Modelling of the charge carrier mobility in disordered linear polymer materials

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Fragment orbital approach calculation of hole transfer integrals between covalently bound monomer units in a dimer using Gaussian 09 program

According to the fragment orbital procedure (see e.g. ref \textsuperscript{1,2}), transfer integrals $J_{A,B}$ between monomer units $A$ and $B$ of a dimer can be calculated as off-diagonal matrix elements of the Kohn–Sham Hamiltonian $H$ expressed in the basis of the monomer (fragment) molecular orbitals.

The calculation procedure is following:

1) Single point DFT calculation of both monomers $A$ and $B$ as open-shell radicals is done with the following keywords

\begin{verbatim}
#P ROBPW91/AUG-cc-pVTZ
SCF=(Tight,Conver=8)
IOP(6/7=3)
IOP(3/33=1)
IOP(2/15=1)
NoRaff
IOP(2/12=3)
\end{verbatim}

Monomer units are capped on the outer side with hydrogens and left radical in place of the split central bond of the dimer. Using open-shell radicals rely on the fact, that the $\sigma$-bond between thiophene monomer units, which is cut, is fairly orthogonal to the $\pi$-system, where the charge carrier transfer takes place.

These calculations provide molecular orbital matrices $C_A$ and $C_B$ (in atomic orbital basis sets). The fragment orbital transformation matrix $T$ is then created as a block diagonal matrix with matrices $C_A$ and $C_B$ on its diagonal.

2) Single point DFT calculation of the dimer is done with the following keywords

\begin{verbatim}
#P BPW91/AUG-cc-pVTZ
SCF=(Tight,Conver=8)
IOP(6/7=3)
\end{verbatim}
Dimer is capped on both sides with hydrogens. Cartesian atomic coordinates of the dimer should be the same as atomic coordinates of the monomers. Atoms of monomer A should be placed before atoms of monomer B.

This calculation provides the overlap matrix $S_{AO}$, molecular orbital matrix $C_{AO}$, and the Kohn-Sham Hamiltonian matrix $H_{AO}$ – all in the atomic orbital representation. Also the diagonal molecular orbital energy matrix $E$ (eigenenergies of $H_{AO}$) is calculated.

Alternatively, the resulting Kohn-Sham Hamiltonian matrix can be calculated as $H_{AO} = S_{AO} C_{AO} E C_{AO}^{-1}$ in order to reduce the size of the Gaussian output file.

3) Transformation of matrices $H_{AO}$, $S_{AO}$, and $C_{AO}$ into the basis of the monomer (fragment) molecular orbitals:

\begin{align*}
H &= T^T H_{AO} T, \\
S &= T^T S_{AO} T, \\
C &= T^T C_{AO},
\end{align*}

where $T^T$ is the transposed transformation matrix $T$.

4) Checking of the transformation:
The transformed matrices should satisfy equation $HC = SCE$.

5) The hole transfer integral $J_{A,B}$ is given by the matrix element $\langle \text{HOMO}_A | H | \text{HOMO}_B \rangle$ of the Hamiltonian matrix $H$ corresponding to the HOMOs of the fragments $A$ and $B$.

Finally, the effective (generalized) hole transfer integral $b_{A,B}$ (used in Eq.(1)) is then calculated as

$$b_{A,B} = J_{A,B} - \frac{1}{2} S_{A,B} (\varepsilon_A + \varepsilon_B),$$

where

\begin{align*}
S_{A,B} &= \langle \text{HOMO}_A | S | \text{HOMO}_B \rangle \\
\varepsilon_A &= \langle \text{HOMO}_A | H | \text{HOMO}_A \rangle \\
\varepsilon_B &= \langle \text{HOMO}_B | H | \text{HOMO}_B \rangle
\end{align*}

are the hole site energies.

References
