is argued to be probably not correct. The relaxation rate continues to increase with optical bleaching over the full range of our experiments. Since the *M*-center concentration goes through a maximum within this range, we conclude that the *M* center plays no direct role in the relaxation enhancement.

(2) A thermal bleach at 150°C, which removes the optical absorption bands of *M*, *R*, and *N*, also restores the resonance relaxation rate to its value prior to optical bleaching. Hence, we conclude that the optical bleaching produces no significant *irreversible* changes in the spatial distribution of *F* centers.

Although they give no detailed information about the nature of the derived centers, our results are consistent with a picture of *F*-center coagulation along the lines suggested by Pick. That is, the various optical absorption bands result mainly from larger and larger agglomerates of *F* centers formed as a result of optically excited migration of *F* centers. As in the experiments of Moran *et al.*, we find little evidence for existence of one or more paramagnetic centers with resonance properties significantly different from those of the *F* center. Some of the derived centers are undoubtedly paramagnetic. It seems likely to us that these will be more fruitfully described as perturbed *F* centers (perturbed because of close association with other *F* centers) rather than as different entities.

ACKNOWLEDGMENTS

Particular thanks go to Professor R. H. Silsbee for profitable discussions on many facets of this work. Dr. M. V. Klein and Professor D. M. Lee contributed through helpful discussions concerning low-temperature equipment. For guidance in the lore of alkali-halide physics, the authors wish to express appreciation to Professors R. O. Pohl and W. Martienssen and to Dr. A. Taylor. The help of Mr. T. R. Sliker in construction of part of the equipment is gratefully acknowledged. We have profited from discussions and exchange of information with Dr. J. G. Castle and Dr. D. W. Feldman of the Westinghouse Research Laboratories.

PHYSICAL REVIEW VOLUME 126, NUMBER 6 JUNE 15, 1962

Cooperative Optical Absorption in Solids

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(Received February 14, 1962)

A discussion is given of a mechanism for resonance energy transfer in the absorption of light by a pair of neighboring ions in a crystal, as recently demonstrated by Varsanyi and Dieke. An estimate of the probability for this process is given.

IN a beautiful experiment recently published Varsanyi and Dieke[1] have conclusively demonstrated the optical absorption of a photon by a pair of atoms in cooperation. The experiment consisted of detecting resonance fluorescence from a given state of a Pr^{3+} ion in a crystal irradiated in several photon wavelengths which a single Pr^{3+} ion does not absorb, but which correspond to the sum of the excitation energy of the emitting state and that of discrete lower excited states. It is clear that a "very tight binding" description is applicable, since the pertinent transitions occur in well shielded inner shells, and since, experimentally, the transition energies remain accurately unchanged from the sum of the individual excitation energies. The implications of this process on optical pumping were noted by the authors.

Some indication of a similar process may also have been observed by Milgram and Givens.[2]

The purpose of this note is to discuss the probable mechanism responsible for this effect, and to estimate its probability.

First, let us comment on why this process is an unusual one. It is clear that, to an excellent approximation, the initial electronic state of the crystal can be written as an antisymmetrized product of Heitler-London wave functions, with each ion in its ground state, and that after absorption of the photon two ions, *A* and *B*, are excited. That is, the final state is... $\psi_a\varphi_b\ldots$, differing from the initial state only in changes from... $\psi_o\varphi_o\ldots$ The perturbing Hamiltonian associated with the incident radiation is of the form $\sum_l \mathbf{A}(\mathbf{r}_l)\cdot\nabla_l$, or $\sum_l \mathbf{e}(\mathbf{r}_l)\cdot\mathbf{r}_l$, where $\mathbf{r}_l$ is the positions of the *l*th electron, $\mathbf{A}$ is the vector potential, and $\mathbf{e}$ is the electric field multiplied by the electronic charge. The atomic wave functions ψ_o and ψ_a for atom *A* (also φ_o and φ_b for *B*)) are orthogonal, so it is clear that one-electron operators cannot directly induce transitions involving more than one atom. Let us simplify the problem for clarification. Suppose each

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* Research supported in part by the U. S. Air Force through the Air Force Office of Scientific Research.

[1] F. Varsanyi and G. H. Dieke, Phys. Rev. Letters **7**, 442 (1961).

[2] A. Milgram and M. P. Givens, Phys. Rev. **125**, 1506 (1962).

atom contains only one electron, so that we are concerned with transitions $\psi_o(1)\varphi_o(2) \rightarrow \psi_a(1)\varphi_b(2)$. (The roles of antisymmetrization, overlap, and exchange will be discussed later.) The sum of one-electron operators such as $\sum_l \mathbf{A}\cdot\nabla_l$ can separately induce a transition from $\psi_o(1)$ to $\psi_a(1)$, *or* $\varphi_o(2)$ to $\varphi_b(2)$, but not both simultaneously, because of the orthogonality of the atomic functions. In the double transition, there would be a factor of the form $\int \varphi_o^*(\mathbf{r}_2)\varphi_b(\mathbf{r}_2)d^3r_2$, and, hence, the integral vanishes, as does the matrix element for the double transition. This is a general result, correct to zero-order in the atomic or ionic wave functions.

A nonvanishing transition probability *is* obtained, even in the absence of overlapping wave functions, with the simple use of first-order perturbation theory, Consider two atoms or ions in a crystal, A and B, with nonoverlapping, zero-order wave functions, $\psi_a(\mathbf{r}_1\cdots\mathbf{r}_\alpha)$, $\varphi_b(\mathbf{r}_{\alpha+1}\cdots\mathbf{r}_{\alpha+\beta})$ and zero-order energy levels $E_a^{(0)}$ and $\mathcal{E}_b^{(0)}$. Transitions can occur in atom A between levels $E_a^{(0)}$ and $E_{a'}^{(0)}$, and in atom B between $\mathcal{E}_o^{(0)}$ and $\mathcal{E}_{b'}^{(0)}$. Now, let us consider the interaction between A and B explicitly, assuming that all other interactions have been included exactly. If the wave functions are orthogonal, the nuclear-nuclear interaction vanishes, as do the electron-"other nucleus" interactions, and we are left with

$$H'=\sum_{i=1}^{\alpha}\sum_{j=1}^{\beta}\frac{e^2}{\kappa r_{ij}}. \tag{1}$$

The dielectric constant κ is introduced on the assumption that the atoms are well-separated, and that the transition frequencies are less than those characteristic of the host crystal. We now correct the wave functions ψ_a and φ_b, to account for the electronic interactions, and obtain a total wave function

$$\chi_{ab}(\mathbf{r}_1\cdots\mathbf{r}_{\alpha+\beta}) =\psi_a\varphi_b-\sum_{a'\neq a}\sum_{b'\neq b}\frac{\langle ab|H'|a'b'\rangle\psi_{a'}\varphi_{b'}}{E_{a'}^{(0)}-E_a^{(0)}+\mathcal{E}_{b'}^{(0)}-\mathcal{E}_b^{(0)}}. \tag{2}$$

In particular, we shall be concerned with the ground state of the system, described by χ_{oo}. Let us introduce the notation

$$\chi_{oo}=\psi_o\varphi_o-\sum_{a'\neq o}\sum_{b'\neq o}\frac{\langle oo|H'|a'b'\rangle}{\delta_{a'}+\epsilon_{b'}}\psi_{a'}\varphi_{b'}. \tag{3}$$

Single excitations, of atom A, for example, are of the form

$$\chi_{ao}=\psi_a\varphi_o-\sum_{a'\neq a}\sum_{b'\neq o}\frac{\langle ao|H'|a'b'\rangle}{\delta_{a'}-\delta_a+\epsilon_b}\psi_{a'}\varphi_{b'}. \tag{4}$$

[Let us ignore, for the moment, the possibility of vanishing energy denominators in Eq. (4).]

Double excitations can exist also, as indicated in Eq. (2). Our problem is to compute the transition probability between the states described by Eqs. (3) and (2) under the perturbation associated with an incident electromagnetic field characterized by the vector potential A. This perturbation may be written as $\mathbf{e}\cdot(\mathbf{R}_A+\mathbf{R}_B)$, where

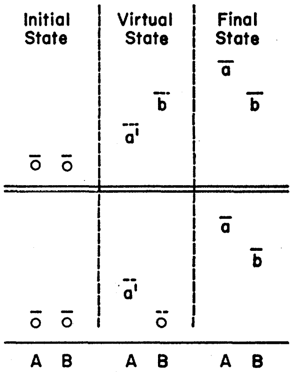

FIG. 1. Double excitation through virtual states. The upper diagram illustrates the first term of Eq. (5) (see text). The lower diagram corresponds to the thrid term.

$$\mathbf{R}_A=\sum_{i=1}^{\alpha}\mathbf{r}_i,\quad \mathbf{R}_B=\sum_{j=1}^{\beta}\mathbf{r}_j.$$

Accordingly, the transition element between the ground state and that of Eq. (2) is given by

$$\begin{aligned}-M_{ab}=&\sum_{a'\neq o}\frac{\langle a|\mathbf{e}\cdot\mathbf{R}_A|a'\rangle\langle oo|H'|a'b\rangle}{\delta_{a'}+\epsilon_b}\\&+\sum_{b'\neq o}\frac{\langle b|\mathbf{e}\cdot\mathbf{R}_B|b'\rangle\langle oo|H'|ab'\rangle}{\delta_a+\epsilon_{b'}}\\&+\sum_{a'\neq a}\frac{\langle o|\mathbf{e}\cdot\mathbf{R}_A|a'\rangle\langle a'o|H'|ab\rangle}{\delta_{a'}-\delta_a-\epsilon_b}\\&+\sum_{b'\neq b}\frac{\langle o|\mathbf{e}\cdot\mathbf{R}_B|b'\rangle\langle ob'|H'|ab\rangle}{-\delta_a+\epsilon_{b'}-\epsilon_b}.\end{aligned} \tag{5}$$

The first term comes from setting $b'=b$, and the second from $a'=a$ in Eq. (3), the third from $b'=o$, and the fourth from $a'=o$ in Eq. (2). Thus, the first term corresponds to the excitation of the state (ab) through the virtual intermediate state $(a'b)$, and the third corresponds to the virtual excitation of $(a'o)$ followed by the real transition to the state (ab). Figure 1 indicates these states.

The vanishing of the energy denominator in the third term for some state a' asserts that $\delta_{a'}=\delta_a+\epsilon_b$, which is the energy of the absorbed photon $h\nu$. "Cascade" processes can, of course, occur. In the event that there happens to exist a state a' of A at $E_{a'}=E_a+\epsilon_b$, it might be a more accurate description to assert that atom A alone absorbs the photon in a *real* process, and, subsequently, makes a transition downward to state a, simultaneously transferring an amount of energy ϵ_b to B. This process is indicated in Fig. 2. On the other hand, this might *not* be the more accurate description, if selection rules should greatly reduce the transition probability for the direct process; in any

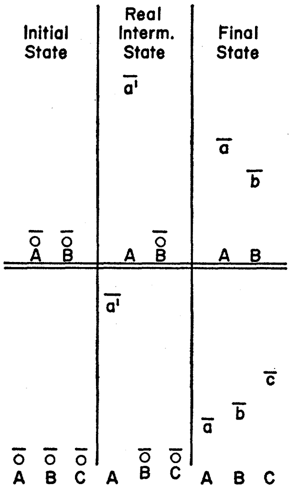

FIG. 2. Illustration of double and triple excitation by successive real processes. The upper diagram corresponds to the vanishing of the energy denominator in the third term of Eq. (5). This can occur if the level a' is at an energy equal to $\delta_a+\epsilon_b$. The lower diagram denotes a three-atom process which would be possible if a' were at an energy equal to $\delta_a+\epsilon_b+\gamma_c$. This process can occur if there is overlap in the wave functions of B and C.

case, degenerate perturbation theory is available if required.

Thus, we see that the transition probability depends on familiar optical matrix elements, but generally not on those directly connecting the ground and excited atomic states of interest. That is, the matrix elements $\langle o|\mathbf{e}\cdot\mathbf{R}_A|a\rangle$ and $\langle o|\mathbf{e}\cdot\mathbf{R}_B|b\rangle$ do not appear explicitly.

To proceed with the calculation, it is necessary to evaluate the matrix elements of H', Eq. (1).

Just as in the case of "sensitized luminescence" calculations,[3,4] it is convenient to develop Eq. (1) in a multipole expansion. According to the conditions of the problem, the charge-charge and charge-dipole terms are zero, and the first potentially nonvanishing terms are the electric dipole-dipole interactions,

$$H'\approx\frac{e^2}{\kappa\rho^3}(\mathbf{R}_A\cdot\mathbf{R}_B-3\mathbf{R}_A\cdot\boldsymbol{\rho}\mathbf{R}_B\cdot\boldsymbol{\rho}/\rho^2), \tag{6}$$

where $\boldsymbol{\rho}$ is the separation of A and B. For convenience, we shall choose this as the x axis. Thus, the matrix elements of H' may be written as

$$\begin{aligned}\langle a'o|H'|ab\rangle\\ =\frac{e^2}{\kappa\rho^3}\{-2\langle a'|X_A|a\rangle\langle o|X_B|b\rangle+\langle a'|Y_A|a\rangle\langle o|Y_B|b\rangle\\ +\langle a'|Z_A|a\rangle\langle o|Z_B|b\rangle\},\end{aligned} \tag{7}$$

etc., where the matrix elements of $\mathbf{R}$ are written in components.

If the matrix elements of H' should vanish in this approximation, it would be necessary to investigate higher order terms, i.e., dipole-quadrupole, quadrupole-quadrupole. . .etc., varying inversely as the 4th, 5th, . . .powers of ρ.

In general, M_{ab} will vary with the angle between $\mathbf{e}$ and $\boldsymbol{\rho}$, and with the nature of the electronic states involved. Let us ignore the angular dependence, and incorporate it in a dimensionless constant c of the order unity while replacing X, Y, Z by an appropriate average value D. That is, we write a typical matrix element of H', as in Eq. (7) above, as

$$\langle a'o|H'|ab\rangle=\frac{ce^2}{\kappa\rho^3}D_A(a'a)D_B(ob). \tag{8}$$

If the dipole-dipole interaction vanishes, but the dipole-quadrupole does not, we represent it as

$$(c'e^2/\kappa\rho^3)[D_A(a'a)][(a_0/\rho)D_B'(ob)].$$

It is important to note that the second factor, the dipole term, is unchanged, and, that the third is reduced by a factor of the order a_0/ρ, where $a_0=\hbar^2/me^2$. $D_B'(ob)$ is still of order a_0, c' of order unity, and the primes will henceforth be dropped. Thus, it should be clearly noted that a transition element, which involves only d-q interactions between A and B is reduced by a_0/ρ as compared with one involving d-d interactions between A and B. Similarly, q-q interactions are down by $(a_0/\rho)^2$ in transition amplitude, etc. The "average value" D is the average over degenerate states, and the sums $\sum_{a'}\sum_{b'}$ now imply sums over nondegenerate states only.

The optical matrix elements such as $\langle a|\mathbf{e}\cdot\mathbf{R}_A|a'\rangle$ can be similarly represented, when the electric dipole transition from a to a' is allowed. In this case, the matrix element is represented as $|\mathbf{e}|L_A(aa')$, $L\sim a_0$. There is a great contrast to the above, however, when the dipole transition a to a' is forbidden. In this case, it is necessary to expand the exponential in $\mathbf{e}=|\mathbf{e}|\mathbf{1}\times\exp(i\mathbf{k}\cdot\mathbf{r})$ (where $\mathbf{1}$ is the unit polarization vector of the incident radiation and $\mathbf{k}$ is the propagation vector of magnitude $\bar{\lambda}^{-1}$, λ the wavelength) in the form $\exp(i\mathbf{k}\cdot\mathbf{r})=1+i\mathbf{k}\cdot\mathbf{r}-\cdots$. Quadrupole matrix elements in *this* case are of magnitude $|\mathbf{e}|L_A(aa')a_0/\bar{\lambda}$, thus reduced by a factor $a_0/\bar{\lambda}$ from those of allowed dipole transitions. It is again emphasized that the comparable reduction in the matrix element of H' is a_0/ρ; for near neighbors a_0/ρ may be only 10^{-1}, but for visible light $a_0/\bar{\lambda}$ is of the order 10^{-3}.

Thus, we may expect the transition element to be of magnitude

$$\begin{aligned}|M_{ab}|=|\mathbf{e}|\{c_1\sum_{a'\neq o}L_A(aa')(e^2/\kappa\rho^3)D_A(oa')\\ \times D_B(ob)/(\delta_{a'}+\epsilon_b)\\ +c_2\sum_{b'\neq o}L_B(bb')(e^2/\kappa\rho^3)D_A(oa)\\ \times D_B(ob')/(\delta_a+\epsilon_{b'})\\ +c_3\sum_{a'\neq a}L_A(oa')(e^2/\kappa\rho^3)D_A(a'a)\\ \times D_B(ob)/(\delta_{a'}-\delta_a-\epsilon_b)\\ +c_4\sum_{b'\neq b}L_B(ob')(e^2/\kappa\rho^3)D_A(oa)\\ \times D_B(b'b)/(-\delta_a+\epsilon_{b'}-\epsilon_b)\},\end{aligned} \tag{9}$$

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[3] Th. Forster, Ann. Physik 2, 55 (1948).

[4] D. L. Dexter, J. Chem. Phys. 21, 836 (1953); D. L. Dexter and J. H. Schulman, J. Chem. Phys. 22, 1063 (1954).

if all indicated transitions were allowed. Any forbidden transition indicated by L should be reduced by a factor of the appropriate power of approximately $a_0/\lambda\!\!\!{}^-$; a forbidden transition denoted by D should be reduced by only a power of a_0/ρ.

There will generally exist *some* combinations in which forbidden L's can be avoided. If for these cases there are also allowed D's, the magnitude of the square of the transition element is approximately

$$|M_{ab}|^2 \approx |\mathbf{e}|^2 a_0^2 \left(\frac{e^2 a_0^2}{\kappa\rho^3}\right)^2 \Big/ W^2, \tag{10}$$

which is reduced from that for a single allowed excitation transition by a factor

$$q \equiv \left(\frac{e^2 a_0^2}{\kappa\rho^3}\right)^2 \Big/ W^2, \tag{11}$$

where W is a characteristic electronic energy difference of the order 0.1 to 1 ev. If $W = 0.3$ ev, $\kappa = 3$, $\rho = 6a_0$, then q can reasonably become as large as 10^{-2}. It may be considerably smaller.

It is important to note that q relates to an *allowed* single excitation. Even though $|M_{ab}|^2$ be reduced by two or more orders of magnitude from that of an allowed single excitation, it might well be much larger than the squared transition element for a given single *forbidden* transition. For simplicity, let us suppose that A contains only one significant electron, present in an s ground state. Similarly with B, suppose further that B has an excited p state b at $\epsilon_b = 1$ ev, and that A has another s state a at $\delta_a = 2$ ev, and a p state a' at $\delta_{a'} = 0.5$ ev. The direct transition in A alone from o to a would be a forbidden one at energy 2 ev, but the double transition to (ab) could readily occur at energy 3 ev, if a B atom were in the neighborhood. If we ignore the existence of any other states, the first term of Eq. (5) and the approximations we have made for H' for this case tell us that

$$|M_{ab}| \approx \left[\frac{e^2 a_0^2}{\kappa\rho^3} \Big/ 1.5\text{ ev}\right] |\mathbf{e}| a_0, \tag{12}$$

which can lead to a very sizeable transition probability, if ρ is not too large.

The same result would obtain, if the final state of A were a d state at 2 ev above the ground state, a transition not allowed in the A atom alone.

Suppose, on the other hand, one wished to induce an s to f transition in atom A. In a free atom, this would be reduced by a factor $\sim (a_0/\rho)^4 \sim 10^{-13}$ from an allowed transition probability in a direct excitation process. If the initial state (oo) is (ss), an intermediate (dp) state can be reached by a quadrupole-dipole virtual transition, and a final state (fp) transition probability is reduced by a factor of only $q(a_0/\rho)^2$ as compared with an allowed electric dipole transition, or perhaps 10^{-4}. This is to be compared with the figure 10^{-13} for the free atom computed just above. (The latter estimate cannot be taken too seriously, however, since lattice vibration and crystalline field effects will destroy at least some of the assumed atomic symmetries.)

Similar arguments apply, making use of the symmetries of other more complex ionic states; there is no fundamental difference.

Basically, what this mechanism accomplishes is: (1) most important, getting around the restrictions represented in the "one-particle operator" point of view; (2) the *removal* of some selection rules held valid in noninteracting, spherically symmetric atomic systems; (3) the *substitution* of degree of forbiddenness from powers of $(a_0/\lambda\!\!\!{}^-)$ to powers of (a_0/ρ). The relevance to optical pumping, as suggested by Varsanyi and Dieke, is clearly confirmed, and its possible importance is reinforced, because of the nature of the states that can be prepared in this way. The prospects of inverting level populations are greatly enhanced, if upper states can be selectively and effectively excited by a mechanism which does not require allowed (or even weakly forbidden) optical transitions to the ground state. The possibility also exists that systems may be found in which broad-band excitation spectra can be used, thus allowing a large amount of absorbed input power, almost independent of the width of the emission spectrum.

Until now we have spoken only of transition matrix elements, and have ignored all energy considerations. The first question on the energetics of this problem surely relates to the additivity of the single-excitation energies in a double-excitation process. Qualitatively stated, one may ask how the interaction between A and B can simultaneously be strong enough to allow double excitation, and weak enough to change the transition energies only negligibly from predictions based on the additivity of single excitation energies. The second question concerns the excitation spectra, i.e., the linewidths for the double transitions.

Let us consider the first matter above, and treat the excitation (ab) in two parts. We assume that we can treat exactly the interaction of all ions in the crystal, including A with all others and B with all others, with the sole exception of A and B. The Coulomb interaction of A with B is also included in the zero-order Hamiltonian, and all that is omitted is the dependence of the interaction on the electronic states of A and B. If this zero-order Hamiltonian leads to a prediction of lowest energy level $W_{oo}^{(0)}$, a corrected (second-order) level is given by

$$W_{oo}^{(2)} = W_{oo}^{(0)} - \sum_{a'\neq o}\sum_{b'\neq o} \frac{|\langle oo|H'|a'b'\rangle|^2}{\delta_{a'}+\epsilon_{b'}}. \tag{13}$$

Similarly, a single excitation of ion A will occur at energy $E_a^{(0)} - E_o^{(0)} \equiv \delta_a = W_{ao}^{(0)} - W_{oo}^{(0)}$, correct to zero order, in the same sense; in second order the transition energy is

$$W_{ao}^{(2)}-W_{oo}^{(2)} =\delta_a-\sum_{b'\neq o}\left\{\frac{|\langle ao|H'|ob'\rangle|^2}{-\delta_a+\epsilon_{b'}}-\frac{|\langle oo|H'|ab'\rangle|^2}{\delta_a+\epsilon_{b'}}\right\}. \tag{14}$$

A similar result is obtained for single excitations in B, and it is a straightforward matter to compute the double excitation energy, $W_{ab}^{(2)}-W_{oo}^{(2)}$, correct to second order. As would be anticipated, it turns out to be equal to the sum of δ_a and ϵ_b with numerous second-order corrections. When the important intermediate states are coupled to the ground state by dipole-dipole interactions, the double excitation energy is predicted to be equal to the sum of the observed single transition energies plus or minus a term of order qW, perhaps 10^{-2} ev or less. Basically, this is a statement that atom B is not much influenced, in its transition $o-b$, by the details of the charge distribution on atom A, as long as the two charge distributions of A and B do not overlap. If the important intermediate states in the (oo)-(ab) transitions are *not* coupled by a dipole-dipole interaction, the transition probability is reduced by more than the factor q, as discussed above, by factors of a_0/ρ. However, the double-excitation energy may still be modified by an amount of the order qW from the sum of the individual excitation energies, because different pairs of virtual states may be important.

Regarding the second question above, that concerning the absorption line shape for double-excitation processes, it is clear that explicit attention must be paid to the interaction of the ions with their environment, particularly with lattice vibration. Suppose the absorption line shape of atom A (or B) in the single-excitation process $o-a$ (or $o-b$) is given by the normalized shape $\alpha_a(E)$ [or $\beta_b(\mathcal{E})$]. The shape function is normalized in the sense that $\int\alpha_a(E)dE=\int\beta_b(\mathcal{E})d\mathcal{E}=1$. Then the probability of absorbing a photon of energy $h\nu$ in a (oo)-(ab) transition is proportional to the convolution integral,

$$\int\alpha_a(E)\beta_b(h\nu-E)dE. \tag{15}$$

This statement asserts the conservation of energy between initial and final states. As written, it ignores the slight second-order energy corrections noted above. If α_a is a narrow absorption band, say a delta function, $\delta(E-\delta_a)$, the line shape is equal to $\beta_b(h\nu-\delta_a)$. If both α_a and β_b are extremely narrow, excitation of the double process will occur very sharply peaked around $W_{ab}^{(2)}-W_{oo}^{(2)}\approx\delta_a+\epsilon_b$. If we assume Gaussian absorption bands for the single excitations, an approximation in reasonable agreement with what is frequently observed, we may expect Gaussian excitation spectra for the double transitions, with a width equal to the square root of the sum of the squares of the two single transitions.

In solids a given absorption band is usually very wide compared with the "natural" linewidth, because of the interaction of the ion or atom with its environment; accordingly, we are most frequently concerned with the integrated absorption cross section for a given transition (i.e., integrated over energy). Thus, the integrated strength of the double excitation is independent of the linewidth of either transition, and an estimate of the integrated transition probability for the double process can properly be based on the transition matrix elements alone, as discussed above. The *maximum* value of the absorption cross section in the double transition is, of course, influenced by both the width of the o-a and the o-b transitions, since the peak value is inversely proportional to the total width.

Throughout this development, atoms A and B have been treated as different. Nothing in this discussion has *required* that they be dissimilar, and the conclusions reached above apply also for identical ions A and B.

When the concentration of A and B ions is large, it may be appropriate to consider the linear combinations of excited states on different lattice sites, i.e., excitons. In the framework of the tight-binding approximation,[5] it is clear that no important modifications need be made.

In Eq. (11) is indicated a reduction factor which would result in the maximum probability for the double excitation probability, as compared with that for an allowed single transition. The probability for a double transition could be reduced much more without preventing its observation. Even in the case of broad absorption bands (width equal to a few tenths ev) and an oscillator strength of the order 0.1, the peak absorption coefficient is of order 10^6 cm^{-1} for high concentration ~ 1 of the absorbing constituent. Thus, reductions by a factor 10^{-6} still allow the observation of double excitation in macroscopic crystals. For the much narrower single absorption lines frequently encountered, correspondingly much weaker double excitations could be observed.

We should mention the difficult problems associated with overlapping wave functions in the tight-binding approximation, requiring consideration of exchange effects. Using Löwdin's method of symmetric orthogonalization,[6] further developed by Knox[7] and Gold,[8] we can formally ensure orthogonality of the various wave functions to any required order, and the inclusion of exchange effects reduces to the treatment of the interaction $e^2/\kappa r_{ij}$ on two different ions. That is, in addition to the terms of the multipole expansion discussed

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[5] D. L. Dexter and W. R. Heller, Phys. Rev. **91**, 273 (1953).

[6] See, for example, P. O. Löwdin, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1956), Vol. 5, p. 1.

[7] R. S. Knox, J. Phys. Chem. Solids **9**, 238 (1959).

[8] A. Gold, J. Phys. Chem. Solids **18**, 218 (1961).

above, we must consider integrals of the form

$$\int\int \psi_o^*(\mathbf{r}_1)\varphi_o^*(\mathbf{r}_2)\frac{e^2}{\kappa r_{12}}\psi_a(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)d^3\mathbf{r}_1 d^3\mathbf{r}_2. \tag{16}$$

Such integrals may be expected to decrease exponentially with increasing separation ρ, since the overlaps of the wave functions do; they can be very small indeed when there is little overlap of the atomic functions. In the rare earth ions, where the electronic wave functions of interest involve shielded inner electrons, the exchange terms should be negligibly small for most transitions. They can be important, however, in two situations: First, and most obviously, when A and B are nearest neighbors and the wave functions are *not* extremely well localized; second, when the various selection rules governing atomic transitions require that all of the first few terms of the multipole expansion vanish. For example, the exchange integral might more effectively couple an *ss* initial state to a *df* intermediate state for a pair of electrons, than would the electric quadrupole-octopole interaction which is proportional to ρ^{-6}. In the exchange integrals the common optical selection rules are not pertinent, and atomic symmetries are not decisive. Accordingly, the integrated absorption coefficient for a double transition can be expected to be reduced from that of an allowed single excitation by no more than the square of an integral of the form (16) divided by W^2. Even this relatively small transition probability should allow the observation of double transitions when the concentration of AB pairs is high, as it would be in a crystal consisting largely of these ingredients.

Finally, let us consider processes involving three atoms simultaneously. First, we may ask if *triple* excitation processes can occur with appreciable probability. From the form of the first-order wave functions of Eq. (2) it is clear that they cannot, at least under these approximations. Nonzero matrix elements exist for coupling states of the form (*obc*) to the ground state (*ooo*), so that the one-electron operator $\mathbf{e}\cdot\mathbf{r}$ could induce a transition to (*abc*), completely independent of the separation of A from B and C. This coupling is an illusion, however, since total cancellation occurs in the sums over all states. There is no way to couple triple excitations to the ground-state wave function with a perturbation depending only on sums of two-electron interactions, and thus the position of one of the three atoms is immaterial. This leads to a net zero matrix element through term-by-term cancellation.

Second-order corrections to the wave functions can indeed allow such transitions, which would presumably be down by a factor possibly no smaller than q^2. This does not seem to be a profitable subject to discuss at the present time, however, when double transitions themselves have so recently been discovered.

It is clear that the double-excitation process with which we have been concerned can give rise to the emission of two or more photons for each absorbed photon. This could obviously be extremely important in many applications. A closely related mechanism to accomplish the same result has been proposed[9]; there appears to be no definite experimental confirmation of this mechansim. In this process, still in the tight-binding framework, one atom A is initially excited in a real transition. It, subsequently, is envisaged to transfer its energy, or part of it, to two other atoms B and C, simultaneously dropping to a lower excited state, as in Fig. 2, or to the ground state. This process, in contrast to the above, requires some overlapping of the electronic wave functions on the separate atoms. Also in contrast, it makes use of zero-order wave functions, rather than first order. In all of these cases resonant energy transfer is involved. Combinations of the two descriptions could presumably be made to describe triple excitations with first order perturbation theory, if overlap is included, with appropriately reduced probability.

The author acknowledges with thanks the comments of R. S. Knox on the first draft of this manuscript.

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[9] D. L. Dexter, Phys. Rev. **108**, 630 (1957).