Ground State of Impurity Atoms in Semiconductors Having Anisotropic Energy Surfaces*

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(Received September 22, 1954)

The nature of the ground state of a substitutional impurity atom in a crystal having an anisotropic energy-band structure is re-examined. A variational calculation has been made for the case of a band whose energy contours consist of several, symmetrically-located ellipsoids. Unlike the previous scalar, hydrogenic impurity model, this calculation at the outset uses the experimentally determined effective-mass-tensor components. Results for the impurity binding energy in germanium and silicon are on the order of thirty percent lower than those obtained directly from activation-slope measurements. Further, theoretical agreement with the experimentally determined critical impurity density for vanishing binding energy in germanium is much improved over the older model, though still not perfect.

IT has been customary to describe the ground state of a Group III or Group V impurity atom, substitutionally introduced into the diamond-type lattice (germanium or silicon) in terms of a hydrogen-like model[1] in which the electron has a scalar effective-mass. However the recent cyclotron resonance experiments[2] have revealed that electrons at the bottom of the lowest conduction band in both germanium and silicon have highly anisotropic effective-mass tensors. Further, for both crystals the E vs $\mathbf{k}$ map for the lowest conduction band exhibits several identical, symmetrically located energy valleys, the number and their axial locations being indicated in the first two columns of Table I. The measured effective-mass values corresponding to principal axes of the constant-energy ellipsoids are given in the third and fourth columns. It is evident that a reconsideration of the theoretical problem is required.

A formalism sufficiently powerful, in principle, to handle the impurity problem in the presence of the above complications has recently been published by Koster and Slater.[3] In this formalism a set of simultaneous difference equations is obtained relating Fourier-expansion coefficients of the Bloch-wave energy $E(\mathbf{k})$ to Wannier-function-expansion coefficients of the impurity wave function. In the case of a single minimum $\mathbf{k}_0$ in the E vs $\mathbf{k}$ map, passage from the difference equations to the standard effective-mass Schrödinger

equation is achieved via a Taylor expansion of $E(\mathbf{k})$ about $\mathbf{k}_0$ and some other simplifying assumptions. Where the E vs $\mathbf{k}$ map exhibits several equal minima, in a first approximation one may follow the same procedure and Taylor-expand $E(\mathbf{k})$ about one minimum, thereby obtaining the effective-mass Schrödinger equation and its solution for that particular energy valley. The correct impurity wave function is then a superposition[4] of the individual wave functions for each energy valley. Because the latter functions are "building blocks" for the correct wave function it was felt worthwhile to study them and also thereby obtain a first approximation to the binding energy of the ground state using the experimental mass values.

The effective-mass Schrödinger equation for one energy valley, with the reduced Coulomb potential $-e^2/\epsilon r$, may be written, after a change to dimensionless units, as

$$H\psi = -\left\{\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{1}{C}\frac{\partial^2}{\partial z^2} + \frac{1}{r}\right\}\psi = \xi\psi, \qquad (1)$$
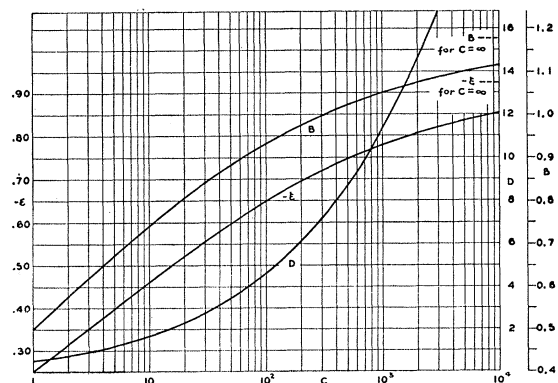

FIG. 1. "Pancake" wave-function parameters vs $C = m_l/m_t (C \geq 1)$.

[1] Wartime contributions to this problem are reviewed in H. C. Torrey and C. A. Witmer's *Crystal Rectifiers* (McGraw-Hill Book Company, Inc., New York, 1948). More recent work is reviewed by G. W. Castellan and F. Seitz in *Semiconducting Materials* (Proceedings of the Reading Conference) (Academic Press, New York, 1951). In the hydrogen-like model for the impurity, the ground state has the radius $a_I = (\epsilon m/m^*)a_0$ and the binding energy $E_I = (m^*/\epsilon^2 m)E_{IH}$. Here ϵ is the dielectric constant of the host crystal, m the free electron mass, m^* the effective mass of the lowest-conduction-band electrons for Group V impurities (or of topmost-valence-band holes for Group III impurities) a_0 is the Bohr radius, $a_0 = 0.53$ A, and $E_{IH} = e^2/2a_0$, e being the electronic charge.

[2] Lax, Zeiger, Dexter, and Rosenblum, Phys. Rev. **93**, 1418 (1954). Also B. Lax, paper read at the Amsterdam Conference on Semiconductors, June 1954, Physica (to be published).

[3] G. F. Koster and J. C. Slater, Phys. Rev. **95**, 1167 (1954), particularly Eqs. (8), (3), (6), and (12).

[4] In superposing these individual wave functions account must be taken of their nonorthogonality—they are coupled together by the Coulomb potential. A study of this coupling has been made by J. Luttinger and W. Kohn. For clarification of this aspect of the problem I am indebted to J. Luttinger (private communication).

TABLE I. Experimental and theoretical results for conduction-band electrons and donor impurities in germanium and silicon.

	No. of Min.	Axial location	m_l/m^a	m_t/m^a	$E(\exp)^b$ ev	$E(\text{calc})$ ev	R_t A	R_l A	m^*/m	a_I A
Ge	8(or 4)[c]	⟨1,1,1⟩	1.4	0.083	As:0.0127	0.0089	64.6	23.9	0.24	35
Si	6	⟨1,0,0⟩	0.99	0.19	P: 0.043	0.0285	24.7	13.5	0.46	14

[a] Cyclotron-resonance data reported by B. Lax at the Amsterdam Conference on Semiconductors, June, 1954, Physica (to be published).
[b] Activation-energy data reported by J. A. Burton at the Amsterdam Conference on Semiconductors, June, 1954, Physica (to be published).
[c] Whether there are $2M$ or M energy valleys depends on whether the minima are located in the interior of the first Brillouin zone or on boundary faces of the zone.

with $C=m_l/m_t$ and $r=(x^2+y^2+z^2)^{\frac{1}{2}}$. The coordinate axes are chosen to coincide with principal axes of the constant-energy ellipsoids for the chosen energy valley. The units of length and energy are, respectively, $a_t=a_I/2$ and $E_t=4E_I$,[1] with $m^*=m_t$.

For $C\neq1$, (1) is not separable and in consequence a variational method has been employed to estimate the binding energy ξ of the ground state. The exact hydrogenic ground-state wave function, $\psi_{(C=1)}=(8\pi)^{-\frac{1}{2}}\times\exp[-(\frac{1}{4}x^2+\frac{1}{4}y^2+\frac{1}{4}z^2)^{\frac{1}{2}}]$, suggests a simple trial wave function for the general case, $C\neq1$, which one would not only expect to represent the true solution quite well, but which also proves quite tractable in calculations, namely the normalized function

$$\psi=\left(\frac{B^2D}{\pi}\right)^{\frac{1}{2}}\exp[-(B^2x^2+B^2y^2+D^2z^2)^{\frac{1}{2}}]. \quad (2)$$

Minimization of the energy integral $I=\int\psi^*H\psi d\tau$ [where H is given by (1)] with respect to B and D results in the following set of equations, valid for the case $C\geq1$, involving an auxiliary variable u:

$$C=\frac{1}{2}(u^2+1)\left[\frac{u^3}{u-\tan^{-1}u}-(u^2+1)\right], \quad (3)$$

$$D=\frac{3}{2}C\frac{u-\tan^{-1}u}{u^3}, \quad B=\frac{D}{(u^2+1)^{\frac{1}{2}}}, \quad (4)-(5)$$

$$-\xi\simeq-I=\frac{D}{u}\tan^{-1}u-\frac{2}{3}B^2-\frac{1}{3}\frac{D^2}{C}. \quad (6)$$

By first plotting C, D, B, and $-\xi$ against u, one then obtains the desired plots of D, B, and $-\xi$ as functions of C, shown for the range $1\leq C\leq10^4$ in Fig. 1. For the case $C<1$, which is not at present of experimental interest, a set of equations somewhat like the set (3)-(6) is obtained, with $\tan^{-1}$ replaced by $\tanh^{-1}$.

With $C>1$, the wavefunction (2) is a "pancake" function. Plausible measures of the transverse and longitudinal spreads of this "pancake" function are, respectively, $R_t=a_t/B$ and $R_l=a_t/D$.

The experimental values for the binding energy E and the calculated values of $E=(-\xi)E_t$, R_t, and R_l are presented, for germanium and silicon, in Table I. Also included are the scalar effective-mass ratios m^*/m of the "old" theory, as determined from $E(\exp)$, and the corresponding ground-state radius a_I.

For electrons in the lowest conduction band in silicon ($\epsilon=12$), $C=5.2$, $a_t=16.7$ A, $E_t=0.0713$ ev and from Fig. 1, $D=1.24$, $B=0.675$, and $-\xi=0.40$. $E(\text{calc})$ is 34 percent lower than $E(\exp)$ corresponding to phosphorus impurity.

For electrons in the lowest conduction band in germanium ($\epsilon=16$), $C=16.9$, $a_t=51$ A, $E_t=0.0175$ ev and from Fig. 1, $D=2.13$, $B=0.79$, and $-\xi=0.508$. $E(\text{calc})$ is 30 percent lower than $E(\exp)$ corresponding to arsenic impurity.

As pointed out above, the impurity ground state is a superposition of the variationally-determined "pancake" functions, each with the spatial orientation determined by the constant-energy ellipsoids for the particular energy valley. The resultant ground state is a highly scalloped wave-function whose spatial extent, for purposes of discussion of the "overlapping impurities" problem may be taken as R_t. "Cubic" packing of impurities would correspond to a density of $(2R_t)^{-3}$ cm³, or 4.6×10^{17} cm⁻³ for germanium (Table I). This is much closer to the published data of Debye and Conwell[5] which indicates a vanishing impurity ionization-energy at a donor concentration of 1.6×10^{17} cm⁻³, than the result predicted by the "old" scalar model. The "cubic" packing density in the latter model is $(2a_I)^{-3}$ cm⁻³, or 2.8×10^{18} cm⁻³ (Table I).

[5] P. P. Debye and E. M. Conwell, Phys. Rev. 93, 705 (1954), Fig. 12.