

Correlation contributions to first ionization potentials of first-row atoms, hydrides and dimers obtained with gradient corrected GGA91 density functionals

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Ionization potentials calculated in the Hartree-Fock approximation can be improved by adding correlation contributions given by density functionals, typical errors being of 0.01 hartree. This accuracy is not present when dissociation energies are considered.

1. Introduction

The ionization potential (IP) of a molecule is one of its most important properties, and many experimental techniques exist for its measurement. It is thus also important to have reliable calculations. Nowadays Hartree-Fock programs can be used routinely for molecules of medium size (see, e.g. ref. [1]). The error of these calculations (mainly due to electron correlation) are typically of the order of 1 eV when the ionization removes an electron from a doubly occupied orbital. An easy method to improve on this result could be the use of density functionals (DFs). The aim of this paper is to show results obtained with the newly developed gradient-corrected density functionals of Perdew and co-workers [2,3]. For atoms results can already be deduced from the published values [4] for this functional while results obtained with different functionals can be found in several places (see, e.g., refs. [5-7]). On the other hand, it is well known that in molecules strong near-degeneracy effects can be present, and that nowadays known correlation energy DFs cannot describe them (see, e.g. refs. [7,8]). As these can appear both in the ion and in the parent molecule a compensation of the errors is often present.

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2. Theory

Kohn and Sham have suggested [9] using density functionals to obtain correlation energies. This approach has been tested by several groups (see, e.g., refs. [5-7,10-12]). The main problem is to find a reliable correlation energy density functional, $E_c[n]$, as we know no systematic way to improve on the simple local density approximation:

$$E_c[n_+, n_-] = \int (n_+ + n_-) \epsilon_c(n_+, n_-) d^3r$$

(n_{\pm} is the spin-up/spin-down electron density, ϵ_c usually the correlation energy per particle of the homogeneous electron gas of density n). While Hohenberg and Kohn [13] suggested a gradient expansion, it soon turned out that the first correction implied by this expansion does not work [14]. It was later suggested (see e.g. ref. [15]) that $\epsilon_c(n)$ should be replaced by $\epsilon_c(n, \nabla n)$ and there are presently several functional forms available for the latter. The most recent ones (GGA91 [2], generalized gradient approximation 1991, and its variant GGA91' [3]) are determined from first principles, use a real-space cutoff of the long-range part of the density-gradient expansion and satisfy several exact conditions. The explicit formulas for GGA91 are shown in table 1.

The expression for the local part ($n\epsilon_c$) is different from the commonly used form given by Vosko et al. (VWN [16]) – without producing, however, significant numerical changes.

Table 1
Explicit formulas for GGA91

$$E_c[n] = \int d^3r n(\epsilon_c + H_0 + H_1), \quad H_0 = g^3 \frac{\beta^2}{2\alpha} \ln \left(1 + \frac{2\alpha}{\beta} \frac{t^2 + At^4}{1 + At^2 + A^2t^4} \right)$$

$$H_1 = 15.7559(C_c - 0.003521)g^3 t^2 \exp[-100g^4(k_s^2/k_F^2 t^2)],$$

$$k_F = (3\pi n)^{1/3}, \quad k_s = (4k_F/\pi)^{1/2}, \quad r_s = (3/4\pi n)^{1/3}, \quad \zeta = (n_+ - n_-)/n, \quad g = \frac{1}{2}[(1+\zeta)^{2/3} + (1-\zeta)^{2/3}],$$

$$t^2 = (\nabla n)^2 / 4g^2 k_s^2 n^2, \quad A = \frac{2\alpha}{\beta} \frac{1}{\exp(2\alpha\epsilon_c/g^3\beta^2) - 1}, \quad \alpha = 0.09, \quad \beta = 15.7559 \times 0.004235$$

$$\epsilon_c = \epsilon^U(1 - f\zeta^4) + \epsilon^P f\zeta^4 + \alpha_c f(1 - \zeta^4)/d, \quad f = [(1+\zeta)^{4/3} + (1-\zeta)^{4/3} - 2]/\gamma,$$

$$\gamma = 0.5198421, \quad d = 1.709921,$$

$$\epsilon^P = -2a_{02}(1 + a_{12}r_s) \ln \left(1 + \frac{1}{2a_{02}(b_{12}x + b_{22}x^2 + b_{32}x^3 + b_{42}x^4)} \right),$$

$$\epsilon^U = -2a_{01}(1 + a_{11}r_s) \ln \left(1 + \frac{1}{2a_{01}(b_{11}x + b_{21}x^2 + b_{31}x^3 + b_{41}x^4)} \right),$$

$$\alpha_c = -2a_{03}(1 + a_{13}r_s) \ln \left(1 + \frac{1}{2a_{03}(b_{13}x + b_{23}x^2 + b_{33}x^3 + b_{43}x^4)} \right),$$

$$x = r_s^{1/2}, \quad a_{01} = 0.031097, \quad a_{02} = 0.01554535, \quad a_{03} = 0.0168869, \quad a_{11} = 0.21370, \quad a_{12} = 0.20548, \quad a_{13} = 0.11125$$

$$b_{11} = 7.5957, \quad b_{12} = 14.1189, \quad b_{13} = 10.357, \quad b_{21} = 3.5876, \quad b_{22} = 6.1977, \quad b_{23} = 3.6231$$

$$b_{31} = 1.6382, \quad b_{32} = 3.3662, \quad b_{33} = 0.88026, \quad b_{41} = 0.49294, \quad b_{42} = 0.62517, \quad b_{43} = 0.49671$$

$$C_c = \frac{c_1 + c_2 r_s + c_3 r_s^2}{1 + c_4 r_s + c_5 r_s^2 + c_6 r_s^3} - c_x, \quad c_x = -0.001667212, \quad c_1 = 0.002568,$$

$$c_2 = 0.023266, \quad c_3 = 7.389 \times 10^{-6}, \quad c_4 = 8.723, \quad c_5 = 0.472, \quad c_6 = 7.389 \times 10^{-2}$$

3. Computational details

As in our previous work [6,7] we first performed Hartree-Fock calculations with good Gaussian basis sets [8,17] at the experimental equilibrium distance (cf. table 2). The energies at Hartree-Fock equilibrium distances are lower by maximally 0.2 eV (O_2^+). As the same effect occurs both for the ion and the parent molecule (0.1 eV for O_2), the error in the adiabatic Hartree-Fock ionization potential remains relatively small when compared with the errors of the density functional (see below) (The error is similar when the Hartree-Fock+DF equilibrium distance is used). Furthermore, our basis set (14s, 9p, 2d contracted to 7s, 5p, 2d) could be improved. By replacing the 2d Gaussian with (6d, 4f) sets contracted to 3d, 2f the maximal energy lowering is 0.2 eV (O_2^+). There is again a compensation when con-

sidering the ionization potential which is changed by only 0.05 eV (O_2 to O_2^+).

The densities obtained with the Hartree-Fock calculation were used to calculate the density functionals. The effect of basis set improvement on the densities or the change of the functionals with the interatomic distance is small: 0.1 eV for the correlation energies and below 0.03 eV for the correlation contributions to the ionization potential.

The symmetry of the Hamiltonian determined both our densities and the Hartree-Fock orbitals (equivalent p or π orbitals). Relaxing these restrictions does not change significantly our results as both effects (each of a few tenth of an eV) cancel out (0.03 eV for the correlation energies)

The ionization potentials are computed as the difference between the energies of the atoms or molecules and the ions, the dissociation energies as the

Table 2

Experimental data at equilibrium distance (R_e , in bohr); dissociation energies (D_e , in eV) and ionization potentials (IP, in eV)^{a)}. In order to compare with the calculated values, we corrected the experimental data for zero-point energies using the experimental constants ω_e and $\omega_e x_e$. Hydride cations dissociate to A + H⁺ for A = Li, Be, B, C; to A⁺ + H for A = N, O, F

Atom	IP	Molecule	R_e	D_e	Molecule	R_e	D_e
Li ¹ S	5.39	LiH ⁺ ² Σ^+	4.140	0.12	Li ₂ ⁺ ² Σ_g^+	5.858	1.31
Be ¹ S	9.32	BeH ⁺ ¹ Σ^+	2.480	3.28	Be ₂ ⁺ ² Σ_u^+	4.216 ^{c)}	1.97 ^{c)}
B ² P	8.30	BH ⁺ ² Σ^+	2.295	2.11	B ₂ ⁺ ² Σ_g^+	4.015 ^{d)}	2.25 ^{d)}
C ³ P	11.26	CH ⁺ ¹ Σ^+	2.137	4.25	C ₂ ⁺ ² Π_u	2.459	5.38
N ⁴ S	14.53	NH ⁺ ² Π_r	2.022	3.71 ^{b)}	N ₂ ⁺ ² Σ_g^+	2.110	8.85
O ³ P	13.62	OH ⁺ ³ Σ^-	1.944	5.28	O ₂ ⁺ ² Π_g	2.110	6.78
F ² P	17.42	FH ⁺ ² Π_i	1.892	3.61	F ₂ ⁺ ² Π_g	2.498	3.41

Molecule	R_e	D_e	IP	Molecule	R_e	D_e	IP
LiH ¹ Σ^+	3.015	2.51	7.76 ^{e)}	Li ₂ ¹ Σ_g^+	5.051	1.06	5.15
BeH ² Σ^+	2.537	2.16	8.20 ^{f)}	Be ₂ ¹ Σ_g^+	4.63 ^{h)}	0.11 ^{h)}	7.46 ⁱ⁾
BH ¹ Σ^+	2.329	3.56	9.76 ^{f)}	B ₂ ³ Σ_g^-	3.005	3.06	8.99 ^{d)}
CH ² Π_r	2.115	3.64	10.65	C ₂ ¹ Σ_g^+	2.348	6.32	12.18
NH ³ Σ^-	1.958	3.63 ^{f)}	13.51 ^{e)}	N ₂ ¹ Σ_g^+	2.074	9.91	15.59
OH ² Π_i	1.832	4.62	12.94	O ₂ ³ Σ_g^-	2.282	5.21	12.05
FH ¹ Σ^+	1.733	6.12	16.10	F ₂ ¹ Σ_g^+	2.668	1.66	15.68

^{a)} r_e and D_e for the hydrides (cations) from ref. [18] if not otherwise specified and IP_e and D_e for the dimers (cations) from ref. [19] if not otherwise specified.

^{b)} From ref. [20]. ^{c)} From ref. [21] (MR-CI calc.). ^{d)} From ref. [22] (MR-CI calc.).

^{e)} From ref. [23]. ^{f)} From ref. [18]. ^{g)} From ref. [20].

^{h)} From ref. [24]. ⁱ⁾ Calculated from $D_e(\text{Be}_2)$, $D_e(\text{Be}_2^+)$ and IP(Be).

Table 3

Calculated dissociation energies and ionization potentials (in eV)^{a)}

Atom	IP _{HF}	IP _{DF}	Molecule	D_{HF}	D_{DF}	Molecule	D_{HF}	D_{DF}
Li	5.34	5.53	LiH ⁺	0.12	0.13	Li ₂ ⁺	1.24	1.29
Be	8.04	8.91	BeH ⁺	2.06	2.93	Be ₂ ⁺	1.52	1.91
B	7.93	8.61	BH ⁺	2.26	2.65	B ₂ ⁺	1.47	1.81
C	10.80	11.47	CH ⁺	3.19	3.95	C ₂ ⁺	0.39	1.70
N	13.96	14.65	NH ⁺	2.91	3.42	N ₂ ⁺	4.92	5.05
O	11.89	13.29	OH ⁺	5.22	5.29	O ₂ ⁺	1.07	3.13
F	15.72	16.96	FH ⁺	3.54	3.61	F ₂ ⁺	-1.49	-0.56

Molecule	D_{HF}	D_{DF}	IP _{HF}	IP _{DF}	Molecule	D_{HF}	D_{DF}	IP _{HF}	IP _{DF}
LiH	1.48	2.25	6.70	7.65	Li ₂	0.16	0.76	4.27	5.00
BeH	2.14	2.47	8.13	8.47	Be ₂	-0.33	-0.04	6.19	6.96
BH	2.78	3.47	8.45	9.42	B ₂	0.87	1.54	7.34	8.34
CH	2.47	3.40	10.07	10.92	C ₂	0.68	2.39	11.08	12.17
NH	2.09	3.21	12.78	13.58	N ₂	5.03	7.51	16.03	17.11
OH	3.04	4.11	11.40	12.68	O ₂	1.15	3.13	11.97	12.74
FH	4.34	5.35	14.41	15.55	F ₂	-1.37	-0.69	15.85	16.84

^{a)} D_{HF} = Hartree-Fock dissociation energy, D_{DF} = dissociation energy including DF, IP_{HF} = Hartree-Fock ionization potential, IP_{DF} = ionization potential including DF.

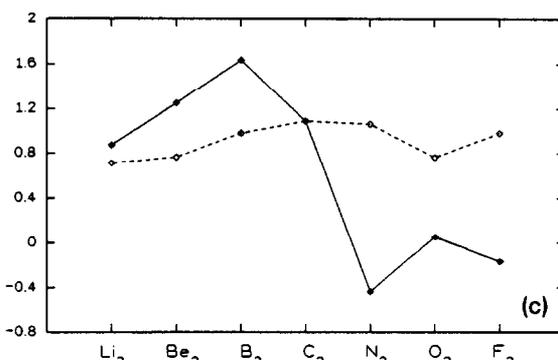
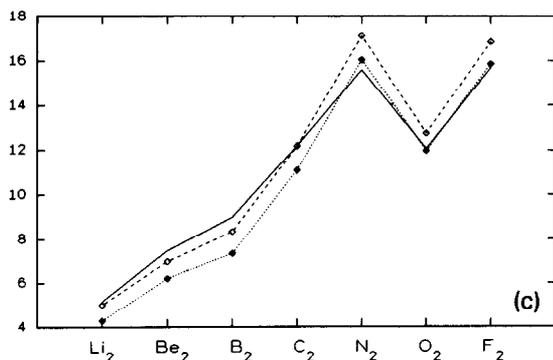
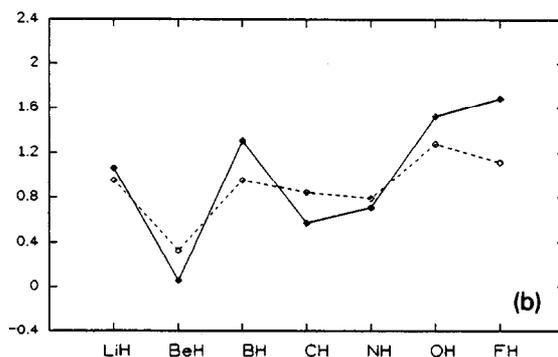
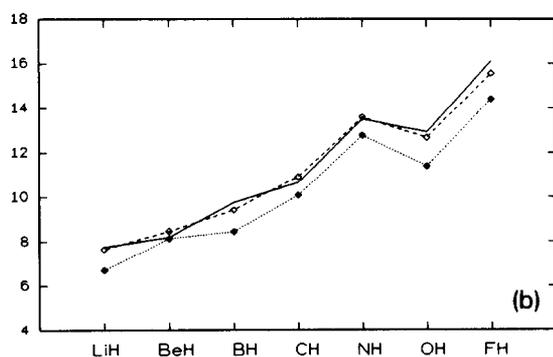
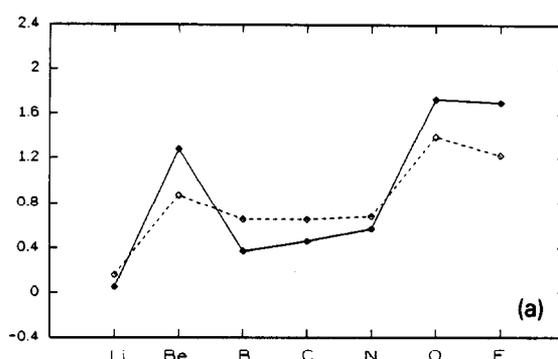
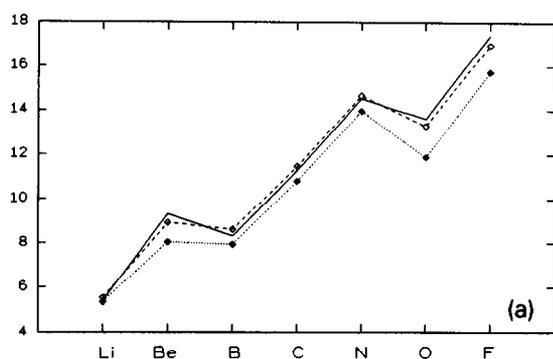


Fig. 1. Experimental and calculated ionization potentials (eV) for (a) atoms, (b) hydrides and (c) dimers. Solid line: experimental; dashed line: Hartree-Fock+DF; dotted line: Hartree-Fock.

Fig. 2. Correlation contributions to ionization potentials (Δ IP in eV) for (a) atoms, (b) hydrides and (c) dimers. Solid line: exact; dashed line: DF.

difference between the energies of the molecules and the atoms or ions. The difference between the correlated and the Hartree-Fock values will be denoted Δ IP and Δ D_e , respectively.

4. Results

We have selected from literature some experimental data for the judgement of the quality of our results (cf. table 2). Our calculated results are shown in table 3. As the ionization potentials and dissociation energies differ at most by 0.03 eV for GGA91

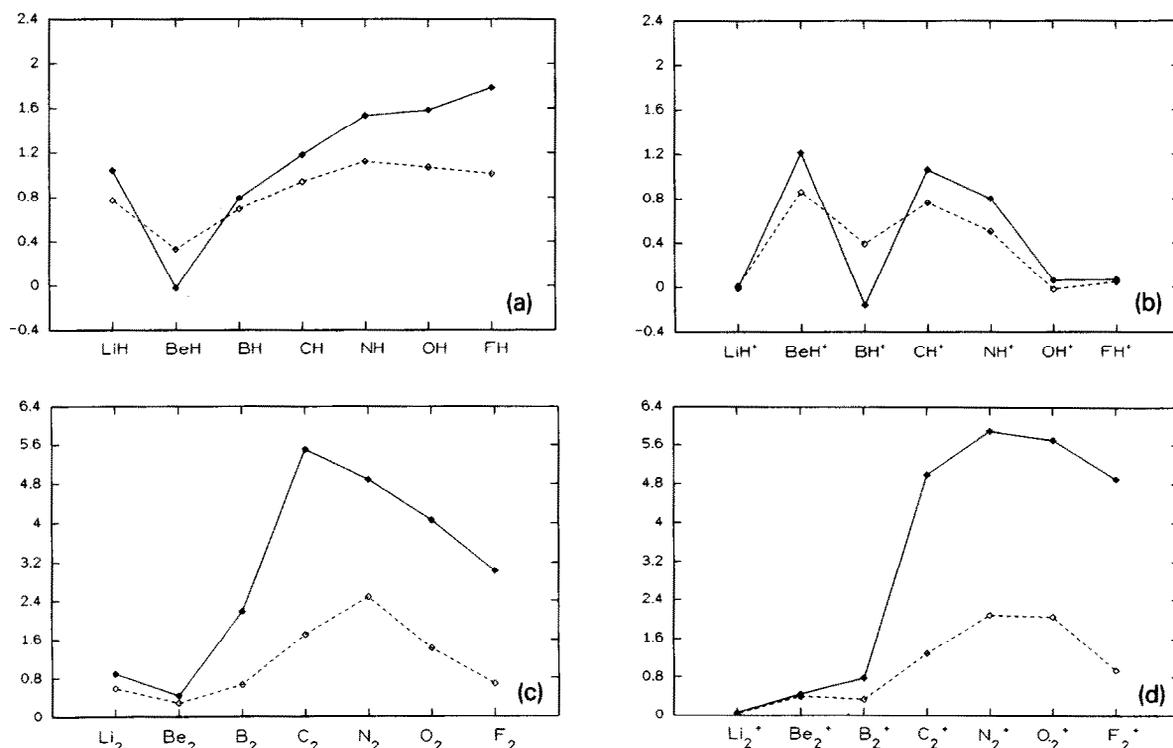


Fig. 3. Correlation contributions to dissociation energies ($\Delta\Delta_e$ in eV) for (a) hydrides ((c) cations) and (b) dimers ((d) cations). Solid line: exact; dashed line: DF.

and GGA91' we list only the GGA91 values. In fig. 1 we compare the calculated to the experimental IPs. Hartree-Fock already reproduces the main trends, but yields numbers which are generally smaller than the experimental IPs. It can be seen that after using GGA91 for the correlation energies, the errors have both signs. The average error of the Hartree-Fock IP is around 0.9 eV. The density functional reduces it to ≈ 0.3 eV for the atoms and hydrides; for dimers it is less effective (error ≈ 0.6 eV).

The exact Δ IP of atoms and hydrides show a clear distinction between the removal of an electron from a singly occupied orbital (0.05–0.7 eV) or from a doubly occupied orbital (1.1–1.8 eV) (compare Li, B, C, N, BeH, CH, NH with Be, O, F, LiH, BH, OH, FH). Values rise slightly as the nuclear charge and the number of electrons increase. These trends are reproduced by the density functional, being, however, less pronounced in the calculated Δ IP (cf. fig. 2).

The exact correlation contributions to the disso-

ciation energies of the hydrides and their cations are 0.8–1.8 eV when an electron pair is split, otherwise -0.2 to 0.1 eV (cf. fig. 3). Although the DF follows this trend, the errors are larger at the right end of the row (0.8 eV for FH). As the bond in FH is partly ionic and the negative charge must be shifted back from F to H when the bond breaks, this error can be compared with the DF error in the correlation contribution to the electron affinity of F (1.1 eV).

The results are worse for the dimers. The exact correlation contribution to the IP has a maximum for B₂ and negative values for N₂ and F₂ while DF yields a nearly constant value (≈ 1 eV). We relate this discrepancy to the fact that the present DFs cannot reproduce near-degeneracy effects. The latter are nearly equal in C₂ and C₂⁺. Multi-configuration-self-consistent-field (MCSCF) calculations using all the determinants which are generated in the valence space give correlation energies of 6.5 and 6.2 eV, respectively. This compensation is not present in Δ IP for N₂, O₂ and F₂: the MCSCF present energies

for the molecules (cations) are: 4.1 eV (5.8 eV), 2.9 eV (4.6 eV) and 2.2 eV (3.7 eV). This can be easily understood by looking at the number of determinants which can be generated in the valence space. They are similar for C_2 and C_2^+ , but roughly a factor of two smaller for X_2 than for X_2^+ ($X=N, O, F$).

B_2 is a special case. A CI calculation shows that the double excitation from $2\sigma_u$ to $3\sigma_g$ is very important. It is also dominant for the ${}^2\Pi_u$ state of B_2^+ . The ground state of B_2^+ is, however, ${}^2\Sigma_g$ where the $3\sigma_g$ orbital is singly occupied and the excitation mentioned above cannot contribute to the correlation energy. Thus, ΔIP becomes larger for the ionization into ${}^2\Sigma_g$ than into ${}^2\Pi_u$ (1.6 versus 0.7 eV estimated from a CI calculation [22]). On the other hand one does not observe this effect with the DFs: both states of B_2^+ have similar correlation energies. One could thus reproduce quite well the ionization to the ${}^2\Pi_u$ state but not that to the ${}^2\Sigma_g$ state of B_2^+ .

When the dissociation of the dimers and their cations is regarded, the near-degeneracy contributions cannot cancel. So they can cause errors in the DF correlation contributions as large as 4 eV.

In this paper, we have combined an exact treatment of exchange with a GGA density-functional approximation for correlation. An alternative approach treats exchange and correlation both by GGAs, and so allows for an expected cancellation of errors between them. As shown for example in ref. [4], this second approach can yield more accurate ionization and dissociation energies than the first, especially when Hartree-Fock theory is a poor starting point. Another possibility to improve the results is a coupling of the DFs for correlation with multi-determinant methods (cf. refs. [8,10,25,26]).

5. Conclusion

Tests on molecules showing a variety of bonding characteristics indicate that the new GGA91 density functional can be used to improve Hartree-Fock values of first ionization potentials. The errors are typically reduced by a factor of two. In the case of the homonuclear dimers the errors for ionization potentials are not as large as for dissociation energies, as a substantial compensation of near-degeneracy effects is present.

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