

THE EFFECT OF AN EXTERNAL ELECTRIC FIELD ON THE SHAPE OF THE INTRINSIC ABSORPTION EDGE IN NON-CONDUCTING CRYSTALS

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The problem stated in the title is solved using many-electron wave functions. The external electric field is taken into account exactly, but the Coulomb interactions of the electrons and holes are neglected. In the region of the intrinsic absorption edge, the absorption coefficient is obtained for all values of the electric field and frequencies of the absorbed light.

THE change in the shape of the intrinsic absorption edge of non-conducting crystals has been considered by Keldysh.¹ He used the approximate wave functions obtained by Houston² for the electron moving in the periodic and uniform fields. As a result, Keldysh concludes that there is a shift of the absorption edge in the red direction. An explicit form was obtained for the absorption coefficient as a function of electric field E and the frequency of the absorbed light ω , for frequencies sufficiently far from the limiting frequency ω_0 of intrinsic absorption without any external field (or for a sufficiently weak electric field). A previous paper by the author³ was devoted to the same problem; however, it referred only to the case of forbidden transitions and did not contain the bases of the method used.

In the present paper we give a more general discussion. The result obtained for the absorption coefficient holds for all values of E and ω . In the limiting case $E \rightarrow 0$ it goes over to the known expression for the intrinsic absorption by the crystal without an external field.⁴

We assume that our crystal contains N valence electrons and an optical transition involves this system as a whole. The conduction and valence bands we take as simple and non-degenerate. Electron spin is not taken into account. Further, we use single-electron orthogonal localized Wannier functions of the valence band (cf. the review by Haken⁵):

$$a(\mathbf{n}, \mathbf{r}) = N^{-1/2} \sum_{\mathbf{k}} e^{i\mathbf{k}\mathbf{r}} f(\mathbf{k}, \mathbf{r}). \quad (1)$$

where $f(\mathbf{k}, \mathbf{r})$ is the Bloch function of the valence band corresponding to the wave vector \mathbf{k} , and the sum is taken over the first Brillouin zone. Wannier functions for the conduction band $\tilde{a}(\mathbf{n}, \mathbf{r})$ are constructed in a similar way.

We write the wave function of the initial ground state of the crystal in the form

$$\Psi_0(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = A(0; \mathbf{r}_1, \dots, \mathbf{r}_N) = N^{-1/2} \det |(\mathbf{n}_\alpha, \mathbf{r}_\beta)|. \quad (2)$$

The index $\alpha = 1, 2, \dots, N$, labels the Wannier functions. The index $\beta = 1, 2, \dots, N$, labels the electrons. The wave function of the final excited state are taken in the form

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = \sum_{\mathbf{m}\mathbf{n}} c(\mathbf{m}, \mathbf{n}) A(\mathbf{m}, \mathbf{n}; \mathbf{r}_1, \dots, \mathbf{r}_N). \quad (3)$$

The determinant $A(\mathbf{m}, \mathbf{n})$ entering into (3) is similar to the determinant $A(0)$, except that the valence-band Wannier function numbered \mathbf{m} is changed into the conduction-band Wannier function numbered \mathbf{n} . The wave function (3) describes the excited state of the crystal, where in the absence of an external field the coefficients $c(\mathbf{m}, \mathbf{n})$ are determined from the Wannier equation.⁵ We shall show that the presence of an external electric field only affects the equation for $c(\mathbf{m}, \mathbf{n})$ if the process of direct transfer of electrons by the field into higher bands is considered as improbable. Then the optical transition from the state $\Psi_0(\mathbf{r}_1, \dots, \mathbf{r}_N)$ to the state $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$, when the function $c(\mathbf{m}, \mathbf{n})$ corresponds to the continuous spectrum of the Wannier equation, also gives the intrinsic absorption of light by the crystal.

We calculate the matrix element of the transition. The perturbation operator has the form

$$H = \frac{e}{mc} \sum_{i=1}^N \mathbf{p}_i \mathbf{A}(\mathbf{r}_i), \quad (4)$$

$\mathbf{r}_i, \mathbf{p}_i$ are the coordinate and momentum of the i -th electron and $\mathbf{A}(\mathbf{r})$ is the vector potential field of the light wave. Using (2), (3), and the relation between the Bloch and Wannier functions, we can obtain

$$(\Psi | H | \Psi_0) = -\frac{ieh}{mc} \mathbf{A}_0 \sum_{\mathbf{m}\mathbf{n}} e^{i\mathbf{x}\mathbf{n}} c^*(\mathbf{m}, \mathbf{n}) \sum_{\mathbf{k}} e^{i(\mathbf{k}, \mathbf{n}-\mathbf{m})} \mathbf{M}(\mathbf{k}), \quad (5) \quad \text{known:}^6$$

κ is the wave vector of the photon; \mathbf{A}_0 is the amplitude of the vector potential. Here

$$\mathbf{M}(\mathbf{k}) = \int \tilde{u}^*(\mathbf{k}, \mathbf{r}) \nabla u(\mathbf{k}, \mathbf{r}) d\mathbf{r}, \quad (6)$$

$u(\mathbf{k}, \mathbf{r})$, $\tilde{u}(\mathbf{k}, \mathbf{r})$ are the periodic factors of the Bloch functions of the valence and conduction bands. The integral is taken throughout one cell.

We now obtain an equation for the functions $c(\mathbf{m}, \mathbf{n})$. We assume that $c(\mathbf{m}, \mathbf{n})$ changes little in a distance of the order of the lattice constant, so that it is possible to transfer from discrete vector arguments \mathbf{m} and \mathbf{n} to continuous \mathbf{r}_2 and \mathbf{r}_1 , which correspond to the coordinates of holes in the valence band and electrons in the conduction band. We do not take into account their interaction. If there were no external field, the equation would contain only terms corresponding to the free motion of electrons and holes. Its solution $c(\mathbf{r}_1, \mathbf{r}_2)$ would be a product of plane waves, and (3) would give the usual band states. The absorption coefficient calculated thus by our method will agree with that obtained in reference 4. We will now include the external field. It is not difficult to find in our system the matrix element of the interaction operator of the electrons with the electric field using the functions $A(\mathbf{m}, \mathbf{n})$:

$$\begin{aligned} \left(\mathbf{m}, \mathbf{n} \left| \left(\sum_{i=1}^N \mathbf{E} r_i \right) \right| \mathbf{m}', \mathbf{n}' \right) &= \delta_{\mathbf{m}\mathbf{m}'} \int \tilde{a}^*(\mathbf{n}, \mathbf{r}) (\mathbf{E} r) \tilde{a}(\mathbf{n}', \mathbf{r}) d\mathbf{r} \\ &- \delta_{\mathbf{n}\mathbf{n}'} \int a^*(\mathbf{m}', \mathbf{r}) (\mathbf{E} r) a(\mathbf{m}, \mathbf{r}) d\mathbf{r}. \end{aligned} \quad (7)$$

Finally, under the assumptions made, the equation for the functions $c(\mathbf{r}_1, \mathbf{r}_2)$ takes the form (field along the z axis):

$$\left(-\frac{\hbar^2}{2m_1} \nabla_1^2 - \frac{\hbar^2}{2m_2} \nabla_2^2 + eEz_1 - eEz_2 \right) c(\mathbf{r}_1, \mathbf{r}_2) = \epsilon c(\mathbf{r}_1, \mathbf{r}_2). \quad (8)$$

Here m_1 and m_2 are the effective masses of electrons and holes.

By transforming to relative coordinates \mathbf{R} and \mathbf{r} , it is easy to separate the motion of the center of gravity and the relative motion in the plane transverse to the field

$$c(\mathbf{R}, \mathbf{r}) = L^{-3/2} e^{i\mathbf{K}\mathbf{R}} L^{-1} e^{i\lambda_1 x + i\lambda_2 y} \varphi(z). \quad (9)$$

Here \mathbf{K} is the wave vector of the center of gravity, λ_1 and λ_2 are the components of the two-dimensional wave vector of the relative motion in the transverse plane, and L is the side of the normalization cube. The solution of the equation then remaining, normalized in the energy interval, is well

$$\begin{aligned} \varphi(z) &= A\Phi(q), \quad q = (z - \epsilon_2 / eE) (2\mu eE / \hbar^2)^{1/2}, \\ A &= (2\mu)^{1/2} / \pi^{1/2} (eE)^{1/2} \hbar^{1/2}, \end{aligned} \quad (10)$$

ϵ_2 is the energy of the relative motion along the field, μ is the reduced mass of the electron and hole, and Φ is the Airy function.⁷

We consider here the case of allowed optical transitions when

$$\mathbf{M}(0) = \mathbf{M}_0 \neq 0. \quad (11)$$

Using the properties of the sum over \mathbf{k} in (5), it is easy to show that the many-electron matrix element of the optical transition in this case is equal to the product of the usual one-electron matrix elements in the value of the function $c(\mathbf{R}, \mathbf{r})$ at the point $\mathbf{r} = 0$. The probability of the transition is determined from the known formula of quantum mechanics by summing the square of the matrix elements over all possible states. We introduce the expression thus obtained into the usual formula for the optical absorption coefficient:⁸

$$\alpha = 4\pi\hbar\omega / nc\mathcal{E}^2, \quad (12)$$

where ω is the probability of an optical transition in unit volume and unit time, n is the refractive index and \mathcal{E} is the electric field of the light wave.

We will express the Airy function entering into (10) in terms of Bessel functions of order $1/3$.⁷ After carrying out the calculation indicated, we obtain the following results.

In the region $\omega < \omega_0$, in which the crystal is transparent in the absence of external field, the absorption is now different from zero and is given by the formula

$$\begin{aligned} \alpha &= \frac{4\mu e^2}{\pi n m^2 c \omega} |\mathbf{e}\mathbf{M}_0|^2 \frac{(\mu eE)^{1/2}}{(3\hbar)^{1/2}} \int_{x_0}^{\infty} \xi^{1/2} K_{1/2}^2(\xi) d\xi, \\ x_0 &= (2\sqrt{2\mu} / 3\hbar eE) (\hbar\omega_0 - \hbar\omega)^{1/2}. \end{aligned} \quad (13)$$

Here \mathbf{e} is the polarization vector of the light and K is the MacDonal function. For sufficiently large values of $\omega_0 - \omega$ an asymptotic formula can be given:

$$\alpha = \frac{2\mu e^2}{\pi n m^2 c \omega} |\mathbf{e}\mathbf{M}_0|^2 \frac{(\mu eE)^{1/2}}{(3\hbar)^{1/2}} \int_{x_0}^{\infty} \xi^{-3/2} e^{-2\xi} d\xi. \quad (14)$$

If it is assumed that in this case the exponential is the most important, formula (14) is close to the corresponding formula in Keldysh's paper. For $\omega = \omega_0$ the absorption coefficient is equal to

$$\alpha_0 = \frac{4}{\pi} \frac{\mu e^2}{n m^2 c \omega} |\mathbf{e}\mathbf{M}_0|^2 \frac{(\mu eE)^{1/2}}{(3\hbar)^{1/2}} \int_0^{\infty} \xi^{1/2} K_{1/2}^2(\xi) d\xi. \quad (15)$$

In the range $\omega > \omega_0$ the absorption coefficient takes the form

$$\alpha = \alpha_0 + \frac{4\pi}{3} \frac{\mu e^2}{nm^2 c \omega} |eM_0|^2 \frac{(\mu e E)^{1/2}}{(3h)^{3/2}} \int_0^{y_0} \xi^{1/2} [J_{-1/2}(\xi) + J_{1/2}(\xi)]^2 d\xi,$$

$$y_0 = (2\sqrt{2\mu} / 3heE) (h\omega - h\omega_0)^{1/2}. \quad (16)$$

We will now take our formula to the limit $E \rightarrow 0$. Then $x_0 \rightarrow \infty$, and it is seen from (13) that the absorption tends to zero for $\omega < \omega_0$. From (15) it is apparent that α_0 is also zero in this case and the absorption starts at the limiting frequency ω_0 . By substituting into (16) the asymptotic expression for the Bessel functions, we verify that it is possible to select the terms tending to zero with the external field and the terms not depending on the field. These latter terms give the correct value of the absorption coefficient for allowed band transitions without an external field

$$\alpha = \frac{4\sqrt{2}}{n} \frac{\mu^{3/2} e^2}{m^2 h c \omega} |eM_0|^2 (h\omega - h\omega_0)^{1/2}. \quad (17)$$

Expression (17) agrees exactly with the result obtained by Bardeen, Blatt, and Hall.⁴ Similarly, it is possible to show that the usual band formula is true also for sufficiently large $\omega - \omega_0$, which agrees with Keldysh's conclusion.

We shall not present here the results for the case of forbidden transitions (they are given in reference 3). The basis of the method used there follows from a consideration of formula (5) of the present paper. The matrix element in this case

will contain the derivatives of the function $c(\mathbf{r}_1, \mathbf{r}_2)$ at the point $\mathbf{r}_1 = \mathbf{r}_2$. We note that the formulae thus obtained contain several integrals more complicated than Bessel functions of order $1/3$. The absorption coefficient is different from zero for $\omega < \omega_0$, depends on the polarization of the incident light relative to the electric field, and for $E \rightarrow 0$ transforms to the usual band expression varying with frequency as $(\omega - \omega_0)^{3/2}$.⁴

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