energy surfaces. From (V.13), there are at once seen to be

$$\epsilon_{1,2}=\tfrac{1}{3}(A+2B)k^2\pm\{[\tfrac{1}{3}(A-B)]^2k^4+\tfrac{1}{3}[C^2-(A-B)^2]I\}^{\frac{1}{2}}, \quad I\equiv k_x^2k_y^2+k_y^2k_z^2+k_z^2k_x^2, \tag{C.14}$$

where each is doubly degenerate.

For our simple case, $C^2=(A-B)^2$, and the expressions (C.14) become

$$\begin{aligned}\epsilon_1&=\tfrac{1}{3}(2A+B)k^2=\tfrac{1}{2}(3\alpha-\beta)k^2,\\ \epsilon_2&=Bk^2=\tfrac{1}{2}(3\beta-\alpha)k^2.\end{aligned} \tag{C.15}$$

Using each of these are our Hamiltonian, we see at once that the energy levels in an external field are (again a factor of s is dropped)

$$\left.\begin{aligned}\epsilon_1(n_0)&=\tfrac{1}{2}(3\alpha-\beta)(2n_0+1)\\ \epsilon_2(n_0)&=\tfrac{1}{2}(3\beta-\alpha)(2n_0+1)\end{aligned}\right\}n_0=0,1,2,\cdots, \tag{C.16}$$

each level being doubly degenerate. Expanding the roots in (C.13) in reciprocal powers of $2n_0+1$, we immediately obtain (C.16) for high quantum numbers. It is also clear from these formulas, however, that for small n_0 the deviations from the classical results are of the order of magnitude of the level spacings themselves.

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Hyperfine Splitting of Donor States in Silicon

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The hyperfine splitting of donor states in Si has been theoretically estimated. The results agree with the recent spin resonance experiments of Fletcher *et al.* within a factor of about 2, which is better than the estimated uncertainty of the calculation.

1. INTRODUCTION

ELECTRON spin resonances exhibiting hyperfine structure in n-type Si have recently been observed by Fletcher *et al.*[1] The number of hyperfine lines of these resonances corresponds exactly to the nuclear spin of the added Group V atoms, so that it is clear that the resonances are due to electrons localized near such atoms. The purpose of the present study is to examine whether the observed magnitude of the hyperfine splitting is consistent with the picture that the electrons in question are in the well-known donor states with ionization energies of about 0.04–0.05 ev. In calculating this splitting there are two main difficulties. The first is that the band functions for Si are not well known. The second is breakdown of the effective mass formulation in the neighborhood of the impurity atom. We estimate that due to these difficulties our final result has an uncertainty of about a factor of five. The experimental results fall well within these limits. Thus our calculation supports the view that the observed resonances are due to electrons in donor states.

2. FORMULATION OF THE PROBLEM

Let us consider an electron bound to a Group V donor atom such as P, As, or Sb. We denote the normalized wave function of the electron by $\psi(\mathbf{r})$, where the origin of $\mathbf{r}$ is taken at the donor nucleus. Then the magnetic interactions of the spin moment of the electron $\boldsymbol{\mu}_s$, the nuclear moment of the donor $\boldsymbol{\mu}_D$, and the external magnetic field $\mathbf{H}$, are given by

$$W=-\boldsymbol{\mu}_s\cdot\mathbf{H}+(8\pi/3)\psi^2(0)\boldsymbol{\mu}_s\cdot\boldsymbol{\mu}_D. \tag{2.1}$$

Thus the donor nucleus produces an additional effective field

$$\mathbf{H}^1=-(8\pi/3)\psi^2(0)\langle\boldsymbol{\mu}_D\rangle, \tag{2.2}$$

where $\langle\ \rangle$ indicates expectation value over the nuclear wave function. Therefore the total hyperfine separation (between the extreme lines of the multiplet) is given by

$$(\Delta H)_{\text{total}}=(16\pi/3)\psi^2(0)\mu_D, \tag{2.3}$$

where μ_D is the magnitude of the nuclear moment of the donor. Table I lists experimental values of ΔH (reference 1), experimental values of μ_D,[2] and $\psi^2(0)$ calculated from (2.3). The object of the following considerations is to make theoretical estimates of $\psi^2(0)$ and to compare them to the values listed in Table I.

The function $\psi(\mathbf{r})$ satisfies the Schrödinger equation

$$[-(\hbar^2/2m)\nabla^2+V(\mathbf{r})+U(\mathbf{r})-E]\psi(\mathbf{r})=0, \tag{2.4}$$

where $V(\mathbf{r})$ is the effective periodic potential for a conduction electron in Si and $U(\mathbf{r})$ is the additional potential due to the replacement of one Si atom by a donor ion. For r large compared to the interatomic

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[1] Fletcher, Yager, Pearson, Holden, Read, and Merritt, Phys. Rev. **94**, 1392 (1954); Fletcher, Yager, Pearson, and Merritt, Phys. Rev. **95**, 844 (1954).

[2] J. E. Mack, Revs. Modern Phys. **22**, 64 (1950).

TABLE I. Experimental results for $\psi^2(0)$.

Donor	μ_D (nuclear magnetons)	ΔH (oersted)	$[\psi^2(0)]_{\text{expt}}$ (10^{24} cm^{-3})
P^{31}	1.13	42	0.44
As^{75}	1.5	228	1.80
Sb^{121}	3.40	345	1.20

distance d,

$$U(\mathbf{r})=-e^2/\kappa r, \tag{2.5}$$

where κ is the dielectric constant, equal to 12.0 in Si. In this and the following two sections we shall use (2.5) for *all* values of r (since the donor orbit is large compared to d), and make rough corrections for the failure of (2.5) when r is small in Sec. 5.

The donor state function $\psi(\mathbf{r})$ is mostly made up of Bloch waves from the bottom of the conduction band of a perfect Si lattice. It is therefore essential to know the nature of the conduction band energy surface near its minimum point or points. Fortunately recent measurements of "cyclotron" resonances[3] provide this information. They show that the conduction band of Si has 6 minima on the (1,0,0) and equivalent axes in $\mathbf{k}$-space. If the minimum point $\mathbf{k}^{(1)}$ on the (1,0,0) axis is given by $(k_0,0,0)$, the energy near this point is given by

$$E=E_0+\frac{\hbar^2}{2m_1}(k_x-k_0)^2+\frac{\hbar^2}{2m_2}(k_y^2+k_z^2), \tag{2.6}$$

where according to reference 3,

$$m_1=0.98m,\quad m_2=0.19m, \tag{2.7}$$

m being the free electron mass.

It can be shown that in the limit where the orbit of the donor state is large compared to the interatomic spacing and $U(\mathbf{r})$ is given by (2.5), the energy of a donor state is the lowest eigenvalue of the equation:

$$\left(-\frac{\hbar^2}{2m_1}\frac{\partial^2}{\partial x^2}-\frac{\hbar^2}{2m_2}\left(\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+U(r)-\epsilon\right)F^{(1)}(r)=0. \tag{2.8}$$

If $\mathbf{k}^{(1)}$ were the only minimum point, then in the same approximation[4] the corresponding wave function would be

$$\psi^{(1)}=F^{(1)}(\mathbf{r})\psi(\mathbf{k}^{(1)},\mathbf{r}), \tag{2.9}$$

where $\psi(\mathbf{k}^{(1)},\mathbf{r})$ is the Bloch function at $\mathbf{k}^{(1)}$, normalized so that

$$\int_{\text{unit cell}}|\psi(\mathbf{k}^{(1)},\mathbf{r})|^2d\mathbf{r}=\Omega, \tag{2.10}$$

Ω being the volume of the unit cell. If $F^{(1)}$ is normalized to unity over the whole crystal, then so is ψ. Since, however, there are six equivalent minima $\mathbf{k}^{(i)}$, the ground state wave function will actually be a linear combination of solutions of the form (2.9) corresponding to each of these points. If the phases of the $\psi^{(i)}$ are all chosen to be the same at the origin, then the correct normalized ground state function is

$$\psi=\frac{1}{\sqrt{6}}\sum_{i=1}^{6}\psi^{(i)}$$

$$=\frac{1}{\sqrt{6}}\sum_{i=1}^{6}F^{(i)}(\mathbf{r})\psi(\mathbf{k}^{(i)},\mathbf{r}). \tag{2.11}$$

Therefore,

$$|\psi(0)|^2=6|F^{(1)}(0)|^2|\psi(\mathbf{k}^{(1)},0)|. \tag{2.12}$$

The normalization of (2.11) follows from the fact that the $F^{(i)}(\mathbf{r})$ are slowly varying compared to a typical lattice spacing, in which case the members of (2.11) are orthonormal.

The problem of calculating $|\psi(0)|^2$ can be divided into three parts: (a) The computation of $|\psi(\mathbf{k}^{(1)},0)|^2$, (b) the computation of $|F^{(1)}(0)|^2$, (c) an estimate of the effects of the simplifying assumptions leading to (2.12). These questions will be taken up in the next three sections.

3. ESTIMATION OF $|\psi(\mathbf{k}^{(1)},0)|^2$

The conduction band wave functions of Si go over, in the limit of large interatomic distance, into $3s$ and $3p$ orbitals. Only the former contribute to the square of the wave function at the nucleus. It is therefore of interest first to estimate $|\psi_{3s}(0)|^2$ for atomic Si. For brevity we shall denote this quantity by $P(\text{Si};3s)$.

Unfortunately no self-consistent calculation for neutral Si exists. However, a fairly good idea of $P(\text{Si};3s)$ can be indirectly obtained as follows. We list below certain values of P obtained from solutions of Hartree-Fock equations[5]:

$$\begin{aligned}&[P(\text{Ge};4s)]_{\text{H.F.}}=70\times10^{24}\text{ cm}^{-3},\\&[P(\text{Ge}^{++};4s)]_{\text{H.F.}}=82\times10^{24}\text{ cm}^{-3},\end{aligned} \tag{3.1}$$

and[6]

$$[P(\text{Si}^{+++};3s)]_{\text{H.F.}}=39\times10^{24}\text{ cm}^{-3}. \tag{3.2}$$

From these values and the analogy of the electronic configurations of Si and Ge, we estimate

$$[P(\text{Si};3s)]_{\text{H.F.}}=(31\pm3)\times10^{24}\text{ cm}^{-3}. \tag{3.3}$$

Direct comparison with experiment in the case of the alkalies shows that the Hartree-Fock equation gives too low a value for P. Hence (3.3) very probably represents a low estimate for the true P.

An upper limit for $P(\text{Si};3s)$ can be obtained by

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[3] Dexter, Lax, Kip, and Dresselhaus, Phys. Rev. **96**, 222 (1954).

[4] J. M. Luttinger and W. Kohn, Phys. Rev. **97**, 869 (1955).

[5] Hartree, Hartree, and Manning, Phys. Rev. **59**, 299 (1941).

[6] Hartree, Hartree, and Manning, Phys. Rev. **60**, 857 (1941).

evaluating $P(\mathrm{Si}^{+++}; 3s)$ from the Goudsmit formula[7]

$$P_{\mathrm{G}}=\frac{1}{\pi a_0^3}\frac{ZZ_0^2}{n_0^3}=\frac{1}{\pi a_0^3}\frac{Z}{Z_0}\left(\frac{Z_0}{n_0}\right)^3, \tag{3.4}$$

where a_0 is the Bohr radius, Z_0 is the charge of the entire ion core (4 in our case), and n_0 is the effective quantum number of the outside s-electron defined by

$$W=(Z_0/n_0)^2\ \mathrm{Ry}, \tag{3.5}$$

where W is the ionization energy. For Si^{+++},

$$W=3.32\ \mathrm{Ry}, \tag{3.6}$$

$$[P(\mathrm{Si}^{+++}; 3s)]_{\mathrm{G}}=46\times 10^{24}\ \mathrm{cm}^{-3}. \tag{3.7}$$

This value should represent the true $P[\mathrm{Si}^{+++}; 3s]$ to within 5–10 percent. It agrees rather well with (3.2), and as expected is somewhat higher. Combining (3.2), (3.3), and (3.7) gives finally:

$$P(\mathrm{Si},3s)=(37\pm 5)\times 10^{24}\ \mathrm{cm}^{-3}. \tag{3.8}$$

In the absence of better crystal wave-functions, we must now use this value to estimate $|\psi(\mathbf{k}^{(1)},0)|^2$. We note that in the tight-binding approximation the conduction band wave functions are made up of atomic $3s$ and $3p$ functions; thus, in the vicinity of each Si atom,

$$\psi(\mathbf{k}^{(1)},\mathbf{r})=(\Omega/2)^{\frac{1}{2}}[\alpha\psi_{3s}(\mathbf{r})+\beta\psi_{3p}(\mathbf{r})], \tag{3.9}$$

$\Omega/2$ being the volume per atom, and

$$|\alpha|^2+|\beta|^2=1. \tag{3.10}$$

We have not been able to estimate α and β reliably. However, the values

$$|\alpha|^2=|\beta|^2=\tfrac{1}{2} \tag{3.11}$$

are probably not in error by more than a factor of 2.

Combining (3.9) and (3.8), and introducing the value $\Omega=40.0\times 10^{-24}\ \mathrm{cm}^3$, we find finally:

$$|\psi(\mathbf{k}^{(1)},0)|^2=(2|\alpha|^2)\times 370, \quad (2|\alpha|)^2\sim 1. \tag{3.12}$$

This final estimate is probably also good to within a factor of 2.[8]

4. ESTIMATION OF $|F^{(1)}(0)|^2$

This is the most straightforward and reliable part of the problem. It requires the solution of Eq. (2.8) with the values (2.7) for m_1 and m_2. An exact solution has not been found, but the function[9]

$$\bar{F}^{(1)}=(a^2b/\pi)^{\frac{1}{2}}\exp\{-[a^2(y^2+z^2)+b^2x^2]^{\frac{1}{2}}\} \tag{4.1}$$

is, with suitable a and b, a good approximate wave function for all values of $m_1\geq m_2$. Details will be described elsewhere. For our present purposes the following results will indicate the reliability of this function. For $m_1=m_2$, $(\bar{F}^{(1)}(0)/F^{(1)}(0))^2=1$; for $m_1/m_2\rightarrow\infty$, $[\bar{F}^{(1)}(0)/F^{(1)}(0)]^2\rightarrow 1.15$. Thus the error of $|\bar{F}^{(1)}(0)|^2$ is less than 15 percent for all $m_1/m_2\geq 1$. At the actual values of m_1 and m_2, $|\bar{F}^{(1)}(0)|^2=3.8\times 10^{+19}\ \mathrm{cm}^{-3}$. Allowing for the fact that for large m_1/m_2, $|\bar{F}^{(1)}(0)|^2$ is a slight overestimate, we arrive at

$$|F^{(1)}(0)|^2=(3.7\pm 0.2)\times 10^{19}\ \mathrm{cm}^{-3}. \tag{4.2}$$

Combining this, Eq. (3.12), and Eq. (2.12) gives

$$\begin{aligned}&|\psi(0)|^2=(2|\alpha|^2)\times 0.082\times 10^{24}\ \mathrm{cm}^{-3},\\&(2|\alpha|^2)\sim 1.\end{aligned} \tag{4.3}$$

We are now in a position to make a preliminary comparison with experiment. The case to which our model of a perfect Si lattice plus a $-e^2/\kappa r$ potential applies best is that of a phosphorus donor, which differs from the neutral Si atom just by one extra nuclear charge. Comparison with Table I shows that our present estimate is too low by a factor of 5. Even if $(2|\alpha|^2)=2$, which is its maximum value in the tight-binding approximation and very likely an overestimate, there still remains a discrepancy of a factor of 2.5. It is therefore necessary to examine the validity of the simplified approach, which led to Eq. (2.11), and to make rough allowance for effects neglected by it. This will be done in the following section.

5. CORRECTIONS TO THE EFFECTIVE MASS FORMALISM

The effective mass formalism on which the work in the preceding sections was based is least reliable in the vicinity of the singularity of the perturbing potential $U(\mathbf{r})$ (see reference 4). Furthermore, the form $-e^2/\kappa r$ for U which we have assumed up to now, is certainly incorrect for small $\mathbf{r}$. Actually

$$U(\mathbf{r})=-f(\mathbf{r})e^2/r, \tag{5.1}$$

where

$$\lim_{\mathbf{r}\rightarrow 0}f(\mathbf{r})=(Z_D-Z_{\mathrm{Si}}), \tag{5.2}$$

$$\lim_{\mathbf{r}\rightarrow\infty}f(\mathbf{r})=1/\kappa, \tag{5.3}$$

Z_D and Z_{Si} being the atomic numbers of the donor atom and of Si respectively. For both of these reasons, the following procedure should represent a distinct improvement:

(a) Solve the effective mass equation (2.8) with the asymptotic potential, $-e^2/\kappa r$, in an exterior region Ω_e, which excludes a small volume Ω_i surrounding the donor atom, and obtain a wave function of the form (2.11) in this region.

(b) Solve the original Schrödinger equation (2.4) with the correct $U(\mathbf{r})$, (5.1) and (5.2), in the interior region Ω_i.

(c) Join these solutions smoothly. This will of course determine the energy.

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[7] S. Goudsmit, Phys. Rev. 43, 636 (1933).

[8] Dr. C. Herring has kindly informed us of an independent estimate of (3.12) giving the value 200, which he expects to be too low rather than too high. This value would improve the agreement with experiment [see Eq. (6.1) ff].

[9] This function was independently introduced by M. Lampert of the Radio Corporation of America.

To carry out this program in detail is at present impossible since both $U(\mathbf{r})$ for small $\mathbf{r}$ and $\psi(\mathbf{k}^{(i)},\mathbf{r})$ are unknown. We shall therefore have to be content with very rough estimates, using as an important guide the measured ionization energy of donor electrons.

For the time being we shall concentrate on phosphorus donors, which introduce the least violent perturbation into the Si lattice. A few remarks about the other donors will be made in Sec. 6.

(a) Exterior Region, Ω_e

Here we are forced at the outset to make a simplification, namely to replace the two masses m_1 and m_2 by a mean mass m^*, which we choose to give the same binding energy as that calculated with m_1 and m_2 using (2.8).

$$\epsilon_0=e^4m^*/(2\hbar^2\kappa^2)=-0.029 \text{ ev},\quad m^*=0.31m. \tag{5.4}$$

In this case all the $F^{(i)}$ become identical, say F, and satisfy the simple hydrogenic equation

$$\left(-\frac{\hbar^2}{2m^*}\nabla^2-\frac{e^2}{\kappa r}-\epsilon\right)F(\mathbf{r})=0. \tag{5.5}$$

At this point it should be noted that the measured ionization energy of phosphorus donor states is[10]

$$\epsilon_{\text{expt}}=-0.044 \text{ ev}, \tag{5.6}$$

substantially larger than the -0.029 ev calculated in the effective mass formalism with the measured m_1 and m_2. Thus we require the s-like solution of (5.5) for a value of ϵ which lies substantially below the lowest eigenvalue. This solution, if it were continued to the origin would diverge there.

To study this function let us first introduce the "Bohr radius" of (5.5) as unit of length:

$$a^*=\hbar^2\kappa/m^*e^2=21\times10^{-8} \text{ cm},\quad r/a^*=x, \tag{5.7}$$

and ϵ_0, the "Rydberg" of (5.5), as unit of energy:

$$\epsilon/\epsilon_0=\epsilon'\equiv 1/n^2. \tag{5.8}$$

In the present case,

$$n=(0.029/0.044)^{\frac{1}{2}}=0.81. \tag{5.9}$$

The solution of (5.5) is then given by

$$F(x)=A(n/2x)W_{n,\frac{1}{2}}(2x/n), \tag{5.10}$$

where W is the Whittaker function[11] and A is a normalization constant. When $|1-n|\ll1$ this function has the following limiting behavior:

$x\rightarrow0$:

$$F(x)=Ae^{-x/n}\left[\left(\frac{1-n}{2x}\right)-(1-n)\log2x+1\right], \tag{5.11}$$

$x\rightarrow\infty$:

$$F(x)=Ae^{-x/n}(2x/n)^{n-1}.$$

When $F(x)$ is normalized over all space, one finds $A^2\approx0.7$.

The choice of the bounding surface between Ω_i and Ω_e is determined by the following considerations: It must not be too close to the origin, since the effective mass formalism with the asymptotic potential $-e^2/\kappa r$ would then break down in Ω_e. On the other hand it cannot be too far from the origin since then the integration problem would be insuperable in Ω_i. A reasonable compromise is to take Ω_i as the Wigner-Seitz sphere enclosing the impurity atom. This has a radius

$$\begin{aligned}a&=(3\Omega/8\pi)^{\frac{1}{3}}=1.68\times10^{-8} \text{ cm}\\&=0.08a^*.\end{aligned} \tag{5.12}$$

In the previous sections we had assumed that $F(x)$ was the normalized solution of the effective mass equation, regular at the origin. With our average mass m^* this corresponds to

$$F_{\text{reg}}(x)=e^{-x}/\sqrt{\pi}. \tag{5.13}$$

The present normalized $F(x)$, Eq. (5.10), is much larger than $F_{\text{reg}}(x)$ at the bounding surface. In fact from (5.10) and (5.13) one finds

$$[F(a)/F_{\text{reg}}(a)]^2\sim10, \tag{5.14}$$

a result which we shall use later in our revised estimate of $|\psi(0)|^2$.[12]

For purposes of joining, it is also of interest to evaluate the logarithmic derivative of $F(x)$ at a. We find

$$F'(a)/F(a)=-8.0a^{*-1}=-0.37\times10^8 \text{ cm}^{-1}. \tag{5.15}$$

It may be noted that while the logarithmic derivative is very large on a scale appropriate to the donor orbit (a^*), it is quite moderate on an atomic scale (10^{-8} cm).

(b) Interior Region, Ω_i

In the case of phosphorus the effect of the additional potential $U(\mathbf{r})$ on the wave function in Ω_i can be treated by perturbation methods. To zeroth order the wave function with the correct symmetry properties is

$$\psi_0=B\sum_{i=1}^{6}\psi(\mathbf{k}^{(i)},\mathbf{r}), \tag{5.16}$$

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[10] Morin, Maita, Shulman, and Hannay, Phys. Rev. **96**, 833(A) (1954).

[11] E. T. Whittaker and G. N. Watson, *Modern Analysis* (Cambridge University Press, New York, 1945), p. 337.

[12] The result (5.14) depends of course on the choice of the joining point a, but this dependence is not overly critical. An increase (decrease) of a by 20 percent would decrease (increase) (5.14) by about 25 percent.

where B is a constant [see (2.11)]. Because of its high symmetry, ψ_0 is predominantly s-like in Ω_i. The perturbation due to the donor atom is also nearly spherical, so that no serious error is incurred by treating the entire problem as having rotational symmetry.

Let us call the radial functions with and without perturbation

$$R(r)\equiv r\psi(r),\quad R_0(r)=r\psi_0(r), \tag{5.17}$$

respectively. It is convenient to choose $\psi(0)=\psi_0(0)$. Since the difference between the energy parameters of R and R_0 is quite negligible compared to $U(r)$, it follows directly from the Schrödinger equation for R and R_0 that

$$\begin{aligned} R_0(r)\frac{dR(r)}{dr}-R(r)\frac{dR_0(r)}{dr}&=\frac{2m}{\hbar^2}\int_0^r U(r')RR_0dr' \\ &\approx\frac{2m}{\hbar^2}\int_0^r U(r')R_0^2dr' \\ &=-\frac{2me^2}{\hbar^2}\int_0^r\frac{f(r')}{r'}R_0^2dr', \end{aligned} \tag{5.18}$$

where $f(r)$ is defined in (5.1). At $r=a$ we may write this as

$$\left(\frac{1}{R}\frac{dR}{dr}-\frac{1}{R_0}\frac{dR_0}{dr}\right)_{r=a} \cong-\bar{f}\left[\frac{2me^2}{\hbar^2}\int_0^a\frac{R_0^2}{r'}dr'\Big/R_0^2(a)\right], \tag{5.19}$$

where $\bar{f}$ is an average value of f. We have estimated the square bracket with an s-like Si function giving a value of 2.5×10^8 cm^{-1}. Since $f\approx1/\kappa$ at a and increases inward a choice of $\bar{f}\approx2/\kappa$ is not unreasonable. This gives for the right hand side of (5.19) a value of -0.4×10^8 cm^{-1}.

The agreement of this very rough estimate with (5.15) is surely fortuitous. But it does at least show that the change of logarithmic derivative (5.15), calculated from the outside, agrees in order of magnitude with that obtained by integrating the Schrödinger equation from the donor atom outwards.

To find $|\psi(0)|^2$ it is also necessary to have an estimated $\psi(a)/\psi_0(a)$ [see Eq. (6.1)]. Unfortunately there is considerable uncertainty in estimating this quantity. However, a reasonable bound may be obtained as follows. Let $\bar{r}$ be the last node of R_0 before a. Then (5.18) becomes

$$-R(\bar{r})\frac{dR_0(\bar{r})}{d\bar{r}}=-\frac{2me^2}{\hbar^2}\int_0^{\bar{r}}\frac{f(r)}{r}R_0^2dr,$$

which may be written

$$\frac{R(\bar{r})}{R_0(a)}=\frac{2me^2}{\hbar^2}\int_0^{\bar{r}}\frac{f(r)}{r}R_0^2dr\Big/\left[R_0(a)\left(\frac{dR_0(r)}{dr}\right)_{\bar{r}}\right]. \tag{5.20}$$

The difference between R and R_0 are of the order of magnitude of $R(\bar{r})$, since $R_0(\bar{r})$ vanishes. Therefore (5.20) is an estimate of the quantity $[\psi(a)-\psi_0(a)]/\psi_0(a)$. Further transformations give

$$\begin{aligned} \left|\frac{\psi(a)-\psi_0(a)}{\psi_0(a)}\right| &\approx\frac{2me^2}{\hbar^2}\left|\frac{\int_0^{\bar{r}}\frac{f(r)}{r}R_0^2dr}{R_0(a)(dR_0/dr)_{\bar{r}}}\right| \\ &\lessapprox\frac{2me^2}{\hbar^2}\left|\frac{\int_0^{a}\frac{f(r)}{r}R_0^2dr}{R_0(a)(dR_0/dr)_{\bar{r}}}\right| \\ &=\left|\frac{R_0(a)}{(dR_0/dr)_{\bar{r}}}\left[\frac{1}{R}\frac{dR}{dr}-\frac{1}{R_0}\frac{dR_0}{dr}\right]_a\right| \\ &=\frac{R_0(a)}{(dR_0/dr)_{\bar{r}}}(0.37\times10^8\text{ cm}^{-1}), \end{aligned} \tag{5.21}$$

from (5.19) and (5.15). Using the same function as was used to estimate (5.19), we find

$$\left|\frac{\psi(a)-\psi_0(a)}{\psi_0(a)}\right|\lessapprox0.15,$$

or

$$\psi(a)/\psi_0(a)=1\pm0.15. \tag{5.22}$$

We see that the deviation from 1 is not large. Since we have chosen $\psi(0)=\psi_0(0)$, we therefore have

$$\psi(0)/\psi(a)\approx\psi_0(0)/\psi_0(a). \tag{5.23}$$

Similarly, in the effective mass formalism, we find

$$\begin{aligned} \psi_{\text{reg}}(0)/\psi_{\text{reg}}(a)&=(\psi_0(0)/\psi_0(a))\frac{F_{\text{reg}}(0)}{F_{\text{reg}}(a)} \\ &\approx\psi_0(0)/\psi_0(a), \end{aligned} \tag{5.24}$$

where "reg" indicates the function obtained with the regular solution of the effective mass equation (Secs. 2–4). Hence, finally,

$$\psi(0)/\psi(a)\approx\psi_{\text{reg}}(0)/\psi_{\text{reg}}(a). \tag{5.25}$$

(c) Joining the Solutions

In principle we should have calculated $R'(a)/R(a)$ from the inside and then have adjusted the energy to get the same logarithmic derivative from the outside. Here we have actually side-stepped the joining problem by using the observed energy for our outside wave function, and therefore had to be content to verify that this could well join smoothly with the interior solution.

We may mention here one more correction. The orthogonality of the six functions $F^{(i)}(\mathbf{r})\psi(\mathbf{k}^{(i)},\mathbf{r})$, which

TABLE II. Atomic wave functions at the origin, and ionization energy of the donor state.

Element	$\psi_{\text{atomic}}^2(0)$ (10^{24} cm^{-3})	Ionization energy of donor (ev)
P	$\sim$ 44	0.044
As	$\sim$110	0.049
Sb	$\sim$110	0.039
Li	1.7	0.033

was used in establishing (2.12), depended on having slowly varying functions $F^{(i)}(\mathbf{r})$. This is no longer the case (particularly near $\mathbf{r}=0$) and hence the orthogonality no longer holds so well. However, the main Fourier components of $F(\mathbf{r})$ still correspond to rather long wavelengths so that the violation of orthogonality should not be too serious.

6. FINAL ESTIMATES FOR $\psi^2(0)$

Phosphorus

Combining our results we obtain

$$\psi^2(0)=\left[\frac{\psi^2(0)/\psi^2(a)}{\psi_{\text{reg}}^2(0)/\psi_{\text{reg}}^2(a)}\right]\left(\frac{\psi^2(a)}{\psi_{\text{reg}}^2(a)}\right)|(\psi_{\text{reg}}^2(0)|$$

$$\approx 1\times 10\times 0.082\times 10^{24}\ \text{cm}^{-3}$$

$$\approx 0.82\times 10^{24}\ \text{cm}^{-3} \qquad (6.1)$$

[see (5.25), (5.14), and (4.3)]. This is to be compared to the experimental value of 0.44×10^{24} cm^{-3}. It will be clear from the crudeness of the estimates in previous sections, that our results can only claim to be valid to within perhaps a factor of five. In view of this, we feel confident that the hyperfine splitting in phosphorus-doped Si can be interpreted as being due to electrons in the usual donor states.

Other Donors

For As and Sb it is considerably more difficult to calculate the wave function in the vicinity of the donor, since the perturbation is much more violent. However important factors are certainly the ionization energy of the donor state, and the values of the atomic wave functions at the origin. These are listed in Table II.[13] For As both the atomic function and the binding are greater than in phosphorus so that we would definitely expect a larger $|\psi^2(0)|$, as is observed (about a factor of 4, see Table I). In Sb, the atomic function is larger, but the binding is less, so that it is hard to say whether the $|\psi(0)|^2$ is greater or less than with phosphorus. However, the fact that the binding is smaller for Sb than for As may account for the fact that the observed $|\psi(0)|^2$ is smaller in Sb than in As.

Finally for Li both the atomic $|\psi(0)|^2$ and the ionization energy are quite low. Very roughly, we would therefore expect a $|\psi(0)|^2$ for lithium smaller than that for phosphorus by a factor of the order of magnitude of

$$\frac{|\psi_{\text{atomic}}(0)|_{\text{Li}}^2}{|\psi_{\text{atomic}}(0)|_{\text{P}}^2}\times\frac{1}{10}=0.004.$$

The 1/10 arises because for Li the ratio (5.13) will be of the order unity. This factor is small enough to account for the fact that Honig and Kip[14] have observed a line without hfs with Li-doped Si.

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Note added in proof.—Honig and Kip[14] and Honig [Phys. Rev. **96**, 234 (1954)] have reported widths of resonance lines associated with Li and As donors in Si. A theoretical study of these widths, which will shortly be published, indicates that very probably $|\psi(k^{(1)},0)|^2=200\pm 50$ [see. Eq. (3.12)], corresponding to $2|\alpha|^2\sim\frac{1}{2}$. This reduces our theoretical estimate (6.1) by a factor of 200/370 giving $[\psi^2(0)]_{\text{theor}}\approx 0.4\times 10^{-24}$ cm^{-3}, in the case of P donors. The agreement with the experimental value $[\psi^2(0)]_{\text{exp}}=0.44\times 10^{24}$ cm^{-3}, is thereby improved.

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[13] The values of $\psi_{\text{atomic}}^2(0)$ have been estimated by methods similar to those leading to (3.8). Those of the ionization energies are taken from reference 9.

[14] A. Honig and A. F. Kip, Phys. Rev. **95**, 1686 (1954).