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Calculation of the Internal Energy and State Populations of a Strongly Coupled Electron-Phonon System in Thermal Equilibrium

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Expressions are derived for the total energy and the thermal-equilibrium single-electron and phonon distribution functions for a defect electron-phonon system with a strong electron-lattice distortion V_d . An application of the result is made to the case of a single-phonon mode coupled strongly to a two-level electron system.

I. INTRODUCTION

In the calculation of properties of trapped-electron defect centers in crystals one finds it necessary to consider the effect of the electron-phonon interaction upon the system both directly, through

its effect upon the energy eigenvalues and eigenstates, and indirectly, through its effect on the thermal averages of observables. If one assumes the electron-phonon interaction Hamiltonian to have the usual form, linear in the phonon coordinates, then this interaction Hamiltonian can be divided

rather naturally into two parts which enter into the determination of the energy and thermal averages in somewhat different ways. The part which is *diagonal* in the electron operators arises primarily from the distortion of the lattice and can produce relatively large shifts in the energy levels of the system and somewhat smaller shifts in the electronic distribution functions. This portion of the interaction can be handled exactly.^{1,2} The part of the interaction which is *nondiagonal* in the electron operators usually has a much smaller effect on the energy levels, but its effect on the system can only be determined through some appropriate order in perturbation theory. The presence of the nondiagonal part of the interaction in the density operator for thermal averages can, therefore, be a considerable nuisance in calculations, and it is desirable to have a criterion for determining how significant its contribution to the thermal averaging process is in a particular situation (and thus, e.g., whether it might be neglected in the density operator for some system).

For this reason, we have performed a calculation of the changes in the average total energy and in the population of electron and phonon levels induced by the interaction of a trapped-electron center with the lattice vibrations. More specifically, expressions have been obtained for the changes in the occupation of phonon levels produced by the nondiagonal part of the electron-phonon interaction, and for the changes in the average energy and the occupation of electron levels produced by the diagonal and nondiagonal parts of the interaction separately. Knowledge of the magnitudes of these changes is adequate to determine the importance of the diagonal and nondiagonal parts of the electron-phonon interaction in the thermal averaging process in the large majority of problems of interest. The derivation has been performed by noting that though the changes of the energy and thermal properties due to the nondiagonal part of the interaction are not exactly calculable, even for strong electron-phonon coupling (i.e., large lattice distortion by the electron), they are frequently small enough so that they may be adequately handled in the lowest nonvanishing order in perturbation theory. By combining an exact treatment of the large, diagonal part of the interaction Hamiltonian with a perturbation treatment of the smaller, nondiagonal part, one may then make an accurate calculation of the energy and thermal effects of the electron-phonon interaction even in the strong-coupling case. The mathematical details of this approach are developed in Sec. II, and the relations derived there are applied in Sec. III to the study of a simple but nontrivial model comprised of a single phonon mode interacting with a two-level electron system. The numerical results

obtained for this model indicate that even though the nondiagonal part of the interaction typically has a much smaller effect on the energy eigenvalues of the system than does the diagonal part, its effect in the density operator can be comparable to that of the diagonal part.

II. CALCULATION OF THERMAL EFFECTS DUE TO ELECTRON-PHONON INTERACTION

Consider a single impurity or defect electron trapped in a crystalline lattice that may be strongly distorted by the presence of the electron. The Hamiltonian operator H for such a system in quantized form may be expressed as

$$\begin{aligned} H &= H' + V_u, \quad H' = H_0 + V_d, \quad H_0 = H_a + H_b, \\ H_a &= \sum_i \epsilon_i a_i^\dagger a_i, \quad H_b = \sum_n \omega_n (b_n^\dagger b_n + \frac{1}{2}), \\ V_d &= \sum_{i,n} v_{i,n} a_i^\dagger a_i (b_n + b_n^\dagger), \quad v_{i,n} \text{ real}, \\ V_u &= \sum_{i,j,n; i \neq j} v_{i,j,n} a_i^\dagger a_j (b_n + b_n^\dagger), \quad v_{i,j,n} = v_{j,i,n} \text{ real}, \end{aligned} \quad (1)$$

where b_n^\dagger and b_n are the standard raising and lowering operators for the emission or absorption of a phonon of energy ω_n in mode n , and a_i^\dagger and a_i are the creation and annihilation operators for an electron of energy ϵ_i in the state i . The interaction V_d , linear in the phonon coordinates, whose matrix elements $v_{i,n}$ connect an electronic state to itself is the electron-phonon interaction operator responsible for the displacement of the centers of oscillation of the lattice ions by the electron. As stated in the Introduction, for large $v_{i,n}$ it is capable of producing a strong electron-phonon coupling and of introducing large distortions into the lattice. The perturbation V_u , also linear in its phonon coordinates, contains matrix elements $v_{i,j,n}$ which connect different electronic states. In contrast to the $v_{i,n}$, the $v_{i,j,n}$ can ordinarily be adequately handled by perturbation theory because they appear in the perturbation expansions divided by electronic energy differences rather than, merely, by phonon energies.

We can make the effect of the interaction V_d more transparent by defining a set of phonon operators c_n^\dagger , c_n corresponding to the emission or absorption of phonons by lattice oscillators whose centers of oscillation are shifted by the electron. In terms of these phonon operators and a corresponding set of transformed electron operators \hat{a}^\dagger , \hat{a} , the physics of the strongly coupled system has a simple description. To this end, then, let us first introduce the canonical transformation generated by the Hermitian operator^{2,3}

$$\mathfrak{R} = \sum_i g_i \hat{a}_i^\dagger \hat{a}_i = \sum_n C_n (c_n - c_n^\dagger),$$

where

$$g_i = i \sum_n v_{i,n} (c_n - c_n^\dagger) / \omega_n, \quad C_n = i \sum_i v_{i,n} \hat{a}_i^\dagger \hat{a}_i / \omega_n.$$

We set

$$\begin{aligned} a_i &\equiv e^{i\mathcal{R}} \hat{a}_i e^{-i\mathcal{R}} = e^{-i\epsilon_i} \hat{a}_i, \quad a_i^\dagger = e^{i\epsilon_i} \hat{a}_i^\dagger, \\ b_n &\equiv e^{i\mathcal{R}} c_n e^{-i\mathcal{R}} = c_n + i C_n, \quad b_n^\dagger = c_n^\dagger + i C_n, \end{aligned} \quad (2)$$

and note that

$$\begin{aligned} H' &\equiv \mathcal{H}'(a, a^\dagger; b, b^\dagger) \\ &= e^{i\mathcal{R}} \mathcal{H}'(\hat{a}, \hat{a}^\dagger; c, c^\dagger) e^{-i\mathcal{R}} = \bar{H}_a + \bar{H}_c, \end{aligned} \quad (3)$$

where

$$\bar{H}_a = \sum_i \left(\epsilon_i - \sum_n v_{i,n}^2 / \omega_n \right) \hat{a}_i^\dagger \hat{a}_i, \quad \bar{H}_c = \sum_n \omega_n (c_n^\dagger c_n + \frac{1}{2}). \quad (4)$$

The perturbation V_u , similarly, becomes

$$V_u \equiv \mathcal{V}(a, a^\dagger; b, b^\dagger) = e^{i\mathcal{R}} \mathcal{V}(\hat{a}, \hat{a}^\dagger; c, c^\dagger) e^{-i\mathcal{R}}.$$

Now in the absence of any electron-phonon interaction, the average energy and the one-particle electron and phonon distribution functions are

$$\begin{aligned} \langle H_0 \rangle_0 &\equiv Z_0^{-1} \text{Tr} e^{-\beta H_0} H_0, \\ \langle a_i^\dagger a_i \rangle_0 &\equiv Z_0^{-1} \text{Tr} e^{-\beta H_0} a_i^\dagger a_i, \\ \langle b_n^\dagger b_n \rangle_0 &\equiv Z_0^{-1} \text{Tr} e^{-\beta H_0} b_n^\dagger b_n, \end{aligned}$$

where

$$Z_0 \equiv \text{Tr} e^{-\beta H_0}.$$

With the total electron-phonon interaction present, the corresponding quantities are

$$\langle H \rangle \equiv Z^{-1} \text{Tr} e^{-\beta H} H,$$

etc., where of course $Z = \text{Tr} e^{-\beta H}$. The changes produced by the electron-phonon interaction are then

$$\begin{aligned} \Delta \langle H(\beta) \rangle &\equiv \langle H \rangle - \langle H_0 \rangle_0 \\ &= (\langle H \rangle - \langle H' \rangle') + (\langle H' \rangle' - \langle H_0 \rangle_0), \\ \Delta N_i(\beta) &\equiv \langle a_i^\dagger a_i \rangle - \langle a_i^\dagger a_i \rangle_0 \\ &= (\langle a_i^\dagger a_i \rangle - \langle \hat{a}_i^\dagger \hat{a}_i \rangle) + (\langle \hat{a}_i^\dagger \hat{a}_i \rangle - \langle \hat{a}_i^\dagger \hat{a}_i \rangle'), \\ &\quad + (\langle \hat{a}_i^\dagger \hat{a}_i \rangle' - \langle a_i^\dagger a_i \rangle_0), \\ \Delta N_n(\beta) &\equiv \langle b_n^\dagger b_n \rangle - \langle b_n^\dagger b_n \rangle_0 \\ &= (\langle b_n^\dagger b_n \rangle - \langle c_n^\dagger c_n \rangle) + (\langle c_n^\dagger c_n \rangle - \langle c_n^\dagger c_n \rangle'), \\ &\quad + (\langle c_n^\dagger c_n \rangle' - \langle b_n^\dagger b_n \rangle_0), \end{aligned}$$

where the quantities of interest have been expressed as sums of several terms by introducing, in addition to the thermal averages with respect to H and H_0 defined earlier, the average

$$\langle \dots \rangle' = (\text{Tr} e^{-\beta H'})^{-1} \text{Tr} e^{-\beta H'} \dots.$$

From (1), (3), and (4) one finds immediately that

$$\begin{aligned} \langle H' \rangle' - \langle H_0 \rangle_0 &= \sum_i \bar{\epsilon}_i e^{-\beta \bar{\epsilon}_i} / \sum_j e^{-\beta \bar{\epsilon}_j} \\ &\quad - \sum_i \epsilon_i e^{-\beta \epsilon_i} / \sum_j e^{-\beta \epsilon_j}, \end{aligned} \quad (5)$$

$$\begin{aligned} \langle \hat{a}_i^\dagger \hat{a}_i \rangle' - \langle a_i^\dagger a_i \rangle_0 &= e^{-\beta \bar{\epsilon}_i} / \sum_j e^{-\beta \bar{\epsilon}_j} \\ &\quad - e^{-\beta \epsilon_i} / \sum_j e^{-\beta \epsilon_j}, \end{aligned}$$

$$\text{where } \bar{\epsilon}_i = \epsilon_i - \sum_n v_{i,n}^2 / \omega_n.$$

Also one sees from (2) that $a_i^\dagger a_i = \hat{a}_i^\dagger \hat{a}_i$, so that

$$\langle a_i^\dagger a_i \rangle - \langle \hat{a}_i^\dagger \hat{a}_i \rangle = 0.$$

Finally, from (3) and (4) one concludes that

$$\langle c_n^\dagger c_n \rangle' = \langle b_n^\dagger b_n \rangle_0.$$

Thus the only unknown contributions to $\Delta \langle H(\beta) \rangle$ and $\Delta N_i(\beta)$ are, respectively,

$$\delta \langle H(\beta) \rangle \equiv Z^{-1} \text{Tr} e^{-\beta H} - Z'^{-1} \text{Tr} e^{-\beta H'} H' \quad (6a)$$

and

$$\delta N_i^c(\beta) \equiv Z^{-1} \text{Tr} e^{-\beta H} \hat{a}_i^\dagger \hat{a}_i - Z'^{-1} \text{Tr} e^{-\beta H'} \hat{a}_i^\dagger \hat{a}_i. \quad (6b)$$

The contributions to $\Delta N_n(\beta)$ are the quantity

$$\delta N_n^c(\beta) \equiv Z^{-1} \text{Tr} e^{-\beta H} c_n^\dagger c_n - Z'^{-1} \text{Tr} e^{-\beta H'} c_n^\dagger c_n \quad (6c)$$

and the term $\langle b_n^\dagger b_n \rangle - \langle c_n^\dagger c_n \rangle$. Now, the evaluation of this last term is tedious. Furthermore, in the presence of the electron the c_n^\dagger may more properly be thought of as the creation operators for phonons than may the b_n^\dagger . The quantity $\delta N_n^c(\beta)$ defined by Eq. (6c) will, therefore, be considered effectively the change in the physical phonon distribution function produced by the electron-phonon interaction. (Recall that for the *electronic* distribution function, the distinction between the states produced by \hat{a}_i^\dagger and a_i^\dagger is, for our purposes, immaterial, since $a_i^\dagger a_i = \hat{a}_i^\dagger \hat{a}_i$.)

We now wish to derive explicit expressions for the variations (6a)–(6c) which are correct through second order in the nondiagonal interaction V_u (and to all orders in the diagonal interaction V_d). For this purpose we define the density operator

$$\begin{aligned} \rho(\eta) &= \exp \left[-\sum_i \eta_i^a \hat{a}_i^\dagger \hat{a}_i - \sum_n \eta_n^c c_n^\dagger c_n \right] / \\ &\quad \text{Tr} \exp \left[-\sum_i \eta_i^a \hat{a}_i^\dagger \hat{a}_i - \sum_n \eta_n^c c_n^\dagger c_n \right] \end{aligned} \quad (7)$$

depending on the parameters (η_i) , (η_n) , and use $\rho(\eta)$ to construct the expectation value

$$\langle S(x) \rangle_\eta = \text{Tr} \rho(\eta) S(x) \quad (8)$$

for the scattering operator

$$S(x) = e^{xH'} e^{-xH}. \quad (9)$$

In terms of (8), expressions (6a)–(6c) become

$$\delta \langle H(\beta) \rangle - \frac{d}{d\beta} \left\{ [\ln \langle S(x) \rangle_{\eta}] \right. \\ \left. \eta^{\hat{a}} = \beta \bar{\epsilon}, \eta^c = \beta \omega, x = \beta \right\}, \quad (10a)$$

$$\delta N_i^a(\beta) = - \left[\frac{\partial}{\partial \eta^{\hat{a}}} \ln \langle S(x) \rangle_{\eta} \right]_{\eta^{\hat{a}} = \beta \bar{\epsilon}, \eta^c = \beta \omega, x = \beta} \quad (10b)$$

$$\delta N_n^c(\beta) = - \left[\frac{\partial}{\partial \eta^{\hat{a}}} \ln \langle S(x) \rangle_{\eta} \right]_{\eta^{\hat{a}} = \beta \bar{\epsilon}, \eta^c = \beta \omega, x = \beta} \quad (10c)$$

Expanding $S(x)$ through second order in V_u , using the interaction representation, we obtain

$$\langle S(x) \rangle_{\eta} \approx 1 + \int_0^x dz_1 \int_0^{z_1} dz_2 \langle V_u(z_1) V_u(z_2) \rangle_{\eta}, \quad (11)$$

where $V_u(x) = e^{xH'} V_u e^{-xH'}$.

Since $\rho(\eta)$ commutes with H' , we can perform one of the integrations in (11) and write

$$\langle S(x) \rangle_{\eta} = 1 + \int_0^x dz (x-z) \langle V_u(z) V_u \rangle_{\eta}. \quad (12)$$

Now $\rho(\eta)$ can be factored [see (7)] into

$$\rho(\eta) = \rho_{\hat{a}}(\eta^{\hat{a}}) \rho_c(\eta^c),$$

and $\rho_c(\eta^c)$ satisfies the conditions given by Bloch and de Dominicis⁴ which make it possible to apply a thermal variant of Wick's theorem^{5,6} to the phonon system. Specifically, one defines the "contraction" of a pair of operators A, B containing the c_n, c_m^{\dagger} as

$$A^* B^* \equiv \text{Tr} \rho_c(\eta^c) AB,$$

and deduces that for a product of field operators A, B_j one has

$$\text{Tr} \rho_c(\eta^c) AB_1 \cdots B_n = \sum_{i=1}^n \text{Tr} \rho_c(\eta^c) A^* B_1 \cdots B_i^* \cdots B_n, \quad (13)$$

with similar relations holding for other orientations of A relative to B_j . In particular, one finds

$$c_n^* c_m^{\dagger} \equiv \text{Tr} \rho_c(\eta^c) c_n c_m^{\dagger} = (1 - e^{-\eta_n^c})^{-1} \delta_{nm},$$

$$c_n^* c_m^{\dagger} = c_n^{\dagger} c_m^{\dagger} = 0.$$

We can now apply these relations to the evaluation of $\langle V_u(z) V_u \rangle_{\eta}$ in Eq. (12). If V_u is written as a function of the a_i and c_n , then in the one-electron case it takes the form

$$V_u(x) = \sum_{i,j,n; i \neq j} v_{ij,n} a_i^{\dagger}(x) a_j(x) \\ \times [c_n(x) + c_n^{\dagger}(x) - 2v_{j,n}/\omega_n]. \quad (14)$$

One may evaluate the contractions necessary to calculate the contribution of V_u in (12) by replacing a_i^{\dagger} and a_j in (14) by their expressions in terms of \hat{a}_i^{\dagger} and \hat{a}_j , expanding the component of $\exp[i(g_i - g_j)]$ corresponding to the n th phonon mode in a series,

and using the property of contractions illustrated by (13). By resumming the resulting expressions and transforming from the $\hat{a}_i^{\dagger}, \hat{a}_j$ to the a_i^{\dagger}, a_j , one then finds

$$\begin{aligned} c_n^*(x) [a_i^{\dagger}(z) a_j(z)]^* &= [(v_{i,n} - v_{j,n})/\omega_n] \\ &\times c_n^*(x) c_n^{\dagger}(z) [a_i^{\dagger}(z) a_j(z)], \\ [a_i^{\dagger}(z) a_j(z)]^* c_n^*(x) &= [(v_{i,n} - v_{j,n})/\omega_n] \\ &\times c_n^{\dagger}(z) c_n^*(x) [a_i^{\dagger}(z) a_j(z)], \\ c_n^{\dagger}(x) [a_i^{\dagger}(z) a_j(z)]^* &= -[(v_{i,n} - v_{j,n})/\omega_n] \\ &\times c_n^{\dagger}(x) c_n^*(x) [a_i^{\dagger}(z) a_j(z)], \\ [a_i^{\dagger}(z) a_j(z)]^* c_n^{\dagger}(x) &= -[(v_{i,n} - v_{j,n})/\omega_n] \\ &\times c_n^{\dagger}(x) c_n^*(x) [a_i^{\dagger}(z) a_j(z)]. \end{aligned} \quad (15)$$

By using (13)–(15) in (12) and noting that $c_n(x) = e^{-x\omega_n} c_n$, one obtains the result

$$\begin{aligned} \langle S(x) \rangle_{\eta} &= 1 + \sum_{i,j,nm; i \neq j} v_{ij,n} v_{ji,m} \langle \hat{a}_i^{\dagger} \hat{a}_i \rangle_{\eta} \\ &\times \int_0^x dz (x-z) L_{ij,nm}(z; \eta^c), \end{aligned} \quad (16)$$

where

$$\begin{aligned} \langle \hat{a}_i^{\dagger} \hat{a}_i \rangle_{\eta} &= \text{Tr} \rho(\eta) \hat{a}_i^{\dagger} \hat{a}_i = e^{-\eta^{\hat{a}}_i} / \sum_j e^{-\eta^{\hat{a}}_j}, \\ L_{ij,nm}(z; \eta^c) &= \{ [e^{z\omega_n} N_0(\eta_n^c) \\ &+ e^{-z\omega_n} (N_0(\eta_n^c) + 1)] \delta_{nm} + F_{ij,n}(z; \eta^c) \\ &\times F_{ij,m}(z; \eta^c) \} K_{ij}(z; \eta^c), \\ F_{ij,n}(z; \eta^c) &= \omega_n^{-1} [(v_{i,n} + v_{j,n}) + (v_{i,n} - v_{j,n}) \\ &\times \{ e^{-z\omega_n} [N_0(\eta_n^c) + 1] - e^{z\omega_n} N_0(\eta_n^c) \}], \\ K_{ij}(z; \eta^c) &= \frac{\text{Tr} \rho(\eta) a_i^{\dagger}(z) a_j(z) a_i^{\dagger} a_i}{\text{Tr} \rho(\eta) a_i^{\dagger} a_i}, \\ N_0(\eta_n^c) &= (e^{\eta_n^c} - 1)^{-1}. \end{aligned} \quad (17)$$

We have removed c and c^{\dagger} from (12) through contraction and then applied (3), (4), and (7). The function $K_{ij}(z; \eta^c)$ given by (17) can be calculated by a number of procedures.^{7,8} [See also the calculation of $K_{ij}^0(s)$ in Ref. 3; then let $s \rightarrow -iz, \beta\omega \rightarrow \eta^c$.] Its value is found to be

$$\begin{aligned} K_{ij}(z; \eta^c) &= e^{z(\bar{\epsilon}_i - \bar{\epsilon}_j)} \\ &\times \exp \left\{ - \sum_m \left(\frac{v_{i,m} - v_{j,m}}{\omega_m} \right)^2 \frac{N_0(z\omega_m) - N_0(\eta_m^c)}{[N_0(z\omega_m) + 1] N_0(z\omega_m)} \right\}. \end{aligned} \quad (18)$$

This completes the formal solution to the problem, as expressions (10) can now be calculated by first substituting (18) into (17) and (17) into (16) and then taking the logarithm and differentiating and evaluating or evaluating and differentiating as the case may be. In the case of $\delta N_i^{\hat{a}}(\beta)$ the differentiation with respect to $\eta_i^{\hat{a}}$ is trivial. In the case of $\delta N_n^c(\beta)$ we use the fact that

$$\frac{d}{d\eta_n^c} N_0(\eta_n^c) = -N_0(\eta_n^c)[N_0(\eta_n^c) + 1] .$$

The energy $\delta \langle H(\beta) \rangle$ can be obtained from the slope of the \ln function defined in (10). In the calculation of $\delta \langle H(\beta) \rangle$ and the $\delta N_i^a(\beta)$ the summations over phonon modes can be approximated in the usual fashion by an integration with an appropriate phonon-mode density, when this is convenient. The actual evaluation of the integral(s) over z can be performed by numerical methods. Explicit expressions for the integrated quantities in terms of elementary functions can apparently be obtained only by making various approximations.

It is interesting to note that the average value of V_u can be expressed in terms of the calculated quantities in the form

$$Z^{-1} \text{Tr } e^{-\beta H} V_u = \delta \langle H(\beta) \rangle$$

$$- \sum_i \bar{\epsilon}_i \delta N_i^a(\beta) - \sum_n \omega_n \delta N_n^c(\beta) .$$

It should also be commented that the so-called non-radiative transition probability per unit time between electronic states i and j , $w_{ij}(\beta)$, can be obtained from the relations

$$2 \frac{d}{dx} \langle S(x) \rangle_\eta = \sum_{i \neq j} \langle \hat{a}_i^\dagger \hat{a}_i \rangle_\eta W_{ij}(x, \eta^c) ,$$

$$w_{ij}(\beta) = \text{Im}[W_{ij}(i_\infty, \beta\omega)] . \quad (19)$$

In Ref. 3, the $w_{ij}(\beta)$ were calculated from the optical spectral functions by assuming that there exists a single relatively small range of phonon frequencies for which the electron-phonon interaction is large, and that in this frequency range the approximate relation

$$v_{ij,n} \cong \lambda_{ij}^0 (v_{i,n} - v_{j,n}) , \quad \lambda_{ij}^0 = -\lambda_{ji}^0 ,$$

is valid. The $w_{ij}(\beta)$ were then used to determine the nonradiative transition rates $^4A_2 \rightarrow ^4T_2$ (Cr^{3+} in Al_2O_3) and $^3T_1 \rightarrow ^3T_2$ (V^{3+} in Al_2O_3) using a set of phonon modes centered around 194 cm^{-1} . Use of Eqs. (19) to evaluate the $w_{ij}(\beta)$ allows one to avoid both these restrictions on the range of validity of

the results. For instance, the techniques of Ref. 3 would allow one to calculate transition rates for electronic coupling to *either* acoustical- *or* optical-phonon modes. The methods of the present paper make it possible to consider cases where both types of coupling appear simultaneously.

III. APPLICATION TO A DEFECT-LATTICE MODEL

Since the relations describing the thermal effects of the electron-phonon interaction which have been derived in Sec. II can hardly be said to yield a transparent picture of the behavior of the system under introduction of the electron-phonon interaction, it is helpful to apply the results given there to the actual numerical calculation of $\delta \langle H(\beta) \rangle$, $\delta N_i^a(\beta)$, and $\delta N_n^c(\beta)$ for a particular system. Such an application can also serve the purpose of illustrating that the nondiagonal part of the electron-phonon interaction can usually be treated by perturbation methods even in the case of strong electron-phonon coupling. The system considered will be one comprised of a two-level electron system interacting with a single phonon mode. In Eqs.(16)–(18), the indices i and j will then take on the values 1 and 2 only, while the indices n and m can only assume the value 1 and will, therefore, be dropped. Furthermore, it will be assumed that the ϵ_i and b_n appearing in the Hamiltonian have been chosen so that v_{11} , the diagonal interaction matrix element coupling the electronic ground state to the phonon mode is zero. (Such a choice can always be made.) It is then possible to express all the quantities referring to the interaction matrix elements in terms of two parameters

$$S = v_2^2/\omega^2$$

(where ωS is half the Stokes shift for the system) and

$$\lambda = v_{12} = v_{21} .$$

The calculation of the derivatives necessary for the evaluation of $\delta N_i^a(\beta)$ and $\delta N_n^c(\beta)$ is straightforward, though tedious. One finds that

$$\delta N_1^a(\beta) = -\frac{\lambda^2}{2 \cosh^2(\frac{1}{2}\beta\omega_{12})} \int_0^\beta dz (\beta - z) \left\{ \frac{\sinh \omega_{12} z \cosh \omega(z - \frac{1}{2}\beta)}{\sinh(\frac{1}{2}\beta\omega)} + S \sinh \omega_{12} z \left[1 + \frac{\sinh^2 \omega(z - \frac{1}{2}\beta)}{\sinh^2(\frac{1}{2}\beta\omega)} \right] \right. \\ \left. - 2S \frac{\cosh z \omega_{12} \sinh \omega(z - \frac{1}{2}\beta)}{\sinh(\frac{1}{2}\beta\omega)} \right\} \exp \left\{ S \frac{[e^{z\omega} + e^{\omega(\beta-z)} - e^{\beta\omega} - 1]}{(e^{\beta\omega} - 1)} \right\} , \quad (20)$$

$$\delta N_2^a(\beta) = -\delta N_1^a(\beta) , \quad (21)$$

$$\delta N^c(\beta) = -\frac{\lambda^2}{\cosh \frac{1}{2}\beta\omega_{12}} \int_0^\beta dz (\beta - z) \left\{ \frac{\cosh \omega_{12} (z - \frac{1}{2}\beta)}{\sinh^2(\frac{1}{2}\beta\omega)} \left[\frac{1}{2} \cosh z \omega + S \left(\frac{\sinh^2(\frac{1}{2}z\omega) \cosh \omega(z - \frac{1}{2}\beta)}{\sinh \frac{1}{2}\beta\omega} \right) \right] \right\} ,$$

$$\begin{aligned}
 & + \frac{\sinh z\omega \sinh \omega(z - \frac{1}{2}\beta)}{\sinh(\frac{1}{2}\beta\omega)} \Big) + S^2 \left(\sinh^2(\frac{1}{2}z\omega) + \frac{\sinh^2(\frac{1}{2}z\omega) \sinh^2 \omega(z - \frac{1}{2}\beta)}{\sinh^2(\frac{1}{2}\beta\omega)} \right) \Big] + \frac{\sinh \omega_{12}(\frac{1}{2}\beta - z)}{\sinh^2(\frac{1}{2}\beta\omega)} \\
 & \times \left[S \sinh z\omega + 2S^2 \frac{\sinh^2(\frac{1}{2}z\omega) \sinh \omega(z - \frac{1}{2}\beta)}{\sinh(\frac{1}{2}\beta\omega)} \right] \Big\} \exp \left\{ \frac{S [e^{z\omega} + e^{\omega(\beta-z)} - e^{\beta\omega} - 1]}{(e^{\beta\omega} - 1)} \right\}, \quad (22)
 \end{aligned}$$

where $\omega_{12} = \bar{\epsilon}_2 - \bar{\epsilon}_1$.

Somewhat more easily, one can verify that

$$\begin{aligned}
 \delta \langle H(\beta) \rangle = & - \frac{d}{d\beta} \frac{\lambda^2}{\cosh(\frac{1}{2}\beta\omega_{12})} \int_0^\beta dz (\beta - z) \left\{ \cosh \omega_{12} (z - \frac{1}{2}\beta) \left[\frac{\cosh \omega(z - \frac{1}{2}\beta)}{\sinh \frac{1}{2}\beta\omega} + S \left(1 + \frac{\sinh^2 \omega(z - \frac{1}{2}\beta)}{\sinh^2 \frac{1}{2}\beta\omega} \right) \right] \right. \\
 & \left. + 2S \frac{\sinh \omega_{12}(\frac{1}{2}\beta - z) \sinh \omega(z - \frac{1}{2}\beta)}{\sinh \frac{1}{2}\beta\omega} \right\} \exp \left\{ \frac{S [e^{z\omega} + e^{\omega(\beta-z)} - e^{\beta\omega} - 1]}{(e^{\beta\omega} - 1)} \right\}. \quad (23)
 \end{aligned}$$

These expressions permit one to make a straightforward numerical evaluation of the quantities of interest.

Calculation of $\delta \langle H(\beta) \rangle$, $\delta N_1^a(\beta)$, and $\delta N^c(\beta)$ was carried out for a phonon frequency ω of 10^{13} sec $^{-1}$. The electronic-transition frequency was taken to be 10^{14} sec $^{-1}$, far out in the infrared. Choosing such a low electronic transition energy maximizes the problems encountered in treating the nondiagonal interaction V_u by perturbation theory, so that the fact that V_u can (as will be seen) be adequately handled by this method here is a strong indication that the method can be used quite successfully for the more usual situation of electronic transitions

in the visible or near infrared regions. S values of 0, 1, and 6 are used to cover the range from a vanishing to a rather large distortion of the lattice by the electron. The off-diagonal interaction matrix element v_{12} is somewhat arbitrarily taken to be the same for all three S values, namely, one-half the diagonal matrix element v_2 for $S = 6$. (If the electronic transition frequency had been chosen in the near infrared, then v_{12} could have been taken equal to or somewhat greater than v_2 without any complications.)

Before displaying the results of calculating the expressions given by Eqs. (20), (22), (23), we first give in Figs. 1 and 2 the change produced in the average energy and the population of the electronic ground state by the *diagonal* part of the electron-phonon interaction. These changes have been calculated for the parameters mentioned earlier and for a range of temperatures from 20 to 600 °K by using Eqs. (5). The quantities $\delta \langle H(\beta) \rangle$, $\delta N_1^a(\beta)$, and $\delta N^c(\beta)$ are then given in Figs. 3, 4, and 5, respectively. The total change in the average energy as a consequence of the electron-phonon interaction is the sum of the contributions shown in Figs. 1 and 3, and the total change in the electronic ground-state population is the sum of the contributions shown in Figs. 2 and 4. As noted earlier, the change in the *physical* phonon number is essentially given in full by $\delta N^c(\beta)$, shown in Fig. 5. To aid in the interpretation of these calculated shifts, plots of the unperturbed phonon and ground-state-electron populations as functions of temperature are given in Fig. 6.

Figures 2 and 4 show that from about liquid-nitrogen temperatures upward over a wide temperature interval both the diagonal and nondiagonal parts of the electron-phonon interaction produce quite significant variations of the average electronic ground-state population from its noninteracting value. (The effect of V_u is of course non-vanishing even at 0 °K since, unlike V_d , this part

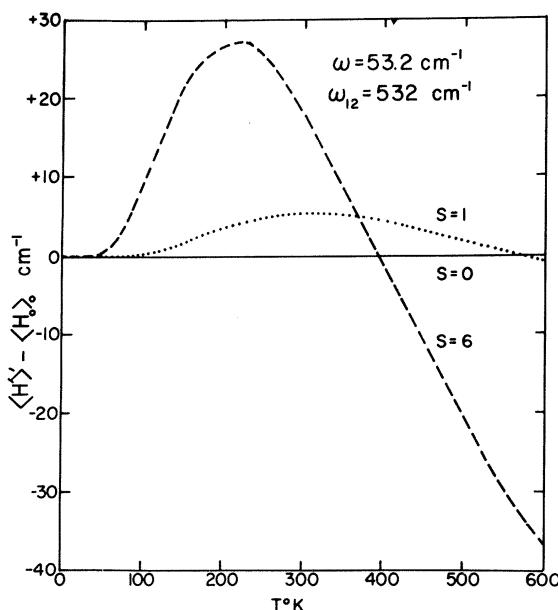


FIG. 1. The change $\langle H' \rangle - \langle H_0 \rangle_0$ in the average energy of the system produced by the diagonal part of the electron-phonon interaction.

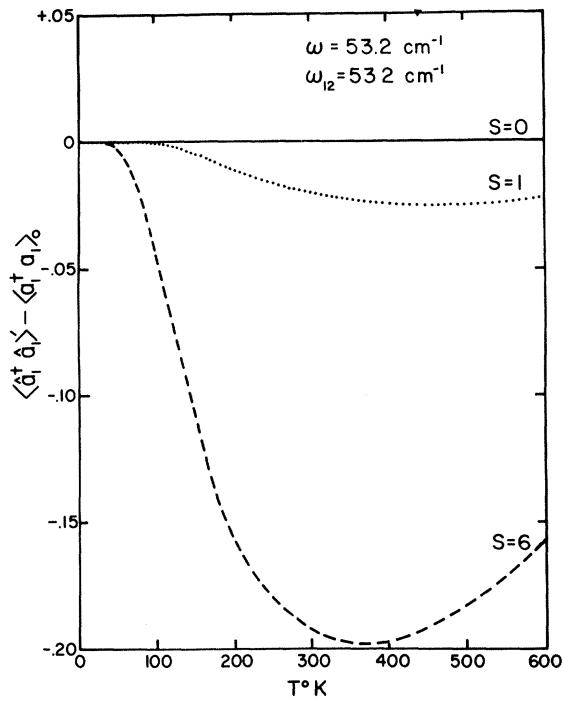


FIG. 2. The change $\langle \hat{a}_1^\dagger \hat{a}_1 \rangle' - \langle \hat{a}_1^\dagger \hat{a}_1 \rangle_0$ in the population of the electronic ground state produced by the diagonal part of the electron-phonon interaction.

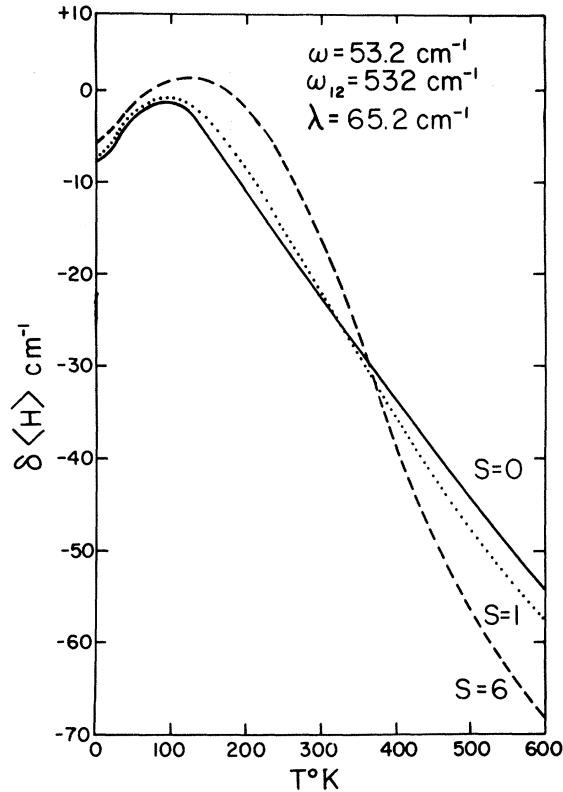


FIG. 3. The change $\delta \langle H(\beta) \rangle$ in the average energy of the system produced by V_u .

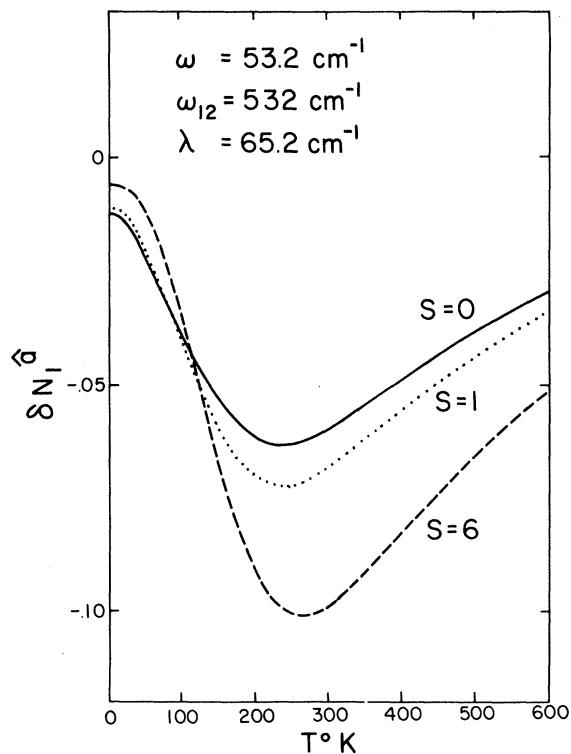


FIG. 4. The change $\delta N_1^2(\beta)$ in the population of the electronic ground state produced by V_u .

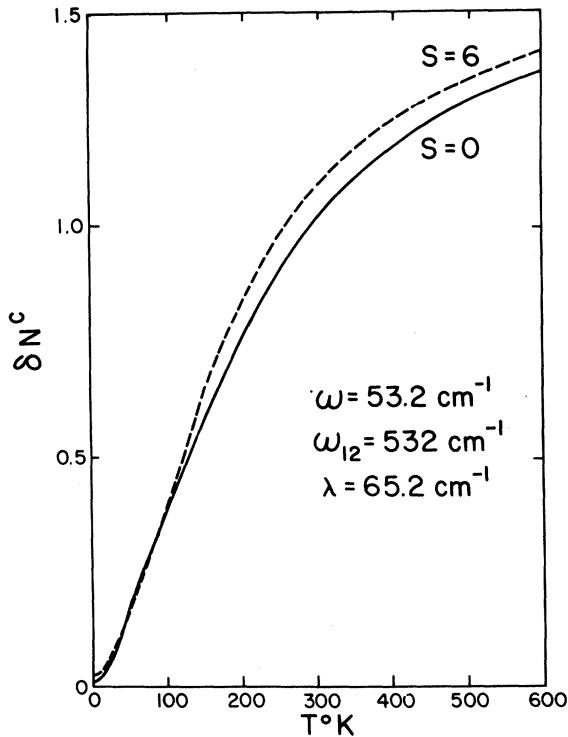


FIG. 5. The change $\delta N^c(\beta)$ in the average phonon number produced by V_u .

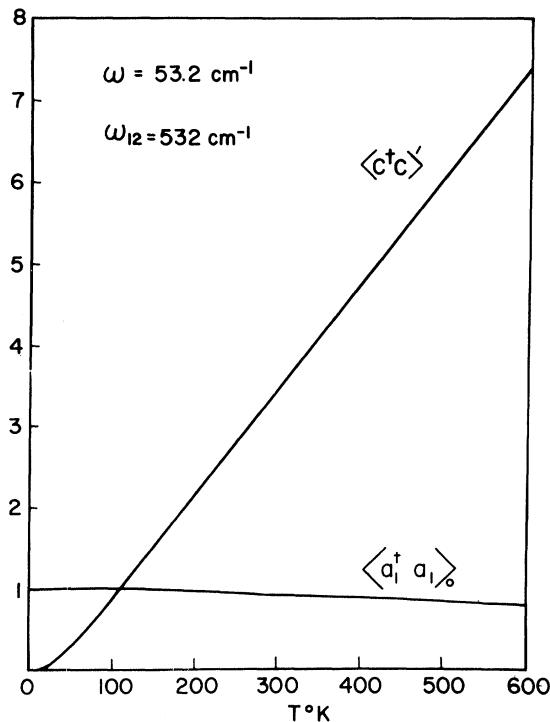


FIG. 6. The unperturbed phonon and ground-state-electron populations as functions of temperature. As mentioned in the text, $\langle c^\dagger c \rangle' = \langle b^\dagger b \rangle_0$.

of the interaction has the ability to mix electronic states.) It is also interesting to observe that the contributions of V_d and V_u to the population change of the ground state are of comparable size, and that the effect of V_u is not strongly dependent on the strength of the diagonal part V_d . Presumably the first of these characteristics is due to the fact just mentioned that V_u is capable of directly mixing the electronic states, while V_d can only alter the behavior of the electronic ground-state population by changing the temperature at which thermal excitation out of the electronic ground state becomes appreciable (by shifting the energy difference between the electronic states).

Figures 1 and 3 show that over the temperature range considered the contributions of V_d and V_u to the change of the average energy are also comparable, with the effect of V_u actually dominating in much of the region. The comparability of these contributions arises from two causes. The first is peculiar to the model, and is simply due to the fact that the choice $v_1 = 0$ forces H' and H_0 to have the same ground-state energy and thus the same low-temperature averages. The second is that only V_u shifts the phonon levels,¹⁰ and though the shift of the lowest-lying phonon levels by V_u is, in general, small compared to the shift of the electronic levels by V_d (in this case approximately 15

and 3% of the latter for $S = 1$ and 6, respectively), the proximity of excited-phonon levels to the ground state allows them to have a relatively greater effect on energy averages at low temperatures. The initial rise of the curves in Figs. 1 and 3 (except for the $S = 0$ curve in Fig. 1) from their values at 0°K occurs because both V_d and V_u depress the energy eigenvalues of the low-lying states relative to the ground state, and thus cause more rapid population of these excited states with increasing temperature. The subsequent falling behavior of the curves is due to this same depression of the energy levels; however, the decreased energy of the excited states becomes more important than the accelerated population of these states once a certain temperature is passed.

The change in phonon number shown in Fig. 5 again is a nonnegligible correction to the phonon number for the noninteracting system (cf. Fig. 6). As in the case of δN_1^2 , the strength of the diagonal part of the interaction has little effect on the shift of the phonon occupation number by V_u ; in fact, the $S = 1$ curve is omitted from the figure because it is so nearly coincident with the curve for $S = 0$.

One point worth noting is that the curves in Figs. 1, 3, 4, and 5 all contain crossover points; and in Fig. 5, the curves shown cross twice. In the case of Figs. 1 and 3, this crossing is due to the manner, described earlier, in which the depression of the energy levels by the interaction initially (i.e., for low temperatures) raises the average energy and then subsequently brings it down again. Presumably the behavior of the curves in Figs. 4 and 5 is related to this effect.

Examination of the six figures shows then, that in the model considered the statistical effects of the diagonal and nondiagonal parts of the electron-phonon-interaction Hamiltonian are comparable to each other, and produce a significant alteration in the average values calculated from a density matrix based on the noninteracting Hamiltonian H_0 alone. Because of the simple character of the model, it is not possible to extrapolate these conclusions to a general class of physical systems; calculations based on the expressions derived in Sec. II are necessary in each such case to determine the significance of the statistical effects of the two parts of the interaction Hamiltonian. However, the model studied here is sufficiently realistic to indicate, on the basis of the above results, that the many calculations done in the past in which the thermal effects of the diagonal and/or nondiagonal parts of the electron-phonon interaction were neglected¹¹ should be considered as at best of semiquantitative significance pending justification of the use of such an approximate density operator.

Two final comments need to be made about the

results obtained here from the application of the general theory of Sec. II to our model. The first one is the obvious statement that the numerical results given may easily be adapted to other values of λ by simply noting that λ^2 appears multiplicatively in $\delta \langle H \rangle$, $\delta N_1^{\frac{1}{2}}$, and δN_c . A less obvious fact is that the numerical results for $\delta \langle H \rangle$ and $\delta N_1^{\frac{1}{2}}$ for this case of a two-level electron interacting with a single-phonon mode can also be applied to the situation of a two-level electron interacting with an Einstein-model lattice if one assumes that for the

phonon modes coupled to the electron the approximation¹²

$$v_{12,n} = \alpha v_{2,n}$$

is adequate. In this case

$$S = \sum_n v_{2,n}^2 / \omega^2 ,$$

where $\omega \equiv \omega_n$ is the Einstein frequency, and

$$\lambda^2 = \sum_n v_{12,n}^2 = \alpha^2 \omega^2 S .$$

It has again been assumed that $v_{1,n} = 0$, all n .

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⁴C. Bloch and C. DeDominicis, Nucl. Phys. 7, 459 (1958).

⁵For a discussion of the pertinent points regarding Wick's theorem see, e.g., N. N. Bogoliubov and D. V. Shirkov, *Introduction to the Theory of Quantized Fields* (Interscience, New York, 1959), p. 421.

⁶For a more detailed discussion of an application of this "thermal Wick's theorem," see D. W. Howgate and C. A. Coulter, Lettere al Nuovo Cimento 1, 210 (1969).

⁷M. Lax, J. Chem. Phys. 20, 1752 (1952).

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⁹Compare expressions (12) and (19) of this paper with expression (19) of Ref. 3.

¹⁰The statement that V_u "shifts the phonon levels" is

used loosely here to express the fact that if $|i, n\rangle'$ and $|i, n+1\rangle'$ are eigenstates of H' corresponding to electronic state i and phonon number n and $n+1$, respectively, then the energy difference ω between these states is different from the energy difference between the H eigenstates $|i, n\rangle$ and $|i, n+1\rangle$ obtained continuously from the H' eigenstates $|i, n\rangle'$, $|i, n+1\rangle'$ by gradually turning on the interaction V_u .

¹¹K. Huang and A. Rhys, Proc. Roy. Soc. (London) A204, 406 (1950); M. Lax and E. Burstein, Phys. Rev. 100, 592 (1955); E. D. Trifonov, Fiz. Tverd. Tela 6, 462 (1964) [Soviet Phys. Solid State 6, 366 (1964)]; D. E. McCumber, Phys. Rev. 133, A163 (1964); to mention only a few references selected at random.

¹²For use of such an approximation in the treatment of electron-phonon interactions see, in addition to Ref. 3, A. Kiel, in *Proceedings of the Third International Conference on Quantum Electronics*, edited by P. Grivet and N. Bloembergen (Columbia U. P., New York, 1964), p. 765.