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## ARTICLES

**Correct dissociation behavior of radical ions such as  $H_2^+$  in density functional calculations**

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In this contribution it is shown that the unphysical dissociation energy curves of dimeric ions bearing a small odd number of electrons as obtained with DFT calculations can be cured by *a posteriori* corrections. The self-interaction error, which is known to be at the origin of the unphysical dissociation behavior, is corrected by a Slater's transition state calculation. A very satisfactory dissociation energy curve is obtained for  $He_2^+$ . However for  $H_2^+$ , it is also necessary to introduce fractional occupation numbers to obtain a good description of the system. © 2001 American Institute of Physics. [DOI: 10.1063/1.1332989]

**I. INTRODUCTION**

In a recent paper, Bally and Sastry<sup>1</sup> showed that standard DFT calculations may fail to predict a correct dissociation behavior of radical ions where charge and/or spin must be separated especially in the case of symmetric molecules. These authors used models such as  $H_2^+$  or  $He_2^+$ , which are usually used as reference models because accurate dissociation curves can be obtained at low computational cost using unrestricted Hartree–Fock (UHF) theory for  $H_2^+$  or full configuration interaction (CI) for  $He_2^+$ . When using DFT, it is well known that the hydrogen atom is by far one of the most difficult elements to tackle with this approach, because it is certainly the most inhomogeneous system available. Modern density functional theory aims to improve the description of electronic systems through exchange–correlation (XC) functionals properly designed to handle an improved description of the electronic density with respect to an homogeneous system. Though, one probably cannot expect to obtain a very accurate dissociation curve for the present systems, at least we require curves exhibiting a physically realistic trend. Unfortunately, the curves obtained by Bally and Sastry<sup>1</sup> show a totally unphysical behavior at distances larger than 2.5 or 2.0 Å for  $H_2^+$  or  $He_2^+$ , respectively, since a spurious energy barrier seems to appear at these distances, and totally unrealistic energies are obtained at larger distances, going asymptotically to energies lying even lower than the bonded radical ions at equilibrium distances. In fact, this pathological failure of standard Kohn–Sham theory to describe dimer cations at a large distance was already shown by Merkle *et al.* in 1992.<sup>2</sup> A  $1/4R$  asymptotic behavior can be demonstrated<sup>3</sup> to occur at distances larger than ca. 5 Å.<sup>2</sup> The aim of this paper is:

- to show that, provided clearly defined computational parameters are properly controlled, the correct dissociation limit can be obtained with DFT calculations;
- to enlarge the description of the energy states involved in the dissociation and to provide an explication of the spurious kinks (curves) obtained in uncontrolled calculations;
- to show that *a posteriori* corrections to the energy curves yield totally satisfactory dissociation curves.

Improper dissociation of radical ions in density functional theory (DFT) originates from the fact that in such systems, the exchange–correlation hole is delocalized over several centers whereas any approximate XC functional is centered around the electron. For this reason, hybrid functionals, which contain an amount of (delocalized) true exchange, fail less dramatically and accordingly, the dissociation curve of  $H_2^+$  or  $He_2^+$  is shifted toward the (asymptotically correct) unrestricted Hartree–Fock (UHF) curve if the amount of pure exchange is increased in the hybrid functional. This is clearly visible from Fig. 1 in Bally and Sastry's paper.<sup>1</sup> As pointed out by Becke,<sup>4</sup> such a failure would be even more dramatic in a one-electron system delocalized over three or more centers.

Another reason for the failure of the underbinding of radical ions, complementary to the previous one, is the fact that approximate functionals contain self-interaction (SI) errors, as shown by Zhang and Yang.<sup>5</sup> This error is maximal for one-electron systems such as  $H_2^+$ . Presently, there is no exchange functional which is SI-error free, if one excepts the self-interaction corrected (SIC) formalism, first introduced by Perdew and Zunger,<sup>6,7</sup> which has the drawback to use an

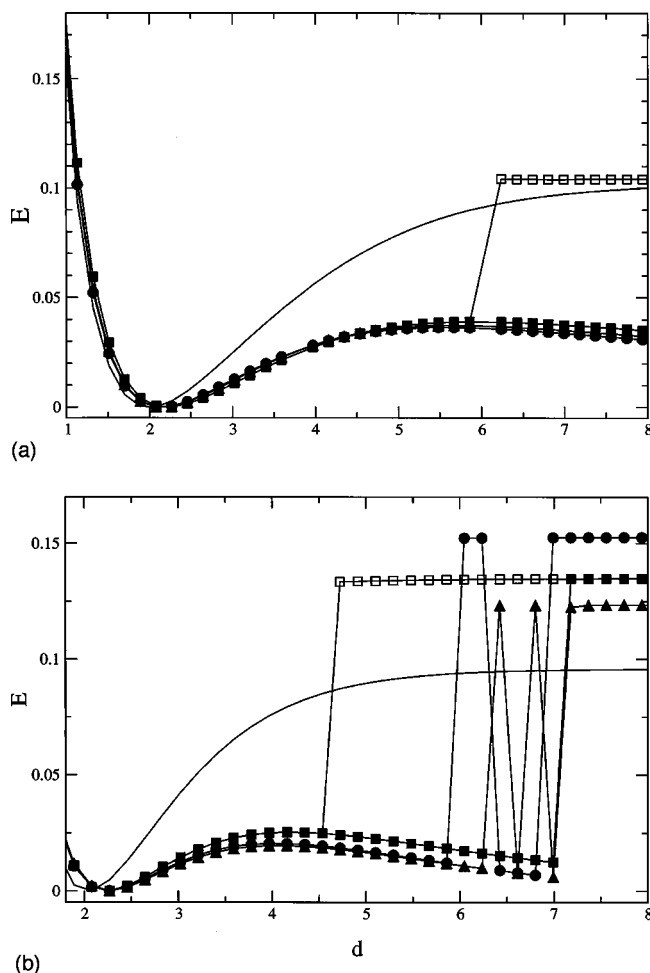


FIG. 1. (a)  $H_2^+$  dissociation curve computed at a LDA and GGA level in  $C_{\infty v}$  compared to UHF and to localized LDA (open square); (b)  $He_2^+$  dissociation curve computed at a LDA and GGA levels in  $C_{\infty v}$  compared to CCSD(T) and to localized LDA (open square). LDA (square); GGA: BLYP (circle), PW91 (up triangle). Energy in a.u., distance in bohr.

orbital dependent exchange-correlation potential, which is computationally demanding for large systems. Moreover, it has been shown<sup>8,9</sup> that there is no possibility to obtain a local or semilocal (exchange) functional which might cancel exactly the SI energy. Actually, the uniform electron gas is not the best reference system for the description of highly separated atoms.

At least two different approaches have been proposed to solve the radical ions problem in DFT:

- The first one is the use of the SIC formalism which has led to moderately satisfying results at a computational cost which removes most of the benefit of the DFT technology. Such SIC functionals are well-known to suffer from the difficulty of rigorously defining the notion of SI in a multielectron system, as well as a lack of unitary invariance in the SIC functionals leading to additional programming complications. Goedecker and Umrigar recently published a critical assessment of the method and its algorithmic implementation.<sup>10</sup> They showed that the molecular properties obtained with the SIC method are rather poorly described;
- The incorporation of the kinetic energy density into the

exchange-correlation functional, as a measure of the delocalization of the exchange-correlation hole. This is the method proposed by Becke and others.<sup>11–15,4</sup>

The aim of this work is not to develop new functionals (for self-consistent calculations), but to point out that it is possible to correct *a posteriori* the dissociation energy curves of such systems obtained by *existent* approximate functionals. The method we propose is based on an *a posteriori* estimate of SI errors—not by the Perdew–Zunger approach, but by the so-called Slater Transition State (STS) method. This correction indeed produces quite good results for systems as small as  $He_2^+$ , but overestimates the correction in the case of  $H_2^+$ . In this latter case the use of the fractional occupation number (FON) will help to fix the problem. In Sec. III we will discuss the problem of localization, whereas self-interaction corrections (SIC) will be discussed in the next section. Finally, Sec. V will be devoted to the special case of  $H_2^+$ ; We will especially show how the left–right correlation problem and how the SIC present in this case can be tackled.

## II. CALCULATIONS DETAILS

Calculations were performed with the ADF1999 code,<sup>16</sup> using a triple  $\zeta$  STO basis set + ( $p, d$ ) polarization functions (basis V, according to ADF classification). For the sake of comparison, DFT as well as HF and CCSD(T) calculations were performed with GAUSSIAN98<sup>17</sup> using Dunning's quadruple  $\zeta$  GTO basis set.<sup>18</sup> A LDA functional has been used with the VWN<sup>19</sup> formulation. GGAs functionals were used with BLYP,<sup>20,21</sup> B88P86,<sup>20,22</sup> and PW91<sup>23</sup> parametrizations. If not differently specified, all dissociation curves for both the ground and the excited state were computed in  $C_{\infty v}$  symmetry (see below for explanation). Localization of the ground states (later referred to as localized calculations) was induced applying the MODIFYSTARTPOTENTIAL keyword available in the ADF code, or using a starting potential altered through the GUESS=MIX keyword in the GAUSSIAN code. For the so-called self-interaction corrected (SIC) energy curves,  $D_{\infty h}$  symmetry was retained all along in the calculations. Slater's transition states calculations were obtained in solving self-consistently (SCF) Kohn–Sham equations after removal of half an electron, corresponding to a 1.5+ charge for the ion.

## III. LOCALIZATION PROBLEM

If one wants to describe properly the dissociation behavior of  $H_2^+$  or  $He_2^+$ , it is necessary to let the system free to localize the unpaired electron near one of the two nuclei. While any computation performed in  $D_{\infty h}$  will lead to symmetry equivalent H or He atoms, removing the center of inversion and thus lowering the symmetry to  $C_{\infty v}$  will give the system an extra degree of freedom and allow localization. The dissociation curves obtained for different LDA and GGA functionals for the ground state of  $H_2^+$  and  $He_2^+$  are depicted in Figs. 1(a) and 1(b), respectively. Whereas for  $H_2^+$  no spontaneous localization occurs, an asymptotic localized behavior is obtained in the case of  $He_2^+$ . However, if we induce localization, as previously described in Sec. II, the correct asymptotic behavior can also be obtained for the case

of  $H_2^+$ , as shown in Fig. 1(a) using LDA. It becomes clear by now that the dissociation energies obtained with such localized calculations are related, as they should be, by the equations:



whereas the curves obtained by Bally and Sastry<sup>1</sup> would read:



The differences between the  $D_{\infty h}$  Kohn–Sham (KS) curves and the exact ones, such as those obtained by UHF for  $H_2^+$ , originate from the fact that, at the HF level, the system can be described either by the superposition of two  $H^{0.5+}$  or by localized  $H^+ + H\cdot$  because the delocalized and localized solutions become degenerate at large internuclear distances (when the overlap becomes negligible). On the other hand, at the LDA level for instance, the Dirac–Slater exchange energy (depending on the total density distribution) amounts to  $2 \times C_x(\rho/2)^{4/3}$ , whereas for a  $H^+ + H\cdot$  system, one gets  $0 + C_x(\rho)^{4/3}$  ( $C_x$  being the Dirac–Slater exchange constant) which differs by a factor of  $2^{1/3}$  (cf. Fig. 1) between the energies in energy of the localized  $C_{\infty v}$  and the  $D_{\infty h}$  asymptotic energies. This difference in exchange energy is just the shift between the bonding  $\Sigma$  and antibonding  $\Sigma^*$  asymptotic states, which should be zero. In the case of HF calculation, this difference is exactly canceled by the exchange energy.

For systems with more electrons, such as  $He_2^+$ , the shift in energy between the two dissociation limits remains similar because one always has one electron interacting with two screened atoms bearing either a  $1+$  and  $0$ , or  $2 \times 0.5+$  charges.

This weakness is partly reduced by more modern functionals than LDA, i.e., by those belonging to the second generation (GGAs) or to the third generation of functionals.<sup>24,25</sup> The observed behavior mainly depends on the nature of the exchange functional chosen. The correlation functionals are more short ranged, hence they contribute less. Hybrid functionals, by construction, lead to a weighted average of the dissociation curves obtained with HF and DFT with Becke exchange GGA. This is shown in Ref. 1 where the hybrid functional used involves the Becke88 exchange GGA, as is usually the case, but the PBE exchange could similarly be taken instead.<sup>26,27</sup> As just said, the correlation functional plays a limited role in this analysis since it is supposed to take mostly the dynamical correlation into account, which is short ranged. The near degeneracy (or left–right) correlation is not taken into account. The problem we have here is typical for such a type of correlation since, for the  $H_2^+$  case, the two dissociated states should lie at the same energy.

However, when one draws the full dissociation curve passing through a series of single points (or through forward and backward linear transit), one obtains a discontinuity in the weakly bonding region (between 2 and 3 Å) which

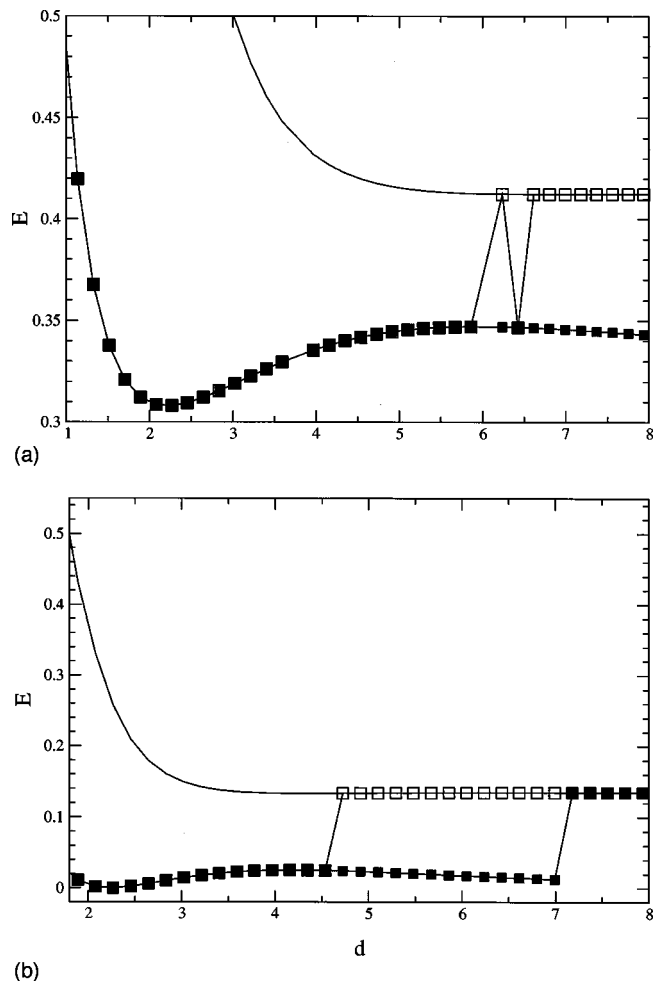


FIG. 2. Excited state LDA dissociation curves for  $H_2^+$  (a) and  $He_2^+$  (b) compared to the ground state in  $C_{\infty v}$  without localization (square) and with localization (open square). Energy in a.u., distance in bohr.

makes the system jump from a covalent description toward an ionic description of the dissociated ionic state. This unphysical discontinuity deserves some comments. These discontinuity jumps are related to the modelization of the exchange–correlation hole, delocalized over the two nuclei vicinity in the case of covalent description, but localized around only one nucleus in the case of ionic description. Because of the approximate forms used in the standard DFT modelization of the exchange–correlation hole, centered around the electron, there is no possibility of a continuous evolution between both of the descriptions, hence leading to the observed jumps.

The Kohn–Sham (KS) description involves by construction a single Slater determinant which, for the  $H_2^+$  system, arises from the occupation of the  $\sigma_g$  bonding molecular orbital (MO), or from the occupation of the  $\sigma_u$  MO for the ionic (dissociative) state. In  $D_{\infty h}$  symmetry these two states belong to the  $\Sigma_g$  and  $\Sigma_u$  irreps. The remarkable point is that these two states belong to the same irrep  $\Sigma$  in  $C_{\infty v}$ , and hence are able to interact. It is easy to compute the energy of both  $C_{\infty v}$  states in the distance range from 0.5 to 5 Å as reported in Fig. 2. An avoided crossing region (in the 2–3 Å zone) corresponds to the change of the system from a domi-

nantly covalent state to an ionic one, both of which are described by a unique KS determinant.

However, as one can see from Fig. 2, the two states which should interact do not cross because of the large SI error which does affect the two states. This error is larger for the  $\Sigma_u$  state than for the  $\Sigma_g$  one so that these two states, which would be degenerate at large distances, remain separated. The correction of this SI energy will be the subject of Sec. IV.

The problem of a single determinantal approach in this region is strongly connected to the treatment of near degeneracy correlation. It has been argued recently in papers by Gritsenko *et al.*<sup>28</sup> that modern correlation functionals provide only a description of the so-called dynamic correlation, which is short ranged. The near degeneracy correlation, on the other hand, is effectively taken into account by the exchange functional, and the fact that the exchange functionals are more long ranged is directly connected to the need of exchange functionals capable to properly handle interactions between species at much larger distances than equilibrium distances. Unfortunately, most of the XC functionals are designed to reproduced ground state properties, such as energies, equilibrium distances, and so forth. Therefore, it would be surprising that the present exchange functionals are already able to provide realistic dissociation curves in all cases. As we shall show later, this stems from the fact that the self-interaction error is roughly proportional to a  $1/N$  (where  $N$  is the number of electrons) times the exchange energy, and is consequently negligible in cases of sufficiently large and homogeneous systems.

On the other hand, methods like HF, which correctly reproduce the symmetry breaking, seem to compensate for this behavior by localization of the electron repulsion associated with a nondynamical correlation error. Indeed, the HF approach overestimates the localization with respect to correlated post-HF approaches. This is also evident when reading the paper of Bally and Sastry where the localization of  $\text{He}_2^+$  occurs at a shorter distance for a UHF calculation as compared to a UCCSD(T) one. A detailed discussion of this topic can be found in papers by Buijse and Baerends,<sup>29,30</sup> where the bonding in  $\text{MnO}^+$  and  $\text{MnO}_4^-$  ions has been studied. These authors underlined that this (excessive) orbital localization within the Hartree–Fock approximation is a two-electron effect, which should increase with decreasing overlap. They also emphasize that such an (over)localization was favored by multiple bonding, large on-site repulsion, and/or weak interaction in the case of small overlap. Indeed, this behavior should be more general since it can already be observed for  $\text{He}_2^+$ , which is a three-electron system.

Anyway, as shown in Ref. 29, the tendency of HF to localize orbitals is favored in the case of small overlaps, and this is why the HF approach provides a realistic dissociation curve for  $\text{He}_2^+$ . The  $\text{H}_2^+$  case is less trivial because no electron repulsion energy is involved. In this case, the dissociation curve is satisfactory because no exchange and correlation energies are present in this method. Whereas standard (i.e., excluding the orbital dependent approximations such as OPM, KLI<sup>31–34</sup>) DFT methods use XC functionals which are not self-interaction free. This self-interaction (SI) energy,

which is maximal for the (LDA) Slater–Dirac exchange, is reduced, but by far not completely, in the case of GGAs and more elaborated exchange functionals. On the other hand, correlation functionals, which are in fact designed to describe both the correlation energy and the exchange energy deficiency, are sometimes properly self-interaction corrected [e.g., with a  $(N-1)/N$  Fermi–Amaldi term],<sup>35,21</sup> and accordingly, not able to cancel the self-interaction energy carried by the exchange functional.

Let us now return to the localization problem at large distances. One should keep in mind that the linear combination of left-localized and right-localized solutions should also be a solution. Therefore the symmetric ( $D_{\infty h}$ ) density should also provide the correct energy if one has a satisfactory exchange functional. This point has already been underlined by Zhang and Yang,<sup>5</sup> who showed that any exchange functional for the description of a system containing less than one electron should obey the scaling relation:

$$E_x[q\rho_1] = q^2 E_x[\rho_1], \quad (5)$$

which is not fulfilled by any of the present exchange functionals ( $0 < q < 1$  being the charge of a one-electron subsystem with density  $\rho_1$ ). Moreover, Perdew and Zunger<sup>6</sup> showed that the origin of the unphysical behavior of the dissociation curve originates from the self-interaction energy. We will see in the next section that the self-interaction error is a feature which cannot be avoided for systems with a very small number of electrons; but this can be cured by *a posteriori* corrections, as discussed in Sec. IV.

#### IV. SELF-INTERACTION CORRECTIONS

It has been known for a long time now that ionization energies differ from the eigenvalue of the highest occupied molecular orbital (HOMO) because any (approximate) exchange–correlation functional introduces an error due to the self-interaction energy which causes the KS orbitals eigenvalues to be too high. Exact (but unknown) exchange–correlation functionals should lead to identical HOMO eigenvalues and ionization energies.<sup>36–38</sup>

One also knows that, according to Janak’s theorem,<sup>39</sup> that removing half an electron from the system leads to a HOMO eigenvalue which is lowered with respect to the HOMO of the original system, and which approximates quite well the ionization energy. This technique is called Slater’s transition state (TS) method. It was proposed by Slater in the early seventies for the  $X\alpha$  formalism<sup>40</sup> and has been extensively used since. The lowering of the HOMO eigenvalue exactly amounts to the self-interaction energy, i.e., the shift with which we are dealing. This is easily seen for a GGA:

$$\epsilon_k = \frac{\partial E}{\partial n_k} = h_k + \sum_j J_{jk} - \frac{2}{3} C_x \int \left[ \sum_i \sum_{\sigma}^{\uparrow\downarrow} \rho_{i\sigma} \right]^{1/3} F(s) d\mathbf{r}, \quad (6)$$

where  $n_k$  is the occupation number of spin orbital  $k$ ,  $h_k$  are the one electron integrals,  $J_{ij}$  are the classical Coulomb integrals,  $C_x$  is the Dirac–Slater constant for exchange (cf. Sec. III),  $\rho_j$  is the electron density associated to the  $j$ th spin orbital,  $\rho_{\uparrow} = \sum_i n_i \rho_{i\uparrow}$ , and  $F(s)$  is the enhancement factor of



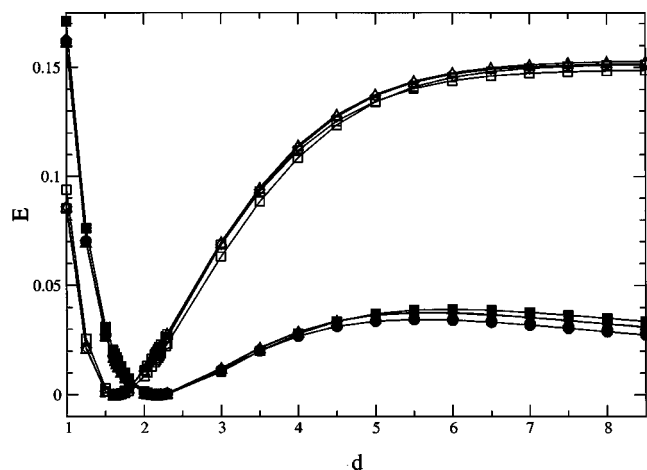


FIG. 3. Ground state  $H_2^+$  (b) dissociation curve computed at a LDA (square) and GGA (BP86 (diamond), BLYP (circle), PW91 (up triangle) levels (in  $D_{\infty h}$ ) without (full marks) and with (open marks) SI corrections calculated via Slater's transition states calculations. Energy in a.u., distance in bohr.

a GGA functional  $E_{xc}(GGA)/E_{xc}(LDA)$ ,  $s$  being the reduced gradient density  $|\nabla\rho/\rho^{4/3}|$  which gives, with  $n_k = 1/2$ , and assuming that orbital  $k$  belongs to  $\uparrow$  spin,

$$\epsilon_k^{TS} = h_k + \sum_j J_{jk} - \frac{1}{2}J_{kk} - \frac{2}{3}C_x \int \left\{ \left[ \rho_{\uparrow} - \frac{1}{2}\rho_k \right]^{1/3} + [\rho_{\downarrow}]^{1/3} \right\} F(s') d\mathbf{r}. \quad (7)$$

The difference between the eigenvalues is, accordingly

$$\epsilon_k - \epsilon_k^{TS} = \frac{1}{2}J_{kk} + \frac{2}{3}C_x \int \left( \left[ \rho_{\uparrow} - \frac{1}{2}\rho_k \right]^{1/3} F(s) - [\rho_{\uparrow}]^{1/3} F(s') \right) d\mathbf{r}. \quad (8)$$

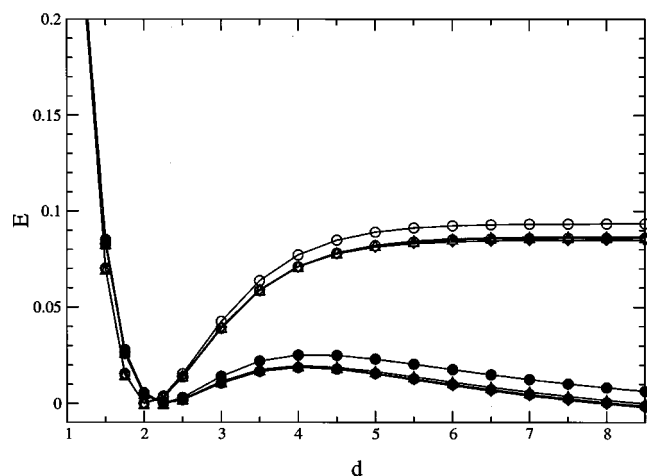


FIG. 4. Ground state  $He_2^+$  (b) dissociation curve computed at a LDA (square) and GGA (BP86 (diamond), BLYP (circle), PW91 (up triangle) levels (in  $D_{\infty h}$ ) without (full marks) and with (open marks) SI corrections calculated via Slater's transition states calculations. Energy in a.u., distance in bohr.

TABLE I. Dissociation energy curves of  $H_2^+$ : Binding energies BE (eV), equilibrium distances ( $\text{\AA}$ ). Calculations at LDA and GGA levels of approximation.

	Eq. dist	BE
LDA	0.88	4.12
B88P86	0.86	4.13
BLYP	0.86	4.05
PW91	0.86	4.16
HF	1.02	2.81
LDA-FON	0.88	2.83
Exp.	1.052	2.65

This difference is dominated by the self-interaction energy,  $\frac{1}{2}J_{kk}$ , and the difference in exchange energy, the sum of both terms being the self-interaction energy error.

However, we have pointed out that it is not equal to the SI energy which could be obtained by the Perdew-Zunger model, because, contrarily to the STS technique, the Perdew-Zunger SI energy is obtained through a self-consistent calculation, using a SIC exchange-correlation potential for each orbital.

Therefore, one could attempt to correct the crude dissociation curves with the STS estimation of the self-interaction energy. This is easily done by calculating the HOMO eigenvalues of both the ground state of the ion and of Slater's transition state for the same ion. Figure 3 and Fig. 4 report such plots for  $H_2^+$  and  $He_2^+$ , respectively, for both LDA and GGA levels. One can see that:

- (1) a physically correct dissociation curve is now obtained;
- (2) the dissociation energy, taken as the difference between the equilibrium energy and the energy of the asymptote, now compares favorably to experiment (see Tables I and II) in the case of  $He_2^+$  but is strongly overestimated in case of  $H_2^+$ ;
- (3) the equilibrium bond length, which is too short, is slightly shifted toward the experimental or CCSD(T) value (see Tables I and II).

If one solves the KS equations of the system for the transition state configuration, both  $J_{kk}$  and the densities  $\rho_{\uparrow}$  and  $\rho_{k\uparrow}$  are modified (as well as the reduced density gradient  $s$ , and therefore the enhancement factor), and the difference includes also some electronic relaxation occurring during the ionization process.

TABLE II. Dissociation energy curves of  $He_2^+$ : Binding energies BE (eV), equilibrium distances ( $\text{\AA}$ ). Calculations at LDA and GGA levels of approximation, CCSD(T), and exper.

	Eq. dist	BE
LDA	1.08	2.550
B88P86	1.085	2.320
BLYP	1.09	2.351
PW91	1.09	2.367
CCSD(T)	1.08	2.42
Exp.	1.08	2.368

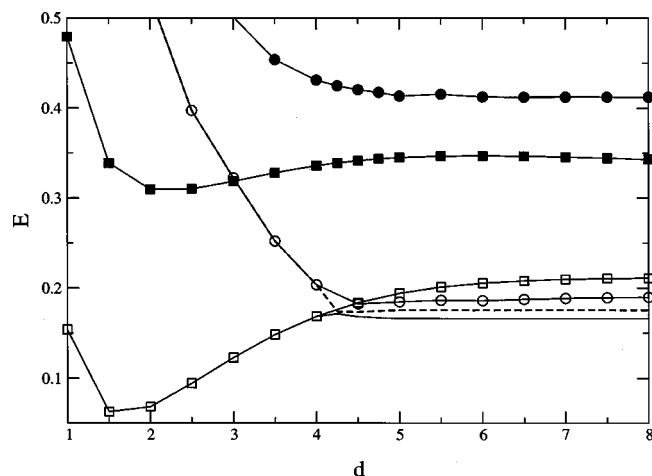


FIG. 5.  $H_2^+$  ground (square) and excited (circle) dissociation energy curves computed at LDA without (full marks) and with (open marks) SI corrections. FON energy curve as full line for the ground state, dashes for the excited state. Energy in a.u., distance in bohr.

Assuming that the reduced density gradient ( $s$ ) does not significantly differ between the ground state of the ion and the corresponding STS [i.e., assuming  $F(s) \approx F(s')$ ], one can write

$$[\rho_{\uparrow} - \frac{1}{2}\rho_k]^{1/3} - [\rho_{\uparrow}]^{1/3} = [\rho_{\uparrow}]^{1/3} [(1 - \rho_k/2\rho_{\uparrow})^{1/3} - 1] \quad (9)$$

$$= -[\rho_{\uparrow}]^{1/3} \left( \frac{1}{6} \frac{\rho_k}{\rho_{\uparrow}} - \frac{1}{18} \frac{\rho_k^2}{\rho_{\uparrow}^2} - \dots \right). \quad (10)$$

Inspection of this expression indicates that the larger the system, the better the approximation. Indeed, in the case of systems with high density, this eigenvalues difference is dominated by the self-interaction energy itself, whereas the change in exchange density is essential for systems with a small number of electrons, for which one cannot neglect  $\rho_k/2\rho_{\uparrow}$  with respect to 1: For  $He_2^+$  this ratio amounts to 1/2, and reaches 1 for  $H_2^+$ . We verified through nonself-consistent calculations that, for these systems, this is the major part of the SI error. This remarkable agreement already obtained for helium should also be found in the case of heavier radicals (corresponding work is in progress).

## V. THE $H_2^+$ CASE: SI AND FON

We have shown in the previous section that applying a simple correction for SI yields both qualitative and quantitative agreement with the CCSD(T) dissociation energy curve in the case of  $He_2^+$ . In the case of  $H_2^+$  this correction is still not satisfactory and leads to an overestimation of the binding energy. Looking for an explanation of this wrong behavior brought us to consider the  $\Sigma$  ground and excited state dissociation curves computed at an LDA level in  $C_{\infty v}$  symmetry, as shown in Fig. 5. The localized, non-SI corrected curves do not cross, whereas the SI corrected curves do. Therefore, in the region where the excited state gets close the two states will interact. As already pointed out in the work of Wang and Schwarz<sup>41</sup> or Baerends,<sup>42</sup> a single determinant KS-DFT

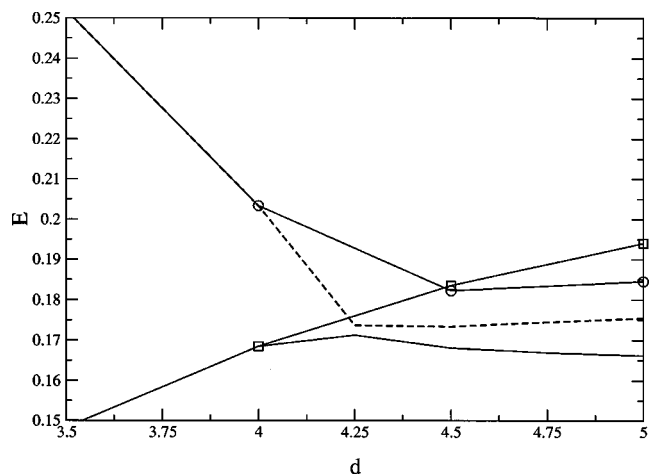


FIG. 6.  $H_2^+$  ground (square), excited (circle), FON ground state (full line) and excited state (dashes) SI corrected dissociation energy curves. Energy in a.u., distance in bohr.

approach is somehow deficient in the description of nondynamical (near degeneracy) correlation. In other words, the region where a low lying excited state of the same symmetry is approaching to the ground state is not correctly described by the current KS-DFT approach. As suggested by Wang and Schwarz, a possible way to solve the problem is to use fractional occupation numbers (FON), thus expressing the ground state and the excited state density as a linear combination of the density obtained from two different Slater determinants corresponding to an optimized fractional occupation of the bonding and antibonding spin orbitals. The idea was already introduced by Slater *et al.*<sup>43</sup> It was explored by Dunlap and Mei<sup>44</sup> for molecules, by Filatov and Shaik<sup>45</sup> for diradicals, and is extensively used for solids or metal clusters.<sup>46</sup> The FON notion rests on a firm basis in cases when the ground state density has to be represented by an ensemble weighted sum of single determinant densities.<sup>47</sup>

In the present work, in order to find the optimal fractional occupation number for the  $\sigma$  and  $\sigma^*$  orbitals, we have chosen the total SIC energy as criterion; that is, we optimized the fractional occupation in order to obtain the minimal self-interaction “free” total energy. The SI error has been estimated *a posteriori* as an average, weighted by the occupation number, of the excited and ground state SI errors obtained with the STS method as previously described. For instance, in the case of an occupation  $(\sigma)^{0.4}(\sigma^*)^{0.6}$ , the SI correction has been taken equal to  $0.4SIC_{gs} + 0.6SIC_{es}$  (where “gs” denotes the ground state and “es” the excited state, respectively). As expected, the interaction between these two states does not affect the ground state energy curve until the excited state very closely approaches the ground state, i.e., for a distance around 3.0 Å, as shown in Fig. 6. Therefore, the curve obtained with FON still underestimates the equilibrium distance, but does finally predict quite correctly the dissociation energy. The calculated dissociation energy is thus 2.83 eV and agrees well with 2.81 eV obtained for UHF and 2.61 eV for the experimental estimation. It is gratifying, but not a surprise, to see that, by applying such a treatment, one obtains the  $\Sigma$  and  $\Sigma^*$  states quasi-degenerate at large

distances. This was not the case for the standard (localized or not), or for the SI corrected calculations, although the corresponding  $\sigma$  and  $\sigma^*$  orbitals are degenerate. A more accurate SI correction than the one presented here would probably have lead to close lying, but not crossing, states since the  $\Sigma^*$  state should produce a more localized density, possessing a higher kinetic energy. However, their closeness would be sufficient to allow the  $\Sigma$  and  $\Sigma^*$  states to interact, justifying the FON calculation whose effect is to reduce the difference in SIC for both states, and therefore to place  $\Sigma$  below  $\Sigma^*$ .

## VI. CONCLUSIONS

The self-interaction energy plays a dominant role for systems with a small, odd number of electrons. It is certainly one of the goals for the new exchange-correlation functionals to describe those systems with the same accuracy as the more homogeneous ones which are already satisfactorily described with GGA functionals. In this respect, the recent attempt of Becke<sup>4</sup> to parametrize an exchange functional more efficiently than standard GGA functionals for tackling the cases of delocalized exchange (Fermi) hole over two or more centers is promising. In this contribution we have shown that removing the symmetry constrain yields the correct asymptotical behavior for the dissociation of homonuclear dinuclear cation, but fails to predict the correct behavior at intermediate distances. On the other hand, simple *a posteriori* corrections obtained from Slater's transition states calculations, applied to existent approximate exchange-correlation functionals, lead to fully satisfactory dissociation energy curves, including both dissociation energies and equilibrium geometries.

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