Density-functional theory of the dielectric constant: Gradient-corrected calculation for silicon

Andrea Dal Corso,* Stefano Baroni, and Raffaele Resta

Scuola Internazionale Superiore di Studi Avanzati (SISSA), Via Beirut 4, I-34014 Trieste, Italy

(Received 13 September 1993)

We study the screening of a macroscopic electric field in a crystalline dielectric. Density-functional perturbation theory provides the static dielectric constant (or tensor) as a bulk property; we give a formulation which extends the local-density approximation, and specifically we discuss its implementation within gradient-corrected schemes. We briefly consider the relevance (if any) of the so-called "gap problem" to static linear response. As a case study, we perform an *ab initio* calculation of the dielectric constant in silicon within a popular gradient-corrected local-density scheme. We find that the gradient corrections reduce the discrepancy found so far between local-density predictions and experiments in covalently bonded materials. The amount of this reduction is sizable if the calculations are performed at the experimental equilibrium lattice constant of the crystal, while however, it is only marginal when the calculations are carried out, at the calculated lattice constants, consistently within each given theoretical scheme.

I. INTRODUCTION

The electronic ground-state properties of a condensed-matter system at zero temperature are, in principle, exactly described by the density-functional theory (DFT).[1] Any change in the electronic ground state induced by a static external influence is within the scope of DFT as well: it is therefore obvious that the macroscopic dielectric constant (or the macroscopic dielectric tensor in noncubic solids) is a well defined macroscopic ground-state observable, which has an exact expression within DFT.

DFT is an exact theory, and as such, it would be only formal and useless to tackle real systems until a workable computational scheme is provided to implement it. Its genuine power stems from the fact that such schemes are provided by simple *physical* approximations which can be implemented completely from first principles. For case studies of moderate complexity—including those considered in this work—a very high computational accuracy can be achieved with affordable computer resources.

By far the most popular approximation to DFT is the local-density approximation (LDA),[1] which has provided over the past 15 years a large number of results: even limiting ourselves to the work done on Si systems (solids, surfaces, clusters), literally thousands of papers have appeared. Most physical properties of Si are reproduced (or predicted) by DFT-LDA within a few percent:[2-4] a notable exception is the dielectric constant ε_∞, whose value is substantially overestimated by LDA. This feature was found by Baroni and Resta in 1986,[5] and then confirmed by several other calculations.[6-9] As for the magnitude of such an overestimate, it depends on which value of the lattice constant is used in the calculation, and also to which experimental data are the theoretical results compared. Both these issues are discussed below. At this point, let us just mention that the amount of the overestimate is something between 12% and 18%. In order to cope with this rather surprising failure, some

authors[9,10] have performed calculations within a quasiparticle scheme, i.e., in a framework which is deliberately outside the scope of DFT. In this paper we assume a different viewpoint: we calculate the dielectric constants of Si *within* DFT, but abandoning the LDA. Specifically, the approximation used in this work includes gradient corrections (GC) to the LDA. Whether such GC are definitely an improvements over the LDA or not—particularly for Si and other covalently bonded materials—is presently under debate:[11,12] this work provides therefore an important piece of information on such an issue.

Among the large number of proposed forms of the GC (Refs. 13 and 14) we decided to concentrate on the proposal of Becke[15] for the exchange part and Perdew[16] for the correlation part. Actually, at present these expressions seem the most appealing candidates to describe both finite and extended systems. Furthermore the pseudopotentials generated within this scheme are smooth and transferable, and they require little extra workload as compared with standard LDA.

The main success of GC is a definite improvement of the calculated cohesive energy of molecules and solids, while the improvement on other physical quantities of interest in solids is not so striking.[12] In part this could be due to the fact that GC has been often tested on materials and properties where LDA is already a very good approximation (such as, e.g., most properties of simple semiconductors). In some cases where LDA was known to fail badly (such as, e.g., hydrogen-bonded systems), GC *did* provide an outstanding improvement.[17] For this reason we decided to concentrate on one material property which is in the range of DFT, but where LDA could be effectively improved upon.

Our computational scheme is the density-functional perturbation theory (DFPT) of Baroni, Giannozzi and Testa,[7] which allows a very good control on the numerical convergence of the results. In particular it offers the possibility of performing very accurate calculations

of the linear-response properties of solids, overcoming some problems of the more traditional dielectric-matrix approach. Furthermore we will show that within DFPT the GC can be introduced in a very simple and natural way.

Our main result is that GC does contribute to reduce the discrepancy between theoretical and experimental dielectric constant, even if the reduction of the error is not so marked as in the case of cohesive energies. The main problem is due to the fact that GC weakens the strength of covalent bonds, so that the lattice constants are generally slightly overestimated and bulk moduli are largely underestimated. This effect also affects the value of the computed dielectric constant. This fact can be seen by comparing the values of the dielectric constant calculated within LDA and GC at the experimental lattice constant and at the theoretical equilibrium lattice constant. In the former case the GC scheme would appear an important improvement over LDA, while it is only marginally better in the latter.

In Sec. II we outline the theory of the electronic dielectric constant within DFT, stressing that it is indeed a bulk ground-state property of a solid. In Sec. III we give a very brief summary of the DFPT restricting to the case in which the perturbation is represented by a uniform static electric field. In Sec. IV we clarify some misunderstanding about possible relationships between static linear response and the so-called "gap problem."[21] In Sec. V we discuss the implementation of DFPT within a GC scheme for exchange and correlation energy. Finally in Sec. VI we report our results on Si and compare them with previous calculations and with a critical interpretation of experimental data.

II. THE MACROSCOPIC DIELECTRIC CONSTANT

The macroscopic dielectric tensor is defined as

$$\overleftrightarrow{\varepsilon}_\infty = 1 + 4\pi \frac{\partial \mathbf{P}}{\partial \mathbf{E}}, \tag{1}$$

where $\mathbf{P}$ is the macroscopic electronic polarization linearly induced by the (screened) field $\mathbf{E}$; in a cubic material such a tensor obviously reduces to a constant. The early computations of ε_∞ in semiconductors, including Refs. 5 and 6, used a dielectric-matrix formalism. In more recent studies, DFPT (Refs. 7 and 20) has proved to be a very convenient alternative: such an approach will be extended here beyond its original LDA formulation. When a perturbation (such as a macroscopic field) is applied to the solid, the Kohn-Sham (KS) Hamiltonian[1] is written as $H_{\rm KS} + \Delta V_{\rm KS}$, where $\Delta V_{\rm KS}$ is a *screened* potential, to be determined self-consistently; the corresponding KS orbitals are then $\varphi_i + \Delta\varphi_i$. Basically, DFPT is a self-consistent scheme which directly provides—as shown below—orbital derivatives: in our case $\partial\varphi_i/\partial\mathbf{E}$. Once these orbital derivatives are known, one can write the polarization derivative in Eq.(1) for a finite sample of volume $\mathcal{V}$ as:

$$\frac{\partial \mathbf{P}}{\partial \mathbf{E}} = \frac{e}{\mathcal{V}} \sum_i f_i \left\langle \varphi_i \left| \mathbf{r} \right| \frac{\partial\varphi_i}{\partial\mathbf{E}} \right\rangle + \text{c.c.}, \tag{2}$$

where f_i is an occupancy factor (either 2 or 0), and c.c. indicates the complex conjugate. It proves useful to transform the dipole matrix elements using the identity

$$\langle \varphi_i | \mathbf{r} | \varphi_j \rangle = -i\hbar \frac{\langle \varphi_i | \mathbf{v} | \varphi_j \rangle}{E_i - E_j} \ , \ i \neq j \ , \tag{3}$$

where E_i are the KS eigenvalues, and the velocity operator $\mathbf{v}$ is defined as

$$\mathbf{v} = \frac{i}{\hbar}[H_{\rm KS}, \mathbf{r}] = \frac{\mathbf{p}}{m_e} + \frac{i}{\hbar}[V_{\rm KS}, \mathbf{r}]; \tag{4}$$

$\mathbf{p}$ is the canonical momentum operator, m_e is the electron mass, and the last term is nonvanishing only if nonlocal potentials appear in the KS Hamiltonian. This is indeed the case whenever norm-conserving pseudopotentials are used,[18,19] as in the calculations reported here.

Straightforward manipulations transform Eq.(2) into

$$\frac{\partial \mathbf{P}}{\partial \mathbf{E}} = -\frac{ie\hbar}{\mathcal{V}} \sum_{i,j} \frac{f_j - f_i}{E_j - E_i} \langle \varphi_i | \mathbf{v} | \varphi_j \rangle \left\langle \varphi_j \left| \frac{\partial\varphi_i}{\partial\mathbf{E}} \right\rangle \right., \tag{5}$$

where we have exploited the fact that $|\partial\varphi_i/\partial\mathbf{E}\rangle$ may be chosen as orthogonal to $|\varphi_i\rangle$.

III. OUTLINE OF DENSITY-FUNCTIONAL PERTURBATION THEORY (DFPT)

In order to proceed further, we need a self-consistent scheme providing the derivatives of the wave functions and of the KS potential with respect to the perturbation. The first step consists in writing the first-order corrections to the wave functions as

$$\Delta\varphi_i = \sum_{j \neq i} \varphi_j \frac{\langle \varphi_j | \Delta V_{\rm KS} | \varphi_i \rangle}{E_i - E_j}; \tag{6}$$

from which the first-order density Δn is trivially obtained in terms of $\Delta V_{\rm KS}$. As a second step, we look for an independent relationship providing instead $\Delta V_{\rm KS}$ in terms of Δn: iterating over these two steps, the self-consistency goal is reached.

The self-consistent perturbation potential $\Delta V_{\rm KS}$ is written as

$$\Delta V_{\rm KS} = \Delta V_{\rm ext} + \Delta V_H + \Delta V_{\rm xc}, \tag{7}$$

where $\Delta V_{\rm ext}$ is the bare perturbation (in the present case the potential of the *unscreened* field), and the remaining two terms are the Hartree and exchange-correlation contributions, respectively. The Hartree term is linear in the induced charge density:

$$\Delta V_H(\mathbf{r}) = e^2 \int d\mathbf{r}' \Delta n(\mathbf{r})/|\mathbf{r} - \mathbf{r}'|, \tag{8}$$

or in shorthand

$$\Delta V_H = v_c \Delta n, \tag{9}$$

while the exchange-correlation contribution is linearized as

$$\Delta V_{\mathrm{xc}} \simeq f_{\mathrm{xc}} \Delta n. \tag{10}$$

The functional derivative defining this linear term is

$$f_{\mathrm{xc}}(\mathbf{r}, \mathbf{r}') = \frac{\delta V_{\mathrm{xc}}(\mathbf{r})}{\delta n(\mathbf{r}')} = \frac{\delta E_{\mathrm{xc}}[n]}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}, \tag{11}$$

where E_{xc} is the exchange-correlation energy functional. The operator f_{xc} is real symmetric, and negative definite: its expression in a GC scheme is discussed below; more details about DFPT within LDA can be found in Refs. 7 and 20.

When a macroscopic field **E** acts on the solid, it proves useful to write the self-consistent perturbation potential ΔV_{KS} in a slightly different way from Eq. (7), separating the macroscopic field from the microscopic one (also called *local field*). The potential of the *screened* macroscopic field—due to both the bare and the Hartree terms in Eq. (7)—is written as $-e\mathbf{E}\cdot\mathbf{r}$, while the remaining *microscopic* term is lattice periodical in the thermodynamic limit. We therefore replace Eq. (7) with

$$\Delta V_{\mathrm{KS}} = -e\mathbf{E}\cdot\mathbf{r} + v_c\Delta n + f_{\mathrm{xc}}\Delta n, \tag{12}$$

where the term $v_c\Delta n$ amounts to solving Poisson's equation.

The self-consistent loop is performed cycling over Eq. (12) and Eq. (6), while the value of the screened field **E** is kept constant during the iteration. Whenever Eq. (12) is inserted in Eq. (6), the matrix elements of **r** are transformed to the velocity form using again Eq. (3). Once self-consistency is reached, one gets the orbital variations $\Delta\varphi_i$ induced by a given macroscopic field **E**, which are exact to linear order in the field magnitude: hence the field derivative to be used in Eq. (5).

All of the equations actually implemented in the method have a simple and well defined expression for the infinite periodic crystal in the thermodynamic limit, where the index i is identified with the band index and the Bloch vector altogether. A further very important feature of DFPT is the fact that the (slowly convergent) perturbation sums in Eqs. (5) and (6) are *not* explicitly evaluated, and an alternative Green's function scheme is used in their stead. More details about these points are given in Refs. 7 and 20.

IV. THE GAP PROBLEM AND ITS IRRELEVANCE

We pause at this point to discuss the relevance (if any) of the so-called "gap problem"[21] to macroscopic linear response in solids. The authors have found this to be the subject of a frequently asked question at seminars and talks. We take therefore the present occasion for a thorough clarification of the issue.

Many of the linear-response calculations do actually perform perturbation sums such as in Eqs. (5) and (6). Such sums are strongly affected by the terms having the smallest energy denominators, and therefore have a strong dependence upon the value of the minimum valence-conduction gap: a gap reduction enhances screening. It is well known for several years that DFT-LDA calculations for semiconductors provide gap values which are substantially smaller than the measured optical gaps. Hence it is tempting to trace back the LDA overestimate of ε_∞ to this kind of failure: such reasoning is nonetheless *incorrect*.

The first important point is that the differences in KS eigenvalues must *not* be identified with optical transition energies. In fact, even the *exact* KS gap is believed to be typically smaller than the optical gap,[21,22] but this fact does not spoil the formulation given above from providing, in principle, an exact value of ε_∞. Besides energy denominators, a key role is played by the f_{xc} operator, as emphasized in Ref. 5. A second point worth discussing is the reason why one-particles energies—such as the KS eigenvalues—enter the formulation at all. In fact, the KS eigenvalues are *unphysical* quantities, and explicitly appear in perturbation theory because of a *mathematical* reason, i.e., expansion over a complete basis set. Static linear response is a ground-state property, and has nothing to do with the physical excited states of the system.

Of course, an alternative approach could be abandoning DFT since the very beginning, and studying the dielectric response in a many-body Green's function framework. This would even provide the dynamical (or frequency-dependent) dielectric constant $\varepsilon_\infty(\omega)$, which is outside the scope of DFT. In order to pursue this aim, one should find approximate expressions for the two-body Green's function, and expand the perturbed state over the physical (hole-particle) excited states of the unperturbed crystal. This is in fact the path currently followed when studying linear response in molecules, at the Hartree-Fock level,[23,24] and beyond.[25]

V. GRADIENT-CORRECTED LINEAR RESPONSE

The first step beyond LDA is to assume that the exchange and correlation functional E_{xc} depends locally on the local density *and* on the density gradient:

$$E_{\mathrm{xc}} = \int d\mathbf{r}\, n\,\varepsilon_{\mathrm{xc}}(n, \nabla n). \tag{13}$$

From this, the exchange and correlation term in the KS potential can be derived from standard calculus of variations:

$$V_{\mathrm{xc}} = \frac{\partial F}{\partial n} - \sum_{\alpha=1}^{3} \frac{\partial}{\partial x_\alpha}\left[\frac{\partial F}{\partial(\partial_\alpha n)}\right], \tag{14}$$

where the function F is defined as $F = n\,\varepsilon_{\mathrm{xc}}(n, \nabla n)$, and $\partial_\alpha n$ is the α component of the density gradient. In

order to evaluate linear response, DFPT requires the f_{xc} operator, Eq. (11). The functional dependence of Eq. (10) is expressed as an explicit linear function of Δn and its **r** derivatives, as

$$\Delta V_{xc} \simeq \frac{\partial^2 F}{\partial n^2} \Delta n - \sum_{\alpha=1}^{3} \frac{\partial}{\partial x_\alpha} \left[\frac{\partial^2 F}{\partial n \partial(\partial_\alpha n)} \right] \Delta n$$

$$- \sum_{\alpha=1}^{3} \sum_{\beta=1}^{3} \frac{\partial}{\partial x_\alpha} \left[\frac{\partial^2 F}{\partial(\partial_\alpha n)\partial(\partial_\beta n)} \right] \frac{\partial \Delta n}{\partial x_\beta}$$

$$- \sum_{\alpha=1}^{3} \sum_{\beta=1}^{3} \left[\frac{\partial^2 F}{\partial(\partial_\alpha n)\partial(\partial_\beta n)} \right] \frac{\partial^2 \Delta n}{\partial x_\alpha \partial x_\beta}. \qquad (15)$$

Within LDA F is independent of the density gradient, and only the first term in Eq. (15) is nonvanishing: one thus recovers the standard LDA expression for f_{xc}.[5,20] To compute this general expression within any GC scheme it is necessary to evaluate analytically the derivatives of F, while the derivatives of Δn can be computed numerically in reciprocal space using a plane-wave representation of the charge density.

Among the different GC implementations which have been proposed in the literature, we have chosen the recipe "Becke exchange plus Perdew correlation,"[15,16] which has been the favorite choice of several other workers in recent papers, including Refs. 11 and 17. Following Becke and Perdew (BP), the explicit form of the energy density reads

$$\varepsilon_{xc}^{BP} = \varepsilon_{xc}^{LDA} + 2^{-\frac{1}{3}} n^{\frac{1}{3}} X_n^2 \left\{ 2^{-\frac{1}{3}} C(n) e^{-\phi} - \frac{\eta}{G} \right\}. \qquad (16)$$

Here we indicated with ε_{xc}^{LDA} the expression of the exchange and correlation functional taken from the best available electron-gas results, with the parametrization of Perdew and Zunger.[26] In Eq. (16) there are three terms which depend upon the gradient of the charge density. Switching from now on to atomic units ($e^2=\hbar=m=1$) they are written as

$$X_n = 2^{\frac{1}{3}} \frac{|\nabla n|}{n^{\frac{4}{3}}}, \qquad (17)$$

$$\phi = 0.192 \frac{C(n)}{C(\infty)} \frac{|\nabla n|}{n^{\frac{7}{6}}}, \qquad (18)$$

$$G = 1 + 6\eta X_n \sinh^{-1} X_n. \qquad (19)$$

The function $C(n)$ can be written in terms of

$$r_s = \left(\frac{3}{4\pi n} \right)^{\frac{1}{3}} \qquad (20)$$

as

$$C(n) = 0.001667 + \frac{0.002568 + \alpha r_s + \beta r_s^2}{1 + \gamma r_s + \delta r_s^2 + 10^4 \beta r_s^3}, \qquad (21)$$

and $\alpha = 0.023266$; $\beta = 7.389 \times 10^{-6}$; $\gamma = 8.723$; $\delta = 0.472$; $\eta = 0.0042$. The reasons for the choice of this functional form of ε_{xc}^{BP} are explained in the original papers, and well summarized by Ortíz and Ballone.[27] The important point to underline here is that this complex expression has the correct low density limit, whereas the exact electron-gas result[26] is recovered in the limit $\nabla n(\mathbf{r}) \to 0$. The numerical value of the parameters is chosen in such a way to fit the calculated exchange and correlation energies of selected atoms in their ground state.

It is interesting to evaluate the f_{xc} operator for a uniform electron gas. Owing to translational and rotational invariance, this operator is diagonal and isotropic in reciprocal space, i.e., it depends only on $k=|\mathbf{k}|$. In the GC case one applies Eq. (15), where only the first and last terms are nonzero, and the Becke-Perdew f_{xc} can be written in the form:

$$f_{xc}(k) = \frac{\partial^2 F^{LDA}}{\partial n^2} + 2^{\frac{7}{3}} (\pi r_s)^2 \left[C(n) - 2^{\frac{1}{3}} \eta \right] \left(\frac{k}{k_F} \right)^2, \qquad (22)$$

where k_F is the Fermi wave vector. The first (LDA) term in Eq. (22) is a constant; within GC one gets the following leading term, quadratic in k. This term in Eq. (22) is proportional to the difference between the parameters $2^{\frac{1}{3}}\eta$ and $C(n)$. This quantity turns out to be negative for typical valence densities in solids. As already noted by Ortíz,[11] this seems to suggest that the Becke-Perdew GC scheme enhances screening, in the case of a uniform electron gas at least. In a nonuniform electron system, the sign of the difference between the parameters $2^{\frac{1}{3}}\eta$ and $C(n)$ is not enough to assess whether the GC correction actually enhances or reduces screening. Several factors contribute to the final result and not even its sign can be easily predicted beforehand. After the full calculation, we find that GC, in fact, *reduces* screening in Si (see below).

The above paragraph suggests an appealing way of assigning the value of the parameter η, which could in fact be taken from the second k derivative of f_{xc} at $k=0$, as calculated for the electron gas at different densities. Unfortunately this quantity is *not* known at the same level of accuracy as the LDA value of f_{xc}, which is taken from Monte Carlo quantum simulations.[26] So far, a quantum Monte Carlo study of the electron-gas linear response has been performed only in two dimensions,[28] while for three dimensions the only available data are derived from more approximated approaches.[29] The calculations on the market grossly differ from each other in their low-k behavior, and even disagree in the sign of the $k=0$ second derivative of f_{xc}. Although the majority of the available theories suggests a positive sign, some authors propose a negative sign.[30] For this reason we preferred to perform our calculation with the value of $\eta = 0.0042$, as originally proposed by Perdew.[16] If and when more accurate and reliable electron-gas data will become available, a reparametrization of the GC functional could possibly improve the quality of the results.

TABLE I. Lattice constant a_0 and bulk modulus B_0 of Si calculated in the present work. We compare the gradient-corrected results both with standard LDA and with experiment.

	LDA	GC	Expt.
a_0 (a.u.)	10.20	10.38	10.26
B_0 (kbar)	960	880	990

VI. RESULTS AND CRITICAL COMPARISON WITH EXPERIMENTAL DATA

We have generated the pseudopotential for Si, in the GC scheme. We used the method of von Barth and Car already described elsewhere,[31] performing both the all-electron and the pseudopotential calculations within a GC scheme. To check the accuracy of the pseudopotential we reproduced the lattice constants and bands of Si already reported by Ortíz,[11] obtaining exactly the same results for the lattice constants and differences smaller than 0.02 eV for the band energies. In Table I we report our results for some structural properties, using both standard LDA and the GC approximation. All the results have been checked for convergence with respect to the cutoff energy and grid of special points. In particular the reported results are referred to 24 Ry cutoff and 28 special points in the irreducible Brillouin zone which ensure a complete convergence in this semiconductor. It is worth pointing out that while the lattice constant in the GC approximation is only slightly overestimated, and the error is comparable with the LDA underestimate, the error in the theoretical value of the bulk modulus is much larger. This finding is in agreement with the calculations reported in Ref. 12.

The available theoretical DFT-LDA values of the dielectric constants of Si are reported in Table II, together with the results of our calculations performed both within LDA and in the GC scheme. Even if there are small differences between the reported theoretical values, mainly due to the slightly different lattice constants and pseudopotentials used in the computation, it seems quite clear that for Si LDA values have an error of the order of 12–18 %.

It is interesting to note that different authors do not agree upon the experimental value to compare with the theoretical result. In particular two different values for Si are reported. The reason of the discrepancy can be attributed to the difficulty of extrapolating to the zero temperature limit measurements which are performed at finite temperature. In this case, in fact, the derivative

TABLE II. Electronic dielectric constants of Si. In the table we report previous theoretical LDA values (BGT and BR from Refs. 7 and 5, HL from Ref. 6, and LA from Ref. 10), together with our results for different lattice constants. LDA refers to standard theory, while GC are the gradient-corrected results. For every entry, we report also the lattice constant, when available. The * indicates computations performed at the experimental lattice constant (see text).

	a_0 (a.u.) Previous results	ε_∞		a_0 (a.u.) Present results	ε_∞
BGT,BR	10.20	12.7	LDA*	10.26	12.9
HL	?	12.9	GC*	10.26	12.4
LA	10.26	13.5	LDA	10.20	12.7
Expt.	10.26	11.4	GC	10.38	12.6

of the dielectric constant with respect to the temperature is quite large. In Ref. 32 the dielectric constant of Si has been measured as a function of the temperature, and a simple extrapolation gives the experimental values reported in Table II. The different value reported for Si is attributed to Ref. 33, but in this case no temperature dependence is studied, and the value reported agrees well with the $T = 300$ K value of Ref. 32.

We have calculated the static dielectric constant, both at theoretical equilibrium volume and at the experimental one. These values show that the variation of the dielectric constant with the pressure is quite high and for this reason it is very important to choose the correct lattice constant in the calculation. This choice is a kind of ideological matter. Some authors prefer indeed to use the experimental lattice constant: for such a choice, we have shown in the present work that the GC is an important improvement over the LDA, the error being reduced to only 9% for Si. Our own policy, on the contrary, has been to use throughout the computed equilibrium geometry within the chosen theoretical scheme. Besides the aesthetical concern of a completely *ab initio* picture—in the sense sketched in Sec. I—we have found such a choice absolutely essential when dealing with the piezoelectric effect.[8,34] In the present study, we have found that the sizable improvement (i.e., the screening reduction) due to GC is partly compensated by the small lattice expansion due to GC as well, so that the final theoretical GC result is only slightly closer to the experiment than the LDA one.

ACKNOWLEDGMENTS

* Present address: IRRMA, PHB-Ecublens, CH-1015 Lausanne, Switzerland.
[1] *Theory of the Inhomogeneous Electron Gas*, edited by S. Lundqvist and N.H. March (Plenum, New York, 1983).
[2] R.M. Martin, in *Electronic Structure, Dynamics and Quantum Structural Properties of Condensed Matter*, edited by J.T. Devreese and P. Van Camp (Plenum, New York, 1985), p. 175.
[3] R.O. Jones and O. Gunnarson, Rev. Mod. Phys. **61**, 689 (1989).
[4] M.L. Cohen, in *Electronic Materials*, edited by J.R. Chelikowsky and A. Franciosi (Springer, Berlin, 1991), p. 57.
[5] S. Baroni and R. Resta, Phys. Rev. B **33**, 7017 (1986).
[6] M.S. Hybertsen and S.G. Louie, Phys. Rev. B **35**, 5585 (1987); *ibid.* **35**, 5602 (1987).
[7] S. Baroni, P. Giannozzi, and A. Testa, Phys. Rev. Lett. **58**,

1861 (1987).

[8] S. de Gironcoli, S. Baroni, and R. Resta, Phys. Rev. Lett. **62**, 2853(1989).

[9] Z.H. Levine and D.C. Allan, Phys. Rev. Lett. **63**, 1719 (1989).

[10] Z.H. Levine and D.C. Allan, Phys. Rev. B **43**, 4187 (1991).

[11] G. Ortíz, Phys. Rev. B **45**, 11328 (1992).

[12] A. García, C. Elsässer, S.G. Louie, and M.L. Cohen, Phys. Rev. B **46**, 9829 (1992).

[13] D.C. Langreth and M.J. Mehl, Phys. Rev. B **28**, 1809 (1983); **29**, 2310(E) (1984).

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

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

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

[17] C. Lee, D. Vanderbilt, K. Laasonen, R. Car, and M. Parrinello, Phys. Rev. B **47**, 4863 (1993).

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

[19] W.E. Pickett, Comp. Phys. Rep. **9**, 115 (1989).

[20] P. Giannozzi, S. de Gironcoli, P. Pavone, and S. Baroni, Phys. Rev. B **43**, 7231 (1991).

[21] J.P. Perdew and M. Levy, Phys. Rev. Lett. **51**, 1884 (1983); L.J. Sham and M. Schlüter, *ibid.* **51**, 1888 (1983).

[22] S.G. Louie, in *Electronic Materials*, edited by J.R. Chelikowsky and A. Franciosi (Springer, Berlin, 1991), p. 23.

[23] A.D. McLachian and M.A. Ball, Rev. Mod. Phys. **36**, 844(1964).

[24] R. Moccia, R. Resta, and M. Zandomeneghi, Chem. Phys. Lett. **37**, 556 (1976).

[25] R.D. Amos, in *Ab-Initio Methods in Quantum Chemistry-I*, edited by K.P. Lawley (Wiley, New York, 1987), p. 99.

[26] D.M. Ceperley and B.J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[27] G. Ortíz and P. Ballone, Phys. Rev. B **43**, 5881 (1991).

[28] S. Moroni, D. Ceperley, and G. Senatore, Phys. Rev. Lett. **69**, 1837 (1992).

[29] 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.

[30] S. Ichimaru and K. Utsumi, Phys. Rev. B **24**, 7385 (1981).

[31] A. Dal Corso, S. Baroni, R. Resta, and S. de Gironcoli, Phys. Rev. B **47**, 3588 (1993).

[32] H.W. Icenogle, B.C. Platt, and W.L. Wolfe, Appl. Opt. **15**, 2384 (1976).

[33] C. Kittel, *Introduction to Solid State Physics*, 6th ed. (Wiley, New York, 1986).

[34] A. Dal Corso, R. Resta, and S. Baroni, Phys. Rev. B **47**, 16 252 (1993).