routines:

### 1. COMMON/NBINFO/

The INTEGER variables of this block store general information related to basis set dimensionality, spin manifold, number of atoms, and energy units:

---

variable	meaning
ISPIN	+2 for $\alpha$ spin, -2 for $\beta$ spin
* NATOMS	number of atoms ( $\leq$ MAXATM)
* NDIM	declared dimensionality of matrices (overlap, density, etc.)
* NBAS	number of basis AOs ( $\leq$ NDIM $\leq$ MAXBAS)
MXBO	maximum number of AOs per 2-c or 3-c NBO
MXAO	maximum AOs per atom
MXAOLM	maximum AOs of the same symmetry per atom

---

\* MUNIT            0 for Hartree energy units, 1 for eV units, 2 for kcal/mol.

---

## 2. COMMON/NBFLAG/

The LOGICAL variables of this block are set .TRUE. or .FALSE. depending on whether the ``condition" (type of wavefunction, spin set, etc.) is satisfied:

---

variable (FLAG)    condition that FLAG=.TRUE.

---

* ROHF	Restricted open-shell Hartree-Fock wavefunction
* UHF	Unrestricted Hartree-Fock wavefunction
* CI	Configuration Interaction wavefunction
* OPEN	open-shell calculation
* COMPLX	complex-valued wavefunction (not currently implemented)
ALPHA	$\alpha$ spin set
BETA	$\beta$ spin set
* MCSCF	Multi-Configuration Self-Consistent-Field wavefunction
* AUHF	Spin-Annihilated UHF wavefunction
* ORTHO	basis set is orthonormal

---

Note (Section B.6.11) that for the open-shell case, both  $\alpha$  and  $\beta$  spin density matrices should be available if OPEN is set .TRUE., unless MSPNBO is enabled.

## 3. COMMON/NBOPT/

The INTEGER variables (flags) of this block are used for storing the keyword options selected by the user in the \$NBO keylist. In many cases, a variable of the form IWOPT (``IW" stands for ``I Want") is set to one or zero (or to some Hollerith content; see below) depending on whether the ``requested option" has

been specified or not. The table also lists the keyword (if any) that requests the option:

variable	keyword	requested option
* IWDM	BODM	1 to transform input bond-order matrix, 0 otherwise
IW3C	3CBOND	3-center bonds
IWAPOL		`apolar' bonds, $c_A = c_B$ (not used)
IWHYBS	\$NBO	set equal to JPRINT(5)
IWPNAO	(PAOPNAO)	PAO→PNAO transformation
IWTNAO	AONAO	AO→NAO transformation
IWTNAB	NAONBO	NAO→NBO transformation
IWTNBO	AONBO	AO→NBO transformation
IWFOCK		+1 if Fock matrix available on DAF, 0 otherwise
* IWCUBF	CUBICF	cubic $f$ functions
* IPSEUD		effective core potential
KOPT		(not used)
IPRINT	PRINT=n	print level
IWDETL	DETAIL	detailed output
IWMULP	MULAT	Mulliken population analysis
ICHOOS	\$CHOOSE	directed NBO (\$CHOOSE) search
IWNBBP	NBBP	natural bond-bond polarizability
IWMSP	MSPNBO	maximum spin-paired NBOs
IWFIXDM	FIXDM	correct input density matrix
JCORE	\$SCORE	user-specified core list
JPRINT(100)	various	printing option flags

The JPRINT(I) printing option flags are similar to (but somewhat more systematic than) the ``IWOPT" flags of COMMON/NBOPT/. Each entry *I* of this array is associated with an NBO keyword, as specified below:

### JPRINT Parameters and Associated Keywords

I	keyword	I	keyword	I	keyword	I	keyword
1	SKIPBO	23	AONLMO	45	NBOMO	67	KNBO
2	ESS version	24	NHONLMO	46	DIPOLE	68	KNLMO
3	E2PERT	25	AOPNBO	47	NBONLMO	69	KMO
4	NPA	26	AOMO	48	SPNLMO	70	VAO
5	NBO	27	DMAO	49	AOPNLMO	71	VNAO
6	NBOSUM	28	AONHO	50	DIAO	72	VNHO
7	ARCHIVE	29	FNHO	51	DINAO	73	VNBO
8	NLMO	30	AOPNHO	52	DINHO	74	VNLMO
9	NAOMO	31	FNAO	53	DINBO	75	VMO
10	NOBOND	32	NRT	54	DINLMO	76	STERIC
11	RPNAO	33	NAONHO	55	NRTOPT	77	NRTFDM
12	BNDIDX	34	DMNHO	56	NRTMEM	78	FPNHO
13	NLMOMO	35	DMNAO	57	NRTDTL	79	FPNBO
14	RESONANCE	36	BEND	58	SPAO	80	NRTCHG
15	FNLMO	37	FNBO	59	AOPAO	81	DIST
16	DMNBO	38	NHOMO	60	FMO	82	CMO
17	DMNLMO	39	SAO	61	DMMO	83	DMPNAO
18	NAONLMO	40	FAO	62	DIMO	84	SPARTAN
19	SPNAO	41	NHONBO	63	checkpointing	85	SVEC
20	SPNHO	42	BOAO	64	KAO	86	NCS
21	SPNBO	43	PLOT	65	KNAO		
22	AOINFO	44	AOPNAO	66	KNHO		

---

In general, if the flag is set to zero, its associated keyword option has not been specified. However, if an option is requested, its flag can be set to a variety of positive, negative, or Hollerith values, depending on the parameters specified with the keyword option. In particular, the option flags associated with the matrix output keywords, described in Section B.2.4, are set according to the following scheme:

---

value	effect
0	Do nothing
$0 < n$	Print $n$ columns of the matrix
$-1000 < n < 0$	Write matrix to external file $ n $
$n < -999$	Read matrix from external file $ n/1000 $
'FULL'	Print the full matrix to the output file
'VAL'	Print only core plus valence orbitals
'LEW'	Print only the occupied (Lewis) orbitals

---

#### 4. COMMON/NBAO/

The INTEGER arrays of this block store information on the atomic centers and angular symmetry of each AO:

---

variable	meaning
* LCTR(MAXBAS)	list of atomic centers of the basis AOs (LCTR(3)=2 if AO 3 is on atom 2)
* LANG(MAXBAS)	angular symmetry labels (Sec. B.7.5) of the basis AOs

---

## 5. COMMON/NBATOM/

The INTEGER arrays of this block store information about the orbitals on each atomic center:

---

variable	meaning
* IATNO(MAXATM)	atomic number for each atom
INO(MAXATM)	number of atomic hybrids on each atom
NORBS(MAXATM)	number of AOs on each atom
LL(MAXATM)	number of the first NAO on each atom
LU(MAXATM)	number of the last NAO on each atom
* IZNUC(MAXATM)	nuclear charge on each atom ( $\leq$ IATNO)
IATCR(MAXATM)	atomic core list for modified SCORE table

---

## 6. COMMON/NBIO/

The INTEGER variables of this block are the stored default logical file numbers for I/O operations. The table below identifies the value (default file assignment) and the contents of the file associated with each LFN (cf. Section B.2.4):

---

LFN	value	file contents
* LFNIN		standard ESS input file
* LFNPR		standard ESS output (print) file
LFNAO	31	AO info file
LFNPNA	32	AO $\rightarrow$ PNAO transformation
LFNNAO	33	AO $\rightarrow$ NAO transformation

---

LFNPNH	34	AO→PNHO transformation
LFNNHO	35	AO→NHO transformation
LFNPNB	36	AO→PNBO transformation
LFNNBO	37	AO→NBO transformation
LFNPNL	38	AO→PNLMO transformation
LFNNLM	39	AO→NLMO transformation
LFNMO	40	AO→MO transformation (LCAO-MO coeffs.)
LFNDM	41	density matrix in AO basis
LFNNAB	42	NAO→NBO transformation
LFNPPA	43	PAO→PNAO transformation
LFNARC	47	archive file
LFNDAF	48	direct access file (DAF)
LFNLBL	46	PLOT labels file
LFNDEF	49	'default' for other file output

---

The remaining 'secondary' COMMON blocks 7-18 contain variables that remain wholly within the system-independent code, and thus can be ignored with respect to interfacing to a new ESS. Blocks 7-13 involve communication with the Group I, II subprograms, whereas blocks 14-18 are wholly within the 'support' routines of Groups III-VII.

### 7. COMMON/NBBAS/

The INTEGER arrays of this block generally store information about the atomic, bond, and molecular units with which the NBOs or NAOs are associated. The meaning of all entries in COMMON/NBBAS/ *changes* between the NAO and NBO segments of the program, so this block functions virtually as 'scratch storage,' and its entries must be approached with extreme caution! The following table indicates the meaning of COMMON/NBBAS/ entries during NBO segments (only!):

---

variable	meaning
----------	---------

---

LABEL(MAXBAS,6)	NBO label information (lbl; *; bond no.; at1; at2; at3)
NBOUNI(MAXBAS)	molecular unit of each NBO
NBOTYP(MAXBAS)	no. centers + 10 (if low-occ LP) + 20 (if BD* or RY*)
LSTOCC(MAXBAS)	1 (NMB) or 0 (NRB) NAO labels
IBXM(MAXBAS)	NBO label permutation list
LARC(MAXBAS)	re-ordering list
LBL(MAXBAS)	atomic center of AO
LORBC(MAXBAS)	angular momentum label of AO
LORB(MAXBAS)	(variable)

---

## 8. COMMON/NBTHR/

The DOUBLE PRECISION variables of this block store the default values of various numerical thresholds that can be set by the user:

---

variable	meaning
THRSET	NBO occupancy threshold
PRJSET	projection threshold
ACCTHR	threshold [0.1] for assigning acceptor orbital NBOTYP
CRTSET	threshold for core-occupancy warning
E2THR	minimum E for 2nd-order energy analysis printing
ATHR	minimum bend angle for BEND printing
PTHR	minimum % <i>p</i> -character for BEND printing
ETHR	minimum NBO occupancy for BEND printing
DTHR	minimum dipole moment for DIPOLE printing
DLTHR	NRT delocalization list threshold (NRTTHR)

CHSTHR occupancy threshold for CHOOSE  
 REFTHR NRT multi-reference weighting (NRTWGT) threshold  
 STTHR steric analysis threshold  
 PRTHR NRTLST threshold for \$NRTSTR printouts  
 THRNCS print threshold (ppm) for NCS analysis

---

## 9. COMMON/NBLBL/

The INTEGER variables of this block store the number of orbitals associated with the ``LEW" and ``VAL" print parameters (Section B.2.4) and the 10 Hollerith fragments required to compose each of the 4 possible types of localized orbital labels (AO, NAO, NHO, NBO):

---

variable	meaning
NLEW	number of Lewis NBOs (= number of occupied MOs)
NVAL	number of minimal basis (NMB) NAOs
LBL(10,MAXBAS,4)	label fragments (AO; NAO; NHO; NBO)

---

## 10. COMMON/NBNAO/

The INTEGER arrays of this block store information pertaining to the labelling of NAOs in the NPA output:

---

variable	meaning
NAOC(MAXBAS)	atomic center of each NAO
NAOA(MAXBAS)	angular symmetry label (Sec. B.7.5) of each NAO
LTYP(MAXBAS)	`Cor', `Val', or `Ryd' label for each NAO

IPRIN(MAXBAS)            principal quantum number ( $n$ ) of each NAO

---

### 11. COMMON/NBMOL/

The INTEGER scalars, vectors, and arrays of this block store information pertaining to ``molecular units":

---

variable	meaning
NMOLEC	number of molecular units
MOLAT(MAXATM)	number of atoms in each unit
MOLEC(MAXATM,MAXATM)	list of atoms (J) in each molecular unit (I)
NMOLA	scratch storage for open-shell case
MOLATA(MAXATM)	scratch storage for open-shell case
MOLECA(MAXATM,MAXATM)	scratch storage for open-shell case

---

### 12. COMMON/NBTOPO/

The INTEGER variables of this block contain atom search lists to direct the search for NBOs and information pertaining to the `topology' (bond connectivity) of the molecule:

---

variable	meaning
IORDER(MAXATM)	permuted atom order for NBO search
JORDER(MAXATM)	atom ordering for `best' resonance structure
NTOPO(MAXATM,MAXATM)	number of bonds between atoms I,J (or number of lone pairs on I, if I = J)

N3CTR	number of 3-center bonds ( $\leq 10$ )
IC3TR(10,3)	the 3 atoms of each 3-c bond

---

### 13. COMMON/NBDXYZ/

The DOUBLE PRECISION variables of this block store information pertaining to the molecular dipole moment and charge distribution:

---

variable	meaning
XDIP	<i>x</i> -component of molecular dipole moment ( $\alpha$ spin)
YDIP	<i>y</i> -component of molecular dipole moment ( $\alpha$ spin)
ZDIP	<i>z</i> -component of molecular dipole moment ( $\alpha$ spin)
CHARGE(MAXATM)	list of 'uncompensated' nuclear charges (dipole loops)
XDNLMO(MAXATM), <i>etc.</i>	NLMO, NBO, and difference vectors

---

### 14. COMMON/NBCRD1/

The INTEGER variables of this block store general information related to the 'card image' (line) being processed by the free-format input routines:

---

variable	meaning
ICD(256)	array of Hollerith characters ( $\leq 256$ ) of the input line
LOOK(256)	scratch buffer for card image
LENGTH	length of the non-blank string in LOOK
IPT	pointer to current location in ICD
LFN	input file assignment

NEXP                    exponent of a number in exponential format

---

### 15. COMMON/NBCRD2/

The LOGICAL variables of this block store information related to the current line being read by the free-format input routines. In each case, the variable is set .TRUE. if the specified condition is met:

---

variable	condition that variable is .TRUE.
----------	-----------------------------------

---

POINT	a number containing a decimal point is present
-------	--

END	word 'END' or EOF has been encountered
-----	--

NEXT	ready for reading next word in line (ICD)
------	---

EXP	a number in exponential notation is present
-----	---

---

### 16. COMMON/NBODAF/

The INTEGER variables of this block store information related to the NBO direct access file (FILE48). The PARAMETER statement

```
PARAMETER (NBDAR = 300)
```

sets the maximum number of logical records accessible in FILE48:

---

variable	meaning
----------	---------

---

INBO	logical file number [48] for DAF
------	----------------------------------

NAV	last-accessed physical record of DAF
-----	--------------------------------------

IONBO(NBDAR)	mapping of physical and logical record numbers
--------------	--

---

## 17. COMMON/NBONAV/

The INTEGER variables of this block provide scratch storage for writing to the NBO direct access file (FILE48). The PARAMETER statement

```
PARAMETER (LENGTH = 256)
```

sets the FILE48 physical record LENGTH to 256 longwords:

---

variable	meaning
IXDNBO(LENGTH)	scratch array for DAF writes
NBNAV	number of physical records in IXDNBO
ISINGL	32-bit (ISINGL=2) or 64-bit (ISINGL=1) machine

---

## 18. COMMON/NBGEN/

The LOGICAL variables of this block store information related to running the GENNBO program in stand-alone mode. In each case, the variable is set .TRUE. if the specified condition is met:

---

variable	condition that variable is .TRUE.
REUSE	request use of an existing DAF
UPPER	specifies upper-triangular matrices
BOHR	specifies atomic units of length
DENOP	density matrix is provided (i.e., ``BODM" not set)
FORM	formatted matrix input for GENNBO

---

## 19. COMMON/NBELEM/

The INTEGER variables of this block store index information for user-requested matrix elements of various output options.

---

variable	meaning
IJELEM(2,100)	index pairs for requested matrix elements
NELEM	number of elements

---

#### C.4 DIRECT ACCESS FILE AND OTHER I/O

The principal I/O routines of Groups III-V are described in Sections C.7-C.9. The *input* to the NBO programs is primarily from the standard ESS input file (LFN 5), and the *output* is primarily to the standard ESS output file (LFN 6). Other "matrix output" (read/write) I/O is by default assigned to LFNs 31-49 (see Table of Section B.2.4), or to a user-selectable LFN, based on keyword entries in the \$NBO keylist.

The remaining two files that are routinely created or modified by the NBO programs are the FILE48 direct access file (LFN 48) and the FILE47 'archive' file (LFN 47, described in Section B.7). The latter file can also serve as the main input file (reassigned as LFN 5) when the NBO program is run in stand-alone GENNBO mode.

From the programmer's viewpoint, the most important information concerns the organization of the FILE48 direct access file. The records of this file are assigned as shown in the following table. The items marked with an asterisk (\*) must be provided from the ESS program (e.g., through the FEAOIN driver), and hence are of particular importance to the programmer:

---

record	content
1	NBODAF common block
2	* Job title

---

3 \* NATOMS,NDIM,NBAS,MUNIT,wavefunction flags  
4 \* IATNO,IZNUC,LCTR,LANG  
5 \* AO basis set info  
8 \* Deletion energy, total energy  
9 \* Atomic coordinates  
10 \* AO overlap matrix  
11 PNAO overlap matrix  
18 \* Kinetic energy integrals  
19 \* Nuclear attraction integrals  
20 \* AO density matrix (alpha)  
21 \* AO density matrix (beta)  
22 Pure AO density matrix  
23 NAO density matrix (alpha)  
24 NAO density matrix (beta)  
25 AO density matrix with NBO deletions (alpha)  
26 AO density matrix with NBO deletions (beta)  
27 NBO occupancies (alpha)  
28 NBO occupancies (beta)  
30 \* AO Fock matrix (alpha)  
31 \* AO Fock matrix (beta)  
32 NAO Fock matrix (alpha)  
33 NAO Fock matrix (beta)  
34 NBO Fock matrix (alpha)  
35 NBO Fock matrix (beta)  
39 AO to PAO transformation matrix  
40 \* AO to MO transformation matrix (alpha)  
41 \* AO to MO transformation matrix (beta)  
42 AO to PNAO transformation matrix

43	AO to NAO transformation matrix
44	AO to NBO transformation matrix (alpha)
45	AO to NBO transformation matrix (beta)
46	AO to NLMO transformation matrix
47	NAO to NHO transformation matrix
48	NAO to NBO transformation matrix
49	NBO to NLMO transformation matrix
50	* X dipole integrals
51	* Y dipole integrals
52	* Z dipole integrals
60	NBO labels (alpha)
61	NBO labels (beta)
62	NHO to NBO transformation matrix (alpha)
63	NHO to NBO transformation matrix (beta)
70	NEDA fragment energies
71	NEDA NBO→MO transformation (alpha)
72	NEDA NBO→MO transformation (beta)
73	NEDA AO Fock matrix (alpha)
74	NEDA AO Fock matrix (beta)
75	NEDA nuclear charge info
76	NEDA IZCORE data
77	NEDA LPSKIP data
78	NEDA LMAX data
80	checkpointing transformation (alpha)
81	checkpointing transformation (beta)
82	NEDA truncated Fock eigenvalues (alpha)
83	NEDA truncated Fock eigenvalues (beta)
84	NEDA AO→MO transformation (alpha)

85	NEDA AO→MO transformation (beta)
86	Density matrixes for psi(def) (alpha)
87	Density matrixes for psi(def) (beta)
88	Density matrixes for psi(cp) (alpha)
89	Density matrixes for psi(cp) (beta)
90	Nuclear attraction integrals (NEDA)
101- 300	NBO transformations and labels for NRT

---

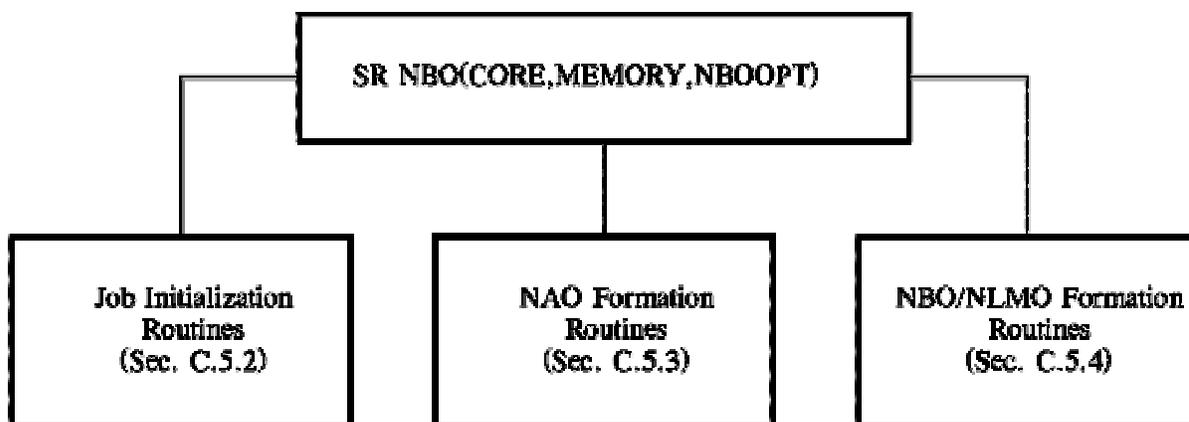
[Cartesian coordinates (record 9) and dipole integrals (records 50-52) should be in angstrom units.]

The direct access file serves as a principal medium of communication between all segments of the NBO program. Input received from the ESS program (Section C.11) is immediately saved in the direct access file and subsequently fetched by other subprograms, using the fetch/save I/O routines of Section C.7. Further information on the structure of the direct access file is specified in COMMON blocks 16, 17 of Section C.3.

## **C.5 NAO/NBO/NLMO ROUTINES (GROUP I)**

### *C.5.1 SR NBO Master Subroutine*

The subroutine of highest precedence in the core NBO program is SR NBO. This routine initially requests that the input file be searched for the \$NBO keylist (See NBOINP, Section C.9). If found, SR NBO continues by calling three main clusters of programs, as shown below:



In addition, SR NBO creates a new NBO direct access file (DAF) each time it is called, and closes this file upon completion (See NBOPEN and NBCLOS, Section C.9).

SR NBO is provided a memory vector, CORE, which is 'MEMORY' double precision words in length. For modest-sized calculations (e.g. 10 heavy atoms with a double-zeta basis set), a vector of 50,000 words should be adequate. Although SR NBO performs an initial partitioning of this memory vector, the majority of the dynamic memory allocation occurs in the NAO and NBO/NLMO formation routines, described in Sections C.5.3 and C.5.4.

An array of job options, NBOOPT(10), is also passed to SR NBO. These job options identify the current version of the NBO program (i.e., the identity of the ESS calling program), control program input and execution, and determine several of the default options of the NBO analysis, as summarized in the following table. [Entries marked with an asterisk (\*) contain information pertaining to the identity or job options of the calling ESS program, and thus are of special concern to the programmer.]

<i>OPTION</i>	<i>ENTRY</i>	<i>DESCRIPTION</i>
*NBOOPT(1)	-2	Do nothing (return control to calling program)
	-1	Perform Natural Population Analysis (NPA) only
	0	Perform NPA/NBO/NLMO analyses, normal program run
	1	Perform NPA/NBO/NLMO analyses, don't read \$NBO keylist
	2	Initiate energetic analysis, read one deletion from \$DEL
	3	

*NBOOPT(2)	0	SCF density
	1	MP first order density
	3	MP2 density
	4	MP3 density
	5	MP4 density
	6	CI one-particle density
	7	CI density
	8	QCI/CC density
	9	Density correct to second order
*NBOOPT(3)	1	Perform the NBO/NLMO dipole analysis (force the DIPOLE keyword)
*NBOOPT(4)	1	Allow strongly delocalized Lewis structures (force the RESONANCE keyword)
*NBOOPT(5)	1	Spin-annihilated UHF (AUHF) wavefunction (unused)
*NBOOPT(6)		(unused)
*NBOOPT(7)	0	Delete the NBO direct access file
	1	Save the NBO direct access file
*NBOOPT(8)	$N$	File unit number containing density matrix (Gaussian version)
*NBOOPT(9)	$I$	$I^{\text{th}}$ excited state CI density (Gaussian version)
*NBOOPT(10)	0	General version of the NBO program (GENNBO)
	1	AMPAC version
	6	GAMESS version
	7	HONDO version
	8x	GAUSSIAN-8x version
	9x	GAUSSIAN-9x version

These options are read by job initialization routines (Section C.5.2) and stored in COMMON/NBOPT/, where they control events throughout the program. [Note that NBOOPT(2) is only used by the Gaussian versions.]

### *C.5.2 Job Initialization Routines*

The routines of this section initialize the default options and parameters, read and store the user's \$NBO keyword options:

#### SR NBOSET(NBOOPT)

This routine sets default option flags (COMMON/NBOPT/), default logical file numbers (COMMON/NBIO/), and default thresholds (COMMON/NBTHR/) for the NBO program. In addition, SR NBOSET interprets the NBOOPT array, setting option flags appropriately.

#### SR JOBOPT(NBOOPT)

This routine is primarily responsible for reading and setting option flags (COMMON/NBOPT/) according to the keywords specified in the \$NBO keylist. It reads the \$NBO keywords using the free format routines described in Section C.8, continuing until the word ``\$END" terminates the keylist. Options that are incompatible with the chosen wavefunction or program version are turned off, and other options are turned on in accord with the requested print level (\$NBO keyword PRINT). All keywords selected in the \$NBO keylist are echoed in the output file. SR JOBOPT now calls three subsidiary subroutines (JOBOPT1, JOBOPT2, JOBOPT3) to avert compiler overflow. LFN=99 is used intermittently as scratch file, but freed for other usage after JOBOPT is complete.

#### SR NBODIM(MEMORY)

Determines the scratch memory requirements of the NBO program, as determined by the options selected in the \$NBO keylist. Program execution halts if the memory requirements exceed the available memory.

#### SR FIXDM(DM, S, V, EV, SCR, V1, V2, NDIM, NBAS)

In response to FIXDM keyword, corrects faulty input density matrix to remove unphysical (negative or Pauli-violating) occupancies. Offending eigenvalues are shifted to zero or two (one for open-shell) and remaining eigenvalues are scaled to give nearest integer trace. Eigenvectors are unaltered. Corrected density matrix is stored in DAF with SR SVDRAW.

SR AXWBX (NDIM, N, A, B, W, IWMATX, X, V1, V2, IERR)

Utility routines (called by FIXDM) to solve eigenvalue problem for input density matrix.

### *C.5.3 NAO Formation Routines*

The principal task of this cluster of routines is to control the formation of the NAOs from the input AO basis. In addition, these routines are responsible for the writing (to an external file) or printing (to the output file) of a variety of matrices in the AO, PNAO, and NAO basis sets, according to job options requested in the \$NBO keylist. The first set of routines are called by SR NBO:

SR NAODRV (DM, T, A)

This is the principal controller routine for non-orthogonal basis sets. The scratch vector A is partitioned within this routine according to the memory requirements of the NAO subprograms.

SR NAOSIM (DM, T, A)

This routine 'simulates' SR NAODRV in the case of a semi-empirical calculation, where the (orthonormal) basis AOs are the presumed effective valence shell atomic orbitals, and no NAO transformation is needed.

SR DMNAO (DM, T, A)

Performs the transformation and analysis of the open-shell AO density matrix (alpha or beta spin) to the NAO basis. This routine employs the AO to NAO transformation, T, determined by SR NAODRV:

SR DMSIM (DM, T, A)

Simulates SR DMNAO for the open-shell semi-empirical case, when no transformation is required.

SR NBODRV (DM, T, A)

Principal driver program for NBO formation; Section C.5.4.

The next set of routines are called by the main NAO driver, SR NAODRV. They include the principal subroutine, SR NAO, which generates the NAOs:

SR SIMTRM (A, S, V, NDIM, N, IWMULP, IWCUBF)

Performs the similarity transformation  $S^t * A * S$  leading to Mulliken populations, with S = overlap matrix, A = bond-order matrix.

SR MULANA (BS, VMAYER, BMAYER, IWMULP, IWCUBF)

Evaluates Mulliken gross populations and performs Mayer-Mulliken bond-order analysis (requires bond order matrix).

SR\_DFGORB (DM, T, RENORM, TPAO)

Performs the decomposition of 'raw' cartesian  $d, f$ , or  $g$  AO sets to pure angular symmetry AOs (e.g., 6 cartesian  $d \rightarrow 5$  pure  $d + 1 s$ ); cf. Section B.7.5.

SR\_NAO (T, S, OCC, BLK, SBLK, EVAL, C, EJECT, EVAL2, LISTAO, NBLOCK)

This is the principal routine for formation of NAOs, following closely the algorithm described by A. E. Reed, R. B. Weinstock, and F. Weinhold, *J. Chem. Phys.* **83**, 735-746 (1985).

SR\_NAOANL (DM, SPNAO, BINDEX, BINDT, BMO, OVPOP, F, ENAO, SCR)

This is the principal routine for performing and printing out natural population analysis (NPA). The routine assigns orbital labels and energies and writes out the NPA, natural electron configuration (NEC), NAO-Wiberg bond index and overlap-weighted bond population tables. [Thresholds TEST, TEST2, ALLOW, ALLOW2 test for numerical conservation of an integer number of electrons.]

SR\_FRMTMO (T, TMO, C, SCR, INDEX, NCOL, IFLG)

Forms and outputs NCOL columns of the transformation matrix to MOs from a chosen localized set, specified by INDEX = 2 (NAO), 3 (NHO), 4 (NBO), or 5 (NLMO). Input matrix T is the transformation from AOs to the basis set specified by INDEX, and matrices TMO, C, and SCR are scratch arrays employed by this routine.

The remaining routines of this section are auxiliary subroutines called by SR\_NAO to perform individual steps of the NAO algorithm:

SR\_LOADAV (LISTAO, NL, M, S, NDIM, A, B, MXAOLM)

Averages the AO density matrix elements over the  $2^\circ + 1$  components of  $^\circ$  for a particular atom, and loads the density matrix and overlap integrals for the orbitals of LISTAO into matrices A, B, respectively.

SR\_ATDIAG (N, A, B, EVAL, C)

Solves the generalized eigenvalue problem  $(A - EVAL*B)*C = 0$  to diagonalize an atomic block.

SR\_SETBAS (LSTOCC, LSTEMT, NOCC, NEMT, IAT, L, NL, NF, NDIM)

Selects the 'occupied' NAOs to be included in the natural minimal basis set for a particular atom (up to  $Z = 105$ ) and angular momentum symmetry type (L), and stores them in LSTOCC.

SR\_NEWWTS (S, T, WT)

Recomputes symmetry-averaged occupancy weights for PNAOs. This routine is only used in conjunction with the 'PAOPNAO=R' keyword.

SR WORTH (S, T, BLK, LIST, NDIM, NBAS, N, OCC, EVAL, BIGBLK)

This subroutine implements the occupancy-weighted symmetric orthogonalization (OWSO), a key feature of the NAO algorithm. [Note that BLK and BIGBLK share the same storage area, though they are dimensioned differently. The routine includes three numerical thresholds, WTTHR ( $10^{-3}$ ) for occupancy weight, DIAGTH ( $10^{-12}$ ) for Jacobi diagonalization, and DANGER ( $10^3$ ) for linear dependence difficulties.]

SR SHMDT (T, S, NDIM, NBAS, NOCC, LSTOCC, NEMT, LSTEMT, SBLK)

Schmidt orthogonalization of column vectors of T.

SR NEWRYD (T, S, TPNAO, DMBLK, SBLK, ETECT, OCC, EVAL, EVAL2, LIST, IRPNAO)

Computes new Rydberg NAOs after Schmidt orthogonalization of the Rydberg space to the NMB set.

SR RYDIAG (T, S, TPNAO, DMBLK, SBLK, OCC, EVAL, ETECT, EVAL2,

IORB, NC, NM, NSTART, NRYDC, LARC, LIST, IRPNAO)

Diagonalizes an atomic Rydberg block and updates the PNAO transformation matrix.

SR RYDSEL (LSTEMT, NEMT, NSEL1, LIST1, NSEL2, LIST2, WT)

Partitions Rydbergs into 'significantly occupied' ( $> WTTHR$ ) and 'negligibly occupied' ( $\leq WTTHR$ ) sets, assigning the latter to have equal (non-zero) occupancy weighting. This avoids numerical singularities associated with the OWSO occupancy weighting for orbitals of negligible occupancy, effectively replacing OWSO by ordinary Löwdin-orthogonalization of these 'residual' Rydbergs among themselves. [Threshold WTTHR ( $10^{-4}$ ) controls singularities of the inverse square-root weighting matrix.]

SR REDIAG (DM, T, TPNAO, EVAL, BLK, C, IRANK, IRPNAO)

Rediagonalizes the atomic density matrix blocks after symmetry averaging.

SR REDBLK (T, TPNAO, IL, DM, BLK, EVAL, C, NF, IOORB, NC, IRANK, IRPNAO)

Finds the rediagonalization transformation for a specific  $\sigma$ -symmetry atomic subblock of the density matrix.

#### *C.5.4 NBO/NLMO Formation Routines*

The master routine of this cluster is SR NBODRV(DM,T,A), which partitions the scratch storage vector (A) according to the memory requirements of the NBO formation and analysis subprograms and controls the calculation of the transformation (T) from NAOs to NBOs using the NAO density matrix (DM).

SR NBODRV calls either SR NATHYB (for the default NBO search) or SR CHSDRV (for the \$CHOOSE directed NBO search) to form the NBOs. It also calls the NLMO formation routine (SR NLMO) and dipole analysis routine (SR DIPANL). According to job options selected in the \$NBO keylist, SR NBODRV also transforms and outputs a variety of matrices in the PNHO, NHO, PNBO, NBO, PNLMO, and NLMO basis sets. [Note that the first NATOMS\*NATOMS elements of the A vector store the Wiberg bond index elements determined in the NAO routines; these should not be destroyed until calculation of NBOs is complete.]

The following routines are called by SR NBODRV:

SR

NATHYB (DM, T, GUIDE, BND OCC, POL, Q, V, BLK, C, EVAL, BORB, P, TA, HYB, VA, VB, TOPO)

This routine performs the basic NBO search, the central task of NBO analysis, closely following the description given by J. P. Foster and F. Weinhold, *J. Am. Chem. Soc.* **102**, 7211-7218 (1980). The routine constructs the orthogonal matrix (T) for the NAO to NBO transformation from the input NAO density matrix (DM). The efficiency of the search procedure is enhanced by using the NAO-Wiberg bond index as a 'GUIDE' to order the NBO search.

[Beware the IBXM bond orbital permutation list (!), which reorders the LABEL array of COMMON/NBBAS/. The occupancy threshold, THRESH, determines whether an NBO is accepted during the search for bond orbitals (cf. SR CYCLES). Two numerical thresholds (PRJTHR, PRJINC) control possible linear dependencies: In the main loops over 1-c, 2-c (and 3-c) functions, each prospective NBO is checked for possible redundancy with previous NHOs by the PRJEXP (projection operator expectation value) test. The threshold PRJTHR for a 'new' hybrid is initially set conservatively low (0.20), but will be auto-incremented by PRJINC (0.05) as needed to prevent linear dependency; any numerical singularity triggers IALARM and causes PRJTHR to be incremented and the entire NBO search repeated.]

SR

CHSDRV (DM, T, GUIDE, BND OCC, POL, Q, V, BLK, C, EVAL, BORB, P, TA, HYB, VA, VB, TOPO)

This routine, the "\$CHOOSE driver," reads the \$CHOOSE keylist, setting up the arrays NTOPO and I3CTR of COMMON/NBTOPO/ which will control the directed NBO search of SR NBCHSE.

SR

NBCHSE (DM, T, GUIDE, BND OCC, POL, Q, V, BLK, C, EVAL, BORB, P, TA, HYB, VA, VB, TOPO, IFLG, BRANCH)

This routine is essentially similar to SR NATHYB, but the search loops are directed by the \$CHOOSE specification.

SR SRTNBO (T, BNDOCC)

Reorders (dangerous!) the NBOs according to bond type and constituent atomic centers. NBOs are ordered BD (and 3C), CR, LP, LP\*, RY\*, BD\* (and 3C\*). Note that this step is not required for the proper execution of any of the NBO analysis or NLMO formation routines, but it leads to more readable output.

SR XCITED (DM, T, HYB, THYB, S, OCC, SCR, ISCR)

Examines PNHO overlaps to determine whether NBOs were properly labelled as 'bonds' (unstarred, Lewis) or 'antibonds' (starred, non-Lewis) in the NBO formation routines (SR NATHYB and SR NBCHSE). If incorrect nodal character is recognized in a bond or antibond (generally indicative of an excited state), a warning is printed and the orbital is relabelled. Note that this will probably mix the NBO ordering set by SR SRTNBO.

SR ANALYZE (T, BNDOCC, HYB, HYCOEF, THYB)

Prints out the principal table (Section A.3.3) of NBO analysis [using the IBXM ordering!], expressing each NHO in  $sp^i$  form.

SR HTYPE (HYB, LTYP, MXAO, NH, COEF, PCT, NL, ISGN)

Analyzes input hybrid for polarization coefficient and percentages of each angular momentum component (accepts up to g orbitals).

SR FRMHYB (HYB, THYB, COEFF, HYCLEFT, KL, KU, NHYB)

Forms the NAO to NHO transformation (THYB) and saves it on the DAF.

SR HYBDIR (BNDOCC, ATCOOR, THYB, TBND, SCR)

Computes hybrid directionality and bond bending angles as determined from percentage  $p$ -character for selected NBOs, and prints the BEND table (Section A.3.4). [Keyword-selectable thresholds ATHR (angular deviation), PTHR (%  $p$ -character), and ETHR (occupancy) control printing.]

SR HYBCMP (XYZ, PCENT, IHYB, JCTR, HYB)

Finds direction and percentage  $p$ -character of a given hybrid.

SR FNDMOL (IATOMS)

Finds 'molecular units' from NBO connectivity.

SR NBOCLA (BNDOCC, ACCTHR)

Classifies NBOs according to donor/acceptor type, number of atomic centers, and parent molecular unit.

SR FNBOAN (BNDOCC, F, MOLNBO)

Performs the 2nd-order perturbation theory energy analysis of the NBO Fock matrix and prints the table (Section A.3.5). [Thresholds ETHR1 (intramolecular) and ETHR2 (intermolecular) control printing.]

SR NBOSUM (F, BND OCC, LIST, LISTA, SCR)

Prepares and prints the NBO summary table (Section A.3.6).

SR GETDEL (IBO, OCC, THR1, THR2, NL, LIST, DEL, DELOC, IFLG)

Assembles the delocalization list, LIST(NL), for the IBO<sup>th</sup> NBO. Only intramolecular and intermolecular delocalizations which are stronger than THR1 and THR2 (in kcal mol<sup>-1</sup>), respectively, are included in the list.

SR DLCSTR (IBO, IL, NL, LIST, ML, ISTR)

Builds a character string containing delocalization information for the NBO summary table.

SR NLMO (N, A, EVAL, EVEC, TSYM, RESON, NOCC, IALARM)

This is the main routine for determination of the NLMOs, following closely the description given by A. E. Reed and F. Weinhold, *J. Chem. Phys.* **83**, 1736-1740 (1985). [Numerical thresholds DIFFER (10<sup>-5</sup>), DONE (10<sup>-10</sup>), and EPS (10<sup>-11</sup>) control the modified Jacobi diagonalizations.]

SR LMOANL (T, S, RESON, OCC, TS, BORDER, OWBORD, ATLMO, SIAB, NOCC, NAB)

Prints out details of the NAO→NLMO transformation and the NAO/NLMO bond order table (Section B.6.2).

SR DIPANL (DM, T, C, TNBO, DX, DY, DZ, SCR, LISTA, INDEX)

Calculates and prints out the DIPOLE analysis table (Section B.6.3).

SR DIPELE (DXYZ, C, T, SCR, ETA, NOCC, INDEX)

Evaluates the x,y,z (INDEX = 1,2,3) electronic dipole moment contributions, including delocalization contributions, for each occupied NBO.

SR DIPNUC (DX, DY, DZ, ATCOOR, ETA, NOCC)

Evaluates the nuclear contributions (DX, DY, DZ) to the molecular dipole moment.

The following routines are called by SR NATHYB and SR NBCHSE in calculating the NBOs. Overall supervision of this set of routines is exercised by SR CYCLES. Other routines are associated with specific steps of the NBO algorithm:

SR CORE (DM, T, BORB, POL, Q, HYB, BND OCC, IBD, DETAIL, LFNPR)

Performs the first step in the search for NBOs. This routine identifies core orbitals and depletes the NAO density matrix of their contributions.

FN IWPRJ (NCTR)

This function returns zero (no projection wanted) if still on the same atomic center, or one (projection operator should be formed) if this is a new center.

SR DEPLET (DM, T, Q, POL, BORB, BND OCC, NBD)

'Depletes' density matrix of contribution from bond orbital (BORB), by subtracting its diagonal contribution from the spectral expansion of the density operator. This insures that the same electron pair will not be found twice in the NBO loops.

SR LOAD (DM, IAT1, IAT2, IAT3, BLK, NB)

Loads the appropriate atomic blocks of the density matrix into the local (2-c, 3-c) density matrix subblock (BLK), in preparation for diagonalization.

SR PRJEXP (BORB, IAT1, IAT2, IAT3, Q, P, PK, HYB, VA, VB, HYBEXP)

Determines how much of a prospective bond orbital (BORB) is composed of hybrids already used. The projection operator onto the space of previously accepted hybrids is used to evaluate the expectation value of each hybrid component of BORB.

SR STASH (BORB, IBD, IAT1, IAT2, IAT3, POL, Q, HYB)

Decomposes bond orbital (BORB) into constituent normalized hybrids and stores them in the hybrid array (Q).

SR ORTHYB (Q, S, TA, EVAL, C, IALARM, IFLG)

Performs symmetric (Löwdin) orthogonalization on occupied atomic hybrids (PNHOs) to give final NHOs. [Threshold TOOSML ( $10^{-4}$ ) turns on the alarm (IALARM) to warn of numerical instabilities due to linear dependence.]

SR FRMPRJ (P, IA, Q, NK, PK, VK, PI)

Forms projection matrix to annihilate components of the occupied atomic hybrids on a given center.

SR AUGMNT (P, BLK, C, EVAL, DM, TA, BORB, V, LARC, IA, NOCC, NORB)

This routine augments the set of occupied atomic hybrids on a center with a sufficient number of Rydberg AOs (in order of occupancy) to complete the span of the basis set on that atom.

SR REPOL (DM, Q, POL, BLK, EVAL, C, NBD)

Diagonalizes each 2x2 block of the density matrix in the basis of final NHOs to get the optimal polarization coefficients for each NBO.

SR FORMT (T, Q, POL)

Constructs the final NAO to NBO transformation matrix (T) from the final array of NHOs (Q) and polarization coefficients (POL).

SR CYCLES (ITER, THRESH, GUIDE, BND OCC, TOPO, ICONT)

Controls the overall search for an acceptable resonance structure, including the lowering of the occupancy threshold (THRESH) for the RESONANCE

keyword. Decides whether a structure is acceptable, initiates reordered searches over atoms for alternative resonance structures, and returns with the best overall structure. Prints the initial table (Section A.3.3) of the NBO output.

The final routines of this group are auxiliary to the formation of NLMOs, called by SR NLMO:

SR  
SYMUNI (TSYM, A, COS, SIN, OVLP, BLK, EVAL, NROT, NIUNIQ, NJUNIQ, ILIST, JLIST, NOFF, IOFF, JOFF, NDIM)

Symmetrizes the unitary transformation matrix (TSYM) to preserve symmetries inherent in the density matrix, using symmetric orthogonalization of columns (if necessary) to preserve unitarity.

SR SYMORT (S, T, BLK, NDIM, N, EVAL, IERR, IPFLG)

Symmetric orthogonalization of a set of column vectors (T). [Thresholds DIAGTH ( $10^{-12}$ ) for off-diagonal Jacobi diagonalization and DANGER ( $10^3$ ) to detect singularities of the overlap matrix; all eigenvalues of S must be less than DIAGTH\*DANGER.]

## C.6 ENERGY ANALYSIS ROUTINES (GROUP II)

The small set of routines in this group carry out the second main task of NBO analysis, the NBO Energetic Analysis ("deletions," associated with inclusion of a \$DEL keylist; Section B.5). These routines depend on the presence of a Fock matrix, and are bypassed in any non-SCF calculation.

Overall control of Group II routines is with SR NBOEAN, which in turn calls the remaining programs of this group:

SR NBOEAN (A, MEMORY, NBOOPT, IDONE)

The task performed by this subroutine is dependent of the value of NBOOPT(1). If set to 2, this routine initiates (by calling SR NBODEL) the calculation of the next NBO deletion of the \$DEL keylist. If set to 3, this routine completes the NBO deletion by computing the energy for the deletion. INTEGER variable IDONE is set to 1 if no additional deletions are found in the \$DEL keylist.

SR NBODEL (A, MEMORY, IDONE)

Controls the calculation of the new AO density matrix from the requested deletion in the \$DEL keylist. A modified NBO Fock matrix is created (SR NBDELE) and diagonalized (SR NBJACOBI), leading to a new AO density matrix (SR NEWDM). This routine also prints the NBO deletions table (Section B.6.10).

SR NBDELE (F, TRF, NDIM, IDEL, LEN, ITYPE, NDEL, NTRUNC, DONE, ISPIN)

Reads the \$DEL list for the next deletion, deletes (sets to zero) the appropriate elements from the Fock matrix, and prints out the deletion specification Section B.6.10).

SR NEWDM (DM, U, EIG, NDIM, IDEL, LEN, NDEL, ITYPE, ISPIN)

Constructs a new density matrix corresponding to the deleted Fock matrix.

SR RNKEIG (RANK, EIG, N, NDIM, ARCRNK)

Ranks the eigenvalues found in vector EIG (lowest eigenvalue having first rank).  $I = ARCRNK(N)$  is the entry whose rank is N.

SR SIMLTR (N, NDIM, F, U, R, S, KNTROL)

Performs the similarity transform  $U^t F U$  on a packed upper-triangular matrix F.

### C.7 DIRECT ACCESS FILE ROUTINES (GROUP III)

The routines of Group III are involved in communication between the NBO programs and the FILE48 direct access file (DAF), whose contents are described in Section C.4. Two levels of I/O routines are employed.

The higher-level 'fetch/save' routines are called directly by the NBO subroutines. In most cases, the function of the fetch/save routines can be recognized by its name or argument list; e.g., 'FETITL(TITLE)' fetches the job title line, 'FEFAO(F,IWFOCK)' fetches the AO Fock matrix (FAO), and so forth. Each routine can also be associated with a logical record number (IDAR) of the direct access file (Section C.4), where the I/O item is stored. We list these routines and associated direct access file record number(s) IDAR without further description:

---

routine	IDAR	routine	IDAR
SR FETITL(TITLE)	2	SR SVTLMO(T)	49
SR FEE0(EDEL,ETOT)	8	SR FETLMO(T)	49
SR SVE0(EDEL)	8	SR SVTNHO(T)	47
SR FECOOR(ATCOOR)	9	SR FETNHO(T)	47

---

SR FESRAW(S)	10	SR SVPPAO(DM)	22
SR FEDRAW(DM,SCR)	20,21	SR FEPPAO(DM)	22
SR FEFAO(F,IWFOCK)	30,31	SR SVTNAO(T)	43
SR FEAOMO(T,IT)	40,41	SR FETNAO(T)	43
SR FEDXYZ(DXYZ,I)	50-52	SR SVNLMO(T)	46
SR SVNBO(T,OCC,ISCR)	44,45	SR FENLMO(T)	46
SR FENBO(T,OCC,ISCR,NELEC)	44,45	SR SVDNAO(DM)	23,24
SR FETNBO(T)	44,45	SR FEDNAO(DM)	23,24
SR SVPNAO(T)	42	SR SVFNBO(F)	34,35
SR FEPNAO(T)	42	SR FEFNBO(F)	34,35
SR SVSNAO(S)	11	SR SVNEWD(DM)	25,26
SR FESNAO(S)	11	SR FENEWD(DM)	25,26
SR SVTNAB(T)	48	SR FEINFO(ICORE,ISWEAN)	3
SR FETNAB(T)	48	SR FEBAS(NSHELL,NEXP,ISCR)	5
SR SVKAO(T,IT)	18	SR SVTPAO(T)	39
SR FEKAO(T,IT)	18	SR FETPAO(T)	39
SR SVVAO(V,IV)	19	SR SVCHK(T,IS)	80,81
SR FEVAO(V,IV)	19	SR FECHK(T,IS,IT)	80,81
SR FELBLS(ISCR)	60,61	SR FESPIN(DM,SCR)	20,21

---

*related NEDA routines*

---

SR SVNEWT(T)	71,72	SR SVNEWF(F)	73,74
SR FENEWT(T)	71,72	SR FENEWF(F)	73,74
SR SVTEDA(T)	84,85	SR SVEIG(U)	82,83
SR FETEDA(T)	84,85	SR FEEIG(U)	82,83
SR SVDDEF(SCR,NFRG)	86,87	SR SVDCP(SCR,NFRG)	88,89
SR FEDDEF(SCR,NFRG)	86,87	SR FEDCP(SCR,NFRG)	88,89

In turn, the fetch/save routines call the following lower-level, primitive subprograms, which open, close, read, write, and test the contents of the DAF (these are heavily modified versions of the direct access file subroutines of HONDO):

SR NBOPEN(NEW, ERROR)

Opens a new or existing unformatted DAF depending in the value of logical variable NEW. Record lengths are currently set at 256 (LENGTH) single precision words (1024 bytes), and up to 100 (NBDAR) logical records can be written. Note that logical records and physical records of the DAF are not equivalent; single logical records can span several physical records and need not be ordered sequentially. The array IONBO (in COMMON/NBODAF/) maps each logical record with its associated physical records. The first physical record of the DAF is reserved for COMMON/NBODAF/. [Note: Some machines may require that you alter the parameters LENGTH (the chosen record length) and ISINGL (a record length scaling factor).]

SR NBWRIT(IX, NX, IDAR)

Writes NX double precision words of array IX to logical record number IDAR of the NBO DAF.

SR NBREAD(IX, NX, IDAR)

Reads NX double precision words of the logical record number IDAR of the NBO DAF.

SR NBCLOS(DEL)

Rewrites common block /NBODAF/ on the first physical record of the DAF, and closes the file.

SR NBINQR(IDAR)

Inquires whether information has been stored in logical record IDAR of the direct access file, and sets IDAR=0 if the record is empty.

## **C.8 FREE FORMAT INPUT ROUTINES (GROUP IV)**

The routines of Group IV are the small set of system-independent free-format input routines that are used in reading the various keylists and datalists of the input file. The routines of this group are the 'primitives' that read and interpret

individual keywords or entries of a keylist. They are called by higher-level I/O routines (such as SR JOBOPT of Group I) throughout the NBO program.

The free-format input primitive routines are:

SR STRTIN(LFNIN)

Initializes input from the LFNIN input file.

SR NXTCRD

Reads the next 'card' (line) of the input file, and stores this line in the integer array ICD in COMMON/NBCRD1/ with all lower case characters converted to upper case. Logical variable END in COMMON/NBCRD2/ is set to .TRUE. if the end-of-file is encountered.

SR IFLD(INT,ERROR)

Searches input file LFNIN for the next string of non-blank characters, and checks to see if they form an integer. If so, the numerical value of the integer is placed in INT. If not, the logical variable ERROR is set to .TRUE. and INT is set positive (indicating an 'END' terminating mark or end-of-file was encountered) or negative (indicating that the character string is not an integer).

SR RFLD(REAL,ERROR)

Similar to SR IFLD, but for a real number REAL. This routine will accept real numbers in a variety of different formats. For example, 1000 can be represented by 1000, 1000.0, 1.0E3, D3, 1+3, etc.

SR HFLD(KEYWD, LENG, ENDD)

Similar to SR IFLD and RFLD, but for a Hollerith array KEYWD(LENG). The logical variable ENDD is set to .TRUE. if the 'END' terminating mark or the end-of-file is encountered. On return to the calling subroutine, LENG is set to the length of the string in KEYWD or to zero if the end-of-file is encountered.

SR FNDFLD

Searches for the next non-blank field on the input file, reading additional lines if necessary. Commas and equal signs are treated as blanks, and any character string which follows an exclamation point is treated as an arbitrary comment, and is ignored. The contents of this field are stored in the integer array LOOK of length LENGTH in COMMON/NBCRD1/.

FN EQUAL(IA, IB, L)

This logical function tests the equivalence of the first 'L' elements of the Hollerith strings IA and IB.

## **C.9 OTHER SYSTEM-INDEPENDENT I/O ROUTINES (GROUP V)**

This section summarizes the I/O routines of Group V. These routines perform a variety of auxiliary I/O tasks, such as the reading or writing of matrices, or perform functions closely related to I/O.

The first set of programs in this group are responsible for searching for the \$GENNBO, \$NBO, \$CORE, \$CHOOSE, and \$DEL identifiers of the job input file LFNIN:

SR GENINP (NEWDAF)

Searches for the \$GENNBO identifier. In addition, this routine reads in the keywords of the \$GENNBO keylist (see Section B.7), setting the option flags of COMMON/NBOPT/ and COMMON/NBGEN/ appropriately.

SR NBOINP (NBOOPT, IDONE)

Searches for the \$NBO identifier according to the program version number, NBOOPT(10). The integer variable IDONE is set to 0 if this identifier is located, or 1 otherwise.

SR CORINP (IESS, ICOR)

Searches for the \$CORE identifier according to the program version number, IESS. The integer variable ICOR is set to 1 if this identifier is located, or 0 otherwise.

SR CHSINP (IESS, ICHS)

Searches for the \$CHOOSE identifier according to the program version number, IESS. The integer variable ICHS is set to 1 if this identifier is located, or 0 otherwise.

SR DELINP (NBOOPT, IDONE)

Searches for the \$DEL identifier according to the program version number, NBOOPT(10). The integer variable IDONE is set to 0 if this identifier is located, or 1 otherwise.

The remaining routines of this group perform miscellaneous I/O functions:

SR RDCORE (JCORE)

Initializes the atomic core array (IATCR on COMMON/NBATOM/), and reads the entries of the \$CORE keylist.

SR WRPPNA (T, OCC, IFLG)

Writes the transformation from 'pure' AOs to PNAOs, the NAO labels (NAOCTR, NAOL, and LSTOCC from COMMON/NBBAS/), and PNAO occupancies (diagonal PNAO density matrix elements) to an external file (LFN

= -IFLG). Pure AOs (PAOs) are obtained from 'raw' cartesian AOs by the transformations of SR DFGORB.

SR RDPPNA(T, OCC, IFLG)

Reads the transformation from 'pure' AOs (PAOs) to PNAOs, NAO labels, and PNAO occupancies from an external file (LFN = -IFLG/1000) (cf. SR WRPPNA).

SR WRTNAO(T, IFLG)

Writes the AO to NAO transformation (fetched from the DAF), NAO labels, and the PNAO overlap matrix (also fetched from the DAF) to an external file (LFN = -IFLG). Note that T is the PNAO overlap matrix when control is returned to the calling routine.

SR RDTNAO(DM, T, SCR, IFLG)

Reads the AO to NAO transformation, NAO labels, and PNAO overlap matrix from an external file (LFN = -IFLG/1000). The transformation and overlap matrices are saved on the DAF, and the input AO density matrix is transformed to the NAO basis. Note that T is the PNAO overlap matrix on return to the calling routine (cf. SR WRTNAO).

SR WRTNAB(T, IFLG)

Writes the NAO to NBO transformation and NBO info (LABELS and IBXM arrays of COMMON/NBBAS/) to an external file (LFN = -IFLG).

SR RDTNAB(T, DM, BND OCC, SCR, IFLG)

Reads the NAO to NBO transformation and NBO info from an external disk file (LFN = -IFLG/1000). The input NAO density matrix is also transformed to the NBO basis, and the NBO occupancies are stored in BND OCC (cf. WRTNAB).

SR WRTNBO(T, BND OCC, IFLG)

Writes the AO to NBO transformation, the NBO occupancies, and additional NBO info (NBOUNI, NBOTYP, LABEL, IBXM, and IATNO arrays) to an external disk file (LFN = -IFLG).

SR WRNLMO(T, DM, IFLG)

Similar to SR WRTNBO but for NLMOs. Note that the NLMO labels are identical to the NBO labels.

SR WRBAS(SCR, ISCR, LFN)

Writes the atomic coordinates and AO basis set information to the 'AOINFO' file LFN. The information contained in this file is identical to that of the \$COORD, \$BASIS, and \$CONTRACT datalists of the GENNBO input file

(see Section B.7). For more information on the file format, see the subroutine source code.

SR WRARC (SCR, ISCR, LFN)

Writes the 'ARCHIVE' file LFN (see Section B.7).

SR WRLBL (LFNLBL)

Writes the orbital label info to LFNLBL for PLOT keyword (ORBLOT).

SR AOUT (A, MR, NR, NC, TITLE, INDEX, IFLG)

General utility to write matrix  $A(MR,1)$  to an external file ( $LFN = -IFLG$ ) or print it to the output file ( $IFLG =$  number of columns to print, 'FULL', 'VAL', or 'LEW'). TITLE is a CHARACTER\*80 matrix label, and the rows of A are labelled according to the value of INDEX = 0 (atoms), 1 (AOs), 2 (NAOs), 3 (NHOs), 4 (NBOs), or 5 (NLMOs). This routine calls SR APRINT or SR AWRITE.

SR APRINT (A, MR, NR, NC, TITLE, INDEX, MCOL)

Prints MCOL columns of matrix A to the output file. The format of the matrix is chosen according to the magnitude of the largest matrix element in A (cf. SR AOUT).

SR AWRITE (A, MR, NR, NC, TITLE, LFN)

Writes matrix A to external disk file LFN (cf. SR AOUT).

SR AREAD (A, MR, NR, NC, JOB, LFN, ERROR)

Reads NC columns of the matrix  $A(MR,1)$  from the external file LFN. The job title in the external file is returned to the calling subroutine in the Hollerith array, JOB(20), and the LOGICAL variable ERROR is set to .TRUE. if an error occurred while reading.

SR ALTOUT (A, MR, MC, NR, NC)

Prints the matrix  $A(MR,MC)$  to the standard output file. This routine is called only when the print formats of SR APRINT are unsuitable for matrix A.

SR KEYPAR (STRING, LEN, IFLG, ICHKPT, LFN, READ, ERROR)

Interprets the Hollerith array STRING(LEN), storing the result in IFLG. The contents of STRING can be any of the read/write/print parameters such as 'W38', 'PVAL', 'R43', etc., described in Section B.2.4, and the resulting value of IFLG is determined according to the discussion of COMMON/NBOPT/ in Section C.3. When this routine is called, IFLG should be set to its default value, LFN should be the default file for writing or reading, and LOGICAL variable READ should be set to .TRUE. if reading from an external file is allowed. The LOGICAL variable ERROR is set to .TRUE. if STRING is uninterpretable.

FN HIOINQR(IFLG)

Interprets IFLG as to whether the I/O item should be printed (IOINQR = `PRNT'), read (IOINQR = `READ'), or written out (IOINQR = `WRIT') to an external file.

SR LBLAO

Forms labels for AOs and stores them in COMMON/NBLBL/.

SR LBLNAO

Forms labels for NAOs and stores them in COMMON/NBLBL/.

SR LBLNBO

Forms labels for NBOs and stores them in COMMON/NBLBL/.

SR LBLNHO(INHO, INBO, ICTR, NCTR)

Forms labels for NHOs and stores them in COMMON/NBLBL/.

SR LBLPAO

Forms labels for PAOs and stores them in COMMON/NBLBL/.

## **C.10 GENERAL UTILITY ROUTINES (GROUP VI)**

The utility routines of Group VI perform a variety of mathematical and other general tasks (such as solving sets of linear equations), and are called from routines throughout the NBO program.

SR ANGLES(X, Y, Z, THETA, PHI)

Converts cartesian coordinates (X,Y,Z) to corresponding polar angle THETA and azimuthal angle PHI in spherical polar coordinates.

FN BDFIND(IAT, JAT)

LOGICAL function BDFIND is set to .TRUE. if there is at least one bond between atoms IAT, JAT.

SR CHEM(NAT, NATOMS, LISTA, NL, ISTR)

Builds a `chemical formula' for the list of atoms in LISTA having been identified as belonging to a particular `molecular unit'. The chemical formula is stored in the Hollerith array ISTR(NL).

SR CONSOL(AUT, ALT, NDIM, N)

Consolidates an upper-triangular (AUT) and lower-triangular (ALT) matrix in a single matrix, stored in AUT.

SR CONVIN (IJ, LEN, IK, ERROR)

Converts the Hollerith array IJ(LEN) into an integer IK. This is the inverse of SR IDIGIT.

SR CONVRT (N, NC1, NC2)

Converts a 2-digit integer N to two Hollerith characters NC1, NC2.

SR CONVRT3 (N, NC1, NC2, NC3)

Converts a 3-digit integer N to three Hollerith characters NC1, NC2, NC3.

SR CONVRT3S (N, SC1, SC2, SC3)

Converts a 3-digit integer N to three string characters SC1, SC2, SC3.

SR COPY (A, B, NDIM, NR, NC)

Copies matrix A to matrix B.

SR CORTBL (IAT, ICORE, IECP)

Stores the nominal "core table," giving the number of core *s*, *p*, *d*, *f* orbitals for elements 1-105 (H to Lw, and elements 104, 105). This table controls the number of high-occupancy unhybridized NAOs that will be isolated and removed as core NBOs (taking account also of any effective core potential).

SR IDIGIT (KINT, IK, ND, MAXD)

Converts the INTEGER variable KINT in the first ND elements of the Hollerith array IK(MAXD). This is the inverse of SR CONVIN.

FN IHTYP (IBO, JBO)

This Hollerith function determines whether the IBO→JBO delocalization is vicinal ('v'), geminal ('g'), or remote ('r'), based on the derived NBO connectivity.

SR NBJACOBI (N, A, EIVU, EIVR, NDIM, NVDIM, ICONTR)

Diagonalizes a real symmetric matrix by the Jacobi rotations method. If ICONTR=0, a standard Jacobi diagonalization (unconstrained 2x2 rotations) is carried out. If ICONTR=1, the algorithm is prevented from mixing orbitals that are degenerate within 'DIFFER' if the off-diagonal element connecting them is less than 'DIFFER'. [Threshold DIFFER ( $10^{-5}$ ) controls degenerate mixing, DONE ( $10^{-13}$ ) is the maximum allowed off-diagonal element, and EPS ( $0.5 \times 10^{-13}$ ) is a number between DONE and the machine precision.]

SR KEYERR (WORD)

Prints error message and returns if keyword reading error occurs.

SR LIMTRN (T, M, A, B, NDIM, NBAS, NCDIM, NC, IOPT)

This routine carries out a 'limited' transformation of a matrix (T), using only

the rows and columns specified by vector M. The operations performed are  $T^*A$ ,  $A^tT^*A$ , or  $A^tT$  according to the value of IOPT.

SR MATMLT (A, B, V, NDIM, N)

Multiplies square matrices  $A^*B$  (using scratch vector V) and stores result in A.

SR MATML2 (A, B, V, NDIM, N)

Multiplies  $A^tB$  (using scratch vector V) and stores the result in B. The algorithm assumes that  $A^*B$  is a symmetric, so about half the work is saved. [SR MATML2 is typically the second step in a similarity transform of B by A, where B (and thus  $A^tB^*A$ ) is symmetric.]

FN NAMEAT (IZ)

Returns the (Hollerith) atomic symbol for atomic number  $IZ \leq 103$ .

SR NBHALT (WORD)

Halts execution of the NBO program if an unrecoverable error is encountered, or returns control to host program (Gaussian).

SR NORMLZ (A, S, M, N)

Normalizes the columns of A using the overlap matrix S.

SR ORDER (RANK, LIST, N, NDIM, ARCRNK)

Ranks the positive elements of integer LIST(N), lowest values first. [RANK and ARCRNK are integer vectors, with  $I = \text{ARCRNK}(N)$  if LIST(I) is the element of rank N.]

SR PACK (T, NDIM, NBAS, L2)

Packs the upper-triangular portion of the symmetric matrix T(NBAS,NBAS) the first L2 elements of T.

SR RANK (EIG, N, NDIM, ARCRNK)

Orders the entries of vector EIG, highest values first. ARCRNK(I) is the old location of the I<sup>th</sup> highest value in EIG. On return, EIG(I) is the I<sup>th</sup> highest value. [Entries are not switched unless they differ by more than a DIFFER ( $5 \times 10^{-8}$ ) threshold.]

SR SCNVRT (IVEC, STR, NL, ERR)

Converts Hollerith IVEC to string STR(1:NL).

SR SIMTRN (A, T, V, NDIM, N)

Performs the general similarity transform  $T^tA^*T$  of A by T, using scratch vector V.

SR SIMTRS (A, S, V, NDIM, N)

Performs the 'fast' similarity transform  $S^t * A * S$ , assuming the result is symmetric.

SR NBTRSP (A, NDIM, N)

Transposes the matrix A:  $A \rightarrow A^t$ .

SR UNPACK (T, NDIM, NBAS, L2)

Unpacks an upper triangular matrix (vector of length L2) into a symmetric matrix T(NBAS,NBAS).

SR VALTBL (IAT, IVAL)

Specifies the nominal "valence table," giving the number of valence AOs of each symmetry type for elements 1-105.

FN VECLLEN (X, N, NDIM)

Evaluates Euclidean length of vector X.

The following four routines constitute the linear equations package for solving the system  $A * X = B$  for matrix X by the method of Gaussian elimination:

SR LINEQ (A, X, B, SCR, N, M, NDIM, MDIM, ZERTOL, EPS, MAXIT, LFNPR, IERR)

Driver program for solving linear equations.

SR FACTOR (A, W, D, IPIVOT, N, NDIM, ZERTOL, IFLAG)

Supports SR LINEQ.

SR FNDSOL (A, X, B, W, R, E, IPIVOT, N, NDIM, EPS, MAXIT, LFNPR, IERR)

Supports SR LINEQ.

SR SUBST (X, W, B, IPIVOT, N, NDIM)

Supports SR LINEQ.

The following four routines contain some ESS or operating system dependence:

SR DACLOS (INBO, DEL)

Closes the NBO DAF, deleting it if DEL set to .TRUE.

SR DAFILE (NAME, LEN, INBO, ISINGL, LENREC, ERROR)

Defines bit precision, record length, and filename for the NBO DAF.

SR DEBYTE (I, IBYTE)

Decomposes a Hollerith variable I into its four individual Hollerith 'bytes' IBYTE(4).

SR SQFILE (NEW, ERROR)

Selects name and opens external files for NBO matrix output. If necessary, FILE input name is modified (with appended integer) to avoid conflict with existing disk files.

## **C.11 SYSTEM-DEPENDENT DRIVER ROUTINES (GROUP VII)**

The routines of Group VII comprise the set of ESS-dependent driver routines which initiate the NBO and NBO energetic analyses and provide the NBO program with a variety of information about the electronic wavefunction. This section provides a brief, generic description of the three main driver routines. [In addition, subroutines DACLOS, DAFILE, DEBYTE, SQFILE of the utility group (Sec. C.10) and SR CHKNBO of the checkpointing group (Sec. C.18) are ESS- or system-dependent.] If you intend to write a set of routines for an ESS program not supported by this distribution, refer to the driver source code for additional guidance. Also, see Section C.13 for helpful hints for attaching the NBO program to an ESS package.

System-dependent driver routines are grouped together near the end of the NBO source code. Since multiple versions of each driver are provided (one for each supported ESS package and GENNBO), all of the executable lines in these routines are 'commented out' with an asterisk in the first column. In addition, every line of the drivers has an identifier 'XXXDRV' in columns 73-78, where 'XXX' is a 3-letter identifier for the associated ESS package. It is the responsibility of the program ENABLE to 'uncomment' the appropriate lines of the code for the requested program version (see Section A.2).

The system-dependent driver routines are:

SR RUNNBO

Determines the logical file numbers for the input and output files (LFNIN and LFNPR) of the parent program, initializes the NBOOPT job option array (Section C.5.1), and initiates the NBO analysis (SR NBO) and energetic analysis (SR NBOEAN). This routine is the only routine of the NBO program called directly by the parent ESS package.

SR FEAOIN (CORE, ICORE, MEMORY, NBOOPT)

Interrogates the scratch files and COMMON blocks of the parent program, providing the NBO program with required information of the electronic wavefunction via the NBO COMMON blocks and FILE48 direct access file. (Note that for GENNBO, this routine directs the input of information from the GENNBO input file, FILE47.) The NBO COMMON blocks and FILE48 records which must be initialized by SR FEAOIN are discussed in Sections

C.3, C.4. Additional information on the COMMON blocks and scratch files of the parent ESS package is provided in the Appendices.

SR DELSCF(CORE, ICORE, NBOOPT)

Performs one of two tasks, depending of the value of NBOOPT(1). If NBOOPT(1) is set to 2, SR DELSCF provides the parent ESS program with the modified density matrix generated by the NBO energetic analysis routines. The parent program will then compute the "deletion energy" for this modified wavefunction. If NBOOPT(1) is set to 3, SR DELSCF fetches the deletion energy from the parent program and writes it to the FILE48 direct access file. (The NBOOPT array is discussed in Section C.5.1).

## C.12 GENNBO AUXILIARY ROUTINES

An additional set of routines is provided for the GENNBO stand-alone program. These routines are called by the GENNBO driver routine FEAOIN and are responsible for reading the datalists of the GENNBO input file. Each of these routines rewinds the input file before searching sequentially for its associated datalist. Thus, the order of datalists (as well as keylists) in the input file is immaterial. Each routine also checks that all required information in the datalist is given and stores this information on the FILE48 direct access file or in the NBO COMMON blocks.

Below we list each GENNBO auxiliary routine, indicating its associated datalist, but without further explanation:

<i>Datalist</i>	Auxiliary routine to read datalist
\$COORD	SR CRDINP(TITLE,ATCOOR,BOHR)
\$BASIS	SR BASINP
\$CONTRACT	SR CONINP(CORE,ICORE)
\$OVERLAP	SR SINP(CORE,UPPER)
\$DENSITY	SR DMINP(CORE,UPPER)
\$FOCK	SR FINP(CORE,UPPER,END)
\$LCAOMO	SR TINP(CORE)
\$DIPOLE	SR DIPINP(CORE,UPPER,BOHR)

\$KINETIC	SR KINP(CORE,UPPER)
\$NUCLEAR	SR VINP(CORE,UPPER)

---

### C.13 ATTACHING NBO TO A NEW ESS PROGRAM

This section briefly outlines the steps to be considered when attaching the NBO program to a new ESS package that is not supported by this distribution.

In general, you should try to identify the supported ESS package that is most similar to the ESS package you wish to use, and try to create driver routines modelled as closely as possible on those provided for the ESS. [In fact, examining the source code for driver routines of *all* supported ESS packages is good preparation for writing your own drivers.]

1. Decide where in the parent ESS package you wish to perform the NBO analysis. This will necessarily be placed after the calculation of the wavefunction (and the associated density matrix), usually near the wavefunction analysis routines (e.g., the perennial "Mulliken population analysis" section) or wavefunction properties section of the code. If possible, restrict the modification of your ESS source code to insertion of a single "CALL RUNNBO" statement at some point where the information required for NBO analysis is known to be available.
2. Check carefully for possible conflicts between the parent ESS program and the NBO program in (1) function or subroutine names, (2) COMMON block names, and (3) logical file assignments (LFNs) for I/O. NBO common block names all begin with /NB../, and default LFN assignments are in the range 31-49. (Duplicate FN or SR names are detected by a linker.)
3. Create new driver (interfacing) subroutines RUNNBO, FEAOIN, and DELSCF to perform the functions briefly described in Section C.11, using the drivers provided with this distribution as templates insofar as possible. The following are a few helpful hints for each driver:
  - a. The RUNNBO routine should be relatively straightforward to write, following an analogous example provided in this distribution. Note that you can simply omit the calls to SR NBOEAN and SR DELSCF from RUNNBO if you do not plan to use the NBO energetic analysis (for example, because the DELSCF driver is unmanageable).

If your parent program is quite different from any of those supported by this distribution, choose an alternate version number [NBOOPT(10)], and carefully consider step 4 below.

b. Routine FEAOIN should fetch information about the electronic wavefunction from your ESS package and load it into the NBO COMMON blocks and FILE48 direct access file. This requires intimate knowledge of where these items are stored in the ESS program, so the FEAOIN examples of the distribution may provide little direct guidance. See Sections C.3, C.4 for description of the NBO COMMON blocks and file records which must be initialized by this routine.

Note that the NBO analysis will perform properly without the information stored on logical records 2, 5, 9, 30, 31, 40, 41, and 50-52 of the direct access file. If information is not provided on these records, the NBO program will simply shut off (with warnings) any requested keyword options which are thereby incompatible. In addition, the overlap matrix of record 10 need not be provided if the input basis set is orthogonal, and the energies of record 8 are not required if the NBO energetic analysis is not implemented for your ESS package.

c. Creating routine DELSCF will require intimate knowledge of the SCF routines in the parent ESS program; again, versions of DELSCF provided with this distribution may only be of minimal assistance. As described in Section C.11, SR DELSCF is responsible for providing a modified AO density matrix to an SCF energy evaluator (one pass through the SCF routines) and returning this new energy to the NBO deletion routines via the FILE48 direct access file. If you do not intend to employ the NBO energetic analysis, you need not provide this routine to the NBO program. [Note that the 2nd-order perturbation theory energy analysis will be carried out (provided the Fock matrix is available) even if you do not include the NBOEAN and DELSCF energy analysis routines.]

4. In addition to the explicitly system-dependent subroutines RUNNBO, FEAOIN, and DELSCF, there are a few routines within the NBO program which can be considered *quasi*-system dependent, and might, therefore, require modification. These are SR NBOSET (Section C.5.2) and the 'INP' routines NBOINP, CORINP, CHSINP, and DELINP (Section C.9):

a. SR NBOSET assigns the logical file numbers (LFNs) 31-49 to be used by the NBO program. As mentioned above, if these are in conflict with the files

employed by the parent ESS program, the conflicting LFNs will have to be reassigned in this subroutine.

b. The `INP' routines may have to be modified according to the manner in which the input file of the parent program should be processed by the NBO program. More specifically, these routines either rewind the input file before searching for their associated keylist identifier, or they simply begin searching the input file sequentially at the point where the parent program left off, depending on the version number specified in NBOOPT(10). Be sure this parameter is consistent with the way you wish to modify the ESS input file for NBO input.

## C.14 NRT ROUTINES

The NRT module comprises about 10000 lines of portable Fortran code (about 30% comment cards) which has been appended to the host NBO program. In this section, we provide a brief description of the labelled COMMON blocks and routines of the NRT module. More detailed descriptions of the NRT algorithms can be found within the NRT source code itself. Since the NRT analysis is not completely self-contained but calls several subprograms of the NBO analysis frequently and uses several of the NBO COMMON blocks, some knowledge of the NBO source code is assumed.

Some communication within the NRT analysis is provided by labelled COMMON blocks. We list these with a brief description of their contents in Section C.14.1.

The NRT source code has been partitioned into five groups of routines which are related either by their precedence in the NRT program or by the tasks which they perform. These groups are ordered in the NRT source code as follows:

---

Group	description	no.	Section
I.	Main NRT driver	1	C.14.2
II.	NRT routines	26	C.14.3
III.	NRT optimization routines	17	C.14.4
IV.	Branching routines	7	C.14.5

---

Subroutines and functions are abbreviated SR and FN, respectively.

The NRT routines have been written to minimize I/O with external disk files. Furthermore, the minimal I/O that the NRT routines will perform is restricted to input from the NBO direct access file, which typically occupies less than 1 MByte.

Although the memory requirements of the NRT analysis are generally rather modest, some consideration of the memory made available to the program is recommended at installation time (see Sec. A.2). The maximum number of resonance structures,  $n_{RS}$ , that can be generated during program execution is limited by the length of the scratch vector made available to the NBO and, ultimately, NRT programs. For a calculation with  $n_{ref}$  reference resonance structures,  $n_b$  basis functions, and  $n_a$  atomic centers, NRT analysis requires a scratch vector (array CORE in SR RUNNBO of the NBO program) of roughly

$$2 n_{RS}^2 + n_{RS}(n_{ref} n_b + n_{ref} n_a^2 + 6 n_a) + 4 n_b^2$$

REAL\*8 words. For example, the analysis of a wavefunction with 75 basis functions, 10 atoms, and 100 resonance structures (assuming  $n_{ref}=1$ ) requires a scratch vector of about 50,000 elements (less than 500 kbytes). *We recommend that a scratch vector of at least 100,000 elements be made available to the program.*

In practice, the number of resonance structures generated by the NRT analysis is not known prior to program execution ( $n_{ref}$  is determined by the NRTREF keyword,  $n_b$  and  $n_a$  are intrinsic to the wavefunction). Thus, for the given scratch vector, an expression similar to the one above is inverted to determine the maximum number of resonance structures that the calculation can accommodate. Warning messages appear when insufficient memory is available to complete a calculation.

#### *C.14.1 NRT Labelled Common Blocks*

The NRT routines contain four COMMON blocks in addition to those documented elsewhere in this manual. Array dimensions within these blocks are determined by the statements

PARAMETER (MAXATM = 200, MAXBAS = 2000)

which specify the maximum number of atomic centers and basis functions which the NRT program can handle. See Sec. C.3 for additional notes on MAXATM and MAXBAS.

Below, we briefly describe each of the NRT COMMON blocks:

### 1. COMMON/NBSTR/

The INTEGER array of this block is used to store the topo matrix of a resonance structure:

---

variable	meaning
ITOP0(MAXATM,MAXATM)	current working resonance structure

---

### 2. COMMON/NBALT/

The INTEGER variables of this block contain the branching indices which guide SR NBCHSE in the search for "iso-Lewis" resonance structures:

---

variable	meaning
IDX(MAXATM)	limiting branching indices
JDX(MAXATM)	current branching indices
KDX(MAXBAS)	atom connectivity list
JCNT	number of branch points

---

### 3. COMMON/NBALT1/

The INTEGER variables of this block contain a temporary copy of COMMON/NBALT/, available for restoration if problems occur during the search for electron pairs in SR NBCHSE:

---

variable	meaning
IIDX(MAXATM)	limiting branching indices
JJDX(MAXATM)	current branching indices
KKDX(MAXBAS)	atom connectivity list
JJCNT	number of branch points

---

#### 4. COMMON/NBSTOR/

The INTEGER arrays of this block are used to store temporary copies of the NBO labels and NHO atomic centers:

---

variable	meaning
NBOLBL(MAXBAS,6)	NBO labels
NHOCTR(MAXBAS)	NHO atomic centers

---

Slight modifications have been made to two COMMON blocks of the main NBO program, which are listed below:

#### 5. COMMON/NBOPT/

The following entries of the original JPRINT array are pertinent to NRT analysis:

---

variable	meaning
JPRINT(32)	activate NRT analysis
JPRINT(55)	method of variational optimization
JPRINT(56)	number of reference structures
JPRINT(57)	NRT print level
JPRINT(77)	use full NAO density matrix
JPRINT(80)	control maximum atomic formal charge

## 6. COMMON/NBTHR/

The following thresholds have been appended to this block:

variable	meaning
DLTHR	delocalization list threshold
CHSTHR	threshold for iso-Lewis search
REFTHR	reference structure weighting threshold
PRTHR	\$NRTSTR printing threshold

### *C.14.2 Main NRT Driver Routine*

SR NRTDRV is the NRT routine of highest precedence in the NRT program:

SR NRTDRV (DM, T, WIBERG, RHOSTR, KPAR, NRES, IRESET, A, MAXRES, MAXREF, NLOW, NNAO, LEN, NELEC, MEMORY, IVALSP)

Controls the calculation of resonance structures and evaluation of resonance weights and bond orders. The following is an overview of the NRT algorithm, controlled by SR NRTDRV:

1. Partition the scratch vector, A(MEMORY), according to the needs of the program. Warning messages alert the user if insufficient memory is available to perform NRT analysis.
2. Collect an initial set of resonance structures from the \$NRTSTR keylist (SR NRTSTR), the search over the Wiberg bond indices (SR LEWIS), and possibly from the regular NBO analysis (SR NBORES). Each resonance structure is represented in "TOPO matrix" form, the diagonal elements, TOPO(I,I), indicating the number of lone pairs on center I, and the off-diagonal elements, TOPO(I,J), indicating the number of bonds between centers I,J.
3. Loop over the initial set of resonance structures, passing each structure in turn to SR PARENT (ultimately to SR NBCHSE), which searches the density matrix for the best representation of the wavefunction corresponding to the specified resonance form. SR SELECT selects reference resonance structures based on the delocalization densities,  $\rho^*$ , and on the number of reference structures requested by the user.
4. Search (in SR KEKULE) the set of reference structures for structures that are related by concerted bond shifts (benzenoid resonance). This search is based on characteristic patterns in the TOPO matrices and on the strengths of NBO interactions.
5. Loop over reference structures, generating additional, secondary structures (SR ARROWS) according to the entries of the delocalization list. NBOs for these secondary structures are calculated by SR SECRES, and NBO expectation values and polarization information are computed by SR EXPECT and SR IONIC.
6. Append resonance forms from SR KEKULE to the list of structures, and compute NBOs, NBO expectation values, and polarization information, according to Step 5.
7. Request (from SR CONDNS) that all ionic structures of covalent-ionic pairs be removed from the list of structures, and that exponential (Boltzmann-like) resonance weights be evaluated (by SR INITWT).
8. Request that the resonance weights be variationally optimized by SR WGTOPT. Linear dependence of the NRT resonance structures is recognized from vanishing eigenvalues of the analytic Hessian matrix, and indeterminacies are resolved by inclusion of a penalty function.

9. Perform the multi-reference weighting (with SR MULTI and RESWGT).
10. Add reference structures (according to resonance weight) as needed, and repeat Steps 4-9.
11. Complete the analysis by printing structures and weights (SR NRTOUT) and bond orders and atomic valencies (SR NBDORD).

### C.14.3 NRT Routines

The routines of this group form the core of the NRT program:

SR VALDM (DM, GAMMA, SCR, V, U, IOCC, NVAL, LVAL)

Extracts valence NAO density matrix elements from DM (if full density matrix not specified), places them in GAMMA, and renormalizes to maintain idempotency.

SR NRTSTR (NRES, IDXRES, MAXRES, MAXREF, LSTRES, LEN, NELEC)

Processes the \$NRTSTR (or \$NRTSTRA and \$NRTSTRB) keylist. Resonance structures in this keylist are placed in the ITOPO array (of COMMON/NBSTR/) and are appended to the list of candidate structures stored in LSTRES. This routine also determines whether the resonance structures entered via the \$NRTSTR keylist have the appropriate number of electron pairs. If not, error messages are printed and program execution halts.

SR LEWIS (DM, WIBERG, NRES, IDXRES, MAXRES, MAXREF, LSTRES, LEN, IVALSP)

Searches the Wiberg bond indices ( $b_{AB}$ ) for resonance structures which (1) satisfy the octet rule, and (2) contain formal charges equal to the net charge on the molecule plus up to NRTCHG pairs of +/- formal charges. The routine places  $b$  bonds between atoms  $A$  and  $B$  if  $|b_{AB}^{(w)} - b| \leq thresh$ , where  $thresh$  is THR1, THR2, THR3 for near-single, double, or triple bond character, respectively. If no satisfactory resonance structures are found, the electroneutrality and formal charge constraints are relaxed, and the search repeated.

SR LEWATM (IAT, JAT, KDX, LEFTBD, ICNT, NATOMS)

Determines, for SR LEWIS, the order in which atomic centers are searched for electron pairs.

SR LEWBDS (IAT, JAT, IDX, JDX, WIBERG, LEFTBD, NATOMS, THR1, THR2, THR3, IALARM)

Selects, for SR LEWIS, LEFTBD bonds from atomic center JAT to its adjacent atomic centers. The connectivity information of the Wiberg bond indices is used to determine bonded atoms.

SR LEWDIS (ICH, N, IATNO, NATOMS, IERR, INIT)

Distributes charges over atomic centers.

SR LEWTOP (JAT, JDX, KDX, LEFTBD, ICNT, NATOMS)

Stores the bond selections of SR LEWBDS in the ITOPO matrix of COMMON/NBSTR/.

SR NBORES (NRES, IDXRES, MAXRES, MAXREF, LSTRES, LEN, ISCR, IVALSP)

Adds the Lewis structure obtained by NBO analysis to the list of candidate structures, but only if SR LEWIS failed to find any resonance structures and no \$NRTSTR keylist was available in the input deck.

SR HBRES (NRES, IDXRES, MAXRES, LSTRES, LEN, NRTCTL)

Adds to the list of candidate structures any missing structure(s) detected by the 3-center hyperbond search (3CHB, automatically activated).

SR KEKULE (ILIST, IDXRES, IRESET, MAXRES, NREF, MAXREF, LSTRES, LEN)

Searches the list of candidates for structures which are related by concerted three-bond shifts (benzenoid-type resonance). Related structures are listed in ILIST.

SR PARENT (IREF, RHOST, DM, T, WIBERG, BND OCC, POL, Q, V, BLK, C, EVAL, BORB, P, TA, HYB, VA, VB, TOPO, SCR, IDON, IACC, IDXRES, KPAR, MAXRES, MAXREF, IBDRES, ISRC H)

Directs SR NBCHSE to search for the resonance structure specified in matrix ITOPO of COMMON/NBSTR/.

SR SHREWD (DM, T, BND OCC, POL, Q, V, BLK, C, EVAL, BORB, P, TA, HYB, VA, VB, IREF, IDON, IACC, IFLG)

``Shrewd'' version of SR NBCHSE that searches for the NBOs of a particular (target) Lewis structure given the NBOs of a related (parent) structure and the single delocalization that relates the two.

SR SELECT (RHOSTR, NRES, IRESET, KPTR, IDXRES, MAXRES, NREF, MAXREF, NRTCTL)

Selects list of reference structures to be used in evaluation of resonance weights.

SR REFRS (IREF, T, BND OCC, OCCR, TR, SCR1, SCR2, SCR3, GAMMA, GAMMAW, IST, IOCC, NREF, NNAO, IVALSP)

Collects information about each reference resonance structure to be used in the optimization of the resonance weights.

SR EXPECT (IRES, T, BND OCC, OCC, OCCR, TR, SCR, IPTR, MAXRES, IREF, NREF, NELEC)

Evaluates the expectation values of the density operator for the IRES-th resonance structure in the NBO bases of the reference structures.

Computationally, this reduces to a back-transformation of the electron density of the IRES-th structure to the NBO basis of each reference.

SR IONIC (IRES, T, XION, NLOW, MAXRES, IREF, NREF)

Computes the fractional ionic character (returned in XION) of the bonds in the IRES-th resonance structure.

SR PREPAR (DM, TNBO, HYB, T, THYB, SCR)

Prepares the NHO density and NHO to NBO transformation matrices, used to calculate secondary resonance structures.

SR ARROWS (DM, T, DELOC, SCR, NRES, IRESET, IDON, IACC, IDXRES, MAXRES, IREF, NREF, LSTRES, LEN, IAT1, IAT2, IDXCOV, IIONC, NRTCTL)

Forms TOPO matrices for secondary resonance structures according to the entries of the delocalization lists of the reference structures.

SR NEWLBL

Restores the NBO labels of the parent reference structure.

SR IONTST (IRES, IREF, IAT1, IAT2, IDXRES, MAXRES, NREF, LSTRES, LEN, IDEL)

Tests for adjacent formal charges from a LP-LP\* interaction.

SR CONDNS (RHOSTR, KPTR, NRES, NBONDS, ICOV, IION, IDXRES, MAXRES, MREF, NREF, LSTRES, LEN)

Permanently removes any ionic resonance structure from the list of candidates, if the ionic structure is reducible to another in the list by bond formation.

SR SECRES (IRES, DM, T, RHOSTR, BND OCC, TNBO, SCR, IDON, IACC, IDXRES, LSTRES, MAXRES, IREF, NREF, LEN)

Computes NBOs for each secondary structure from the hybrids of its parent.

SR SETAPP (NUMRES, NRES, ILIST, IDXRES, MAXRES, IREF, NREF)

Augments the list of secondary structures with structures which are related by concerted three-bond shifts.

SR APPEND (IRES, DM, T, RHOSTR, DELOC, BND OCC, TNBO, SCR, ICTR, IMAKE, IBRAK, IDN, QDN, IAC, QAC, IPAR, IHYB, IDON, IACC, IDXRES, MAXRES, IREF, NREF, LSTRES, LEN)

Computes NBOs for each of the structures generated by SRs KEKULE and SETAPP.

SR INITWT (ERRREF, ERR, RHOSTR, OCC, WGT, IST, IRANK, NRES, IRESET, MAXRES, NREF)

Computes a set of exponential resonance weights which will serve as the initial guess for the variational optimization procedures.

SR WGT OPT (ERRREF, ERR, RHOSTR, OCC, WGT, T, SCR1, SCR2, SCR3, SCR4, SCR5, SCR6, SCR7, SCR8, SCR9, IST, IPTR, KPAR, NRES, MAXRES, IRESET, MAXRES, NREF)

Calls the NRT optimization routines and computes the final optimized resonance weights. The exponential weights from SR INITWT are used as an initial guess.

SR HESSIN (RHOSTR, OCC, WGT, T, HESS, EVEC, EVAL, DER, G, IST, IPTR, NRES, MAXRES, IREF, NREF, IND)

Evaluates the Hessian of the variational functional for the optimized resonance weights. Zero eigenvalues of this matrix indicate numerical indeterminacy.

SR SUPPL (FW, WGT, WGTM, MAP, WGTP, IDXRES, KPAR, NRES, IRESET, IPTR, MAXRES, ICNT, NREF, MAXREF, NRTCTL, IVALSP)

Supplements the list of reference structures, as needed, using the secondary structures of highest resonance weight.

SR RESWGT (RHOSTR, WGT, WGTP, WGTM, ISCR, MAP, IRANK, NRES, IRESET, IDXRES, MAXRES, ICNT, NREF)

Performs multi-reference averaging, storing the final NRT weights in WGTM.

SR SYMWGT (RHOSTR, WGTP, WGTM, MAP, NRES, IRESET, IDXRES, MAXRES, ICNT, NREF, NRTCTL)

Loops over pairs of reference structures checking for symmetry inconsistency (equal  $\rho^*$  but unequal weights).

SR NRTOUT (RHOSTR, OCC, WGT, WGTP, SCR, WGTM, MAP, IST, NRES, IRESET, IDXRES, LSTRES, MAXRES, ICNT, NREF, LEN)

Prints a listing of the resonance structures and resonance weights.

SR NBDORD (BORDER, VALENZ, TOPO, WGT, XION, WGTP, NRES, IRESET, IDXRES, MAXRES, NREF, LSTRES, LEN, NLOW)

Computes and prints the natural bond orders, fractional ionic character, and atomic valencies.

SR NRTLST (MAP, WGTM, ICNT, NRES, IRESET, IDXRES, MAXRES, NREF, LSTRES, LEN)

Punches specified structures (default is references only) to output file as \$NRTSTR keylist.

#### *C.14.4 NRT optimization routines*

The routines of this group are responsible for minimizing the variational functional,  $d(\underline{w})$  (see SR GETERR, Sec. C.14.6), by optimization of the resonance weights. Several of these routines are modified versions of the algorithms presented in W. H. Press, B. P. Flannery, S. A. Teukolsky, and W. T. Vetterling, *Numerical Recipes*, Cambridge: New York, 1988, pp. 274-312. We refer the reader to this reference for an excellent discussion of minimization methods.

Due to the positivity and normalization conditions of the resonance weights, the variational treatment of these weights is a constrained optimization. To maintain the positivity condition, we do not explicitly optimize the resonance weights, but instead, treat the quantities

$$t_\alpha = -\ln w_\alpha$$

as variational parameters. Since we require normalization of the resonance weights, only  $(n_{RS}-1)$  variational parameters are optimized, the weight of the leading resonance structure ultimately determined by normalization. The symmetry of the resonance weights is maintained during optimization by constraining the weights of resonance structures with degenerate  $\rho^*$  values (usually indicative of symmetry-related resonance forms) to be identical.

Note that multi-reference treatments of the resonance weights require that  $n_{ref}$  separate optimizations be performed, one for each reference structure.

The following routines are used in the steepest descent optimizations:

SR SETOPT (RHOSTR, WGT, T, IPTR, NRES, MAXRES, IREF, NREF, NVAR)

Prepares a list of NVAR variational parameters in T. IPTR is used to map the values in T onto an array of resonance weights in WGT.

SR BFGS (FRET, FREF, OCC, WGT, P, HESSIN, XT, XIT, G, DG, HDG, DF, W, SCR, IPTR, IST, NRES, MAXRES, IREF, NREF, NVAR, ITER)

Performs the optimization of the variational parameters employing analytic derivatives of the variational functional. Optimization continues until the value of the functional (in FRET) is converged to a fractional tolerance of  $10^{-6}$ . The optimized resonance weights are returned to the calling routine in array WGT.

SR POWELL (FRET, FREF, OCC, WGT, P, XI, PT, XIT, PTT, W, WP, IPTR, IST, NRES, MAXRES, IREF, NREF, NVAR, ITER)

Optionally performs a numerical optimization of the variational functional using numerical derivatives. The optimized value (FRET) is converged to within a fractional tolerance of  $10^{-5}$ . The optimized resonance weights are returned to the calling routine in array WGT.

SR NLINMN (FRET, OCC, WGT, XT, P, XIT, IPTR, IST, NRES, MAXRES, IREF, NREF, NVAR)

Performs a linear minimization of the variational functional.

SR DLINMN (FRET, OCC, WGT, XT, P, XIT, DF, SCR, IPTR, IST, NRES, MAXRES, IREF, NREF, NVAR)

Performs a linear minimization of the variational functional, employing analytic derivatives.

SR MNBRAK (AX, BX, CX, FA, FB, FC, OCC, WGT, XT, P, XIT, IPTR, IST, NRES, MAXRES, IREF, NREF, NVAR)

Brackets the minimum along a line through configuration space.

FN BRENT (AX, BX, CX, FB, TOL, XMIN, OCC, WGT, XT, PT, XIT, IPTR, IST, NRES, MAXRES, IREF, NREF, NVAR)

Locates the minimum along a line in configuration space, using parabolic interpolation and golden section techniques.

FN DBRENT (AX, BX, CX, FB, TOL, XMIN, OCC, WGT, XT, P, XIT, DF, SCR, IPTR, IST, NRES, MAXRES, IREF, NREF, NVAR)

Locates the minimum along a line in configuration space using analytic gradient information, parabolic interpolation, and golden section techniques.

FN F1DIM (X, OCC, WGT, XT, P, XIT, IPTR, IST, NRES, MAXRES, IREF, NREF, NVAR)

Returns the value of the functional to FN BRENT and FN DBRENT.

FN DF1DIM (X, OCC, WGT, XT, P, XIT, DF, SCR, IPTR, IST, NRES, MAXRES, IREF, NREF, NVAR)

Returns the derivative of the functional to FN DBRENT.

FN PHI (T, OCC, WGT, IPTR, IST, NRES, MAXRES, IREF, NREF, NVAR)

Computes the value of the functional (with the aid of SR GETERR) at the point T in configuration space.

SR DPHI (DER, T, OCC, WGT, SCR, IPTR, IST, NRES, MAXRES, IREF, NREF, NVAR)

Computes the derivatives of the functional (with the aid of SR GETERR and SR GETGRD) at the point T in configuration space.

The following routines are used in the simulated annealing optimization of the resonance weights:

SR ANNEAL (XLAM, ERRREF, ERR, RHOSTR, OCC, WGT, T, SCR, IPTR, IST, NRES, MAXRES, IREF, NREF, ISEED, NVAR, ITT)

Controls the simulating anneal (SA) optimization. SA optimization continues until both the fractional improvement  $f(w)$  and step size is converged to  $10^{-5}$ . The optimized resonance weights are returned to the calling routine in WGT.

SR SETANN (RHOSTR, WGT, T, IPTR, NRES, MAXRES, IREF, NREF, NVAR)

Prepares the array T with the NVAR resonance weights to be optimized.

SR ADJUST (T, IT, NVAR, SSIZE, STEP, ISEED)

Randomly adjusts the IT-th element of T. STEP is the largest acceptable change in the weight and SSIZE is the actual step size.

SR METROP (NSUC, FW2, FW1, FT, ISEED)

Employs the Metropolis algorithm to determine whether the given set of weights is acceptable. FT is the annealing 'temperature'.

SR RESTOR (T, IT, NVAR, SSIZE)

Restores T(IT) to its original value if SR METROP found the set of weights to be unacceptable.

### *C.14.5 Branching routines*

The routines of this group perform a variety of tasks which guide the NBCHSE routine in the search for "iso-Lewis" resonance structures (i.e., structures that share the same skeletal pattern of bonds and lone pairs but correspond to distinct electron configurations).

Briefly, these routines maintain a set of "branching indices" (in COMMON/NBALT/) that are used to select orbitals at "branch points" which occur each time SR NBCHSE has to select NUM orbitals from a list of NC candidates (NUM

Each branch point (requesting NUM orbitals from NC candidates) is assigned a branching index (stored in JDX in COMMON/NBALT/), which is an INTEGER variable of NUM digits, each digit specifying one of the NC candidates to accept. For example, a branch point (NUM=2, NC=3) is initially assigned an index of 21, indicating that the first and second candidate orbitals should be accepted. On subsequent passes through SR NBCHSE, this index may be incremented to 31, thereby indicating that the first and third candidates should be selected. Incrementing continues until the branching index reaches its limiting value (stored in IDX of COMMON/NBALT/).

Note that if the first NH of the NC candidate orbitals ( $NH \leq NC$ ) have orbital occupancies greater than 1.7 electrons, the branching index is constrained such that SR NBCHSE will always accept these NH candidates as NBOs.

The following routines maintain the branching indices:

SR IDCTRL (IREF)

Controls the loops through SR NBCHSE, resetting the JCNT index counter (in COMMON/NBALT/) as needed. If IREF is positive on return to the calling program, the NRT program should continue looping over the current TOPO matrix.

SR IDINIT (ICNT, NC, NH, NUM)

Initializes the ICNT-th branching index and computes its limiting value. There are NUM orbitals to select from NC candidates of which NH have occupancy greater than 1.7 electrons.

SR IDINCR (ICNT, NC, NH, NUM)

Increment the ICNT-th branching index. ICNT should never be less the index counter JCNT of COMMON/NBALT/.

FN IDTEST (JDXT, IC, NUM)

Test the branching index in JDXT to determine whether the IC-th orbital should be accepted (IDTEST=1) or rejected (IDTEST=0). The orbital IC is accepted if either JDXT is negative or the digit IC appears in the integer JDXT.

SR IDCLR

Clears the arrays in COMMON/NBALT/.

SR IDCOPY

Copies the arrays of COMMON/NBALT/ into COMMON/NBALT1/.

SR IDREST

Copies the arrays of COMMON/NBALT1/ into COMMON/NBALT/.

#### *C.14.6 NRT utility routines*

These utility routines perform a variety of computational tasks pertinent to the calculation of resonance structures and weights. These routines are grouped alphabetically in the NRT source code.

SR ATMORD (WIBERG, NRT)

Determines the atom ordering which will be used by SR NBCHSE during the search for electron pairs. The search should begin with the pair of atoms whose formal bond order (TOPO matrix element) is larger than its Wiberg bond index. The search continues, following the atom connectivity of the TOPO matrix.

FN CHARAT (IZ)

Returns the atomic symbol (CHARACTER\*2) for a center with atomic number IZ.

FN CMPFW (XLAM, ERRREF, ERR, T, OCC, WGT, IPTR, IST, NRES, MAXRES, IREF, NREF)

Computes the fractional improvement  $f(\underline{w})$  for the resonance weights (of reference structure IREF) listed in array WGT. If XLAM is positive, a penalty function is added to the calculation of  $f(\underline{w})$ .

SR EXPWGT (RHOW, RHOSTR, WGT, IRANK, NRES, MAXRES, IREF, NREF, N)

Computes a set of normalized exponential (Boltzmann-like) weights

$$w_{\alpha} \propto \exp(-\rho_{\alpha}^*/\rho_w) \rho_w = 1/3$$

which provide the initial guess for the NRT optimization routines.

SR FETREF (T, LABEL, IBXM, IREF)

Fetches the NAO-NBO transformation and labels for reference structure IREF.

SR GETDM (T, DM, TR, SCR1, SCR2, SCR3, IST, IOCC, NVAL, IERR)

Calculate the valence NAO density matrix from the full NAO-NBO transformation, the orbital type index (core, valence, extra-valence) and the orbital occupancy index (unoccupied or occupied).

SR GETDW (DW, GAMMAW, WGT, LVAL, NREF)

Calculates the value of the multi-reference variational functional

$$D(\underline{W}^{(r)}) = \min \{n^{-1} \text{Tr} (\mathbf{\Gamma} - \sum_r W^{(r)} \mathbf{\Gamma}^{(r)})^2\}^{1/2}$$

SR GETERR (ERROR, WGT, OCC, IST, NRES, MAXRES, IREF, NREF, ICTRL)

Computes the value (returned in ERROR) of the variational functional

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

for the weights listed in WGT.

SR GETFDM (DM, DELOC, TNAO, TBO, SCR)

Retrieves the Fock matrix (in the NBO basis) from the NBO DAF, storing it in DELOC. If not available, the NBO density is placed in DELOC.

SR GETGRD (DER, T, WGT, OCC, G, IST, IPTR, NRES, MAXRES, IREF, NREF, NVAR)

Computes the derivatives of the variational functional with respect to the resonance weights.

SR GETHES (HESSIN, DER, T, WGT, OCC, G, IST, IPTR, NRES, MAXRES, IREF, NREF, NVAR, IFLG)

Computes the Hessian of the variational functional,  $d(\underline{w})$ .

SR GETREL (IBO, IBOP, IUNIT1, IUNIT2, IREL, IA, IB, IC, ID)

Determines the relationship (geminal, vicinal, remote) of the delocalizing NBOs IBO and IBOP. IREL is set according to the type of delocalization, and IA,IB,IC,ID are the atomic centers of the interacting orbitals. IUNIT1 and IUNIT2 are not implemented.

FN INTRN (ILLIM, IULIM, ISEED)

Returns an INTEGER random number in the range (ILLIM, IULIM), inclusive. ISEED is the seed for the random number generator.

SR MULTI (FW, GAMMAW, WGT, SCR, IRESET, LVAL, NREF)

Computes the relative weights (WGTP) of the reference manifolds in a multi-reference analysis.

SR NRTINP (IESS, INRT)

Searches the input file for the \$NRTSTR identifier (or \$NRTSTRA or \$NRTSTRB identifiers for open-shell wavefunctions) according to the program version number IESS.

SR PRTWGT (IRES, IR, WGT, II, IAT, JJ, JAT, IFLG)

Collects information (weight, connectivity) about the IRES-th resonance structure and prints it to the output file. This routine is initialized by IRES=0, collects info when IRES>0, and prints when IRES

FN RAN (IDUM)

Returns a uniform random deviate between 0.0 and 1.0. IDUM is the random number seed, set negative to initialize or reinitialize the random sequence. Note that this is RAN2 from p. 197, Numerical Recipes.

FN REALRN (XLLIM, XULIM, ISEED)

Returns a REAL\*8 random number in the range (XLLIM, XULIM), inclusive. ISEED is the seed for the random number generator.

SR SVTREF (T, LABEL, IBXM, IREF)

Saves the NAO-NBO transformation and labels for reference structure IREF.

SR TOPCMP (IDUP, IRES, IDXRES, MAXRES, IREF, NREF, LSTRES, LEN)

Compares the IRES-th TOPO matrix for reference structure IREF with the others in the LSTRES array. If an identical copy is found, IDUP is set to one.

SR TOPGET (IRES, IDXRES, MAXRES, IREF, NREF, LSTRES, LEN)

Retrieves the IRES-th TOPO matrix for reference structure IREF from LSTRES and stores it in COMMON/NBSTR/.

SR TOPOUT

Prints the TOPO matrix, stored in the ITOPO array of COMMON/NBSTR/, in the output file.

SR TOPSTR (IRES, IDXRES, MAXRES, IREF, NREF, LSTRES, LEN)

Stores the IRES-th TOPO matrix (from COMMON/NBSTR) in condensed form in the array LSTRES.

SR TOPZER (NATOMS)

Sets the elements of the ITOPO array to zero in COMMON/NBSTR/.

SR WGTOUT (WGT, NRES, MAXRES, IREF, NREF)

Prints a condensed list of resonance weights for the IREF resonance structure.

SR WGTPR (WGTM, MAP, NWGT)

Prints the multi-reference optimized resonance weights.

SR WNORM (WGT, IRESET, IW, IP, SKIP)

Renormalizes multi-reference weights after a change in the multi-reference variational functional.

## C.15 NBBP ROUTINES

The NBBP module consists of about 450 lines of portable Fortran-77 code. The routines of this module use NBO scratch storage and external scratch files, and thus have no impact on NBO memory allocation. The NBBP routines are invoked by a single CALL NBBP statement in SR NBODRV, and aside from the explicit argument list of this call, all communication is through scratch files or unmodified COMMON blocks. Thus, the NBBP routines have minimal impact on overall NBO program structure, and they present no added difficulties in interfacing NBO to a new ESS.

The NBBP module consists of the main SR NBBP and four utility programs (two subroutines and two functions), as described below. Communication between these routines is through explicit argument lists or scratch files.

SR NBBP (T, TMO, BBP, SCR, LFN)

Fetches the AO Fock matrix from storage, transforms to the NHO basis, and evaluates the  $\Pi_{b,b'}$  expression for each occupied NBO, printing the result to the output file. If supplementary elements are requested in a file-input bracket, the routine will scan the bracketed entries (as rewritten to scratch file LFN with the help of SR FNDFIL) for each set of 4 NHO indices, compute the NBBP values and the signs of Fock matrix elements needed to assign the "corrected"  $[\text{sgn}(F_{rs}F_{tu})\Pi_{rs,tu}]$  values, and print the results as a supplementary table in the output file.

SR FNDFIL (LFN, ERROR)

General utility to read entries of a file-input bracket and write them as separate

lines to scratch file LFN. File LFN is rewound for subsequent reading and parsing by other programs. SR FNDFIL automatically selects a unique scratch filename (NB\$\_01.\$\$\$, NB\$\_02.\$\$\$, etc.) and LFN number (61, 62, etc.) for up to 20 file-input brackets. The program returns with LFN=0 (and logical ERROR=.FALSE.) if no file-input bracket is detected, and returns with logical ERROR=.TRUE. if a syntax error is encountered.

SR NBPARS (STR, NV, IVAL)

General utility to parse string STR into NV integer values: IVAL(1), IVAL(2),..., IVAL(NV).

FN NBINTV (STR)

General utility to convert string STR to an integer value.

FN LENNB (STRING)

General utility to evaluate the non-blank length of string variable STRING.

## **C.16 NATURAL STERIC ANALYSIS ROUTINES**

The NBSTER module consists of one main routine SR NBSTER and one utility routine SR WORTUN, comprising about 500 lines of portable Fortran-77 code. SR NBSTER uses existing NBO scratch storage and an external scratch file (previously created) from which integer indices are read, while SR WORTUN uses six 2 x 2 arrays. One parameter, STTHR, is added to COMMON/NBTHR/ to specify the threshold for printing. NBO/NLMO steric analysis is invoked by a single CALL NBSTER statement in SR NBODRV (placed just before the 2nd-order perturbation analysis call). Communication with other routines is through six arguments in the call and existing COMMON blocks of the NBO program, and so presents no added difficulties in interfacing NBO to a new ESS.

SR NBSTER (T, S, FNLMO, SCR, MOLNBO, LFNSTR)

Fetches the NLMO Fock matrix and forms the PNLMO overlap and Fock matrices; calculates orbital energy changes due to exchange effects and calculates steric exchange energy; breaks down steric effects pairwise and prints a table of steric orbital interactions. [Thresholds STTHR1 (intramolecular) and STTHR2 (intermolecular) control printing.] If supplementary orbital interactions were requested using bracketed input format (previously read in by SR FNDFIL called from SR JOBOPT; see Sec. C.15 for details), the routine will read the pairs of NBO indices from a scratch file with LFN number LFNSTR, compute the pairwise steric interaction energies, and print the results as a supplementary table in the output file.

SR WORTUN (FO, S, W, FP, IERR)

Utility routine to calculate the 2 x 2 "pre-orthogonal" Fock matrix for two orbitals by doing a reverse occupancy-weighted orthogonalization of two (NLMO) orbitals.

## C.17 NEDA ROUTINES

Natural Energy Decomposition Analysis is implemented in the energetic analysis module of the NBO program. SRs NBOEDA and EDAOUT guide the calculation of the energy components and a highly modified version of SR DELSCF controls the calculation of fragment wavefunctions. Communication between these routines is provided by the existing COMMON blocks of the NBO program, COMMON block /NBEDA/, and several reserved records of the NBO direct access file.

NEDA is fully implemented only in the GAMESS version of the NBO program.

SR NBOEDA (T, DM, SCR1, SCR2)

Loops over fragments, preparing the wavefunction  $\psi^{(\text{def})}$  for each. Transformation and density matrices are stored on the NBO DAF to be retrieved later by SR DELSCF.

SR EDAOUT (ETOT, E, LISTA)

Collects energies calculated by SR DELSCF and writes the NEDA summary table.

SR SVNEWF (F)

Saves the current AO Fock matrix to records 73,74 of the NBO DAF.

SR FENEWF (F)

Retrieves AO Fock matrices from the DAF

SR SVNEWT (T)

Saves the NBO to MO transformation matrix on records 71,72 of the NBO DAF.

SR FENEWT (T)

Retrieves the NBO to MO transformation from the DAF

SR SVTEDA (T)

Save fragment MOs (AO-MO transformation matrices) to record 84,85 of the NBO DAF.

SR FETEDA(T)

Retrieves the fragment MOs from the DAF.

SR SVEIG(U)

Save MO energies for each fragment to record 82,83 of the NBO DAF.

SR FEEIG(U)

Retrieves the MO energies from the DAF.

The following are extended versions of the NBO 3.0 routines:

SR DELSCF

This routine calculates the energy of the fragment wavefunction  $\psi^{(\text{def})}$  with a single pass through the SCF routines and then variationally optimizes the wavefunction. Modifications include (in order performed):

1. Calculates the 1-e integrals for the fragment wavefunction. The nuclear attraction integrals differ from those of the full complex (supermolecule).
2. Calculates the dipole moment of  $\psi^{(\text{def})}$ . The origin is translated to the center of mass for charged fragments.
3. Evaluates  $E[\psi^{(\text{def})}]$  with a single pass through the SCF routines.
4. Variationally optimizes the fragment wavefunction (in the full basis set of the complex) using standard damping, DIIS, and direct energy minimization convergence accelerators.
5. Calculates the dipole moment of the optimized wavefunction.
6. Recalculates the 1-e integrals for the complex.

SR NBOEAN(A, MEMORY, NBOOPT, IDONE)

Prepares the scratch vector for NEDA and calls SRs NBOEDA and EDAOUT.

SR NBODEL(A, MEMORY, IDONE)

Saves MOs and MO energies to DAF:

SR NBDELE

Reads NEDA input from the \$DEL keylist.

The following records of the NBO DAF have been reserved for NEDA:

---

70	Wavefunction energies
71	NBO-MO transformation matrix (alpha)
72	NBO-MO transformation matrix (beta)
73	AO Fock matrix (alpha)
74	AO Fock matrix (beta)
75	ZAN nuclear charges of /INFOA/
76	IZCORE of /ECP2/
77	LPSKIP of /ECP2/
78	LMAX of /ECP2/
82	MO energies (alpha)
83	MO energies (beta)
84	AO-MO transformation (alpha)
85	AO-MO transformation (beta)

---

One COMMON block has been added to facilitate communication between the various NEDA routines:

```
COMMON /NBEDA/ KFRG, NFRG, IFRG (MAXBAS) , NFE (MAXBAS) , NFEB (MAXBAS)
```

---

KFRG	Index indicating current fragment
NFRG	Number of fragments
IFRG	Array mapping NBO molecular units onto NEDA fragments
NFE	Number of electrons assigned with each of the NFRG fragments
NFEB	Number of beta electrons assigned to each of the fragments

---

## C.18 CHECKPOINTING ROUTINES

The checkpointing module consists of about 600 lines of portable Fortran-77 code. The routines of this module generally use NBO scratch storage and

external scratch files, and thus have negligible impact on NBO memory allocation. A single labelled common block

COMMON/NBPRMC/LFNPRM

is used to store the logical file number of the permutation information read from a file-input bracket and stored on an external scratch file for processing by SR RDPERM. The checkpointing option is flagged in JPRINT(63), and checkpoint storage is assigned to records 80 (alpha spin) and 81 (beta spin) of the NBO direct-access file.

The main subroutines associated with checkpointing options are listed below. SR RDPERM uses general utilities (SR FNDFIL, etc.) associated with file-input brackets. I/O to the DAF is handled by SR FECHK, SR SVCHK (Sec. C.7), which read/write the checkpoint transformation to record 80 (alpha) or 81 (beta) according to spin flag IS.

SR CHKNBO (CORE)

This is the main ESS-specific routine to store transformation information in the host direct-access file, using general DAF I/O routines.

SR SRTCHK (DM, T, S, SCR, IRNK)

Sorts the checkpointed orbitals stored in T according to occupancy, using diagonal populations stored in density matrix DM. On return, the permuted orbitals in T have highest occupancy first, lowest occupancy last.

SR RDPERM (T, S, IRNK, ARC, ITMP, IORG, LIST)

Reads the list of labels or numbers originally provided in a checkpointing bracket, now stored in scratch file LFNPRM. SR RDPERM locates the Fermi marker ``|'' (if any), reads the labels or numbers and associates them with entries of the specified localized orbital list, then permutes the transformation matrix T to desired order, using IRNK, etc., as scratch.

SR FILFLD (LFN, STR, LENGTH, IAMNEW, END)

Finds next non-blank field STR(1:LENGTH) in LFN. Set IAMNEW=1 for first read from a new file, 0 otherwise.

## **C.19 CANONICAL MO ANALYSIS ROUTINE**

SR CMOANL (TMO, TMP, SCR, IFLG)

This routine organizes and prints the two tables describing CMO composition: (1) the table of LCNBO-MO compositions, and (2) the table of atom-atom bonding character character. The subroutine is essentially self-contained, with calls only to general utility routines and fetches from the DAF file. Note that

this routine uses CMOs provided by the host ESS program, rather than determined by direct diagonalization of the Fock matrix. This insures closest agreement with other displays of the host CMOs, but may result in some details of CMOANL output differing from one host ESS to another (depending on the numerical treatment of degeneracies in the host program).

## **C.20 NATURAL CHEMICAL SHIELDING ANALYSIS ROUTINES**

At present the NCS method is implemented only under Gaussian 98.

The NCS module consists of about 1350 lines of code and employs LFN 26-31 disk files as scratch storage. Two main subroutines (called successively from NBODRV) control the overall NCS task: SR NCSMAT supervises import of GIAO derivative matrices from the host ESS program through calls to the G98 subroutine DENBAS and direct fetches from the G98 read-write file. (This is the only subroutine that must be rewritten to attach NCS to a new host ESS.) SR NCSANL is the main driver for assembling and printing the tables requested by the user.

SR NCSMAT (C10, V, MDV)

This ESS-dependent subroutine is called in NBODRV immediately before NCSANL to carry out two tasks:

- (1) Read the C10 matrix of MO coefficient derivatives with respect to magnetic field from the G98 read-write file;
- (2) Calculate (with SR DENBAS) the H01 and H11 matrices containing magnetic field derivatives of the 1-e Hamiltonian and write out the results to disk with SR MATWR. (Note that Link 1002 does not save these quantities after calculating chemical shifts.)

SR NMRWR (D, IX, JY, KZ, IFI, NCF)

Called by NCSMAT to write records to temporary disk files NMR\_H01 (LFN 28) and NMR\_H11 (LFN 27) containing one-electron derivative matrices H11, H01 calculated by G98 DenBas.

SR NCSANL (NATOMS, NBAS, NOCC, A, B, C, D, T, H01J, C10X, C10Y, C10Z, ENER, LFNPR, SCR1, SCR2, SCR3, SCR4, LFNCS, IATNO)

This is the main NCS driver. It reads the < options > bracket list, assembles the necessary matrices from the NBO DAF file, opens scratch files (LFN 24-26), and calls the routines NCSATM, NCSXYZ, and NCSISO to compute and print the requested optional tables.

SR NCSATM (IAT, A, B, D, T, C, C10X, C10Y, C10Z, NBAS, NOCC, LFNU, LFNI, SCR1, SCR2, SCR3, SCR4, H01J, IWCMO)

Called by NCSANL to analyze the shielding tensor for a particular atom. Uses H01 matrices and SR NCSUAJ, NCSIAJ.

SR NCSUAJ (IAT, JY, A, B, D, C, NBAS, NOCC, LFNU, H11XJ, H11YJ, H11ZJ, SCRA, IWCMO)

Compute and print unperturbed (diamagnetic) contributions for a chosen atom.

SR NCSIAJ (IAT, JY, A, B, T, C, C10X, C10Y, C10Z, NBAS, NOCC, LFNI, H01JY, SCRX, SCRY, SCRZ, SCR, IWCMO)

Compute and print induced (paramagnetic) contributions for a chosen atom.

SR NCSISO (NOCC, NATM, NUC, SIGISO, LFNISO, LFNPR, IWCMO)

Compute and print summary table of contributions to isotropic shielding (default).

SR NCSCSA (IAT, SIGTOT, LFNX, LFNY, LFNZ, LFNPR, IWCSA, IZ, ITYP, R, IORDER, IWCMO)

Diagonalize shielding tensor and calculate chemical shift anisotropy (CSA) and isotropic contributions.

SR NCSXYZ (IAT, NBAS, NOCC, SIGXL, SIGYL, SIGZL, LFNU, LFNI, LFNPR, LFNISO, IWXYZ, IWCSA, IWD, IWP, IZ, R, IORDER, IWCMO)

Compute and print contributions to cartesian shielding tensor components.

SR FEH01 (IAT, IY, H01I, NBAS, IERR)

Called by NCSATM to fetch derivative matrix with respect to magnetic field (x,y,z) for induced (paramagnetic) term.

SR FEH11 (IAT, IX, JY, H11I, NBAS, IERR)

This is called by NCSATM to fetch individual H11 matrices (for ``11" = xx, yx, yz, xy, yy, zy, xz, yz, zz) from file NMR\_H11 for a particular unperturbed atom (diamagnetic term).

FN TRCNCS (A, B, NDIM)

Calculate trace of matrix product AB.

## **C.21 NATURAL J-COUPLING ROUTINES**

At present the Natural J-Coupling (NJC) analysis is implemented only under Gaussian 9X.

The NJC module consists of about 2000 lines of code and employs LFN 91,92 disk files as scratch storage. The necessary ``integrals" over the Dirac delta

function operator are performed by SR AOVVAL. The main output table is prepared by SR NJCTAB from data pre-processed and stored by routines NJC and NJCANL in successive JOB-*n* steps.

SR NJC (TBL, FCG, FCB, FCL, TBLA, TBLB, FCBA, FCBB, FCLA, FCLB,  
DJI\_NL, DI\_L, DPJI\_NL, DPI\_L, SCR1, SCR2, V1, V2, V3, V4, LFNPR)

This routine is the only direct call from NBODRV. It carries out the evaluation of Fermi-contact amplitudes in the Gaussian AO basis (FCG), NBO basis (FCB), and NLMO basis (FCL), prepares the NBO to NLMO transformation (TBL) to be written to the disk (LFN 91, 92) for each spin set, and reads the identity of the spin-perturbed atom (IATNP) from the NBO filename. All other arguments are passed through to SR NJCANL, which controls the subsequent steps of NJC analysis.

SR NJCANL (IATNP, TBLA, TBLB, FCBA, FCBB, FCLA, FCLB,  
DJI\_NL, DI\_L, DPJI\_NL, DPI\_L, SCR1, SCR2, V1, V2, V3, V4, LFNPR)

This routine is called from NJC after beta spin FC-amplitudes are written to disk. It first prepares the array of  $\Delta_{ji}^{(NL)}$  (DJI\_NL) and  $\Delta_i^{(L)}$  (DI\_L) values from the alpha and beta FC-amplitudes (FCGA, FCGB, etc.) and NBO→NLMO transforms (TBLA, TBLB) for each spin set. It then writes these arrays for each atom into a disk file D\_*n*.DAT, where *n* is the perturbed atom IATNP. The disk is then searched for previously written D\_*m*.DAT files, and from these files the symmetrized DJI\_NL, DI\_L arrays are prepared and passed to SR NJCTAB for analysis of J[*n,m*] coupling for each IATN, IATNP pair.

SR NJCTAB (IATN, IATNP, DJI\_NL, DI\_L, DELOC, REPOL, SUMBI, SUMBJ, DM, T, LFNPR)

Called by SR NJCANL (with input DJI\_NL, DI\_L arrays) to print the table of localized J-coupling contributions for atoms IATN, IATNP, based on print control threshold THRNJC. This routine also prepares the NHO Fock matrix (using DM, T) that is used to determine the through-bond coupling path across H-bonds.

SR NJCATM (IATNP)

Reads the FILENM parameter from COMMON/NBNAME/ to determine the perturbing atom IATNP for this job (JOB\_*n*).

SR NJCLNK (IA, IB, LINKS, NLINKS)

Finds the shortest bond-connected linkage, LINKS(I), I = 1, NLINKS, between atoms IA, IB in the same molecular unit (up to 7 links).

SR NJCLAB (IATN, IATNP, LINKS, NLINKS, MOLLOC, TITLE)

Prepares the through-bonds label (in string variable TITLE) for the composite LINKS between atoms IATN, IATNP, employing the vector MOLLOC that identifies the molecular unit for each atom.

SR FNDHYBS (INBO, IH1, IH2, IH3)

Determines the NHOs (IH1, IH2, IH3) that compose input NBO (INBO).

SR CONSTFC (CGYRO, IZ1, IZ2, IPR, LFNPR)

Evaluates the multiplicative constant that converts atomic units to Hz, using magnetogyric ratios for nuclei IZ1, IZ2. If IPR is non-zero, the subroutine prints the isotopic magnetogyric ratios.

SR RMBLNK (STR, NS)

Removes blanks from string variable STR(1:NS).

FN IPHTYP (IBO, JBO)

Modified form of FN IHTYP that identifies relationship of NBOs IBO, JBO as vicinal ('v'), geminal ('g'), remote ('r'), or internal ('i'), allowing gathering of the latter into the "repolarization" contribution. JBO is "internal" to IBO if the atom(s) of JBO are a proper subset of those of IBO.

SR FCAOEL (FCAO, SCR, ISCR, NBAS, NDIM, NATOMS)

Evaluates the FC-amplitudes of Gaussian AO basis functions FCAO(NBAS,NATOMS) at all atoms.

SR NBRSTR (FVAL, STR, NS)

Converts a real value FVAL to string form STR(1:NS).

SR NBISTR (INT0, STR, NS)

Converts an integer value INT0 to string form STR(1:NS).

SR AOVAL (AOAMP, R, ORIGIN)

This is the basic program to evaluate the amplitudes (AOAMP) of atomic orbitals (centered on points ORIGIN) at the vector position R. All remaining routines of this module assist AOVAL.

FN AOAFAC (R, ITYPE)

Computes "atomic orbital structure factor" for this orbital type.

SR ITYPERR (ITYPE)

Prints error message for illegal values found by STRUCF.

SR STRUCF (ITYPE, NKAL, CAL, NXAL, NYAL, NZAL)

This routine returns the parameters making up the structure factors for the atomic orbital labeled by ITYPE. The comments in this subroutine describe the meaning of parameters and general expansion form for Gaussian AOs.

SR BNORM

Normalizes the Gaussian AO basis functions stored in COMMON/NBORBP/.

FN AONORM (ITYPE, ZETA1, ZETA2)

This routine computes the overlap between two Gaussian atomic orbitals located on the same center. Each has the same angular symmetry specified by ITYPE, but different Gaussian exponents (ZETA1 and ZETA2).

FN ATMFACT (R, N)

Utility routine for atomic orbital structure factor.

FN OLAPCG (N1, ZETA1, C1, N2, ZETA2, C2)

Computes the overlap of two cartesian Gaussians, one described by X, Y, Z exponents in N1, Gaussian exponent ZETA1, and centered at C1 (in atomic units), and a second Gaussian described by N2, ZETA2, and C2.

FN OLAP1D (NX1, ZETA1, X1, NX2, ZETA2, X2, ALFA)

Evaluates the 1-dimensional overlap of two Gaussians.

## **C.22 NATURAL 3-CENTER HYPERBOND ANALYSIS ROUTINE**

The Natural 3-Center Hyperbond subroutine NB3CHB consists of about 150 lines of code, with no calls to other routines. SR NB3CHB starts from potential hyperbonding patterns (A-B :C) of the NBO Lewis structure, searching for triples of NHOs h(A), h(B), h(C) with sufficient overlap, population, and symmetry to constitute a significant 3-center hyperbond (with apparent percentage of A-B :C vs. A: B-C character within a 2:1 ratio, approximately the weighting for both to be considered as NRT reference structures). Information gathered by SR NB3CHB is passed to NRT and other routines through the labelled COMMON block

COMMON/NBHB/N3CHB,I3CHB(MAXHB,3)

where N3CHB is the number of 3-center hyperbonds and I3CHB(MAXHB,3) is the integer array of three atomic hybrids for each hyperbond. The row dimension of I3CHB (maximum allowed number of hyperbonds MAXHB) is set to MAXATM/3.

SR NB3CHB (DM, LFNPR)

Searches the input NHO density matrix (DM) for hyperbonding A-B :C  $\longleftrightarrow$  A: B-C patterns of sufficient strength (%-weighting > 33%), writes output table to LFNPR, and stores tabulated results in COMMON/NBHB/.