Electronic Supplementary Information

Modelling of the charge carrier mobility in disordered linear polymer materials

Petr Toman[a,*], Miroslav Menšík[a], Wojciech Bartkowiak[b], Jiří Pfleger[a]

[a] Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, v.v.i., Heyrovský Sq. 2, 162 06 Prague 6, Czech Republic
[b] Department of Physical and Quantum Chemistry, Faculty of Chemistry, Wrocław University of Science and Technology, Wyb. Wyspiańskiego 27, 50-370 Wroclaw, Poland

[*] E-mail: toman@imc.cas.cz

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 [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

```
#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)
```

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 σ-bond between thiophene monomer units, which is cut, is fairly orthogonal to the π-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

```
#P BPW91/AUG-cc-pVTZ
SCF=(Tight,Conver=8)
IOP(6/7=3)
```

IOP(3/33=1)
IOP(2/15=1)
NoRaff
IOP(2/12=3)
IOP(5/33=3)
IOP(3/32=2)

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:
$H = T^T H_{AO}\, T$,
$S = T^T S_{AO}\, T$,
$C = T^{-1} C_{AO}$,
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 $\langle HOMO_A|H|HOMO_B\rangle$ 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
$S_{A,B} = \langle HOMO_A|S|HOMO_B\rangle$ is the overlap integral of both HOMOs and
$\varepsilon_A = \langle HOMO_A|H|HOMO_A\rangle$ and $\varepsilon_B = \langle HOMO_B|H|HOMO_B\rangle$ are the hole site energies.

References

1 F. C. Grozema and L. D. A. Siebbeles, *Int. Rev. Phys. Chem.*, 2008, **27**, 87–138.

2 K. Senthilkumar, F. C. Grozema, F. M. Bickelhaupt and L. D. A. Siebbeles, *J. Chem. Phys.*, 2003, **119**, 9809–9817.