

Green's-function—quantum-defect treatment of impurity photoionization in semiconductors

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An analytic expression is derived for the photoionization cross section of impurity atoms in semiconductors. The use of a quantum-defect wave function for the impurity ground state permits impurity atoms to be conveniently characterized in terms of ground-state energies. The Coulomb Green's-function and time-dependent perturbation theory are used to calculate the wave function of photoexcited electrons or holes from which the photoionization cross section is obtained. The results apply to shallow or deep levels associated with carriers bound to charged impurity centers. Results for photodetachment of carriers bound to neutral impurities are obtained in the limit where the impurity charge goes to zero. Theoretical cross-section maxima are found to be in remarkably good agreement with experimental results, considering that no free parameters or empirical effective field ratios are employed.

Electromagnetic radiation can be absorbed by an impurity atom when an incoming photon has sufficient energy to excite an electron residing in the ground state of a donor impurity atom into either an excited state or into the conduction band. In the case of an acceptor, a hole can be photoexcited out of the ground state into an excited state or into the valence band. The process of photoexcitation of a ground-state electron into the continuum is shown schematically in Fig. 1 along with the potential due to the impurity atom.

Various attempts have been made at theoretical calculation¹⁻⁶ of the photoionization cross section and its wavelength dependence. Here we present an approach different from previous attempts. First, the photoexcited carrier wave function is calculated using the Coulomb Green's function, the ground-state wave function, and time-dependent perturbation theory. Then the ionization rate and the photoionization cross section are calculated by integrating the outward probability current associated

with the photoexcited carrier wave function.

In the case of a "hydrogenlike" impurity, the theory of photoionization of the hydrogen atom, modified to include the properties of the medium such as the dielectric constant and the effective mass, is reasonable only for shallow impurities with small central cell corrections. For deeper impurities such a treatment is not reasonable. This is due to the fact that for deeper impurities electrons (or holes) spend more time near the impurity atom and experience non-Coulombic, short-range effects due to the core of the impurity atom and intervalley scattering. Also, the simple effective mass equation [Eq. (1)] predicts a unique binding energy for all impurities, whereas the experimentally observed binding energies⁷ of impurities depend on the chemical species of the impurity ion:

$$\left[-\frac{\hbar^2}{2m^*} \nabla^2 - \frac{Ze^2}{4\pi\epsilon\epsilon_0 r} \right] \psi(\mathbf{r}) = E\psi(\mathbf{r}), \quad (1)$$

where m^* is the effective mass, ϵ is the dielectric constant of the medium, and ψ and E are the wave function and energy of the ground state, respectively.

Since the core potential is unknown, we attempt to estimate its effect by looking for solutions of Eq. (1) with the energy eigenvalue (E) replaced with the experimentally observed binding energy (E_0). In effect, the absence of knowledge about the short-range potential is replaced by empirical information about the binding energy which is sensitive to short-range effects. This is a standard and well-known technique in atomic physics and certain areas of solid-state physics.^{8,2,9} The resulting quantum-defect wave functions are solutions of

$$\left[-\frac{\hbar^2}{2m^*} \nabla^2 - \frac{Ze^2}{4\pi\epsilon\epsilon_0 r} \right] \psi_0(\mathbf{r}) = E_0\psi_0(\mathbf{r}), \quad (2)$$

except at $r=0$. This is equivalent to approximating short-range effects by an empirical zero-range deviation from the Coulomb potential. Since the observed energy is not, in general, an eigenvalue of Eq. (2), we cannot require

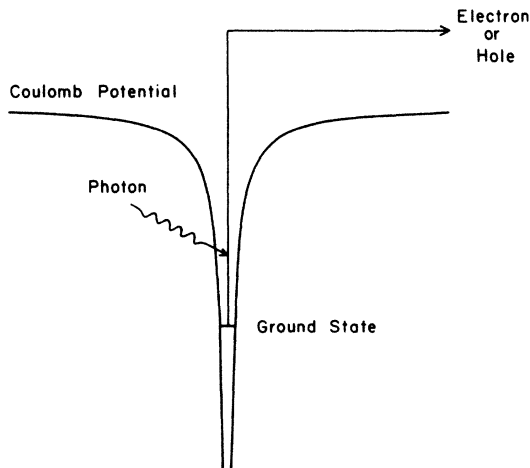


FIG. 1. Photoexcitation of an electron (or hole).

the function ψ_0 to remain finite at the origin. However, the divergence of the solution at the origin does not affect its validity away from the origin, where the major contribution to optical transition integrals occurs. This is because photoionization matrix elements involve spatially extended excited state wave functions which vanish at the origin.

Solutions of Eq. (2) can be written in terms of a noninteger principal quantum number $n^* = (E/E_0)^{1/2}$ (Ref. 9). The first term in the asymptotic expansion⁹ of the ground-state wave function provides a good approximation for our purposes. Approximate wave functions of this form have also been used by Bebb and Chapman.^{1,2} We use the exact wave function normalization constant while Bebb and Chapman use a constant which normalizes the approximate wave function. The difference is small for shallow levels. Our preference is based solely on a factor of 2 effect on the photoionization rate for deep levels. The approximate ground-state wave function is

$$\psi_0(\mathbf{r}) = \frac{N(n^*)}{\sqrt{4\pi}} r^{n^*-1} e^{-r/n^*a}, \quad (3)$$

where

$$N(n^*) = \left[\frac{2}{n^*a} \right]^{n^*} \frac{C(n^*)}{(n^*a)^{1/2} \Gamma(n^*+1)} \quad (4)$$

and⁹

$$C(n^*) = \frac{\pi}{\sin(n^*\pi)} \left[\frac{1}{2} \sum_{m=0}^{\infty} \frac{1}{(n^*-m-1)^2(n^*-m)^2} \right]^{-1/2}. \quad (5)$$

Here $a = 4\pi\epsilon_0\hbar^2/Zm^*e^2$ is the Bohr radius and n^* is the effective principal quantum number of the ground state. $C(n^*)$ is exactly equal to 1 for positive integer n^* and close to 1 for $n^* > \frac{1}{2}$. It has the value $\sqrt{2}$ for $n^* = 0$.

In the limit $n^* \rightarrow 1$, the above wave function exactly reduces to the usual hydrogenic ground-state wave function and it is possible to obtain the wave function corresponding to neutral centers in the limit where the impurity charge, Ze goes to zero. In order to maintain nonzero binding (ionization) energy in this limit, we must take n^* to zero as well, as can be seen from $E_I = m^*Z^2e^4/2(4\pi\epsilon_0)^2\hbar^2n^{*2}$. In this limit, the ground-state wave function reduces to

$$\psi_0(\mathbf{r}) = \left[\frac{k_0}{2\pi} \right]^{1/2} \frac{e^{-k_0r}}{r}, \quad (6)$$

where $k_0 = (n^*a)^{-1} = (2mE_I)^{1/2}/\hbar$. The limit of n^*a is finite and nonzero because n^*a is proportional to n^*/Z . This ψ_0 is exactly equal to the wave function for a zero-range potential which was used by Lucovsky³ to describe impurity centers with the Coulomb effects neglected.

The wave equation of the electron (or hole) including interaction with the incident photons can be written as¹⁰

$$\left[-\frac{\hbar^2}{2m^*} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} + V(\mathbf{r})e^{-i\omega t} \right] \psi(\mathbf{r}, t) = i\hbar \frac{\partial \psi(\mathbf{r}, t)}{\partial t}, \quad (7)$$

where ψ is the Kohn-Luttinger envelope wave function¹¹ and

$$V(\mathbf{r}) = \frac{e}{m^*} \left[\frac{I\hbar}{2c\epsilon_0 n_r \omega} \right]^{1/2} \hat{\mathbf{a}} \cdot \mathbf{p} e^{i\mathbf{q} \cdot \mathbf{r}} \quad (8)$$

is the interaction potential between an electron or hole and a photon.⁵ I is the intensity of the incident beam, $\hat{\mathbf{a}}$ is the polarization vector of the incident photon, \mathbf{p} is the momentum of the electron, ϵ is the dielectric constant, m^* is the carrier effective mass, and n_r is the refractive index of the medium.

After exposure to monochromatic radiation, the electron (or hole) will be in a state which has energy $E_0 + n\hbar\omega$, where n is an integer, which is the number of photons that an electron absorbs in order for the transition to occur. The general solution to Eq. (7) can be written as

$$\psi(\mathbf{r}, t) = \sum_{n=-\infty}^{\infty} \psi_n(\mathbf{r}) e^{-i(E_0 + n\hbar\omega)t/\hbar}. \quad (9)$$

If we neglect multiphoton absorption then we need to consider only $n=0$ and $n=1$ terms of the above equation:

$$\psi(\mathbf{r}, t) = \psi_0(\mathbf{r}) e^{-iE_0 t/\hbar} + \psi_1(\mathbf{r}) e^{-i(E_0 + \hbar\omega)t/\hbar}, \quad (10)$$

where ψ_0 and ψ_1 are the spatial wave function of the ground state and the excited state, respectively. Here E_0 is the ground-state energy and $E_0 = -E_I$, and E_I is the ionization energy. Substituting Eq. (10) in Eq. (7) we get

$$\left[\nabla^2 + (2k\nu) \frac{1}{r} + k^2 \right] \psi_1(\mathbf{r}) = \frac{2m^*}{\hbar^2} V(\mathbf{r}) \psi_0(\mathbf{r}), \quad (11)$$

where

$$\nu = \frac{Zm^*e^2}{4\pi\epsilon_0\hbar^2k} \quad \text{and} \quad k^2 = \frac{2m^*E}{\hbar^2},$$

and $E = \hbar\omega + E_0$ is the energy of the photoexcited electron (or hole). Solutions of Eq. (11) can be written in the integral form

$$\psi_1(\mathbf{r}) = \frac{2m^*}{\hbar^2} \int G(\mathbf{r}, \mathbf{r}') V(\mathbf{r}') \psi_0(\mathbf{r}') d^3r', \quad (12)$$

where $G(\mathbf{r}, \mathbf{r}')$ is the Coulomb Green's function which satisfies the following equation:

$$\left[\nabla^2 + (2k\nu) \frac{1}{r} + k^2 \right] G(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}'), \quad (13)$$

and has the form^{12,13}

$$G(\mathbf{r}, \mathbf{r}') = \frac{i\Gamma(1-i\nu)}{4\pi k |\mathbf{r} - \mathbf{r}'|} \left[\frac{\partial}{\partial x} - \frac{\partial}{\partial y} \right] \times W_{i\nu, 1/2}(-ikx) M_{i\nu, 1/2}(-iky) \quad (14)$$

with

$$\begin{aligned} x &= r + r' + |\mathbf{r} - \mathbf{r}'|, \\ y &= r + r' - |\mathbf{r} - \mathbf{r}'|, \end{aligned} \quad (15)$$

where $W_{i\nu,1/2}(-ikx)$ and $M_{i\nu,1/2}(-iky)$ are the two solutions of the Whittaker equation.¹⁴ The free-particle Green's function can be obtained in the limit as the impurity charge (Z) goes to zero.

A photon causes transitions from s -wave ground states to p waves. This means that in Eq. (12) the p -wave but not the s -wave part of the Green's function is important. Quantum defects reflect deviations from Coulombic potentials near the origin. Since p waves vanish at the origin but s waves do not, we must take quantum defects into account in the ground-state wave function but not in the Green's function.

An approximate evaluation of the integral in Eq. (12) can be carried out because the ground-state wave function $\psi(r')$ has a small spatial extent compared to the larger distances at which we need to evaluate $\psi_1(r)$ which describes the escape of the photoexcited carrier. Thus we take $r' \ll r$. If we also choose the z' axis to lie along the r direction, it is possible to simplify x and y as

$$\begin{aligned} x &\simeq 2r, \\ y &\simeq r'(1 + \cos\theta'), \end{aligned} \quad (16)$$

where θ' is the angle between vectors r and r' .

In order to obtain the asymptotic form of M and W , the two conditions $r \gg r'$ and $r \gg |i\nu(i\nu-1)|/2k$ should hold. This specifies the range of validity of the approximate form of ψ_1 for a given excited state energy. From Eq. (14) we obtain the asymptotic form

$$\begin{aligned} G(\mathbf{r}, \mathbf{r}') &= \sum_{n=0}^{\infty} \frac{\Gamma(n+1-i\nu)}{[\Gamma(n+1)]^2} e^{ikr'} (-ikr')^n (1 + \cos\theta')^n \\ &\quad \times \frac{ik}{2\pi} (-2ikr)^{i\nu-1} e^{-ikr}. \end{aligned} \quad (17)$$

The impurities that we are interested in have ionization energies of the order of a few hundreds of meV at most. This corresponds to wavelengths of the order of microns. The range of integration in Eq. (12) is determined by the spatial extent of the ground-state wave function and is of the order of a few tens of angstroms or less. This implies that in the interaction potential, the factor $\exp(i\mathbf{q}\cdot\mathbf{r})$ can be approximated by 1. This is the standard dipole approximation, and holds for most cases of interest to semiconductor physics. Then Eq. (8) becomes

$$V(\mathbf{r}) = \frac{e}{m^*} \left[\frac{I\hbar}{2c\epsilon_0 n_r \omega} \right]^{1/2} \hat{\mathbf{a}} \cdot \mathbf{p}. \quad (18)$$

In order to obtain the asymptotic form of $\psi_1(\mathbf{r})$, we can use (12) with $G(\mathbf{r}, \mathbf{r}')$ given by Eq. (17) and $V(\mathbf{r})$ as in Eq. (18). By evaluating the integral, we get

$$\psi_1(\mathbf{r}) = I^{1/2} S(n^*) \hat{\mathbf{a}} \cdot \hat{\mathbf{e}}_r (-ikr)^{i\nu-1} e^{ikr}, \quad (19)$$

where

$$\begin{aligned} S(n^*) &= \left[\frac{4n^* + i\nu e^2}{2\pi\epsilon_0 n_r c \hbar \omega} \right]^{1/2} \frac{k_0 n^* + 3/2 k^2}{(k_0 - ik)^{n^* + 3}} \\ &\quad \times (n^* + 1) \Gamma(2 - i\nu) F(n^*) \end{aligned} \quad (20)$$

and

$$\begin{aligned} F(n^*) &= C(n^*) [(n^* - 1)(k/3k_0) {}_2F_1(2 - i\nu, n^* + 2, 4; z) \\ &\quad - i {}_2F_1(2 - i\nu, n^* + 2, 3; z)], \end{aligned} \quad (21)$$

$z = 2k/(k + ik_0)$, and ${}_2F_1$ is the confluent hypergeometric function.¹⁴ The photoionization cross section (σ) can be defined as

$$\sigma = \frac{\text{Total outgoing probability current } (I_r)}{\text{Incident photon flux } (I)}. \quad (22)$$

The outgoing probability current (I_r) can be obtained by integrating the radial part of the current density \mathbf{J}_r on a sphere with the impurity atom at the center:

$$\mathbf{J}_r = \frac{1}{m^*} \text{Re} \left[\psi_1(\mathbf{r}) \frac{\hbar}{i} \hat{\mathbf{e}}_r \cdot \frac{\partial}{\partial \mathbf{r}} \psi_1(\mathbf{r}) \right]. \quad (23)$$

Since only the asymptotic form of ψ_1 is known, the sphere on which \mathbf{J}_r is integrated should be positioned far enough from the origin in order to use the asymptotic form of ψ_1 . Due to the fact that the total probability current is conserved, it should be independent of the position of the sphere on which \mathbf{J}_r is integrated. Substituting for ψ_1 in Eq. (23) we get

$$J_r \simeq \frac{I |S(n^*)|^2 (\hat{\mathbf{a}} \cdot \hat{\mathbf{e}}_r)^2 \left[\frac{\hbar e^{\pi\nu}}{kr^2} \right]}{m^*}. \quad (24)$$

We typically consider unpolarized photon beams incident on the impurities in semiconductors. In this case, it is useful to obtain the photoionization cross section averaged over possible polarization directions. Averaging over the

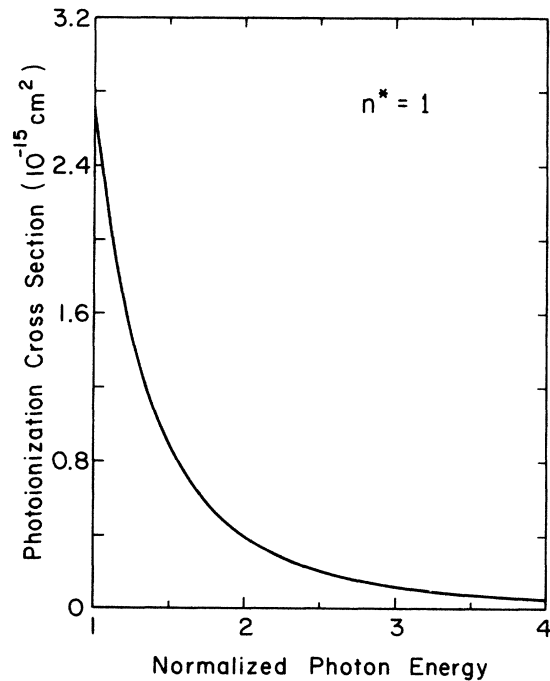


FIG. 2. Photoionization cross section as a function of normalized photon energy for $n^* = 1$, i.e., no central cell correction (pure Coulomb).

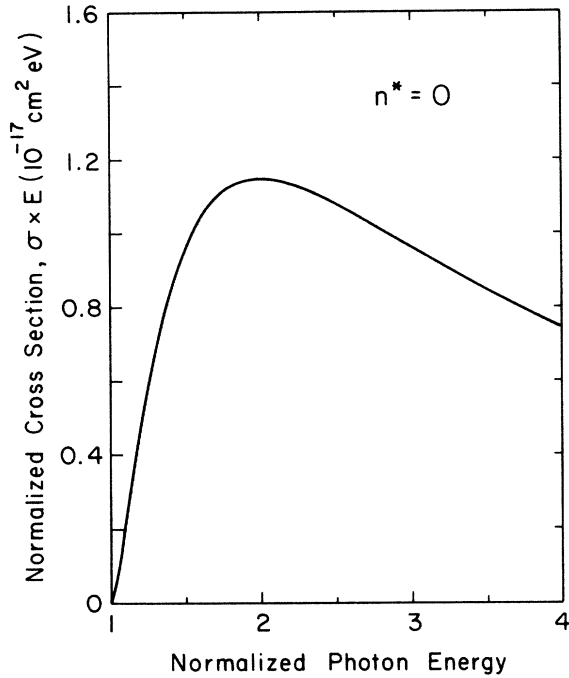


FIG. 3. Photoionization cross section as a function of normalized photon energy for a neutral impurity ($n^* = 0$), for example, an isoelectronic (isovalent) impurity.

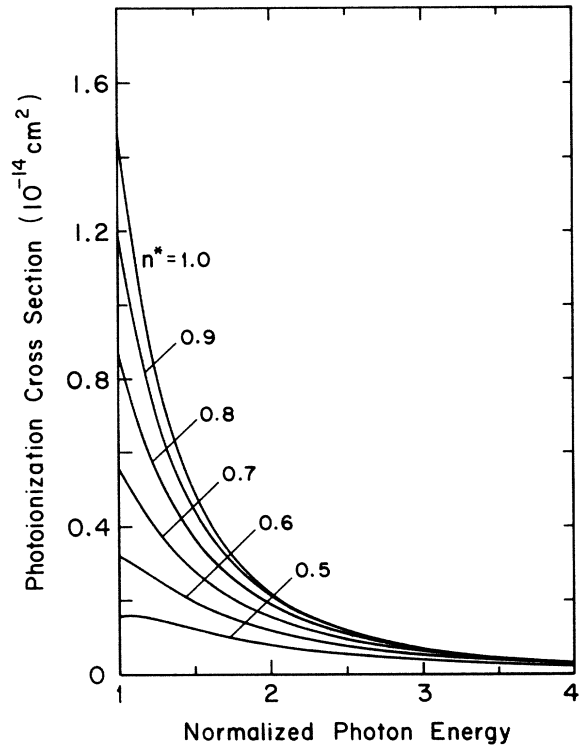


FIG. 5. Photoionization cross section as a function of normalized photon energy for donor impurities in germanium, i.e., a Coulomb potential with a central cell correction. Small central cell corrections correspond to n^* near 1.

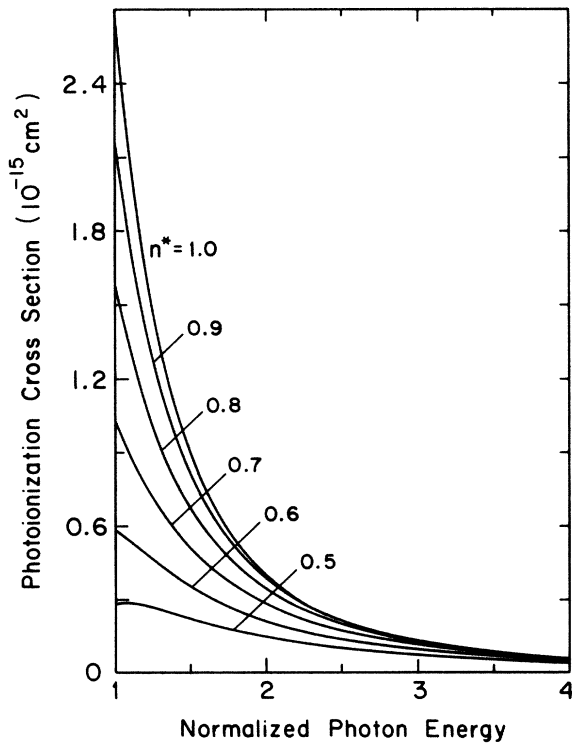


FIG. 4. Photoionization cross section as a function of normalized photon energy for donor impurities in silicon, i.e., a Coulomb potential with a central cell correction. Small central cell corrections correspond to n^* near 1.

possible polarizations of the incident photon we get the photoionization cross section as

$$\sigma = \frac{\pi \hbar e^2}{3n_r \epsilon_0 m^* c} \frac{4^{n^*+1} (n^*+1) 2n^* [(n^*)^2 - 1 + x] |F(n^*)|^2}{E_I x^{n^*+4} (1 - e^{-2\pi\nu})} \quad (25)$$

For a given value of n^* and photon energy, $F(n^*)$ can be obtained using the integral representation of hypergeometric function

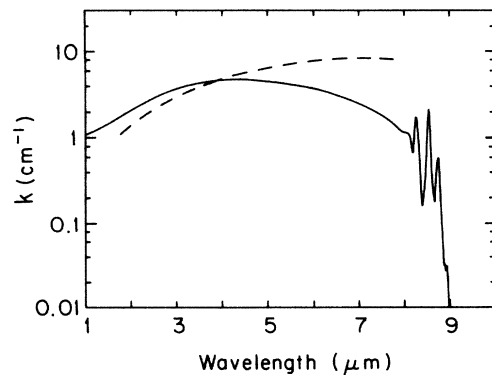


FIG. 6. Theoretical and experimental (solid curve) absorption constant (k) as a function of wavelength for indium impurities in silicon.

TABLE I. Theoretical and experimental photoionization cross sections at the peak for different impurities in Si and Ge.

Impurity	Theoretical (cm ²)	Experimental (cm ²)
Si:P	1.78×10^{-15}	1.7×10^{-15}
Si:B	1.63×10^{-15}	1.4×10^{-15}
Si:Ga	8.11×10^{-16}	5.0×10^{-16}
Si:Al	9.16×10^{-16}	8.0×10^{-16}
Si:In	1.89×10^{-16}	4.5×10^{-17}
GeAs	1.05×10^{-14}	1.1×10^{-14}
Ge:P	1.17×10^{-14}	1.5×10^{-14}
Ge:Sb	1.51×10^{-14}	1.8×10^{-14}
Ge:Tl	1.36×10^{-14}	8.7×10^{-15}

$${}_2F_1(a, b, c; z) = \frac{\Gamma(c)}{\Gamma(b)\Gamma(c-b)} \int_0^1 t^{b-1}(1-t)^{c-b-1}(1-tz)^{-a} dt \quad (26)$$

and the recurrence relation¹⁴

$$c(1-z){}_2F_1(a, b, c; z) - c{}_2F_1(a, b-1, c; z) + z(z-a){}_2F_1(a, b, c+1; z) = 0. \quad (27)$$

The expression given in Eq. (25) can be used to obtain photoionization cross sections for both shallow and deep impurities in semiconductors. In contrast with our results, the pioneering calculations of Bebb and Chapman¹ are not applicable near threshold, since the asymptotic form of the excited state wave function was used to calculate the matrix element.

Our result (25) exactly reduces to the formula obtained for the hydrogen atom¹⁵ in the limit $n^* \rightarrow 1$ and to the one obtained by Lucovsky for a zero-range potential in the limit $n^* \rightarrow 0$. At $n^* = 1$ the maximum of the cross section occurs at threshold and falls off rapidly with the increasing photon energy (see Fig. 2). This agrees with earlier results obtained for the hydrogen atom in atomic physics¹⁵ and also for hydrogenlike impurities in semiconductors.¹⁶ The nonzero behavior at the threshold is a feature of the long-range nature of the Coulomb potential. If instead of the Coulomb Green's function, the free-particle Green's function is used, the cross section would vanish at the threshold as is the case in Bebb's treatment² using plane waves for the excited state wave function. In the limit $n^* \rightarrow 0$, the cross section vanishes at threshold and its maximum appears when the photon energy is equal to twice the ionization energy (see Fig. 3). In the $n^* \rightarrow 0$, $Z \rightarrow 0$ limit, our result agrees exactly with the formula obtained by Lucovsky³ for the case of a zero-range potential. As shown before,^{17,10} in this limit the ground-

TABLE II. Approximate empirical values of effective masses, effective Rydbergs, and effective quantum numbers in terms of impurity ionization energies $E_I = -E_0$. Heavy hole masses are employed for acceptors.

	Effective Rydberg (meV)	Effective mass	$(n^*)^2$
Si Donors	31	0.3	$31 \text{ meV}/E_I$
Si Acceptors	36	0.34	$36 \text{ meV}/E_I$
Ge Donors	8.8	0.15	$8.8 \text{ meV}/E_I$
Ge Acceptors	9.4	0.16	$9.2 \text{ meV}/E_I$

state wave function exactly reduces to the one used by Lucovsky. The normalization of the Bebb and Chapman result is off by a factor of 2 in this limit. (This is a different factor of 2 than has been discussed by Cordes and Calkin.¹⁸)

Figures 4 and 5 show the photoionization cross section as a function of normalized photon energy ($x = \hbar\omega/E_I$) for donor impurities in Si and Ge. As n^* becomes smaller, the absolute value of the cross section decreases and also the maximum of the cross section moves away from threshold. The energy dependence of the cross section becomes weaker for small values of n^* . Figure 6 shows a comparison of the theoretical and experimental¹⁹ absorption constant for In impurities in silicon.

Table I shows a comparison between theoretical, using the above formula, and experimental²⁰ photoionization cross sections at the peak for several impurities in Si and Ge. In order to estimate n^* , effective Rydbergs and masses (see Table II) are obtained from the literature.^{11,21} Note that no effective field ratios are used in contrast with other work,^{1,2} where an empirical factor between 3 and 9 is introduced in order to obtain agreement with experiments. Also no free parameters are employed. We attribute this success to the fact that $GV\psi_0$ provides a good treatment of normalization because G accurately relates the small-distance behavior to large-distance behavior. This agreement is also due in part to the fact that the cross-section maxima are at or relatively near threshold, where our use of effective mass theory is more accurate than it is for energies much larger than the threshold energy.

The above procedure can be extended to obtain cross sections in the presence of applied electric fields.¹⁰ In this case, we expect nonzero cross sections for photon energies below the ionization energy. Future work should be aimed at incorporation of anisotropy about valley minima.

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