It can be verified that (42) is identical with the expression given by Rossi.[36]

Equation (43) should be used if one is interested in the loss due to collisions with a fixed maximum energy transfer T_0, as in the case of emulsion or of the droplet count in gases. Upon writing (41), (42), and (43) in terms of A and B, one obtains

$$\frac{1}{\rho}\frac{dE}{dx}=\frac{A}{\beta^2}\left[B+0.69+2\ln\frac{p}{\mu c}+\ln T_{\mathrm{Mev}}-2\beta^2-\delta\right], \quad \text{(heavy)} \quad (48)$$

$$\frac{1}{\rho}\frac{dE}{dx}=\frac{A}{\beta^2}\left[B+0.43+2\ln\frac{p}{mc}+\ln E_{\mathrm{Mev}}-\beta^2-\delta\right], \quad \text{(electrons)} \quad (49)$$

$$\frac{1}{\rho}\left(\frac{dE}{dx}\right)_{T_0}=\frac{A}{\beta^2}\left[B+0.69+2\ln\frac{p}{\mu c}+\ln T_{0,\mathrm{Mev}}-\beta^2-\delta\right], \quad (50)$$

where the subscript in T_{Mev}, E_{Mev}, and $T_{0,\mathrm{Mev}}$ indicates that T, E, and T_0 are to be expressed in Mev.

[36] Reference 32, p. 27, Eq. (11).

Equation (16) of II for the most probable loss ϵ_{prob} should be corrected. ϵ_{prob} is given by[37]

$$\epsilon_{\mathrm{prob}}=\frac{2\pi n_0 e^4 t}{mv^2\rho}\left[\ln\frac{2mv^2(2\pi n_0 e^4 t/mv^2\rho)}{I^2(1-\beta^2)}-\beta^2+0.37-\delta\right], \quad (51)$$

where t is the thickness in g cm^{-2}. Equation (51) can also be written

$$\epsilon_{\mathrm{prob}}=\frac{At}{\beta^2}\left[B+1.06+2\ln\frac{p}{\mu c}+\ln\frac{At}{\beta^2}-\beta^2-\delta\right]. \quad (52)$$

I would like to thank Dr. Ernest D. Courant for several very helpful discussions and comments.

Note added in proof:—In recent measurements of the grain count in emulsion, B. Stiller and M. M. Shapiro [Bull. Am. Phys. Soc. **28**, No. 3, 72 (1953)] found good agreement with the curve of $(1/\rho)(dE/dx)$ presented here (Fig. 2). Besides confirming the theoretical ratio of plateau to minimum ionization, these data lend support to the gradual rise of the ionization to the asymptotic value.

[37] L. Landau, J. Phys. (U.S.S.R.) **8**, 201 (1944); K. R. Symon, thesis, Harvard University, 1948 (unpublished).

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Absorption of Light by Trapped Electrons

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A new method of approach to the problem of absorption of light by trapped electrons in crystals is presented. The method is based upon the use of the Slater sum for an oscillator (density matrix). The absorption cross section is calculated under the assumption of an electron-lattice coupling which is linear in the normal coordinates of the lattice; this yields the shape of the absorption curve, but the maximum does not shift with temperature as required by experiment. This shift is then accounted for in a somewhat fundamental manner by considering the small change in the lattice frequencies which accompanies the photon induced electronic transition. The result is that the absorption maximum shifts with temperature, but the shape of the absorption curve is not effected by the change in the lattice frequencies.

HUANG and Rhys[1] published the first detailed quantum-mechanical calculation of the absorption of light in F centers. Their work was followed by two articles of Lax[2,3] in which a more general viewpoint is taken in the sense that the F center can be of more complicated structure (i.e., more than one electron) and the lattice is represented in a more general form (i.e., all modes optical and acoustical and a general frequency distribution). Lax obtains some of their results as a special case by setting all the frequencies $\omega_j=\omega$ (optical), where j indicates mode. He thereby avoids almost all of the analysis in their paper.[4] One finds in Lax's papers a complete formulation[2] of the problem and a complete discussion of the moments[3] of the absorption and emission spectral distributions.

The purpose of this paper is to present a third method of approach to the problem which is, in this author's opinion, simpler than either that of Huang-Rhys or Lax; the present method accomplishes the following things: (1) it avoids entirely the rather formal use of ordered operators in Lax by a straightforward application of the density matrix of a simple oscillator; (2) it yields the results of Huang-Rhys and the more general

[1] K. Huang, and A. Rhys, Proc. Roy. Soc. (London) **A204**, 406 (1950).
[2] M. Lax, Naval Research Laboratory Report 3973, 1952 (unpublished).
[3] M. Lax, J. Chem. Phys. **20**, 1752 (1952).
[4] Reference 3, p. 1760.

results of Lax without recourse to the condition $N\to\infty$, where N is the number of normal coordinates needed to describe the lattice; (3) finally, the present theory is in such a general yet simple form that other problems, such as the change in lattice frequencies (which accompanies an electronic transition, see Sec. II) and the effect of the Condon approximation (made by Huang-Rhys and by Lax; see below) can be more easily investigated if and when detailed knowledge of the dependence of the electronic Born-Oppenheimer wave functions on the lattice coordinates is available.

I. GENERAL RESULTS

To save space the present paper will begin with Eqs. (2.1) and (2.2) of Lax[3] for the absorption cross section $\sigma(\nu)$ and the total emission probability per unit time W, respectively. These read

$$\sigma(\nu)=\left[\frac{n}{\epsilon}\left(\frac{E_e}{E}\right)^2\right]\frac{8\pi^3\nu}{3c}I_{ba}(\nu), \tag{1}$$

$$W=\int\left[\frac{n^3}{\epsilon}\left(\frac{E_e}{E}\right)^2\right]\frac{64\pi^3\nu^4}{hc^3}I_{ab}(\nu)d(h\nu), \tag{2}$$

where

$$I_{ba}(\nu)=\mathrm{Av}_{\mathbf{n}'}\sum_{\mathbf{n}''}|\langle b\mathbf{n}''|M_{ba}(\mathbf{R})|a\mathbf{n}'\rangle|^2 \times\delta(E_{b\mathbf{n}''}-E_{a\mathbf{n}'}-h\nu), \tag{3}$$

$$\langle b\mathbf{n}''|M_{ba}(\mathbf{R})|a\mathbf{n}'\rangle \equiv\int d\mathbf{R}\,\varphi_{b\mathbf{n}''}{}^*(\mathbf{R})M_{ba}(\mathbf{R})\varphi_{a\mathbf{n}'}(\mathbf{R}), \tag{4}$$

and

$$M_{ba}(\mathbf{R})=\int d\mathbf{r}\psi_b{}^*(\mathbf{r},\mathbf{R})\sum_i e\mathbf{r}_i\psi_a(\mathbf{r},\mathbf{R}). \tag{5}$$

The wave functions ψ and φ are the usual Born-Oppenheimer functions for the electrons and lattice, respectively; $\mathbf{r}$, $\mathbf{R}$, are abbreviations for the coordinates of all electrons and lattice atoms (ions), respectively. For the problem of F centers one can drop the sum in (5) since only one electron is involved. Everything else is the same as in Lax and from this point on the present method is quite different from his. The symbol $\mathrm{Av}_{\mathbf{n}'}$ means "thermal average" over the initial lattice states. Equation (3) will be written in the following form:

$$I_{ba}(\nu)=\sum_{\mathbf{n}'',\mathbf{n}'}p_{\mathbf{n}'}|\langle b\mathbf{n}''|M_{ba}(\mathbf{R})|a\mathbf{n}'\rangle|^2 \times\delta(E_{b\mathbf{n}''}-E_{a\mathbf{n}'}-h\nu), \tag{6}$$

where

$$p_{\mathbf{n}'}=\left[\sum_{\mathbf{n}'}\exp\left(-\frac{E_{a\mathbf{n}'}}{kT}\right)\right]^{-1}\exp\left(-\frac{E_{a\mathbf{n}'}}{kT}\right). \tag{7}$$

The Hamiltonian for the perfect lattice plus "linear" electron-lattice coupling can be written in the following form:

$$\mathfrak{H}^{a,b}=\tfrac{1}{2}\sum_{j=1}^{N}[p_j{}^2+\omega_j{}^2q_j{}^2]-\frac{1}{N^{\frac{1}{2}}}\sum_{j=1}^{N}A_j{}^{a,b}q_j, \tag{8}$$

where the superscripts a, b refer to the electronic state of the F center electron [or electrons as in (5)]. The index j stands for the usual $(l,\boldsymbol{\sigma})$ in Seitz.[5] The "coupling constants" can actually be calculated in the Huang-Rhys case, but here they play the role of phenomenological constants. This case of a linear electron-lattice coupling is being investigated in order to compare the present method with that of Huang-Rhys and Lax where it is also assumed.

To continue, one can introduce modified normal coordinates into (8) in the following manner:

$$\begin{aligned}q_j'&=q_j-N^{-\frac{1}{2}}\omega_j{}^{-2}A_j{}^a\equiv q_j-c_j',\\ q_j''&=q_j-N^{-\frac{1}{2}}\omega_j{}^{-2}A_j{}^b\equiv q_j-c_j''.\end{aligned} \tag{9}$$

When (9) is used in (8), one finds

$$\mathfrak{H}^{a,b}=\tfrac{1}{2}\sum_{j=1}^{N}[p_j{}'^2+\omega_j{}^2q_j{}'^2]-\frac{1}{2N}\sum_{j=1}^{N}\frac{(A_j{}^{a,b})^2}{\omega_j{}^2}, \tag{10}$$

which is again that of a system of simple oscillators since the last constant term can be absorbed into the electronic energy of the F center electron (electrons). One can then write

$$E_{b\mathbf{n}''}-E_{a\mathbf{n}'}=\hbar\omega_{ba}+\sum_{j=1}^{N}[(n_j''+\tfrac{1}{2})\hbar\omega_j-(n_j'+\tfrac{1}{2})\hbar\psi_j], \tag{11}$$

wherein

$$\hbar\omega_{ba}\equiv\epsilon_b-\epsilon_a-\frac{1}{2N}\sum_{j=1}^{N}\frac{(A_j{}^b)^2-(A_j{}^a)^2}{\omega_j{}^2}, \tag{12}$$

and ϵ_b, ϵ_a are the electronic energies of the trapped electron(s) when there are no lattice vibrations. One can consider (Sec. II) the final state frequencies in (11) as different from the initial state frequencies, i.e., ω_j'', ω_j', respectively, where $\omega_j''-\omega_j'\equiv\rho_j\omega_j'$ defines a new set of phenomenological constants ρ_j. Now, from (10) one knows the lattice wave functions are products of simple oscillator functions in the modified coordinates, namely,

$$\begin{aligned}\varphi_{b\mathbf{n}''}(\mathbf{R})&=\prod_{j=1}^{N}X_{nj''}(q_j'')\equiv\prod_{j=1}^{N}\langle bn_j''|,\\ \varphi_{a\mathbf{n}'}(\mathbf{R})&=\prod_{j=1}^{N}X_{nj'}(q_j')\equiv\prod_{j=1}^{N}|an_j'\rangle,\end{aligned} \tag{13}$$

where

$$X_{mj}(q_j)=\left(\frac{\omega_j}{\pi\hbar}\right)^{\frac{1}{4}}(2^{m_j}m_j!)^{-\frac{1}{2}}H_{mj}\left[q_j\left(\frac{\omega_j}{\hbar}\right)^{\frac{1}{2}}\right] \times\exp\left\{-\tfrac{1}{2}\left[q_j\left(\frac{\omega_j}{\hbar}\right)^{\frac{1}{2}}\right]^2\right\}.$$

[5] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), pp. 133 and 477.

The next thing is the use of the Fourier integral representation of the Dirac delta-function in (6),

$$\delta(E_{b\mathbf{n}''}-E_{a\mathbf{n}'}-h\nu)$$
$$=\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}dt\exp\left[\frac{it}{\hbar}(E_{b\mathbf{n}''}-E_{a\mathbf{n}'}-h\nu)\right]. \quad (14)$$

From (6), (11), and (14) one then obtains

$$I_{ba}(\nu)=\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}dte^{i\omega_{ba}t-i2\pi\nu t}\sum_{\mathbf{n}''\mathbf{n}'}p_{\mathbf{n}'}$$
$$\times\exp[it\sum_{j=1}^{N}(n_j''-n_j')\omega_j]\cdot|\langle b\mathbf{n}''|M_{ba}(\mathbf{R})|a\mathbf{n}'\rangle|^2, \quad (15)$$

or, more explicitly,

$$I_{ba}(\nu)=\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}dte^{-i2\pi(\nu-\nu_{ba})t}G_{ba}(t), \quad (16)$$

where

$$G_{ba}(t)=\sum_{n_j'',n_j'=0}^{\infty}\exp\{-\sum_{j=1}^{N}[(n_j'+\tfrac{1}{2})\beta_j-it(n_j''-n_j')\omega_j]\}$$
$$\times\prod_{j=1}^{N}|\langle bn_j''|M_{ba}(\mathbf{R})|an_j'\rangle|^2$$
$$\times\{\prod_{j=1}^{N}\sum_{n_j'=0}^{\infty}e^{-(n_j'+\frac{1}{2})\beta_j}\}^{-1}, \quad (17)$$

and

$$\beta_j\equiv\hbar\omega_j/kT. \quad (18)$$

Now, since the electronic wave functions are not known in any detail for the present problem, i.e., their dependence on the lattice coordinates $\mathbf{R}$ or normal coordinates q_j is not known, one is practically forced to make the so-called Condon approximation in which $M_{ba}(\mathbf{R})$ is treated as a constant. It will be made evident in what follows how one would proceed if M_{ba} were a known function of the q_j.

When the Condon approximation is made, therefore, one obtains from (17)

$$G_{ba}(t)=|\langle b|\sum_i e\mathbf{r}_i|a\rangle|^2\prod_{j=1}^{N}G_j\equiv|M|^2\prod_{j=1}^{N}G_j, \quad (19)$$

where

$$G_j=2\sinh(\tfrac{1}{2}\beta_j)\sum_{n_j'',n_j'=0}^{\infty}e^{-(n_j''+\frac{1}{2})\mu_j}e^{-(n_j'+\frac{1}{2})\lambda_j}$$
$$\times|\langle bn_j''|an_j'\rangle|^2, \quad (20)$$

and

$$\lambda_j\equiv\beta_j+i\omega_jt,\quad \mu_j\equiv-i\omega_jt. \quad (21)$$

Introducing the oscillator functions (13) into (20) and writing out the square of the matrix element leads to

$$G_j=2\sinh(\tfrac{1}{2}\beta_j)\sum_{n_j'',n_j'=0}^{\infty}\alpha_j\frac{e^{-\mu_j(n_j''+\frac{1}{2})}}{\pi^{\frac{1}{2}}2^{n_j''}n_j''!}\alpha_j\frac{e^{-\lambda_j(n_j'+\frac{1}{2})}}{\pi^{\frac{1}{2}}2^{n_j'}n_j'!}$$
$$\times\int_{-\infty}^{\infty}dq_jH_{n_j''}(\alpha_jq_j'')H_{n_j'}(\alpha_jq_j')$$
$$\times\exp\left\{-\frac{\alpha_j^2}{2}(q_j''^2+q_j'^2)\right\}\int_{-\infty}^{\infty}d\bar{q}_jH_{n_j''}(\alpha_j\bar{q}_j'')$$
$$\times H_{n_j'}(\alpha_j\bar{q}_j')\exp\left\{-\frac{\alpha_j^2}{2}(\bar{q}_j''^2+\bar{q}_j'^2)\right\}, \quad (22)$$

$\alpha_j^2\equiv\omega_j/\hbar$, and then to

$$G_j=2\alpha_j^2\sinh(\tfrac{1}{2}\beta_j)\int_{-\infty}^{\infty}\int dq_jd\bar{q}_j$$
$$\times\rho(\alpha_jq_j'',\alpha_j\bar{q}_j''|\mu_j)\rho(\alpha_jq_j',\alpha_j\bar{q}_j'|\lambda_j), \quad (23)$$

where Mehler's formula (Slaters' sum) for the density matrix of an oscillator has been used, namely,

$$\rho(x,x'/\xi)=\sum_{k=0}^{\infty}\frac{e^{-(k+\frac{1}{2})\xi}}{\pi^{\frac{1}{2}}2^kk!}H_k(x)H_k(x')\exp\{-\tfrac{1}{2}(x^2+x'^2)\}$$
$$=(2\pi\sinh\xi)^{-\frac{1}{2}}\exp\{-\tfrac{1}{4}[(x+x')^2$$
$$\times\tanh(\tfrac{1}{2}\xi)+(x-x')^2\coth(\tfrac{1}{2}\xi)]\}. \quad (24)$$

Using (24), (23), and (9) one finds the following result:

$$G_j=\tfrac{1}{2}\sinh(\tfrac{1}{2}\beta_j)[\sinh\lambda_j\sinh\mu_j]^{-\frac{1}{2}}\int_{-\infty}^{\infty}\int dq_jd\bar{q}_j$$
$$\times\exp\{-\tfrac{1}{4}[(q_j+\bar{q}_j-2\alpha_jc_j'')^2\tanh(\tfrac{1}{2}\mu_j)$$
$$+(q_j-\bar{q}_j)^2\coth(\tfrac{1}{2}\mu_j)]\}$$
$$\times\exp\{-\tfrac{1}{4}[(q_j+\bar{q}_j-2\alpha_jc_j')^2\tanh(\tfrac{1}{2}\lambda_j)$$
$$+(q_j-\bar{q}_j)^2\coth(\tfrac{1}{2}\lambda_j)]\}. \quad (25)$$

The integration is easily carried out and yields the interesting and simple result:

$$G_j=\exp\left\{-\frac{\alpha_j^2(C_j''-C_j')^2}{\coth(\frac{1}{2}\beta_j+\frac{1}{2}i\omega_jt)-\coth(\frac{1}{2}i\omega_jt)}\right\}, \quad (26)$$

so that from (19) one finds

$$G_{ba}(t)=|M|^2$$
$$\times\exp\left\{-\sum_{j=1}^{N}\frac{\alpha_j^2(C_j''-C_j')^2}{\coth(\frac{1}{2}\beta_j+\frac{1}{2}i\omega_jt)-\coth(\frac{1}{2}i\omega_jt)}\right\}. \quad (27)$$

It is clear that this result would be more involved if the Condon approximation had not been made since (23) would have then contained $M_{ba}(q_j)\cdot M_{ba}(\bar{q}_j)$.

Finally, using the identity

$$(-)\frac{\sinh(x-y)}{\sinh x\sinh y}=\coth x-\coth y,$$

and Eq. (16) one is led to the following result:

$$I_{ba}(\nu)=|M|^2\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}dt e^{-i2\pi(\nu-\nu_{ba})t}\times\exp\left\{\sum_{j=1}^{N}\alpha_j^2(C_j''-C_j')^2\frac{\sinh(\frac{1}{2}\beta_j+\frac{1}{2}i\omega_j t)}{\sinh(\frac{1}{2}\beta_j)}\times\sinh(\tfrac{1}{2}i\omega_j t)\right\},\quad(28)$$

or, after simple manipulation,

$$I_{ba}(\nu)=|M|^2\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}dt e^{-i2\pi(\nu-\nu_{ba})t}\times\exp\{-\sum_{j=1}^{N}\tfrac{1}{2}\alpha_j^2(C_j''-C_j')^2[\coth(\tfrac{1}{2}\beta_j)-i\sin(\omega_j t)-\coth(\tfrac{1}{2}\beta_j)\cos(\omega_j t)]\}.\quad(29)$$

Introducing the C's from (9) allows one to write the last exponential in the form of an average over the lattice spectrum (as in Lax)

$$\frac{1}{N}\sum_{j=1}^{N}\tfrac{1}{2}\alpha_j^2\frac{(A_j^b-A_j^a)^2}{\omega_j^4}\{\coth(\tfrac{1}{2}\beta_j)-i\sin(\omega_j t)-\coth(\tfrac{1}{2}\beta_j)\cos(\omega_j t)\}\equiv\langle f(t)\rangle\equiv\frac{1}{N}\sum_{j=1}^{N}f(\omega_j,t).\quad(30)$$

One can then use the complete formulas in Lax for the moments of the distribution (29).

II. THE HUANG-RHYS PROBLEM

One can now consider the problem of Huang and Rhys in which all lattice modes have the same frequency (these being the single frequency longitudinal optical vibrations) i.e., $\omega_j=\omega$ for all j. From Eq. (29) one has

$$I_{ba}(\nu)=|M|^2\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}dt e^{-i2\pi(\nu-\nu_{ba})t}\times\exp\{-S[\coth(\tfrac{1}{2}\beta)-i\sin\omega t-\coth(\tfrac{1}{2}\beta)\cos(\omega t)]\},\quad(31)$$

where S has been defined so that the result will agree with the notation of Huang-Rhys, namely,

$$2S\equiv\sum_{j=1}^{N}\alpha_j^2(C_j''-C_j'')^2;\quad\beta=\hbar\omega/kT;\quad\alpha_j^2\equiv\omega/\hbar.\quad(32)$$

To carry out the integration one can introduce a phase ϕ such that

$$\tan\phi=\frac{i}{\coth(\frac{1}{2}\beta)};\quad\sin\phi=i\sinh(\tfrac{1}{2}\beta),\quad(33)$$

and a new variable,

$$\omega t-\phi=x.\quad(34)$$

Then one has from (31)

$$I_{ba}(\nu)=\frac{|M|^2}{2\pi\hbar\omega}\int_{-\infty}^{\infty}dx\exp\{-ipx-S\coth(\tfrac{1}{2}\beta)+S\,\mathrm{csch}(\tfrac{1}{2}\beta)\cos x\},\quad(35)$$

where, as in Huang-Rhys and Lax, the quantity p is defined as follows:

$$p=(2\pi/\omega)(\nu-\nu_{ba}),\quad(36)$$

and represents the net number of phonons involved in the transition at frequency ν. Of course only integral values of p are allowed. One can carry the integration in (35) out as in Lax. One finds

$$I_{ba}(\nu)=\frac{|M|^2}{\hbar\omega}e^{-ip\phi}\exp\{-S\coth(\tfrac{1}{2}\beta)\}\times[\sum_{k=-\infty}^{\infty}\delta(p-k)]I_p(S\,\mathrm{csch}(\tfrac{1}{2}\beta)),\quad(37)$$

where $I_p(z)$ is the modified Bessel function. One obtains complete agreement between these results and those of Huang-Rhys and Lax by using the well-known expression for the average number of phonons, of mode j, at temperature T

$$\langle n_j\rangle=(e^{\beta j}-1)^{-1},\quad(38)$$

and replacing the various hyperbolic terms in (37) by functions of $\langle n_j\rangle$. For example,

$$e^{-ip\phi}=[\sinh(\tfrac{1}{2}\beta)+\cosh(\tfrac{1}{2}\beta)]^p=[(\langle n\rangle+1)/\langle n\rangle]^{p/2},\quad\mathrm{csch}(\tfrac{1}{2}\beta)=2[\langle n\rangle(\langle n\rangle+1)]^{\frac{1}{2}},\quad\coth(\tfrac{1}{2}\beta)=2\langle n\rangle+1.\quad(39)$$

Equation (37) can then be written.

$$I_{ba}(\nu)=\frac{|M|^2}{\hbar\omega}\left[\frac{\langle n\rangle+1}{\langle n\rangle}\right]^{p/2}\exp\{-S(2\langle n\rangle+1)\}\times[\sum_{k=-\infty}^{\infty}\delta(k-p)]I_p\{2S[\langle n\rangle(\langle n\rangle+1)]^{\frac{1}{2}}\}.\quad(40)$$

As in Lax,[3] one considers the integrated spectrum in order to remove the delta-functions; *viz.*,

$$\int I_{ba}(\nu)d(h\nu)=|M|^2\sum_{p=-\infty}^{\infty}\exp\left\{-S(2\langle n\rangle+1)+\frac{p}{2}\ln\frac{1+\langle n\rangle}{\langle n\rangle}\right\}\times I_p\{2S[\langle n\rangle(\langle n\rangle+1)]^{\frac{1}{2}}\},\quad(41)$$

where p has been substituted for k and p is now integer. Each value of p corresponds to a discrete absorption line at a definite frequency given by (36). The sum in (41) was shown to be unity by Huang-Rhys by employing the series expansion for the Bessel function.

This must be true since

$$\frac{1}{|M|^2}\int I_{ba}(\nu)d(h\nu)=1$$

is a statement of the normalization of the moments (see Lax and below) of the absorption curve. For completeness and since these moments will be needed below, a brief derivation of them will be given.

One performs the Fourier inversion of (16) and finds

$$G_{ba}(t)=\int_{-\infty}^{\infty} e^{2\pi i(\nu-\nu_{ba})t}I_{ba}(\nu)d(h\nu). \tag{42}$$

Then $G_{ba}(t)$ and the exponential are expanded as power series in t; *viz.*,

$$\sum_{k=0}^{\infty}\frac{t^k}{k!}\left\{\frac{d^kG_{ba}(t)}{dt^k}\right\}_{t=0}=\sum_{k=0}^{\infty}\frac{t^k}{k!}\int_{-\infty}^{\infty}[2\pi i(\nu-\nu_{ba})]^kI_{ba}(\nu)d(h\nu). \tag{43}$$

Comparison yields

$$\langle p^k\rangle\equiv\int_{-\infty}^{\infty}p^kI_{ba}(\nu)d(h\nu)=\left\{\frac{d^k}{d(i\omega t)^k}G_{ba}(t)\right\}_{t=0}, \tag{44}$$

$$p\equiv 2\pi/\omega(\nu-\nu_{ba}).$$

Equations (16), (31) yield

$$G_{ba}(t)/|M|^2\equiv\mathcal{G}_{ba}(t)=\exp\{-S\coth(\tfrac{1}{2}\beta)+S\sinh(i\omega t)+S\coth(\tfrac{1}{2}\beta)\cosh(i\omega t)\}. \tag{45}$$

If one divides $I_{ba}(\nu)$ by $|M|^2$, then all moments are normalized and one has from (45) and (44)

$$\begin{aligned}&\langle p^0\rangle=1,\quad \langle p\rangle=\pm S,\\ &\langle(p-\langle p\rangle)^2\rangle=S\coth(\tfrac{1}{2}\beta),\quad \langle(p-\langle p\rangle)^3\rangle=\pm S,\\ &\langle(p-\langle p\rangle)^4\rangle=3[S\coth(\tfrac{1}{2}\beta)]^2+S\coth(\tfrac{1}{2}\beta).\end{aligned} \tag{46}$$

These results are given by Lax with $2\langle n\rangle+1$ instead of $\coth(\frac{1}{2}\beta)$. The important thing about these moments is that $\langle p\rangle=S$ does not change with temperature, whereas Pohl's experiments on F centers[1] show a shift in the position of the maximum of the absorption band with temperature. Huang-Rhys made a physical argument to show how the small change in the lattice frequencies which accompanies and electronic transition would account for such a shift. They simply shifted the position of the maximum without changing the shape of the absorption curve (but they were correct in doing so) as will be seen below.

It will now be shown how one can calculate this shift by a slight extension of the above theory. Equation (11) becomes

$$E_{bn''}-E_{an'}=\hbar\omega_{ba}+\sum_{j=1}^{N}\{(n_j''+\tfrac{1}{2})\hbar\omega_j''-(n_j'+\tfrac{1}{2})\hbar\omega_j'\}, \tag{47}$$

where now

$$\hbar\omega_{ba}=\epsilon_b-\epsilon_a-\frac{1}{2N}\sum_{j=1}^{N}\left\{\left(\frac{A_j{}^b}{\omega_j''}\right)^2-\left(\frac{A_j{}^a}{\omega_j'}\right)^2\right\}. \tag{48}$$

One then simply replaced α_j by α_j'' and α_j by α_j' in the final and initial states, respectively, of Eq. (22). Then

$$\begin{aligned}G_j=2\sinh(\tfrac{1}{2}\beta_j)\sum_{n_j'',n_j'=0}^{\infty}&\frac{e^{-(n_j''+\frac{1}{2})\mu_j}}{\pi^{\frac{1}{2}}2^{n_j''}(n_j'')!}\frac{e^{-(n_j'+\frac{1}{2})\lambda_j}}{\pi^{\frac{1}{2}}2^{n_j'}(n_j')!}\alpha_j''\alpha_j'\\ &\times\int_{-\infty}^{\infty}dq_jH_{n_j''}(\alpha_j''q_j'')H_{n_j'}(\alpha_j'q_j')\\ &\times\exp\{-\tfrac{1}{2}[(\alpha_j''q_j'')^2+(\alpha_j'q_j')^2]\}\\ &\times\int_{-\infty}^{\infty}d\bar{q}_jH_{n_j''}(\alpha_j''\bar{q}_j'')H_{n_j'}(\alpha_j'\bar{q}_j')\\ &\times\exp\{-\tfrac{1}{2}[(\alpha_j''\bar{q}_j'')^2+(\alpha_j'\bar{q}_j')^2]\},\end{aligned} \tag{49}$$

where

$$\lambda_j\equiv\beta_j+i\omega_j't,\quad \mu_j\equiv-i\omega_j''t,\quad \beta_j\equiv\hbar\omega_j'/kT,$$
$$(\alpha_j'')^2=\omega_j''/\hbar,\quad (\alpha_j')^2=\omega_j'/\hbar.$$

Then, by using Slater's sum, Eq. (40) reduces to

$$\begin{aligned}G_j=2\alpha_j''\alpha_j'\sinh(\tfrac{1}{2}\beta_j)&\int_{-\infty}^{\infty}\int dq_jd\bar{q}_j\\ &\times\rho(\alpha_j''q_j'',\alpha_j''\bar{q}_j''|\mu_j)\rho(\alpha_j'q_j',\alpha_j'\bar{q}_j'|\lambda_j),\end{aligned} \tag{50}$$

which in turn after a straightforward integration along with the use of (9) and (24) yields

$$\begin{aligned}G_j=2\alpha_j''\alpha_j'\sinh(\tfrac{1}{2}\beta_j)&[\sinh\lambda_j\sinh\mu_j\Lambda_j^2\Omega_j^2]^{-\frac{1}{2}}\\ &\times\exp\{-(\alpha_j''\alpha_j')^2(C_j''-C_j')^2/\Omega_j^2\},\end{aligned} \tag{51}$$

where

$$\Lambda_j^2\equiv(\alpha_j'')^2\tanh(\tfrac{1}{2}\mu_j)+(\alpha_j')^2\tanh(\tfrac{1}{2}\lambda_j),$$
$$\Omega_j^2\equiv(\alpha_j'')^2\coth(\tfrac{1}{2}\mu_j)+(\alpha_j')^2\coth(\tfrac{1}{2}\lambda_j).$$

Some further reduction using trigonometric identities leads to

$$\begin{aligned}G_j=2^{\frac{1}{2}}\sinh(\tfrac{1}{2}\beta_j)&[\cosh\lambda_j\cosh\mu_j-1\\ &+\tfrac{1}{2}(\kappa_j+1/\kappa_j)\sinh\lambda_j\sinh\mu_j]^{-\frac{1}{2}}\\ &\times\exp\{-(\alpha_j''\alpha_j')^2(C_j''-C_j')^2/\Omega_j^2\},\end{aligned} \tag{52}$$

wherein

$$\kappa_j\equiv\omega_j''/\omega_j'\equiv(\alpha_j''/\alpha_j')^2\equiv(1-\rho_j). \tag{53}$$

This defines a new constant ρ_j similar to the C_j above. One expects physically that $\omega_j''\leqslant\omega_j'$ or $\rho_j>0$ for all j

but this need not concern us since ρ_j will be treated as a phenomenological constant. From the fact that the linear electron-lattice coupling entered as $O(N^{-\frac{1}{2}})$, one expects the frequency change to enter the theory as $O(N^{-1})$; this will be assumed true for the present and allows one to write

$$\rho_j \equiv \epsilon_j/N, \tag{54}$$

where ϵ_j is a new constant. Then one has

$$\kappa_j + \frac{1}{\kappa_j} = 1-\rho_j + \frac{1}{1-\rho_j} = 2+O(\rho_j^2) = 2+O(1/N^2). \tag{55}$$

If one drops terms of order $1/N^2$, Eq. (52) reduces first of all to

$$G_j = \frac{\sinh(\frac{1}{2}\beta_j)}{\sinh\left(\frac{1}{2}\beta_j + \frac{i}{2}\rho_j\omega_j' t\right)} \exp\left\{-\frac{(\alpha_j''\alpha_j')^2(C_j''-C_j')^2}{\Omega_j^2}\right\}, \tag{56}$$

so that

$$\begin{aligned}\mathcal{G}_{ba}(t) = \frac{G_{ba}(t)}{|M|^2} &= \prod_{j=1}^{N} G_j \\ &= \exp\left\{-\sum_{j=1}^{N} \ln\left[\frac{\sinh\left(\frac{1}{2}\beta_j + \frac{i}{2}\rho_j\omega_j' t\right)}{\sinh(\frac{1}{2}\beta_j)}\right]\right\} \\ &\quad \times \exp\left\{-\sum_{j=1}^{N} \frac{(\alpha_j''\alpha_j')^2(C_j''-C_j')^2}{\Omega_j^2}\right\}. \end{aligned} \tag{57}$$

Finally, one develops the argument of the logarithm up to and including order $1/N$ and neglects the difference between α_j'' and α_j' in the second exponential since the C_j^2 contain $1/N$. The result is simply

$$\begin{aligned}\mathcal{G}_{ba}(t) &= \exp\left\{-\frac{it}{2}\sum_{j=1}^{N} \rho_j\omega_j' \coth(\tfrac{1}{2}\beta_j)\right\} \\ &\quad \times \exp\left\{-\sum_{j=1}^{N} \frac{(\alpha_j')^2(C_j''-C_j')^2}{\coth(\frac{1}{2}\mu_j)+\coth(\frac{1}{2}\lambda_j)}\right\}. \end{aligned} \tag{58}$$

This reduces, of course, to (27) when $\rho_j=0$. One can easily calculate the moments of the absorption curve using (58) and (44). It is of more immediate interest, however, to apply (58) to the Huang-Rhys case $\omega_j=\omega$ for all j. One uses ϵ_j above and writes

$$\frac{1}{2N}\sum_{j=1}^{N} \epsilon_j \equiv B. \tag{59}$$

Then one finds immediately that

$$\begin{aligned}\mathcal{G}_{ba}(t) = \exp\{&-i\omega t B \coth(\tfrac{1}{2}\beta) - S\coth(\tfrac{1}{2}\beta) \\ &+ S\sinh(i\omega t) + S\coth(\tfrac{1}{2}\beta)\cosh(i\omega t)\}. \end{aligned} \tag{60}$$

The moments now becomes with the use of (44)

$$\begin{aligned}&\langle p^0\rangle = 1, \quad \langle p\rangle = S - B\coth(\tfrac{1}{2}\beta) = S - B(2\langle n\rangle + 1), \\ &\langle (p-\langle p\rangle)^2\rangle = S\coth(\tfrac{1}{2}\beta), \quad \text{etc.}\end{aligned}$$

The result for $\langle p\rangle$ is just what Huang-Rhys employed. Their intuitive arguments are therefore borne out in a more fundamental derivation. One notes that the second moment is not affected by B so that if the absorption curve is approximately Gaussian the curves maximum shifts with temperature but does not change its half-width. Also, no change in the higher moments is produced by the lattice frequency shift. The higher moments would change if one included higher order terms in ρ_j in the above derivation, but this seems hardly necessary to carry out.

Finally, one notes that the exact shape is still described by the Bessel functions in (41) but shifted according to the new value of $\langle p\rangle$; this is clear from the result of substituting (60) into (16) etc. and, of course, also from the above moment considerations, since none of them higher than the first was modified by the frequency change.

SUMMARY

This paper has presented a new method of handling the problem of the absorption of light by trapped electrons. The results of Huang-Rys, except for nonradiative processes, have been obtained in a more straightforward manner. Also the complete results of Lax are obtained in a more direct manner avoiding the use of ordered operators which are not really required for these problems although their use is formally interesting.

The basic problems still to be investigated are the investigation of the validity of the Condon approximation and the study of radiationless transitions (thermal ionization, thermal excitation, etc.). The latter problem has been started by Kubo,[6] making use of the Einstein representation of the lattice.

[6] R. Kubo, Phys. Rev. **86**, 929 (1952).