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Defining the Domain of Density Functionals: Charge-Transfer Complexes

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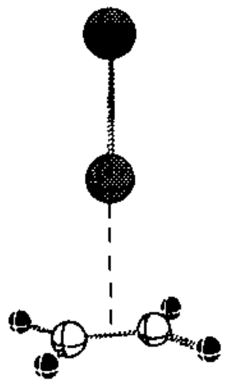
Density functional theory (DFT) has known wide success for the description of strongly-bonded systems,[1,2] and because of this, DFT is currently being used by a rapidly growing community that cuts across many subdisciplines of chemistry. The challenge of describing hydrogen bonds has also been taken up.[3,4] For these weak interactions the accuracy of current functionals, though not perfect, is sufficient for many purposes, which has raised serious interest in DFT for biochemical applications as well.

Another class of weak intermolecular interactions, those present in charge-transfer complexes, has not, until now, been explored with DFT. In this communication we show that charge-transfer complexes represent an important testing ground for density functionals. We delineate the performance of the widely used functionals based in the generalized gradient approximation (GGA) (they turn out to be inadequate) and of hybrid functionals that incorporate a contribution for Hartree−Fock exchange (these show potential, but the results are very sensitive to the precise mixture of exchange and correlation components used).

The charge-transfer complexes between ethylene and a halogen play an important role in the mechanism of the electrophilic addition of halogen molecules to ethylene.[5] It is generally admitted (and corroborated by our results) that the first step of this reaction comprises the formation of an axial-perpendicular complex (**1**).



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In spite of the considerable amount of experimental information (particularly for the chlorine complex[6−10]) about the charge-transfer complexes $C_2H_4\cdots X_2$ (X = F, Cl, Br, and I), the lack of an accurate theoretical analysis of these weak interactions has motivated us to carry out an ab initio study of these systems using density functional methods.

As can be seen in Table 1, the local spin density method (VWN)[13] yields a large overestimation of the intermolecular interaction, which is partially corrected by the GGA. Within this level of theory, the Becke−Perdew (BP)[14,15] and Perdew−Perdew (PP)[15,16] functionals give the most improvement with respect to the local spin density method, while the Perdew−Wang functional (PW)[17,18] yields only a better result for the interaction energy. As discussed elsewhere,[19] the underestimate of the intermolecular distance and Cl−Cl frequency and the overestimate of the binding energy correlate with a transfer a charge which is undoubtedly too large. Recent work[20,21] has proposed the advantages of so-called hybrid methods which incorporate a contribution of the Hartree−Fock exchange through the "adiabatic connection" formula,[22]

$$\mathbf{E}_{XC} = \int_0^1 \mathbf{U}_{XC}^{\lambda}\, d\lambda$$

where λ is a coupling parameter that allows the switching from the Kohn−Sham non-interacting system ($\lambda = 0$) to the fully interacting system ($\lambda = 1$), and U_{XC}^{λ} is the potential energy of exchange correlation. We consider two hybrid approaches: the Becke three-parameter functional (B3LYP)[21] and the half-and-half functional (HH)[20] as implemented in Gaussian92/DFT.[23,24] There is a clear relation between the intermolecular interaction and the amount of the Hartree−Fock exchange involved. The B3LYP method incorporates 20% of the Hartree−Fock exchange, and the results are intermediate between those of the pure density functional methods and the HH method where 50% of the Hartree−Fock exchange is included. As a further test we have performed calculations with pure Hartree−Fock exchange along with the Lee−Yang−Parr correlation functional.[25] These yield an intermolecular distance of 3.142 Å, in excellent agreement with experiment, but completely wrong results are found for the frequencies and the bonded distances, as discussed elsewhere.[19] The drawbacks of this method have been reported previously.[26,27] The complete neglect of correlation using the Hartree−Fock method underestimates considerably the intermolecular interaction. For this complex, the inclusion of the Hartree−Fock exchange with a weight of 50%

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Table 1. Optimized Intermolecular Distance, Rotational Constants, Harmonic Stretching Cl−Cl Frequencies, and BSSE (Basis Set Superposition Error) Corrected Interaction Energies for the Complex $C_2H_4 \cdot\cdot Cl_2$ Calculated with Different Methodologies and the Available Experimental Data[a]

	VWN[b]	BP[b]	PP[b]	PW[b]	B3LYP[c]	HH[c]	HF[c]	MP2[c]	expt
d(Cl· ·plane) (Å)	2.435	2.649	2.730	2.448	2.835	3.055	3.601	3.003	3.128[d,e]
rot. const A_0 (GHz)	24.5335	24.4732	24.4988	24.7310	24.8790	25.3455	25.4689	24.7689	25.520[d,e]
rot. const B_0 (GHz)	1.5409	1.4042	1.4043	1.5148	1.3167	1.2383	1.0152	1.2613	1.2244[d,e]
rot. const C_0 (GHz)	1.4796	1.3528	1.3530	1.4554	1.2722	1.1996	0.9892	1.2202	1.1841[d,e]
ν(Cl−Cl) (cm^{-1})	386 (544)	385 (519)	392 (520)	373 (528)	422 (500)	515 (550)	594 (598	506 (539)	527[f] (559)[g]
E_{int} (kcal/mol)	−12.6	−5.2	−6.3	−6.8	−3.7	−2.1	−0.6	−1.6	−1.7 to −2.7[h]

[a] The values of the stretching frequencies for the free molecules are indicated in parentheses. Triple-ζ basis sets with polarization functions have been used for all the atoms. [b] Using deMon (refs 1 and 12). [c] Using Gaussian92/DFT (ref 23). [d] Reference 6. [e] Reference 7. [f] Reference 9. [g] Reference 13. [h] Reference 8.

Table 2. Optimized Intermolecular Distance, Halogen−Halogen Harmonic Stretching Frequences, and BSSE (Basis Set Superposition Error) Corrected Interaction Energies for the Complexes $C_2H_4 \cdot\cdot X_2$ (X = F, Br, and I) Calculated with Different Methodologies and the Available Experimental Data[a]

	VWN[b]	BP[b]	PP[b]	PW[b]	HH[c]	MP2[c]
$C_2H_4 \cdot\cdot F_2$						
d(F· ·plane) (Å)	1.798	1.922	1.891	1.836	2.945	2.894
ν(F−F) (cm^{-1})	486 (1056)	471 (991)	511 (982)	492 (1042)	1051 (1095)	873 (918)
E_{int} (kcal/mol)	−38.4	−25.7	−32.6	−25.3	−0.5	−0.4
$C_2H_4 \cdot\cdot Br_2$						
d(Br· ·plane) (Å)	2.496	2.712	2.842	2.536	3.081	2.966
ν(Br−Br) (cm^{-1})	260 (338)	256 (319)	253 (305)	252 (322)	320 (344)	303 (330)
E_{int} (kcal/mol)	−14.0	−6.0	−7.4	−7.8	−2.6	−2.5
$C_2H_4 \cdot\cdot I_2$						
d(I· ·plane)	2.765	2.995	3.036	2.821	3.340	3.171
ν(I−I) (cm^{-1})	188 (227)	184 (213)	191 (220)	184 (214)	214 (224)	208 (222)
E_{int} (kcal/mol)	−11.2	−4.3	−5.4	−5.7	−2.3	−2.9

[a] The values of the stretching frequencies for the free molecules are indicated in parentheses. Triple-ζ basis sets with polarization functions have been used for all the atoms except for bromine and iodine, where a double-ζ basis was employed. [b] Using deMon. [c] Using Gaussian92/DFT.

in the HH approach provides the best results among the density functional methods, being similar to those obtained with second-order Moller−Plesset (MP2) theory and to the available experimental data.

When one goes from fluorine to iodine (see Table 2), the trends observed in the interaction energies between HH and MP2 methods are in agreement with the known experimental information,[28] whereas those from the pure density functional methods disagree, particularly dramatically for F_2. The MP2 and hybrid methods have in common the inclusion of the exchange energy of the Slater determinant corresponding to Hartree−Fock and Kohn−Sham orbitals, respectively. In the HH method this is moderated by a factor of $^1/_2$ and the inclusion of the density functional exchange and correlation; in the MP2 method it is tempered by correlation brought in through perturbation theory. With the hybrid methods one corrects, at least asymptotically, the well-known error of the too rapid asymptotic decay of the effective potential in the currently used pure density functional methods.[29] A clear manifestation of the improved behavior of the effective potential, as discussed elsewhere,[19] is that the HOMO−LUMO energy differences are more reasonable and these lead to much more reasonable charge transfers. An interesting feature of our results is that the discrepancies between the different methods narrow as one goes from fluorine to iodine. A plausible explanation is that, in the case of fluorine, the intermolecular bond is located in a region for which the too rapid decay of the potential is important. A considerable shortening of the intermolecular distance results, along with a large overestimation of the interaction energy. On the other hand, since iodine is bigger, the intermolecular bond forms in a region where the description of the effective potential is more accurate, diminishing the discrepancies among the different methodologies.

Even though hydrogen-bonded systems have been described with reasonable success using the GGA,[3] closer examination of the results reveals that the intermolecular distances are underestimated for hydrogen bonds, also. However, the more electrostatic nature of the hydrogen bond yields a better description in comparison with the charge-transfer interactions. The charge-transfer complexes represent a stringent and important testing ground for new functionals. The hybrid methods are promising but do not represent a panacea. New pure density functionals for exchange and correlation are needed, and we hope that our results will help motivate the search. In the meantime, the results also contain a warning: applying DFT to (bio)molecular modeling where large charge transfers are possible could lead to serious errors.

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