14 Semiconductor crystals: I. Energy bands, cyclotron resonance, and Impurity states 10 h 15	Các bán dẫn tinh thể: I.Các vùng năng lượng, cộng hưởng cyclotron, và các trạng thái tạp chất
In this and the following chapter we discuss the band structures of several important semiconductors, and we then treat phenomena which involve the structure at the band edge: cyclotron resonance, spin resonance, impurity states, optical transitions, oscillatory magnetoabsorption, and excitons.	Trong chương này và những chương sau, chúng ta sẽ thảo luận về cấu trúc vùng của một vài bán dẫn quan trọng, và sau đó chúng ta sẽ xét các hiện tượng liên quan đến cấu trúc tại biên vùng: cộng hưởng cyclotron, cộng hưởng spin, các trạng thái tạp chất, các dịch chuyển quang học, hấp thụ magneto (từ) dao động, và các exciton.

ENERGY BANDS

The most important semiconductor crystals have the diamond struc¬ture or structures closely related to diamond. The diamond structure is based on a fee bravais lattice (ISSP, pp. 36-37) with a basis of two atoms at 000; i i t, as shown in Fig. 1. The structures of the valence bands are similar in diamond, Si, and Ge, with the point of maximum energy at k = 0. The point of maximum energy is called the band edge. The valence band edge for these crystals would be threefold degenerate (p-like) in the absence of spin and of spin-orbit interaction; with the spin-orbit interaction we shall see that this 3X2 = sixfold degenerate band edge splits into fourfold (p^-like) and twofold (p^-like) levels.

The valence electrons in the ground state of the free atoms have the configuration ns2np2, with n = 2, 3, 4 for diamond, Si, and Ge, respectively. In the crystal the ground state is formed from the configuration nsnp3. Using the language of chemistry, we say that the valence electrons form directed spz tetrahedral bonding orbitals of the form

s + px + py + Pz) 8 + px - py - pz;

s - px + py- pz',

FIG. 1. Atomic positions in the unit cell of the diamond structure projected on a cube face; fractions denote height above base in units of a cube edge. The points at 0 and ^ are on the fee lattice; those at -J and f are on a similar lattice displaced among the body diagonal by one-fourth of its length.

Each atom in the diamond structure is at

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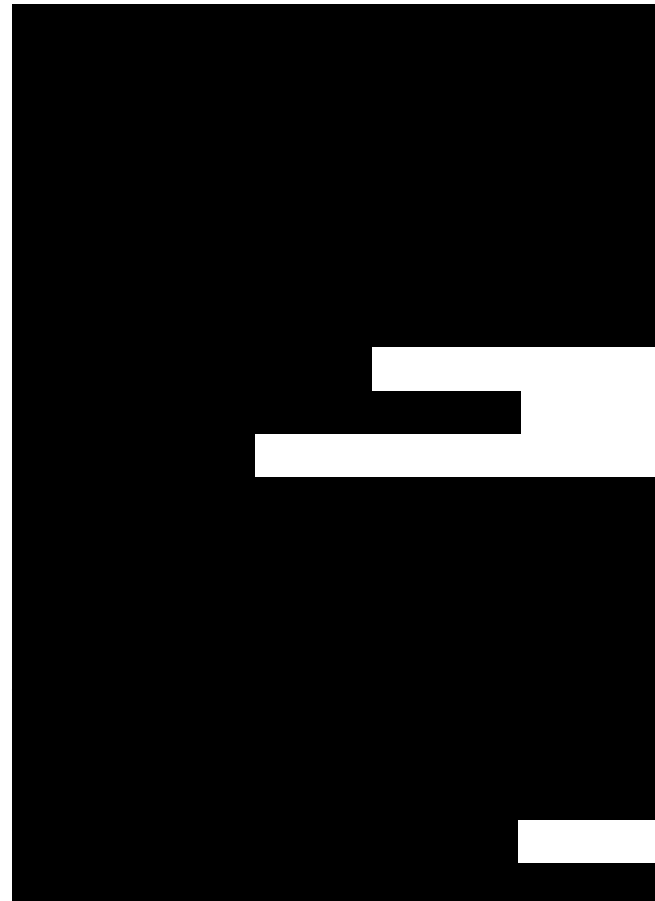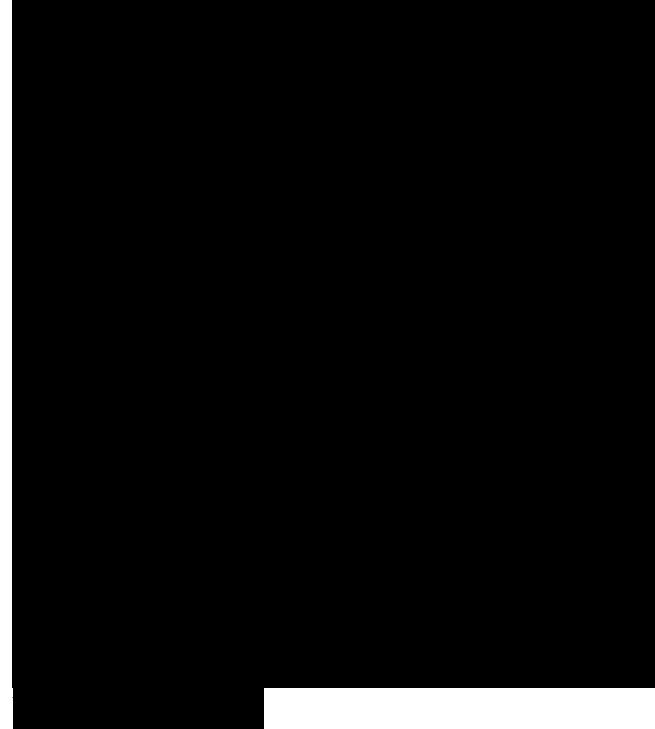
the center of a tetrahedron with the nearest-neighbor atoms at the vertices. The four orbitals Just enumerated have lobes pointing in the tetrahedral directions. These orbitals form the basis of a reducible representation of the tetrahedral point group 43m; the representation may be reduced into the identical representation Vi and the vector representation…..The representation is believed to occur at the bottom of the valence band (Fig. 2) at the center of the zone; Ti is like an s state and is formed from the sum of the sp3 orbitals above. Each of the two atoms in the primitive cell of the diamond structure furnishes one electron to the lowest band. This band turns out to be s-like at the points T, X, and L.

The valence band edge lies at the center of the zone and has the threefold representation r^, transforming as xy, yz, xz about the center of the line joining the two atoms in the primitive cell. The representa¬tion may be formed from p orbitals on the individual atoms, taken to be symmetrical with respect to inversion about the center of the line connecting the two atoms; the symmetrical combination is said to be bonding. The antibonding combination forms the representation r15 and in diamond lies about 5.7 ev above T'2b.

It is useful to consider the form of the wavefunctions at the points T in terms of a tight-binding model, also called a linear combination of atomic orbitals. The two interpenetrating fee lattices of diamond are displaced from the other by the vector

(1)   t = Ml, 1,1),

referred to the edges of the unit cube shown in Fig. 1. At k = 0 the tight-binding functions have the form
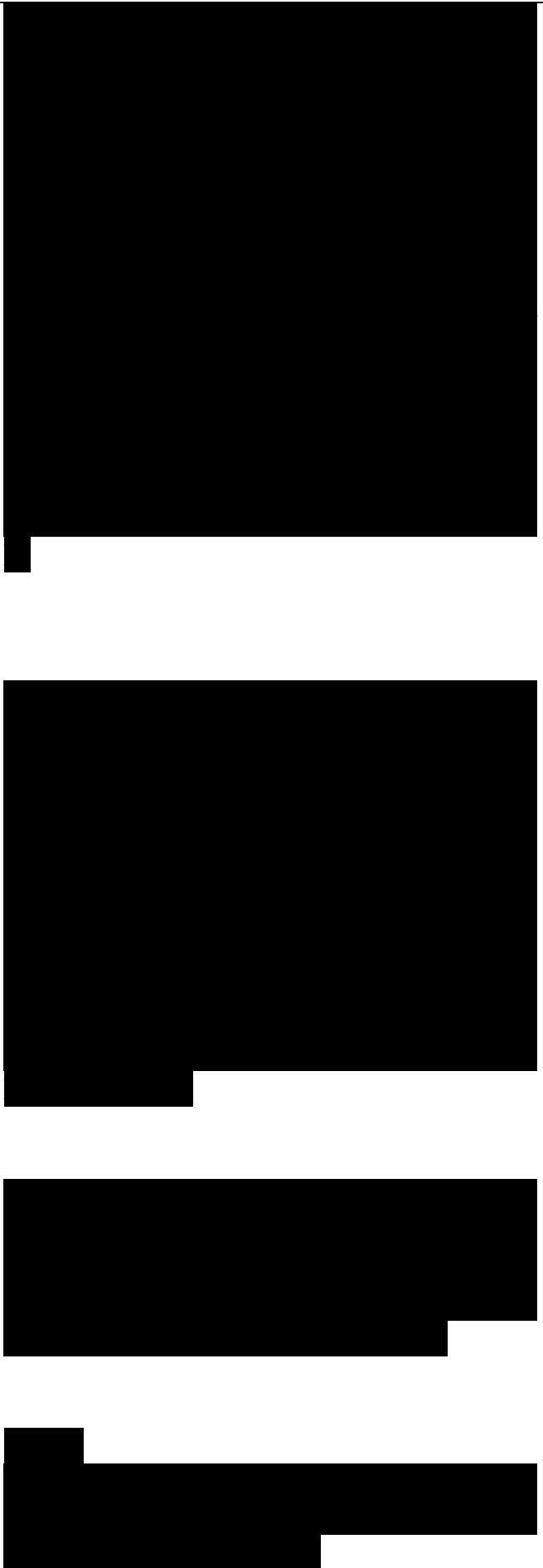
(2)   **(x) = (2JV)-" I fo(x - xn) + Vi(x - x. - t)],

where xn runs over all the lattice points of one fee lattice; the <ps are atomic or Wannier functions with j = s, px, pv, or pz. The + sign indicates the two independent ways in which the atomic functions may be combined on the two lattices. Tight-binding functions are not a good approximation to the actual wavefunctions, but they form an easy pictorial representation of the symmetry properties of the exact solutions. One may readily show by examining the transformation properties that ¥+ forms a representation of Ti; of r£;   of rj5; and ¥+tfi, of ri5.

We can understand qualitatively some of the features of the band structure of diamond by reference to the free-electron energy bands in an fee bravais lattice, as illustrated in Fig. 10.8. We omit from the treatment the electrons of the Is2 core, because these go into narrow Tj and r'2 bands quite low in energy. The lowest point (ri) shown in Fig. 10.8 is formed in the tight-binding approximation by taking 2s functions on each lattice, with a positive choice of the sign in (2):

(3)   »(r,) - (2N)-» I MX - x,,) + «>.(x - x,, - t)J,

&

where xn runs over all lattice points of an fee lattice. This combination is called bonding. There is no other plausible way of forming the low-lying state rh

Next in energy at r on the free-electron model are eight degenerate states having G = (2T/O)(±1; ±1; ±1). The states belong to four different representations of the cubic group; in the crystal the eight¬fold degeneracy will be lifted and we will have the threefold levels and ri5,

and the nondegenerate levels Tj and The Ti component will require 3s orbitals and is therefore expected to lie quite high in energy.

We expect to lie below Tu. The arrangement of p orbitals
Bonding p orbitals

for V'25; this arrangement is even under inversion at the center of the line. For Ti5 the arrangement must be odd under inversion:
GXDGX*)
Antibonding p orbitals
but this contains fourier components at twice the wavevector as for rj5. Our rough argument suggests that lies lower than ri5; in fact, in all crystals of the diamond and zinc blende structures that is believed to be realized.

We cannot order the T'2 antibonding s level by the same argument. In diamond and silicon £(r15) < e^); the order is inverted in the heavier elements, probably because the stronger core potentials lower s relative to p.

STRUCTURE OF VALANCE BAND EDGE

The valence band edge in diamond-type crystals has a threefold orbital degeneracy; with spin the degeneracy is sixfold. The spin-orbit interaction lifts some of the degeneracy by splitting the p-like states into PM and py2 states. In diamond (Table 1) the spin-orbit splitting A is estimated to be 0.006 ev, which is very much less than the band

TABLE 1
ENERGY-BAND DATA OF SEVERAL

SEMICONDUCTOR CRYSTALS (At helium temperature unless specified)

	Diamond	Si	Ge	InSb
Eg: minimum energy gap (ev)	5.33*	1.14	0.744	0.23
Vertical gap at k = 0 (ev)	(2.5)	0.898	0.23-10"	
Valence band width (ev)	(20)	17	7.0	
A: valence band spin-orbit splitting (ev)	0.006	0.04	0.29	(0.9)
mi/m at conduction band edge	0.98	1.64	0.014	
mt/m at conduction band edge	0.19	0.082	0.014	
'2 mA/h2		-4.0	-13.1	
Valence band edge parameters ■				
2m B√h2		1.1	8.3	
.2 m C√h2		4.1	12.5	

* Room temperature.

gap, 5.3 ev. As we advance along the periodic table, the spin-orbit splitting increases markedly and the energy gap may decrease. In InSb the spin-orbit splitting is 0.9 ev and the band gap is 0.23 ev.

Thus the spin-orbit splitting may be larger than the band gap; in heavy elements the splitting is one of the important factors deter-mining the gap. Even in diamond the splitting is important for experiments on holes if their effective temperature is less than about 50°K. There is, however, a mathematical convenience in first setting up the k * p perturbation theory for the valence band edge with the neglect of spin-orbit interaction, and later including it.

We make an arbitrary choice of a basis for the representation at k = 0, taking the three degenerate orbital states to

transform as

(4)   e[~ yz\ Sg ~ zx; £3 ~ xy.

The second-order perturbation matrix (Schiff, pp. 156-158) has the form

where r, s denote 1, 2, or 3 above and the sum is over all states at k = 0 except those in the valence band edge level under consideration. The dependence of (r|iZ"|s) on the components of k is found by con¬sidering the form of the sum if all energy denominators were equal. Then by the completeness relation

(6)

with (4) we have, on examining the derivatives,

(l|iJ"|2> = 2kxky(l\pypx\2),

and similarly for the other matrix elements. The secular equation is then of the form

The cubic symmetry of the crystal enables us to express the coefficients in terms of the three constants L, M, N. The energy eigenvalue is given by £(k) = £(0) + (1/2m)k2 + X. Expressions for L, M, N, as simplified by the use of symmetry, are given by Dresselhaus, Kip, and Kittel, Phys. Rev. 98, 368 (1955).

To include spin-orbit effects, we take as the basis the six functions S[a, ef2a, e'za, sJ/3, £3$, where a, ft are the spin functions. We include in the perturbation the spin-orbit interaction

Hso = -——(d X grad V) • p,
4   me

and neglect the corresponding term having k written for p. Suppose that we transform from the basis just given to a basis in which the quantum numbers J,mj are diagonal, where J is the operator for the total angular momentum. Then in the

new 6X6 secular equation the spin-orbit interaction simply subtracts the splitting A from the two diagonal terms involving the states | 2 li) and 11; —|).

If we restrict ourselves to energies k2/2mA « 1, the 6X6 secular equation has the approximate eigenvalues1

(10) S(k) = Ak2 ± [B2k4 + C2(kx%2 + k2k2 + k2k2)t\

s(k) — —A ~(- Ak2.

There are three roots, given by (10) and (11); each root is double, as required by the time reversal and inversion invariance of the hamil-tonian. The solutions (10) converge at k = 0 to a fourfold degenerate state which belongs to the r8 representation of the cubic group; the representation may be built up from p3/i atomic functions on each atom. The solutions (11) converge at k = 0 to a twofold degenerate state which belongs to the r7 representation; it may be viewed as built up from atomic p^ functions. The band at r7 is called the split-off band and lies lower in energy than r8. The presence of r7 was first deduced from the analysis of experiments on optical absorption in p-Ge. Values of A, B, C, as determined by cyclotron resonance, are given in Table 1. The form (10) is established at the end of this chapter.

Diamond. Representative theoretical calculations of the band structure of diamond are given by F. Herman, Phys. Rev. 93, 1214 (1954); and J. C. Phillips and L. Kleinman, Phys. Rev. 116, 287 (1959). The results are shown in Fig. 2. The valence band edge is Tf2b. The conduction band edge is believed to lie along the A axis; the electron energy surfaces are six equivalent spheroids, one along each 100 axis. The calculated band gap of 5.4 ev agrees well with the

observed 5.33 ev. It is known experimentally that the band edges are indirect; that is, the

1 Solutions valid over a wider range of k have been given by E. O. Kane, Phys. Chem. Solids 1, 82 (1956).

FIG. 2. Energy bands of diamond along (100) and (111) axes of the Brillouin zone. The valence band edge is at k = 0 and has the representation r'25; the conduction band edge should lie along A. (After Phillips and Kleinman.)

FIG. 3. Schematic representation of the energy bands of diamond including spin-orbit coupling effects. (Based on Herman's calculations, after R. J. Elliott.)

valence and conduction band edges are connected by a nonzero k. Cyclotron resonance experiments on p-type diamond give $m^*/m = 0.7$ and 2.2 for the light and heavy hole bands at the band edge and $m^*/m = 1.06$ for the band split off by the spin-orbit interaction. The splitting caused by spin-orbit interaction is shown in Fig. 3.

Silicon. The energy bands of silicon are shown in Fig. 4 without spin-orbit interaction. The band structure is similar to that of dia-mond: the valence band edge belongs to the representation Vr2& and the conduction band edge belongs to Ai at a general point along the axis between T and X. There is a good deal of evidence that one minimum is at $(2x/a)$ (0.86,0,0); there are six equivalent minima, one along each cube edge. The transverse and longitudinal effective masses are
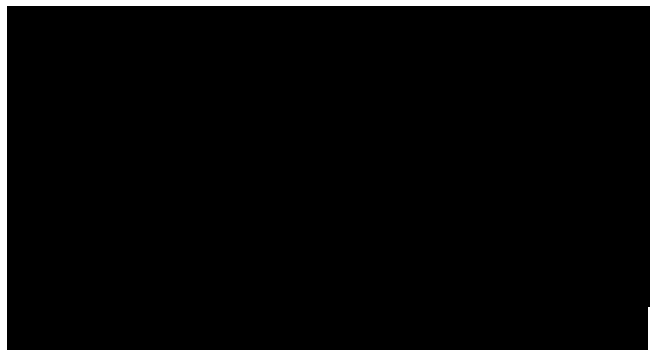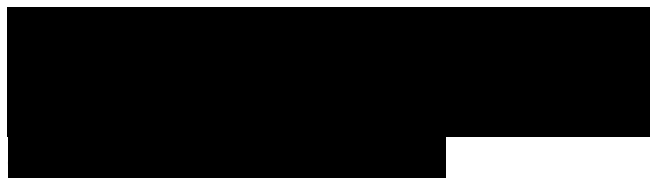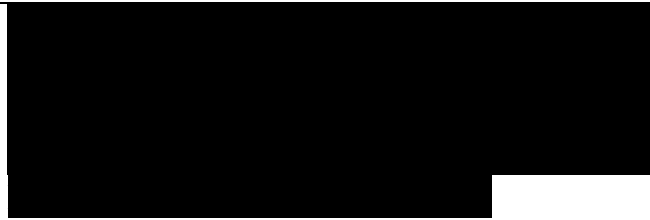
m_t — 0.19 m; m_t = 0.98m.

FIG. 4. Energy band structure of silicon. (After Kleinman and Phillips.) The valence band edge is at r'25; the conduction band edge is along Ai. Spin-orbit interaction has not been considered in this figure.

The minimum energy gap is 1.14 ev; it does not occur vertically in an energy-band diagram in k space. The gap at the center of the zone between Tis and is believed to be about 2.5 ev. Values of the valence-band constants A, B, C calculated by Kleinman and Phillips [Phys. Rev. 118, 1153 (I960)] are in excellent agreement with the values determined by cyclotron resonance.

Germanium. The band structure is shown in Fig. 5, without spin- orbit interaction. The valence-band edge is with a spin-orbit splitting of 0.29 ev. The minimum of the conduction band occurs in the 111 directions at the edge of the zone; that is, the conduction-band edge occurs at the point L and is presumed to have the representation L\. The effective masses of the prolate spheroidal surfaces are highly anisotropic: mjm = 1.64; mt/m = 0.082. The effective mass in the state 1^2 at k = 0 is isotropic and has the value m*/m = 0.036; this state is normally vacant, but the splitting of the optical absorption

FIG. 5. Energy bands in germanium along the [100] and [111] axes according to the experimental information and the calculations of Herman. Spin-orbit cou¬pling is neglected. Levels determined by experiment are circled. (After J.Callaway.)

in a magnetic field gives the mass. One major change which occurs in going from Si to Ge is that the lowest conduction-band state at k = 0 changes from Tis in Si to the nondegenerate in
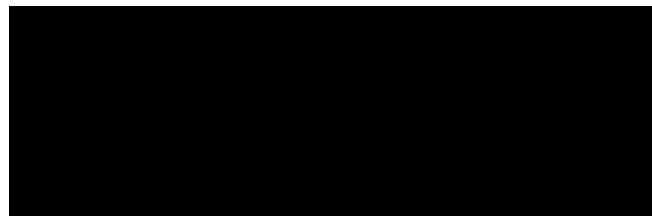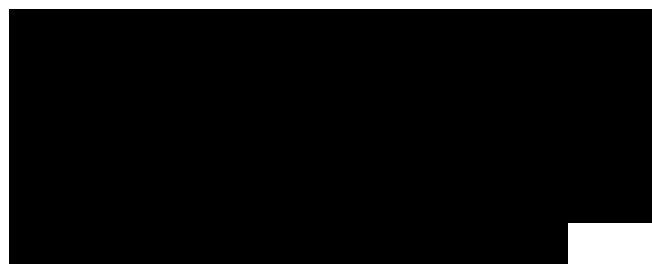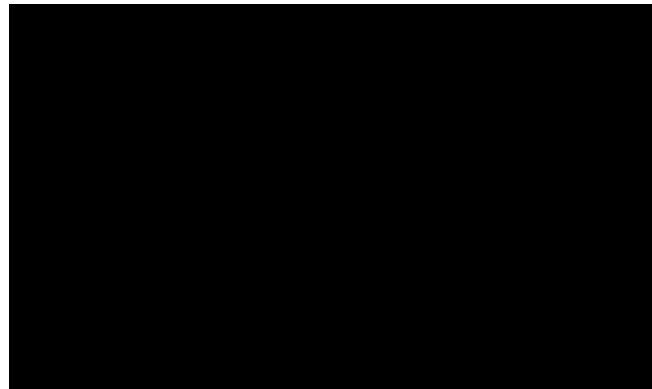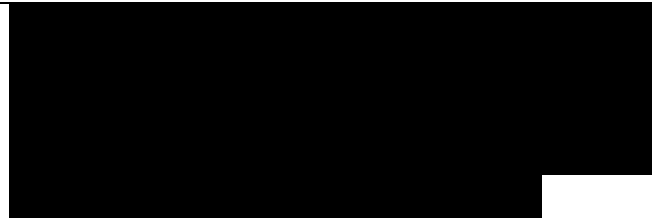
Ge. In grey Sn, beyond Ge, it is believed that V'2 remains lower than Tig.

Indium Antimonide. The crystal InSb has the zinc blende struc-ture, which differs from the diamond structure in an important respect. The diamond structure is composed of two identical interpenetrating fee lattices, but in InSb one of the lattices contains In atoms and the other lattice contains Sb atoms. The chemical valences are 3 and 5; InSb is an example of 3-5 compound. The crystal symmetry resembles that of diamond, but no longer has an inversion center. Thus we can no longer say that the energy levels at fixed k have the twofold conjugation invariance. The time reversal operation K still commutes with the hamiltonian, so that £k f is degenerate with £_k j. A number of changes in the band structure occur with respect to the correspond¬ing 4-4 crystals because of the loss of the inversion J as a symmetry element; this introduces a component of the crystal potential anti¬symmetric with respect to a point midway between the two atoms in a cell.

In 3-5 crystals in which the lowest conduction-band state at k = 0 belongs to Tis it is expected that the antisymmetric potential will mix the representation of the original valence-band edge and the representation r 15. The antisymmetric potential by itself will split these representations if, as for a plane wave model, they were degen¬erate; if the representations are already split, it will act to increase the splitting. The gap at k = 0 in BN is calculated to be about 10 ev, \ about twice as large as in diamond. We note that the gap observed in A1P is 3.0 ev, compared with 1.1 ev in Si. In InSb and grey tin the conduction band at

k = 0 is r£; the antisymmetric potential increases the gap from 0.07 ev in grey tin to 0.23 ev in InSb. The conduction-band edge is at k = 0 in both crystals.

The spin-orbit splitting A of the valence-band edge in InSb is estimated to be 0.9 ev, or about four times as large as the band gap. In this situation it makes no sense to treat the representations of the problem without spin. With spin, the valence-band edge belongs to the fourfold cubic representation r8, with the split-off band belong¬ing to r7. The conduction-band edge may belong to r6 or r7, both twofold.

The k • p perturbation does not give a term in the energy first order in k for either of the twofold representations. This follows because p transforms as the vector representation IV, and IV X r6 does not contain Te; similarly I> X r7 does not contain r7. Thus first-order matrix elements k • (re|p|r6) = 0, and k • (r7|p[r7) = 0. There are second-order contributions to the energy, but the degeneracy is not lifted in this order. To third order for r6 or r7 the energy is
Energy

FIG. 6. Plot of energy versus wavevector in InSb showing the first-order energy for the spin-orbit split r'25 level in [100], [110], and [111] directions. The circled numbers indicate the dimension of the representation. (After Dresselhaus.)

split in all but the 100 and 111 directions:

$$(12) \quad e(k) = CQJC2 \pm Ci[k2(kx\%2 + kyV + kzV) - 9kx\%V]H.$$

It is known from cyclotron resonance that $m^* = 1/2C0 = 0.014m$.

The fourfold representation r8 gives contributions to the energy in first order in k, because I> X r8 = r6 + r7 + 2r8, which contains r8. Thus there will be

first-order matrix elements k * (r8|p|r8) ^ 0. Very close to k = 0 the four bands at the valence-band edge have the general form, to first order in k,

(13)   e(k) = ±C{k% ± [3(/<vV + kyV + kzV)]H}H.

The four signs are independent. The splitting is shown in Fig. 6. The constant C is very small, and the linear region of (13) is soon dominated by the normal quadratic terms as in (10). The C terms shift the band edge slightly from k = 0; the expectation is that there will be a nest of band edges in InSb along 111 directions about 0.003 of the way out to the zone boundary, with an energy at the maximum about 10-4 ev above the energy at k = 0. For hole energies 5S> 10~4 ev the valence band of InSb will resemble that of Ge.

CYCLOTRON AND SPIN RESONANCE IN SEMI¬CONDUCTORS, WITH SPIN-ORBIT COUPLING

We consider a conduction-band edge at k = 0 in an orthorhombic crystal and suppose the band has only the twofold time reversal degeneracy. The crystal is assumed to have a center of inversion. In the absence of a magnetic field the energy to second order in k is

(14)   £(k) = 2 Dtfkakfs, (a, ft = x, y, z).

The two-component Wannier effective wave equation (Chap. 9) in a magnetic field is written by viewing k = p — (e/c)A as an operator:

^(x,s) = #(x,s),

where s is a spin coordinate; we have written the spin magnetie- moment operator as

In using form (15) it is usually assumed implicitly that the com¬ponents of k commute. In the absence of a magnetic field they do:

(!6) [ka,kp] = \pa,pfi] = 0;
but in a magnetic field the commutator of the k's includes [pa,A$[
which is not necessarily zero. For the gauge A = H(0,x,0) we have

(17)   [kx,kz] = 0; [ky,kz] = 0;

(18)   [*,,*,]= —MJ

C   C

We need, therefore, to write (14) in a form which will permit the possibility of a contribution from the antisymmetric form [kx,ky]:

(19)   e(k) = 2 (DjIM*} + DUKW,

where in the summation each pair afi is to be taken only once; that is, fia is not counted if afU is counted. Here

(20)   {ka>kp\ = kakf} "4" kpkat

Ds and DA denote the symmetrical and antisymmetrieal coefficients, respectively. In the absence of a magnetic field only the symmetrical term of (19) will contribute, as then [&«,&/}] = 0.

The coefficient Dap is given by k * p perturbation theory:

(21)   D,,, = J-i,,6 + -LX'^1W^-5L^

2m m j By — B$ 2m

where y denotes the state under consideration at k = 0. Then

(22)   D«p — UDa, + D$a);   =   i(Dap — As«);

(23)   DA - 1 T/   ~   = _DA

a(i 2 m2 7   By — B&   &a'

In our gauge and with the coordinate axes along the crystal axes, we have

(24)   D% = D'Ae,

and the total antisymmetric contribution to s(k) is

ip

(25)

c

using (18). Thus

The equation of motion of x in zero magnetic field is

(27) $ix = [x,H] = i Vx + (d x grad F).) = i \sim$

The term following px arises from the spin-orbit term in the hamil-tonian :

(28) $Hs0 = \sim 2c2 (d X grad F) \cdot p,$

where F(x) is the periodic crystal potential; the commutator

(29) $[x,Hs0] = {}^{\wedge\wedge}2 (d X grad V)x.$

The operator « is defined by (27), as in (9.29); for most purposes the term in d X grad F is a small correction to p. The *'s have essen¬tially the properties with spin-orbit interaction which the p's have without it.

Now write (27) in a representation in which H is diagonal, for zero magnetic field:

i   i i

(30)   —   (y|tx|5)   =   <7|®|5)£j   — eT<7|:r|S>.

If we neglect the difference between p and *, then

(31) $V' (7lp\text{«lg})(5[y>fllr) -$

&   By — £a

$= im J' ((7|a:\text{«}|5)(5|^|7) - <7|^|5)(5|pa|7\text{»}$

$= im(y\backslash LaX^\wedge\backslash y);$

$

here we have made use of $(O^\wedge O) = 0$, which follows by parity for $k = 0$ if the crystal has a center of inversion. If a = x; ft = y, then Lz is the component of the orbital angular momentum L in (31).

With (23) and (31), we have

(32) $iD*y = - \sim (y\backslash Lz\backslash y).$

Now if IC7) is the state conjugate to I7) in the sense introduced in (9.44), then

(33) $(Cy\backslash Lz\backslash Cy) = \{y\backslash C\sim lLzC\backslash y) = -(y^\wedge C^\wedge Cly) = -<7|l*|7>,$ because $CLZ = —Lz; C \ 1LZ = —LZf$ according to (9.135). Therefore

we may write

(34) $s(k)$ = Daakaka — -—
{y\Lz\y)<rzH — HB^ZH,
2 me

because 7 and Cy have opposite spins. Thus

(35) $e(k)$ = DM. - M*d • H,

where the anomalous magnetic moment n* is defined by

(36)   ^ = «7| L,\y) + 1)

MB

= ! _l_ JL V'~ ('y|p»|fi)(*lp«l'r)/
im $ By — £j

(37)   m! _ j + J_ , (%

HB   2im \ s By — Sj

where 8 signifies "the imaginary part of"; here we have used the fact that p is hermitian. The terms Daakaka in (35) gives the splitting observed in cyclotron resonance; the term —/a*d • H gives the splitting observed in spin resonance.

We now consider the anomalous magnetic moment for a specific model which is quite typical of many semiconductors. In the model we are concerned with the g value and magnetic moment of the state IO7) which we suppose is an s-like state at the eonduction-band edge with spin t- The state lies an energy Eg above a p% valence-band edge, also at $k = 0$; at an energy A below this there lies the level p^, split off by the spin-orbit interaction. We assume that there are interactions only among these bands. In the absence of spin-orbit interaction A is zero and then (0|LZ|0) vanishes because the representa¬tion can then be chosen so that either $<7|pa:|5) = 0$ or $\{y\py\8\} = 0$ for any state 8 in the representation. To see this, let $8 = x, y, z$.

We may represent schematically the states \J ;mj) by

(38)

The phases of these states satisfy $K|j;mj)$ $=$ — where $K = -WyKo$ is the Kramers time reversal operator. Note that these are not the phases obtained from successive applications of the $J\sim$ lowering operator. Now

with the matrix elements used for (41). Thus we have the Roth relation

for InSb, in good agreement with experiment. Here the effective hamiltonian is

The crystal having the narrowest band gap known at present is CdajHgi—sTe; with $x = 0.136$, the energy gap between conduction and valence bands is believed to be ~0.006 ev; further, $m*/m \sim 0.0004$ and $g \sim 2500$ at the bottom of the conduction band. The low mass and high g value are direct consequences of the low value of the energy gap, according to $k * p$ perturbation theory.

A careful detailed study of the g values of conduction electrons is given by Y. Yafet, Solid state physics 14, 1 (1963).
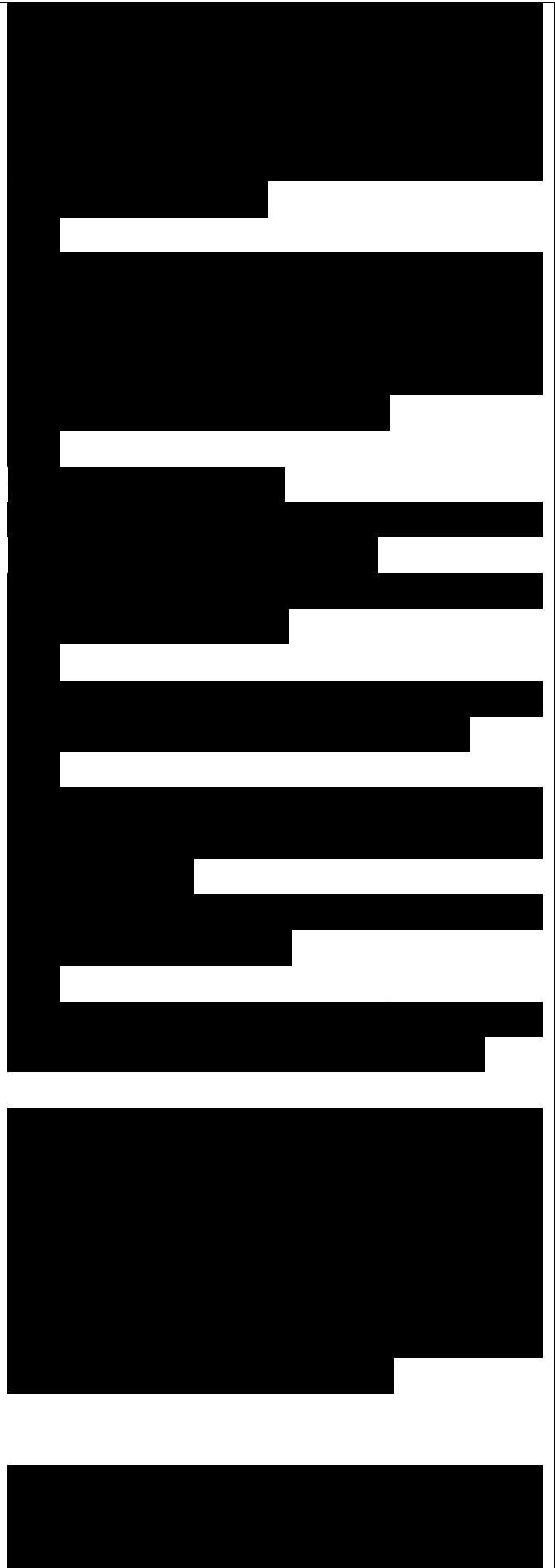
The method which led to (35) was developed by J. M. Luttinger, Phys. Rev. 102, 1030 (1956), for a more difficult problem, the study of magnetic effects on the pw band edge of a diamond-type semiconductor. He found that the hamiltonian in a magnetic field to terms quadratic in k may be written as

(46) H = fakjta + PMtJTaJ. + 40,({*,,*,,} \JX)JV\
+ {hM\Jv,Jz) + {kz,kx}{Jz>Jx}) + 0 AHJa + faHaJJJ*,

where Jx, Jv, Jz are 4X4 matrices which satisfy J X J = ij. In (46) the { } denote anticommutator, as usual.

Valence-Band Edge with Spin-Orbit Interaction. We want to derive the form (10) of the energy near the Tg valence-band edge of a crystal with diamond structure. In the absence of a magnetic field the second- order hamiltonian has the form (46) of the 4X4 matrix

(47) H = 0tk2 + Mcx2Jx2 + k*J* + ke2Jz2) + 403(1 kM {JX,JV}
+ \kv,kz}{JmJz} + \Kkx}{Jz,Jx}).

Here J is a 4 X 4 matrix which satisfies the angular momentum commutation relation J X J = ij. The expression (47) contains all the forms quadratic in the k's and J's which are invariant under the operations of the cubic point groups. The dimensionality of the matrix representing J is 4 X 4 because the r8 state is fourfold degenerate.

We know that H is invariant under the conjugation operation, so that every root of the eigenvalue problem is double. We now give a procedure due to Hopfield for the reduction of (47) to a 2 X 2 matrix for the two independent roots.

In the basis | Jmj) for J = § as given by (38) the time reversal operator is represented by

(«)   K = I h r : "]

where K0 denotes complex conjugation, if

(49)   < is an eigenvector of H, then

(50)   Kip = K

is an eigenvector having the same energy, because K commutes with the hamiltonian. But the states <p and K<p are independent:

(51)

We may then combine <p and K<p to form a state having the same energy, but with one coefficient, say d, equal to zero:

(52)   <p> = (1 + peiaK)ip,

where p and a are constants. We write

The first two components of this equation are sufficient. They may be written

(57)

With the representation (39) of the J's we have that

(58)   Hu = H 2z = 0; H21 = -HA3; tf42 = -Hu*, so that (57) has the solutions

(59)   X = i(Hn + H22) ± [i(Hn - W22)2 + |#12|2 + |H13|2]k,

which is equivalent to the standard form (10).

IMPURITY STATES AND LANDAU LEVELS IN SEMICONDUCTORS

We are now concerned with the theory of the shallow donor and acceptor states associated with impurities in semiconductors, particu¬larly trivalent and pentavalent impurities in germanium and silicon. The ionization energies of these impurities are of the order of 0.04 ev in Si and 0.01 ev in Ge. Such energies are much less than the energy gap; thus it is reasonable to expect the impurity states to be formed from one-particle states of the appropriate band,

conduction or valence. The impurity states will in a sense be hydrogen-like, but loosely bound, largely because the dielectric constant e of the medium is high. The rydberg constant involves 1/e2; for e = 15 the binding energy will be reduced from that of hydrogen by the factor When m* < m, there is a further reduction of the binding energy.

The Wannier theorem gives us the effective hamiltonian for the problem. We treat first a simplified model of a pentavalent impurity in silicon; we consider for the conduction band the single spheroidal energy surface

(60)   e(k) = (k,2 + ky2) + -i-k2.
2mt   2 mi

In the actual crystal there are six equivalent spheroids, each along a [100] axis. The Wannier equation associated with (60) is

' (pj + Vy2) +^-P,2- -1 m = EF(X), 2mt
        2 mi   er J

in the absence of a magnetic field.

We now examine the validity of (61). First, there is the question of the dielectric constant. It is fairly obvious that we should use the dielectric constant e(w) or, better, e(o>,q) as measured at the fre-quency &3 corresponding to the energy E of the impurity level referred to the band edge. In situations of interest to us this energy is smaller than the band gap, so that the electronic polarizability will contribute to e(«) in full. The ionic polarizability will contribute only if the binding energy of the impurity level is small in comparison with the optical phonon frequency near k = 0.

We now consider the validity of the effective mass approach itself. The Schrodinger equation of one electron in the perturbed periodic lattice is
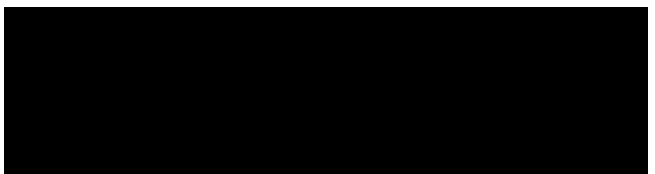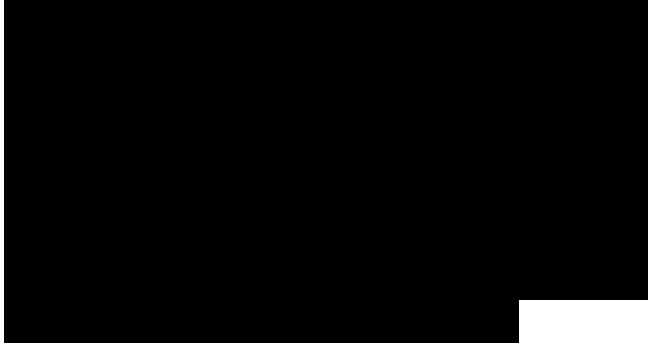
(62) $(H0 + V)* = EV,$

where H0 refers to the perfect lattice and V to the impurity. Here ^ is just a one-electron wavefunction. Consider the solution of the unperturbed problem

(63) $= eY(k)^ki,$ where

(64) $<pki\ s\ |kI) = e*'Xi(x)$

is the Bloch function with wavevector k and band index I. We assume the band is not degenerate. The solutions ^(x) of the per-turbed problem may be written

(65) $¥(x) = £\ [kT)<rk'|>.$
kT

We substitute (65) in the Schrodinger equation (62) and take the scalar product with (flc|, finding directly the secular equation

(66) $£i(k)(flc|> + S\ (Jk|\ V\kT\)(l'k'\) = E\{lk\).$

We next expand the perturbation V in a fourier series:

(67) $V = J\ F£eiK-*,$
K

whence

(68) $(lk\V\kr) = 2\ VK\ f\ d3x\ ei(k'-k+K)*X^k'P.$
K J

Because uki(x) is periodic in the direct lattice, the integral vanishes unless

We are concerned only with small k, k', and K, so that $G = 0$ for the matrix elements of interest. We note that for the coulomb potential Fk oc $l/K2$. The secular equation may be written

(70) $Si(k)(Zk|) + I\ FKA^K,k<r,k + K|> = E(tk\),$
w

where the function

(71) $^k+K,k — j\ dzx\ u£+x.,i(x)uki>(x).$
As |K| 0,

(72) $^k+K,k\ hi'-$

In this limit the secular equation reduces to

(73) $Si(k)(ik|> + X + K|> = E(lk\).$
K

The use of (72) is our central approximation. In this approximation the different bands are entirely independent. The secular equation (73)is precisely the Schrodinger equation in the momentum represen¬tation of the following Wannier problem in a coordinate representation:

(74) $[e,(p) + V(x)]Fl(x) = EFi(x),$
where

(75) $F,(x) = 2eik-'<ik|>.$
k

We suppose we have solved (74) for Fi(x). In a specimen of unit volume

(76) $<*k|> = / tfzFMe-*-1,$
so that the solutions $^(x)$ of our original problem are

(77) $*,(x) = Vn,(i) / ds|F,({)*-*•'$
k

where Fi is an eigenfunction of the Wannier problem, Eq. (74).

For slowly varying perturbations only a small range of k will enter the solution for low-lying states in a given band. If we make the approximation that uki may be replaced by u0i(x) in (77), then

$*,(x)~«0,(x) / d3{Fi(0 2eik"_t) = "0l(x)^(x),$
because

(79) $I j*"-1-" = = *(i - «•$

This displays the role of Fi(x) as a slow modulation on Wo(x). The replacement of uki(x) by u0i(x) introduces no approximation more important than we have made already in neglecting the interband mixing terms in (72).

The Wannier equation (74) is seen to be rigorous in an approxima-tion which can be stated precisely, namely that (73)

should hold. Kittel and Mitchell, Phys. Rev. 96, 1488 (1954), show for I V that

(80) $A'' \approx \left(\dfrac{\text{impurity ionization energy}}{\text{band gap}}\right)$,

which may be of the order of 0.1 for Si and perhaps less for Ge.

The method is easily extended to degenerate bands, where one deals with coupled Wannier equations connecting the several degener¬ate components. For a discussion of the acceptor levels in Si and Ge, and for a treatment of short-range effects within the atomic core of the impurity, the reader should consult the review by W. Kohn, Solid state physics 5, 258 (1957).

We go on to the solution of (61). For a spherical energy surface $mi = mt — m^*$, and we have exactly the hydrogen-atom problem with $e2/e$ written for $e2$ and m^* written for m. The anisotropic Hamiltonian (61) is not exactly solvable in closed form. We may determine an upper bound to the ground-state energy relative to the band edge by a variational calculation. With $mt = aim$; $mt = atm$; and $r0 = e/me2$, we try a variational function of the form

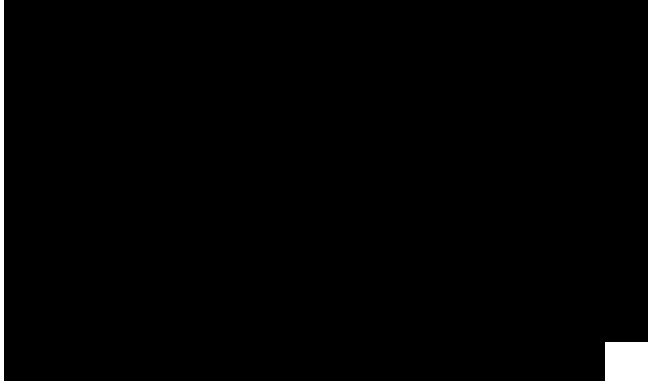(81) $F(x) = (ab2/irr0z)'A \exp \{ — [aV + b2(x2 + y2)]!/Vro\}$.

We find on carrying out the variational calculation the following results:

For w-Ge with $ax = 1.58$; $a2 = 0.082$; $s = 16$:

(82) $E0 = -0.00905$ ev; $a2 = 0.135$; $b2 = 0.0174$.

For n-Si with $ai — 1$; $a2 = 0.2$; $s = 12$:

(83) $E0 = -0.0298$ ev; $a2 = 0.216$; $b2 = 0.0729$.

The theory may be generalized directly for degenerate band edges. The Wannier equation becomes an equation for a

multicomponent wave function F:

(84) $(H(p) + V)F(x) = EF(I)$,

where H(p) is the square matrix from second-order k • p perturbation theory and F(x) is a column matrix.

LANDAU LEVELS

By Landau levels we mean the quantized orbits of a free particle in a crystal in a magnetic field. In the chapter on electron dynamics in a magnetic field we gave the Landau solution for a free particle in a vacuum in a magnetic field, and we considered the semiclassical theory of magnetic orbits on general fermi surfaces. At present we consider only the quantization of a spinless electron near the non-degenerate conduction band edge of a semiconductor having the spheroidal energy surface

(84a) $e(k) = (k* + ky2) + k?$,

2m t   2m i

in the absence of the magnetic field.

The hamiltonian with the magnetic field is

(85) $H.\pm(p -?a)*+F(*)$;

the vector potential for a uniform magnetic field ,TC in the z direction in the Landau gauge is

(80) $A = (0,rfC:r,0)$.

If we write

(87) $s = e.TC/c$, the hamiltonian is

s   s2

(88) $II = HQ$ xpy + — x2.

m   2m

The eigenfunctions of H0 are the Bloch functions jk,l)\ the eigenvalues are Sj(k)- Because of the presence of terms in x and x2 it is a difficult and lengthy problem to analyze the validity of the effective mass equation in a uniform magnetic field. In order to avoid singular matrix

but we have seen in Chapter 9 that

<ncipJw>=*"&!/

to first order in k. Thus for a spherical energy surface

i i   IP

(98)   <ik C/j k'Z> S-Tk. Aq(Jt.!t+, - Sk,k_,,).

m*c

We need also

(99)   (lk\U2\k'i) = - |Aq|2 (Ik\e2i(l'x + e~m'x - 2\k'l);

2 me '

in the limit q —> 0

(100) <ik| J/2|k7> ^ - ^£2 Aa(\M,+2, + V;k-2, - 2Sk.;k).

Similarly

,, </k|C/i|kT)<rkiC/i|k'7)

(101) X'

using the /-sum rule. Thus

(102) (£k|(P|k7)   -j-   Aq   •

k(5k';k+q — 5k';k_q)

m*c

e2

+ 2m*cZ lA«r(2^k — ^k';k-2q — V;k+2q),

and (95) is identical with the effective mass equation in the plane wave representation

(103) F,(x) -X^Zkl),

k

so that Fi(x) satisfies the Wannier equation

(104) 2^(P-^)2^« = ™

The above derivation is due to Argyres (unpublished); the deriva¬tion of Luttinger and Kohn [Phys. Rev. 97, 869 (1955)] avoids the limiting process q — ► 0 at the price of treating singular matrix elements.

PROBLEMS

1.   Consider the hamiltonian

H = p2 + x2

of a harmonic oscillator; solve for the eigenvalues using a plane wave repre¬sentation :

= j dxeikx(k\),
with
(U\x*\k) = - Ji S(k - k'),
and show that one obtains the correct energy eigenvalues. This is an exercise in a method of handling matrix elements of the coordinates.

2.   Show that states which transform as / = | are split into two twofold levels by an axial crystal field. Evaluate the splitting for the crystal potential

V - a(x2 + y2 — z2),

and the spin-orbit splitting X between the / = f and J = i levels in the absence of the crystal field.

3.   (a) Show for a cubic crystal at k = 0 that

DS,, = 0; D% * 0,

using the definitions (21) and (22), with coordinate axes along the cube edge directions. Hint: Consider the effect on D%y of rotating about the z axis by 7t/2. (6) Show that in the absence of spin-orbit coupling D^y = 0.

4.   In CdS the conduction band edge may be written in the form, to 0(fc2),

£k = [A(kx2 + ky2) + Bkz*\   ^   + C(kxav - kvax),

where the z direction is parallel to the symmetry axis of the crystal; the ax, Oy are pauli matrices. Plot a section of a constant energy surface in the plane kv = 0, for the band with spin parallel to the positive y axis. Con¬sidering only this spin orientation, does this band carry a net current when filled at 0°K to a level ZF?

5.   Verify the statement made in connection with 3-5 crystals that the antisymmetric crystal potential component will act to increase the splitting between and r15 states.