Sum Rules for the Dielectric Screening Properties of Crystals

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The question of the screening of contributions from the second-order electron-phonon interaction (i.e., background scattering corrections) in a recent many-body theory of phonon spectra is reexamined. An identity deduced in this latter work requires correction appropriate to the case of unscreened background scattering terms, and a recent sum rule given by Pick *et al.* is shown to arise as one special case of this corrected identity, which consists of a *set* of sum rules on the screening function elements in the long-wavelength limit.

I. INTRODUCTION

IN a recent article,[1] hereafter referred to as I, a quantum theory of the phonon spectrum of a general crystal was presented, in which the problem of calculating the phonon spectrum in the harmonic approximation was reduced, by means of a renormalization procedure, to the problem of the calculation of the more fundamental linear dielectric screening properties.[2] In the course of this work, a new identity was obtained which allowed the cancellation of divergent self-interaction terms and ensured that the acoustic-phonon frequencies vanish in the long-wavelength limit, i.e., ensured translational invariance. Pick *et al.*[3] have also considered the lattice dynamics of crystals and have given a sum rule referred to as "the acoustic sum rule." In the present work, we reexamine the role which screening plays in the corrections due to contributions from the second-order electron-phonon interaction $H_{\mathrm{eph}}{}^{(2)}$ (i.e., scattering against the background), and conclude, contrary to I, that these contributions should not involve screening because the screening effects are actually canceled by a self-consistent-field contribution. Thus, both the term in the phonon self-energy due to $H_{\mathrm{eph}}{}^{(2)}$ and the identity require correction, although both the cancellation and the results for the phonon spectra derived in I are unaffected. The corrected identity is shown to consist of a *set* of sum rules, one of which is the sum rule given by Pick *et al.*[3]

II. BACKGROUND SCATTERING CONTRIBUTION TO PHONON SELF-ENERGY

The nonrelativistic Hamiltonian used in the theory described in I for the system of electrons and nuclei was $H=H_e+H_N+H_I$, where[1]

$$H_e=\sum_i\left(\tfrac{1}{2}\mathbf{p}_i^2-\sum_s\frac{Z_s}{|\mathbf{r}_i-\mathbf{R}_s(0)|}+V_{\mathrm{SF}}(\mathbf{r}_i)\right),$$

$$H_N=\sum_s\left[\frac{\mathbf{P}_s^2}{2M_s}+\tfrac{1}{2}\sum_{r\neq s}\left(\frac{Z_rZ_s}{R_{rs}}+f(\mathbf{R}_{rs})\right)\right],$$

$$H_I=\sum_{i>j}\frac{1}{r_{ij}}-\sum_{i,s}Z_s\left(\frac{1}{|\mathbf{r}_i-\mathbf{R}_s|}-\frac{1}{|\mathbf{r}_i-\mathbf{R}_s(0)|}\right)-\sum_i V_{\mathrm{SF}}(\mathbf{r}_i)-\tfrac{1}{2}\sum_{r\neq s}f(\mathbf{R}_{rs}).$$

The $V_{\mathrm{SF}}(\mathbf{r}_i)$ added to and subtracted from H is a self-consistent-field term introduced[1] in order to make the zero-order Bloch eigenstates of the zero-order electron Hamiltonian H_e close to exact eigenstates. The contribution $f(\mathbf{R}_{rs})$ is a similar term for the phonon eigenstates,[4] in order to avoid difficulties with hybridization such as those encountered by Garland.[5] The electron-electron interaction is treated exactly within the nonrelativistic approximation (using an unretarded Coulomb interaction) and the electron-phonon interaction is correct to second order in the phonon fields, consistent with the harmonic approximation.[1] The electron and phonon fields are quantized and many-body perturbation theory is used to evaluate the phonon self-energy Π in order to renormalize the phonon spectrum. The diagrammatic expression for Π obtained in I is shown in Fig. 1. The first two diagrams involve the first-order electron-phonon interaction $H_{\mathrm{eph}}{}^{(1)}$, while the third and fourth (which make up Π') involve the second-order interaction $H_{\mathrm{eph}}{}^{(2)}$ and correspond to scattering of the phonons off the background. The use of a new identity[1] allowed the derivation of a result which explicitly exhibits translational invariance, i.e., the acoustic-phonon frequencies vanish in the long-wavelength limit.

[1] P. N. Keating, Phys. Rev. **175**, 1171 (1968).

[2] It is to be noted, however, that the screening is due to electrons which are dressed by phonon exchange (see Ref. 1), although the phonon-exchange effects are probably quite small [J. C. Phillips, (private communication)].

[3] R. M. Pick, M. H. Cohen, and R. M. Martin (to be published).

[4] A. J. Rajagopal (private communication) has pointed out that the zero-order eigenstate polarization vectors should form a biorthogonal set when lifetime effects arise, as in metals outside the adiabatic approximation, instead of an orthonormal set [see also S. K. Joshi and A. J. Rajagopal, Solid State Phys. **22**, 225 (1969)]. In this case, we can expect the necessary f contribution to be time-dependent.

[5] J. W. Garland, Phys. Rev. **153**, 460 (1967).

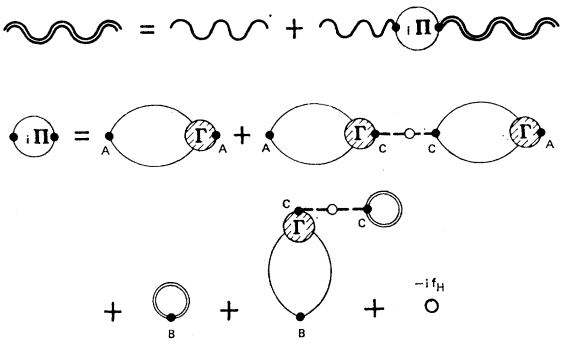

FIG. 1. Contributions to the phonon self-energy considered in Ref. 1.

The contributions from the V_{SF} term in H_I to the first two diagrams are included in the Γ vertex corrections, which are left improper, i.e., they include both electron self-energy terms and proper vertex corrections. The V_{SF} contribution to the $H_{eph}^{(2)}$ terms, which is shown in Fig. 2, was consequently overlooked. This oversight is somewhat unfortunate since Hubbard[6] has shown that, if V_{SF} is suitably chosen, the V_{SF} terms cancel certain diagrams which contain what Hubbard terms "H parts"; such a part is connected to the rest of the diagram (connected to external lines) by a single Coulomb interaction line only. A similar[7] choice of V_{SF}, which is a generalized Hartree field,[6] should be taken in the phonon theory of I, and both the diagram shown in Fig. 2 and the fourth diagram of Fig. 1 should then be excluded, since this latter is an H part.[6] The cancellation, of course, is also acceptable to our intuition since the Hartree field represents the effect of the background and the fourth diagram includes electron scattering off the background. Thus, the expression for Π' given in I should be replaced by

$$\Pi' = -\sum_{\kappa} L_{\mathbf{qq}}(\boldsymbol{\kappa}) \int \frac{d^3k}{(2\pi)^3} n_{\mathbf{k}} B_0(-\boldsymbol{\kappa}, \mathbf{k})$$

[where $L_{\mathbf{qq}}(\boldsymbol{\kappa})$ is a coefficient of $H_{eph}^{(2)}$ (see I), $B_0(\boldsymbol{\kappa},\mathbf{k}) = \langle \mathbf{k}|e^{-i\boldsymbol{\kappa}\cdot\mathbf{r}}|\mathbf{k}\rangle$, $\boldsymbol{\kappa}$ is a reciprocal-lattice vector, and $n_{\mathbf{k}}$ is the occupation factor] because the fourth term in the expression for Π cancels against the term displayed in Fig. 2; there is an additional factor of 2 if we perform the sum over spins.

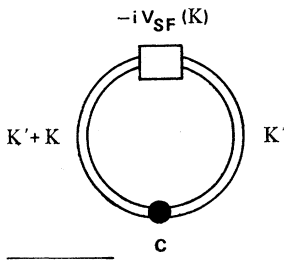

FIG. 2. Additional term in the second-order contribution Π'.

We now reexamine the analysis carried out in the Appendix of I in which the new identity was derived and, in particular, reconsider the role of screening on the explicit electron contribution to the electrostatic potential. The identity is obtained[1] by calculating this electronic contribution in two different ways: (a) as the difference between the bare and screened potentials and (b) explicitly, with the electronic charge as source. The two results are then equated to give the identity. The first result for the electronic contribution to the change in potential due to the electrons when the nuclei are displaced by $\mathbf{u}e^{i\mathbf{q}\cdot\mathbf{r}}$ in the long-wavelength low-frequency limit is[1]

$$\delta V_e = \delta V_{\text{scr}} - \delta V_{\text{bare}} = \lim_{\mathbf{q},\omega\to 0} \sum_{n\kappa\kappa'} \frac{4\pi i Z_n \mathbf{u}\cdot[\![\boldsymbol{\kappa}+\mathbf{q}]\!]}{V_A|\boldsymbol{\kappa}'+\mathbf{q}|} \times e^{-i\boldsymbol{\kappa}\cdot\mathbf{x}_n}(S_{\kappa'\kappa}(\mathbf{q},\omega)-\delta_{\kappa'\kappa})e^{i(\boldsymbol{\kappa}'+\mathbf{q})\cdot\mathbf{r}}, \quad (1)$$

where $[\![\boldsymbol{\kappa}+\mathbf{q}]\!]$ is the unit vector $(\boldsymbol{\kappa}+\mathbf{q})/|\boldsymbol{\kappa}+\mathbf{q}|$, $S_{\kappa'\kappa}(\mathbf{q},\omega) = (|\boldsymbol{\kappa}'+\mathbf{q}|/|\boldsymbol{\kappa}+\mathbf{q}|)\mathcal{K}_{\kappa'\kappa}(\mathbf{q},\omega)$, and $\mathcal{K}_{\kappa'\kappa}$ is the inverse dielectric screening function.[1] We now recalculate the explicit electron contribution. In the long-wavelength limit, the electron density is[1]

$$\rho(\mathbf{r}) = \lim_{\mathbf{q}\to 0} \frac{1}{V_A} \sum_{\kappa'} e^{i(\boldsymbol{\kappa}'+\mathbf{q})\cdot\mathbf{r}} \int \frac{d^3k}{(2\pi)^3} n_{\mathbf{k}} B_0^*(\boldsymbol{\kappa}',k).$$

In I, this was used as an external source which sets up a screened potential.[8] However, this regards all the electrons as test charges, which is inconsistent with the point made by Nozières and Pines[9] that the test charges must form only a small fraction of the electrons. Thus, we should instead consider the direct, unscreened potential from $\rho(\mathbf{r})$ as δV_e. In other words,

$$\delta V_e = \lim_{\mathbf{q}\to 0} \sum_{\kappa} \frac{-4\pi i \mathbf{u}\cdot[\![\boldsymbol{\kappa}'+\mathbf{q}]\!]}{V_A|\boldsymbol{\kappa}'+\mathbf{q}|} \times e^{i(\boldsymbol{\kappa}'+\mathbf{q})\cdot\mathbf{r}} \int \frac{d^3k}{(2\pi)^3} n_{\mathbf{k}} \langle \mathbf{k}|e^{i\boldsymbol{\kappa}'\cdot\mathbf{r}}|\mathbf{k}\rangle. \quad (2)$$

Equating (1) and (2) for δV_e, as in I, we obtain the corrected identity

$$\lim_{\mathbf{q},\omega\to 0} \left(\sum_{n\kappa} Z_n e^{-i\boldsymbol{\kappa}\cdot\mathbf{x}_n} [\![\boldsymbol{\kappa}+\mathbf{q}]\!][S_{\kappa'\kappa}(\mathbf{q},\omega)-\delta_{\kappa'\kappa}] + [\![\boldsymbol{\kappa}'+\mathbf{q}]\!] \int \frac{d^3k}{(2\pi)^3} n_{\mathbf{k}} \langle \mathbf{k}|e^{i\boldsymbol{\kappa}'\cdot\mathbf{r}}|\mathbf{k}\rangle \right) = 0, \quad (3)$$

which replaces the complex conjugate of Eq. (17) of I.

[6] See Sec. 3 of J. Hubbard, Proc. Roy. Soc. (London) **244**, 199 (1958).

[7] The choice appropriate to the present work will differ from Hubbard's choice in that phonon-exchange effects are included. However, in the long-wavelength limit appropriate to the terms due to $H_{eph}^{(2)}$, the cancellation will proceed in the same way in the harmonic approximation.

[8] See also, for example, Sec. III of J. J. Quinn and R. A. Ferrel, Phys. Rev. **112**, 812 (1958).

[9] See Sec. 6 of P. Nozières and D. Pines, Phys. Rev. **109**, 762 (1958).

When both the corrected identity and the corrected Π' are substituted in the remaining analysis in I, the other results obtained there are, of course, unchanged.

III. DISCUSSION AND RELATIONSHIP WITH ACOUSTIC SUM RULE

The identity given above as Eq. (3) is seen to relate the screening properties of the crystal in the long-wavelength limit to the electron density distribution in the crystal, since $\int[d^3k/(2\pi)^3]B_0(-\boldsymbol{\kappa},\mathbf{k})n_{\mathbf{k}}$ is just the $\boldsymbol{\kappa}$th Fourier transform of this distribution.[10] The identity arises in a highly physical way from the fact that the explicit potential due to the screening electronic charge must be equal to the difference between the screened and bare potentials since the screening is due to the electrons. The use of $\mathbf{S}(\mathbf{q},\omega)$ in these expressions is convenient (a) because it is Hermitian, $S_{\kappa\kappa'}=S_{\kappa'\kappa}{}^*$, if vertex corrections are real,[1] and (b) because it is everywhere finite. The matrix $\mathbf{K}(\mathbf{q},\omega)$ is never Hermitian, and the elements $\mathcal{K}_{0\kappa}(\mathbf{q},\omega)$ blow up[3] as $1/|\mathbf{q}|$ in the long-wavelength limit for $\boldsymbol{\kappa}\neq 0$.

In the limit of large $\boldsymbol{\kappa}'$, i.e., at small distances, the screening becomes less and less effective and $S_{\kappa'\kappa}$ becomes closer to $\delta_{\kappa'\kappa}$ in value. Moreover, the $\boldsymbol{\kappa}'$th Fourier transform of the electron density goes to zero—which is, of course, how identity (3) removes the self-interaction divergences in the phonon spectrum[1]—and thus the identity is automatically satisfied for very large $|\boldsymbol{\kappa}'|$.

This identity, Eqs. (3), is seen to be an infinite set of sum rules on $S_{\kappa'\kappa}(0)$. In the special case of $\boldsymbol{\kappa}'\equiv 0$, we obtain

$$\lim_{\mathbf{q},\omega\to 0}\left(\sum_{n\kappa} Z_n e^{-i\boldsymbol{\kappa}\cdot\mathbf{x}_n}[\![\boldsymbol{\kappa}+\mathbf{q}]\!][S_{0\kappa}(\mathbf{q},\omega)-\delta_{0\kappa}] + \hat{q}\int\frac{d^3k}{(2\pi)^3}n_{\mathbf{k}}B_0(0,\mathbf{k})\right)=0.$$

Because of charge neutrality,

$$\int\frac{d^3k}{(2\pi)^3}n_{\mathbf{k}}B_0(0,\mathbf{k})=\sum_n Z_n,$$

and hence

$$\lim_{\mathbf{q},\omega\to 0}\sum_{n\kappa} Z_n e^{-i\boldsymbol{\kappa}\cdot\mathbf{x}_n}S_{0\kappa}(\mathbf{q},\omega)[\![\boldsymbol{\kappa}+\mathbf{q}]\!]=0. \tag{4}$$

Because

$$S_{0\kappa}(\mathbf{q})=\frac{|\mathbf{q}|}{|\mathbf{q}+\boldsymbol{\kappa}|}\varepsilon^{-1}(\mathbf{q},\mathbf{q}+\boldsymbol{\kappa})$$

in the notation of Pick *et al.*,[3] this expression is identical with Eq. (6.12) of Ref. 3, which was obtained by a somewhat more indirect procedure. We see that the acoustic sum rule of Pick *et al.* is actually one of an infinite set of sum rules on the electronic screening properties of a crystal. As Pick *et al.* have pointed out,[3] Eq. (4) implies that the assumption that off-diagonal elements of $\mathbf{S}$ are zero is inconsistent with this sum rule for insulating crystals, since S_{00} does not vanish in the long-wavelength limit in this type of crystal. Furthermore,[3] Eq. (4) does not impose conditions in the case of metals since S_{00} and $S_{0\kappa}$ vanish in the $\mathbf{q}\to 0$ limit for these solids. However, it is to be noted that the additional sum rules contained in identity (3) *do* impose conditions in the case of both metals and insulators. In particular, if the off-diagonal elements are assumed negligible, as is usually the case for contributions from the valence band in metals, Eq. (3) becomes

$$\lim_{\mathbf{q},\omega\to 0}\sum_n Z_n'e^{-i\boldsymbol{\kappa}\cdot\mathbf{x}_n}S_{\kappa\kappa}'(\mathbf{q},\omega)=\sum_n Z_n'e^{-i\boldsymbol{\kappa}\cdot\mathbf{x}_n} - \int_{\text{val. zone}}\frac{d^3k}{(2\pi)^3}\langle\mathbf{k}|e^{i\boldsymbol{\kappa}\cdot\mathbf{r}}|\mathbf{k}\rangle, \tag{5}$$

where Z_n' is the valence electron change per atom and $S_{\kappa\kappa}'$ is the contribution to the screening from the valence electrons. In the case of diagonal $\mathbf{S}'$, the effects of screening may be incorporated into a form factor for the ion and we can write

$$\bar{Z}_n(\boldsymbol{\kappa})=Z_n'e^{-i\boldsymbol{\kappa}\cdot\mathbf{x}_n}[1-S_{\kappa\kappa}'(0)].$$

The condition represented by Eq. (5) then becomes

$$\sum_n\bar{Z}_n(\boldsymbol{\kappa})=\int_{\text{val. zone}}\frac{d^3k}{(2\pi)^3}\langle\mathbf{k}|e^{i\boldsymbol{\kappa}\cdot\mathbf{r}}|\mathbf{k}\rangle. \tag{6}$$

As already mentioned, Eqs. (5) and (6) impose no additional constraints in metals for $\boldsymbol{\kappa}=0$, but they do provide a check on $\epsilon'(\mathbf{Q})$ for $\mathbf{Q}$ at reciprocal lattice points other than the origin.

In the case of insulating crystals, the identity (3) again imposes additional conditions on the screening over and above that for the $\boldsymbol{\kappa}'=0$ case (corresponding to the sum rule of Pick *et al.*), of course.

ACKNOWLEDGMENT

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[10] It has very recently been pointed out [R. M. Martin (private communication)] that this identity is related to Eqs. (3.6), (3.10), and (3.11) of Ref. 3. In fact, these equations are directly equivalent to a weakened version of Eq. (3) in which the latter is multiplied by $Z_{n'}e^{i\boldsymbol{\kappa}'\cdot\mathbf{x}_{n'}}[\![\boldsymbol{\kappa}'+\mathbf{q}]\!]$ and there are sums over n', $\boldsymbol{\kappa}'$ as well as n, $\boldsymbol{\kappa}$. Eq. (3) of the present work represents a condition on the electrostatic potential at an arbitrary point and Eqs. (3.6), (3.10), and (3.11) of Ref. 3 represent a condition on the total potential energy of all the nuclei.