PHYSICAL REVIEW VOLUME 178, NUMBER 3 15 FEBRUARY 1969

Microscopic Dielectric Function of a Model Semiconductor

G. SRINIVASAN

James Franck Institute and Department of Physics, University of Chicago, Chicago, Illinois 60637

(Received 25 October 1968)

Penn's model of an isotropic semiconductor is used to calculate $\epsilon(q)$, the diagonal part of the static microscopic dielectric function. Penn's results have been extended beyond $q=K_F$. This region is important in developing a quantum theory of lattice vibrations of diamond and zinc-blende crystals. Explicit results are given for the range $0<q<4K_F$.

I. INTRODUCTION

THE microscopic dielectric tensor $\epsilon_{ij}(\mathbf{q}+\mathbf{G},\ \mathbf{q}+\mathbf{G}')$ describes the response of a crystal to a static electric field $\mathbf{F}e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}}$ at wave number $\mathbf{q}+\mathbf{G}$:

$$D_i e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}=\epsilon_{ij}(\mathbf{q},\mathbf{G},\mathbf{G}')F_j e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}}. \tag{1.1}$$

Here $\mathbf{q}$ is a reduced wave vector in the first Brillouin zone, while $\mathbf{G}$ and $\mathbf{G}'$ are reciprocal lattice vectors. It is an empirical observation that in many covalent crystals the static dielectric constant

$$\epsilon_0=\tfrac{1}{3}\,\mathrm{Tr}\epsilon_{ij}(0,0) \tag{1.2}$$

is large compared to unity. This suggests that it should be fruitful to study the diagonal part ($\mathbf{G}=\mathbf{G}'$) of $\epsilon_{ii}=\epsilon_i(\mathbf{q}+\mathbf{G})$.

In this paper we discuss $\epsilon(\mathbf{q}+\mathbf{G})$ for a model isotropic semiconductor. The exact form of $\epsilon(\mathbf{q}+\mathbf{G})$ is known only for a free-electron gas. To describe semiconductors in which the static dielectric constant is much larger than unity, Penn has proposed a simple isotropic model.[1] The principal features of Penn's model have been confirmed for Si [2] and Ge [3] by calculations which have used realistic energy bands and oscillator strengths. These numerical calculations show that the effects of anisotropy and off-diagonal matrix elements ($\mathbf{G}\neq\mathbf{G}'$) are indeed small, as anticipated by Penn.

In attempting to utilize Penn's results, we found it necessary to extend his calculations to larger values of q. Also, it appears that there are some algebraic errors in his formulas. Even the simple model considered by him leads to rather intricate expressions for the model dielectric function $\epsilon_P(q)$. Since it now seems that $\epsilon(q)$ can have much more general significance than was anticipated at the time the model was proposed, we have reconsidered Penn's model in detail, and have obtained consistent expressions for $\epsilon_P(q)$ for the entire range of q. In particular, we believe our results to be more accurate than the results obtained by Penn from an interpolation formula. Penn's interpolation formula has had wide applications: It has been used to calculate screened pseudopotential form factors[4] and screened impurity potentials.[5]

In Sec. II we clarify the definition of Penn's model. Explicit expressions for $\epsilon_P(q)$ are quite lengthy and are given in Appendix A, hopefully free of errors. In Sec. III a convenient method for transforming $\epsilon(q)$ into $\tilde{\epsilon}(r)$, a related function which exhibits the effects of spatial dispersion, is presented. In Sec. IV results for diamond, Si, Ge, and several zinc-blende crystals are given and applications are discussed in Sec. V.

II. MODEL

The model due to Penn replaces the actual energy bands of a semiconductor by those of a nearly free electron gas, isotropically extended to three dimensions. A graph of energy versus wave vector for this model is shown in Fig. 1. There is an energy gap at what corresponds to the Jones zone, i.e., an energy gap between the occupied valence states and the unoccupied conduction states.

Such a model is described by the eigenvalues and eigenfunctions

$$E_{\mathbf{k}}^{\pm}=\tfrac{1}{2}\{E_{\mathbf{k}}^{0}+E_{\mathbf{k}'}^{0}\pm[(E_{\mathbf{k}}^{0}-E_{\mathbf{k}'}^{0})^2+E_g^{2}]^{1/2}\}, \tag{2.1}$$

$$\psi_{\mathbf{k}}=(e^{i\mathbf{k}\cdot\mathbf{r}}+\alpha_{\mathbf{k}}^{\pm}e^{i\mathbf{k}'\cdot\mathbf{r}})/[1+(\alpha_{\mathbf{k}}^{\pm})^2]^{1/2}, \tag{2.2}$$

where

$$\alpha_{\mathbf{k}}^{\pm}=\tfrac{1}{2}E_g/(E_{\mathbf{k}}^{\pm}-E_{\mathbf{k}'}^{0}),$$
$$E_{\mathbf{k}}^{0}=(\hbar^2/2m)\mathbf{k}^2,\quad \mathbf{k}'=\mathbf{k}-2K_F\hat{k},$$

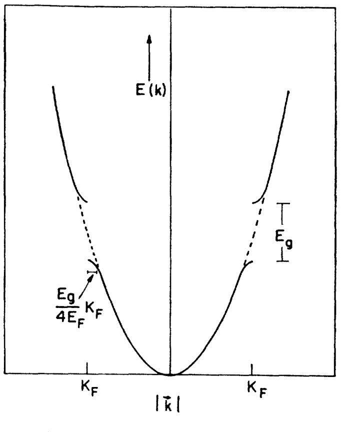

FIG. 1. Energy as a function of wave number for nearly free electron model, isotropically extended to three dimensions.

---

[1] D. R. Penn, Phys. Rev. 128, 2093 (1962).

[2] H. Nara, J. Phys. Soc. Japan 20, 778 (1965).

[3] H. Nara, J. Phys. Soc. Japan 20, 1097 (1965).

[4] J. C. Phillips, Phys. Rev. 166, 832 (1968).

[5] A. Morita, M. Azuma, and H. Nara, J. Phys. Soc. Japan 17, 1570 (1962).

and $\hat{k}$ is the unit vector along $\mathbf{k}$. The superscripts + and − refer to the cases $k>K_F$ and $k<K_F$, respectively. The energy gap E_g is treated as a parameter whose value is adjusted to yield the experimental value for $\epsilon(q=0)$, viz., the macroscopic dielectric constant. We note here that because of the isotropy of the model, every direction $\mathbf{k}$ assigns a reciprocal lattice vector of magnitude $2K_F$, directed antiparallel to $\mathbf{k}$.

One can write the general expression for $\epsilon(q)$ as

$$\epsilon(q)=1+\frac{4\pi e^2}{q^2}\sum_{\mathbf{k}_1,\mathbf{k}_2}|\langle\mathbf{k}_1|e^{-i\mathbf{q}\cdot\mathbf{r}}|\mathbf{k}_2\rangle|^2\frac{N_{\mathbf{k}_2}-N_{\mathbf{k}_1}}{E_{\mathbf{k}_2}-E_{\mathbf{k}_1}}, \quad (2.3)$$

where $N_{\mathbf{k}}$ is the occupation number of state $|\mathbf{k}\rangle$. We have for the matrix element between states $|\mathbf{k}_1\rangle$ and $|\mathbf{k}_2\rangle$

$$\langle\psi_{\mathbf{k}_1}{}^{\pm}|e^{-i\mathbf{q}\cdot\mathbf{r}}|\psi_{\mathbf{k}_2}{}^{\pm}\rangle=[1+(\alpha_{\mathbf{k}_1}{}^{\pm})^2]^{-1/2}[1+(\alpha_{\mathbf{k}_2}{}^{\pm})^2]^{-1/2}$$
$$\times\left(\int d^3r(e^{-i\mathbf{k}_1\cdot\mathbf{r}}+\alpha_{\mathbf{k}_1}{}^{\pm}e^{-i\mathbf{k}_1'\cdot\mathbf{r}})e^{-i\mathbf{q}\cdot\mathbf{r}}(e^{i\mathbf{k}_2\cdot\mathbf{r}}+\alpha_{\mathbf{k}_2}{}^{\pm}e^{i\mathbf{k}_2'\cdot\mathbf{r}})\right). \quad (2.4)$$

Carrying out the integration, one gets

$$\langle\psi_{\mathbf{k}_1}{}^{\pm}|e^{-i\mathbf{q}\cdot\mathbf{r}}|\psi_{\mathbf{k}_2}{}^{\pm}\rangle=[1+(\alpha_{\mathbf{k}_1}{}^{\pm})^2]^{-1/2}[1+(\alpha_{\mathbf{k}_2}{}^{\pm})^2]^{-1/2}$$
$$\times(\delta_{\mathbf{k}_1+\mathbf{q},\mathbf{k}_2}+\alpha_{\mathbf{k}_1}{}^{\pm}\alpha_{\mathbf{k}_2}{}^{\pm}\delta_{\mathbf{k}_1'+\mathbf{q},\mathbf{k}_2'}+\alpha_{\mathbf{k}_2}{}^{\pm}\delta_{\mathbf{k}_1+\mathbf{q},\mathbf{k}_2'}+\alpha_{\mathbf{k}_1}{}^{\pm}\delta_{\mathbf{k}_1'+\mathbf{q},\mathbf{k}_2}), \quad (2.5)$$

where

$$\delta_{\mathbf{k}_1,\mathbf{k}_2}=0, \quad \mathbf{k}_1\neq\mathbf{k}_2$$
$$=1, \quad \mathbf{k}_1=\mathbf{k}_2.$$

If one examines the limit of the four terms in Eq. (2.5) as q tends to zero, one finds that they tend to nonzero values. In particular, one finds that the first, second, third, and fourth terms, in the limit $q\to 0$, of the interband matrix element, tend to $+\frac{1}{2}$, $-\frac{1}{2}$, $-\alpha_{\mathbf{k}}{}^{-}/[1+(\alpha_{\mathbf{k}}{}^{-})^2]$, and $+\alpha_{\mathbf{k}}{}^{-}/[1+(\alpha_{\mathbf{k}}{}^{-})^2]$, respectively. We know that in order for $\epsilon(q)$ to have a finite value at $q=0$, it is necessary that the total interband matrix element vanish at $q=0$ (corresponding to the orthogonality of wave functions belonging to different bands). This can easily be achieved by grouping together the first and second terms and the third and fourth terms in Eq. (2.5). However, for $q=0+$, i.e., for q not identically zero, the four momentum-conserving δ functions in Eq. (2.5) are manifestly incompatible. Such incompatibility arises from the assumption that for every vector $\mathbf{k}$ there exists an unique vector $\mathbf{k}'=\mathbf{k}-2K_F\hat{k}$.

In a real crystal there is only a discrete number of reciprocal lattice vectors. In this spirit we shall assume that for a given $\mathbf{k}_1$, $\mathbf{k}_2=\mathbf{k}_1+\mathbf{q}$ does not have an independent reciprocal lattice vector. This is a reasonable assumption when the angle between $\mathbf{k}_1$ and $\mathbf{k}_2$ is smaller than the smallest angle between the reciprocal lattice vectors of interest in the real crystal. In that case, the reciprocal lattice vector $\mathbf{G}$ used to construct $\mathbf{k}_1'=\mathbf{k}_1+\mathbf{G}$ and $\mathbf{k}_2'=\mathbf{k}_2+\mathbf{G}$ is assumed to be the same. The meaning of this construction is illustrated in Fig. 2. This convention enables us to group the terms in the matrix element as described above even when $q\neq 0$. This leads to the following expression[1] for the matrix element which is consistent with the requirement of orthogonality of wave functions of different bands:

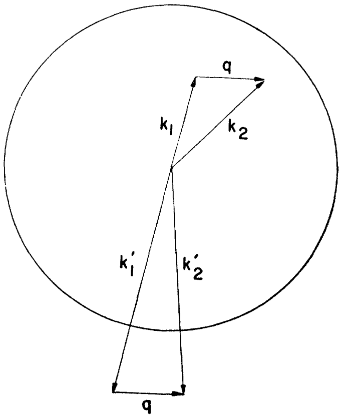

FIG. 2. Possible construction of $\mathbf{k}_2'$, where $\mathbf{k}_2=\mathbf{k}_1+\mathbf{q}$. $\mathbf{k}_2$ has the same reciprocal lattice vector as $\mathbf{k}_1$, viz., a vector of magnitude $2K_F$ along $-\hat{k}_1$.

$$\langle\psi_{\mathbf{k}_1}{}^{\pm}|e^{-i\mathbf{q}\cdot\mathbf{r}}|\psi_{\mathbf{k}_2}{}^{\pm}\rangle$$
$$=\frac{1+\alpha_{\mathbf{k}_1}{}^{\pm}\alpha_{\mathbf{k}_2}{}^{\pm}}{[1+(\alpha_{\mathbf{k}_1}{}^{\pm})^2]^{+1/2}[1+(\alpha_{\mathbf{k}_2}{}^{\pm})^2]^{+1/2}}\delta_{\mathbf{k}_1+\mathbf{q},\mathbf{k}_2}$$
$$+\frac{\alpha_{\mathbf{k}_1}{}^{\pm}+\alpha_{\mathbf{k}_2}{}^{\pm}}{[1+(\alpha_{\mathbf{k}_1}{}^{\pm})^2]^{+1/2}[1+(\alpha_{\mathbf{k}_2}{}^{\pm})^2]^{+1/2}}\delta_{\mathbf{k}_1+\mathbf{q},\mathbf{k}_2'}. \quad (2.6)$$

We then get the expression for $\epsilon(q)$

$$\epsilon(q)=1+\frac{8\pi e^2}{q^2}\left[\sum_{\mathbf{k}}N_{\mathbf{k}}(1-N_{\mathbf{k}+\mathbf{q}})\frac{|\langle\mathbf{k}|e^{-i\mathbf{q}\cdot\mathbf{r}}|\mathbf{k}+\mathbf{q}\rangle|^2}{E_{\mathbf{k}+\mathbf{q}}{}^{+}-E_{\mathbf{k}}{}^{-}}\right.$$
$$\left.+\sum_{\mathbf{k}}N_{\mathbf{k}}(1-N_{(\mathbf{k}+\mathbf{q})'})\frac{|\langle\mathbf{k}|e^{-i\mathbf{q}\cdot\mathbf{r}}|(\mathbf{k}+\mathbf{q})'\rangle|^2}{E^{+}{}_{(\mathbf{k}+\mathbf{q})'}-E_{\mathbf{k}}{}^{-}}\right], \quad (2.7)$$

in agreement with Penn. The first term in brackets in (2.7) corresponds to the "normal" process, and the second term involves the reciprocal lattice vector $-2K_F$ and describes "umklapp processes."

In the actual computation of $\epsilon(q)$, we have used an approximation to the matrix elements previously suggested by Penn. It can be verified that both $\langle\mathbf{k}|e^{-i\mathbf{q}\cdot\mathbf{r}}|\mathbf{k}+\mathbf{q}\rangle$ and $\langle\mathbf{k}|e^{-i\mathbf{q}\cdot\mathbf{r}}|(\mathbf{k}+\mathbf{q})'\rangle$ approach $2E_F\mathbf{q}\cdot\mathbf{k}/E_gK_F{}^2$ as $\mathbf{q}\to 0$. In this limiting case it is a good approximation to replace the oscillator strengths (the square of the matrix element) by their average on the Fermi surface. Such an averaging implicitly assumes that for $\mathbf{q}\to 0$ the main contribution arises from transitions from states lying just below the Fermi surface to states just above it. This is clearly true for the normal process, and our calculations indicate that this is true for the umklapp processes too.

Penn's approximation consists of obtaining an interpolation formula for the oscillator strengths between this limiting behavior as $q \to 0$ and the limiting form as $q \to \infty$, where we must get the free-electron behavior. This leads, upon angular averaging, to an approximate expression for the oscillator strengths

$$|\langle \mathbf{k}|e^{-i\mathbf{q}\cdot\mathbf{r}}|\mathbf{k}+\mathbf{q}\rangle|^2 \approx |\langle \mathbf{k}|e^{-i\mathbf{q}\cdot\mathbf{r}}|(\mathbf{k}+\mathbf{q})'\rangle|^2 \approx \frac{\frac{4}{3}(E_g/E_F)^2(q/K_F)^2}{1+\frac{4}{3}(E_g/E_F)^2(q/K_F)^2}. \quad (2.8)$$

Note that for $q \to 0$ this goes to zero as q^2, reflecting the orthogonality condition. This guarantees that $\epsilon(q)$ will show no anomalous behavior as $q \to 0$.

In order to evaluate the sum in (2.7) we introduce the following approximations for $E_{\mathbf{k}}^{\pm}$:

$$\begin{aligned} E_{\mathbf{k}}^{-} &\approx (\hbar^2/2m)\mathbf{k}^2, & k &< (1-\tfrac{1}{4}\bar{E})K_F \\ E_{\mathbf{k}}^{-} &\approx (\hbar^2/2m)(1-\tfrac{1}{4}\bar{E})^2K_F^2, & (1-\tfrac{1}{4}\bar{E})K_F &< k < K_F \\ E_{\mathbf{k}}^{+} &\approx (\hbar^2/2m)(1+\tfrac{1}{4}\bar{E})^2K_F^2, & K_F &< k < (1+\tfrac{1}{4}\bar{E})K_F \\ E_{\mathbf{k}}^{+} &\approx (\hbar^2/2m)\mathbf{k}^2, & (1+\tfrac{1}{4}\bar{E})K_F &< k, \end{aligned} \quad (2.9)$$

where $\bar{E} = E_g/E_F$. These approximations will introduce an error in $\epsilon(q)$ of order E_g/E_F.

We next divide the Fermi sphere into several regions, consistent with the approximations made in Eq. (2.9). The actual geometry of these regions depends on the value of q that we are considering. We illustrate this in Fig. 3 for the case $(1+\frac{1}{4}\bar{E})K_F < q < (2-\frac{1}{2}\bar{E})K_F$. We may then write (2.7) as

$$\epsilon(q) = 1 + \frac{8\pi e^2}{q^2}|M|^2 \sum_{\mathbf{k},i} \frac{1}{E_i}\delta_{\mathbf{k},i}, \quad (2.10)$$

where $\delta_{\mathbf{k},i} = 1$ if $\mathbf{k}$ lies in region i and zero otherwise, and $|M|^2$ is the approximate oscillator strength as given in (2.8). The approximate energy denominators E_i are given by[6]

$$\begin{aligned} E_1 &= (\hbar^2/2m)[(\mathbf{k}+\mathbf{q})'^2 - (1-\tfrac{1}{4}\bar{E})^2K_F^2], \\ E_2 &= E_4 = E_g, \\ E_3 &= E_5 = (\hbar^2/2m)[(1+\tfrac{1}{4}\bar{E})^2K_F^2 - \mathbf{k}^2], \\ E_6 &= (\hbar^2/2m)[(\mathbf{k}+\mathbf{q})^2 - \mathbf{k}^2], \\ E_7 &= (\hbar^2/2m)[(\mathbf{k}+\mathbf{q})^2 - (1-\tfrac{1}{4}\bar{E})^2K_F^2]. \end{aligned}$$

Upon performing the various sums one gets the final expression for $\epsilon(q)$. These are given in Appendix A. It is noteworthy that even the simple model described here leads to algebraic expressions of considerable complexity.

To complete the specification of $\epsilon(q)$ we have carried out the calculations in two additional regions:

$$(1+\tfrac{1}{4}\bar{E})K_F < q < (2-\tfrac{1}{2}\bar{E})K_F \quad (2.11)$$

and

$$(2+\tfrac{1}{4}\bar{E})K_F < q. \quad (2.12)$$

The results for these regions are also given in Appendix A. For (2.12), where $q > 2K_F$, there is no contribution to $\epsilon(q)$ from umklapp processes.

For large q one has

$$\epsilon - 1 \ll 1, \quad (2.13)$$

but the exact value of the left-hand side of (2.13) is still important, e.g., for the calculations of restoring forces for transverse lattice modes.

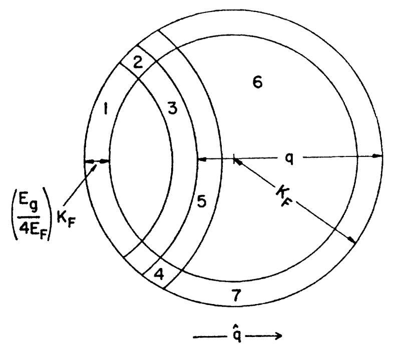

FIG. 3. Division of the Fermi surface into regions for the purpose of evaluating the sum in (2.7), for the case $(1+\frac{1}{4}\bar{E}) < q/K_F < (2-\frac{1}{2}\bar{E})$. Regions 4–7 contribute to normal processes and regions 1–3 to umklapp processes.

III. SPATIAL DIELECTRIC FUNCTION

In the discussion of $V(r)$, the effective potential modified by the screening effects of valence electrons, it is useful to introduce the concept of a spatial dielectric function $\tilde{\epsilon}(r)$ which is defined by the relation

$$v(r) = Ze/\tilde{\epsilon}(r)r, \quad (3.1)$$

where $v(r)$ is the screened Coulomb potential of a point charge Ze.

The general prescription for the screened pseudopotential $V(r)$ is

$$V(r) = \frac{1}{(2\pi)^3}\int V^S(q)e^{-i\mathbf{q}\cdot\mathbf{r}}d^3q, \quad (3.2)$$

where $V^s(q)$ is the screened form factor defined in terms of the ion-core form factor $v_i(q)$ and the model dielectric function $\epsilon(q)$ by[4]

$$V^s(q) = v_i(q)/\epsilon(q). \quad (3.3)$$

This reduces for the case of a point charge to

$$V^s(q) = 4\pi Ze^2/q^2\epsilon(q). \quad (3.4)$$

---

[6] Since, in the actual calculation, we use an interpolation formula for the oscillator strength, we take $(\mathbf{k}_1+\mathbf{q})' = (\mathbf{k}_1+\mathbf{q}) - 2K_F \times (\mathbf{k}_1+\mathbf{q})/|\mathbf{k}_1+\mathbf{q}|$ instead of the construction given in Fig. 2.

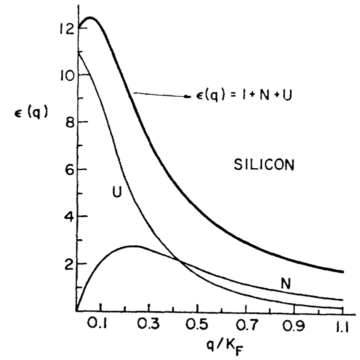

FIG. 4. Dielectric function versus wave number for Si. The curve labeled N is the contribution of the normal processes to $\epsilon(q)-1$, and the curve U refers to the umklapp processes.

The function $\bar{\epsilon}(r)$ is then given by

$$\frac{1}{\bar{\epsilon}(r)}=\frac{rv(r)}{Ze}=\frac{r}{(2\pi)^3}\int\frac{4\pi}{q^2\epsilon(q)}e^{-i\mathbf{q}\cdot\mathbf{r}}d^3q. \tag{3.5}$$

We have computed $\bar{\epsilon}(r)$ for diamond, Si, Ge, and some zinc-blende crystals. Instead of using the exact expression for $\epsilon(q)$, which would make the above integration very difficult, we have fitted a rational function to the calculated values of $\epsilon(q)$ and have used this function in the Fourier transform. The details of this procedure are shown in Appendix B. In general, the use of a rational fitting function facilitates determination of the fitting parameters by a least-squares procedure.

IV. NUMERICAL RESULTS

We have evaluated $\epsilon(q)$ for Si, with results shown in Fig. 4. In Fig. 5 we have compared our results for Si with those obtained by Nara and those obtained by using Penn's interpolation formula. The values for the parameter E_g that were used and their agreement with peaks observed in optical spectra[7–9] are shown in Table I.

TABLE I. Comparison of the parameter E_g used by us with the main peak in optical absorptivity experiment.

Element	E_g used by us (Ry)	Main peak in optical absorptivity (Ry)
Si	0.35	0.32
Ge	0.28	0.32
Diamond	0.99	0.88

In Fig. 4 we have shown for the case of Si the separate contributions of the normal and umklapp processes to $\epsilon(q)$ [see (2.7)]. It is clear that in the region $q<0.4K_F$ the umklapp processes dominate, and beyond this value of q the contribution of the umklapp processes drops rapidly. For $q>2K_F$ only the normal processes contribute. The detailed form of $\epsilon(q)$ for $q<K_F$ is strongly affected by the assumed interpolation formula (2.8) which defines interband oscillator strengths. Thus, great significance probably should not be attached to the maximum in $\epsilon(q)$ near $q=0.05K_F$, which results from a delicate cancellation of the normal and umklapp terms in a region where the former is quite small.

In order to study the effects of changes in $E_g/\hbar\omega_p$ and $E_F/\hbar\omega_p$ on the results, we have calculated $\epsilon(q)$ for BeO, BN, ZnSe, and GaAs, all assumed to be in the zinc-blende structure. We have set the lattice constants of the first two crystals equal to that of diamond and set the lattice constants of the last two equal to that of Ge. (The actual lattice constants differ from the assumed values by less than $\frac{1}{2}\%$.) The results for $\epsilon(q)$ are shown

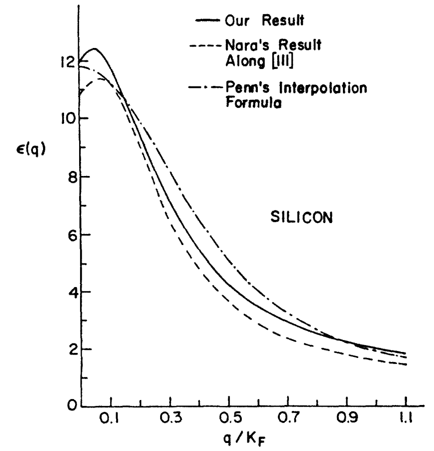

FIG. 5. $\epsilon(q)$ versus q for Si. We show a comparison of our results with those of Nara and those obtained from Penn's interpolation formula.

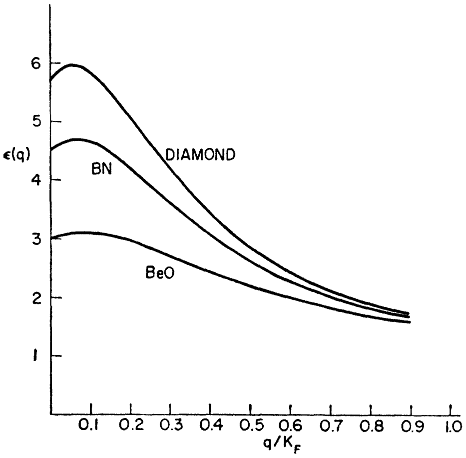

FIG. 6. $\epsilon(q)$ versus q for diamond, BeO, and BN.

---

[7] H. R. Philipp and E. A. Taft, Phys. Rev. **120**, 37 (1960).

[8] H. R. Philipp and E. A. Taft, Phys. Rev. **113**, 1002 (1959).

[9] R. A. Roberts and W. C. Walker, Phys. Rev. **161**, 730 (1967).

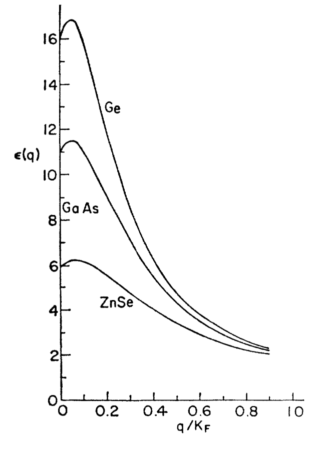

FIG. 7. $\epsilon(q)$ versus q for Ge, GaAs, and ZnSe.

in Figs. 6 and 7, and those for $\tilde{\epsilon}(r)$ are shown in Figs. 8–10.

To facilitate the application of the elaborate formulas given in Appendix A, we show in Table II values of $\epsilon(q)$ for diamond, Si, and Ge up to $q=4K_F$.

V. APPLICATIONS

We have remarked that in spite of the apparent simplicity of Penn's model, calculation of the phase-space sums involved requires no little labor. The agreement of the screened ion form factors (calculated using Penn's interpolation formula) with empirical pseudopotential form factors determined from electronic spectra[10] appears to be reasonable,[4] and the energy bands obtained using these form factors agree with experiment as well as with those obtained from the best available first-principles calculations. The advantage of the present approach is that it makes possible the qualitative assessment of the effect of covalent bonding energy gaps on valence screening. Because the magnitude of the gap used in each case is determined from optical data, the method should yield results closer to self-consistency (especially in discussing the effects of chemical shifts) than one would obtain from a superposition of free-atom charge densities.

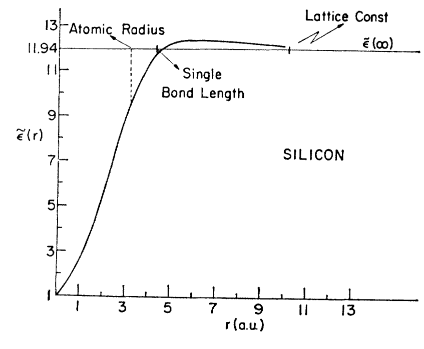

FIG. 8. Spatial dielectric function of Si. Note that $\tilde{\epsilon}(r)$ reaches its value at infinity by the nearest-neighbor distance. At the present time we do not attach any importance to the overshoot in $\tilde{\epsilon}(r)$ above $\tilde{\epsilon}(\infty)$.

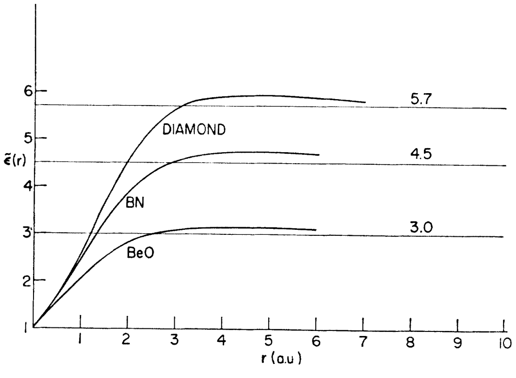

FIG. 9. $\tilde{\epsilon}(r)$ versus r for diamond, BN, and BeO.

The present calculations make it possible to evaluate the apparent atomic pseudopotential form factor, $V_p(G_1)$ more accurately in Si. Here G_1 is the magnitude of the first reciprocal lattice vector, $G_1=(2\pi/a)(111)$. Using the free-electron screening of the ion-core form factor $v_i(q)$, Animalu and Heine[11] found

$$v_m^*(q)=v_i(q)/\epsilon_f^*(q)\,, \qquad (5.1)$$

where $\epsilon_f^*(q)$ includes many-body corrections to the Hartree free-electron dielectric function $\epsilon_f(q)$:

$$\epsilon_f^*(q)-1=[\epsilon_f(q)-1][1-f_H(q)]\,, \qquad (5.2)$$

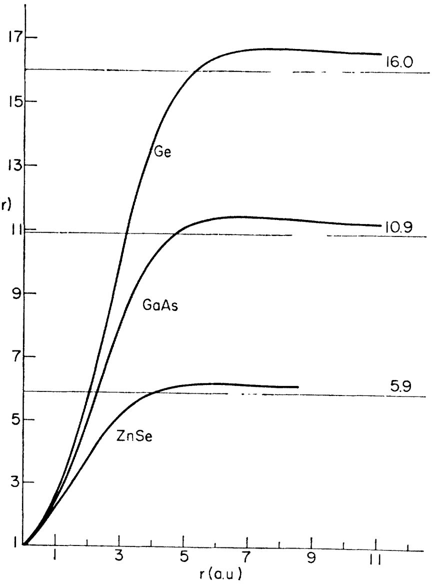

FIG. 10. $\tilde{\epsilon}(r)$ versus r for Ge, GaAs, and ZnSe.

---

[10] M. L. Cohen and T. K. Bergstresser, Phys. Rev. 141, 789 (1966).

[11] A. O. E. Animalu and V. Heine, Phil. Mag. 12, 1249 (1965).

Table II. Calculated values for the model dielectric function $\epsilon(q)$ as a function of wave number measured in units of K_F.

q/K_F		$\epsilon(q)$	
	Si	Ge	Diamond
0	11.94	16.00	5.70
0.1	11.93	15.80	5.86
0.2	9.54	11.90	5.08
0.3	7.24	8.56	4.19
0.4	5.52	6.28	3.44
0.5	4.33	4.78	2.87
0.6	3.50	3.79	2.44
0.7	2.92	3.12	2.13
0.8	2.51	2.65	1.90
0.9	2.20	2.31	...
1.1	1.80	1.86	1.49
1.2	1.66	1.71	1.41
1.3	1.55	1.59	1.34
1.4	1.46	1.49	1.28
1.5	1.38	1.41	1.24
1.6	1.32	1.34	1.20
1.7	1.27	1.29	1.17
1.8	1.22	1.23	1.14
2.1	1.117	1.124	1.076
2.3	1.076	1.080	1.049
2.5	1.052	1.055	1.034
2.7	1.037	1.039	1.024
2.9	1.028	1.029	1.018
3.1	1.021	1.022	1.014
3.3	1.016	1.017	1.010
3.5	1.013	1.013	1.008
3.7	1.010	1.010	1.007
3.9	1.008	1.008	1.005

where the factor $f_H(q)$ is set equal (following a suggestion by Hubbard[12]) to

$$f_H(q)=\tfrac{1}{2}q^2/(q^2+K_s^2+K_F^2)\,, \tag{5.3}$$

where $K_s^2=2K_F/\pi$ (a.u.). We propose to replace $\epsilon_P(q)$ by $\epsilon_P{}^*(q)$ defined in a manner analogous to (5.2):

$$\epsilon_P{}^*(q)-1=[\epsilon_P(q)-1][1-f_H(q)]\,. \tag{5.4}$$

In (5.4) we use for $f_H(q)$ the expression (5.3) derived for a free-electron gas, which means that we are neglecting the effect of bonding on the many-body corrections.

In the diamond structure, $G_1=1.1K_F$. For a free-electron gas of density corresponding to the density of valence electrons in Si, $\epsilon_f(G_1)=1.98$ and $\epsilon_P(G_1)=1.80$. From (5.3) one has $1-f_H(G_1)=0.79$. This gives $\epsilon_f{}^*(G_1)=1.78$ and $\epsilon_P{}^*(G_1)=1.63$.

The complete expression for $V_p(G_1)$ includes a bonding contribution[4] to the effective atomic form factor,

$$V_p{}^*(G_1)=V_a{}^*(G_1)+(S_b/S_a)V_b{}^*\,. \tag{5.5}$$

Here $S_b/S_a=2^{-1/2}$ is the ratio of bonding to atomic-structure factors for $q=G_1$. The Hartree value of V_b calculated from Poisson's equation [four bonding charges of magnitude $Z_b=e/\epsilon(0)$ per atomic volume] is

$$V_b=(32/3\pi)Z_be/a\,, \tag{5.6}$$

where a is the lattice constant. This differs from a value given previously[4] by a factor of 4.

We now ask about the many-body corrections to (5.6). With a well-localized (point) bonding charge, half of the Coulomb repulsion will be cancelled by exchange terms. [This is the meaning of (5.3) in the limit $q\rightarrow\infty$.] We therefore get

$$V_b{}^*=\tfrac{1}{2}V_b\,. \tag{5.7}$$

Our complete formula for $V_p{}^*(G_1)$ then is

$$V_p{}^*(G_1)=\frac{v_i(G_1)}{\epsilon_P{}^*(G_1)}+\frac{S_b}{S_a}V_b{}^* \tag{5.8}$$

and this can be evaluated given[11] $v_m{}^*(G_1)=-0.180$ Ry/atom. The result is

$$V_p{}^*(G_1)=-0.177 \text{ Ry/atom}\,. \tag{5.9}$$

Thus, we find that $V_p{}^*(G_1)$ is essentially equal to $V_m{}^*(G_1)$.

It is interesting to compare the value of $\epsilon_P(G_1)=1.80$ calculated here with the value obtained by Nara, using numerical sampling techniques.[2] Nara's Fig. 3 shows that $\epsilon(G_1)=1.5$. This value, however, is not reliable, for the following reason. Nara solved the pseudopotential equations and calculated $\epsilon(q)$ from a small number of pairs of interband transitions $(1\text{–}4)\rightarrow(5\text{–}8)$. As a result, he obtained a value of $\epsilon(0)=8.9$, which is smaller than the correct value of 11.94. This was corrected by adding more points to the sample. But, of course, the omitted transitions $(1\text{–}4)\rightarrow(9+)$ contribute an amount to $\epsilon(q)$ which, although small, decreases rather slowly with increasing q. Nara's procedure for normalizing $\epsilon(q)$ at small q therefore underestimates $\epsilon(q)$ at large q.

To obtain agreement with the empirical value of $V_p{}^*(G_1)$ one needs a value of $\epsilon(G_1)=1.5$. It so happens that this is close to the value given by Nara and that obtained from Penn's interpolation formula. We feel, however, that in order to be certain that Nara's result is more accurate than that obtained from the present model, it would be necessary to repeat his calculation with more attention paid to the question of convergence at large q.

The above bond charge model together with the microscopic dielectric function yields a basis for the calculation of lattice vibration spectra of covalent crystals. Martin has calculated phonon dispersion curves for Si in this manner.[13] He finds that $\epsilon_P(q)$ for Si (shown in Fig. 4 and Table II) yields a lattice vibration spectrum in good agreement with experiment, after adjusting the curvature near $q=0$ to fit the longitudinal sound velocities. The results *are* sensitive to the values of $\epsilon(q)$ at large q, and are materially improved when our (larger) values are used rather than Nara's (smaller) values.

It is likely that oversimplifications involved in a point bond charge approximation to umklapp terms are responsible for the disagreement between the empirical values of $\epsilon(q)$ at large q (of order G_1) obtained from

---

[12] J. Hubbard, Proc. Roy. Soc. (London) **A276**, 238 (1964); V. Heine and I. Abarenkov, Phil. Mag. **9**, 451 (1964).

[13] R. M. Martin, Phys. Rev. Letters **21**, 536 (1968).

electronic spectra $[\epsilon(G_1)=1.5]$ on the one hand and lattice vibration spectra $[\epsilon(G_1)=1.8]$ on the other. To keep proper perspective on this problem, it is perhaps useful to note that when $\epsilon(G_1)$ is computed for Ge from the semiclassical shell model, the value [longitudinal screening in (111) direction[14]] is 2.7. Thus the present disagreement between the two microscopic values is about four times smaller than their disagreement with the shell-model value.

ACKNOWLEDGMENTS

The author gratefully acknowledges many helpful conversations with Professor J. C. Phillips and R. M. Martin. This research was supported in part by the Office of Naval Research, the National Aeronautics and Space Administration, and also benefitted from general support of Materials Science at the University of Chicago by the Advanced Research Projects Agency.

APPENDIX A

To simplify the problem of obtaining an expression for $\epsilon(q)$ we approximate E_4, E_5, E_6, and E_7 by $E_8=(\hbar^2/2m)[(\mathbf{k}+\mathbf{q})^2-\mathbf{k}^2+E_g]$. Equation (2.10) now reads

$$\epsilon(q)=1+\tfrac{4}{3}\left(\frac{\bar{q}}{\bar{E}}\right)^2\left[1+\tfrac{4}{3}\left(\frac{\bar{q}}{\bar{E}}\right)^2\right]^{-1} \times(A_1+A_2+A_3+A_8)\,, \tag{A1}$$

where

$$A_i=\frac{8\pi e^2}{q^2}\sum_{\mathbf{k}}\frac{1}{E_i}\delta_{\mathbf{k},i}\,,$$

$\bar{q}=q/K_F$, $\bar{E}=E_g/E_F$, and $\delta_{\mathbf{k},i}=1$ if $\mathbf{k}$ lies in the region i and zero otherwise.

For convenience, we define the following variables:

$$\begin{aligned}
&B_1=2+\bar{q}\,,\quad B_2=2-\bar{q}\,,\\
&B_3=1+a+\bar{q}\,,\quad B_4=1-a+\bar{q}\,,\\
&B_5=2-2a+\bar{q}\,,\quad B_6=2-\bar{q}+\tfrac{1}{4}\bar{E}\,,\\
&B_7=\bar{E}+2a\bar{q}-\bar{q}^2\,,\quad B_8=\bar{E}+2\bar{q}-\bar{q}^2\,,\\
&B_9=\bar{E}+2\bar{q}+\bar{q}^2\,,\quad B_{10}=\bar{E}-2\bar{q}+\bar{q}^2\,,
\end{aligned} \tag{A2}$$

where $a=1-\frac{1}{4}\bar{E}$.

In the region $\bar{q}<\frac{1}{4}\bar{E}$ the A_i are given by

$$\begin{aligned}
A_1=\tfrac{3}{2}\left(\frac{\hbar\omega_p}{E_F}\right)^2\bar{q}^{-3}\Big(&2\bar{q}+\tfrac{1}{2}a\bar{q}+\tfrac{3}{4}\bar{q}^2-\frac{(1+B_3)^2}{2a}\ln\tfrac{1}{2}B_1\\
&+\frac{(1+B_4)^2}{2a}\ln\frac{2B_5}{\bar{E}}-\tfrac{1}{2}a(1+\bar{q})\ln\frac{\bar{E}B_1}{4B_5}\\
&-\tfrac{1}{4}B_1^2\ln\frac{B_1B_5}{\bar{E}}\Big)\,,
\end{aligned} \tag{A3}$$

$$A_2=-\frac{3}{4}\frac{(\hbar\omega_p)^2}{E_FE_g}\bar{q}^{-3}[\tfrac{4}{3}\bar{q}(1-a^3)-\bar{q}^2(1+a^2)+\tfrac{1}{6}\bar{q}^4]\,, \tag{A4}$$

$$\begin{aligned}
A_3=\tfrac{3}{4}\left(\frac{\hbar\omega_p}{E_F}\right)^2\bar{q}^{-3}\Big(&-a\bar{q}-\tfrac{3}{2}\bar{q}^2+\tfrac{1}{2}(\bar{E}+\bar{q}^2)\ln\frac{B_7}{\bar{E}}\\
&+\bar{q}(1+\tfrac{1}{4}\bar{E})\ln\frac{4B_5}{\bar{E}B_2}\Big)\,,
\end{aligned} \tag{A5}$$

$$A_8=\tfrac{3}{8}\left(\frac{\hbar\omega_p}{E_F}\right)^2\bar{q}^{-3}\left(\tfrac{1}{2}\bar{E}+\bar{q}-\bar{E}\ln\frac{B_8}{\bar{E}}+\frac{B_9B_{10}}{4\bar{q}^2}\ln\frac{B_8}{B_9}\right). \tag{A6}$$

Here, $W_p^2=4\pi ne^2/m$ is the plasma frequency and n is the density of electrons.

In the region $\frac{1}{4}\bar{E}<\bar{q}<1-\frac{1}{4}\bar{E}$ the A_i are given by

$$\begin{aligned}
A_1=\tfrac{3}{4}\left(\frac{\hbar\omega_p}{E_F}\right)^2\bar{q}^{-3}\Big(&\tfrac{1}{4}\bar{E}(5-\tfrac{1}{8}\bar{E})+\tfrac{1}{4}\bar{q}\bar{E}\\
&-\frac{1-a^2}{a}\ln(1-a)+a\ln\frac{B_1}{B_5}-\frac{1}{a}\ln\frac{B_3}{B_4}+\frac{1}{a}(1+B_4)^2\ln\frac{B_5}{B_4}\\
&+\frac{1}{a}(1+B_3)^2\ln\frac{B_3}{B_1}+aB_1\ln\frac{B_3B_5}{B_4B_1}\\
&+\tfrac{1}{2}B_1^2\ln\frac{B_3B_4}{B_1B_5}-\tfrac{1}{2}(1-a^2)\ln\frac{B_3B_4}{4(1-a)}\Big)\,,
\end{aligned} \tag{A7}$$

$$A_2=-\frac{3}{8}\frac{(\hbar\omega_p)^2}{E_FE_g}\bar{q}^{-3}(1-a^2)^2\,, \tag{A8}$$

$$\begin{aligned}
A_3=\tfrac{3}{2}\left(\frac{\hbar\omega_p}{E_F}\right)^2\bar{q}^{-3}\Big(&-\tfrac{1}{8}\bar{E}+\tfrac{1}{64}\bar{E}^2-\tfrac{1}{8}\bar{E}\bar{q}\\
&-\tfrac{1}{4}(\bar{E}+\bar{q}^2)\ln\frac{B_6B_4}{B_2B_5}+\tfrac{1}{2}\bar{q}(1+\tfrac{1}{4}\bar{E})\ln\frac{B_6B_5}{B_2B_4}\\
&+\tfrac{1}{4}(1-a^2)\ln\frac{B_6B_4}{\bar{E}}\Big)\,,
\end{aligned} \tag{A9}$$

and A_8 is as given in Eq. (A6).

In the region $(1+\frac{1}{4}\bar{E})K_F<q<(2-\frac{1}{2}\bar{E})K_F$, A_1, A_2, and A_8 are given by Eqs. (A7), (A8), and (A6), respectively, and A_3 is given by

$$\begin{aligned}
A_3=\tfrac{3}{2}\left(\frac{\hbar\omega_p}{E_F\bar{q}}\right)^2\Big(&-\tfrac{1}{8}\bar{E}+\frac{a^2-1}{4\bar{q}}\\
&+\tfrac{1}{2}(1+\tfrac{1}{4}\bar{E})\ln\frac{B_5B_6}{B_2B_4}+\frac{1-a^2}{4\bar{q}}\ln\frac{B_5B_2}{\bar{E}}\\
&+\frac{(1+\tfrac{1}{4}\bar{E})^2-1+\bar{q}^2}{4\bar{q}}\ln\frac{B_5B_2}{B_4B_6}\Big).
\end{aligned} \tag{A10}$$

---

[14] W. Cochran and J. C. Phillips, Phys. Rev. **134**, A1402 (1964).

In the region $q>(2+\frac{1}{4}\bar{E})K_F$, Eq. (A1) reduces to

$$\epsilon(q)=1+\tfrac{4}{3}\left(\frac{\bar{q}}{\bar{E}}\right)^2\left[1+\tfrac{4}{3}\left(\frac{\bar{q}}{\bar{E}}\right)^2\right]^{-1}(A_{\rm I}+A_{\rm II})\,, \quad \text{(A11)}$$

where, once again, $A_i=(8\pi e^2/q^2)\sum(1/E_i)\delta_{\mathbf{k},i}$, with $\bar{q}$ and $\delta_{\mathbf{k},i}$ as defined previously. Here $A_{\rm I}$ refers to $0<k<(1-\frac{1}{4}\bar{E})K_F$ and $A_{\rm II}$ refers to $(1-\frac{1}{4}\bar{E})K_F<k<K_F$. The approximate energy denominators in these two regions are given by

$$E_{\rm I}=(\hbar^2/2m)[(\mathbf{k}+\mathbf{q})^2-k^2], \quad 0<k<(1-\tfrac{1}{4}\bar{E})K_F$$

and

$$E_{\rm II}=(\hbar^2/2m)[(\mathbf{k}+\mathbf{q})^2-K_F^2(1-\tfrac{1}{4}\bar{E})^2],$$
$$(1-\tfrac{1}{4}\bar{E})K_F<k<K_F.$$

We give below the resultant expression for $A_{\rm I}+A_{\rm II}$:

$$\begin{aligned}A_{\rm I}+A_{\rm II}=\tfrac{3}{4}\left(\frac{\hbar\omega_p}{E_F}\right)^2\bar{q}^{-3}\Bigg(&\tfrac{1}{2}\bar{q}+\tfrac{3}{8}\bar{q}\bar{E}\\ &+(\tfrac{1}{2}a^2+\tfrac{3}{8}\bar{q}^2)\ln\frac{\bar{q}+2a}{\bar{q}-2a}+[\tfrac{1}{2}(1-a^2)-\tfrac{1}{2}\bar{q}^2]\\ &\times\ln\frac{(\bar{q}+1+a)(\bar{q}+1-a)}{(\bar{q}-1+a)(\bar{q}-1-a)}+a\bar{q}\ln\frac{(\bar{q}+1-a)(\bar{q}-1+a)}{(\bar{q}+1+a)(\bar{q}-1-a)}\\ &+a\bar{q}\ln\frac{(\bar{q}+2a)(\bar{q}-2a)}{\bar{q}^2}\Bigg)\,, \quad \text{(A12)}\end{aligned}$$

where $a=1-\frac{1}{4}\bar{E}$.

APPENDIX B

In order to obtain $\tilde{\epsilon}(r)$, we fitted a rational function of the form

$$\epsilon(q)=\frac{q^4+Cq^2+D}{q^4+Aq^2+B} \quad \text{(B1)}$$

to the calculated values of the model dielectric function $\epsilon_P(q)$. This determines the parameters A, B, C, and D. We see from Eq. (3.5) that $\tilde{\epsilon}(r)$ is given by

$$\frac{1}{\tilde{\epsilon}(r)}=\frac{r}{2\pi^2}\int\frac{1}{q^2\epsilon_P(q)}e^{-i\mathbf{q}\cdot\mathbf{r}}d^3q. \quad \text{(B2)}$$

In the integrand of the above equation, instead of using the exact expression for $\epsilon_P(q)$, as given in Appendix A, we use the rational function given in Eq. (B1). We may rewrite the expression for $\epsilon(q)$ as

$$\epsilon(q)=\frac{(q^2+\alpha^2)(q^2+\beta^2)}{q^4+Aq^2+B}.$$

In order to perform the integration in Eq. (B2) we resolve $1/[q^2\epsilon(q)]$ into partial fractions, and it reads

$$\frac{1}{q^2\epsilon(q)}=\frac{a}{q^2}+\frac{b}{q^2+\alpha^2}+\frac{c}{q^2+\beta^2},$$

where

$$a=1/\epsilon(0)\,,$$

$$b=\frac{\alpha^4\beta^2+B\beta^2-A\alpha^2\beta^2}{\alpha^2\beta^2(\alpha^2-\beta^2)}\,,$$

and

$$c=\frac{A\alpha^2\beta^2-B\alpha^2-\alpha^2\beta^4}{\alpha^2\beta^2(\alpha^2-\beta^2)}.$$

Performing the integration, we obtain

$$1/\tilde{\epsilon}(r)=1/\epsilon(0)+be^{-\alpha r}+ce^{-\beta r}.$$