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Comments on exciton phonon coupling: Temperature dependence

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We discuss upper bounds to the free energy of an exciton interacting with a lattice of phonons with a linear coupling. From these upper bounds, we find the effective number of phonons clothing an exciton to vary with exciton bandwidth and temperature. The possibility of an *abrupt* transition from a delocalized to a localized exciton with an increase in temperature is discussed.

I. INTRODUCTION

In the present paper, we will discuss the free energy of an exciton interacting with a lattice of phonons. We will consider only linear exciton phonon coupling, and we will be content to compute upper bounds to free energy using the Peierls and Bogoliubov theorems. We will be interested in the importance of our results for exciton mobility and spectral properties, and will show the possibility of an abrupt change in the nature of the exciton as temperature increases.

In Sec. II, we define the Hamiltonian with which we will work and discuss certain unitary transformations of that Hamiltonian. In Sec. III we discuss the Bogoliubov and Peierls bounds to the free energy and apply these to our model Hamiltonian. In Sec. IV, we discuss the computation of the number of phonons surrounding the exciton. This is a measure of (a) the effective mass of the exciton (as the number of phonons increases so does the effective mass and thus the mobility decreases) (b) the extent of lattice deformation of the exciton (and the localization of the exciton) and (c) the intensity of the zero phonon line [which varies as $\exp(-\langle N_{ph}\rangle)$, where $\langle N_{ph}\rangle$ is the number of phonons in the cloud surrounding the exciton]. In Sec. V, we apply these results to a particularly simple model of exciton–phonon interaction and find how the free energy and $\langle N_{ph}\rangle$ change with exciton bandwidth, exciton phonon coupling strength and temperature.

II. THE HAMILTONIAN

We will deal solely with a model of exciton–phonon interaction in which the coupling is linear in the phonon coordinate. This model has been examined by Merrifield,[1] Grover and Silbey,[2,3] Fisher and Rice,[4] and Nakamura[5] and the analogous electron phonon model has been examined by Holstein,[6] Toyozawa,[7] Emin,[8] and Cho and Toyozawa.[9] Of these, only the work of Merrifield and Nakamura are variational in nature. The Hamiltonian, in second quantized form is given by

$$H = H_{ex} + H_{ph} + H_{int} \ , \qquad (2.1)$$

where

$$H_{ex} = \sum_n E_0 a_n^+ a_n + \sum_{n,m} J_{nm} a_n^+ a_m \ , \qquad (2.2)$$

$$H_{ph} = \sum_q \omega_q (b_q^+ b_q + \tfrac{1}{2}) \ , \qquad (2.3)$$

and

$$H_{int} = N^{-1/2} \sum_{n,q} X_q^n \omega_q (b_q + b_{-q}^+) a_n^+ a_n \ . \qquad (2.4)$$

Here, H_{ex} is the Hamiltonian for a single band of Frenkel excitons in a perfect rigid crystal with E_0 the electronic excitation energy of a single molecule and J_{nm} being the usual resonance transfer integral between molecules at site n and site m. H_{ph} is the free harmonic phonon Hamiltonian with ω_q being the frequency of the normal mode of wave vector q. The operators a_n and a_n^+ destroy and create an excitation on site n, while b_q and b_q^+ destroy and create a phonon of wave vector q. The interaction term represents the interaction of an electronic excitation at site n with phonons of wave vector q. Translational symmetry requires that J_{nm} be a function of $\mathbf{R}_n - \mathbf{R}_m$ only and that $X_q^n = e^{i\mathbf{R}_n \cdot \mathbf{q}} c_q$, where $c_q = c_{-q}^*$.

There are three characteristic energies in the problem: (a) the Debye frequency (or molecular vibrational frequency) ω_0 ($\hbar = 1$ in all that follows); (b) the exciton (or electron) bandwidth Δ where

$$\Delta = 2\sum_n J_{nm} = 2\sum_n J(\mathbf{R}_n - \mathbf{R}_m) \ ; \qquad (2.5)$$

and (c) the strength of the exciton phonon coupling S where

$$S = N^{-1} \sum_q |X_q^n|^2 \omega_q \ . \qquad (2.6)$$

In molecular crystals, it is often the case that $\Delta < \omega_0$ (although some exceptions do arise) and that Δ and S are of the same magnitude.

In the polaron problem,[7] it is usually assumed that $\Delta \gg \omega_0$ and S varies from small compared to Δ (large polaron) to large compared to Δ (small polaron). As the coupling strength S increases (at 0 K), the polaron becomes localized. If $\Delta \gg \omega_0$ the prediction is that this localization (as measured by the effective bandwidth or number of phonons carried by the electron) is an abrupt transition. If $\Delta \lesssim \omega_0$, the transition (at 0 K) is not abrupt, but instead occurs in a smooth manner. The effect of temperature on this transition is not well understood.

In the exciton case, E_0 is large compared with $k_B T (\equiv \beta^{-1})$ so that we need only consider single exciton states. A typical basis function is given by

$$a_n^+ \prod_q (n_q!)^{-1/2} (b_q^+)^{n_q} |0\rangle_{ph} |0\rangle_e \ , \tag{2.7}$$

where $|0\rangle_{ph}$ is the phonon vacuum state and $|0\rangle_e$ the ground electronic state of the isolated molecule.

In the P, Q representation of the phonon momentum and coordinates, we can write

$$H_{ph} = \sum_q \tfrac{1}{2}(P_q^2 + \omega_q^2 Q_q^2) \tag{2.8}$$

and

$$H_{int} = N^{-1/2} \sum_{nq} K_q^n Q_q a_n^+ a_n \ , \tag{2.9}$$

where

$$Q_q = (2\omega_q)^{-1/2} (b_q + b_{-q}^+) \ , \tag{2.10}$$

$$P_q = i(\omega_q/2)^{1/2} (b_q - b_{-q}^+) \ , \tag{2.11}$$

$$K_q^n = X_q^n 2^{1/2} \omega_q^{3/2} \ , \tag{2.12}$$

and the system is quantized by requiring

$$[Q_q, P_{q'}] = i\,\delta_{qq'} \ . \tag{2.13}$$

We now transform the basis functions Eq. (2.7) by a unitary transformation $\exp(-U_1)$, where

$$U_1 = N^{-1/2} \sum_{n,q} \bar{X}_q^n a_n^+ a_n (b_q - b_{-q}^+) \tag{2.14a}$$

$$= i N^{-1/2} \sum_{n,q} \bar{K}_q^n a_n^+ a_n P_{-q} \ , \tag{2.14b}$$

and where $\bar{X}_q^n = e^{i R_n \cdot q} f_q$ and $\bar{K}_q^n$ and $\bar{X}_q^n$ are in the same relation (2.12) as K_q^n and X_q^n. This transformation diagonalizes the Hamiltonian in the case $J_{n-m} = 0$ and $\bar{X}_q^n = X_q^n$. In the case $J_{n-m} \neq 0$, it corresponds to translating the origin of phonon coordinates in the direction of the shift of equilibrium position of a localized exciton. Transforming the basis functions is the same as transforming the Hamiltonian, so we find

$$\begin{aligned} \tilde{H} \equiv e^{U_1} H^{-U_1} &= \sum_n \epsilon\, a_n^+ a_n + \sum_q \omega_q (b_q^+ b_q + \tfrac{1}{2}) \\ &+ \sum_{n,m} J_{n-m} a_n^+ a_m \theta_n^+ \theta_m \\ &+ N^{-1/2} \sum_{n,q} (X_q^n - \bar{X}_q^n)\, \omega_q a_n^+ a_n (b_q^+ + b_{-q}) \ , \end{aligned} \tag{2.15}$$

where

$$\begin{aligned} \epsilon &= E_0 - 2N^{-1} \sum_q (X_q^n \bar{X}_q^n - \tfrac{1}{2} |X_q^n|^2)\, \omega_q \ , \\ \theta_n^+ &= \exp\left\{ -N^{-1/2} \sum_q \bar{X}_q^n (b_q^+ - b_{-q}) \right\} \ . \end{aligned} \tag{2.16}$$

Note that if $J_{n-m} = 0$, for all $n - m$, then setting $\bar{X}_q^n = X_q^n$ would result in a diagonal Hamiltonian. In the above we have used the fact that only one exciton states are present. The representation in which $\bar{X}_q^n = X_q^n$ will be referred to as the dressed exciton representation.

Now if the transformation to exciton states of wave vector k is made by defining

$$a_k = N^{-1/2} \sum_n e^{ik \cdot R_n} a_n \ , \tag{2.17}$$

we find

$$\tilde{H} = \tilde{H}_0 + V \equiv \tilde{H}_0 + \sum_{k,k'} V_{kk'} a_k^+ a_{k'} \ , \tag{2.18}$$

where

$$\tilde{H}_0 = \epsilon \sum_k a_k^+ a_k + \sum_q \omega_q (b_q^+ b_q + \tfrac{1}{2}) \ , \tag{2.19}$$

and

$$\begin{aligned} V_{kk'} &= N^{-3/2} \sum_{n,q} (X_q^n - \bar{X}_q^n)\, e^{i(k-k') \cdot R_n} \omega_q (b_q^+ + b_{-q}) \\ &+ N^{-1} \sum_{n,m} J_{n-m} \theta_n^+ \theta_m\, e^{i(k \cdot R_n - k' \cdot R_m)} \ . \end{aligned} \tag{2.20}$$

Note that the average of $V_{kk'}$ over the canonical phonon ensemble can be performed to find

$$\begin{aligned} \langle V_{kk'} \rangle_{ph} &\equiv \mathrm{Tr}_L (e^{-\beta H_{ph}} V_{kk'}) / \mathrm{Tr}_L (e^{-\beta H_{ph}}) \\ &= \delta_{kk'} \sum_n J_{n-m} \langle \theta_n^+ \theta_m \rangle\, e^{ik \cdot (R_n - R_m)} \ , \end{aligned} \tag{2.21}$$

where

$$\begin{aligned} H_{ph} &= \sum_q \omega_q (b_q^+ b_q + \tfrac{1}{2}) \\ \langle \theta_n^+ \theta_m \rangle &= \exp - \left\{ N^{-1} \sum_q |f_q|^2 (1 - \cos \mathbf{q} \cdot \mathbf{R}_{nm}) \coth(\beta \omega_q / 2) \right\} \\ &\equiv \exp - \{ S_0(\mathbf{R}_{nm}, f_q) \} \ , \end{aligned} \tag{2.22}$$

and Tr_L means a trace over the lattice states.

III. UPPER BOUNDS ON THE FREE ENERGY

A. General considerations

The Helmholtz free energy A for a system defined by a Hamiltonian H operating on a separable Hilbert space spanned by the orthonormal set $|i\rangle$ at temperature T and volume V is given by

$$A = -\beta^{-1} \ln \sum_i \langle i | e^{-\beta H} | i \rangle \equiv -\beta^{-1} \ln \mathrm{Tr}\, e^{-\beta H} \ . \tag{3.1}$$

The following inequalities can be demonstrated as a consequence of the convexity of the function $\exp(-x)$[10]:

(i) Bogoliubov's theorem: Let $H = H_0 + V$, then if $\exp(-\beta H)$ and $\exp(-\beta H_0)$ have finite trace for $\beta > 0$,

$$A \leq -\beta^{-1} \ln \mathrm{Tr}\, e^{-\beta H_0} + \langle V \rangle_{H_0} \equiv A_0 + \langle V \rangle_0 \equiv A_B \ , \tag{3.2}$$

where

$$\langle V \rangle_{H_0} = \mathrm{Tr}(e^{-\beta H_0} V) / \mathrm{Tr}(e^{-\beta H_0}) \ . \tag{3.3}$$

(ii) Peierls' theorem: Let $|a\rangle$ be any orthonormal set in the space, then with the same restrictions as above,

$$A \leq -\beta^{-1} \ln \sum_a \exp(-\beta \langle a | H | a \rangle) \ . \tag{3.4}$$

The equality holds if the set $|a\rangle$ is a complete set of eigenfunctions of H. Note that if the Hamiltonian is transformed by a unitary transformation, e^{-U} where $U^+ = -U$,

$$\tilde{H} = e^{-U} H e^{U} = \tilde{H}_0 + \tilde{V} \ , \tag{3.5}$$

then the above upper bounds become

$$A_B \leqslant -\beta^{-1}\ln \mathrm{Tr}\, e^{-\beta \tilde{H}_0} + \langle V\rangle_{\tilde{H}_0} \qquad (3.6)$$

and

$$A_p \leqslant -\beta^{-1}\ln \sum_a \exp -\beta\langle a|\tilde{H}|a\rangle \ . \qquad (3.7)$$

In this paper, the upper bounds will be computed using these forms. A search will be made for the U, which minimizes the right hand side of both inequalities.

Note that if the Hilbert space is partitioned into a set of orthogonal subspaces, e.g., those for different values of the total wave vector, and if the unitary transformation does not mix these subspaces, then the preceding results are valid for the free energy in these subensembles.

B. Application to the exciton–phonon Hamiltonian

In this section, the structure of the Bogoliubov and Peierls bounds to A is considered for the total system defined in Sec. II as well as for the subsystems corresponding to distinct eigenvalues of the total crystal wave vector. Note that the transformation U_1 defined in Eq. (2.14) conserves the total wave vector P and exciton number:

$$e^{U_1} X e^{-U_1} = X \ , \qquad (3.8)$$

where X is either exciton number N_{ex} where

$$N_{ex} \equiv \sum_{\mathbf{k}} a_{\mathbf{k}}^+ a_{\mathbf{k}} = \sum_n a_n^+ a_n \ , \qquad (3.9)$$

or total wave vector $\mathbf{P}$ where

$$\mathbf{P} = \sum_{\mathbf{k}} \mathbf{k}\, a_{\mathbf{k}}^+ a_{\mathbf{k}} + \sum_{\mathbf{q}} \mathbf{q}\, b_{\mathbf{q}}^+ b_{\mathbf{q}} \ . \qquad (3.10)$$

(a) Consider first the Bogoliubov bounds for the free energy of the entire system (A_B^t) and that for a particular eigenvalue of $\mathbf{P}$, say $\mathbf{K}$ ($A_B^{\mathbf{K}}$) with H given in Eq. (2.18):

$$A_B^t = -\beta^{-1}\ln \sum_{\mathbf{k},\{n_{\mathbf{q}}\}} \langle \mathbf{k};\{n_{\mathbf{q}}\}|\, e^{-\beta\tilde{H}_0}|\mathbf{k};\{n_{\mathbf{q}}\}\rangle + \langle V\rangle_{\tilde{H}_0} \ , \qquad (3.11)$$

or

$$A_B^t = \epsilon - \beta^{-1}\ln N - \beta^{-1}\ln q_{ph} + \sum_k \langle \tilde{V}_{\mathbf{kk}}\rangle_{ph}$$
$$= \epsilon - \beta^{-1}\ln N - \beta^{-1}\ln q_{ph} \ , \qquad (3.12)$$

where

$$q_{ph} = \mathrm{Tr}_L\, e^{-\beta H_{ph}} = \prod_{\mathbf{q}} (1 - e^{-\beta\omega_{\mathbf{q}}})^{-1} e^{-\beta\omega_{\mathbf{q}}/2} \qquad (3.13)$$

$$N = \sum_{\mathbf{k}} 1 \ , \qquad (3.14)$$

and $-\beta^{-1}\ln q_{ph}$ is just the phonon contribution to the free energy.

Note that if the zeroth order Hamiltonian is defined differently by adding and subtracting the phonon average of V to H as defined in Eq. (2.18), so that

$$\tilde{H} = h_0 + v \ , \qquad (3.15)$$

$$h_0 = \epsilon \sum_{\mathbf{k}} a_{\mathbf{k}}^+ a_{\mathbf{k}} + \sum_{\mathbf{q}} \omega_{\mathbf{q}}(b_{\mathbf{q}}^+ b_{\mathbf{q}} + \tfrac{1}{2}) + \sum_k \langle V_{\mathbf{kk}}\rangle_{ph}\, a_{\mathbf{k}}^+ a_{\mathbf{k}} \ , \qquad (3.16)$$

$$v = \sum_{\mathbf{k},\mathbf{k}'} [V_{\mathbf{kk}'} - \delta_{\mathbf{kk}'}\langle V_{kk}\rangle_{ph}]\, a_k^+ a_{k'} \ , \qquad (3.17)$$

then $\langle v\rangle_{h_0} = 0$ and the *new* Bogoliubov bound is given by

$$\tilde{A}_B^t = \epsilon - \beta^{-1}\ln q_{ph} - \beta^{-}\ln \sum_{\mathbf{k}} e^{-\beta\langle V_{\mathbf{kk}}\rangle} \ . \qquad (3.18)$$

It is tempting to think of a particular term in the sum over $\mathbf{k}$ as the contribution to the free energy of the subspace corresponding to *total* crystal wave vector $\mathbf{k}$. This is incorrect, as will be shown below.

The evaluation of $A_B^{\mathbf{K}}$, the free energy of system with total crystal wave vector $\mathbf{K}$ will now be considered. The essential difficulty is that each basis function used in the sums must belong to the subspace with a particular value of $\mathbf{P}$, namely $\mathbf{K}$. This difficulty can be circumvented, and the details are given in Appendix A. There it is also shown that the same result can be interpreted as an *upper bound* to the corresponding Peierls bound to A for fixed K ($A_P^{\mathbf{K}}$). In either case, one has to take the traces in the general formulas for the Bogoliubov bounds over only those states with a particular total wave vector. For example, the states of total wave vector K can be written as

$$a_{\mathbf{K}-\mathbf{Q}}^+ \prod_{\mathbf{q}} (n_{\mathbf{q}}!)^{-1/2} (b_{\mathbf{q}}^+)^{n_{\mathbf{q}}} |0\rangle_{ph}|0\rangle_e \equiv |\mathbf{K}-\mathbf{Q};\{n_{\mathbf{q}}\}\rangle \ , \quad (3.19)$$

where

$$\mathbf{Q} = \sum_{\mathbf{q}} \mathbf{q}\, n_{\mathbf{q}} \qquad (3.20)$$

represents the contribution of the phonons to the total wave vector. If one takes $\tilde{H}_0$ and $\tilde{V}$ as given in Eq. (2.18), then the Bogoliubov bound for wave vector $\mathbf{K}$ is

$$A_B^{\mathbf{K}} = \epsilon - \beta^{-1}\ln q_{ph} + \sum_n J_{n-m}\, e^{i\mathbf{K}\cdot\mathbf{R}_{nm}} \langle \theta_n^+ \theta_m\, e^{-i\hat{\mathbf{Q}}\cdot\mathbf{R}_{nm}}\rangle \ , \qquad (3.21)$$

where

$$\hat{\mathbf{Q}} = \sum_q \mathbf{q}(b_{\mathbf{q}}^+ b_{\mathbf{q}}) \ . \qquad (3.22)$$

The average $\langle \theta_n^+ \theta_m\, e^{-i\hat{\mathbf{Q}}\cdot\mathbf{R}_{nm}}\rangle$ is performed in Appendix A, where it is found

$$\langle \theta_n^+ \theta_m\, e^{-i\hat{\mathbf{Q}}\cdot\mathbf{R}_{nm}}\rangle = \prod_{\mathbf{q}} \frac{(1 - e^{-\beta\omega_{\mathbf{q}}})}{(e^{i\mathbf{q}\cdot\mathbf{R}_{nm}} - e^{-\beta\omega_{\mathbf{q}}})} \exp\{-S_{\mathbf{Q}}(\mathbf{R}_{nm}, f_{\mathbf{q}})\} \ , \qquad (3.23)$$

where

$$S_{\mathbf{Q}}(\mathbf{R}_{nm}, f_q) = N^{-1}\sum_q f_q^2 (1 - \cos \mathbf{q}\cdot\mathbf{R}_{nm})$$
$$\times \coth[(\beta\omega_{\mathbf{q}} + i\mathbf{q}\cdot\mathbf{R}_{nm})/2] \ . \qquad (3.24)$$

In the Einstein phonon limit $\omega_q = \omega$, we can evaluate this averages explicitly to find (see Appendix A)

$$A_B^{\mathbf{K}} = \epsilon - \beta^{-1}\ln q_{ph}^E + (1 - e^{-\beta\omega})^N \sum_{\mathbf{a}} J_a\, e^{i\mathbf{K}\cdot\mathbf{a}} e^{-S_{\mathbf{Q}}} \qquad (3.25)$$

or

$$A_B^{\mathbf{K}} = \epsilon - \beta^{-1}\ln q_{ph}^E \ , \qquad (3.26)$$

if $T > 0K$ (see Appendix A).

If the phonon average of $V_{kk'}$ were included in h_0, as was done above, then the Bogoliubov bound on A^K is given, using the states defined above [Eq. (3.19)], by

$$\tilde{A}_B^{\mathbf{K}} = \epsilon - \beta^{-1} \ln q_{\text{ph}} - \beta^{-1} \ln \sum_{n_q} \frac{e^{-\beta \Sigma n_q \omega_q}}{q_{\text{ph}}} e^{-\beta V(\mathbf{K}-\mathbf{Q})} , \quad (3.27)$$

where

$$V(\mathbf{K}-\mathbf{Q}) \equiv \langle V_{\mathbf{K}-\mathbf{Q},\mathbf{K}-\mathbf{Q}} \rangle_{\text{ph}} = \sum_a J_a e^{-S_0(a)} e^{i(\mathbf{K}-\mathbf{Q})\cdot \mathbf{a}} . \quad (3.28)$$

Since $\mathbf{Q}$ is given by a number $(\sum_{\mathbf{q}} \mathbf{q} n_q)$, $\tilde{A}_B^{\mathbf{K}}$ can be written as

$$\tilde{A}_B^{\mathbf{K}} = \epsilon - \beta^{-1} \ln q_{\text{ph}} - \beta^{-1} \ln \langle e^{-\beta V(\mathbf{K}-\hat{\mathbf{Q}})} \rangle_{\text{ph}} , \quad (3.29)$$

where, as in (3.22), $\mathbf{Q} = \sum_q \mathbf{q} b_q^+ b_q$ (the *operator* representing total phonon wave vector). The term $\langle v \rangle_{h_0}$ is very small for $T > 0$ K, for the same reasons as above [see Eq. (3.26)].

These bounds for A^t and $A^{\mathbf{K}}$ are interesting in a number of ways. First, it is clear that choosing H_0 instead of h_0 as the zeroth order Hamiltonian results in a worse upper bound and in a less interesting temperature dependence, as well as a less interesting dependence on the $\{f_q\}$. For example, A_B^t [Eq. (3.12)] depends on the $\{f_q\}$ only in ϵ, and the optimal choice will be $f_q = c_q$. The $\{f_q\}$ dependence in $\tilde{A}_B^t$ occurs also in the $\langle V_{\mathbf{kk}} \rangle$. A similar result occurs for the Bogoliubov bounds on $A^{\mathbf{K}}$.

Note that from the form of $A_B^{\mathbf{K}}$ and $\tilde{A}_B^{\mathbf{K}}$, we can derive the expressions for A_B and $\tilde{A}_B^t$, since

$$e^{-\beta A^t} = \sum_K \exp - \{ \beta A^{\mathbf{K}} \} . \quad (3.30)$$

Thus, from Eq. (3.21), for $T > 0$

$$A_B^t = \epsilon - \beta^{-1} \ln N - \beta^{-1} \ln q_{\text{ph}} , \quad (3.31)$$

where we have assumed that $\langle \theta_n^+ \theta_m e^{-i\hat{\mathbf{Q}}\cdot R_{nm}} \rangle \approx 0$ for $T > 0$. This is in agreement with (3.12). In the same manner, we find

$$\tilde{A}_B^t = \epsilon - \beta^{-1} \ln q_{\text{ph}} - \beta^{-1} \ln \sum_K \langle e^{-\beta V(\mathbf{K}-\hat{\mathbf{Q}})} \rangle_{\text{ph}} . \quad (3.32)$$

It is possible to show that this is equal to Eq. (3.18); however, it also points out the reason why it is incorrect to associate a particular term (in the sum over $\mathbf{K}$) in (3.18) with the free energy for a particular value of *total* wave vector ($\mathbf{K}$).

Now, consider the Peierls bounds for the free energy of the entire system:

$$A_P^t = \epsilon - \beta^{-1} \ln \sum_{\mathbf{k},\{n_q\}} \exp - \beta \left\{ \sum n_q \omega_q + \langle \{n_q\} | V_{\mathbf{kk}} | \{n_q\} \rangle \right\} . \quad (3.33)$$

In Appendix A, the integrals appearing in the exponent of (3.33) are computed and we find

$$A_P^t = \epsilon - \beta^{-1} \ln q_{\text{ph}} - \beta^{-1} \ln \sum_{\mathbf{k}} \langle e^{-\beta \hat{T}(\mathbf{k})} \rangle_{\text{ph}} , \quad (3.34)$$

where

$$\hat{T}(\mathbf{k}) = \sum_a J_a e^{i\mathbf{k}\cdot\mathbf{a}} \exp - \left\{ N^{-1} \sum_q f_q^2 (1 - \cos \mathbf{q}\cdot\mathbf{a})(2 b_{\mathbf{q}}^+ b_{\mathbf{q}} + 1) \right\} . \quad (3.35)$$

Since e^{-x} is a convex function, an upper bound to A_p^t can be found easily by replacing $\hat{T}(\mathbf{k})$ by $\langle \hat{T}(\mathbf{k}) \rangle_{\text{ph}}$ in the exponential. Repeating this, we find that an upper bound for A_p^t is $\tilde{A}_B^t$ [as given in Eq. (3.18)].

Peierls upper bounds on A^K can be found in the same way:

$$A_P^{\mathbf{K}} = \epsilon - \beta^{-1} \ln q_{\text{ph}} - \beta^{-1} \ln \langle e^{-\beta \hat{T}(K-\hat{Q})} \rangle_{\text{ph}}, \quad (3.36)$$

where $\hat{\mathbf{Q}}$ is given by Eq. (3.22).

The expressions for the bounds on $A^{\mathbf{K}}$, Eqs. (3.29) and (3.36) appear to have a more interesting K independence than that found using the simplest Bogoliubov bound, Eqs. (3.21) and (3.26) for an Einstein lattice. However, the evaluation of the averages in Eqs. (3.29) and (3.36) shows that the $\mathbf{K}$ dependence of these bounds is vanishingly small for $T > 0$. The reason for this is that all the terms in the expansion of $\exp(-\beta \hat{T}(\mathbf{K}-\hat{\mathbf{Q}}))$ or $\exp(-\beta V(K-\hat{Q}))$ which have $\exp(i \hat{Q}\cdot a)$ dependences will give, when averaged over the phonon density matrix, a vanishingly small contribution compared to those terms which do not have this dependence. This is shown in Appendix A. Thus, for example, a typical term in the average of the expansion of $\exp(-\beta V(\mathbf{K}-\hat{\mathbf{Q}}))$ will be

$$\frac{(-\beta)^n}{n!} \langle [V(\mathbf{K}-\hat{\mathbf{Q}})]^n \rangle_{\text{ph}} = \frac{(-\beta)^n}{n!} \left\langle \left[\sum_a J_a e^{-S_0(a)} e^{i(\mathbf{K}-\hat{\mathbf{Q}})\cdot a} \right]^n \right\rangle_{\text{ph}} , \quad (3.37)$$

which can be written

$$\frac{(-\beta)^n}{n!} \sum_{\mathbf{a}_1} \cdots \sum_{\mathbf{a}_n} J_{a_1} \cdots J_{a_n} \times e^{-S_0(\mathbf{a}_1)} \cdots e^{-S_0(\mathbf{a}_n)} e^{i\mathbf{K}\cdot\Sigma_{i=1}^n \mathbf{a}_i} \langle e^{-i\hat{\mathbf{Q}}\cdot\Sigma_{i=1}^n \mathbf{a}_i} \rangle_{\text{ph}} . \quad (3.38)$$

The only terms which survive (for $T > 0$) are those for which $\sum_{i=1}^n \mathbf{a}_i = 0$, from the above argument, so that the $\mathbf{K}$ dependence is lost:

$$\frac{(-\beta)^n}{n!} \sum_{\mathbf{a}_1} \cdots \sum_{\mathbf{a}_n} \tilde{J}_{a_1} \cdots \tilde{J}_{a_n} \delta(\mathbf{a}_1 + \mathbf{a}_2 + \cdots + \mathbf{a}_n), \quad (3.39)$$

where

$$\tilde{J}_{\mathbf{a}} = J_{\mathbf{a}} e^{-S_0(\mathbf{a})} . \quad (3.40)$$

Eq. (3.39) can be rewritten as the diagonal matrix element of the matrix $(\tilde{\mathbf{J}})^n$ where

$$(\tilde{\mathbf{J}})_{nm} = \tilde{J}_{n-m} \quad (3.41)$$

so that the typical term becomes

$$(-\beta)^n / n! [\tilde{\mathbf{J}}^n]_{00} , \quad (3.42)$$

since all site diagonal elements of $\tilde{\mathbf{J}}^n$ are equal. Thus, we find finally

$$\langle e^{-\beta V(\mathbf{K}-\hat{\mathbf{Q}})} \rangle_{\text{ph}} = (e^{-\beta \tilde{\mathbf{J}}})_{00} . \quad (3.43)$$

It can also be shown in the same manner that

$$\langle e^{-\beta \hat{T}(\mathbf{K}-\hat{\mathbf{Q}})} \rangle_{\text{ph}} \leq (e^{-\beta \tilde{\mathbf{J}}})_{00} , \quad (3.44)$$

so that the two bounds $A_p^{\mathbf{K}}$ and $A_B^{\mathbf{K}}$ are related by $A_p^{\mathbf{K}} \leq \tilde{A}_B^K$, both independent of $\mathbf{K}$. Thus, the final form taken for the bound on the free energy for a system in a particular **K** subspace is ($T>0$):

$$A^{\mathbf{K}}(T) \leq \epsilon - \beta^{-1}\ln q_{\rm ph} - \beta^{-1}\ln(e^{-\beta\tilde{\mathbf{J}}})_{00}. \tag{3.45}$$

The RHS of this can be minimized by differentiating with respect to $\{f_q\}$ so that the parameters will be the same for every **K** (within the bounds that have been established). Better bounds may be possible in which the f_q are different for each **K** subspace. Taking the derivative of the RHS of (3.45) with respect to f_q and setting the result equal to zero gives

$$\frac{\partial\epsilon}{\partial f_q} = \beta^{-1}\frac{\partial}{\partial f_q}\ln(e^{-\beta\tilde{\mathbf{J}}})_{00} \tag{3.46}$$

or

$$2(c_q - f_q) = -\left[\frac{\partial}{\partial f_q}[e^{-\beta\tilde{\mathbf{J}}}]_{00}/(e^{-\beta\tilde{\mathbf{J}}})_{00}\right]. \tag{3.47}$$

To lowest order in $\beta\tilde{\mathbf{J}}$, the best choice of f_q is $f_q = c_q$ which results in completely removing the linear exciton–phonon coupling. This is also the result when the Bogoliubov bound, $A_B^{\mathbf{K}}$, of Eq. (3.26) is used. For larger $\beta\tilde{\mathbf{J}}$, there will be corrections to this result. Examples will be given in Sec. V.

There exists another bound on the free energy which is that the free energy must decrease with temperature (at constant volume), so that

$$A^{\mathbf{K}}(T=0) \geq A^{\mathbf{K}}(T). \tag{3.48}$$

This is a special case of the Peierls bound on A. Therefore, an examination of $A(T=0)$ is in order. Since $A^K(T=0)=E^{\mathbf{K}}$, the eigenvalue of the Hamiltonian (for one exciton in the system and total wave vector **K**), the bounds on $A^K(T=0)$ reduce to the usual variational principle of quantum mechanics. This has been discussed in detail by Merrifield; however, we will briefly discuss the difference between the $T=0$ and the $T>0$ calculations here. If the bounds, given in Eq. (3.21), (3.29) or (3.36) are computed at $T=0$, they all give the same result, which is

$$E^K = A^{\mathbf{K}}(T=0) \leq \epsilon + \sum_n J_{n-m}\, e^{i\mathbf{K}\cdot\mathbf{R}_{nm}}\, e^{-S_0(\mathbf{R}_{nm})}, \tag{3.49}$$

in which $S_0(\mathbf{R}_{nm})$ is evaluated at $T=0$,

$$S_0(\mathbf{R}_{nm}) = N^{-1}\sum_q f_q^2(1-\cos\mathbf{q}\cdot\mathbf{R}_{nm}). \tag{3.50}$$

This agrees with the results of Merrifield. Combining Eq. (3.49) with Eq. (3.48) gives another bound on the free energy, which has a K dependence in contrast to the earlier bounds we have derived. In Sec. V, an analysis of these various bounds will be made.

IV. APPROXIMATING ENSEMBLE AVERAGES

Consider the quantity

$$\langle\Delta N_{\rm ph}\rangle = \langle N_{\rm ph}\rangle - \langle N_{\rm ph}\rangle_{\rm ph}, \tag{4.1}$$

where $N_{\rm ph}=\sum_q b_q^+ b_q$, which, as pointed out in the introduction, will be important in the discussion of exciton mobility. For temperature T we have

$$\langle N_{\rm ph}\rangle = e^{\beta A}\,{\rm Tr}(N_{\rm ph}\,e^{-\beta H}) \tag{4.2}$$

and

$$\langle N_{\rm ph}\rangle_{\rm ph} = e^{\beta A_{\rm ph}}\,{\rm Tr}_L(N_{\rm ph}\,e^{-\beta H_{\rm ph}}), \tag{4.3}$$

where as before

$$A = -\beta^{-1}\ln{\rm Tr}\,e^{-\beta H} \tag{4.4}$$

and

$$A_{\rm ph} = -\beta^{-1}\ln{\rm Tr}_L\,e^{-\beta H_{\rm ph}}. \tag{4.5}$$

Even for the simple model Hamiltonian defined in Sec. II, it is not possible to evaluate the traces required exactly. Instead an approximation scheme will be employed which is based on the perturbation expansion of the exponential of an operator.

$$e^{-\beta H} = e^{-\beta H_0}\left[1-\int_0^\beta d\alpha\, V(\alpha) + \int_0^\beta d\alpha_1\int_0^{\alpha_1} d\alpha_2\, V(\alpha_1)\,V(\alpha_2)+\cdots\right]$$

$$\equiv e^{-\beta H_0}\exp_o\left[-\int_0^\beta d\alpha\, V(\alpha)\right], \tag{4.6}$$

where

$$H = H_0 + V \tag{4.7}$$

and

$$V(\alpha) = e^{\alpha H_0}\,V e^{-\alpha H_0}. \tag{4.8}$$

The subscript on the exponential represents the usual time ordered expansion. Since the trace is invariant to the choice of basis, we have

$$\langle N_{\rm ph}\rangle = [{\rm Tr}\,e^{u}e^{-\beta H}e^{-u}]^{-1}\,{\rm Tr}(e^{u}e^{-\beta H}N_{\rm ph}\,e^{-u})$$
$$= [{\rm Tr}\,e^{-\beta\tilde{H}}]^{-1}\,{\rm Tr}(e^{-\beta\tilde{H}}\tilde{N}_{\rm ph}), \tag{4.9}$$

where $U^+=-U$. If Eq. (4.6) is inserted in Eq. (4.9) and the result taken to first order in the perturbation, the result is

$$\langle N_{\rm ph}\rangle = \left(1+\left\langle\int_0^\beta \tilde{V}(\alpha)\,d\alpha\right\rangle_Q\right)\left\{\langle\tilde{N}_{\rm ph}\rangle_0 - \int_0^\beta d\alpha\,\langle\tilde{V}(\alpha)\,\tilde{N}_{\rm ph}\rangle_0\right\},$$

where

$$\langle X\rangle_0 \equiv ({\rm Tr}e^{-\beta\tilde{H}_0})^{-1}\,{\rm Tr}(e^{-\beta\tilde{H}_0}). \tag{4.10}$$

This is the desired result. Note that while Eq. (4.9) is independent of U, Eq. (4.10) is not, since the expansion is carried out only to first order. The criterion for the choice of U will be the variational principles on the Helmholtz free energy discussed in Sec. III.

Using the form of U given in Eq. (2.14a), the first order form for $\langle N_{\rm ph}\rangle$ can be found. In Appendix B, this is done explicitly and it is found that for $T>0$ (see the discussions in Appendix A and Appendix B)

$$\langle\Delta N_{\rm ph}\rangle = \frac{1}{N}\sum_q (2c_q f_q - f_q^2), \tag{4.11}$$

while at $T=0$

$$\langle\Delta N_{\rm ph}\rangle = \frac{1}{N}\sum_q f_q^2. \tag{4.12}$$

V. RELATION TO EXCITON MOBILITY AND EXAMPLES

A. Introduction

We will now apply the results of the last three sections to a simplified model Hamiltonian which will ex-

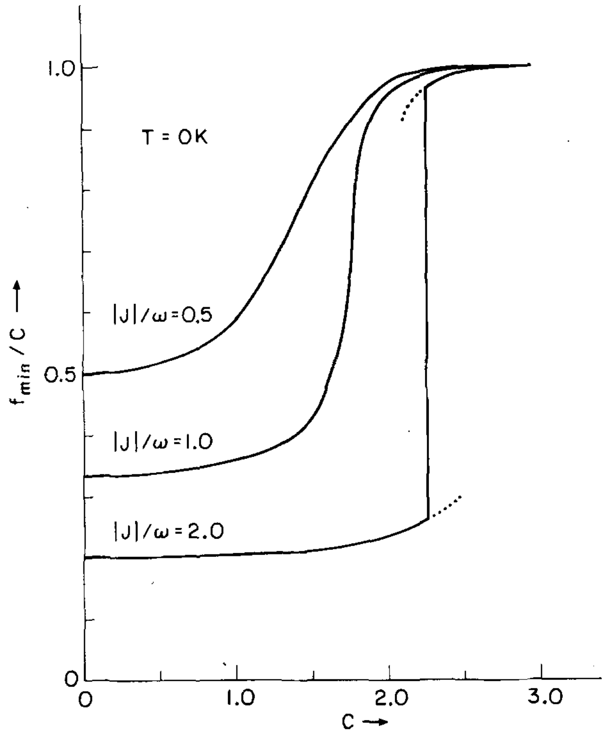

FIG. 1. The best value of f/c (f_{min}/c) as a function of c for various values of bandwidth ($|J|/\omega$) at $T=0$ K.

hibit the properties of interest. First, we note that the larger $\langle \Delta N_{ph}\rangle$ is, the larger will be the exciton effective mass and, hence, the more slowly the exciton will move. Another way of seeing this is that the larger the f_q are (with a maximum at c_q) the smaller will be the effective exciton transfer integrals $\tilde{J}$, which depend on $\exp(-f_q^2)$, and thus the more slowly the exciton moves.

In the present section, we will show that for given exciton transfer integrals J_{nm} as the exciton phonon coupling strength c_q is increased from zero, the best value of the f_q changes from being very small to being equal to c_q. This change in f_q is smooth for small values of J_{nm}, but becomes discontinuous for values of J_{nm} (or exciton bandwidth) greater than some critical value. In addition, we will show that as temperature is increased, this discontinuous change eventually disappears and is replaced by a smooth change. If we ascribe high mobility to an exciton with small values of f_q and low mobility to an exciton with large values of f_q, as proposed above, then this change from small f_q to large f_q as coupling or temperature increases amounts to a change from delocalized to quasilocalized excitons. This possibility has been discussed in the polaron literature and we will discuss the connection between these two cases in the next section.

B. Example

Consider the Hamiltonian for a one dimensional nearest neighbor interacting crystal with Einstein phonons:

$$H = E_0\sum_n a_n^+ a_n + \omega\sum_q b_q^+ b_q + J\sum_n (a_n^+ a_{n+1} + a_{n+1}^+ a_n) + \frac{1}{N^{1/2}}\sum_{n,q} a_n^+ a_n\, c\, e^{i\mathbf{q}\cdot\mathbf{R}_n}(b_q + b_{-q}^+) \;. \quad (5.1)$$

This is a special case of the Hamiltonians considered in Secs. II–IV and we can immediately apply the results therein to this Hamiltonian. We apply a unitary transformation of type (2.14a) with $f_q = f$, all q, and we find for $T=0$,

$$A^K = \epsilon + 2J\cos K\, e^{-f^2} \quad (5.2)$$

and for $T>0$ (see Appendices A and B)

$$A^K = \epsilon - k_B T\ln I_0(2\beta J) - k_B T \ln q_{ph}\;. \quad (5.3)$$

At $T=0$, the value of f which minimizes A_K is given by

$$f\left(1 - \frac{2J}{\omega}(\cos K)\, e^{-f^2}\right) = c\;, \quad (5.4)$$

while at $T>0$ the value of f minimizing A_K (or A_t) is

$$f\left(1 + \frac{2|J|e^{-f^2}}{\omega}\,\frac{I_1(2\beta|J|e^{-f^2})}{I_0(2\beta|J|e^{-f^2})}\right) = c\;, \quad (5.5)$$

where $I_n(x)$ is the nth order modified Bessel function.

Because the uninteresting phonon free energy overwhelms the exciton free energy, except at $T=0$, we will ignore the term $k_BT\ln q_{ph}$ in Eq. (5.3) and discuss only the "exciton" free energy (the remaining terms of (5.3) and all of Eq. [(5.2)]. In addition, we will be concerned with the bottom of the band only, so we set $K=0$ for $J<0$ and $K=\pi$ for $J>0$, so that $J\cos k$ becomes $-|J|$ in Eq. (5.2) and (5.5).

In Fig. 1 we plot the value of f (f_{min}), which gives the minimum free energy at $T=0$ for various values of $|J|/\omega$ and c. For $|J|/\omega$ less than ~1.12, the change in f_{min}/c as a function of c is smooth and continuous. However, for $|J|/\omega>1.12$, the free energy [Eq. (5.2)] has two minima with respect to variations in f and there are three solutions to Eq. (5.4) (with $K=0$). One of these is a relative maximum, the other two are relative minima. As c increased for $|J|/\omega>1.12$, the free energies of the two minima become equal and the lower solution changes abruptly from a small value of f to a large value of f.

The values of f_{min} and $A_{K=0}$ for various values of c and $|J|/\omega$ are given in Table I for $T=0$.

In Fig. 2, we plot the value of f_{min}/c for various values of $|J|/\omega$, c, and T. For those values of $|J|/\omega$ below the critical value, 1.12, the curves vary very little as T increases. The major qualitative change is that f_{min} becomes close to c as T increases. As T gets large the curves of f_{min}/c vs c become qualitatively like the subcritical curves, even for values of $|J|/\omega$ above critical. Thus, there is the possibility that in real systems increasing the temperatures brings about an abrupt change in the character of the exciton: it will change from a delocalized to a quasilocalized excitation. The number of phonons bound to the exciton $\langle\Delta N_{ph}\rangle$, is plotted in Fig. 3 as a function of temperature for a few representative cases. Table II has the values of f_{min} and A_K for various values of $|J|/\omega$, c, and T. This shows that for small bandwidth ($|J|/\omega<1$), the zero phonon line intensity varies smoothly with temperature; for large bandwidth this intensity will vary very little

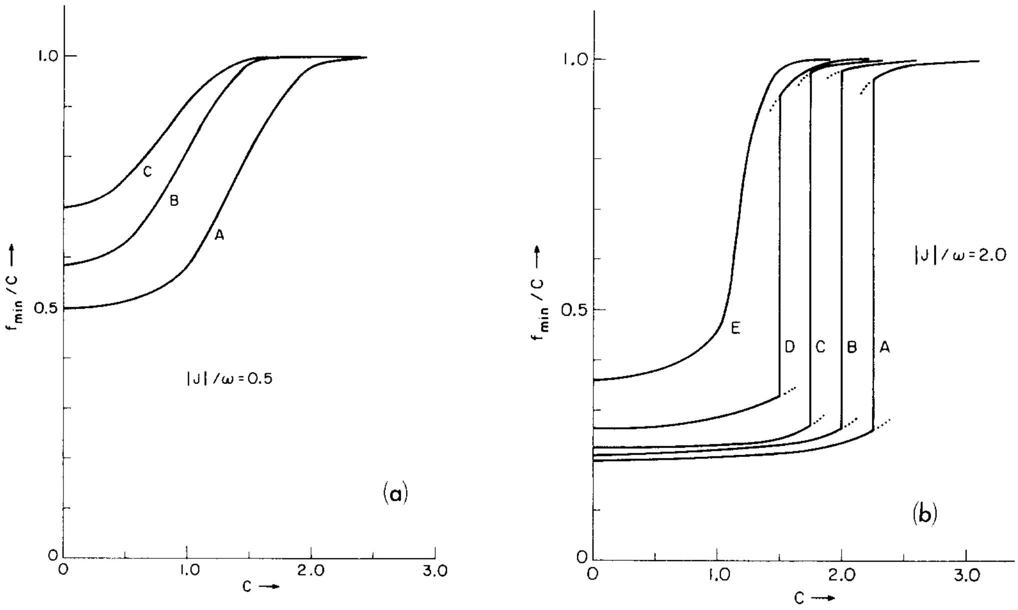

FIG. 2(a) The best value of $f/c(f_{min}/c)$ as a function of c for $|J|/\omega = 0.5$ at three temperatures: the curve A is $T=0$ K; B is for $T=1/2\ (\omega/k_B)$; c is for $T=(\omega/k_B)$ (b) The best value of f/c (f_{min}/c) as a function of c for $|J|/\omega = 2.0$ at five temperatures: A is $T=0$ K; B is $T=1/2\ (\omega/k_B)$; c is $T=+\omega/k_B$); D is $T=2(\omega/k_B)$; and E is $T=4\ (\omega/k_B)$.

with temperature until the critical temperature is reached at which point, it will abruptly drop to a very small value.

VI. CONCLUSIONS

In this paper, we have discussed upper bounds on the free energy of an exciton interacting with a lattice of phonons. The model Hamiltonian has been used before as a model of exciton phonon interaction and only contains interaction terms linear in phonon coordinate and diagonal in the exciton site representation. Although this is a very simplified model, properties such as spectral line shapes and exciton mobility are considered to be qualitatively similar to more realistic and complicated Hamiltonians.

A number of conclusions arise from our considerations. First of all, although $\exp(-\beta A)$ can be written as a sum over exciton wave vectors as in Eq. (3.18), each term in the sum does *not* correspond to $\exp(-\beta A_K)$ where this is the trace within a subspace of the total Hilbert space corresponding to a particular total wave vector of the system. When the correct upper bound on A_K is found at temperatures greater than 0 K (actually

TABLE I. Values of f_{min} and $A_{K=0}$ for $T=0$ K and various values of $|J|/\omega$ and c. From Eqs. (5.2) and (5.4).

$\|J\|/\omega$	c	f_{min}	$A_{K=0}+c^2$
0.5	0	0	−1.0
	0.5	0.258	−0.877
	1.0	0.586	−0.538
	1.5	1.228	−0.147
	2.0	1.958	−0.020
1.0	0	0	−2.0
	0.5	0.170	−1.83
	1.0	0.363	−1.347
	1.5	0.648	−0.537
	2.0	1.896	−0.044
2.0	0	0	−4.0
	1.0	0.207	−3.203
	1.5	0.326	−2.219
	2.0	0.478	−0.867
	2.1	0.517	−0.556
	2.2	0.561	−0.234
	2.3	2.25	−0.022
	2.5	2.50	−0.008

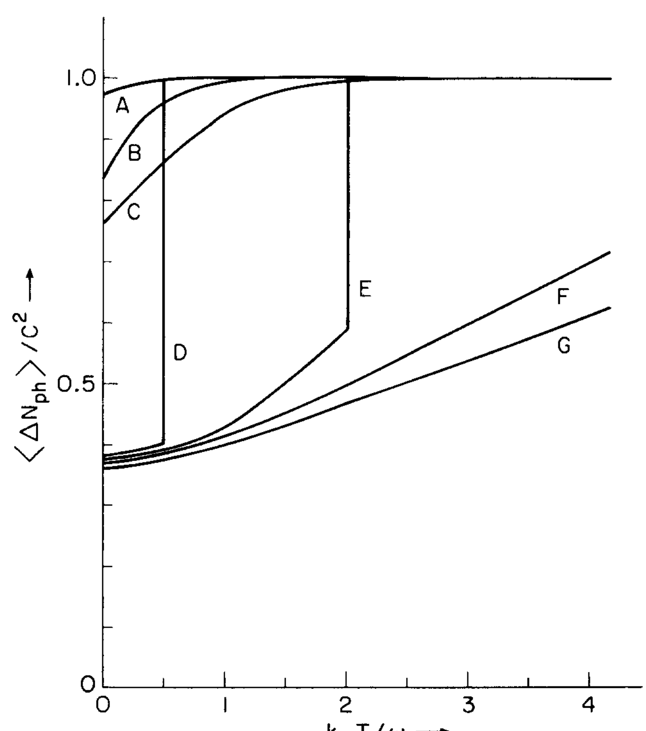

FIG. 3. The average excess number of phonons in units of c^2 as a function of temperature for the following cases:

A. $|J|/\omega = 1/2$; $c=2$ E. $|J|/\omega = 2$; $c=1.5$
B. $|J|/\omega = 1/2$; $c=1$ F. $|J|/\omega = 2$; $c=1$
C. $|J|/\omega = 1/2$; $c=1/2$ G. $|J|/\omega = 2$; $c=1/2$
D. $|J|/\omega = 2$; $c=2$

TABLE II. Values of $f_{\min}$ for $T>0$ K and various values of $|J|/\omega$ and c. From Eqs. (5.3) and (5.5).

$\|J\|/\omega$	c	k_BT/ω	$f_{\min}$
0.5	0.5	0.5	0.3147
	1.0	0.5	0.8064
	1.5	0.5	1.4181
	2.0	0.5	2.000
0.5	0.5	1.0	0.374
	1.0	1.0	0.913
	1.5	1.0	1.492
	2.0	1.0	2.0
2.0	0.5	0.5	0.1065
	1.0	0.5	0.2198
	1.5	0.5	0.3507
	2.0	0.5	0.5343
	2.1	0.5	2.095
	2.5	0.5	2.5
2.0	0.5	1.0	0.113
	1.0	1.0	0.236
	1.5	1.0	0.367
	1.75	1.0	0.976
	2.0	1.0	0.997
2.0	0.5	2.0	0.135
	1.0	2.0	0.291
	1.5	2.0	(1.377, 0.538)
	2.0	2.0	1.997

greater than $\omega/[k_B \ln N]$, where ω is a typical phonon frequency), it is found that the bound on A_K is independent of K. This is due to the exciton free energy being so much smaller than the phonon free energy at these temperatures that the effect of the phonons is to "average" the free energy over the exciton band (see Appendix A for details).

Using the simplified model of an Einstein lattice ($\omega_q=\omega$ all q), nearest neighbor interactions ($J_{n-m} = J\delta_{n,m\pm1}$), and a one dimensional lattice, we found the upper bound for the free energy at all temperatures. In particular, we found the value of f in the unitary transformation of the basis set (or Hamiltonian) given by Eq. (2.16a) which minimized the free energy. There are three independent parameters in the Hamiltonian: J/ω [or the exciton bandwidth Δ in units of the phonon frequency $\Delta = 4(J/\omega)$], c^2 (or the energy of interaction between exciton and phonons in units of the phonon frequency), and the temperature k_BT/ω.

We find that for $k_BT/\omega=0$, the optimum value of f/c is much less than one for $c=0$ and $|J|/\omega>0$; as c gets larger for fixed $|J|/\omega$, f/c goes smoothly to unity, for $|J|/\omega<1.12$. However, for $|J|/\omega>1.12$, f/c changes *discontinuously* as c gets larger than some critical value ($c_{\text{crit}} > |J|/\omega$). For $k_BT/\omega>0$, the optimum value of f/c for a particular $|J|/\omega$ and for $c=0$ is larger than that for $T=0$; as c increases f/c gets larger and goes to unity for large c. There is again a discontinuous change in f/c as a function of c for larger $|J|/\omega$. Finally, for fixed c and $|J|/\omega$ the optimum value of f/c increases with temperature, and if $|J|/\omega$ is greater than 1.12 this change will be *abrupt*. This behavior is shown in Figs. 1–3.

Since the optimum value of f/c is related to the number of phonons surrounding the exciton, we can interpret the increase in f/c as temperature increases as a further clothing of the exciton by phonons, thus decreasing the exciton mobility, lowering the intensity of the zero phonon line and increasing the lattice distortion surrounding the exciton. There is the possibility that this can take place in an abrupt manner for large enough exciton bandwidth. This has been suggested previously for the polaron problem, which is formally analogous to the exciton phonon problem treated herein. Unfortunately, in the polaron case, the analysis was marred by confusing the sum over k in Eq. (3.19) with a sum over subspaces corresponding to different total wave vectors. At $T=0$ the results are the same, and at higher temperatures qualitatively similar conclusions are found.

Finally, we remark on the importance of this work for exciton dynamics. Recent work has focused on computing the coherent and incoherent contributions to exciton mobilities. Grover and Silbey[3] and others[4,5] have used the above unitary transformation with $f_q=c_q$ for all temperatures. It is clear that this is valid at high temperatures and strong coupling, but not at low temperatures and weak coupling. In the case of anthracene singlet excitons, the evidence is great that this is an example of weak exciton phonon scattering ($c<1$) so that the optimum choice of f_q will be very small. This will mean that the correlation functions involved in computing the diffusion coefficient will be close to those for the bare exciton, rather than the clothed exciton (although for c_q small, the difference between these two representations is small). In addition, this will mean a smaller temperature dependence for the bandwidth than previously assumed.

Finally, although the explicit results found are for a one dimensional, nearest neighbor coupled lattice with Einstein phonons, all of these approximations are inessential to the general results and can be dispensed with, at the cost of a large amount of computational labor.

APPENDIX A

I. Calculation of $\langle e^{i\hat{Q}\cdot a}\rangle_{\text{ph}}$

We will need the value of

$$\langle e^{i\hat{Q}\cdot \mathbf{a}}\rangle_{\text{ph}} = [\text{Tr}_L(e^{i\hat{Q}\cdot\mathbf{a}}\, e^{-\beta H_{\text{ph}}})][\text{Tr}_L(e^{-\beta H_{\text{ph}}})]^{-1}, \tag{A1}$$

where

$$\hat{Q} = \sum_q \mathbf{q}\, b_q^{+} b_q \tag{A2}$$

and the trace is over the phonon states of the lattice. We find

$$\langle e^{i\mathbf{Q}\cdot\mathbf{a}}\rangle_{\text{ph}} = \left[\sum_{\{n_q\}} \exp\left(-\beta\sum_q n_q\omega_q + i\sum_q n_q(\mathbf{q}\cdot\mathbf{a})\right)\right] \times\left[\sum_{\{n_q\}}\exp\left(-\beta\sum_q n_q\omega_q\right)\right]^{-1}$$

$$=\prod_{\mathbf{q}} \frac{(1-e^{-\beta\omega_q})}{(1-e^{-\beta\omega_q}e^{i\mathbf{q}\cdot\mathbf{a}})}, \quad \beta>0 . \tag{A3}$$

The denominator of (A.3) can be written

$$\prod_q (1-e^{-\beta\omega_q}e^{i\mathbf{q}\cdot\mathbf{a}})$$

$$=\prod_{q>0}{}' \left|1-e^{-\beta\omega_q}e^{i\mathbf{q}\cdot\mathbf{a}}\right|^2(1-e^{-\beta\omega_0})(1+e^{-\beta\omega_\pi}) , \tag{A4}$$

where the prime on the product means that we leave out $q=0$ and $q=\pi$ and only take positive q (we have assumed that $\omega_q=\omega_{-q}$). Thus the denominator becomes

$$\prod_q (1-e^{-\beta\omega_q}e^{i\mathbf{q}\cdot\mathbf{a}}) = (1-e^{-\beta\omega_0})(1+e^{-\beta\omega_\pi})\prod_{q>0}{}' [(1-e^{-\beta\omega_q})^2 + 2e^{-\beta\omega_q}(1-\cos\mathbf{q}\cdot\mathbf{a})]$$

$$=\frac{(1+e^{-\beta\omega_\pi})}{(1-e^{-\beta\omega_\pi})}\left[\prod_q (1-e^{-\beta\omega_q})\right] \times \prod_{q>0}{}' \left[1+\frac{2(1-\cos\mathbf{q}\cdot\mathbf{a})e^{-\beta\omega_q}}{(1-e^{-\beta\omega_q})^2}\right] .$$

Thus

$$\langle e^{i\hat{\mathbf{Q}}\cdot\mathbf{a}}\rangle_{\text{ph}} = \frac{(1-e^{-\beta\omega_\pi})}{(1+e^{-\beta\omega_\pi})}\prod_{q>0}{}' \left[1+\frac{2e^{-\beta\omega_q}(1-\cos\mathbf{q}\cdot\mathbf{a})}{(1-e^{-\beta\omega_q})^2}\right]^{-1} . \tag{A5}$$

Since the product in (A.5) is the product of $N-2$ factors, each of which is less than unity, this is very small, hence $\langle e^{i\hat{\mathbf{Q}}\cdot\mathbf{a}}\rangle_{\text{ph}}$ is much smaller than 1 at temperatures, such that $e^{-\beta\omega_q}>1/N$ for ω_q.

In the case of Einstein phonons we can evaluate the denominator exactly. Denote the log of the denominator by L, then

$$L=\sum_q \log(1-e^{-\beta\omega}e^{i\mathbf{q}\cdot\mathbf{a}}) \tag{A6}$$

and

$$\frac{dL}{d(e^{-\beta\omega})} = -\sum_q \frac{e^{i\mathbf{q}\cdot\mathbf{a}}}{(1-e^{-\beta\omega}e^{i\mathbf{q}\cdot\mathbf{a}})}$$

$$= -\sum_q e^{i\mathbf{q}\cdot\mathbf{a}}\sum_{n=0}^{\infty} e^{-\beta n\omega}e^{in\mathbf{q}\cdot\mathbf{a}}$$

$$= -\sum_{n=0}^{\infty} e^{-\beta n\omega} N\delta_{\mathbf{a},0}$$

$$= -N\delta_{\mathbf{a},0}(1-e^{-\beta\omega})^{-1} . \tag{A7}$$

Thus

$$L=\delta_{\mathbf{a},0}N\log(1-e^{-\beta\omega}) , \tag{A8}$$

and the denominator of (A.3) in the limit of a dispersionless phonon band becomes

$$\prod_q (1-e^{-\beta\omega}e^{i\mathbf{q}\cdot\mathbf{a}}) = 1 \quad \text{if } \mathbf{a}\neq 0$$
$$= (1-e^{-\beta\omega})^N \quad \text{if } \mathbf{a}=0 , \tag{A9}$$

and so

$$\langle e^{i\hat{\mathbf{Q}}\cdot\mathbf{a}}\rangle_{\text{ph}} = (1-e^{-\beta\omega})^N \quad \mathbf{a}\neq 0 \tag{A10}$$

in this limit. Thus for all T such that $e^{-\beta\omega}>(10N)^{-1}$, this is much smaller than unity. This means for all $T\gtrsim \omega/(k_B\log N)$,

$$\langle e^{+i\hat{\mathbf{Q}}\cdot\mathbf{a}}\rangle_{\text{ph}} \ll 1 \quad \mathbf{a}\neq 0 . \tag{A11}$$

At $T=0\ K$, we find by direct calculation that

$$\langle e^{i\hat{\mathbf{Q}}\cdot\mathbf{a}}\rangle_{\text{ph}} = 1, \quad T=0K . \tag{A12}$$

In this paper, from the argument following (A.5), we will assume that (A.11) and (A.12) hold for a phonon band with dispersion also.

II. Calculation of the free energy of a noninteracting exciton–phonon system

Consider a Hamiltonian for noninteracting excitons and phonons:

$$H=\sum_k \epsilon(\mathbf{k})a_{\mathbf{k}}^+a_{\mathbf{k}} + \sum_q \omega_q b_q^+b_q$$
$$\equiv \sum_{n,m} J_{nm}a_n^+a_m + \sum_q \omega_q b_q^+b_q . \tag{A13}$$

Then

$$e^{-\beta A} = \text{Tr}\, e^{-\beta H}$$
$$=\sum_k \sum_{\{n_q\}} e^{-\beta\epsilon(\mathbf{k})}e^{-\beta\Sigma n_q\omega_q}$$
$$=\sum_k e^{-\beta\epsilon(\mathbf{k})}\prod_q (1-e^{-\beta\omega_q})^{-1} . \tag{A14}$$

Thus

$$A=-\beta^{-1}\left[\ln\left(\sum_k e^{-\beta\epsilon(\mathbf{k})}\right)-\sum_q \ln(1-e^{-\beta\omega_q})\right]. \tag{A15}$$

It is tempting to consider each term in the sum over k either in (A.14) or (A.15) as the contribution from a subspace with total wave vector $\mathbf{k}$. This is not correct as can be seen by calculating $\exp(-\beta A)$ as a sum over each invariant subspace. Then we write

$$e^{-\beta A} = \sum_{\mathbf{K},\{n_q\}} \exp-\beta\left[\epsilon(\mathbf{K}-\mathbf{Q})+\sum n_q\omega_q\right] , \tag{A16}$$

where $\mathbf{Q}=\sum q n_q$. Here the exciton wave vector is just that to make the total wave vector $\mathbf{K}$ when added to the total phonon wave vector. Note that (A.16) is identical to (A.14) in numerical value, but the contribution to $\exp(-\beta A)$ from an invariant subspace of $\mathbf{K}$ is not the term with $\mathbf{k}=\mathbf{K}$ in (A.14). In fact, we find

$$e^{-\beta A} = \sum_{\mathbf{K}}\sum_{\{n_q\}} \exp-\beta\left[\sum_r J_r e^{i(\mathbf{K}-\mathbf{Q})\cdot\mathbf{R}_r}+\sum_q n_q\omega_q\right] \tag{A17}$$

where $J_r\equiv J_{(r+p)-p}$. The presence of the $e^{-i\mathbf{Q}\cdot(\mathbf{R}_n-\mathbf{R}_m)}$ in the exponent of (A.17) is feature which spoils the easy separation of exciton and phonon contributions in each subspace. It is possible to evaluate the contribution of each term in the sum over $\mathbf{K}$ in (A.17). We expand $\exp(-\beta\epsilon(\mathbf{K}-\mathbf{Q}))$ in a power series and find

$$e^{-\beta A} = \sum_{\mathbf{K}}\sum_{\{n_q\}} e^{-\beta\Sigma n_q\omega_q}\sum_{m=0}^{\infty}\frac{1}{m!}\left(\sum_n J_n e^{i(\mathbf{K}-\mathbf{Q})\cdot\mathbf{R}_n}\right)^m . \tag{A18}$$

From the argument of Appendix A1, any term in (A.18) which contains an $e^{-i\mathbf{Q}\cdot\mathbf{a}}$ with $\mathbf{a}\neq 0$ will give a vanishingly small contribution when compared to those terms with $\mathbf{a}=0$ at nonzero temperatures. Hence the only terms which are to be kept in the sum over m at such temperatures are those for which there is no $\mathbf{Q}$ dependence:

$$\left(\sum_n e^{i(\mathbf{K}-\mathbf{Q})\cdot\mathbf{R}_n} J_n\right)^m = \sum_{n_1}\cdots\sum_{n_m} J_{n_1}J_{n_2}\cdots J_{n_m} \times \delta(\mathbf{R}_1+\mathbf{R}_2+\ldots+\mathbf{R}_m), \qquad \text{(A19)}$$

where the delta function is the Kronecker delta function. Thus at $T>\omega/[k_B \log N]$,

$$e^{-\beta A}\sum_{\mathbf{K}} (e^{-\beta J})_{dd} \sum_{\{n_q\}} e^{-\beta\Sigma n_q\omega_q} \qquad \text{(A20)}$$

where $\mathbf{J}$ is the matrix formed by $J_{n,m}\equiv J_{n-m}$, and the matrix element "dd" is the diagonal matrix element in the site representation. Since each term in the sum over $\mathbf{K}$ is independent of $\mathbf{K}$, we finally have

$$e^{-\beta A} = N(e^{-\beta J})_{dd}\prod_q (1-e^{-\beta\omega_q})^{-1}. \qquad \text{(A21)}$$

Note that this is identical to the result from (A.14), when we see that

$$\sum_k e^{-\beta\epsilon(\mathbf{k})} = N(e^{-\beta\mathbf{J}})_{dd}. \qquad \text{(A22)}$$

Therefore, we see that the contribution to the total free energy from each invariant subspace of total wave vector $\mathbf{K}$ is independent of $\mathbf{K}$ for $T>\omega/[k_B\log N]$. From the example treated herein, we see that the cause of this behavior is the swamping of the exciton contribution by the phonon contributions even at low, but nonzero temperature; because the total wave vector is restricted to a certain value, the exciton wave vector is forced to sample the entire band as the phonon wave vector is changed. Only at extremely low T (below $\omega/[k_B\log N]$) does the exciton sample a restricted part of the band.

Note also that if a exciton phonon interaction with diagonal matrix elements which are zero, then the Peierls upper bound on A would be given by the expression in (A20). We will show in Appendix C that this is the value for the free energy of an exciton interacting with a classical lattice.

Finally we note that in the one dimensional nearest neighbor model ($J_{nm}=J[\delta_{n,m+1}+\delta_{n,m-1}]$), we have

$$(e^{-\beta\mathbf{J}})_{dd} = I_0(2\beta J). \qquad \text{(A23)}$$

III. Evaluation of bounds on the free energy

Consider the Hamiltonian as given in Eqs. (2.19) and (2.20); then the Bogoliubov bound is given as

$$A_B^t = -\beta^{-1}\ln\sum_{\mathbf{K},\{n_q\}}\langle\mathbf{K}-\mathbf{Q};\{n_q\}|e^{-\beta\tilde{H}_0}|\mathbf{K}-\mathbf{Q};\{n_q\}\rangle + \sum_{\mathbf{K},\{n_q\}}\frac{1}{z}\langle\mathbf{K}-\mathbf{Q};\{n_q\}|e^{-\beta\tilde{H}_0}V|\mathbf{K}-\mathbf{Q};\{n_q\}\rangle, \qquad \text{(A24)}$$

where $\mathbf{Q}=\sum_q \mathbf{q}n_q$ as before and

$$z=\sum_{\mathbf{K},\{n_q\}}\langle\mathbf{K}-\mathbf{Q};\{n_q\}|e^{-\beta\tilde{H}_0}|\mathbf{K}-\mathbf{Q};\{n_q\}\rangle = Ne^{-\beta\epsilon}q_{\text{ph}}. \qquad \text{(A25)}$$

Thus

$$A_B^t = -\beta^{-1}\ln\left[\sum_K e^{-\beta\epsilon}q_{\text{ph}}\right] + \sum_K N^{-1}\sum_{n,m}J_{nm}e^{i\mathbf{K}\cdot\mathbf{R}_{nm}} \times\langle\theta_n^+\theta_m e^{-i\hat{\mathbf{Q}}\cdot\mathbf{R}_{nm}}\rangle \qquad \text{(A26)}$$

where $\hat{\mathbf{Q}}=\sum_q q b_q^+ b_q$. To compute the last average, we note that

$$\langle\theta_n^+\theta_m e^{-i\hat{\mathbf{Q}}\cdot\mathbf{R}_{nm}}\rangle = \frac{1}{q_{\text{ph}}}\sum_{\{n_q\}}\exp-\beta\left\{\sum n_q[\omega_q + i(\mathbf{q}\cdot\mathbf{R}_{nm})\beta^{-1}]\right\} \times\langle\{n_q\}|\exp\left[-N^{-1/2}\sum_q(\bar{X}_q^n - X_q^n)(b_q^+ - b_{-q})\right]|\{n_q\}\rangle. \qquad \text{(A27)}$$

The effect of the term $e^{-\hat{\mathbf{Q}}\cdot\mathbf{R}_{nm}}$ is to make a formal change in the frequency from ω_q to $\omega_q + i(q\cdot R_{nm})/\beta$ in the mathematics. Hence

$$\langle\theta_n^+\theta_m e^{-i\hat{\mathbf{Q}}\cdot\mathbf{R}_{nm}}\rangle_{\text{ph}} = \prod_q[(1-e^{-\beta\omega_q})(1-e^{-\beta\omega_q}e^{-i\mathbf{q}\cdot\mathbf{R}_{nm}})^{-1}] \times\exp\left[-N^{-1}\sum_q f_q^2(1-\cos\mathbf{q}\cdot\mathbf{R}_{nm})\coth(\tfrac{1}{2}\beta\omega_q - i_q\cdot R_{nm})\right]. \qquad \text{(A28)}$$

It is the first factor which we discussed in Appendix A1 and found to be so small compared to unity for $T<\omega/[k_B\log N]$. [See Eq. (3.23) *et seq.*]

If we had added and subtracted the phonon average of V to H_0 as in Eqs. (3.16) and (3.17) we get the result given in (3.32) for $\tilde{A}_B^t$.

In computing the Peierls bound with the Hamiltonian of Eq. (2.19) and (2.20), we must evaluate the matrix elements of V explicitly. We find

$$\langle K-Q;\{n_q\}|V|K-Q;\{n_q\}\rangle = N^{-1}\sum_{n,m}J_{nm}e^{i(\mathbf{K}-\mathbf{Q})\cdot\mathbf{R}_{nm}} \times\langle\{n_q\}|\theta_n^+\theta_m|\{n_q\}\rangle, \qquad \text{(A29)}$$

but

$$\langle\{n_q\}|\theta_n^+\theta_m|\{n_q\}\rangle = \langle\{n_q\}|\exp\left[-N^{-1/2}\sum_q(\bar{X}_q^n - \bar{X}_q^m)(b_q^+ - b_{-q})\right]|\{n_q\}\rangle = \exp\left[-(2N)^{-1}\sum_q|\bar{X}_q^n - \bar{X}_q^m|^2\right]\langle\{n_q\}|e^{\theta^+}e^{-\theta}|\{n_q\}\rangle, \qquad \text{(A30)}$$

where $\theta^+ = -N^{1/2}\sum_q(\bar{X}_q^n - \bar{X}_q^m)b_q^+$. Expanding the exponentials, evaluating the terms and re-exponentiating, we find

$$\langle\{n_q\}|\theta_n^+\theta_m|\{n_q\}\rangle = \exp\left[-N^{-1}\sum_q f_q^2(1-\cos\mathbf{q}\cdot\mathbf{R}_{nm})(2n_q+1)\right]. \qquad \text{(A31)}$$

APPENDIX B. EVALUATION OF $\langle N_{\rm ph}\rangle$

We evaluate $\langle N_{\rm ph}\rangle$ from Sec. IV, Eq. (4.10), writing the Hamiltonian, H as

$$\tilde{H}=\epsilon\sum_n a_n^+a_n+\sum_q \omega_q b_q^+b_q+\sum_{n,m}\tilde{J}_{nm}a_n^+a_m+N^{-1/2}\sum_{n,q}(c_q-f_q)\omega_q e^{i\mathbf{q}\cdot\mathbf{R}_n}a_n^+a_n(b_q+b_q^+)+\sum_{n,m}J_{nm}[\theta_n^+\theta_m-\langle\theta_n^+\theta_m\rangle]a_n^+a_m\,, \quad (B1)$$

where $\tilde{J}_{nm}=J_{nm}\langle\theta_n^+\theta_m\rangle$. We take $\tilde{H}_0$ to be used in Eq. (4.12) as the first three terms of $\tilde{H}$; thus, $\langle v\rangle=0$. Also,

$$N_{\rm ph}=\sum_q b_q^+b_q-N^{-1/2}\sum_{n,q}a_n^+a_n f_q e^{i\mathbf{q}\cdot\mathbf{R}_n}(b_q+b_{-q}^+)+N^{-1}\sum_q f_q^2\,. \quad (B2)$$

Thus, from Eq. (4.12),

$$\langle N_{\rm ph}\rangle=\langle\tilde{N}_{\rm ph}\rangle_0-\int_0^\beta d\alpha\,\langle\tilde{V}(\alpha)\tilde{N}_{\rm ph}\rangle_0$$
$$=\langle\tilde{N}_{\rm ph}\rangle_{\rm ph}+N^{-1}\sum_q f_q^2-\int_0^\beta d\alpha\,\langle\tilde{V}(\alpha)\tilde{N}_{\rm ph}\rangle_0\,. \quad (B3)$$

The last term contains six terms (two in $\tilde{V}(\alpha)$ and three in $\tilde{N}_{\rm ph}$), but most of these give no contribution. The evaluation of these averages encounters no special difficulties except the term with the phonon operators $\theta_n^+\theta_m(b_q+b_{-q}^+)$. This is small in each subspace of particular value of K due to the argument in Appendix A1. We finally find

$$\langle N_{\rm ph}\rangle=\langle N_{\rm ph}\rangle_{\rm ph}+N^{-1}\sum_q f_q^2+2N^{-1}\sum_q(c_qf_q-f_q^2) \quad (B4)$$

or

$$\langle\Delta N_{\rm ph}\rangle=N^{-1}\sum_q(2c_qf_q-f_q^2) \quad (B5)$$

to first order in V. This is the form we used in Secs. IV and V. This form is also equal to $\langle\Delta N_{\rm ph}\rangle$ found by splitting the Hamiltonian into $\tilde{H}_0$ and $\tilde{V}$ as in (2.18) and (2.19).

APPENDIX C. FREE ENERGY OF AN EXCITON INTERACTING WITH A CLASSICAL LATTICE

In this Appendix, the free energy of an exciton interacting with a classical phonon bath is determined. The starting point is the Hamiltonian of Sec. II in the P, Q representation [Eqs. (2.2), (2.8), and (2.9)]. The transformation of Eq. (2.14b) is performed and we find

$$H=\epsilon\sum a_n^+a_n+\sum_q\tfrac{1}{2}(P_q^2+\omega_q^2Q_q^2)+\sum_{n,m}J_m\theta_{n+m}^+\theta_n a_{n+m}^+a_n \quad (C1)$$

with θ_n^+ given in Eq. (2.16). If we assume the phonons behave classically, then $[Q_\lambda, P_{\lambda'}]=0$, and

$$A^t=-\beta^{-1}\ln\sum_n\langle 0|a_n\int d^NPd^NQ\,e^{-\beta H}a_n^+|0\rangle$$
$$=\epsilon-\beta^{-1}\ln\sum_n\langle 0|a_n\int d^NPd^NQ\,e^{-\beta H_{\rm ph}}$$
$$\times\exp\,-\beta\sum_{n'm'}J_{m'}\theta_{n'+m'}^+\theta_{n'}a_{n'+m'}^+a_n')a_n^+|0\rangle\,. \quad (C2)$$

This can be simplified by noting that if $R=\sum_{n,m}g_{nm}a_n^+a_m$, then

$$e^Ra_l^+e^{-R}=\sum_n a_n^+(e^{\mathbf{g}})_{nl}\,. \quad (C3)$$

Substituting this into (C2) gives

$$A^t=\epsilon-\beta^{-1}\ln\langle 0|\int d^NPd^NQ\sum_{n,m}a_n^+a_m(e^{-\beta\mathbf{g}})_{mn}e^{-\beta H_{\rm ph}}|0\rangle$$
$$=\epsilon-\beta^{-1}\ln q_{\rm ph}-\beta^{-1}\ln\int\sum_n(e^{-\beta\mathbf{g}})_{nn}\frac{e^{-\beta H_{\rm ph}}}{q_{\rm ph}}\,d^NPd^NQ\,, \quad (C4)$$

where $g_{nm}=\theta_n^+\theta_mJ_{nm}$. Since $\theta_n^+\theta_n=1$, we find

$$A^t=\epsilon-\beta^{-1}\ln q_{\rm ph}-\beta^{-1}\ln\sum_n(e^{-\beta\mathbf{J}})_{nn}\,. \quad (C5)$$

Since all diagonal matrix elements in the last term of (C5) are equal, the free energy is equal to that computed in Appendix A2 for a noninteracting exciton phonon system.

[1]R. E. Merrifield, J. Chem. Phys. 40, 445 (1964).
[2]M. Grover and R. Silbey, J. Chem. Phys. 52, 2099 (1970).
[3]M. Grover and R. Silbey, J. Chem. Phys. 54, 4843 (1971).
[4]S. Fischer and S. A. Rice, J. Chem. Phys. 52, 2089 (1970).
[5]A. Nakamura, J. Chem. Phys. 64, 185 (1976).
[6]T. Holstein, Ann. Phys. (N.Y.) 8, 325 (1959).
[7]Y. Toyozawa, Prog. Theor. Phys. 26, 29 (1961); also in *Polarons and Excitons*, edited by C. Kuper and G. Whitfield (Plenum, New York, 1962).
[8]D. Emin, Adv. Phys. 22, 57 (1973).
[9]K. Cho and Y. Toyozawa, J. Phys. Soc. Jpn. 30, 1555 (1971).
[10]For a good review, see the article by A. Huber in *Mathematical Methods in Solid State and Superfluid Theory*, edited by R. Clark and G. Derrick (Oliver and Boyd, London, 1969).