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Gradient-corrected pseudopotential calculations in semiconductors

G. Ortiz
Institut Romand de Recherche Numérique en Physique des Matériaux (IRRMA),
PHB-Ecublens, 1015 Lausanne, Switzerland

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We have computed cohesive properties for Si, Ge, and GaAs in the framework of pseudopotential density-functional theory, including gradient corrections to the local-density approximation (LDA). Computed cohesive energies are in significantly better agreement with experiment than those given by the LDA, while lattice constants show only a minor improvement. The Kohn-Sham single-particle spectrum reveals a systematic k-dependent repulsion between occupied and unoccupied states. Finally we discuss the screening properties of a gradient-corrected homogeneous electron gas.

In recent years, the local-density approximation (LDA) to the density-functional theory (DFT) has gained general recognition as an accurate, reliable, and simple method to perform total-energy computations for atoms, molecules, and solids.[1]

Although the limitations of this approximation are now well assessed, inhomogeneity corrections [mainly gradient corrections (GC): see Langreth and Mehl[2] (LM), Becke,[3] Perdew;[4] for a general reference see Parr and Yang[5]] to the LDA have not been systematically explored, especially in extended systems.

Early computations within the LM recipe produced significantly improved results for the cohesive energy and electron density of bulk beryllium and silicon.[6] Excitation energy computations via band structure, however, showed little or no improvement in the case of the transition metals vanadium and copper.[7] After these studies, nearly a decade elapsed before the interest in GC was revived by the failure of the LDA to predict the correct ground-state geometry for ferromagnetic solids.[8] A series of computations[9–12] have shown that GC stabilized the ferromagnetic bcc phase for iron, giving the correct structure and therefore providing an important improvement over the LDA. Recent gradient-corrected studies of $CaCuO_2$ have shown that the correction to the LDA brings this material closer to an antiferromagnetic instability.[13]

In this paper we investigate the effects and the importance of GC to the LDA for selected semiconductors. We focus our attention on cohesive and structural properties, although a short discussion of the resulting band structures will also be given. In the last part of the paper we discuss the screening properties of a gradient-corrected recipe in the limit of a homogeneous electron gas.

Pseudopotential–plane-wave computations have been performed for bulk Si, Ge, and GaAs. Our results show that GC provide a significant improvement in the calculated cohesive energies. Lattice constants show little or no improvement, with a systematic error opposite in sign with respect to that of the LDA.

According to pseudopotential DFT,[5] the total energy in atomic units of a solid of lattice constant a is the minimum of the functional:

$$E[a \mid \rho] = \sum_{n,\mathbf{k}} f_{n\mathbf{k}} \langle \psi_{n\mathbf{k}} \mid -\tfrac{1}{2}\nabla^2 + \tfrac{1}{2}V_H + \widehat{V}_{\mathrm{ps}} \mid \psi_{n\mathbf{k}} \rangle + E_{\mathrm{xc}}[\rho] + E_{\mathrm{ions}} \ , \tag{1}$$

where ρ is the valence electron density, $\{\psi_{n\mathbf{k}}\}$ and $\{f_{n\mathbf{k}}\}$ are the Kohn-Sham eigenfunctions of the Bloch type and their occupation numbers, respectively. V_H is the classical Coulomb-Hartree potential. $\widehat{V}_{\mathrm{ps}}$ is the sum of the atomic pseudopotentials of the *ab initio*, norm-conserving, semirelativistic type.[14] E_{ions} is the classical potential energy of nonoverlapping ions. $E_{\mathrm{xc}}[\rho]$ is the exchange-correlation functional, here approximated by two closely related schemes: the well-known local-density approximation and the gradient-corrected scheme. For the gradient-corrected computation we used the semiempirical exchange correction by Becke[3] and the correlation correction by Perdew[4] (BP), that in the spin-unpolarized version reads (Hartree atomic units)

$$E_{\mathrm{xc}}[\rho] = \int \rho \, \epsilon_{\mathrm{xc}}(\rho \, ; \nabla\rho) \, d\mathbf{r} \ , \tag{2}$$

with

$$\epsilon_{\mathrm{xc}}(\rho \, ; \nabla\rho) = \epsilon_{\mathrm{xc}}^{\mathrm{LDA}}(\rho) + 2^{-1/3}\rho^{1/3}X_\rho^2 \left\{ 2^{-1/3} e^{-\Phi}\, C(\rho) - \frac{\eta}{1 + 6\eta X_\rho \sinh^{-1} X_\rho} \right\} , \tag{3}$$

where $X_\rho = 2^{1/3} \mid \nabla\rho \mid / \rho^{4/3}$, $\eta = 0.0042$,

$$\Phi = 0.192 \frac{C(\infty)}{C(\rho)} \frac{|\nabla\rho|}{\rho^{7/6}}$$

and

$$C(\rho) = 0.001\,667 + \frac{0.002\,568 + \alpha r_s + \beta r_s^2}{1 + \gamma r_s + \delta r_s^2 + 10^4 \beta r_s^3} \ ,$$

with $r_s^{-3} = 4\pi\rho/3$, $\alpha = 0.023\,266$, $\beta = 7.389 \times 10^{-6}$, $\gamma =$

TABLE I. Structural properties of three selected semiconductors in the LDA and the BP approximation; nlcc stands for nonlinear pseudocore correction on Ga atom only.

System	$-E_{\text{cohesive}}$ (eV)			a_0 (a.u.)		
	LDA	BP	Expt.	LDA	BP	Expt.
Si	5.35	4.41	4.63	10.15	10.38	10.26
Ge	4.65	3.68	3.85	10.52	10.80	10.69
GaAs	8.16	6.45	6.7	10.41	10.70	10.68
GaAs-nlcc		6.13			10.80	

8.723, and $\delta = 0.472$.

The reasons for the selection of this functional are listed in Ref. 15. Here we note that this choice gives smooth and transferable ionic pseudopotentials. To study the structural properties of Si, Ge, and GaAs we performed self-consistent calculations for a periodically repeated fcc cell containing two atoms. All LDA computations used the Perdew-Zunger[17] parametrization of the exchange-correlation energy functional, also used in the computation of $\epsilon_{\text{xc}}^{\text{LDA}}$ in Eq. (3). The Kohn-Sham eigenfunctions $\{\psi_{n\mathbf{k}}\}$ were expanded in a plane-wave basis set with kinetic energy up to 48 Ry for structural properties and 24 Ry for band-structure calculations. Special point techniques were used to sample the irreducible part of the Brillouin zone and 10 Monkhorst-Pack special **k** points proved to be enough to provide an accuracy of the order of 0.01 eV for all the systems studied (checks were done with 60 **k** points). We took the LDA pseudopotentials from Ref. 18, while we generated those used for the gradient-corrected computations according to the prescriptions of Ref. 15.

In Table I we report results for the cohesive energy (E_{cohesive}) and equilibrium lattice constant (a_0). As usual, the cohesive energy is computed as a total-energy difference between the solid in equilibrium and the isolated atoms in their respective ground spin configuration. We observe that the corrected a_0 is as good as the LDA one for Si and Ge, while in GaAs the error is considerably reduced by GC. While the LDA systematically underestimates a_0, gradient corrections tend always to overestimate it, resulting in a weaker bond picture.

For the cohesive energy the improvement is indeed substantial. We observe that the roughly 20% error of the LDA is reduced to ~ 5%. Again, we find that the error of BP has the opposite sign with respect to that of the LDA. We recall that we have found the same qualitative trends in finite systems (atoms and molecules)[15,16] though in that case the improvement was more impressive.

So far we have discussed the role of the nonlocal corrections to the LDA from the total-energy point of view. Although the Kohn-Sham eigenvalues do not have, in general, a direct physical interpretation, we can try to analyze the consequences of these corrections on the LDA Kohn-Sham spectrum of the solid and compare it to the experimental single-particle excitations. In order to understand the effect of inhomogeneity we have performed band-structure calculations at the same lattice constant (in particular at the experimental one), because spurious pressure effects mask the character of the many-body corrections. From Tables II and III we observe a systematic repulsion between occupied and unoccupied states. This repulsion is not a constant scissor operator but a **k**-dependent one, and the sign of the correction brings the computed values closer to the experimental excitation energies.

In order to improve transferability of the pseudopotentials we consider explicitly the nonlinear exchange-correlation interaction between the core and valence charge densities. Following Ref. 19, we introduce the functional

$$E_{\text{xc}}[\rho] = \int [\rho_t \, \epsilon_{\text{xc}}(\rho_t \, ; \nabla \rho_t) - \rho_c \, \epsilon_{\text{xc}}(\rho_c \, ; \nabla \rho_c)] \, d\mathbf{r} \ , \quad (4)$$

where $\rho_t = \rho + \rho_c$ with ρ_c the bulk pseudocore charge density. ρ_c is the true core charge density outside a given cutoff radius r_c, while for $r < r_c$ it is the sum of two spherical Bessel functions:

$$\rho_c(r) = A \, j_0(Kr) + B \, j_0(2Kr) \ , \quad (5)$$

where A, B, and K are parameters adjusted to enforce continuity of ρ_c, ρ_c', and ρ_c'' at r_c.

Because the core-valence nonlinear interaction is negligible in Si, Ge, and As we applied the previous formalism only to Ga for the bulk GaAs computations within the BP scheme.[23] From Table I we observe that BP-nlcc (nonlinear pseudocore correction) tends to slightly worsen the BP result though it is still superior to the LDA.

Concerning the single-particle spectrum we notice in Table III that the occupied-unoccupied repulsion effect

TABLE II. Electronic energies of Kohn-Sham states of different symmetry at Γ, X, and L. All values are in eV and are measured with respect to the top of the valence band ($\Gamma_{25'v}$). Calculations are done at the experimental lattice constant a_0; spin-orbit effects were not considered. Experimental values for the corresponding excitation energies are taken from Refs. 20–22.

Si	Γ_{1v}	Γ_{15c}	X_{1v}	X_{4v}	X_{1c}	$L_{2'v}$	L_{1v}	$L_{3'v}$	L_{1c}
LDA	−11.88	2.55	−7.75	−2.82	0.63	−9.55	−6.93	−1.17	1.46
BP	−11.96	2.65	−7.81	−2.85	0.83	−9.62	−6.96	−1.20	1.59
Expt.	−12.5±0.6	3.4		−3.3±0.2	1.3	−9.3±0.4	−6.7±0.2	−1.2±0.2	2.4±0.2
Ge	Γ_{1v}	$\Gamma_{2'c}$	X_{1v}	X_{4v}	X_{1c}	$L_{2'v}$	L_{1v}	$L_{3'v}$	L_{1c}
LDA	−12.67	0.00	−8.83	−3.02	0.71	−10.61	−7.55	−1.37	0.15
BP	−12.73	0.03	−8.85	−3.04	0.86	−10.65	−7.55	−1.39	0.23
Expt.	−12.9±0.2	0.89	−9.3±0.2	−3.5±0.2	1.3±0.2	−10.6±0.5	−7.7±0.2	−1.4±0.3	0.84

TABLE III. GaAs Kohn-Sham eigenenergies. (See Tables I and II for details.)

GaAs	Γ_{1v}	Γ_{1c}	X_{1v}	X_{3v}	X_{5v}	X_{1c}	L_{1v}	L_{1v}	L_{3v}	L_{1c}
LDA	−12.55	0.55	−10.24	−6.70	−2.58	1.43	−10.94	−6.52	−1.08	1.02
BP	−12.62	0.64	−10.26	−6.72	−2.62	1.63	−10.98	−6.54	−1.11	1.13
BP-nlcc	−12.66	0.53	−10.27	−6.77	−2.63	1.61	−11.00	−6.57	−1.12	1.06
Expt.		1.63			−2.80	2.09			−1.30	1.93

still persists but there is a slight downward shift with respect to the top of the valence band.

Up to now we have presented results of self-consistent computations within the BP scheme. We should mention that there exist other gradient-corrected calculations for Si (pseudopotential)[24] and Ge (all-electron)[25] that make use of different approximations to the exchange-correlation functional. In the case of Si, conclusions are not only qualitatively but also quantitatively equivalent at least within the quoted error bars. For Ge similar trends are observed if we compare our results to the ones obtained within the LM recipe. It is not evident from these computations whether a given recipe is better than another.

The static dielectric response is a ground-state property, and as such it is within the scope of DFT.[26] Due to the importance of this quantity in understanding the response to external perturbations, we have analyzed the screening properties of a fermion gas within the GC schemes, and, in particular, we have considered its homogeneous electron-gas limit. The relevant quantity to study is the second-order functional derivative $f_{\mathrm{xc}}(\mathbf{r},\mathbf{r}') = \delta^2 E_{\mathrm{xc}}/\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')$, which contains all the difficult many-body contributions. Its computation from Eq. (3) is an exercise in the calculus of variations and the result is not an ordinary function but a distribution.[27]

The Fourier transform of f_{xc} in the homogeneous electron-gas limit is

$$\lim_{\rho\to\mathrm{const}} f_{\mathrm{xc}}(\mathbf{k},\mathbf{k}') = \left\{ \frac{\partial^2}{\partial\rho^2}[\rho\,\epsilon_{\mathrm{xc}}^{\mathrm{LDA}}(\rho)] + 2^{7/3}(\pi r_s)^2[C(\rho) - 2^{1/3}\eta]\left(\frac{k}{k_F}\right)^2 \right\} \times\delta(\mathbf{k}-\mathbf{k}'), \tag{6}$$

where $k_F^3 = 3\pi^2\rho$ is the Fermi wave vector. The first term is a negative constant, and corresponds to the LDA contribution. The second (k^2) term represents the gradient-correction contribution. The value of this second term, within the BP scheme with the choice of coefficients listed above, is negative. In terms of physical density response operators:

$$\chi_{\mathrm{BP}} = \chi_{\mathrm{LDA}}\left(\mathbb{1} - \Delta f_{\mathrm{xc}}\,\chi_{\mathrm{LDA}}\right)^{-1}. \tag{7}$$

From Eq. (6) $\Delta f_{\mathrm{xc}} = f_{\mathrm{xc}} - f_{\mathrm{xc}}^{\mathrm{LDA}}$ is negative, so $\chi_{\mathrm{BP}} - \chi_{\mathrm{LDA}}$ is negative definite. That means that the BP correction to the LDA enhances screening.

This has to be contrasted to the results of refined many-body computations[28] showing that, up to k_F, $f_{\mathrm{xc}}(k)$ is a rather flat function of k, with, however, a positive k^2 contribution. This would suggest that the screening properties of the BP scheme are in fact worse than those of the LDA, whose constant $f_{\mathrm{xc}}^{\mathrm{LDA}}(k)$ well approximates the more reliable forms for slowly varying perturbations up to k of the order of k_F.

Although semiempirical, a simple way to amend this failure would be to decrease η in Eq. (6) with respect to the value used in the present computation. This possibility, already suggested by Becke[3] for extended systems computations, could, at the same time, improve cohesive energies, lattice constants, and screening properties. Computations to explore this possibility are under way.

In conclusion, we have computed converged structural properties for some selected semiconductors (Si, Ge, and GaAs) using both the LDA and the BP approximation. We observe that, though not so important as in finite systems, the BP scheme improves the energetics with respect to the LDA. We found a band repulsion between occupied and unoccupied orbitals when gradient corrections are added to the LDA one-particle spectrum. Finally we discussed electron screening within gradient-corrected recipes, concluding that the BP approximation, in the homogeneous electron-gas limit, overscreens an arbitrary external perturbation. This is a possible explanation of the slight overcorrection in the structural properties of the semiconductors studied.

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[1] G. P. Srivastava and D. Weaire, Adv. Phys. **36**, 463 (1987); R. O. Jones and O. Gunnarsson, Rev. Mod. Phys. **61**, 689 (1989).

[2] D. C. Langreth and M. J. Mehl, Phys. Rev. B **28**, 1809 (1983).

[3] A. D. Becke, Phys. Rev. A **38**, 3098 (1988).

[4] J. P. Perdew, Phys. Rev. B **33**, 8822 (1986).

[5] R. G. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules* (Oxford University Press, Oxford, 1989).

[6] U. von Barth and A. C. Pedroza, Phys. Scr. **32**, 353 (1985); U. von Barth and R. Car (unpublished).

[7] M. Norman and D. D. Koelling, Phys. Rev. B **28**, 4357 (1983).

[8] C. S. Wang, B. M. Klein, and H. Krakauer, Phys. Rev. Lett. **54**, 1852 (1985).

[9] P. Bagno, O. Jepsen, and O. Gunnarsson, Phys. Rev. B **40**, 1997 (1989).

[10] B. Barbiellini, E. G. Moroni, and T. Jarlborg, J. Phys. Condens. Matter **2**, 7597 (1990).

[11] D. J. Singh, W. E. Pickett, and H. Krakauer, Phys. Rev. B **43**, 11 628 (1991).

[12] T. C. Leung, C. T. Chan, and B. N. Harmon, Phys. Rev. B **44**, 2923 (1991).

[13] D. J. Singh and W. E. Pickett, Phys. Rev. B **44**, 7715 (1991).

[14] D. R. Hamann, Phys. Rev. B **40**, 2980 (1989).

[15] G. Ortiz and P. Ballone, Phys. Rev. B **43**, 6376 (1991).

[16] G. Ortiz and P. Ballone, Phys. Rev. B **44**, 5881 (1991); Z. Phys. D **19**, 169 (1991).

[17] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[18] G. B. Bachelet, D. R. Hamann, and M. Schlüter, Phys. Rev. B **26**, 4199 (1982).

[19] S. G. Louie, S. Froyen, and M. L. Cohen, Phys. Rev. B **26**, 1738 (1982).

[20] M. S. Hybertsen and S. G. Louie, Phys. Rev. B **34**, 5390 (1986).

[21] R. W. Godby, M. Schlüter, and L. J. Sham, Phys. Rev. B **37**, 10 159 (1988).

[22] F. Gygi and A. Baldereschi, Phys. Rev. Lett. **62**, 2160 (1989).

[23] For Ga we used a pseudocore cutoff radius $r_c = 2.2$ a.u.

[24] X. J. Kong, C. T. Chan, K. M. Ho, and Y. Y. Ye, Phys. Rev. B **42**, 9357 (1990).

[25] D. J. Singh and W. E. Pickett, in *Proceedings of the 20th International Conference on the Physics of Semiconductors, Thessaloniki, 1990*, edited by E. M. Anastassakis and J. D. Joannopoulos (World Scientific, Singapore, 1990), p. 1787.

[26] R. Resta, in *Festkörperprobleme*, edited by P. Grosse (Vieweg, Braunschweig, 1985), Vol. XXV, p. 183; Z. H. Levine and D. C. Allan, Phys. Rev. B **43**, 4187 (1991), and references therein.

[27] G. Ortiz (unpublished).

[28] K. S. Singwi and M. P. Tosi, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1981), Vol. 36, p. 177.