Singly ionized first-row dimers and hydrides calculated with the fully-numerical density-functional program NUMOL

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Gradient corrected density functionals yield average errors in the ionization potentials of 0.3–0.8 eV. The average errors in the dissociation energies of the diatomic cations are similar to the corresponding errors of the neutral molecules, i.e., 0.2–0.6 eV. The wrong behavior of the potential curves of the dimer cations at large distances calculated with these functionals does not affect the accuracy of $D_e$.

I. INTRODUCTION

For molecules, the bond dissociation energies are an important quantity, and in the collection of diatomic molecules that we treat here, different types of bonding and strengths of bonds can be found. The good results of density-functional theory in calculating dissociation energies have been explained by the correct dissociation of the charge density along the potential curve. But these two effects must not always occur simultaneously. Slater remarks that for example in a NaCl molecule at large distance charge must be transferred from Na to Cl to get the minimum of the total energy. In a calculation using the local spin density approximation (LDA), the minimum is reached for the partially ionic pair Na$^+0.4Cl^-0.4$. When we look at the dimer cations X$_2^+$ at large interatomic distances, we find that the system X$^+0.5X^+0.5$ with equally distributed charge has clearly the lower energy compared with the observed dissociation products X$^+X^+$. This phenomenon shows that a proper balance of Coulomb and exchange-correlation energies is not maintained at large interatomic distances in the density-functional methods we used. The Coulomb repulsion between the electrons is dominant and favors the distribution of the charge of a cation on both atoms.

II. THEORY

In the Kohn–Sham density-functional theory the total energy is calculated as follows:

$$E = T_s + \int v_F + \frac{1}{2} \int \frac{\rho(1)\rho(2)}{r_{12}} + E_{XC},$$

where $T_s = -\sum_i \frac{1}{2} \nabla^2 \psi_i$ is the kinetic energy of the noninteracting reference system that yields the same electronic density

$$\rho = \sum_i |\psi_i|^2$$

as the system with all electron–electron interactions. The Kohn–Sham orbitals $\psi_i$ are calculated from

$$-\frac{1}{2} \nabla^2 \psi_i + v_{ext}(\psi_i = \varepsilon_i \psi_i,$$

$$v_{ext} = v_{nuc} + \int \frac{\rho(2)}{r_{12}} d^3 r_2 + \delta E_{XC}$$

and $\int \rho(1)\rho(2)/r_{12}$ represent the Coulomb interaction between nuclei and electrons and the electrons with each other, while $E_{XC}(\rho)$ is the exchange-correlation energy. Of the several approaches for the exchange-correlation functional $E_{XC}(\rho)$ we will mention these that are used in the present paper.

One of the simplest ways of getting $E_{XC}(\rho)$ is the local spin density approach

$$E_{XC}(\rho) = \int \rho \varepsilon_{XC}(\rho_{\alpha\beta}) d^3 r,$$

where $\varepsilon_{XC}(\rho_{\alpha\beta})$ is the exchange-correlation energy per electron in the uniform electron gas with the densities $\rho_{\alpha\beta}$ (see Appendix for explicit formulas). Naturally the uniform electron gas is not a very good reference system for atoms and molecules with nonuniform electronic density. A successful expression for $E_{XC}$ was developed by Becke and contains a gradient correction for the exchange part (see Appendix). Results of this approach will be denoted BX.

In their generalized gradient approximation (GGA91) Perdew and Wang use a correction for exchange similar to that of Becke, and correct the correlation energy with an expression derived from a modeled correlation hole (see Appendix).

III. COMPUTATIONAL DETAILS

In this work we performed calculations for the diatomic molecules and their ions at the experimental equilibrium distance with the fully-numerical basis-set-free density-functional program NUMOL which was developed by Becke (for further details). Only the valence orbitals are optimized, the core orbitals are transferred from numerical atomic calculations using the LDA. During the iterations $v_{ext}$ is calculated at the LDA level, after the last step the gradient corrections are applied for obtaining $E_{XC}$. Open-shell systems are treated in the spin-unrestricted formalism.
The molecular orbitals were occupied in such a way (broken occupation numbers if necessary) that the molecules had cylindrical symmetry. The difference to the system treated with broken symmetry is for example for C$_2^+$ 0.04 eV (LDA) and 0.17 eV (BX). For the dimer cations O$_2^+$ and F$_2^+$ calculated with broken symmetry extensive rearrangements in the $\pi$ orbitals take place (about four times more iterations necessary for convergence than usually) and the resulting binding energy is 0.5 and 2.5 eV larger, respectively.

For calculating the dissociation energies, atomic energies are also needed. Unfortunately, approximate density functionals do not yield the same energy for the densities obtained from different degenerate states. Spherical atoms would give values different from that obtained with the molecules at large interatomic distances. While the latter choice seems natural to use with potential curves, it has the disadvantage of giving different atomic reference values for different molecules. We thus made a compromise by using a set of values from nonspherical atoms and ions (B, C', F, O, N, p, O, F, p, p, F, p, p, F). This occupation lowers the energy with respect to the spherical atoms (B: 0.07/0.24/0.19; C: 0.04/0.22/0.16; O: 0.18/0.46/0.45; F: 0.04/0.32/0.31 eV; LDA/BX/GGA91 values, respectively).10,11

IV. DIMER CATIONS AT LARGE DISTANCES

When a molecule is formed, charge is shifted in space until the minimum of the energy is reached. In density functional theory this happens also for molecules at large interatomic distances that should be rather regarded as separate, only weakly interacting atoms and ions. The exact density functional changes linearly with the (fractional) occupation in a state intermediate between an atom A and its ion A$^+$ (Ref. 12) and thus no energy change will be present when redistributing the positive charge between A and A$^+$. This is not the case for most approximate density functionals like the ones used in this paper. Here the fragments with a noninteger number of electrons have a lower energy than the physically correct atoms and ions with integer charge. This effect is related to the nonlinearity of parts of the energy functional as $\int \rho(1)\rho(2)/r_{12}$ or $E_{xc}$. We will illustrate this for the Coulomb term.

Removing a charge $\Delta \rho_A$ only from atom A in a homonuclear dimer X$_A$-X$_B$ at large interatomic distance, the Coulomb term yields

$$\int \int \frac{\rho_A^2 + \rho_B^2 + \alpha^2(\Delta \rho_A)^2 + \beta^2(\Delta \rho_B)^2 + 2\alpha \rho_A \Delta \rho_A + 2\beta \rho_B \Delta \rho_B}{2r_{12}}.$$

Considering $\int \int [\rho_A \Delta \rho_A/r_{12}] = \int \rho_B \Delta \rho_B/r_{12}$ and $\int \int [(\Delta \rho_A)^2/r_{12}] = \int \int (\Delta \rho_B)^2/r_{12}$, the difference between these terms is a contribution to the Coulomb energy of

$$\int \int \frac{(\alpha^2 + \beta^2 - 1)(\Delta \rho_A)^2}{2r_{12}}.$$

This contribution becomes minimal for $\alpha = \beta = 1/2$ in the case of X$_A^+$ molecules and favors the equal distribution of ionic charge on both atoms even for large interatomic distances.

TABLE I. Dimer cations at large interatomic distance. Energy difference $\Delta = E_\text{pol}(A) + E_\text{pol}(A^+) - E_{\text{pol}}(A^+ + 20 \text{ Å})$ between the separated atom and ion and the dimer cation at 20 Å (in eV), using LDA, BX, and GGA91 density functionals.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\Delta_{\text{LDA}}$</th>
<th>$\Delta_{\text{BX}}$</th>
<th>$\Delta_{\text{GGA91}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2^+$</td>
<td>2.54</td>
<td>2.77</td>
<td>2.69</td>
</tr>
<tr>
<td>He$_2^+$</td>
<td>4.10</td>
<td>4.42</td>
<td>3.95</td>
</tr>
<tr>
<td>Li$_2^+$</td>
<td>0.93</td>
<td>0.99</td>
<td>0.99</td>
</tr>
<tr>
<td>Be$_2^+$</td>
<td>1.43</td>
<td>1.61</td>
<td>1.53</td>
</tr>
<tr>
<td>B$_2^+$</td>
<td>2.18</td>
<td>2.18</td>
<td>2.16</td>
</tr>
<tr>
<td>C$_2^+$</td>
<td>2.70</td>
<td>2.56</td>
<td>2.58</td>
</tr>
<tr>
<td>N$_2^+$</td>
<td>3.22</td>
<td>3.10</td>
<td>3.11</td>
</tr>
<tr>
<td>O$_2^+$</td>
<td>3.19</td>
<td>3.16</td>
<td>3.11</td>
</tr>
<tr>
<td>F$_2^+$</td>
<td>3.65</td>
<td>3.40</td>
<td>3.39</td>
</tr>
</tbody>
</table>

FIG. 1. Potential curve of He$_2^+$ (in eV; 0 eV = He + He$^+$). Solid line, BX; dashed line, GGA91.
TABLE II. Calculated dissociation energies ($D$) and ionization potentials ($IP$) in eV using LDA, BX, and GGA91 density functionals.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$D_{\text{LDA}}$</th>
<th>$D_{\text{BX}}$</th>
<th>$D_{\text{GGA91}}$</th>
<th>$IP_{\text{LDA}}$</th>
<th>$IP_{\text{BX}}$</th>
<th>$IP_{\text{GGA91}}$</th>
<th>Ion</th>
<th>$D_{\text{LDA}}$</th>
<th>$D_{\text{BX}}$</th>
<th>$D_{\text{GGA91}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiH $1 \Sigma^+$</td>
<td>2.63</td>
<td>2.75</td>
<td>2.36</td>
<td>7.87</td>
<td>8.44</td>
<td>7.81</td>
<td>LiH $^+ 2 \Sigma^+$</td>
<td>0.21</td>
<td>0.15</td>
<td>0.06</td>
</tr>
<tr>
<td>BeH $^+ \Sigma^+$</td>
<td>2.61</td>
<td>2.62</td>
<td>2.45</td>
<td>8.33</td>
<td>8.78</td>
<td>8.48</td>
<td>BeH $^+ 1 \Sigma^+$</td>
<td>3.31</td>
<td>3.23</td>
<td>3.03</td>
</tr>
<tr>
<td>BH $^+ \Pi_1$</td>
<td>3.90</td>
<td>3.77</td>
<td>3.56</td>
<td>9.68</td>
<td>10.12</td>
<td>9.63</td>
<td>BH $^+ 1 \Sigma^+$</td>
<td>2.85</td>
<td>2.75</td>
<td>2.66</td>
</tr>
<tr>
<td>CH $^+ \Pi_1$</td>
<td>3.98</td>
<td>3.66</td>
<td>3.56</td>
<td>11.03</td>
<td>11.16</td>
<td>10.65</td>
<td>CH $^+ 1 \Sigma^+$</td>
<td>4.64</td>
<td>4.40</td>
<td>4.23</td>
</tr>
<tr>
<td>NH $^+ \Sigma^+$</td>
<td>4.14</td>
<td>3.96</td>
<td>3.85</td>
<td>13.96</td>
<td>14.24</td>
<td>13.99</td>
<td>NH $^+ 1 \Pi_1$</td>
<td>3.21</td>
<td>3.84</td>
<td>3.49</td>
</tr>
<tr>
<td>OH $^+ \Pi_1$</td>
<td>5.34</td>
<td>4.59</td>
<td>4.59</td>
<td>13.37</td>
<td>13.50</td>
<td>13.05</td>
<td>OH $^+ 2 \Sigma^-$</td>
<td>5.00</td>
<td>5.21</td>
<td>5.16</td>
</tr>
<tr>
<td>FH $^+ \Sigma^+$</td>
<td>7.03</td>
<td>6.16</td>
<td>6.21</td>
<td>16.57</td>
<td>16.89</td>
<td>16.47</td>
<td>FH $^+ 2 \Pi_1$</td>
<td>3.48</td>
<td>3.49</td>
<td>3.37</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Atom</th>
<th>$IP_{\text{LDA}}$</th>
<th>$IP_{\text{BX}}$</th>
<th>$IP_{\text{GGA91}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li $^3S$</td>
<td>5.48</td>
<td>5.83</td>
<td>5.63</td>
</tr>
<tr>
<td>Be $^3S$</td>
<td>9.03</td>
<td>9.48</td>
<td>9.07</td>
</tr>
<tr>
<td>B $^3P$</td>
<td>8.58</td>
<td>8.86</td>
<td>8.55</td>
</tr>
<tr>
<td>C $^3P$</td>
<td>11.76</td>
<td>12.05</td>
<td>11.75</td>
</tr>
<tr>
<td>N $^4S$</td>
<td>14.92</td>
<td>15.22</td>
<td>15.00</td>
</tr>
<tr>
<td>O $^3P$</td>
<td>13.90</td>
<td>14.33</td>
<td>13.75</td>
</tr>
<tr>
<td>F $^3P$</td>
<td>18.06</td>
<td>18.45</td>
<td>17.95</td>
</tr>
</tbody>
</table>

*Data for most of the neutral molecules and atomic systems are also presented in Refs. 15 and 11 and are given here only for completeness.

bIP from spherical atoms to spherical ions.

This Coulomb term is compensated by a corresponding exchange-correlation term in the exact density functional. With approximate forms of the latter one can only expect an incomplete cancellation. For the density functionals studied here one always observes a dominance of the Coulomb term. A discussion of the possibilities of correcting this error is given by Perdew (for some recent advances see Ref. 14).

The energy differences of $\sim 1-4$ eV that are gained in the systems $X^+X^+$, $X^+X^+$ and $X^+X^+$ at a distance of 20 Å with respect to $X+X^+$ are shown in Table I. They rise with the compactness of the atoms along the row. We would like to stress that here energy lowering cannot be used as a criterion for obtaining the solution with broken symmetry ($X^+X^+$).

Only for He$^+$ the energy difference exceeds the dissociation energy of 2.5 eV. The potential curve of this molecule (see Fig. 1, 0 eV=He+He$^+$) calculated with BX and GGA91 and equal charge distribution has a well of 0.4 eV before it becomes a Coulomb repulsion curve of two X$^+X^+$ at large distance. The turning point is at about twice the value of $R_e$. The curves of the other dimer cations also become a Coulomb curve at large distances, but the global energy minimum remains at $R_e$. As we shall see in the comparison of the errors of the dissociation energies of the dimers and dimer cations, this misbehavior of the potential curve near the equilibrium bond distance does not influence the accuracy of $D_e$ very much.

FIG. 2. Errors in the dissociation energies of the hydrides and their cations (in eV). Dotted line, LDA; solid line, BX; dashed line, GGA91.
V. RESULTS

In Table II we list our calculated values. Most of the values for the neutral molecules were already published by Becke and Perdew et al. We include them in our discussion for completeness. The errors of the calculated data are defined with respect to the experimental values collected in Ref. 7. In Fig. 2 we show the errors $\Delta D_e = D_e^{\text{calc}} - D_e^{\text{exp}}$ in the dissociation energies of the hydrides and their cations. The gradient corrections lower the average errors $\Delta D_e$ of the hydrides and hydride cations from $\sim 0.5$ and $0.3$ eV, respectively, using LDA to $0.1-0.2$ eV. The largest error with all three approximations is found for BH$^+$ with $0.6-0.7$ eV.

While no systematical trend in the errors can be seen for the hydrides, the $\Delta D_e$(LDA) of the dimers and dimer cations (Fig. 3) rise in the second half of the row, being maximal for $F_2^+$ with 2.6 eV. This observation could be related to effects of near-degeneracy that are not completely recovered in LDA. The gradient correction approaches yield better results with maximal errors for $F_2^+$ of $0.8$ and $1.3$ eV. The average errors are $0.3$ eV/$0.4$ eV (BX) and $0.5$ eV/$0.6$ eV (GGA91) for the dimers and their cations, respectively. The incorrect dissociation of the dimer cations with the density functionals mentioned above does not seem to influence the dissociation energies much; the errors are of the same order of magnitude for $X_2$ and $X_2^+$. For most molecules the gradient-corrected functionals yield significantly better dissociation energies.

When we look at the ionization potentials of the atoms, hydrides, and dimers (see Fig. 4), LDA and GGA91 show average errors $\Delta \text{IP} = \text{IP}_{\text{calc}} - \text{IP}_{\text{exp}}$ of $0.2-0.4$ eV. The BX ionization potentials run almost parallel to the GGA91 values, but are generally $0.2-0.4$ eV larger, and so the BX values differ from the experimental data by $0.4-0.8$ eV.

Although configuration interaction (CI) calculations yield correct potential curves, the errors in the dissociation energies and ionization potentials can be of the same order.
of magnitude as with the density functionals. In additional CI calculations we found average errors in $D_e$ of 1.1 eV and in $IP$ of 0.3 eV, but with reversed sign (i.e., the calculated values are too low).

VI. CONCLUSION

The calculated values for dissociation energies and ionization potentials are usually too large, i.e., the electron richer systems are stabilized more by the used density functionals than the systems with more distributed or fewer electrons. While the exchange-only gradient correction of Becke yields the better dissociation energies for the dimers and their ions, the generalized gradient approximation of Perdew and Wang works better for the ionization potentials. The wrong behavior of the density functional energies for the dimer cations at large distances does not affect the accuracy of the $D_e$ at equilibrium bond lengths.

ACKNOWLEDGMENTS

We are grateful to Professor A. D. Becke for giving us the program NUMOL and to Professor J. P. Perdew for sending us the subroutines for calculating the GGA91 density functional. We would like to thank Professor H.-J. Werner for making available the program MOLPRO. We would also like to thank Professors A. D. Becke, J. P. Perdew, and H. Stoll for comments on the manuscript.

APPENDIX

(1) Local spin density approximation (LDA). Exchange energy

$$e_X^{\text{LDA}} = \frac{3}{2} \left( \frac{3}{4\pi} \right)^{1/3} \int \rho_x^{4/3} + \rho_y^{4/3} \rho_z^{4/3} d^3r.$$

Correlation energy

$$E_C^{\text{LDA}} = \int \rho_x^{\text{LDA}}(\rho_x^{\alpha} \rho_y^{\beta}) d^3 v,$$

$$E_C^{\text{LDA}} = e_U^{\text{LDA}}(1-f(s)) + e_F f(s)+\alpha \sigma f(1-\xi^3)/d,$$

$$f = [(1+\xi)4/3+(1-\xi)4/3-2]/\gamma,$$

$$\gamma = 0.519 842 1, \quad d = 1.709 921,$$

$$e_U = -2a_{02}(1+a_{12}r_4)$$

$$\times \ln \left[ 1 + \frac{1}{2a_{02}(b_{12}x + b_{23}y^2 + b_{33}y^3 + b_{43}y^4)} \right],$$

$$e_U = -2a_{10}(1+a_{11}r_4)$$

$$\times \ln \left[ 1 + \frac{1}{2a_{10}(b_{11}x + b_{23}y^2 + b_{33}y^3 + b_{43}y^4)} \right],$$

$$\alpha_c = -2a_{03}(1+a_{13}r_4)$$

$$\times \ln \left[ 1 + \frac{1}{2a_{03}(b_{13}x + b_{23}y^2 + b_{33}y^3 + b_{43}y^4)} \right],$$

$$x=r_s^{1/2}, \quad r_s = \left( \frac{3}{4ap} \right)^{1/3}, \quad \xi = (\rho_\alpha - \rho_\beta)/\rho,$$

$$a_{01} = 0.031 097, \quad a_{02} = 0.015 545 35, \quad a_{03} = 0.016 886 9,$$

$$a_{11} = 0.213 70, \quad a_{12} = 0.205 48, \quad a_{13} = 0.111 25,$$

$$b_{11} = 7.595 7, \quad b_{12} = 14.118 9, \quad b_{13} = 10.357,$$

$$b_{21} = 3.587 6, \quad b_{22} = 6.197 7, \quad b_{23} = 3.623 1,$$

$$b_{31} = 1.638 2, \quad b_{32} = 3.366 2, \quad b_{33} = 0.880 26,$$

$$b_{41} = 0.492 94, \quad b_{42} = 0.625 17, \quad b_{43} = 0.496 71.$$

(2) Becke gradient correction for exchange (BX)

$$E_X^{\text{BX}} = E_X^{\text{LDA}} - \sum_{\sigma} 0.0042$$

$$\times \int \rho_\sigma^{4/3} x_\sigma^{1/3} d^3r,$$

$$x_\sigma = \left| \nabla \rho_\sigma \right| / \rho_\sigma^{4/3}, \quad \sigma = \text{spin } \alpha \text{ or spin } \beta.$$

(3) Generalized gradient approximation (GGA91). Exchange energy

$$E_X^{\text{GGA91}} = E_X^{\text{LDA}} + \sum_{\sigma} 0.738 558 8 \cdot 2^{1/3}$$

$$\times \int \rho_\sigma^{4/3}[F(s) - 1] d^3r,$$

$$F(s) = \frac{1 + 0.196 455 \cdot \text{arsinh}(7.7965s) + (0.2743 - 0.1508e^{-100s})s^2}{1 + 0.196 455 \cdot \text{arsinh}(7.7965s) + 0.0045^2},$$

$$s = (3\pi^2)^{-1/3} \left| \nabla \rho_\sigma \right| / \rho_\sigma^{4/3},$$

$$\sigma = \text{spin } \alpha \text{ or spin } \beta.$$

Correlation energy

$$E_C^{\text{GGA91}} = E_C^{\text{LDA}} + \int (H_0 + H_1) \rho d^3r,$$

$$H_0 = \frac{\beta^2}{2\alpha} \ln \left[ 1 + \frac{2\alpha}{\beta \frac{1}{1 + A^2 + A^2 r^2}} \right],$$

$$H_1 = 15.7559 (C_\sigma - 0.003 521) \cdot 0.559 e^{-100s}(\xi^2 r^2/k^2),$$


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k_F = (3πρ)^{1/3}, \quad k_z = (4k_F/π)^{1/2}, \quad r_z = \left(\frac{3}{4πρ}\right)^{1/3}, \\
ξ = (ρ_α - ρ_β)/ρ, \quad g = [(1 + ξ)^{2/3} + (1 - ξ)^{2/3}]^{-1}, \\
\rho^2 = (\nabla ρ)^2/4g^2k_ρ^2, \quad A = \frac{2α}{β} \frac{1}{c^2ρ_ρ^2(c^2ρ_ρ^2)^{-1}}, \\
α = 0.09, \quad β = 15.755 \quad 9 \quad 0.004 \quad 235, \\
C_x = \frac{c_1 + c_2r_s + c_3r_s^2}{1 + c_4r_s + c_5r_s^2 + c_6r_s^3} - c_x, \quad c_x = -0.001 \quad 667 \quad 212, \\
c_1 = 0.002 \quad 568, \quad c_2 = 0.023 \quad 266, \quad c_3 = 7.389 \cdot 10^{-6}, \\
c_4 = 8.723, \quad c_5 = 0.472, \quad c_6 = 7.389 \cdot 10^{-2}. \\

1M. Cook and M. Karplus, J. Phys. Chem. 91, 31 (1987). \\

For experimental data see Table I in Ref. 16; data for Heo from Ref. 8, R_o = 1.08 Å, D_o = 2.47 eV. 


10A. D. Becke (private communication). 


15A. D. Becke (to be published). 


17The CI calculations were performed with the program MOLPRO [Hartree–Fock part by W. Meyer and H.-J. Werner, CI calculation by H.-J. Werner and P. J. Knowles (Ref. 18)], including all excitations in valence space (1s and 2s orbitals kept closed), basis (1s, 3p, 2d) contracted to [7s, 3p, 2d] from Ref. 19. 
