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Communication: Correct charge transfer in CT complexes from the Becke'05 density functional

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Abstract

It has been known for over twenty years that density functionals of the generalized-gradient approximation (GGA) type, and exact-exchange-GGA hybrids with low exact-exchange mixing fraction, yield enormous errors in the properties of charge-transfer (CT) complexes. Manifestations of this error have also plagued computations of charge-transfer excitation energies. GGAs transfer far too much charge in CT complexes. This error has therefore come to be called "delocalization" error. It remains, to this day, a

vexing unsolved problem in density-functional theory (DFT). Here we report that a 100-percent exact-exchange-based density functional known as Becke'05 or "B05" [J. Chem. Phys. **119**, 2972 (2003) and **122**, 064101 (2005)] predicts excellent charge transfers in classic CT complexes involving the electron donors NH_3, C_2H_4, HCN, and C_2H_2 and electron acceptors F_2 and Cl_2. Our approach is variational, as in our recent "B05min" dipole moments paper [J. Chem. Phys. **147**, 154103 (2017)]. Therefore B05 is not only an accurate DFT for thermochemistry, but is promising as a solution to the delocalization problem as well.

Over twenty years ago, Ruiz, Salahub, and Vela[1] observed that standard density-functional theory (DFT) exchange approximations such as GGAs (generalized gradient approximations) and exact-exchange-GGA hybrids give atrociously poor structures, binding energies, and charges in charge transfer (CT) complexes. They considered classic CT complexes of the electron donors ammonia and ethylene with dihalogen electron acceptors F_2 through I_2. GGA and hybrid functionals were found[1] to predict far too much binding and far too much charge transfer. Related errors were subsequently found in the time-dependent DFT treatment of charge-transfer excitations also[2-4]. The latter problem inspired a whole new class of DFT approximations known as long-range-corrected (or

LC) functionals[5-7]. LC functionals work quite well for charge transfer processes for which they were designed.

Except for the LC functionals, no fundamental solution to the "delocalization error" (so called because of a tendency to overly delocalize electronic charge) in standard functionals is known. This is a problem of paramount importance if forward progress is to be made in DFT[8]. It is doubtful that GGA or hybrid functionals will survive the challenge.

In this paper, charge distributions in CT complexes will be examined again, twenty years after Ruiz, Salahub, and Vela,[1] as a test of delocalization error. We consider eight CT complexes involving the electron donors NH_3, C_2H_4, HCN, and C_2H_2, and the electron acceptors F_2 and Cl_2. All computations are performed with the Gaussian 09 program.[9] Coupled-cluster singles and doubles theory (CCSD) will be our standard of reference. CCSD has very recently been deemed by several groups[10,11] an adequate and convenient reference method for tests of DFT densities. The aug-cc-pVDZ basis set[12] has been used for all computations. Larger basis sets are not necessary since comparisons between different levels of theory, not with experiment, will be made. Geometries were optimized at the CCSD level using geometries from Ref. 1 to start. We calculate the extent of donor→acceptor electron transfer in each complex for a variety of DFT approximations and compare with the CCSD values. The amount of charge transfer is determined by Hirshfeld atomic population analysis.[13]

Table 1 lists donor→acceptor electron transfer values for the BLYP (Becke-Lee-Yang-Parr) GGA,[14,15] the popular "B3LYP" hybrid of BLYP and 20 percent exact exchange,[16,17] the "BHHLYP" half-and-half hybrid of BLYP and 50 percent exact exchange,[18] and the long-range-corrected variant[19] of BLYP known as "LC-BLYP". The severe over-delocalizing tendencies of BLYP and B3LYP are evident in the table. Errors as large as six times too high are seen for BLYP and three times too high for B3LYP. The BHHLYP functional performs reasonably well, but its 50 percent exact-exchange fraction is problematic in general thermochemical applications. LC-BLYP performs best of all. Remember, however, that LC functionals were designed to alleviate CT errors, so this is not surprising. Delocalization error is not intrinsic to Hartree-Fock (HF) theory as it treats exchange exactly. So the HF results in the last column agree well with CCSD also.

In 2003[20] and 2005[21], Becke developed *pure correlation* functionals ("B05") for static (non-dynamical) and dynamical electron correlation, to be added to 100 percent exact exchange (i.e. no GGA exchange component). Since exact exchange does not suffer delocalization error, B05 holds promise to solve the delocalization problem in DFT. This will be investigated in the following.

The B05 exchange-correlation energy has the form

$$E_{XC}^{B05} = E_X^{exact} + a_{statC}^{opp} U_{statC}^{opp} + a_{statC}^{par} U_{statC}^{par} + a_{dynC}^{opp} E_{dynC}^{opp} + a_{dynC}^{par} E_{dynC}^{par} \tag{1}$$

where static and dynamical correlation energies are denoted by subscripts "*statC*" and "*dynC*", and each is explicitly modeled by an opposite-spins and a parallel-spins part (superscripts "*opp*" and "*par*"). Our implementation here is precisely as in Ref. 21, with

minor notation changes that should be obvious to readers. The static terms U_{statC}^{opp} and U_{statC}^{par} are *potential* energy models, whereas E_{dynC}^{opp} and E_{dynC}^{par} are *total* energy models incorporating kinetic energy through the Kohn-Sham adiabatic connection[22]. Thus the prefactors a_{statC}^{opp} and a_{statC}^{par} should in principle have value 1/2 in accordance with the virial theorem, whereas a_{dynC}^{opp} and a_{dynC}^{par} should have value 1, as follows:

$$E_{XC}^{B05} = E_X^{exact} + \frac{1}{2}(U_{statC}^{opp} + U_{statC}^{par}) + E_{dynC}^{opp} + E_{dynC}^{par} . \tag{2}$$

We adopt this non-empirical expression throughout the present work, even though the prefactors in Eq.(1) were originally fit to experimental data in Ref. 21. On the 222 heats of formation of the G3 thermochemical benchmark set[23] the mean absolute error of the non-empirical Eq.(2) is 4.5 kcal/mol, compared to 3.0 kcal/mol for Eq.(1) with the fitted prefactors of Ref. 21 (computed with the grid-based NUMOL program[24]). The difference is acceptably small.

B05 is a functional of density, density gradient, kinetic-energy density, Laplacian of the density, and the Coulomb (spin) potential of the exact exchange hole, also known as the Slater potential:

$$V_{X\sigma}^{Slater}(\boldsymbol{r}_1) = -\frac{1}{\rho_\sigma(\boldsymbol{r}_1)} \sum_{ij} \psi_{i\sigma}^*(\boldsymbol{r}_1)\psi_{j\sigma}(\boldsymbol{r}_1) \int \frac{\psi_{i\sigma}(\boldsymbol{r}_2)\psi_{j\sigma}^*(\boldsymbol{r}_2)}{|\boldsymbol{r}_2 - \boldsymbol{r}_1|} d^3\boldsymbol{r}_2 . \tag{3}$$

It is the Slater potential that communicates non-locality information to the B05 static correlation terms, through a renormalized local exchange-hole reconstruction introduced in Refs. 20 and 21. Unfortunately, B05 is a complicated functional and self-consistent field (SCF) implementation is extremely difficult. Nevertheless an "optimized effective

potential" implementation has been reported by Arbuznikov and Kaupp,[25] and very encouraging progress on SCF implementation has been reported by Proynov et al.[26-28]

In the absence of readily available self-consistent B05 technology, we have recently introduced an alternative variational approach for obtaining (near) optimum B05 densities.[29] We use orbitals and densities from *hybrid* or *long-range-corrected* functionals, sampled over a "spectrum" of a_X or ω values (a_X for the former, ω for the latter) as input to the B05 functional and select the orbitals and density that *minimize the B05 energy*. We call the method "B05min". It has proven superior to standard functionals in small-molecule dipole moment tests.[29] More importantly, B05min is the first *a priori* method for determining optimal a_X values in hybrid density functionals, and among the first for *a priori* determination of ω values in LC functionals (see Ref. 30 for the very first).

B05min computations have been carried out on our eight CT complexes using orbitals from the "h-BLYP" hybrid functional

$$E_{XC}^{h-BLYP} = a_X E_X^{exact} + (1-a_X)E_X^{B88} + E_C^{LYP} \tag{4}$$

where $B88$ and LYP are the exchange and correlation GGAs from Refs. 14 and 15, and also the long-range-corrected LC-BLYP functional[19] with the range-separated Coulomb potential

$$\frac{1}{r_{12}} = \frac{1-erf(\omega r_{12})}{r_{12}} + \frac{erf(\omega r_{12})}{r_{12}} \ . \tag{5}$$

Searches over the a_X and the ω parameters (to be denoted h-B05min and LC-B05min) are in intervals of 0.01. B05 energies are obtained from an in-house "postG" program that reads WFN files from Gaussian 09 and computes all energy components using the grid-based methods of Becke and Dickson.[31,32] The optimum h-B05min a_X and LC-B05min ω, and resulting Hirshfeld charge-transfer values, are in Table 2 (a_X and ω values bracketed in the table). Typically, h-B05min yields a_X just above 20 percent, in agreement with the decades-old 20-percent empirical exchange fraction in B3LYP.[16,17] Therefore the h-B05min transferred charges have errors very similar to B3LYP.

The h-B05min and LC-B05min results in Table 2 are rather disappointing. In C_2H_4-F_2, for example, the transferred charge is still three times too high. We hypothesize that the h-B05min a_X and LC-B05min ω are optimum for minimization of the *total* energy, which involves *all* the orbitals, but are probably *not* optimum for the high-lying valence orbitals actually responsible for the charge transfer. Core and low-lying valence orbitals overwhelm these in the B05 total energy. They need to be identified and excluded somehow if we want to focus on charge transfer.

Figure 1 depicts Hartree-Fock orbital energies for the HCN-F_2 complex, with atomic $1s$ cores omitted. We choose Hartree-Fock because its orbital energies are physically meaningful as approximate ionization potentials. Observe that a distinct gap occurs between the 3rd and 4th orbitals in the figure, or 7th and 8th including the four atomic $1s$ cores. It is reasonable to assume that orbitals above this gap contribute to charge transfer, and that orbitals below the gap do not. We shall call the latter orbitals

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"core" (even though this is not the usual definition) and the former "valence" (again, even though this is not the usual definition). In the case of the HCN-F$_2$ complex, 7 orbitals are "core". The Hartree-Fock gaps in our eight complexes range from 0.2 to 0.4 au, resulting in the core-orbital counts listed in the caption to Table 2. Coincidentally (or perhaps not) it transpires that our "core" obitals are all the orbitals with energy below -1 au.

Also, we have examined "core-only" Hirshfeld charges in each of our complexes at each a_X and ω search value. We find a charge of almost exactly +10 on all dihalogen monomers (+5 on each atom) in all complexes, at all a_X and ω, with an overall (~1600 calculations) mean absolute error of only 0.002. This verifies that our core charges are constant throughout, and that they play no role in charge transfer. They contain F or Cl atoms with their p electrons expunged but their valence s electrons in place. This makes sense, as the highest valence ns orbital in main-group atoms has somewhat lower energy than the np orbital, especially in halogens.

Having now identified our core orbitals, how can we remove their effect on the B05 minimization? Since the total energy is composed of core-core, core-valence, and valence-valence interactions, we compute the core B05 energy and subtract it from the total B05 energy to obtain the *valence-only* energy:

$$E_{B05}^{valence} = E_{B05} - E_{B05}^{core} \; . \tag{6}$$

This subtraction is carried out at each of our a_X and ω search values, using the orbitals previously computed in the B05min round, and this *valence-only* B05 energy is

minimized. We call this step "B05minV". The minimizing B05minV a_X or ω *differ* from the B05min values (see Table 2) tending to be larger. The final transferred Hirshfeld charge for each complex is then taken from the Gaussian 09 computation corresponding to the B05minV a_X or ω (the last two columns of Table 2).

Tables 1 and 2 show that h-B05minV gives charge transfers of quality similar to Hartree-Fock, as might be expected. Given that exact exchange is free of delocalization error, the optimum a_X in many cases logically equals 100 percent. The LC variant, LC-B05minV, outperforms *all* the functionals assessed here. Its optimum ω's are significantly larger than for LC-B05min, again as expected given that larger ω implies more exact-exchange character. The mean absolute error for LC-B05minV is twice as small as for the best-performing standard functional, LC-BLYP.

This work suggests that the Becke'05 density functional[21] offers a solution to the DFT electron delocalization problem based on correlation-hole models that are fundamental, non-empirical, and general. As such, we encourage the continued development of B05 SCF technology along the lines of Refs. 25-28.

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Table 1: Hirshfeld electron transfer to F_2 or Cl_2 for standard functionals

| Complex	CCSD	BLYP	B3LYP	BHHLYP	LC-BLYP	HF
NH_3-F_2	0.040	0.119	0.080	0.050	0.047	0.034
NH_3-Cl_2	0.097	0.155	0.133	0.109	0.103	0.086
C_2H_4-F_2	0.013	0.080	0.047	0.027	0.016	0.019
C_2H_4-Cl_2	0.033	0.076	0.063	0.050	0.037	0.041
HCN-F_2	0.017	0.029	0.022	0.018	0.019	0.015
HCN-Cl_2	0.043	0.054	0.048	0.043	0.046	0.039
C_2H_2-F_2	0.010	0.054	0.029	0.018	0.011	0.014
C_2H_2-Cl_2	0.028	0.058	0.047	0.039	0.031	0.034
MAE[a]		0.043	0.024	0.009	0.004	0.006

a) Mean absolute error with respect to CCSD.

Table 2: Hirshfeld electron transfer to F_2 or Cl_2 for B05min variants

Complex[a]	CCSD	h-B05min[b]	LC-B05min[c]	h-B05minV[b]	LC-B05minV[c]
NH$_3$-F$_2$	0.040	0.078 (0.21)	0.074 (0.25)	0.043 (0.65)	0.040 (0.68)
NH$_3$-Cl$_2$	0.097	0.132 (0.21)	0.130 (0.22)	0.088 (1.00)	0.099 (0.57)
C$_2$H$_4$-F$_2$	0.013	0.046 (0.21)	0.043 (0.19)	0.023 (0.64)	0.015 (0.66)
C$_2$H$_4$-Cl$_2$	0.033	0.062 (0.21)	0.052 (0.20)	0.042 (1.00)	0.037 (0.54)
HCN-F$_2$	0.017	0.021 (0.22)	0.021 (0.34)	0.015 (1.00)	0.017 (0.71)
HCN-Cl$_2$	0.043	0.048 (0.21)	0.051 (0.26)	0.039 (1.00)	0.044 (0.62)
C$_2$H$_2$-F$_2$	0.010	0.028 (0.22)	0.019 (0.25)	0.016 (0.69)	0.011 (0.64)
C$_2$H$_2$-Cl$_2$	0.028	0.046 (0.21)	0.040 (0.22)	0.034 (1.00)	0.031 (0.53)
MAE[d]		0.023	0.019	0.006	0.002

a) "Core"-orbital counts are, respectively: 6, 14, 7, 15, 7, 15, 7, 15.

b)   Bracketed entries are the minimizing exact-exchange fractions a_X.

c)   Bracketed entries are the minimizing LC range parameters ω (bohr^{-1}).

d)   Mean absolute error with respect to CCSD.

Figure 1: Hartree-Fock orbital energies in HCN-F_2 ($1s$ atomic cores omitted)
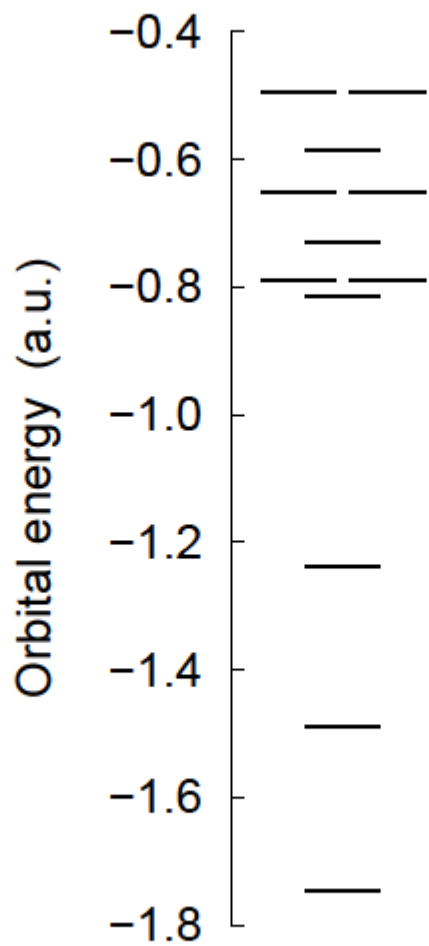
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