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A Density Functional Theory for Symmetric Radical Cations from Bonding to Dissociation†

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It has been known for quite some time that approximate density functional (ADF) theories fail disastrously when describing the dissociative symmetric radical cations R_2^+. By considering this dissociation limit, previous work has shown that Hartree−Fock (HF) theory favors the $R^{+1}-R^0$ charge distribution, whereas DF approximations favor the $R^{+0.5}-R^{+0.5}$. Yet, general quantum mechanical principles indicate that both these (as well as all intermediate) average charge distributions are asymptotically energy degenerate. Thus, HF and ADF theories mistakenly break the symmetry but in a contradicting way. In this letter, we show how to construct system-dependent long-range corrected (LC) density functionals that can successfully treat this class of molecules, avoiding the spurious symmetry breaking. Examples and comparisons to experimental data is given for R = H, He, and Ne, and it is shown that the new LC theory improves considerably the theoretical description of the R_2^+ bond properties, the long-range form of the asymptotic potential curve, and the atomic polarizability. The broader impact of this finding is discussed as well, and it is argued that the widespread semiempirical approach which advocates treating the LC parameter as a system-independent parameter is in fact inappropriate under general circumstances.

At large internuclear distance r, the electronic ground-state wave function of symmetric radical cations R_2^+ is excellently approximated by the superposition

$$|\theta\rangle = |10\rangle \cos\theta + |01\rangle \sin\theta \tag{1}$$

where θ is an arbitrary angle and $|01\rangle$ ($|10\rangle$) is the exact wave function having positive charge on the right (left) R fragment. In the asymptotic $r \to \infty$ limit, the average charge of the left R fragment is $Q_L(\theta) = e\cos^2\theta$, whereas that on the right is $Q_R(\theta) = e\sin^2\theta$. Because $|10\rangle$ and $|01\rangle$ are energy degenerate, the ground-state energy $E(r,\theta)$ is almost independent of θ at large r (at $r \to \infty$, this is exact). How well this degeneracy is preserved in various approximations is a central issue in this paper. The energy difference at some large internuclear distance $r_0 = 20$Å,

$$\Delta E(r_0) = E\left(r_0, \frac{\pi}{4}\right) - E(r_0, 0) \tag{2}$$

will serve as a measure for this. Note that $\theta = \pi/4$ is the symmetric charge distribution, whereas $\theta = 0$ (or $\pi/2$) is a localized (integer) average charge distribution. An additional exact property of the potential is its functional form at large r, which must approach an atom−ion interaction potential[1]

$$E(r,\theta) \to 2E_R - IP_R - \frac{2\alpha_R}{r^4} + O(r^{-6}) \tag{3}$$

where E_R is the electronic energy of the atom R, IP_R is its ionization potential, and α_R is its polarizability (atomic units are used throughout).

The above exact properties, derived from compelling physical considerations, make the class of symmetric cation systems an interesting and generic benchmark for DFT. Surprisingly, local approximations to DFT have been found to grossly defy them exhibiting a repulsive asymptotic Born−Oppenheimer (BO) force $F(r) = -E'(r) \propto r^{-2}$ at large distances instead of the attractive force deduced from eq 3.[2] It was further found that the approximate density functionals (ADF) break the θ degeneracy, stabilizing the delocalized charge distribution $\Delta E_{ADF} > 0$. Equally interesting was the fact that Hartree−Fock (HF) theory also broke symmetry but in an opposite way, stabilizing the localized charge density, $\Delta E_{HF} < 0$. As shown below, this spurious behavior often spoils the accuracy of the potential also at small r.

It was established in previous studies that the spurious asymptotic repulsion is a result of self-repulsion in conventional DF approximations.[2−8] It is therefore appealing to determine how fares the long-range corrected (LC) hybrid functional,[9−13] with these systems. In the LC approach, one separates the electron repulsion potential appearing in the exchange terms into short- and long-range parts: $r^{-1} = r^{-1}erf(\gamma r) + r^{-1}erfc(\gamma r)$. The short-range term is represented by a local potential whereas the long-range part is treated via an explicit or exact exchange term. One critical issue in this scheme is the determination of γ and any additional parameter inserted into the scheme. If one assumes that γ is system independent, one can use a molecular training set for optimizing its value. Such semiempirical approaches were shown to achieve impressive results for a limited class of systems.[11,14−18] However, assuming γ is system independent is most likely only an approximation. Indeed, in ref 12, a rigorous theory for γ was developed on the basis of the adiabatic connection theorem. The value of $\gamma(n)$ was subsequently computed for the homogeneous electron gas[18,19] by using high-accuracy Monte Carlo results,[20] finding strong density dependence. Furthermore, an ab initio method for determining system-specific γ showed good predictions of ionization potentials.[18]

One of the goals of the present letter is to show that a system-dependent parameter γ is in fact necessary for treating the symmetric radical cation systems. We also provide a simple ab initio approach for determining its proper value. Although our

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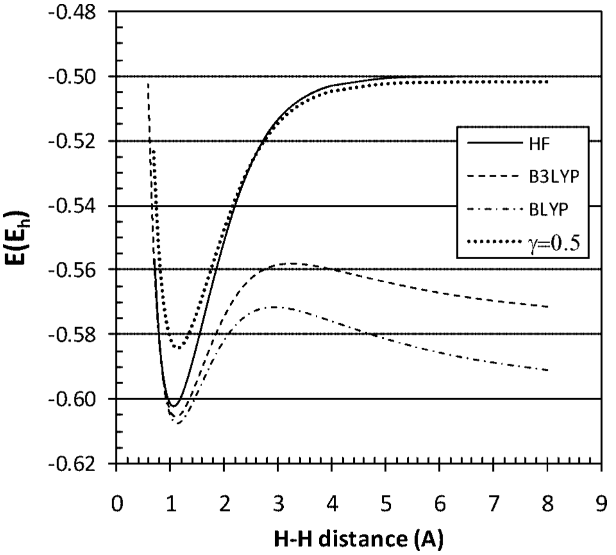

Figure 1. Potential curves of H_2^+ (cc-pVTZ level) obtained by using different theories. The HF theory is the exact variational solution in this case because this is a 1-electron system.

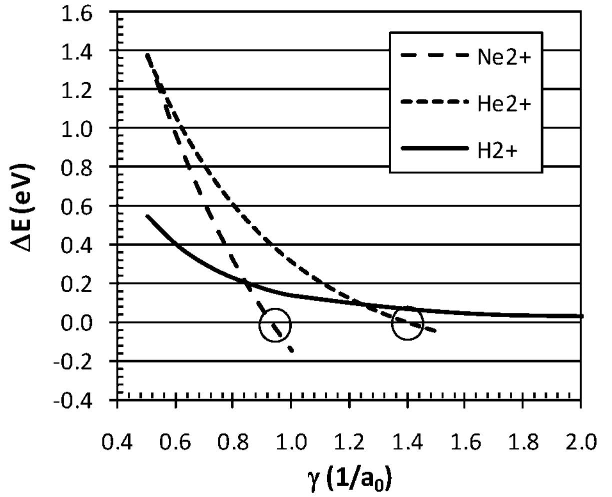

Figure 2. Dependence of the localization-delocalization energy difference ΔE on the value of the parameter γ in the LC functional.

approach can be used with any existing LC functional, we focus here on a specific functional developed in ref 18 which we label here as BNL. All results below were calculated by using the Q-CHEM program version 3.1,[21] and the basis set used was cc-pVTZ for all calculations except polarizability, for which we used d-aug-cc-pVTZ.[22,23]

Let us first consider the simplest R_2^+ system, namely, H_2^+, for which HF results are essentially exact within the basis set. In Figure 1, we show the potential energy curves $E(r)$ of H_2^+ calculated by using HF, BLYP,[24,25] B3LYP,[26] and LC BNL ($\gamma = 0.5$) functionals. In the face of the exact HF curve, all DFT curves look faulty. The BLYP and B3LYP expose their unwieldy dissociation pattern, and the BNL functional based curve, although being qualitatively correct, is quantitatively disappointing with its underestimated well depth.

Therefore, let us now discuss how to improve the functional performance for these systems. We found that it is essential to concentrate on fixing the spurious symmetry breaking. For any value of γ, we calculate ΔE of eq 2, denoting it ΔE_γ. In Figure 2, we show the results for R_2^+ with R = H, He, and Ne. It is seen that only for a particular value of γ does the exact condition $\Delta E_\gamma = 0$ materialize (we denote this as the proper value γ^*).

TABLE 1: Data for R_2^+, R = H, He, and Ne, calculated in the cc-pVTZ basis[22,23][a]

Property	R	BLYP	B3LYP	HF	BNL	BNL*	Exp.[29,30]
BDE by $E_{\text{atoms}}^{(\text{sum})}$							
	H	66	65	60.9	60.9	60.9	61
	He	82	75	43	74	59	55
	Ne	75	60	2	59	34	32
BDE by $E_{\text{atoms}}^{(\text{ass})}$							
	H	NA	NA	60.9	50	60.9	61
	He	NA	NA	43	42	59	55
	Ne	NA	NA	2	27	34	32
r_{eq} (Å)							
	H	1.1	1.1	1.06	1.2	1.06	1.05
	He	1.2	1.1	1.075	1.2	1.078	1.080
	Ne	1.9	1.9	1.7	1.760	1.72	1.765
$\hbar\omega/2$							
	H	2.7	2.9	3.3	2.9	3.3	3.32
	He	1.7	2.0	2.5	2.1	2.5	2.42
	Ne	0.5	0.6	0.9	0.726	0.8	0.729
$\alpha_R/\alpha_{\text{eff}}$							
	H	NA	NA	1	0.6	1	1
	He	NA	NA	0.98	NA	0.98	1
	Ne	NA	NA	1.01	NA	1.02	1
$a_R^{\text{daug}}(a_0^3)$							
	H	5.3	5.6	4.51	5.8	4.51	4.50
	He	1.6	1.5	1.34	1.8	1.41	1.38
	Ne	3.1	2.9	2.4	3.2	2.70	2.66

[a] All energies in kcal/mole. r_{eq} is the inter-nuclear distance at which the $E(r)$ is minimal. $\omega = \sqrt{2\mu^{-1}E''(r_{\text{eq}})}$ is the harmonic frequency, and BDE is calculated as $E_{\text{atoms}} - E(r_{\text{eq}}) + 1/2\ \hbar\omega$ where E_{atoms} is estimated by the two methods discussed in the text (eq 4).α_R is the calculated polarizability of the atom R, and α_{eff} is defined in eq 5. Finally, α_R^{daug} is the polarizability computed with a large basis-set.

For R = H, $\gamma^* \to \infty$, and for R = He and Ne, the proper values are $\gamma^* \approx 1.4a_0^{-1}$ and $\gamma^* \approx 0.93a_0^{-1}$, respectively. BNL with the proper LC parameter γ^* will be denoted henceforth BNL*.

We now show that the proper functional BNL* improves considerably the asymptotic properties of the potential energy surface (PES) and at the same time gives a good description of the bonding characteristics. In Table 1, we show the essential results. Consider first the bond dissociation energy (BDE), *BDE* = $E_{\text{atoms}} - E_{\text{molec}}$. E_{molec} is the ground-state energy of the molecule estimated as $E_{\text{molec}} = E(r_{\text{eq}}) + \hbar\omega/2$, where r_{eq} is the internuclear bond length for which the PES $E(r)$ reaches its minimum and $\hbar\omega/2$ is the zero-point harmonic vibrational energy, (with $\omega^2 = (2/M_R)E''(r_{\text{eq}})$, where M_R is the mass of the R nucleus). As for E_{atoms}, we have two ways for estimating it: as the asymptotic value of the PES and as the sum of the atomic energies (calculated separately).

$$E_{\text{atoms}}^{(\text{sum})} = 2E_R - \text{IP}_R$$
$$E_{\text{atoms}}^{(\text{ass})} = E(r \to \infty) \qquad (4)$$

From Table 1, we see that HF theory is exact for R = H, not so good for R = He where the error exceeds 20%, and completely wrong for R = Ne, where the predicted BDE is less than 10% of its experimental value. When BLYP and B3LYP are used to estimate BDE by using $E_{\text{atoms}}^{(\text{ass})}$, they produce an utterly wrong result, whereas they predict too large BDEs (up to a factor of 2 for R = Ne) when $E_{\text{atoms}}^{(\text{sum})}$ is used. The BNL functional does not give utterly wrong results in both of these approaches, because it has long-range self-repulsion removed, but the two methods for calculating BDEs differ by a considerable amount, a manifestation of the spurious symmetry breaking. The proper functional BNL* seems to be very robust and yields in both methods the same BDE estimates deviating from experimental values typically by less than 10%. Next, consider the equilibrium bond length r_{eq} and the vibrational frequency ω. Here too, the conventional DFT approximations have larger than usual errors, whereas HF and the two LC approaches are pretty robust. Finally, the asymptotic shape of the PES, namely, whether eq 3 is obeyed, can be checked by computing the ratio α_R/α_{eff}, where α_R is the polarizability of R calculated separately in the same basis and

$$\alpha_{eff} = \lim_{r\to\infty} E'(r)r^5/2 \qquad (5)$$

From Eq 3, it is evident that α_R/a_{eff} should approach 1 as the internuclear distance is increased. Thus, the proximity of the ratio α_R/a_{eff} to its ideal value of 1 is a quality indicator for the asymptotic form of the potential. For BNL ($\gamma = 0.5$), we see in Table 1 that the ratio is 0.6 for H_2^+, whereas for the other species, the potential does not show a converged value for α_{eff}, indicating that it exhibits the wrong asymptotic behavior. The approximate DFTs get the asymptotic all wrong, and therefore, the ratio is meaningless. This is specified by NA in the table. The HF and BNL* methods have ratios close to 1, indicating proper asymptotic behavior.

Finally, we have checked an atomic property, namely, the polarizability against experiments. For the polarizability estimation, convergence tests showed that a large basis is required, and we were forced to use the doubly augmented cc-pVTZ basis set. It is seen that BLYP, B3LYP, and BNL all tend to overestimate the polarizability, whereas HF underestimates it. The performance of BNL* is exceptionally good with deviations smaller than 3%. Thus, it is seen that a correct selection of γ for these systems has an overall positive effect on the estimation of a variety of electronic structure-related properties.

In summary, we have shown that by optimizing γ so that the asymptotic degeneracy is respected, we obtain a functional with improved properties: it automatically adheres to the asymptotic form (eq 3), describes the basic bond properties reasonably well, and gives very good atomic polarizability. Overall, the LC functional with optimized γ is considerably more robust and physically appealing than any of its counterparts considered here.

The broader impact of these findings is that the γ parameter must not be considered a system-independent quantity. It seems that for universality to be achieved, γ must be system specific, and techniques for its ab initio determination from the calculation itself, as done here, need to be developed. Our previous work[18] indicated that having a system-dependent γ may impair size consistency. Yet, here, we found that by choosing γ so as to impose this consistency, we obtain a good description from bonding to dissociation of the symmetric radical cation system. This approach can perhaps be made into a general strategy so that before any system R is calculated, the parameter γ can be determined by the above procedure for R_2^+. This will in effect serve to impose the linear energy dependence on the fractional particle number as determined by Perdew et al.[27] exhibiting both derivative discontinuity and correct long-range behavior (we refer the reader to a recent comprehensive review discussing these two aspects[28]). In future work, we will examine whether this approach or similar approaches have the capability of improving other asymptotic properties such as reaction barriers.

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