

“Direct” evaluation of the inverse dielectric matrix in semiconductors

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The static inverse dielectric matrix is a ground-state property and, as such, can be calculated directly, using the local-density-functional theory, in a similar way as energies of “frozen phonons” have been determined recently. The present method includes quite naturally the exchange-correlation effects and applies to both linear and nonlinear screening. Results are presented on Ge and GaAs and are compared with previous random-phase-approximation calculations.

The local-density-functional (LDF) scheme has in recent years proved to be an efficient method for precise determination of many ground-state properties of solids, such as crystal structure, phonon energies, forces, stresses, etc.^{1,2} We show here that also the static *microscopic* (nonlocal) dielectric response of a solid, particularly the linear (but also the nonlinear) response, can be derived in a similar way, starting from first principles, with a local form for exchange correlation as the only essential approximation.

The linear response of a crystal to an external perturbation V^{ext} is given by the inverse dielectric matrix ϵ^{-1} as

$$V^{\text{scr}}(\vec{q} + \vec{G}) = \sum_{\vec{G}'} \epsilon^{-1}(\vec{q} + \vec{G}, \vec{q} + \vec{G}') V^{\text{ext}}(\vec{q} + \vec{G}'), \quad (1)$$

where V^{scr} is the (electrostatic) potential change actually felt by a classical test charge; \vec{G}, \vec{G}' are reciprocal-lattice vectors and the wave vector \vec{q} lies inside the first Brillouin zone. The very general usefulness of ϵ^{-1} for calculating phonons,³⁻⁷ and other local-field properties,^{8,9} has in the past prompted a considerable amount of effort towards its calculation. So far, calculating accurately ϵ^{-1} has been possible only within the simple random-phase approximation (RPA), through the Adler-Wiser formula.¹⁰ This method is based on extensive and cumbersome sums over band structure, to be performed individually for each dielectric matrix element; in principle, the exchange-correlation effects then can be incorporated as corrections.¹¹ In spite of simplifying mean-value techniques that have been introduced,¹² this approach is very time consuming and has convergence problems concerning both the number of conduction bands to be included and the dimension of the ϵ^{-1} matrix to be inverted. Also, unless the exchange-correlation corrections mentioned above are included (which can readily be done only in tight-binding formulation, and is performed only rarely¹³), it totally misses any exchange-correlation effects other than those—averaged and trivial—that are already contained in the starting band structure.

Yet, any self-consistent band-structure scheme allows a straightforward evaluation of the dielectric response directly from the definition (1). All one needs to do is to consider two distinct crystal potentials, differing by just the chosen V^{ext} , and to bring them to self-consistency. Achieving self-consistency merely expresses the fact that the electron

ground state has adapted to the given situation, whether perturbed or unperturbed. Specifically, in the LDF scheme one solves for the states of an electron in an effective potential

$$\left\{ -\frac{1}{2} \nabla^2 + [v_{\text{ion}}(\vec{r}) + v_{\text{H}}(\vec{r}) + v_{\text{xc}}(n(\vec{r}))] \right\} \psi_i = E_i \psi_i, \quad (2)$$

where $n(\vec{r}) = \sum_i |\psi_i(\vec{r})|^2$ is the self-consistent charge density, v_{xc} the exchange-correlation potential, and

$$v_{\text{H}}(\vec{r}) = \int d^3 \vec{r}' n(\vec{r}') |\vec{r} - \vec{r}'|^{-1}$$

the Hartree potential. Changing v_{ion} into $(v_{\text{ion}} + \Delta v_{\text{ion}})$ with $\Delta v_{\text{ion}} = V^{\text{ext}}$, and achieving a new self-consistency, changes the effective potential felt by an electron by $(\Delta v_{\text{ion}} + \Delta v_{\text{H}} + \Delta v_{\text{xc}})$, and that felt by a (classical) external charge by $(\Delta v_{\text{ion}} + \Delta v_{\text{H}})$ —which then equals the sought V^{scr} .

Using a plane-wave expansion for the solution of (2) then makes it particularly easy to extract the ϵ^{-1} matrix elements through the definition (1). If, in that case, we take

$$\Delta v_{\text{ion}}(\vec{r}) = V^{\text{ext}}(\vec{r}) = V_0 \exp[+i(\vec{q} + \vec{G}')r], \quad (3)$$

the resulting linear response will generally be of the form

$$\Delta v_{\text{ion}} + \Delta v_{\text{H}} = V^{\text{scr}}(\vec{r}) = \sum_{\vec{G}} V(\vec{q} + \vec{G}) \exp[i(\vec{q} + \vec{G})\vec{r}], \quad (4)$$

whence the whole column $\epsilon^{-1}(\vec{q} + \vec{G}, \vec{q} + \vec{G}') = V(\vec{q} + \vec{G})/V_0$ is directly obtained.

The major problem is that a perturbation of the form (3) leads to a new, increased lattice periodicity dictated by the commensurability between \vec{q} and the \vec{G} 's. It has already been shown in other contexts, however,¹⁴⁻¹⁶ that for simple enough choices of \vec{q} , e.g., \vec{q} a zone boundary point or even a simple fraction of the zone-boundary distance, a self-consistent *supercell* calculation is still feasible, whence $\epsilon^{-1}(\vec{q} + \vec{G}, \vec{q} + \vec{G}')$ at those particular \vec{q} values can also be calculated. One merely has to choose a (nonelementary) unit cell in such a way that both \vec{q} and \vec{G} are vectors of the (new) reciprocal lattice. Especially, for $\vec{q} = (q, 0, 0)2\pi/a$, the cell must be doubled ($q = 1, X$ point), quadrupled ($q = \frac{1}{2}$), or octupled ($q = \frac{1}{4}$).

We have carried out the calculation outlined above for Ge and for GaAs, chosen as convenient reference systems whose dielectric response has been thoroughly studied,¹²

and for which a reasonable LDF ground state is obtainable with a local pseudopotential plus Slater exchange (we use $\alpha = 0.8$). This and other details of the ground-state calculation underlying the present determination are the same as in previous studies of phonons^{1,14} and of macroscopic dielectric properties.¹⁵ In particular the band gap is reproduced fairly for GaAs (-20%) and rather badly in Ge (-50% for the direct gap at Γ and -80% for the minimum indirect gap $\Gamma-L$). Plane-wave expansions include waves with kinetic energy up to 9.2 Ry, of which only those up to 2.6 Ry are treated exactly, the rest by Löwdin perturbation. Symmetry is used to reduce the size of the integration over reciprocal space and the Brillouin-zone sampling thus runs over special point sets which are characterized, in the Monkhorst-Pack notation,¹⁷ by indices (2,2,2) (simple cell, $\vec{q}=0$) and (4,4,2) [double, quadruple, and octuple supercells, $\vec{q}=(100)$, $(\frac{1}{2}, 0, 0)$, $(\frac{1}{4}, 0, 0)$, respectively]. We note, however, that crystal plus "perturbation" Δv_{ion} has lower symmetry than the crystal alone, so that the actual number of special points can be up to six times larger than in the unperturbed case. The perturbation (3) is exerted by applying separately $V_0 \cos[(\vec{q} + \vec{G}) \cdot \vec{r}]$ and $V_0 \sin[(\vec{q} + \vec{G}) \cdot \vec{r}]$ and compounding the response with coefficients 1 and $\pm i$, respectively. The result is real in Ge and complex in GaAs due to lack of inversion symmetry. The amplitude V_0 is chosen to be 1 mRy in single-cell calculations ($\vec{q}=0$) and 5 mRy in the supercell ones [$\vec{q}=(100)$, $(\frac{1}{2}, 0, 0)$, $(\frac{1}{4}, 0, 0)$], after checking (particularly in Ge) that even for 10 mRy the response was still essentially linear.

All elements of a large-size dielectric matrix are calculated very efficiently with this direct method. Besides symmetry, which of course relates many ϵ^{-1} matrix elements as explained in Ref. 12, the increased efficiency has two origins: (1) double summations over all valence and typically 90 conduction bands are replaced by single summations over the valence bands only, in evaluation of the charge density; (2) for a fixed \vec{q} a calculation with one given \vec{G}' yields all ϵ^{-1} matrix elements of that column $\epsilon^{-1}(\vec{q} + \vec{G}, \vec{q} + \vec{G}')$ at once. The only exception is for $\vec{q}=0$, $\vec{G}'=0$; in particular,

$\epsilon^{-1}(0, 0)$ cannot be obtained at all with the present method. This is precisely the macroscopic screening, for which separate methods of "direct" determination have already been developed.^{15,16} An example of a very favorable situation is the point Γ : for $\vec{q}=0$ and with the size of ϵ^{-1} limited to 113×113 , the gain in efficiency can be estimated by a factor $\frac{201}{16} \times \frac{90}{10} = 113$. [Instead of 201 symmetry-independent matrix elements only 16 independent perturbations (i.e., eight independent columns in ϵ^{-1}) have to be treated; rather than dealing with ≥ 90 conduction bands and inverting a matrix, the self-consistency has to be achieved, which requires ≤ 10 iterations.] For larger sizes of dielectric matrix the advantage becomes even more pronounced; on the contrary, for $\vec{q} \neq 0$ the efficiency is reduced due to the use of supercells. Nevertheless, we are still gaining a factor of about 10 when \vec{q} is at the zone boundary (point X).

We present some of our results at $\vec{q}=0$ in Table I, in terms of the Hermitian "symmetrized" inverse dielectric matrix defined by Baldereschi and Tosatti:¹²

$$\bar{\epsilon}^{-1}(\vec{q} + \vec{G}, \vec{q} + \vec{G}') = \frac{|\vec{q} + \vec{G}|}{|\vec{q} + \vec{G}'|} \epsilon^{-1}(\vec{q} + \vec{G}, \vec{q} + \vec{G}') \quad (5)$$

Comparison with the earlier RPA results of Ref. 12 shows general overall agreement, with some differences of detail. These differences originate in principle from two distinct facts. The first is that the empirical-pseudopotential (EPS) band structure and gap of Ref. 12 are not identical to our LDF band structure and band gap. However, we can argue that this origin does probably not account for the largest fraction of the differences of ϵ^{-1} with Ref. 12. In fact, the direct band gaps are quite different in Ge (0.5 eV in LDF, 1.2 eV in EPS) but not so different in GaAs (1.3 eV in LDF, 1.4 eV in EPS), while the relative differences of, e.g., $\epsilon^{-1}(111, 111)$ are about the same in Ge and GaAs. [Note that the Adler-Wiser virtual transition formulation of dielectric response indicates that the response at $\vec{q}=0$ is dominated by the *direct* gap; on the contrary, the indirect gap in Ge is expected to be dominating at $\vec{q}=(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$.]

TABLE I. Some elements of inverse dielectric matrix $\bar{\epsilon}^{-1}(\vec{G}, \vec{G}')$ Eq. (5) calculated by the present direct method for Ge and GaAs. The origin of coordinates is chosen between the two basis atoms, with Ga on the site $+\frac{1}{8}(111)a$ and As on $-\frac{1}{8}(111)a$; imaginary part of Fourier coefficients refers to the choice of + sign in Eq. (3).

\vec{G}	\vec{G}'	Ge		GaAs		RPA ^a	
		Present work	RPA ^b	Real	Imaginary	Real	Imaginary
000	000	...	+0.063	+0.087	0.0
111	111	+0.517	+0.610	+0.528	0.0	+0.619	0.0
200	200	+0.570	+0.669	+0.592	0.0	+0.681	0.0
200	111	-0.048	-0.045	-0.049	+0.011	-0.046	+0.013
222	111	+0.049	+0.043 ^c	+0.045	-0.008
022	111	-0.048	-0.043 ^c	-0.045	-0.006
111	111	+0.077	+0.048	+0.060	-0.037	+0.040	-0.026
200	111	-0.014	-0.007	-0.009	+0.004	-0.003	+0.003
311	200	+0.050	+0.041 ^c	+0.045	-0.010
020	200	+0.023	+0.013	+0.015	0.0	+0.010	0.0
200	200	+0.015	+0.011	-0.010	0.0	0.0	0.0

^aAfter R. Resta and A. Baldereschi, Ref. 12.

^cR. Resta (private communication).

^bA. Baldereschi and E. Tosatti, Ref. 12.

TABLE II. Sample elements of inverse dielectric matrix $\epsilon^{-1}(\vec{q} + \vec{G}, \vec{q})$ Eq. (5) for GaAs, as derived from self-consistent calculations on supercells. \vec{q} in units $2\pi/a$.

\vec{G}	$\vec{q} = (1, 0, 0)$		$\vec{q} = (\frac{1}{2}, 0, 0)$		$\vec{q} = (\frac{1}{4}, 0, 0)$	
	Real	Imaginary	Real	Imaginary	Real	Imaginary
0	+0.293	0.0	+0.137	0.0	+0.081	0.0
111	+0.045	-0.013	+0.037	-0.015	+0.028	-0.013
$\bar{2}00$	0.0	-0.060	0.0	-0.025	0.0	-0.010
$\bar{3}1\bar{1}$	+0.016	0.0	+0.015	0.0	+0.010	0.0
$20\bar{2}$	+0.010	0.0	+0.014	0.0	+0.014	0.0
$00\bar{2}$	0.0	+0.011	0.0	+0.008	0.0	+0.004

The other origin of the difference is in the fact that our approach includes exchange-correlation effects in ϵ^{-1} which, of course, are absent in $\epsilon_{\text{RPA}}^{-1}$ of Ref. 12. These corrections can qualitatively be seen as due to a certain amount of excitonic red shift of the main interband excitation energies, thus resulting in an enhanced *diagonal* dielectric screening, leading to smaller values of $\epsilon^{-1}(\vec{q} + \vec{G}, \vec{q} + \vec{G})$. We note that, indeed, this is brought out systematically, with a decrease of order 15% for $\epsilon^{-1}(\vec{G}, \vec{G})$ in both Ge and GaAs; the nondiagonal elements, on the contrary, are (in absolute value) systematically larger than in RPA. We, therefore, can interpret these differences as largely due to genuine exchange-correlation corrections, evaluated within the LDF approximation. It may be worth noting that this increased screening, sizable as it is, is probably still an underestimate, smaller than that predicted by other forms of exchange, like, for example, that of Hanke and Sham.¹³

Some of our results for $q = 1, \frac{1}{2}, \frac{1}{4}$ are summarized in Table II. At present, very little comment is possible, except that they seem again generally similar to the RPA values that are presently being calculated for GaAs by Fleszar and Resta,¹⁸ following an alternative "direct" route which can provide the ϵ^{-1} in random-phase approximation.

In conclusion, we have shown how the full static inverse dielectric matrix of a solid, including "screened-exchange" corrections, can be straightforwardly and simply extracted as a ground-state property from a standard self-consistent local-density ground-state calculation. This method is one to two orders of magnitude faster and more accurate than the best previous methods, exemplified by Ref. 12. The possibility of calculating the full nonlocal screening in such a simple way should soon find useful applications, that so far were prevented by the difficulty of calculations based on the Adler-Wiser formula.

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