Abstract Submitted
for the MAR12 Meeting of
The American Physical Society

Density-functional Theory and Beyond for Donor-Acceptor Complexes: The Example of TTF/TCNQ[1] VIKTOR ATALLA, Fritz-Haber-Institut der MPG, MINA YOON, Oak Ridge National Laboratory, MATTHIAS SCHEFFLER, Fritz-Haber-Institut der MPG — We study the performance of density-functional theory (DFT) with various exchange-correlation (XC) functionals in describing electronic and structural properties of the prototypical donor/acceptor complex TTF/TCNQ. We find that the binding energetics and the amount of electron transfer between TTF and TCNQ depends strongly on the functional. In particular, all semilocal functionals give rise to significant, aritificial electron transfer due to a wrong ordering of Kohn-Sham (KS) levels. We consider the HSE [1] "family" of XC functionals using the fraction of exact exchange (α) as adjustable parameter. The optimum XC functional is then identified as that for which the G_0W_0 quasiparticle correction to the energy gap of the KS LUMO of the acceptor and the HOMO of the donor is minimized. We obtain $\alpha \sim 0.8$ which gives an electronic level alignment that is consistent with experiment and free from spurious asymptotic charge transfer. We conclude that the proposed scheme improves the KS spectrum, and that the investigated TTF-TCNQ dimer exhibits intra-molecular electron-density rearrangement rather than electron transfer.

[1] A.V. Krukau, et al., J. Chem. Phys. **125**, 224106 (2006)

[1]Research sponsored by the Max Planck Society and the US Department of Energy, Basic Energy Sciences, Materials Sciences and Engineering Division.

Viktor Atalla
Fritz-Haber Institut der MPG

Date submitted: 09 Dec 2011 Electronic form version 1.4