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Generalized Screening Model for Lattice Dynamics*

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(Received 25 February 1971)

A very general *Ansatz* is made for the form of the dielectric response matrix $\epsilon(\vec{Q}, \vec{Q}')$ for a solid in terms of which it is possible to explicitly find the inverse matrix $\epsilon^{-1}(\vec{Q}, \vec{Q}')$. The various existing models of lattice dynamics may be obtained as special cases of this *Ansatz*. The phonon dispersion curves for Si are calculated from a simple generalized shell model based on this theory and agree with experiment to within 20 %.

The response of electrons in a solid to an external potential can be described in terms of the dielectric matrix given by

$$\epsilon(\vec{Q}, \vec{Q}') = \delta_{\vec{Q}, \vec{Q}'} + v(\vec{Q}) \chi(\vec{Q}, \vec{Q}'), \tag{1}$$

where $\chi(\vec{Q}, \vec{Q}')$ is the generalized susceptibility matrix and $v(\vec{Q})$ is the Fourier transform of the electron-electron interaction including corrections for exchange and correlation effects. The main problem in connection with screening in real solids is associated with the calculation of the inverse of $\epsilon(\vec{Q}, \vec{Q}')$ including its off-diagonal elements. For free electrons $\epsilon(\vec{Q}, \vec{Q}')$ becomes diagonal and the problem is trivial, whereas for tightly bound atomic electrons, one of us[1] has shown that a factorization *Ansatz* can be made for $\chi(\vec{Q}, \vec{Q}')$ which enables $\epsilon(\vec{Q}, \vec{Q}')$ to be inverted and leads to a generalized dipole screening model. For intermediate cases, such as covalently bound solids, or transition metals, neither model is satisfactory. For covalent solids, the quasiphenomenological bond-charge model of Phillips[2] and Martin[3] have been used to approximate the effect of the off-diagonal elements of $\epsilon(\vec{Q}, \vec{Q}')$. We present here a very general *Ansatz* which makes an explicit inversion of $\epsilon(\vec{Q}, \vec{Q}')$ possible and from which all of the above models may be derived as special cases and hence may be adapted to calculate the electron response for almost any solid. In doing so we also provide a quantum-mechanical basis for the bond-charge model and derive models which have not hitherto been employed but may be useful in certain types of solids.

We make the *Ansatz* that $\epsilon(\vec{Q}, \vec{Q}')$ may be approximated by the form

$$\epsilon(\vec{Q}, \vec{Q}') = \epsilon_0(\vec{Q})\delta_{\vec{Q},\vec{Q}'} + v(\vec{Q})\sum_{\substack{\alpha\beta \\ ss'}} Q_\alpha Q_{\beta'} f_s{}^*(\vec{Q})f_{s'}(\vec{Q}')\exp(i\vec{Q}\cdot\vec{r}_s)\exp(-i\vec{Q}'\cdot\vec{r}_{s'})a_{\alpha\beta}{}^{ss'}, \tag{2}$$

where α and β run over all Cartesian indices; $\vec{r}_s$ and $\vec{r}_{s'}$ run over suitably chosen sites in the unit cell; and these sites as well as the functions $\epsilon_0(\vec{Q})$, $f_s(\vec{Q})$, and $a_{\alpha\beta}{}^{ss'}$ are chosen to provide the best representation of $\epsilon(\vec{Q}, \vec{Q}')$ for the solid in question. The Bloch symmetry of the crystal requires that $\vec{Q}'$ must be related to $\vec{Q}$ through a reciprocal lattice vector, and that $a_{\alpha\beta}{}^{ss'}$ must be a periodic function of $\vec{q}$, the wave vector $\vec{Q}$ reduced to the first zone. The only restriction on the sites s and s' and on $a_{\alpha\beta}{}^{ss'}(\vec{q})$ is that they must be chosen consistent with crystalline symmetry. It is also convenient to normalize the functions $f_s(\vec{Q})$ so that they tend to unity as $\vec{Q}\to 0$.

It may be verified that with this approximation

$$\epsilon^{-1}(\vec{Q}, \vec{Q}') = \frac{1}{\epsilon_0(\vec{Q}')}\left[\delta_{\vec{Q},\vec{Q}'} - \frac{v(\vec{Q})}{\epsilon_0(\vec{Q})}\sum_{\substack{\alpha\beta \\ ss'}} Q_\alpha Q_{\beta'} f_s{}^*(\vec{Q})f_{s'}(\vec{Q}')\exp(i\vec{Q}\cdot\vec{r}_s)\exp(-i\vec{Q}'\cdot\vec{r}_{s'})S_{\alpha\beta}{}^{ss'}(\vec{q})\right] \tag{3}$$

where the matrix

$$S = (V + a^{-1})^{-1}. \tag{4}$$

The matrix a has already been defined by Eq. (2). The matrix V is defined as

$$V_{\alpha\beta}{}^{ss'}(\vec{q}) = \sum_{\vec{H}} (\vec{q}+\vec{H})_\alpha(\vec{q}+\vec{H})_\beta f_s(\vec{q}+\vec{H})f_{s'}{}^*(\vec{q}+\vec{H})\frac{v(\vec{q}+\vec{H})}{\epsilon_0(\vec{q}+\vec{H})}\exp[-i(\vec{q}+\vec{H})\cdot(\vec{r}_s-\vec{r}_{s'})], \tag{5}$$

the sum being over all reciprocal lattice vectors.

In order to examine the physical basis of such an *Ansatz* we imagine a weak external perturbation $U(\vec{Q}')$ applied to the crystal and examine the Fourier components of the corresponding perturbation in the electron density, as given by

$$\Delta\rho(\vec{Q}) = [1/v(\vec{Q})][\delta_{\vec{Q},\vec{Q}'} - \epsilon^{-1}(\vec{Q}, \vec{Q}')]U(\vec{Q}'). \tag{6}$$

Using Eq. (3) we get

$$\Delta\rho(\vec{Q}) = \frac{1}{v(\vec{Q})}\left[1 - \frac{1}{\epsilon_0(\vec{Q})}\right]\delta_{\vec{Q},\vec{Q}'}U(\vec{Q}') - i\sum_{\alpha,s} Q_\alpha\left[\frac{f_s{}^*(\vec{Q})\epsilon_0}{\epsilon_0(\vec{Q})}\right]\exp(i\vec{Q}\cdot\vec{r}_s)w_\alpha{}^s, \tag{7}$$

where

$$w_\alpha{}^s = -i\sum_{\beta,s'} S_{\alpha\beta}{}^{ss'}(\vec{q})Q_{\beta'}[f_{s'}(\vec{Q}')/\epsilon_0(\vec{Q}')]\exp(-i\vec{Q}'\cdot\vec{r}_{s'})U(\vec{Q}')\epsilon_0, \tag{8}$$

where $\epsilon_0 = \epsilon_0(\vec{Q}=0)$. The first term in Eq. (7) can be interpreted as the usual electron response given by a simple scalar dielectric function, while the second term corresponds to the electron density associated with oscillatory *distributions* of dipoles centered on the sites s, with amplitudes $\vec{w}^s$ and form factors $[f_s{}^*(\vec{Q})\epsilon_0/\epsilon_0(\vec{Q})]$. Note that, in principle, higher order multipoles are included in this formulation.

Let us now consider various special cases. If the $a_{\alpha\beta}{}^{ss'}$ becomes vanishingly small, i.e., $\epsilon(\vec{Q}, \vec{Q}')$ becomes mainly diagonal, then $S_{\alpha\beta}{}^{ss'}(\vec{q})\to 0$ and the $w_\alpha{}^s \to 0$ so that the free-electron screening is recovered from Eq. (7) in the limit. On the other hand, for tightly bound solids, $\epsilon_0(\vec{Q}) \to 1$ so that only the second term of Eq. (7) is left, and if the sites s are chosen as the atomic sites

we obtain induced dipole distributions on the atoms. For covalent solids or transition metals, it is reasonable to suppose that both the $\epsilon_0(\vec{Q})$ and the $a_{\alpha\beta}{}^{ss'}$ are necessary to approximate $\epsilon(\vec{Q}, \vec{Q}')$. If the sites s are chosen to be the centers of the covalent bonds in a covalent crystal, then Eq. (7) reduces to a bond-charge model (BCM) where the $\vec{w}^s$ arise from bond-charge displacements. On the other hand situating the sites s on the atoms themselves leads to a kind of *generalized shell model* (GSM) where part of the response is diagonal, as in the case of a free-electron gas, and part is due to dipolar distributions developed on the atom sites, as in the shell model.

We may use the above formalism to obtain the dielectric constant ϵ_∞ for cubic nonmetallic crys-

tals, where ϵ_0 is finite. This is given by

$$\epsilon_\infty = \lim_{\vec{q}\to 0} 1/\epsilon^{-1}(\vec{q}, \vec{q}).\qquad(9)$$

Using Eq. (3) we get, after some manipulation,

$$\epsilon_\infty = \epsilon_0 + \frac{4\pi e^2}{\Omega}\frac{1}{K+1/a}.\qquad(10)$$

Here

$$K = \sum_{\vec{H}}' \tfrac{1}{3}\vec{H}^2\frac{v(\vec{H})}{\epsilon_0(\vec{H})}\left|\frac{1}{n}\sum_s f_s(\vec{H})\exp(-i\vec{H}\cdot\vec{r}_s)\right|^2,\quad(11)$$

where Ω is cell volume, n is the number of sites s in the unit cell, and the prime over the summation indicates $\vec{H}=0$ is to be excluded;

$$a = \lim_{\vec{q}\to 0}\sum_{ss'} a^{ss'}(\vec{q}),\qquad(12)$$

where we have assumed that the $a_{\alpha\beta}{}^{ss'}(\vec{q})$ may be written as $a^{ss'}(\vec{q})\delta_{\alpha\beta}$ for cubic crystals. The quantity a is equal to $(\Omega/e^2)\alpha$, where α is the polarizability of a unit cell.

It may be shown that Eq. (10) yields the usual Lorentz-Lorenz formula in the point dipole approximation [$\epsilon_0 = f_s(\vec{Q}) = 1$, s runs over atomic sites], while for extended dipolar distributions [$\epsilon_0 = 1$, $f_s(\vec{H}) = 0$ $(\vec{H}\neq 0)$],

$$\epsilon_\infty = 1 + 4\pi\alpha,\qquad(13)$$

so that both classical limits are obtained. A very important application of the above formalism is in the calculation of the vibrational spectra of solids. In this case $U(\vec{Q}')$ of Eq. (6) stands for the perturbing potential due to the displaced ions of the lattice and may be written as

$$U(\vec{Q}') = -i\sum_{\gamma,k} Q_{\gamma}' W_k(\vec{Q}')\exp(+i\vec{Q}'\cdot\vec{r}_k)e_\gamma{}^k(\vec{q}),\qquad(14)$$

where $\vec{r}_k$ runs over atomic sites, $\vec{e}^k$ is the unit polarization vector for site k, and $W_k(\vec{Q}')$ is the pseudopotential form factor associated with the ion at site k. We shall not discuss here the complications arising from nonlocal pseudopotentials. Combining Eqs. (8) and (14) we may write Eq. (8) in the form

$$w_\alpha{}^s = -(1/\epsilon_0)\sum_{k\gamma}(SW^\dagger)_{\alpha\gamma}{}^{sk}e_\gamma{}^k,\qquad(15)$$

where

$$W_{\alpha\beta}{}^{ks}(\vec{q}) = \sum_{\vec{H}}(\vec{q}+\vec{H})_\alpha(\vec{q}+\vec{H})_\beta\frac{W_k(\vec{q}+\vec{H})}{\epsilon_0(\vec{q}+\vec{H})}f_s{}^*(\vec{q}+\vec{H})\exp[-i(\vec{q}+\vec{H})\cdot(\vec{r}_k-\vec{r}_s)].\qquad(16)$$

Using Eqs. (7) and (14) the lattice equations of motion may be shown by standard methods to be

$$\omega^2 M_k e_\alpha{}^k = \sum_{k'\gamma}(C_{\alpha\gamma}{}^{kk'}+E_{\alpha\gamma}{}^{kk'})e_\gamma{}^{k'}+e_0\sum_{s\gamma}W_{\alpha\gamma}{}^{ks}W_\gamma{}^s,\qquad(17)$$

where M_k is the atomic mass, C is the electrostatic coupling coefficient between ion cores, and E is given by the usual expression used for simple metals except that the free-electron dielectric function is replaced by $\epsilon_0(\vec{Q})$. For nonmetallic crystals, one has to ensure vanishing microscopic electric fields in the limit $\vec{q}\to 0$ for the acoustic modes,[4] which leads to the sum rule

$$\lim_{\vec{q}\to 0}\sum_k\left[Z_k\frac{q_\alpha q_\beta}{q^2}+\sum_{s\gamma}\frac{q_\alpha q_\gamma}{q^2}(SW^\dagger)_{\gamma\beta}{}^{sk}\right] = 0\qquad(18)$$

for the above model, where Z_k is the ionic core charge at site k. In general this sum rule leads to a restriction on the $a_{\alpha\beta}{}^{ss'}$ for which evaluation is complicated. However, evaluation is simpler in the case of a lattice with the diamond structure if we adapt the GSM (sites s on atomic sites) to become

$$a = -1/(j+K),\qquad(19)$$

where K, a are defined in Eqs. (11) and (12), and

$$j = \frac{1}{Z}\sum_{\vec{H}}\tfrac{1}{3}\vec{H}^2\left[\tfrac{1}{2}\sum_k\frac{W(\vec{H})}{\epsilon_0(\vec{H})}\exp(i\vec{H}\cdot\vec{r}_k)\right]\left[\tfrac{1}{2}\sum_{k'}f_{k'}(\vec{H})\exp(-i\vec{H}\cdot\vec{r}_{k'})\right].\qquad(20)$$

Equations (15) and (17) together look similar to the shell-model equations but are in fact representative of a very general model. As pointed out above, keeping only $\epsilon_0(\vec{Q})$ and neglecting the $a_{\alpha\beta}{}^{ss'}$ leads to the usual free-electron model, while putting $\epsilon_0(\vec{Q}) = 1$ leads to vanishing E and the usual dipolar models. Keeping both $\epsilon_0(\vec{Q})$ and the $a_{\alpha\beta}{}^{ss'}$ leads to different models depending on our choice of the sites s, i.e., GSM or BCM.

It may be shown that if one takes the sites s as the bond-charge sites and makes a special assump-

tion about the form of the matrix a, and also certain simplifying assumptions about the form of the pseudopotential, and the exchange and correlation effects and the $\vec{Q}$ dependence of $\epsilon_0(\vec{Q})$, one arrives at the equations of motion obtained by Martin for his bond-charge model.

Finally, we present a calculation for silicon based on a GSM with the sites s being the atomic sites, where for reasons of simplicity and rapid convergence we have taken the $f_k(\vec{Q})$ to be form factors associated with a uniform distribution inside a sphere of radius r_G, i.e.,

$$f_k(\vec{Q}) = 3(\sin x - x \cos x)/x^3, \quad x = Q r_G. \quad (21)$$

The $a_{\alpha\beta}{}^{kk'}(\vec{q})$ were taken simply as $a_1 \delta_{\alpha\beta} \delta_{kk'}$, and the pseudopotential form factor taken as

$$W(\vec{Q}) = -(4\pi Z e^2/\Omega Q^2) \sin(Q r_c)/Q r_c. \quad (22)$$

The pseudopotential in Eq. (22) was chosen to approximate best the pseudopotential for silicon as given by Heine and Abarenkov (HA) as modified by Shaw[5] for which Eq. (22) provides a reasonable analytical representation. The value of r_c was chosen to be 2.14 a.u. to make the first node of Eq. (22) coincide closely with that of the HA potential. The dispersion curves did show some sensitivity to the choice of r_c however. We have used the most recent $\epsilon(\vec{Q}, \vec{Q})$ as calculated for silicon by Walter and Cohen[6] and the sum rule as given by Eq. (19) to determine a_1 and $\epsilon_0(\vec{Q})$. The procedure was an iterative one involving calculating a_1 from the sum rule [which involves $\epsilon_0(\vec{Q})$], using this and the published $\epsilon(\vec{Q}, \vec{Q})$ to calculate $\epsilon_0(\vec{Q})$ from Eq. (2), and repeating the procedure until self-consistency was achieved. The r_G used in Eq. (21) was chosen as an adjustable parameter, and a value of $r_G = 2.67$ a.u. was chosen to obtain reasonable agreement with experiment. The induced dipolar distribution in real space corresponding to the Fourier transform of $f_k(\vec{Q})\epsilon_0/\epsilon_0(\vec{Q})$ turns out to be mainly contained inside the sphere of radius r_G, with a discontinuity at r_G and a small oscillatory tail outside r_G. The discontinuity and oscillations are a consequence of our simplifying assumption for $f_k(\vec{Q})$. It should be noted, however, that the $f_k(\vec{Q})$ are simply functions chosen to represent the off-diagonal elements of $\epsilon(\vec{Q}, \vec{Q})$ through the Ansatz in Eq. (2), and hence involve transitions to excited states, so one should not identify the above form factors with the static x-ray form factors for the electron density.
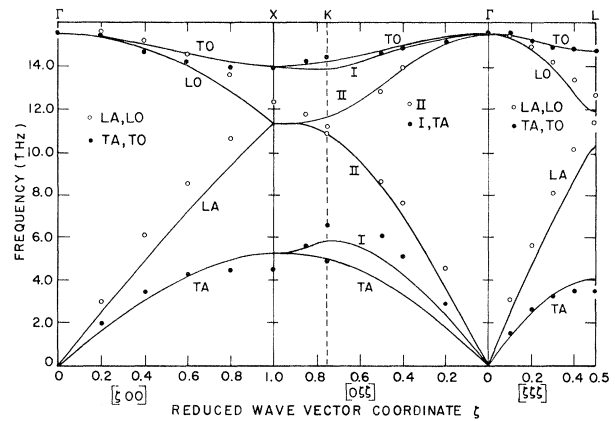

Fig. 1. Phonon dispersion curves for Si calculated from the generalized shell model referred to in the text. The experimental points refer to the data of Dolling (Ref. 7) and the [110] TA point is from the data of Palevsky et al. (Ref. 8).

The calculated dispersion curves are shown in Fig. 1. It may be seen that the agreement is quite reasonable for a simple one-parameter model. The LA modes show a remarkable lack of dispersion which is also borne out by the experimental observations. We also remark that the term in the dynamical matrix obtained by eliminating w from Eqs. (15) and (17) contains a purely imaginary antisymmetric component in $D_{\alpha\beta}{}^{kk}$, i.e., gives rise to forces between atoms on the same sublattice, in particular the second neighbors, which cannot be obtained from a bond-stretching–type interaction alone and therefore involves bond-bending forces also.

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