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Quantum Theory of Cyclotron Resonance in Semiconductors: General Theory*

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The most general form of the Hamiltonian of an electron or hole in a semiconductor such as Si or Ge, in the presence of an external homogeneous magnetic field, is given. Two methods of obtaining the corresponding energy levels are discussed. The first should yield very accurate values for the magnetic field in the (111) direction for either Si or Ge. The second is a perturbation method and is expected to give good results only for Ge.

INTRODUCTION

In collaboration with W. Kohn, the author has recently[1] treated the problem of cyclotron resonance for degenerate bands in semiconductors such as Ge and Si. In particular, it was predicted that for such bands there would be characteristic quantum deviations from the usual classical result at sufficiently low temperatures. These effects now seem to have been observed by Fletcher[2] for Ge. Working at 1.3°K to 4.2°K, and at very low power levels, he found that in addition to the usual "classical" absorption frequencies for light and heavy holes placed in an external magnetic field, there were also new absorption lines which increased in intensity as the temperature was lowered. This is just what one would expect on the basis of the quantum theory, since lowering the temperature populates the lower energy levels of the system more abundantly, and these are the ones that show marked deviations from the classical theory.

It is the purpose of the present paper to set up in the most general manner possible the theory of the energy levels in a magnetic field for holes—which occupy a degenerate band—in a semiconductor such as Ge or Si. This is done in Sec. I. In Sec. II this general theory will be specialized, and the techniques available for actually solving the resultant equations will be given.

No numerical results or detailed comparison with experiment will be given in this paper. Such comparison will be the subject of a later paper. It may be said, however, that although the numerical work is not yet complete, there are already very strong indications that many of Fletcher's new lines are indeed those predicted by the theory given here.

I. GENERAL THEORY

(1) We shall first consider, for illustrative purposes, the case in which there is no spin-orbit coupling, and indeed, all effects of electron spin are neglected. In this case the energy levels are determined by Eq. (IV.14) of LK. The result may be stated as follows: consider an electron (of charge $-e$) in an external homogeneous magnetic field of magnitude H, the direction of which we shall call the "3" direction. The "1" and "2" directions will be any two perpendicular to each other and to $\mathbf{H}$, which form a right-handed coordinate system with $\mathbf{H}$. Let the vector potential representing $\mathbf{H}$ be $\mathbf{A}$. We shall always choose for $\mathbf{A}$ the "Landau" gauge

$$A_1=-Hx_2,\quad A_2=A_3=0. \tag{1}$$

The energy levels of the electron, in this external field, are then given by solving the coupled equations[3]

$$\sum_{j'}\left[D_{jj'}^{\alpha\beta}\left(p_\alpha+\frac{e}{c}A_\alpha\right)\left(p_\beta+\frac{e}{c}A_\beta\right)\right]F_{j'}(\mathbf{r})=EF_j(\mathbf{r}). \tag{2}$$

In (2) the repeated indices α and β are summed over x, y, z. The summation over j' is a summation over the number of degenerate states for the band edge in question, which would be three for Ge (say). The quantity p_α is just the usual momentum operator $(1/i)(\partial/\partial x_\alpha)$, and the F_j are related to the wave function of the system by the equation

$$\psi=\textstyle\sum_j F_j(\mathbf{r})\phi_j, \tag{3}$$

the ϕ_j being the degenerate solutions of the unperturbed problem. Finally the quantities $D_{jj'}^{\alpha\beta}$, are a set of numbers defined by

$$D_{jj'}^{\alpha\beta}=\frac{1}{2m}\delta_{jj'}\delta_{\alpha\beta}+\frac{1}{m^2}\sum_i\frac{p_{ji}^\alpha p_{ij'}^\beta}{\epsilon_0-\epsilon_i}, \tag{4}$$

where the summation over i is over all those states of the unperturbed problem not belonging to the degenerate set j, ϵ_0 is the energy of the degenerate set, ϵ_i the energy of the ith unperturbed state, and finally the p_{ji}^α are just the momentum matrix elements between the different bands, evaluated at the degeneracy point.

In deriving (2), LK assumed that the symmetry property $D_{jj'}^{\alpha\beta}=D_{jj'}^{\beta\alpha}$ was valid. By inspection of (4) one can see that there is no general reason for this to be so, and it will be true only in very special circumstances.

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[1] J. M. Luttinger and W. Kohn, Phys. Rev. **97**, 869 (1955). See also W. Kohn and J. M. Luttinger, Phys. Rev. **96**, 529 (1954). We shall refer to the former paper as LK from now on.

[2] Fletcher, Yager, and Merritt, Phys. Rev. **100**, 747 (1955).

[3] Units are chosen so that $\hbar=1$.

The only general symmetry which is valid is $(D_{jj'}{}^{\alpha\beta})^* = D_{j'j}{}^{\beta\alpha}$, which follows at once from the Hermiticity of the momentum matrix elements $p_{ji}{}^{\alpha}$. Nonetheless, Eq. (2) is still correct, as may very easily be seen by carrying through the derivation just as in LK, but without the aforementioned symmetry.[4]

From this result, it follows that the cyclotron resonance equations contain extra constants which are not included in either the expression for the energy surfaces or in the impurity state problem. To see this we proceed as follows. Define

$$k_\alpha = p_\alpha + (e/c)A_\alpha. \tag{5}$$

If there is no external magnetic field the different components of $\mathbf{k}$ commute. Then in (2) only the part of $D_{jj'}{}^{\alpha\beta}$ symmetric in α and β will contribute, the antisymmetric part giving nothing since $k_\alpha k_\beta$ is symmetric. Thus the expression for the energy as a function of k_α is a function only of the "symmetric constants" $D_{jj'}{}^{\alpha\beta} + D_{jj'}{}^{\beta\alpha}$. If the external magnetic field is present, however, then the different components of $\mathbf{k}$ *do not* commute. In fact, we have

$$(k_x, k_y) = (1/i)(e/c)H_z \tag{6}$$

the other commutators being obtained by cyclic permutation of the indices. Therefore the "antisymmetric constants" $D_{jj'}{}^{\alpha\beta} - D_{jj'}{}^{\beta\alpha}$ also contribute to the energy levels in a magnetic field.

Now for a band like the valence band of Ge or Si, it is well known that the symmetrical constants may all be expressed in terms of three independent ones. The explicit representation is given by (V.9) and (V.10) of LK, for example. At $\mathbf{k}=0$ there are three real degenerate functions which transform like x, y, z under the operations of the cubic point group. Denote these functions by X, Y, Z, respectively. Defining a matrix D by its elements

$$D_{jj'} = D_{jj'}{}^{\alpha\beta} k_\alpha k_\beta, \tag{7}$$

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

$$D = \left\| \begin{matrix} Ak_x^2 + B(k_y^2 + k_z^2) & Ck_xk_y & Ck_xk_z \\ Ck_xk_y & Ak_y^2 + B(k_z^2 + k_x^2) & Ck_yk_z \\ Ck_xk_z & Ck_yk_z & Ak_z^2 + B(k_x^2 + k_y^2) \end{matrix} \right\|. \tag{8}$$

Here A, B, and C are the three real constants:

$$\begin{aligned} A &= D_{XX}{}^{xx}, \\ B &= D_{XX}{}^{yy}, \\ C &= D_{XY}{}^{xy} + D_{XY}{}^{yx}. \end{aligned} \tag{9}$$

This result was obtained by ignoring the noncommutivity the components of $\mathbf{k}$ in the presence of a magnetic field. Now the question arises: how many new independent constants are brought in by the antisymmetric parts of the $D_{jj'}{}^{\alpha\beta}$, and what is the explicit representation of the operator D in terms of them? Since all the $D_{jj'}{}^{\alpha\beta}$, are real, there will be no correction to the diagonal elements of D. Let us take a typical off-diagonal term:

$$D_{XY} = D_{XY}{}^{xy} k_x k_y + D_{XY}{}^{yx} k_y k_x, \tag{10}$$

all other constants vanishing by symmetry. Defining a new "antisymmetric constant" K by

$$K = D_{XY}{}^{xy} - D_{XY}{}^{yx}, \tag{11}$$

we may write (10) as

$$D_{XY} = C\{k_x k_y\} + \tfrac{1}{2}K(k_x, k_y), \tag{12}$$

where we have employed the notation

$$\{k_x k_y\} = \tfrac{1}{2}(k_x k_y + k_y k_x) \tag{13}$$

for the symmetrized product. Using (6), (12) becomes

$$D_{XY} = C\{k_x k_y\} + (K/2i)(e/c)H_z. \tag{14}$$

The same analysis for D_{YX} gives

$$D_{YX} = C\{k_x k_y\} - (K/2i)(e/c)H_z, \tag{15}$$

and the results for the other off-diagonal components may be written down by cyclic permutation. Thus there is *one* extra constant K which enters the energy-level formulas. D then consists of two parts

$$D = D^{(S)} + D^{(A)}. \tag{16}$$

$D^{(S)}$ is just given by (8) with $k_\alpha k_\beta \to \{k_\alpha k_\beta\}$. For $D^{(A)}$ we obtain

$$D^{(A)} = -\frac{e}{c}\frac{K}{2} \left\| \begin{matrix} 0 & -iH_z & iH_y \\ iH_z & 0 & -iH_x \\ -iH_y & iH_x & 0 \end{matrix} \right\|. \tag{17}$$

Both the expression for $D^{(A)}$ and that for $D^{(S)}$ become much more transparent if we express all matrices in terms of "spin" matrices corresponding to spin unity. Let us define the three matrices

$$I_x = \left\| \begin{matrix} 0 & 0 & 0 \\ 0 & 0 & -i \\ 0 & i & 0 \end{matrix} \right\|, \quad I_y = \left\| \begin{matrix} 0 & 0 & i \\ 0 & 0 & 0 \\ -i & 0 & 0 \end{matrix} \right\|, \quad I_z = \left\| \begin{matrix} 0 & -i & 0 \\ i & 0 & 0 \\ 0 & 0 & 0 \end{matrix} \right\|. \tag{18}$$

These matrices have the commutation rules of angular

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[4] Thus, though the final equation (IV.14) is generally valid, the preliminary equation (IV.13) is not.

momentum, i.e.,

$$(I_x,I_y)=iI_z,\quad (I_y,I_z)=iI_x,\quad (I_z,I_x)=iI_y, \tag{19}$$

and also satisfy

$$I_x^2+I_y^2+I_z^2=\left\|\begin{matrix}2 & 0 & 0\\ 0 & 2 & 0\\ 0 & 0 & 2\end{matrix}\right\|, \tag{20}$$

so that they correspond to unit spin.[5]

In terms of the matrices just defined we have

$$\begin{aligned}D^{(S)}=Ak^2-(A-B)(k_x^2I_x^2+k_y^2I_y^2+k_z^2I_z^2)\\ -2C(\{k_xk_y\}\{I_xI_y\}+\{k_yk_z\}\{I_yI_z\}\\ +\{k_zk_x\}\{I_zI_x\}),\end{aligned} \tag{21}$$

$$D^{(A)}=(e/2c)K(I_xH_x+I_yH_y+I_zH_z)=(e/2c)K\mathbf{I}\cdot\mathbf{H}. \tag{22}$$

It is possible to give the extra term $D^{(A)}$ a simple physical interpretation, in the limit where the binding of the electrons is very tight. In that case the "effective masses" A, B, C must be very small, and the electron is essentially always bound to one ion or the other. Thus we are finding how the degenerate levels of an electron bound to an atom are split in the presence of a magnetic field. If μ is the Bohr magneton, then this splitting is just given by

$$\mu\mathbf{I}\cdot\mathbf{H}=(e/mc)\mathbf{I}\cdot\mathbf{H}, \tag{23}$$

which is exactly of the form (22). To check this interpretation, we have to show that K, as calculated from (11) with the use of tight binding wave functions for $\mathbf{k}=0$ has the value $1/m$. A straightforward calculation reveals this to be true.

(2) The problem of finding energy levels in a magnetic field is completely described, for no spin-orbit coupling, by the "Hamiltonian" (16), and (21) and (22). Before we go on to the spin-orbit case, which is the practical one, it is very convenient to obtain these results by another method of analysis.

The Hamiltonian D must be a three-by-three matrix, every element of which is a quadratic function of the components of $\mathbf{k}$. Now let us consider the matrices I_x, I_y, I_z and their products. The nine matrices 1, I_x, I_y, I_z, I_x^2, I_y^2, $\{I_xI_y\}$, $\{I_yI_z\}$, $\{I_zI_x\}$ are easily seen to be linearly independent, and, therefore, any arbitrary 3×3 matrix may be expressed in terms of them. (Products of more than two I's can occur, but since the I's are 3×3 matrices, any cubic expression may clearly be reduced to lower orders, e.g., $I_z^3=I_z$, etc.) Now, further, we can allow the I_x, I_y, I_z to transform (if we make a coordinate transformation) just like an axial vector,[6] since the I's are angular momentum matrices. That is, whenever we transform coordinate systems we transform I_α as well as k_α. This just corresponds to a numerical canonical transformation on D, and cannot change any of its characteristic values. We now require that, expressed in terms of the I_α and the k_α, the Hamiltonian D should be invariant under the operations of the cubic group. Clearly this will insure that the Hamiltonian will give us results which transform correctly with respect to the transformations of the cubic point group, which is the symmetry group of $\mathbf{k}$.

Now $\mathbf{k}$ transforms like an ordinary vector and, therefore (see Appendix A), like the representation T_1 of the cubic group. Since $\mathbf{I}$ transforms like an axial vector, it belongs to the representation T_2 of the cubic group. Let us classify the irreducible representations which may be constructed with the I_α.

(a) The zeroth power of I_α contains only the unit matrix. Therefore, it only contains the identity or A_1 representation.

(b) The first powers of I_α are just the irreducible representation T_2.

(c) The second powers of I_α (that is the reduction of $I_\alpha I_\beta$) contains the representation

$$T_2\times T_2=A_1+E+T_1+T_2, \tag{24}$$

which (see Appendix A again) may be decomposed into a symmetric part and an antisymmetric part, i.e.,

$$(T_2\times T_2)_S=A_1+E+T_1,\quad (T_2\times T_2)_A=T_2. \tag{25}$$

The antisymmetric part just consists of terms like $I_\alpha I_\beta-I_\beta I_\alpha$, which may be reduced by means of the commutation rules to the vector $\mathbf{I}$ again, so this is nothing new. For the symmetric part one easily sees the quantities belonging to A_1, E, and T_1 are, respectively,

$$\begin{aligned}A_1&: I_x^2+I_y^2+I_z^2=I^2=2,\\ E&: I_x^2-I_y^2,\ I_y^2-I_z^2,\\ T_1&: \{I_xI_y\},\ \{I_yI_z\},\ \{I_zI_x\}.\end{aligned}$$

That is, the A_1 is just proportional to the unit matrix and gives us nothing new. Thus, out of the I_α we can construct four independent irreducible representations, one belonging to each of A_1, E, T_1, T_2.

Consider on the other hand the k_α. Since the Hamiltonian must depend on k_α quadratically, we ask what irreducible representations are contained in $T_1\times T_1$.

$$T_1\times T_1=A_1+E+T_1+T_2, \tag{26}$$

$$(T_1\times T_1)_S=A_1+E+T_1, \tag{27}$$

$$(T_1\times T_1)_A=T_2. \tag{28}$$

Therefore, we have 4 independent irreducible representations, one belonging to each of A_1, E, T_1, T_2. Combining this with our result for the I's, we see that there are at most 4 independent invariants made of their products. That is, we must construct out of the I's and k's quantities which are invariant, i.e., which belong to A_1. Only the product of two identical irre-

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[5] See, for example, L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, New York, 1949), p. 144. The representation chosen there differs from ours.

[6] If we let them transform like an ordinary vector, they would all change sign under an inversion, which would violate the commutation rules. Therefore, a canonical transformation cannot change the sign of all the I's.

ducible representations can contain the identity representation, as may be easily verified for this particular group, from the direct products given in Appendix A. It is very easy to write these four invariants explicitly. From the symmetrical part of k_α products we have the three invariants

$$\begin{aligned}&k_x^2+k_y^2+k_z^2=k^2,\\&k_x^2I_x^2+k_y^2I_y^2+k_z^2I_z^2,\\&\{k_xk_y\}\{I_xI_y\}+\{k_yk_z\}\{I_yI_z\}+\{k_zk_x\}\{I_zI_x\},\end{aligned}\tag{29}$$

while from the antisymmetrical products we have the single invariant

$$(k_y,k_z)I_x+(k_z,k_x)I_y+(k_x,k_y)I_z.\tag{30}$$

Using (6) we see that (30) is equivalent to

$$H_xI_x+H_yI_y+H_zI_z.\tag{31}$$

Therefore, the most general Hamiltonian possible is given by

$$\begin{aligned}D=\alpha_1k^2&+\alpha_2(k_x^2I_x^2+k_y^2I_y^2+k_z^2I_z^2)\\&+\alpha_3(\{k_xk_y\}\{I_xI_y\}+\{k_yk_z\}\{I_yI_z\}+\{k_zk_x\}\{I_zI_x\})\\&\qquad+\alpha_4(H_xI_x+H_yI_y+H_zI_z).\end{aligned}\tag{32}$$

This is clearly identical with (21) and (22), by suitable choice of the α_i.[7] The advantage of this method over the original one is that it can be generalized almost word for word to the case where spin-orbit coupling of arbitrary strength is present.

(3) If spin-orbit coupling is present, the original sixfold degenerate level (the extra factor of two coming from spin) breaks up into a fourfold and a twofold degenerate one. It is generally believed that the fourfold degenerate level lies higher and hence is the important one for the cyclotron resonance experiments at low temperatures. We shall deal with the fourfold case here. The result for the twofold case is given in Appendix B. It may in fact prove possible by suitable external excitation to make observations on the latter case, though there is no evidence that this has been done as yet.

Since the band edge is fourfold degenerate, the Hamiltonian D will now be four by four. We now introduce any three 4×4 matrices, J_x, J_y, J_z, which satisfy the commutation rules of angular momentum, i.e.,

$$(J_x,J_y)=iJ_z,\text{ etc.,}\tag{33}$$

and

$$J_x^2+J_y^2+J_z^2=\tfrac{3}{2}(\tfrac{3}{2}+1)=15/4.\tag{34}$$

That is, these are the angular momentum matrices for a state with spin $\frac{3}{2}$. It is easily seen that the following 16 matrices are linearly independent:

$$\begin{aligned}&1,\ J_x,\ J_y,\ J_z,\ J_x^2,\ J_y^2,\ \{J_xJ_y\},\ \{J_yJ_z\},\ \{J_zJ_x\},\\&\{(J_y^2-J_z^2)J_x\}\equiv V_x,\ \{(J_z^2-J_x^2)J_y\}\\&\qquad\equiv V_y,\ \{(J_x^2-J_y^2)J_z\}\equiv V_z,\\&J_x^3,\ J_y^3,\ J_z^3,\ J_xJ_yJ_z+J_zJ_yJ_x,\end{aligned}\tag{35}$$

and, therefore, any arbitrary 4×4 matrix may be expanded in terms of them.

Now all the results we have derived for the no spin-orbit case apply equally well to the spin-orbit case. J_α transforms as T_2 for the same reason that I_α did. Thus the invariants (29) and (31) are all still possible, with the simple replacement of $I_\alpha\rightarrow J_\alpha$. To see whether anything new arises, we must then investigate whether any invariants can be constructed out of the cubic expressions occurring in (35). It is very easy to see by calculating characters that

$$\begin{aligned}&V_x,\ V_y,\ V_z\text{ belong to }T_1,\\&J_x^3,\ J_y^3,\ J_z^3\text{ belong to }T_2,\\&J_xJ_yJ_z+J_zJ_yJ_x\text{ belongs to }A_2.\end{aligned}$$

Since A_2 occurs nowhere in the reduction of $k_\alpha k_\beta$ we have at once that this last term cannot occur, since we cannot form an invariant with it. In the $k_\alpha k_\beta$ decomposition only $\{k_yk_z\}$, $\{k_zk_x\}$, $\{k_xk_y\}$ transform like T_1, and only (k_y,k_z), (k_z,k_x), (k_x,k_y) or H_x, H_y, H_z, transform like T_2. Therefore we get only two new invariants:

$$V_x\{k_yk_z\}+V_y\{k_zk_x\}+V_z\{k_xk_y\}\tag{36}$$

and

$$J_x^3H_x+J_y^3H_y+J_z^3H_z.\tag{37}$$

Thus there would seem to be in general six constants necessary to describe the Hamiltonian for the spin-orbit case. However, an investigation of the time-reversal properties of (36) shows that this cannot occur. In the case where there is no magnetic field present, the Hamiltonian of the system certainly must be invariant under the operation of time-reversal, since the original Hamiltonian has this invariance property. Now time-reversal must simply change the J_α into $-J_\alpha$. This is true because the J_α are the matrix representations of the orbital angular momentum operator L_α for a state with $j=\frac{3}{2}$. But L_α is an odd operator (it contains the velocity or momentum linearly) and therefore J_α is odd. If there is no magnetic field, the terms like (29) and (36) still occur, while (31) and (37) do not. All the invariants in (29) contain J_α an even number of times, so they are allowed by time-reversal. The invariant (36), on the other hand contains J_α three times; it therefore changes sign under time-reversal, and is not allowed. Thus the most general Hamiltonian for the spin-orbit case is

$$\begin{aligned}D=\beta_1k^2&+\beta_2(k_x^2J_x^2+k_y^2J_y^2+k_z^2J_z^2)\\&+\beta_3(\{k_xk_y\}\{J_xJ_y\}+\{k_yk_z\}\{J_yJ_z\}\\&+\{k_zk_x\}\{J_zJ_x\})+\beta_4(H_xJ_x+H_yJ_y+H_zJ_z)\\&\qquad+\beta_5(H_xJ_x^3+H_yJ_y^3+H_zJ_z^3).\end{aligned}\tag{38}$$

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[7] That the α_i are real follows from the requirement that the Hamiltonian be Hermitian.

That is, five constants are necessary to describe the energy levels. It should be emphasized that we have nowhere made any assumption about the strength of the spin-orbit coupling, and this means that in general the constants β_i are in no way related to the α_i. (If the spin-orbit coupling is small, however, we can relate them.) If we are not dealing with an external magnetic field, but just want the shape of the energy surface, or want to deal with the impurity problem, then the last two terms of (38) vanish, and the band is described by three constants. If now we choose the following representation for the J_x, J_y, J_z:

$$J_x=\left\|\begin{matrix} 0 & \sqrt{3}i/2 & 0 & 0 \\ -\sqrt{3}i/2 & 0 & i & 0 \\ 0 & -i & 0 & \sqrt{3}i/2 \\ 0 & 0 & -\sqrt{3}i/2 & 0 \end{matrix}\right\|,$$

$$J_y=\left\|\begin{matrix} 0 & \sqrt{3}/2 & 0 & 0 \\ \sqrt{3}/2 & 0 & 1 & 0 \\ 0 & 1 & 0 & \sqrt{3}/2 \\ 0 & 0 & \sqrt{3}/2 & 0 \end{matrix}\right\|, \qquad (39)$$

$$J_z=\left\|\begin{matrix} \frac{3}{2} & 0 & 0 & 0 \\ 0 & \frac{1}{2} & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & 0 \\ 0 & 0 & 0 & -\frac{3}{2} \end{matrix}\right\|,$$

and write

$$\begin{aligned} \beta_1 &= (3A+B)/4, \\ \beta_2 &= -\tfrac{1}{3}(A-B), \\ \beta_3 &= -\tfrac{2}{3}C, \end{aligned} \qquad (40)$$

then we see at once that (38) is identical with the first four rows and columns of (v. 13) in LK, which was obtained on the basis of very weak spin-orbit coupling. The only difference is that A, B, and C are no longer necessarily given by (9). Since these are parameters which we fit to experiment, this makes, in general, little difference. Thus the form of the Hamiltonian is totally unchanged no matter how strong the spin-orbit coupling is, as long as no magnetic field is present. This is no longer true when a field is present, since the last term of (38) represents a new invariant which gives no contribution when the spin-orbit coupling gets extremely weak (i.e., β_5 approaches zero as the spin-orbit coupling does). To see this in detail, and also to see the relationships between the α_i and β_i (which are very convenient to have if we want to make estimates of the β_i), let us consider the case of very small spin-orbit coupling. Then the Hamiltonian corresponding to the no-spin orbit point of view is

$$\begin{aligned} D=Ak^2-(A-B)(k_x^2I_x^2+k_y^2I_y^2+k_z^2I_z^2) \\ -2C(\{k_xk_y\}\{I_xI_y\}+\{k_yk_z\}\{I_yI_z\}+\{k_zk_x\}\{I_zI_x\}) \\ +(e/2c)K\mathbf{I}\cdot\mathbf{H}+\mu(\boldsymbol{\sigma}\cdot\mathbf{H}). \quad (41) \end{aligned}$$

In (41) the last term is new, and represents the interaction of the electron's spin magnetic moment with the external magnetic field. The quantity $\boldsymbol{\sigma}$ is of course the Pauli spin matrix vector. The space on which (41) operates is the direct product of the 3×3 space of the I_α and the 2×2 space of $\boldsymbol{\sigma}$, so that (41) is really a 6×6 matrix operator. This electron spin term is usually quite small, but we include it for completeness. Now, in the limit of infinitely weak spin-orbit coupling, (41) may be transformed directly into the correct spin-orbit Hamiltonian. This is done in Appendix B. The result is the following:

$$\begin{aligned} D=(3A+B/4)k^2-\tfrac{1}{3}(A-B)(k_x^2J_x^2+k_y^2J_y^2+k_z^2J_z^2) \\ -\tfrac{2}{3}C(\{k_xk_y\}\{J_xJ_y\}+\{k_yk_z\}\{J_yJ_z\}+\{k_zk_x\}\{J_zJ_x\}) \\ +(e/3mc)(mK+1)\mathbf{J}\cdot\mathbf{H}. \quad (42) \end{aligned}$$

Comparison with (38) shows that for the case in which the spin-orbit coupling is very weak, we have

$$\begin{aligned} \beta_1 &= (3A+B)/4, \\ \beta_2 &= -\tfrac{1}{3}(A-B), \\ \beta_3 &= -\tfrac{2}{3}C, \\ \beta_4 &= (e/3mc)(mK+1), \\ \beta_5 &= 0. \end{aligned} \qquad (43)$$

Therefore, the constant β_5 is only introduced by the spin-orbit coupling. For Si, this correction will probably be utterly negligible, but for Ge, in which the spin-orbit splitting is comparable though somewhat less than the band separation, it might have observable effects.

II. DETERMINATION OF THE ENERGY LEVELS

(1) In the previous section we have set up the general Hamiltonian (38), the characteristic values of which give the allowed energy levels of the system. We now turn to the actual problem of determining these characteristic values. Unfortunately it has not proven possible to find a general solution of the problem. We have, however, developed what seem to be excellent approximation methods which are applicable to the experimental situation so far realized. Since we are dealing with the upper band edge (i.e., with holes in the valence band) the energy levels will in general decrease as we go to more excited states. In order to think of the energy level scheme in the more usual way, we shall deal from now on with the negative of (38) as our Hamiltonian. It then proves convenient to introduce the dimensionless constants γ_1, γ_2, γ_3, κ, and q by

$$\begin{aligned} &(1/2m)\gamma_1=-\tfrac{1}{3}(A+2B), \quad && (1/m)(3\kappa+1)=-K, \\ &(1/2m)\gamma_2=-\tfrac{1}{6}(A-B), && (e/mc)q=-\beta_5, \qquad (44) \\ &(1/2m)\gamma_3=-\tfrac{1}{6}C. && \end{aligned}$$

When we replace D by $-D$, (38), (44), and (40) yield

$$D=\frac{1}{m}\left\{\left(\gamma_1+\frac{5\gamma_2}{2}\right)\frac{k^2}{2}-\gamma_2(k_x^2J_x^2+k_y^2J_y^2+k_z^2J_z^2)\right.$$
$$-2\gamma_3(\{k_xk_y\}\{J_xJ_y\}+\{k_yk_z\}\{J_yJ_z\}+\{k_zk_x\}\{J_zJ_x\})$$
$$\left.+\frac{e}{c}\kappa\mathbf{J}\cdot\mathbf{H}+\frac{e}{c}q(J_x^3H_x+J_y^3H_y+J_z^3H_z)\right\}. \quad (45)$$

We shall limit ourselves to the case in which the momentum along the magnetic field (k_3) is zero. Clearly by the commutation relations (6), which hold in any rectangular coordinate system, k_3 commutes with k_1 and k_2 and is, therefore, a constant of the motion. The energy levels will depend parametrically on k_3 in some involved way. The same is true for degenerate bands, even in the classical limit. Since the allowed values of k_3 will be thermally distributed, there will be a broadening and shift of the absorption line due to k_3. This effect has been investigated in the classical limit.[8] The shift in resonance frequency depends on $\omega_r\tau$, where ω_r is the resonant frequency and τ is a measure of the relaxation time for the holes. For $\omega_r\tau=7.5$ the shift was only about 3% (for Ge), and it decreases rapidly with increasing $\omega_r\tau$. For Fletcher's experiments there are $\omega_r\tau$'s of perhaps 30 or 40, so the effect should be very small indeed. Further, it is possible that the effect is still *smaller* in the low-temperature quantum case since large k_3 are not excited. In fact, at absolute zero, there should be no shift at all. We therefore feel justified in tentatively taking $k_3=0$. It is easy, though tedious, to include the k_3 dependence in the calculations given in Sec. II(2), and we hope to return later to a detailed verification of this assumption.

With $k_3=0$ the Hamiltonian (45) is still not soluble for an arbitrary direction of the magnetic field. However, if the magnetic field is in the (111) crystallographic direction, it becomes possible to reduce the problem rigorously to a much simpler algebraic one which requires at most finding the characteristic values of a 4×4 numerical matrix. To see this we must first express $\mathbf{k}$ in its (1,2,3) components. One simple choice for the 1 and 2 axes gives

$$\begin{aligned}
k_x&=\frac{1}{\sqrt{6}}k_1-\frac{1}{\sqrt{2}}k_2+\frac{1}{\sqrt{3}}k_3=\frac{1}{\sqrt{6}}k_1-\frac{1}{\sqrt{2}}k_2,\\
k_y&=\frac{1}{\sqrt{6}}k_1+\frac{1}{\sqrt{2}}k_2+\frac{1}{\sqrt{3}}k_3=\frac{1}{\sqrt{6}}k_1+\frac{1}{\sqrt{2}}k_2,\\
k_z&=-\left(\frac{2}{3}\right)^{\frac{1}{2}}k_1+\frac{1}{\sqrt{3}}k_3=-\left(\frac{2}{3}\right)^{\frac{1}{2}}k_1.
\end{aligned} \quad (46)$$

The situation is considerably simplified if we also transform the J in the same way as the k_α when we choose a new direction of magnetic field. (This actually corresponds to quantizing our original degenerate states along the direction of the magnetic field). That is, we put

$$\begin{aligned}
J_x&=\frac{1}{\sqrt{6}}J_1-\frac{1}{\sqrt{2}}J_2+\frac{1}{\sqrt{3}}J_3,\\
J_y&=\frac{1}{\sqrt{6}}J_1+\frac{1}{\sqrt{2}}J_2+\frac{1}{\sqrt{3}}J_3,\\
J_z&=-\left(\frac{2}{3}\right)^{\frac{1}{2}}J_1+\frac{1}{\sqrt{3}}J_3.
\end{aligned} \quad (47)$$

It is easily seen that the transformation is a canonical one—it is just a rotation—so that the characteristic values of (45) are left unchanged by it. Further, by (6)

$$(k_1,k_2)=(1/i)(e/c)H,$$

so that p and q defined by

$$k_1=(eH/c)^{\frac{1}{2}}p,\quad k_2=(eH/c)^{\frac{1}{2}}q, \quad (48)$$

are canonical variables, i.e.,

$$(p,q)=1/i. \quad (49)$$

We shall often make use of the creation and destruction operators $a^\dagger$ and a defined by

$$a^\dagger=(1/\sqrt{2})(p+iq),\quad a=(1/\sqrt{2})(p-iq). \quad (50)$$

These operators have the commutation rule

$$(a,a^\dagger)=1. \quad (51)$$

They also have the following properties: If we call the harmonic oscillator eigenfunctions u_n, then we know that

$$\tfrac{1}{2}(p^2+q^2)u_n=(a^\dagger a+\tfrac{1}{2})u_n=(n+\tfrac{1}{2})u_n, \quad (52)$$

or

$$a^\dagger a u_n=nu_n. \quad (53)$$

Further

$$au_n=n^{\frac{1}{2}}u_{n-1},\quad a^\dagger u_n=(n+1)^{\frac{1}{2}}u_{n+1}, \quad (54)$$

if the phases of the u_n are properly choosen.

In terms of these operators, we may write (45) as

$$D=\frac{eH}{mc}\{[\gamma_1-\gamma_3(5/4-J_3^2)](N+\tfrac{1}{2})$$
$$-\gamma_2S_1-\gamma_3S_2+\kappa J_3+qS_3\}, \quad (55)$$

where $N=a^\dagger a$,

$$\begin{aligned}
S_1&=\tfrac{1}{6}[(a^2+a^{\dagger 2})(J_1^2-J_2^2-\sqrt{2}\{J_1J_3\})\\
&\qquad+2i(a^2-a^{\dagger 2})(\{J_1J_2\}+\sqrt{2}\{J_2J_3\})],\\
S_2&=\tfrac{1}{3}[(a^2+a^{\dagger 2})(J_1^2-J_2^2+\sqrt{2}\{J_1J_3\})\\
&\qquad+i(a^2-a^{\dagger 2})(2\{J_1J_2\}-\sqrt{2}\{J_2J_3\})],\\
S_3&=1/3\sqrt{2}[-(5/2)J_1^3-2\sqrt{2}J_3^3+(41/4)\sqrt{2}J_3\\
&\qquad+(41/8)J_1+\tfrac{3}{2}\{J_1(J_2^2-J_3^2)\}].
\end{aligned} \quad (56)$$

We shall measure all energies in units of eH/mc from now on, so we may drop this factor from (55) and all subsequent energy expressions.

It is convenient to introduce a specific representation for the J_α at this point. Although it is possible to solve the problem with the conventional representation for the J_α, we prefer to choose another which simplifies

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[8] J. M. Luttinger and R. R. Goodman, Phys. Rev. **100**, 673 (1955). H. J. Zeiger, Phys. Rev. **98**, 560(A) (1955), also private communication.

the results somewhat in both this and the following section. Let us put

$$J_1=\begin{Vmatrix} 0 & 0 & \sqrt{3}/2 & 0 \\ 0 & 0 & 1 & \sqrt{3}/2 \\ \sqrt{3}/2 & 1 & 0 & 0 \\ 0 & \sqrt{3}/2 & 0 & 0 \end{Vmatrix},$$

$$J_2=\begin{Vmatrix} 0 & 0 & -\sqrt{3}i/2 & 0 \\ 0 & 0 & i & -\sqrt{3}i/2 \\ \sqrt{3}i/2 & -i & 0 & 0 \\ 0 & \sqrt{3}i/2 & 0 & 0 \end{Vmatrix}, \qquad (57)$$

$$J_3=\begin{Vmatrix} \frac{3}{2} & 0 & 0 & 0 \\ 0 & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & \frac{1}{2} & 0 \\ 0 & 0 & 0 & -\frac{3}{2} \end{Vmatrix}.$$

In terms of (57) we have

$$S_1=\frac{1}{\sqrt{3}}\begin{Vmatrix} 0 & a^2 & -\sqrt{2}a^{\dagger 2} & 0 \\ a^{\dagger 2} & 0 & 0 & \sqrt{2}a^{\dagger 2} \\ -\sqrt{2}a^2 & 0 & 0 & a^2 \\ 0 & \sqrt{2}a^2 & a^{\dagger 2} & 0 \end{Vmatrix},$$

$$S_2=\frac{1}{\sqrt{3}}\begin{Vmatrix} 0 & 2a^2 & \sqrt{2}a^{\dagger 2} & 0 \\ 2a^{\dagger 2} & 0 & 0 & -\sqrt{2}a^{\dagger 2} \\ -\sqrt{2}a^2 & 0 & 0 & 2a^2 \\ 0 & -\sqrt{2}a^2 & 2a^{\dagger 2} & 0 \end{Vmatrix}, \qquad (58)$$

$$S_3=\frac{1}{4}\begin{Vmatrix} 23/2 & 0 & 0 & -2\sqrt{2} \\ 0 & -13/2 & 0 & 0 \\ 0 & 0 & 13/2 & 0 \\ -2\sqrt{2} & 0 & 0 & -23/2 \end{Vmatrix}.$$

Finally, (55) becomes

$$D=\begin{Vmatrix} (\gamma_1+\gamma_3)(N+\frac{1}{2})+\frac{3}{2}\kappa+23q/8 & -g_1a^2 & -g_2a^{\dagger 2} & -q/\sqrt{2} \\ -g_1a^{\dagger 2} & (\gamma_1-\gamma_3)(N+\frac{1}{2})-\frac{1}{2}\kappa-13q/8 & 0 & g_2a^{\dagger 2} \\ -g_2a^2 & 0 & (\gamma_1-\gamma_3)(N+\frac{1}{2})+\frac{1}{2}\kappa+13q/8 & -g_1a^2 \\ -q/\sqrt{2} & g_2a^2 & -g_1a^{\dagger 2} & (\gamma_1+\gamma_3)(N+\frac{1}{2})-\frac{3}{2}\kappa-23q/8 \end{Vmatrix}, \qquad (59)$$

where

$$g_1=(2\gamma_3+\gamma_2)/\sqrt{3},$$

and

$$g_2=(\tfrac{2}{3})^{\frac{1}{2}}(\gamma_3-\gamma_2).$$

We must solve the Schrödinger equation

$$D\psi=E\psi. \qquad (60)$$

Inspection shows that the following Ansatz satisfies this equation:

$$\psi=\begin{Vmatrix} C_1u_n \\ C_2u_{n+2} \\ C_3u_{n-2} \\ C_4u_n \end{Vmatrix}, \qquad (61)$$

for $n\geqslant 2, 3, 4, \cdots$.

The C's are then the characteristic vectors of the matrices

$$\begin{Vmatrix} (\gamma_1+\gamma_3)(n+\frac{1}{2})+\frac{3}{2}\kappa+23q/8 & -g_1[(n+1)(n+2)]^{\frac{1}{2}} & -g_2[n(n-1)]^{\frac{1}{2}} & -q/\sqrt{2} \\ -g_1[(n+1)(n+2)]^{\frac{1}{2}} & (\gamma_1-\gamma_3)(n+5/2)-\frac{1}{2}\kappa-13q/8 & 0 & g_2[(n+1)(n+2)]^{\frac{1}{2}} \\ -g_2[n(n-1)]^{\frac{1}{2}} & 0 & (\gamma_1-\gamma_3)(n-\frac{3}{2})+\frac{1}{2}\kappa+13q/8 & -g_1[n(n-1)]^{\frac{1}{2}} \\ -q/\sqrt{2} & g_2[(n+1)(n+2)]^{\frac{1}{2}} & -g_1[n(n-1)]^{\frac{1}{2}} & (\gamma_1+\gamma_3)(n+\frac{1}{2})-\frac{3}{2}\kappa-23q/8 \end{Vmatrix}, \qquad (62)$$

and ϵ the characteristic values.

For $n<2$ the Ansatz (61) no longer makes sense. If, however, we choose $C_3=0$, it still does, and we get further solutions for $n=0$, 1 by simply striking out the third row and column of (62) and solving the 3×3 matrix problem.

For $n=-1$, -2 (61) still makes sense if we put $C_1=C_3=C_4=0$. In this case, the characteristic values may be written down at once, and are

$$\epsilon=(\gamma_1-\gamma_3)\frac{1}{2}-\frac{\kappa}{2}-\frac{13q}{8} \quad \text{for} \quad n=-2,$$

$$(63)$$

$$\epsilon=(\gamma_1-\gamma_3)\frac{3}{2}-\frac{\kappa}{2}-\frac{13q}{8} \quad \text{for} \quad n=-1.$$

It may easily be shown that the solutions given form a complete set. This is best accomplished by considering the special case $g_1=g_2=q=0$, for which the set is clearly complete. Therefore, we have reduced the problem to a very simple algebraic one which lends itself very easily to numerical computation once the values of the parameters are decided on.

(2) We now consider a general method of approximation, valid for any direction of magnetic field. This is based on the fact that if $\gamma_2=\gamma_3$ and $q=0$, the characteristic values of (45) can be found immediately. If the experiments performed at higher temperatures are interpreted as being already in the classical region, then it is possible to get estimates of γ_1, γ_2, γ_3 for Ge and Si from them.[9] We have, for germanium: $\gamma_1\cong 13.2$,

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[9] Dresselhaus, Kip, and Kittel, Phys. Rev. 98, 368 (1955). From the classical limit only the magnitude of γ_2 and γ_3 can be

$\gamma_2 \cong 4.4$, $\gamma_3 \cong 5.4$. For silicon: $\gamma_1 \cong 4.0$, $\gamma_2 \cong \pm 0.62$, $\gamma_3 \cong \pm 1.3$.

For Ge we see that γ_2 and γ_3 differ from their mean value by about 10%. Further, estimates of q based on the band theory indicate that it is indeed very small. We may, therefore, hope in this case to solve the problem first for $\gamma_2 = \gamma_3$, $q=0$, and then to treat the rest by perturbation theory. The present indications are (based on constants about equal to those given above) that for Ge second order-perturbation theory in $(\gamma_3 - \gamma_2)$ and first-order in perturbation theory in q are already quite accurate. For Si this method probably doesn't work at all, and for theoretical comparison one only has the (111) direction readily available.

Let us then put $\gamma_2 = \gamma_3 = \bar{\gamma}$ and $q=0$. The Hamiltonian (45) becomes

$$D = \frac{1}{m}\left\{ [\gamma_1 + (5/2)\bar{\gamma}]k^2 - \bar{\gamma}\{k_\alpha k_\beta\}\{J_\alpha J_\beta\} + \frac{e}{c}\kappa \mathbf{J}\cdot\mathbf{H} \right\}. \tag{64}$$

By means of the identity

$$\{k_\alpha k_\beta\}\{J_\alpha J_\beta\} = (\mathbf{k}\cdot\mathbf{J})^2 - \frac{e}{2c}(\mathbf{J}\cdot\mathbf{H}),$$

we may write (64) as

$$D = \frac{1}{m}\left\{ [\gamma_1 + (5/2)\bar{\gamma}]k^2 - \bar{\gamma}(\mathbf{k}\cdot\mathbf{J})^2 + \left(\kappa - \frac{\bar{\gamma}}{2}\right)\frac{e}{c}\mathbf{J}\cdot\mathbf{H} \right\}. \tag{65}$$

From (65) we see at once that in this approximation the energy levels are all independent of the direction of the magnetic field. This is true because, if we rotate the coordinate system in such a way that $\mathbf{H}$ is always in the same direction in the new system, then by a canonical transformation on (65) we can rotate $\mathbf{J}$ in the same way [just as in (47)]. Further, of course, $\mathbf{k}$ transforms like a vector under a rotation of the coordinate system. But all the terms in (65) are rotational invariants, so that D takes exactly the same form for every direction of $\mathbf{H}$ and the characteristic values are therefore independent of the direction of $\mathbf{H}$.

To actually find the levels we note that with the Hamiltonian (65), the quantity

$$Q = \tfrac{1}{2}k^2 + \frac{e}{c}\mathbf{J}\cdot\mathbf{H} \tag{66}$$

is a constant of the motion since

$$(\tfrac{1}{2}k^2, \mathbf{J}\cdot\mathbf{k}) = (ie/c)(\mathbf{H}\times\mathbf{J})\cdot\mathbf{k},$$
$$(\mathbf{J}\cdot\mathbf{H}, \mathbf{J}\cdot\mathbf{k}) = -i(\mathbf{H}\times\mathbf{J})\cdot\mathbf{k}.$$

On the other hand, the characteristic functions and values of (66) are extremely easy to find. Using (48) we have

$$Q = \frac{eH}{c}\left(\frac{p^2+q^2}{2} + J_3\right) + \tfrac{1}{2}k_3^2. \tag{67}$$

Choosing the representation (57) for J_3, we see that the most general characteristic function of Q belonging to the same characteristic value is

$$\psi = \left\| \begin{matrix} C_1 u_n \\ C_2 u_{n+2} \\ C_3 u_{n+1} \\ C_4 u_{n+3} \end{matrix} \right\|, \tag{68}$$

where the C's are arbitrary constants. Equation (68) must then be a characteristic function of (65). This fact is easily verified, and one obtains a 4×4 numerical matrix to determine the C's and the characteristic values of (65). Rather than writing this out explicitly, which is quite tedious, we shall at once make the approximation of putting $k_3=0$. It is important to stress, however, that this approximation is not necessary here as it was in the previous section, and that an investigation of the "k_3-shift" could be carried out with this method.

Putting $k_3=0$, (64) becomes

$$D = \frac{1}{m}\left\{ [\gamma_1 + (5/2)\bar{\gamma}]\frac{k_1^2+k_2^2}{2} - \bar{\gamma}(k_1^2 J_1^2 + k_2^2 J_2^2 + 2\{k_1 k_2\}\{J_1 J_2\}) + \frac{eH}{c}\kappa J_3 \right\} \tag{69}$$

$$= \frac{eH}{mc}\left\{ [\gamma_1 - \bar{\gamma}(5/4 - J_3^2)](N+\tfrac{1}{2}) - \bar{\gamma}\left[\frac{a^2+a^{\dagger 2}}{2}(J_1^2 - J_2^2) + i(a^2 - a^{\dagger 2})\{J_1 J_2\}\right] + \kappa J_3 \right\}. \tag{70}$$

Choosing the representation (57) and again measuring energy in units of eH/mc, (70) becomes

$$D = \left\| \begin{matrix} (\gamma_1+\bar{\gamma})(N+\frac{1}{2}) + \frac{3}{2}\kappa & -\sqrt{3}\bar{\gamma}a^2 & 0 & 0 \\ -\sqrt{3}\bar{\gamma}a^{\dagger 2} & (\gamma_1-\bar{\gamma})(N+\frac{1}{2}) - \frac{1}{2}\kappa & 0 & 0 \\ 0 & 0 & (\gamma_1-\bar{\gamma})(N+\frac{1}{2}) + \frac{1}{2}\kappa & -\sqrt{3}a^2 \\ 0 & 0 & -\sqrt{3}a^{\dagger 2} & (\gamma_1+\bar{\gamma})(N+\frac{1}{2}) - \frac{3}{2}\kappa \end{matrix} \right\|. \tag{71}$$

We notice that, for $k_3=0$, D breaks up into two 2×2 matrix operators, which are uncoupled. The Ansatz (68) still works, of course, but because of this decoupling it is simpler to treat the two 2×2 blocks independently. We call the upper block "1" and write ϵ_1, ψ_1 for the characteristic values and functions, respectively, and similarly we call the lower block "2", with ϵ_2, ψ_2.

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determined. The choice of sign given for Ge is, however, very strongly supported by our current ideas of the band structure of Ge (Sec. 5 of this reference). For Si the situation is not so certain and we leave both signs as possible.

Clearly for "1" we may take

$$\psi_1=\left\|\begin{matrix} a_1 & u_{n-2} \\ a_2 & u_n \end{matrix}\right\|, \tag{72}$$

and for "2,"

$$\psi_2=\left\|\begin{matrix} b_1 & u_{n-2} \\ b_2 & u_n \end{matrix}\right\|. \tag{73}$$

In (72) and (73) if we let $n=0, 1, 2, \cdots$ we get all the characteristic functions as long as we put a_1 and b_1 equal to zero for $n=0, 1$. Using (72) we get

$$\begin{aligned}&[(\gamma_1+\bar{\gamma})(n-\tfrac{3}{2})+\tfrac{3}{2}u]a_1-\sqrt{3}\bar{\gamma}[n(n-1)]^{\frac{1}{2}}a_2=\epsilon_1 a_1,\\ &-\sqrt{3}\bar{\gamma}[n(n-1)]^{\frac{1}{2}}a_1+[(\gamma_1-\bar{\gamma})(n+\tfrac{1}{2})-\tfrac{1}{2}\kappa]a_2=\epsilon_1 a_2,\end{aligned} \tag{74}$$

for $n\geqslant 2$. For $n=0$, 1 we must only take the second equation, which yields

$$\epsilon_1(0)=\tfrac{1}{2}(\gamma_1-\bar{\gamma})-\tfrac{1}{2}\kappa, \quad \epsilon_1(1)=\tfrac{3}{2}(\gamma_1-\bar{\gamma})-\tfrac{1}{2}\kappa. \tag{75}$$

The characteristic values of (74) may be written down explicitly since we have only a 2×2 matrix. They are

$$\begin{aligned}\epsilon_1^{\pm}(n)=\gamma_1 n-(\tfrac{1}{2}\gamma_1+\bar{\gamma}-\tfrac{1}{2}\kappa)\\ \pm\{[\bar{\gamma}n-(\gamma_1-\kappa+\tfrac{1}{2}\bar{\gamma})]^2+3\bar{\gamma}^2 n(n-1)\}^{\frac{1}{2}},\end{aligned} \tag{76}$$

for $n\geqslant 2$. From (75) and (76) we see that $\epsilon_1(0)$ and $\epsilon_1(1)$ are just $\epsilon_1^{+}(n)$ for $n=0$, 1. Similarly, using (73) we get

$$\begin{aligned}&[(\gamma_1-\bar{\gamma})(n-\tfrac{3}{2})+\tfrac{1}{2}\kappa]b_1-\sqrt{3}\bar{\gamma}[n(n-1)]^{\frac{1}{2}}b_2=\epsilon_2 b_1,\\ &-\sqrt{3}\bar{\gamma}[n(n-1)]^{\frac{1}{2}}b_1+[(\gamma_1+\bar{\gamma})(n+\tfrac{1}{2})-\tfrac{3}{2}\kappa]b_2=\epsilon_2 b_2,\end{aligned} \tag{77}$$

for $n\geqslant 2$. For $n=0$, 1 we have

$$\epsilon_2(0)=\tfrac{1}{2}(\gamma_1+\bar{\gamma})-\tfrac{3}{2}\kappa, \quad \epsilon_2(1)=\tfrac{3}{2}(\gamma_1+\bar{\gamma})-\tfrac{3}{2}\kappa. \tag{78}$$

The characteristic values of (77) are

$$\begin{aligned}\epsilon_2^{\pm}(n)=\gamma_1 n-(\tfrac{1}{2}\gamma_1-\bar{\gamma}+\tfrac{1}{2}\kappa)\\ \pm[[\bar{\gamma}n+(\gamma_1-\kappa-\tfrac{1}{2}\bar{\gamma})]^2+3\bar{\gamma}^2 n(n-1)]^{\frac{1}{2}},\end{aligned} \tag{79}$$

and again $\epsilon_2(0)$, $\epsilon_2(1)$ are just $\epsilon_2^{+}(0)$ and $\epsilon_2^{+}(1)$, respectively.

We shall call a set of characteristic values which are obtained by just increasing n by integer steps in some function a "ladder." The spectrum then consists of 4 ladders, the 1^{+}, 1^{-}, 2^{+}, 2^{-}.[10] It turns out that it is quite convenient to keep the levels grouped this way, not only for ease of visualization, but also in considering selection rules for absorption.

The case discussed here reduces exactly to that of Appendix C in LK, if we put $\kappa=0$. We now see, however, that it has considerably more application than was indicated there.

(3) Now actually experiment shows that the levels even in Ge are not the same in all directions, so that the results of the previous section cannot be accurate enough for detailed comparison with experiment. Therefore, one must use perturbation theory on the difference between (45) and (64). We shall not even write down the perturbation for an arbitrary direction of **H**, but shall confine ourselves entirely to the magnetic field in the (110) plane. This plane contains all the directions for which experiments have been done so far. If we call θ the angle between the field and the z-axis, then we can choose the (1,2,3) coordinate system so that

$$\begin{aligned}k_x&=(1/\sqrt{2})(ck_1-k_2+sk_3),\\ k_y&=(1/\sqrt{2})(ck_1+k_2+ck_3),\\ k_z&=-sk_1+ck_3,\end{aligned} \tag{80}$$

where $s\equiv\sin\theta$, $c\equiv\cos\theta$. We shall also make a canonical transformation on the J's, so that the relation between J_x, J_y, J_z and J_1, J_2, J_3 is also given by (80). Using this, and putting $k_3=0$, we get

$$\begin{aligned}D&=D_0+D_1+D_2,\\ D_0&=[\gamma_1+\gamma'(J_3^2-5/4)](N+\tfrac{1}{2})\\ &\qquad-\gamma''[l_1(J_1^2-J_2^2)+2l_2\{J_1J_2\}]+\kappa J_3,\\ D_1&=\frac{\mu}{2}\bigg((3c^2-1)(s)[4c\{J_1J_3\}-s(J_1^2-J_2^2)](N+\tfrac{1}{2})\\ &\qquad-3s^2[4sc\{J_1J_3\}-(3c^2-1)(J_3^2-5/4)]l_1\\ &\qquad+8sc\{J_2J_3\}l_2+\frac{3c^4-10c^2+3}{2}\\ &\qquad\qquad\times[(J_1^2-J_2^2)l_1-2\{J_1J_2\}l_2]\bigg),\\ D_2&=q\bigg((5/4)sc(3c^2-2)J_1^3+\tfrac{1}{4}(15c^4-10c^2-1)J_3^3\\ &\qquad+\frac{9sc^3}{4}\{J_1(J_2^2-J_3^2)\}+\frac{3s^2}{4}(3c^2-1)\{J_3(J_1^2-J_2^2)\}\\ &\qquad+\frac{41}{16}[sc(2-3c^2)J_1+s^2(1+3c^2)J_3]\bigg).\end{aligned} \tag{81}$$

Here

$$\begin{aligned}\gamma'&=\tfrac{1}{4}[(3c^2-1)^2\gamma_2+3s^2(3c^2+1)\gamma_3],\\ \gamma''&=\tfrac{1}{8}[(3-2c^2+3c^4)\gamma_2+(5+2c^2-3c^4)\gamma_3],\\ \mu&=\tfrac{1}{2}(\gamma_3-\gamma_2),\\ l_1&=\tfrac{1}{2}(a^2+a^{\dagger 2}),\\ l_2&=(i/2)(a^2-a^{\dagger 2}).\end{aligned} \tag{82}$$

Several remarks should be made about (81). D_0 is the unperturbed Hamiltonian. It only reduces to (70) if $\gamma_2=\gamma_3=\bar{\gamma}$. However, as one easily sees, it is soluble by exactly the same technique as was used on (70). The reason we absorb some of the perturbation into the zeroth-order Hamiltonian is that as a consequence D_1 has no diagonal matrix elements in the D_0 representation, so we need not do first- and second-order

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[10] In the classical limit the spacing between levels becomes uniform within any ladder. The plus ladders then correspond to the level spacing of the "light" holes, the minus ladders to the level spacing of the heavy" holes.

perturbation theory on D_1, but only second order. It is also possible to split D_2 into a first-order part (by taking the $J_3{}^3$ and J_3 terms) and a part which has no diagonal elements. The zeroth-order Hamiltonian can still be rigorously diagonalized, if we include this diagonal part of D_2 in it. However, since we have not as yet gone beyond the first order in q this split has no advantage, and we have not made it.

The characteristic functions of D_0 are again given by (72) and (73) where we have

$$\begin{aligned}&[(\gamma_1+\gamma')(n-\tfrac{3}{2})+\tfrac{3}{2}\kappa]a_1-\sqrt{3}\gamma''[n(n-1)]^{\frac{1}{2}}a_2=\epsilon_1a_1\\&\qquad\qquad\qquad\qquad n=2,\,3,\,\cdots\\&-\sqrt{3}\gamma''[n(n-1)]^{\frac{1}{2}}a_1+[(\gamma_1-\gamma')(n+\tfrac{1}{2})-\tfrac{1}{2}\kappa]a_2\\&\qquad\qquad\qquad=\epsilon_1a_2\quad n=0,\,1,\,2,\,\cdots,\end{aligned}\tag{83}$$

with the characteristic values

$$\begin{aligned}\epsilon(n,1^{\pm})=&\gamma_1n-(\tfrac{1}{2}\gamma_1+\gamma'-\tfrac{1}{2}\kappa)\\&\pm\{[\gamma'n-(\tfrac{1}{2}\gamma'+\gamma_1-\kappa)]^2+3\gamma''^2n(n-1)\}^{\frac{1}{2}},\end{aligned}\tag{84}$$

where for the plus sign $n=0,\,1,\,2,\,\cdots$, and for the minus sign $n=2,\,3,\,4\cdots$. Similarly,

$$\begin{aligned}&[(\gamma_1-\gamma')(n-\tfrac{3}{2})+\tfrac{1}{2}\kappa]b_1-\sqrt{3}\gamma''[n(n-1)]^{\frac{1}{2}}b_2=\epsilon_2b_1\\&\qquad\qquad\qquad\qquad n=2,\,3,\,\cdots\\&-\sqrt{3}\gamma''[n(n-1)]^{\frac{1}{2}}b_1+[(\gamma_1+\gamma')(n+\tfrac{1}{2})-\tfrac{3}{2}\kappa]b_2\\&\qquad\qquad\qquad=\epsilon_2b_2\quad n=0,\,1,\,2,\,\cdots,\end{aligned}\tag{85}$$

with the characteristic values

$$\begin{aligned}\epsilon(n,2^{\pm})=&\gamma_1n-(\tfrac{1}{2}\gamma_1-\gamma'+\tfrac{1}{2}\kappa)\\&\pm\{[\gamma'n+(\gamma_1-\kappa-\tfrac{1}{2}\gamma')]^2+3\gamma''n(n-1)\}^{\frac{1}{2}},\end{aligned}\tag{86}$$

where $n=0,\,1,\,2,\,\cdots$ for the plus sign, and $n=2,\,3,\,4\cdots$ for the minus sign. The explicit matrix representation of D_1 is

$$D_1=\frac{\sqrt{3}\mu}{2}\begin{Vmatrix}r_1 & r_2 & r_3 & 0\\ r_2{}^+ & -r_1 & 0 & -r_3\\ r_3{}^+ & 0 & -r_1 & r_2\\ 0 & -r_1{}^+ & r_2{}^+ & r_1\end{Vmatrix},\tag{87}$$

where

$$r_1=\tfrac{1}{2}\sqrt{3}s^2(3c^2-1)(a^2+a^{\dagger2}),$$
$$r_2=(3c^2-1)[\tfrac{1}{2}(c^2-3)a^{\dagger2}-s^2(N+\tfrac{1}{2})],$$
$$r_3=sc[(3c^2-1)(2N+1+a^2)+(3c^2-5)a^{\dagger2}].$$

Similarly, for D_2 we have

$$D_2=\frac{q}{4}\begin{Vmatrix}p_1 & p_2 & p_3 & p_4\\ p_2 & p_5 & p_6 & p_3\\ p_3 & p_6 & -p_5 & -p_2\\ p_4 & p_3 & -p_2 & p_1\end{Vmatrix},\tag{88}$$

where

$$p_1=\tfrac{3}{2}(3c^4-2c^2+8),$$
$$p_2=\tfrac{3}{2}\sqrt{3}s^2(3c^2-1),$$
$$p_3=-\tfrac{3}{2}\sqrt{3}sc(3c^2-1),$$
$$p_4=\tfrac{3}{2}sc(3c^2-5),$$
$$p_5=\tfrac{1}{2}(27c^4-18c^2-10),$$
$$p_6=(9/2)sc(3c^2-1).$$

Finally, a word may be said about the energy levels in the twofold degenerate case. From Eq. (b.9) of Appendix B, the Hamiltonian is just that of a free particle with an isotropic effective mass, spin one-half and an intrinsic magnetic moment. Since orbit and spin are not coupled, we can find the energy levels of each part separately. These are

$$\begin{aligned}\epsilon_n{}^{\pm}=&\tfrac{2}{3}(A+2B)(n+\tfrac{1}{2})\frac{eH}{c}\\&\pm\frac{eH}{2mc}(2mK-1)+\frac{A+2B}{3}k_3{}^2.\end{aligned}\tag{89}$$

Oscillating electric fields will cause transitions between n and $n\pm1$, so that the second and third terms will not affect cyclotron resonance experiments at all. On the other hand, oscillating magnetic fields ("spin resonance") will produce transitions between the $\pm$ states and would, therefore, provide a direct measure of K. An estimate[11] of K for Ge, based on the band theory gives something like $K=-13/m$. This indicates that such spin-resonance experiments on free holes would see an effective g-factor which was very large. A similar but more complicated situation will hold for the fourfold degenerate band. This large effective magnetic moment may conceivably be connected with the failure to obtain spin resonance at the expected place for holes bound loosely to impurity centers. These questions remain to be investigated, however.

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APPENDIX A. THE CUBIC GROUP

We list in Table I the character table for the cubic group, and the reduction of all direct products.

TABLE I. Character table for the cubic group.[a]

Representation	$1E$	$1R$	$16C_3$	$12\sigma_d$	$12S_4$	$6C_2$
A_1	1	1	1	1	1	1
A_2	1	1	1	−1	−1	1
E	2	2	−1	0	0	2
T_1	3	3	0	1	−1	−1
T_2	3	3	0	−1	1	−1

[a] The following relations hold: $A_1\times A_1=A_1$; $A_1\times A_2=A_2$; $A_1\times E=E$; $A_1\times T_1=T_1$; $A_1\times T_2=T_2$; $A_2\times A_2=A_1$; $A_2\times E=E$; $A_2\times T_1=T_2$; $A_2\times T=T_1$; $E\times E=A_1+A_2+E$; $E\times T_1=T+T_2$; $E\times T_2=T_1+T_2$; $T_1\times T_1=A_1+E+T_1+T_2$; $T_1\times T_2=A_2+E+T_1+T_2$; $T_2\times T_2=A_1+E+T_1+T_2$.

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[11] I am grateful to Professor Kohn for this estimate. It is closely related to the estimates of Dresselhaus, Kip, and Kittel in reference 9.

When two identical representations, (say R) occur in a direct product, we can ask: what irreducible representations occur if we consider only those functions symmetrical in the two representations, and which occur when we consider only those antisymmetrical in the two representations? We call the former $(R\times R)_S$ and the latter $(R\times R)_A$. One can easily see that the characters of any element T are given by

$$\chi_S=\tfrac{1}{2}[\chi(T)^2+\chi(T^2)]$$

in the symmetrical case, and

$$\chi_A=\tfrac{1}{2}[\chi(T)^2-\chi(T^2)]$$

in the antisymmetrical case. Using this, we obtain at once, the following:

$$\begin{aligned}(T_1\times T_2)_S&=A_1+E+T_1,\\(T_1\times T_1)_A&=T_2,\\(T_2\times T_2)_S&=A_1+E+T_1,\\(T_2\times T_2)_A&=T_2.\end{aligned}$$

APPENDIX B

In this appendix we obtain the Hamiltonian for the very weak spin-orbit case directly from that for the no-spin orbit case (41). Call the six degenerate wave functions for the no spin-orbit case g_i, $i=1, 2, \cdots, 6$. The correct "zero-order" functions for the weak spin-orbit case are given by (V.11) and (V.12) of LK. Call these collectively f_l, $l=1, 2, \cdots, 6$. Then the f_l are related to the g_i by a relationship

$$f_l=\textstyle\sum_i g_i(i|l), \tag{b.1}$$

where the $(i|l)$ are some numerical coefficients.

Let the matrix elements of D (from 41) be $D_{ii'}$ in the g_i representation. Then in the f_l representation they will clearly be

$$D_{ll'}=\sum_{i,i'}(l|i)D_{ii'}(i'|l'), \tag{b.2}$$

where $(l|i)\equiv(i|l)^*$.

By means of the explicit representations (V.11) and (V.12) it would now be a very straightforward matter to obtain the $(i|l)$ and, therefore, $D_{ll'}$. It is, however, much more convenient to proceed as follows: If we think for a moment of the original functions X, Y, Z as functions which transform under the full rotation group like x, y, z, then the functions g_i are states of orbital $L=1$ and spin $\frac{1}{2}$ in the (m_L,m_S) representation. Further, the functions (V.11) and (V.12) are then formally those for $j=\frac{3}{2}$ and $\frac{1}{2}$, respectively, in the (j,m) representation. Therefore, the transformation matrix $(i|l)$ is identical with the transformation from the (m_L,m_S) basis to the (j,m) basis. If we want the fourfold degenerate part we need only consider the submatrix with $j=\frac{3}{2}$, if we want the twofold degenerate part, then we take the submatrix with $j=\frac{1}{2}$.

Let us consider the $j=\frac{3}{2}$ part first. Then we need quantities like, $\mathbf{I}$, $\boldsymbol{\sigma}$, $\{I_\alpha I_\beta\}$ expressed in the (j,m) representation for $j=\frac{3}{2}$. These are easy to find. Consider any vector V_α. Then the matrix elements $(jm|V_\alpha|jm')$ are given by

$$(jm|V_\alpha|jm')=\gamma(jm|J_\alpha|jm'), \tag{b.3}$$

where γ is independent of m[12]; and J_α is the total angular momentum operator, orbit plus spin. To determine γ one considers some simple matrix element. Thus for $\boldsymbol{\sigma}$, let us consider $(\frac{3}{2}\frac{3}{2}|\sigma_z|\frac{3}{2}\frac{3}{2})$, which equals unity from (V.11). On the other hand, $(\frac{3}{2}\frac{3}{2}|J_z|\frac{3}{2}\frac{3}{2})=\frac{3}{2}$, so that $\gamma=\frac{2}{3}$ for $\boldsymbol{\sigma}$. Thus we may write that as far as matrix elements for $j=\frac{3}{2}$ are concerned,

$$\boldsymbol{\sigma}\rightarrow\tfrac{2}{3}\mathbf{J}, \tag{b.4}$$

where $\mathbf{J}$ is any 4×4 representation of the angular momentum for $j=\frac{3}{2}$. Similarly

$$(jm|I_\alpha|jm')=\gamma'(jm|J_z|jm').$$

Considering again the $\frac{3}{2}\frac{3}{2}$ state, we get

$$(\tfrac{3}{2}\tfrac{3}{2}|I_z|\tfrac{3}{2}\tfrac{3}{2})=1$$

from (V.11), so that γ' also is unity, and we have

$$\mathbf{I}\rightarrow\tfrac{2}{3}\mathbf{J}. \tag{b.5}$$

Finally, to find such quantities as $\{I_\alpha I_\beta\}$, we make use of the fact that $\{I_\alpha I_\beta\}-\frac{1}{3}\delta_{\alpha\beta}I^2$ is an irreducible tensor of the second rank. Then, once again,[12]

$$(jm|\{I_\alpha I_\beta\}-\tfrac{1}{3}\delta_{\alpha\beta}I^2|jm')=\gamma''(jm|\{J_\alpha J_\beta\}-\tfrac{1}{3}J^2\delta_{\alpha\beta}|jm').$$

To determine γ'' we once more consider $\alpha=\beta=z$ and the $\frac{3}{2}\frac{3}{2}$ state.

$$\begin{aligned}(\tfrac{3}{2}\tfrac{3}{2}|I_z^2-\tfrac{1}{3}I^2|\tfrac{3}{2}\tfrac{3}{2})&=1^2-\tfrac{1}{3}(2)=\tfrac{1}{3},\\(\tfrac{3}{2}\tfrac{3}{2}|J_z-\tfrac{1}{3}J^2|\tfrac{3}{2}\tfrac{3}{2})&=(\tfrac{3}{2})^2-\tfrac{1}{3}(15/4)=1,\end{aligned}$$

so that $\gamma''=\frac{1}{3}$. Therefore, we may write

$$\{I_\alpha I_\beta\}-\tfrac{1}{3}\delta_{\alpha\beta}I^2\rightarrow\tfrac{1}{3}(\{J_\alpha J_\beta\}-\tfrac{1}{3}J^2\delta_{\alpha\beta}),$$

or

$$\{I_\alpha I_\beta\}\rightarrow\tfrac{1}{3}\{J_\alpha J_\beta\}+\tfrac{1}{4}\delta_{\alpha\beta}. \tag{b.6}$$

Substituting (b.4), (b.5), and (b.6) in (41) we get

$$\begin{aligned}D=\tfrac{1}{4}(3A+B)k^2-\tfrac{1}{3}(A-B)(k_x^2J_x^2+k_y^2J_y^2+k_z^2J_z^2)\\-\tfrac{2}{3}c(\{k_xk_y\}\{J_xJ_y\}+\{k_yk_z\}\{J_yJ_z\}+\{k_zk_x\}\{J_zJ_x\})\\+(e/3mc)(mK+1)\mathbf{J}\cdot\mathbf{H},\end{aligned} \tag{b.7}$$

which is just (42).

It is even easier to obtain the two by two matrix corresponding to the twofold degenerate state. We obtain at once,

$$\boldsymbol{\sigma}\rightarrow-\tfrac{1}{3}\mathbf{J},\quad \mathbf{I}\rightarrow\tfrac{2}{3}\mathbf{J},\quad \{I_\alpha I_\beta\}\rightarrow\tfrac{2}{3}\delta_{\alpha\beta}, \tag{b.8}$$

where $\mathbf{J}$ in (b.8) is a 2×2 representation of angular

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[12] See E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1951), p. 59 ff.

momentum $j=\frac{1}{2}$. (We could write, for example, $\mathbf{J}=\frac{1}{2}\boldsymbol{\sigma}$.) Substituting in (41) again, we get

$$D\rightarrow\tfrac{1}{3}(A+2B)k^2+(e/6mc)(2Km-1)\mathbf{J}\cdot\mathbf{H}$$
$$=\tfrac{1}{3}(A+2B)k^2+(e/12mc)(2Km-1)\boldsymbol{\sigma}\cdot\mathbf{H}. \quad \text{(b.9)}$$

If we leave off the $\mathbf{J}\cdot\mathbf{H}$ term and choose the representation (39) for $\mathbf{J}$ [in (b.7)], then (b.7) and (b.9) agree exactly with (V.13) of LK. It is easily seen by the methods of Sec. I that the form of (b.9) is the most general possible for the twofold degenerate case.

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Experimental Cross Sections for Charge-Changing Collisions of He^+ and He^{++} Ions Traversing Gases*

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Ion beams of He^+ and He^{++}, in the kinetic energy range 100 to 450 kev, are held in arcs of circular orbits in a magnetic field. When a few microns of gas are admitted the beam is attenuated by charge-changing collisions, since with change of charge the ion is lost from its orbit. Cross sections for such charge-changing collisions are designated by σ_{if}, where i is the initial positive ionic charge in electron units and f the charge after the collision. $(\sigma_{10}+\sigma_{12})$ has been directly measured for He^+ in hydrogen, helium, and air, and $(\sigma_{21}+\sigma_{20})$ for He^{++} in the same gases.

Other observers have measured the equilibrium ratio He^+/He^{++} attained in a field-free beam after many collisions, and combining these data with our observations allows calculation of σ_{10} and σ_{12} separately if one assumes σ_{02} negligible compared to the other cross sections. The electron loss cross sections σ_{12} increase with energy for helium and air throughout the measured region and are of the order 10^{-17} cm^2; σ_{12} for hydrogen *vs* energy shows a broad maximum at about 370 kev and 0.98×10^{-17} cm^2 per hydrogen atom.

The capture cross sections σ_{10} decrease rapidly in the measured energy range and in the region 200–450 kev those measured in helium agree, within the estimated experimental error, with theoretical calculations of H. Schiff.

In attempting the resolution of the sums $(\sigma_{21}+\sigma_{20})$ into the separate cross sections it is found that the errors in the measurements accumulate to such an extent that the individual values become very unreliable. An auxiliary experiment designed to increase the accuracy of our knowledge of the separated capture cross sections σ_{20} and σ_{21} is in progress.

1. INTRODUCTION

THE discovery by Henderson,[1] in 1922, that an appreciable fraction of the alpha particles emitted from natural sources have an orbital electron attached, and thus are He^+ ions, initiated a series of researches in which the capture and loss of electrons by moving helium ions were studied. The results on α particles prior to 1933 have been summarized in the *Handbuch der Physik* by Geiger,[2] and the same volume contains a review of work on the more general aspects of charge changing collisions, by Rüchardt.[3]

The status of the problem as of June, 1953, has been recorded by Allison and Warshaw.[4]

Experimental researches on this problem may be roughly divided into two categories: (A) studies of the equilibrium ratios of the various charge states attained after a sufficiently large number of charge-changing collisions; (B) studies of the collision cross sections for individual charge-changing events.

Subsequent to the work summarized by Allison and Warshaw other reports of researches on helium ions under a category (A) have appeared from the Cavendish Laboratory[5] and the Oak Ridge National Laboratory.[6] Specific applications to the production of He^{++} beams for acceleration to high energies are reported by Bittner[7] and by Geller and Prevot.[8]

The experimental studies reported here belong in category (B), and are in the kinetic energy range 100 to 450 kev. We shall use the notation σ_{if} in discussing the cross sections, where subscript i refers to the initial positive charge on the ion in units of the magnitude of the electronic charge, and f to the positive charge after the collisions in the same units. Very little was known of the helium cross sections in the range 100 to 600 kev when the summary by Allison and Warshaw was written. Some helium cross sections in the kinetic energy range up to 100 kev had been reported,[9–14] and

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