time axis could be detected. Hence, one concludes that if the deformation introduced changes in the elastic constants C_{33} or C_{44} these changes must be less than one or two percent for strains up to 10^{-2} radian. Such a result is to be expected since the appearance of slip bands on the surface indicates that the deformation was confined to numerous very narrow bands. Within these bands one might expect very different elastic modulii but since their total thickness is small compared to the total thickness of undisturbed crystal, the sound wave spends most of its time traveling in an undeformed lattice.

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Motion of Electrons and Holes in Perturbed Periodic Fields

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A new method of developing an "effective-mass" equation for electrons moving in a perturbed periodic structure is discussed. This method is particularly adapted to such problems as arise in connection with impurity states and cyclotron resonance in semiconductors such as Si and Ge. The resulting theory generalizes the usual effective-mass treatment to the case where a band minimum is not at the center of the Brillouin zone, and also to the case where the band is degenerate. The latter is particularly striking, the usual Wannier equation being replaced by a set of coupled differential equations.

I. INTRODUCTION

IN recent years, there has been a renewed interest in the problem of motion of charge carriers in perturbed periodic fields. The principle tool has been the so-called "effective mass" theory, which replaces the effect of the periodic field by a mass tensor, the elements of which are determined by the unperturbed band structure.[1] The rigorous theory has so far been limited almost entirely to the case where the relevant band is simple and has its lowest point at the center of the first Brillouin zone. In this form it is not directly applicable to the treatment of semiconductors such as Si and Ge. For these substances, recent "cyclotron" resonance experiments[2] indicate that both the conduction band and the valence band are not of this simple form. The conduction band for Si does not have its minimum at $\mathbf{k}=0$, but has six equivalent minima along the (100) directions of the first Brillouin zone. Similarly the conduction band in Ge consists of eight equivalent minima along (111) directions. In both these cases the principal curvatures —which determine the effective mass tensor—are known with some accuracy. For the valence band, the situation is rather more complex. The top of the valence band is at $\mathbf{k}=0$, but this is also a degeneracy point, i.e., there are several eigenfunctions with the same energy at this point. The theory of band structure in the neighborhood of such a degeneracy is due to Shockley.[3] There is in addition the complication that for such degenerate functions the spin-orbit coupling must be taken into account.[4]

We have investigated the form of the effective mass theory for these more complicated situations. For clarity, we begin with a new treatment of the case of a simple band with its lowest point at $\mathbf{k}=0$. This treatment, we believe, expresses the results of the effective mass theory in particularly compact form, and also has the advantage of being easily generalized to more complicated cases. (An alternative derivation more closely related to the work of Adams[1] is described in Appendix A. This derivation is perhaps simpler for impurity states in nondegenerate bands but is not as easily generalized for the cases of cyclotron resonance and degenerate bands.) In Sec. II, this theory will be developed for the discussion of impurity centers and "cyclotron" resonance. In Sec. III, the changes necessary for the "many-valley" case (i.e., the conduction band of Si or Ge) will be discussed. Section IV then extends the treatment to degenerate bands without spin-orbit coupling, and finally in Sec. V the modifications brought about by spin-orbit coupling are introduced.

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II. SIMPLE BANDS

(A) Impurity Centers

We begin by considering an impurity center in a substance with a simple band, the minimum of which is at $\mathbf{k}=0$. Let H_0 be the Hamiltonian of the electron in the periodic potential, and let U be the additional potential due to the impurity. We shall assume in what follows that the fractional change of U over a unit cell is small, since it is only in this case that an effective mass theory might be expected to hold. The eigenfunctions of H_0 (the Bloch functions) will be denoted by $\psi_{n\mathbf{k}}$ and the corresponding eigenvalues by $\epsilon_n(\mathbf{k})$, n labelling the band and $\mathbf{k}$ wandering through the first Brillouin zone of the crystal. Thus

$$H_0\psi_{n\mathbf{k}}=\epsilon_n(\mathbf{k})\psi_{n\mathbf{k}}. \tag{II.1}$$

To find the impurity state wave function ψ we must solve the Schrödinger equation

$$(H_0+U)\psi=\epsilon\psi. \tag{II.2}$$

In order to proceed further, it is necessary to choose some complete set of functions in which to expand ψ. Rather than taking the Bloch functions or Wannier functions corresponding to H_0, as has been done previously,[1] we choose a set as follows. Write the Bloch functions as

$$\psi_{n\mathbf{k}}=e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}, \tag{II.3}$$

where $u_{n\mathbf{k}}$ is a function of $\mathbf{r}$ with the lattice periodicity. The $\psi_{n\mathbf{k}}$ form, of course, a complete set of functions, in which any wave function may be expanded. Consider now the set of functions

$$\chi_{n\mathbf{k}}=e^{i\mathbf{k}\cdot\mathbf{r}}u_{n0}. \tag{II.4}$$

We assert that these form a complete orthonormal set if the $\psi_{n\mathbf{k}}$ do. Imagine any function $f(\mathbf{r})$ expanded in the $\psi_{n\mathbf{k}}$:

$$f(\mathbf{r})=\sum_n\int d\mathbf{k}g_n(\mathbf{k})\psi_{n\mathbf{k}}=\sum_n\int d\mathbf{k}g_n(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}. \tag{II.5}$$

On the other hand, any periodic function can be expressed in terms of the Bloch functions at the bottom of the band, which are complete with respect to periodic functions. Therefore

$$u_{n\mathbf{k}}=\textstyle\sum_n b_{nn'}(\mathbf{k})u_{n'0}, \tag{II.6}$$

which yields, when substituted in (II.5), the result

$$f(\mathbf{r})=\sum_n\int d\mathbf{k}\bar{g}_n(\mathbf{k})\chi_{n\mathbf{k}},$$

with

$$g_n(\mathbf{k})=\sum_{n'}g_{n'}(\mathbf{k})b_{n'n}(\mathbf{k}).$$

The orthonormality is also easily established. For the Bloch waves this means

$$(\psi_{n\mathbf{k}},\psi_{n'\mathbf{k}'})=\int_{\substack{\text{entire}\\ \text{crystal}}}\psi_{n\mathbf{k}}^*\psi_{n'\mathbf{k}'}d\mathbf{r}=\delta_{nn'}\delta(\mathbf{k}-\mathbf{k}'). \tag{II.7}$$

The corresponding quantity for the χ_{nk} is

$$(\chi_{n\mathbf{k}},\chi_{n'\mathbf{k}'})=\int e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}}u_{n0}^*u_{n'0}d\mathbf{r}. \tag{II.8}$$

Since $u_{n0}^*u_{n'0}$ has the lattice periodicity, we may expand it in a Fourier series, say

$$u_{n0}^*u_{n'0}=\textstyle\sum_m B_m^{nn'}e^{-i\mathbf{K}_m\cdot\mathbf{r}}, \tag{II.9}$$

where the $B_m^{nn'}$ are just numerical coefficients, and the $\mathbf{K}_m$ are the reciprocal lattice vectors. Inserting (II.9) in (II.8), we obtain

$$(\chi_{n\mathbf{k}},\chi_{n'\mathbf{k}})=(2\pi)^3\textstyle\sum_m B_m^{nn'}\delta(\mathbf{k}'-\mathbf{k}-\mathbf{K}_m). \tag{II.10}$$

However, since $\mathbf{k}'$ and $\mathbf{k}$ are both in the first Brillouin zone, $\mathbf{k}'-\mathbf{k}=\mathbf{K}_m$ is only possible if $m=0$. Thus

$$(\chi_{n\mathbf{k}},\chi_{n\mathbf{k}'})=\delta(\mathbf{k}'-\mathbf{k})B_0^{nn'}(2\pi)^3. \tag{II.11}$$

Using Fourier's theorem (with Ω the volume of the unit cell) the $B_m^{nn'}$ are given by

$$B_m^{nn'}=\frac{1}{\Omega}\int_{\text{cell}}e^{i\mathbf{K}_m\cdot\mathbf{r}}u_{n0}^*u_{n'0}d\mathbf{r},$$

$$B_0^{nn'}=\frac{1}{\Omega}\int_{\text{cell}}u_{n0}^*u_{n'0}d\mathbf{r}=\frac{1}{(2\pi)^3}\delta_{nn'}$$

from (II.7). Finally, then,

$$(\chi_{n\mathbf{k}},\chi_{n'\mathbf{k}'})=\delta(\mathbf{k}'-\mathbf{k})\delta_{nn'}, \tag{II.12}$$

which is the required orthonormality.

We now make in (II.2) the Ansatz

$$\psi=\sum_{n'}\int d\mathbf{k}'A_{n'}(\mathbf{k}')\chi_{n'\mathbf{k}'}, \tag{II.13}$$

which gives the equation

$$\sum_{n'}\int d\mathbf{k}'(n\mathbf{k}|H_0+U|n'\mathbf{k}')A_{n'}(\mathbf{k}')=\epsilon A_n(\mathbf{k}). \tag{II.14}$$

The notation $(n\mathbf{k}|H_0+U|n'\mathbf{k}')$ means matrix elements with respect to the $\chi_{n\mathbf{k}}$. These may be evaluated in the following manner. For H_0 we have

$$\begin{aligned}(n\mathbf{k}|H_0|n'\mathbf{k}')&=\int e^{-i\mathbf{k}\cdot\mathbf{r}}u_{n0}^*H_0e^{i\mathbf{k}'\cdot\mathbf{r}}u_{n'0}d\mathbf{r}\\&=\int e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}}u_{n0}^*\left(H_0+\frac{\mathbf{k}'\cdot\mathbf{p}}{m}+\frac{k'^2}{2m}\right)u_{n'0}d\mathbf{r}\\&=\int e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}}u_{n0}^*\left(\epsilon_{n'}+\frac{\mathbf{k}'\cdot\mathbf{p}}{m}+\frac{k'^2}{2m}\right)u_{n'0}d\mathbf{r}.\qquad\text{(II.15)}\end{aligned}$$

Here $\epsilon_{n'}=\epsilon_{n'}(0)$, the energy at the bottom of the nth band, and $\mathbf{p}$ is the momentum operator $-i\boldsymbol{\nabla}$.[5] Since the entire factor multiplying $e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}}$ is periodic, the same argument that lead from (II.8) to (II.12) yields

$$\begin{aligned}(n\mathbf{k}|H_0|n'k')&=\frac{(2\pi)^3}{\Omega}\delta(\mathbf{k}-\mathbf{k}')\int u_{n0}^*\left(\epsilon_{n'}+\frac{\mathbf{k}'\cdot\mathbf{p}}{m}+\frac{k'^2}{2m}\right)u_{n'0}d\mathbf{r}\\&=\delta(\mathbf{k}-\mathbf{k}')\left[\left(\epsilon_n+\frac{k^2}{2m}\right)\delta_{nn'}+\frac{k_\alpha p_{nn'}{}^\alpha}{m}\right].\qquad\text{(II.16)}\end{aligned}$$

In (II.16), a summation over $\alpha=x,y,z$ is implied, and the quantity $p_{nn'}{}^\alpha$ is defined by

$$p_{nn'}{}^\alpha=\frac{(2\pi)^3}{\Omega}\int_{\text{cell}}u_{n0}^*\left(\frac{1}{i}\nabla_\alpha\right)u_{n'0}d\mathbf{r}.\qquad\text{(II.17)}$$

The $p_{nn'}{}^\alpha$'s are just the momentum matrix elements at the bottom of the band. They have the following properties:

$$p_{nn}{}^\alpha=0,\quad p_{nn'}{}^\alpha=p_{n'n}{}^\alpha=(p_{nn'}{}^\alpha)^*.\qquad\text{(II.18)}$$

The former follows from the fact that $p_{nn}{}^\alpha(\mathbf{k})=m\partial\epsilon_n(\mathbf{k})/\partial k_\alpha$, which is zero at the minimum of a band. The latter follows if—as in Si and Ge—a center of symmetry exists in the crystal. These results are of use in what follows.

For the matrix elements of U we proceed similarly:

$$\begin{aligned}(n\mathbf{k}|U|n'\mathbf{k}')&=\int e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}}Uu_{n0}^*u_{n'0}d\mathbf{r}\\&=\sum_m\int e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}}B_m{}^{nn'}e^{-i\mathbf{K}_m\cdot\mathbf{r}}Ud\mathbf{r},\end{aligned}$$

by (II.9). This may be written

$$(n\mathbf{k}|U|n'\mathbf{k}')=(2\pi)^3\textstyle\sum_m B_m{}^{nn'}\mathcal{U}(\mathbf{k}-\mathbf{k}'+\mathbf{K}_m),\qquad\text{(II.19)}$$

$$\mathcal{U}(\mathbf{k})\equiv\frac{1}{(2\pi)^3}\int d\mathbf{r}e^{-i\mathbf{k}\cdot\mathbf{r}}U(\mathbf{r}),\qquad\text{(II.20)}$$

the Fourier transform of U. It is at this point that we make the assumption that U is a "gentle" potential. If this is so, only the terms with $m=0$ in (II.19) need be kept. The reason for this is the following. As will be seen later, the solution of our problem with this assumption leads to values of $\mathbf{k}$ and $\mathbf{k}'$ much smaller than any $\mathbf{K}_m$ with $m\neq0$. Therefore, the terms in (II.19) with $m\neq0$ contain much higher Fourier components than those with $m=0$, and are thus much smaller. For example, for a Coulomb-like potential the error involved is of the order of the square of the ratio of the lattice spacing to the dimensions of the impurity state. Equation (II.19) then becomes

$$\begin{aligned}(n\mathbf{k}|U|n'\mathbf{k}')&=(2\pi)^3B_0{}^{nn'}\mathcal{U}(\mathbf{k}-\mathbf{k}')\\&=\delta_{nn'}\mathcal{U}(\mathbf{k}-\mathbf{k}').\qquad\text{(II.21)}\end{aligned}$$

From (II.16) and (II.21), (II.14) becomes

$$\left(\epsilon_n+\frac{k^2}{2m}\right)A_n(\mathbf{k})+\sum_{n'\neq n}\frac{k_\alpha p_{nn'}{}^\alpha}{m}A_{n'}(\mathbf{k})+\int d\mathbf{k}'\mathcal{U}(\mathbf{k}-\mathbf{k}')A_n(\mathbf{k}')=\epsilon A_n(\mathbf{k}).\qquad\text{(II.22)}$$

Equation (II.22) is not yet of the form we want, since it still contains terms involving $p_{nn'}{}^\alpha$, which represent a coupling between bands. These terms are proportional to $\mathbf{k}$, however, and since we can expect the effective mass theory to hold only if the important $\mathbf{k}$'s are small, it is natural to regard these coupling terms also as small quantities of the first order in $\mathbf{k}$. Now in the effective mass theory one works correctly to terms in k^2, the theory being no longer rigorously valid for higher powers of $\mathbf{k}$, and therefore we shall treat (II.22) accurately up to and including quadratic terms in $\mathbf{k}$, but no further.

We proceed as follows. Since the interband matrix elements $p_{nn'}{}^\alpha$ are causing the trouble, we remove them to the first order by a canonical transformation T. That is, we put

$$A_n(\mathbf{k})=\sum_{n'}\int d\mathbf{k}'(n\mathbf{k}|T|n'\mathbf{k}')B_{n'}(\mathbf{k}'),\qquad\text{(II.23)}$$

and try to find T such that the equations for the $B_n(\mathbf{k})$ contain no interband elements to the first order. It is convenient to regard this somewhat more abstractly, and write (II.22) as

$$HA=\epsilon A,\qquad\text{(II.24)}$$

and (II.23) as

$$A=TB\equiv e^SB.\qquad\text{(II.25)}$$

Substitution of (II.25) in (II.24) yields

$$(e^{-S}He^S)B=\epsilon B\equiv\bar{H}B.\qquad\text{(II.26)}$$

Clearly,

$$\bar{H}=H+(H,S)+\tfrac{1}{2}((H,S),S)+\cdots.\qquad\text{(II.27)}$$

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[5] We choose units such that $\hbar=1$.

Let us write $H=H^{(0)}+H^{(1)}+U$, where

$$(n\mathbf{k}|H^{(0)}|n'\mathbf{k}')=\left(\epsilon_n+\frac{k^2}{2m}\right)\delta_{nn'}\delta(\mathbf{k}-\mathbf{k}'),$$

$$(n\mathbf{k}|H^{(1)}|n'\mathbf{k}')=\frac{k_\alpha p_{nn'}{}^{\alpha}}{m}\delta(\mathbf{k}-\mathbf{k}'),\qquad\text{(II.28)}$$

$$(n\mathbf{k}|U|n'k')=\mathcal{U}(\mathbf{k}-\mathbf{k}')\delta_{nn'}.$$

Then

$$\bar{H}=H^{(0)}+U+H^{(1)}+(H^{(0)},S)+(H^{(1)},S)$$
$$+\tfrac{1}{2}((H^{(0)}S),S)+(U,S)+\tfrac{1}{2}((U,S),S)+\cdots,\qquad\text{(II.29)}$$

the omitted terms being of order S^3 or more. By choosing S such that

$$H^{(1)}+(H^0,S)=0,\qquad\text{(II.30)}$$

we succeed in eliminating the interband transitions to first order in $\mathbf{k}$. Going back to the $\chi_{n\mathbf{k}}$ representation, we see at once that

$$(n\mathbf{k}|S|n'\mathbf{k}')=-\frac{k_\alpha p_{nn'}{}^{\alpha}\delta(\mathbf{k}-\mathbf{k}')}{m\omega_{nn'}},\quad n\neq n',$$
$$=0,\quad n=n'.\qquad\text{(II.31)}$$

where $\omega_{nn'}\equiv\epsilon_n-\epsilon_{n'}$. Consequently, the second order terms from $H^{(0)}$ and $H^{(1)}$ are

$$(H^{(1)},S)+\tfrac{1}{2}((H^{(0)},S),S)=\tfrac{1}{2}(H^{(1)},S),$$

which becomes

$$\tfrac{1}{2}(n\mathbf{k}|(H^{(1)},S)|n'\mathbf{k}')=\frac{k_\alpha k_\beta}{2m^2}\Bigg[\sum_{\substack{n''\\ n''\neq n,\,n'}}p_{nn''}{}^{\alpha}p_{n''n'}{}^{\beta}$$
$$\times\left(\frac{1}{\omega_{nn''}}+\frac{1}{\omega_{n'n''}}\right)\Bigg]\delta(\mathbf{k}-\mathbf{k}')\qquad\text{(II.32)}$$

in the $\chi_{n\mathbf{k}}$ representation. The correction terms to U are also easily found. Consider first $(n\mathbf{k}|(U,S)|n'\mathbf{k}')$. Using (II.31) and (II.28), we obtain at once

$$(n\mathbf{k}|(U,S)|n'\mathbf{k}')$$
$$=(k_\alpha-k_\alpha')\mathcal{U}(\mathbf{k}-\mathbf{k}')p_{nn'}{}^{\alpha}/m\omega_{nn'},\quad n\neq n',\qquad\text{(II.33)}$$
$$=0,\quad n=n'.$$

(II.33) has only interband matrix elements, and they are of first order in $\mathbf{k}$. At first sight, it would seem therefore that we have made little progress over (II.22). The difference is, however, in the order of magnitude of these new interband elements. These are reduced by a factor of the order of $\mathcal{U}(\bar{k})/\bar{\omega}$, where $\mathcal{U}(\bar{k})$ is a typical Fourier component of U and $\bar{\omega}$ a typical interband separation. This ratio is quite small, a typical value being perhaps 1/25, say, for a donor electron in Si. Since this must come in squared—there being no diagonal elements—we see that the contribution to the Hamiltonian is really quite negligible. Another way—easily seen from (II.33)—of stating the result is that the error committed in dropping these terms is of the order of the square of the ratio of the lattice spacing a to the extent of the impurity state a_i. Similarly, the next term $\frac{1}{2}((U,S),S)$ is again reduced over (U,S) by a factor S, which is of the order of a typical k describing the impurity state, times a. Since $\bar{k}\sim 1/a_i$, this again gives a factor of a/a_i, so that the error is again of the order of this ratio squared. Thus in the limit of very extended impurity states (II.22) becomes

$$\left(\epsilon_n+\frac{k^2}{2m}+\frac{k_\alpha k_\beta}{m^2}\sum_{\substack{n''\\ n''\neq n}}\frac{p_{nn''}{}^{\alpha}p_{n''n}{}^{\beta}}{\omega_{nn''}}\right)B_n(\mathbf{k})$$
$$+\int\mathcal{U}(\mathbf{k}-\mathbf{k}')B_n(\mathbf{k}')d\mathbf{k}=\epsilon B_n(\mathbf{k}').$$

In this equation we have neglected terms of the order k^3 and interband elements of order k^2, since they would lead to higher order terms when eliminated. The coefficient of $B_n(\mathbf{k})$ on the left-hand side is just exactly the expansion of $\epsilon_n(\mathbf{k})$ to second order. This must be so, since if $U\equiv 0$ this is exactly the equation for determining $\epsilon_n(\mathbf{k})$ to second order. This may also be verified directly by using the f-sum rule,

$$\frac{2}{m}\sum_{n''\neq n}\frac{p_{nn''}{}^{\alpha}(\mathbf{k})p_{n''n}{}^{\beta}(\mathbf{k})}{\epsilon_{n''}(\mathbf{k})-\epsilon_n(\mathbf{k})}=\delta_{\alpha\beta}-m\frac{\partial^2\epsilon_n(\mathbf{k})}{\partial k_\alpha\partial k_\beta},\qquad\text{(II.34)}$$

for $\mathbf{k}=0$. Therefore, we may write

$$\epsilon_n(\mathbf{k})B_n(\mathbf{k})+\int\mathcal{U}(\mathbf{k}-\mathbf{k}')B_n(\mathbf{k}')d\mathbf{k}'=\epsilon B_n(\mathbf{k}),\qquad\text{(II.35)}$$

where it is understood that $\epsilon_n(\mathbf{k})$ is to be expanded to second order in $\mathbf{k}$. Equation (II.35) is the well-known effective-mass equation, written, however, in "momentum" space. To get the more usual formulation, we introduce a function

$$F_n(\mathbf{r})\equiv\int e^{i\mathbf{k}\cdot\mathbf{r}}B_n(\mathbf{k})d\mathbf{k},\qquad\text{(II.36)}$$

the integration, as always, being over the first Brillouin zone. Inverting (II.36), we obtain

$$B_n(\mathbf{k})=\frac{\Omega}{(2\pi)^3}\sum_m e^{-i\mathbf{k}\cdot\mathbf{R}_m}F_n(\mathbf{R}_m),\qquad\text{(II.37)}$$

since $B_n(\mathbf{k})$ is periodic in $\mathbf{k}$, $\mathbf{R}_m$ being the vector to the lattice point m. Upon using this definition, (II.35) becomes simply

$$\epsilon_n(-i\boldsymbol{\nabla})F_n(\mathbf{r})+\int d\mathbf{r}'\Delta(\mathbf{r}-\mathbf{r}')U(\mathbf{r}')F_n(\mathbf{r}')=\epsilon F_n(\mathbf{r}),$$

where

$$\Delta(\mathbf{r}-\mathbf{r}')\equiv\frac{1}{(2\pi)^3}\int d\mathbf{k}e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')},$$

and the expression $\epsilon_n(-i\nabla)$ meaning that $\mathbf{k}$ is to be replaced by $-i\nabla$ in the expression for $\epsilon_n(\mathbf{k})$. Clearly

$$\int_{\text{all space}} \Delta(\mathbf{r})d\mathbf{r}=1,$$

and $\Delta(\mathbf{r})$ drops off as $|\mathbf{r}|^3$ at large distances. Since the only length in $\Delta(\mathbf{r})$ is the lattice spacing, it is clear that $\Delta(\mathbf{r})$ is a δ-like function of extension $\sim a$. Therefore, in any integrals such as the above, where Δ is multiplied by functions which do not vary appreciably over a unit cell Δ behaves as a δ function, and we have

$$[\epsilon_n(-i\nabla)+U(\mathbf{r})]F_n(\mathbf{r})=\epsilon F_n(\mathbf{r}). \qquad \text{(II.38)}$$

One may easily see—by taking for $U(r)$ a Coulomb potential cutoff gently at the origin, say—that the error involved in replacing Δ by δ is of the order of $(a/a_i)^2$ again.

Since $A_n(\mathbf{k})=B_n(\mathbf{k})+O(a/a_i)$, the leading term in the wave function becomes, from (II.13):

$$\psi=\sum_n \int d\mathbf{k}B_n(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{r}}u_{n0}(\mathbf{r})$$
$$=\sum_n F_n(\mathbf{r})u_{n0}(\mathbf{r})=\sum_n F_n(\mathbf{r})\psi_{n0}(\mathbf{r}). \qquad \text{(II.39)}$$

Equation (II.38) contains no interband coupling, so that if we are interested in, say, electrons in the conduction band we get only one term

$$\psi=F(\mathbf{r})\psi_c(\mathbf{r}), \qquad \text{(II.40)}$$

where $F(\mathbf{r})$ is a solution of (II.38) for $\epsilon_n(\mathbf{k})$ appropriate to the conduction band, and ψ_c is the Bloch function at the bottom of the conduction band.[6]

If there is a place where the potential changes considerably within a cell—as for example in the cell containing the impurity atom itself—then of course (II.38) is no longer valid. One may easily see, however, by considering the effect of an added short-range potential of the form

$$ce^{-r/\alpha}/r,$$

where $\alpha\sim a$, that (II.38) is still valid in regions of space sufficiently distant from the region of violent change.

(B) External Magnetic Field

We now consider the case where an electron in such a simple band is subjected to an homogeneous magnetic field. We shall take this field in the z direction and assume that the crystal is arbitrarily oriented with respect to it. To avoid complications of many indices, and also for convenience in later work, we shall choose a specific gauge for the vector potential. We shall choose

$$A_x=-\mathcal{H}y, \quad A_y=0, \quad A_z=0, \qquad \text{(II.41)}$$

where $\mathcal{H}$ is the magnitude of the external field. With this gauge, the Hamiltonian becomes

$$H=H_0+\frac{s}{m}yp_x+\frac{s^2}{2m}y^2, \qquad \text{(II.42)}$$

where

$$s\equiv e\mathcal{H}/c.$$[7]

In order to find the matrix elements of H in the $\chi_{n\mathbf{k}}$ representation, we need those of yp_x and y^2. Thus

$$(n\mathbf{k}|yp_x|n'\mathbf{k}')$$
$$=\int e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}}u_{n0}{}^*y\left(k_x+\frac{1}{i}\nabla_x\right)u_{n'0}d\mathbf{r}$$
$$=\frac{1}{i}\frac{\partial}{\partial k_y}\int e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}}u_{n0}{}^*\left(k_x+\frac{1}{i}\nabla_x\right)u_{n'0}d\mathbf{r}$$
$$=\frac{1}{i}\frac{\partial}{\partial k_y'}[(k_x\delta_{nn'}+p_{nn'}{}^x)\delta(\mathbf{k}'-\mathbf{k})]$$
$$=(k_x\delta_{nn'}+p_{nn'}{}^x)\frac{1}{i}\frac{\partial\delta(\mathbf{k}'-\mathbf{k})}{\partial k_y'}, \qquad \text{(II.43)}$$

as in the discussion of Eq. (II.15). Similarly,

$$(n\mathbf{k}|y^2|n'\mathbf{k}')=\int y^2e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}}u_{n0}{}^*u_{n'0}d\mathbf{r}$$
$$=\left(\frac{1}{i}\frac{\partial}{\partial k_y'}\right)^2\int e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}}u_{n0}{}^*u_{n'0}d\mathbf{r}$$
$$=-\frac{\partial^2\delta(\mathbf{k}'-\mathbf{k})}{\partial k_y'^2}\delta_{nn'}. \qquad \text{(II.44)}$$

The Hamiltonian in the $\chi_{n\mathbf{k}}$ representation is therefore

$$(n\mathbf{k}|H|n\mathbf{k}')$$
$$=\left[\left(\epsilon_n+\frac{k^2}{2m}\right)\delta_{nn'}+\frac{k_\alpha p_{nn'}{}^\alpha}{m}\right]\delta(\mathbf{k}-\mathbf{k}')$$
$$+\frac{s}{m}(k_x\delta_{nn'}+p_{nn'}{}^x)\frac{1}{i}\frac{\partial\delta(\mathbf{k}'-\mathbf{k})}{\partial k_y'}-\frac{s^2}{2m}\frac{\partial^2\delta(\mathbf{k}-\mathbf{k}')}{\partial k_y'^2}\delta_{nn'}$$
$$=\left[\left(\epsilon_n+\frac{k^2}{2m}\right)\delta(\mathbf{k}-\mathbf{k}')+\frac{sk_x}{m}\frac{1}{i}\frac{\partial\delta(\mathbf{k}'-\mathbf{k})}{\partial k_y'}\right.$$
$$\left.-\frac{s^2}{2m}\frac{\partial^2\delta(\mathbf{k}'-\mathbf{k})}{\partial k_y'^2}\right]\delta_{nn'}+\frac{1}{m}\left[k_\alpha p_{nn'}{}^\alpha\delta(\mathbf{k}-\mathbf{k}')\right.$$
$$\left.+sp_{nn'}{}^x\frac{1}{i}\frac{\partial\delta(\mathbf{k}'-\mathbf{k})}{\partial k_y'}\right]. \qquad \text{(II.45)}$$

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[6] Functions of the form of a slowly varying function times the Bloch function at the bottom of the band have been used previously by J. A. Krumhansl, Phys. Rev. **93**, 245 (1954). See also D. L. Dexter, Phys. Rev. **93**, 244 (1954).

[7] In ordinary units we may define $s=e\mathcal{H}/\hbar c$, s then having units of a reciprocal length squared. This length $L=[(\hbar c)/(e\mathcal{H})]^{+\frac{1}{2}}$ $\sim10^{-5}$ cm, under typical experimental circumstances for "cyclotron" resonance. It is therefore much larger than the lattice spacing.

The first line gives the intraband elements, and the second the interband ones. Now the interband elements are "small" in the same sense that they were in the discussion of (II.22): those proportional to k are identical with the old ones, and those proportional to s are of the same order.[8] We therefore once again make a canonical transformation, say $T'=e^{S'}$, such that these interband elements are removed to the first order. Define

$$\begin{aligned}(n\mathbf{k}|H_a|n'\mathbf{k}')&=\frac{sk_x}{m}\frac{1}{i}\frac{\partial\delta(\mathbf{k}'-\mathbf{k})}{\partial k_y'}\delta_{nn'},\\ (n\mathbf{k}|H_b|n\mathbf{k}')&=-\frac{s^2}{2m}\frac{\partial^2\delta(\mathbf{k}'-\mathbf{k})}{\partial k_y'^2}\delta_{nn'},\\ (n\mathbf{k}|H'|n'\mathbf{k}')&=\frac{1}{m}\bigg[k_\alpha p_{nn'}{}^{\alpha}\delta(\mathbf{k}-\mathbf{k}')\\ &\qquad+sp_{nn'}{}^{x}\frac{1}{i}\frac{\partial\delta(\mathbf{k}'-\mathbf{k})}{\partial k_y'}\bigg].\end{aligned}\tag{II.46}$$

Then $H=H^{(0)}+H_a+H_b+H'$, and the transformed Hamiltonian $\bar{H}$ is

$$\begin{aligned}\bar{H}&=e^{-S'}He^{+S'}\\ &=H+(H,S')+\tfrac{1}{2}((H,S'),S')+\cdots\\ &=H^{(0)}+H_a+H'+(H^{(0)},S')+H_b+(H_a,S')\\ &\qquad+(H',S')+\tfrac{1}{2}((H^0,S'),S')+\cdots.\end{aligned}\tag{II.47}$$

The interband elements are removed to first order by choosing

$$H'+(H^{(0)},S')=0,\tag{II.48}$$

after which (II.47) simplifies to

$$\bar{H}=H^{(0)}+H_a+H_b+(H_a,S')+\tfrac{1}{2}(H',S')+\cdots.\tag{II.49}$$

We shall drop the higher order terms which have been indicated by the dots. These terms will actually contribute very little under normal conditions. This may be seen easily as follows. The matrix elements of S' are essentially of the order

$$kp_{nn'}/m\omega_{nn'}.$$

Now, typically

$$k\sim\surd s,\quad p_{nn'}\sim 1/a,\quad \omega_{nn'}\sim 1/ma^2,$$

so that $S'\sim a\surd s=a/L$. The terms which are of third order in S' (those we have retained being of second order) vanish on the average, since S' is odd in $\mathbf{k}$ and the wave functions are even or odd. The fourth order terms contribute an amount of order $(a/L)^2$ compared to those we keep, since there are two extra factors of S'. Further, the interband matrix elements of the terms indicated in (II.49) contribute an amount of order $s/m\omega_{nn'}\sim(a/L)^2$. Thus the entire error made by confining ourselves to the intraband elements of the terms indicated in (II.49) is of the order $(a/L)^2$.

Under usual conditions,[7] these corrections are in fact extremely small.

Writing (II.48) in the $\chi_{n\mathbf{k}}$ representation, we obtain

$$\begin{aligned}(n\mathbf{k}|S'|n'\mathbf{k}')&=-(n\mathbf{k}|H'|n'k')/\omega_{nn'},\quad n\neq n',\\ &=0,\quad n=n'.\end{aligned}\tag{II.50}$$

We shall only be interested in the intraband matrix elements of $\bar{H}$. Thus,

$$(n\mathbf{k}|(H_a,S')|n\mathbf{k}')=0,$$

and

$$\begin{aligned}&\tfrac{1}{2}(n\mathbf{k}|(H',S')|n\mathbf{k}')\\ &=\frac{1}{m^2}\sum_{n'\neq n}\frac{1}{\omega_{nn'}}\bigg[k_\alpha k_\beta p_{nn'}{}^{\alpha}p_{n'n}{}^{\beta}\delta(\mathbf{k}-\mathbf{k}')\\ &\qquad+s(k_\alpha+k_\alpha')p_{nn'}{}^{\alpha}p_{n'n}{}^{x}\frac{1}{i}\frac{\partial\delta(\mathbf{k}'-\mathbf{k})}{\partial k_y'}\\ &\qquad\qquad-s^2p_{nn'}{}^{x}p_{n'n}{}^{x}\frac{\partial^2\delta(\mathbf{k}'-\mathbf{k})}{\partial k_y'^2}\bigg]\\ &=-\frac{1}{2m}\bigg\{k_\alpha k_\beta\bigg[\delta_{\alpha\beta}-m\bigg(\frac{\partial^2\epsilon_n(\mathbf{k})}{\partial k_\alpha\partial k_\beta}\bigg)_0\bigg]\delta(\mathbf{k}-\mathbf{k}')\\ &\qquad+s\bigg[(k_x+k_x')-m(k_\alpha+k_\alpha')\bigg(\frac{\partial^2\epsilon_n(\mathbf{k})}{\partial k_\alpha\partial k_x}\bigg)_0\bigg]\frac{1}{i}\\ &\qquad\times\frac{\partial\delta(\mathbf{k}'-\mathbf{k})}{\partial k_y'}-s^2\bigg[1-m\bigg(\frac{\partial^2\epsilon_n(\mathbf{k})}{\partial k_x^2}\bigg)_0\bigg]\frac{\partial^2\delta(\mathbf{k}'-\mathbf{k})}{\partial k_y'^2}\bigg\},\end{aligned}\tag{II.51}$$

by means of the f-sum rule (II.34). Inserting these results in (II.49), we see at once that $\bar{H}$ may be written in the form

$$\begin{aligned}&(n\mathbf{k}|\bar{H}|n\mathbf{k}')\\ &=\epsilon_n(\mathbf{k})\delta(\mathbf{k}-\mathbf{k}')+sk_\alpha\bigg(\frac{\partial^2\epsilon_n(k)}{\partial k_\alpha\partial k_x}\bigg)_0\frac{1}{i}\frac{\partial\delta(\mathbf{k}-\mathbf{k}')}{\partial k_y'}\\ &\qquad+\frac{is}{2}\bigg(\frac{\partial^2\epsilon_n(\mathbf{k})}{\partial k_x\partial k_y}\bigg)_0\delta(\mathbf{k}-\mathbf{k}')\\ &\qquad-\frac{1}{2}s^2\bigg(\frac{\partial^2\epsilon_n(\mathbf{k})}{\partial k_x^2}\bigg)_0\frac{\partial^2\delta(\mathbf{k}-\mathbf{k}')}{\partial k_y'^2}.\end{aligned}\tag{II.52}$$

In deriving this, we have used the identities

$$(k_x-k_x')\partial\delta(\mathbf{k}-\mathbf{k}')/\partial k_y'=0$$

and

$$(k_y-k_y')\partial\delta(\mathbf{k}-\mathbf{k}')/\partial k_y'=+\delta(\mathbf{k}-\mathbf{k}').$$

As in (II.35), $\epsilon_n(\mathbf{k})$ is understood as expanded to the second order in $\mathbf{k}$.

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[8] This follows because the spread of the wave function is actually $\sim 1/\surd s$, so that a mean k will be of the order of $\surd s$. The derivative of δ will then give, when applied to the wave function, a factor of order $1/\surd s$ so that both first and second terms are of the same order.

Equation (II.52) is essentially the effective mass theory Hamiltonian written in momentum space. To get the usual result in coordinate space we again introduce the functions $F_n(\mathbf{r})$ via (II.36). Writing the Schrödinger equation corresponding to (II.52) we obtain

$$\epsilon_n(\mathbf{k})B_n(\mathbf{k})+s\left[k_\alpha\left(\frac{\partial^2\epsilon_n(\mathbf{k})}{\partial k_\alpha\partial k_x}\right)_0 i\frac{\partial B_n(\mathbf{k})}{\partial k_y}+\frac{i}{2}\left(\frac{\partial^2\epsilon_n(\mathbf{k})}{\partial k_x\partial k_y}\right)_0 B_n(\mathbf{k})\right]+\frac{1}{2}s^2\left(\frac{\partial^2\epsilon_n(\mathbf{k})}{\partial k_x^2}\right)_0 i^2\frac{\partial^2 B_n(\mathbf{k})}{\partial k_y^2}=\epsilon B_n(\mathbf{k}). \quad \text{(II.53)}$$

Using (II.36), we get

$$\left[\epsilon_n\left(\frac{1}{i}\boldsymbol{\nabla}\right)+\frac{1}{2}s\left(\frac{\partial^2\epsilon_n(\mathbf{k})}{\partial k_\alpha\partial k_x}\right)_0\left(y\frac{1}{i}\nabla_\alpha+\frac{1}{i}\nabla_\alpha y\right)+\frac{s^2}{2}\left(\frac{\partial^2\epsilon_n(\mathbf{k})}{\partial k_x^2}\right)_0 y^2\right]F_n(\mathbf{r})=\epsilon F_n(\mathbf{r}). \quad \text{(II.54)}$$

This corresponds exactly to the following prescription. In the presence of an external field, the function F_n satisfies the differential equation which is obtained by using the expansion of $\epsilon_n(\mathbf{k})$ to quadratic terms as the Hamiltonian, and replacing k_α by the operator $(1/i)\nabla_\alpha-(e/c)A_\alpha$. In the expansion of $\epsilon_n(\mathbf{k})$ to the second order, any product of noncommuting factors which arises is to be interpreted as the symmetrized product. The leading term in the wave function is once again given by (II.40).

III. BAND WITH MINIMUM NOT AT CENTER

Let us assume that there is a minimum at $\mathbf{k}=\mathbf{k}_0$. Instead of expanding in the functions $\chi_{n\mathbf{k}}$ given by (II.4), it proves convenient to use the set of functions

$$\varphi_{n\mathbf{k}}\equiv e^{i\mathbf{k}\cdot\mathbf{r}}(e^{i\mathbf{k}_0\cdot\mathbf{r}}u_{n\mathbf{k}_0})=e^{i\mathbf{k}\cdot\mathbf{r}}\psi_{n\mathbf{k}_0}. \quad \text{(III.1)}$$

This set of functions is also complete, since if we can expand any function in $\chi_{n\mathbf{k}}$-like functions, we can certainly expand any function times $e^{i\mathbf{k}_0\cdot\mathbf{r}}$. Further, the orthonormality,

$$(\varphi_{n\mathbf{k}},\varphi_{n'\mathbf{k}'})=\delta_{nn'}\delta(\mathbf{k}-\mathbf{k}'), \quad \text{(III.2)}$$

follows just as in II from that of the $\psi_{n\mathbf{k}}$. The only other thing we need is the analog of the properties (II.18) of the momentum matrix elements. The relationship

$$p_{nn}{}^\alpha(\mathbf{k}_0)=0 \quad \text{(III.3)}$$

follows again since $\mathbf{k}_0$ is by definition a minimum point, and therefore $p_{nn}{}^\alpha(\mathbf{k}_0)$, which is proportional to the derivative of $\epsilon_n(\mathbf{k})$, at that point vanishes. The symmetry of the matrix elements,

$$p_{nn'}{}^\alpha(\mathbf{k}_0)=p_{n'n}{}^\alpha(\mathbf{k}_0), \quad \text{(III.4)}$$

also follows at once from the existence of a center of inversion. Noting these results, we see that every step of IIA and IIB may be carried through. The only difference is that the quantities which enter are evaluated at $\mathbf{k}=\mathbf{k}_0$ instead of $\mathbf{k}=0$.

For the impurity problem the result will again be that

$$\psi=F(\mathbf{r})\psi_{n\mathbf{k}_0}(\mathbf{r}), \quad \text{(III.5)}$$

where F is a solution of the effective mass equation

$$\left[\epsilon_n\left(\mathbf{k}_0+\frac{1}{i}\boldsymbol{\nabla}\right)+U\right]F=\epsilon F. \quad \text{(III.6)}$$

As always, it is meant that the ϵ_n be expanded around $\mathbf{k}_0$ to second order terms in $(1/i)\boldsymbol{\nabla}$.

Similarly, the result for an external magnetic field is that the wave function is of the form (III.5), where F satisfies the equation

$$\epsilon_n\left(\mathbf{k}_0+\frac{1}{i}\boldsymbol{\nabla}-\frac{e}{c}\mathbf{A}\right)F=\epsilon F, \quad \text{(III.7)}$$

again an expansion to second order in $(1/i)\boldsymbol{\nabla}-(e/c)\mathbf{A}$ being meant, with any noncommuting factors being written as symmetrized products.

In the case that there are minima at several different $\mathbf{k}_0$ within the band (which is always so when $\mathbf{k}_0\neq 0$), one obtains equations like (III.5), (III.6), and (III.7) corresponding to each of these. For the most general U, or direction of the magnetic field, the solutions corresponding to the different $\mathbf{k}_0$ will have different energies, and will clearly represent independent solutions of the Schrödinger equation. These solutions will be incidently, approximately orthogonal because of the fact F varies very little within a cell. On the other hand if U is spherically symmetric or has the symmetry of the crystal point group, as is usually the case, then solutions corresponding to different minima will have the same energy. The same is of course true when the magnetic field points in crystallographically simple directions. Under these conditions the correct wave function will clearly be a linear combination of those from the different "valleys" which lead to the same energy. It is impossible within the framework of the effective mass theory to decide which the correct zero order linear combinations are. This can only be decided by considering the first correction to the effective mass theory and seeing what their matrix elements are between the degenerate states. In any case if the effective mass theory is really a good approximation, then the splitting will be small, and the many valley situation will lead to a fine multiplet instead of a single level as in the case of a simple band.

IV. DEGENERATE BANDS

(A) Impurity States

We shall now consider the case of a degenerate band, neglecting spin-orbit coupling. For simplicity we shall limit ourselves to the case where the degeneracy occurs at the point $\mathbf{k}=0$, though this is no essential limitation. Let us call the degenerate functions at this point ϕ_1, ϕ_2, $\cdots$, ϕ_r, a typical one being denoted by ϕ_j. The degeneracy implies that they all have the same energy:

$$H_0\phi_j=\epsilon_0\phi_j. \qquad \text{(IV.1)}$$

Let us further make the convention that the wave functions at $\mathbf{k}=0$ for the other bands be denoted by ϕ_i, i never equalling $1, 2, \cdots, r$. For brevity we denote this by $i\neq j$.

Now if the crystal has a center of symmetry the matrix elements of the momentum between different ϕ_j will vanish. It is clear that unless there is an accidental degeneracy the different ϕ_j will belong to some irreducible representation of the crystal point group. However, all the functions in such an irreducible representation will be even or odd[9] under an inversion, since the operation of inversion commutes with all the elements of the point group. The matrix elements of $\mathbf{p}$ vanish however between states of the same parity, so that we may write

$$p_{jj'}{}^{\alpha}=0. \qquad \text{(IV.2)}$$

We shall now introduce a complete set of functions $\phi_{n\mathbf{k}}$ defined by

$$\phi_{n\mathbf{k}}=e^{i\mathbf{k}\cdot\mathbf{r}}\phi_n, \qquad \text{(IV.3)}$$

the index n running over both j and i. We then make the Ansatz

$$\psi=\sum_n\int d\mathbf{k}A_n(\mathbf{k})\phi_{n\mathbf{k}}. \qquad \text{(IV.4)}$$

For the impurity problem this leads to the Schrödinger equation:

$$\sum_{n'}\int d\mathbf{k}'(n\mathbf{k}|H_0+U|n\mathbf{k}')A_{n'}(\mathbf{k}')=\epsilon A_n(\mathbf{k}'). \qquad \text{(IV.5)}$$

The analysis leading from (II.14) to (II.22) is again valid due to the orthonormality of the $\phi_{n\mathbf{k}}$, and we obtain [on specializing n to j in (IV.5)]

$$\left(\epsilon_0+\frac{k^2}{2m}\right)A_j(\mathbf{k})+\sum_i\frac{k_\alpha p_{ji}{}^{\alpha}}{m}A_i(\mathbf{k}) +\int d\mathbf{k}'\mathcal{U}(\mathbf{k}-\mathbf{k}')A_j(\mathbf{k}')=\epsilon A_j(\mathbf{k}). \qquad \text{(IV.6)}$$

This is the equation which replaces (II.22) for the degenerate case. We again transform away the interband elements $p_{ji}{}^{\alpha}$ by a transformation analogous to (II.25) and (II.31). This is

$$(n\mathbf{k}|S|n'\mathbf{k}')=-\frac{k_\alpha p_{nn'}{}^{\alpha}}{m\omega_{nn'}}\delta(\mathbf{k}-\mathbf{k}'),\quad n,n'\neq j, \qquad \text{(IV.7)}$$
$$=0,\quad n \text{ or } n'=j.$$

This yields, to second order terms in k, the result:

$$\sum_{j'}\left(\epsilon_0\delta_{jj'}+\frac{k^2}{2m}\delta_{jj'}+\frac{k_\alpha k_\beta}{m^2}\sum_i\frac{p_{ji}{}^{\alpha}p_{ij'}{}^{\beta}}{\epsilon_0-\epsilon_i}\right)B_{j'}(\mathbf{k}) +\int\mathcal{U}(\mathbf{k}-\mathbf{k}')B_j(\mathbf{k}')d\mathbf{k}'=\epsilon B_j(\mathbf{k}). \qquad \text{(IV.8a)}$$

If there were no potential U present, the second term would vanish, and the B_j would be determined by a certain $r\times r$ secular equation, the matrix elements of which depend only on the unperturbed values of the momentum matrix elements at the degeneracy point. These are numbers, presumably known as soon as the unperturbed band structure is known. If we set the energy zero at ϵ_0, then we may write

$$\sum_{j'=1}^{r}(D_{jj'}{}^{\alpha\beta}k_\alpha k_\beta)B_{j'}(\mathbf{k})+\int\mathcal{U}(\mathbf{k}-\mathbf{k}')B_j(\mathbf{k}')d\mathbf{k}' =\epsilon B_j(\mathbf{k}), \qquad \text{(IV.8b)}$$

where

$$D_{jj'}{}^{\alpha\beta}\equiv\frac{1}{2m}\delta_{jj'}\delta_{\alpha\rho}+\frac{1}{m^2}\sum_i\frac{p_{ji}{}^{\alpha}p_{ij'}{}^{\beta}}{\epsilon_0-\epsilon_i}. \qquad \text{(IV.9)}$$

This set of numbers $D_{jj'}{}^{\alpha\beta}$ play the same role in the theory of degenerate bands that the effective masses do for a simple band.[10] Once they have been determined by, say, cyclotron resonance experiments (see below), the impurity problem can be handled in as straightforward a manner as in the simple band case. In fact, if we again introduce functions $F_j(\mathbf{r})$ as in (II.36),

$$F_j(\mathbf{r})=\int e^{i\mathbf{k}\cdot\mathbf{r}}B_j(\mathbf{r})d\mathbf{k}, \qquad \text{(IV.10)}$$

then (IV.8b) becomes

$$\sum_{j'=1}^{r}\left[D_{jj'}{}^{\alpha\beta}\left(\frac{1}{i}\nabla_\alpha\right)\left(\frac{1}{i}\nabla_\beta\right)+U(\mathbf{r})\delta_{jj'}\right]F_{j'}(\mathbf{r})=\epsilon F_j(\mathbf{r}), \qquad \text{(IV.11)}$$

and the leading term in the wave function is

$$\psi=\sum_{j=1}^{r}F_j(\mathbf{r})\phi_j(\mathbf{r}). \qquad \text{(IV.12)}$$

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[9] For the valence band of Si or Ge they will actually be even.

[10] The form of the matrix $D_{jj'}{}^{\alpha\beta}$, for the simple case where the coordinate axes coincide with the cubic axes, and where there is no spin-orbit coupling, is given in V.

The set of coupled second order differential equations (IV.11) for the functions F_j is the analog for degenerate bands of the effective mass equation (II.38).‡

(B) External Magnetic Field

For the case where an external homogeneous magnetic field is present, very similar results obtain. If we use as our basis the functions $\phi_{n\mathbf{k}}$, then the matrix elements of the Hamiltonian are the same as those in (II.45), except that none connect different j with each other. Making a canonical transformation S', which differs from (II.50) only that S' contains no elements connecting different j, we find to second order that the $B_j(\mathbf{k})$ satisfy

$$\sum_{j'}\bigg[D_{jj'}^{\alpha\beta}k_\alpha k_\beta B_j(\mathbf{k}) + is\bigg(2k_\alpha D_{jj'}^{\alpha x}\frac{\partial B_{j'}(\mathbf{k})}{\partial k_y}+D_{jj'}^{xy}B_{j'}(\mathbf{k})\bigg) - s^2 D_{jj'}^{xx}\frac{\partial^2 B_{j'}(\mathbf{k})}{\partial k_y{}^2}\bigg]=\epsilon B_j(\mathbf{k}), \qquad \text{(IV.13)}$$

where we have made use of the definition (IV.9). Going over again to coordinate space via the definition (IV.10), we find that the F_j satisfy the differential equations

$$\sum_{j'=1}^{r}\bigg[D_{jj'}^{\alpha\beta}\bigg(\frac{1}{i}\nabla_\alpha+sy\delta_{\alpha x}\bigg)\bigg(\frac{1}{i}\nabla_\beta+sy\delta_{\beta x}\bigg)\bigg]F_{j'}(\mathbf{r}) = \epsilon F_j(\mathbf{r}), \qquad \text{(IV.14)}$$

where any products of noncommuting factors on the left hand side are to be interpreted as a symmetrized product. This equation is exactly what one would obtain if one took as unperturbed Hamiltonian the matrix $D_{jj'}^{\alpha\beta}k_\alpha k_\beta$, and made the replacement $k_\alpha\rightarrow(1/i)\nabla_\alpha-(e/c)A_\alpha$. It is therefore the natural generalization of the effective-mass equation (II.54). As in the case of impurity levels we have a system of coupled differential equations instead of a single differential equation.

V. SPIN-ORBIT COUPLING

In the preceeding discussion, we have not included any effects of spin-orbit coupling. As is well known,[11] this leads to an extra term in the Hamiltonian ($H_{\text{s.o.}}$), given by

$$H_{\text{s.o.}}=\frac{1}{4m^2c^2}(\boldsymbol{\sigma}\times\nabla V)\cdot\mathbf{p}; \qquad \text{(V.1)}$$

here $\boldsymbol{\sigma}$ is the Pauli spin matrix vector, and V the potential energy of the electron. In our case, V is just the periodic potential energy arising from the crystal. For the case of a nondegenerate band the effects of spin-orbit coupling are not very profound. Since V is periodic and $\mathbf{p}$ invariant under translations, the total unperturbed Hamiltonian,

$$\bar{H}_0=H_0+H_{\text{s.o.}}, \qquad \text{(V.2)}$$

will still possess Bloch waves as solutions. Call these $\bar{\psi}_{n\mathbf{k}}=e^{i\mathbf{k}\cdot\mathbf{r}}\bar{u}_{n\mathbf{k}}$, with the energy $\bar{\epsilon}_n(\mathbf{k})$. The $\bar{u}_{n\mathbf{k}}$ are spin-dependent periodic functions. We may again introduce a set of functions analogous to the $\chi_{n\mathbf{k}}$, say $\bar{\chi}_{n\mathbf{k}}$, defined by

$$\bar{\chi}_{n\mathbf{k}}=e^{i\mathbf{k}\cdot\mathbf{r}}\bar{u}_{n0}. \qquad \text{(V.3)}$$

Then the Ansatz,

$$\psi=\sum_n\int d\mathbf{k}A_n(\mathbf{k})\bar{\chi}_{n\mathbf{k}}, \qquad \text{(V.4)}$$

leads to the same Schrödinger equation for $A_n(\mathbf{k})$ as we had without spin-orbit coupling in both the impurity and magnetic cases, except that the matrix elements $p_{nn'}{}^{\alpha}$ are replaced by $\pi_{nn'}{}^{\alpha}$ defined by

$$\pi_{nn'}{}^{\alpha}=\frac{(2\pi)^3}{\Omega}\int_{\text{cell}}\bar{u}_{n0}{}^*\bigg(\frac{1}{i}\nabla_\alpha+\frac{1}{4mc^2}(\boldsymbol{\sigma}\times\nabla V)_\alpha\bigg)\bar{u}_{n'0}d\mathbf{r}. \qquad \text{(V.5)}$$

This extra term arises from the fact that the spin-orbit coupling contains the differential operation $\mathbf{p}$. Actually the $\pi_{nn'}{}^{\alpha}$ have the essential properties in the spin-orbit case that the $p_{nn'}{}^{\alpha}$ have in the case without spin-orbit coupling. These properties were (II.18) and the f-sum rule (II.34). The second of the relations (II.18) is established at once from the existence of a center of symmetry, just as it was for (II.18). Further, one may show that[12]

$$\pi_{nn}{}^{\alpha}=m\bigg(\frac{\partial\epsilon_n(k)}{\partial k_\alpha}\bigg)_0. \qquad \text{(V.6)}$$

Therefore if we are at the bottom or top of a band the energy is stationary, and we have $\pi_{nn}{}^{\alpha}=0$. Finally, in the spin-orbit case the correct f-sum rule must be written in terms of the $\pi_{nn'}{}^{\alpha}$, i.e.,

$$\frac{2}{m}\sum_{n''\neq n}\frac{\pi_{nn''}{}^{\alpha}(\mathbf{k})\pi_{n''n}{}^{\beta}(\mathbf{k})}{\bar{\epsilon}_{n''}(\mathbf{k})-\bar{\epsilon}_n(\mathbf{k})}=\delta_{\alpha\beta}-m\frac{\partial^2\bar{\epsilon}_n(\mathbf{k})}{\partial k_\alpha\partial k_\beta}. \qquad \text{(V.7)}$$

(See Appendix B.) These results mean that the entire theory goes through just as without spin-orbit coupling, it only being necessary to use the correct energy $\bar{\epsilon}_n(\mathbf{k})$ instead of $\epsilon_n(k)$. The experimentally determined effective masses—from cyclotron resonance, say—will of course refer to $\bar{\epsilon}_n(\mathbf{k})$.

When there is a degenerate band in the absence of spin-orbit coupling, its introduction can lead to more radical changes by partially lifting the degeneracy. In a case such as Si or Ge, the originally six-fold[13] degenerate state at $\mathbf{k}=0$ is split into a four-fold and a two-fold

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‡ *Note added in proof.*—Since this manuscript was completed a paper has appeared by C. Kittel and A. H. Mitchell [Phys. Rev. 96, 1488 (1954)] dealing with the effective mass equation for the impurity problem, in the case of degenerate bands. Their equation (46) is identical with our (IV.11). The problem of an external magnetic field is not dealt with by them.

[11] See for example, L. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, New York, 1949), p. 321.

[12] This has been proven recently by R. Karplus and J. M. Luttinger, Phys. Rev. **95**, 1154 (1954).

[13] This includes the spin degeneracy.

degeneracy. Thus degenerate bands are split in general into several bands by the spin-orbit coupling. If we fix our attention on one of these "spin-orbit bands" then formally the entire theory goes through without a hitch, and equations identical with (IV.11) and (IV.14) are obtained. The only difference is that the $D_{jj'}^{\alpha\beta}$ are now defined in terms of the $\pi_{nn'}^{\alpha}$ and $\bar{\epsilon}_n(0)$ instead of the of the $p_{nn'}^{\alpha}$ and $\epsilon_n(0)$. Since these quantities are in any case determined by experiment this makes little practical difference. It is important to note the fact that the spin-orbit coupling is in general not large, and will lead to small splittings between the spin-orbit bands. Now the entire validity of our effective mass like theory rests ultimately on the assumption that the interband separations are large compared with the energies involved in the solution of the effective mass equation. A very rough estimate of the splitting between the spin-orbit bands is perhaps 0.2 ev in Ge and 0.05 ev in Si. There is no doubt that in cyclotron resonance experiments the energies involved are much smaller than this, and the effective mass theory will be extremely good. For impurity states the situation is not as favorable. In Ge, acceptor levels are found at roughly 0.01 ev, so that the approximation is not too bad in all likelihood. In Si, however, typical acceptor levels are at roughly 0.05 ev, so that the impurity will produce an appreciable mixing of bands. In this case, the effective mass theory in its simple form (where only the properties of the neighborhood of one point of a single band play a role) cannot be valid.

Perhaps it is instructive to illustrate these remarks in more detail by the specific situation in crystals such as Si and Ge. For simplicity we shall assume that the cubic axes of the crystal are oriented along the coordinate axes. At $\mathbf{k}=0$ in the absence of spin-orbit coupling there are three degenerate space functions belonging to Γ_{25}', and which transform like x, y, and z respectively under the operations of the tetrahedral point group. We shall denote these functions by X, Y, Z, respectively. Of course each has an additional double degeneracy due to spin. Let us define a matrix D by its elements,

$$D_{jj'}=k_\alpha k_\beta D_{jj'}^{\alpha\beta}. \tag{V.8}$$

Then the symmetry of the diamond lattice requires that D have the form

$$D=\left\|\begin{matrix} Ak_x^2+B(k_y^2+k_z^2) & Ck_xk_y & Ck_xk_z \\ Ck_xk_y & Ak_y^2+B(k_x^2+k_z^2) & Ck_yk_z \\ Ck_xk_z & Ck_yk_z & Ak_z^2+B(k_y^2+k_x^2)\end{matrix}\right\|, \tag{V.9}$$

for each spin, where A, B, C are three real constants defined by

$$\begin{aligned} A&=\frac{1}{2m}+\frac{1}{m^2}\sum_i\frac{p_{Xi}^x p_{iX}^x}{\epsilon_0-\epsilon_i},\\ B&=\frac{1}{2m}+\frac{1}{m^2}\sum_i\frac{p_{Xi}^y p_{iX}^y}{\epsilon_0-\epsilon_i},\\ C&=\frac{1}{m^2}\sum_i\frac{p_{Xi}^x p_{iY}^y+p_{Xi}^y p_{iY}^x}{\epsilon_0-\epsilon_i},\end{aligned} \tag{V.10}$$

as may be seen from (IV.9).

The introduction of spin-orbit coupling splits some of the degeneracy of the band at $\mathbf{k}=0$. Treating $H_{\mathrm{s.o.}}$ as a perturbation, we see at once that the correct *zero order* wave functions fall into a group of four and a group of two:

$$\begin{aligned} \phi_{\frac{3}{2}}^{(\frac{3}{2})}&=\frac{1}{\sqrt{2}}(X+iY)\alpha,\\ \phi_{\frac{1}{2}}^{(\frac{3}{2})}&=\frac{i}{\sqrt{6}}[(X+iY)\beta-2Z\alpha],\\ \phi_{-\frac{1}{2}}^{(\frac{3}{2})}&=\frac{1}{\sqrt{6}}[(X-iY)\alpha+2Z\beta],\\ \phi_{-\frac{3}{2}}^{\frac{3}{2}}&=\frac{i}{\sqrt{2}}(X-iY)\beta,\end{aligned} \tag{V.11}$$

and

$$\begin{aligned} \phi_{\frac{1}{2}}^{(\frac{1}{2})}&=\frac{1}{\sqrt{3}}[(X-iY)\beta+Z\alpha],\\ \phi_{-\frac{1}{2}}^{(\frac{1}{2})}&=\frac{i}{\sqrt{3}}[-(X-iY)\alpha+Z\beta],\end{aligned} \tag{V.12}$$

where α and β are the spin functions corresponding to spin "up" and "down" respectively. The set of functions (V.11) correspond to what would be the $J=\frac{3}{2}$ multiplet in the case of tight binding, while the functions (V.12) correspond to the $J=\frac{1}{2}$ multiplet. The phases of the functions have been so chosen that the functions $\phi_{-\frac{3}{2}}^{(\frac{3}{2})}$ and $\phi_{\frac{1}{2}}^{(\frac{3}{2})}$ are obtained from $\phi_{\frac{3}{2}}^{(\frac{3}{2})}$ and $\phi_{-\frac{1}{2}}^{(\frac{3}{2})}$ by time reversal.[14] Similarly for $\phi_{-\frac{1}{2}}^{(\frac{1}{2})}$ and $\phi_{\frac{1}{2}}^{(\frac{1}{2})}$. This time reversal degeneracy is of course present because the original Hamiltonian (V.2) is invariant under time reversal. Cyclotron resonance seem to indicate at the present moment that the top of the valence band actually corresponds to the $J=\frac{3}{2}$ multiplet, the $J=\frac{1}{2}$ band being depressed by an amount, say λ. It is this λ which is very roughly 0.2 ev in Ge and 0.05 ev in Si. If we assume that the U (or magnetic field) is sufficiently small to produce no appreciable mixing of these bands, then we obtain an independent set of four coupled equations to describe the situation for the $J=\frac{3}{2}$ band and a set of two equations to describe the $J=\frac{1}{2}$ band.

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[14] In the representation where σ_x, σ_z are real and $\sigma_y=\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}$, this simply means taking the complex conjugate and multiplying by σ_y.

For larger U, on the other hand, we shall have to deal with the full set of six coupled equations.

We shall first consider the situation in which the spin-orbit coupling is sufficiently small so that the zeroth order functions (V.11) and (V.12) may be used. This is almost certainly an excellent approximation in Si, and is also very likely not bad in Ge. For heavier elements, on the other hand, it may break down seriously. Considering both the $J=\frac{3}{2}$ and $\frac{1}{2}$ bands together, we find

$$D=\begin{array}{r} (\frac{3}{2}),\frac{3}{2} \\ (\frac{3}{2}),\frac{1}{2} \\ (\frac{3}{2}),-\frac{1}{2} \\ (\frac{3}{2}),-\frac{3}{2} \\ (\frac{1}{2}),\frac{1}{2} \\ (\frac{1}{2}),-\frac{1}{2} \end{array}\left\| \begin{array}{cccccc} \frac{1}{2}P & L & M & 0 & iL/\sqrt{2} & -i\sqrt{2}M \\ L^* & \frac{1}{6}P+\frac{2}{3}Q & 0 & M & -i(P-2Q)/3\sqrt{2} & i\sqrt{3}L/\sqrt{2} \\ M^* & 0 & \frac{1}{6}P+\frac{2}{3}Q & -L & -i\sqrt{3}L^*/\sqrt{2} & -i(P-2Q)/3\sqrt{2} \\ 0 & M^* & -L^* & \frac{1}{2}P & -i\sqrt{2}M^* & -iL^*/\sqrt{2} \\ -iL^*/\sqrt{2} & i(P-2Q)/3\sqrt{2} & i\sqrt{3}L/\sqrt{2} & i\sqrt{2}M & \frac{1}{3}(P+Q)-\lambda & 0 \\ i\sqrt{2}M^* & -i\sqrt{3}L^*/\sqrt{2} & i(P-2Q)/3\sqrt{2} & iL/\sqrt{2} & 0 & \frac{1}{3}(P+Q)-\lambda \end{array}\right\|, \tag{V.13}$$

where

$$P(\mathbf{k})\equiv(A+B)(k_x^2+k_y^2)+2Bk_z^2, \qquad L(\mathbf{k})\equiv-(iC/\sqrt{3})(k_x-ik_y)k_z,$$
$$Q(\mathbf{k})\equiv B(k_x^2+k_y^2)+Ak_z^2, \qquad M(\mathbf{k})=[(A-B)(k_x-k_y^2)-2iCk_xk_y]/\sqrt{12}, \tag{V.14}$$
$$\lambda\equiv\text{spin-orbit splitting at }\mathbf{k}=0.$$

For the impurity state problem, the matrix (V.13) with k_α replaced by $-i\nabla_\alpha$ now takes place of the matrix $D_{jj'}{}^{\alpha\beta}(-i\nabla_\alpha)(-i\nabla_\beta)$ in Eq. (IV.11). In Si, where the binding energy is comparable to the spin-orbit splitting λ it is necessary to treat these six coupled differential equations together. On the other hand, in Ge, λ is very likely sufficiently larger than the binding energy, so that these six equations decouple to a good approximation. Specifically, if the top of the $J=\frac{3}{2}$ band lies higher than that corresponding to $J=\frac{1}{2}$ as appears likely, the acceptor states are solutions of the following four coupled differential equations:

$$\left\|\begin{array}{cccc} \frac{1}{2}P(-i\boldsymbol{\nabla})+U-\epsilon & L(-i\boldsymbol{\nabla}) & M(-i\boldsymbol{\nabla}) & 0 \\ L^\dagger(-i\boldsymbol{\nabla}) & \frac{1}{6}P(-i\boldsymbol{\nabla})+\frac{2}{3}Q(-i\boldsymbol{\nabla})+U-\epsilon & 0 & M(-i\boldsymbol{\nabla}) \\ M^\dagger(-i\boldsymbol{\nabla}) & 0 & \frac{1}{6}P(-i\boldsymbol{\nabla})+\frac{2}{3}Q(-i\boldsymbol{\nabla})+U-\epsilon & -L(-i\boldsymbol{\nabla}) \\ 0 & M^\dagger(-i\boldsymbol{\nabla}) & -L^\dagger(-i\boldsymbol{\nabla}) & \frac{1}{2}P(-i\boldsymbol{\nabla})+U-\epsilon \end{array}\right\| \begin{bmatrix} F_1 \\ F_2 \\ F_3 \\ F_4 \end{bmatrix}=0. \tag{V.15}$$

For cyclotron resonance experiments, the energies involved are always much less than λ, and therefore one needs only to deal with the 4×4 matrix corresponding to the $J=\frac{3}{2}$ band. Taking, for example, the magnetic field in the (001) direction and choosing the vector potential as in (II.41), the differential equations describing the energy states are clearly cyclic in x and z. If we write

$$F_j=\exp[i(p_xx+p_zz)]f_j(y), \tag{V.16}$$

then corresponding to (IV. 14) we obtain the following coupled differential equations:

$$\left\|\begin{array}{cccc} \begin{array}{c}\frac{A+B}{2}\left(-\frac{\partial^2}{\partial y^2}+s^2y^2\right)\\ +Bp_z^2-\epsilon\end{array} & \frac{-iC}{\sqrt{3}}p_z\left(sy-\frac{\partial}{\partial y}\right) & \begin{array}{c}\frac{1}{\sqrt{12}}\left[(A-B)\left(s^2y^2+\frac{\partial^2}{\partial y^2}\right)\right.\\ \left.-Cs\left(y\frac{\partial}{\partial y}+\frac{\partial}{\partial y}y\right)\right]\end{array} & 0 \\ \frac{iC}{\sqrt{3}}p_z\left(sy+\frac{\partial}{\partial y}\right) & \begin{array}{c}\frac{A+5B}{6}\left(-\frac{\partial^2}{\partial y^2}+s^2y^2\right)\\ +\frac{B+2A}{3}p_z^2-\epsilon\end{array} & 0 & \begin{array}{c}\frac{1}{\sqrt{12}}\left[(A-B)\left(s^2y^2+\frac{\partial^2}{\partial y^2}\right)\right.\\ \left.-Cs\left(y\frac{\partial}{\partial y}+\frac{\partial}{\partial y}y\right)\right]\end{array} \\ \begin{array}{c}\frac{1}{\sqrt{12}}\left[(A-B)\left(s^2y^2+\frac{\partial^2}{\partial y^2}\right)\right.\\ \left.+Cs\left(y\frac{\partial}{\partial y}+\frac{\partial}{\partial y}y\right)\right]\end{array} & 0 & \begin{array}{c}\frac{A+5B}{6}\left(-\frac{\partial^2}{\partial y^2}+s^2y^2\right)\\ +\frac{B+2A}{3}p_z^2-\epsilon\end{array} & \frac{iCp_z}{\sqrt{3}}\left(sy-\frac{\partial}{\partial y}\right) \\ 0 & \begin{array}{c}\frac{1}{\sqrt{12}}\left[(A-B)\left(s^2y^2+\frac{\partial^2}{\partial y^2}\right)\right.\\ \left.+Cs\left(y\frac{\partial}{\partial y}+\frac{\partial}{\partial y}y\right)\right]\end{array} & \frac{-iCp_z}{\sqrt{3}}\left(sy+\frac{\partial}{\partial y}\right) & \begin{array}{c}\frac{A+B}{2}\left(-\frac{\partial^2}{\partial y^2}+s^2y^2\right)\\ +Bp_z^2-\epsilon\end{array} \end{array}\right\| \begin{bmatrix} f_1 \\ f_2 \\ f_3 \\ f_4 \end{bmatrix}=0. \tag{V.17}$$

In this equation, p_x+sy has been replaced simply by sy a shift in the origin of y not affecting the energy levels. The dependence of the energy levels on p_z, on the other hand, is quite complicated in the present case. We shall not pursue in this paper the solution of Eq. (V.17). It may be remarked however that it is easy to see that in the limit of high quantum numbers these equations lead exactly to the usual semiclassical treatment of cyclotron resonance due to Shockley.[15] The procedure is identical with that used by Pauli[16] in finding the classical limit of the Dirac equation. On the other hand, for low quantum numbers the energy spectrum of (V.17) shows marked deviations from the classical limit. In addition the direct interaction of the electronic magnetic moment with the external magnetic field must be taken into account for the low lying states. An example, which may be worked through in detail, is given in Appendix C.§

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APPENDIX A. ALTERNATIVE DERIVATION OF THE EFFECTIVE MASS EQUATION

Let us consider an energy band which has n equivalent minima at the points $\mathbf{k}^{(i)}$, $i=1, 2, \cdots, n$. The wave function $\psi(\mathbf{r})$ of an impurity state satisfies the equation

$$(H_0+U)\psi=\epsilon\psi, \qquad \text{(A.1)}$$

where H_0 is the unperturbed periodic Hamiltonian. ψ may be expanded in the Bloch functions $\psi_{\mathbf{k}}(\mathbf{r})$, which are eigenfunctions of H_0 (see Adams, reference 1). It is convenient to label these functions by the wave vector $\mathbf{k}$ which is allowed to vary over all momentum space. Thus we have

$$\psi(\mathbf{r})=\int C(\mathbf{k})\psi_{\mathbf{k}}(\mathbf{r})d\mathbf{k}. \qquad \text{(A.2)}$$

If now

$$H_0\psi_{\mathbf{k}}=\epsilon(\mathbf{k})\psi_{\mathbf{k}}, \qquad \text{(A.3)}$$

substitution into (A.1) gives

$$[\epsilon(\mathbf{k})-\epsilon]C(\mathbf{k})+\int \mathcal{U}(\mathbf{k},\mathbf{k}')C(\mathbf{k}')d\mathbf{k}'=0, \qquad \text{(A.4)}$$

where

$$\begin{aligned}\mathcal{U}(\mathbf{k},\mathbf{k}')&=\int \psi_{\mathbf{k}}^*U\psi_{\mathbf{k}'}d\mathbf{r}\\ &=\int (u_{\mathbf{k}}^*u_{\mathbf{k}'})Ue^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}}d\mathbf{r}. \qquad \text{(A.5)}\end{aligned}$$

The product $u_{\mathbf{k}}^*u_{\mathbf{k}'}$ is a periodic function of $\mathbf{r}$ and hence can be written as

$$u_{\mathbf{k}}^*(\mathbf{r})u_{\mathbf{k}'}(\mathbf{r})=\sum\nolimits_m M_{\mathbf{k}\mathbf{k}'}{}^{(m)}e^{-i\mathbf{K}_m\cdot\mathbf{r}}, \qquad \text{(A.6)}$$

where the $\mathbf{K}_m$ are the vectors of the reciprocal lattice. The normalization of the $\psi_{\mathbf{k}}(\mathbf{r})$ implies that

$$M_{\mathbf{k}\mathbf{k}'}{}^{(0)}=1/(2\pi)^3. \qquad \text{(A.7)}$$

For $m\neq 0$, the order of magnitude of the M's is evidently similar or smaller. Now using (A.6), we find

$$\mathcal{U}(\mathbf{k},\mathbf{k}')=\sum_m M_{\mathbf{k}'\mathbf{k}}{}^{(m)}\int U(\mathbf{r})e^{i(\mathbf{k}'-\mathbf{k}-\mathbf{K}_m)\cdot\mathbf{r}}d\mathbf{r}. \qquad \text{(A.8)}$$

We shall see later that $B(\mathbf{k})$ is very small except in the immediate vicinity of the $\mathbf{k}^{(i)}$ ($|\mathbf{k}-\mathbf{k}^{(i)}|\ll\mathbf{K}_1$). Let us assume further that $U(\mathbf{r})$ is a "gentle" potential whose main Fourier components correspond to wavelengths much larger than the lattice spacing. Under these circumstances $\mathcal{U}(\mathbf{k},\mathbf{k}')$ is negligible unless $\mathbf{k}$ and $\mathbf{k}'$ lie near the same $\mathbf{k}^{(i)}$, and in the latter case (A.8) and (A.7) give to a good approximation

$$\begin{aligned}\mathcal{U}(\mathbf{k},\mathbf{k}')&=\frac{1}{(2\pi)^3}\int U(\mathbf{r})e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}}d\mathbf{r}\\ &=\mathcal{U}(\mathbf{k}-\mathbf{k}').\end{aligned} \qquad \text{(A.9)}$$

Since the $C(\mathbf{k})$ corresponding to $\mathbf{k}$ near different minima are only weakly coupled, it is a good approximation to write

$$C(\mathbf{k})=\sum_{i=1}^{n}\alpha^{(i)}C^{(i)}(\mathbf{k}), \qquad \text{(A.10)}$$

where the $\alpha^{(i)}$ are numerical coefficients (governed by the symmetry of the lattice), and the $C^{(i)}(\mathbf{k})$ satisfy equations of the following kind:

$$[\epsilon^{(1)}(\mathbf{k})-\epsilon]C^{(1)}(\mathbf{k})+\int \mathcal{U}(\mathbf{k}-\mathbf{k}')C^{(1)}(\mathbf{k}')d\mathbf{k}'=0, \qquad \text{(A.11)}$$

with

$$\epsilon^{(1)}(\mathbf{k})=\epsilon_0+\sum_{i,j}\alpha_{ij}(k_i-k_i{}^{(1)})(k_j-k_j{}^{(1)}), \qquad \text{(A.12)}$$

ϵ_0 being the energy at the bottom of the band. If we now introduce

$$F^{(1)}(\mathbf{r})=\int C^{(1)}(\mathbf{k})\exp[i(\mathbf{k}-\mathbf{k}^{(1)})\cdot\mathbf{r}]d\mathbf{k}, \qquad \text{(A.13)}$$

(A.12) becomes the effective mass equation

$$\left[\sum_{i,j}\alpha_{ij}\left(\frac{1}{i}\nabla_i\right)\left(\frac{1}{i}\nabla_j\right)+U(\mathbf{r})-(\epsilon-\epsilon_0)\right]F^{(1)}(\mathbf{r})=0. \qquad \text{(A.14)}$$

Clearly $B^{(1)}(\mathbf{k})\approx 0$ for $|\mathbf{k}-\mathbf{k}^{(1)}|\gg a_i^{-1}$, a_i being the extent of the function $F^{(1)}$. a_i must be assumed large

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[15] W. Shockley, Phys. Rev. **79**, 191 (1950); **90**, 491 (1953).

[16] W. Pauli, *Handbuch der Physik* (J. Springer, Berlin, 1933), second edition, Vol. 24, part 1, p. 240.

§ *Note added in proof.*—Recently we have found the exact solution to the practical case of A, B, C arbitrary, $p_z=0$, and the field in the [111] direction.

compared to the lattice spacing for the above derivation to be consistent.

The total wave function is, by (A.2), (A.11), and (A.13),

$$\psi(\mathbf{r})=\sum_{i=1}^{n}\alpha^{(i)}\int C^{(i)}(\mathbf{k})u_{\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}d\mathbf{k}$$

$$\cong\sum_{i=1}^{n}\alpha^{(i)}u_{\mathbf{k}^{(i)}}(\mathbf{r})\exp(i\mathbf{k}^{(i)}\cdot\mathbf{r})\int C^{(i)}(\mathbf{k})$$

$$\times\exp[i(\mathbf{k}-\mathbf{k}^{(i)})\cdot\mathbf{r}]d\mathbf{k} \quad \text{(A.15)}$$

$$=\sum_{i=1}^{n}\alpha^{(i)}\psi_{\mathbf{k}^{(i)}}(\mathbf{r})F^{(i)}(\mathbf{r});$$

i.e., it is a linear combination of products of modulating functions $F^{(i)}(\mathbf{r})$ and the Bloch waves $\psi_{\mathbf{k}^{(i)}}(\mathbf{r})$ at the minima of the conduction band.

APPENDIX B. *f*-SUM RULE WITH SPIN-ORBIT COUPLING

We note first that the quantity occurring in $\pi_{nn'}{}^{\alpha}$ is related to the commutator of $\bar{H}_0$ and x_α. Clearly,

$$(\bar{H}_0,x_\alpha)=\frac{1}{i}\left(\frac{p_\alpha}{m}+\frac{1}{4m^2c^2}(\boldsymbol{\sigma}\times\boldsymbol{\nabla}V)_\alpha\right). \quad \text{(B.1)}$$

Thus the matrix elements between two Bloch waves $\bar{\psi}_{n\mathbf{k}}$, $\bar{\psi}_{n'\mathbf{k}'}$ are

$$[\bar{\epsilon}_n(\mathbf{k})-\bar{\epsilon}_{n'}(\mathbf{k}')](n\mathbf{k}|x_\alpha|n'\mathbf{k}')$$

$$=\frac{1}{i}\left(n\mathbf{k}\left|\frac{p_\alpha}{m}+\frac{1}{4m^2c^2}(\boldsymbol{\sigma}\times\boldsymbol{\nabla}V)_\alpha\right|n'\mathbf{k}'\right)$$

$$=\delta(\mathbf{k}-\mathbf{k}')\frac{1}{mi}\pi_{nn'}{}^{\alpha}(\mathbf{k}). \quad \text{(B.2)}$$

However,

$$(n\mathbf{k}|x_\alpha|n'\mathbf{k}')=\int e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}}x_\alpha\bar{u}_{n\mathbf{k}}{}^*\bar{u}_{n'\mathbf{k}'}d\mathbf{r}$$

$$=\frac{1}{i}\frac{\partial}{\partial k_\alpha'}\delta(\mathbf{k}'-\mathbf{k})\delta_{nn'}-\frac{1}{i}\int e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}}\bar{u}_{n\mathbf{k}}{}^*\frac{\partial\bar{u}_{n'\mathbf{k}'}}{\partial k_\alpha'}d\mathbf{r}$$

$$=\frac{1}{i}\frac{\partial\delta(\mathbf{k}'-\mathbf{k})}{\partial k_\alpha'}\delta_{nn'}+i\delta(\mathbf{k}-\mathbf{k}')\frac{(2\pi)^3}{\Omega}$$

$$\times\int_{\text{cell}}\bar{u}_{nk}{}^*\frac{\partial\bar{u}_{n'k}}{\partial k_\alpha}d\mathbf{r}. \quad \text{(B.3)}$$

Therefore, putting (B.2) and (B.3) together, we have for $n\neq n'$:

$$\frac{(2\pi)^3}{\Omega}\int_{\text{cell}}\bar{u}_{n\mathbf{k}}{}^*\frac{\partial\bar{u}_{n'\mathbf{k}}}{\partial k_\alpha}d\mathbf{r}=-\frac{\pi_{nn'}{}^{\alpha}}{m[\bar{\epsilon}_n(\mathbf{k})-\epsilon_{n'}(\mathbf{k})]}. \quad \text{(B.4)}$$

Therefore, we have

$$\frac{2}{m}\sum_{n'\neq n}\frac{\pi_{nn'}{}^{\alpha}\pi_{n'n}{}^{\beta}}{\bar{\epsilon}_{n'}(\mathbf{k})-\bar{\epsilon}_n(\mathbf{k})}$$

$$=-2\frac{(2\pi)^3}{\Omega}\sum_{n'}\int_{\text{cell}}\bar{u}_{n\mathbf{k}}{}^*\left(\frac{1}{i}\nabla_\alpha+\frac{1}{4mc^2}(\boldsymbol{\sigma}\times\boldsymbol{\nabla}V)_\alpha\right)$$

$$\times\bar{u}_{n'\mathbf{k}}d\mathbf{r}\int_{\text{cell}}\bar{u}_{n'\mathbf{k}}\frac{\partial\bar{u}_{n\mathbf{k}}}{\partial k_\beta}d\mathbf{r}. \quad \text{(B.5)}$$

Here we have extended the sum over n' to include $n'=n$, since when $n=n'$ and a center of symmetry is present, the integral

$$\int\bar{u}_{n\mathbf{k}}{}^*\frac{\partial\bar{u}_{n\mathbf{k}}}{\partial k_\alpha}d\mathbf{r}\equiv 0. \quad \text{(B.6)}$$

Now we may carry out the sum on the right hand side of (B.5) using the completeness of the $\bar{u}_{n\mathbf{k}}$, i.e.,

$$\sum_{n'}\bar{u}_{n'\mathbf{k}}{}^{a*}(\mathbf{r}')\bar{u}_{n'\mathbf{k}}{}^{a'}(\mathbf{r})=\frac{\Omega}{(2\pi)^3}\delta(\mathbf{r}-\mathbf{r}')\delta_{aa'}, \quad \text{(B.7)}^{17}$$

for $\mathbf{r}$, $\mathbf{r}'$ in the same cell. Thus

$$\frac{2}{m}\sum_{n'\neq n}\frac{\pi_{nn'}{}^{\alpha}\pi_{n'n}{}^{\beta}}{\bar{\epsilon}_{n'}(\mathbf{k})-\bar{\epsilon}_n(\mathbf{k})}$$

$$=-2\frac{(2\pi)^3}{\Omega}\int_{\text{cell}}\bar{u}_{n\mathbf{k}}{}^*\left(\frac{1}{i}\nabla_\alpha+\frac{1}{4mc^2}(\boldsymbol{\sigma}\times\boldsymbol{\nabla}V)_\alpha\right)\frac{\partial\bar{u}_{nk}}{\partial k_\beta}d\mathbf{r}. \quad \text{(B.8)}$$

Since $\pi_{nn'}{}^{\alpha}=\pi_{n'n}{}^{\alpha}$, the original expression is symmetric in α and β. Therefore, we may write (B.8) as

$$\frac{2}{m}\sum_{n'\neq n}\frac{\pi_{nn'}{}^{\alpha}\pi_{n'n}{}^{\beta}}{\bar{\epsilon}_{n'}(\mathbf{k})-\bar{\epsilon}_n(\mathbf{k})}$$

$$=-\frac{(2\pi)^3}{\Omega}\left[\int_{\text{cell}}\bar{u}_{n\mathbf{k}}{}^*\left(\frac{1}{i}\nabla_\alpha+\frac{1}{4mc^2}(\boldsymbol{\sigma}\times\boldsymbol{\nabla}V)_\alpha\right)\frac{\partial\bar{u}_{nk}}{\partial k_\beta}d\mathbf{r}\right.$$

$$\left.+\int_{\text{cell}}\bar{u}_{n\mathbf{k}}{}^*\left(\frac{1}{i}\nabla_\beta+\frac{1}{4mc^2}(\sigma\times\boldsymbol{\nabla}V)_\beta\right)\frac{\partial\bar{u}_n\mathbf{k}}{\partial k_\alpha}d\mathbf{r}\right]. \quad \text{(B.9)}$$

The right hand side of (B.9) is easily evaluated by means of the Schrödinger equation for $\bar{u}_{n\mathbf{k}}$. This is

$$\left[\bar{H}_0+\frac{1}{m}\mathbf{k}\cdot\left(\mathbf{p}+\frac{1}{4mc^2}(\boldsymbol{\sigma}\times\boldsymbol{\nabla}V)\right)+\frac{k^2}{2m}\right]\bar{u}_{n\mathbf{k}}=\bar{\epsilon}_n(k)\bar{u}_{nk}. \quad \text{(B.10)}$$

Differentiating this successively with respect to k_α and k_β, multiplying with respect to $\bar{u}_{n\mathbf{k}}{}^*$ and integrating

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[17] The index a indicates the spin state involved.

over a cell, we find

$$\int_{\text{cell}} \bar{u}_{n\mathbf{k}}{}^{*}\left(\frac{1}{i}\nabla_{\alpha}+\frac{1}{4mc^{2}}(\boldsymbol{\sigma}\times\boldsymbol{\nabla}V)_{\alpha}\right)\frac{\partial\bar{u}_{nk}}{\partial k_{\beta}}d\mathbf{r}$$

$$+\int_{\text{cell}} \bar{u}_{n\mathbf{k}}{}^{*}\left(\frac{1}{i}\nabla_{\beta}+\frac{1}{4mc^{2}}(\boldsymbol{\sigma}\times\boldsymbol{\nabla}V)_{\beta}\right)\frac{\partial\bar{u}_{n\mathbf{k}}}{\partial k_{\alpha}}d\mathbf{r}$$

$$=\frac{\Omega}{(2\pi)^{3}}\left(m\frac{\partial^{2}\bar{\epsilon}_{n}(\mathbf{k})}{\partial k_{\alpha}\partial k_{\beta}}-\delta_{\alpha\beta}\right). \quad \text{(B.11)}$$

Using Eq. (B.11), Eq. (B.9) becomes the f-sum rule.

$$\frac{2}{m}\sum_{n'\neq n}\frac{\pi_{nn'}{}^{\alpha}\pi_{n'n}{}^{\beta}}{\bar{\epsilon}_{n'}(\mathbf{k})-\bar{\epsilon}_{n}(\mathbf{k})}=\delta_{\alpha\beta}-m\frac{\partial^{2}\bar{\epsilon}_{n}(\mathbf{k})}{\partial k_{\alpha}\partial k_{\beta}}. \quad \text{(B.12)}$$

APPENDIX C. A SOLUBLE CASE FOR DEGENERATE BANDS

We consider now a special case of the cyclotron resonance problem where everything may be calculated completely. For simplicity we shall restrict ourselves to the case where $p_z=0$, and shall ignore the electron spin effects. Neither of these restrictions are essential, but they simplify the work considerably without obscuring the nature of the quantum deviations in cyclotron resonance. The case of interest is where $A-B=C$. ($A-B=-C$ may be treated with equal ease.) Under these circumstances, it is convenient to introduce instead of p_y and y creation and destruction operators defined by

$$y=(a+a^{\dagger})/(2s)^{\frac{1}{2}}, \quad p_y=(\tfrac{1}{2}s)^{\frac{1}{2}}(a-a^{\dagger})/i; \quad \text{(C.1)}$$

then

$$(a,a^{\dagger})=1 \quad \text{(C.2)}$$

and

$$\begin{aligned} p_y{}^2+s^2y^2&=s(aa^{\dagger}+a^{\dagger}a)=s(2N+1),\\ s^2y^2-p_y{}^2&=s(a^{\dagger 2}+a^2), \qquad \text{(C.3)}\\ s(yp_y+p_yy)&=-is(a^2-a^{\dagger 2}), \end{aligned}$$

where $N\equiv a^{\dagger}a$ has integer eigenvalues 0, 1, 2, $\cdots$.

All terms now have a common factor of s, which we shall drop; the final energy levels should be multiplied by s. In terms of these new operators, the matrix operator (V.17) becomes (on changing the labeling as indicated):

$$\begin{array}{r} \frac{3}{2} \\ -\frac{1}{2} \\ \frac{1}{2} \\ -\frac{3}{2} \end{array}\left\|\begin{array}{cccc} \alpha(2N+1) & \gamma a^{\dagger 2} & 0 & 0 \\ \gamma a^{2} & \beta(2N+1) & 0 & 0 \\ 0 & 0 & \beta(2N+1) & \gamma a^{\dagger 2} \\ 0 & 0 & \gamma a^{2} & \alpha(2N+1) \end{array}\right\|. \quad \text{(C.4)}$$

Here $\alpha\equiv\frac{1}{2}(A+B)$, $\beta\equiv\frac{1}{6}(A+5B)$, $\gamma\equiv\sqrt{3}(\alpha-\beta)$. Therefore the eigenvalue problem factors into two 2×2 problems, which differ from each other only in that α and β are interchanged. We consider only the first one.

If we expand the wave function in eigenfunctions ψ_n of N,

$$f_j=\textstyle\sum_n f_j(n)\psi_n, \quad \text{(C.5)}$$

and make use of the well-known properties,

$$a^{\dagger}\psi_n=(n+1)^{\frac{1}{2}}\psi_{n+1}, \quad a\psi_n=n^{\frac{1}{2}}\psi_{n-1}, \quad \text{(C.6)}$$

of the creation and destruction operators, we obtain

$$\begin{aligned} &[\alpha(2n+1)-\epsilon]f_1(n)+\gamma[n(n-1)]^{\frac{1}{2}}f_2(n-2)=0,\\ &\gamma[(n+1)(n+2)]^{\frac{1}{2}}f_1(n+2), \qquad \text{(C.7)}\\ &\qquad\qquad [\beta(2n+1)-\epsilon]f_2(n)=0, \end{aligned}$$

for the eigenvalue problem of the first 2×2 block.

These equations are solved at once by the following Ansatz:

$$f_1(n)=C_1\delta_{n,\,n_0}, \quad f_2(n)=C_2\delta_{n+2,n_0}, \quad \text{(C.8)}$$

which yields

$$\begin{aligned} &[\alpha(2n_0+1)-\epsilon]C_1+\gamma[n_0(n_0-1)]^{\frac{1}{2}}C_2=0,\\ &\gamma[n_0(n_0-1)]^{\frac{1}{2}}C_1+[\beta(2n_0-3)-\epsilon]C_2=0. \end{aligned} \quad \text{(C.9)}$$

The first equation is valid for $n_0=0, 1, 2, \cdots$, while the second is valid for $n_0=2, 3, \cdots$. The condition that C_1, C_2 do not vanish identically yields

$$\left|\begin{array}{cc} \alpha(2n_0+1)-\epsilon & \gamma[n_0(n_0-1)]^{\frac{1}{2}} \\ \gamma[n_0(n_0-1)]^{\frac{1}{2}} & \beta(2n_0-3)-\epsilon \end{array}\right|=0 \quad \text{(C.10)}$$

for $n_0=2, 3, \cdots$, and

$$\epsilon=\alpha(2n_0+1) \quad \text{(C.11)}$$

for $n_0=0$, 1. Solving (C.10), we get

$$\begin{aligned} \epsilon^{\pm}(n_0)=\tfrac{1}{2}\{&(\alpha+\beta)(2n_0+1)-4\beta\\ &\pm[((\alpha-\beta)(2n_0+1)+4\beta)^2+4\gamma^2n_0(n_0-1)]^{\frac{1}{2}}\}, \quad \text{(C.12)}\\ &n_0=2, 3, \cdots. \end{aligned}$$

The expressions (C.11) and (C.12) represent all eigenvalues of (C.7), as may easily be seen by considering the limiting case where $\gamma=0$. Therefore the totality of eigenvalues of (V.17) for this case is

$$\begin{aligned} \epsilon^{\pm}(n_0)=\tfrac{1}{2}\{&(\alpha+\beta)(2n_0+1)-4\beta\\ &\pm[((\alpha-\beta)(2n_0+1)+4\beta)^2+4\gamma^2n_0(n_0-1)]^{\frac{1}{2}}\},\\ \epsilon'^{\pm}(n_0)=\tfrac{1}{2}\{&(\alpha+\beta)(2n_0+1)-4\alpha\\ &\pm[((\beta-\alpha)(2n_0+1)+4\alpha)^2+4\gamma^2n_0(n_0-1)]^{\frac{1}{2}}\}, \quad \text{(C.13)} \end{aligned}$$

for $n_0=2, 3, \cdots$;

$$\epsilon(n_0)=\alpha(2n_0+1), \quad \beta(2n_0+1) \text{ for } n_0=0, 1.$$

The levels are no longer each doubly degenerate, the time reversal symmetry having been lifted by the external magnetic field. To see what the "classical" expression for these levels are we first need the form of the energy surfaces. From (V.13), there are at once seen to be

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

where each is doubly degenerate.

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

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

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)

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

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

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

Thus the donor nucleus produces an additional effective field

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

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

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

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

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

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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