

Deduction of Impurity Wave Functions from Photoionization Properties*

E. F. Rynne, J. R. Cox, J. B. McGuire, and J. S. Blakemore

Department of Physics, Florida Atlantic University, Boca Raton, Florida 33432

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Photoionization properties for an impurity in a semiconductor are used to reconstruct the radial dependence of the bound-state wave function, through inversion of a Hankel transform. For a heuristic wave function, with effective mass approximated by a scalar, optical data for boron in Si transform to $\psi(r)$ characteristic of a nonhydrogenic shallow acceptor. Data for "deeper" acceptors in Si, Ge, and GaAs dictate a compact, sharply defined charged and an effective potential steeper than Coulombic.

The ground state(s) and excited states for an electron or hole bound to an impurity site in a semiconductor each have a characteristic energy, and a characteristic localized wave function $\psi(r, \theta, \varphi)$. Among other properties, the magnitude and spectral dependence of the photoionization cross section $\sigma(\hbar\omega)$ are both direct consequences of the bound charge distribution for the ground state. This cross section is customarily calculated¹ in time-dependent perturbation theory using the electric-dipole approximation, which happens to be an excellent approximation under the circumstances. The procedure is simplest when Coulombic interaction between a photoelectron and its former site is neglected, and a plane-wave form $\psi_k = L^{-3/2} e^{i\vec{k} \cdot \vec{r}}$ assumed for the band state; this Born-approximation simplification works very well in many cases, is used in most treatments of photoionization,¹⁻⁵ and will be used here. (Explicit consideration of the Coulombic interaction necessitates a Coulomb-wave-function final state, as used by Lax⁶ for hydrogenic impurities and by Bebb and Chapman⁷ for photoionization from a quantum-defect bound state.)

Theoretical impurity models, both for shallow effective-mass-type impurities⁵⁻⁸ and for "deep" impurities^{2-4,7,8} are commonly judged by how well the model predicts (a) the ionization energy E_I , (b) the spectrum of excited-state energies, and (c) the magnitude and spectral dependence of $\sigma(\hbar\omega)$. The latter test has typically been made by a graphical comparison of optical absorption data with curves of $\sigma(\hbar\omega)$ derived from seemingly appropriate models. One of us has illustrated such comparisons for the moderately deep-impurity situations of indium in silicon⁹ and manganese in GaAs,¹⁰ and similar comparisons are common in the literature.^{2,4,7,11-14}

The appropriateness of a theoretical model for a given impurity would be provided more directly by deduction of the bound state $\psi(r)$ from empiri-

cal data. This Letter discusses information transfer from k space into real space; deduction of $\psi(r)$ from experimental $\sigma(\hbar\omega)$ data.¹⁵ Transformations in that direction are common in some other areas of physics, but do not seem to have been used previously for the semiconductor-impurity problem. It is our hope that the simplified solution reported here will stimulate others to explore extensions to more complicated cases.

For simplicity, we have assumed that bound and unbound states are all characterized by a scalar and energy-independent¹⁶ effective mass m^* , so that wave vector and energy are related by $k = [2m^*(\hbar\omega - E_f)\hbar^2]^{1/2}$. The Born-approximation form of the electric-dipole ionization model is applied for an $l=0$ ground state. Now $\sigma(\hbar\omega)$ can be expressed as

$$\sigma(\hbar\omega) = (E_{\text{eff}}/E)^2 (n/\kappa) W(\hbar\omega) / \Phi(\hbar\omega), \quad (1)$$

where $\Phi(\hbar\omega) = cE^2/4\pi\hbar\omega$ is the incident monochromatic radiation flux, and $W(\hbar\omega)$ is the ionization probability. For an $l=0$ bound state, integration of the angular dependence yields an expression for the probability and hence for the cross section:

$$\sigma = (E_{\text{eff}}/E)^2 (n/\kappa) (32\pi^2 m^* e^2 \omega k / 3\hbar^2 c) \times \left[\int_0^\infty r^3 j_1(kr) \psi(r) dr \right]^2, \quad (2)$$

which involves the spherical Bessel function

$$j_1(kr) = (kr)^{-2} [\sin(kr) - kr \cos(kr)]. \quad (3)$$

Thus σ can readily be expressed as a function of k or of $\hbar\omega$ when a form is postulated for $\psi(r)$, as has been shown by Lucovsky² for the consequences of a delta-function potential, by Bebb for hydrogenic and quantum-defect situations, and by Ning and Sah⁵ for shallow donors associated with a multivalley conduction band.

Now a property of the spherical Bessel function (see, for example, Stakgold¹⁷) utilized in Hankel

transformations is

$$\int_0^\infty j_1(kr)j_1(kr')k^2 dk = (\pi/2r^2)\delta(r-r'). \quad (4)$$

This property makes it easy to invert the transformation of Eq. (2), thus going from k space to real space. From Eqs. (2) and (4),

$$\psi(r) = (\hbar/\pi^2 e r)(E/E_{\text{eff}})(3nc/8m^* \kappa)^{1/2} \times \int_0^\infty (k^3 \sigma/\omega)^{1/2} j_1(kr) dk. \quad (5)$$

Experimental data for σ as a function of $\hbar\omega$ are readily converted into the equivalent dependence on k , and then Eq. (5) can compute the corresponding picture for $\psi(r)$. Before using this for experimental data, we verified that it does work (both analytically and in our numerical computer program) for both hydrogenic and delta-potential models.

The numerical procedure of Eq. (5) was then applied to published optical absorption data for five impurities, namely Si:B, Si:In, Ge:Hg, GaAs:Mn, and GaAs:Cu. All of these create acceptor impurities,¹⁸ with acceptor states derived primarily from a heavy-hole band at Γ , a band for which m^* is more or less scalar.¹⁹ Theoretical models for both shallow and deep acceptors imply that wave-function radius should be scaled in terms of $a^* = (\hbar^2/2m^*E_a)^{1/2}$, where E_a is the experimentally determined ionization energy. Values for E_a , m^* , and a^* are listed in Table I, and our computations expressed $\psi(\rho)$ as a function of $\rho \equiv r/a^*$. Now if the radial wave function is written as the product

$$\psi(\rho) = F(\rho) \exp(-\rho), \quad (6)$$

then existing impurity models suggest that $F(\rho)$ should be a weaker function of radius than $\exp(-\rho)$

TABLE I. Parameters for the semiconductor:impurity systems: ionization energy E_a ; effective mass ratio m^*/m ; wave-function scale length a^* ; and the exponent s , the slope in Fig. 2.

System	E_a (meV)	m^*/m^a	a^* (Å)	Exponent s
Si:B	45	0.45	13.6	Variable
Ge:Hg	92	0.38	10.5	-1.78
GaAs:Mn	110	0.32	10.4	-1.63
GaAs:Cu	146	0.32	9.05	-1.51
Si:In	155	0.45	7.33	-1.49

^aThe "effective-mass ratio" has been chosen in conjunction with the known dielectric constant of each solid to generate correctly the ionization energy of a shallow hydrogenic acceptor.

for any type of impurity, shallow or deep. [Thus $F(\rho)$ is a constant for the 1s state of a hydrogenic impurity, varies as $\rho^{\nu-1}$ (with $0 < \nu < 1$) for the quantum-defect model,^{3,7} and as ρ^{-1} for the delta-potential deep-impurity model.²] And so we studied both $\psi(\rho)$ and $F(\rho)$ for the information derived from optical data. Figure 1 compares the radial probability function $|\rho\psi(\rho)|^2$ in terms of each impurity's scale of ρ for boron and indium in silicon, while Fig. 2 shows $F(\rho)$ versus ρ on a log-log basis for all five acceptors we studied. It will be clear at once that the "deep" acceptor curves in Fig. 2 fall off more rapidly with increasing ρ than expected from the preceding remarks about $F(\rho)$ in various theories.

The curves of Figs. 1 and 2 use optical data which are usually available only for the limited spectral range $E_a < \hbar\omega < 5E_a$; this sets a limit to the range of ρ for which the results are meaningful. We supplied the computer with an asymptotic "tail" for experimentally inaccessible high photon energies; this act is not as drastic as it sounds, for σ always decreases rapidly at high energies and makes a minor contribution to the integration. Thus we were able to verify that the derived $\psi(\rho)$ and $F(\rho)$ were insensitive to the choice of "tail" parameters for the radial range $\rho > 0.2$, though the absence of real high-energy optical data clearly does set an inner limit to

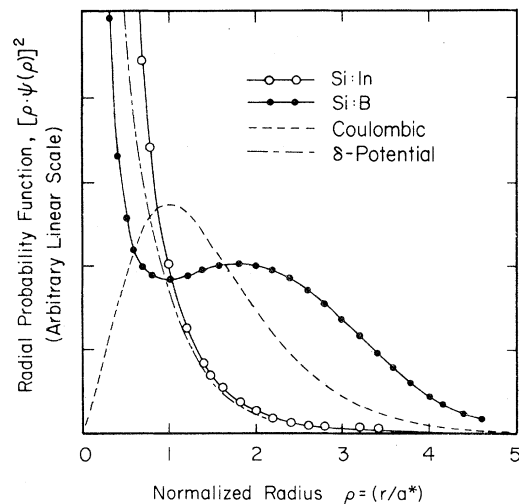


FIG. 1. A comparison of the radial probability functions for In and B in silicon, each abscissa scaled to its own a^* . The dashed curves show the behavior of Coulombic and delta-potential models for comparison. The Si:In curve is derived from optical data of Messenger and Blakemore (Ref. 9) and the Si:B curve from that of Burstein *et al.* (Ref. 20).

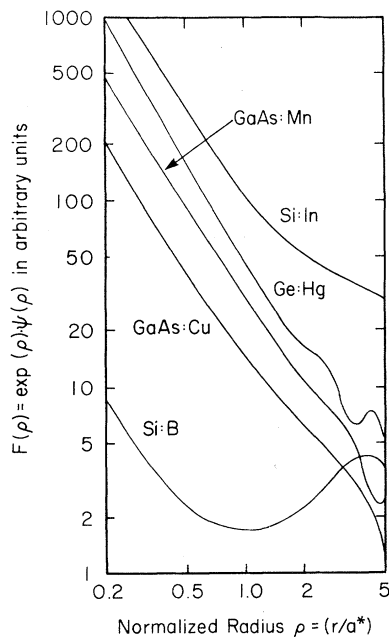


FIG. 2. Log-log plots of $F(\rho)$ versus ρ for all five acceptors; curves displaced vertically by arbitrary amounts for clarity of view. Ge:Hg is derived from optical data of Bebb and Chapman (Ref. 7), while optical data of Brown, Woodbury, and Blakemore are used for GaAs:Mn, and of Queisser (Ref. 12) for GaAs:Cu.

probing of $\psi(r)$. At the other end of the spectral range, we set out to use "cleaned" photoionization data for $\hbar\omega$ just above threshold, with extraneous absorption of excitation lines, etc., removed. The kinks seen in the Ge:Hg and GaAs:Cu curves of Fig. 2 for $\rho > 3$ probably arise from unremoved traces of these extraneous processes in our starting data.

The provisos of the last paragraph still leave a substantial range of intermediate ρ for which the results of the Eq. (5) transformation should be informative about the impurity. Figure 1 shows that charge bound to a deep In acceptor in Si is well confined within a sphere of radius a^* , even though we can not project what the true radial probability does for very small ρ . The boron curve of Fig. 1 is strikingly different from a hydrogenic 1s state,²¹ and it would be interesting to see if the outer lobe with its maximum around $\rho \approx 2$ would be retained in an elaborated transformation procedure which takes specific account of the silicon valence band structure.

As already noted in connection with Fig. 2, $F(\rho)$ fell off quite steeply with increasing ρ for all four deep impurities we studied. The approxi-

mately linear form of the curves implies that $F(\rho)$ approximates a power-law dependence $F(\rho) \approx A\rho^s$ over a substantial range of radius. The values of this (negative) slope s appear in the final column of Table I. Now if indeed $\psi(\rho) = A\rho^s e^{-\rho}$ over some substantial range of ρ , then the Schrödinger equation prescribes a potential with radial dependence $V = (2E/\rho)(1+s)(1-s/2\rho)$, which reduces to the Coulombic form $V = 2E/\rho$ for the hydrogenic $s=0$ case, and vanishes for all finite radii for $s = -1$ (delta-function potential). What surprised us was that $-1 > s > -2$ for all four deep acceptors of Fig. 2; this would be incompatible with a real relationship between potential and energy if it existed over the entire range of radius—but of course it does not. What happens for small radius is modified in practice both by decrease of the effective dielectric constant to unity and by the impurity-atom core structure, as has recently been discussed by Pantelides and Sah⁸; consideration of these complications would take us beyond the intended scope of this Letter. The striking thing about the steep slopes in Fig. 2 is that they reinforce the impression gained from the Si:In curve of Fig. 1, that a deep impurity has a very abrupt cutoff in charge density outside a critical radius. In the present model, this has to be the consequence of a confining potential that is steeper than Coulombic.

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¹See, for example, L. Schiff, *Quantum Mechanics* (McGraw-Hill, New York, 1968), 3rd ed., Chaps. 2 and 8. Also, H. S. W. Massey, *Electronic and Ionic Impact Phenomena* (Oxford Univ. Press, London, 1969), Vol. 2, Chap. 14.

²G. Lucovsky, *Solid State Commun.* **3**, 299 (1965).

³H. B. Bebb, *Phys. Rev.* **185**, 1116 (1969).

⁴H. G. Grimmeiss and L.-A. Ledebø, *J. Phys. C* **8**, 2615 (1975).

⁵T. H. Ning and C. T. Sah, *Phys. Rev. B* **4**, 3468 (1971).

⁶M. Lax, in *Proceedings of the Photoconductivity Conference, Atlantic City, New Jersey, 1954*, edited by R. G. Breckneridge (Wiley, New York, 1956), p. 111.

⁷H. B. Bebb and R. A. Chapman, *J. Phys. Chem. Solids* **28**, 2087 (1967).

⁸S. T. Pantelides and C. T. Sah, Phys. Rev. B 10, 621, 638 (1974).

⁹R. A. Messenger and J. S. Blakemore, Phys. Rev. B 4, 1873 (1971).

¹⁰W. J. Brown, D. A. Woodbury, and J. S. Blakemore, Phys. Rev. B 8, 5664 (1973).

¹¹R. A. Chapman and W. G. Hutchinson, Phys. Rev. 157, 615 (1967).

¹²H. J. Queisser, in *Festkörperprobleme*, edited by O. Madelung (Pergamon, New York, 1971), Vol. XI, p. 45.

¹³J. W. Walker and C. T. Sah, Phys. Rev. B 8, 5597 (1973).

¹⁴H. G. Grimmeiss, in *Metal-Semiconductor Contacts*, edited by M. Pepper, IOP Conference Proceedings No. 22 (Institute of Physics, London, 1974), p. 187.

¹⁵J. S. Blakemore and E. F. Rynne, Bull. Am. Phys. Soc. 19, 1118 (1974).

¹⁶Scalar effective masses are appropriate for relatively few real impurities, one example being the very shallow donors associated with the Γ conduction minimum in III-V compounds. For the acceptors analyzed in this Letter, use of a scalar effective mass is an approximation of debatable validity, but it does get this topic started. Grimmeiss and Lebedo (Ref. 4) have extended the Lucovsky delta-function model to make mass

a function of energy, but most other workers have adopted an energy-independent mass approximation.

¹⁷I. Stakgold, *Boundary Value Problems in Mathematical Physics* (Macmillan, London, 1967), p. 316.

¹⁸Hg is divalent in Ge, and both Mn and Cu have been reported to be multivalent in GaAs. Our concern here is just with photoionization data for the *neutral* acceptor.

¹⁹The heavy-hole band is known to be warped from spherical symmetry in each of these three semiconductors, to varying degrees. However, the liberty we thus take with reality should be less severe than that necessary to describe donor states in a multivalley-conduction-band semiconductor such as Ge or Si by an equivalent scalar m^* . The approach needed for such multivalley bands is indicated by Ning and Sah (Ref. 5), who do calculate effective radial charge densities for shallow donors in silicon.

²⁰E. Burstein, G. Picus, B. Hennis, and R. Wallis, J. Phys. Chem. Solids 1, 65 (1956).

²¹S. T. Pantelides (personal communication) has suggested that the Si:B impurity wave function be thought of as the product of a Bloch function (sp^3 hybrid character near each atom) and an envelope function which is mainly s (hydrogenic) in character with a small d admixture.

Observation of Excitonic Surface States on MgO—Stark-Model Interpretation*

Victor E. Henrich, G. Dresselhaus, and H. J. Zeiger

Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, Massachusetts 02173

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Using the energy and angle-of-incidence dependence of the electron-energy-loss spectra of MgO, we have separated the excitonic transitions from the Mg core levels to the excited states into those of bulk and surface origin. The bulk transitions are very nearly those of the free Mg^{2+} ion. The surface-state transitions can be described by Stark splitting of the energy levels of the surface Mg^{2+} ions in the intense Madelung electric fields at the crystal surface.

While the electronic surface states of covalent semiconductors such as Si, Ge, and GaAs have been widely studied over the last few years, less attention has been paid to the surface electronic structure of highly ionic materials. We have extended the technique of reflection electron-energy-loss spectroscopy (ELS) to the study of intrinsic surface states on MgO. By using both the angle-of-incidence and primary-electron-energy dependence of the ELS spectra, we have been able unambiguously to separate transitions from the $Mg(2p)$ and $Mg(2s)$ core levels to excited states¹ into those of bulk and surface origin. The energies of the bulk excitonic transitions are in good agreement with the optically observed ex-

cited states of the free Mg^{2+} ion.² The surface-state transitions can be described well by a simple, one-parameter model for the Stark splitting of the bulk Mg^{2+} -like excitonic states in an electric field \mathcal{E}_s at the position of a surface Mg^{2+} ion.

By varying the energy and angle of incidence of the primary-electron beam, a wide range of effective depths can be sampled in ELS. The electron mean free path in a solid increases from 4–5 Å for energies between about 40 and 150 eV to 20–30 Å for 2000-eV electrons.³ Thus an ELS spectrum taken with a primary-electron energy $E_p \sim 2000$ eV at normal incidence will be dominated by transitions of bulk origin, whereas a normal-incidence spectrum taken with $E_p \sim 100$ eV