THE MEAN FREE PATH OF AN EXCITON IN A POLAR CRYSTAL

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We have used Low's method to evaluate in the intermediate coupling approximation the scattering amplitude for the scattering of a phonon by an exciton by expressing it in the form of a matrix element between exact eigenfunctions of the energy operator corresponding to the initial and final states of the exciton. Our basic approximation consists in the use of Haken's functions for the exciton wave functions. We have carried out detailed calculations for the case of large quantum numbers and for the ground state of the exciton. It is shown that the mean free path remains finite also for the case where the effective masses of the electron and of the hole are the same.

THE Wannier-Mott approximation, according to which the exciton is a system of an electron and a positively charged hole with a Coulomb interaction between the two, is valid for excitons of large radii. The periodic field of the lattice is, as usual, taken into account by introducing effective masses which may be assumed to be isotropic if we consider a crystal of cuprous oxide.

Both particles, the electron and the hole, interact with the crystalline lattice, and in polar crystals and the main interaction is the one, known from polaron theory, of the particles with the longitudinal optical phonons.[1] The existence of a phonon interaction leads according to Haken[2] to the fact that the potential is of the form $-e^2/\epsilon r$, at large distances and $-e^2/n^2 r$ at small ones. Describing the relative motion of the electron and hole in classical terms one can say that at small distances the motion is fast and the ions do not have time to shift from their equilibrium positions. The potential is thus equal to $-e^2/n^2 r$ where the index of refraction n takes the polarization of the electron shells of the atoms into account. At large distances, however, the motion is slow and the interaction is characterized by the static dielectric constant ϵ.

This difference in the character of the interaction is automatically obtained if one takes into account the recoil connected with the emission of phonons.[4]

It is essential to note that if the effective masses of the electron and of the hole are equal, as will be the case in cuprous oxide,[3] the phonon interaction does not vanish, and the exciton still causes a polarization of the lattice. The statements to the opposite which are in the literature[7] are based upon the approximation which writes the wave function of the system in the form

$$\Psi(r, a) = \psi_n(r)\,\Omega(a), \tag{1}$$

where $\psi_n(r)$ is a function of the spatial coordinates r, $\Omega(a)$ a functional depending only on the phonon field variables a.

Approximation (1) leads to the fact that when the effective masses are equal the probability for a collision of a phonon with the exciton turns out to be equal to zero and the mean free path tends to infinity.[5,6] Taking the interaction of the exciton with the acoustic lattice vibrations into account cannot change this result as in the approximation of a continuous medium the constants for the interaction of an electron and a hole with the phonons turn out to be equal, and under those conditions the mean free path is also equal to infinity.[6]

To obtain a finite collision probability one must use more exact functionals for the exciton state which take into account not the polarization in the medium, but the polarization produced by each of the particles separately.

The most convenient mathematical apparatus to consider this problem is Low's method,[8] which makes it possible to evaluate the phonon scattering cross section without using the usual perturbation theory set-up. This fact is of the greatest importance for polar crystals as in that case the coupling is either strong or intermediate. The evaluation of the matrix elements is performed with respect to the phonon field in the same approximation as in the paper by Low and Pines[10] where the scattering of a phonon by a polaron was considered. The results obtained are valid in the intermediate coupling region.

The energy operator for an exciton in the Wannier-Mott model is of the form

$$H = -\frac{1}{2M}\nabla_R^2 - \frac{1}{2M'}\nabla_r^2 - \frac{e^2}{n^2 r} + \sum_k \omega a_k^+ a_k + \sum_k (V_k(r)\, e^{i\mathbf{kR}} a_k + V_k^*(r)\, e^{-i\mathbf{kR}} a_k^+). \quad (2)$$

Our notation is the following ($\hbar = 1$): $M = m_1 + m_2$ is the total mass, M' the reduced mass, ω the limiting frequency for the longitudinal optical vibrations, a_k^+ and a_k the creation and annihilation operators for the phonons, $\mathbf{R} = \mu_1 \mathbf{r}_1 + \mu_2 \mathbf{r}_2$ the center of mass coordinate, $\mu_i = m_i/M$, $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$, the coefficient V_k is equal to

$$V_k = \gamma_k (e^{i\mathbf{kr}\mu_2} - e^{-i\mathbf{kr}\mu_1}), \quad (3)$$

$$\gamma_k = -i\frac{\omega}{k}(2m\omega)^{-1/4}(4\pi\alpha/V)^{1/2}, \quad (4)$$

α plays the role of the coupling constant:

$$\alpha = {}^1/_2 e^2 (2m/\omega)^{1/2}(1/n^2 - 1/\varepsilon). \quad (5)$$

One can easily show that the matrix element of the scattering matrix S corresponding to a transition from a state with phonon momentum k_0 and total exciton momentum P_0 to a state k,P is equal to (see references 8 and 9)

$$S_{nn} = 1 - 2\pi i \delta(E_i^{(n)} - E_f^{(n)})\, T, \quad (6)$$

where T is the following matrix:

$$T = \int d^3R \int d^3r \left(\Psi_f, e^{-i\mathbf{kR}} V_k^* \frac{1}{H - E - \omega - i\varepsilon} e^{i\mathbf{k}_0\mathbf{R}} V_{k_0} \Psi_i\right) + \int d^3R \int d^3r \left(\Psi_f, e^{i\mathbf{k}_0\mathbf{R}} V_{k_0} \frac{1}{H - E + \omega - i\varepsilon} e^{-i\mathbf{kR}} V_k^* \Psi_i\right) \quad (7)$$

In Eq. (7) Ψ_i and Ψ_f are the exact eigenfunctions of the initial and final states, ϵ is an infinitesimal quantity which leads to an outgoing wave in coordinate representation, $E_i^{(n)}$ and $E_f^{(n)}$ are the energies of the initial and final states*

$$E_i^{(n)} = P_0^2/2M^* + E_n = E, \quad (8)$$

E_n is the exciton energy in the n-th state. We shall use for the functionals Ψ_i and Ψ_f those obtained by Haken[2]†

$$\Psi_i = \exp\left\{ i\left(\mathbf{P}_0 - \sum_k \mathbf{k} a_k^+ a_k\right)\mathbf{R}\right\} U \psi_n(r)\, \Phi_0, \quad (9)$$

where

$$U = \exp\left(\sum_k a_k^+ f_k - a_k f_k^*\right), \quad a_k \Phi_0 = 0,$$

$$f_k(P) = -\gamma_k^* \{\nu_2^{-1} e^{-i\mathbf{kr}\mu_2} - \nu_1^{-1} e^{i\mathbf{kr}\mu_1}\},$$

$$\nu_i = \left\{\omega + k^2\left(\frac{1}{2M} + \frac{\mu_i^2}{2M'}\right) - \frac{\mathbf{Pk}(1-\eta)}{M}\right\}. \quad (10)$$

*We have omitted from the expression for the energy an additive constant which is inessential for our problem.

†Haken considered the case $P = 0$ in the paper quoted.

The functions f_k and $\psi_n(r)$ satisfy the following equations

$$-\frac{1}{2M'}\nabla_r^2 f_k + \left(\omega + \frac{k^2}{2M} - \frac{\mathbf{Pk}}{M}(1-\eta)\right) f_k + V_k^* = 0,$$

$$\left\{-\frac{1}{2M'}\nabla_r^2 - \frac{e^2}{n^2 r} + \sum_k |f_k(0)|^2\left(\omega + \frac{k^2}{2M}\right) + \sum_k f_k(0) V_k + f_k^*(0) V_k^* + \frac{1}{2M'}\sum_k |\nabla f_k(0)|^2\right\}\psi_n = E_n \psi_n. \quad (11)$$

The functional (9) is obtained by assuming that $\psi_n(r)$ is a spherically symmetric function. If we evaluate the expectation value of the energy using the functional (9) and after that using the functional (1), it turns out that the value will be less in the latter case. The choice of the solution in the form (9) is thus the more correct one. The value of the renormalization constant η will be found below.

For small momenta P_0 which are different from zero there will only be the first term in (7). To evaluate this expression we take the terms depending on P_0 through the operator $(H - E - \omega)^{-1}$ and integrate over d^3R. We get as a result

$$S - 1 = -i(2\pi)^4 \delta(E_i - E_f)\, \delta(\mathbf{P}_0 + \mathbf{k}_0 - \mathbf{P} - \mathbf{k})\, Q, \quad (12)$$

where

$$Q = \int d^3r \langle \Phi_0 \psi_n, \quad V_k^* U^{-1}(P) \frac{1}{\overline{H} - E - \omega - i\varepsilon} U(P_0) V_{k_0} \psi_n \Phi_0 \rangle,$$

$$\overline{H}(\mathbf{P}_0) = H(\mathbf{P}_0 + \mathbf{k}_0 - \sum_k \mathbf{k} a_k^+ a_k). \quad (13)$$

It is convenient to write the quantity Q as a sum of two terms $Q = Q_1 + Q_2$, corresponding to the two terms in (3):

$$Q_2 = \gamma_{k_0} \int d^3r \langle \Phi_0 \psi_n, V_k^* U^{-1}(P) \times \frac{1}{\overline{H} - E - \omega - i\varepsilon} U(P_0) e^{i\mathbf{k}_0\mathbf{r}\mu_2} \psi_n \Phi_0 \rangle. \quad (14)$$

Q_1 is obtained from Q_2 by the substitution $\exp\{i\mathbf{k}_0\mathbf{r}\mu_2\} \to \exp\{-i\mathbf{k}_0\mathbf{r}\mu_1\}$. We shall consider the evaluation of Q_2.

We shall transfer the operator U from the right to the left. We must, of course, be careful when differentiating U, since ∇U does not commute with U. We shall use the general formula

$$\frac{d}{dx} e^{\varphi(x)} = e^{\varphi(x)}\left\{\varphi' + \frac{1}{2!}[\varphi', \varphi] + \frac{1}{3!}[[\varphi', \varphi], \varphi] + \ldots\right\}. \quad (15)$$

From (15) it follows that

$$\nabla U = U\left\{\sum_k \nabla f_k a_k^+ - \nabla f_k^* a_k + {}^1/_2\, \mathbf{j}_k\right\},$$

$$\mathbf{j}_k = f_k^* \nabla f_k - f_k \nabla f_k^*.$$

The expression div $\mathbf{j}_k$ can be rewritten in the form

$$-(1/2M')\,\mathrm{div}\, \mathbf{j}_k = {}^1/_2 (f_k V_k - f_k^* V_k^*).$$

because of (11). The average value of div $\mathbf{j}_k$ eval-

uated over a spherically symmetric function tends to zero. We shall now transfer the factor $\exp\{i\mathbf{k}_0\mathbf{r}\mu_2\}$ in (14) from the right to the left. As a result of this we can write Q_2 in the form

$$Q_2 = \gamma_{k_0}\int d^3r \langle \Phi_0\psi_n, V_k^* e^{i\mathbf{k}_0\mathbf{r}\mu_2}\frac{1}{H_0+H_1-E-\omega-i\varepsilon}\psi_n\Phi_0\rangle. \quad (16)$$

Considering in the following the case of small momenta we have replaced $U^{-1}(P_f)U(P_0)$ by unity. This is permissible since the only expression where it is important that P be finite is the denominator in the integrand of (14), which can be studied separately. $H_0 = H_0^{(1)} + H_0^{(2)}$ is the following operator

$$\begin{aligned}H_0 = &-\frac{1}{2M'}\nabla_r^2 - \frac{e^2}{n^2 r} + \sum_k V_k f_k + V_k^* f_k^* \\ &+ \sum_k |f_k|^2\left(\omega - \frac{\mathbf{kP}_0}{M} + \frac{k^2}{2M}\right) + \frac{1}{2M'}\sum_k |\nabla f_k|^2 + \sum_k \omega a_k^+ a_k \\ &+ \frac{1}{2M}\left(\mathbf{P}_0 - \sum_k \mathbf{k}a_k^+ a_k\right)^2 + \frac{k_0^2}{2M} + \frac{k_0^2}{2M'}\mu_2^2 \\ &+ \frac{1}{M}\left(\mathbf{P}_0\mathbf{k}_0 - \sum_k (\mathbf{kk}_0)a_k^+ a_k\right) + \frac{1}{M}\sum_k \mathbf{k}a_k^+ a_k \sum_k \mathbf{k}|f_k|^2 \\ &- \frac{1}{M}\sum_k (\mathbf{kk}_0)|f_k|^2 + \frac{1}{2M}\left(\sum_k \mathbf{k}|f_k|^2\right)^2. \end{aligned} \quad (17)$$

The splitting up of the operator H_0 into $H_0^{(1)}$ and $H_0^{(2)}$ is done as follows. Each of the last three terms in (17) can be written as a sum of two terms: the first which is independent of r must be assigned to $H_0^{(1)}$, and the second one to $H_0^{(2)}$. In the other terms $f_k = f_k(P)$ and $|f_k(P)|^2$ must be expanded in power series in P, while $f_k(0)$, and $|f_k(0)|^2$ must be assigned to $H_0^{(1)}$. Terms quadratic in P can in turn be split into two parts; terms which do not contain an r-dependence are assigned to $H_0^{(1)}$, and the rest to $H_0^{(2)}$; it turns out that the latter are unimportant in the following. Let us, for instance consider the expression

$$\sum_k \mathbf{k}|f_k|^2 = \sum_k \mathbf{k}|\gamma_k|^2\{\nu_1^{-2} + \nu_2^{-2} - \nu_1^{-1}\nu_2^{-1}(e^{i\mathbf{kr}} + e^{-i\mathbf{kr}})\}. \quad (18)$$

If we make the transition from a summation to an integration between infinite limits, the first two terms in (18) give

$$(2\pi)^{-3}\int \mathbf{k}|\gamma_k|^2(\nu_1^{-2}+\nu_2^{-2})\,d^3k = \frac{\alpha(m)}{6}(1-\eta_1)\left\{\left(\frac{m_1}{m}\right)^{1/2}\frac{m_1}{M} + \left(\frac{m_2}{m}\right)^{1/2}\frac{m_2}{M}\right\} \quad (19)$$

Similarly, up to terms of $O(P^4)$

$$\sum_k |f_k(P)|^2(\omega - \mathbf{kP}/M + k^2/2M) = \sum_k |f_k(0)|^2(\omega + k^2/2M) + 3(1-\eta_1)^2 M^{-2}\sum_k |\gamma_k|^2(\mathbf{kP})^2(\omega + k^2/2M)(\nu_1^{-4}(0) + \nu_2^{-4}(0))$$
$$- 2(1-\eta_1)M^{-2}\sum_k |\gamma_k|^2(\mathbf{kP})^2(\nu_1^{-3}(0) + \nu_2^{-3}(0)) + \text{terms depending upon the spatial coordinates.}$$

Taking away the terms quadratic in the momentum we get, apart from an additive constant,

$$\begin{aligned}H_0^{(1)} = &-\frac{1}{2M'}\nabla_r^2 + W(r) + \frac{P_0^2}{2M_1^*} \\ &+ \sum_k a_k^+ a_k\left(\omega - \frac{\mathbf{kP}_0}{M^*} - \frac{\mathbf{kk}_0}{M}\right) + \frac{k_0^2}{2M} \\ &+ \frac{k_0^2}{2M'}\mu_2^2 + \frac{\mathbf{k}_0\mathbf{P}_0}{M^*} + \frac{1}{2M}\left(\sum_k \mathbf{k}a_k^+ a_k\right)^2, \end{aligned} \quad (20)$$

where

$$W(r) = -\frac{e^2}{n^2 r} + \frac{1}{2M'}\sum_k |\nabla f_k|^2 + \sum_k |f_k|^2\left(\omega + \frac{k^2}{2M}\right) + \sum_k f_k V_k + f_k^* V_k^*.$$

If $m_1 = m_2$, the potential W(r) is of the form[2,4] $W(r) = -e^2/\varepsilon r - (1/n^2 - 1/\varepsilon)r^{-1}\exp(-r\sqrt{2m\alpha})$.

From (19) we have

$$M^{*-1} = M^{-1}\{1 - {}^1/_6\,\alpha(m)(1-\eta_1)[(m_1/m)^{1/2}m_1/M + (m_2/m)^{1/2}m_2/M]\}. \quad (21)$$

The mass M_1^* is somewhat different from M^*.

Let us consider the operator $H_I = H_I^{(1)} + H_I^{(2)}$.

$$\begin{aligned}H_I^{(1)} = &-\frac{1}{2M'}\sum_{k,k'}\{\nabla f_k \nabla f_{k'} a_k^+ a_{k'}^+ - 2\nabla f_k \nabla f_{k'}^* a_k^+ a_{k'} \\ &+ \nabla f_k^* \nabla f_{k'}^* a_k a_{k'}\} + \frac{1}{2M}\sum_{k,k'}(\mathbf{kk}')\{f_k f_{k'} a_k^+ a_{k'}^+ \\ &+ 2f_k f_{k'}^* a_k^+ a_{k'} + f_k^* f_{k'} a_k a_{k'} + f_{k'}^* a_k^+ a_k a_{k'} + f_{k'} a_{k'}^+ a_k^+ a_k\} \\ &- \frac{1}{M}\sum_k (\mathbf{kk}_0)(a_k f_k^* + a_k^+ f_k) - \frac{1}{M'}\sum_k (\nabla f_k a_k^+ - \nabla f_k^* a_k)\nabla \\ &- \frac{i\mu_2}{M'}\mathbf{k}_0\sum_k \nabla f_k a_k^+ - \nabla f_k^* a_k - \frac{1}{M'}\sum_k (\nabla f_k a_k^+ - \nabla f_k^* a_k) \\ &\times \sum_{k'}\mathbf{j}_{k'} - \frac{1}{2M'}\sum_k \nabla^2 f_k a_k^+ - \nabla^2 f_k^* a_k \\ &+ \sum_k a_k^+\left\{V_k^* + f_k\left(\omega - \frac{\mathbf{P}_0\mathbf{k}}{M} + \frac{k^2}{2M}\right) + \frac{\mathbf{k}}{M}\sum_{k'}\mathbf{k}'|f_{k'}|^2\right\} \\ &+ \sum_k a_k\left\{V_k + f_k^*\left(\omega - \frac{\mathbf{P}_0\mathbf{k}}{M} + \frac{k^2}{2M}\right) + \frac{\mathbf{k}}{M}\sum_{k'}\mathbf{k}'|f_{k'}|^2\right\}, \end{aligned}$$

$$H_I^{(2)} = -\frac{1}{2M'}\sum_k \operatorname{div}\mathbf{j}_k - \frac{1}{2M'}\left(\sum_k \mathbf{j}_k\right)^2 - \frac{1}{M'}\sum_k \mathbf{j}_k\nabla - \frac{i\mu_2}{M'}\mathbf{k}_0\sum_k \mathbf{j}_k - \frac{i\mu_2}{M'}(\mathbf{k}_0\nabla). \quad (22)$$

Using the equation for the function f_k we can write the last three sums in the expression for $H_I^{(1)}$ in

the following form:

$$\frac{1}{M}\sum_k \gamma_k k^2 a_k \{e^{ikr\mu_2}\nu_2^{-1}\mu_2^2 + e^{-ikr\mu_1}\nu_1^{-1}\mu_1^2\} = \sum_k \delta_k a_k. \quad (23)$$

We shall show in the following that one can neglect the term $\Sigma \mathbf{k}|\gamma_k|^2\nu_1^{-1}\nu_2^{-1}e^{\pm i\mathbf{kr}}a_k$ in (22). Let us now turn to Eq. (16). For the evaluation of the matrix element we shall follow Low and Pines[10] and introduce a functional Ψ by

$$c\Psi = (H_0^{(1)} + H_0^{(2)} + H_I - E - \omega - i\varepsilon)^{-1}\psi_n\Phi_0, \quad (24)$$

which satisfies the following integral equation

$$\Psi = \psi_n\Phi_0 - (H_0^{(1)} - E - \omega - i\varepsilon)^{-1}(H_0^{(2)} + H_I)\Psi,$$
$$c^{-1} = k_0^2/2M + k_{0x}^2\mu_2^2/2M' + \mathbf{k}_0\mathbf{P}_0/M^* - \omega. \quad (25)$$

Putting $\Psi = u(r)\Phi_0 + \sum_k v_k(r)\,a_k^+\Phi_0$ we can obtain the following set of integro-differential equations for the functions u(r) and v(r):

$$\mathcal{H}_0 u + \frac{1}{c}u = \frac{1}{c}\psi_n + \frac{1}{M}\sum_k (\mathbf{kk}_0) f_k^* v_k - i\frac{\mu_2}{M'}\sum_k \mathbf{k}_0\nabla f_k^* v_k$$
$$- \frac{1}{M'}\sum_k \nabla f_k^*\nabla v_k - \frac{1}{M'}\sum_k \mathbf{j}_k\nabla f_k^* v_k - H_I^{(2)}u$$
$$- \langle\Phi_0, H_0^{(2)}\Phi_0\rangle u - \sum_k \delta_k v_k, \quad (26)$$

$$\mathcal{H}_0 v_k + \Delta E v_k = \frac{1}{M}u(\mathbf{kk}_0) f_k + \frac{1}{M'}\nabla f_k\nabla u + \frac{1}{M'}u\nabla f_k\sum_{k'}\mathbf{j}_{k'}$$
$$+ \frac{i\mu_2}{M'}u\mathbf{k}_0\nabla f_k - H_1^{(2)}v_k - \langle a_k^+\Phi_0, H_0^{(2)}a_k^+\Phi_0\rangle v_k$$
$$- \frac{1}{M}f_k\mathbf{k}\sum_{k'}\mathbf{k}' f_{k'}^* v_{k'} - \frac{1}{M'}\nabla f_k\sum_{k'}\nabla f_{k'}^* v_{k'}, \quad (27)$$

where

$$\mathcal{H}_0 = -\nabla_r^2/2M' + W(r) - E_n;$$
$$\Delta E = k_0^2/2M + k_{0x}^2\mu_2^2/2M' + k^2/2M$$
$$- \mathbf{kk}_0/M + \mathbf{P}_0(\mathbf{k}_0 - \mathbf{k})/M^* - i\varepsilon. \quad (28)$$

Let us consider the case of most interest, when the effective masses of the electron and of the hole are the same. From (18) and (17),

$$\langle a_k^+\Phi_0, H_0^{(2)}a_k^+\Phi_0\rangle = -\frac{1}{M}(\mathbf{k} - \mathbf{k}_0)\sum_{k'}\mathbf{k}'\nu_{k'}^{-2}(P_0)\,2\cos\mathbf{k}'\mathbf{r}.$$

If we write the function v_k as $v_k = \exp(-i\mathbf{kr}/2)\,v_k^{(1)}$, we get for u and $v_k^{(1)}$ the following equations

$$\mathcal{H}_0 u + \frac{1}{c}u = \frac{1}{c}\psi_n - \frac{1}{m}\sum_k (\mathbf{kk}_0)\varphi_k v_k^{(1)}$$
$$- \frac{1}{M'}\sum_k (\nabla f_k^*)(\nabla e^{-i\mathbf{kr}/2}v_k^{(1)}) + \frac{i}{2M'}(\mathbf{k}_0\nabla)u - \sum_k \delta_k v_k, \quad (26a)$$

$$\mathcal{H}_0 v_k^{(1)} + \frac{i}{m}(\mathbf{k} - \mathbf{k}_0)\nabla v_k^{(1)} + \Delta E^{(1)}(\mathbf{P}_0)v_k^{(1)}$$
$$- \frac{1}{M}(\mathbf{k} - \mathbf{k}_0)\sum_{k'}\mathbf{k}'\nu_{k'}^{-2}(P_0)\,2\cos\mathbf{k}'\mathbf{r}\,v_k^{(1)} = -\frac{u}{m}(\mathbf{kk}_0)\varphi_k^*$$
$$- \frac{1}{M'}(1 - e^{-i\mathbf{kr}})\varphi_k^*(i\mathbf{k}\nabla u)$$
$$- \frac{1}{m}\varphi_k^*\mathbf{k}\sum_k \mathbf{k}'\varphi_{k'}(1 + \exp\{ir(\mathbf{k} - \mathbf{k}')\})v_{k'}^{(1)}, \quad (27a)$$

where

$$\varphi_k = \gamma_k(\omega + k^2/2m)^{-1},$$
$$\Delta E^{(1)}(\mathbf{P}_0) = (\mathbf{k}_0 - \mathbf{k})^2/2m + (\mathbf{P}_0/M^*)(\mathbf{k}_0 - \mathbf{k}) - i\varepsilon. \quad (28a)$$

One can neglect the P_0 dependence of the functions φ_k for small P_0.

We shall expand the functions u and $v_k^{(1)}$ in terms of a complete set of functions of the operator $\mathcal{H}_0$:

$$u = \sum_n a_n\psi_n, \qquad v_k^{(1)} = \sum_n b_{nk}\psi_n. \quad (29)$$

Since at large distances the potential W(r) behaves like $-e^2/\epsilon r$ we can take for the exciton wave functions ψ_n for the states with n = 2,3,4,... hydrogen functions, taking the radius of the Bohr orbit to be equal to ϵ/me^2. If we substitute, for the zeroth approximation, $u = a_n\psi_n$ into the right hand side of (27a), it is clear that the coefficient b_n will be the main one. Multiplying the left and right hand side of (27a) by ψ_n and integrating over the coordinates we obtain an equation for the coefficient b_{nk}. The magnitude of the renormalized exciton mass will then be determined by the expression

$$\mathbf{P}_0/M_n^* = \mathbf{P}_0/M - \frac{1}{M}\sum_k \mathbf{k}\,|\gamma_k|^2(2\nu_k^{-3}(\mathbf{P}_0)$$
$$- 2\nu_k^{-2}(\mathbf{P}_0)\langle n|\cos\mathbf{kr}|n\rangle).$$

One can show (see Appendix) that $\langle n|\exp(\pm i\mathbf{kr})|n\rangle$ tends to zero as $n\to\infty$. The limiting value of M_n^* will thus be equal to M^*. It is, on the other hand, obvious that for large quantum numbers the electron and the hole move so slowly that they have time to polarize not only the atomic shells, but also to shift the ions. For large n the exciton mass must therefore be equal to twice the polaron mass. The latter is, for instance, in the Lee, Low, and Pines approximation[11] connected with the coupling constant α by the relation $m^* = m(1 + \alpha/6)$ so that the parameter η in (9) and (19) will be equal to $\eta = (\alpha/6)(1 + \alpha/6)^{-1}$. We shall consider the solution of Eqs. (26a) and (27a) in the limiting cases of large and small quantum numbers n.

In the case of large n the quantity $\langle n|\exp(\pm i\mathbf{kr})|n\rangle$ can be considered to be small compared to unity. The equations for the coefficients a_n and b_{nk} take the form

$$a_n = 1 - \frac{c}{m}\sum_k (\mathbf{kk}_0)\varphi_k b_{kn}, \quad (26b)$$

$$\Delta E_n^{(1)} b_{nk} = -\frac{a_n}{m}(\mathbf{kk}_0)\varphi_k^* - \frac{1}{m}\varphi_k^*\mathbf{k}\sum_{k'}\mathbf{k}'\varphi_{k'}b_{nk'}. \quad (27b)$$

The solution of this set of equations is of the form*

$$cu_n = \left(\frac{k_0^2}{2m}\frac{1 - I}{1 + I} - \omega\right)^{-1}\psi_n,$$
$$I = \sum_k (\mathbf{kk}_0)^2\,|\varphi_k|^2/m\Delta E^{(1)}(P_0) = I_1 + iI_2, \quad (31)$$

*The P_0 dependence is only contained in $\Delta E^{(1)}(P_0)$.

where I_2 is proportional to P_0,

$$I_2 = \frac{2\alpha\omega^2}{(2m\omega)^{1/2}(\omega + k^2/2m)^2}\frac{m}{M_n^*}P_0.$$

The required matrix element Q is thus equal to

$$Q = Q_1 + Q_2 = |\gamma_{k_0}|^2\left(\frac{k_0^2}{2m}\frac{1-I}{1+I} - \omega\right)^{-1}\rho_n(k_0), \quad (32)$$

where

$$\rho_n(k_0) = |\gamma_{k_0}|^{-2}\int|\psi_n(r)|^2|V_{k_0}(r)|^2 d^3r. \quad (33)$$

The first factor in (32) has the same form as the amplitude for the scattering of a phonon by a polaron[10] while the factor $\rho_n(k_0)$ plays the role of a form factor.

Integrating (13) over the final state and over the initial phonon momentum k_0 we get the following expression for the scattering probability $1/\tau$ per unit time

$$\frac{1}{\tau} = \frac{M_n^*}{8\pi^4}P_0\int|\gamma_{k_0}|^4\rho_n^2(k_0)e^{-\omega/kT}\left|\frac{k_0^2}{2m}\frac{1-I}{1+I} - \omega\right|^{-2}d^3k_0. \quad (34)$$

The factor $\exp(-\omega/kT)$ gives the volume dependence of the number of phonons on the temperature T. For small P_0 we get by using the well known limit $\lim \epsilon/(x^2+\epsilon^2) = \pi\delta(x)$

$$\frac{1}{\tau} = \left(\frac{M_n^*}{M}\right)^2\frac{2\alpha\omega}{f(\alpha)}e^{-\omega/kT}(2\rho_n(k_0))^2, \quad (35)$$

where $f(\alpha)$ is a slowly changing function of α, the value of which was given in reference 10. The mean free path l is connected with $1/\tau$ through the relation $l = v\tau$ where v is the exciton velocity.

We shall now consider the exciton ground state. The exciton dimensions in the ground state are several times less than the characteristic length $\bar{k}^{-1} = (2m\omega)^{-1/2}$; if we take the wave function in the form $\psi_0(r) = (\pi r_0^3)^{-1/2}\exp(-r/r_0)$ the constant r_0 must then satisfy the inequality $\bar{k}r_0 < 1$. Taking this inequality into account one can put

$$\langle\psi_0|\exp(\pm ir(k - k'))|\psi_0\rangle = 1 + O(\bar{k}^2 r_0^2),$$

and the equations for the coefficients a_0 and b_{0k} take the form

$$a_0 = 1 - \frac{c}{m}\sum_k(kk_0)\varphi_k b_{0k},$$

$$\Delta E_0 b_{0k} = -\frac{a_0}{m}(kk_0)\varphi_k^* - \frac{2}{m}\varphi_k^* k\sum k'\varphi_{k'}b_{0k'}. \quad (36)$$

From (36) we get

$$cu_0 = (k_0^2/2m(1+2I) - \omega)^{-1}\psi_0. \quad (37)$$

The renormalized exciton mass is in the case of the ground state up to terms of $O(r_0^2\bar{k}^2)$ equal to the unrenormalized one according to (30). This result corresponds to the intuitive feeling that in the ground state both particles move "fast" and they do not have time to shift the average positions of the neighboring ions. The function $\rho(k_0)$ can for the ground state be approximately replaced by $r_0^2k_0^2$. Calculations analogous to the foregoing ones lead to the following value of $1/\tau$:

$$1/\tau = 2\alpha\omega e^{-\omega/kT}4(k_r r_0)^4/\varphi(\alpha), \quad (38)$$

where

$$\varphi(\alpha) = (1 + x_r^2)\{1/x_r - x_r^{-2}\partial I_1/\partial x_r\}, \quad (39)$$

x_r is the root of the equation

$$x_r^2 = 1 + 2I_1(x_r), \qquad x = k_0/\sqrt{2m\omega}. \quad (40)$$

The root of Eq. (40) is close to unity so that when we estimate the order of smallness of different terms we can—as we did in the foregoing—substitute instead of k_r the value $\bar{k}$. The function $\varphi(\alpha)$ is close to unity and changes slowly with α.

Representing the crystal as a continuous medium and assuming the mass to be isotropic is, of course, crude for a consideration of the exciton ground state.[12]

Nevertheless, for a qualitative description of the character of the interaction of an exciton in the ground state with the crystalline lattice, the Wannier-Mott model can be useful. According to Zhilich's calculations[13] the wave function of an electron forming an exciton state has its main maximum at a distance of approximately 4.3 atomic units from the central oxygen ion O^{--} in a Cu_2O crystal. This means that the electron moves essentially at the boundaries of the four copper ions which are the nearest neighbors of O^{--}. If we use an approximate representation for the electron and the hole the main part of their interaction will be described by a potential $-e^2/n^2r$, where the refractive index n takes into account the polarization of the copper atoms. The potential W(r) considered above behaved for small r just like $-e^2/n^2r$. When r_0 is decreased the exciton is by and large more and more a neutral system, and the probability for collision with a phonon will according to (38) decrease fast.

For excitons with large radii the mean free path is of the same order of magnitude as the polaron mean free path.

This result is explained by the fact that the electron and the hole polarize the crystal individually [the function U in (9) depends on the spatial coordinates]. Even though the exciton is an electrically neutral system, it deforms the lattice none the less, even if $m_1 = m_2$, and the phonons are scattered by the deformed lattice. The usual per-

turbation theory is not able to take this effect correctly into account which for $m_1 = m_2$ also leads to an infinitely large mean free path.

In conclusion I express my sincere gratitude to Academician V. A. Fock for a discussion of the present paper.

APPENDIX

We shall consider the evaluation of the integral $J_n(k) = \langle n|\exp i\mathbf{kr}|n\rangle$, where $|n\rangle$ is a spherically symmetric function of the discrete hydrogen atom spectrum

$$|n\rangle = NL_n^{(1)}(\rho)\,e^{-\rho/2}, \qquad \rho = 2r/na, \qquad a = \varepsilon/me^2.$$

Using the integral representation of the Laguerre polynomials

$$L_n(\rho) = \frac{1}{2\pi i}\oint_C u^{-n-1}(1+u)^n e^{-\rho u}\,du,$$

where the contour C encloses the coordinate origin, we can perform first of all the integration over the spatial coordinates

$$J_n(k) = N^2\pi a^3 \frac{1}{2\pi i}\oint u^{-n}(1+u)^n\,du \times \frac{1}{2\pi i}\oint v^{-n}(1+v)^n \frac{u+v+1}{[(u+v+1)^2+k_n^2]^2}\,dv,$$

$k_n = kan/2$.

The integration over dv is easily performed if the integration contour is pulled towards the poles of the function $[(u+v+1)^2 + k_n^2]^{-2}$. A change of variables $u = ik_n t/(t-1-ik_n)$ reduces the integral over du to a hypergeometric function

$$J_n(k) = \frac{(-1)^{n+1}}{4ik_n}(1+k_n^2)^{-n-1}\{(1+ik_n)^{2n} - (1-ik_n)^{2n}\} \times F(1-n, 1+n, 2; (1+k_n^2)^{-1}).$$

As $n\to\infty$ the function $J_n(k)$ tends to zero. If we expand $J_n(k)$ in a power series in k we can obtain from the expression given here the well known equations for $\bar{r}^2$, $\bar{r}^4$, and so on.

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