Charge-Transfer Excitations Made “Simple” by Subsystem DFT

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What is PRG interested in?

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Ab-Initio Modeling of Realistically Sized Systems *with subsystem DFT!*

- Charge transfer phenomena
  - **Electronic structure and couplings**
  - Application to biosystems, and organic electrode materials
    → DNA, Sulfite Oxidase (SCM booth)
    → Organic electrode materials based on croconate crystals
- Electronic structure of periodic systems [Davide Ceresoli]
  - AIMD, RT-TDDFT, Ehrenfest
    → RT-TDDFT, Ehrenfest (Thursday afternoon)
    → Ground state (Poster)
  - Application to molecules at surfaces, liquids, ionic crystals, etc
- Linear-response TD-DFT and vdW [Henk Eshuis]

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  - All-electron method
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  - Can be used in conjunction with TD-DFT, but self-interaction error complicates things
  - As accurate as the method for computing the adiabatic states

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- Fragment Orbitals
    - Frozen core method
    - F. Grozema, M. Ratner, J. L. Bredas, J. Blumberger, M. Elstner, . . .
    - The most common method
    - About 20%-40% accurate [J. Chem. Phys. **140** , 104105 (2014)]

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- Frozen Density Embedding (FDE-ET)
  - All-electron method
  - M. Pavanello, J. Neugebauer, L. Visscher
  - New method [J. Chem. Phys. **138** , 054101 (2013)]
  - Better than 10% accurate [Submitted to J. Phys. Chem. B]

Tackling large systems with subsystem DFT: FDE

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- Split the system into (smaller) interacting subsystems
- Partition of the total electron density into subsystem contributions[1]

$$\rho(\mathbf{r}) = \rho_I(\mathbf{r}) + \rho_{II}(\mathbf{r}) \qquad \rho_{I/II}(\mathbf{r}) = \sum_i^{occ_{I/II}} |\phi_{I/II,i}(\mathbf{r})|^2$$

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$$F^{\mathrm{nadd}}[\rho_I, \rho_{II}] = F[\rho] - F[\rho_I] - F[\rho_{II}]$$

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- **Frozen Density Embedding** (FDE): coupled Kohn–Sham equations for each subsystem

$$\frac{\delta E[\rho_I + \rho_{II}]}{\delta\, \rho_I} \rightarrow \left[-\frac{1}{2}\nabla^2 + v_{KS}^I(\mathbf{r}) + v_{emb}^I(\mathbf{r})\right] \phi_i^I(\mathbf{r}) = \varepsilon_i^I \phi_i^I(\mathbf{r})$$

---

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KS equations in Frozen Density Embedding (FDE)^a

$$
\begin{aligned}
v^I_{\mathrm{KS}}(\mathbf{r}) &= v^I_{nuc}(\mathbf{r}) + \int \frac{\rho_I(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}' + \frac{\delta E_{xc}[\rho_I]}{\delta\, \rho_I} \\
v^I_{emb}(\mathbf{r}) &= v^{II}_{nuc}(\mathbf{r}) + \int \frac{\rho_{II}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}' + \frac{\delta E^{nadd}_{xc}[\rho_I, \rho_{II}]}{\delta\, \rho_I(\mathbf{r}')} + \frac{\delta T^{nadd}[\rho_I, \rho_{II}]}{\delta\, \rho_I(\mathbf{r}')}.
\end{aligned}
$$

KS equations in Frozen Density Embedding (FDE)[a]

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\end{aligned}
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Non-additive functionals approximants

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- $E^{\mathrm{nadd}}_{xc}[\rho_I,\rho_{II}]$: GGA functionals

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- $T^{\rm nadd}_{s}[\rho_I,\rho_{II}]$: orbital-free GGA expressions

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. . . if use LDA:

$$\frac{\delta T^{\mathrm{nadd}}[\rho_I,\rho_{II}]}{\delta\rho^I(\mathbf{r}')} = \frac{5}{3}C_F\left\{\left[\,\rho_I\,(\mathbf{r}') + \rho_{II}\,(\mathbf{r}')\,\right]^{2/3} - \left[\,\rho_I\,(\mathbf{r}')\,\right]^{2/3}\right\}$$

Donor–Acceptor Picture
Diabatic states

Donor–Acceptor Picture

Diabatic states

- Model Hamiltonian

$$\hat{H} = H'_{ii}|i\rangle\langle i| + H'_{if}|i\rangle\langle f| + H'_{ff}|f\rangle\langle f|$$

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- Basis set for a hole transfer reaction

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$$\text{Initial state} \quad \rightarrow \left[D\right]^{+} - (\text{bridge}) - \left[A\right]$$

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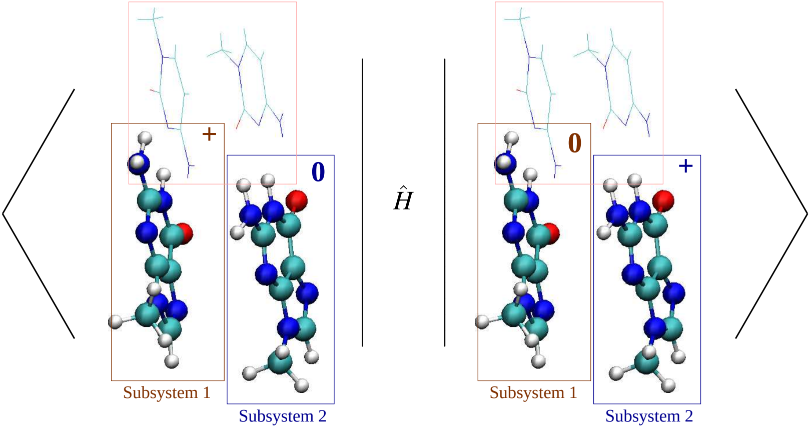
Diabatic representation: making charge-localized states with FDE



Electronic Couplings With Subsystem DFT[a]: FDE-ET

Hartree–Fock

$$H_{if} = \langle \Phi_i | \hat{H} | \Phi_f \rangle = E\left[\rho^{(if)}(\mathbf{r})\right] S_{if}$$

where $S_{if} = \langle \Phi_i | \Phi_f \rangle$, and

$$\rho^{(if)}(\mathbf{r}) = \sum_{kl} \phi_k^{(i)}(\mathbf{r}) \left(\mathbf{S}^{(if)}\right)^{-1}_{kl} \phi_l^{(f)}(\mathbf{r})$$

where $\mathbf{S}_{kl}^{(if)} = \langle \phi_k^{(i)} | \phi_l^{(f)} \rangle$

Subsystem DFT formalism

$$H_{if} = E\left[\rho^{(if)}\right] S_{if} \qquad \ldots \textbf{an approximation}$$

$$H_{if} = \left[\left(\sum_I^{N_S} E\left[\rho_I^{(if)}(\mathbf{r})\right]\right) + T_s^{\mathrm{nadd}}\left[\left\{\rho_I^{(if)}\right\}_{I=1,\ldots,N_S}\right] + E_{xc}^{\mathrm{nadd}}\left[\left\{\rho_I^{(if)}\right\}_{I=1,\ldots,N_S}\right]\right] S_{if}$$

It's linear scaling!!

---

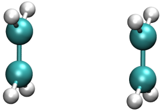
[a] MP, Van Voorhis, Visscher, Neugebauer, JCP **138**, 054101 (2013)

Does FDE-ET work?

Hole transfer in the ethylene dimer radical cation

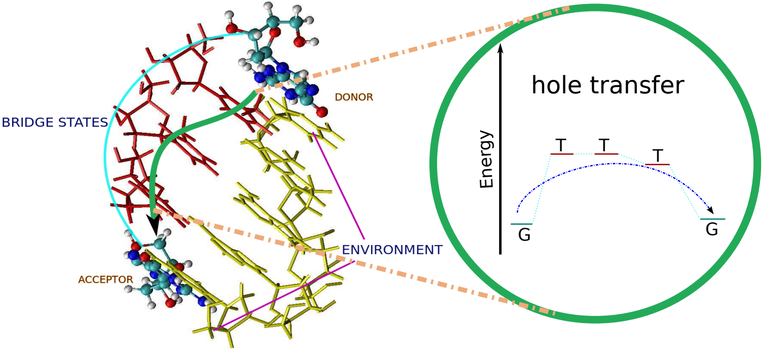
		Excitation Energy (eV)			
R	S_{if}	This Work[a]	CCSD(T)[b]	CCSD(T)[c]	FS-CCSD[d]
3.0	1.60E-1	1.833	1.913	1.939	1.947
4.0	6.27E-2	0.521	0.527	0.558	0.555
6.0	6.55E-3	0.037	0.024	0.038	0.035
9.0	1.82E-4	6E-4	0.009	0.004	3E-4
10.0	5.31E-5	1E-4	0.009	0.003	5E-5
15.0	8.75E-8	2E-6	0.009	0.004	1E-7

[a] PW91/TZP
[b] EOM-CCSD(T)/6-311G(d,p) ROHF
[c] EOM-CCSD(T)/aug-cc-pVDZ ROHF
[d] FS-CCSD(T)/aug-cc-pVDZ UHF



MP, Van Voorhis, Visscher, Neugebauer, JCP **138**, 054101 (2013)

The Superexchange Hole Transfer in DNA



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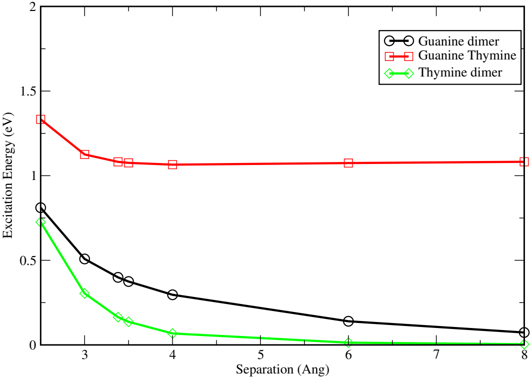
[a] Ramos and MP, JCTC **10**, 2546 (2014)

Calculation of hole transfer couplings with FDE-ET

DNA base pairs: distance dependence of excitation energies and couplings[a]



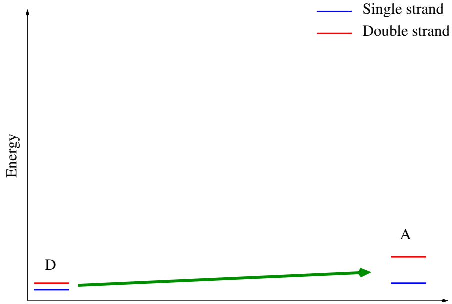
$$2.5 < \beta < 3.5$$

---

[a] Ramos and MP, JCTC **10**, 2546 (2014)

Donor-Bridge-Acceptor Effective Couplings[a] with FDE-ET[b]

Hole transfer in DNA oligomers: $\begin{matrix} G \\ C \end{matrix} \left(\begin{matrix} T \\ A \end{matrix} \right)_n \begin{matrix} G \\ C \end{matrix}$



Deep Tunnelling

$$V_{DA} \simeq H_{DA} - S_{DA} \frac{H_{DD} + H_{AA}}{2}$$

decays too fast: $\beta \simeq 3$

---

[a] A. Nitzan, Chemical Dynamics in Condensed Phases, Oxford University Press (2006)

[b] Ramos and MP, JCTC **10**, 2546 (2014)

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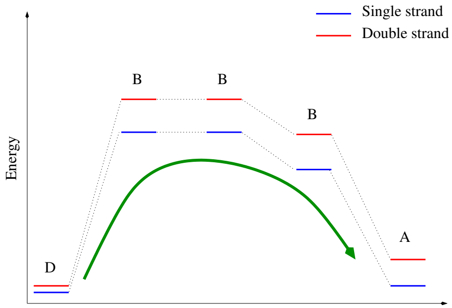

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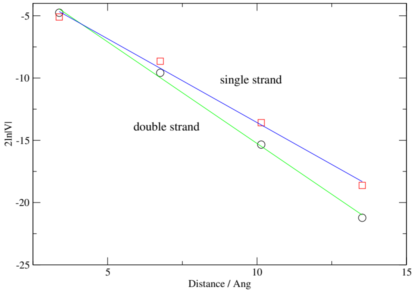

Superexchange mechanism

$$V'_{DA}(E) = V_{DA} + V_{DB}G_B(E)V_{BA}$$

accounts for a lower tunnelling barrier than the vacuum: $\beta \simeq 1$

much closer to experiment[c]

---

[a] A. Nitzan, Chemical Dynamics in Condensed Phases, Oxford University Press (2006)
[b] Ramos and MP, JCTC **10**, 2546 (2014)
[c] B. Giese, Annu. Rev. Biochem. **71**, 51-70 (2002)

Effective Couplings Between Charge Separated States[a] with Subsystem DFT

Effective Couplings Between Charge Separated States^a with Subsystem DFT

- Charge separation (ground state)

$$D + A \rightarrow D^+ + A^-$$

- Charge separation (excited state)

$$D^* + A \rightarrow D^+ + A^-$$

Effective Couplings Between Charge Separated States[a] with Subsystem DFT

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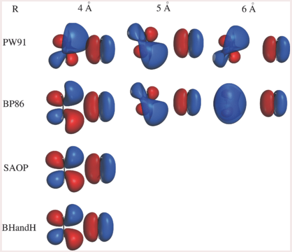
HOMOs for the ethylene dimer in the charge separated state

The FDE calculation needs extra care.

The orbitals of the anions might not be correct due to self-interaction. If a self-interaction corrected functional is used, these issues are drastically reduced.



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[a] Solovyeva, Pavanello, Neugebauer, JCP, 140, 164103 (2014)

Practical Calculations: outline

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Initial FDE calculations

- Compute $D^+ + A$ diabat A
- Compute $D + A^+$ diabat B
- The input file must be prepared manually
- PyADF support is being developped (L. Vissher)

- In output:
  - 1 T21 file for the isolated D: t21.iso.rho1
  - 1 T21 file for the isolated A: t21.iso.rho1
  - 2 T21 files for the embedded D: fragA1.t21, fragB1.t21
  - 2 T21 files for the embedded A: fragA2.t21, fragB2.t21

Practical Calculations: outline

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FDE-ET calculation

Once the FDE calculations for the A and B diabats are complete, the FDE-ET calculation can follow. The keyword needed is

ElectronTransfer

Practical Calculations: Making the FDE-ET input file

Practical Calculations: Making the FDE-ET input file

Fragment key need this setup to load some predefined parameters from the isolated calculation (basis sets, AO maps, . . .)

```
FRAGMENTS
  rho1 t21.iso.rho1
  rho2 t21.iso.rho2
END
```

ElectronTransfer key. NumFrag specifies the number of fragments involved. InvThr is a threshold for handling quasi-orthogonality. Joint/Disjoint: the default is Joint. Disjoint is not recommended yet.

```
ELECTRONTRANSFER
  NumFrag 2
  {Joint|Disjoint}
  {InvThr 1.0e-3}
END
```

See example file at:

`$ADFHOME/examples/adf/ElectronTransfer_FDE_H2O`

Practical Calculations: The output file

The output file from:

```
$ADFHOME/examples/adf/ElectronTransfer_FDE_H2O
```

Practical Calculations: The output file

The output file from:

`$ADFHOME/examples/adf/ElectronTransfer_FDE_H2O`

Is the following:

```
 -------------------------------------------------------------------
 ==> WARNING: one less electron in the transition density matrix <==
 ==>          applying the Penrose inversion of the N-1          <==
 ==>          dimensional subspace                               <==
 -------------------------------------------------------------------

Some references...

 ============  Electron Transfer RESULTS ===================
 Electronic Coupling =         0.000000 eV
 Electronic Coupling =        -0.000006 cm-1
 H11-H22             =        -1.396836 eV
 Excitation Energy   =         1.396836 eV
 Overlap             =         0.000000
 H11 H22 H12 =  -152.443044906236  -152.391712133030  -151.743951196449 Eh
 S11 S22 S12 =     0.981761438554     0.980941502465    -0.000000000038

 =========== END Electron Transfer RESULTS ================
 Exiting Electron Transfer Program
 NORMAL TERMINATION
 END
```

Practical Calculations: The output file

Let’s look at another output file:

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```
============  Electron Transfer RESULTS ===================
Electronic Coupling =         0.344469 eV
Electronic Coupling =      2778.314671 cm-1
H11-H22             =         0.000574 eV
Excitation Energy   =         0.688937 eV
Overlap             =         0.066531
H11 H22 H12 = -1384.925285303533 -1384.925306415906 -1385.114726153074 Eh
S11 S22 S12 =     0.880467985626     0.880488669229    -0.058578952462
=========== END Electron Transfer RESULTS ================
```

Practical Calculations: The output file

Let’s look at another output file:

```
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H11-H22             =         0.000574 eV
Excitation Energy   =         0.688937 eV
Overlap             =         0.066531
H11 H22 H12 = -1384.925285303533 -1384.925306415906 -1385.114726153074 Eh
S11 S22 S12 =     0.880467985626     0.880488669229    -0.058578952462
=========== END Electron Transfer RESULTS ================
```

Things to note

- H11-H22 is the energy difference of the diabatic states
- Excitation Energy may differ from H11-H22

- Overlap is the normalized overlap

$$S'_{ij} = \frac{S_{ij}}{\sqrt{S_{ii} \times S_{jj}}}$$

FDE-ET in summary

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What has been done with FDE-ET

- Applied to hole transfer and charge separation in pilot calculations.
- Tested for hole transfer.

FDE-ET in summary

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Recommendations

- Use the PW91k nonadditive Kinetic Energy functional in the FDE calculations.
- No particular problems applying FDE-ET to cations (hole transfer) → InvThr: might need 1.0e-2 if a near orthogonality is suspected.
- Application to anions is not recommended, however it is possible. Use SIC functionals in the FDE part, and then a GGA functional in the ElectronTransfer part.
- Application to charge separation (+/-) and to other spin states (e.g. triplet) is not available in the released code. Perhaps in the next ADF release.

Pavanello Research Group

I am looking for. . .

- PhD & Master's students

Available Projects

- Non-adiabatic dynamics with Subsystem DFT
- Van der Waals interactions between subsystems
- Subsystem DFT applied to Materials research
- . . .

Rutgers University, Newark, NJ

- 20' from NYC
- Fun learning environment

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