PHYSICAL REVIEW B VOLUME 8, NUMBER 12 15 DECEMBER 1973

Exact Spectral Function for an Electron-Phonon System with an Electron-Diagonal Interaction Hamiltonian

C. Alton Coulter

Department of Physics, University of Alabama in Tuscaloosa, University, Alabama 35486
Quantum Physics Branch, Physical Sciences Directorate, Redstone Arsenal, Alabama 35809

D. W. Howgate

Quantum Physics Branch, Physical Sciences Directorate, Redstone Arsenal, Alabama 35809

(Received 13 November 1972; revised manuscript received 25 June 1973)

An explicit exact expression is obtained for the spectral function of an arbitrary electron-phonon system whose interaction Hamiltonian is linear in the phonon operators and diagonal in the electron operators, and whose statistics are described by any density operator which commutes with the Hamiltonian. The result generalizes, with respect to both lattice type and density operator, the classic calculation of Huang and Rhys for F centers in an Einstein lattice, and in the special case of thermal equilibrium it provides an explicit evaluation of the integral representation for the spectral function given in a fundamental paper by Lax. An application to an example is presented.

I. INTRODUCTION

The Hamiltonian for an electron-phonon system with an interaction linear in the phonon coordinates is

$$H=\sum_i \epsilon_i a_i^\dagger a_i+\sum_\mu \hbar\,\omega_\mu(c_\mu^\dagger c_\mu+\tfrac{1}{2})+\sum_{\substack{i,j\\ \mu}} v_{\mu ij}\, a_i^\dagger a_j(c_\mu^\dagger+c_\mu), \tag{1}$$

where $a_i^\dagger$ and a_i are the creation and annihilation operators for the ith electron state, with energy ϵ_i, and $c_\mu^\dagger$ and c_μ are the standard harmonic oscillator raising and lowering operators for the μth lattice vibrational mode, with frequency ω_μ. The (anti)commutation relations are

$$\begin{aligned}&[a_i, a_j^\dagger]_+=\delta_{ij},\\ &[c_\mu,\ c_{\mu'}^\dagger]_-=\delta_{\mu\mu'},\end{aligned} \tag{2}$$

all other (anti)commutators zero. The third term in (1) is the electron-phonon interaction term, and describes processes in which the electron is scattered from an initial state i into the (same or different) final state j with simultaneous creation or annihilation of a phonon in lattice mode μ. If the first few electronic energy levels ϵ_i are widely spaced compared to the phonon energies $\hbar\omega_\mu$, as in trapped-electron defect centers having absorption bands in the near infrared or visible regions, the dominant terms in the interaction Hamiltonian are usually those for which $i=j$ (since all reasonable density operators will restrict electron populations to these lowest levels, and the diagonal contributions from these low electronic levels enter perturbation expansions in terms with small energy denominators $\pm\hbar\omega_\mu$, while the nondiagonal contributions enter the perturbation expansions in terms with the much larger energy denominators $\epsilon_i-\epsilon_j\pm\hbar\omega_\mu$). Consequently it is a reasonable approximation in many such systems to retain only the electron-diagonal terms in the interaction Hamiltonian and to describe the dynamics of the system by the "electron-diagonal" Hamiltonian

$$H_d=\sum_i \epsilon_i a_i^\dagger a_i+\sum_\mu \hbar\omega_\mu(c_\mu^\dagger c_\mu+\tfrac{1}{2})+\sum_{i,\mu}\hbar d_{\mu i}\, a_i^\dagger a_i(c_\mu^\dagger+c_\mu), \tag{3}$$

where $v_{\mu ii}=\hbar d_{\mu i}$.

Huang and Rhys[1] used a Hamiltonian equivalent to (3) to calculate the absorption spectrum of an F center in an Einstein lattice in thermal equilibrium. They obtained the result (restated in our notation) that absorption lines occur at the (circular) frequencies.

$$\omega_{jip}=\frac{1}{\hbar}(\epsilon_j-\epsilon_i)-\sum_\mu\frac{d_{\mu j}^2-d_{\mu i}^2}{\omega_\mu}+p\omega_l,\qquad p=0,\ \pm1,\ \pm2,\ \ldots \tag{4}$$

with intensities proportional, for fixed i and j, to

$$\omega_{jip}\, e^{-S(2\bar n+1)}[(\bar n+1)/\bar n]^{p/2}\times I_p(2S[\bar n(\bar n+1)]^{1/2}). \tag{5}$$

Here ω_l is the common frequency of all the lattice vibrational modes, $\bar n=(e^{\beta\hbar\omega_l}-1)^{-1}$ with $\beta=(kT)^{-1}$, $S=\sum_\mu(d_{\mu i}-d_{\mu j})^2/\omega_l^2$, and I_p is the modified Bessel function of the first kind of order p. Lax[2] subsequently considered the general case of an arbitrary (non-Einsteinian) lattice and showed that the spectral function for the electron-phonon system is proportional to (ν the ordinary frequency, with $\omega=2\pi\nu$)

$$G(\nu)=h^{-1}\int_{-\infty}^{\infty}\exp[2\pi i(\nu-\nu_0)t+f(t)]\,dt, \tag{6}$$

where in our notation

$$2\pi\nu_0=\hbar^{-1}(\epsilon_j-\epsilon_i)-\sum_{\mu}\frac{d_{\mu j}^2-d_{\mu i}^2}{\omega_\mu}\ , \tag{7a}$$

$$f(t)=\sum_{\mu}\frac{(d_{\mu i}-d_{\mu j})^2}{\omega_\mu^2}\times[i\sin\omega_\mu t-(2\bar{n}_\mu+1)(1-\cos\omega_\mu t)], \tag{7b}$$

with $\bar{n}_\mu=(e^{\beta\hbar\omega_\mu}-1)^{-1}$. He demonstrated that in the special case of an Einstein lattice this expression reduces to the Huang-Rhys result.

In this paper we derive an explicit exact form for the spectral function of any electron-phonon system having the Hamiltonian (3) and a density operator commuting with this Hamiltonian. The only approximation used [besides neglect of the electron-nondiagonal interaction terms, implied by the use of (3) rather than (1)] is the assumption that the electromagnetic field couples to the electron-phonon system only through the electron moment operators, an assumption that appears to be well justified in most cases of interest but which could easily be eliminated were it physically advantageous to do so. For a general density operator commuting with H_d, the result is stated as a set of δ-function absorption lines with line strengths expressed in terms of sums of products of exponentials and Laguerre polynomials. In the special case of thermal equilibrium the expressions for the line strengths simplify to products of terms of type (5) over phonon modes, and thus provide an explicit evaluation in terms of well-known functions for Lax's integral representation (6) for the spectral function.

The calculation is performed by using double-time Green's functions and a second-quantized representation for the phonon fields which was first introduced by Lax.[3] Properties of this second-quantized phonon representation and of the double-time Green's functions are briefly summarized in Sec. II. The spectral function is calculated in Sec. III, and its simplified form in the special case of thermal equilibrium is given in Sec. IV. An application to two hypothetical defect centers in LiF is given in Sec. V.

II. PRELIMINARIES

The usual harmonic oscillator with Hamiltonian

$$h=p^2/2m+\tfrac{1}{2}m\omega^2q^2$$

may be second quantized[4,5] by introducing a field operator $\phi(q)$ with the commutation relations

$$\begin{aligned}&[\phi(q),\ \phi^\dagger(q')]_-=\delta(q-q'),\\&[\phi(q),\ \phi(q')]_-=0\end{aligned} \tag{8}$$

and a Hamiltonian operator

$$H=\int_{-\infty}^{\infty}\phi^\dagger(q)\left(-\frac{\hbar^2}{2m}\frac{d^2}{dq^2}+\tfrac{1}{2}m\omega^2q^2\right)\phi(q)\,dq. \tag{9}$$

By expanding $\phi(q)$ in the complete orthonormal set of eigenfunctions $u_n(q)$ of the differential operator

$$-\frac{\hbar^2}{2m}\frac{d^2}{dq^2}+\tfrac{1}{2}m\omega^2q^2$$

as

$$\phi(q)=\sum_{n=0}^{\infty}u_n(q)b_n, \tag{10}$$

where the b_n are a set of (operator) expansion coefficients, one may transform Eqs. (8) and (9) to

$$[b_m,\ b_n^\dagger]_-=\delta_{nm},\quad [b_m,\ b_n]_-=0 \tag{11}$$

and

$$H=\sum_{n=0}^{\infty}(n+\tfrac{1}{2})\hbar\omega b_n^\dagger b_n\ , \tag{12}$$

respectively. Obviously $b_n^\dagger$ is the creation operator for the nth harmonic-oscillator energy eigenstate, and b_n is the annihilation operator for this state. The customary harmonic-oscillator raising and lowering operators can be written[3]

$$\begin{aligned}c^\dagger&=\sum_{n=0}^{\infty}(n+1)^{1/2}b_{n+1}^\dagger b_n,\\c&=\sum_{n=0}^{\infty}(n+1)^{1/2}b_n^\dagger b_{n+1}\end{aligned} \tag{13}$$

within the set of one-particle states, which is spanned by the $b_n^\dagger|0\rangle$ ($|0\rangle$ the vacuum state); and only this set of states is of physical interest in lattice-vibrational problems.[5] In this set of one-particle states the Hamiltonian (12) can also be written in the familiar form

$$H=\hbar\omega(c^\dagger c+\tfrac{1}{2}).$$

In the case of a lattice, where a large number of vibrational modes labeled by the index μ are present, one introduces a field operator $\phi^\mu(q_\mu)$ for each mode and proceeds as above. By observing the relation (13) between the raising-lowering operators and the creation-annihilation operators for each of these modes, one sees that the Hamiltonian H_d given in (3) may be rewritten as

$$H_d=\sum_i\epsilon_i a_i^\dagger a_i+\sum_\mu\sum_{n=0}^{\infty}\hbar\omega_\mu(n+\tfrac{1}{2})b_n^{\mu\dagger}b_n^\mu+\sum_{i,\mu}\sum_{n=0}^{\infty}\hbar d_{\mu i}(n+1)^{1/2}a_i^\dagger a_i(b_{n+1}^{\mu\dagger}b_n^\mu+b_n^{\mu\dagger}b_{n+1}^\mu), \tag{14}$$

with

$$\begin{aligned}&[b_n^\mu,\ b_m^{\mu'\dagger}]_-=\delta_{\mu\mu'}\delta_{nm},\\&[b_n^\mu,\ b_m^{\mu'}]_-=0.\end{aligned}$$

Equation (14) may, of course, be derived entirely within a quantum-field-theory context without use of the operators $c_\mu^\dagger$, c_μ.[6]

Since the problem considered involves one electron, and the lattice states of interest contain one "particle" per mode, the space of state vectors of interest is spanned by the complete orthonormal set

$$a_i^\dagger \prod_\mu b_{n_\mu}^{\mu\dagger} |0\rangle . \tag{15}$$

Within this set of vectors the Hamiltonian (14) is the same as the operator

$$H_d' = \sum_i \epsilon_i a_i^\dagger a_i + \sum_i a_i^\dagger a_i \sum_\mu \left(\sum_{n=0}^{\infty} [\hbar\omega_\mu (n+\tfrac{1}{2}) b_n^{\mu\dagger} b_n^\mu + \hbar d_{\mu i}(n+1)^{1/2}(b_{n+1}^{\mu\dagger} b_n^\mu + b_n^{\mu\dagger} b_{n+1}^\mu)] \right) . \tag{16}$$

From the properties of the harmonic-oscillator eigenstates $u_n^\mu(q_\mu)$, one sees that the term in large parentheses can also be written

$$\int_{-\infty}^{\infty} \phi^{\mu\dagger}(q_\mu) \left(-\frac{\hbar^2}{2m_\mu} \frac{d^2}{dq_\mu^2} + \tfrac{1}{2} m_\mu \omega_\mu^2 q_\mu^2 + (2m_\mu \hbar\omega_\mu)^{1/2} d_{\mu i} q_\mu \right) \phi^\mu(q_\mu)\, dq_\mu$$

$$= \int_{-\infty}^{\infty} \phi^{\mu\dagger}(q_\mu) \left\{ -\frac{\hbar^2}{2m_\mu} \frac{d^2}{dq_\mu^2} + \tfrac{1}{2} m_\mu \omega_\mu^2 \left[q_\mu + \left(\frac{2\hbar}{m_\mu \omega_\mu} \right)^{1/2} \frac{d_{\mu i}}{\omega_\mu} \right]^2 - \frac{\hbar d_{\mu i}^2}{\omega_\mu} \right\} \phi^\mu(q_\mu)\, dq_\mu . \tag{17}$$

By expanding $\phi^\mu(q_\mu)$ in the complete orthonormal set of functions $\{u_n^\mu(q_\mu + \lambda_{\mu i})\}$ as

$$\phi^\mu(q_\mu) = \sum_{n=0}^{\infty} b_n^{i\mu} u_n^\mu(q_\mu + \lambda_{\mu i}), \tag{18}$$

with $\lambda_{\mu i} = (2\hbar/m_\mu\omega_\mu)^{1/2} d_{\mu i}/\omega_\mu$, one may rewrite (17) as

$$\sum_{n=0}^{\infty} \hbar\omega_\mu (n+\tfrac{1}{2}) b_n^{i\mu\dagger} b_n^{i\mu} - \frac{\hbar d_{\mu i}^2}{\omega_\mu} \sum_{n=0}^{\infty} b_n^{i\mu\dagger} b_n^{i\mu} . \tag{19}$$

By writing expression (19) in place of the large parentheses in Eq. (16) and noting that $\Sigma_{n=0}^{\infty} b_n^{i\mu\dagger} b_n^{i\mu}$ is the identity operator on the set of states (15), one finally concludes that in the set of states of physical interest the Hamiltonian may be written

$$H_d = \sum_i \left(\epsilon_i - \sum_\mu \frac{\hbar d_{\mu i}^2}{\omega_\mu} \right) a_i^\dagger a_i + \sum_i a_i^\dagger a_i \sum_\mu \sum_{n=0}^{\infty} \hbar\omega_\mu (n+\tfrac{1}{2}) b_n^{i\mu\dagger} b_n^{i\mu} . \tag{20}$$

The symbol H_d has again been used for this operator, though it actually differs from both (16) and (14), because in the set of states of interest all three operators are the same. One sees immediately that the eigenstates of the Hamiltonian (20) are the vectors

$$|i, \{n_\mu\}\rangle \equiv a_i^\dagger \prod_\mu b_{n_\mu}^{i\mu\dagger} |0\rangle , \tag{21}$$

with the well-known energy eigenvalues

$$E(i, \{n_\mu\}) = \epsilon_i - \sum_\mu \frac{\hbar d_{\mu i}^2}{\omega_\mu} + \sum_\mu (n_\mu + \tfrac{1}{2}) \hbar\omega_\mu . \tag{22}$$

As noted earlier, it will be assumed that the electron-phonon system is in a statistical equilibrium described by a density operator ρ which commutes with the H_d of Eq. (20) (so that statistical averages are time independent), but is not otherwise restricted. ρ and H_d will then be expressible as functions of a single operator[7]; and in the usual fashion we may by appropriately choosing any degenerate states of H_d assume that $\rho = \rho(H_d)$. For simplicity and definiteness we assume that the action of ρ on the states (21) can be written

$$\rho |i, \{n_\mu\}\rangle = \rho(i, \{n_\mu\}) |i, \{n_\mu\}\rangle , \tag{23}$$

the necessary modification of the following calculation for other cases being obvious. The traces occurring in statistical averages are then conveniently evaluated in the states (21).

The spectral function for the system can be expressed in terms of double-time Green's functions.[8] The Green's function $\langle\langle A|B \rangle\rangle_\omega$ for arbitrary operators A, B is defined as

$$\langle\langle A|B \rangle\rangle_\omega = \begin{cases} \dfrac{i}{2\pi} \displaystyle\int_{-\infty}^{0} dt\, e^{i\omega t} \langle [A(t), B] \rangle, & \mathrm{Im}\omega < 0 \\ -\dfrac{i}{2\pi} \displaystyle\int_{0}^{\infty} dt e^{i\omega t} \langle [A(t), B] \rangle, & \mathrm{Im}\omega > 0 \end{cases} \tag{24}$$

with

$$A(t) = e^{iHt/\hbar} A e^{-iHt/\hbar} \tag{25}$$

and

$$\langle \cdots \rangle = \mathrm{Tr}\rho \cdots . \tag{26}$$

One sees that

$$\omega \langle\langle A|B \rangle\rangle_\omega = (1/2\pi)\langle [A, B] \rangle + (1/\hbar) \langle\langle [A, H] | B \rangle\rangle_\omega . \tag{27}$$

The absorption spectrum is determined by the function $\sigma(\omega)$ whose value at the (real) frequency ω is proportional to[2,8,9]

$$\omega \lim_{\epsilon \to 0^+} \mathrm{Im} \sum_\alpha \langle\langle M_\alpha | M_\alpha \rangle\rangle_{\omega - i\epsilon} , \tag{28}$$

where the M_α are the components of the moment operator coupling the system of interest to the electromagnetic field. For the case of the electron-phonon system the phonon contribution to M_α can usually be neglected, so one may write

$$M_\alpha = \sum_{i,j} M_{\alpha ij} a_i^\dagger a_j \tag{29}$$

in terms of the moment-operator matrix elements $M_{\alpha ij}$. $\sigma(\omega)$ is then proportional to

$$\omega \lim_{\epsilon\to 0^+} \mathrm{Im} \sum_\alpha \sum_{\substack{i,j\\ i',j'}} M_{\alpha ij} M_{\alpha j' i'} \langle\langle a_i^\dagger a_j | a_{j'}^\dagger a_{i'} \rangle\rangle_{\omega - i\epsilon} , \tag{30}$$

so that the Green's functions $\langle\langle a_i^\dagger a_j | a_{j'}^\dagger a_{i'} \rangle\rangle_\omega$ determine the absorption spectrum. The explicit evaluation of these Green's functions for the Hamiltonian H_d and density operator $\rho(H_d)$ is given in Sec. III.

III. CALCULATION OF DOUBLE-TIME GREEN'S FUNCTIONS

Equation (27) cannot conveniently be used for the direct evaluation of $\langle\langle a_i^\dagger a_j | a_{j'}^\dagger a_{i'} \rangle\rangle_\omega$, because it leads in the familiar way to a coupled hierarchy of equations for Green's functions of higher and higher order. This difficulty may be avoided by considering instead the Green's functions

$$\langle\langle a_i^\dagger a_j b_{m_1}^{1\dagger} b_{m_2}^{2\dagger} \cdots b_{m_N}^{N\dagger} b_{n_N}^{N} \cdots b_{n_2}^{2} b_{n_1}^{1} | a_{j'}^\dagger a_{i'} \rangle\rangle_\omega , \tag{31}$$

where N is the number of lattice vibrational modes. For one has[5]

$$\langle\langle a_i^\dagger a_j | a_{j'}^\dagger a_{i'} \rangle\rangle_\omega = \sum_{m_1} \cdots \sum_{m_N} \langle\langle a_i^\dagger a_j b_{m_1}^{1\dagger} \cdots b_{m_N}^{N\dagger} b_{m_N}^{N} \cdots b_{m_1}^{1} | a_{j'}^\dagger a_{i'} \rangle\rangle_\omega , \tag{32}$$

since

$$\sum_{m_1} \cdots \sum_{m_N} b_{m_1}^{1\dagger} \cdots b_{m_N}^{N} b_{m_N}^{N} \cdots b_{m_1}^{1} \tag{33}$$

is the identity operator in the state space of interest. Also, from Eqs. (10) and (18) it follows that the $b_m^{i\mu}$ and the b_n^μ are linearly related:

$$b_m^\mu = \sum_{n=0}^{\infty} C_{mn}^\mu (\lambda_{\mu i}) b_n^{i\mu} , \tag{34}$$

with

$$C_{mn}^\mu(\lambda_{\mu i}) = \int_{-\infty}^{\infty} u_m^{\mu *}(q_\mu) u_n^\mu (q_\mu + \lambda_{\mu i})\, dq_\mu . \tag{35}$$

Equation (32) can then be written

$$\langle\langle a_i^\dagger a_j | a_{j'}^\dagger a_{i'} \rangle\rangle_\omega = \sum_{m_1} \ldots \sum_{m_N} \sum_{n_1} \ldots \sum_{n_N} \prod_\mu C_{m_\mu n_\mu}^\mu (\lambda_{\mu j} - \lambda_{\mu i}) \langle\langle a_i^\dagger a_j b_{m_1}^{i1\dagger} \ldots b_{m_N}^{iN\dagger} b_{n_N}^{jN} \ldots b_{n_1}^{j1} | a_{j'}^\dagger a_{i'} \rangle\rangle_\omega , \tag{36}$$

since

$$\sum_{p=0}^{\infty} C_{pm}^{\mu *}(\lambda_{\mu i}) C_{pn}^\mu (\lambda_{\mu j}) = C_{mn}^\mu (\lambda_{\mu j} - \lambda_{\mu i}) .$$

Equation (27) can now be used directly to evaluate the function

$$\langle\langle a_i^\dagger a_j b_{m_1}^{i1\dagger} \ldots b_{m_N}^{iN\dagger} b_{n_N}^{jN} \ldots b_{n_1}^{j1} | a_{j'}^\dagger a_{i'} \rangle\rangle_\omega ,$$

the commutator with H_d on the right-hand side of (27) giving rise to no higher-order Green's functions because of the one- "particle" -per-mode nature of the states in the trace, and in fact yielding a term proportional to the Green's function itself. Explicitly, one finds

$$\begin{aligned} \langle\langle a_i^\dagger a_j b_{m_1}^{i1\dagger} \ldots b_{m_N}^{iN\dagger} b_{n_N}^{jN} \ldots b_{n_1}^{j1} | a_{j'}^\dagger a_{i'} \rangle\rangle_\omega &= \frac{1}{2\pi} [\rho(i; \{m_\mu\}) - \rho(j; \{n_\mu\})] \\ &\times \delta_{ii'} \delta_{jj'} \prod_\mu C_{m_\mu n_\mu}^{\mu *} (\lambda_{\mu j} - \lambda_{\mu i}) \\ &\times \left(\omega - \hbar^{-1}(\epsilon_j - \epsilon_i) + \sum_\mu \frac{d_{\mu j}^2 - d_{\mu i}^2}{\omega_\mu} - \sum_\mu \omega_\mu (n_\mu - m_\mu) \right)^{-1} . \end{aligned} \tag{37}$$

By combining Eqs. (36) and (37), one finds

$$\begin{aligned} \langle\langle a_i^\dagger a_j | a_{j'}^\dagger a_{i'} \rangle\rangle_\omega &= \frac{\delta_{ii'} \delta_{jj'}}{2\pi} \sum_{\{m_\mu\}} \sum_{\{n_\mu\}} [\rho(i; \{m_\mu\}) - \rho(j; \{n_\mu\})] \\ &\times \prod_\mu | C_{m_\mu n_\mu}^\mu (\lambda_{\mu j} - \lambda_{\mu i}) |^2 \Big/ \left[\omega - \left(\hbar^{-1}(\epsilon_j - \epsilon_i) - \sum_\mu \frac{(d_{\mu j}^2 - d_{\mu i})^2}{\omega_\mu} + \sum_\mu \omega_\mu (n_\mu - m_\mu) \right) \right] . \end{aligned} \tag{38}$$

Reference to expression (30) for $\sigma(\omega)$ shows that the transition from state $| i; \{m_\mu\} \rangle$ to state $| j; \{n_\mu\} \rangle$ produces an absorption line at frequency

$$\omega = \hbar^{-1}(\epsilon_j - \epsilon_i) - \sum_\mu \frac{d_{\mu j}^2 - d_{\mu i}^2}{\omega_\mu} + \sum_\mu \omega_\mu (n_\mu - m_\mu) \tag{39}$$

with strength proportional to

$$\omega\Big(\sum_\alpha |M_{\alpha ij}|^2\Big)[\rho(i;\{m_\mu\})-\rho(j;\{n_\mu\})] \times \prod_\mu |C^\mu_{m_\mu n_\mu}(\lambda_{\mu j}-\lambda_{\mu i})|^2 . \tag{40}$$

Two steps must be taken to complete the calculation. The first is to observe that the $C^\mu_{mn}(\lambda_{\mu i})$ may be computed explicitly in the case of the standard choice[10,11]

$$u^\mu_n(q)=\alpha_\mu^{1/2}(\pi^{1/2}2^n n!)^{-1/2} \times e^{-1/2(\alpha_\mu q)^2}H_n(\alpha_\mu q), \tag{41}$$

$$\alpha_\mu=(m_\mu\,\omega_\mu/\hbar)^{1/2}, \tag{42}$$

$$H_n(Q)=(-1)^n e^{Q^2}\frac{d^n}{dQ^n}e^{-Q^2} \tag{43}$$

for the phases of the $u^\mu_n(q)$ to be

$$C^\mu_{mn}(\lambda_{\mu i})=(-1)^m(m!n!)^{1/2}e^{-(d_{\mu i}/\omega_\mu)^2/2}\sum_r\frac{(-1)^r(d_{\mu i}/\omega_\mu)^{m+n-2r}}{r!\,(m-r)!\,(n-r)!} \tag{44}$$

$$=\left(\frac{n-m}{|m-n|}\right)^{m+n}(m!n!)^{1/2}[(m+n-p)!]^{-2}(d_{\mu i}/\omega_\mu)^{|m-n|}e^{-(d_{\mu i}/\omega_\mu)^2/2}L_p^{|m-n|}\left[\left(\frac{d_{\mu i}}{\omega_\mu}\right)^2\right], \tag{45}$$

where

$$L^k_p(z)\equiv\sum_r(-1)^r\frac{[(p+k)!]^2}{(p-r)!\,r!\,(k+r)!}z^r \tag{46}$$

is the associated Laguerre polynomial[12] of indicated order with

$$p=\min(m,n)=\tfrac{1}{2}(m+n-|m-n|).$$

The second is to note that the absorption frequency (39) depends only on the differences $r_\mu \equiv n_\mu - m_\mu$ of phonon excitation numbers, and consequently all transitions $|j;\{n_\mu\}\rangle \leftarrow |i;\{m_\mu\}\rangle$ having the same set of $\{r_\mu\}$ will contribute additively to the absorption at the same frequency.[13] Thus one may finally state that the absorption spectrum for the system consists of δ-function lines at the frequencies

$$\omega=\hbar^{-1}(\epsilon_j-\epsilon_i)-\sum_\mu(d^2_{\mu j}-d^2_{\mu i})/\omega_\mu+\sum_\mu r_\mu\omega_\mu , \tag{47}$$

where the r_μ are any set of (positive, negative, or zero) integers; and the strength of the absorption line at frequency (47) is proportional to

$$\omega\Big(\sum_\alpha|M_{\alpha ij}|^2\Big)\sum_{m_1=s_1}^{\infty}\cdots\sum_{m_N=s_N}^{\infty}[\rho(i;\{m_\mu\})-\rho(j;\{m_\mu+r_\mu\})]\prod_\mu\frac{m_\mu!(m_\mu+r_\mu)!}{[(m_\mu+\frac{1}{2}r_\mu+\frac{1}{2}|r_\mu|)!]^4} \times\left(\frac{(d_{\mu j}-d_{\mu i})^2}{\omega_\mu^2}\right)^{|r_\mu|}e^{-(d_{\mu j}-d_{\mu i})^2/\omega_\mu^2}\left[L_{p_\mu}^{|r_\mu|}\left(\frac{(d_{\mu j}-d_{\mu i})^2}{\omega_\mu^2}\right)\right]^2, \tag{48}$$

where $s_\mu=\max(0,-r_\mu)$ and $p_\mu=\min(m_\mu,\ m_\mu+r_\mu)$. Equations (47) and (48) give a complete, exact, and explicit solution to the problem of calculating the absorption spectrum for any electron-phonon system with an electron-diagonal Hamiltonian of the type (3) and a density operator ρ commuting with the Hamiltonian.

IV. CASE OF THERMAL EQUILIBRIUM

The expression (48) for the line strengths can be put in a considerably simpler form for the case of thermal equilibrium, where

$$\rho=e^{-\beta H_d}/\mathrm{Tr}\,e^{-\beta H_d},\qquad \beta=(kT)^{-1}. \tag{49}$$

For this situation (48) takes the form

$$\omega\Big(\sum_\alpha|M_{\alpha ij}|^2\Big)\exp\Big[-\beta\Big(\epsilon_i-\sum_\mu\frac{\hbar d^2_{\mu i}}{\omega_\mu}+\sum_\mu\tfrac{1}{2}\hbar\omega_\mu\Big)\Big](\mathrm{Tr}\,e^{-\beta H_d})^{-1} \times\Big\{1-\exp\Big[-\beta\Big(\epsilon_j-\epsilon_i-\sum_\mu\frac{\hbar(d^2_{\mu j}-d^2_{\mu i})}{\omega_\mu}+\sum_\mu\hbar\omega_\mu r_\mu\Big)\Big]\Big\}\exp\Big(-\sum_\mu\frac{(d_{\mu j}-d_{\mu i})^2}{\omega_\mu^2}\Big) \times\prod_\mu\frac{m_\mu!(m_\mu+r_\mu)!}{[(m_\mu+\frac{1}{2}r_\mu+\frac{1}{2}|r_\mu|)!]^4}\left(\frac{(d_{\mu j}-d_{\mu i})^2}{\omega_\mu^2}\right)^{|r_\mu|}\left[L_{p_\mu}^{|r_\mu|}\left(\frac{(d_{\mu j}-d_{\mu i})^2}{\omega_\mu^2}\right)\right]^2 e^{-m_\mu\beta\hbar\omega_\mu} . \tag{50}$$

A special case of a theorem[14] relating sums of products of associated Laguerre polynomials to hypergeometric functions states that

$$\sum_{p=0}^{\infty} \frac{p!\,t^p[L_p^k(x)]^2}{[(p+k)!]^3} = (1-t)^{-1-k}\, e^{-2xt/(1-t)} \left(\frac{1-t}{xt^{1/2}}\right)^k I_k(2xt^{1/2}/(1-t))\,, \tag{51}$$

where, as before, $I_k(z)$ is the modified Bessel function of the first kind of order k. Upon applying this to expression (50) one finds that the line strengths may be written (for either sign of the various r_μ)

$$\begin{aligned}
&\omega\Big(\sum_\alpha |M_{\alpha ij}|^2\Big)\exp\Big[-\beta\Big(\epsilon_i-\sum_\mu \frac{\hbar d_{\mu i}^2}{\omega_\mu}+\sum_\mu \tfrac{1}{2}\hbar\omega_\mu\Big)\Big](\mathrm{Tr}\,e^{-\beta H_d})^{-1}\\
&\quad\times\Big\{1-\exp\Big[-\beta\Big(\epsilon_j-\epsilon_i-\sum_\mu \frac{\hbar(d_{\mu j}^2-d_{\mu i}^2)}{\omega_\mu}+\sum_\mu \hbar\omega_\mu r_\mu\Big)\Big]\Big\}\exp\Big(-\sum_\mu \frac{(2\bar{n}_\mu+1)(d_{\mu j}-d_{\mu i})^2}{\omega_\mu^2}\Big)\\
&\quad\times\prod_\mu (1-e^{-\beta\hbar\omega_\mu})^{-1}\Big(\frac{\bar{n}_\mu+1}{\bar{n}_\mu}\Big)^{r_\mu/2} I_{r_\mu}\Big(2[(\bar{n}_\mu+1)\bar{n}_\mu]^{1/2}\,\frac{(d_{\mu j}-d_{\mu i})^2}{\omega_\mu^2}\Big)
\end{aligned} \tag{52}$$

[where, as before, $\bar{n}_\mu=(e^{\beta\hbar\omega_\mu}-1)^{-1}$] or, after taking into account the explicit form of $\mathrm{Tr}\,e^{-\beta H_d}$, as

$$\begin{aligned}
&\omega\Big(\sum_\alpha |M_{\alpha ij}|^2\Big)\exp\Big[-\beta\Big(\epsilon_i-\sum_{\mu'} \frac{\hbar d_{\mu' i}^2}{\omega_{\mu'}}\Big)\Big]\Big/\sum_k \exp\Big[-\beta\Big(\epsilon_k-\sum_{\mu''} \frac{\hbar d_{\mu'' k}^2}{\omega_{\mu''}}\Big)\Big]\\
&\quad\times\Big\{1-\exp\Big[-\beta\Big(\epsilon_j-\epsilon_i-\sum_\mu \frac{\hbar(d_{\mu j}^2-d_{\mu i}^2)}{\omega_\mu}+\sum_\mu \hbar\omega_\mu r_\mu\Big)\Big]\Big\}\exp\Big(-\sum_\mu \frac{(2\bar{n}_\mu+1)(d_{\mu j}-d_{\mu i})^2}{\omega_\mu^2}\Big)\\
&\quad\times\prod_\mu\Big(\frac{\bar{n}_\mu+1}{\bar{n}_\mu}\Big)^{r_\mu/2} I_{r_\mu}\Big(2[(\bar{n}_\mu+1)\bar{n}_\mu]^{1/2}\,\frac{(d_{\mu j}-d_{\mu i})^2}{\omega_\mu^2}\Big)\;.
\end{aligned} \tag{53}$$

Equations (47) and (53) give explicit exact expressions for the frequencies and strengths, respectively, of the absorption lines of a system with Hamiltonian H_d in thermal equilibrium.

By noting that Lax's function[15] $G(\nu)$ [Eq. (6)] differs from $2\,\mathrm{Im}\,\langle\langle a_i^\dagger a_j\,|\,a_j^\dagger a_i\rangle\rangle_{2\pi\nu}$ by a factor $\hbar^{-1}$, by the omission of thermal averages over the electron states, and by not taking into account stimulated emission (which is treated separately, and is in any case negligible for most cases of interest), one obtains as a corollary that $G(\nu)$ has the explicit value

$$G(\nu)=h^{-1}\sum_{r_1=-\infty}^{\infty}\cdots\sum_{r_N=-\infty}^{\infty} A(\{r_\mu\})\,\delta(\nu-\nu(\{r_\mu\})) \tag{54}$$

where

$$h\nu(\{r_\mu\})=\epsilon_j-\epsilon_i-\sum_\mu \frac{\hbar(d_{\mu j}^2-d_{\mu i}^2)}{\omega_\mu}+\sum_\mu r_\mu\,\hbar\omega_\mu \tag{55}$$

and

$$\begin{aligned}
A(\{r_\mu\})=&\exp\Big(-\sum_\mu \frac{(2\bar{n}_\mu+1)(d_{\mu j}-d_{\mu i})^2}{\omega_\mu^2}\Big)\\
&\times\prod_\mu\Big(\frac{\bar{n}_\mu+1}{\bar{n}_\mu}\Big)^{r_\mu/2}\\
&\times I_{r_\mu}\Big(2[(\bar{n}_\mu+1)\bar{n}_\mu]^{1/2}\,\frac{(d_{\mu j}-d_{\mu i})^2}{\omega_\mu^2}\Big).
\end{aligned} \tag{56}$$

V. ADAPTATION TO NUMERICAL CALCULATIONS AND APPLICATION TO AN EXAMPLE

While Eqs. (47) and (53) give an exact expression for the absorption spectrum of the system with Hamiltonian (3) in thermal equilibrium, they clearly cannot be used for actual numerical calculations for a lattice with 10^{23} (or even 10^2) distinct vibrational modes. Fortunately, it is usually possible to approximate the physical lattice by a lattice containing only a few vibrational modes in such a fashion that the absorption spectrum of the "approximate" lattice is essentially indistinguishable from that of the actual physical lattice. To see how this may be done, note that a comparison of the form (4), (5) of the absorption spectrum given by Lax's Green's function $G(\nu)$ [Eqs. (6), (7a), (7b)] in the case where all the lattice frequencies are equal with the general form (54)–(56) restricted to the same case yields the identity

$$I_p(2S[\bar{n}(\bar{n}+1)]^{1/2})=\sum_{r_1}\cdots\sum_{r_N}\prod_\mu I_{r_\mu}\Big(2[\bar{n}(\bar{n}+1)]^{1/2}\,\frac{(d_{\mu j}-d_{\mu i})^2}{\omega_l^2}\Big),\qquad \sum_{\mu=1}^{N} r_\mu=p \tag{57}$$

where as in Eq. (5), $\bar{n}=(e^{\beta\hbar\omega_l}-1)^{-1}$, $S=\sum_\mu(d_{\mu i}-d_{\mu j})^2/\omega_l^2$, and ω_l is the common frequency of the lattice modes, and where the summations over $r_1, \ldots, r_N$ include only those values of these variables for which

$r_1+\cdots+r_N=p$. It follows that if $\omega_{\mu_1}, \ldots, \omega_{\mu_m}$ all lie in a small enough interval $\Delta\omega_\tau$ about an average frequency $\bar{\omega}_\tau$ then

$$\sum_{r_{\mu_1}} \cdots \sum_{r_{\mu_m}} \prod_{l=1}^{m} \left(\frac{\bar{n}_{\mu_l}+1}{\bar{n}_{\mu_l}}\right)^{r_{\mu_l}/2} I_{r_{\mu_l}}\left(2[\bar{n}_{\mu_l}(\bar{n}_{\mu_l}+1)]^{1/2} \frac{(d_{\mu_l j}-d_{\mu_l i})^2}{\omega_{\mu_l}^2}\right),$$

$$\approx \left(\frac{\bar{n}_\tau+1}{\bar{n}_\tau}\right)^{r_\tau/2} I_{r_\tau}\left(2[\bar{n}_\tau(\bar{n}_\tau+1)]^{1/2} \frac{(\bar{d}_{\tau j}-\bar{d}_{\tau i})^2}{\omega_\tau^2}\right), \qquad \sum_{l=1}^{m} r_{\mu_l} = r_\tau \tag{58}$$

with

$$\bar{n}_\tau = (e^{\beta\hbar\bar{\omega}_\tau}-1)^{-1}$$

and

$$\frac{(\bar{d}_{\tau j}-\bar{d}_{\tau i})^2}{\bar{\omega}_\tau^2} = \sum_{l=1}^{m} \frac{(d_{\mu_l j}-d_{\mu_l i})^2}{\omega_{\mu_l}^2}. \tag{59}$$

In addition, for each combination of $r_{\mu_1}, \ldots, r_{\mu_m}$ above satisfying

$$\sum_{l=1}^{m} r_{\mu_l} = r_\tau ,$$

one has[16]

$$\sum_{l=1}^{m} r_{\mu_l}\omega_{\mu_l} \approx r_\tau \bar{\omega}_\tau .$$

If the definition of $\bar{d}_{\tau j}$, $\bar{d}_{\tau i}$ is completed (up to a nonessential over-all sign) by requiring that

$$\frac{\bar{d}_{\tau j}^2-\bar{d}_{\tau i}^2}{\bar{\omega}_\tau} = \sum_{l=1}^{m} \frac{d_{\mu_l j}^2-d_{\mu_l i}^2}{\omega_{\mu_l}}, \tag{60}$$

one sees that the exact absorption spectrum may be approximated by applying Eqs. (47) and (53) not to the full set of modes μ with frequencies and coupling constants $d_{\mu i}$, $d_{\mu j}$, but to the smaller set of "modes" τ with frequencies $\bar{\omega}_\tau$ and coupling constants $\bar{d}_{\tau i}$, $\bar{d}_{\tau j}$. The effect of this approximation is to replace a large group of absorption lines due to a set of phonon modes lying in a narrow frequency range by a single line in that range whose amplitude contribution is the "integrated" amplitude contribution of the entire set of lines it replaces. It seems reasonable to assume that the approximation will be a good one if the spacing of the resulting absorption lines in the "approximate" spectrum is significantly smaller than the instrumental resolution available. As will be seen shortly, this condition is marginally satisfied for four "approximate modes." For five or more modes it will be well satisfied over the whole band except for the immediate region of the zero-phonon line. Additional modes can be introduced to determine the form of that exceptional region of the spectrum to any desired accuracy.

To illustrate the application of this approximate form of the results of Sec. IV, calculations of the absorption spectra of two hypothetical one-electron centers in LiF—one with an S value of 5 and the other with an S value of 15—were performed. The phonon spectrum of LiF as calculated by Karo and Hardy[17] is shown in Fig. 1. For the purposes of the present calculation this spectrum was replaced by four "modes" whose frequencies are indicated by vertical bars in Fig. 1. These four frequencies and the frequency ranges which they "represent" are given in Table I. Each $\bar{\omega}_\tau$ is the average of the frequencies in its frequency range,[18] and the particular frequency ranges used were chosen to correspond to the prominent features of the LiF phonon spectrum. For simplicity it was decided to take the $\bar{d}_{\tau i}=0$, and each $\bar{d}_{\tau j}$ proportional to the number of phonon modes in the frequency range to which it corresponds.[19] The $\bar{d}_{\tau j}$ were then adjusted by an over-all factor to obtain the desired S values. The relative sizes of the $\bar{d}_{\tau j}$ are indicated by the relative heights of the lines indicating the positions of the $\bar{\omega}_\tau$ in Fig. 1, and the specific numerical values of the $\bar{d}_{\tau j}$ used in the two cases are given in Table I. Finally, the "unperturbed" electronic transition frequency was chosen in each case so as to make the circular frequency ω_0 of the zero-phonon transition 3.1416×10^{15} sec^{-1}

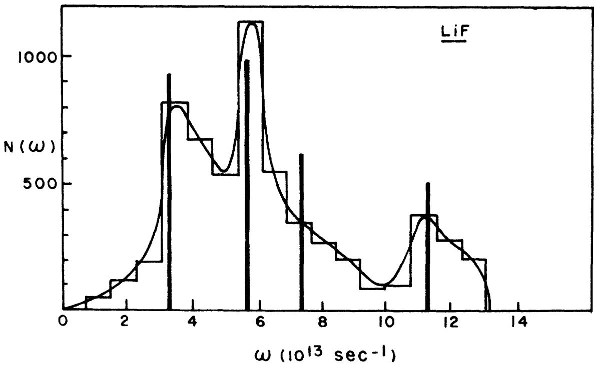

FIG. 1. Phonon spectrum of LiF as calculated by Karo and Hardy (Ref. 17). Four vertical bars have been superimposed on their figure to indicate the frequencies and coupling constants of the four modes which have been used to approximate the spectrum in the present calculation.

TABLE I. Parameters used in the calculation of the approximate absorption spectra of two hypothetical one-electron centers in LiF.

τ	Frequency Range ($\Delta\omega_\tau$)	$\bar{\omega}_\tau$ (all units 10^{13} sec^{-1})	$\bar{d}_{\tau j}$ $S=5$	$S=15$
1	0–4.5	3.32	6.037	10.456
2	4.5–6.5	5.62	6.432	11.141
3	6.5–10	7.33	4.007	6.941
4	10–max	11.33	3.295	5.708

(corresponding to a wavelength of 600 nm). The respective "unperturbed" electronic circular transition frequencies are 3.3565×10^{15} sec^{-1} (561.6 nm) for $S=5$ and 3.7863×10^{15} sec^{-1} (497.8 nm) for $S=15$.

The factors for the individual modes which appear in Eq. (53) were first calculated for a wide range of $\bar{r}_\tau$ values to see what set of values would contribute significantly to the absorption. The range of $\bar{r}_\tau$ values ultimately decided upon (which incorporated a certain degree of "overkill") varied from 33 for the lowest-frequency mode to seven for the highest-frequency mode. This range produced a total of 53 361 absorption lines, of which only a few percent contributed significantly to the absorption. Since a knowledge of the positions and magnitudes of such a large number of lines is not desired, what was done in practice was to calculate the integrated absorption over two nets of frequency intervals of width 1.2×10^{13} sec^{-1} displaced by 0.6×10^{13} sec^{-1} with respect to each other, and to average the results. The number of modes per frequency interval contributing significantly to the absorption spectrum in the main part of the band ranged from 5 to 10 for the $S=5$, $T=20$ °K case to about five times that many for the $S=15$, $T=80$ °K case. The average spacing of the lines was thus approximately 10^{12} sec^{-1}, or 0.19 nm at the long-wavelength end of the spectrum and proportionately less at the short-wavelength end. Each additional "approximate mode" included increases the number of lines per unit frequency interval by a factor of 10–15. The four-mode case illustrated here thus gives only a moderately accurate representation of details of the absorption spectrum, but the use of six modes could be expected to yield acceptable accuracy to about the 0.1-nm level over the bulk of the band. As noted earlier, the accurate treatment of the immediate vicinity of the zero-phonon line would require the use of a larger number of modes, with a correspondingly smaller range of values for the associated $\bar{r}_\tau$.

The results of the calculation for $S=5$ are shown in Fig. 2 for the two cases (a) $T=20$ °K and (b) $T=80$ °K.[20] The results obtained for $S=15$ and the same two temperatures are shown in Figs. 3(a) and 3(b). In each of these figures the histogram depicts on an arbitrary vertical scale the calculated absorption per unit frequency interval; and the dashed curve shows, also on an arbitrary vertical scale, the number of calculated absorption lines per unit frequency interval. Approximately half the calculated lines lie at higher frequencies not shown in the figures and contribute an absorption which is not significant on the scale of the figures.

As discussed previously, the small-scale details of the spectrum can be assumed to be only moderately accurate because of the use of only four phonon modes in the calculation. However, that the indicated existence of considerable structure in the spectrum for the $S=5$ case has physical significance and is associated with the structure of the phonon spectrum can be verified by comparing the large variations in the absorption with the smooth variation of the number of lines per unit

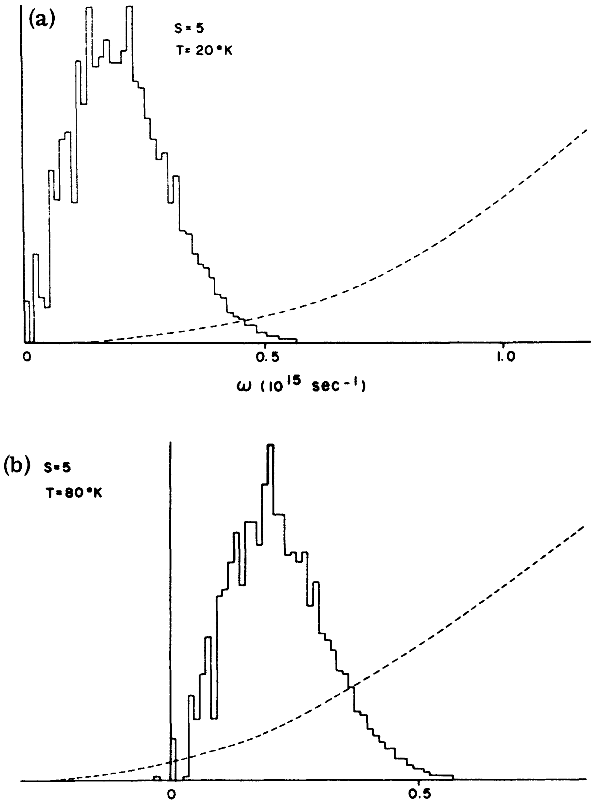

FIG. 2. (a) Absorption spectrum (histogram) and number of calculated absorption lines per unit frequency interval (dashed line) at 20 °K for the hypothetical defect center in LiF having $S=5$. The vertical scales are arbitrary. (b) Results for the same center at a temperature of 80 °K. $\omega=0$ is the location of the zero-phonon line.

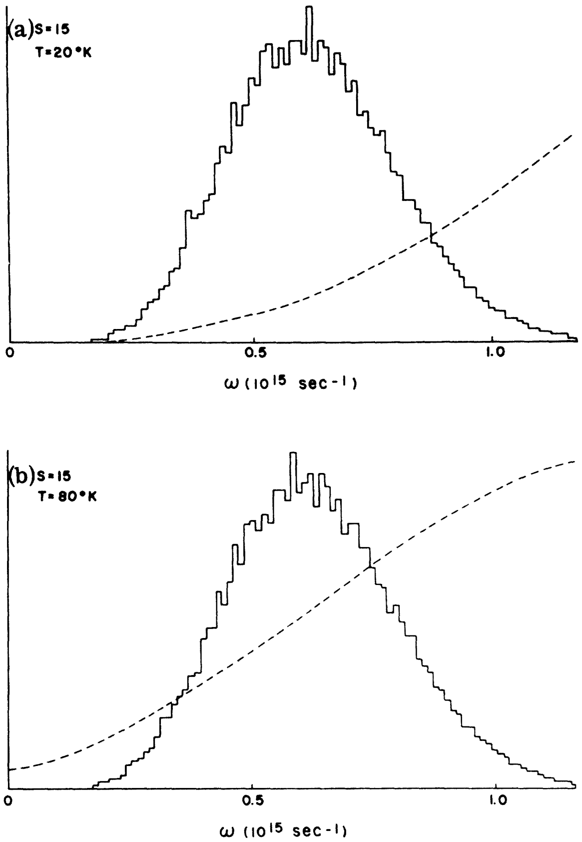

FIG. 3. (a) Absorption spectrum (histogram) and number of calculated absorption lines per unit frequency interval (dashed line) at 20 °K for the hypothetical defect center in LiF having $S = 15$. The vertical scales are arbitrary. (b) Results for the same center at a temperature of 80 °K. $\omega = 0$ is the location of the zero-phonon line.

frequency interval. By utilizing five or six modes, integrating over smaller intervals, and folding the resulting spectrum with a Gaussian to represent the effects of instrumental and radiative lifetime broadening, crystal inhomogenieties, etc., one could expect to obtain a quite accurate representation of the spectrum over practically the entire width of the band. (For the purposes of illustration it seemed more instructive not to perform this additional smoothing here.)

Many of the experimentally (and in some cases theoretically) well-known features of defect-center absorption spectra are clearly displayed in Figs. 2 and 3. For the $S = 5$ case these include the presence of a zero-phonon line which grows in intensity from 20 to 80 °K (by a factor 1.17), and the appearance of a phonon-absorption peak in the 80 °K spectrum. For the $S = 15$ case the zero-phonon line is so small as to be unobservable, the band is broader, and there is less structure. In each of the two cases the position of the band peak is essentially independent of temperature[2]; in addition, the integrated absorption is temperature-independent.[2]

Calculation of the four spectra shown required a total of 30 sec CPU time on a Univac 1108 computer; but this time could be shortened somewhat, without sacrificing appreciable accuracy, by reducing the ranges of $\bar{r}_\tau$ values considered. It was noted earlier that each additional phonon mode introduced increases the number of lines by a factor of 10–15, and so will increase the computation time by approximately the same factor. Calculation of spectra using six "approximate modes" is therefore easily done with currently available computers; and by means of careful programming to avoid computation of lines of negligible intensity, one could probably handle seven or perhaps even eight modes without encountering exorbitant computation times. The preceding discussion and example show that with six modes a satisfactory representation of the absorption band could be obtained.

ACKNOWLEDGMENTS

During the course of the research reported here the authors have benefited greatly from discussions with John D. Stettler and Romas A. Shatas.

---

[1] K. Huang and A. Rhys, Proc. R. Soc. Lond. A **204**, 406 (1950).

[2] M. Lax, J. Chem. Phys. **20**, 1752 (1952).

[3] M. Lax, Phys. Rev. **129**, 2342 (1963). It is actually possible to evaluate the integral in Eq. (6) explicitly by using a generalization of the method used by Lax in Ref. 2 for treating the Einstein-lattice case, without employing Lax's second-quantized phonon representation [D. W. Howgate (unpublished research)]. However, the authors know of no way of obtaining the more general results of Sec. 3 without use of the second-quantized formalism.

[4] S. Schweber, *An Introduction to Relativistic Quantum Field Theory* (Harper and Row, New York, 1961), pp. 121–150; *Topics in Fields and Solids*, edited by C. A. Coulter and R. A. Shatas (Gordon and Breach, New York, 1968), pp. 7–39.

[5] C. A. Coulter, D. W. Howgate, and R. A. Shatas, Phys. Rev. **140**, A2000 (1965).

[6] R. A. Shatas and C. A. Coulter, Int. J. Quantum Chem. 2S, 323 (1968).

[7] F. Riesz and B. Sz.-Nagy, *Functional Analysis* (Ungar, New York, 1955), pp. 355ff.

[8] See, e.g., K. Nishikawa and R. Barrie, Can. J. Phys. **41**, 1135 (1963), and references given there.

[9] By using Eq. (28) to calculate the absorption spectrum, one neglects spontaneous emission as well as higher-order effects in the electromagnetic field. This standard approximation is well justified in most cases of interest.

[10] A. Messiah, *Quantum Mechanics* (Wiley, New York, 1961), Vol. I, pp. 440 and 491–492.

[11] Any other choice of the phases clearly produces the same physical results, since only $|C^{\mu}_{m\,n}|^2$ appears in Eq. (40).

[12] A. Messiah, in Ref. 10, p. 483.

[13] Special relationships among the ω_μ and/or the $\epsilon_j - \epsilon_i$ may of course lead to additional coincidences of lines in certain cases.

[14] E. D. Rainville, *Special Functions* (MacMillan, New York, 1960), p. 212. In using Rainville's statement of the theorem one must observe that his definition of $L_p^k(z)$ differs from ours by a factor $(k + p)!$.

[15] Equation (6) has also been derived by a variety of methods by several other investigators. See, e.g., R. Barrie and I. W. Sharpe, Can. J. Phys. **50**, 222 (1972), and references given there.

[16] Since the r_μ's vary over an infinite range of integer values, this equation could not be literally true for any nonzero value of $\Delta\omega_r$. However, in practice only the r_μ values lying in a fairly small finite range make any appreciable contribution to the absorption; and for these r_μ the stated approximation can be made valid by an appropriate choice of the size of $\Delta\omega_r$.

[17] A. M. Karo and J. R. Hardy, Phys. Rev. **129**, 2024 (1963).

[18] The averages were computed from a listing supplied to us by A. M. Karo of calculated phonon frequencies and corresponding eigenvectors at sample points representing 125 points in the wave-vector space for LiF. We are very grateful to Dr. Karo for providing this information.

[19] On the basis of Eqs. (59) and (60), one might also have chosen the d_{rj} to be proportional to the *square roots* of the number of phonon modes in the intervals which they represent.

[20] The absorption spectra were calculated at 20 °K rather than 4 °K to avoid the difficulties involved in exceeding the exponent range of the computer in the evaluation of certain thermal factors at the lower temperature. The spectra at 4 °K would not differ by a detectable amount from those at 20 °K.