Theory of Bloch Electrons in a Magnetic Field: The Effective Hamiltonian*

WALTER KOHN
Department of Physics, Carnegie Institute of Technology, Pittsburgh, Pennsylvania
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The Hamiltonian of a Bloch electron in a static magnetic field is $H=\frac{1}{2}\mathbf{P}^2+V(\mathbf{r})$, where $V(\mathbf{r})$ is the periodic potential, $\mathbf{P}=\mathbf{p}+\mathbf{A}/c$, and $\mathbf{A}$ is the vector potential giving rise to the magnetic field $\mathfrak{H}$. We consider the case of a nondegenerate band m. It is then shown that, with an error vanishing with $\mathfrak{H}$ like $\mathfrak{H}^{N+1}$ (N arbitrary), the eigenstates of H can be calculated from an equivalent Hamiltonian $\bar{H}_m(\mathbf{P})$ with the following properties: (1) It is a one-band Hamiltonian, obtained by transforming away all relevant interband matrix elements. (2) It depends only on the gauge-covariant operators P^α. (3) It has the periodicity property $\bar{H}_m(\mathbf{P}+\mathbf{K})=\bar{H}_m(\mathbf{P})$, where $\mathbf{K}$ is an arbitrary reciprocal lattice vector. (4) It can be written as a series $\bar{H}_m(\mathbf{P})=\sum_{i=0}^N s^i \bar{H}_{m;i}(\mathbf{P})$ where $s\equiv\mathfrak{H}/c$ and the functions $\bar{H}_{m;i}(\mathbf{P})$ are completely symmetrized in the noncommuting operators P^α. Properties (3) and (4) can also be summarized in the equations $\bar{H}_m(\mathbf{P})=\sum_l a^{(l)} \times\exp[i\mathbf{R}^{(l)}\cdot\mathbf{P}]$, where the $\mathbf{R}^{(l)}$ are lattice vectors and the $a^{(l)}$ can be expanded as $a^{(l)}=\sum_{i=0}^N s^i a_i^{(l)}$. An algorithm is given for the construction of the $\bar{H}_{m;i}$ and carried through for $i=0, 1, 2$. The formalism is not restricted to the neighborhood of the bottom and top of the band. We believe that the equivalent Hamiltonian $\bar{H}_m(\mathbf{P})$ provides a sound basis for a discussion of wave functions and energy levels of Bloch electrons in a magnetic field.

1. Introduction

THE study of the physical properties of metals and semiconductors in external magnetic fields has been among the most fruitful methods for obtaining insight into their electronic structure. In many cases the experiments give us information about the electronic energy levels in a magnetic field. Examples are the diamagnetic susceptibility, De Haas-Van Alphen effect, cyclotron resonance, and magneto-optic effects.

It is therefore not surprising that the theory of the motion of Bloch electrons in a uniform magnetic field has received a good deal of attention. Following the classic work of Landau[1] on the quantum theory of free electrons in a magnetic field, the first analysis of Bloch electrons in a magnetic field was carried through by Peierls.[2] This latter work was based on the tight-binding approximation and therefore its results have only qualitative validity. Since then a great many contributions to this problem have been made, some of them dealing with the individual energy levels,[3–10] others emphasizing the free energy of the entire system.[11–14] However, because of the great mathematical complexity of the problem, many authors have found it necessary to use one or the other uncontrolled approximation, so that the reliability of their results remains often in doubt. Thus much work is based on the so-called single-band Hamiltonian

$$H\equiv\epsilon_m(\mathbf{P}), \tag{1.1}$$

where $\epsilon_m(\mathbf{k})$ is the energy band in question,[15a]

$$\mathbf{P}=\mathbf{p}+\mathbf{A}/c, \tag{1.2}$$

and $\mathbf{A}$ is the vector potential giving rise to the uniform magnetic field. At least some interband matrix elements are left out of account in such theories and in certain cases it has been shown that this may lead to very serious errors.

Two relatively recent developments have been of particular interest. One is an expression due to Onsager,[4] which relates the levels in a magnetic field to simple geometrical properties of the energy bands and applies to bands of arbitrary shape. This expression has been extremely helpful in analyzing De Haas-Van Alphen experiments. However it is derived by means of a semi-classical argument whose range of validity is, as the author points out, not entirely clear.

The other question which has been recently discussed by several authors[6,8,9] concerns the extent to which magnetic levels, highly degenerate in the absence of a periodic potential, are spread into bands. That such banding occurs is beyond any doubt, and may be demonstrated in some simple examples. But the width of the bands is a matter which is not settled at present and there is substantial disagreement between different authors.

The present work was undertaken in the hope of clarifying some of the existing uncertainties. It is in a sense an outgrowth of some earlier work,[5,7] but unlike it is not restricted to the vicinity of the bottom or top

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[15a] Atomic units are used in this paper.

of an energy band. In this paper we derive an effective single-band Hamiltonian as well as the corresponding basis functions. The diagonalization of this Hamiltonian and the resulting energy levels, wave functions, and free energies will be discussed in a second paper.

Following is a summary of the results obtained in this paper. We are concerned with the solution of the Schrödinger equation

$$H\psi\equiv(\tfrac{1}{2}\mathbf{P}^2+V)\psi=E\psi, \tag{1.3}$$

where $\mathbf{P}$ is defined in Eq. (1.2) and V is a periodic potential. For $\mathbf{A}=0$, the eigenfunctions of H are the Bloch waves

$$\varphi_{n\mathbf{k}}=u_{n\mathbf{k}}(r)e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{1.4}$$

and the corresponding eigenvalues are the energy bands $\epsilon_n(\mathbf{k})$. We fix our attention on solutions of (1.3) which in the limit of vanishing $\mathbf{A}$ go over into Bloch waves belonging to a nondegenerate band denoted by m.

In the presence of a magnetic field, the Hamiltonian H in (1.3) has nonvanishing matrix elements between Bloch waves associated with the band m and those belonging to other bands. We shall explicitly construct a new set of functions $\bar{\varphi}_{n\mathbf{k}}$ such that, *in a certain sense*, $H\bar{\varphi}_{m\mathbf{k}}$ can be expressed as a linear combination of the $\bar{\varphi}_{m\mathbf{k}'}$ with the *same m*. In fact we shall show that

$$H\bar{\varphi}_{m\mathbf{k}}\approx\sum_{k'}\bar{\varphi}_{m\mathbf{k}'}(\mathbf{k}'|\bar{H}_m(\mathbf{P})|\mathbf{k}), \tag{1.5}$$

where $\bar{H}_m(\mathbf{P})$ is an explicitly constructed function of the operator $\mathbf{P}$, and the notation $(\mathbf{k}'|\ |\mathbf{k})$ denotes a matrix element between *plane*-wave states $\mathbf{k}'$ and $\mathbf{k}$.[15b]

The meaning of the phrase "in a certain sense" and of the $\approx$ sign in (1.5) is the following. We construct $\bar{\varphi}_{n\mathbf{k}}$ and $\bar{H}_m(\mathbf{P})$ by a step-by-step process, which can be carried to arbitrary order N in the magnetic field $\mathcal{H}$. If we stop at the Nth order, the equation (1.5) is correct apart from terms which vanish with $\mathcal{H}$ like $\mathcal{H}^{N+1}$. We do not yet know if for small enough $\mathcal{H}$ our process converges strictly or only in an asymptotic sense. To simplify our langugage, we shall assume the former, but if in fact the convergence is only asymptotic our results may have errors which vanish however more rapidly than $\mathcal{H}^N$, where N is arbitrary.[16]

The new basis functions $\bar{\varphi}_{m\mathbf{k}}$ have a "periodicity" property similar to that of ordinary Bloch waves. That is, if $\mathbf{K}$ is a reciprocal lattice vector,

$$\bar{\varphi}_{m\mathbf{k}+\mathbf{K}}=\pm\bar{\varphi}_{m\mathbf{k}}. \tag{1.6}$$

The sign here depends on the details of $V(\mathbf{r})$ as well as on $\mathbf{K}$. It is extremely convenient not to restrict $\mathbf{k}$ to a single Brillouin zone but to allow it to run over a very large volume in $\mathbf{k}$ space. Because of (1.6) the $\bar{\varphi}_{m\mathbf{k}}$ are then of course not linearly independent, but the difficulties associated with this *redundancy* are more than balanced by its advantages.

The effective one-band Hamiltonian, $\bar{H}_m(\mathbf{P})$ *includes* all interband effects. If we define

$$s\equiv\mathcal{H}/c, \tag{1.7}$$

it can be expanded in the form

$$\bar{H}_m(\mathbf{P})=\bar{H}_{m;0}(\mathbf{P})+s\bar{H}_{m;1}(\mathbf{P})+s^2\bar{H}_{m;2}(\mathbf{P})+\cdots, \tag{1.8}$$

where each $H_{m;i}$ is a completely symmetrized function of the noncommuting operators P^α. Furthermore, if we denote the lattice vectors of the crystal by $\mathbf{R}^{(l)}$, each $H_{m;i}$ has a Fourier series expansion of the form

$$\bar{H}_{m;i}(\mathbf{P})=\sum_l a_i^{(l)}\exp(i\mathbf{R}^{(l)}\cdot\mathbf{P}). \tag{1.9}$$

Explicit constructions for the functions

$$\bar{H}_{m;i}(\mathbf{k})=\sum_l a_i^{(l)}\exp(i\mathbf{R}^{(l)}\cdot\mathbf{k}) \tag{1.10}$$

(and hence for the a_i^l) are given. For $i=0$, we find of course

$$\bar{H}_{m;0}(\mathbf{k})=\epsilon_m(\mathbf{k}), \tag{1.11}$$

which gives rise to the simple one-band Hamiltonian (1.1).

In view of (1.8) and (1.9), $\bar{H}_m(\mathbf{P})$ can also be expressed as a Fourier series,

$$\bar{H}_m(\mathbf{P})=\sum_l a^{(l)}\exp(i\mathbf{R}^{(l)}\cdot\mathbf{P}), \tag{1.12}$$

where

$$a^{(l)}=a_0^{(l)}+sa_1^{(l)}+s^2a_2^{(l)}+\cdots. \tag{1.13}$$

From this form the important periodicity property

$$\bar{H}_m(\mathbf{P}+\mathbf{K})=\bar{H}_m(\mathbf{P}) \tag{1.14}$$

is apparent.

The Hamiltonian $\bar{H}_m(\mathbf{P})$ of Eq. (1.8) is far from unique. Any unitary transformation $U(\mathbf{P})$ with the appropriate periodicity properties will lead to an equivalent but different Hamiltonian. The leading term $\bar{H}_{m;0}(\mathbf{P})$ is of course common to all these forms.

When the crystal in question has a center of inversion, only even powers of s occur in our expansion (1.8). In this paper the expansion is explicitly carried out up to order s^2. When a center of inversion is absent, also odd powers of s occur. For this case the expansion is explicitly carried through up to order s.

This is the point where the present paper stops. It remains to find the solutions of Eq. (1.3) corresponding to the band m. These can be written in the form

$$\psi=\sum_{\mathbf{k}}\bar{A}_m(\mathbf{k})\,\bar{\varphi}_{m\mathbf{k}}, \tag{1.15}$$

and by (1.5) will satisfy the Schrödinger equation, if $\bar{A}_m(\mathbf{k})$ satisfies the equation

$$\sum_{\mathbf{k}'}(\mathbf{k}|\bar{H}_m(\mathbf{P})|\mathbf{k}')\bar{A}_m(\mathbf{k}')=E\bar{A}_m(\mathbf{k}). \tag{1.16}$$

The solution of this equation and related questions will be discussed in a subsequent paper.

The results derived in this paper have a very simple structure. It is therefore a pity that the methods by

[15b] For earlier discussions of an effective Hamiltonian, see especially references 3 and 4.

[16] This possibility is of importance in the question of the "banding" of the magnetic levels.

which they are derived here are shockingly complicated. Also the particular expressions we obtain for the higher-order Hamiltonians in Eq. (1.8) are very involved and depend rather surprisingly on such unexpected quantities as the values of the normalized Bloch waves at the arbitrarily chosen origin of coordinates. We have already mentioned the lack of uniqueness of the Hamiltonian. Perhaps much simpler expressions exist and much simpler derivations. If so, we hope that they will in time be found.

PART I

2. Formulation of the Mathematical Problem

Our problem is the solution of the Schrödinger equation

$$H\psi \equiv (\tfrac{1}{2}\mathbf{P}^2+V)\psi = E\psi, \tag{2.1}$$

where V is a periodic potential, $\mathbf{P}$ is the velocity operator

$$\mathbf{P}=\mathbf{p}+\mathbf{A}/c, \tag{2.2}$$

and $\mathbf{A}$ is the vector potential giving rise to a uniform magnetic field $\mathfrak{H}$:

$$\mathfrak{H}=\mathrm{curl}\mathbf{A}. \tag{2.3}$$

The boundary conditions are the usual periodicity conditions on the surface of a large box of volume $\bar{\Omega}$.

We shall be interested in the solutions of (2.1) which correspond to a simple band whose band index we denote by m. By "correspond" we mean that in the limit of vanishing $\mathbf{A}$ the solutions go over into Bloch waves with the band index m; and by a "simple" band we mean a band which has only one wave function for a given $\mathbf{k}$ and which does not touch or intersect another band.

Of course, except in some very special cases, such as $V\equiv 0$, an exact solution of (2.1) is not possible. We shall seek approximate solutions which are valid if the magnetic field is sufficiently weak. However, what constitutes a weak field for one part of the spectrum may not for another. Loosely speaking, we may say that a weak field is one in which the magnetic energy of the electron is small compared to some characteristic energy when the magnetic field is switched off. In atomic units, if we call

$$s\equiv \mathfrak{H}/c, \tag{2.4}$$

this means that

$$s \ll \gamma, \tag{2.5}$$

where γ is a pure number of the general order of magnitude 1. However in some cases, for example when dealing with very small effective masses, γ may be as small as 10^{-1} or 10^{-2}. We shall by a sequence of unitary transformations construct new Hamiltonian, equivalent to H, in the form of a series whose nth term contains a factor s^n. The validity of the expansion can then in each case be checked by inspection of successive terms. In most practical cases a few terms are sufficient.

It is perhaps worth mentioning that the validity of our procedure is quite independent of the temperature. For example, the observation of the De Haas-Van Alphen effect requires a "strong" field, but in the sense

$$s \gtrsim kT. \tag{2.6}$$

Since kT at 1°K equals 10^{-5} in atomic units, the condition (2.5) need by no means rule out the inequality (2.6).

3. Initial Basis Functions

Returning now to Eq. (2.1), it is of course well known that it cannot be solved by simple Schrödinger perturbation theory in powers of s. The effect of even a very weak magnetic field on the eigenfunctions is too profound. Nevertheless it seems natural to begin by writing Eq. (2.1) in the representation of the unperturbed eigenfunctions of H, the Bloch waves, and carry on from there. However, this approach led to technical difficulties which we could not overcome.

The procedure which we could carry through begins with the following basis, introduced in reference 5:

$$\chi_{n\mathbf{k}} \equiv u_{n0}e^{i\mathbf{k}\cdot\mathbf{r}}. \tag{3.1}$$

Here u_{n0} is the periodic part of the Bloch wave

$$\varphi_{n\mathbf{k}} = u_{n\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{3.2}$$

for $\mathbf{k}=0$. The normalization is fixed by the equation

$$\frac{(2\pi)^3}{\Omega}\int_{\text{cell}} u_{n\mathbf{k}}{}^* u_{n'\mathbf{k}} d\mathbf{r} = \delta_{nn'}, \tag{3.3}$$

where Ω is the volume of the unit crystal cell. Finally it follows from time reversal symmetry that we may fix the phase of $u_{n0}(\mathbf{r})$ such that

$$\mathrm{Im}\, u_{n0}(\mathbf{r}) = 0. \tag{3.4}$$

When $\mathbf{k}$ is restricted to the fundamental Brillouin zone, the set $\chi_{n\mathbf{k}}$ forms a complete orthogonal basis. This was the set used in the papers by Luttinger and Kohn[5] and Kjeldaas and Kohn[7] that were concerned with levels near the bottom or top of a band, which involved only small values of $\mathbf{k}$.[17] In the present paper we shall not limit ourselves to levels near the band edges. In particular we want to be able to describe levels which, in a semiclassical description, correspond to Bloch wave packets circulating under the influence of the magnetic field through *several* Brillouin zones. Two courses of action suggest themselves: One is to hold fast to the basis of Luttinger and Kohn and consider very carefully what happens when $\mathbf{k}$ is *on* the Brillouin zone boundary. This procedure we found not tractable. The other course, which we adopt, is to extend the basis (3.1) by letting $\mathbf{k}$ run over a very large volume $\bar{\tau}$ in $\mathbf{k}$ space. Now since the $\chi_{n\mathbf{k}}$ form a complete set when $\mathbf{k}$ runs over any one Brillouin zone, of volume τ, this extended basis has a redundancy of $(\bar{\tau}/\tau)$. The

[17] The results of the present work are in agreement with the conclusions of these earlier papers.

magnitude of $\bar{\tau}$ will of course drop out of our final results just as does the coordinate volume $\bar{\Omega}$ of the crystal.

When we come to count states, the finiteness of both $\bar{\tau}$ and $\bar{\Omega}$ will be made use of. But during most of the following developments it is convenient to regard them first as infinite. Then both $\mathbf{r}$ and $\mathbf{k}$ become continuous variables ranging over their entire respective spaces.

4. Schrödinger Equation in the Initial Representation

Since the functions $\chi_{n\mathbf{k}}$ of our extended basis are more than complete, the solutions ψ of the Schrödinger equation can certainly be expanded in terms of them:

$$\psi=\sum A_n(\mathbf{k})\chi_{n\mathbf{k}}, \tag{4.1}$$

where the symbol $\sum$ includes both summation over n and integration over $\mathbf{k}$. However, it is obvious that the coefficients $A_n(\mathbf{k})$ are not unique.

When we substitute (4.1) into the Schrödinger equation (2.3), we are led to consider the effect of $(H-E)$ operating of $\chi_{n\mathbf{k}}$. The resulting function has of course again a highly ambiguous expansion in terms of the $\chi_{n\mathbf{k}}$, but we are entirely at liberty to choose one which is particularly simple.

We follow in this largely the procedure of Kjeldaas and Kohn.[7] We wish first to compute the result of $\frac{1}{2}(\mathbf{p}+\mathbf{A}/c)^2$ acting on $\chi_{n\mathbf{k}}$. We make the following preliminary definitions. If Q is an operator which is a function of x^α and p^α, we define

$$(\mathbf{k}'|Q|\mathbf{k})\equiv\frac{1}{(2\pi)^3}\int e^{-i\mathbf{k}'\cdot\mathbf{r}}Qe^{i\mathbf{k}\cdot\mathbf{r}}d\mathbf{r}. \tag{4.2}$$

Further we call

$$p_{n'n}{}^\alpha\equiv\frac{(2\pi)^3}{\Omega}\int_{\text{cell}}u_{n'0}{}^*p^\alpha u_{n0}d\mathbf{r}. \tag{4.3}$$

With these notations we *may* write

$$\begin{aligned}p^\alpha\chi_{n\mathbf{k}}&=p^\alpha u_{n0}e^{i\mathbf{k}\cdot\mathbf{r}}\\&=\sum\chi_{n''\mathbf{k}''}[\delta_{n''n}k^\alpha(\mathbf{k}''-\mathbf{k})+p_{n''n}{}^\alpha\delta(\mathbf{k}''-\mathbf{k})]\\&=\sum\chi_{n''\mathbf{k}''}[\delta_{n''n}(\mathbf{k}''|p^\alpha|\mathbf{k})+p_{n''n}{}^\alpha\delta(\mathbf{k}''-\mathbf{k})],\end{aligned} \tag{4.4}$$

and

$$\begin{aligned}x^\alpha\chi_{n\mathbf{k}}&=x^\alpha u_{n0}e^{i\mathbf{k}\cdot\mathbf{r}}\\&=(1/i)(\partial/\partial k^\alpha)u_{n0}e^{i\mathbf{k}\cdot\mathbf{r}}\\&=\sum\chi_{n''\mathbf{k}''}\delta_{n''n}(1/i)(\partial/\partial k^\alpha)\delta(\mathbf{k}''-\mathbf{k})\\&=\sum\chi_{n''\mathbf{k}''}[\delta_{n''n}(\mathbf{k}''|x^\alpha|\mathbf{k})].\end{aligned} \tag{4.5}$$

Now in a uniform magnetic field we can write

$$P^\alpha=p^\alpha+s^{\alpha\alpha'}x^{\alpha'} \tag{4.6}$$

(summation over repeated indices implied), where

$$\mathcal{H}_1=c(s^{32}-s^{23}),\text{ etc.} \tag{4.7}$$

Hence by (4.4) and (4.5) we can write

$$P^\alpha\chi_{n\mathbf{k}}=\sum\chi_{n''\mathbf{k}''}\times[\delta_{n''n}(\mathbf{k}''|P^\alpha|\mathbf{k})+p_{n''n}{}^\alpha\delta(\mathbf{k}''-\mathbf{k})]. \tag{4.8}$$

A second application of P^α results in

$$\begin{aligned}\tfrac{1}{2}P^\alpha P^\alpha\chi_{n\mathbf{k}}&=\sum\chi_{n'\mathbf{k}'}[\delta_{n'n}(\mathbf{k}'|\tfrac{1}{2}P^\alpha P^\alpha|\mathbf{k})+p_{n'n}{}^\alpha(\mathbf{k}'|P^\alpha|\mathbf{k})\\&\quad+\tfrac{1}{2}\textstyle\sum_{n''}p_{n'n''}{}^\alpha p_{n''n}{}^\alpha\delta(\mathbf{k}'-\mathbf{k})].\end{aligned} \tag{4.9}$$

To this must be added

$$[V(\mathbf{r})-E]\chi_{n\mathbf{k}}=\sum\chi_{n'\mathbf{k}'}(V_{n'n}-E\delta_{n'n})\delta(\mathbf{k}'-\mathbf{k}), \tag{4.10}$$

giving

$$\begin{aligned}(H-E)\chi_{n\mathbf{k}}&=\sum\chi_{n'\mathbf{k}'}[\delta_{n'n}(\mathbf{k}'|\tfrac{1}{2}P^\alpha P^\alpha|\mathbf{k})+p_{n'n}{}^\alpha(\mathbf{k}'|P^\alpha|\mathbf{k})\\&\quad+(\tfrac{1}{2}\textstyle\sum_{n''}p_{n'n''}{}^\alpha p_{n''n}{}^\alpha+V_{n'n}-E\delta_{n'n})\delta(\mathbf{k}'-\mathbf{k})].\end{aligned} \tag{4.11}$$

This may be further simplified by noting that the special case $\mathbf{A}=0$, $\mathbf{k}=0$ gives

$$\tfrac{1}{2}\textstyle\sum_{n''}p_{n'n''}{}^\alpha p_{n''n}{}^\alpha+V_{n'n}=\epsilon_n\delta_{n'n}, \tag{4.12}$$

where ϵ_n is the energy of the nth band at $\mathbf{k}=0$. With this relation (4.11) now becomes

$$(H-E)\chi_{n\mathbf{k}}=\sum\chi_{n'\mathbf{k}'}(n'\mathbf{k}'|H-E|n\mathbf{k}), \tag{4.13}$$

where

$$\begin{aligned}(n'\mathbf{k}'|H|n\mathbf{k})&\equiv\delta_{n'n}[\epsilon_n\delta(\mathbf{k}'-\mathbf{k})+\tfrac{1}{2}(\mathbf{k}'|P^\alpha P^\alpha|\mathbf{k})]\\&\quad+p_{n'n}{}^\alpha(\mathbf{k}|P^\alpha|\mathbf{k}'),\end{aligned} \tag{4.14}$$

and

$$(n'\mathbf{k}'|E|n\mathbf{k})=E\delta_{n'n}\delta(\mathbf{k}'-\mathbf{k}). \tag{4.15}$$

It should be noted that the matrix $(n'\mathbf{k}'|H|n\mathbf{k})$ is Hermitian.

When we substitute ψ, in the form of Eq. (4.1), into the Schrödinger equation (2.1) we obtain with the help of (4.13) the following *necessary and sufficient* condition on the coefficients $A_n(\mathbf{k})$:

$$\sum_{n'\mathbf{k}'}\sum_{n\mathbf{k}}\chi_{n'\mathbf{k}'}(n'\mathbf{k}'|H-E|n\mathbf{k})A_n(\mathbf{k})=0. \tag{4.16}$$

Now in the customary representation theory one infers from the orthogonality of the basis functions that (4.16) is equivalent to

$$\sum_{n\mathbf{k}}(n'\mathbf{k}'|H-E|n\mathbf{k})A_n(\mathbf{k})=0. \tag{4.17}$$

In the present case, since the $\chi_{n'\mathbf{k}'}$ are not linearly independent, the situation is different:

(a) Any set of coefficients $A_n(\mathbf{k})$, satisfying (4.17) will also satisfy (4.16) and hence the corresponding wave function,

$$\psi=\sum A_n(\mathbf{k})\chi_{n\mathbf{k}}, \tag{4.1}$$

will satisfy the Schrödinger equation (2.1). However the possibility exists (and is in fact realized) that a nonvanishing solution $A_n(\mathbf{k})$ of (4.17) may give rise to an identically vanishing wave function ψ. Equivalently, two different solutions of (4.17) can give rise to the same ψ.

(b) The totality of solutions of (4.17) give rise—via (4.1)—to the totality of solutions of the original Schrödinger equation (2.1). This result is demonstrated in Appendix A. It is not entirely trivial, since solutions of (4.16) may (and do) exist which are not solutions of (4.17). However, these solutions are equivalent (in the sense of giving rise to the same ψ) to other solutions of (4.17).

In view of this situation, the problem of finding all solutions of (2.1) can be divided into two parts: We first determine all solutions of (4.17). Then we construct the corresponding ψ's by means of (4.1) (some of which may vanish identically) and select from these a linearly independent set in terms of which they all can be expanded.

5. Elimination of Interband Matrix Elements

We now turn to the problem of solving Eq. (4.17), which on interchange of the primed and unprimed variables becomes

$$\sum_{n'\mathbf{k}'} (n\mathbf{k}|H|n'\mathbf{k}')A_{n'}(\mathbf{k}')=EA_n(\mathbf{k}); \qquad (5.1)$$

here the matrix $(n\mathbf{k}|H|n'\mathbf{k}')$ is given by Eq. (4.14). This equation is an integral equation in $\mathbf{k}$ space and a matrix equation in the band index. Our first aim is to eliminate by a series of canonical transformations the interband matrix elements in (5.1) which connect the band in question, m, with other bands and thus to transform (5.1) into an equation of the form

$$\sum_{\mathbf{k}'}(\mathbf{k}|\bar{H}_m|\mathbf{k}')\bar{A}_m(\mathbf{k}')=E\bar{A}_m(\mathbf{k}). \qquad (5.2)$$

First some preliminaries. As we have chosen the functions $u_{n0}(\mathbf{r})$ to be entirely real [see Eq. (3.4)] it follows that all matrix elements $p_{n'n}{}^\alpha$, Eq. (4.3), are purely imaginary and that

$$p_{nn'}{}^\alpha=-p_{n'n}{}^\alpha=p_{n'n}{}^{\alpha*}; \qquad (5.3)$$

in particular,

$$p_{nn}{}^\alpha=0. \qquad (5.4)$$

Further, it will be convenient to define the matrix operator $H(\mathbf{P})$ whose elements with respect to the band indices n are given by the operators

$$H_{nn'}(\mathbf{P})\equiv\delta_{nn'}[\epsilon_n+\tfrac{1}{2}\delta^{\alpha\beta}P^\alpha P^\beta]+(1-\delta_{nn'})p_{nn'}{}^\alpha P^\alpha. \quad (5.5)$$

By comparison with (4.14) we have

$$(n\mathbf{k}|H|n'\mathbf{k}')=(\mathbf{k}|H_{nn'}(\mathbf{P})|\mathbf{k}'). \qquad (5.6)$$

Now we see from (5.5) that $H(\mathbf{P})$ consists of a part diagonal in n, of zeroth and second order in the operators P^α, and an off-diagonal part linear in P^α. Our next program is to regard P^α as formally small and, by successive unitary transformations, to remove, to higher and higher order in P^α, the off-diagonal elements of $H(\mathbf{P})$ which involve the band m.

As a first step we write

$$\bar{H}^{(1)}(\mathbf{P})\equiv\exp[-S^{(1)}(\mathbf{P})]H(\mathbf{P})\exp[S^{(1)}(\mathbf{P})], \quad (5.7)$$

where $S^{(1)}(\mathbf{P})$ is an anti-Hermitian matrix operator, which is taken to be linear in P^α:

$$S_{nn'}{}^{(1)}(\mathbf{P})=D_{nn'}{}^\alpha P^\alpha. \qquad (5.8)$$

Expanding the right-hand side of (5.7) in powers of $S^{(1)}(\mathbf{P})$ gives

$$\bar{H}^{(1)}(\mathbf{P})=H(\mathbf{P})+[H(\mathbf{P}),S^{(1)}(\mathbf{P})] +\tfrac{1}{2}[[H(\mathbf{P}),S^{(1)}(\mathbf{P})],S^{(1)}(\mathbf{P})]+\cdots. \quad (5.9)$$

In this expansion the terms linear in P^α have the matrix elements

$$(p_{nn'}{}^\alpha+\omega_{nn'}D_{nn'}{}^\alpha)P^\alpha, \qquad (5.10)$$

where

$$\omega_{nn'}\equiv\epsilon_n-\epsilon_{n'}. \qquad (5.11)$$

In order that $\bar{H}^{(1)}(\mathbf{P})$ have no linear interband matrix elements involving the band m we must choose the coefficients $D_{nn'}{}^\alpha$ so that

$$p_{mn}{}^\alpha+\omega_{mn}D_{mn}{}^\alpha=0, \quad n\neq m, \qquad (5.12)$$

and, because of the anti-Hermitian property of $S^{(1)}$,

$$D_{nm}{}^\alpha=-(D_{mn}{}^\alpha)^*. \qquad (5.13)$$

Obviously these requirements still leave us considerable freedom in the choice of the constants $D_{nn'}{}^\alpha$. The simplest choice would be $D_{mn}{}^\alpha=-(D_{nm}{}^\alpha)^*=-p_{mn}{}^\alpha/\omega_{mn}$, for $n\neq m$, and all other $D_{nn'}{}^\alpha=0$. However for reasons which will become apparent later on we make a slightly more general choice, namely

$$D_{mn}{}^\alpha=\delta_{mn}iC_m{}^\alpha-(1-\delta_{mn})p_{mn}{}^\alpha/\omega_{mn}; \qquad (5.14)$$

$$D_{nm}{}^\alpha=-(D_{mn}{}^\alpha)^*; \qquad (5.15)$$

and

$$D_{nn'}{}^\alpha=0, \quad n\neq m \text{ and } n'\neq m. \qquad (5.16)$$

Here the $C_m{}^\alpha$ are real numbers, for the time being quite arbitrary, so that $iC_m{}^\alpha P^\alpha$ is properly anti-Hermitian.

The matrix elements of $\bar{H}^{(1)}(\mathbf{P})$ involving the band m are now, by Eq. (5.9),

$$\bar{H}_{mn}{}^{(1)}(\mathbf{P})=\delta_{mn}\left\{\epsilon_m+\left[\tfrac{1}{2}\delta^{\alpha\beta}+\sum_{n'}\frac{p_{mn'}{}^\alpha p_{n'm}{}^\beta}{\omega_{mn'}}\right]P^\alpha P^\beta+\cdots\right\} +(1-\delta_{mn})\left\{\left[-iC_m{}^\alpha p_{mn}{}^\beta+\sum_{n'}\frac{p_{mn'}{}^\alpha p_{n'n}{}^\beta}{\omega_{mn}}\right]P^\alpha P^\beta+\cdots\right\}, \qquad (5.17)$$

$$\bar{H}_{nm}{}^{(1)}(\mathbf{P})=[\bar{H}_{nm}{}^{(1)}(\mathbf{P})]^\dagger. \qquad (5.18)$$

Thus by our construction $\bar{H}_{mn}{}^{(1)}(\mathbf{P})$ contains, for $n\neq m$, only terms of second order in P^α. To emphasize this feature we write $\bar{H}_{mn}^{(1)}(\mathbf{P})$ in the form

$$\bar{H}_{mn}^{(1)}(\mathbf{P})=\delta_{mn}\bar{H}_m^{(1)}(\mathbf{P})+(1-\delta_{mn})\{Q_{mn}^{\alpha\beta}P^\alpha P^\beta+\cdots\}. \quad (5.19)$$

We now make a second unitary transformation and define

$$\bar{H}^{(2)}(\mathbf{P})\equiv\exp[-S^{(2)}(\mathbf{P})]\bar{H}^{(1)}(\mathbf{P})\exp[S^{(2)}(\mathbf{P})], \quad (5.20)$$

where $S^{(2)}$ is of second order in P^α and so chosen that $\bar{H}_{mn}^{(2)}$ has, for $n\neq m$, no terms of lower order than the third in P^α. Proceeding as before, this may be achieved by taking

$$S_{nn'}^{(2)}(\mathbf{P})=D_{nn'}^{\alpha\beta}P^\alpha P^\beta, \quad (5.21)$$

where

$$D_{mn}^{\alpha\beta}=\delta_{mn}iC_m^{\alpha\beta}-(1-\delta_{mn})Q_{mn}^{\alpha\beta}/\omega_{mn}; \quad (5.22)$$

$$D_{nm}^{\alpha\beta}=-(D_{mn}^{\alpha\beta})^*; \quad (5.23)$$

$$D_{nn'}^{\alpha\beta}=0, \quad n\neq m \text{ and } n'\neq m. \quad (5.24)$$

Here the constants $C_m^{\alpha\beta}$ are for the time being largely arbitrary, except that in view of the anti-Hermitian nature of $S^{(2)}$, $C_m^{\alpha\beta}P^\alpha P^\beta$ must be Hermitian:

$$(C_m^{\beta\alpha})^*P^\alpha P^\beta=C_m^{\alpha\beta}P^\alpha P^\beta. \quad (5.25)$$

Clearly, this procedure may be continued so that after the tth transformation we have

$$\bar{H}_{mn}^{(t)}(\mathbf{P})=\delta_{mn}\bar{H}_m^{(t)}(\mathbf{P})+(1-\delta_{mn})[Q_{mn}^{\alpha_1\cdots\alpha_{t+1}}P^{\alpha_1}\cdots P^{\alpha_{t+1}}+\cdots]. \quad (5.26)$$

The subsequent transformation is then given by

$$S_{nn'}^{(t+1)}(\mathbf{P})=D_{nn'}^{\alpha_1\cdots\alpha_{t+1}}P^{\alpha_1}\cdots P^{\alpha_{t+1}}, \quad (5.27)$$

where

$$D_{mn}^{\alpha_1\cdots\alpha_{t+1}}=\delta_{mn}iC_m^{\alpha_1\cdots\alpha_{t+1}}-(1-\delta_{mn})Q_{mn}^{\alpha_1\cdots\alpha_{t+1}}/\omega_{mn}; \quad (5.28)$$

$$D_{nm}^{\alpha_1\cdots\alpha_{t+1}}=-D_{mn}^{\alpha_1\cdots\alpha_{t+1}}; \quad (5.29)$$

$$D_{nn'}^{\alpha_1\cdots\alpha_{t+1}}=0, \quad n\neq m \text{ and } n'\neq m; \quad (5.30)$$

and the numbers $C_m^{\alpha_1\cdots\alpha_{t+1}}$ are arbitrary, apart from the requirement that

$$C_m^{\alpha_1\cdots\alpha_{t+1}}P^{\alpha_1}\cdots P^{\alpha_{t+1}}=C_m^{\alpha_{t+1}\cdots\alpha_1}P^{\alpha_1}\cdots P^{\alpha_{t+1}}. \quad (5.31)$$

From the power series of $\exp(-S^{(t+1)}\bar{H}^{(t)}\exp(S^{(t+1)})$ we see that

$$\bar{H}_m^{(t+1)}(\mathbf{P})=\bar{H}_m^{(t)}(\mathbf{P})+O(P^{t+2}). \quad (5.32)$$

Thus all $\bar{H}_m^{(t)}$ for $t\geqslant t_0$ are identical up to order $(P^\alpha)^{t_0+1}$ inclusive. We now define $\bar{H}_m(\mathbf{P})$ as the formal limit of $\bar{H}_m^{(t)}$ as $t\to\infty$. It can be written in the form

$$\bar{H}_m(\mathbf{P})=\epsilon_m+E_m^{\alpha_1\alpha_2}P^{\alpha_1}P^{\alpha_2}+E_m^{\alpha_1\alpha_2\alpha_3}P^{\alpha_1}P^{\alpha_2}P^{\alpha_3}+\cdots, \quad (5.33)$$

where in view of (5.32) $E_m^{\alpha_1\cdots\alpha_t}$ can be obtained by calculating $H_m^{(t-1)}$.

We shall not discuss here the question of convergence of this procedure. However, in Sec. 10 we shall estimate the error of the solutions obtained.

6. Commutation Expansion of $H_m(P)$

We now wish to write $\bar{H}_m(\mathbf{P})$ in a series of terms each of which is "effectively" smaller by a factor $s(=\mathcal{H}/c)$ than the preceding one. Since, by (4.6),

$$P^\alpha=p^\alpha+s^{\alpha\alpha'}x^{\alpha'},$$

one's first inclination might be to order the series (5.33) in powers of s. However, in such a series successive terms are not effectively smaller by a factor of s. The reason for this can be most easily seen in the free electron case. Here

$$H(\mathbf{P})=\tfrac{1}{2}P^\alpha P^\alpha=\tfrac{1}{2}p^\alpha p^\alpha+s^{\alpha\alpha'}(p^\alpha x^{\alpha'}+x^\alpha p^{\alpha'})+s^{\alpha\alpha'}s^{\alpha\alpha''}x^{\alpha'}x^{\alpha''}. \quad (6.1)$$

If we now consider solutions of (approximately) fixed energy, then as $s\to 0$, the dimensions over which the orbits extend behave as s^{-1}, so that terms of the type sx occurring in (6.1) are in fact independent of s.

A more appropriate procedure is to make what we call a commutator expansion of Eq. (5.33). Let us begin with some preliminaries. First we define

$$\langle P^{\alpha_1}\cdots P^{\alpha_t}\rangle_{\text{Av}}, \quad (6.2)$$

as the average of $P^{\alpha_1}\cdots P^{\alpha_t}$ over all possible permutations of the factors. Since for $s=0$ the P^α's commute, it is clear that the difference between $P^{\alpha_1}\cdots P^{\alpha_t}$ and its average must be at least linear in s. For example,

$$P^{\alpha_1}P^{\alpha_2}-\langle P^{\alpha_1}P^{\alpha_2}\rangle_{\text{Av}}=\tfrac{1}{2}(P^{\alpha_1}P^{\alpha_2}-P^{\alpha_2}P^{\alpha_1})=\tfrac{1}{2}i(s^{\alpha_1\alpha_2}-s^{\alpha_2\alpha_1})=\frac{is}{2}\left(\frac{s^{\alpha_1\alpha_2}-s^{\alpha_2\alpha_1}}{s}\right), \quad (6.3)$$

where the factor in parentheses is independent of the magnitude of s. In general, we can write

$$P^{\alpha_1}\cdots P^{\alpha_t}=\langle P^{\alpha_1}\cdots P^{\alpha_t}\rangle_{\text{Av}}+s\Delta_1, \quad (6.4)$$

where Δ_1 is a linear combination of products of P^α, each of order $(P^\alpha)^{t-2}$. Now we define Δ_{r+1} by the equation

$$s\Delta_{r+1}=\Delta_r-\langle\Delta_r\rangle_{\text{Av}}. \quad (6.5)$$

Then clearly we can develop $P^{\alpha_1}\cdots P^{\alpha_t}$ in a series of the form

$$P^{\alpha_1}\cdots P^{\alpha_t}=\langle P^{\alpha_1}\cdots P^{\alpha_t}\rangle_{\text{Av}}+s\langle\Delta_1\rangle_{\text{Av}}+\cdots s^{[t/2]}\langle\Delta_{[t/2]}\rangle_{\text{Av}}, \quad (6.6)$$

where

$$\begin{aligned}[t/2]&=t/2 && \text{for } t \text{ even,}\\ &=(t-1)/2 && \text{for } t \text{ odd.}\end{aligned} \quad (6.7)$$

Such an expansion we call a commutator expansion.

We now develop each term of the power series (5.33) of $\bar{H}_m(\mathbf{P})$ in a commutator expansion and then collect all terms corresponding to a given power of s. This results in the commutator expansion of $\bar{H}_m(\mathbf{P})$ which has the form

$$\bar{H}_m(\mathbf{P})=\bar{H}_{m;0}(\mathbf{P})+s\bar{H}_{m;1}(\mathbf{P})+s^2\bar{H}_{m;2}(\mathbf{P})+\cdots. \quad (6.8)$$

Each term $\bar{H}_{m;i}(P)$ in this expansion is a linear combination of completely symmetrized products of the P^α. We shall see later that in general all $\bar{H}_{m;i}(\mathbf{P})$ are of similar magnitude so that (6.8) is a suitable expansion for sufficiently weak fields.

Let us now recall that any completely symmetrized *operator* $M(\mathbf{P})$ is completely defined by the *function* $M(\mathbf{k})$ to which it reduces when the operators P^α are replaced by the c-numbers k^α.[18] Hence each of the Hamiltonians $\bar{H}_{m;i}(\mathbf{P})$ is completely characterized by the corresponding function $\bar{H}_{m;i}(\mathbf{k})$. The procedure which we have followed gives us power series expansions for these functions. For example, from (5.17) and (6.8) we see that[19]

$$\bar{H}_{m;0}(\mathbf{k})=\epsilon_m+\left[\tfrac{1}{2}\delta^{\alpha\beta}+\sum_{n'}\frac{p_{mn'}{}^{\alpha}p_{n'm}{}^{\beta}}{\omega_{mn'}}\right]k^\alpha k^\beta+\cdots, \quad (6.9)$$

$$\bar{H}_{m;1}(\mathbf{k})=\left[\frac{i}{2}\frac{s^{\alpha\beta}}{s}\sum_{n'}\frac{p_{mn'}{}^{\alpha}p_{n'm}{}^{\beta}-p_{mn'}{}^{\beta}p_{n'm}{}^{\alpha}}{\omega_{mn'}}\right]+\cdots. \quad (6.10)$$

The deficiency of this formalism, as developed so far, is then that it is restricted to sufficiently small $\mathbf{k}$-vectors for which these series converge adequately. One of the main objectives of Part II of this paper is to obtain expressions for the functions $\bar{H}_{m;i}(\mathbf{k})$ without recourse to power series expansions.

PART II

To obtain explicit expressions for the functions $\bar{H}_{m;i}(\mathbf{k})$ we shall be following a rather complicated procedure. It may therefore be helpful if we give here a brief outline.

In Sec. 7 we show very easily that $\bar{H}_{m;0}(\mathbf{k})$ is just the energy band function $\epsilon_m(\mathbf{k})$. This has the well-known periodicity property

$$\epsilon_m(\mathbf{k}+\mathbf{K})=\epsilon_m(\mathbf{k}),$$

where $\mathbf{K}$ is a reciprocal lattice vector.

This suggests that also the functions $\bar{H}_{m;i}(\mathbf{k})$ for $i>0$ might have this property. However, these functions depend on the as yet largely arbitrary coefficients $C_m{}^{\alpha_1\cdots\alpha_t}$ occurring in the canonical transformations $S^{(t)}$ [see Eqs. (5.28), (5.31)]. In Secs. 8–14 it is shown how these constants can be chosen so that (a) the $\bar{H}_{m;i}(\mathbf{k})$ can be evaluated in terms of the Bloch waves $\varphi_{n\mathbf{k}}$ and without recourse to power series expansions in k^α, (b) they have the periodicity property

$$\bar{H}_{m;i}(\mathbf{k}+\mathbf{K})=\bar{H}_{m;i}(\mathbf{k}).$$

This is accomplished in several steps. In Sec. 8 it is shown that, when $s=0$, the $C_m{}^{\alpha_1\cdots\alpha_t}$ can be so chosen that the new basis functions generated by the unitary transformations $S^{(t)}$,

$$\varphi_{m\mathbf{k}}=\sum\chi_{n'\mathbf{k}'}(n'\mathbf{k}'|\exp(S^{(1)})(\exp S^{(2)})\cdots|m\mathbf{k}),$$

have the property of being *real* at the arbitrarily chosen origin $\mathbf{r}=0$. This fixes the phase of these functions—which are just Bloch waves—so as to assure their periodicity in the sense that

$$\varphi_{m\mathbf{k}+\mathbf{K}}=\pm\varphi_{m\mathbf{k}}.$$

In Secs. 9, 10, and 11 the same results are obtained when $s\neq 0$. The new basis functions,

$$\bar{\varphi}_{m\mathbf{k}}=\sum\chi_{n'\mathbf{k}'}(n'\mathbf{k}'|\exp(S^{(1)})\exp(S^{(2)})\cdots|m\mathbf{k}),$$

are constructed so as to be real at $\mathbf{r}=0$, and they are periodic in the same sense as $\varphi_{m\mathbf{k}}$. Furthermore the unitary transformation matrix connecting $\bar{\varphi}_{m\mathbf{k}}$ with $\chi_{n'\mathbf{k}'}$ is constructed without recourse to a power series expansion in k^α.

In Sec. 12 the algorithm for constructing the functions $\bar{H}_{m;i}(\mathbf{k})$, having the properties (a) and (b) above is developed; and in Secs. 13 and 14 it is applied to construct the first few $\bar{H}_{m;i}(\mathbf{k})$ $(i=0, 1, \cdots)$ for crystals with and without a center of inversion, respectively.

7. Discussion of the Leading Term $\bar{H}_{m;0}(P)$

In this section we shall derive very easily an explicit expression for $\bar{H}_{m;0}(\mathbf{P})$ which makes evident the important periodicity property

$$\bar{H}_{m;0}(\mathbf{P}+\mathbf{K})=\bar{H}_{m;0}(\mathbf{P}), \quad (7.1)$$

where $\mathbf{K}$ is any reciprocal lattice vector. In subsequent sections, we shall discuss the higher order Hamiltonians, $\bar{H}_{m;i}(\mathbf{P})$ with $i>0$.

When the magnetic field is switched off, clearly

$$\bar{H}_m(\mathbf{P})\rightarrow\bar{H}_{m;0}(\mathbf{p}). \quad (7.2)$$

Now the eigenfunctions of $H_{m;0}(\mathbf{p})$—as those of $\mathbf{p}$ itself—are plane waves $\exp(i\mathbf{k}\cdot\mathbf{r})$ and the corresponding eigenvalues are $\bar{H}_{m;0}(\mathbf{k})$. But these must be just the energies of the Bloch waves $\varphi_{m;\mathbf{k}}$ so that

$$\bar{H}_{m;0}(\mathbf{k})=\epsilon_m(\mathbf{k}). \quad (7.3)$$

We recall again that a completely symmetrized operator $M(\mathbf{P})$ is uniquely determined by the function $M(\mathbf{k})$ to which it reduces when $\mathbf{P}$ is replaced by $\mathbf{k}$. In particular, if

$$M(\mathbf{k})=\sum_{\mathbf{R}}A(\mathbf{R})e^{i\mathbf{R}\cdot\mathbf{k}}, \quad (7.4)$$

then

$$M(\mathbf{P})=\sum_{\mathbf{R}}A(\mathbf{R})e^{i\mathbf{R}\cdot\mathbf{P}}. \quad (7.5)$$

[18] The function $k^{\alpha_1}\cdots k^{\alpha_t}$ defines uniquely the operator $\langle P^{\alpha_1}\cdots P^{\alpha_t}\rangle_{\mathrm{Av}}$.

[19] It so happens that the leading term of order k^0, which is here given, vanishes.

This fact may be applied in the present situation. For $\epsilon_m(\mathbf{k})$ is a periodic function of $\mathbf{k}$ and hence may be written as a Fourier series of the form

$$\epsilon_m(\mathbf{k})=\sum_l a_0^{(l)} \exp(i\mathbf{R}^{(l)}\cdot\mathbf{k}), \tag{7.6}$$

where the $\mathbf{R}^{(l)}$ are the lattice vectors of the crystal. Therefore we have

$$\bar{H}_{m;0}(\mathbf{P})=\sum_l a_0^{(l)} \exp(i\mathbf{R}^{(l)}\cdot\mathbf{P}). \tag{7.7}$$

From this form we see at once that $\bar{H}_{m;0}(\mathbf{P})$ has the important periodicity property (7.1), analogous to the periodicity of $\epsilon_m(k)$.

It is sometimes a convenient notation to write

$$\bar{H}_{m;0}(\mathbf{P})=\langle\epsilon_m(\mathbf{P})\rangle_{\text{Av}}, \tag{7.8}$$

where $\epsilon_m(\mathbf{P})$ is any function of the operator $\mathbf{P}$ which reduces to $\epsilon_m(\mathbf{k})$ when $\mathbf{P}$ is replaced by $\mathbf{k}$.

We wish next to draw attention to the *uniqueness* of $\bar{H}_{m;0}(\mathbf{P})$, in spite of the fact that the sequence of unitary transformations $S^{(t)}$ leading to $\bar{H}_m(\mathbf{P})$ contained a great deal of arbitrariness [see comments after Eqs. (5.13) and (5.30)]. How this uniqueness comes about may be understood as follows. Suppose we consider a different sequence of canonical transformations $S'^{(t)}$ which also uncouple the band m from the rest. The resulting effective Hamiltonian $\bar{H}_m'(\mathbf{P})$ must then be related to $\bar{H}_m(\mathbf{P})$ by a unitary transformation, $\exp T_m(\mathbf{P})$. Thus

$$\begin{aligned}\bar{H}_m'(\mathbf{P})&=\exp[-T_m(\mathbf{P})]\bar{H}_m(\mathbf{P})\exp[T_m(\mathbf{P})]\\&=\bar{H}_m(\mathbf{P})+[\bar{H}_m(\mathbf{P}),T_m(\mathbf{P})]+\cdots.\end{aligned} \tag{7.9}$$

When we now make a commutator expansion of $\bar{H}_m'(\mathbf{P})$ only $\bar{H}_m(\mathbf{P})$ in (7.9) can contribute to the leading term $\bar{H}_{m;0}'(\mathbf{P})$. For all the following terms, because of their form as commutators, contain one or more factors of s. The identity of $\bar{H}_{m;0}'(\mathbf{P})$ and $\bar{H}_{m;0}(\mathbf{P})$ is now obvious. On the other hand, the higher order terms in the commutator expansion (6.8) do depend on the particular choice of the transformations $S^{(t)}$.

8. Periodicity in k of Bloch Waves

We have just seen that for $i>0$, the functions $\bar{H}_{m;i}(\mathbf{k})$ depend on the choice of the coefficients $C_m^{\alpha_1\cdots\alpha_t}$. We shall find it extremely useful that they may be chosen in such a way that, in a certain gauge, the new basis functions are real at $\mathbf{r}=0$. These functions can then be shown to be "periodic" in the variable $\mathbf{k}$. We begin by demonstrating this in the absence of a magnetic field.

For $\mathbf{A}=0$ we have of course $\mathbf{P}=\mathbf{p}$, and therefore the Hamiltonian (4.14) is diagonal in $\mathbf{k}$:

$$(n\mathbf{k}|H|n'\mathbf{k}')=\delta(\mathbf{k}-\mathbf{k}')H_{nn'}(\mathbf{k}). \tag{8.1}$$

Consequently the solutions of the Schrödinger equation (5.1) are of the form

$$A_{n'}^{(n)}(\mathbf{k})=B_{n'}^{(n)}(\mathbf{k}^0)\delta(\mathbf{k}-\mathbf{k}^0), \tag{8.2}$$

and the corresponding eigenfunctions of H are just the Bloch waves $\varphi_{n\mathbf{k}^0}$ associated with the vector $\mathbf{k}^0$:

$$\begin{aligned}\varphi_{n\mathbf{k}^0}&=\sum_{n'} A_{n'}^{(n)}(\mathbf{k})\chi_{n\mathbf{k}}\\&=\exp(i\mathbf{k}^0\cdot\mathbf{r})\sum_{n'} B_{n'}^{(n)}(\mathbf{k}^0)u_{n'0}(\mathbf{r}).\end{aligned} \tag{8.3}$$

In this case, where the Hamiltonian is already initially diagonal in $\mathbf{k}$, the removal of the interband matrix elements leads to a complete diagonalization. Therefore

$$\varphi_{m\mathbf{k}}=\{\exp[S^{(1)}(\mathbf{p})]\exp[S^{(2)}(\mathbf{p})]\cdots\}\chi_{m\mathbf{k}}, \tag{8.4}$$

where $\varphi_{m\mathbf{k}}$ is a Bloch wave associated with quantum numbers m and $\mathbf{k}$. We say *a* Bloch wave, because its *phase* will depend on the disposition of the arbitrary constants in the transformations $S^{(t)}$.

We shall now show how the $C_m^{\alpha_1\cdots\alpha_t}$ can be chosen to make

$$\mathrm{Im}[\varphi_{m\mathbf{k}}(0)]\equiv 0. \tag{8.5}$$

The procedure will be to assure the property (8.5) up to any power of k^α, from which the reality for all $\mathbf{k}$ follows by analytic continuation in the variables $k^{(1)}$, $k^{(2)}$, and $k^{(3)}$.[20]

We have previously chosen the functions $u_{n0}(\mathbf{r})$ as real. Let us now further assume that $u_{m0}(0)>0$.[21] Next we write

$$\begin{aligned}\varphi_{m\mathbf{k}}^{(t)}&\equiv\sum\chi_{n\mathbf{k}'}\\&\times(n\mathbf{k}'|\{\exp[S^{(1)}(\mathbf{p})]\exp[S^{(2)}(\mathbf{p})]\cdots\}_t|m\mathbf{k}),\end{aligned} \tag{8.6}$$

where the notation $\{\ \}_t$ implies a power series expansion of $\exp[S^{(1)}]\exp[S^{(2)}]\cdots$ in powers of p^α up to order $(p^\alpha)^t$ inclusive. Clearly $\varphi_{m\mathbf{k}}^{(t)}$ has the form

$$\begin{aligned}\varphi_{m\mathbf{k}}^{(t)}(\mathbf{r})=e^{i\mathbf{k}\cdot\mathbf{r}}[&u_{m0}(\mathbf{r})+k^\alpha u_m^\alpha(\mathbf{r})\\&+\cdots k^{\alpha_1}\cdots k^{\alpha_t}u_m^{\alpha_1\cdots\alpha_t}(\mathbf{r})],\end{aligned} \tag{8.7}$$

where the functions $u_m^{\alpha_1\cdots\alpha_t}$ are periodic in $\mathbf{r}$. We must now show that $\varphi_{m\mathbf{k}}^{(t)}(0)$ can be made real for all t.

To lowest order we have

$$\varphi_{m\mathbf{k}}^{(0)}(0)=[u_{m0}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}]_{\mathbf{r}=0}, \tag{8.8}$$

and this is clearly real.

To first order we obtain, with the help of Eqs. (5.8), (5.14), and (5.15),

$$\begin{aligned}&\varphi_{m\mathbf{k}}^{(1)}(0)\\&=\{\textstyle\sum_n u_{n0}(\mathbf{r})[\delta_{nm}+S_{nm}^{(1)}(\mathbf{p})]e^{i\mathbf{k}\cdot\mathbf{r}}\}_{\mathbf{r}=0}\\&=\left\{e^{i\mathbf{k}\cdot\mathbf{r}}\left[u_{m0}(\mathbf{r})+k^\alpha\left(iC_m^\alpha u_{m0}-\sum_{n\neq m}u_{n0}\frac{p_{nm}^\alpha}{\omega_{nm}}\right)\right]\right\}_{\mathbf{r}=0}\\&=u_{m0}(0)+k^\alpha\left(iC_m^\alpha u_{m0}(0)-\sum_{n\neq m}u_{n0}(0)\frac{p_{nm}^\alpha}{\omega_{nm}}\right).\end{aligned} \tag{8.9}$$

[20] This assumes of course, without proof, the analyticity of $\varphi_{m\mathbf{k}}$ as a function of $\mathbf{k}$. For one-dimensional Bloch waves this analyticity has been established under mild restrictions by W. Kohn, Proc. Phys. Soc. (London) 72, 301 (1958), and to be published.

[21] If $u_{m0}(0)$ should accidentally vanish, we choose another origin.

As $u_{m0}(0)$ and $u_{n0}(0)$ are real, and the $p_{nm}{}^{\alpha}$ are imaginary, this can be made real by choosing

$$C_m{}^{\alpha}=\frac{1}{i}\sum_{n\neq m} r_n\frac{p_{nm}{}^{\alpha}}{\omega_{nm}}, \quad (8.10)$$

where

$$r_n\equiv u_{n0}(0)/u_{m0}(0). \quad (8.11)$$

It will be seen that $C_m{}^{\alpha}$, defined by (8.10), is real as required. [See comment after Eq. (5.16).]

Proceeding in this manner it is easily seen that $\varphi_{m\mathbf{k}}{}^{(t)}(0)$ can be made real by an appropriate choice of real coefficients $C_m{}^{\alpha_1\cdots\alpha_t}$, which may be taken as invariant under permutation of the indices $\alpha_1\cdots\alpha_t$.

It may be mentioned in passing that if the crystal has a center of inversion at $\mathbf{r}=0$, the $C_m{}^{\alpha_1\cdots\alpha_t}$ can be taken as zero.

This procedure defines $\varphi_{m\mathbf{k}}(\mathbf{r})$ in terms of a power series in k^{α} of the form (8.7). By analytic continuation this function is then defined for all $\mathbf{k}$. It clearly satisfies the following conditions: It satisfies the wave equation; it is normalized; it is real at $\mathbf{r}=0$; and it has the quasi-periodicity property

$$\varphi_{m\mathbf{k}}(\mathbf{r}+\mathbf{R}^{(l)})=\exp[i\mathbf{k}\cdot\mathbf{R}^{(l)}]\varphi_{m\mathbf{k}}(\mathbf{r}). \quad (8.12)$$

These conditions define $\varphi_{m\mathbf{k}}$ uniquely, apart from sign. Consequently it must have the following "periodicity" property, as a function of $\mathbf{k}$:

$$\varphi_{m\mathbf{k}+\mathbf{K}}(\mathbf{r})=\theta\varphi_{m\mathbf{k}}(\mathbf{r}), \quad (8.13)$$

where for a given crystal and band index m, $\theta=\pm1$ depending on the vector $\mathbf{K}$. Examples show that both signs do in fact occur. However for simplicity of writing we shall assume in the following that $\theta\equiv1$, so that

$$\varphi_{m\mathbf{k}+\mathbf{K}}(\mathbf{r})=\varphi_{m\mathbf{k}}(\mathbf{r}). \quad (8.14)$$

Where the case $\theta=-1$ leads to significant differences, they will be explicitly mentioned.

9. Expansion of the New Basis Functions in Powers of P^{α}

The canonical transformations $S^{(1)}, S^{(2)},\cdots$ discussed in Sec. 5 define a new set of basis functions which we shall denote by $\bar{\varphi}_{n\mathbf{k}}$:

$$\bar{\varphi}_{n\mathbf{k}}=\sum\chi_{n'\mathbf{k}'}\times(n'\mathbf{k}'|\exp[S^{(1)}(\mathbf{P})]\exp[S^{(2)}(\mathbf{P})]\cdots|n\mathbf{k}). \quad (9.1)$$

For $\mathbf{A}=0$ these were just the Bloch waves $\varphi_{n\mathbf{k}}$ discussed in the preceding section. In this section we begin a study of the $\bar{\varphi}_{n\mathbf{k}}$ in the presence of a magnetic field. We shall first show that if we define

$$\bar{\varphi}_{n\mathbf{k}}{}^{(t)}\equiv\sum\chi_{n'\mathbf{k}'}\times(n'\mathbf{k}'|\{\exp[S^{(1)}(\mathbf{P})]\exp[S^{(2)}(\mathbf{P})]\cdots\}_t|m\mathbf{k}), \quad (9.2)$$

where the symbol $\{\ \}_t$ denotes the truncated power series of the argument up to $(P^{\alpha})^t$, the constants $C_m{}^{\alpha_1\cdots\alpha_{t'}}$ can be so chosen as to make

$$\mathrm{Im}[\bar{\varphi}_{m\mathbf{k}}{}^{(t)}(0)]=0, \quad (9.3)$$

for all values of t. Since the phases of the $\bar{\varphi}_{n\mathbf{k}}$ depend on the gauge of the vector potential, we must settle on a particular choice. It is convenient to take

$$\mathbf{A}=\tfrac{1}{2}(\mathcal{H}\times\mathbf{r}); \quad (9.4)$$

in this gauge we write $s^{\alpha\alpha'}=\sigma^{\alpha\alpha'}$, so that

$$P^{\alpha}=p^{\alpha}+\sigma^{\alpha\alpha'}x^{\alpha'}, \quad (9.5)$$

and

$$\sigma^{32}=-\sigma^{23}=\mathcal{H}_1/c,\quad \text{etc.}, \quad (9.6)$$

$$\sigma^{11}=\sigma^{22}=\sigma^{33}=0. \quad (9.7)$$

Our final results will, however, be gauge invariant.

The procedure of removing off-diagonal elements to higher and higher order in P^{α}, which was described in Sec. 5, gives us $\bar{\varphi}_{n\mathbf{k}}{}^{(t)}$ in the form of a series

$$\bar{\varphi}_{n\mathbf{k}}{}^{(t)}=\sum_{t'=0}^{t} w_{n\mathbf{k}}{}^{(t')}, \quad (9.8)$$

where $w_{n\mathbf{k}}{}^{(t')}$ is of order $(P^{\alpha})^{t'}$. Let us begin by studying the first two of these, for $n=m$.

Clearly for $t'=0$ we have

$$w_{m\mathbf{k}}{}^{(0)}(\mathbf{r})=\chi_{m\mathbf{k}}(\mathbf{r})=u_{m0}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}, \quad (9.9)$$

and since all $u_{n0}(0)$ are real, so is $w_{m\mathbf{k}}{}^{(0)}(0)$. The next term is, in view of Eqs. (5.8), (5.14), and (5.15),

$$w_{m\mathbf{k}}{}^{(1)}(\mathbf{r})=\sum u_{n0}(\mathbf{r})\times[iC_m{}^{\alpha}\delta_{nm}-(1-\delta_{nm})p_{nm}{}^{\alpha}/\omega_{nm}]P^{\alpha}e^{i\mathbf{k}\cdot\mathbf{r}}, \quad (9.10)$$

whose imaginary part at $\mathbf{r}=0$ is

$$\mathrm{Im}w_{m\mathbf{k}}{}^{(1)}(0)=u_{m0}(0)\left(iC_m{}^{\alpha}-\sum_{n\neq m} r_n\frac{p_{nm}{}^{\alpha}}{\omega_{nm}}\right)k^{\alpha}; \quad (9.11)$$

where r_n is defined by Eq. (8.11). This may be made to vanish by the same choice of $C_m{}^{\alpha}$, as in the absence of the magnetic field [see Eq. (8.10)].

So far there has been no significant difference between the cases of nonvanishing and vanishing magnetic fields. But in higher orders ($t'\geqslant2$), the noncommutativity of the components of $\mathbf{P}$ does introduce such differences. We shall now show that nevertheless there exists a set of constants $C_m{}^{\alpha_1},\cdots C_m{}^{\alpha_1\cdots\alpha_t}$ which will make $\varphi_{m\mathbf{k}}{}^{(t)}(0)$ real for arbitrary t, that these constants satisfy the requirement that the quantity

$$\sum_{\alpha_1\cdots\alpha_t} C_m{}^{\alpha_1\cdots\alpha_t}P^{\alpha_1}\cdots P^{\alpha_t} \quad (9.12)$$

is Hermitian [see Eq. (5.31)], and are real for odd t and imaginary for even t.

We give a proof by induction. Suppose we have chosen appropriate constants $C_m{}^{\alpha_1},\cdots C_m{}^{\alpha_1\cdots\alpha_{t-1}}$. Then

$w_{m\mathbf{k}}^{(t)}$ has the form

$$w_{m\mathbf{k}}^{(t)}=\sum_n u_{n0}\sum_{\alpha_1\cdots\alpha_t}(i\delta_{nm}C_m^{\alpha_1\cdots\alpha_t}+Q_{nm}^{\alpha_1\cdots\alpha_t})\times P^{\alpha_1}\cdots P^{\alpha_t}e^{i\mathbf{k}\cdot\mathbf{r}}, \quad (9.13)$$

where the constants $Q_{nm}^{\alpha_1\cdots\alpha_t}$ are real if t is even and imaginary if t is odd. Let us take the case of even t. From (9.13) we have, at $\mathbf{r}=0$,

$$w_{m\mathbf{k}}^{(t)}(0)=u_{m0}(0)\sum_{\alpha_1\cdots\alpha_t}(iC_m^{\alpha_1\cdots\alpha_t}+R_m^{\alpha_1\cdots\alpha_t})\times[P^{\alpha_1}\cdots P^{\alpha_t}e^{i\mathbf{k}\cdot\mathbf{r}}]_{\mathbf{r}=0}, \quad (9.14)$$

where

$$R_m^{\alpha_1\cdots\alpha_t}\equiv\sum_n r_nQ_{nm}^{\alpha_1\cdots\alpha_t} \quad (9.15)$$

is real. We want to choose the $C_m^{\alpha_1\cdots\alpha_t}$ to make

$$\mathrm{Im}(w_{m\mathbf{k}}^{(t)})=0. \quad (9.16)$$

Now the product $P^{\alpha_1}\cdots P^{\alpha_t}$ may be divided, in a gauge-invariant manner, into a Hermitian and anti-Hermitian operator. One way of effecting this division is by a commutator expansion. For example,

$$\begin{aligned}P^{\alpha_1}P^{\alpha_2}&=\langle P^{\alpha_1}P^{\alpha_2}\rangle_{\mathrm{Av}}+\tfrac{1}{2}(P^{\alpha_1}P^{\alpha_2}-P^{\alpha_2}P^{\alpha_1})\\&=\langle P^{\alpha_1}P^{\alpha_2}\rangle_{\mathrm{Av}}+(i/2)\sigma^{\alpha_1\alpha_2}\\&=(P^{\alpha_1}P^{\alpha_2})_H+(P^{\alpha_1}P^{\alpha_2})_A,\end{aligned} \quad (9.17)$$

since

$$\sigma^{\alpha_1\alpha_2}=\tfrac{1}{2}(s^{\alpha_1\alpha_2}-s^{\alpha_2\alpha_1})=(1/i)[P^{\alpha_1},P^{\alpha_2}], \quad (9.18)$$

and is gauge invariant; the subscripts H and A denote, respectively, the Hermitian and anti-Hermitian parts. Similarly

$$\begin{aligned}&P^{\alpha_1}P^{\alpha_2}P^{\alpha_3}P^{\alpha_4}\\&=\langle P^{\alpha_1}P^{\alpha_2}P^{\alpha_3}P^{\alpha_4}\rangle_{\mathrm{Av}}\\&+i(\sigma^{\alpha_1\alpha_2}\langle P^{\alpha_3}P^{\alpha_4}\rangle_{\mathrm{Av}}+\sigma^{\alpha_1\alpha_3}\langle P^{\alpha_2}P^{\alpha_4}\rangle_{\mathrm{Av}}+\sigma^{\alpha_1\alpha_4}\langle P^{\alpha_2}P^{\alpha_3}\rangle_{\mathrm{Av}}\\&+\sigma^{\alpha_2\alpha_3}\langle P^{\alpha_1}P^{\alpha_4}\rangle_{\mathrm{Av}}+\sigma^{\alpha_2\alpha_4}\langle P^{\alpha_1}P^{\alpha_3}\rangle_{\mathrm{Av}}+\sigma^{\alpha_3\alpha_4}\langle P^{\alpha_1}P^{\alpha_2}\rangle_{\mathrm{Av}})\\&-(\sigma^{\alpha_1\alpha_2}\sigma^{\alpha_3\alpha_4}+\sigma^{\alpha_1\alpha_3}\sigma^{\alpha_2\alpha_4}+\sigma^{\alpha_1\alpha_4}\sigma^{\alpha_2\alpha_3})\\&=(P^{\alpha_1}P^{\alpha_2}P^{\alpha_3}P^{\alpha_4})_H+(P^{\alpha_1}P^{\alpha_2}P^{\alpha_3}P^{\alpha_4})_A,\end{aligned} \quad (9.19)$$

where the Hermitian part contains all terms even in σ, and the anti-Hermitian part all terms which are odd in σ. The general product $P^{\alpha_1}\cdots P^{\alpha_t}$ can be similarly decomposed.

We can therefore write $R_m^{\alpha_1\cdots\alpha_t}$ as the sum of two terms,

$$R_m^{\alpha_1\cdots\alpha_t}=H_m^{\alpha_1\cdots\alpha_t}+A_m^{\alpha_1\cdots\alpha_t}, \quad (9.20)$$

where

$$\sum_{\alpha_1\cdots\alpha_t}H_m^{\alpha_1\cdots\alpha_t}P^{\alpha_1}\cdots P^{\alpha_t}=\sum_{\alpha_1\cdots\alpha_t}R_m^{\alpha_1\cdots\alpha_t}(P^{\alpha_1}\cdots P^{\alpha_t})_H \quad (9.21)$$

and

$$\sum_{\alpha_1\cdots\alpha_t}A_m^{\alpha_1\cdots\alpha_t}P^{\alpha_1}\cdots P^{\alpha_t}=\sum_{\alpha_1\cdots\alpha_t}R_m^{\alpha_1\cdots\alpha_t}(P^{\alpha_1}\cdots P^{\alpha_t})_A; \quad (9.22)$$

both $H_m^{\alpha_1\cdots\alpha_t}$ and $A_m^{\alpha_1\cdots\alpha_t}$ are real.

We now choose

$$C_m^{\alpha_1\cdots\alpha_t}=iA_m^{\alpha_1\cdots\alpha_t}. \quad (9.23)$$

By (9.22) we have

$$\sum_{\alpha_1\cdots\alpha_t}C_m^{\alpha_1\cdots\alpha_t}P^{\alpha_1}\cdots P^{\alpha_t}=i\sum_{\alpha_1\cdots\alpha_t}R_m^{\alpha_1\cdots\alpha_t}(P^{\alpha_1}\cdots P^{\alpha_t})_A, \quad (9.24)$$

and this is properly Hermitian. Furthermore this choice gives, by (9.14),

$$w_{m\mathbf{k}}^{(t)}(0)=u_{m0}(0)\sum_{\alpha_1\cdots\alpha_t}R_m^{\alpha_1\cdots\alpha_t}\times[(P^{\alpha_1}\cdots P^{\alpha_t})_He^{i\mathbf{k}\cdot\mathbf{r}}]_{\mathbf{r}=0}. \quad (9.25)$$

It remains to verify that, *in the gauge* (9.4), the imaginary part of (9.25) vanishes. Since the $R_m^{\alpha_1\cdots\alpha_t}$ are real, inspection of (9.17) and (9.19) shows that this will be so provided that for arbitrary t

$$\mathrm{Im}[\langle P^{\alpha_1}\cdots P^{\alpha_t}\rangle_{\mathrm{Av}}e^{i\mathbf{k}\cdot\mathbf{r}}]_{\mathbf{r}=0}=0. \quad (9.26)$$

To establish this fact substitute in the product $P^{\alpha_1}\cdots P^{\alpha_t}$ the expression (9.5) and pull all factors x to the right of all factors p. This results in

$$[(P^{\alpha_1}\cdots P^{\alpha_t})e^{i\mathbf{k}\cdot\mathbf{r}}]_{\mathbf{r}=0}=k^{\alpha_1}\cdots k^{\alpha_t}+i\sigma^{\alpha_1\alpha_2}k^{\alpha_3}\cdots k^{\alpha_t}+\cdots. \quad (9.27)$$

When we now perform the operation $\langle\ \rangle_{\mathrm{Av}}$ on (9.27), all terms containing one or more factors $\sigma^{\alpha\beta}$ vanish because of the antisymmetry of $\sigma^{\alpha\beta}$. Hence we have

$$[\langle P^{\alpha_1}\cdots P^{\alpha_t}\rangle_{\mathrm{Av}}e^{i\mathbf{k}\cdot\mathbf{r}}]_{\mathbf{r}=0}=k^{\alpha_1}\cdots k^{\alpha_t}, \quad (9.28)$$

which proves (9.26).

When t is odd an analogous demonstration can be given.

We have therefore succeeded in constructing functions of the form (9.2), or equivalently of the form

$$\begin{aligned}\bar{\varphi}_{n\mathbf{k}}^{(t)}&=\sum_{n'}u_{n'0}[\delta_{n'n}+\sum_{\alpha_1}G_{n'n}^{\alpha_1}P^{\alpha_1}+\cdots+\sum_{\alpha_1\cdots\alpha_t}G_{n'n}^{\alpha_1\cdots\alpha_t}P^{\alpha_1}\cdots P^{\alpha_t}]e^{i\mathbf{k}\cdot\mathbf{r}}\\&=\sum\chi_{n'\mathbf{k}'}(\mathbf{k}'|\delta_{n'n}+\sum_{\alpha_1}G_{n'n}^{\alpha_1}P^{\alpha_1}+\cdots+\sum_{\alpha_1\cdots\alpha_t}G_{n'n}^{\alpha_1\cdots\alpha_t}P^{\alpha_1}\cdots P^{\alpha_t}|\mathbf{k}),\end{aligned} \quad (9.29)$$

which for $n=m$ have the property (9.3).

10. Commutator Expansion of the New Basis Functions; Degree of Decoupling

The expansion (9.29) has the drawback of converging only for small values of k. Our previous experience suggests rearranging the terms in (9.29) in a commutator expansion. We therefore write formally

$$\delta_{n'n}+\sum_{\alpha_1} G_{n'n}{}^{\alpha_1}P^{\alpha_1}+\sum_{\alpha_1\alpha_2} G_{n'n}{}^{\alpha_1\alpha_2}P^{\alpha_1}P^{\alpha_2}+\cdots$$
$$=U_{n'n;0}(\mathbf{P})+sU_{n'n;1}(\mathbf{P})+s^2U_{n'n;2}(\mathbf{P})+\cdots, \quad (10.1)$$

where the operators $U_{n'n;i}(\mathbf{P})$ are completely symmetrized in the P^α. Because of this property they can be completely characterized by the functions $U_{n'n;i}(\mathbf{k})$ of the c-numbers k^α. For example, we see from (10.1) that

$$U_{n'n;0}(\mathbf{k})=\delta_{n'n}+\sum_{\alpha_1} G_{n'n}{}^{\alpha_1}k^{\alpha_1}+\sum_{\alpha_1\alpha_2} G_{n'n}{}^{\alpha_1\alpha_2}k^{\alpha_1}k^{\alpha_2}+\cdots,$$
$$U_{n'n;1}(\mathbf{k})=\sum_{\alpha_1\alpha_2}(i\sigma^{\alpha_1\alpha_2}/2s)G_{nn'}{}^{\alpha_1\alpha_2}+\cdots, \quad (10.2)$$

etc. The functions $U_{n'n;i}(\mathbf{k})$ are defined by their power-series in k^α where these converge, and by analytic continuation[22] elsewhere.

Combining (9.29) and (10.1) gives the following formal expansion for $\bar{\varphi}_{n\mathbf{k}}$:

$$\bar{\varphi}_{n\mathbf{k}}(\mathbf{r})=\sum u_{n'0}[U_{n'n;0}(\mathbf{P})+sU_{n'n;1}(\mathbf{P})+s^2U_{n'n;2}(\mathbf{P})+\cdots]e^{i\mathbf{k}\cdot\mathbf{r}} \quad (10.3)$$
$$=\sum \chi_{n'\mathbf{k}'}(\mathbf{k}'|U_{n'n;0}(\mathbf{P})+sU_{n'n;1}(\mathbf{P})+\cdots|\mathbf{k}).$$

For some purposes it is convenient to define

$$F_{n;i}(\mathbf{r};\mathbf{P})\equiv\sum_{n'} u_{n'0}(\mathbf{r})U_{n'n;i}(\mathbf{P}). \quad (10.4)$$

They are functions of $\mathbf{r}$ and completely symmetrized functions of the operators P^α. As the definition (10.4) shows, the P^α are to be thought of as on the *right* of the $\mathbf{r}$, i.e., not acting on it. With the help of these objects, we can rewrite (10.3) also in the compact form

$$\bar{\varphi}_{n\mathbf{k}}(\mathbf{r})=[F_{n;0}(\mathbf{r};\mathbf{P})+sF_{n;1}(\mathbf{r};\mathbf{P})+s^2F_{n;2}(\mathbf{r};\mathbf{P})+\cdots]e^{i\mathbf{k}\cdot\mathbf{r}}. \quad (10.5)$$

So far our entire development has been purely formal. We are now in a position to examine to what extent the functions $\bar{\varphi}_{m\mathbf{k}}$ have in fact been "decoupled" from the $\bar{\varphi}_{n\mathbf{k}}$ with $n\neq m$.

Let us first note that the transformation functions $S^{(t)}(\mathbf{P})$ have been so constructed that the equation

$$H_{nn'}(\mathbf{P})(n'|\exp[S^{(1)}(\mathbf{P})]\exp[S^{(2)}(\mathbf{P})]\cdots|m)$$
$$-(n|\exp[S^{(1)}(\mathbf{P})]\exp[S^{(2)}(\mathbf{P})]\cdots|m)\times\bar{H}_m(\mathbf{P})=0 \quad (10.6)$$

is a formal identity when both terms are formally expanded in powers of P^α. If now these power series are regrouped in a commutator expansion, (10.6) is also clearly a formal identity to all orders of s of this expansion. Let us now denote by $[Q(\mathbf{P})]_i$ the commutator expansion of any function Q of the operators P^α up to order s^i. Then clearly we must have

$$H_{nn'}(\mathbf{P})(n'|[\exp[S^{(1)}(\mathbf{P})]\exp[S^{(2)}(\mathbf{P})]\cdots]_i|m)$$
$$-(n|[\exp[S^{(1)}(P)]\exp[S^{(2)}(P)]\cdots]_i|m)\times[H_m(P)]_i=O(s^{i+1}). \quad (10.7)$$

Now let us denote by $\bar{\varphi}_{n\mathbf{k};i}$ the series (10.5) truncated after the power s^i:

$$\bar{\varphi}_{n\mathbf{k};i}\equiv[F_{n;0}(\mathbf{r};\mathbf{P})+\cdots s^iF_{n;i}(\mathbf{r};\mathbf{P})]e^{i\mathbf{k}\cdot\mathbf{r}}$$
$$=\sum u_{n'0}(n'|[\exp[S^{(1)}(\mathbf{P})]\exp[S^{(2)}(\mathbf{P})]\cdots]_i|n)\times e^{i\mathbf{k}\cdot\mathbf{r}}. \quad (10.8)$$

Then (10.7) can be rewritten as

$$H\bar{\varphi}_{m\mathbf{k};i}=\sum_{k'}\bar{\varphi}_{m\mathbf{k}';i}(\mathbf{k}'|\bar{H}_{m;0}(\mathbf{P})+\cdots+s^i\bar{H}_{m;i}(\mathbf{P})|\mathbf{k})+O(s^{i+1}). \quad (10.9)$$

This answers our question concerning the degree of decoupling: $\bar{\varphi}_{m\mathbf{k};i}$ is decoupled up to order s^i inclusive. Consequently, if we solve the one-band equation

$$\sum_{\mathbf{k}'}(\mathbf{k}|[\bar{H}_m(\mathbf{P})]_i|\mathbf{k}')\bar{A}_m(\mathbf{k}')=E\bar{A}_m(\mathbf{k}), \quad (10.10)$$

where

$$[\bar{H}_m(\mathbf{P})]_i=\bar{H}_{m;0}(\mathbf{P})+s\bar{H}_{m;1}(\mathbf{P})+\cdots s^i\bar{H}_{m;i}(\mathbf{P}), \quad (10.11)$$

the energy E and the corresponding wave function

$$\psi=\sum\bar{A}_m(\mathbf{k})\,\bar{\varphi}_{m\mathbf{k};i} \quad (10.12)$$

will have errors which vanish with s like s^{i+1}.

It may be remarked that if we define

$$F_m(\mathbf{r})\equiv\sum A_m(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{r}}, \quad (10.13)$$

then (10.10) is equivalent to the equation

$$[\bar{H}_m(\mathbf{P})]_iF_m(\mathbf{r})=EF_m(\mathbf{r}). \quad (10.14)$$

11. Analytic Continuation of New Basis Functions

In the preceding section we have seen that the new basis functions $\bar{\varphi}_{n\mathbf{k}}(\mathbf{r})$ can be developed in a commutator expansion of the form (10.5). As the operators $F_{n;i}(\mathbf{r};\mathbf{P})$ are completely symmetrized in the components of P^α, they are uniquely determined by the functions $F_{n;i}(\mathbf{r};\mathbf{k})$. The procedure of the previous section gave us a series development of these functions in powers of k^α. In the present section we shall show how they can be obtained for arbitrary $\mathbf{k}$ without recourse to a power series.

To determine $F_{m;0}(\mathbf{r};\mathbf{k})$ we first consider the case $s=0$ which has already been treated in Sec. 8. Here one finds

$$\bar{\varphi}_{m\mathbf{k}}=\varphi_{m\mathbf{k}}=F_{m;0}(\mathbf{r};\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{r}}, \quad (11.1)$$

so that

$$F_{m;0}(\mathbf{r};\mathbf{k})=u_{m\mathbf{k}}(\mathbf{r}), \quad (11.2)$$

where, by our construction, $\mathrm{Im}[u_{m\mathbf{k}}(0)]=0$.

[22] Again the analyticity is assumed without proof; see reference 20.

This gives us at once the result that in the presence of a magnetic field

$$\bar{\varphi}_{m\mathbf{k}}(\mathbf{r})=u_{m\mathbf{P}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}+O(s), \tag{11.3}$$

where $\mathbf{P}$ does not act on the argument $\mathbf{r}$ of $u_{m\mathbf{P}}$, and the operator $u_{m\mathbf{P}}$ is considered completely symmetrized in the components P^α. Now since

$$u_{m\mathbf{P}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}=u_{m,\mathbf{k}+(1/c)\mathbf{A}(\mathbf{r})}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}+O(s), \tag{11.4}$$

we can also write

$$\begin{aligned}\bar{\varphi}_{m\mathbf{k}(\mathbf{r})}&=u_{m,\mathbf{k}+(1/c)\mathbf{A}(\mathbf{r})}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}+O(s)\\&=\varphi_{m,\mathbf{k}+(1/c)\mathbf{A}(\mathbf{r})}(\mathbf{r})\exp[-i(1/c)\mathbf{A}(\mathbf{r})\cdot\mathbf{r}]\\&\qquad+O(s).\end{aligned} \tag{11.5}$$

We now turn to the higher-order terms in the commutator expansion of $\bar{\varphi}_{m\mathbf{k}}$. As we are interested in the case of small s but arbitrary values of $\mathbf{k}$, it is natural to try and discuss the whole problem in a new representation based on the Bloch waves at an arbitrary point $\mathbf{g}$ in $\mathbf{k}$ space, rather than the $\chi_{n\mathbf{k}}$ representation which was based on the Bloch waves u_{n0} at $\mathbf{k}=0$. In analogy with (3.1) we therefore define the following new basis functions:

$$\chi_{n\mathbf{h}}(\mathbf{r};\mathbf{g})\equiv\varphi_{n\mathbf{g}}(\mathbf{r})\exp(i\mathbf{h}\cdot\mathbf{r}), \tag{11.6}$$

where the phases of the $\varphi_{n\mathbf{g}}$ are so chosen that

$$\operatorname{Im}\varphi_{n\mathbf{g}}(0)=0, \tag{11.7}$$

and the sign of $\operatorname{Re}\varphi_{m\mathbf{g}}(0)$ is that which one obtains by analytic continuation of $\varphi_{m\mathbf{k}}$ from $\mathbf{k}=0$, under the condition (11.7). For $n\neq m$ the sign of $\varphi_{n\mathbf{g}}$ may be arbitrarily chosen. In complete analogy with Eqs. (5.5) and (5.6), we find that in this representation the Hamiltonian matrix is

$$(n\mathbf{h}|H|n'\mathbf{h}')=(\mathbf{h}|H_{nn'}(\mathbf{P};\mathbf{g})|\mathbf{h}'), \tag{11.8}$$

where

$$\begin{aligned}H_{nn'}(\mathbf{P};\mathbf{g})=\delta_{nn'}[\epsilon_n(\mathbf{g})+p_{nn}{}^\alpha(\mathbf{g})P^\alpha+\tfrac{1}{2}\delta^{\alpha\beta}P^\alpha P^\beta]\\+(1-\delta_{nn'})p_{nn'}{}^\alpha(\mathbf{g})P^\alpha;\end{aligned} \tag{11.9}$$

here $\epsilon_n(\mathbf{g})$ is the energy of band n at wave vector $\mathbf{g}$ while

$$p_{nn'}{}^\alpha(\mathbf{g})\equiv\frac{(2\pi)^3}{\Omega}\int_{\text{cell}}\varphi_{n\mathbf{g}}{}^*p^\alpha\varphi_{n\mathbf{g}}d\mathbf{r}. \tag{11.10}$$

As before, we shall now eliminate the interband matrix elements of (11.9) and in this way be led to new basis functions $\bar{\varphi}_{n\mathbf{h}}(\mathbf{r};\mathbf{g})$. For $m=n$ it will be shown that these are related as follows to the functions $\bar{\varphi}_{m\mathbf{k}}(\mathbf{r})$ of Sec. 10:

$$\bar{\varphi}_{m\mathbf{h}}(\mathbf{r};\mathbf{g})=\bar{\varphi}_{m\mathbf{g}+\mathbf{h}}(\mathbf{r}). \tag{11.11}$$

This connection will enable us to construct the function $F_{m;i}(\mathbf{r};\mathbf{k})$ of Eq. (10.5) as well as the functions $\bar{H}_{m;i}(\mathbf{k})$ of Eq. (6.8) without recourse to power series expansions in k^α.

We begin by eliminating the first-order off-diagonal matrix elements of $H_{nn'}(\mathbf{P};\mathbf{g})$ by means of the unitary transformation $\exp[S^{(1)}(\mathbf{P};\mathbf{g})]$:

$$\begin{aligned}\bar{H}^{(1)}(\mathbf{P};\mathbf{g})&\equiv\exp[-S^{(1)}(\mathbf{P};\mathbf{g})]H(\mathbf{P};\mathbf{g})\exp[S^{(1)}(\mathbf{P};\mathbf{g})]\\&=H(\mathbf{P};\mathbf{g})+[H(\mathbf{P};\mathbf{g}),S^{(1)}(\mathbf{P};\mathbf{g})]\\&\quad+\cdots.\end{aligned} \tag{11.12}$$

We take $S^{(1)}$ of the form

$$S_{nn'}{}^{(1)}(P;g)=D_{nn'}{}^\alpha(\mathbf{g})P^\alpha, \tag{11.13}$$

where the $D_{nn'}{}^\alpha(\mathbf{g})$ must satisfy the condition

$$p_{mn}{}^\alpha(\mathbf{g})+\omega_{mn}(\mathbf{g})D_{mn}{}^\alpha(\mathbf{g})=0\quad n\neq m, \tag{11.14}$$

and

$$D_{nn'}{}^\alpha(\mathbf{g})=-[D_{n'n}{}^\alpha(\mathbf{g})]^*; \tag{11.15}$$

here

$$\omega_{nn'}(\mathbf{g})\equiv\epsilon_n(\mathbf{g})-\epsilon_{n'}(\mathbf{g}). \tag{11.16}$$

We choose

$$\begin{aligned}D_{mn}{}^\alpha(\mathbf{g})=\delta_{mn}iC_m{}^\alpha(\mathbf{g})\\-(1-\delta_{mn})p_{mn}{}^\alpha(\mathbf{g})/\omega_{mn}(\mathbf{g}),\end{aligned} \tag{11.17}$$

$$D_{nm}{}^\alpha=-(D_{mn}{}^\alpha)^*, \tag{11.18}$$

$$D_{nn'}{}^\alpha=0,\quad n\neq m\text{ and }n'\neq m \tag{11.19}$$

[see Eq. (5.14) ff]. As before, we choose the real constants $C_m{}^\alpha(\mathbf{g})$ so as to make the new basis functions

$$\begin{aligned}\bar{\varphi}_{m\mathbf{h}}{}^{(1)}(\mathbf{r};\mathbf{g})=\sum_{n,\mathbf{h}'}\chi_{n\mathbf{h}'}(\mathbf{r};\mathbf{g})\\\times(n\mathbf{h}'|1+S^{(1)}(\mathbf{P};\mathbf{g})|m\mathbf{h}),\end{aligned} \tag{11.20}$$

real at $\mathbf{r}=0$, to first order in P^α. This requires

$$iC_m{}^\alpha(\mathbf{g})=\frac{1}{\varphi_{m\mathbf{g}}(0)}\operatorname{Im}\sum_{n\neq m}\varphi_{n\mathbf{g}}(0)\frac{p_{nm}{}^\alpha(\mathbf{g})}{\omega_{nm}(\mathbf{g})}. \tag{11.21}$$

Continuing in this manner we construct, in analogy with Eq. (9.29), the functions

$$\begin{aligned}\bar{\varphi}_{n\mathbf{h}}{}^{(t)}(\mathbf{r};\mathbf{g})=\sum_{n'}\varphi_{n'\mathbf{g}}[\delta_{n'n}+\sum_{\alpha_1}G_{n'n}{}^{\alpha_1}(\mathbf{g})P^{\alpha_1}\\+\cdots+\sum_{\alpha_1\cdots\alpha_t}G_{n'n}{}^{\alpha_1\cdots\alpha_t}(\mathbf{g})P^{\alpha_1}\cdots P^{\alpha_t}]\\\times\exp(i\mathbf{h}\cdot\mathbf{r}).\end{aligned} \tag{11.22}$$

These series may be rearranged in a commutator series leading to an expansion analogous to Eq. (10.3)

$$\begin{aligned}\bar{\varphi}_{n\mathbf{h}}(\mathbf{r};\mathbf{g})=\textstyle\sum_{n'}\varphi_{n'\mathbf{g}}[U_{n'n;0}(\mathbf{P};\mathbf{g})\\+sU_{n'n;1}(\mathbf{P};\mathbf{g})+\cdots]\exp(i\mathbf{h}\cdot\mathbf{r}),\end{aligned} \tag{11.23}$$

where the functions $U_{n'n;i}(\mathbf{P};\mathbf{g})$ are completely symmetrized in the P^α.

Now let us set

$$\mathbf{h}=\mathbf{k}-\mathbf{g}, \tag{11.24}$$

and use the following identity, valid for any function $Z(\mathbf{P})$:

$$\begin{aligned}Z(\mathbf{P})\exp[i(\mathbf{k}-\mathbf{g})\cdot\mathbf{r}]\\=\exp[-i\mathbf{g}\cdot\mathbf{r}]Z(\mathbf{P}-\mathbf{g})\exp[i\mathbf{k}\cdot\mathbf{r}].\end{aligned} \tag{11.25}$$

This allows us to re-write (11.23) as

$$\bar{\varphi}_{n\mathbf{k}-\mathbf{g}}(\mathbf{r};\,\mathbf{g})=\sum_{n'}\varphi_{n'\mathbf{g}}\exp(-i\mathbf{g}\cdot\mathbf{r})[U_{n'n;0}(\mathbf{P}-\mathbf{g};\,\mathbf{g})+sU_{n'n;1}(\mathbf{P};\,\mathbf{g})+\cdots]e^{i\mathbf{k}\cdot\mathbf{r}}. \quad (11.26)$$

Next we observe that the functions $\varphi_{n'\mathbf{g}}\exp(-i\mathbf{g}\cdot\mathbf{r})=u_{n'\mathbf{g}}(\mathbf{r})$ are completely periodic in $\mathbf{r}$, so that we can write

$$\varphi_{n'\mathbf{g}}\exp(-i\mathbf{g}\cdot\mathbf{r})=\sum_{n''}u_{n''0}(\mathbf{r})C_{n''n'}(\mathbf{g}),$$
$$C_{n''n'}(\mathbf{g})=\frac{(2\pi)^3}{\Omega}\int_{\text{cell}}u_{n''0}^*u_{n'\mathbf{g}}d\mathbf{r}, \quad (11.27)$$

where $C_{n''n'}$ is a unitary matrix. If we now define

$$\bar{U}_{n''n;i}(\mathbf{P};\,\mathbf{g})\equiv\sum C_{n''n'}(\mathbf{g})U_{n'n;i}(\mathbf{P}-\mathbf{g};\,\mathbf{g}), \quad (11.28)$$

Eq. (11.26) assumes the form

$$\bar{\varphi}_{n\mathbf{k}-\mathbf{g}}(\mathbf{r};\,\mathbf{g})=\sum u_{n'0}[\bar{U}_{n'n;0}(\mathbf{P};\,\mathbf{g})+s\bar{U}_{n'n;1}(\mathbf{P};\,\mathbf{g})+\cdots]e^{i\mathbf{k}\cdot\mathbf{r}}=\sum\chi_{n'\mathbf{k}'}(\mathbf{k}'|\bar{U}_{n'n;0}(\mathbf{P};\,\mathbf{g})+s\bar{U}_{n'n;1}(\mathbf{P};\,\mathbf{g})+\cdots|\mathbf{k}). \quad (11.29)$$

These expressions have the same form as those occurring in Eq. (10.3). We shall now show that, for $n=m$, $\bar{\varphi}_{m\mathbf{k}-\mathbf{g}}(\mathbf{r};\,\mathbf{g})$ and $\bar{\varphi}_{m\mathbf{k}}(\mathbf{r})$ are in fact identical.

We begin by inverting the power series expansion (9.29) and rearranging the inverted series in a commutator expansion of the following form[23]:

$$\chi_{n'\mathbf{k}'}=\sum\bar{\varphi}_{n''\mathbf{k}''}\times(\mathbf{k}''|X_{n''n';0}(\mathbf{P})+sX_{n''n';1}(\mathbf{P})+\cdots|\mathbf{k}). \quad (11.30)$$

Substituting $\chi_{n'\mathbf{k}'}$ from (11.30) into (11.29) and regrouping in a commutator expansion gives an equation of the form

$$\bar{\varphi}_{n\mathbf{k}-\mathbf{g}}(\mathbf{r};\,\mathbf{g})=\sum\bar{\varphi}_{n'\mathbf{k}'}\times(\mathbf{k}'|W_{n'n;0}(\mathbf{P})+sW_{n'n;1}(\mathbf{P})+\cdots|\mathbf{k}). \quad (11.31)$$

Now for $s=0$, and $n=m$, we have by construction

$$\bar{\varphi}_{m\mathbf{k}-\mathbf{g}}(\mathbf{r};\,\mathbf{g})=\bar{\varphi}_{m\mathbf{k}}(\mathbf{r})=\varphi_{m\mathbf{k}}(\mathbf{r}), \quad (11.32)$$

where the phase of the Bloch wave is in accordance with (11.7) ff. Hence

$$W_{n'm;0}(\mathbf{P})\equiv\delta_{n'm}. \quad (11.33)$$

Furthermore the transformation matrix

$$W_{nn'}(\mathbf{P})=W_{nn';0}(\mathbf{P})+sW_{nn';1}(\mathbf{P})+\cdots \quad (11.34)$$

is formally unitary, i.e.,

$$\sum_{n''}W_{n'n''}^{\dagger}(\mathbf{P})W_{n''n'''}(\mathbf{P})=\delta_{n'n'''}, \quad (11.35)$$

where † denotes the Hermitian conjugate.

[23] This is of course again a formal expansion which has the following property: If $\bar{\varphi}_{n''\mathbf{k}''}$ is expressed as a formal commutator expansion, according to (10.3), substituted into (11.30) and the resulting terms regrouped in a commutator expansion, (11.30) is an identity to all orders in s.

Finally, since the original Hamiltonian H has no interband matrix elements connecting $\bar{\varphi}_{m\mathbf{k}}(\mathbf{r})$ with $\bar{\varphi}_{n\mathbf{k}}(\mathbf{r})$, $n\neq m$, or connecting $\bar{\varphi}_{m\mathbf{k}-\mathbf{g}}(\mathbf{r};\,\mathbf{g})$ with $\bar{\varphi}_{n\mathbf{k}-\mathbf{g}}\times(\mathbf{r};\,\mathbf{g})$, $n\neq m$, it follows that $\bar{\varphi}_{m\mathbf{k}-\mathbf{g}}(\mathbf{r};\,\mathbf{g})$ must be a linear combination of $\bar{\varphi}_{m\mathbf{k}'}(\mathbf{r})$ with the same m. Thus

$$W_{n'm;i}(\mathbf{P})=\delta_{n'm}W_i(\mathbf{P}), \quad (11.36)$$

and we have

$$\bar{\varphi}_{m\mathbf{k}-\mathbf{g}}(\mathbf{r};\,\mathbf{g})=\sum\bar{\varphi}_{m\mathbf{k}'}\times(\mathbf{k}'|1+sW_1(\mathbf{P})+s^2W_2(\mathbf{P})+\cdots|\mathbf{k}). \quad (11.37)$$

Now let us turn to $W_1(\mathbf{P})$. From the unitary property (11.35), it follows that

$$W_1(\mathbf{P})+W_1^*(\mathbf{P})=0. \quad (11.38)$$

Setting $s=0$ gives

$$W_1(\mathbf{k})+W_1^*(\mathbf{k})=0, \quad (11.39)$$

so that $W_1(\mathbf{k})$ is purely imaginary. Next let us use the reality of $\varphi_{m\mathbf{k}-\mathbf{g}}(\mathbf{r};\,\mathbf{g})$ and $\bar{\varphi}_{m\mathbf{k}}(\mathbf{r})$ at $\mathbf{r}=0$. This gives

$$\text{Im}[\sum\bar{\varphi}_{m\mathbf{k}'}(0)(\mathbf{k}'|W_1(\mathbf{P})|\mathbf{k})]=0. \quad (11.40)$$

Now letting $s\to 0$ gives

$$\text{Im}[W_1(\mathbf{k})]=0, \quad (11.41)$$

so that $W_1(\mathbf{k})$ is purely real. Hence

$$W_1(\mathbf{k})\equiv 0. \quad (11.42)$$

In the same way one shows next that $W_2(\mathbf{k})$ vanishes, etc. This gives finally the required result

$$\bar{\varphi}_{m\mathbf{k}-\mathbf{g}}(\mathbf{r};\,\mathbf{g})=\bar{\varphi}_{m\mathbf{k}}(\mathbf{r}), \quad (11.43)$$

which is equivalent to (11.11).

One important consequence of this result is the following. Since by construction

$$\bar{\varphi}_{m\mathbf{h}}(\mathbf{r};\,\mathbf{K})=\theta\,\bar{\varphi}_{m\mathbf{h}}(\mathbf{r}) \quad (11.44)$$

[see Eq. (8.13)], it follows from (11.43) that

$$\bar{\varphi}_{m\mathbf{K}+\mathbf{k}}(\mathbf{r})=\theta\,\bar{\varphi}_{m\mathbf{k}}(\mathbf{r}). \quad (11.45)$$

Thus, also in the presence of a magnetic field, the new basis functions have the quasi-periodic property (11.45).

It is obvious how (11.43) can be used to obtain the analytic continuation of $\bar{\varphi}_{m\mathbf{k}}(\mathbf{r})$ for arbitrary $\mathbf{k}$. Setting $\mathbf{g}=\mathbf{k}$, (11.43) gives

$$\bar{\varphi}_{m\mathbf{k}}(\mathbf{r})=\bar{\varphi}_{m0}(\mathbf{r};\,\mathbf{k}). \quad (11.46)$$

Now by Eq. (11.29) we have

$$\bar{\varphi}_{m0}(\mathbf{r};\,\mathbf{k})=\sum\chi_{n'\mathbf{k}'}(\mathbf{k}'|\bar{U}_{n'm;0}(\mathbf{P};\,\mathbf{k})+s\bar{U}_{n'm;1}(\mathbf{P};\,\mathbf{k})+\cdots|\mathbf{k}), \quad (11.47)$$

while by (10.3)

$$\bar{\varphi}_{m\mathbf{k}}(\mathbf{r})=\sum\chi_{n'\mathbf{k}'}(\mathbf{k}'|U_{n'm;0}(\mathbf{P})+2U_{n'm;1}(\mathbf{P})+\cdots|\mathbf{k}). \quad (11.48)$$

On subtracting and using (11.46), we get

$$0=\sum \chi_{n'\mathbf{k}'}(\mathbf{k}'|[U_{n'm;0}(\mathbf{P})-\bar{U}_{n'm;0}(\mathbf{P};\mathbf{k})] +s[U_{n'm;1}(\mathbf{P})-\bar{U}_{n'm;1}(\mathbf{P};\mathbf{k})]+\cdots|\mathbf{k}). \quad (11.49)$$

As the $\chi_{n'\mathbf{k}'}$ are not orthonormal, we cannot immediately conclude that the coefficients of $\chi_{n'\mathbf{k}'}$ vanish. However, this fact may be established as follows. Set $s=0$ in (11.49), which then reads

$$0=\sum_{n'} \chi_{n'\mathbf{k}}[U_{n'm;0}(\mathbf{k})-\bar{U}_{n'm;0}(\mathbf{k};\mathbf{k})]. \quad (11.50)$$

Hence

$$U_{n'm;0}(\mathbf{k})=\bar{U}_{n'm;0}(\mathbf{k};\mathbf{k}), \quad (11.51)$$

and

$$U_{n'm;0}(\mathbf{P})=\bar{U}_{n'm;0}(\mathbf{P};\mathbf{k}). \quad (11.52)$$

Now, by using (11.52) in (11.49) and dividing the latter equation by s, we get

$$0=\sum \chi_{n'\mathbf{k}'}(k'|[U_{n'm;1}(\mathbf{P})-\bar{U}_{n'm;1}(\mathbf{P};\mathbf{k})] +s[U_{n'm;2}(\mathbf{P})-\bar{U}_{n'n;2}(\mathbf{P};\mathbf{k})]+\cdots|k). \quad (11.53)$$

Now set $s=0$ and obtain

$$U_{n'm;1}(\mathbf{P})=\bar{U}_{n'm;1}(\mathbf{P};\mathbf{k}), \quad (11.54)$$

etc. Thus we see that for all i,

$$U_{n'm;i}(\mathbf{k})=\bar{U}_{n'm;i}(\mathbf{k};\mathbf{k}). \quad (11.55)$$

Finally, by (11.28), we have

$$\bar{U}_{n'm;i}(\mathbf{k};\mathbf{k})=\sum C_{n'n''}(\mathbf{k})U_{n''m;i}(0;\mathbf{k}). \quad (11.56)$$

But at $\mathbf{h}=0$, each coefficient $U_{n''m;i}(\mathbf{h};\mathbf{k})$ can be evaluated explicitly in terms of a finite number of the coefficients of the power series (11.22). Thus

$$U_{n''m;0}(0;\mathbf{k})=\delta_{n''m}, \quad (11.57)$$

$$U_{n''m;1}(0;\mathbf{k})=\sum_{\alpha_1\alpha_2} \frac{i\sigma^{\alpha_1\alpha_2}}{2s} G_{n''m}{}^{\alpha_1\alpha_2}(\mathbf{k}), \quad (11.58)$$

etc. We see then that for example to obtain $U_{n''m;1}(\mathbf{k})$ we require a knowledge of $G_{n''m}{}^{\alpha_1\alpha_2}(\mathbf{k})$ which may be obtained by two canonical transformations. This should be compared to Eq. (10.2) which required the summation of an infinite power series in k^α, i.e., the performance of an infinite sequence of canonical transformations.

12. Explicit Construction of the Effective Hamiltonian

In Sec. 6 we saw that the effective Hamiltonian $\bar{H}_m(\mathbf{P})$ could be expanded in a series of the form

$$\bar{H}_m(\mathbf{P})=H_{m;0}(\mathbf{P})+s\bar{H}_{m;1}(\mathbf{P})+s^2\bar{H}_{m;2}(\mathbf{P})+\cdots. \quad (12.1)$$

We have already remarked that since the $\bar{H}_{m;i}(\mathbf{P})$ are completely symmetrized functions of the P^α, they are determined by the functions $\bar{H}_{m;i}(\mathbf{k})$. In fact, if

$$\bar{H}_{m;i}(\mathbf{k})=\sum_{\mathbf{R}} B(\mathbf{R})e^{i\mathbf{R}\cdot\mathbf{k}}, \quad (12.2)$$

then

$$\bar{H}_{m;i}(\mathbf{P})=\sum_{\mathbf{R}} B(\mathbf{R})e^{i\mathbf{R}\cdot\mathbf{P}}. \quad (12.3)$$

However at the stage of Sec. 6, we had only expansions of $\bar{H}_{m;i}(\mathbf{k})$ in powers of k^α. We are now in a position to calculate these functions explicitly for arbitrary $\mathbf{k}$.

Let us begin by writing Eq. (10.3) for $n=m$ in the form

$$\bar{\varphi}_{m\mathbf{k}}(\mathbf{r})=\sum \chi_{n'\mathbf{k}'}(n'k'|U(\mathbf{P})|m\mathbf{k}), \quad (12.4)$$

where

$$U_{n'n}(\mathbf{P})=U_{n'n;0}(\mathbf{P})+sU_{n'n;1}(\mathbf{P})+\cdots =(n'|\exp[S^{(1)}(\mathbf{P})]\exp[S^{(2)}(\mathbf{P})]\cdots|n). \quad (12.5)$$

Similarly, (11.23) can for $n=m$ be written as

$$\bar{\varphi}_{m\mathbf{h}}(\mathbf{r};\mathbf{g})=\sum_{n'} \chi_{n'\mathbf{h}'}(\mathbf{r};\mathbf{g})(n'\mathbf{h}'|U(\mathbf{P};\mathbf{g})|m\mathbf{h}), \quad (12.6)$$

where

$$U_{n'n'}(\mathbf{P};\mathbf{g}) =U_{n'n;0}(\mathbf{P};\mathbf{g})+sU_{n'n;1}(\mathbf{P};\mathbf{g})+\cdots =(n'|\exp[S^{(1)}(\mathbf{P};\mathbf{g})]\exp[S^{(2)}(\mathbf{P};\mathbf{g})]\cdots|n). \quad (12.7)$$

By (11.5) and (11.28), $U(\mathbf{P})$ and $U(\mathbf{P};\mathbf{g})$ are connected by the relation

$$U_{n''n}(\mathbf{P})=\sum C_{n''n'}(\mathbf{g})U_{n'n}(\mathbf{P}-\mathbf{g};\mathbf{g}). \quad (12.8)$$

We shall now prove the following identity. Let

$$\bar{H}_m(\mathbf{P})=U_{mn}{}^{-1}(\mathbf{P})H_{nn'}(\mathbf{P})U_{n'm}(\mathbf{P}), \quad (12.9)$$

where $U_{n'n}(\mathbf{P})$ is defined in (12.5) and

$$H_{nn'}(\mathbf{P})=\delta_{nn'}[\epsilon_n+\tfrac{1}{2}P^\alpha P^\alpha]+p_{nn'}{}^\alpha P^\alpha; \quad (12.10)$$

and let

$$\bar{H}_m(\mathbf{P};\mathbf{g})=U_{mn}{}^{-1}(\mathbf{P};\mathbf{g})H_{nn'}(\mathbf{P};\mathbf{g})U_{n'm}(\mathbf{P};\mathbf{g}), \quad (12.11)$$

where $U_{n'n}(\mathbf{P};\mathbf{g})$ is defined by (12.7) and

$$H_{nn'}(\mathbf{P};\mathbf{g})=\delta_{nn'}[\epsilon_n(\mathbf{g})+\tfrac{1}{2}P^\alpha P^\alpha]+p_{nn'}{}^\alpha(\mathbf{g})P^\alpha. \quad (12.12)$$

Then

$$\bar{H}_m(\mathbf{P})\equiv\bar{H}_m(\mathbf{P}-\mathbf{g};\mathbf{g}). \quad (12.13)$$

We first transform (12.9) with the help of (12.8):

$$\bar{H}_m(\mathbf{P})=U_{mn}{}^{-1}(\mathbf{P}-\mathbf{g};\mathbf{g})C_{nn''}{}^{-1}(\mathbf{g}) \times H_{n''n'''}(\mathbf{P})C_{n'''n'}(\mathbf{g})U_{n'm}(\mathbf{P}-\mathbf{g};\mathbf{g}). \quad (12.14)$$

Next we note the identity

$$\delta_{n''n'''}\epsilon_{n''}=(u_{n''0},(p^2/2m+V)u_{n'''0}). \quad (12.15)$$

This allows us to write

$$C_{nn''}{}^{-1}(\mathbf{g})\delta_{n''n'''}\epsilon_{n''}C_{n'''n'}(\mathbf{g}) =(u_{ng},u_{n''0})(u_{n''0},(p^2/2m+V)u_{n'''0})(u_{n'''0},u_{n'g}) =(\varphi_{ng}\exp(-i\mathbf{g}\cdot\mathbf{r}),(p^2/2m+V)\varphi_{n'g}\exp(-i\mathbf{g}\cdot\mathbf{r})) =(\epsilon_{ng}+\tfrac{1}{2}\mathbf{g}^2)\delta_{nn'}-p_{nn'}{}^\alpha(\mathbf{g})g^\alpha. \quad (12.16)$$

Similarly

$$C_{nn''}^{-1}(\mathbf{g})p_{n''n'''}{}^{\alpha}C_{n'''n'}(\mathbf{g})=p_{nn'}{}^{\alpha}(\mathbf{g})-g^{\alpha}\delta_{nn'}. \quad (12.17)$$

Therefore (12.14) gives

$$\begin{aligned}\bar{H}_m(\mathbf{P})=&U_{mn}{}^{-1}(\mathbf{P}-\mathbf{g};\mathbf{g})\\&\times\{\delta_{nn'}[\epsilon_n(\mathbf{g})+\tfrac{1}{2}(P^{\alpha}-g^{\alpha})(P^{\alpha}-g^{\alpha})\\&+p_{nn'}{}^{\alpha}(g)(P^{\alpha}-g^{\alpha})]\}U_{n'm}(\mathbf{P}-\mathbf{g};\mathbf{g})\\&=\bar{H}_m(\mathbf{P}-\mathbf{g};\mathbf{g}),\end{aligned} \quad (12.18)$$

as was to be shown.

This relation allows one to calculate explicitly the functions $\bar{H}_{m;i}(\mathbf{k})$ which determine the successive terms of the commutator expansion of $\bar{H}_m(\mathbf{P})$. We make a commutator expansion of both sides of (12.18),

$$\begin{aligned}\bar{H}_{m;0}(\mathbf{P})+s\bar{H}_{m;1}(\mathbf{P})+\cdots\\=\bar{H}_{m;0}(\mathbf{P}-\mathbf{g};\mathbf{g})+s\bar{H}_{m;1}(\mathbf{P}-\mathbf{g};\mathbf{g})+\cdots.\end{aligned} \quad (12.19)$$

We equate corresponding terms, setting $\mathbf{P}=\mathbf{k}$ and $\mathbf{g}=\mathbf{k}$. This gives

$$\bar{H}_{m;i}(\mathbf{k})=\bar{H}_{m;i}(0;\mathbf{k}). \quad (12.20)$$

Now suppose that $\bar{H}_m(\mathbf{P};\mathbf{k})$ has the following *power* series expansion in P^{α}

$$\begin{aligned}\bar{H}_m(\mathbf{P};\mathbf{k})=\epsilon_m(\mathbf{k})+E_m{}^{\alpha_1}(\mathbf{k})P^{\alpha_1}+E_m{}^{\alpha_1\alpha_2}(\mathbf{k})P^{\alpha_1}P^{\alpha_2}+\cdots\\+E_m{}^{\alpha_1\cdots\alpha_t}(\mathbf{k})P^{\alpha_1}\cdots P^{\alpha_t}+\cdots.\end{aligned} \quad (12.21)$$

This may be rearranged in a commutator expansion

$$\bar{H}_m(\mathbf{P};\mathbf{k})=\bar{H}_{m;0}(\mathbf{P};\mathbf{k})+s\bar{H}_{m;1}(\mathbf{P};\mathbf{k})+\cdots, \quad (12.22)$$

where

$$\begin{aligned}\bar{H}_{m;0}(\mathbf{P};\mathbf{k})=\epsilon_m(\mathbf{k})+E_m{}^{\alpha_1}(\mathbf{k})\langle P^{\alpha_1}\rangle_{\text{Av}}\\+E_m{}^{\alpha_1\alpha_2}(\mathbf{k})\langle P^{\alpha_1}P^{\alpha_2}\rangle_{\text{Av}}+\cdots,\end{aligned} \quad (12.23)$$

$$\bar{H}_{m;1}(\mathbf{P};\mathbf{k})=i\sum_{\alpha_1\alpha_2}\frac{\sigma^{\alpha_1\alpha_2}}{s}E_m{}^{\alpha_1\alpha_2}(\mathbf{k})+O(P^{\alpha}), \quad (12.24)$$

$$\begin{aligned}\bar{H}_{m;2}(\mathbf{P};\mathbf{k})=-\sum_{\alpha_1\alpha_2\alpha_3\alpha_4}\frac{\sigma^{\alpha_1\alpha_2}\sigma^{\alpha_3\alpha_4}+\sigma^{\alpha_1\alpha_3}\sigma^{\alpha_2\alpha_4}+\sigma^{\alpha_1\alpha_4}\sigma^{\alpha_2\alpha_3}}{s^2}\\\times E_m{}^{\alpha_1\alpha_2\alpha_3\alpha_4}(\mathbf{k})+O(P^{\alpha}).\end{aligned} \quad (12.25)$$

Hence by (12.20)

$$\bar{H}_{m;0}(\mathbf{k})=\epsilon_m(\mathbf{k}),$$

$$\bar{H}_{m;1}(\mathbf{k})=i\sum_{\alpha_1\alpha_2}\frac{\sigma^{\alpha_1\alpha_2}}{s}E_m{}^{\alpha_1\alpha_2}(\mathbf{k}),$$

$$\begin{aligned}\bar{H}_{m;2}(\mathbf{k})=-\sum_{\alpha_1\alpha_2\alpha_3\alpha_4}\frac{\sigma^{\alpha_1\alpha_2}\sigma^{\alpha_3\alpha_4}+\sigma^{\alpha_1\alpha_3}\sigma^{\alpha_2\alpha_4}+\sigma^{\alpha_1\alpha_4}\sigma^{\alpha_2\alpha_3}}{s^2}\\E_m{}^{\alpha_1\alpha_2\alpha_3\alpha_4}(\mathbf{k}),\end{aligned} \quad (12.26)$$

etc. These functions can all be explicitly calculated.

Now by construction of $\bar{H}_m(\mathbf{P};\mathbf{k})$ the coefficients $E_m{}^{\alpha_1\alpha_2\cdots}(\mathbf{k})$ have the periodicity of the reciprocal lattice, so that we may write

$$\bar{H}_{m;i}(\mathbf{k})=\sum a_i{}^{(l)}\exp(i\mathbf{R}^{(l)}\cdot\mathbf{P}), \quad (12.27)$$

where the $\mathbf{R}^{(l)}$ are the lattice vectors of the crystal. Hence the effective Hamiltonian can be written in the form

$$\bar{H}_m(\mathbf{P})=\sum_l a^{(l)}(s)\exp(i\mathbf{R}^{(l)}\cdot\mathbf{P}), \quad (12.28)$$

where

$$a^{(l)}(s)=a_0{}^{(l)}+sa_1{}^{(l)}+s^2a_2{}^{(l)}+\cdots. \quad (12.29)$$

Denoting by τ the volume of the fundamental Brillouin zone, we have

$$a_0{}^{(l)}=\frac{1}{\tau}\int_{\text{zone}}\epsilon_m(\mathbf{k})\exp(-i\mathbf{k}\cdot\mathbf{R}^{(l)})d\mathbf{k}, \quad (12.30)$$

$$a_1{}^{(l)}=\frac{1}{\tau}\int_{\text{zone}}(is^{\alpha_1\alpha_2}/s)E_m{}^{\alpha_1\alpha_2}(\mathbf{k})\times\exp(-i\mathbf{k}\cdot\mathbf{R}^{(l)})d\mathbf{k}, \quad (12.31)$$

etc.

Equation (12.28) has as a consequence the important periodicity property

$$\bar{H}_m(\mathbf{P}+\mathbf{K})=\bar{H}_m(\mathbf{P}), \quad (12.32)$$

where $\mathbf{K}$ is an arbitrary reciprocal lattice vector.

13. Application to Crystals with a Center of Inversion

Using the methods of the preceding sections, we shall now work out the first few terms of the commutator expansion of the effective Hamiltonian $\bar{H}_m(\mathbf{P})$ for crystals with a center of inversion.

For such crystals it is easily shown (Appendix B) that with our convention of

$$\text{Im}[\varphi_{n\mathbf{g}}(0)]=0, \quad (13.1)$$

one has the result[24]

$$\text{Im}[p_{n'n''}{}^{\alpha}(\mathbf{g})]=0. \quad (13.2)$$

This results in the vanishing of the terms of odd degree in s in the commutator expansion of $\bar{H}_m(\mathbf{P})$.

Working in the representation of the $\chi_{n\mathbf{h}}(\mathbf{r};\mathbf{g})$, we begin with the Hamiltonian

$$H(\mathbf{P};\mathbf{g})=H_0+H_1+H_2, \quad (13.3)$$

where

$$(H_0)_{nn'}=\delta_{nn'}\epsilon_n(\mathbf{g}), \quad (13.4)$$

$$(H_1)_{nn'}=p_{nn'}{}^{\alpha}(\mathbf{g})P^{\alpha}, \quad (13.5)$$

$$(H_2)_{nn'}=\tfrac{1}{2}\delta_{nn'}P^{\alpha}P^{\alpha}. \quad (13.6)$$

To this H we apply a sequence of unitary transformations $\exp[S^{(i)}(\mathbf{P};\mathbf{g})]$ to eliminate off-diagonal elements to higher and higher order in P^{α}. We take $S^{(i)}$ to be of

[24] For isolated values of $\mathbf{g}$, for which $\varphi_{n\mathbf{g}}(0)=0$, (13.1) does not fix the phase of $\varphi_{n\mathbf{g}}$. In such cases we define $\varphi_{n\mathbf{g}}=\lim_{\mathbf{g}'\to\mathbf{g}}\varphi_{n\mathbf{g}'}$. With this understanding, (13.2) holds also at such points.

order $(P^\alpha)^i$. Then, up to order $(P^\alpha)^4$ we have

$$\begin{aligned}\bar{H}(\mathbf{P};\mathbf{g})\\ &=\cdots\exp(-S^{(2)})\exp(-S^{(1)})H\exp(S^{(1)})\exp(S^{(2)})\cdots\\ &=H_0\\ &+\{H_1+[H_0,S^{(1)}]\}\\ &+\{H_2+[H_1,S^{(1)}]+\tfrac{1}{2}[[H_0,S^{(1)}],S^{(1)}]+[H_0,S^{(2)}]\}\\ &+\{[H_1,S^{(2)}]+[H_2,S^{(1)}]+[[H_0,S^{(1)}],S^{(2)}]\\ &+\tfrac{1}{2}[[H_1,S^{(1)}],S^{(1)}]+\tfrac{1}{6}[[[H_0,S^{(1)}],S^{(1)}],S^{(1)}]\\ &+[H_0,S^{(3)}]\}+\{[H_2,S^{(2)}]+\tfrac{1}{2}[[H_0,S^{(2)}],S^{(2)}]\\ &+[[H_1,S^{(1)}],S^{(2)}]+\tfrac{1}{2}[[H_2,S^{(1)}],S^{(1)}]\\ &+\tfrac{1}{2}[[[H_0,S^{(1)}],S^{(1)}],S^{(2)}]+\tfrac{1}{6}[[[H_1,S^{(1)}],S^{(1)}],S^{(1)}]\\ &+(1/24)[[[[H_0,S^{(1)}],S^{(1)}],S^{(1)}],S^{(1)}]\\ &+[[H_0,S^{(1)}],S^{(3)}]+[H_1,S^{(3)}]+[H_0,S^{(4)}]\}\\ &+\cdots.\end{aligned}\tag{13.7}$$

The first-order off-diagonal elements are eliminated by the choice

$$\begin{aligned}S_{mi}^{(1)}&=-(S^{(1)})_{im}{}^\dagger=-(p_{mi}{}^\alpha/\omega_{mi})P^\alpha, && i\neq m\\ S_{n'n''}{}^{(1)}&=0, && \text{all other } n', n''.\end{aligned}\tag{13.8}$$

Here we write $p_{nn'}{}^\alpha$ and $\omega_{nn'}$ short for $p_{nn'}{}^\alpha(\mathbf{g})$ and $\omega_{nn'}(\mathbf{g})$. Because of (13.1) and (13.2) we see that the corresponding new basis functions,

$$\begin{aligned}\bar{\varphi}_{m\mathbf{g}+\mathbf{h}}&=\exp(S^{(1)})\exp(S^{(2)})\cdots\chi_{m\mathbf{h}}=(1+S^{(1)}+\cdots)\chi_{m\mathbf{h}}\\ &=\varphi_{m\mathbf{g}}\exp(i\mathbf{h}\cdot\mathbf{r})-\textstyle\sum_i\varphi_{i\mathbf{g}}(p_{im}{}^\alpha/\omega_{im})P^\alpha\exp(i\mathbf{h}\cdot\mathbf{r})\\ &\quad+\cdots,\end{aligned}\tag{13.9}$$

have to first order in P^α the required property

$$\mathrm{Im}[\bar{\varphi}_{m\mathbf{g}+\mathbf{h}}(0)]=0.\tag{13.10}$$

The second transformation matrix $S^{(2)}$ must be chosen to eliminate the second-order off-diagonal elements from $\bar{H}(\mathbf{P};\mathbf{g})$. By (13.7), this requires that

$$\{H_2+[H_1,S^{(1)}]+\tfrac{1}{2}[[H_0,S^{(1)}],S^{(1)}]+[H_0,S^{(2)}]\}_{mi}=0,\quad i\neq m,\tag{13.11}$$

or

$$\{p_{mm}{}^\alpha(-p_{mi}{}^\alpha/\omega_{mi})+(p_{mi}{}^\alpha/\omega_{mj})p_{ji}{}^\beta\}P^\alpha P^\beta+\omega_{mi}S_{mi}{}^{(2)}(\mathbf{P})=0,\quad i\neq m.\tag{13.12}$$

Here the band index j runs over all values except m. This equation can now be solved for $S_{mi}{}^{(2)}$. Recalling the anti-Hermitian property of $S^{(2)}$, we find

$$S_{mi}{}^{(2)}=-(S_{im}{}^{(2)})^\dagger=D_{mi}{}^{\alpha\beta}P^\alpha P^\beta,\tag{13.13}$$

where

$$D_{mi}{}^{\alpha\beta}=(1/\omega_{mi})\{(1/\omega_{mi})p_{mm}{}^\alpha p_{mi}{}^\beta-(1/\omega_{mj})p_{mj}{}^\alpha p_{ji}{}^\beta\},\quad i\neq m.\tag{13.14}$$

All other off-diagonal matrix elements of $S^{(2)}$ can be taken as zero. $S_{mm}{}^{(2)}$ is chosen so as to satisfy the condition (13.10) up to second order in P^α. This requires evidently that

$$\mathrm{Im}\{[\tfrac{1}{2}(S^{(1)})^2+S^{(2)}]\chi_{m\mathbf{h}}\}_{\mathbf{r}=0}=0.\tag{13.15}$$

Now,

$$\begin{aligned}&[\tfrac{1}{2}(S^{(1)})_j\chi_{m\mathbf{h}}]_{\mathbf{r}=0}\\ &=\tfrac{1}{2}\varphi_{m\mathbf{g}}(0)\sum_{i\neq m}\frac{p_{mi}{}^\alpha}{\omega_{mi}}\frac{p_{im}{}^\beta}{\omega_{im}}[P^\alpha P^\beta\exp(i\mathbf{h}\cdot\mathbf{r})]_{\mathbf{r}=0}\\ &=\tfrac{1}{2}\varphi_{m\mathbf{g}}(0)\sum_{i\neq m}\frac{p_{mi}{}^\alpha}{\omega_{mi}}\frac{p_{im}{}^\beta}{\omega_{im}}[\langle P^\alpha P^\beta\rangle_{\mathrm{Av}}\exp(i\mathbf{h}\cdot\mathbf{r})]_{\mathbf{r}=0}\\ &=\tfrac{1}{2}\varphi_{m\mathbf{g}}(0)\sum_{i\neq m}\frac{p_{mi}{}^\alpha}{\omega_{mi}}\frac{p_{im}{}^\beta}{\omega_{im}}\mathbf{h}^\alpha\mathbf{h}_\beta,\end{aligned}\tag{13.16}$$

and this is clearly real. The second term in (13.15) gives

$$\begin{aligned}[S^{(2)}\chi_{m\mathbf{h}}]_{\mathbf{r}=0}&=\varphi_{m\mathbf{g}}(0)[S_{mm}{}^{(2)}(\mathbf{P})\exp(i\mathbf{h}\cdot\mathbf{r})]_{\mathbf{r}=0}\\ &+\sum_{i\neq m}\varphi_{i\mathbf{g}}(0)\frac{1}{\omega_{im}}\left\{\frac{1}{\omega_{im}}(p_{ii}{}^\alpha p_{im}{}^\beta-p_{im}{}^\alpha p_{mm}{}^\beta)+\frac{1}{\omega_{km}}p_{ik}{}^\alpha p_{km}{}^\beta\right\}\\ &\times[P^\alpha P^\beta\exp(i\mathbf{h}\cdot\mathbf{r})]_{\mathbf{r}=0}.\end{aligned}\tag{13.17}$$

But

$$[P^\alpha P^\beta\exp(i\mathbf{h}\cdot\mathbf{r})]_{\mathbf{r}=0}=h^\alpha h^\beta+is^{\alpha\beta}.\tag{13.18}$$

Therefore, if we call

$$r_{i\mathbf{g}}\equiv\varphi_{i\mathbf{g}}(0)/\varphi_{m\mathbf{g}}(0),\tag{13.19}$$

then condition (13.15) requires that we choose

$$\begin{aligned}S_{mm}{}^{(2)}(\mathbf{P})=-\sum_{i\neq m}r_{i\mathbf{g}}(0)\frac{1}{\omega_{im}}\frac{1}{\omega_{im}}\Big\{&(p_{ii}{}^\alpha p_{im}{}^\beta-p_{im}{}^\alpha p_{mm}{}^\beta)\\ &+\frac{1}{\omega_{km}}p_{ik}{}^\alpha p_{km}{}^\beta\Big\}\tfrac{1}{2}[P^\alpha,P^\beta].\end{aligned}\tag{13.20}$$

Similarly we construct $S^{(3)}$. The result is

$$S_{im}{}^{(3)}=D_{im}{}^{\alpha\beta\gamma}P^\alpha P^\beta P^\gamma,\tag{13.21}$$

where

$$\begin{aligned}D_{im}{}^{\alpha\beta\gamma}&=\frac{1}{\omega_{im}}\\ &\times\left\{-p_{ij}{}^\alpha\left[\frac{1}{\omega_{jm}{}^2}(p_{ij}{}^\beta p_{jm}{}^\gamma-p_{jm}{}^\beta p_{mm}{}^\gamma)+\frac{1}{\omega_{jm}\omega_{km}}p_{jk}{}^\beta p_{km}{}^\gamma\right]\right.\\ &+\left[\frac{1}{\omega_{im}{}^2}(p_{ii}{}^\alpha p_{im}{}^\beta-p_{im}{}^\alpha p_{mm}{}^\beta)+\frac{1}{\omega_{im}\omega_{km}}p_{ik}{}^\alpha p_{km}{}^\beta\right]p_{mm}{}^\gamma\\ &+\delta^{\alpha\beta}\frac{p_{im}{}^\gamma}{\omega_{im}}-\frac{p_{im}{}^\alpha}{\omega_{im}}\delta^{\beta\gamma}\\ &\left.+\frac{1}{3}\left(\frac{3}{\omega_{im}\omega_{jm}}+\frac{1}{\omega_{jm}{}^2}\right)p_{im}{}^\alpha p_{mj}{}^\beta p_{jm}{}^\gamma\right\},\quad i\neq m\end{aligned}\tag{13.22}$$

while

$$S_{mm}^{(3)}(\mathbf{P})$$

$$=\left[\sum_{i\neq m} r_{ig}\left(\frac{1}{6}\frac{p_{im}^{\alpha}}{\omega_{im}}\frac{p_{mj}^{\beta}}{\omega_{mj}}\frac{p_{jm}^{\gamma}}{\omega_{jm}}-D_{im}^{\alpha\beta\gamma}\right)+D_{mi}^{\alpha\beta}\frac{p_{im}^{\gamma}}{\omega_{im}}\right]$$

$$\times(\tfrac{1}{2}[P^{\beta},P^{\gamma}]P^{\alpha}+\tfrac{1}{2}[P^{\alpha},P^{\gamma}]P^{\beta}+\tfrac{1}{2}[P^{\alpha},P^{\beta}]P^{\gamma}). \quad (13.23)$$

The transformation $S^{(4)}$ is not required for computing the m-m block of $\bar{H}(\mathbf{P};\,\mathbf{g})$ up to fourth order in P^{α} [see Eq. (13.7)].

Substituting our results for $S^{(1)}$, $S^{(2)}$, and $S^{(3)}$ in Eq. (13.7) gives the following result:

$$\bar{H}_m(\mathbf{P};\,\mathbf{g})=\bar{H}_{m;0}(\mathbf{P};\,\mathbf{g})+s\bar{H}_{m;1}(\mathbf{P};\,\mathbf{g})+s^2\bar{H}_{m;2}(\mathbf{P};\,\mathbf{g})+\cdots, \quad (13.24)$$

where

$$\bar{H}_{m;0}(0;\,\mathbf{g})=\epsilon_{mg},$$

$$\bar{H}_{m;1}(0;\,\mathbf{g})=0, \quad (13.25)$$

$$\bar{H}_{m;2}(0;\,\mathbf{g})=-\sum_{\alpha\beta\gamma\delta}\frac{\sigma^{\alpha\beta}\sigma^{\gamma\delta}+\sigma^{\alpha\gamma}\sigma^{\beta\delta}+\sigma^{\alpha\delta}\sigma^{\beta\gamma}}{s^2}E_m^{\alpha\beta\gamma\delta}(\mathbf{g}),$$

and

$$E_m^{\alpha\beta\gamma\delta}(\mathbf{g})=\frac{1}{\omega_{mi}}\left\{\frac{1}{\omega_{mj}}p_{mm}^{\alpha}p_{mj}^{\beta}-\frac{1}{\omega_{mi}}p_{mi}^{\alpha}p_{im}^{\beta}\right\}$$

$$\times\left\{\frac{1}{\omega_{mj}}p_{jm}^{\gamma}p_{mm}^{\delta}-\frac{1}{\omega_{mk}}p_{jk}^{\gamma}p_{km}^{\delta}\right\}$$

$$-\frac{1}{4}\frac{1}{\omega_{mi}^2}\{p_{mi}^{\alpha}p_{im}^{\beta}\delta^{\gamma\delta}-2p_{mi}^{\alpha}\delta^{\beta\gamma}p_{im}^{\delta}+\delta^{\alpha\beta}p_{mi}^{\gamma}p_{im}^{\delta}\}$$

$$-\frac{1}{2}\left(\frac{1}{\omega_{mi}^2\omega_{mk}}+\frac{1}{\omega_{mi}\omega_{mk}^2}\right)p_{mi}^{\alpha}p_{im}^{\beta}p_{mk}^{\gamma}p_{km}^{\delta}$$

$$-\sum_{i\neq m}\left[r_{ig}\left(\frac{1}{6}\frac{p_{im}^{\alpha}}{\omega_{im}}\frac{p_{mj}^{\beta}}{\omega_{mj}}\frac{p_{jm}^{\gamma}}{\omega_{jm}}-D_{im}^{\alpha\beta\gamma}\right)+D_{mi}^{\alpha\beta}\frac{p_{im}^{\gamma}}{\omega_{im}}\right]p_{mm}^{\delta}. \quad (13.26)$$

The coefficients $D_{im}^{\alpha\beta}$ and $D_{im}^{\alpha\beta\gamma}$ are defined in Eqs. (13.14) and (13.22).

Finally, using (13.25) and (13.26) in (12.26), we have now explicit expressions for $\bar{H}_{m;i}(\mathbf{k})$ for $i=0$, 1, and 2.

The absence of a term linear in s will be noted. It is easy to see in general that for the case of a crystal with a center of inversion, our construction leads to an expansion in even powers of s.

14. Application to Crystals without a Center of Inversion

In this section we construct the effective Hamiltonian for a crystal without a center of inversion. We again choose the phases of the φ_{ng} in accordance with the reality condition (13.1). But now, in contrast to the case of an inversion center, we have

$$p_{nn'}^{\alpha}(\mathbf{g})=q_{nn'}^{\alpha}(\mathbf{g})+it_{nn'}^{\alpha}(\mathbf{g}), \quad (14.1)$$

where q and t are real and in general neither vanishes.

We make the transformation (13.7) and find, as before, that

$$S_{mi}^{(1)}=-(S^{(1)})_{im}^{\dagger}=-(p_{mi}^{\alpha}/\omega_{mi})P^{\alpha}, \quad i\neq m. \quad (14.2)$$

However $S_{mm}^{(1)}$ does not now vanish. Instead, since

$$\bar{\varphi}_{m\mathbf{h}}(0;\,\mathbf{g})=\varphi_{mg}(0)+\left[\left(-\sum_{i\neq m}\varphi_{ig}(0)\frac{p_{im}^{\alpha}}{\omega_{im}}P^{\alpha}+\varphi_{mg}(0)S_{mm}^{(1)}(\mathbf{P})\right)\exp(i\mathbf{h}\cdot\mathbf{r})\right]_{\mathbf{r}=0}+\cdots, \quad (14.3)$$

the reality requirement leads to

$$S_{mm}^{(1)}(P)=D_{mm}^{\alpha}P^{\alpha}, \quad (14.4)$$

where

$$D_{mm}^{\alpha}=-i\sum_{i\neq m} r_{ig}\frac{t_{im}^{\alpha}}{\omega_{im}}. \quad (14.5)$$

This is enough to determine $\bar{H}_m(\mathbf{P};\,\mathbf{g})$ up to second order in P^{α}, which is as far as we shall go. By (14.7) we find

$$\bar{H}_m(\mathbf{P};\,\mathbf{g})=\epsilon_m(\mathbf{g})+p_{mm}^{\alpha}P^{\alpha}+\{\tfrac{1}{2}\delta^{\alpha\beta}+p_{mi}^{\alpha}p_{im}^{\beta}/\omega_{mi}-i(D_{mm}^{\alpha}p_{mm}^{\beta}-p_{mm}^{\alpha}D_{mm}^{\beta})\}P^{\alpha}P^{\beta}+\cdots. \quad (14.6)$$

$$\bar{H}_{m;0}(\mathbf{k})=\bar{H}_{m;0}(0;\,\mathbf{k})=\epsilon_m(\mathbf{k}),$$

$$\bar{H}_{m;1}(\mathbf{k})=\bar{H}_{m;1}(0;\,\mathbf{k})=\frac{\sigma^{\alpha\beta}}{s}\left\{\frac{1}{2\omega_{mi}}(p_{mi}^{\alpha}p_{im}^{\beta}-p_{mi}^{\beta}p_{im}^{\alpha})-i(D_{mm}^{\alpha}p_{mm}^{\beta}-D_{mm}^{\beta}p_{mm}^{\alpha})\right\}. \quad (14.7)$$

It will be noted that $H_{m;1}$ does now *not* vanish. In general it cannot be removed by any unitary transformation. This fact is of importance for the location of the energy levels in the presence of a magnetic field.

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APPENDIX A. DEMONSTRATION THAT NO SOLUTIONS ARE OMITTED

In Sec. 4 it was stated that the solutions of Eq. (4.17) give rise, through Eq. (4.1), to all solutions of the original Schrödinger equation $H\psi=E\psi$. As $\mathbf{k}$ was taken to be a continuous variable, the dimensionality of the Hilbert space spanned by the $\chi_{n\mathbf{k}}$ is nondenumerable. To avoid the associated mathematical difficulties, we shall here prove the corresponding result for a vector space of finite dimensionality and assume that it can be generalized to a Hilbert space of the above type.

Consider then a vector space of dimensionality D, spanned by the orthonormal basis vectors

$$\mathbf{e}_\alpha, \qquad \alpha=1,2,\cdots D \tag{A.1}$$

$$\mathbf{e}_\alpha{}^*\mathbf{e}_{\alpha'}=\delta_{\alpha\alpha'}, \quad \alpha,\alpha'=1,\cdots D. \tag{A.2}$$

Let H be a Hermitian Hamiltonian operator in this space, with matrix elements $(\alpha'|H|\alpha)$ defined by

$$H\mathbf{e}_\alpha=\sum_{\alpha'=1}^{D}\mathbf{e}_{\alpha'}(\alpha'|H|\alpha), \quad \alpha=1,2,\cdots D. \tag{A.3}$$

This operator has D orthonormal eigenvectors $\psi^{(i)}$:

$$H\psi^{(i)}=E^{(i)}\psi^{(i)}, \quad i=1,\cdots D \tag{A.4}$$

$$\psi^{(i)*}\psi^{(i')}=\delta_{ii'} \qquad i,i'=1,\cdots D. \tag{A.5}$$

Now consider a *redundant* set of normalized vectors

$$\mathbf{e}_\alpha, \quad \alpha=1,2,\cdots ND \tag{A.6}$$

the first D of which are identical with the basis (A.1). Let the effect of operating on these $\mathbf{e}_\alpha$ with H be described by a matrix $(\alpha'|H|\alpha)$, such that

$$H\mathbf{e}_\alpha=\sum_{\alpha'=1}^{ND}\mathbf{e}_{\alpha'}(\alpha'|H|\alpha), \quad \alpha=1,\cdots ND. \tag{A 7}$$

Because of the redundancy of the $\mathbf{e}_\alpha$, the matrix $(\alpha'|H|\alpha)$ is not completely defined by (A.7). But, in view of the completeness of the $\mathbf{e}_\alpha$, *some* matrix $(\alpha'|H|\alpha)$ certainly exists for which (A.7) holds. Finally assume that the matrix $(\alpha'|H|\alpha)$ is *Hermitian:*

$$(\alpha'|H|\alpha)^*=(\alpha|H|\alpha'). \tag{A.8}$$

This corresponds exactly to the situation of Sec. 4.

Now consider ND solutions of the eigenvalue problem

$$\sum_{\alpha'=1}^{ND}(\alpha|H|\alpha')A_{\alpha'}{}^{(l)}=E^{(l)}A_\alpha{}^{(l)}, \quad \alpha=1,\cdots ND. \tag{A.9}$$

These may be taken as orthonormal in the sense

$$\sum_{\alpha=1}^{ND}A_\alpha{}^{(l)*}A_\alpha{}^{(l')*}=\delta_{ll'}; \quad l,l'=1,\cdots ND. \tag{A.10}$$

In view of (A.7), the corresponding vectors

$$\boldsymbol{\varphi}^{(l)}=\sum_{\alpha'=1}^{ND}A_{\alpha'}{}^{(l)}\mathbf{e}_{\alpha'}, \quad l=1,\cdots ND \tag{A.11}$$

satisfy the equation

$$H\boldsymbol{\varphi}^{(l)}=E\boldsymbol{\varphi}^{(l)}, \quad l=1,\cdots ND. \tag{A.12}$$

Clearly, because of (A.1), *at most* D of these can be linearly independent.

We next show that also *at least* D of these $\psi^{(l)}$ are linearly independent. For, from (A.10) follow the reciprocal relationships

$$\sum_{l=1}^{ND}A_\alpha{}^{(l)*}A_{\alpha'}{}^{(l)}=\delta_{\alpha\alpha'}; \quad \alpha,\alpha'=1,\cdots ND. \tag{A.13}$$

Now multiplying (A.11) by $A_\alpha{}^{(l)*}$ and summing over l from 1 to ND gives, by (A.13),

$$\mathbf{e}_\alpha=\sum_{l=1}^{ND}A_\alpha{}^{(l)*}\boldsymbol{\varphi}^{(l)}, \quad \alpha=1,\cdots ND. \tag{A.14}$$

In particular therefore the D independent vectors $\mathbf{e}_1,\cdots,\mathbf{e}_D$ can be expressed linearly in terms of the $\boldsymbol{\varphi}^{(l)}$. Hence the latter must contain a linearly independent subset of D independent vectors, say

$$\boldsymbol{\varphi}^{(l_1)},\cdots\boldsymbol{\varphi}^{(l_D)}. \tag{A.15}$$

Since the $\boldsymbol{\varphi}^{(l_j)}$ are D independent solutions of the same eigenvalue problem (A.12) as the $\psi^{(i)}$, each $\psi^{(i)}$ must be a linear combination of the $\boldsymbol{\varphi}^{(l_j)}$. (If there is no degeneracy there must in fact be a one-to-one correspondence.) It follows *a fortiori* that each $\psi^{(i)}$ is a linear combination of *all* the $\boldsymbol{\varphi}^{(l)}$ $(l=1,\cdots ND)$ obtained from the solutions $A_\alpha{}^{(l)}$ of Eq. (A.9). Thus by solving (A.9) no solutions of the original eigenvalue problem (A.4) are lost.

APPENDIX B. REALITY OF MOMENTUM MATRIX ELEMENTS

Consider a crystal with a center of symmetry at $\mathbf{r}=0$. Let $\mathbf{g}$ be a general point in $\mathbf{k}$ space and choose the phases of the Bloch waves $\varphi_{n\mathbf{g}}$ such that

$$\mathrm{Im}[\varphi_{n\mathbf{g}}(0)]=0. \tag{B.1}$$

We shall then show that the momentum matrix elements are all real:

$$\mathrm{Im}[p_{nn'}{}^{\alpha}(\mathbf{g})]=0. \tag{B.2}$$

Let us first assume that at $\mathbf{g}$ none of the set of Bloch energies $\epsilon_n(\mathbf{g})$ coincide and that none of the $\varphi_{n\mathbf{g}}(0)$ vanish. Then if the function

$$\varphi_{n\mathbf{g}}(\mathbf{r})=u_{n\mathbf{g}}(\mathbf{r})\exp(i\mathbf{g}\cdot\mathbf{r}) \tag{B.3}$$

satisfies the Schrödinger equation and periodicity condition described by $\mathbf{g}$, so does

$$\varphi_{n\mathbf{g}}(-\mathbf{r})^* = u_{n\mathbf{g}}^*(-\mathbf{r}) \exp(i\mathbf{g}\cdot\mathbf{r}). \quad \text{(B.4)}$$

From the assumed nondegeneracy of the $\epsilon_n(\mathbf{g})$ we conclude that

$$u_{n\mathbf{g}}^*(-\mathbf{r}) = C u_{n\mathbf{g}}(\mathbf{r}), \quad \text{(B.5)}$$

where C is a numerical constant. Setting $\mathbf{r}=0$, we see that $C=1$, so that

$$u_{n\mathbf{g}}(-\mathbf{r}) = u_{n\mathbf{g}}^*(\mathbf{r}). \quad \text{(B.6)}$$

Now let us divide $u_{n\mathbf{g}}$ into a real and imaginary part:

$$u_{n\mathbf{g}}(\mathbf{r}) = v_{n\mathbf{g}}(\mathbf{r}) + i w_{n\mathbf{g}}(\mathbf{r}). \quad \text{(B.7)}$$

Then, by (B.6) we have

$$v_{n\mathbf{g}}(-\mathbf{r}) = v_{n\mathbf{g}}(\mathbf{r}), \quad \text{(B.8)}$$

$$w_{n\mathbf{g}}(-\mathbf{r}) = -w_{n\mathbf{g}}(\mathbf{r}). \quad \text{(B.9)}$$

But as the operator

$$p_\alpha \equiv (1/i)(\partial/\partial x_\alpha) \quad \text{(B.10)}$$

is odd under inversion we have

$$p_{nn'}{}^\alpha(\mathbf{g}) = \frac{(2\pi)^3}{\Omega}\int \varphi_{n\mathbf{g}}^* p^\alpha \varphi_{n'\mathbf{g}} d\mathbf{r} = \delta_{nn'} g^\alpha + \frac{(2\pi)^3}{\Omega}\int u_{n\mathbf{g}}^* p^\alpha u_{n'\mathbf{g}} d\mathbf{r} = \delta_{nn'} g^\alpha + \frac{(2\pi)^3}{\Omega}\int (v_{n\mathbf{g}} p^\alpha i w_{n'\mathbf{g}} - i w_{n\mathbf{g}} p^\alpha v_{n'\mathbf{g}}) d\mathbf{r}, \quad \text{(B.11)}$$

and in view of (B.10) this is clearly real.

At special points $\mathbf{g}$, where either of the conditions mentioned after Eq. (B.2) fails, the property (B.2) will still hold if one chooses $\varphi_{n\mathbf{g}}$ as the limit of $\varphi_{n\mathbf{g}'}$ where $\mathbf{g}' \to \mathbf{g}$.

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Self-Diffusion and Nuclear Relaxation in He^3

R. L. Garwin and H. A. Reich
International Business Machines Watson Laboratory at Columbia University, New York, New York
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Direct spin-echo measurements of diffusion coefficient (D) and spin relaxation time (T_1 and T_2) have been performed on He^3, with an accuracy $\sim$2% in the range 0.5°K to 4.2°K and at pressures to 67 atmos in the liquid, the solid, and in dilute solutions of He^3 in He^4. Unactivated diffusion is observed to the lowest temperatures in the liquid, but not in the solid. By measurement of D at 19 atmos we find an activation energy of 13.7°K for the production of scatterers in He II. There is an extended discussion of experimental details.

I. INTRODUCTION

In order to resolve some questions raised by thermodynamic measurements,[1] we began some time ago an experiment to measure by the spin-echo technique the nuclear susceptibility of pure liquid He^3 and so to exhibit the expected Fermi degeneracy. By the use of spin echoes[2] it is possible to obtain, in addition to the nuclear spin susceptibility, accurate values of the spin relaxation times, transverse T_2 and longitudinal T_1, and also of the diffusion coefficient[2,3] of a He^3 atom among other identical He^3 atoms or in He^4. It is on this last that we concentrated after the cw resonance measurements of the spin susceptibility appeared.[4]

In addition to studying the diffusion of a purely quantum particle among its identical neighbors, we expected to find for dilute solutions of He^3 in He^4 that the He^3 diffusion coefficient (under isothermal conditions with uniform concentrations) would increase rapidly with decreasing temperature below the λ point,[5] and we wanted to exhibit the absence of scattering of He^3 by He^4 at low temperatures.

Since both the actual diffusion coefficient and the spin relaxation time (both in liquid and in solid) are measured accurately ($\sim$2%) and independently in this experiment, we have also some information of interest in the general mechanisms of nuclear spin relaxation.[6]

Some examples of qualitative (and hence interesting) questions we hoped to answer are:

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