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# Absorption of Light by Atoms in Solids*

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The interactions of an atom with its neighbors in an idealized solid are taken into account explicitly in treating the absorption of light, as contrasted with the usual introduction of an "effective" field and mass. In the discussion of the magnitude of the absorption coefficient, two cases are treated: one, the absorption by an impurity atom, in which case we are led to an equation similar to Smakula's; and two, the absorption by one of the atoms of the perfect crystal. The computations are based on a simple idealized model whose validity is discussed for existing systems.

## I. INTRODUCTION

CONSIDERABLE progress has been made in recent years in the understanding of the shape of absorption bands of atoms in solids, particularly of impurity atoms.[1–5] Relatively little attention has been directed to the problem of the total amount of absorption by the atom, that is, to the integrated cross section. This is a somewhat more difficult problem, requiring explicit knowledge of the details of the wave functions, which are, in most cases, severely modified by the medium from their values *in vacuo*.

The usual method[2] for the treatment of the magnitude of the absorption has been to make use of the atomic wave functions of the atom, completely uninfluenced by the presence of the medium, and to attempt to take account of the effect of the medium by the introduction of an "effective field" and an "effective mass" for the electron. This procedure is satisfactory in limiting cases, where the values of these effective parameters are known, but suffers from the difficulty that in general the parameters are not known. In an alternative description, presented here, the transition probability of the system is calculated, using wave functions for the whole crystal in which interactions among the atoms are taken into account. Since the interactions are explicitly accounted for in the wave functions, the introduction of effective masses and fields is unnecessary, and this difficulty is avoided; for this difficulty there is substituted the problem of calculating wave functions in which the interactions are included. This is, in general, a formidable task since the interactions are many and large, so large, in fact, that perturbation theory may not be applicable in a simple way in some systems.

In one idealized model, however, the calculation of the wave functions and the transition probability can easily be carried out, and the results can be expressed in a form similar to Smakula's equation[6,7] for impurity atom absorption. This is included in Sec. II, where there is also presented a discussion of the simplifying assumptions inherent in the idealized model. In Sec. III is a similar calculation for the absorption of the pure host crystal itself. In this case we obtain a result, not previously emphasized to the knowledge of the writer, which is equivalent to the statement that the integrated absorption cross section of an oscillator is unchanged by the dipole-dipole interactions with other identical oscillators.

## II. IMPURITY ABSORPTION

Here we shall be concerned particularly with an impurity atom which absorbs light of a longer wavelength than that at which the host crystal absorbs; thus its absorption is not lost in the fundamental absorption of the host crystal. We shall also assume that the impurity concentration is sufficiently low, say less than

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$10^{19}$ per $\text{cm}^3$, that interactions between one impurity atom and another may be ignored.

The model we shall assume is based on a familiar one, which has been used by numerous workers in treating optical properties of pure crystals.[8–13] The crystal is effectively infinite, and of cubic crystal structure. The ground states of the atoms are assumed to be $S$-type, and the excited states of interest are thus $P$-type. Thermal vibration may be left out of the calculation since only integrated absorption cross sections are to be calculated here.[2] Any possible spin effects are ignored. According to this model, the dominant interactions between atoms is a dipole-dipole, or van der Waals' interaction, with exchange and higher multipole effects less important. All effects are assumed small, so that their squares are neglected. (This statement will be made more precise a little later, but essentially we treat $4\pi\alpha/3$, the Lorentz correction, as small, so that its square may be dropped out.) Further, the overlap of wave functions centered on one atom with those on another atom is assumed negligible, so that normalized atomic functions are still orthonormal in the crystal. Thus to a zero-order approximation (indicated by the superscript on $\Psi^{(0)}$) the wave function for the ground state of the system (denoted by the subscript 0) is given by an antisymmetrized product of ground state wave functions for one impurity atom and $N-1$ host crystal atoms.

$$\Psi_0{}^{(0)}=\frac{1}{\sqrt{N!}}\sum_P(-1)^P P\psi_1{}^0(1)\psi_2{}^0(2)\cdots \times\psi_{N-1}{}^0(N-1)\varphi^0(N). \quad (1)$$

Here we sum over the $N!$ permutations $P$, the lower case $\psi$'s are host crystal atomic wave functions, the subscript indicating the location of the atom, the superscript labelling the atomic state, and the argument specifying the electron occupying the state. The letter $\varphi$ will be used to denote the wave functions of the impurity atom in its ground state ($\varphi^0$) or excited states ($\varphi^l$). According to the assumption just above, this wave function Eq. (1) is normalized if each $\psi$ and $\varphi$ is normalized. We shall now use stationary perturbation theory to compute the ground-state wave function to a first-order approximation, taking the dominant interations into account.

The wave function Eq. (1) is an eigenfunction of the Hamiltonian

$$H_0=\sum_{i=1}^N H_i, \quad (2)$$

where each term $H_i$ is an atomic Hamiltonian. The actual crystal Hamiltonian, which includes interactions, is

$$H=H_0+\frac{1}{2}\sum_i\sum_j{}'\frac{e^2}{r_{ij}}+\frac{1}{2}\sum_I\sum_J{}'\frac{e^2}{r_{IJ}}-\sum_i\sum_J{}'\frac{e^2}{r_{iJ}}. \quad (3)$$

Here lower case indices are used for electron coordinates, and upper case letters for those of the atomic cores. The primes above the summation symbols act to exclude the equivalence of the two summation indices. Considering the Hamiltonian $H_1=H-H_0$ as a small perturbation, we may express the corrected ground-state wave function formally as

$$\Psi_0{}^{(1)}=\Psi_0{}^{(0)}+\sum_\alpha\frac{\langle\alpha|H_1|0\rangle}{E_0-E_\alpha}\Psi_\alpha{}^{(0)}. \quad (4)$$

We must now discuss the wave functions $\Psi_\alpha{}^{(0)}$ which are coupled to $\Psi_0{}^{(0)}$ by the interaction $H_1$. Since $H_1$ is a function of pairs of coordinates, $H_{ij}$, only those $\Psi_\alpha{}^{(0)}$ appear in which two of the wave functions $\psi$ and $\varphi$ changed. Thus the $\Psi_\alpha{}^{(0)}$ are of two types, one containing two excited atoms $\psi_L{}^m$ and $\psi_I{}^n$, and the other containing one $\psi_L{}^m$ and one $\varphi^j$. We shall see later that it is only the latter type which contributes to the low-energy transitions associated with the impurity atom. (The former type which we may call $\Psi_\beta{}^{(0)}$, is similar to the "double exciton" wave functions discussed in reference 13.) Thus let us rewrite Eq. (4) including the first type only formally, and the second explicitly.

$$\Psi_0{}^{(1)}=\Psi_0{}^{(0)}+\sum_\beta c_\beta\Psi_\beta{}^{(0)} -\sum_L\sum_m\sum_j\frac{\langle L,m,j|H_1|0\rangle}{\epsilon_m+w_j}\Psi_{L,m,j}{}^{(0)}. \quad (5)$$

Here we have inserted the energy difference $E_0-E_\alpha$ as $-(\epsilon_m+w_j)$, each atomic energy being measured from the ground atomic state; the letter $\epsilon_m$ is used for the energy levels of the host crystal atoms, and $w_j$ for the impurity atom levels. The wave function $\Psi_{L,m,j}{}^{(0)}$ is the antisymmetrized product

$$\Psi_{L,m,j}{}^{(0)}=\frac{1}{\sqrt{N!}}\sum_P(-1)^P P\psi_1{}^0(1)\cdots\psi_L{}^m(l)\cdots\varphi^j(N), \quad (6)$$

and the matrix elements of $H_1$,

$$\langle L,m,j|H_1|0\rangle =\frac{1}{2N!}\sum_P\sum_{P'}(-1)^{P+P'}\int P\psi_1{}^{0*}(1)\cdots\psi_L{}^{m*}(l)\cdots \times\varphi^{j*}(N)(\sum_i\sum_j{}' H_{ij})P'\psi_1{}^0(1)\cdots \times\psi_L{}^0(l)\cdots\varphi^0(N)d\tau, \quad (7)$$

are nonzero under two circumstances, corresponding to dipole-dipole or exchange interactions. If the per-

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mutations $P$ and $P'$ are identical, we find, by expanding $H_{ij}$ in a power series in $1/r_{ij}$, the dipole-dipole coupling; if $P$ and $P'$ are identical except for the pair of electrons occupying the excited states $\psi_L{}^m$ and $\varphi^j$, we obtain the exchange coupling. Thus Eq. (7) becomes

$$\langle L, m, j|H_1|0\rangle = \frac{e^2}{R_L{}^3}(\mathbf{r}_m\cdot\mathbf{x}_j - 3\mathbf{r}_m\cdot\mathbf{R}_L\mathbf{x}_j\cdot\mathbf{R}_L/R_L{}^2) - \int \psi_L{}^{m*}(1)\varphi^{j*}(2)\frac{e^2}{r_{12}}\psi_L{}^0(2)\varphi^0(1)d\tau_{12}. \quad (8)$$

Here $\mathbf{r}^m$ is the matrix element of $\mathbf{r}$ between $\psi^{m*}$ and $\psi^0$, and $\mathbf{x}_j$ that between $\varphi^{j*}$ and $\varphi^0$; $\mathbf{R}_L$ is the vector separating the impurity atom and the $L$th atom.

The energy of the ground state, $W_0$, is given by the expectation value of $H$ in the state $\Psi_0{}^{(1)}$, and is equal to

$$W_0 = -\tfrac{1}{2}\sum_I\sum_L{}'' e^2\int\psi_I{}^{0*}(1)\psi_L{}^{0*}(2)\frac{1}{r_{12}}\psi_I{}^0(2)\psi_L{}^0(1)d\tau_{12} - \sum_I e^2\int\psi_I{}^{0*}(1)\varphi^{0*}(2)\frac{1}{r_{12}}\psi_I{}^0(2)\varphi^0(1)d\tau_{12}. \quad (9)$$

Here the double prime on the first summation reminds us that $I$ and $L$ are not equal and that neither refers to the impurity atom. Thus $-W_0$ is the amount by which the energy of the system is lowered by the exchange interaction among all the atoms, the zero of energy being chosen equal to that of the $N$ isolated atoms in their ground states. To Eq. (9) might be added additional terms coming from the small terms in Eq. (5), but since these would appear as squares of quantities such as $\langle L, m, j|H_1|0\rangle/(\epsilon_m+w_j)$, they are neglected. This same approximation is made throughout, consistent with the use of first-order perturbation theory.

We now discuss the excited states of the system. The lowest excited states are those in which the impurity atom is excited, according to our stipulation that we wish to be able to see its effect in absorption. Thus a zero-order excited wave function is the antisymmetrized product,

$$\Psi_j{}^{(0)} = \frac{1}{\sqrt{N!}}\sum_P(-1)^P P\psi_1{}^0(1)\cdots\psi_{N-1}{}^0(N-1)\varphi^j(N). \quad (10)$$

The wave functions to be mixed with this by the interactions are of two types: the first, wave functions having two host atoms excited as well as the impurity atom; the second, wave functions having one host atom excited and the impurity atom in a different excited state or the ground state. The first type will not contribute to the final result and will be included only formally, as $\Psi_\gamma{}^{(0)}$. The others are described explicitly below in Eq. (11), where the summation over $n$ includes the ground state (which is, in fact, the only term which will contribute in the final result).

$$\Psi_j{}^{(1)} = \Psi_j{}^{(0)} + \sum_\gamma d_\gamma\Psi_\gamma{}^{(0)} - \sum_L\sum_m\sum_{n\neq j}\frac{\langle L, m, n|H_1|j\rangle}{\epsilon_m+w_n-w_j}\Psi_{L,m,n}{}^{(0)}. \quad (11)$$

The matrix elements here are computed in the same way as in Eq. (7), and are equal to

$$\langle L, m, n|H_1|j\rangle = \frac{e^2}{R_L{}^3}(\mathbf{r}_m\cdot\mathbf{x}_{jn} - 3\mathbf{r}_m\cdot\mathbf{R}_L\mathbf{x}_{jn}\cdot\mathbf{R}_L/R_L{}^2) - e^2\int\psi_L{}^{0*}(1)\varphi^{j*}(2)\frac{1}{r_{12}}\psi_L{}^m(2)\varphi^n(1)d\tau_{12}, \quad (12)$$

and the energy of the state $\Psi_j{}^{(1)}$ is given by

$$W_j = w_j - \frac{e^2}{2}\sum_I\sum_J{}''\int\psi_I{}^{0*}(1)\psi_J{}^{0*}(2)\frac{1}{r_{12}}\psi_I{}^0(2)\psi_J{}^0(1)d\tau_{12} - e^2\sum_I\int\psi_I{}^{0*}(1)\varphi^{j*}(2)\frac{1}{r_{12}}\psi_I{}^0(2)\varphi^j(1)d\tau_{12}. \quad (13)$$

Thus the energy difference $W_j - W_0$ is just equal to the atomic energy level difference plus an exchange correction.

$$W_j - W_0 = w_j - e^2\sum_I\int\psi_I{}^{0*}(1)\psi_I{}^0(2)\frac{1}{r_{12}} \times(\varphi^{j*}(2)\varphi^j(1) - \varphi^{0*}(2)\varphi^0(1))d\tau_{12}. \quad (14)$$

Now that we have the corrected wave functions of the system, we may apply time-dependent perturbation theory[14] in the usual way to calculate the probability of a transition of the system under the influence of an electromagnetic field

$$\boldsymbol{\varepsilon} = \mathbf{u}\mathcal{E}_0[\exp i(\mathbf{k}\cdot\mathbf{r}-\omega t)+\text{c.c.}].$$

The transition probability per unit time is given by

$$p_j = (2\pi/\hbar)\rho_E|\mathbf{u}\cdot\mathbf{C}_j|^2, \quad (15)$$

where $\rho_E$ is the density of radiation at the energy given by Eq. (14) polarized in the direction of the unit vector $\mathbf{u}$, and where $\mathbf{C}_j$ is given by

$$\mathbf{C}_j = \frac{-e\hbar}{\omega_j m}\int\Psi_j{}^{(1)*}\Big(\sum_i\nabla_i e^{i\mathbf{k}\cdot\mathbf{r}_i}\Big)\Psi_0{}^{(1)}d\tau. \quad (16)$$

Here $\omega_j$ is the (mean) frequency of the absorption line $(W_j - W_0)/\hbar$, $\nabla_i$ the gradient operator for the $i$th electron, and $\mathbf{k}$ the propagation vector of the radiation. Inserting the wave functions given by Eqs. (5)–(8)

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[14] See for example p. 215 of reference 10.

and (10)–(12), we obtain the result derived in Appendix A,

$$|\mathbf{u}\cdot\mathbf{C}_j|^2=e^2x_j^2\left\{1+\frac{4\pi n_0}{3}\alpha_h(w_j)+2\sum_m\frac{r_m\epsilon_m\mathcal{E}(m,j)}{(\epsilon_m^2-w_j^2)x_j}+\frac{1}{w_j}[F(0,j)-F(0,0)]\right\}^2. \quad (17)$$

For the isolated atom we would obtain the simple result $e^2x_j^2$, so that the quantity in curly brackets represents the effect of the medium. The first correction term is the familiar "local field" correction, evaluated at the energy of the transition. Here $\alpha_h$ is the atomic polarizability of the host crystal atoms, of density $n_0$, at the energy $w_j$. The other terms are exchange terms defined in the appendix. The integrated absorption cross-section is obtained by dividing the energy absorbed per second, that is, $(W_j-W_0)$ times the transition probability, by the incident energy flux corresponding to one photon per unit volume. Since the energy carried by the photon is $\kappa\mathcal{E}_0^2/2\pi$ and the velocity is $c/n$, we obtain

$$\int\sigma_j(E)dE=\frac{n}{\kappa}\frac{4\pi^2}{\hbar c}|\mathbf{C}_j\cdot\mathbf{u}|^2(W_j-W_0). \quad (18)$$

Thus substituting for $(W_j-W_0)$ and for $|\mathbf{C}_j\cdot\mathbf{u}|^2$ we obtain the area under the absorption band $\mu_j(E)$ for a density $N_0$ of impurity atoms

$$\int\mu_j(E)dE=\frac{1}{n}\frac{4\pi^2}{\hbar c}\left\{1+\frac{4\pi}{3}n_0\alpha_h(w_j)-2\sum_m\frac{r_m\epsilon_m\mathcal{E}(m,j)}{(\epsilon_m^2-w_j^2)x_j}+\frac{1}{2w_j}[F(0,j)-F(0,0)]\right\}^2\times N_0e^2x_j^2w_j, \quad (19)$$

where we have made use of the relation $\kappa\cong n^2$. These last two factors may be related to the atomic oscillator strength $f_{0j}$ and we obtain finally

$$\int\mu_j(E)dE=\frac{1}{n}\frac{2\pi^2e^2\hbar}{mc}\left\{1+\frac{4\pi}{3}n_0\alpha_h(w_j)-2\sum_m\frac{r_m\epsilon_m\mathcal{E}(m,j)}{(\epsilon_m^2-w_j^2)x_j}+\frac{1}{2w_j}[F(0,j)-F(0,0)]\right\}^2N_0f_{0j}. \quad (20)$$

This result may be compared with that obtained by use of the effective field and mass parameters, as discussed by Lax,[2]

$$\int\mu_j(E)dE=\frac{1}{n}\frac{2\pi^2e^2\hbar}{m^*c}\left\{\frac{\mathcal{E}_{\text{eff}}}{\mathcal{E}}\right\}^2N_0f_{0j}, \quad (21)$$

and it is seen that the quantity in curly brackets in Eq. (20) is the effective field ratio in cases where the effective mass to be inserted in Eq. (21) is the electronic mass. (This will be the case in systems for which the foregoing calculation is justified.) Thus the effective field ratio in the present calculation is

$$\left\{\frac{\mathcal{E}_{\text{eff}}}{\mathcal{E}}\right\}_j=1+\frac{4\pi}{3}n_0\alpha_h(w_j)+J+K, \quad (22)$$

where we have grouped together all the exchange terms in Eq. (19) in the symbol $J$. We may consider that $K$ contains higher order corrections in the form of dipole-quadrupole and higher multipole effects, squares of parameters such as $4\pi n_0\alpha_h(w_j)/3$ and the exchange terms in Eq. (19), and effects of overlap and nonorthogonality.

If $J$ and $K$ may be ignored, we may derive a generalized "Smakula equation" by making use of the relations

$$\begin{gathered}\kappa=n^2=1+4\pi\alpha,\\ \frac{n^2+2}{3}=1+4\pi n_0\alpha_h(w_j)/3+K'.\end{gathered} \quad (23)$$

Here $\alpha$ is the polarizability of the crystal and $K'$ is another term of the magnitude of $K$, and is dropped in the following. Thus by substituting Eqs. (23) in Eq. (22) and Eq. (21), we obtain

$$\int\mu_j(E)dE=\frac{1}{n}\left(\frac{2\pi^2e^2\hbar}{mc}\right)\left(\frac{n^2+2}{3}\right)^2N_0f_{0j}. \quad (24)$$

Equation (24) may be considered as describing an experimental method for measuring the concentration of impurity centers $N_0$ in cases where the above simplifying assumptions are valid. That is, the oscillator strength in the transition may be measured *in vacuo*, the index of refraction $n$ of the host crystal may be determined optically, and the absorption band area found in the usual way. If the absorption coefficient is expressed in reciprocal centimeters and the energy in electron volts, Eq. (24) may be written

$$N_0=0.821\times10^{17}\text{ cm}^{-3}\frac{n}{(n^2+2)^2}\frac{1}{f_{0j}}\int\mu_j(E)dE. \quad (25)$$

Two simple cases may be treated further. Smakula[6] treated the case for which $\mu_j(E)$ is of the classical, Lorentzian shape, so that the integral $\int\mu_j(E)dE$ is equal to $(\pi/2)\mu_j(\text{max})U_j$, where $\mu_j(\text{max})$ is the peak absorption coefficient and $U_j$ the width of the absorption band at half-maximum. Thus we obtain the numerical coefficient as it has been commonly used,

$$N_0=1.29\times10^{17}\text{ cm}^{-3}\frac{n}{(n^2+2)^2}\frac{1}{f_{0j}}\mu_j(\text{max})U_j. \quad (26)$$

However, in solids the width of the band does not arise in the classical dispersion manner, but rather from interactions of the center with lattice vibration. Thus in simple centers the absorption band is more nearly Gaussian in shape, so that the integral in Eq. (25) is $(\frac{1}{2})(\pi \ln 2)^{\frac{1}{2}}\mu_j(\max)U_j$, and Eq. (25) becomes

$$N_0=0.87\times 10^{17}\ \mathrm{cm}^{-3}\frac{n}{(n^2+2)^2}\frac{1}{f_{0j}}\mu_j(\max)U_j. \quad (27)$$

This point has been recognized independently by Herring.[7]

The drastic simplifying assumptions made in deriving these last few equations are probably not even approximately valid in ionic crystals. (For example, we have treated $4\pi\alpha/3$ as a small quantity; even in the alkali halides $4\pi\alpha/3=(\kappa-1)/3$ is almost unity, and is larger than unity in other ionic crystals.) Appreciably better equations would entail vastly greater work, and would very likely be appreciably better only for the particular crystal system for which the calculations were performed. One's intuitive feeling is that because of overlap effects the interactions with the medium are less than those used here, so that the numerical coefficients should be increased over their values in Eqs. (25)–(27). Another way of viewing the overlap effects is that as the wave functions of the impurity atom extend over regions comparable with or larger than the unit cell, the field which is effective in inducing the transition is just the average field within the medium. However, in this case the wave functions become so distorted that they bear little resemblance to the initial atomic wave functions, and the type of calculation attempted here is not valid; Lax[15] has recently discussed some of the problems of the diffuse center, such as impurities in germanium, and concludes that an equation such as Eq. (21) may describe the absorption, but that here the effective field ratio is unity, and the effective mass to be used is a harmonic mean of the effective mass tensor components in simple cases. However, in this case the oscillator strength is *not* associated with a transition of the isolated atom itself but rather with that of the diffuse center. That is, the oscillator strength may not be measured independently of the crystal.

The type of calculation presented here may have quantitative validity, particularly if exchange is included as in Eq. (20), in the solid rare gases or other molecular crystals in which van der Waals' interactions are predominant. The investigation of the optical properties of xenon impurities in solid argon, for example, would be extremely interesting, but unfortunately the experiments would be difficult to perform.

One additional restriction should perhaps be mentioned here. If the energy of the transition in the impurity atom is close to the energy of the fundamental absorption band of the host crystal, the denominator in Eq. (11) becomes small, and resonant effects will become important. In fact, if we consider the energy of the transition to be just equal to that of the fundamental absorption band, we have essentially the same problem as is discussed in the next section, where the resonance effects necessitate the introduction of exciton wave functions

## III. HOST CRYSTAL ABSORPTION

In this section we shall treat the magnitude of the absorption in transitions to the exciton states of the system. The crystal model is that which we made use of above, except that we now have no impurity atoms present, but just $N$ host crystal atoms. Since extensive calculations have already been made with this model, we shall draw on previous results for the sake of brevity. The ground state of the system is an antisymmetrized product of ground state atomic functions, $\Psi_0^{(0)}$, plus an admixture of higher excited state wave functions coupled in by the dipole-dipole and exchange interactions [see Eqs. (4)–(7) of reference 13]. Specification of the excited states of the system by the location and state of an excited atom is not an adequate description because of the $N$-fold degeneracy arising from the periodicity of the crystal structure, and we are led to the exciton wave functions by choosing a suitable linear combination of the localized atomic excited wave functions. The $N$ linear combinations of one excited atom in state $l$ and $N-1$ atoms in the ground state, each combination characterized by a propagation vector, $\mathbf{k}'$, are known as exciton wave functions [see Eqs. (8)–(10) of reference 13 for further details]. These wave functions take into account the interactions among the atoms to the same approximation as in the previous section. Making use of these wave functions, we now apply time-dependent perturbation theory to calculate the transition probability of the system when an electromagnetic field is applied (as contrasted with reference 13, where the polarizability was computed). We find, as in reference 13, the value for $|\mathbf{u}\cdot\mathbf{C}_l|$,

$$|\mathbf{u}\cdot\mathbf{C}_l(\mathbf{k}')|=\frac{N^{\frac{1}{2}}\delta_{\mathbf{k}',\mathbf{k}}r_l\epsilon_l}{W_l(\mathbf{k}')-W_0}\left\{1-\frac{4\pi}{3}n_0e^2\sum_j\frac{r_j^2\epsilon_j}{\epsilon_l(\epsilon_j+\epsilon_l)}\right.$$
$$\left.+\frac{4\pi}{3}n_0e^2\sum_{j\neq l}\frac{r_j^2\epsilon_j}{(\epsilon_j-\epsilon_l)\epsilon_l}+L\right\}. \quad (28)$$

Here the Kronecker delta function $\delta_{\mathbf{k}',\mathbf{k}}$ states that transitions are only allowed to exciton states which have the same momentum as the absorbed photon; $L$ is a symbol for the several exchange terms. The denominator $W_l(\mathbf{k}')-W_0$ is found to be

$$W_l(\mathbf{k}')-W_0=\epsilon_l\left(1-\frac{4\pi}{3}\frac{n_0e^2}{\epsilon_l}r_l^2\right)+I+T, \quad (29)$$

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[15] M. Lax, Proceedings of the Atlantic City Conference on Photoconductivity, November, 1954 (John Wiley and Sons, Inc., New York, 1955).

where $I$ denotes the exchange terms, and $T$ the kinetic energy of the exciton. Since we are interested only in the states for which $\hbar\mathbf{k}'$ is equal to the very small photon momentum, we may set $T$ equal to zero with high accuracy, as Heller and Marcus[12] have shown. The transition probability per unit time per unit volume in the energy range $dE$ is given by

$$P_l dE=\frac{2\pi}{\hbar}\rho_E n_0 e^2 r_l^2 dE\left\{1+\frac{2\pi}{3}n_0 e^2\frac{r_l^2}{\epsilon_l}\right.$$
$$\left.+\frac{4\pi}{3}n_0 e^2\left(2\sum_{j\neq l}\frac{\mu_j^2\epsilon_j}{\epsilon_j^2-\epsilon_l^2}\right)+L'\right\}^2. \qquad (30)$$

Note that the possibility of the same transition 0 to $l$ in the other atoms increases the transition probability for each of the atoms. This is shown by the first correction term in the curly brackets. The other transitions to states $j\neq l$ account for the second correction term, and $L'$ is a sum of exchange terms which we shall not describe explicitly. The second correction term is of the familiar form, $(4\pi n_0/3)$ times the polarizability at energy $\epsilon_l$ arising from all transitions $j\neq l$ in the atoms, but there is the additional correction, just mentioned, from the same transition to state $l$ in the other atoms. This same dependence is exhibited by the extinction coefficient, equal to $\mu_l\hbar c/(W_l-W_0)$, though not by the absorption coefficient.

To obtain the absorption coefficient, we proceed as before.

$$\int\mu_l(E)dE=\int\frac{2\pi n}{\kappa c}\frac{(W_l-W_0)}{\rho_E}P_l(E)dE. \qquad (31)$$

In the vicinity of the absorption band, $n$ and $\kappa$ are functions of the energy, but the contributions to $n$ and $\kappa$ by the other transitions $j\neq l$ must be slowly varying if $\epsilon_j$ is not too close to $\epsilon_l$, so that their contributions may be called constant. (If the energies *are* closely equal, the use of perturbation theory in deriving the wave functions is not justified anyway.) The dispersion near the absorption maximum makes the contribution to $n$ and $\kappa$ from the $l$th transition change sign on the two sides of the $l$th absorption band, and, to the approximation we have been following here, this contribution vanishes. Thus the integration may be carried out, and we obtain

$$\int\mu_l(E)dE=\frac{n}{\kappa}\frac{4\pi^2}{\hbar c}n_0 e^2 r_l^2\epsilon_l\left\{1+L''\right.$$
$$\left.+\frac{4\pi}{3}n_0\left(2\sum_{j\neq l}\frac{e^2 r_j^2\epsilon_j}{\epsilon_j^2-\epsilon_l^2}\right)\right\}^2. \qquad (32)$$

In terms of the oscillator strength, $f_{0l}$, Eq. (32) may be written

$$\int\mu_l(E)dE=\frac{n}{\kappa}\frac{2\pi^2 e^2\hbar}{mc}$$
$$\times\left\{1+\frac{4\pi}{3}n_0\left(2\sum_{j\neq l}\frac{e^2 r_j^2\epsilon_j}{\epsilon_j^2-\epsilon_l^2}\right)+L'''\right\}^2 n_0 f_{0l}. \qquad (33)$$

This exhibits the interesting result that if only one transition in the atom has appreciable oscillator strength, the total absorption per atom is uninfluenced by the presence of the other atoms.

Thus, aside from the effects of transitions to states $j\neq l$ and aside from exchange and higher order effects, the effective field ratio is $1+(4\pi n_0/3)(2e^2r_l^2/\epsilon_l)$ in treating the low-frequency polarization of an atom, is $1+(\pi n_0/3)(2e^2r_l^2/\epsilon_l)$ for purposes of calculating the transition probability, but is unity as regards the absorption coefficient. Another way of stating this is that although the transition probability is increased by the presence of the other atoms, the energy of the transition by the presence of the other atoms, the energy of the transition is reduced by the same interactions just enough to leave the total absorption unchanged. This result was not previously known to the writer and demonstrates that one must be careful in applying the "effective field" concept. Essentially this result may be obtained classically, as shown in Appendix B.

This idealized model probably bears little resemblance to most real crystals, except perhaps the solid rare gases and possibly other molecular crystals. However, even if there should be little practical application, the calculation seems worthwhile since with this model it is possible to carry out in detail the computations for the very commonly used van der Waals' interaction, showing results rather different from those commonly assumed. The formal result that the van der Waals interaction between an oscillator and other identical oscillators produces no change in the amount of energy absorbed cannot obviously be carried over to other interactions, but it is at least suggestive.

## APPENDIX A

In this section we wish to compute the transition amplitude $\mathbf{C}_j$ given by Eqs. (16) and (A1),

$$\mathbf{u}\cdot\mathbf{C}_j=\frac{-e\hbar}{\omega_j m}\int\Psi_j^{(1)*}(\mathbf{u}\cdot\textstyle\sum_i\nabla_i e^{i\mathbf{k}\cdot\mathbf{r}_i})\Psi_0^{(1)}d\tau. \qquad (A1)$$

There are three types of terms in $\Psi_j^{(1)*}$ and three in $\Psi_0^{(1)}$, in each case one wave function with a large coefficient, and the others with small coefficients. We shall keep none of the product terms involving the product of two of the small coefficients. The leading term is

$$\int\Psi_j^{(0)*}(\mathbf{u}\cdot\sum\nabla_i e^{i\mathbf{k}\cdot\mathbf{r}_i})\Psi_0^{(0)}d\tau, \qquad (A2)$$

and there are additional terms with one small coefficient

$$\int \Psi_j^{(0)*}(\mathbf{u}\cdot\textstyle\sum_i \boldsymbol{\nabla}_i e^{i\mathbf{k}\cdot\mathbf{r}_i}) \times\sum_L\sum_m\sum_n \frac{\langle L,m,n|H_1|0\rangle}{\epsilon_m+w_n}\Psi_{L,m,n}{}^{(0)}, \tag{A3}$$

and

$$\int \sum_J\sum_s\sum_{n\neq j} \frac{\langle J,s,n|H_1|j\rangle}{\epsilon_s+w_n-w_j}\Psi_{J,s,n}{}^{(0)*} \times(\mathbf{u}\cdot\sum_i \boldsymbol{\nabla}_i e^{i\mathbf{k}\cdot\mathbf{r}_i})\Psi_0{}^{(0)}d\tau. \tag{A4}$$

The terms like

$$\int \Psi_j^{(0)*}(\mathbf{u}\cdot\textstyle\sum_i \boldsymbol{\nabla}_i e^{i\mathbf{k}\cdot\mathbf{r}_i})\sum_\beta c_\beta\Psi_\beta{}^{(0)}d\tau \tag{A5}$$

and

$$\int \textstyle\sum_\gamma d_\gamma\Psi_\gamma{}^{(0)*}(\mathbf{u}\cdot\sum_i \boldsymbol{\nabla}_i e^{i\mathbf{k}\cdot\mathbf{r}_i})\Psi_0{}^{(0)}d\tau \tag{A6}$$

do not contribute, since $\Psi_\beta{}^{(0)}$ involves 2 excited host crystal atoms, so that it does not combine with $\Psi_j{}^{(0)*}$ with a one-electron operator such as $\boldsymbol{\nabla}_i$. The same argument applies to the term labelled (A6). The leading term is

$$\begin{aligned}\frac{-e\hbar}{\omega_j mN!}&\int\sum_p\sum_{p'}(-1)^{p+p'}P\psi_1{}^{0*}(1)\cdots\\ &\times\varphi^{j*}(N)(\mathbf{u}\cdot\textstyle\sum_i\boldsymbol{\nabla}_i e^{i\mathbf{k}\cdot\mathbf{r}_i})P'\psi_1{}^0(1)\cdots\varphi^0(N)d\tau\\ &=\frac{-e\hbar}{\omega_j m}\int\varphi^{j*}(N)(\mathbf{u}\cdot\textstyle\sum_i\boldsymbol{\nabla}_i e^{i\mathbf{k}\cdot\mathbf{r}_i})\varphi^0(N)d\tau\\ &=\frac{-e\hbar}{\omega_j m}(\mathbf{u}\cdot\langle j|\boldsymbol{\nabla}|0\rangle)e^{i\mathbf{k}\cdot\mathbf{r}_N}.\end{aligned} \tag{A7}$$

The first step involves first the recognition that the $N!$ permutations $P$ and $P'$ must be identical, because of orthogonality, in order to give a nonzero result, and second the integration over all the electronic coordinates except those describing the electron, say the $N$th, on the impurity atom. In the next step we find a contribution in the sum $\sum_i \boldsymbol{\nabla}_i e^{i\mathbf{k}\cdot\mathbf{r}_i}$ only for that same electron, the $N$th. In the following, we shall choose our coordinate system to be centered on the impurity atom, so that $\exp i\mathbf{k}\cdot\mathbf{r}_N$ is unity. Note that the $\boldsymbol{\nabla}$ matrix element is computed between *atomic* states, so that we may apply the well-known theorem,

$$\langle j|\boldsymbol{\nabla}|0\rangle=\frac{-m}{\hbar^2}\mathbf{x}_j(w_j-w_0), \tag{A8}$$

relating the gradient and dipole matrix elements. Thus the leading term is

$$[ew_j/(W_j-W_0)]\mathbf{u}\cdot\mathbf{x}_j \tag{A9}$$

and only those states $j$ contribute which are polarized in the direction of polarization of the field $\mathbf{u}$.

The next term (A3) gives a contribution for all states $L$, $m$, in which the direction of polarization is parallel to $\mathbf{u}$, but only for the impurity state $n$ the same as the state $j$. Similarly in (A4) the state $n$ must be the ground state for the impurity atom, in order to get a nonzero contribution, because of orthogonality. The correction terms are found in the same way as above to be

$$\frac{e}{W_j-W_0}\left(\sum_m \mathbf{u}\cdot\mathbf{r}_m\epsilon_m\left[\frac{1}{\epsilon_m+w_j}-\frac{1}{\epsilon_m-w_j}\right]\right)\sum_L e^{i\mathbf{k}\cdot\mathbf{r}_L} \times\left(\frac{e^2}{R_L{}^3}[\mathbf{r}_m\cdot\mathbf{x}_j-3\mathbf{r}_m\cdot\mathbf{R}_L\mathbf{x}_j\cdot\mathbf{R}_L/R_L{}^2]-\mathcal{E}_L(m,j)\right). \tag{A10}$$

Here $\mathcal{E}_L(m,j)$ is an exchange term

$$\mathcal{E}_L(m,j)=\int\psi_L{}^{m*}(1)\varphi^{j*}(2)\frac{e^2}{r_{12}}\psi_L{}^0(2)\varphi^0(1)d\tau_{12}, \tag{A11}$$

which drops off exponentially with the separation $R_L$. The summation over the atoms $\sum_L$ may be performed with an integral for small $\mathbf{k}$, as shown by Heller and Marcus[12]; for the dipole-dipole terms the result can be simply expressed, but the details of the wave functions must be known to evaluate the exchange terms. We shall use the symbol $\mathcal{E}(m,j)$ for $\sum_L e^{i\mathbf{k}\cdot\mathbf{r}_L}\mathcal{E}_L(m,j)$, and assert that it does not depend appreciably upon $\mathbf{k}$, since the wavelength of the light is much longer than the range of the exchange interaction. Thus we obtain

$$\mathbf{u}\cdot\mathbf{C}_j=\frac{ew_j\cdot\mathbf{u}\cdot\mathbf{x}_j}{W_j-W_0}+\frac{e}{W_j-W_0}\sum_m\frac{2\mathbf{u}\cdot\mathbf{r}_m\epsilon_m w_j}{\epsilon_m{}^2-w_j{}^2} \times\left(-\frac{8\pi}{3}n_0e^2P_2[\cos(\mathbf{k},\mathbf{u})]\mathbf{r}_m\cdot\mathbf{x}_j \times[j_0(\rho)-j_2(\rho)]+\mathcal{E}(m,j)\right). \tag{A12}$$

Here $P_2$ is the Legendre polynomial of order 2, and its argument is the cosine of the angle between $\mathbf{k}$ and $\mathbf{u}$. This angle is, of course, $\pi/2$ for photons, so that $P_2$ is $-\frac{1}{2}$. The Bessel functions $j_0$ and $j_2$ are functions of $\rho\equiv k(3/4\pi n_0)^{\frac{1}{3}}$ which is of the order of the lattice spacing divided by the wavelength of the light, so that $\rho$ is very small and $j_0-j_2$ can be replaced by unity. Thus we obtain

$$\mathbf{u}\cdot\mathbf{C}_j=\frac{ew_j}{W_j-W_0}\mathbf{u}\cdot\mathbf{x}_j\left[1+\sum_m\frac{8\pi}{3}n_0\frac{e^2\epsilon_m}{\epsilon_m{}^2-w_j{}^2}r_m{}^2 +\sum_m\frac{2\mathbf{u}\cdot\mathbf{r}_m\epsilon_m}{\mathbf{u}\cdot\mathbf{x}_j(\epsilon_m{}^2-w_j{}^2)}\mathcal{E}(m,j)\right]. \tag{A13}$$

Now the polarizability $\alpha_h$ of a host crystal atom at energy $w_j$ is $2e^2\sum_m r_m{}^2\epsilon_m/(\epsilon_m{}^2-w_j{}^2)$, so the second term in the square brackets is $(4\pi n_0/3)\alpha_h(w_j)$. Finally, we substitute for $W_j - W_0$ from Eq. (14), and, defining the exchange terms

$$F(0,a) = \sum_I \int \psi_I^{0*}(1)\varphi^{a*}(2)\frac{e^2}{r_{12}}\psi_I^0(2)\varphi^a(1)d\tau_{12}, \quad \text{(A14)}$$

we obtain

$$\mathbf{u}\cdot\mathbf{C}_j = e\mathbf{u}\cdot\mathbf{x}_j\left[1 + \frac{4\pi}{3}n_0\alpha_h(w_j) + 2\sum_m \frac{\mathbf{u}\cdot\mathbf{r}_m\epsilon_m\mathcal{E}(m,j)}{\mathbf{u}\cdot\mathbf{x}_j(\epsilon_m^2 - w_j^2)} + \frac{1}{w_j}(F(0,j) - F(0,0))\right], \quad \text{(A15)}$$

the square of which is given in Eq. (17).

## APPENDIX B

A result similar to Eq. (33) may be obtained classically, as follows. An oscillator in a vacuum satisfies the differential equation

$$m\ddot{x} + mb\dot{x} + m\omega_0^2 x = e\mathcal{E}, \quad \text{(B1)}$$

and has the solution

$$x = \frac{(e/m)\mathcal{E}}{\omega_0^2 - \omega^2 + i\omega b}, \quad \text{(B2)}$$

where $\omega_0$ is its resonance frequency and $b$ is a damping term. Thus the polarization per oscillator is $p = ex$, the polarizability per oscillator is $\alpha_a = p/\mathcal{E}$, and the total polarizability $\alpha$ is $n_0 p/\mathcal{E}$ (for an oscillator strength of unity). The dielectric constant $\kappa = (n - ik)^2$ is $1 + 4\pi\alpha$ so we have

$$(n - ik)^2 = 1 + 4\pi n_0 \frac{e^2}{m}\frac{1}{\omega_0^2 - \omega^2 + i\omega b}, \quad \text{(B3)}$$

in terms of the extinction coefficient $k$ and the index $n$. Solving for $k$, we obtain

$$\int_0^\infty k(\omega)d\omega = 2\pi n_0 \frac{e^2}{m}\int_0^\infty \frac{\omega b d\omega}{(\omega_0^2 - \omega^2)^2 + \omega^2 b^2} \quad \text{(B4)}$$

$$= \pi^2 n_0 e^2/m\omega_0.$$

Thus the integrated extinction coefficient is independent of the damping constant, and is inversely proportional to the resonance frequency. The absorption coefficient is $\omega k/c$, so that its integral is

$$\int \mu(\omega)d\omega = \pi^2 n_0 e^2/mc. \quad \text{(B5)}$$

If the oscillator is inserted in a medium where the effective field for polarization is not $\mathcal{E}$ but $\mathcal{E} + 4\pi P/3$, the right hand member of Eq. (B1) should have added to it the quantity $4\pi P e/3 = 4\pi n_0 e^2 x/3$. This term may be combined with the last term on the left of Eq. (B1), to give the solution

$$x = (e/m)\mathcal{E}/(\bar{\omega}^2 - \omega^2 + i\omega b), \quad \text{(B6)}$$

where

$$\bar{\omega}^2 = \omega_0^2 - 4\pi n_0 e^2/3. \quad \text{(B7)}$$

Thus the resonance frequency is shifted by an amount given by

$$\bar{\omega}/\omega_0 = 1 - 2\pi n_0 e^2/3\omega_0^2, \quad \text{(B8)}$$

so that the integrated extinction coefficient is increased by the reciprocal of this ratio, or

$$\int k'(\omega)d\omega = \frac{\pi^2 n_0 e^2}{m\omega_0}\left(1 + \frac{\pi n_0 e^2}{3\omega_0^2}\right)^2, \quad \text{(B9)}$$

to the desired order of approximation. However, the quantity $e^2/m\omega_0^2$ is the atomic polarizability at zero frequency, $\alpha_a$, so that the modified extinction coefficient integrates to

$$\int k'(\omega)d\omega = \left(1 + \frac{\pi n_0}{3}\alpha_a\right)^2 \int k(\omega)d\omega. \quad \text{(B10)}$$

Since both the transition probability, quantum mechanically speaking, and the extinction coefficient are proportional to the absorption coefficient divided by the frequency of the transition, they are proportional to each other, and hence the transition probability must be increased by the same ratio as in Eq. (B10). The agreement with Eq. (30), for the case of just one type of oscillator and no exchange, may be observed by noting that $2e^2 r_l^2/\epsilon_l$ in Eq. (30) is the quantum mechanical value for $\alpha_a$ at zero frequency.

On the other hand, since according to Eq. (B5) the integrated absorption cross section is independent of the resonance frequency $\omega_0$ or $\bar{\omega}$, it is unchanged by the presence of the other identical oscillators, in agreement with Eq. (33).