Adiabatic Theory of the Electron-Phonon Interaction

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Second-order corrections to the electronic energy due to the electron-phonon interaction have been obtained by several authors using the formalism of the adiabatic theory. Their result differs from the commonly accepted expression first given by Fröhlich in 1950. It will be demonstrated in the present paper that terms were omitted in the adiabatic theories which reconcile the two results. In addition, a comparison will be made between this paper and a recent paper along similar lines by Englman.

SEVERAL authors[1-6] have treated the electron-phonon interaction problem from a point of view that is more commonly used in molecular theory, the Born-Oppenheimer adiabatic theory.[7] In these theories the form of the electron-phonon interaction term differs from that used by Fröhlich[8] in 1950 to calculate the second-order correction to the electronic energy E_2. A corresponding difference in the form of E_2 results, the implications of which are discussed briefly in Ref. 1 and extensively in Ref. 4. Since the Fröhlich expression agrees with that obtained from the later, more careful derivation of Nakajima[9]—as extended by Bardeen and Pines[10] (Refs. 9 and 10 are discussed in a review article by Bardeen[11])—a disagreement exists between terms calculated by two apparently equally valid approximations. It will be shown in this paper that the discrepancy can be resolved by noting that the authors of Refs. 1-4 have omitted a term while the author of Ref. 6 obtains the missing term but does not compute E_2. A similar approach was taken in a recent paper by Englman[12]; several points at which we disagree with Englman's argument will be discussed.

The particular presentation of the adiabatic theory which is used in Ref. 12 is that given by Ziman.[1] This approach will be followed here. The part of the total Hamiltonian,

$$H = \sum (1/2m)p^2 + \sum (1/2M)P^2 + U(X) + V_c(x) + V(X,x), \quad (1)$$

which depends on electronic coordinates is used to define electronic eigenstates $\psi_X(x)$ which depend parametrically on the nuclear coordinates X so that

$$[(1/2m)p^2 + V_c(x) + V(X,x)]\psi_X(x) = E_X\psi_X(x). \quad (2)$$

In Eqs. (1) and (2), U denotes the ion-ion potential,

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V the electron-ion potential, and V_c the Coulomb interactions between electrons. Subscripts on the nuclear coordinates (X) and momenta (P) and electronic coordinates (x) and momenta (p) are suppressed.

The total Hamiltonian acting on trial wave functions of the form $\psi_X(x)\Phi(X)$ gives three terms

$$\psi_X(x)[\sum (1/2M)P^2 + E_X + U(X)]\Phi(X), \quad (3)$$

$$-(\hbar^2/M)\nabla_X\psi_X(x) \cdot \nabla_X\Phi(X), \quad (4)$$

and

$$-(\hbar^2/2M)\Phi(X)\nabla_X^2\psi_X(x). \quad (5)$$

If Φ_i are chosen to be eigenfunctions of (3) with eigenvalue $(n+\frac{1}{2})\hbar\omega_i$, and if (4) and (5) are small, the trial wave functions represent an electron-phonon system in which the electrons follow the nuclear motion adiabatically.

Expression (4) appears in one form or another in Refs. 1-6. When expressed in terms of electron creation operators a_k^* it is equal to[6]

$$i\hbar \sum_{k,\kappa} \frac{a^*_k a_{k-\kappa} v_\kappa}{\epsilon_k - \epsilon_{k-\kappa}} p_\kappa^*, \quad (6)$$

where v_κ is a renormalized electron-phonon matrix element. In this form the departure of the ions from X_0, their equilibrium position, has been expanded in a Fourier series with coefficients q_κ; the ϵ_k are the E_{X_0} and the p_κ are canonically conjugate to q_κ. This term, when treated as a perturbation, gives a second-order correction to the electronic energy

$$E_2' = \sum_{k,\kappa} \frac{\hbar^4\omega_\kappa^2 |v_\kappa|^2 f(k)(1-f(k-\kappa))}{(\epsilon_k - \epsilon_{k-\kappa})^2[(\epsilon_k - \epsilon_{k-\kappa})^2 - \hbar^2\omega_\kappa^2]} \quad (7)$$

which was pointed out in Refs. 1-4.

Expression (5) which was either considered negligible or completely ignored in Refs. 1-4 yields a correction to the energy

$$E_2'' = \sum_{k,\kappa} \frac{\hbar^2 |v_\kappa|^2}{(\epsilon_k - \epsilon_{k-\kappa})^2} f(k)(1-f(k-\kappa)). \quad (8)$$

In Eqs. (7) and (8) the $f(k)$ are electron occupation numbers and a spin summation has been carried out. This result was pointed out in Refs. 12 and 6.

It may be easily verified that the sum of E_2' and E_2'' is

$$E_2 = \sum_{k,\kappa} \frac{\hbar^2 |v_\kappa|^2}{(\epsilon_k - \epsilon_{k-\kappa})^2 - \hbar^2 \omega_\kappa^2} f(k)(1 - f(k-\kappa)), \quad (9)$$

the electronic interaction energy originally derived by Fröhlich.

In Ref. 12 a procedure equivalent to the following is employed. The second-order energy,

$$W = 2 \sum \frac{|v_\kappa|^2 \langle n_\kappa \pm 1 | q_\kappa | n_\kappa \rangle^2 f(k)(1 - f(k-\kappa))}{\epsilon_k - \epsilon_{k-\kappa} \mp \hbar \omega_\kappa}, \quad (10)$$

due to an electron-phonon interaction of the form $v_\kappa q_\kappa a_k^* a_{k-\kappa}$, is expanded in powers of $\hbar\omega_\kappa/\epsilon_k - \epsilon_{k-\kappa}$. Three terms

$$W_0 = \sum W_{k,\kappa}$$
$$= 2 \sum \frac{|v_\kappa|^2 \langle n_\kappa \pm 1 | q_\kappa | n_\kappa \rangle^2 f(k)(1 - f(k-\kappa))}{\epsilon_k - \epsilon_{k-\kappa}},$$

$$W_1 = \sum \pm \frac{\hbar \omega_\kappa}{\epsilon_k - \epsilon_{k-\kappa}} W_{k,\kappa},$$

$$W_2 = \sum \frac{\hbar^2 \omega_\kappa^2}{(\epsilon_k - \epsilon_{k-\kappa})^2} W_{k,\kappa},$$

are retained and an approximation is made in the denominator of the definition of W_2 to give

$$W_2' = \sum \frac{\hbar^2 \omega_\kappa^2 W_{k,\kappa}}{(\epsilon_k - \epsilon_{k-\kappa})(\epsilon_k - \epsilon_{k-\kappa} \mp \hbar \omega_\kappa)}.$$

In the above n_κ is a phonon occupation number.

For terms which are of particular interest—those which lead to superconductivity in the BCS model—the expansion in powers of $\hbar\omega_\kappa/(\epsilon_k - \epsilon_{k-\kappa})$ is clearly not valid because the expansion parameter would be larger than unity. However, this apparent error is of little consequence in Ref. 12 because retaining only three terms in the expansion and approximating the third term as indicated results in an identity;

$$W = W_0 + W_1 + W_2'.$$

If the three terms are examined it will be found that W_0 is proportional to $(n_\kappa + \frac{1}{2})$, that W_1 is independent of n_κ, and that while part of W_2' is proportional to $(n_\kappa + \frac{1}{2})$, another part is not. The sum of the two terms independent of n_κ is equal to E_2. The terms proportional to $n_\kappa + \frac{1}{2}$ are identified with a second-order change in phonon frequency. [A term proportional to $n_\kappa + \frac{1}{2}$ was omitted in obtaining Eq. (7)].

In Ref. 12 it is stated that the phonon frequencies which result from solving Eq. (3) depend on E_X and that W_0 is equal to the change in phonon energy caused by the part of E_X which is quadratic in $X - X_0$. This statement misses an important point of the adiabatic formalism—it is precisely the X dependence of E which renormalizes the phonon frequencies so that energy changes caused by this dependence are already taken into account if renormalized ($\omega_\kappa \propto \kappa$, κ small) rather than unrenormalized ($\omega_\kappa =$ the ion plasma frequency at small κ) frequencies are used. Thus the electronic energies ϵ_k are to be evaluated at nuclear equilibrium, and they are independent of X.

The phonon-electron interaction assumed in deriving Eq. (10) does not appear in any of the derivations considered here in a Hamiltonian with renormalized phonon frequencies. For this reason we feel that the derivation of Eq. (10) is unsound and agreement with this equation should not be a criterion for another theory. General agreement between the adiabatic theory and the Nakajima transformation, as modified by Bardeen and Pines, is indicated by the present argument. The relationship between these derivations will be discussed in more detail by one of us (RKN) in a separate paper.