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Use of gradient-corrected functionals in total-energy calculations for solids

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We have used two gradient-corrected exchange-correlation functionals to compute the lattice constant, bulk modulus, and cohesive energy for the simple metal Al, the *sp*-bonded semiconductors Si, Ge, and GaAs, and the 4*d* transition metals Nb and Pd. We find no consistent improvement over the predictions of the local-density approximation.

Despite its enormous success in the accurate calculation of structural parameters, phonon frequencies, and other ground-state properties of crystalline systems, the local-density approximation (LDA) of density-functional theory (DFT) (Ref. 1) has clear shortcomings. If the eigenvalues of the Kohn-Sham equations are assumed to be related to the true many-body excitation spectrum of the system—admittedly a widespread but unwarranted assumption, since the DFT concerns itself only with the ground state—the LDA severely underestimates the band gap in semiconductors and insulators.[2] Even some genuine ground-state properties are not accurately predicted by the LDA. For example, there is generally an overestimation of the cohesive energies of molecules and solids, and the ground-state structure of crystalline iron is predicted to be paramagnetic fcc, instead of ferromagnetic bcc.[3]

Several nonlocal functionals for the exchange and correlation energies have been proposed. The gradient expansion approximation (GEA) (Ref. 1) was the first scheme to be tested, with unsatisfactory results.[4,5] Langreth and co-workers[6,7] were the first to see a theoretical need to move away from a simple expansion in powers of the density gradient. Generalized gradient approximations were proposed for the correlation energy by Perdew,[8] and for the exchange energy by Perdew and Wang,[9] and by Becke.[10]

Use of the gradient-corrected (GC) functional of Perdew and Wang[8,9] (PW) or the combined Becke-Perdew functional[8,10] (BP) resulted in improvements for the calculated values of the total energies of atoms and molecules,[6–9,11–13] in better estimates of the cohesive energies in some crystals,[14,15] and in the prediction of the correct ground state of iron.[16–19] Since they involve minor changes in existing LDA codes and the computational cost of their use instead of a LDA functional is moderate, the GC schemes have been recommended as more accurate substitutes for the LDA. However, we feel that these approaches need to be applied to more systems, to ascertain whether they consistently improve on the LDA, before they find routine use.

In this work we have used the PW and BP functionals to perform total-energy calculations for Al as a typical simple metal, for Si, Ge, and GaAs as prototype *sp*-bonded semiconductors, and for Nb and Pd as prototype 4*d* transition metals. We have employed the *ab initio* pseudopotential method, which has proven to be very successful in the study of the structural properties of solids.[20,21] The Al, Si, and Ge pseudopotentials were generated using the method of Hamann, Schlüter, and Chiang.[22] For Ga and As, we used the scheme of Troullier and Martins,[23] and the Vanderbilt method[24] was employed for Nb and Pd.

For Al, Si, Nb, and Pd we generated LDA pseudopotentials employing the exchange-correlation functional by Ceperley and Alder[25] (CA), and GC pseudopotentials with both the PW and BP functionals. For Ge, Ga, and As we only generated LDA pseudopotentials (CA) and used them for both the LDA and GC calculations for the valence electrons.[26] For Nb and Pd the CA, PW, and BP pseudopotentials were found to show only marginal differences in their shapes. For Al and Si, on the other hand, the BP potentials are slightly less smooth than the CA potentials, whereas the PW potentials have very strong wiggles close to the nucleus. Such behavior was reported as well by Ortiz and Ballone.[27] It indicates a very delicate dependence of the functional form of the Perdew-Wang exchange potential[9] on the densities and their derivatives. Their softer character makes the BP potentials more suitable for solid-state calculations involving plane-wave expansions.[15,27]

The Ga, As, Nb, and Pd pseudopotentials were constructed with partial core corrections for exchange and correlation.[28] Both nonrelativistic and scalar relativistic calculations were performed for Ge, Nb, and Pd, while only scalar relativistic pseudopotentials were used for GaAs. For Al and the semiconductors, the basis set consisted of plane waves, with a kinetic-energy cutoff of 24 Ry for Al and Si, 16 Ry for Ge, and 20 Ry for GaAs.[29] It should be noted that the need for an accurate gradient requires a high-quality representation of the charge density. For that reason, we repeated the GaAs GC calculation with a cutoff of 49 Ry. We found no significant change in the lattice constant or the bulk modulus, and a

TABLE I. Cohesive properties of Al.

Core	Valence	a_0 (Å)	B_0 (GPa)	E_0 (eV)
CA	CA	3.96	87	4.05
CA	BP	3.96	86	3.49
BP	BP	4.04	79	3.39
CA	PW	3.95	89	3.29
PW	PW	4.04	79	3.09
LMTO, CA, relat.		3.98	87	4.11
LMTO, PW, relat.		4.02	82	3.15
Experiment[a]		4.05	72	3.39

[a] Reference 36.

TABLE II. Cohesive properties of Si.

Core	Valence	a_0 (Å)	B_0 (GPa)	E_0 (eV)
CA	CA	5.37	98	5.37
CA	BP	5.39	95	4.72
BP	BP	5.46	89	4.59
CA	PW	5.42	90	4.59
PW	PW	5.52	81	4.35
Experiment[a]		5.430	98.8	4.63

[a] Reference 36.

TABLE III. Cohesive properties of Ge.

Core	Valence	a_0 (Å)	B_0 (GPa)	E_0 (eV)
CA	CA	5.57	81	4.87
CA	BP	5.58	78	4.20
CA	PW	5.62	74	4.18
CA, relat.	CA	5.55	78	4.79
CA, relat.	BP	5.57	75	4.11
CA, relat.	PW	5.61	70	4.09
Experiment[a]		5.658	76.8	3.85

[a] Reference 36.

TABLE IV. Cohesive properties of GaAs.

Core	Valence	a_0 (Å)	B_0 (GPa)	E_0 (eV)
CA, relat.	CA	5.60	75	8.21
CA, relat.	BP	5.68	66	6.51
CA, relat.	PW	5.79	56	6.25
Experiment[a]		5.653	74.8	6.7

[a] See Ref. 37 and references therein.

TABLE V. Cohesive properties of Nb.

Core	Valence	a_0 (Å)	B_0 (GPa)	E_0 (eV)
CA	CA	3.27	172	8.15
CA	BP	3.31	160	6.59
BP	BP	3.32	166	6.64
CA	PW	3.37	156	6.33
PW	PW	3.37	159	6.41
CA, relat.	CA	3.26	186	8.54
CA, relat.	BP	3.31	173	6.99
CA, relat.	PW	3.36	164	6.70
LMTO, CA, relat.		3.26	172	8.55
LMTO, PW, relat.		3.37	159	6.85
Experiment[a]		3.30	170	7.57

[a] Reference 36.

small increase (around 0.15 eV) in the absolute value of the cohesive energy. A mixed-basis approach[30] was used for Nb and Pd, with five localized d functions per atom and plane waves up to 10.5 Ry. Up to 49 Ry cutoffs were used to extrapolate the convergence of the total energy to about 1 mRy for all materials considered, and zero-point energies were also taken into account. In addition, for Al, Nb, and Pd we performed scalar-relativistic all-electron calculations with the linear-muffin-tin-orbital–atomic-sphere-approximation (LMTO-ASA) method,[31] including partial waves up to $l_{\max} = 3$ and the combined correction term.

Our results for the structural properties (equilibrium lattice constant a_0 and bulk modulus B_0) and cohesive energies (E_0) are displayed in Tables I–VI. The first columns indicate the exchange-correlation functionals used for the core electrons, i.e., for the construction

TABLE VI. Cohesive properties of Pd.

Core	Valence	a_0 (Å)	B_0 (GPa)	E_0 (eV)
CA	CA	3.94	178	3.91
CA	BP	4.05	124	2.74
BP	BP	4.04	127	2.78
CA	PW	4.15	94	2.53
PW	PW	4.14	100	2.62
CA, relat.	CA	3.89	213	4.86
CA, relat.	BP	3.97	161	3.62
CA, relat.	PW	4.06	128	3.31
LMTO, CA, relat.		3.85	234	5.10
LMTO, PW, relat.		4.02	145	3.55
Experiment[a]		3.89	181	3.89

[a] Reference 36.

of the pseudopotentials. The second columns show the treatment of the valence electrons. Several trends can be immediately discerned. First, neither of the GC functionals gives the overbinding of the LDA, although in the case of Nb and Pd there is significant underbinding. Second, the lattice constant is consistently increased with respect to the LDA value. Whether or not this effect brings better agreement with experiment depends on the material. Third, and most distressing, is the reduction in the value of the bulk modulus brought about by the GC. While in the cases of Al, Si, and Ge the effect is rather small, for GaAs, Nb, and Pd the reduction is much too drastic. These trends have been previously reported in a variety of systems: 4*d* (including Nb) and 5*d* metals,[17] and BN.[32]

The comparison of the mixed-basis and LMTO results demonstrates that despite their different basic approximations, namely the frozen-core pseudopotential approximation and the atomic-sphere approximation, respectively, the two methods yield very similar results with both the LDA and the GC functionals. In contrast to the conclusion of Ref. 34 that the remaining discrepancies of their GC calculations with experiment may be attributed to the spherical approximation in the LMTO method, we do not find a significant improvement in the agreement with experiment by comparing our LMTO-ASA results with our results obtained with pseudopotential methods (which involve no spherical approximations for the densities and their derivatives).

In view of the above results, we conclude that the two GC schemes[33] do not provide a consistent and unequivocal improvement over the LDA in the calculated structural properties of crystalline solids. Still, because of the relative ease of implementation of the GC schemes compared to other proposed extensions to the LDA such as the weighted-density approximation,[35] further studies with the GC functionals are desirable to elucidate systematics throughout the periodic system.

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