

## Dielectric Response in the Wannier Representation: Application to the Optical Spectrum of Diamond\*

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A method of calculating local-field effects in the time-dependent Hartree-Fock approximation utilizing the Wannier representation is presented and applied to the optical spectrum of diamond. The results establish the importance of including both the local-field effects and the exchange effects beyond the random-phase approximation.

In a crystal, which possesses lattice translational symmetry, a small electric perturbation of wave vector  $\vec{q} + \vec{G}'$  and frequency  $\omega$  can excite responses of wave vector  $\vec{q} + \vec{G}$  and frequency  $\omega$ , where  $\vec{G}$  and  $\vec{G}'$  denote reciprocal-lattice vectors. Thus, the dielectric matrix, describing this response, is of the form  $\epsilon(\vec{q} + \vec{G}, \vec{q} + \vec{G}'; \omega)$ . An external macroscopic electric field may be regarded as a perturbation of vanishingly small wave vector  $\vec{q}$  and, therefore, the screening of the external macroscopic field is given by the matrix element  $\epsilon^{-1}(\vec{q}, \vec{q}; \omega)$  of the inverse dielectric matrix. In insulating crystals, this results in a formula for the macroscopic dielectric constant,

$$\epsilon(\omega) = \lim_{\vec{q} \rightarrow 0} [1/\epsilon^{-1}(\vec{q}, \vec{q}; \omega)]. \quad (1)$$

In the special case of an ideal insulator in which the electrons are so tightly bound that the dipole approximation is valid, the inversion of the dielectric matrix has been shown<sup>1</sup> to lead to the local-field (or Lorentz-field) effect. The resulting Lorentz-Lorenz relation has been used to demonstrate<sup>2</sup> empirically the importance of the local-field effect in the optical spectrum of CsCl.

It is still common practice to relate electronic band structures to the optical spectra of ionic and covalent crystals without including the local-field effects. This corresponds to neglecting the off-diagonal terms of the dielectric matrix and to using as the macroscopic dielectric constant

$$\bar{\epsilon}(\omega) = \lim_{\vec{q} \rightarrow 0} \epsilon(\vec{q}, \vec{q}; \omega), \quad (2)$$

an approximation which is rigorously justified only in the free-electron limit. On the other

hand, for covalent crystals, with the electron wave functions sufficiently spread out to form bonds, physically it appears that the Lorentz-Lorenz relation is invalid. In fact, we have found that its use yields a poorer agreement with the measured optical spectrum. To examine the fundamental relation between band structure and the optical spectrum, a first-principles investigation of the local-field effect is, therefore, very important.

We report here a method of calculating the local-field effect in the time-dependent Hartree-Fock approximation by expressing the dielectric response in terms of Wannier functions in much the same way as we did in the case of lattice dynamics in metals.<sup>3</sup> This method is used to calculate the optical spectrum of the covalent crystal diamond. Van Vechten and Martin<sup>4</sup> have investigated the local-field effect in diamond by directly evaluating and inverting a dielectric matrix with size  $59 \times 59$  in the plane-wave representation using the pseudopotential method. The contrast between the two methods of studying the local-field effect is as much as that between the linear combination of atomic orbitals (LCAO) and pseudopotential methods for calculating the band structure. In the plane-wave formulation, there is an intrinsic problem of slow convergence both for the dielectric matrix and for the wave function. The LCAO or Wannier-function method seems to be the more natural concept to describe the local-field effects, because it is precisely the localization of the wave functions which is the physical origin for these effects.

The proper polarization part  $\tilde{\chi}$  is related to the dielectric matrix by

$$\epsilon(\vec{q} + \vec{G}, \vec{q} + \vec{G}'; \omega) = \delta_{\vec{G}, \vec{G}'} - v(\vec{q} + \vec{G})\tilde{\chi}(\vec{q} + \vec{G}, \vec{q} + \vec{G}'; \omega), \quad (3)$$

where  $v(\vec{q} + \vec{G})$  is the Fourier transform of the Coulomb potential. Thus, the inverse dielectric matrix is determined by

$$\epsilon^{-1} = 1 + v\tilde{\chi}\epsilon^{-1}. \quad (4)$$

We have noted<sup>3</sup> that in the time-dependent Hartree approximation [or random-phase approximation (RPA)], when the electron wave functions are expressed in terms of Wannier functions or LCAO's, the polarization is of the separable form

$$\tilde{\chi}(\vec{q} + \vec{G}, \vec{q} + \vec{G}'; \omega) = \sum_{ss'} F_s(\vec{q} + \vec{G}) N_{ss'}(\vec{q}, \omega) F_{s'}^*(\vec{q} + \vec{G}'). \quad (5)$$

The inverse dielectric matrix then becomes

$$\epsilon^{-1}(\vec{q} + \vec{G}, \vec{q} + \vec{G}'; \omega) = \delta_{\vec{G}, \vec{G}'} + v(\vec{q} + \vec{G}) \sum_{ss'} F_s(\vec{q} + \vec{G}) S_{ss'}(\vec{q}, \omega) F_{s'}^*(\vec{q} + \vec{G}'), \quad (6)$$

where the matrix  $S$  is given by

$$S = N(1 - VN)^{-1} \quad (7)$$

with

$$V_{ss'}(\vec{q}) = \sum_{\vec{G}} F_s^*(\vec{q} + \vec{G}) v(\vec{q} + \vec{G}) F_{s'}(\vec{q} + \vec{G}). \quad (8)$$

Thus, the inversion problem is reduced to the inversion of a matrix of the same dimension as  $N$ . If the density matrix element between Wannier functions at different sites decreases rapidly with distance, the size of  $N$  is quite manageable.

We have gone beyond the RPA and studied the effect of exchange on the proper polarization part. Within the time-dependent Hartree-Fock approximation, the exchange effect can be taken into account by an integral equation for the vertex.<sup>5</sup> We again express the kernel for the exchange in terms of the Wannier functions. The dominant term is then given by exchange processes within the same bond in the covalent crystal. This exchange contribution has the same structure as the Coulomb interaction in RPA and the net effect of this term is a modification of corresponding terms in the Coulomb matrix  $V$  given by Eq. (8).

We follow Ambegaokar and Kohn<sup>6</sup> in treating the divergence in the long-range Coulomb interaction and obtain for the macroscopic dielectric constant

$$\epsilon(\omega) = \lim_{\vec{q} \rightarrow 0} [1 - v(\vec{q}) \hat{\chi}(\vec{q}, \vec{q}; \omega)], \quad (9)$$

where  $\hat{\chi}$  is the sum of all polarization processes *not* involving the long-range part of the Coulomb interaction  $v(\vec{q})$ .

For certain types of symmetry for the bands, e.g.,  $s$  and  $p$  symmetry for the conduction and valence bands, respectively, or vice versa, as is approximately the case for the alkali halides, the density form factor  $F_s$  in the separable polarization part (4) takes the dipole form. Such a form was assumed by Sinha, Gupta, and Price.<sup>7</sup>

From this, we can derive the Lorentz-Lorenz relation with a specific prescription for the self-interaction term. In general, the separable form is not necessarily dipolar in nature.

Since there are not yet available Wannier functions for covalent crystals of the diamond type, we follow Hall's method<sup>8</sup> to construct a set of LCAO's for the band structure. The  $s$  and three  $p$  atomic wave functions of the valence shell are combined according to Pauling's prescription<sup>9</sup> to form four hybridized wave functions localized in four tetrahedral directions. The atomic wave functions are expressed in the Gaussian basis which allows for analytic integration of all the multicenter integrals involved in Eqs. (6) and (9) and furthermore enables us to test easily the convergence of higher overlap corrections to  $\epsilon(\omega)$ . The hybridized orbitals from two neighboring atoms in the same direction are added and subtracted to form the bonding and antibonding orbitals  $\varphi_\nu$ , where the index  $\nu$  stands for  $\pm$  and a tetrahedral direction. Linear combinations of the bonding orbitals are used to form the four valence bands, and of the antibonding orbitals to form the four conduction bands. We include up through the third-nearest-neighbor overlap integrals of the Hamiltonian to fit the energy spectrum of a first-principles calculation by Painter, Ellis, and Lubinsky.<sup>10</sup> This yields a Hamiltonian matrix in our LCAO basis from which the energies and wave functions are determined.

Using the Wannier-function formulation of dielectric response described above, we obtain the macroscopic dielectric constant

$$\epsilon(\omega) = 1 - (4\pi e^2 / \Omega_0) \sum_{ss'} f_s^\alpha S_{ss'} f_{s'}^{\alpha*}, \quad (10)$$

where

$$f_s^\alpha = \int \varphi_\nu^*(\vec{r}) r_\alpha \varphi_\mu(\vec{r} - \vec{x}_l) d^3r \quad (11)$$

with  $\vec{x}_l$  being the lattice vector,  $\Omega_0$  the volume of the unit cell, and  $s$  short for  $(\nu, \mu, l)$ . The screening matrix  $S$  is given by Eq. (7) with

$$N_{ss'}(\omega) = \sum_{n, n', \vec{k}} c_\nu^*(n\vec{k}) c_\mu(n'\vec{k}) \exp(i\vec{k} \cdot \vec{x}_l) \frac{f(n\vec{k}) - f(n'\vec{k})}{E(n\vec{k}) - E(n'\vec{k}) + \omega} \exp(-\vec{k} \cdot \vec{x}_l) c_{\nu'}(n\vec{k}) c_{\mu'}^*(n'\vec{k}), \quad (12)$$

where  $E(n\vec{k})$  denotes the electron energy,  $f(n\vec{k})$  the occupation number, and  $c_{\mu}(n\vec{k})$  the wave function in the bonding and antibonding orbital basis.

In the RPA, the Coulomb matrix defined in Eq. (8) can be written as

$$V_{ss'} = \sum_m \iint d^3r d^3r' \varphi_{\nu}^*(\vec{r} - \vec{x}_m) \varphi_{\mu}(\vec{r} - \vec{x}_l - \vec{x}_m) v(\vec{r} - \vec{r}') \varphi_{\nu'}^*(\vec{r}') \varphi_{\mu'}(\vec{r}' - \vec{x}_{l'}). \quad (13)$$

When exchange is taken into account as described above,  $V$  is modified by subtracting from Eq. (13) half of the  $\vec{x}_m = 0$  term if either (a)  $\vec{x}_l = \vec{x}_{l'}$  and  $\mu = \mu'$  or (b)  $\nu = \nu'$ .

For the calculation of the dielectric constant we have included only nearest-neighbor overlaps of wave functions  $\varphi_{\nu}$ , having found the rest negligible within the error range of our approximate band structure and wave functions. The dimension of the matrices  $N$ ,  $V$ ,  $S$ , etc. is then 28. The  $\vec{k}$  summation of (12) was done by the Gilat-Raubenheimer method<sup>11</sup> with the smallest box having a width of 0.078 a.u. The dielectric matrix can be expressed in terms of either the density-density response or the current-current response. We adjust the  $s$  and  $p$  orbitals such that, indeed, either representation gives the same answer. This adjustment, which is used in all the calculated dielectric functions below, generally increases the strength of the absorption spectrum without changing its characteristic features.

The results of our calculation of the optical spectrum  $\epsilon_2(\omega)$ , i.e., the imaginary part of  $\epsilon(\omega)$ , for diamond are plotted in Fig. 1 and compared with experiment.<sup>12</sup> The optical spectrum is quite sensitive to local-field corrections. Consider the main peak which is close to 12 eV. The RPA calculation without local-field effects ( $\bar{\epsilon}_{\text{RPA}}$  in Fig. 1) places the peak a little too high. Local-field effects within the RPA ( $\epsilon_{\text{RPA}}$  in Fig. 1) produce an additional shift by approximately 0.5 eV to higher energies contrary to what is required to reconcile theory with experiment. The shift to higher energies and the reduction of strength below the main peak introduced by local-field effects in the RPA have also been reported by Van Vechten and Martin,<sup>4</sup> however to a less drastic extent. Inclusion of local-field effects in the time-dependent Hartree-Fock approximation ( $\epsilon$  in Fig. 1), on the other hand, results in a 1.5-eV shift of the main peak to lower energies and an improvement of the overall agreement with experiment, especially on the low-energy side.

In view of our approximate band structure and wave functions, we do not claim to have calculated quantitatively the absolute magnitude of  $\epsilon_2(\omega)$ . To do this our formulation of the dielectric func-

tion can be used in exactly the same manner directly utilizing the results of a first-principles Hartree-Fock band calculation based on LCAO's or Wannier functions. The use of more accurate wave functions than ours gives significantly better agreement of  $\bar{\epsilon}_{\text{RPA}}$  without local fields with experiment, as has been shown by Lubinsky, Ellis, and Painter<sup>13</sup>; however, it is not clear that replacement of the statistical exchange potential used in the underlying band structure calculation by the exact Fock potential does not spoil that particular agreement.<sup>14</sup> We believe that the sign and the order of magnitude of the shift introduced in the peak structure of  $\epsilon_2(\omega)$  by local-field and exchange effects is not affected by our approximate treatment of band structure and wave functions.

In summary, our results demonstrate the necessity for incorporating both local-field and exchange effects in the dielectric function of covalent crystals. These microscopic effects are important not only for the identification of struc-

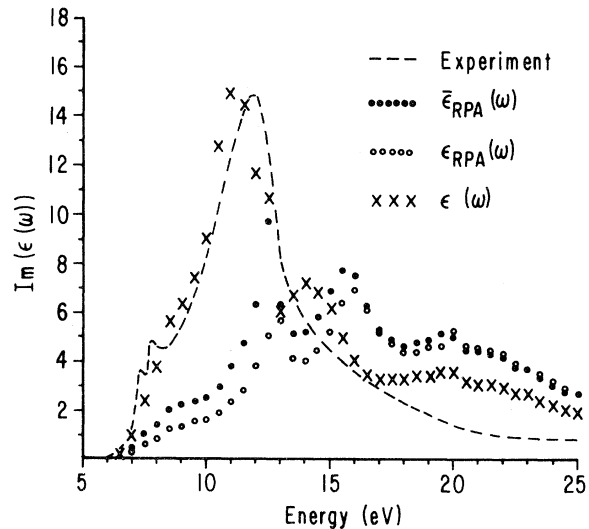


FIG. 1. Imaginary part of the dielectric constant versus energy; experimental data from Ref. 12;  $\bar{\epsilon}_{\text{RPA}}$  calculated within RPA without local-field correction;  $\epsilon_{\text{RPA}}$  calculated within RPA with local-field correction;  $\epsilon(\omega)$  calculated with local-field correction in the time-dependent Hartree-Fock approximation.

tures in the measured optical spectrum with the electronic transitions between energy bands but also for other purposes, such as a calculation of the phonon frequencies.

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## Direct Transform-Deconvolution Method for Surface-Structure Determination

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We describe direct method for surface-structure determination from low-energy electron-diffraction (LEED) intensities. Fourier transforms of LEED intensities are shown to contain convolution products of functions of the interatomic vectors with data truncation and potential windows. A deconvolution method and substrate-subtraction procedure is described, yielding an accurate structural determination of clean surfaces and overlayer systems. Applicability of the method to experimental data is demonstrated by using LEED intensities from Al(100).

Since the discovery<sup>1</sup> of low-energy electron diffraction (LEED), the extraction of surface structures has been the subject of intensive efforts, mainly via an *indirect approach*,<sup>2</sup> which is intrinsically dependent on model assumptions and proceeds by comparisons of microscopic model calculations with experimental intensities. However, a full variation over the geometrical and electronic parameters is not carried out because of the prohibitive expense in computation time and storage.

In this paper we present the principles of a rapid, *direct method* of surface-structure determination<sup>3</sup> and demonstrate its applicability to the analysis of experimental data.<sup>4</sup>

In the diffraction of low-energy electrons from solids, momentum is conserved in the plane parallel to the surface, giving rise to diffracted beams characterized by discrete ( $hk$ ) Miller indices of the two-dimensional net. Electron propagation in the direction normal to the surface is strongly attenuated<sup>1</sup> and is, therefore, characterized by the continuous variable  $S$ , where  $2\pi S$  is the normal momentum transfer and  $S > 0$  as a result of the half-space nature of LEED measurements and the inner potential