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Mean-value point and dielectric properties of semiconductors and insulators

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The mean-value-point technique for Brillouin-zone averages is shown to be applicable to the calculation of electronic dielectric screening matrices. The dielectric-matrix elements for which the technique is not accurate are only a few and for them a separate simple prescription is given. Detailed results are presented for the $\omega = 0$, $\vec{q} = 0$, and $\vec{q} \to 0$ ϵ matrices of diamond, Si, Ge, α-Sn, MgO, and NaCl. Comparison with a nearly-free-electron model is also discussed.

I. INTRODUCTION

The calculation of physical properties of crystals generally requires difficult and time-consuming Brillouin-zone integrations. A considerable simplification was proposed by one of the authors[1] who showed that average values over the Brillouin zone are often well approximated by the value at the Baldereschi or mean-value point which is dictated by crystal symmetry. The coordinates of this point were explicitly given for cubic lattices and possible applications of the method were indicated in the calculation of the electronic valence charge density $\rho(\vec{r})$ and of the average one-electron valence-band energy $\bar{E}$.

This idea stimulated several subsequent investigations which can be classified into three categories. The first includes the works in which the position of the Baldereschi point is determined for crystals other than cubic[2,3] or for crystals subject to external perturbations.[4] The second category corresponds to improvements of the method by using several representative points[2,5] which allow simple convergence tests. Finally, the third category includes the many applications of the method in calculations of those physical properties which were indicated in the original publication, i.e., $\rho(\vec{r})$ and $\bar{E}$. Most applications are concerned with the computation of $\rho(\vec{r})$ to gain information on chemical bonding,[6] or in self-consistent band-structure calculations (for example, calculations of surface states[7]) where a simple method to obtain $\rho(\vec{r})$ is of great help. First-principles calculations of elastic constants and phonon frequencies[8] also need a fast method of obtaining $\rho(\vec{r})$ and $\bar{E}$. Applications to cohesive energies and structural problems do not seem to have been attempted yet.

Little attention has also been paid to the question of whether the Baldereschi point can be of help in other areas of solid-state physics. We know of only one attempt in this direction, by Straus and Ashcroft[9] who show the validity of the method to calculate temperature-dependent structure factors.

In this paper we show that the Baldereschi point is extremely useful in studying the electronic dielectric properties of solids in the static limit ($\omega = 0$), i.e., in evaluating the elements $\epsilon(\vec{q}+\vec{G},\vec{q}+\vec{G}')$ of the dielectric matrix (DM).[10] Our results indicate that even if the method is not equally powerful for all elements of the DM, the elements which require a more careful treatment are few and appropriate prescriptions for them are given. This additional application of the Baldereschi point supports the conjecture by Phillips[11] that these special points may have conceptual implications besides being convenient computational tools. In the following sections we apply the mean-value point technique to a direct calculation of $\epsilon(\vec{q}+\vec{G},\vec{q}+\vec{G}')$ for the group-IV semiconductors, and for the insulators MgO and NaCl. Section II illustrates the details of the method, the convergence checks made, and presents the results, for the lowest reciprocal vectors. These results are discussed in Sec. III, and compared with those of a nearly-free-electron approximation.

II. CALCULATION AND RESULTS

The linear electronic response of a crystal to a static external perturbation is described, in the random-phase approximation, by the matrix[10]

$$\epsilon(\vec{q}+\vec{G},\vec{q}+\vec{G}') = \delta_{\vec{G},\vec{G}'} + 2\,\frac{8\pi e^2}{N\Omega\,|\vec{q}+\vec{G}|^2} \sum_{\vec{k},v,c} \frac{\langle v,\vec{k}\,|e^{-i(\vec{q}+\vec{G})\cdot\vec{r}}|\,c,\vec{k}+\vec{q}\rangle\langle c,\vec{k}+\vec{q}\,|e^{i(\vec{q}+\vec{G}')\cdot\vec{r}}|\,v,\vec{k}\rangle}{E_c(\vec{k}+\vec{q}) - E_v(\vec{k})}\,, \tag{1}$$

where the factor 2 reflects spin degeneracy and $N\Omega$ is the crystal volume. In (1) $\vec{G}$ and $\vec{G}'$ are reciprocal-lattice vectors whereas $\vec{q}$ and $\vec{k}$ are defined within the first Brillouin zone, $|v,\vec{k}\rangle$ and $|c,\vec{k}\rangle$ indicate Bloch states with momentum $\vec{k}$ in the valence and conduction bands, respectively, $E_v(\vec{k})$ and $E_c(\vec{k})$ are the corresponding one-electron energies. The summations over $\vec{k}$ and v reflect the fact that the total polarizability of the crystal is obtained by adding up the contributions of all the electrons present in the system. The $\vec{k}$ summation in particular is extremely time consuming since for each $\vec{k}$ we must calculate the electron Bloch functions in order to compute the matrix elements indicated in (1). The necessity of lengthy calculations is probably the reason why up to now dielectric matrices have been evaluated for a few crystals only. Also, in most of these cases, only the diagonal elements $\epsilon(\vec{q}+\vec{G},\vec{q}+\vec{G})$ have been calculated. A complete calculation of $\epsilon(\vec{q}+\vec{G},\vec{q}+\vec{G}')$ turns out in fact to be a typical application of the mean-value-point technique. Since this technique is valid only for slowly varying functions we must verify whether it can be applied in our case.

For computational purposes, we prefer to work with the "symmetrical dielectric matrix" $\tilde{\epsilon}(\vec{q}+\vec{G},\vec{q}+\vec{G}')$ which is simply related to ϵ by

$$\tilde{\epsilon}(\vec{q}+\vec{G},\vec{q}+\vec{G}')=(|\vec{q}+\vec{G}|/|\vec{q}+\vec{G}'|)\epsilon(\vec{q}+\vec{G},\vec{q}+\vec{G}')\,. \tag{2}$$

The advantage of working with $\tilde{\epsilon}$ is to avoid the divergencies[12] presented by $\epsilon(\vec{q},\vec{q}+\vec{G}')$ in the limit $\vec{q}\rightarrow 0$.

We have performed extensive calculations of $\tilde{\epsilon}(\vec{q}+\vec{G},\vec{q}+\vec{G}')$ for various semiconductors and insulators for both $\vec{q}=0$ and $\vec{q}\rightarrow 0$ and for the lowest 113 values of $\vec{G}$ and $\vec{G}'$. The values of $\tilde{\epsilon}(\vec{q}+\vec{G},\vec{q}+\vec{G}')$ for diamond, Si, Ge, α-Sn, MgO, and NaCl for $\vec{q}\parallel(1,0,0)$ in the limit $\vec{q}\rightarrow 0$ and for the 15 lowest values of the vectors $\vec{G}$ and $\vec{G}'$ are given in Tables I–VI. The DM elements with $\vec{G}$ and $\vec{G}'$ belonging to the $(0,0,0)$, $(1,1,1)$, and $(2,0,0)$ shells

TABLE I. Symmetrical-dielectric-matrix elements $\tilde{\epsilon}(\vec{q}+\vec{G},\vec{q}+\vec{G}')$ for diamond calculated with the Baldereschi point in the limit $\vec{q}\rightarrow 0$ for $\vec{q}\parallel(1,0,0)$. These values are compared to those obtained with the two-point and ten-point techniques of Chadi and Cohen. All nonvanishing and symmetry-independent values of $\tilde{\epsilon}$ are given for $\vec{G}$ and $\vec{G}'$ belonging to the stars of $(0,0,0)$, $(1,1,1)$, and $(2,0,0)$. Some additional values belonging to the DM "wing" are also given. The values have been obtained using the local pseudopotential band-structure calculation by Van Vechten (Ref. 13). The dielectric-matrix elements for $\vec{q}=0$ are the same except the elements $\tilde{\epsilon}(0,\vec{G})$ and $\tilde{\epsilon}(\vec{G},0)$ which vanish for $\vec{G}\neq 0$.

$\vec{G}$	$\vec{G}'$	*B* point	Two-point	Ten-point
(0, 0, 0)	(0, 0, 0)	3.180	6.366	5.274
(1, 1, 1)	(0, 0, 0)	−0.211	−0.243	−0.241
(1, 1, 1)	(1, 1, 1)	1.438	1.442	1.441
($\bar{1}$, 1, 1)	(1, 1, 1)	0.004	0.003	0.004
(1, $\bar{1}$, 1)	($\bar{1}$, 1, 1)	−0.025	−0.024	−0.024
(1, $\bar{1}$, $\bar{1}$)	($\bar{1}$, 1, 1)	−0.118	−0.136	−0.132
(2, 0, 0)	(1, 1, 1)	0.073	0.075	0.074
(2, 0, 0)	($\bar{1}$, 1, 1)	0.006	0.009	0.009
(2, 0, 0)	(2, 0, 0)	1.337	1.345	1.344
($\bar{2}$, 0, 0)	(2, 0, 0)	0.001	−0.013	−0.010
(0, 2, 0)	(2, 0, 0)	−0.020	−0.022	−0.021
(2, 2, 0)	(0, 0, 0)	0.007	0.035	0.023
(3, 1, 1)	(0, 0, 0)	0.046	0.072	0.064
(1, 3, 1)	(0, 0, 0)	0.031	0.051	0.046

TABLE II. Symmetrical-dielectric-matrix elements $\tilde{\epsilon}(\vec{q}+\vec{G},\vec{q}+\vec{G}')$ of Si for $\vec{q}\parallel(1,0,0)$ in the limit $\vec{q}\rightarrow 0$. The first three columns refer to the local band-structure calculation by Cohen and Bergstresser (Ref. 13); the nonlocal calculation is based on the band structure by Chelikowsky and Cohen (Ref. 21). The dielectric-matrix elements for $\vec{q}=0$ are the same except the elements $\tilde{\epsilon}(0,\vec{G})$ and $\tilde{\epsilon}(\vec{G},0)$ which vanish for $\vec{G}\neq 0$.

$\vec{G}$	$\vec{G}'$	*B* point	Two-point	Ten-point	Ten-point nonlocal
(0, 0, 0)	(0, 0, 0)	4.793	10.909	12.102	11.305
(1, 1, 1)	(0, 0, 0)	−0.365	−0.464	−0.441	−0.392
(1, 1, 1)	(1, 1, 1)	1.711	1.708	1.710	1.718
($\bar{1}$, 1, 1)	(1, 1, 1)	−0.016	−0.018	−0.018	0.007
(1, $\bar{1}$, 1)	($\bar{1}$, 1, 1)	−0.020	−0.025	−0.023	0.025
(1, $\bar{1}$, $\bar{1}$)	($\bar{1}$, 1, 1)	−0.113	−0.151	−0.138	−0.156
(2, 0, 0)	(1, 1, 1)	0.085	0.090	0.089	0.118
(2, 0, 0)	($\bar{1}$, 1, 1)	0.008	0.013	0.012	0.034
(2, 0, 0	(2, 0, 0)	1.529	1.544	1.541	1.552
($\bar{2}$, 0, 0)	(2, 0, 0)	−0.008	−0.031	−0.023	−0.023
(0, 2, 0)	(2, 0, 0)	−0.025	−0.030	−0.028	0.008
(2, 2, 0)	(0, 0, 0)	0.043	0.194	0.117	0.124
(3, 1, 1)	(0, 0, 0)	0.087	0.197	0.151	0.138
(1, 3, 1)	(0, 0, 0)	0.033	0.094	0.068	0.084

TABLE III. Symmetrical-dielectric-matrix elements $\tilde{\epsilon}(\vec{q}+\vec{G},\vec{q}+\vec{G}')$ of Ge for $\vec{q}\,\|(1,0,0)$ in the limit $\vec{q}\rightarrow 0$. The first three columns refer to the local band-structure calculation by Cohen and Bergstresser (Ref. 13); the nonlocal calculation is based on the band structure by Pandey and Phillips (Ref. 22). The dielectric-matrix elements for $\vec{q}=0$ are the same except the elements $\tilde{\epsilon}(0,\vec{G})$ and $\tilde{\epsilon}(\vec{G},0)$ which vanish for $\vec{G}\neq 0$.

G	$\vec{G}'$	*B* point	Two-point	Ten-point	Ten-point nonlocal
(0, 0, 0)	(0, 0, 0)	5.202	29.420	15.906	15.045
(1, 1, 1)	(0, 0, 0)	−0.384	−0.426	−0.430	−0.335
(1, 1, 1)	(1, 1, 1)	1.707	1.702	1.706	1.685
$(\bar{1}, 1, 1)$	(1, 1, 1)	−0.008	−0.008	−0.008	0.002
$(1, \bar{1}, 1)$	$(\bar{1}, 1, 1)$	−0.006	−0.009	−0.008	0.000
$(1, \bar{1}, \bar{1})$	$(\bar{1}, 1, 1)$	−0.127	−0.163	−0.149	−0.135
(2, 0, 0)	(1, 1, 1)	0.104	0.111	0.109	0.100
(2, 0, 0)	$(\bar{1}, 1, 1)$	0.018	0.025	0.022	0.031
(2, 0, 0)	(2, 0, 0)	1.532	1.556	1.547	1.532
$(\bar{2}, 0, 0)$	(2, 0, 0)	−0.019	−0.056	−0.038	−0.039
(0, 2, 0)	(2, 0, 0)	−0.010	−0.019	−0.013	−0.012
(2, 2, 0)	(0, 0, 0)	0.042	0.323	0.169	0.199
(3, 1, 1)	(0, 0, 0)	0.097	0.301	0.200	0.187
(1, 3, 1)	(0, 0, 0)	0.043	0.157	0.101	0.098

and which do not appear in the tables, either vanish identically or are related by symmetry to those given in the tables. The DM symmetry group is the same as that of the vector $\vec{q}$, and becomes the full crystal symmetry group only at $\vec{q}\equiv 0$. It should also be noted that the DM elements depend on the particular choice of origin in $\vec{r}$ space. In fact, we see from Eq. (1) that if we displace the origin through a vector $\vec{d}$, the DM elements (both ϵ and $\tilde{\epsilon}$) transform according to

$$\epsilon_{\vec{d}}(\vec{q}+\vec{G},\vec{q}+\vec{G}')=e^{i(\vec{G}-\vec{G}')\cdot\vec{d}}\epsilon_0(\vec{q}+\vec{G},\vec{q}+\vec{G}')\,. \quad (3)$$

TABLE IV. Symmetrical-dielectric-matrix elements $\tilde{\epsilon}(\vec{q}+\vec{G},\vec{q}+\vec{G}')$ of α-Sn for $\vec{q}\,\|(1,0,0)$ in the limit $\vec{q}\rightarrow 0$. The values have been obtained using the local pseudopotential band-structure calculation by Cohen and Bergstresser (Ref. 13). The dielectric-matrix elements for $\vec{q}=0$ are the same except the elements $\tilde{\epsilon}(0,\vec{G})$ and $\tilde{\epsilon}(\vec{G},0)$ which vanish for $\vec{G}\neq 0$.

$\vec{G}$	$\vec{G}'$	*B* point	Two-point	Ten-point
(0, 0, 0)	(0, 0, 0)	5.901	40.561	21.232
(1, 1, 1)	(0, 0, 0)	−0.433	−0.443	−0.459
(1, 1, 1)	(1, 1, 1)	1.773	1.769	1.774
$(\bar{1}, 1, 1)$	(1, 1, 1)	0.000	0.002	0.001
$(1, \bar{1}, 1)$	$(\bar{1}, 1, 1)$	−0.005	−0.006	−0.006
$(1, \bar{1}, \bar{1})$	$(\bar{1}, 1, 1)$	−0.153	−0.187	−0.172
(2, 0, 0)	(1, 1, 1)	0.132	0.140	0.138
(2, 0, 0)	$(\bar{1}, 1, 1)$	0.027	0.033	0.030
(2, 0, 0)	(2, 0, 0)	1.589	1.626	1.609
$(\bar{2}, 0, 0)$	(2, 0, 0)	−0.033	−0.084	−0.056
(0, 2, 0)	(2, 0, 0)	−0.002	−0.017	−0.008
(2, 2, 0)	(0, 0, 0)	0.044	0.433	0.220
(3, 1, 1)	(0, 0, 0)	0.120	0.420	0.266
(1, 3, 1)	(0, 0, 0)	0.058	0.223	0.138

In our case, we place the origin halfway between the two atoms in the primitive cell of semiconductors and on the cation for insulators so that $\tilde{\epsilon}$ is a real symmetric matrix. Electronic energies and wave functions have been calculated by the empirical local pseudopotential method.[13] Core effects (i.e., core polarizability and orthogonalization of the valence states to the core) have been neglected since they are expected to be rather small and in any case they will not modify the conclusions of

TABLE V. Symmetrical-dielectric-matrix elements $\tilde{\epsilon}(\vec{q}+\vec{G},\vec{q}+\vec{G}')$ of MgO for $\vec{q}\,\|(1,0,0)$ in the limit $\vec{q}\rightarrow 0$. The values have been obtained using the local pseudopotential band-structure calculation by Cohen, Lin, Roessler, and Walker (Ref. 13). The dielectric-matrix elements for $\vec{q}=0$ are the same except the elements $\tilde{\epsilon}(0,\vec{G})$ and $\tilde{\epsilon}(\vec{G},0)$ which vanish for $\vec{G}\neq 0$.

$\vec{G}$	$\vec{G}'$	*B* point	Two-point	Ten-point
(0, 0, 0)	(0, 0, 0)	2.753	3.313	3.187
(1, 1, 1)	(0, 0, 0)	−0.309	−0.329	−0.325
(1, 1, 1)	(1, 1, 1)	1.434	1.432	1.433
$(\bar{1}, 1, 1)$	(1, 1, 1)	0.081	0.081	0.081
$(1, \bar{1}, 1)$	$(\bar{1}, 1, 1)$	−0.040	−0.042	−0.041
$(1, \bar{1}, \bar{1})$	$(\bar{1}, 1, 1)$	−0.128	−0.132	−0.131
(2, 0, 0)	(0, 0, 0)	0.321	0.346	0.342
(2, 0, 0)	(1, 1, 1)	−0.107	−0.107	−0.107
(2, 0, 0)	$(\bar{1}, 1, 1)$	0.028	0.030	0.029
(2, 0, 0)	(2, 0, 0)	1.299	1.297	1.298
$(\bar{2}, 0, 0)$	(2, 0, 0)	−0.052	−0.055	−0.054
(0, 2, 0)	(2, 0, 0)	0.003	0.002	0.002
(2, 2, 0)	(0, 0, 0)	0.036	0.030	0.031
(3, 1, 1)	(0, 0, 0)	0.025	0.034	0.033
(1, 3, 1)	(0, 0, 0)	−0.004	0.000	−0.001

TABLE VI. Symmetrical-dielectric-matrix elements $\tilde\epsilon(\vec q+\vec G, \vec q+\vec G')$ of NaCl for $\vec q \parallel (1,0,0)$ in the limit $\vec q \to 0$. The values have been obtained by using the local pseudopotential band-structure calculation by Fong and Cohen (Ref. 13). The dielectric-matrix elements for $\vec q = 0$ are the same except the elements $\tilde\epsilon(0,\vec G)$ and $\tilde\epsilon(\vec G, 0)$ which vanish for $\vec G \neq 0$.

$\vec G$	$\vec G'$	B point	Two-point	Ten-point
(0, 0, 0)	(0, 0, 0)	2.444	2.520	2.514
(1, 0, 0)	(0, 0, 0)	−0.328	−0.331	−0.330
(1, 1, 1)	(1, 1, 1)	1.471	1.470	1.470
$(\bar 1, 1, 1)$	(1, 1, 1)	0.091	0.091	0.091
$(1, \bar 1, 1)$	$(\bar 1, 1, 1)$	−0.052	−0.052	−0.052
$(1, \bar 1, \bar 1)$	$(\bar 1, 1, 1)$	−0.181	−0.182	−0.182
(2, 0, 0)	(0, 0, 0)	0.407	0.412	0.411
(2, 0, 0)	(1, 1, 1)	−0.143	−0.143	−0.143
(2, 0, 0)	$(\bar 1, 1, 1)$	0.062	0.062	0.062
(2, 0, 0)	(2, 0, 0)	1.347	1.347	1.347
$(\bar 2, 0, 0)$	(2, 0, 0)	−0.089	−0.090	−0.090
(0, 2, 0)	(2, 0, 0)	0.005	0.005	0.005
(2, 2, 0)	(0, 0, 0)	0.068	0.067	0.067
(3, 1, 1)	(0, 0, 0)	−0.010	−0.009	−0.009
(1, 3, 1)	(0, 0, 0)	−0.008	−0.007	−0.007

this paper. As indicated in Tables I–VI, each DM element has been calculated using the Baldereschi-point[1] as well as the two-point and ten-point methods of Chadi and Cohen[2] in order to test the convergence.

The results of Tables I–VI show that different DM elements have different convergence behavior and can be classified into three groups depending on whether $\vec G$ and $\vec G'$ vanish or not. The most pathological case is the single element $\vec G = \vec G' = 0$ for which it is necessary to use as many as ten points to obtain satisfactory results. The second group of elements consists of the two DM "wings" corresponding to either $\vec G = 0$ or $\vec G' = 0$. For this group the convergence is better, and two points usually give reasonable results. Finally, the full DM "body" $\vec G, \vec G' \neq 0$ is already accurate to within a few percent with the single-point alone. This accuracy is similar to that originally found in approximating the electronic charge density.[1] It is more than enough for all practical purposes, in view of the many uncertainties involved in a DM calculation like core effects, exchange and correlation corrections, etc., which involve errors which are one order of magnitude larger.

The differences in convergence among the three groups can be understood as follows. Note that for $\vec G = 0$ and $\vec q \to 0$, the dipole limit gives

$$\langle v, \vec k + \vec q | e^{i(\vec q + \vec G)\cdot \vec r} | c, \vec k\rangle \to \langle v, \vec k | i\vec q \cdot \vec r | c, \vec k \rangle = -\frac{\hbar}{m}\frac{\langle v, \vec k | \vec q \cdot \vec p | c, \vec k\rangle}{E_c(\vec k) - E_v(\vec k)} . \qquad (4)$$

The matrix element $\langle v, \vec k | \vec q \cdot \vec p | c, \vec k\rangle$ is usually a slowly varying function of $\vec k$ whereas the energy denominator strongly oscillates in the Brillouin zone. Substituting (4) into (1) we see that each $\vec G = 0$ (or $\vec G' = 0$) adds one more power in the energy denominator. The oscillations of the integrand become larger, and the averaging more difficult. Incidentally, the limit (4) clarifies the nonanalyticity of the "wings" of ϵ and $\tilde\epsilon$ at $\vec q = 0$.[12] In fact, they do not vanish as $\vec q \to 0$, and yet

$$\lim_{\vec q \to 0} \tilde\epsilon(\vec q, \vec q + \vec G') = -\lim_{\vec q \to 0} \tilde\epsilon(-\vec q, -\vec q + \vec G') , \quad (\vec G' \neq 0) , \qquad (5)$$

as is easily seen by inserting (4) into expression (1). Related formulas also hold for ϵ, $\tilde\epsilon^{-1}$, and ϵ^{-1}. This nonanalyticity requires a separate prescription for $\vec q = 0$. This is provided by gauge invariance, which requires no electronic response to a constant perturbing potential, and, therefore,

$$\epsilon^{-1}(0, \vec G) = \epsilon^{-1}(\vec G, 0) = 0 , \qquad (6)$$

for all $\vec G \neq 0$. As a consequence of (6) also the "wings" of $\tilde\epsilon^{-1}$, ϵ, and $\tilde\epsilon$ vanish for $\vec q = 0$. No such problems arise for the $\vec G = \vec G' = 0$ and the $\vec G, \vec G' \neq 0$ matrix elements of ϵ and $\tilde\epsilon$ which are analytic at $\vec q = 0$. The dielectric matrices ϵ and $\tilde\epsilon$ at $\vec q = 0$ are therefore simply obtained from the corresponding matrices calculated for $\vec q \to 0$ by setting their "wings" equal to 0 and keeping all the other matrix elements unchanged. The $\tilde\epsilon$-matrix elements at $\vec q = 0$ are therefore implicitly contained in Tables I–VI which give the $\tilde\epsilon$-matrix elements for $\vec q \to 0$. The inverse matrices ϵ^{-1} and $\tilde\epsilon^{-1}$ are in all cases obtained by inverting the corresponding matrices ϵ and $\tilde\epsilon$ and, as a result, not only their "wings" but in general all their matrix elements are not analytic at $\vec q = 0$. No simple prescription can be given to directly relate the inverse dielectric matrices at $\vec q = 0$ to those for $\vec q \to 0$ and therefore we give in Tables VII and VIII the independent elements of $\tilde\epsilon^{-1}$ for $\vec q = 0$ and $\vec q \to 0$, respectively. The values given in these tables have been obtained by inverting matrices of order 113 calculated with the ten-point averaging method. In particular, we note that the screening of a periodic potential ($\vec q = 0$) has to be performed with the $\vec q = 0$ ϵ^{-1}-matrix (i.e., the inverse of the $\vec q = 0$ ϵ matrix) and this differs from just taking the "body" of the $\vec q \to 0$ ϵ^{-1} matrix as is evident from a comparison of Tables VII and VIII.

Finally, we note that the values of the DM elements reported in Tables I–VI should reflect the different properties of the crystals, i.e., increasing metallicity upon going from diamond to α-Sn and the high ionicity of MgO and NaCl. We note that while $\epsilon(0,0)$ changes rather drastically, the

TABLE VII. Inverse-dielectric-matrix elements $\tilde{\epsilon}^{-1}(\vec{q}+\vec{G},\vec{q}+\vec{G}')$ at $\vec{q}=0$. The elements $\tilde{\epsilon}^{-1}(0,\vec{G})$ and $\tilde{\epsilon}^{-1}(\vec{G},0)$ vanish for $\vec{G}\neq 0$. The $\tilde{\epsilon}^{-1}$ matrices have been obtained by inverting $\tilde{\epsilon}$ matrices of order 113 calculated with the ten-point method.

$\vec{G}$	$\vec{G}'$	Diamond	Si local	Si nonlocal	Ge local	Ge nonlocal	α-Sn	MgO	NaCl
$(0,0,0)$	$(0,0,0)$	0.190	0.083	0.088	0.063	0.066	0.047	0.314	0.398
$(1,1,1)$	$(1,1,1)$	0.715	0.605	0.605	0.610	0.613	0.595	0.734	0.737
$(\bar{1},1,1)$	$(1,1,1)$	−0.001	0.008	0.004	0.006	0.003	0.005	−0.034	−0.033
$(1,\bar{1},1)$	$(\bar{1},1,1)$	0.015	0.010	−0.004	0.006	0.005	0.008	0.021	0.021
$(1,\bar{1},\bar{1})$	$(\bar{1},1,1)$	0.060	0.045	0.049	0.048	0.044	0.051	0.053	0.065
$(2,0,0)$	$(1,1,1)$	−0.041	−0.038	−0.045	−0.045	−0.041	−0.052	0.053	0.064
$(2,0,0)$	$(\bar{1},1,1)$	−0.003	−0.005	−0.008	−0.007	−0.010	−0.008	−0.010	−0.021
$(2,0,0)$	$(2,0,0)$	0.761	0.667	0.666	0.669	0.672	0.652	0.798	0.791
$(\bar{2},0,0)$	$(2,0,0)$	0.001	0.006	0.003	0.011	0.010	0.015	0.024	0.030
$(0,2,0)$	$(2,0,0)$	0.017	0.016	0.005	0.013	0.012	0.013	0.004	0.003

other values seem to change much less from crystal to crystal. Therefore, it is only the *relative* importance of $\epsilon(0,0)$ to the off-diagonal elements which determines the magnitude and relevance of the local-field corrections. They are much more important in insulators than in semiconductors and among the group-IV semiconductors they are bigger in diamond than in α-Sn, in agreement with the metallicity trend mentioned above.

III. DISCUSSION

The success of the mean-value point in the calculation of $\epsilon(\vec{G},\vec{G}')$ can be traced back to that of $\rho(\vec{r})$.[1] A hint that the mean-value-point technique should be equally valid in the calculation of $\rho(\vec{r})$ and of the DM elements is provided by the existence of the relationship[14]

$$\vec{G}\frac{4\pi e^2}{|\vec{G}|}\rho(\vec{G}) = |\vec{G}|\lim_{\vec{q}\to 0}\sum_{\vec{G}'}(\vec{q}+\vec{G}')[\epsilon^{-1}(\vec{q}+\vec{G},\vec{q}+\vec{G}')-\delta_{\vec{G},\vec{G}'}]W(\vec{G}')\,, \tag{7}$$

TABLE VIII. Inverse-dielectric-matrix elements $\tilde{\epsilon}^{-1}(\vec{q}+\vec{G},\vec{q}+\vec{G}')$ for $\vec{q}\to 0$ along the [100] direction. The elements corresponding to grouped together $\vec{G}$, $\vec{G}'$ pairs are related by symmetry at $\vec{q}=0$ but not for $\vec{q}\to 0$. Notice the different symmetry properties between diamond and rocksalt crystals. The $\tilde{\epsilon}^{-1}$ matrices have been obtained by inverting $\tilde{\epsilon}$ matrices of order 113 calculated with the ten-point method.

$\vec{G}$	$\vec{G}'$	Diamond	Si local	Si nonlocal	Ge local	Ge nonlocal	α-Sn	MgO	NaCl
$(0,0,0)$	$(0,0,0)$	0.205	0.092	0.098	0.070	0.072	0.052	0.388	0.522
$(1,0,0)$	$(0,0,0)$	0.031	0.022	0.021	0.016	0.014	0.013	0.069	0.084
$(1,1,1)$	$(1,1,1)$	0.720	0.610	0.610	0.614	0.615	0.598	0.746	0.751
$(\bar{1},1,1)$	$(1,1,1)$	0.004	0.013	0.009	0.010	0.006	0.008	−0.046	−0.046
$(1,\bar{1},1)$	$(1,1,1)$	−0.005	0.003	−0.001	0.002	0.001	0.002	−0.022	−0.020
$(1,\bar{1},1)$	$(\bar{1},1,1)$	0.010	0.005	−0.008	0.003	0.002	0.005	0.009	0.007
$(1,1,\bar{1})$	$(1,\bar{1},1)$	0.020	0.015	0.001	0.010	0.007	0.011	0.033	0.034
$(1,\bar{1},\bar{1})$	$(\bar{1},1,1)$	0.056	0.040	0.044	0.044	0.042	0.047	0.041	0.052
$(2,0,0)$	$(0,0,0)$	0.	0.	0.	0.	0.	0.	−0.072	−0.101
$(2,0,0)$	$(1,1,1)$	−0.041	−0.038	−0.045	−0.045	−0.041	−0.052	0.040	0.047
$(0,2,0)$	$(1,1,1)$	−0.041	−0.038	−0.045	−0.045	−0.041	−0.052	0.053	0.064
$(2,0,0)$	$(\bar{1},1,1)$	−0.003	−0.005	−0.008	−0.007	−0.010	−0.008	0.003	−0.004
$(0,2,0)$	$(1,\bar{1},1)$	−0.003	−0.005	−0.008	−0.007	−0.010	−0.008	−0.010	−0.021
$(2,0,0)$	$(2,0,0)$	0.761	0.667	0.666	0.669	0.672	0.652	0.811	0.811
$(0,2,0)$	$(0,2,0)$	0.761	0.667	0.666	0.669	0.672	0.652	0.798	0.791
$(\bar{2},0,0)$	$(2,0,0)$	0.001	0.006	0.003	0.011	0.010	0.015	0.011	0.010
$(0,\bar{2},0)$	$(0,2,0)$	0.001	0.006	0.003	0.011	0.010	0.015	0.024	0.030
$(0,2,0)$	$(2,0,0)$	0.017	0.016	0.005	0.013	0.012	0.013	0.004	0.003

which linearly connects $\rho(\vec{r})$ and ϵ^{-1} via the bare crystal potential $W(\vec{G})$. Even if Eq. (7) does not imply that contributions to ρ and to ϵ^{-1} are proportional in each region of $\vec{k}$ space, it does suggest that a close parallelism should exist between ρ and ϵ averages. To see this parallelism in more detail, let us consider the limit where the crystal is obtained by perturbing a free-electron gas by a weak, real self-consistent periodic potential $V(\vec{G})$. In practice, most crystals have a potential which is far too strong for such an approximation to hold, but the validity of the argument remains. In Brillouin-Wigner perturbation theory, the Bloch states are (apart from a normalization factor)

$$|\vec{k}+\vec{G}\rangle = e^{i(\vec{k}+\vec{G})\cdot\vec{r}} + \sum_{\vec{G}'\neq\vec{G}} [E(\vec{k}+\vec{G}) - E^0(\vec{k}+\vec{G}')]^{-1} \times V(\vec{G}'-\vec{G})e^{i(\vec{k}+\vec{G}')\cdot\vec{r}}, \quad (8)$$

where $E^0(\vec{k}) = \hbar^2k^2/2m$ and $E(\vec{k})$ is the perturbed one-electron energy. The valence electron charge density to lowest order in V is

$$\rho(\vec{r}) = \frac{e}{N\Omega} \sum_{\vec{G}} \sum_{\vec{k}} \left(1 + \sum_{\vec{G}'\neq\vec{G}} [E(\vec{k}+\vec{G}) - E^0(\vec{k}+\vec{G}')]^{-1} \times V(\vec{G}'-G) \cos(\vec{G}-\vec{G}')\cdot\vec{r}\right), \quad (9)$$

where $N\Omega$ is the crystal volume and the summations over $\vec{k}$ and $\vec{G}$ cover all the occupied states. Expression (9) shows that the Fourier components of the electronic charge are proportional to the Brillouin-zone averages of $[E(\vec{k}+\vec{G}) - E^0(\vec{k}+\vec{G}')]^{-1}$. The DM elements (1) have been calculated by Bertoni *et al.*[15] using the same approximations leading to expression (9). Their results for $\vec{q}\rightarrow 0$ are

$$\tilde{\epsilon}(\vec{q},\vec{q}+\vec{G}) = -\frac{4\pi e^2}{|\vec{q}|\,|\vec{q}+\vec{G}|}\left[-\frac{\hbar^2}{m}(\vec{q}\cdot\vec{G})V(\vec{G})\sum_{\vec{k}}\frac{f(\vec{k}+\vec{G})-f(\vec{k})}{[E(\vec{k}+\vec{G})-E(\vec{k})][E(\vec{k}+\vec{G})-E^0(\vec{k})]^2}\right], \quad (10)$$

and

$$\tilde{\epsilon}(\vec{q}+\vec{G},\vec{q}+\vec{G}') = \delta_{\vec{G},\vec{G}'} - \frac{4\pi e^2}{|\vec{q}+\vec{G}|\,|\vec{q}+\vec{G}'|} \times \left\{2V(\vec{G}-\vec{G}')\left[\sum_{\vec{k}}\frac{f(\vec{k}+\vec{G})-f(\vec{k})}{[E(\vec{k}+\vec{G})-E(\vec{k})][E(\vec{k})-E^0(\vec{k}+\vec{G}-\vec{G}')]}+\dots\right]\right\}, \quad (11)$$

where the dots mean "same with $\vec{G}\rightleftarrows\vec{G}'$" and $f(\vec{k})$ is the Fermi function. From expression (11) we see that the DM elements for $\vec{G},\vec{G}'\neq 0$ are proportional to the Brillouin-zone average of the product of two energy denominators, which however are different, so that their oscillations do not add up. Since the calculation of $\rho(\vec{r})$, expression (9), involves a single energy-denominator average, we do expect that $\rho(\vec{r})$ and $\epsilon(\vec{G},\vec{G}')$ should be calculable by the same averaging technique with comparable accuracy in the results. On the other hand, we see from (10) that for either $\vec{G}=0$ or $\vec{G}'=0$, the calculation of the DM element involves the average of the product of three energy denominators, two of which are equal. It is therefore not surprising that the mean-value point is less accurate in this case. Finally, for $\vec{G}=\vec{G}'=0$ the DM element contains terms which involve the product of as many as five energy denominators,[15] which justifies why so many representative points are necessary in this case.

We can now check the accuracy of perturbation theory in the calculation of DM elements. To calculate expressions (10) and (11) one should usually proceed numerically since finding the perturbed one-electron energies $E(\vec{k})$ requires solving the nearly-free-electron secular problem. The obvious replacement $E(\vec{k})\rightarrow E^0(\vec{k}) = \hbar^2k^2/2m$ causes unphysical divergences unless $x = |\vec{G}|/2k_F < 1$. For $x \ll 1$, however, the replacement is legitimate and expression (10) can be evaluated analytically,

$$\tilde{\epsilon}(\vec{q},\vec{q}+\vec{G}) = \frac{1}{2\pi}\frac{\vec{q}\cdot\vec{G}}{|\vec{q}|\,|\vec{G}|}\frac{\vec{V}(\vec{G})}{x^3k_F^3}\left(\frac{x}{x^2-1}+\ln\left|\frac{1-x}{1+x}\right|\right), \quad (12)$$

where V and k_F are in atomic units. Since for $\vec{G}=(2\pi/a)(1,1,1)$ one has $x=0.55$, expression (12) should be a reasonable approximation. We obtain the values −0.15, −0.14, −0.17, and −0.24 for diamond, Si, Ge, and α-Sn, respectively, to be compared with the values −0.24, −0.44, −0.43, and −0.46 given in Tables I–IV. Thus, the accuracy of the free-electron perturbation approach is at most fair, as already found by Bertoni *et al.*[15] who, in their DM calculation for Si, had to multiply by the constant factor 3.0 all ϵ matrix elements obtained by perturbation theory in order to satisfy the acoustical sum rule.[16] It is interesting to observe that this scaling changes the Si value from −0.14 to −0.42 in excellent agreement with the value obtained from the "exact" band structure. The reason for the limited success of the free-electron perturbation approach in the quantitative prediction of the DM elements is that the Bloch functions (8) are expanded up to linear terms in the crystal potential only. Higher-order terms cannot be neglected in calculating the band structure of semiconductors and insulators as shown, for example, by Heine and Jones[17] in their calculation of the covalent energy gap at the Jones-zone surface of semiconductors. The 3.0 scaling factor introduced by Bertoni *et al.* indicates the relevance of these higher-order terms for covalent and ionic crystals.

So far, we have shown that the Baldereschi-point technique[1] and the representative point technique by Chadi and Cohen[2] are suitable for the numerical evaluation of the dielectric matrices for $\vec{q}=0$ and in the limit $\vec{q}\to 0$. These techniques are expected to work even better for $\vec{q}\neq 0$. In fact, the convergence difficulties encountered in the limit $\vec{q}\to 0$ were connected with the dipole limit (4), giving rise to powers in the energy denominators higher than 1. These difficulties should disappear altogether along with the dipole expansion for $\vec{q}\neq 0$, and we expect that the mean-value-point technique should be excellent as $\vec{q}$ approaches the Brillouin-zone boundary.

We can compare our values of the DM elements for diamond with those calculated in the limit $\vec{q}\to 0$ by Van Vechten and Martin[18] and reported by Johnson.[19] The pseudopotential form factors used in the two calculations are the same and the resulting values for the DM elements are very similar. The small differences can be attributed to the use of different averaging techniques and to the larger number of conduction states used in the present work in the evaluation of expression (1). We find, in fact, that the number of conduction bands to be included in the summation (1) to attain convergence strongly depends upon $\vec{G}$ and $\vec{G}'$, a point already stressed by Srinivasan.[20] For Si, for example, for both $\vec{G}$ and $\vec{G}'$ in the $(1,1,1)$ shell, the lowest 15 conduction states must be included in the summation (1) to obtain DM elements with 10% accuracy. At the same time, for $\vec{G},\vec{G}'$ in the $(4,2,0)$ shell, we had to include as many as 90 conduction states to get the same accuracy. This is to be expected since the matrix elements of $e^{i(\vec{q}+\vec{G})\cdot\vec{r}}$ in (1) are essentially the Fourier transforms of the valence wave functions at wave vector $|\vec{q}+\vec{G}|-[2mE_c(\vec{k})/\hbar^2]^{1/2}$. For large $\vec{G}$ one needs to go to higher and higher conduction bands before the matrix element falls to negligible values.

We have also tested the sensitivity of the values of the DM elements to the particular band structure used in the calculation. We have reevaluated $\tilde{\epsilon}(\vec{q}+\vec{G},\vec{q}+\vec{G}')|_{\vec{q}\to 0}$ using the nonlocal pseudopotential band structures recently proposed by Chelikowsky and Cohen[21] for Si and by Pandey and Phillips[22] for Ge. The results obtained by the ten-point technique are given in Tables II and III. The differences with the local band structure results are of the order of 10%. This figure can therefore be taken as an indication of the overall accuracy of the values reported in Tables I–VI.

Before concluding, a few words are in order concerning the feasibility of DM calculations of this type with $\omega\neq 0$ for semiconductors, and at any ω for metals. Let us consider first a semiconductor or an insulator, and introduce a finite ω. The denominator in Eq. (1) is replaced by

$$\Delta E(\vec{k},\vec{q},\omega)=[E_c(\vec{k}+\vec{q})-E_v(\vec{k})+\hbar\omega+i\eta]\ ,$$

where η is infinitesimal. As ω increases from zero, the minimum value of $\Delta E(\vec{k},\vec{q},\omega)$ decreases from the energy gap E_g to $E_g-\hbar\omega$. The denominator will then vanish for $\omega>E_g/\hbar$ at a number of $\vec{k}$ points proportional to the "joint density of states," and the DM will correspondingly become complex. Because now the integrand of (1) oscillates wildly, one can anticipate that an averaging technique will in general be unsuitable. This is true for any system at $\hbar\omega\gtrsim E_g$, and it remains true for a metal all the way down to $\omega=0$. In fact, one or more averaging points may by chance fall very close to the Fermi surface, and yield large meaningless contributions to the sum. There is however another circumstance, besides $\omega\ll E_g/\hbar$, where the mean-value-point technique should work well. That is the opposite limit, of very large frequencies, or $\omega\gg E_g/\hbar$. At such frequencies, well above the most important interband transitions, the integrand in (1) becomes again a smooth function, except for a few conduction bands that however give a negligible contribution, and may be left out of the summation. This idea might enable future accurate calculations of, e.g., umklapp effects on plasmons,[23] both in metals and in insulators.

In conclusion, we have shown how the mean-value-point technique can be successfully employed for fast and efficient computations of dielectric matrices of semiconductors and insulators and we hope that this will open the way to extensive investigations of the dielectric properties of these materials. The screening of periodic perturbations through the concept of DM eigenvalues and eigenpotentials,[24] the study of chemical trends, the investigation of local field corrections and the calculation of phonon frequencies are among the applications that are presently under study and which will be reported elsewhere.

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