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Incorrect Dissociation Behavior of Radical Ions in Density Functional Calculations

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The current lineup of popular density functional theories, in particular those based on Becke's exchange functionals, fail to predict a correct dissociation behavior in radical ions where charge and spin must be separated (model: $H_2^{\bullet+}$) or where both must be localized on one fragment (model: $He_2^{\bullet+}$). The repercussions of this on the location of certain transition states on radical ion potential energy surfaces are pointed out.

1. Introduction

In the course of our ongoing work on rearrangement of organic radical cations,[1] we encountered unusual difficulties in locating transition states for certain simple reactions when using density functional theory (DFT) based methods that otherwise proved to be very successful in these types of applications. As the same transition states were often relatively easy to find by Hartree–Fock based methods, we began to ask ourselves about the origin of these difficulties. A closer examination revealed a common feature of such elusive structures, i.e., that they required either a separation of spin and charge in different (say, allylic) moieties or a localization of spin and charge in one part (say, a double bond) of a radical ion. Apparently, the DFT methods available to us "refused" to carry out such separations and localizations in cases where these were clearly required.

Independently, we found that a similar feature of DFT methods comes to bear when radical ions are *dissociated* into fragments, either by separating spin and charge or by localizing them on one of the fragments. Thus, we were unable to model the loosely bound region of the acetylene dimer cation because even at very large distances, spin and charge remained completely delocalized over both acetylene moieties.[2] This led us to investigate the nature of this problem on the example of the most simple model cases, i.e., $H_2^{\bullet+}$ and $He_2^{\bullet+}$, the former of which has the additional advantage that electron correlation effects are entirely absent. This Letter reports the results of this model study, which should serve to attract the attention of the authors of exchange functionals to this particular problem in the hope of remedying it in future versions.

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2. Methods

Reference calculations for $H_2^{\bullet+}$ were performed by the unrestricted Hartree–Fock (UHF) method using Dunning's quadruple-ζ basis set,[3] which yields D_e in excellent agreement with experiment (cf. Table 1). For $He_2^{\bullet+}$, dynamic electron correlation was accounted for by the coupled cluster method including all single and double excitations augmented by a noniterative estimate of the contribution of connected triple excitations (CCSD(T)).[4] This reproduces r_e and ω_e within experimental error and gives a value of D_e only 0.3 kcal/mol above a recent large MRCI calculation.[5] DFT calculations were carried out using Becke's gradient-corrected exchange functional[6] as well as the hybrid three-parameter (B3) and the so-called "half-and-half" functionals (BH&H), which incorporate 20% or 50% Hartree–Fock exchange density, respectively.[7] For $He_2^{\bullet+}$, these were used in conjunction with the Lee, Yang, and Parr correlation functional.[8] Calculations were carried out with the standard 6-31G* and with Dunning's cc-pVnZ basis sets,[3] but for the sake of consistency we report only the results obtained with the cc-pVQZ basis set (qualitatively similar results were obtained with all basis sets). All calculations were done with the Gaussian 94 set of programs.[9] The effect of spin contamination (which is absent in $H_2^{\bullet+}$ as there is only one electron) is practically negligible for $He_2^{\bullet+}$ as indicated by the $\langle S^2 \rangle$ values, which are less than 0.767 at any given internuclear distance.

3. Results and Discussion

The problem becomes most clearly evident when the dissociation curves for the two model cations are normalized to

TABLE 1: Equilibrium Bond Lengths (r_e), Harmonic Frequencies (ω_e), and Bond Dissociation Energies (D_0) as Well as Bond Lengths (r_T) and Harmonic Frequencies (ω_T) of the "Fictitious Transition States" of $H_2^{\bullet+}$ with the cc-pVQZ Basis Set

method	r_e/Å	ω_e/cm^{-1}	D_0/kcal·mol^{-1}	r_T/Å	ω_T/cm^{-1}
exptl[a]	1.052	2321.7	61.13		
HF	1.0571	2323.8	61.04[b]		
BLYP	1.1357	1876.7	66.42	2.9586	−459.7
B3LYP	1.1142	1997.4	65.02	3.2861	−387.9
BH&H	1.0890	2135.1	63.38	3.8554	−272.4

[a] Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979. [b] Most of the difference between the experimental and calculated D_0 is due to the neglect of anharmonicity.

TABLE 2: Equilibrium Bond Lengths (r_e), Harmonic Frequencies (ω_e), and Bond Dissociation Energies (D_0) as Well as Bond Lengths (r_T) and Harmonic Frequencies (ω_T) of the "Fictitious Transition States" of $He_2^{\bullet+}$ with the cc-pVQZ Basis Set

method	r_e/Å	ω_e/cm^{-1}	D_0/kcal·mol^{-1}	r_T/Å	ω_T/cm^{-1}
exptl[a]	1.0806	1698.5	54.62[b]		
UHF	1.0757	1737.7	43.03		
UCCSD(T)	1.0806	1701.2	54.33		
BLYP	1.1830	1192.8	81.58	2.1586	−372.3
B3LYP	1.1454	1359.9	75.46	2.3677	−320.4
BH&H	1.1062	1555.9	67.00	2.7601	−227.7

[a] Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979. [b] Combination of the best calculated value for D_e[5] with the experimental zero-point energy.

Figure 1. Dissociation curves for $H_2^{\bullet+}$ (upper panel) and $He_2^{\bullet+}$ (lower panel) as obtained at the levels indicated under the curves. All calculations were done with Dunning's cc-pVQZ basis set. In the lower panel, the solid and dashed line mark the percentage of spin and charge on one of the two He atoms as a function of the interatomic distance (50% indicates full delocalization, 0% full localization) as obtained at the UHF (dashed) and QCISD levels (solid).

their respective minima and drawn to large interatomic distances, as it is done in the two panels in Figure 1. These show the (essentially correct) curves obtained by UHF ($H_2^{\bullet+}$) or CCSD-(T) calculations ($He_2^{\bullet+}$) at the top and those obtained by the B(LYP) functional at the bottom. The two curves in the middle correspond to admixture of increasing amounts of HF exchange density (B3LYP and BeckeH&H, respectively). After tracing the bottom of the potential energy wells rather accurately, the DFT "dissociation" curves go through fictitious transition states (cf. Tables 1 and 2) before converging very slowly to a completely unrealistic fragment energy, which may even lie below the binding energy of the original cation.

Inspection of the spin and charge distribution from the DFT calculations reveals that it remains completely uniform from the equilibrium distance to infinity, thus confirming our recent experience with the acetylene dimer cation where we had noted the same odd behavior.[2] In contrast, localization of spin and charge in one of the atoms of $He_2^{\bullet+}$ occurs between the inflection point of the potential energy curve and the dissociation limit.[10] Interestingly, when comparing the charge and spin distribution obtained by UHF and by a high-level correlated method (QCISD), one finds, as expected, that correlation delays the onset of charge and spin localization, as found previously for acetylene dimer cation.[2] It therefore appears that DFT methods continue to correlate the motions of the electrons where this should cease to be of energetic advantage.

However, if a DFT calculation is started from a UHF density matrix for a localized wave function, it converges also to that localized solution for large interatomic distances. Series of such calculations result in curves that give a qualitatively correct picture; i.e., they converge to the dissociation limit for each method, but these curves lie invariably at higher energy than those depicted in the two plots. Hence, for large interatomic distances, the (converged!) localized Kohn−Sham wave functions are unstable with regard to equalization of spin and charge
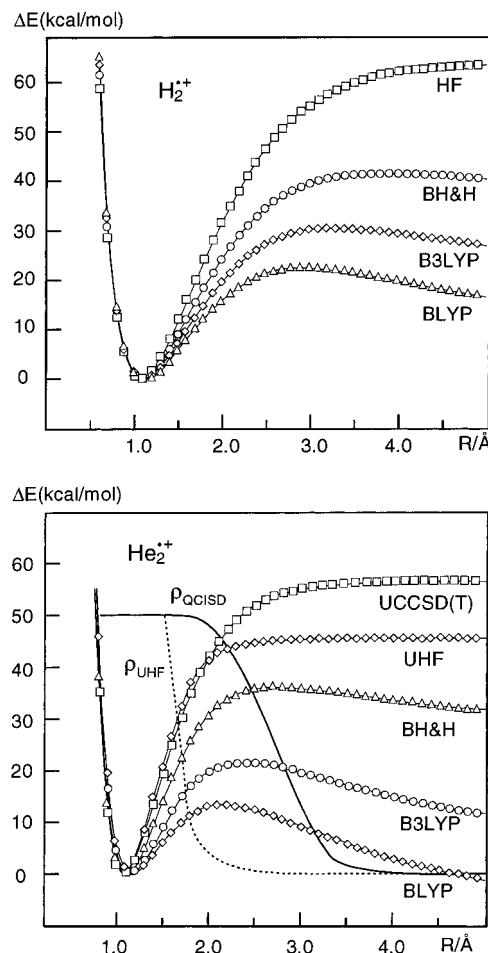
and thus DFT methods appear to be prone to what might be called "inverse symmetry breaking".

But even if we disregard the strange dissociation behavior depicted in Figure 1, the D_e values obtained by taking the energy difference between the fragment atoms or ions and the molecular radical cations are in much poorer agreement with experiment than HF ($H_2^{\bullet+}$) or CCSD(T) ($He_2^{\bullet+}$). In Tables 1 and 2 we list r_e, ω_e, and D_0 values obtained by the different methods as well as r_T and ω_T, the distances and imaginary frequencies at the fictitious transition states obtained by DFT. The very poor prediction of D_0 obtained at the BLYP level is improved somewhat by admixture of increasing amounts of HF density but is still about 0.5 eV from the experimental value when the density is 50% HF.

We also performed some exploratory calculations to delineate the scope of the problem we encountered with the DFT methods. It occurs likewise in homonuclear radical anions (F_2^-), but *not* in unsymmetric radical ions ($LiH^{\bullet+}$, $CH_3OH^{\bullet+}$ dissociating into $OH^\bullet + CH_3^+$) or closed-shell cations (HeH^+) or uncharged radicals ($BeH^\bullet$). It seems that a strong inherent dissymmetry puts a strongly delocalized form at a disadvantage even in DFT methods. However, our experience with larger organic radical cations shows that if the dissymmetry is not pronounced the tendency of DFT for delocalization of spin and charge prevails.[11]

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4. Conclusion

We have encountered a problem with density functional methods that may seriously hamper the applicability of these otherwise very promising techniques in radical ions. It seems to originate from an erroneous dissociation behavior produced by a propensity of different density functionals to keep spin and charge delocalized over the entire molecule even at very large fragment distances. Our experience with radical ions indicates that tightly bonded equilibrium structures are well modeled by density functional methods in most cases. However, locating transition structures where spin and charge should localize at one or different sites of a molecule is very difficult with density functional methods that do not seem to tackle the problem correctly.[11] Also existing DFT methods cannot properly describe loosely bonded complexes between a radical ion and a neutral molecule[2] (or, alternatively, between a closed-shell ion and a radical). Model calculations on $H_2^{\bullet+}$ and $He_2^{\bullet+}$ suggest that the problem is of a sufficiently fundamental nature to warrant the attention of those who develop and apply density functional methods. We hope that this Letter will spur the search for a remedy to this problem.

References and Notes

(1) See, for example: Bally, T.; Truttmann, L.; Dai, S.; Williams, F. *J. Am. Chem. Soc.* **1995**, *117*, 7916.

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(4) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.

(5) Carrington, A.; Pyne, C. H.; Knowles, P. J. *J. Chem. Phys.* **1995**, *102*, 5979.

(6) Becke, A. D. *Phys. Rev. A* **1988**, *39*, 3098.

(7) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(8) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. In $He_2^{\bullet+}$ we tested also other correlation functionals (Perdew, Perdew-Wang, Vosko, Wilk and Nusair) but these gave very similar results. Thus, the problem appears to be with the Becke exchange functional.

(9) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montogomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Repogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; DeFrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzales, M. C.; Pople, J. A. *Gaussian Program*, Version Gaussian 94, Rev. B1 and D4; Gaussian, Inc.: Pittsburgh, PA, 1995.

(10) In $H_2^{\bullet+}$ even the HF density remains fully delocalized along the entire dissociation curve. At larger distances the localized and the delocalized "states" become degenerate.

(11) Consider the cis−trans interconversion in butadiene radical cation, which involves a crossing from a ^2A to a ^2B surface along a C_2 reaction coordinate. To effect this the system must lose all symmetry, which it does by localizing spin on charge on one of two double bonds (such as to be able to change the sign of the π-MO in the other one). We could locate the corresponding TS structure (which shows the expected properties) by all conventional ab initio methods (UHF, ROHF, UMP2, and QCISD) but *not* by BLYP or B3LYP because those methods refuse to effect the required localization of spin and charge.

$^2A_2 \longrightarrow C_2:{}^2A \qquad TS \qquad C_2:{}^2B \longleftarrow {}^2B_g$