PHYSICAL REVIEW B VOLUME 26, NUMBER 12 15 DECEMBER 1982

Optical-transition cross sections involving impurities in semiconductors

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(Received 10 May 1982)

A formula is derived in a general framework for various optical-transition cross sections involving an impurity bound state (acceptor or donor) and a continuum state belonging to a band (valence or conduction) in semiconductors. A quantum-defect wave function with the correct normalization has been used for the bound state. The results are used to obtain explicitly several improved formulas of interest in the literature. A method is presented and also applied to the case of GaAs to compute the overlap integrals of the cell periodic functions which are needed in our derived formula. Approximate analytical expressions which should be valid with good accuracy for transitions near the band extrema have also been obtained. It has been shown that the formula for photoionization cross section reduces exactly to that for the well-known Lucovsky's δ-function model in the appropriate limit. Other limiting cases have been discussed and compared with previous results. Comparison with experiment has been made for the photoionization of manganese impurities in gallium arsenide.

I. INTRODUCTION

Considerable effort has been given in recent years to the studies of various quantities of interest related to optical transitions involving impurity atoms in semiconductors, and, consequently, there exist many calculations with varying degrees of compromise between simplicity and accuracy.[1] Calculations of the transition cross section require the knowledge of impurity wave functions, the lack of which is one of the major sources of difficulty. There are many impurities which may be described by hydrogenic effective-mass theory (HEMT) in which the impurity potential is approximated to be Coulombic and the effect of the medium is taken into account through the effective masses and the dielectric constant. HEMT provides a simpler approach to the impurity problem and hence to the optical-transition problems. Irrespective of whether it is shallow or deep, a single-band approximation is valid for a so-called *isocoric* impurity. As the core of an impurity deviates from that of the host, a many-band expansion of the impurity wave function becomes necessary. A detailed discussion on the validity of the HEMT may be found in a review article by Pantelides.[2] The binding energies for all impurities describable by the HEMT would be same, whereas the experimental values vary from impurity to impurity and are generally higher than that given by the HEMT. This extra binding arises from the impurity core where the potential is not Coulombic, as well as from the so-called umklapp contribution, intervalley interaction, etc.[2,3] All of these are short-ranged effects in real space. Bebb and Chapman[4] borrowed the well-known phenomenological quantum-defect method (QDM) from atomic physics and applied it to the case of such impurities with Coulomb potential plus a short-ranged potential.

Bebb[5] has utilized the QD wave functions to calculate the optical-transition cross sections involving an impurity. This is one of the simple approaches, but his calculations include some crucial approximations, which are as follows. (1) The transition matrix element between a band state and the impurity state has been written as the product of the momentum matrix element $p_{12}(\vec{k})$ between the band states (1,2 are the relevant band indices) and the Fourier transform of the envelope part of the impurity wave function. This approximation has been used for the *band-impurity transitions* which involve both the conduction and the valence bands. (2) In the photoionization calculations (involving a single band) the Bloch functions are taken out of the integral which is equivalent to neglecting the umklapp terms. (3) $p_{12}(\vec{k})$ has been replaced by its value at the band extremum, which is a standard approximation for small $\vec{k}$. (4) The normalization used in his QD wave function is simply that of the hydrogenic wave function, i.e., the QD wave function is not normalized to unity. By approximately calculating the umklapp contribution we see that it is small and (2) is a valid approximation as is expected, but we do not find any justification for the first approximation. Therefore we have eliminated this and obtained an analytical expression valid for small energies along with more accurate numerical results valid for all energies. The third approximation is valid for small $\vec{k}$ values only. Since the photoionization cross-section measurements are not, in general, restricted to energies near the band extremum, we feel that it is desirable to do the calculation without the second approximation. We have found considerable differences for large $\vec{k}$ values. We have presented a method to compute the overlap integral of the cell periodic functions in which one of them is at a general $\vec{k}$ value. The overlap integral is needed in our formula for the cross sections. We have applied this method to the case of GaAs and shown that the cross sections deviate considerably from the corresponding results with the third approximation. Amato and Ridley[6] have argued that the incorrect normalization of the QD wave function is the major flaw in the QD model. In our calculation we have used the QD wave function with the correct normalization obtained by Chaudhuri, Coon, and Derkits.[7] This normalization introduces an extra factor which varies from 1 to 2 for the hydrogenic model (i.e., the quantum defect being zero) to the other extreme limiting case, the δ-function model. Owing to this normalization factor our result for the photoionization cross section reduces exactly to that of the Lucovsky's δ-function model[8] in the appropriate limit. We have pointed out some errors that have occurred in the photoionization cross-section formula obtained with QD wave functions.[5] We also point out that unlike the previous QD calculations, we are able to treat both types of transitions (i.e., the *band-impurity transition* and photoionization) in the same general framework.

The continuum states should, in principle, be products of Whittaker functions and Bloch functions.[2] Here we approximate them to be pure Bloch waves. This is a standard approximation. Bebb has found that this is a much better approximation in semiconductors than the approximations with the plane waves in the free-atom case.[5] In the pure hydrogenic system the peak of the photoionization cross section appears at $\hbar\omega = \epsilon_I$, where ϵ_I is the impurity binding energy. The experimental studies show that the position of the peak ranges from less than 1.43 to $\sim 2\epsilon_I$. This result is in agreement with the QD calculation with the continuum states taken as Bloch waves.

Here we will not consider the temperature dependence of the cross sections which may be easily obtained by utilizing the formula given by Ridley[9] in terms of the zero-temperature cross section which, in turn, may be obtained from the present calculation.

II. GENERAL FORMULA FOR OPTICAL-TRANSITION CROSS SECTIONS

A. Cross-section formula

In semiconductors the optical transitions involving an impurity may be divided into two types according to the charge state of the impurity when it absorbs a photon or emits a photon. If a neutral impurity atom becomes ionized when a photon is absorbed in the process or if an ionized impurity becomes neutral when a photon is emitted, the processes may be called, in general, photoionization or photodeionization, respectively. On the other hand, the process in which an ionized impurity becomes neutral with the absorption of a photon or its reverse process may be called *band-impurity absorption* or *recombination,* respectively.[10] These two types of transitions are shown in Fig. 1. Since within EMT a donor state is associated with the conduction band, we note that in the first type only one band (conduction or valence) is involved in a single process, and in the second type both of the valence and the conduction bands are involved in a

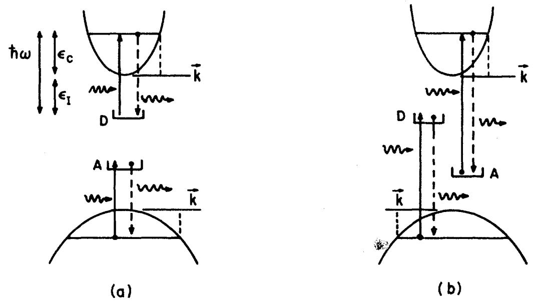

FIG. 1. Diagrams for transitions involving a single band (photoionization) and for transitions involving both of the bands *(band-impurity transition)* are shown in (a) and (b), respectively. In (a) solid arrows represent photoionization and the dashed arrows represent photodeionization. In (b) solid arrows are for *band-impurity absorptions* and dashed ones are for *band-impurity recombinations.* *D* and *A* denote donors and acceptors, respectively. Also shown is the wave vector $\vec{k}$ involved in the transitions (see text).

single process.

We are interested in obtaining the transition cross section $\sigma(\hbar\omega)$ for either type of process described above. If σ is known, other quantities of interest, e.g., spontaneous-emission rate, absorption coefficient, etc., may be easily obtained in terms of σ.[5] The transition cross section, in the well-known dipole approximation, is

$$\sigma(\hbar\omega)=\frac{4\pi^2\alpha_0\hbar\omega}{n}\left[\frac{E_{\text{eff}}}{E_0}\right]^2\frac{|\langle i\,|p_z|\,f\rangle|_{\text{av}}^2}{m^2\omega^2}\rho(E_j)\;,\qquad j=i,f \tag{1}$$

where α_0 $(=e^2/\hbar c)$ is the fine-structure constant, $\hbar\omega$ is the energy of the photon, n is the frequency-dependent refractive index of the semiconductor, and $\rho(E_j)$ is the density of the continuum states at the band energy E_j, at which the transition takes place. The subscript of the matrix element indicates average over all degenerate states including all photon directions. Here the direction of the z axis is chosen along the photon polarization direction. The factor E_{eff}/E_0 is the so-called effective-field ratio, which takes into account the fact that the electric field E_{eff}, which is effective in inducing a transition, is different from the average field E_0 in the medium.[11] The momentum matrix element between the initial and the final states $(\langle i\,|p_z|\,f\rangle)$ can be written in terms of the position matrix element $(\langle i\,|z|\,f\rangle)$ by the relation

$$|\langle i\,|p_z|\,f\rangle|^2=m_1^{*2}\omega^2|\langle i\,|z|\,f\rangle|^2\;. \tag{2}$$

Ridley[9] has correctly pointed out that the mass in Eq. (2) should be the effective mass. There are many calculations where this point has been neglected. Kohn has discussed this point in his review article.[12]

Thus we obtain

$$\sigma(\hbar\omega)=\frac{4\pi^2\alpha_0\hbar\omega}{n}\left[\frac{E_{\text{eff}}}{E_0}\right]^2\left[\frac{m_1^*}{m}\right]^2|\langle i\,|z|\,f\rangle|_{\text{av}}^2\times\rho(E_j)\;,\quad j=i,f\;. \tag{3}$$

Our task is then to calculate $|\langle i\,|z|\,f\rangle|_{\text{av}}^2$ for the general case. Since $|\langle i\,|z|\,f\rangle|^2=|\langle f\,|z|\,i\rangle|^2$, we can use the initial and final states interchangeably and we arbitrarily consider the impurity state to be the initial state (denoted by 1) and the continuum state to be the final state (denoted by 2).

B. Bound-state wave function

For simplicity we will assume that the bands are nondegenerate at their extrema, unless otherwise stated. In the effective-mass approximation the impurity-atom wave function ψ may be written as an envelope function F modulated by the Bloch wave $u(\vec{k}_0,\vec{r})e^{i\vec{k}_0\cdot\vec{r}}$, where $u(\vec{k}_0,\vec{r})$ is the cell periodic function and $\vec{k}_0$ is the wave vector at the relevant band extremum.[12] The envelope wave function satisfies the hydrogenlike effective-mass equation[12]

$$\left[-\frac{\hbar^2}{2m_1^*}\nabla^2-\frac{e^2}{Kr}-\epsilon^0\right]F=0\;, \tag{4}$$

where m_1^* is the effective mass corresponding to the appropriate band, K is the dielectric constant of the crystal, and ϵ^0 is the energy eigenvalue. Since we are interested in the ground-state wave function, we restrict ourselves to the case of S-like states. Then we write the envelope wave function[13]

$$F_n=\frac{2}{\sqrt{4\pi}\,(na_1^*)^{3/2}}e^{-r/na_1^*}\times{}_1F_1(1-n;2;2r/na_1^*)\;, \tag{5}$$

where ${}_1F_1$ is a confluent hypergeometric function, n $(=1,2,\ldots)$ is the principal quantum number, and $a_1^*=K\hbar^2/m_1^*e^2$. The energy eigenvalues are given by

$$|\epsilon_n^0|=\frac{m_1^*e^4}{K^2\hbar^2}\frac{1}{2n^2}\;. \tag{6}$$

The true ground-state binding energy ϵ_I is generally larger than $|\epsilon_1^0|$. In the QD method, to obtan an empirical wave function which would yield the observed binding energy ϵ_I (measured from the associated band extremum), the eigenvalue $-\epsilon^0$ is replaced by ϵ_I in Eq. (4). Hence the integral quantum number n has to be replaced, in general, by the nonintegral defect quantum number ν, such that

$$\epsilon_I=\frac{m_1^*e^4}{K^2\hbar^2}\frac{1}{2\nu^2}=\frac{|\epsilon_1^0|}{\nu^2}\;. \tag{7}$$

Replacing n in Eq. (5) by ν would yield an unnormalizable wave function which is irregular at infinity. But writing ${}_1F_1$ in terms of the ${}_2F_0$ hypergeometric functions, we obtain a wave function which is irregular at the origin, but normalizable.[14] With the exact normalization the QD function F_ν may be written as[15]

$$F_\nu=\frac{2^\nu}{\sqrt{4\pi}\,(\nu a_1^*)^{\nu+1/2}}\frac{1}{\Gamma(\nu+1)}|D(\nu)|r^{\nu-1}e^{-r/\nu a_1^*} \tag{8a}$$

and

$$\psi_\nu = F_\nu u_1(\vec{k}_0,\vec{r})e^{i\vec{k}_0\cdot\vec{r}} , \tag{8b}$$

where

$$|D(\nu)| = \frac{\pi}{|\sin\nu\pi|} \times \left[\frac{1}{2}\sum_{m=0}^{\infty}\frac{1}{(\nu-m-1)^2(\nu-m)^2}\right]^{-1/2} . \tag{9}$$

The formal hypergeometric series for ${}_2F_0$ provides an asymptotic series for $2r \gg \nu a_1^*$ and since the important region contributing to the transition matrix element is the large-r region, we have retained in Eq. (8) the leading term of ${}_2F_0$, which is unity. We also note that ${}_2F_0$ is exactly unity when $\nu \to 0$ or 1. In the limit of ν approaching an integer the factor $|D(\nu)|$ approaches unity. Another interesting limit is that in which the binding energy remains fixed while $\nu \to 0$.[15] In this limit the charge e and hence Coulombic part of the potential vanishes with the binding energy maintained at a given fixed value by the short-ranged potential. This is the case of the so-called δ-function potential and the wave function given by Eq. (8) reduces to that for the δ-function potential with the correct normalization. We will utilize this wave function in calculating the transition matrix element.

C. Continuum states

The band energy $\epsilon_2(\vec{k})$ at which the transition occurs is related to the photon energy $\hbar\omega$, by

$$\epsilon_2(\vec{k}) = \hbar\omega - \epsilon_I \tag{10a}$$

for photoionization and

$$\epsilon_2(\vec{k}) = \hbar\omega - \epsilon_g + \epsilon_I \tag{10b}$$

for *band-impurity transitions*,

where ϵ_g is the band gap. Note that for the valence band as well as for the conduction band, this energy is positive as $\vec{k}$ increases, in this convention.

Neglecting the effects of the impurity potential on the continuum states, the final states are simply the Bloch states,

$$\langle r|f\rangle = e^{i\vec{k}\cdot\vec{r}}u_2(\vec{k},\vec{r}) . \tag{11}$$

Since the functions u are cell periodic, they can be expanded as

$$u_j(\vec{k},\vec{r}) = \sum_i a_j(\vec{k}+\vec{K}_i)e^{i\vec{K}_i\cdot\vec{r}} , \tag{12}$$

where the $\vec{K}_i$'s are the reciprocal-lattice vectors and j is the band index. We will need this expansion later.

In our calculations we assume a parabolic band structure;

$$\epsilon_2(\vec{k}) = \frac{\hbar^2k^2}{2m_2^*} . \tag{13}$$

D. Calculation of the matrix element and the general formula

With the initial and final wave functions given by Eqs. (8b) and (11), the matrix element can be written explicitly as

$$\langle i|z|f\rangle = \int e^{i\vec{k}\cdot\vec{r}}u_2^*(\vec{k},\vec{r})u_1(0,\vec{r}) \times zF_\nu(\vec{r})d^3r . \tag{14}$$

We have taken the extremum position of the band 1 to be at $\vec{k}_0 = 0$, without any loss of generality. For the case of $\vec{k}_0 \neq 0$, the calculation is similar. Using the expansions of u, given by Eq. (12), we obtain

$$\langle i|z|f\rangle = \int e^{-i\vec{k}\cdot\vec{r}}zF_\nu(\vec{r})\mu_{21}(\vec{k}) + {\sum_{i,j}}' \beta_{ij}e^{i\vec{K}_{ji}\cdot\vec{r}}d^3r , \tag{15}$$

where

$$\vec{K}_{ji} = \vec{K}_j - \vec{K}_i , \tag{16a}$$

$$\mu_{21}(\vec{k}) = \sum_i a_2^*(\vec{k}+\vec{K}_i)a_1(\vec{K}_i) , \tag{16b}$$

$$\beta_{ij} = a_2^*(\vec{k}+\vec{K}_i)a_1(\vec{K}_j) , \tag{16c}$$

and the prime on the summation of the second term indicates that $i \neq j$. The second term is the so-called umklapp contribution. It can be easily shown that $\mu_{21}(\vec{k})$ is the overlap integral of the cell periodic function at $\vec{k}$ of the band 2, and the cell periodic function at $\vec{k}=0$ of the band 1, i.e.,

$$\mu_{21}(\vec{k}) = \frac{(2\pi)^3}{\Omega}\int_\Omega u_2^*(\vec{k},\vec{r})u_1(0,\vec{r})d^3r , \tag{17}$$

where Ω is the volume of a unit cell of the crystal. To reduce Eq. (15) to a one-dimensional integration we separate the angle-dependent part in $\exp(i\vec{k}\cdot\vec{r})$ by using its well-known expansion in terms of the spherical Bessel functions $j_l(kr)$,[13]

$$e^{-i\vec{k}\cdot\vec{r}} = 4\pi\sum_{l=0}^{\infty}\sum_{m=-l}^{l}(-i)^l j_l(kr) \times Y_l^{m*}(\theta,\phi)Y_l^m(\hat{k}) , \tag{18}$$

where $\hat{k}$ is the unit vector along $\vec{k}$ and θ,ϕ are the polar angles of $\vec{r}$. Since $z=(4\pi/3)^{1/2}rY_1^0(\theta,\phi)$, if we perform the angular integration in Eq. (15), only the $l=0,m=0$ term survives because of the orthogonality relations of the spherical harmonics Y_l^m's. Averaging over all directions of $\hat{k}$ [i.e., $(4\pi)^{-1}\int d\Omega_{\vec{k}}$], and also over the spin degeneracies assuming that no spin flip occurs in the process,[5] and performing the r integration, we finally obtain

$$|\langle i|z|f\rangle|^2_{\text{av}}=\frac{2\pi}{3}\frac{2^{2\nu}(\nu a_1^*)^5|D(\nu)^2|f(y_1)}{y_1(1+y_1)^{\nu+1}}\times[|\mu_{21}(\vec{k})|^2+B_{21}(\vec{k})]\,, \tag{19}$$

where

$$f(y_1)=\cos^2\theta\left[\frac{\sin(\nu+1)\theta}{\sin\theta}-(\nu+1)\cos(\nu+2)\theta\right]^2, \tag{20a}$$

in which

$$\theta=\arctan(\sqrt{y_1}) \tag{20b}$$

and

$$y_1=(k\nu a_1^*)^2\,. \tag{20c}$$

B_{21} is a quantity much smaller than $|\mu_{21}|^2$. B_{21} is explicitly written down in the Appendix. In averaging over the directions of $\hat{k}$ we have assumed that $\mu_{21}(\vec{k})$ is isotropic. Neglecting the umklapp contribution, we write our general formula for the transition cross section, with the use of Eq. (3),

$$\sigma(\hbar\omega)=\frac{8\pi^3\alpha_0\hbar\omega}{3n}\left[\frac{E_{\text{eff}}}{E_0}\right]^2\left[\frac{m_1^*}{m}\right]^2\times\frac{2^{2\nu}(\nu a_1^*)^5|D(\nu)|^2f(y_1)|\mu_{21}(\vec{k})|^2}{y_1(1+y_1)^{\nu+1}}\times\rho(E_j)\,,\quad j=1,2\,. \tag{21}$$

E. Calculation of $|\mu_{21}(\vec{k})|^2$

The quantities $\mu_{21}(\vec{k})$ may be computed by utilizing the pseudopotential form factors given by Cohen and Bergstresser,[16] and more recently by Chelikowsky and Cohen.[17] The Schrödinger equation with the pseudopotential for a perfect crystal may be written as the matrix eigenvalue equation

$$\sum_j A_{ij}a(\vec{k}+\vec{K}_j)=\epsilon a(\vec{k}+\vec{K}_i)\,, \tag{22a}$$

with the known matrix A_{ij} given by

$$A_{ij}=\frac{\hbar^2}{2m}(\vec{k}+\vec{K}_i)^2\delta_{ij}+\tilde{V}(\vec{K}_i-\vec{K}_j)\,. \tag{22b}$$

The Bloch functions have been expanded according to Eq. (12). The quantities $\tilde{V}(\vec{K}_i)$ can be broken into a symmetric and an antisymmetric part, and each part is a product of a pseudopotential form factor and a structure factor.[16] Diagonalizing this matrix we obtain the eigenvectors $a_n(\vec{k}+\vec{K}_j)$ and the corresponding eigenvalues $\epsilon_n(\vec{k})$ for a given $\vec{k}$. With the appropriate eigenvectors chosen, it is then straightforward to compute various $|\mu_{21}(\vec{k})|^2$ using Eq. (16b). The dimensions of the matrices are restricted in our numerical calculation such that $|\vec{K}_i-\vec{K}_j|\leq\sqrt{11}(2\pi/a)$. The contributions from higher reciprocal-lattice vectors are small and can be added, as was done in Ref. 16. By neglecting this small contribution we obtain fairly good agreement with previous results,[16] and so we believe that our computed values of $|\mu_{21}|^2$ are not affected much by the truncation of the matrix. We have plotted $|\mu_{cv}|^2$ and $|\mu_{cc}|^2$ as functions of the band energy $\epsilon_c(\vec{k})$ (Fig. 2). For $i=j$, $|\mu|$ differs from unity in the second-order perturbation term which is $\sim O(k^2)$. Since this contribution is negative,[18] $|\mu_{ii}|^2\leq 1$. Our computed values of $|\mu|^2$ agree with the analytical result for small $\vec{k}$. An analytical form for μ_{ij} obtained by the $\vec{k}\cdot\vec{p}$ perturbation method is[18]

$$\mu_{ij}(\vec{k})=\delta_{ij}+\frac{\hbar}{m}\{\vec{k}\cdot\vec{p}_{ij}/[\epsilon_i(0)-\epsilon_j(0)]\}\times(1-\delta_{ij})\,, \tag{23}$$

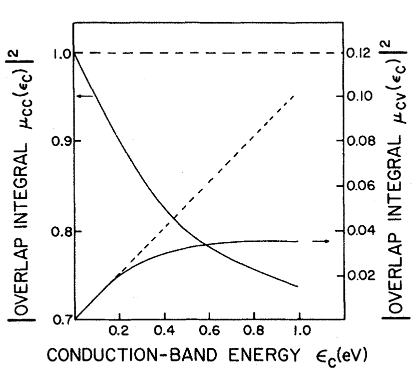

FIG. 2. Squares of the overlap integrals $|\mu_{cc}|^2$ and $|\mu_{cv}|^2$ for GaAs, appearing as a factor in the photoionization cross section (see text) versus the conduction-band energy ϵ_c in eV. Solid line represents calculation using pseudopotential form factors described in Sec. II E of the text and the dashed line is from the $\vec{k}\cdot\vec{p}$ perturbation.

where $\vec{p}_{ij}$ is the usual momentum matrix element between the two Bloch states of bands i and j at $\vec{k}_0$. This is, of course, valid only for small $\vec{k}$.

III. SPECIAL CASES

A. Photoionization

As we have described earlier, in the case of photoionization only one band is involved. So we replace both of the indices 1 and 2 by b which denotes the relevant band. The density of states, including the spin degeneracy, is

$$\rho(\epsilon_b)=\frac{2}{(2\pi)^2}\left[\frac{2m_b^*}{\hbar^2}\right]^{3/2}|\epsilon_b(\vec{k})|^{1/2}\,. \tag{24}$$

On substitution of this expression for ρ, and after some manipulation, we obtain the photoionization cross section

$$\sigma(\hbar\omega)=\frac{4\pi\alpha_0}{3n}\left[\frac{E_{\mathrm{eff}}}{E_0}\right]^2\left[\frac{m_b^*}{m}\right]^2 \times\frac{2^{2\nu}(\nu a_b^*)^2|D(\nu)|^2 f(y_b)}{y_b^{1/2}(1+y_b)^\nu} \times|\mu_{bb}(\vec{k})|^2\,. \tag{25}$$

The quantity y_b is related to the binding energy ϵ_I by the relation

$$y_b=\frac{\hbar\omega-\epsilon_I}{\epsilon_I}\,. \tag{26}$$

Before comparing our formula with the corresponding formula [Eq. (57)] of Ref. 5, we note that some errors have occurred in the latter. First of all, there is an extra factor of ν. This can be easily seen to be incorrect. If the limit is taken as $\nu\to 0$ with the binding energy held fixed (or equivalently $\nu a_b^*=\mathrm{const}$) we find that $\sigma\to 0$ instead of reducing to Lucovsky's formula. Of course, this is correct for $\nu=1$. Second, the expression for $f(y)$ is incorrect. The correct form is given in Eq. (20a) of this paper. Third, we have already mentioned about the factor $(m_b^*/m)^2$, which is missing. Here we would like to point out that for acceptor photoionization, the calculation becomes somewhat more involved because of the valence-band degeneracy. But, writing the acceptor wave function as a sum of effective-mass-like wave functions for each band, the calculation proceeds in a straightforward way. Figure 3 compares the photoionization cross section given by Eq. (25) with the experimental data for the acceptor Mn in GaAs.[19] We have avoided the complexity of calculation arising from the valence-band degeneracy by considering the average effective mass to be 0.33, corresponding to the acceptor binding energy ~29 meV obtained from the HEMT for degenerate bands. The quantity $|\mu_{bb}|^2$ has been set equal to one. The quantum defect (corresponding to the binding energy 0.11 eV) is 0.52. Even without introducing the complexity of the degenerate valence bands, but simply incorporating their effects through a single average effective mass, we find that the theory is in excellent agreement with the experiment in predicting the peak position, in contrast to either the hydrogenic or the δ-function model. It is possible that away from the band extremum, the heavy hole valence band is the dominant one, and, accordingly, the cross section is higher than that calculated with the average effective mass. This may, at least partially, account for the underestimation at higher energies. The theoretical curve has been adjusted such that the maximum value of the cross section is the same as that of the experiment. From this fit we have obtained the effective-field ratio (E_{eff}/E_0) to be 2.7. In the same figure we have also shown the curve for the δ-function model. For the δ-function model, the value of the effective-field ratio is 4.9.

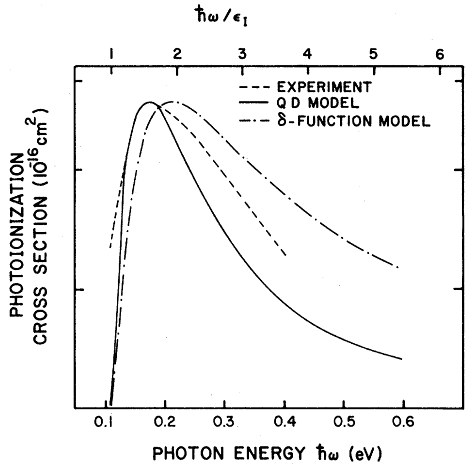

FIG. 3. Photoionization cross section σ versus the photon energy for the manganese impurity in gallium arsenide. The values of the effective-field ratio obtained by fitting the maximum values of σ are 2.7 and 4.9 for the QD model and the δ-function model, respectively.

Let us now examine the following two limiting cases.

(i) First, we consider the limit $\nu\to 0$ while keeping the binding energy fixed at a given value (i.e.,

νa_B^* is also fixed). Noting that

$$\lim_{\nu\to 0} f(y_b)=\frac{4y_b^2}{(1+y_b)^3} \tag{27a}$$

and

$$\lim_{\nu\to 0} |D(\nu)|^2=2\ , \tag{27b}$$

we obtain

$$\sigma_\delta(\hbar\omega)=\frac{16\pi e^2\hbar}{3nm_b^*c}\left[\frac{E_{\text{eff}}}{E_0}\right]^2\left[\frac{m_b^*}{m}\right]^2 \times\frac{\epsilon_I^{1/2}(\hbar\omega-\epsilon_I)^{3/2}}{(\hbar\omega)^3}\,|\mu_{bb}(\hbar\omega-\epsilon_I)|^2\ . \tag{28}$$

This is exactly the formula obtained by Lucovsky for the δ-function model, except for the factor of $(m_b^*/m)^2$ and $|\mu_{bb}|^2=1$.

(ii) In the hydrogenic limit, i.e., $\nu\to 1$,

$$\lim_{\nu\to 1} f(y_b)=\frac{64y_b^2}{(1+y_b)^4} \tag{29a}$$

and

$$\lim_{\nu\to 1} |D(\nu)|^2=1\ . \tag{29b}$$

We obtain the photoionization cross section,

$$\sigma_H(\hbar\omega)=\frac{2^8\pi e^2\hbar}{3nm_b^*c}\left[\frac{E_{\text{eff}}}{E_0}\right]^2\left[\frac{m_b^*}{m}\right]^2 \times\frac{(\hbar\omega-\epsilon_I)^{3/2}\epsilon_I^{5/2}}{(\hbar\omega)^5}\,|\mu_{bb}(\hbar\omega-\epsilon_I)|^2\ . \tag{30}$$

In the limit of $\nu\to 1$, σ_H has its maximum at $\hbar\omega=10\epsilon_I/7$ and for $\hbar\omega\gg\epsilon_I$, σ_H falls off as $(\hbar\omega)^{-7/2}$, in contrast to the maximum at $\hbar\omega=2\epsilon_I$ and falloff at large $\hbar\omega$ as $(\hbar\omega)^{-3/2}$ in the δ-function model. For the free hydrogen atom, on the other hand, the maximum occurs at $\hbar\omega=\epsilon_I$ and falloff for large $\hbar\omega$ is as $(\hbar\omega)^{-3}$.

B. Band-impurity transition

In this case both the conduction and the valence bands are involved. Let us specifically consider transitions between an acceptor state and a conduction-band state. For transitions between a donor and the valence-band state, cross sections can be obtained similarly. We replace the index 1 by v for the valence band and 2 by c for the conduction band. Because of the degeneracy of the valence band at $\vec{k}_0$, we have to keep in mind that the quantity $|\langle i|z|f\rangle|^2$ has to be averaged over the degenerate bands. Even in the effective-mass approximation, calculation of the acceptor impurity wave function is a very complex problem due to the degeneracy of the valence band. For some realistic calculations of acceptor states see, for example, Ref. 20. We avoid such complexity by assuming that the ground-state wave function is obtained by summing over the products of Bloch functions at $\vec{k}_0=0$ and the envelope function for each degenerate band at $\vec{k}_0$,

$$\psi_v=\frac{1}{\sqrt{d}}\sum_{l=1}^{d} u_l(0,\vec{r})F_v^l(\vec{r})\ , \tag{31}$$

where d is the number of degenerate bands at the band extremum and the $F_v^l(\vec{r})$ are the ground-state envelope functions. We also make the assumption that the different effective masses for the different degenerate valence bands can be approximated to a single average mass, which one can take to be that obtained from the effective-mass binding energy. One can, of course, do without these approximations following a similar procedure, but with more complexity. We have

$$|\mu_{cv}(\vec{k})|^2=\frac{1}{d}\left|\sum_{l=1}^{d}\mu_{cl}(\vec{k})\right|^2\ . \tag{32}$$

This quantity for GaAs has been calculated in Sec. II E.

Writing the density of states $\rho(\epsilon_c)$ as

$$\rho(\epsilon_c)=\frac{2}{(2\pi)^2}\left[\frac{2m_c}{\hbar^2}\right]^{3/2}|\epsilon_c|^{1/2}\ , \tag{33}$$

we obtain the *band-impurity transition* cross section from Eq. (21),

$$\sigma(\hbar\omega)=\frac{4\pi\alpha_0}{3n}\left[\frac{E_{\text{eff}}}{E_0}\right]^2\left[\frac{m_c^*}{m}\right]^2\left[\frac{m_c^*}{m_v^*}\right]^{1/2} \times\frac{2^{2\nu}(\nu a_v^*)^2|D(\nu)|^2 f(y_v)}{y_v^{1/2}(1+y_v)^{\nu+1}}\,\frac{\hbar\omega}{\epsilon_I} \times|\mu_{cv}(\vec{k})|^2\ . \tag{34}$$

The quantity μ_{bb} appearing in the photoionization cross section [Eq. (25)] is approximately equal to unity for small $\vec{k}$, since the first-order perturbation term is zero. Hence, at least for small $\vec{k}$, we obtain an analytic formula for the photoionization cross section with $|\mu_{bb}|^2\simeq 1$. It is also desirable to obtain such an analytic form valid at low energies for the *band-impurity transition.*

From Eq. (23) and again with the assumption that $\vec{p}_{cv}$ is isotropic, we obtain a relation between $\mu_{cv}(\vec{k})$ and p_{cv}:

$$|\mu_{cv}(\vec{k})|^2 = \frac{\hbar^2 k^2}{m^2 \epsilon_g^2} |p_{cv}|^2 . \tag{35}$$

The momentum matrix element p_{cv} may be written in terms of the band gap and effective masses by using the formula for effective mass,[18]

$$\frac{m}{m_c^*} = 1 + \frac{2}{m} \sum_{l=1}^{d} \frac{|p_{cl}|^2}{\epsilon_c(0) - \epsilon_l(0)} . \tag{36}$$

Neglecting the spin-orbit splitting and using the relation $|p_{ci}|^2 = |p_{cj}|^2$ obtained by Kane,[21] we have

$$|p_{cv}|^2 \simeq \frac{\epsilon_g m^2}{2d\bar{m}_c} , \tag{37}$$

where $\bar{m}_c$ is given by

$$\frac{m}{\bar{m}_c} = \frac{m}{m_c^*} - 1 . \tag{38}$$

Equation (37) was derived by Bebb.[5] Using Eqs. (35) and (37), we finally obtain

$$\begin{aligned} |\mu_{cv}(\vec{k})|^2 &= \frac{1}{2d} \frac{m_c^*}{\bar{m}_c} \frac{\epsilon_c}{\epsilon_g} \\ &= \frac{1}{2d} \frac{m_v^*}{\bar{m}_c} \frac{\epsilon_I}{\epsilon_g} y_v . \end{aligned} \tag{39}$$

The quantity $|\mu_{cv}(\vec{k})|^2$ is equal to zero at $\vec{k} = 0$, since $\epsilon_c = 0$. This can also be shown to be an exact result from the orthogonality of the u's.

A dashed line in Fig. 2 represents the plot of Eq. (39) for GaAs. From this figure we can see that $|\mu_{cv}|^2$ obtained from Eq. (39) agrees well with that obtained by the numerical method for small values of ϵ_c. Thus we write the cross-section formula which should be valid for small energies,

$$\sigma(\hbar\omega) = \frac{2\pi\alpha_0}{3dn} \left[\frac{E_{\text{eff}}}{E_0}\right]^2 \left[\frac{m_c^*}{m}\right]^2 \left[\frac{m_c^* m_v^*}{m_c^2}\right]^{1/2} \times \frac{2^{2\nu}(\nu a_v^*)^2 |D(\nu)|^2 f(y_v)}{(1+y_v)^{\nu+1}} y_v^{1/2} \frac{\hbar\omega}{\epsilon_g} . \tag{40}$$

To our knowledge, experimental data for *band-impurity transitions* with which direct comparison is possible are not available. We have plotted σ for GaAs versus the normalized band energy $x = \epsilon_c / \epsilon_I$ for $\nu = 1.0, 0.9, 0.6$ (Fig. 4). In the inset of this figure is shown σ versus x for $\nu = 0.3$ and for $\nu \to 0$. For $\nu \to 0$, the binding energy is fixed at a value given by $\nu = 0.3$. To fit in the same scale we have multiplied σ for $\nu = 0.6$, 0.3, and $\nu \to 0$ by a factor of 2. The solid lines are obtained from Eq. (40) and the dashed lines are from Eq. (34).

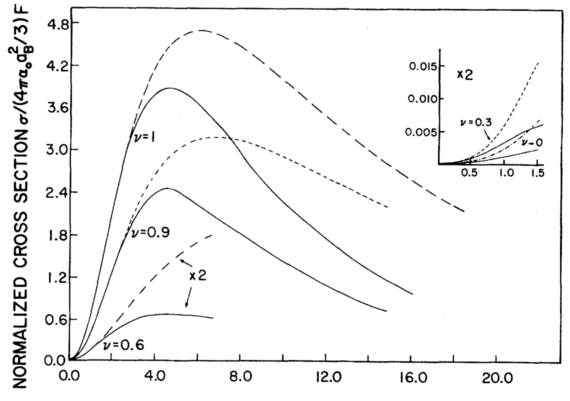

FIG. 4. Normalized *band-impurity transition* cross section for GaAs $[\sigma/(4\pi\alpha_0 a_B^{*2}/3)F]$ vs the normalized band energy (ϵ_c/ϵ_I). Dashed lines are from the analytical result [Eq. (43)] and the solid lines are from the more accurate results [Eq. (37)] for different values of ν (i.e., different values of impurity binding energies ϵ_I). All curves are terminated at a value of $\epsilon_c = 1$ eV. $F = (E_{\text{eff}}/E_0)^2/n$. σ for $\nu = 0.6$, 0.3, and 0.0 has been multiplied by 2.

In the hydrogenic and the δ-function limits, Eq. (40) reduces to the following forms.

(i) In the δ-function limit, i.e., $\nu \to 0$, while keeping the binding energy ϵ_I fixed, we obtain [with the use of Eq. (30a)]

$$\sigma_\delta(\hbar\omega) = \frac{4\pi e^2 \hbar}{3dnm_v^*} \left[\frac{E_{\text{eff}}}{E_0}\right]^2 \left[\frac{m_c^*}{m}\right]^2 \left[\frac{m_c^* m_v^*}{m^2}\right]^{1/2} \times \frac{y_v^{5/2}}{(1+y_v)^4} \frac{\hbar\omega}{\epsilon_I \epsilon_g} . \tag{41}$$

(ii) In the hydrogenic limit, i.e., $\nu \to 1$, we have

$$\sigma_H(\hbar\omega) = \frac{2^8 \pi e^2 \hbar}{3dnm_v^* c} \left[\frac{E_{\text{eff}}}{E_0}\right]^2 \left[\frac{m_c^*}{m}\right]^2 \left[\frac{m_c^* m_v^*}{m^2}\right]^{1/2} \times \frac{y_v^{5/2}}{(1+y_v)^6} \frac{\hbar\omega}{\epsilon_I \epsilon_g} . \tag{42}$$

Note that y_v can be written in terms of $\hbar\omega$ as

$$y_v = \frac{m_c^*}{m_v^*} \frac{\hbar\omega + \epsilon_I - \epsilon_g}{\epsilon_I} . \tag{43}$$

Comparison with the corresponding formulas given in Ref. 5 shows that the dependence of σ on $\hbar\omega$ is quite different. In the hydrogenic limit our result is also different from another corresponding calculation by Eagles,[22] whereas agreement has been achieved between Refs. 5 and 21. The origin of this difference is the assumption in both Refs. 5 and 22 that the momentum matrix element between the bound state and a Bloch function can be written as the products of two integrals, one being the momentum matrix element between the cell periodic functions at the band edges and the other being the Fourier integral of the impurity envelope function. In the present calculation we have eliminated this assumption. Note that in the photoionization cross-section calculation the energy dependences are not different from the corrected results of Bebb.[5] This is due to the fact that, in this case, his assumption is not the same as in the *band-impurity transition* case, but is equivalent to simply neglecting the umklapp contribution.

IV. CONCLUSION

In summary, we have calculated cross sections for both photoionization and band-impurity transition in the QD model. We have presented a method to compute the overlap integrals which may also be of use for other purposes. We have also obtained analytical results in which some crucial approximations of previous calculations have been eliminated. This led to a quite different energy dependence of the cross-section formula for the *band-impurity transitions,* but similar energy dependence in the photoionization. The origin of the different behavior in the two cases is discussed in the previous section. Our formula for the photoionization cross section has been shown to reduce exactly to that of Lucovsky in the appropriate limit. Thus we believe that our formula for the photoionization cross section has been somewhat improved from previous calculations although not drastically different, whereas the *band-impurity transition* cross section has been improved drastically. In our calculations we have assumed isotropic bands. For nonisotropic bands, use of a single effective mass averaged in a specific way may yield reasonable results.

ACKNOWLEDGMENTS

We thank Dr. D. C. Look, Dr. K. K. Bajaj, and Dr. P. W. Yu for comments and constructive criticism on the manuscript. This work was performed at the Avionics Laboratory, Wright-Patterson AFB, Dayton, Ohio under Contract No. F33615-81-C-1406.

APPENDIX

The contribution B_{21} arising from the umklapp terms to the transition cross section [Eq. (20)] is given by

$$B_{21}(\vec{\mathrm{k}})=2\,\mathrm{Re}\left[\mu_{21}^{*}(\vec{\mathrm{k}})\sum_{i=j}\beta_{ij}\left[\frac{g_{ij}d_{ij}^{\nu+1}}{c_{ij}^{+}(1+c_{ij})}\right]^{1/2}\right] +\sum_{i\neq j}|\beta_{ij}|^{2}\frac{g_{ij}d_{ij}^{\nu+1}}{c_{ij}^{+}}\frac{1+3c_{ij}}{1+c_{ij}}\,, \tag{A1}$$

in which

$$y_1=(k\nu a_1^{*})^2\,,$$

$$y_{ij}=(K_{ij}\nu a_1^{*})^2\,,\quad y_{ij}^{+}=(|\vec{\mathrm{k}}+\vec{\mathrm{K}}_{ij}|\,\nu a_1^{*})^2\,,$$

$$c_{ij}=y_{ij}/y_1\,,\quad c_{ij}^{+}=y_{ij}^{+}/y_1\,,$$

$$d_{ij}=\frac{1+y_1}{1+y_{ij}}\,,\quad g_{ij}=\frac{f(y_{ij}^{+})}{f(y_1)}\,,$$

and β_{ij} has been defined in the text. A rough estimation shows that $B_{21}<0.05$.

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