

COMMENTS

Comments are short papers which criticize or correct papers of other authors previously published in the **Physical Review**. Each Comment should state clearly to which paper it refers and must be accompanied by a brief abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.

Comment on “Local exchange-correlation functional: Numerical test for atoms and ions”

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Zhao and Parr [Phys. Rev. A **46**, R5320 (1992)] recently introduced an exchange-correlation functional for the local-density approximation of the density-functional theory. In this paper we report results for atoms, molecules, and crystalline solids using their functional as well as traditional ones. We conclude that their functional yields a better description of neither the ionization energies nor of the chemical bond in polyatomic systems.

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It is widely believed that the local-density approximation (LDA) of the exchange-correlation (XC) energy in density-functional theory (DFT) [1–3] gives a reliable description of the *ground-state properties* of polyatomic systems. Up to now the best founded LDA functional is that of Ceperley and Alder (CA80) [6–9]. However, as the XC energy is evaluated variationally it gives an upper bound of the exact result. In this respect but also with respect to treat inhomogeneous electron densities a search for better LDA functionals, therefore, appears legitimate. Obviously, the ultimate test of such a “better” functional is a comparison with experiments, the most important requirement being an accurate description of the ground-state chemical bond, i.e., in particular of the interatomic binding energy, bond lengths, and elastic constants. Using the general ansatz for the XC functional

$$E_{XC}[\rho] = \int \varepsilon_{XC}[\rho] \rho(r) d^3r, \quad (1)$$

where in the LDA the functional $\varepsilon_{XC}[\rho]$ is approximated by a function $\varepsilon_{XC}^{LDA}(\rho)$, Zhao and Parr (ZP92) [10,11] recently proposed a function $\varepsilon_{XC}(\rho)$ which they claim to work better than those typically applied (e.g., those of Wigner (W34) [4,5] or of CA80)

$$\varepsilon_{XC}^{ZP92}(\rho) = -\alpha_0 \rho^{1/3} \left[1 - \kappa \rho^{1/3} \ln \left(1 + \frac{1}{\kappa \rho^{1/3}} \right) \right], \quad (2)$$

where the parameters $\alpha_0 = 1.86444$ Ry bohr and $\kappa = 9.473\,62 \times 10^{-3}$ bohr are obtained from a least-square fit to accurately known XC energies of light closed-shell sample atoms and ions. Rydberg atomic units are used throughout the paper. In self-consistent calculations for some selected atomic and ionic systems [12,13] the ZP92 functional yields total energies better than those obtained using other LDA functionals based on the homogeneous electron gas. In order to illustrate the differences

between those functionals and ZP92 we display in Fig. 1 the quantity

$$\Delta\varepsilon(r_s) = \varepsilon_{XC}(r_s) - \varepsilon_X^{KS}(r_s), \quad (3)$$

where ε_X^{KS} is the Kohn-Sham exchange, $\varepsilon_X^{KS}(r_s) = -(3/2\pi)(9\pi/4)^{1/3}/r_s$, with the density parameter $r_s = (3/4\pi\rho)^{1/3}$. It is obvious that ZP92 gives rise to a substantial energy gain at intermediate densities ($0.25 < r_s < 3$) when compared to homogeneous-electron-gas-based XC functionals. At very high densities, e.g., close to the nucleus in some atoms, the correlationlike contribution $\Delta\varepsilon$ becomes repulsive for the ZP92 approach.

This is certainly an unphysical result but it is not clear if it really matters in practice. To test the usefulness of

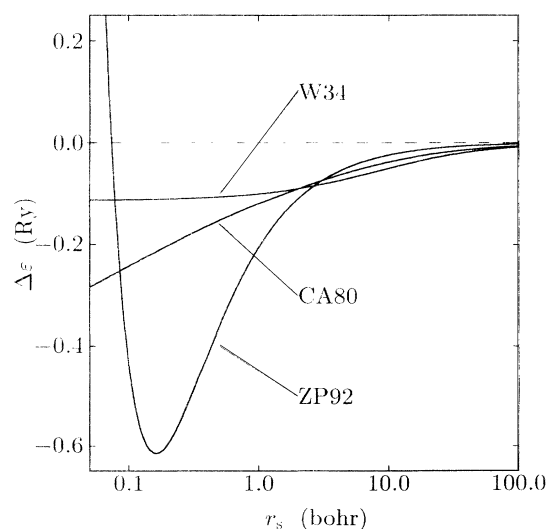


FIG. 1. Exchange-correlation energy per particle beyond Kohn-Sham exchange [see Eq. (3)] of the W34, CA80, and ZP92 functionals as a function of the density parameter r_s .

TABLE I. Energy differences (in eV) between atoms and ions for which both the initial state and the final state have closed shells. Deviations (in %) from experiment [14] are given in parentheses. Atoms and ions marked with an asterisk had been used by ZP92 to determine their functional.

System		Experiment	LDA model		
$ I\rangle$	$ F\rangle$		W34	CA80	ZP92
Be*	Be ^{2+*}	27.53	27.42 (−0.42)	27.30 (−0.86)	27.55 (+0.05)
Mg	Mg ²⁺	22.68	23.28 (+2.65)	23.12 (+1.94)	23.23 (+2.40)
Mg ²⁺	Mg ⁸⁺	1007.98	1006.41 (−0.16)	1010.52 (+0.25)	1028.76 (+2.06)
Mg ⁸⁺	Mg ¹⁰⁺	695.48	690.60 (−0.70)	691.69 (−0.54)	695.63 (+0.02)
Ca	Ca ²⁺	17.98	18.63 (+3.58)	18.41 (+2.39)	18.37 (+2.14)
Zn	Zn ²⁺	27.36	29.01 (+6.05)	28.96 (+5.85)	29.20 (+6.73)
Cd	Cd ²⁺	25.90	27.19 (+4.99)	27.15 (+4.81)	27.45 (+5.97)
Hg	Hg ²⁺	29.19	30.42 (+4.20)	30.44 (+4.28)	30.94 (+5.97)
He*	He ²⁺	79.00	76.67 (−2.95)	77.12 (−2.39)	79.28 (+0.35)
Ne*	Ne ^{6+*}	507.23	507.18 (−0.01)	510.01 (+0.55)	522.86 (+3.08)
Ar*	Ar ⁶⁺	309.96	308.35 (−0.52)	309.82 (−0.05)	316.63 (+2.15)
Kr	Kr ⁶⁺	271.00	267.33 (−1.35)	268.49 (−0.93)	273.88 (+1.06)
mean error			— (+1.28)	— (+1.28)	— (+2.67)
r.m.s.			— (3.03)	— (2.79)	— (3.39)

TABLE II. Bond lengths (in bohr) of H, C, N, and F dimers. Deviations (in %) from experiment [15] are given in parentheses.

System	Experiment	LDA model		
		W34	CA80	ZP92
H–H	1.400	1.461 (+4.3)	1.443 (+3.1)	1.389 (−0.8)
C–C	2.347	2.373 (+1.1)	2.353 (+0.2)	2.281 (−2.8)
N–N	2.067	2.092 (+1.2)	2.077 (+0.5)	2.020 (−2.3)
F–F	2.668	2.657 (−0.4)	2.630 (−1.4)	2.534 (−5.0)

TABLE III. Structural parameters of H₂CO. Deviations (in %) from experiment [15] are given in parentheses.

Parameter	Experiment	LDA model		
		W34	CA80	ZP92
d_{CO} (bohr)	2.29	2.29 (<0.1)	2.28 (−0.4)	2.21 (−3.5)
d_{CH} (bohr)	2.11	2.15 (+1.9)	2.12 (+0.5)	2.06 (−2.4)
α_{HCH} (°)	116.5	115.9 (−0.5)	115.7 (−0.7)	114.0 (−2.2)

TABLE IV. Equilibrium lattice constant and bulk modulus of crystalline Mo (bcc) and Si (diamond). Deviations (in %) from experiment [16–18] are given in parentheses (nrel = nonrelativistic, rel = scalar relativistic).

Parameter	System	Experiment	Modus	LDA model		
				W34	CA80	ZP92
a_0 (bohr)	Si	10.26	nrel	10.33 (+0.7)	10.23 (−0.3)	9.92 (−3.3)
	Mo	5.949	nrel	5.97 (+0.4)	5.91 (−0.7)	5.72 (−3.8)
	Mo		rel	5.94 (−0.2)	5.89 (−1.0)	5.71 (−4.0)
B_0 (Mbar)	Si	0.99	nrel	0.89 (−10.1)	0.96 (−3.0)	— (> 20)
	Mo	2.608	nrel	2.71 (+3.9)	2.83 (+8.5)	— (> 20)
	Mo		rel	2.81 (+7.7)	3.08 (+18.1)	— (> 30)

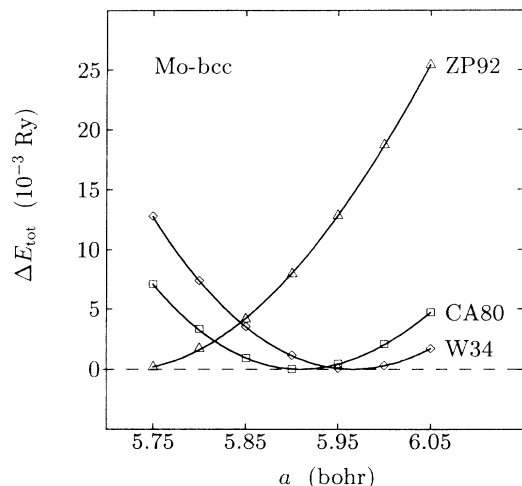


FIG. 2. Total energy of crystalline Mo (bcc) as a function of the lattice parameter, as obtained from a nonrelativistic calculation using different XC functionals. The total energy at equilibrium was chosen as energy zero.

the ZP92 functional, we studied the ground-state properties of a number of non-spin-polarized atoms, molecules, and crystalline solids. The results are compared to experimental data [14–18] and the conventional LDA functionals (W34 and CA80).

As a test we calculated the energy differences between closed-shell atoms and ions. The results are presented in Table I. They do not indicate that the ZP92 functional yields a consistent improvement. Remarkably, this even holds for those atoms and ions that were used by ZP92 to determine their functional (in the table these systems are marked with asterisks).

Proceeding to molecular systems, we calculated the bond lengths of H_2 , C_2 , N_2 , and F_2 as well as of formaldehyde (H_2CO). For these studies we used a DFT-LDA cluster method [19] which is in some respects similar to the program of Salahub *et al.* [20]. The method employs a Gaussian type basis set for the orbital representation and evaluates the XC contributions numerically with a high accuracy and without the need to introduce auxiliary basis sets for the electron density and the XC potential [19,21]. The results of the calculations are listed in Tables II and III. For all molecules the bond lengths obtained with the ZP92 model are considerably smaller than those obtained with CA80 and W34.

Finally, in order to get insights into the applicability of the ZP92 functional to crystalline systems we performed full-potential linear augmented plane-wave calculations [22] of the equilibrium lattice parameter and the bulk

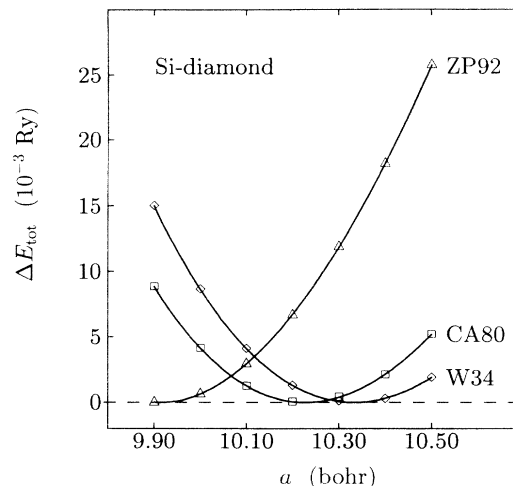


FIG. 3. Same as in Fig. 2 but for Si in the diamond structure.

modulus of a typical metal (bcc Mo) and a typical semiconductor (Si in the diamond structure). For Mo we use 100 \mathbf{k} points in the irreducible part of the Brillouin zone to describe the valence electrons while in the case of Si a set of 10 special \mathbf{k} points was employed. The results presented in Table IV and the solid lines in Figs. 2 and 3 represent a least-square fit to Murnaghan's equation of state [23]. The observed deviations of the ZP92 functional from experimental data are significantly larger than those of the W34 and CA80 functionals. The equilibrium lattice constant decreases by more than 3% compared to experimental and other theoretical results, and the bulk modulus is overestimated by more than 20%.

From the total-energy calculations for free atoms and ions in Ref. [10] the ZP92 form of the XC functional indeed appears to be superior to other approaches. However, with respect to a proper theoretical description of the chemical bond in polyatomic systems our study shows that the new functional works worse than the “traditional” LDA functionals.

Note added. After submission of this Comment Professor Parr sent us a copy of Ref. [24]. This paper by Zhao and Bartolotti describes among other things results for H_2 and N_2 which are very similar to ours. However, Zhao and Bartolotti do not comment on the (rather unsatisfactory) properties of the ZP92 functional to describe chemical bonding. We are grateful to Professor Parr for informing us about this paper, as well as for his remarks on our Comment.

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