Random-phase-approximation dielectric function for diamond, with local field effects included

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The diagonal part of the static wave-vector-dependent random-phase-approximation (RPA) dielectric function was computed for diamond using both Hartree-Fock energies and screened exchange plus Coulomb hole correlated energies, and in both cases, the diagonal RPA was found to be smaller than the experimental value as represented by the Penn model. Next the full RPA dielectric matrix was calculated using seven sets of reciprocal-lattice vectors. The matrix was then inverted and the reciprocal of the first diagonal term of the inverse was taken, yielding the diagonal RPA with local-field effects included. Special techniques were employed to handle the singularities that appear in the dielectric matrix when the wave vector goes to zero. The diagonal RPA with local-field effects included was found to be smaller, and thus farther from experiment, than the diagonal RPA that was calculated initially. Hartree energy bands were also used to compute the diagonal RPA, and the result was a significant improvement over the previous calculations and quite a bit closer to experiment.

I. INTRODUCTION

In the past few years there have been several calculations of correlated energies for crystals. The screened-exchange–plus–Coulomb-hole (SECH) method has been used by Brinkman and Goodman[1] for Si, by Lipari and Fowler[2] for Ar, and more recently by the author for diamond[3] and LiF,[4] and the random-phase-approximation (RPA) method has been used by Monkhorst and Oddershede[5] for H. In many correlation calculations for crystals, such as the ones mentioned above, the dielectric function plays an important part. Therefore, since we are interested in obtaining correlated energy bands for crystals, we have made a study of the dielectric function, and in particular we have looked at the RPA dielectric function.

The expression for the diagonal part of the RPA dielectric function was derived in the late 1950's by Nozières and Pines[6] using a many-body approach and by Ehrenreich and Cohen[7] using a self-consistent-field approach. Since then, the RPA dielectric function has been used extensively to calculate various crystalline quantities such as correlation energies, optical properties, and impurity levels, and in most cases, only the diagonal part of the dielectric function was included in the calculation. Alder[8] and Wiser[9] looked at the off-diagonal terms of the

RPA dielectric matrix, which are known as local-field effects, and Wiser estimated that in most cases, these local-field effects are negligible, however, there have been few actual calculations of the contribution of these off-diagonal dielectric matrix elements. Hanke and Sham[10] have done a local-field-effects calculation in which they used approximate wave functions and energies, adjusted the orbitals, and made the dipole approximation in order to obtain the inverse matrix. In this paper we carry out an exact calculation of local-field effects within the RPA, and thus we can accurately determine the effect of the off-diagonal dielectric matrix elements.

In previous calculations, it has been common practice to use pseudopotential $X\alpha$ or Hartree-Fock wave functions and energies when computing a screening function with the RPA formula. In this paper, we not only compute the RPA dielectric function with Hartree-Fock and correlated energies, but we also do the calculation with Hartree energy bands. The calculations are done for diamond using Euwema's energy bands[11] and the author's correlation corrections.[3]

II. DIAGONAL RPA

The RPA formula for the dielectric function ϵ is given by[4]

$$\epsilon(\vec{q}+\vec{K}_1, \vec{q}+\vec{K}_2, \omega) = \delta_{\vec{K}_1,\vec{K}_2} - \frac{2}{V}v(\vec{q}+\vec{K}_2)\sum_{\vec{k}ll'}\frac{n_{\vec{k}+\vec{q}+\vec{K},l'}-n_{\vec{k}l}}{\epsilon_{\vec{k}+\vec{q}+\vec{K},l'}-\epsilon_{\vec{k}l}-\omega}\langle\vec{k}l|e^{-i(\vec{q}+\vec{K}_1)\cdot\vec{r}}|\vec{k}+\vec{q}+\vec{K},l'\rangle$$

$$\times\langle\vec{k}l|e^{-i(\vec{q}+\vec{K}_2)\cdot\vec{r}}|\vec{k}+\vec{q}+\vec{K},l'\rangle^*,\qquad (1)$$

$$v(\vec{q})=4\pi e^2/q^2,\qquad (2)$$

where $\vec{q}$ and $\vec{k}$ are wave vectors restricted to the

first Brillouin zone, $\vec{K}_1$ and $\vec{K}_2$ are reciprocal-lattice vectors, ω is the frequency, V is the volume of the crystal, l and l' are band indices, the states

$|\vec{k}\,l\rangle$ are one-electron states with corresponding energies $\epsilon_{\vec{k}\,l}$ and occupation numbers $n_{\vec{k}\,l}$ (either 0 or 1), $\vec{K}$ is the reciprocal-lattice vector such that $\vec{k}+\vec{q}+\vec{K}$ lies in the first zone, and e is the charge of an electron. This dielectric function is a matrix in reciprocal-lattice vectors $\vec{K}_1$ and $\vec{K}_2$ such that different points $\vec{q}$ in the first zone do not mix, i.e., the full dielectric matrix in reciprocal-lattice vectors can be calculated and inverted independently for each point $\vec{q}$ in the first zone.

Instead of the full dielectric matrix, often only the first diagonal term is used in calculating screening functions. Setting $\vec{K}_1$ and $\vec{K}_2$ equal to zero in Eq. (1), we obtain this diagonal term,

$$\epsilon(\vec{q},\vec{q},\omega) = 1 - \frac{2}{V}\,v(\vec{q})\sum_{\vec{k}\,l\,l'}\frac{n_{\vec{k}+\vec{q}+\vec{K},\,l'} - n_{\vec{k}\,l}}{\epsilon_{\vec{k}+\vec{q}+\vec{K},\,l'} - \epsilon_{\vec{k}\,l} - \omega}$$

$$\times\,|\langle\vec{k}\,l\,|\,e^{-i\vec{q}\cdot\vec{r}}\,|\vec{k}+\vec{q}+\vec{K},\,l'\rangle|^2 . \qquad (3)$$

Since the dielectric function that appears in the SECH correlation method is the static dielectric function, we set $\omega = 0$ in these calculations.

Initially the diagonal part of the RPA was computed with Hartree-Fock (HF) one-electron states and energies, which are denoted by $u_{\vec{k}\,l}$ and $\epsilon_{\vec{k}\,l}$, respectively, where $\vec{k}$ is a wave vector restricted to the first zone and l is a band index. The calculation was done for diamond using the HF energy bands calculated by Euwema et al.[11] These are exact, self-consistent, LCAO (linear-combination-of-atomic-orbitals) HF energy bands with the wave functions having the form

$$u_{\vec{k}\,l}(\vec{r}) = \frac{1}{N^{1/2}}\sum_{i\nu}b_{l\,i}(\vec{k})\,e^{i\vec{k}\cdot\vec{R}_\nu}\phi_i(\vec{r} - \vec{R}_\nu) , \qquad (4)$$

where the sums are over atomic orbitals ϕ_i and direct lattice vectors $\vec{R}_\nu$, the b's are the coefficients of the Bloch functions associated with the atomic
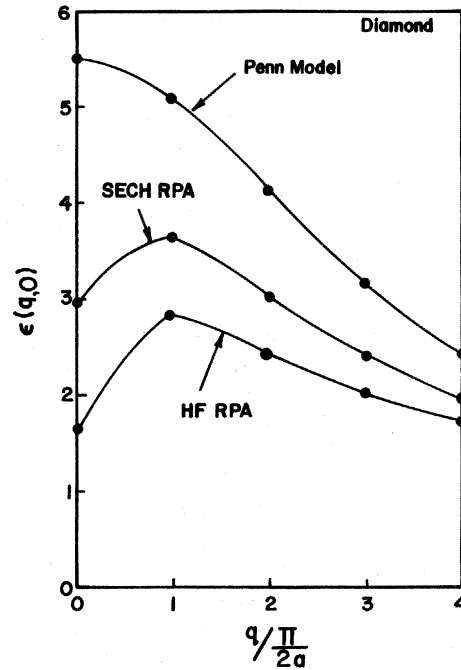

FIG. 1. Diamond dielectric functions along the Δ axis.

orbitals, and N is the number of unit cells in the crystal. All of the HF calculations were done in direct space with the direct lattice sums being carried out to four- or five-place accuracy using three charge-conserving integral approximations.[12] These HF bands were used to calculate several ground-state properties such as Compton profiles,[13] the equilibrium lattice constant and the bulk modulus,[14] all of which were in close agreement with experiment.

The HF wave functions and energies were initially determined at 20 points in $\frac{1}{48}$ of the first zone, and then the coefficients of the Bloch functions were permuted to obtain the wave functions at 341 points throughout the zone. These 341 points were used in the sum over $\vec{k}$ in Eq. (3) with the six occupied bands and first 12 conduction bands being used in the sums over l and l'. Table I shows that the diagonal part of the RPA is well converged after 12 conduction bands.

It is well known that HF band calculations give energy differences that are too large, so that correlation corrections must be added to HF energies in order to obtain better agreement with experiment. Correlation corrections were calculated by the author[3] using the SECH method which was first proposed by Hedin[15] and later treated in a review article by Hedin and Lundqvist.[16] In this method the self-energy is expanded in a power series in a screened, rather than bare, interaction and the first term is used. The dynamically screened interaction is then replaced by an averaged instan-

TABLE I. Diagonal RPA vs total number of conduction bands used in computation. Calculation was done for diamond at $\vec{q} = (\pi/2a)(1,0,0)$, where a is the lattice constant.

Bands	$\epsilon(\vec{q},\vec{q},\omega = 0)$
1	1.885
2	2.348
3	2.668
4	2.760
5	2.776
6	2.791
7	2.803
8	2.812
9	2.817
10	2.820
11	2.821
12	2.822

taneous interaction which leads to a statically screened exchange plus a Coulomb hole. The calculation was done for diamond and the results were in close agreement with experiment for the top of the valence band. For the direct and indirect band gaps, we obtained 7.6 and 5.6 eV compared with experimental values of 7.3–7.4 and 5.5–5.6 eV,[17] respectively. The agreement is best for the indirect gap which is the only piece of "hard" experimental information available for diamond.

The diagonal RPA was calculated at several points along the Δ axis using both HF and correlated energies, and the results are shown in Fig. 1 where the HF RPA was calculated with HF wave functions and energies, and the SECH RPA was calculated with HF wave functions and SECH correlated energies. The Penn model[18] dielectric function, which is also shown in Fig. 1, is derived as an approximation to the diagonal part of the RPA, however, it is then forced to take on the experimental value for the optical dielectric constant when $\vec{q} = 0$. Since the Penn model is forced to match experiment, the RPA calculations can be compared with the Penn model in order to determine how close they are to experiment. As the figure shows, the HF RPA is quite a bit smaller than the experimental value as represented by the Penn model, and the SECH RPA indicates that correlated energies account for about half of the difference between the HF RPA and the Penn model. The rest of the difference could be due to several factors, one of which is higher-order polarization terms beyond the random-phase approximation. Another possibility is the off-diagonal terms of the RPA dielectric matrix.

III. RPA WITH LOCAL-FIELD EFFECTS

Next we did an RPA calculation in which we included the off-diagonal dielectric matrix elements, which are known as local-field effects. For each

of several points $\vec{q}$ along the Δ axis, we calculated the full RPA dielectric matrix, as given in Eq. (1), out to seven sets of reciprocal-lattice vectors for a total of 65 individual vectors. The matrix, which is real for $\omega = 0$, was then numerically inverted and the reciprocal of the first diagonal term of the inverse was taken, yielding the diagonal RPA with local-field effects included. Table II shows that the reciprocal of the first diagonal term of the inverse, $1/[\epsilon^{-1}(\vec{q}+0, \vec{q}+0, \omega=0)]$, is well converged after seven sets of reciprocal-lattice vectors.

When $\vec{q} = 0$, certain problems arise because the matrix has singularities. If $\vec{K}_1$ and $\vec{K}_2$ are both zero in Eq. (1), then in the limit as $\vec{q} \to 0$, there is a $1/q^2$ singularity present, however, both matrix elements are also zero and these are strong enough to cancel the singularity, so that a finite result is obtained for the first diagonal term using $\vec{k} \cdot \vec{p}$ perturbation theory,

$$\epsilon(0, 0, \omega = 0) = 1 - \frac{4\pi e^2}{3m^2} \frac{2}{V}$$

$$\times \sum_{\vec{k}ll'} \frac{n_{\vec{k}l'} - n_{\vec{k}l}}{\epsilon_{\vec{k}l'} - \epsilon_{\vec{k}l}} \frac{|\langle \vec{k}l | \vec{p} | \vec{k}l' \rangle|^2}{(\epsilon_{\vec{k}l'} - \epsilon_{\vec{k}l})^2}, \quad (5)$$

where $\vec{p} = -i\vec{\nabla}$ and m is the mass of an electron. However, when $\vec{K}_2 = 0$ but $\vec{K}_1 \neq 0$, the $1/q^2$ singularity is still present but now only one of the matrix elements is zero and it is not strong enough to cancel the $1/q^2$ term, so that the matrix has singularities in the first column. Also it is easily seen that the matrix has zeroes along the first row where $\vec{K}_1 = 0$ and $\vec{K}_2 \neq 0$. Thus the dielectric matrix cannot be calculated directly and then inverted because of the singularities.

Instead we take the limit as $\vec{q} \to 0$ of the expression for the inverse matrix which contains products of the terms in the first row and first column of the direct matrix. These products are well behaved when $\vec{q} \to 0$ and have the form

$$\lim_{\vec{q} \to 0} 21 \times 13 = \frac{4\pi e^2}{3m^2} \frac{4}{V^2} v(\vec{K}_3) \sum_{\vec{k}lj\vec{k}'l'j'} \frac{(n_{\vec{k}j} - n_{\vec{k}l})(n_{\vec{k}'j'} - n_{\vec{k}'l'})}{(\epsilon_{\vec{k}j} - \epsilon_{\vec{k}l})^2 (\epsilon_{\vec{k}'j'} - \epsilon_{\vec{k}'l'})^2} \langle \vec{k}l | e^{-i\vec{K}_2 \cdot \vec{r}} | \vec{k}j \rangle$$

$$\times \langle \vec{k}'l' | e^{-i\vec{K}_3 \cdot \vec{r}} | \vec{k}'j' \rangle^* \langle \vec{k}l | \vec{p} | \vec{k}j \rangle^* \cdot \langle \vec{k}'l' | \vec{p} | \vec{k}'j' \rangle, \quad (6)$$

where 21×13 is the product of the 21 and 13 elements of the dielectric matrix, the sums on $\vec{k}$ and $\vec{k}'$ are over the first zone, and the sums on l, j, l', and j' are over bands.

Since the terms in the first row and column of the direct matrix have to be handled according to Eq. (6), we use a form for the inverse that allows us to separate the first row and column from the rest of the direct matrix. If the matrix A has the form

where the submatrices A_{11} and A_{22} are square, then the inverse matrix is given by

$$A^{-1} = \begin{pmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{pmatrix},$$

where

$$A = \begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix},$$

TABLE II. Diagonal RPA with local-field effects included vs total number of sets of reciprocal-lattice vectors (RLV's) used in computation. Calculation was done for diamond at $\vec{q} = (\pi/2a)(2, 0, 0)$.

Sets of RLV's	$\dfrac{1}{\epsilon^{-1}(\vec{q}+0, \vec{q}+0, \omega=0)}$
1	2.993
2	2.632
3	2.586
4	2.575
5	2.569
6	2.568
7	2.568

$$B_{11} = A_{11}^{-1} + A_{11}^{-1}A_{12}P^{-1}A_{21}A_{11}^{-1} ,$$

$$B_{12} = - A_{11}^{-1}A_{12}P^{-1} ,$$

$$B_{21} = - P^{-1}A_{21}A_{11}^{-1} ,$$

$$B_{22} = P^{-1} ,$$

$$P = A_{22} - A_{21}A_{11}^{-1}A_{12} ,$$

and A_{11} and P are nonsingular.

Using the above results, we can calculate the $\vec{q} = 0$ limit of the inverse dielectric matrix which has the same form as the direct matrix. The first diagonal term of the inverse is well behaved as it should be since it corresponds to a physical quantity, the optical dielectric constant. The inverse also has zeroes along the first row and singularities in the first column; however, these singularities are permissible since the off-diagonal terms by themselves do not correspond to any physical quantity. The physical quantity of interest here is the screened interaction in direct space, and since we have computed the Fourier transform of the inverse dielectric matrix, we must put this Fourier transform into an integral over $\vec{q}$ when computing the direct-space screened interaction,

$$W(\vec{r}, \vec{r}', \omega = 0) = \frac{1}{(2\pi)^3} \sum_{\vec{K}_1, \vec{K}_2} \int_{1st\,BZ} v(\vec{q}+\vec{K}_1)\epsilon^{-1}(\vec{q}+\vec{K}_1, \vec{q}+\vec{K}_2, \omega = 0) \exp[i(\vec{q}+\vec{K}_1)\cdot\vec{r} - i(\vec{q}+\vec{K}_2)\cdot\vec{r}']\,d\vec{q} , \qquad (7)$$

in which case the volume element $q^2\,dq$ cancels the singularity. In fact, we actually get zero contribution from the terms in the first column as well as from the terms in the first row, so that the screened interaction in direct space is well behaved.

The calculations described above were done using both HF and correlated energies, and Fig. 2 shows that in both cases, the diagonal RPA with local-field effects included, which is denoted by LF RPA, is smaller and thus farther from experiment than the diagonal RPA that was calculated initially. Thus if the RPA is calculated with HF or correlated energies, it does not agree very well with experiment, and adding local-field effects does not improve the agreement, but rather gives results that are even farther from experiment.

IV. RPA COMPUTED WITH HARTREE ENERGY BANDS

However, the RPA actually comes from time-dependent Hartree theory. The RPA formula for the dielectric function is derived from the time-dependent Hartree equation, [16] and therefore, to be consistent with the theory, the RPA should be calculated with Hartree energy bands. So, setting the HF exchange equal to zero, we obtained Hartree energy bands and used them to compute the diagonal RPA, and Fig. 3 shows that the RPA computed with Hartree wave functions and energies, which is denoted by H RPA, is a significant improvement over the previous calculations and quite a bit closer to experiment.
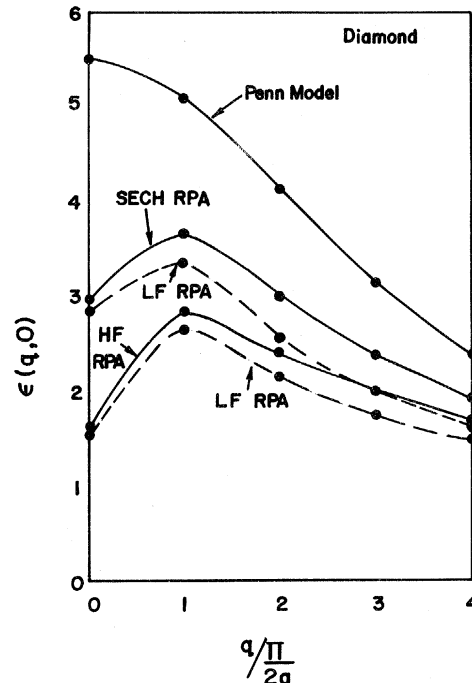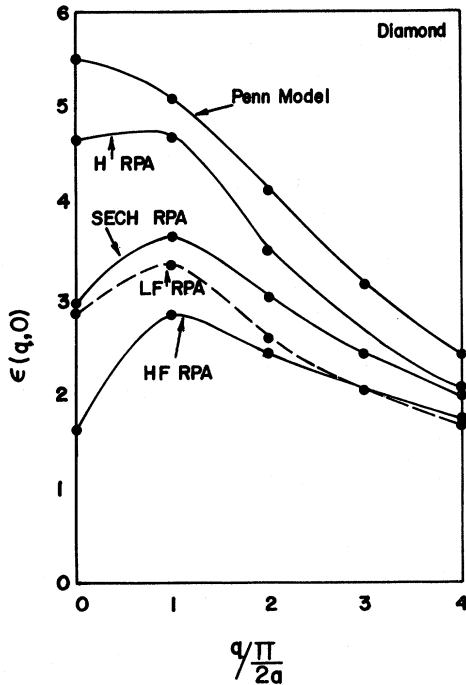
In order to further determine how the H RPA

FIG. 2. Diamond dielectric functions along the Δ axis.

FIG. 3. Diamond dielectric functions along the Δ axis.

compares with experiment, it was used to obtain SECH correlated energy differences. In the SECH method, correlation corrections (energy shifts) are computed and added to HF energies in order to ob-
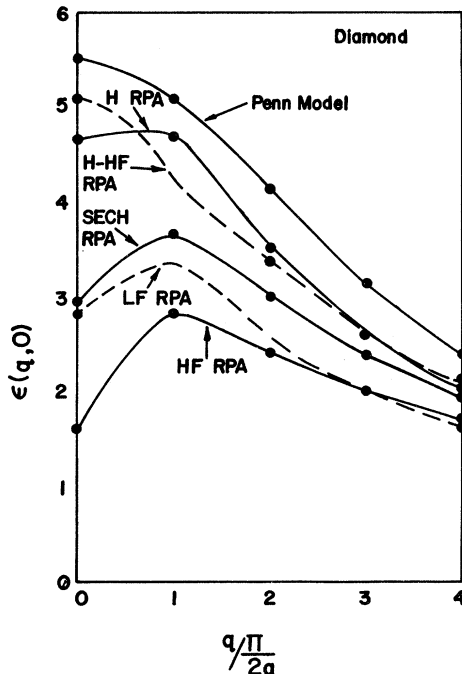

FIG. 4. Diamond dielectric functions along the Δ axis.

TABLE III. Comparison of diamond correlated energy differences in eV obtained with the H RPA and the Penn model. HF uncorrelated energy differences and some experimental values are also shown.

	HF	H RPA	Penn model	Experiment[a]
$\Gamma'_{25} \rightarrow \Delta_1$	12.1	6.0	5.6	5.5–5.6
$\Gamma'_{25} \rightarrow \Gamma_{15}$	13.7	7.9	7.6	7.3–7.4
$\Gamma_1 \rightarrow \Gamma'_{25}$	30.3	27.5	27.2	24.2
$\Gamma'_{25} \rightarrow \Gamma'_2$	25.5	18.5	18.1	
$X_4 \rightarrow X_1$	22.2	14.8	14.3	12.5–12.6
$L'_3 \rightarrow L_3$	22.8	15.8	15.3	
$L'_3 \rightarrow L_1$	24.3	17.2	16.7	
$L'_3 \rightarrow L'_2$	35.6	27.7	27.2	

[a]Reference 17.

tain correlated energies.[3] One of the quantities required in this correlation calculation is the dielectric function, and although it is HF energies that are being correlated, the dielectric function itself can be computed with an independent set of energies and wave functions, such as the Hartree set. Table III compares correlated energy differences obtained with the H RPA and the Penn model, and as the table shows, the H RPA gives correlated energy differences that are within half an eV of the Penn-model results, where the Penn-model results are in close agreement with experiment for the top of the valence band.

In order to determine how sensitive the dielectric function is to the wave functions used in the calculation, we also computed the diagonal RPA using Hartree energies and HF wave functions, and Fig. 4 shows that this dielectric function, which is denoted by H-HF RPA, is close to the H RPA. In fact, both of these dielectric functions give the same correlated energy differences to a tenth of an eV, however, the H-HF RPA gives a slightly better optical dielectric constant, where the optical dielectric constant is the value of the RPA at $\vec{q} = 0$.

Thus if the RPA formula is used to calculate a screening function, then the best results are obtained with Hartree energy bands rather than correlated HF or Hartree-Fock-Slater bands. In order to do better than this, one has to add higher-order polarization terms beyond the RPA. For example, HF energy bands could be used to calculate a time-dependent Hartree-Fock dielectric function; however, it is not clear that the time-dependent Hartree-Fock dielectric function would be significantly better, or even as good, as the time-dependent Hartree dielectric function, and it would require much more computer time.

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