Model calculation of the static macroscopic dielectric function and the optical frequency of diamond*

P. E. Van Camp, V. E. Van Doren, and J. T. Devreese[†]

Rijksuniversitair Centrum Antwerpen, Groenenborgerlaan 171, B-2020 Antwerpen, Belgium

(Received 26 April 1976; revised manuscript received 19 January 1977)

In this paper the dielectric matrix and its inverse are calculated for diamond using electron energies and wave functions obtained by diagonalizing a simple molecular-bonding Hamiltonian. Results of the static longitudinal macroscopic dielectric function and of the phonon frequencies at the Γ point are presented. This macroscopic dielectric function is derived from the linear response of the system to an external perturbation in the Hartree approximation, i.e., neglecting the explicit influence of exchange and correlation in the linear-response formulas. The parameters in the Hamiltonian matrix are fitted to the experimental values of the indirect band gap and valence-band width. Results of the macroscopic dielectric function are given in the Δ, Σ, and Λ direction. The effect of the off-diagonal elements, accounting for the variations in the local electric field, on the macroscopic dielectric constant at zero wave vector, is 14%. A comparison is made with other calculations. The double summation over reciprocal-lattice vectors in the electron-nuclear part of the dynamical matrix is performed through a factorization procedure. Convergence is achieved by summing over 1185 shells. The calculated value of the optical frequencies at the Γ point is 4.45×10^{14} rad/sec, compared with the experimental value of 2.51×10^{14} rad/sec. The results show that in this model a realistic macroscopic dielectric function does not necessarily guarantee agreement between the calculated and experimental phonon frequencies.

I. INTRODUCTION

The diagonal part of the static longitudinal dielectric function in the Hartree approximation for diamond has been calculated before.[1-8] Diamond has a very pronounced covalent bonding character and in that respect serves as the prototype of covalent semiconductors. As such they have a strong anisotropic electron charge density, something which is reflected in band-structure calculations where a local orbital scheme seems to be preferable over plane waves or orthogonalized plane waves. Nevertheless, an isotropic-charge model has served a good purpose to describe the electron-density response function of such systems.[1-4] Other calculations are mostly based on pseudopotentials[5-6] and in one case Hartree-Fock wave functions and energies have been used for the expression of the Hartree dielectric function.[7]

Hanke and Sham[8] have evaluated the imaginary part of the macroscopic dielectric function derived from linear-response theory applied to the Hartree-Fock Hamiltonian, with a tight-binding approximation for the electron wave functions and energies.

It is well known that band-structure calculations based on pseudopotentials or Hartree-Fock or any of its approximations are quite involved. For a linear-combination-of-atomic-orbitals-type calculation for example, a large number of overlap integrals of basis functions and of matrix elements of the Hamiltonian between such functions has to be taken in order to achieve convergence in the

calculation of the energy bands. Because of the necessity to keep all these overlap integrals, the calculation of the dynamical matrix or dielectric matrix becomes very difficult and little room is left to test out such things as integrations over the Brillouin zone or summation over reciprocal-lattice vectors. It is for these reasons that in this calculation a molecular-bonding Hamiltonian is chosen.[9] This model yields a band picture which has the overall features of a full band calculation. It has built in the covalent bonding property, typical for diamond, but still keeps the computation relatively simple.

Based on this model, a calculation of the microscopic dielectric matrix, macroscopic dielectric function, and dynamical matrix has been made in which the integration over the Brillouin zone appearing in the dielectric matrix, the inversion of this matrix, and the summation over reciprocal-lattice vectors in the dynamical matrix has been tested out.

In Sec. II a review of the formalism to calculate the macroscopic dielectric function and the dynamical matrix for a covalent-bonding Hamiltonian is given. In Sec. III the results of the macroscopic dielectric function versus wave vector and of the optical frequencies at the Γ point for diamond are discussed and compared with other calculations.

II. SUMMARY OF THE FORMALISM

The microscopic theory of the longitudinal dielectric matrix and of the dynamical matrix of

insulators and semiconductors has been treated in
several papers.[10-16] One of the basic differences
between this theory and the formalism applicable
to free electronlike metals is, as one knows, the
appearance of off-diagonal elements in the dielec-
tric response matrix.[17-21] These terms arise in a
natural way if one uses Bloch functions instead of
plane waves for the electron states. Physically
the off-diagonal elements describe the local vari-
ations of the microscopic field $E(\vec{q})$.

The function describing the macroscopic dielec-
tric response of the electrons in a crystal to an
electric field is related to the microscopic
screening, as Adler[17] and Wiser[18] showed, by the
expression

$$\epsilon_m(\vec{q}, \omega) = [\epsilon^{-1}(\vec{q}, 0, 0, \omega)]^{-1} , \tag{1}$$

where $\epsilon^{-1}(\vec{q}, 0, 0, \omega)$ is the (1,1) entry of the inverse
of the dielectric matrix $\epsilon(\vec{q}, \vec{G}, \vec{G}', \omega)$. The matrix
elements, for one or both reciprocal-lattice vec-
tors, $\vec{G}$ and $\vec{G}'$ different from zero, measure es-

sentially the harmonics of an incoming wave, gen-
erated by the crystal through Bragg reflection off
the lattice sites.

Owing to these elements, the left-hand side of
Eq. (1) is not just equal to the (1,1) entry of the
dielectric matrix $\epsilon(\vec{q}, 0, 0, \omega)$. The so-called local
field corrections are defined as the difference of
the macroscopic dielectric function and of
$\epsilon(\vec{q}, 0, 0, \omega)$.

The dynamical matrix of the system can be split
up into a nuclear-nuclear part and electron-nu-
clear part. Following Sham[13] the expression for
the latter is given by

$$D_{\alpha\beta}^{en}(\vec{q}, ab) = \sum_{\vec{G}\vec{G}'} \left(X_{\alpha\beta}(ab; \vec{q}, \vec{G}, \vec{G}') - \delta_{ab} \sum_{c} X_{\alpha\beta}(ac; 0, \vec{G}, \vec{G}') \right) , \tag{2}$$

with

$$X_{\alpha\beta}(ab; \vec{q}, \vec{G}, \vec{G}') = [1/(M_a M_b)^{1/2}](1/v_c)[(\vec{q}+\vec{G})_\alpha V_a^*(\vec{q}+\vec{G})e^{i\vec{G}\cdot\vec{R}_a}\chi(\vec{q}, \vec{G}, \vec{G}')e^{-\vec{G}'\cdot\vec{R}_b} V_b(\vec{q}+\vec{G}')(\vec{q}+\vec{G}')_\beta] . \tag{3}$$

α (and β) denote the three Cartesian components;
a (or b, c) refer to the different atoms in the unit
cell; M_a (M_b) is the mass of the ath $(b$th) atom
and v_c the volume of the unit cell; $V_a(\vec{K})$ is the
Fourier transform of the bare ion potential of the
ath ion. This potential is a bare Coulomb poten-
tial if all the electrons, core as well as valence
electrons, are treated on the same footing in the
density response matrix X. If the core electrons
are omitted from the response formulas and con-
sidered to move rigidly with the nucleus, then a
pseudopotential should be chosen in order to ac-
count properly for this part of the screening.

In order to obtain the electron bands and the
wave functions needed in Eq. (1), one must solve
the eigenvalue equation of a single particle Ham-
iltonian, such as the Hartree-Fock Hamiltonian
or any of the local exchange approximations. The
procedure amounts to diagonalizing the Hamil-
tonian matrix calculated between Bloch functions
which are built up from a truncated set of local
orbitals. Many authors prefer Gaussian or Sla-
ter type orbitals.[22,23] However, several groups
use directly molecular orbitals which have the ad-
vantage that crystal binding can be incorporated
in the calculation right from the beginning. Hall[24]
applied this idea of molecular binding to diamond
by using sp^3 hybridized orbitals and only nearest-
neighbor overlap. Weaire and Thorpe[9] extended
this by proposing a model Hamiltonian in terms
of projection operators formed by these sp^3 or-
bitals.

This Hamiltonian consists of two parts: one de-
scribing the strength of the overlap between dif-
ferent lobes centered on the same site, the other
describing overlap between lobes with the same
orbital number on different sites. Overlap be-
tween the same lobes on the same site is omitted
since this would just introduce an additional con-
stant and accordingly shift the energy levels by a
constant amount. If one limits the overlap between
lobes pointing in the same direction to nearest
neighbors, one has only two parameters V_1 and V_2.

This is shown in Fig. 1 where the four different
lobes on the same atomic site are indicated by the
numbers 11-14, and the lobes from the four neigh-
boring sites by the numbers 21-24. Lobes 11-14
match, respectively, with lobes 21-24.

In the case of diamond which has four electrons
in the outer shell, one can construct four hy-
bridized sp^3 orbitals with their lobes directed to-
ward the four nearest neighbors. These lobes can
be written as a linear combination of the $2s$, $2p_x$,
$2p_y$, and $2p_z$ hydrogenic wave functions and point
in the directions of the four nearest neighbors.

With only four lobes per atom and two atoms
per unit cell (the core states are neglected), a
total of eight electron bands will be obtained. The
electron wave functions are

$$\Psi_n(\vec{k}, \vec{r}) = \sum_{ia} c_{nia}(\vec{k})\Phi_{ia}(\vec{k}, \vec{r}) , \tag{4}$$
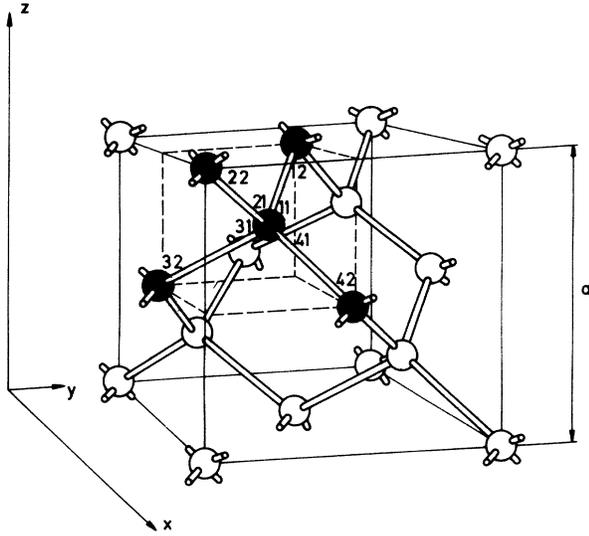
with

FIG. 1. Diamond crystal showing covalent bonds. Numbers 11–14 indicate the four atomic orbitals from a central atom 1, while numbers 21–24 refer to the atomic orbitals from the four nearest neighbors of atom 1.

$$\Phi_{ia}(\vec{K},\vec{r}) = \frac{1}{\sqrt{N}} \sum_{l} e^{i\vec{k}\cdot(\vec{R}_l + \vec{R}_a)} \varphi_{ia}(\vec{r} - \vec{R}_l - \vec{R}_a) \ , \tag{5}$$

where φ_{ia} is the wave function of the ith lobe on the ath atom. N counts the number of unit cells in the crystal.

At this point a further simplification is introduced by assuming that the local orbitals are Wannier functions, i.e.,

$$\int d\vec{r}\,\varphi^{*}_{i_1 a_1}(\vec{r} - \vec{R}_{l_1} - \vec{R}_{a_1})\varphi_{i_2 a_2}(\vec{r} - \vec{R}_{l_2} - \vec{R}_{a_2})$$

$$= \delta_{l_1, l_2}\delta_{a_1, a_2}\delta_{i_1, i_2} \ . \tag{6}$$

This assumption implies that the overlap matrix is diagonal and equal to the unit matrix and furthermore that matrix elements between wave functions centered on different sites are zero. Of course, overlap, as well as exchange and correlation effects, is taken into account implicitly by adjusting the parameters V_1 and V_2 to the experimental band gap and valence bandwidth.

To describe the linear response of the electronic system to an external potential only the Coulomb interaction between the electrons is taken into account, neglecting all exchange and correlation. The result is the well-known Hartree expression for the dielectric matrix.[21] However, the model used here describes the covalent bonding by hybridized orbitals and as such some exchange and correlation is included in the wave functions and energies through the parameters V_1 and V_2. This procedure is, of course, not entirely consistent. Instead, Hartree energies and wave functions should be used.

As was previously done by Lukes and Nix,[25] the following additional assumption will be made in the calculation of the matrix elements of the dielectric matrix:

$$\int d\vec{r}\,\varphi^{*}_{i_1 a_1}(\vec{r} - \vec{R}_{l_1} - \vec{R}_{a_1})e^{i\vec{K}\cdot\vec{r}}\varphi_{i_2 a_2}(\vec{r} - \vec{R}_{l_2} - \vec{R}_{a_2})$$

$$= \delta_{l_1, l_2}\delta_{a_1, a_2}\delta_{i_1, i_2} \int d\vec{r}\,\varphi^{*}_{i_1 a_1}(\vec{r} - \vec{R}_{l_1} - \vec{R}_{a_1})e^{i\vec{K}\cdot\vec{r}}\varphi_{i_1 a_1}(\vec{r} - \vec{R}_{l_1} - \vec{R}_{a_1}) \ . \tag{7}$$

This assumption is more restrictive than the Wannier approximation because only the diagonal terms of the Fourier transforms of the overlap between lobes on the same site are taken into account.

III. DISCUSSION OF RESULTS FOR DIAMOND

In order to calculate the dielectric function of diamond, one could simply fix the values of the two parameters in the Hamiltonian, V_1 and V_2, by fitting $\epsilon(0,0,0,0)$ to the experimental value of the dielectric constant[26] and by choosing the overall best curves of $\epsilon(\vec{q},0,0,0)$. However, the purpose of the present paper is to see whether a simple band model can give a reasonable dielectric function without fitting the dielectric function itself. Therefore, the parameters are chosen such as to

give an acceptable band structure by fitting the experimental indirect band gap of 5.47 eV and the valence bandwidth of 21 eV. The result is a value of −5.25 eV for V_1 and −14.15 eV for V_2. These values are obtained with a lattice constant of 3.56 Å. The corresponding band structure was first given by Weaire and Thorpe.

Compared with other band calculations,[22,23,27−32] this model is quite reasonable for the valence bands. The top valence band, however, is flat. The width of the conduction bands is the same as that of the valence bands which is 1.8 times larger than the result of a linear-combination-of-atomic-orbitals band-structure calculation by Chaney et al. who start from a Hartree-Fock equation with Kohn-Sham exchange. However, according to Walter and Cohen[6] the influence of the higher bands

on the dielectric function is rather small. In this Weaire-Thorpe model, the band gap is direct at the Γ point. The flatness of the top valence and conduction bands can be removed by including nearest-neighbor overlap in the calculation of the Hamiltonian between Bloch states.

The integrand of the microscopic dielectric matrix does not have the full symmetry of the diamond group, O_h^7, for a general $\vec{q}$ vector, but transforms according to certain subgroups depending on the direction of this vector. For $\vec{q} = 0$, however, it has the full O_h^7 symmetry in the same way as the Fourier transform of the charge density. In the latter case, Baldereschi[33] remarked that one could conveniently choose one point in $\frac{1}{48}$th of the Brillouin zone (BZ) for which, in the case of Ge, the integration over $\vec{k}$ space had converged to within 1.7% from the value of a 512-points integration. Chadi and Cohen[34,35] extended the Baldereschi procedure to include several points in the irreducible element of the BZ.

For a $\vec{q}$ vector different from zero, an appropriate subgroup of O_h^7 has to be used in order to find the region of the BZ for which this integrand remains invariant upon transformation by this subgroup. A complete analysis of how to use the symmetry is given in Ref. 36. This procedure reduces substantially the number of mesh points to be used. Depending on the $\vec{k}$ vector one considers, the reduction factor can be as high as 8, 4, or 6, respectively, for a vector in the Δ, Σ, and Λ direction. The weights of the integration points have to be multiplied by the right multiplicity.

The dielectric function $\epsilon(\vec{q}, 0, 0, 0)$ has been calculated for a mesh with, respectively, $M = 4$, 6, 8, 10, and 12, where M defines the number of divisions of the interval between the Γ and X point. The last case corresponds to 864 mesh points in the whole zone or 28 in the irreducible element. The results of this integration differ by 1.8% with respect to the case $M = 10$, which corresponds to 20 points in the irreducible element. This relatively small change can be attributed partly to the matrix elements in the expression of the dielectric matrix, which vary slowly with respect to the wave vector in the BZ and partly to the top valence and conduction bands, which are constant over the entire zone.

The (1,1) element of the dielectric matrix is shown in Fig. 2 for three directions of the vector $\vec{q}$, i.e., Δ, Σ, and Λ. For comparison, the results of Penn's interpolation formula are also given, with the plasma frequency equal to 31.27 eV and the band gap equal to 13.84 eV. Since in all Penn-like calculations the value of $\epsilon(0, 0, 0, 0)$ is fitted to the experimental macroscopic constant, a band gap is found which is about two times
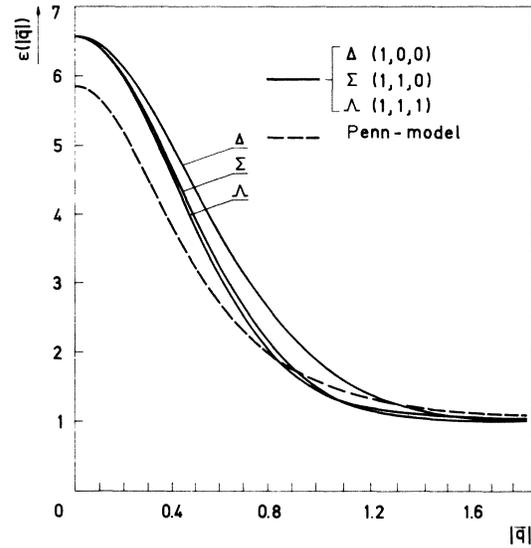
too big.

In Figs. 3–5, $\epsilon(\vec{q}, 0, 0, 0)$ is compared with the calculated macroscopic dielectric function, given in Eq. (1), for the same three directions, as a function of the wave vector. There are three major features in these curves which can be compared with earlier calculations[1-4,9,19,25,37,38]: the values of $\epsilon(0, 0, 0, 0)$ and of the macroscopic dielectric constant $\epsilon_m(0, 0)$, the directional dependence of the macroscopic dielectric function, and the presence of a hump for small $\vec{q}$ values. In all three features the present calculation differs from the one by Lukes and Nix[25] in the following aspects. In the

FIG. 2. Calculated $\epsilon(\vec{q}, 0, 0, 0)$ vs $\vec{q}$ for three directions $(\Delta, \Sigma, \Lambda)$. The dotted line represents the results of Penn's interpolation formula with $E_{gap} = 13.84$ eV.
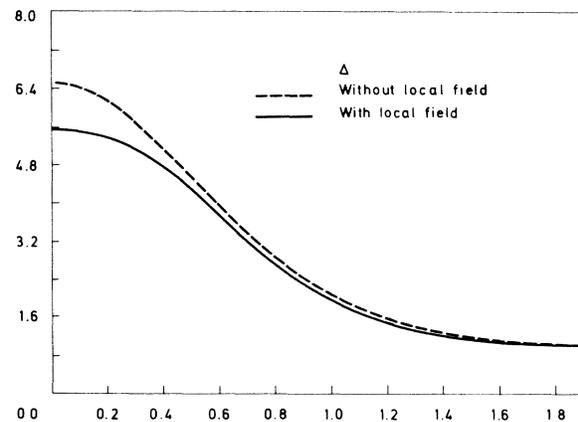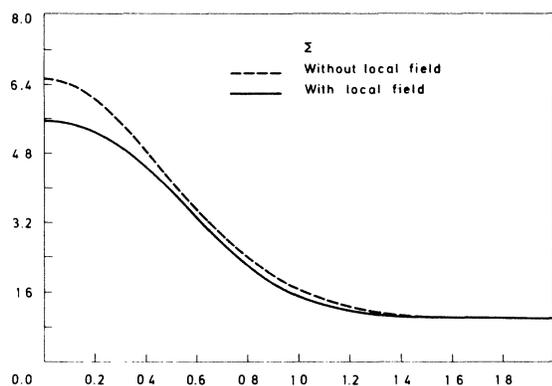

FIG. 3. Diagonal of the dielectric matrix $\epsilon(\vec{q}, 0, 0, 0)$ and the macroscopic dielectric function $\epsilon_m(\vec{q})$ vs $\vec{q}$ in the Δ direction showing local field corrections.

FIG. 4. Diagonal of the dielectric matrix $\epsilon(\vec{q}, 0, 0, 0)$ and the macroscopic dielectric function $\epsilon_m(\vec{q})$ vs $\vec{q}$ in the Σ direction showing local field corrections.

latter calculation the parameters V_1 and V_2 are chosen to match the value of the macroscopic dielectric constant at $\vec{q} = 0$ and to give an overall good fit to the dielectric function, i.e., to the diagonal of the microscopic dielectric matrix. Furthermore the calculation of Lukes and Nix is only valid for the direction of the wave vector in the Δ direction and therefore does not include a directional dependence on the wave vector. Finally, in the present calculation the macroscopic dielectric function, which is the quantity with real physical significance, has been calculated.

In the present calculation a value of 6.425 is obtained for $\epsilon(0, 0, 0, 0)$. The calculated value of the dielectric constant $\epsilon_m(0, 0)$ is 5.537 which should be compared with the experimental value of 5.7. The local field corrections are -0.888, which is a reduction of 14% compared with $\epsilon(\vec{q}, , 0, 0, 0)$ at $\vec{q} = 0$. As Sinha[39] pointed out, the local field corrections in the Lorentz-Lorenz limit tend to be positive. However, the sign of the corrections
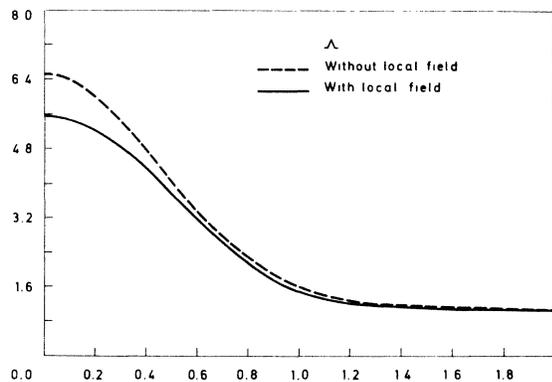

FIG. 5. Diagonal of the dielectric matrix $\epsilon(\vec{q}, 0, 0, 0)$ and the macroscopic dielectric function $\epsilon_m(\vec{q})$ vs $\vec{q}$ in the Λ direction showing local field corrections.

seems to depend heavily on the model for the electronic band structure. In their calculation Van Vechten and Martin[37] found a negative local field correction of -0.4 (from 5.4 to 5.0) at small wave vector and low energy, $\omega = 1.5$ eV. Similar reductions were found by Johnson[19] and by Brener.[7]

Hanke and Sham calculated the optical spectrum of diamond in the time-dependent Hartree-Fock approximation assuming that the orbitals are Wannier functions. On top of the exchange correction from the self-consistent Fock term in the Hamiltonian, the local field corrections, coming from the off-diagonal elements of the dielectric matrix, have also been taken into account. In their calculation the value of the static dielectric constant is 6.0 compared with a value of 5.1 for the diagonal of the dielectric matrix in the Hartree approximation at zero wave vector, i.e., without local field effects. This means that the corrections, due to a combination of both the local field and the exchange, increase the Hartree value of 5.1 by 17%.

The directional dependence on $\vec{q}$ of the diagonal of the dielectric matrix as well as of the macroscopic dielectric function is stronger in this calculation than in the results of Johnson[18] and in calculations on Si by Walter and Cohen.[6] It decreases for a fixed wave vector from the Δ to the Λ direction. This is so because the density response function has its maximum in the $(1, 1, 1)$ direction where the electrons in a covalent bond are located. This is in accordance with Walter and Cohen's result for Si. The present results do not show a hump for small $\vec{q}$ values, contrary to the results of the calculations by Penn,[1] Srinivasan,[2] Nara,[5] and Lukes and Nix.[25] Such a hump can be obtained for small $\vec{q}$ vectors by integrating the dielectric function only over the irreducible element of the BZ, i.e., by assuming that the integrand exhibits the full O_h^7 symmetry for $\vec{q}$ different from zero. Neither is there a strong directional dependence for small $\vec{q}$ as is found by Nara[5] for Si. Martin[40] observed that the existence of such a hump is doubtful because it would lead to negative elastic constants. The local field corrections decrease in magnitude as a function of $\vec{q}$. Physically this means, as one would expect, that the larger the wave vector of the electric field the more the local structure of the crystal is felt by the wave. For large wave vectors, of the order of half a reciprocal-lattice vector, the screening effect of the electrons in the crystal has almost disappeared.

The dynamical matrix has been evaluated and diagonalized at the Γ point of the phonon spectrum. In the form it is given in Eqs. (2) and (3), the density response matrix, which enters in the electron-nuclear part of the dynamical matrix, has to be calculated for all reciprocal-lattice vectors

and a double summation over all these vectors has to be performed. It is clear that such a procedure can be executed only if the matrix elements of χ or the Fourier transform of the electron-nuclear potential, or both, become small rapidly enough with increasing $\vec{G}$. As far as χ is concerned this is unfortunately not the case for the diagonal as well as the off-diagonal elements. Even in the 8th shell the modulus of the off-diagonal elements is still of the same order as the one of the diagonal elements.

As far as the electron-nuclear potential is concerned, one should realize that a bare Coulomb potential cannot be used. This is due to the fact that only the $2s$ and $2p$ valence electrons are included in the dielectric response calculation, leaving out the $1s$ core electrons. In order to take their screening effect of the nucleus into account, a model potential may be used. In the present calculation an empty core potential with zero well depth is chosen:

$$V_a(\vec{K}) = (1/v_c)(4\pi/K^2)Z\cos Kr_c \ ,$$

where r_c is the radius of the atomic $1s$ core electron shell. Its value is 0.38 Å. Z is equal to 4.

As was pointed out by Sinha[41] and by Hayashi and Shimizu[42] for the tight-binding approximation and later shown for the general case independently by Pick et al.,[14] Sham,[43] and Hanke[44] when the electron wave functions are expressed in the Wannier approximation, the polarization matrix can be factorized into a product of three matrices. Consequently, the dielectric matrix can be inverted in a simple way. The net effect of this procedure in the present calculation, where all overlap between lobes on different sites is neglected [Eq. (6)], is that instead of having to invert a matrix in reciprocal-lattice vectors, a matrix in the Wannier lobes has to be inverted, i.e., a 8×8 matrix. As Sham[41] showed, with this simplification the dynamical matrix reduces to a single sum over reciprocal-lattice vectors. As a result the convergence of both the inverse dielectric matrix and the dynamical matrix can be thoroughly investigated. Table I shows the convergence of the determinant of ϵ, the macroscopic dielectric function, and the dynamical matrix, in the limit as $\vec{q}$ goes to zero, in terms of the number of reciprocal lattice vectors and the shells used in the summation. Whereas the determinant of ϵ seems to converge rapidly (the value calculated with only 27 reciprocal-lattice vectors differs only by 2.5% from the one with 59 vectors), this is not the case for the dynamical matrix.

In the determinant of ϵ the terms obtained from products of elements belonging to the same star tend to cancel each other. This symmetry property

TABLE I. The values of the determinant of the dielectric matrix ϵ, the macroscopic dielectric function ϵ_m, and the optical frequency ω_{opt} (in 10^{14} rad/sec) in the limit as $\vec{q}$ goes to zero are given for five different summations. The first two columns give the numbers of shells and lattice vectors, in reciprocal space.

No. shells	No. vectors	detϵ	ϵ_m	ω_{opt}
27	537	13.24	5.518	4.11
104	2891	13.452 48	5.592 593	4.32
261	8393	13.452 643	5.592 585 9	4.448
641	23 049	13.452 658 9	5.592 585 63	4.465
1185	44 975	13.452 660 1	5.592 585 62	4.454

is destroyed in the dynamical matrix because each element of the χ matrix is multiplied by a different factor.

The value obtained for the optical frequencies at the Γ point is 4.45×10^{14} rad/sec. The experimental value is 2.51×10^{14} rad/sec. It should be noted that the main objective of the calculation at this stage is to investigate the possibility to evaluate the dynamical matrix for diamond as far as the convergence goes, and not the value of the optical frequencies as such. Second, this calculation shows that a realistic result for the static dielectric properties does not guarantee per se a similar agreement with experiment for the phonon frequencies. Whereas the value of the macroscopic dielectric constant is determined to a large extent by the average over the Brillouin zone of the energy gap between valence and conduction bands, the situation for the phonons is much more complicated. In order to get a realistic phonon spectrum, one must have the right long-range and short-range forces.

To summarize, in this paper the macroscopic dielectric response function is calculated for diamond starting from a simple molecular bonding Hamiltonian. Diagonalization of this Hamiltonian yields a set of energies and wave functions which are used in the calculation of the dielectric function. This function shows a dependence on the direction of the wave vector. The off-diagonal elements contribute 14% to the macroscopic dielectric constant. In this model the electron-nuclear part of the dynamical matrix has been evaluated at the Γ point via the use of the factorization procedure. The convergence of the summation over reciprocal lattice vectors is investigated.

ACKNOWLEDGMENTS

*Work performed in the framework of the joint project ESIS (Electronic Structure in Solids) of the University of Antwerpen and the University of Liège.

†Also at: Dept. Natuurkunde, Universitaire Instelling Antwerpen, B-2610 Wilrijk, Belgium.

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

[2] G. Srinivasan, Phys. Rev. 178, 1244 (1969).

[3] V. K. Bashenov, M. G. Foigel, and R. A. Alarashi, Phys. Status Solidi B 54, 355 (1972).

[4] R. A. Breckenridge, R. W. Shaw, and A. Sher, Phys. Rev. B 10, 2483 (1974).

[5] H. Nara, J. Phys. Soc. Jpn. 20, 778 (1965).

[6] J. P. Walter and M. L. Cohen, Phys. Rev. B 6, 1821 (1970).

[7] N. E. Brener, Phys. Rev. B 11, 929 (1975).

[8] W. Hanke and L. J. Sham, Phys. Rev. Lett. 38, 582 (1974); W. Hanke and L. J. Sham, Phys. Rev. B 12, 4501 (1975).

[9] D. Weaire and M. F. Thorpe, Phys. Rev. B 8, 2508 (1971).

[10] F. A. Johnson, Proc. R. Soc. A 310, 79 (1969); 310, 89 (1969); 310, 101 (1969); P. D. De Cicco, F. A. Johnson, ibid. 310, 111 (1969).

[11] M. H. Cohen, R. M. Martin, and R. M. Pick, Symposium on Inelastic Neutron Scattering (International Atomic Energy Agency, Vienna, 1968), Vol. 1, p. 119.

[12] P. N. Keating, Phys. Rev. 175, 1171 (1968); 187, 1190 (1969).

[13] L. J. Sham, Phys. Rev. 188, 1431 (1969).

[14] R. M. Pick, M. H. Cohen, and R. M. Martin, Phys. Rev. B 2, 910 (1970).

[15] B. Gliss, R. Zeyher, and H. Bilz, Phys. Status Solidi B 44, 747 (1971).

[16] D. C. Wallace, Thermodynamics of Crystals (Wiley, New York, 1972).

[17] S. L. Adler, Phys. Rev. 126, 413 (1962).

[18] N. Wiser, Phys. Rev. 129, 62 (1963).

[19] D. L. Johnson, Phys. Rev. B 9, 4475 (1974).

[20] L. J. Sham, in Dynamical Properties of Solids, edited by G. K. Horton and A. A. Maradudin (North-Holland, Amsterdam, 1974), Vol. 1, p. 301.

[21] H. Ehrenreich and M. H. Cohen, Phys. Rev. 115, 786 (1959).

[22] R. C. Chaney, C. C. Lin, and E. E. Lafon, Phys. Rev. B 3, 459 (1971).

[23] A. B. Kunz, in Elementary Excitations in Solids, Molecules and Atoms, edited by J. T. Devreese, A. B. Kunz, and T. C. Collins, (Plenum, New York, 1974), Vol. A, p. 159.

[24] G. G. Hall, Philos. Mag. 43, 338 (1952).

[25] T. Lukes and B. Nix, J. Phys. C 7, 1564 (1974).

[26] H. R. Philipp and E. A. Taft, Phys. Rev. 136, A1445 (1964).

[27] F. Bassani and M. Yoshimine, Phys. Rev. 130, 20 (1963).

[28] L. A. Hemstreet, C. Y. Fong, and M. L. Cohen, Phys. Rev. B 6, 2054 (1970).

[29] G. S. Painter, D. E. Ellis, and A. R. Lubinsky, Phys. Rev. B 4, 3610 (1971).

[30] J. R. Neto and L. G. Ferreira, J. Phys. C 6, 3430 (1973).

[31] T. C. Collins, R. N. Euwema, G. G. Wepfer, G. T. Surratt, N. E. Brener, J. L. Yvey, and D. L. Wilhite, in Elementary Excitations in Solids, Molecules and Atoms, edited by J. T. Devreese, A. B. Kunz, and T. C. Collins, (Plenum, New York, 1974), Vol. A, p. 117.

[32] R. N. Euwema, D. L. Wilhite, and G. T. Surratt, Phys. Rev. B 7, 818 (1973).

[33] A. Baldereschi, Phys. Rev. B 7, 5212 (1973).

[34] D. J. Chadi and M. L. Cohen, Phys. Rev. B 7, 692 (1973).

[35] D. J. Chadi and M. L. Cohen, Phys. Rev. B 8, 5747 (1973).

[36] S. P. Singhal, Phys. Rev. B 12, 564 (1975).

[37] J. A. Van Vechten and R. M. Martin, Phys. Rev. Lett. 28, 446 (1972).

[38] P. E. Van Camp, V. E. Van Doren, and J. T. Devreese, J. Phys. C 9, L79 (1976); V. E. Van Doren, P. E. Van Camp, and J. T. Devreese, Bull. Am. Phys. Soc. 21, 411 (1976).

[39] S. K. Sinha, R. P. Gupta, D. L. Price, Phys. Rev. B 9, 2564 (1974).

[40] R. M. Martin, Phys. Rev. 186, 871 (1969).

[41] S. Sinha, Phys. Rev. 169, 477 (1968); 177, 1256 (1969).

[42] E. Hayashi and M. Shimizu, J. Phys. Soc. Jpn. 26, 1369 (1969).

[43] L. J. Sham, Phys. Rev. B 6, 3584 (1972).

[44] W. Hanke, Phys. Rev. B 8, 4585 (1973).