THE ELECTRON-PHONON INTERACTION IN NORMAL METALS

by

J. F. KENNEY

B.A., University of California at Berkeley
(1959)

M.S. Massachusetts Institute of Technology
(1963)

SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF
PHILOSOPHY

at the

MASSACHUSETTS INSTITUTE OF
TECHNOLOGY

February, 1967

Signature of Author________________________________
Department of Physics, 6 February 1967

Certified by________________________________
Thesis Supervisor

Accepted by________________________________
Chairman, Departmental Committee
on Graduate Students

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J.F. Kenney

ABSTRACT

The prohibitively cumbersome exact Hamiltonian for the combined system of electrons and nuclei in a crystalline solid is simplified into a Fröhlich-type Hamiltonian

$$H = \sum_{\vec{q},s} \left(\hbar\omega(\vec{q},s) + 1/2\right) a^+_{\vec{q},s}\, a_{\vec{q},s} + \sum_{\vec{k}} \left(\epsilon(\vec{k}) - \frac{1}{2} v_e(\vec{k})\right) c^+_{\vec{k}}\, c_{\vec{k}} +$$

$$+ i \sum_{\vec{k}} \sum_{\vec{q},s} D(\vec{k},\vec{q},s)\, c^+_{\vec{k}+\vec{q}}\, c_{\vec{k}} \left(a_{\vec{q},s} - a^+_{-\vec{q},s}\right) .$$

The Adiabatic Principle is explained and used to approximate the eigenfunctions of the solid by products $\tau(x,R) = \Psi_e(x,R)\, \Phi_n(R)$ of electronic $\left(\Psi_e(x,R)\right)$ and nuclear $\left(\Phi_n(R)\right)$ eigenfunctions. The electronic system is further approximated by an independent-particle model for which the electronic eigenstates are Slater determinants of one-electron orbitals. Within the framework of this model, the set of terms which describe the coupling of the electronic and nuclear systems,

$$i \sum_{\vec{k}} \sum_{\vec{q},s} D(\vec{k},\vec{q},s)\, c^+_{\vec{k}+\vec{q}}\, c_{\vec{k}} \left(a_{\vec{q},s} - a^+_{-\vec{q},s}\right) ,$$

is shown to arise from the effect of the nuclear momentum operator acting upon the electronic orbitals

$$i\hbar \int \psi^*_{\vec{k}+\vec{q}}(\vec{x};R) \left(\frac{d}{dR_{m,i}}\left(\psi_{\vec{k}}(\vec{x};R)\right)\right) d\vec{x} .$$

In order to solve for the derivative

$$\frac{d}{dR_{m,i}}\left(\psi_{\vec{k}}(\vec{x};R)\right) ,$$

the energy band problem for both the single-particle orbital $\psi(\vec{x}_k;R)$ and for the eigenvalue to which it belongs are set up and solved for the deformed lattice by the method of Augmented Plane-Waves (A.P.W.) Because the eigenvalues and eigenfunctions for the perfect lattice result from the A.P.W. variational calculation, such that the band energies are stationary

$$\frac{\delta\epsilon(\vec{k})}{\delta(\psi_{\vec{k}})} = 0 ,$$

it must be shown that the eigenvalues for the deformed lattice are invariant up to orders quadratic in the nuclear variations $\delta R_{m,i}$. The full secular determinant of order $10^{25} \times 10^{25}$ for the deformed lattice is set up and formerly expanded by minors retaining only terms of order quadratic or less in $\delta R_{m,i}$. The zeroes of this A.P.W. secular determinant are ascertained by transforming the summations over $\vec{k}$-vectors into an integration in the complex energy plane. The secular determinant for the deformed lattice is then inverted to ascertain to eigenfunction, and it is established that the derivative

$$\frac{d}{dR_{m,i}}\left(\psi_{\vec{k}}(\vec{x}_k;R)\right) = \sqrt{\frac{1}{A(k)}}\sum_j a^{\epsilon^0(k)}(\vec{k}+\vec{K}_j) \times \frac{e^{i\vec{k}\cdot\vec{R}_m}}{\sqrt{N}}\Big(i(\vec{k}+\vec{K}_j)_i\varphi_{\vec{k}+\vec{K}_j}(\vec{x}-\vec{R}_m)$$

$$- \vec{\nabla}_i\,\varphi_{\vec{k}+\vec{K}_j}(\vec{x}-\vec{R}_m)\Big) ,$$

neglecting corrections of the order of N^{-1} the size of the above, and where $\varphi_{\vec{k}+\vec{K}_j}(\vec{x})$ represents the A.P.W. trial function $\psi_{\vec{k}+\vec{K}_j}(\vec{x})$ minus its plane-wave component $e^{i(\vec{k}+\vec{K}_j)\cdot\vec{x}}$.

The single-coordinate electronic potential $v_e(\vec{x};R)$ and its requirements of self-consistency are discussed at length. It is shown that the self-consistent potential generated by the electrons in the eigenstates of the deformed lattice is substantially different from the rigidly translated perfect lattice potential. This result considerably qualifies the results of the commonly used Rigid-Ion approximation. However, it is also shown that the correct self-consistent potential for the deformed lattice contributes additional corrections to the derivative above which are of the order of N^{-1} times the original expression.

Submitted to the Department of Physics on 9 January 1967 in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Thesis Supervisor:	George F. Koster
Title:	Professor of Physics.

TABLE OF CONTENTS

Chapter		Page
	ABSTRACT	1
	TABLE OF CONTENTS	4
I	THE ELECTRON-PHONON INTERACTIONS	6
II	THE ADIABATIC PRINCIPLE	13
III	THE TOTAL HAMILTONIAN AND THE INDEPENDENT-PARTICLE MODEL	21
	III.1 The Simplification of the Potential Energy Terms . .	21
	III.2 The Independent Particle Model	24
	III.3 The A.P.W. Method	30
IV	THE MATRIX ELEMENTS OF THE ELECTRON-PHONON INTERACTION IN THE ADIABATIC MODEL	42
	IV.1 The Expectation Values of the Total Hamiltonian for the System of Electrons and Nuclei	42
	IV.2 Evaluation of the Non-Adiabatic Terms Involving the Double Derivatives	48
	IV.3 The Electron-Phonon Vertex Function by the A.P.W. Formalism	59
V	THE ENERGY BAND PROBLEM FOR A DEFORMED LATTICE	65
	V.1 The Matrix Elements for the Band Energies when a Single Nucleus is Displaced	65
	V.2 The Solution to the Variational Eigenvalue Problem for an Electron in a Deformed Lattice: Expansion of the Secular Determinant	74
	V.3 Evaluation of the Expanded Secular Determinant . . .	88
	V.4 The Eigenfunctions for the Deformed Lattice.	95

Chapter | Page

VI THE CRYSTALLINE POTENTIAL IN A DEFORMED LATTICE 108

VI.1 The Problem of the Self-Consistency of the Crystalline Potential in a Deformed Lattice 108
VI.2 Further Remarks Upon Self-Consistency. The Phenomenon of Shielding 135
VI.3 The Virtues of the A.P.W. Method and the Vices of the Rigid-Ion Model 143

APPENDIX 150

ACKNOWLEDGMENTS 157

BIBLIOGRAPHY 158

BIOGRAPHICAL NOTE 161

CHAPTER I

THE ELECTRON-PHONON INTERACTIONS

The dynamics of matter in the crystalline solid state is conventionally described in terms of the normal-mode vibrations of the nuclei or ions forming the crystal lattice, — the phonons, — and in terms of the energetics and characteristics of the mobile electrons, which themselves are usually described by an independent-particle formalism[1-9].

The interactions between these lattice waves and the mobile electrons, — the electron-phonon interactions, — have traditionally been thought to occupy a position of secondary importance, at least for many problems and always for those problems which concern themselves solely with properties of one or the other of the two aspects of the dynamical system alone.

It has long been recognized that the electron-phonon interactions dominate transport theory: the study of electrical and thermal resistivity[1,2,4,5,6]. These interactions are responsible for all thermo-electric effects[1,6,11] and for the attenuation of ultrasonic radiation in metals[12]. Furthermore these interactions produce such phenomena as the Jahn-Teller Effect in solids[13,14,15] and the existence of the polaron in, say, ionic crystals or covalent semiconductors in their intrinsic regions[16,17,18]. The electron-phonon interactions are also responsible for the phenomenon superconductivity[19,20].

The traditionally subordinate position which the electron-lattice interactions have held has been allowed for essentially three reasons.

The first reason, as has been already stated, is because such effects have been considered to be of no consequence when studying some property of one aspect of the dynamics of the solids, e.g., the cyclotron-resonance frequency of the conduction electrons. In short, the two aspects of the dynamics have been usually thought of as two decoupled, independent dynamical systems: one, the system of phonons; the other, that of the conduction electrons. This conceptual picture is flatly wrong, as we shall demonstrate; and most of the empirical constants traditionally believed to be properties of the electronic system independent of the lattice vibrations (e.g., the electron plasma-oscillation frequency, $\omega_{p\ell}$, the Pauli susceptibility, X_p, the linear term, γ, in the specific heat, $(\gamma T + \beta T^3)$ will be shown to depend considerably upon the energies of the lattice waves through the electron-phonon interaction.

The second reason for the traditional disregard of the electron-phonon interactions is that the strength of these interactions has been thought to be small, at least with respect to the energies of the electrons involved, as measured by, say, some coupling constant in a perturbation theory formalism. Such is a fundamental misunderstanding. An important parameter which can be associated with the strength of the electron-phonon interaction (if one takes a certain perspective) is

$$\epsilon_F\left(\frac{\epsilon_F}{Mc_3^2/2}\right) , \qquad \text{(I.1)}$$

where ϵ_F is the Fermi energy, M the nuclear mass, and c_s the velocity of sound of the solid. This parameter is on the order of ϵ_F. As a demonstration, for sodium,[21]

$$c_s = 3 \times 10^5 \text{ cm/sec}$$

$$M = 23 \text{ nuclear masses}$$

$$\epsilon_F = 2.3 \text{ ev.} ,$$

such that

$$\frac{\epsilon_F}{Mc_s^2/2} \sim \frac{1}{3} .$$

The third reason for the usual neglect of these interactions has been the (previous) uncertainty concerning not only the form of the interaction but also the values of the constants appearing in it.

About a decade ago, Frohlich[22] hypothesized that the complete Hamiltonian for the solid could be expressed as

$$\text{H(Frohlich)} = \sum_{\vec{k}} \epsilon(\vec{k})\, c^+_{\vec{k}}\, c_{\vec{k}} + \sum_{\vec{q},s} \hbar\, \omega_s(\vec{q})\, a^+_{\vec{q},s}\, a_{\vec{q},s}$$

$$+ i \sum_{\substack{\vec{q},s \\ \vec{k}}} D_s(\vec{k}+\vec{q},\vec{k})\, c^+_{\vec{k}+\vec{q}}\, c_{\vec{k}} \left(a_{\vec{q},s} + a^+_{-\vec{q},s}\right) . \qquad \text{(I.2)}$$

This Hamiltonian operator is written in the Second-Quantization formalism pertaining to quantum field theory. Its expectation values are taken between states in occupation-number space and have exactly the same values as has the equivalent operator in the Schrodinger representation taken between spatial wave functions. In (I.2) $\epsilon(\vec{k})$ is the single-particle energy of the electron belonging to the wave-vector $\vec{k}$; c_k^+ and c_k are, respectively, the creation and annihilation operators for an electron of wave-vector $\vec{k}$; $\omega_s(\vec{q})$ is the normal mode frequency of the phonon of wave-vector $\vec{q}$ and band index s, and a_q^+ and a_q are, respectively, the creation and annihilation operators for that phonon; $D_s(\vec{k}+\vec{q},\vec{k})$ is the matrix element associated with the electron-phonon interaction involving an electron transition from wave-vector $\vec{k}$ to wave-vector $\vec{k}+\vec{q}$ accompanied by either the absorbtion (a_q) or emission (a_{-q}^+) of a phonon of wave-vector $\vec{q}$ and band index s. Frohlich developed his Hamiltonian (I.2) in an ad hoc fashion using "plausibility," arguments starting from the assumption that the electrons and the phonons were almost independent systems and that their coupling was weak. He further argued that the dependence of the matrix element $D(\vec{k}+\vec{q},\vec{k})$ should be of the form,

$$D(k+q,k) = c\sqrt{\frac{\hbar}{2NM\,\omega_s(q)}}\,|\vec{q}|\;, \tag{I.3}$$

where $\hbar$ is Planck's quantum of action; N is the number of nuclei in the crystal; and M, $\omega_s(q)$, $\vec{q}$ are as defined above. The constant c has the dimensions of energy and, Frohlich argued, should be of the same order of magnitude as the energy of the $\vec{k}$-th electron, $\varepsilon(k)$. The constant c is often called Wilson's Constant, after A.H. Wilson[4] who calculated it to be,

$$c = \left(\frac{2}{3}\right)\frac{\hbar^2}{2m}\int |\vec{\nabla} u_k|^2\, d + \int V_{crys}\, |u_k|^2\, d \;, \tag{I.4}$$

where $u_k(r)$ is a factor in the Bloch eigenfunction,

$$\psi_k(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}\, u_k(\vec{r}) \;\; . \tag{I.5}$$

In his analysis of the coupling between the electrons and the lattice waves, Wilson assumed that the interaction is attributable entirely to the variation of the crystalline potential due to the motion of the nuclei in the presence of a lattice vibration wave. This assumption is both inadequate and conceptually dissatisfying. It is inadequate because there are additional sources for the coupling which must be taken into account. It is conceptually unreasonable because it ascribes the majority of the interaction to that region of the crystal cell where the variation of the crystalline potential is greatest, to wit, near the nucleus. Common sense as well as the detailed studies of crystalline electronic wave functions tells us that near the nucleus the electronic wave function in the crystal is very nearly identical to the wave function in the free atom. In that region, shielded by the outer core electrons, the conduction electron will be impervious to the relative motions of the other atoms in the lattice, and its eigenstate and energy will no more there depend upon the motion of its own nucleus than does the state and energy of the electron in the free atom depend upon its center-of-mass motion.

Frohlich's Hamiltonian has more inadequacies besides the usual misestimate of Wilson's Constant. To begin with, his initial assumption that the conduction electrons and the lattice vibrations are essentially independent aspects of the crystal dynamics is quite incorrect, as we argue further in Chapter II. Furthermore, the total energy of the electronic system cannot be represented simply as the sum of the single-particle energy eigenvalues of each electron but must be corrected by subtracting from that sum one half of the sum of the energies of the Coulomb interactions between all the electrons. This last arises because the potential function which enters into the single-particle Hamiltonian, $H_e(x)$, where

$$H_e(\vec{x})\ \psi_k(\vec{x}) = \varepsilon(k)\ \psi_k(\vec{x}) \quad , \tag{I.6}$$

involves some average of the sum of the two-particle interaction potential between the $\vec{k}$-th (here) electron and all the others. Therefore, when summing the eigenvalues, $\varepsilon(k)$, one is counting the expectation values of the two-particle interaction energies twice. Hence the necessary correction, which Frohlich neglects.

The Frohlich Hamiltonian has been used for many investigations of phenomena involving the electron-phonon interactions and has rendered modestly good predictions. Considering the conceptual and mathematical errors involved in its derivation, this is somewhat surprising, even when allowing for a great elasticity admitted to its conclusions by an empirically fitted Wilson's Constant.

For these reasons, our investigations shall include a logical derivation of Frohlich's Hamiltonian. We shall show explicitly the approximations and simplifications involved in its development; and we shall calculate explicitly the correct Wilson's Constant.

CHAPTER II

THE ADIABATIC PRINCIPLE

The dynamics of matter in the solid state is determined by the Hamiltonian operator,

$$H_{\text{total}} = \sum_{\vec{R}_n} \sum_{\vec{x}_i} \left\{ -\frac{\hbar^2}{2M} \nabla_n^2 - \frac{\hbar^2}{2M} \nabla_i^2 - \frac{Ze^2}{|\vec{R}_n - \vec{x}_i|} + \frac{1}{2} \sum_{j \neq i} \frac{e^2}{|\vec{x}_i - \vec{x}_j|} + \frac{1}{2} \sum_{m \neq n} \frac{Z^2 e^2}{|\vec{R}_m - \vec{R}_n|} \right\} . \quad \text{(II.1)}$$

This operator describes the total energy of the system in its nonrelativistic limit and in the absence of any external fields. The specification of the energy spectrum of the solid obtains from the eigenvalues of this Hamiltonian operator, and the description of the properties of the solid depends upon the eigenstates belonging to those eigenvalues. The eigenvalue equation for the solid is

$$H_{\text{total}} \Psi\left(\left\{\vec{x}_i\right\}\left\{\vec{R}_n\right\}\right) = E_{\text{total}} \Psi\left(\left\{\vec{x}_i\right\}\left\{\vec{R}_n\right\}\right) . \quad \text{(II.2)}$$

Because the operator H_{total} involves a number of independent coordinates on the order of $10^{22} - 10^{23}$, no exact solution to equation (II.2) can be obtained at present, and we must seek useful and accurate approximations to its solutions.

The first approximation introduced is suggested by the division of the Hamiltonian operator into two parts:

$$H_{\text{total}} = H_{\text{nuclear}}(R) + H_{\text{electronic}}(x,R) \quad , \qquad (\text{II}.3)$$

where

$$H_{\text{nuclear}}(R) = \sum_{\vec{R}_n} \left\{ \frac{-\hbar^2}{2M} \nabla_n^2 + \frac{1}{2} \sum_{m \neq n} \frac{Z^2 e^2}{|\vec{R}_n - \vec{R}_m|} \right\} \qquad (\text{II}.4)$$

and

$$H_{\text{electronic}}(x,R) = \sum_{i} \left\{ \frac{-\hbar^2}{2M} \nabla_i^2 - \sum_{R_n} \frac{Ze^2}{|\vec{x}_i - \vec{R}_n|} + \frac{1}{2} \sum_{j \neq i} \frac{e^2}{|\vec{x}_i - \vec{x}_j|} \right\} . \qquad (\text{II}.5)$$

It is observed that the operator $H_{\text{nuclear}}(R)$ involves only the nuclear coordinates, $\{\vec{R}_n\}$. The electronic coordinates, $\{\vec{x}_i\}$, enter only the operator $H_{\text{electronic}}(x,R)$, and, furthermore, the nuclear coordinates enter $H_{\text{electronic}}(x,R)$ only in the potential energy sum,

$$\sum_{R_n} \frac{-Ze^2}{|\vec{x}_i - \vec{R}_n|} .$$

The simplifying hypothesis which permits the separation of the dynamical problem of the nuclei from that of the electrons is as follows:

Because the mass of the electrons is so very much smaller than that of the nuclei, —

$$\frac{m}{M} \sim 10^{-4} - 10^{-5} \quad , \qquad \text{(II.6)}$$

the mobile electrons always follow the motion of the nuclei instantaneously and smoothly, and the state of the electronic system is, at any instant, the equilibrium electronic state for that particular nuclear arrangement.

This is the *Adiabatic Principle*.[23,24,25]

An immediate consequence of the Adiabatic Principle is that, within the limits of the principle's validity, the total eigenstate of the solid can be represented as the product of eigenstates of the nuclear and the electronic systems, respectively, i.e.,

$$\Upsilon\left(\{\vec{x}\}, \{\vec{R}\}\right) = \Psi_{\text{electronic}}\left(\{\vec{x}_i\}, \{\vec{R}_n\}\right) \Phi_{\text{nuclear}}\left(\{R_n\}\right) \qquad \text{(II.7a)}$$

or, simply

$$\Upsilon(x,R) = \Psi_e(x,R)\ \Phi_n(R) \quad . \qquad \text{(II.7b)}$$

Because the electronic coordinates enter only the electronic Hamiltonian, $H_{\text{electronic}}(x,R)$, as noted above, the eigenfunction of the electronic system satisfies the equation,

$$H_e(x,R)\ \Psi_{e,j}(x;R) = \mathcal{E}_{e,j}(R)\ \Psi_{e,j}(x;R) \quad . \qquad \text{(II.8)}$$

We observe that equation (II.8) is not only an eigenvalue equation pertinent to the eigenvalue $\mathcal{E}_{e,j}(R)$, but also that it is a parametric equation in the 3Nz nuclear coordinates, $\{\vec{R}_n\}$ (where z equals the number of atoms per unit Wigner-Seitz cell). The eigenvalue $\mathcal{E}_{e,j}(R)$ is a parametric function of the nuclear coordinates, as are $H_e(x,R)$ and $\Psi_{e,j}(x;R)$.

There area few remarks that should be made at once concerning the consequences, interpretation and usefulness of the Adiabatic Principle and of such approximate eigenstates as (II.7).

First, a consequence which does not derive from the Principle:

This point of view,— and the use of eigenstates such as (II.7), — does not decouple the systems of electrons and nuclei. We expect that this fact needs stating explicitly, for a picture of solids (metals, especially) commonly held is that of a system of electrons decoupled from a system of nuclei (or ions), which systems interact with one another but weakly. This simple picture appears to be supported by a substantial amount of experimental evidence. For one example, the specific heat of a metal can be expressed as the sum of the independent contributions of the electronic and vibrational specific heats, i.e.,

$$C_v(T) = C_v(\text{electronic})\ T + C_v(\text{lattice})\ T^3 \quad , \qquad \text{(II.9)}$$

suggesting that the total energy of the solid is the sum of the energies of the electrons and nuclei — a characteristic of independent systems. In fact, such is a misinterpretation of equation (I.9); and one important conclusion of this investigation is that the interaction between the dynamical behaviour of the nuclear and electronic systems strongly influences the quantities C_v(electronic) and C_v(lattice) entering (II.9). For another misleading example, when deriving the electrical conductivity of metals, the effect of the motion of the nuclei upon the conduction electrons can be fairly accurately calculated using perturbation theory.

What the Adiabatic Principle does, in fact, say is that if the nuclei have just changed one configuration, say $\Phi_n(R)$, to another, say $\Phi_n(R')$, the system of electrons will inevitably be found in the equilibrium configuration pertinent to that nuclear arrangement, i.e., $\Psi_e(x;R')$, however, abrupt the nuclear transition may have been. Which is to say that the electronic system, far from being independent of the nuclear motion, follows it perfectly, and that after such a transition,

$$\Phi_n(R) \rightarrow \Phi_n(R') \quad ,$$

there is no part of the electronic system "left" in the state $\Psi_e(x;R)$. The limits of the validity of the Adiabatic Principle depend upon the ratio of the electron velocity, v_k, to the velocity of sound, c_s, and upon a relaxation time, $\tau(e^- - \text{ph})$, characteristic of the actual (not instantaneous) response of the electrons to nuclear motion. The extent of these limits and their influence upon the results of calculations made using the Adiabatic hypothesis are discussed in Chapter VII.

Second, on the usefulness of the formation of the Adiabatic Principle:

The usefulness of the type of eigenstates for the electronic system pertinent to the Adiabatic model, i.e.,

$$\Psi_e(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_N; \vec{R}_1, \vec{R}_2, \ldots, \vec{R}_m) \ , \qquad \text{(II.10)}$$

is usually limited to physical systems where either the variation of the electronic eigenstates with the parameters R is small or where the motions of the nuclei are severely restricted. The reason for this limitation is simple. Except for the circumstance wherein the temperature of the system is at absolute zero, the nuclei will be always in motion. Therefore an eigenfunction like (II.10) will be constantly changing, and one can not calculate any stationary or universally significant quantity of the electronic system, such as, e.g., total energies, charge or current densities, magnetic moment, etc. In such cases, one is restricted to calculating some time-averaged quantity associated with the property under investigation — a procedure which is both conceptually unsatisfactory and which introduces new complications into the analysis.

An example of a problem for which the Adiabatic Model is useful by virtue of the first condition, — a very small variation of the electronic eigenfunction with respect to variations of the nuclear coordinates, — is that of the conduction electrons in a periodic lattice. That is the problem which we address here.

Because the nuclei in a crystal lattice are always in motion (at temperatures not equal to absolute zero), the electronic eigenfunction is varying at every instant of time. Furthermore, because the interaction between a nucleus and an electron is very large in the vicinity of the nucleus, a change in the nuclear position will expectedly work a considerable change upon the electronic probability amplitudes (wave-functions), at least in its neighborhood. Thus we must address the problem of solving for the electronic eigenfunction at all nuclear spatial arrangements.

This general and extensive problem is rendered tractable by two properties of the crystal lattice. First, all possible motions of the nuclei are known and counted for temperatures below the melting point. These are the Normal-mode lattice vibrations (phonons), characterized each by their respective normal-mode frequencies, $\omega_s(q)$, their wave-vectors within the first Brillouin Zone, $\vec{q}$, and their band indices, s. Second, the functional dependence of the electronic eigenfunctions upon all the nuclear coordinates is known explicitly through the dependence of the tight-binding components of the one-electron orbitals, which have the form,

$$\psi_{\vec{k}}(\vec{x}_k;\vec{R}) \sim \sum_{R_n} e^{i\vec{k}\cdot\vec{R}_n} \varphi_k(\vec{r}-\vec{R}_n) \quad . \qquad (II.11)$$

These two properties will permit us to write the electronic eigenfunction for all nuclear arrangements in terms of the derivatives of the electronic eigenfunctions and the normal mode amplitudes. This particular approach has been described succinctly as, "substituting for the solution of one general and very difficult problem the equivalent solutions to 10^{23} easy ones."

The specific technique which we use is simply to express the electronic eigenfunction at a general set of nuclear coordinates as a Taylor series expansion about the equilibrium (or zero-temperature) set of nuclear coordinates. Furthermore, because the electronic system is conventionally (and most easily) described in terms of the electronic eigenfunctions belonging to the equilibrium-position nuclear coordinates,

$$\left\{ \Psi_{e,j}(\vec{x};R^{\circ}) \right\} , \tag{II.12}$$

we express each term in the Taylor series as a linear combination of these.

Finally, an example of a problem for which the Adiabatic Principle is of little use, although of no less validity, is that of a fully ionized plasma at sufficiently low density and high temperature so as to be in the non-degenerate regime. For this system, the rapid and complicated motions of the positively-charged nuclei render the solutions of the electronic Hamiltonian of the form, $\Psi_e(x,R)$, practically unobtainable.

CHAPTER III

THE TOTAL HAMILTONIAN AND THE INDEPENDENT-PARTICLE MODEL

III.1 The Simplification of the Potential Energy Terms.

As has been stated in equations (II.1) and (II.3), (II.4), the operator representing the total energy of the solid is,

$$H_{\text{total}} = \sum_{R_n} \left(\frac{-\hbar^2}{2M} \nabla_n^2 + \frac{1}{2} \sum_{R_m \neq R_n} \frac{Z^2 e^2}{|\vec{R}_n - \vec{R}_m|} \right) +$$

$$+ \sum_i \left(\frac{-\hbar^2}{2m} \nabla_i^2 - \sum_{R_n} \frac{Z e^2}{|x_i - R_n|} + \frac{1}{2} \sum_{j \neq i} \frac{e^2}{|\vec{x}_i - \vec{x}_j|} \right) . \quad \text{(III.1.1)}$$

The potential energy terms in equation (III.1.1) which describe, respectively, the nuclear-nuclear Coulomb repulsion,

$$+ \frac{1}{2} \sum_{R_m \neq R_n} \frac{Z^2 e^2}{|\vec{R}_n - \vec{R}_m|} , \qquad \text{(III.1.2a)}$$

the electron-electron repulsion,

$$+\frac{1}{2}\sum_{i}\sum_{j\neq i}\frac{e^2}{|\vec{x}_i-\vec{x}_j|}\ , \qquad \text{(III.1.2b)}$$

and the electron-nuclear Coulomb attraction,

$$-\sum_{i}\sum_{\vec{R}_m}\frac{Z\,e^2}{|\vec{x}_i-\vec{R}_m|}\ , \qquad \text{(III.1.2c)}$$

can be combined so as to eliminate the long-range $|R|^{-1}$ interaction. This simplification is affected by using the translational symmetry of the crystal and introducing the coordinate transformation,

$$\vec{x}'_j=\vec{x}_j-\vec{R}_m\ , \qquad \text{(III.1.3a)}$$

where the <u>cellular coordinates</u>, $\vec{x}'_j$, are restricted to the range set by the limits of the Wigner-Seitz cell,

$$0\le x'_j\le a_o\ . \qquad \text{(III.1.3b)}$$

When the operators for the electron-nuclear attraction and the electron-electron repulsion are written, respectively, in a polar and bipolar expansion, the lowest order terms, — which go as,

$$\sum_{R_n \neq R_m} \frac{1}{|\vec{R}_n - \vec{R}_m|}$$

cancel the nuclear-nuclear repulsion exactly, because the periodicity of the crystal requires that each Wigner-Seitz unit cell be electrically neutral.[26] Thus, the total Hamiltonian can be written simply as,

$$H_{\text{total}} = \sum_{\vec{R}_n} \frac{-\hbar^2}{2M} \nabla_n^2 + \sum_i \left[\frac{-\hbar^2}{2m} \nabla_i^2 - \frac{Z\,e^2}{|\vec{x}_i|} + \frac{1}{2} \sum_{j \neq i} \frac{e^2}{|\vec{x}_i' - \vec{x}_j'|} + \right.$$
$$\left. + \sum_{R_n \neq 0} \left(-a(\vec{x}_i', \vec{R}_n) + \frac{1}{2} \sum_{j \neq i} r(\vec{x}_i', \vec{x}_j', \vec{R}_n) \right) \right] , \quad (\text{III}.1.4)$$

where both $-a(\vec{x}_j', \vec{R}_n)$ and $r(\vec{x}_i', \vec{x}_j', \vec{R}_n)$ go as R^{-p} for $p \geq 2$. Accordingly, the total Hamiltonian may be separated as,

$$H_{\text{total}}(x,R) = -\sum_{\vec{R}_n} \frac{h^2}{2M} \nabla_n^2 + H_e(\text{cellular}) \ , \qquad (\text{III}.1.5)$$

where

$$H_e(\text{cellular}) = \sum_i \left[\frac{-\hbar^2}{2m} \nabla_i^2 - \frac{Z\,e^2}{|\vec{x}_i'|} + \frac{1}{2} \sum_{j \neq i} \frac{e^2}{|\vec{x}_i' - \vec{x}_j'|} + \right.$$
$$\left. + \sum_{R_n} \left(-a(\vec{x}_i, \vec{R}_n) + \frac{1}{2} \sum_{j \neq i} r(\vec{x}_i', \vec{x}_j', \vec{R}_n) \right) \right] . \quad (\text{III}.1.6)$$

III.2 The Independent Particle Model.

As has been made clear in Section II, the calculation of the dynamical properties of a system of electrons and nuclei begins, — when using the adiabatic hypothesis, — with the calculation of the eigenfunctions $\Psi_e(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_N; \vec{R}_1, \vec{R}_2, \ldots, \vec{R}_N)$ of the electronic Hamiltonian, $H_e(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_N; \vec{R}_1, \vec{R}_2, \ldots, \vec{R}_N)$, for some specific nuclear arrangement. For crystalline solids, the arrangement of the nuclei chosen is usually (and herein) that pertinent to the temperature absolute zero. The first problem then is to ascertain the eigenstates of the Hamiltonian,

$$\sum_i \left[\frac{-\hbar^2}{2m} \nabla_i^2 - \frac{Z\,e^2}{|\vec{x}_i'|} + \frac{1}{2} \sum_{j \neq i} \frac{e^2}{|\vec{x}_i' - \vec{x}_j'|} + \sum_{R_n \neq 0} \left(-a(\vec{x}_i', \vec{R}_n^o) + \frac{1}{2} \sum_{j \neq i} r(\vec{x}_i', \vec{x}_j', \vec{R}_n^o) \right) \right] \Psi_e(\vec{x}; \vec{R}^o)$$

$$= H_e(\vec{x}, \vec{R}^o)\, \Psi_e(\vec{x}; \vec{R}) = \mathcal{E}_e(R^o)\, \Psi_e(\vec{x}; \vec{R}^o) \;. \qquad \text{(III.2.1)}$$

Now, because the number of electrons in a given crystal is on the order of 10^{21} - 10^{22} cm^{-3}, this problem also presents insuperable difficulties to finding the exact eigensolutions, quite independently of any difficulties associated with the motion of the nuclei. In order to calculate reasonable approximate solutions to equation (III.2.1) we introduce the following simplification: every electron is assumed to move independently of the motion of all the other electrons in the average potential field produced by them. This simplification amounts to performing some average summation of the terms in the electron Hamiltonian which represent the electron-electron Coulomb interaction, i.e.,

$$\sum_{j\neq i} \frac{e^2}{|\vec{x}'_i-\vec{x}'_j|} + \sum_{\vec{R}_n\neq 0} r(\vec{x}'_i,\vec{x}'_j,\vec{R}_n) \equiv$$

$$\equiv \frac{\left(\sum_{j\neq i} \underbrace{\int\cdots\int}_{N-1} \Psi^*_e(\vec{x}'_1,\dots,\vec{x}'_N;\vec{R}_1,\dots,\vec{R}_N) \frac{e^2}{|\vec{x}'_i-\vec{x}'_j|} \Psi_e(\vec{x}'_1,\dots,\vec{x}'_N;\vec{R}_1,\dots,\vec{R}_N)\, d\vec{x}'_1,\dots,\widehat{d\vec{x}'_i},\dots,d\vec{x}'_N\right)}{\left(\underbrace{\int\cdots\int}_{N-1} \Psi^*_e(\vec{x}'_1,\dots,\vec{x}'_N;\vec{R}_1,\dots,\vec{R}_N)\, \Psi_e(\vec{x}'_1,\dots,\vec{x}'_N;\vec{R}_1,\dots,\vec{R}_N)\, d\vec{x}'_1,\dots,\widehat{d\vec{x}'_i},\dots,d\vec{x}'_N\right)}$$

$$= \frac{\left(\sum_{j\neq i} \sum_{R_n\neq 0} \underbrace{\int\cdots\int}_{N-1} \Psi^*_e(\vec{x}',\dots,\vec{R})\, r(\vec{x}'_i,\vec{x}'_j,\vec{R}_N)\, \Psi_e(\vec{x}'\dots,\vec{R})\, d\vec{x}'_1,\dots,\widehat{d\vec{x}'_i},\dots,d\vec{x}'_N\right)}{\left(\underbrace{\int\cdots\int}_{N-1} \Psi^*_e(\vec{x},\dots,\vec{R})\, \Psi_e(\vec{x}',\dots,\vec{R})\, d\vec{x}'_1,\dots,\widehat{d\vec{x}'_i},\dots,d\vec{x}'_N\right)}$$

$$= V_e^{op}(\vec{x}'_i,\vec{R}_1,\dots,\vec{R}_N) \quad . \qquad \text{(III.2.2)}$$

Observe that the caret over the differential $d\vec{x}'_i$ specifies the coordinate <u>not</u> integrated out. The operator, $V_e^{op}(\vec{x}'_i,\vec{R}_1,\dots,\vec{R}_N)$ represents the potential energy of interaction between the i-th electrons (with space and spin coordinates, $\vec{x}'_i$) and all the other electrons. The contribution to the total energy of the electronic system (the expectation value of H_e) of the energy of interaction between all the electrons is the integral over coordinates $\vec{x}_i$ of this operator $V_e^{op}(\vec{x}_i,\vec{R})$ times the density, $\rho_e(\vec{x}_i)$, of electrons at $\vec{x}_i$, where

$$\rho_e(\vec{x}_i) = \underbrace{\int \cdots \int}_{N-1} \Psi_e^*(\vec{x}_1,\ldots,\vec{x}_N;\vec{R}_1,\ldots,\vec{R}_N)\, \Psi_e(\vec{x},\vec{R})\, d\vec{x}_1,\ldots,\widehat{d\vec{x}_i},\ldots,d\vec{x}_N \qquad \text{(III.2.3)}$$

or, explicitly,

$$\Omega_e = \frac{1}{2}\int \rho_e(\vec{x}_i)\, V_e^{op}(\vec{x}_i)\, d\vec{x}_i \ , \qquad \text{(III.2.4)}$$

multiplied by a factor of one-half because the total energy is the sum of the energies of electrons interacting in pairs,[1] [27,28,29]

The development of $V_e^{op}(\vec{x}_i')$ corresponds to a demonstration of Hartree's original postulate: each electron moves in the averaged charge distribution of the other electrons. Because the eigenfunctions, $\Psi_e(\vec{x},\vec{R})$, of the electronic system from which $V_e^{op}(\vec{x}_i;\vec{R})$ is generated according to (III.2.21) are necessarily anti-symmetric under interchange of any pair of electronic space-and-spin coordinates, this single-coordinate potential operator manifests the effects of exchange. And to whatever extent the polarization of the electron cloud or any configuration interaction is included, $V_e^{op}(\vec{x}_i)$ manifests the effects of dynamic cor-

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[1] Equation (III.2.4) is exact (there have been no approximations made in its derivation) and has the form of the classical electrostatic expression for the energy of a distribution of charge interacting with itself. However, although the equations (III.2.2) and (III.2.3) for $V_e(\vec{x}_i)$ and $\rho_e(\vec{x}_i)$, respectively, are exact, they are not related by Poisson's approximation: $\nabla^2 V_e(\vec{x}_i) \neq \rho_e(\vec{x}_i)$.

relation as well. The full analysis which demonstrates that when Hartree's original postulate is properly interpreted one obtains a unique potential for the self-consistent field was done by J.C. Slater.[30,31]

Using the potential operator, $V_e^{op}(\vec{x}_i)$ which represents the potential experienced by an electron of coordinates, $\vec{x}_i$, due to all the other electrons, we define the single-particle energy operator, $h(\vec{x}_i,\vec{R})$, by

$$h_e(\vec{x}_1,\vec{R}_1,\vec{R}_2,\ldots,\vec{R}_N) \equiv h_e(\vec{x}_i,\vec{R}) \equiv$$

$$\equiv \frac{-\hbar^2}{2m}\nabla_i^2 - \frac{Z e^2}{|\vec{x}_i|} + V_e^{op}(\vec{x}_i,\vec{R}) + \sum_{R_n \neq 0} a(\vec{x}_i,\vec{R}_n) \quad . \qquad \text{(III.2.5)}$$

Substituting this one-particle energy operator, $h_e(\vec{x}_i,\vec{R})$, into the expression for the Hamiltonian for the electronic system gives,

$$H_e(\vec{x},\vec{R}) = \sum_i \left(h_e(\vec{x}_i,\vec{R}) - \frac{1}{2} V_e^{op}(\vec{x}_i,\vec{R}) \right) \quad . \qquad \text{(III.2.6)}$$

Note again the subtraction of $\frac{1}{2} V_e^{op}(\vec{x}_i,\vec{R})$ from the single-particle energy operator, $h_e(\vec{x}_i,\vec{R})$. This is required because the total Hamiltonian, $H_e(\vec{x},\vec{R})$, involves $\frac{1}{2} V_e^{op}(\vec{x},\vec{R})$, while $h_e(\vec{x}_i,\vec{R})$ contains $V_e^{op}(\vec{x},\vec{R})$.

The exact eigenfunctions of $H_e(\vec{x},\vec{R})$ are sums (or series) of Slater determinants with coefficients determined variationally to minimize the eigenvalue (i.e., the total energy). We take for elements of the determinants the linearly independent one-electron orbitals which are eigenfunctions of the single-particle energy operator, $h_e(\vec{x}_i,\vec{R})$, that is orbitals which satisfy

$$h_e(\vec{x}_i,\vec{R})\ \psi_k(\vec{x}_i;\vec{R}) = \epsilon_k(R)\ \psi_k(\vec{x}_i;\vec{R}) \quad . \qquad \text{(III.2.7)}$$

Because the orbitals, $\psi_k(\vec{x}_i;\vec{R})$, are all eigenfunctions of the same operator, $h_e(\vec{x}_i,\vec{R})$, they are automatically orthogonal. In the present work, this will be a distinct advantage over the Hartree-Fock formalism of which the excited state orbitals are not orthogonal to the ground state ones.

The variational procedure necessary to ascertain the configuration interaction is impractically difficult, however, and for the present work we shall approximate the eigenfunctions of $H_e(\vec{x},\vec{R})$ by single determinants, or

$$\Psi_e(\vec{x}_1,\ldots,\vec{x}_N;\vec{R}_1,\ldots,\vec{R}_N) = \Psi_e(\vec{x},\vec{R}) = \det \sqrt{\frac{1}{N}}\ |\ \psi_k(\vec{x}_k;\vec{R})\ | \quad . \text{(III.2.8)}$$

Using these single determinants we generate a self-consistent potential function, $V_e(\vec{x}_i,\vec{R})$, to approximate the exact potential operator for the self-consistent field,

$$V_e^{op}(\vec{x}_i,\vec{R}) \cong V_e(\vec{x}_i,\vec{R}) \quad , \qquad \text{(III.2.9)}$$

where

$$V_e(\vec{x}_i,\vec{R}) = \sum_j \int \psi_j^*(\vec{x}_j;\vec{R}) \frac{1}{|\vec{x}_i - \vec{x}_j|} \psi_j(\vec{x}_j;\vec{R})\ d\vec{x}_j + \\ - \sum_j \frac{3}{2\pi^2}\left(3\pi^2\ \psi_j^*(\vec{x}_j;\vec{R})\ \psi_j(\vec{x}_j;\vec{R})\right)^{1/3} \quad . \qquad \text{(III.2.10)}$$

In the potential function, $V_e(\vec{x}_i,\vec{R})$, the effects of exchange are included by the $\rho^{1/3}(\vec{x}_i)$ approximation developed by Slater.[32] The ground state eigenfunction for the electronic system will be chosen as the determinant containing the N distinct orbitals of lowest one-electron energies, $\epsilon_k(R)$. Thus we shall use an independent-particle model.

There is more to justify the use of an independent-particle model for the electronic system besides the fact that such approximation reduces a partial differential equation of 3N independent and inseparable coordinates (where $N \sim 10^{22}$) to an equal number of ordinary differential equations.

The conceptual picture of the electrons in a crystalline solid is that of a set of single-particle states occupied by order of increasing energy up to some maximum value determined by the number of electrons present. Such is the concept of the Fermi Surface. The conceptual picture of the interactions between the electrons and the lattice vibrations is that of an electron in a specific single-particle eigenstate (labelled by a wave vector, $\vec{k}$, in the First Brillouin Zone), $\psi_{\vec{k}}(\vec{x}_i)$, either absorbing or emitting a phonon of wave vector, $\vec{q}$, and changing to the eigenstate of wave vector, $\vec{k} \pm \vec{q}$, $\psi_{\vec{k}+\vec{q}}(\vec{x}_i)$. These types of processes are represented by the interaction diagrams in Fig. 1, respectively.

This way of conceptualizing the phenomena is inherently one of an independent-particle model. And therefore, we employ one such.

III.3 The A.P.W. Method.

Within the framework of the independent-particle formalism, the one-electron orbitals, $\psi_k(\vec{x}_k;\vec{R})$, which form the N-electron determinantal eigenfunctions,

$$\psi_e(\vec{x}_1,\ldots,\vec{x}_N;\vec{R}_1,\ldots,\vec{R}_N) = \det \sqrt{\frac{1}{N}}\, |\psi_k(\vec{x}_k;\vec{R}_1,\ldots,\vec{R}_N)|, \qquad (\text{III}.3.1)$$

are eigenfunctions of the crystalline Schrodinger equation (III.2.7),

$$h_e(\vec{x}_k,\vec{R})\ \psi_k(\vec{x}_k;\vec{R}) = \epsilon_k(R)\ \psi_k(\vec{x}_k;\vec{R}) \ . \qquad (\text{III}.3.2)$$

The potential energy operator in equation (III.3.2),

$$\begin{aligned} U(\vec{x}_k,\vec{R}) &= \frac{-Ze^2}{|\vec{x}_k|} + V_e(\vec{x}_k;\vec{R}) - \sum_{R_m \neq 0} a(\vec{x}_k,\vec{R}_m) \\ &= \sum_{\vec{R}_n} U_{\text{cell}}(\vec{x}_k - \vec{R}_n) \ , \end{aligned} \qquad (\text{III}.3.3)$$

has the symmetry and periodicity of the crystal, and the eigensolutions, $\psi_k(\vec{x}_k;\vec{R})$, must satisfy the crystalline periodic boundary conditions,

$$\psi_k(\vec{x}_k + \vec{R}_m;\vec{R}) = e^{i\vec{k}\cdot\vec{R}_m}\ \psi_k(\vec{x}_k;\vec{R}) \ , \qquad (\text{III}.3.4a)$$

and

$$\vec{\nabla}_n \psi_k(\vec{x}_{k,s} + \vec{R}_m; \vec{R}) = -e^{i\vec{k}\cdot\vec{R}_m} \vec{\nabla}_n \psi_{k,s}(\vec{x}_{k,s}; \vec{R}) \quad . \qquad \text{(III.3.4b)}$$

In equation (III.3.4b) the subscript n specifies the normal gradient, and the index s on $\vec{x}_{k,s}$ that the coordinate is on the surface of the Wigner-Seitz cell. To find solutions to the Schrodinger equation which satisfy both boundary conditions (III.3.4a) and (III.3.4b) at all points within the Wigner-Seitz cell and on its entire surface has been one of the central problems of theoretical solid state physics during the past quarter century. This problem of the Schrodinger equation for a periodic potential has been solved most accurately by the method of Augmented Plane Waves (A.P.W.) developed by Slater and others.[33,34,35]

The A.P.W. method employs a dual, or composite, representation for the eigenfunctions of the crystalline one-electron Hamiltonian. Within the volume of a sphere drawn inside the Wigner-Seitz cell, the A.P.W. procedure solves the central-field Schrodinger equation exactly for a set of trial one-electron eigenenergies, ϵ:

$$h_e(\vec{x}_k, \vec{R})\, \psi_k(\vec{x}_k; \vec{R}) = \left(-\nabla_k^2 + U_{\text{cell}}(\vec{x}_k; \vec{R})\right) \psi_k(\vec{x}_k; \vec{R}) = \epsilon(R)\, \psi_k(\vec{x}_k; \vec{R}) \ ,$$

where (III.3.5)

$$|\vec{x}_k| \le r_s \quad .$$

In the region between the inscribed sphere and the cell boundary, the A.P.W.

eigenfunctions are expanded in plane waves:

$$\psi_k(\vec{x}_k;\vec{R}) = \sum_{\vec{K}_i} v(\vec{k}+\vec{K}_i)\, e^{i(\vec{k}+\vec{K}_i)\cdot\vec{x}_k} \quad , \qquad \text{(III.3.6)}$$

where

$$|\vec{x}_k| \geq r_s \quad .$$

These two representations of the eigenfunction are made to match continuously at the surface of the inscribed sphere, $\vec{r}_s$. The functions described in equations (III.3.5) and (III.3.6) are the trial functions which enter the variational procedure to ascertain the minimal eigenvalue, $\epsilon_k(\vec{R})$, and the eigenfunction belonging to it. Although the exact solutions to the crystalline problem have eigenfunctions which match not only continuously at the A.P.W. sphere radius but match there also with a continuous first derivative, both such conditions cannot be imposed <u>a priori</u> upon the trial functions without corrupting the variational procedure.

The A.P.W. energy eigenvalues, $\epsilon_k(\vec{R})$, and the A.P.W. eigenfunctions which belong to them, $\psi_{\vec{k}}(\vec{x}_k;\vec{R})$, are determined variationally from the trial solutions, (III.3.5), and (III.3.6), by the zeros of the secular determinant,

$$\det|(h-\epsilon)_{ij}| = 0 \quad , \qquad \text{(III.3.7)}$$

where

$$(h-\epsilon)_{ij} = \int_{\substack{\text{Wigner-}\\ \text{Seitz}\\ \text{Cell}}} \psi_i^*(\vec{x}';\vec{R})\left(h(\vec{x}',\vec{R}) - \epsilon(\vec{R})\right)\psi_j(\vec{x}';\vec{R})\,d\vec{x}' \quad . \qquad (\text{III}.3.8)$$

Observe that in all the equations relating to the one-electron problem we carry along the implicit dependence of the 3N nuclear coordinates by the symbolic parametric variable, $\vec{R}$.

The A.P.W. method for solving the variational problem of an electron in a crystalline potential is carried out as follows.

The crystalline potential, $u_{crys}(\vec{x},\vec{R})$, has the symmetry of the crystal's space group, e.g., O_h for a cubic crystal; and from this potential,

$$u_{crys}(\vec{x},R) = \sum_{\ell,m} u_{\ell,m}(|\vec{x}|,R)\; Y_\ell^m(\theta,\varphi) \quad , \qquad (\text{III}.3.9)$$

the spherically symmetric component is taken,

$$u_{\ell=0}(\vec{x},R) = u(r,R) \quad , \qquad (\text{III}.3.10)$$

and enters the one-dimensional radial Schrodinger equation,

$$\left(-\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) + \frac{\ell(\ell+1)}{r^2} + u(r)\right) u_\ell(r) = \epsilon\, u_\ell(r) \quad . \qquad (\text{III}.3.11)$$

The solutions to this radial equation form the trial functions for the A.P.W. variational problem. The trial functions have the form,

$$\left(\psi_{\vec{k}}(\vec{x})\right)_{\text{trial}} = \sum_{\ell,m} \left(i^{\ell}(2\ell+1) \frac{(\ell-|m|)!}{(\ell+|m|)!} P_{\ell}^{|m|}(\cos\theta_k)\, e^{-im\varphi_k} \right)$$

$$\times \left(\frac{j_{\ell}(k\, r_s)}{u_{\ell}^{(\epsilon)}(r_s)}\, u_{\ell}^{(\epsilon)}(r)\, P_{\ell}^{|m|}(\cos\theta)\, e^{im\varphi} \right), \qquad \text{(III.3.12)}$$

inside the A.P.W. sphere, $r \le r_s$, and

$$\left(\psi_{\vec{k}}(\vec{x})\right)_{\text{trial}} = \sum_{\ell,m} \left(i^{\ell}(2\ell+1) \frac{(\ell-|m|)!}{(\ell+|m|)!} P_{\ell}^{|m|}(\cos\theta_k)\, e^{-im\varphi} \right)$$

$$\times \left(j_{\ell}(kr)\, P_{\ell}^{|m|}(\cos\theta)\, e^{im\varphi} \right), \qquad \text{(III.3.13)}$$

between the sphere and the boundaries of the Wigner-Seitz cell, $r_s \le r \le r_B$. One observes that the factors,

$$i^{\ell}(2\ell+1) \frac{(\ell-|m|)!}{(\ell+|m|)!} P_{\ell}^{|m|}(\cos\theta_k)\, e^{-im\varphi_k} \frac{j_{\ell}(k\, r_s)}{u_{\ell}^{\epsilon}(r_s)}, \qquad \text{(III.3.14)}$$

which multiply the trial functions inside the sphere assure that it joins continuously onto the plane wave, $e^{i\vec{k}\cdot\vec{r}}$, at the sphere radius, r_s. The eigenvalue, ϵ, is superscribed on these trial functions, $u_{\ell}^{\epsilon}(r)$, to emphasize that they are implicit functions of ϵ.

These trial functions are the natural ones to use for the crystalline variational problem. The only singularity in the crystalline potential is contained in its spherically symmetric component, u(r), and the behaviour of the solutions to the singular radial equation will dominate that of the solutions to the complete crystalline potential problem.

The variational problem in the case of a single plane wave for the eigenfunction outside the sphere consists of finding the function $\psi_k^{\epsilon}(\vec{x})$ which renders a stationary value to the integral,

$$\int_{\substack{\text{cell,}\\ \Omega}} \psi_k^*(\vec{x})\, h_e(\vec{x})\, \psi_k(\vec{x})\, d\vec{x} \ , \tag{III.3.15}$$

subject to the constraint of normalization,

$$\int_{\Omega} \psi_k^*(\vec{x})\, \psi_k(\vec{x})\, d\vec{x} = 1 \ . \tag{III.3.16}$$

Such is determined by the eigenfunction for which,

$$\int_{\Omega} \psi_k^*(\vec{x}) \left(h_e(\vec{x}) - \epsilon_k\right) \psi_k(\vec{x})\, d\vec{x} = 0 \ , \tag{III.3.17}$$

where the Lagrange multiplier, ϵ_k, is identified as the pertinent eigenvalue to which $\psi_k(\vec{x})$ belongs.

Now because the trial functions which enter equation (III.3.17) are themselves implicit functions of the eigenvalue, ϵ, there exists no known technique for solving for the eigenvalue analytically, — as with, say, the Euler-Lagrange equations. Accordingly, the A.P.W. method determines the eigenvalue by "brute force." The integral function of the energy,

$$I(\epsilon) = \int_{\Omega} \psi_k^*(\vec{x}) \left(h_e(\vec{x}) - \epsilon_k \right) \psi_k(\vec{x})\, d\vec{x} \ , \qquad (\text{III}.3.18)$$

is solved explicitly over an extended range of values of ϵ, and its zeroes are there from ascertained directly. It is to be understood that the integrals (III.3.17) and (III.3.18) can involve the complete crystalline potential, — not necessarily only the spherical component inside the sphere.

The eigenfunction thus found is not, however, the variational solution to the crystalline problem. Although the trial functions (III.3.12) comprise a complete set of functions inside the A.P.W. sphere, by matching them onto a single plane wave, $e^{i\vec{k}\cdot\vec{r}}$, at the sphere radius the solution was pre-determined between the sphere and the cell boundary. A thorough variational freedom is admitted to the method by matching at the sphere radius the trial solutions inside the sphere to the set of plane waves,

$$\sum_{K_j} e^{i(\vec{k}+\vec{K}_j)\cdot\vec{r}} \ , \qquad (\text{III}.3.19)$$

where the vectors, $\vec{K}_j$, are vectors of the reciprocal lattice. Then the eigenvalues are determined by the zeroes of the determinantal function,

$$D(\epsilon) = \det\left| \int_{\Omega} \psi^{*}_{\vec{k}+\vec{K}_i}(\vec{x}) \left(h_e(\vec{x}) - \epsilon_k\right) \psi_{\vec{k}+\vec{K}_j}(\vec{x})\, d\vec{x} \right| , \qquad (\text{III}.3.20)$$

which are also ascertained by calculating the values of $D(\epsilon)$ over a range of energies.

Because the eigenfunctions which belong to the A.P.W. eigenvalues $\epsilon(k)$ obtain from a variational procedure, they are expected by the most exact solutions to the problem of electrons in a crystal lattice.

There is nothing in the formalism of the A.P.W. method which restricts its validity to any particular crystalline symmetry or to any particular set of nuclear coordinates. In fact, should the nuclear coordinates pertinent to some specific crystal problem be altered to a new arrangement, the A.P.W. method would calculate the set of one-electron energies, $\epsilon(k)$, and the distribution of electrons with $\epsilon(k)$ (energy and wave vector) pertinent to the new nuclear arrangement with an accuracy and ease equal to that of the original problem. In short, the A.P.W. method is well adapted to provide the adiabatic-model eigenfunctions, $\Psi_e(\vec{x};\vec{R})$, where

$$H_e(\vec{x},\vec{R})\, \Psi_e(\vec{x};\vec{R}) = E_e(\vec{R})\, \Psi_e(\vec{x};\vec{R}) , \qquad (\text{III}.3.21)$$

and

$$\Psi_e(\vec{x},\vec{R}) = \det \sqrt{\frac{1}{N}}\, | \psi_k(\vec{x}_k;\vec{R}) | \quad . \qquad (\text{III}.3.22)$$

This statement holds especially true when the distribution of electrons with energy, $\epsilon(k)$, — i.e., the Fermi Surface, — is of primary concern.

For the analysis of the electron-phonon interactions, the essential point under investigation is the redistribution of electrons at the Fermi Surface accompanied by the absorbtion or emission of phonons. Or put another way, the deformation of the Fermi Surface when the nuclear arrangement is altered according to one or another of the vibrational normal modes of the lattice. For this problem, the A.P.W. method is well qualified.

The A.P.W. eigenfunctions have a distinct form: each can be represented as a sum of plane waves plus a tight-binding function. Within the A.P.W. sphere inscribed in the Wigner-Seitz cell, the eigenfunction is an exact solution to the Schrodinger equation, or

$$\left(-\nabla^2 + U(\vec{x}_k;R)\right) \psi^{(\epsilon)}_{\vec{k},s}(\vec{x}_k;R) = \epsilon_{\vec{k},s}(R)\, \psi^{(\epsilon)}_{\vec{k},s}(\vec{x}_{\vec{k}};R) \quad . \qquad (\text{III}.3.23)$$

In equation (III.3.23), the eigenfunction is written as,

$$\psi^{(\epsilon)}_{k,s}(x_k;R) \quad , \qquad (\text{III}.3.24)$$

in order to indicate plainly that $\psi_{\vec{k}}(x)$ is an implicit parametric function of the energy eigenvalue, ε (and, precisely, that one which belongs to the argument, $\varepsilon_{\vec{k},s}(R)$). The wave-vector, k, is restricted to points within the first Brillouin Zone, and the subscript, s, designates the branch to which the band energy, $\varepsilon_{\vec{k},s}(R)$ belongs. Together $\vec{k}$ and s specify the irreducible representation of the crystal's space group of which $\psi_{\vec{k},s}(x)$ transforms as a base vector. In terms of the trial functions, $U^{(\varepsilon)}_{\ell}(\vec{r})$, the A.P.W. eigenfunction is represented within the sphere as,

$$\psi^{(\varepsilon)}_{\vec{k},s}(\vec{x}_k;R) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} a^{(\varepsilon;k,s)}\, U^{(\varepsilon)}_{\ell}(|\vec{x}_k|;R)\, Y^{m}_{\ell}(\theta_k,\varphi_k) \quad , \quad (\text{III}.3.25)$$

where

$$|\vec{x}_k| \leq v_s$$

In the region between the A.P.W. sphere and the cell boundary, the A.P.W. eigenfunction is represented as,

$$\psi^{(\varepsilon)}_{k,s}(x_k;R) = \sum_{K_i} a^{(\varepsilon;\vec{k},s)}(\vec{k}+\vec{K}_i)\, e^{i(\vec{k}+\vec{K}_i)\cdot\vec{x}_k} \quad , \qquad (\text{III}.3.26)$$

where

$$r_x \leq |\vec{x}_k| \leq \frac{\vec{R}^{o}_{1}}{2} \ .$$

In equation (III.3.26) the variationally determined coefficients are written as,

$$a^{(\epsilon;\vec{k},s)}(\vec{k}+\vec{K}_i;R) \quad , \tag{III.3.27}$$

to show that they also are implicit functions of the band energy, $\epsilon_{\vec{k},s}(R)$ and parametric functions of the nuclear coordinates $R \equiv \{\vec{R}_1, \vec{R}_2, \ldots, \vec{R}_N\}$. The A.P.W. eigenfunction represented by (III.3.23) or (III.3.25) matches onto the sum of plane waves, (III.3.26), at the sphere radius both with a continuous amplitude and a continuous first derivative. Therefore, one can write,

$$\psi^{(\epsilon)}_{\vec{k},s}(\vec{x}_k;R) = \sum_{\vec{K}_i} a^{(\epsilon;\vec{k},s)}(\vec{k}+\vec{K}_i)\left(e^{i(\vec{k}+\vec{K}_i)\cdot\vec{x}_k} + \varphi^{(\epsilon)}_{\vec{k},s}(\vec{x}_k;R)\right), \tag{III.3.28}$$

where

$$\varphi^{(\epsilon)}_{k,s}(x_k) = 0 \qquad \text{if} \qquad |x_k| \geq r_s \quad . \tag{III.3.29}$$

Observe that equation (III.3.28) is simply equation (III.3.26) for $|\vec{x}_k| \geq r_s$, and that for $|\vec{x}_k| \leq r_s$, $\varphi_{\vec{k}}(\vec{x}_k)$ is simply the difference between equations (III.3.25) and (III.3.26). The tight-binding components of the A.P.W. eigenfunctions,

$$\varphi^{(\epsilon)}_{\vec{k},s}(\vec{x}_k;R) \quad , \tag{III.3.30}$$

which are localized about each nucleus are qualitatively quite like free-atom orbitals. If the energy band or symmetry point to which $\psi_k(x)$ belongs is, say, p-like (e.g., P_4, N' in a body-centered cubic crystal) then $\varphi_k(x)$ will have odd parity and will vanish linearly at the origin. If the energy band is predominantly s-like, then $\varphi_k(x)$ will be an s-like function. In each case, the number of nodes in $\varphi_k(x)$ corresponds to the analogous free-atom state:

$$n - \ell - 1 \equiv \text{number of nodes} \quad , \qquad \text{(III.3.31)}$$

where n is the principal quantum number of the corresponding free-atom energy level.

The Bloch function form of the A.P.W. eigenfunctions obtain as,

$$\psi^{(\epsilon_k)}_{\vec{k},s}(\vec{x}_k;R) = \sum_{K_i} a^{(\epsilon_k;s)}(\vec{k}+\vec{K}_i,R)\left(\frac{e^{i(\vec{k}+\vec{K}_i)\cdot\vec{x}_k}}{\sqrt{V}} + \sqrt{\frac{1}{N}}\sum_{\vec{R}_n} e^{i(\vec{k}+\vec{K}_i)\cdot\vec{R}_n}\,\varphi^{(\epsilon_k)}_{\vec{k}+\vec{K}_i}(\vec{x}_k-\vec{R}_n)\right) \qquad \text{(III.3.32)}$$

written henceforth as,

$$\psi_k(\vec{x};R) = \sum_{K_i} a(k+K_i)\left(\frac{e^{i(\vec{k}+\vec{K}_i)\cdot\vec{x}}}{\sqrt{V}} + \sqrt{\frac{1}{N}}\sum_{R_n} e^{i(\vec{k}+\vec{K}_i)\cdot\vec{R}_n}\,\varphi_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_n)\right) \qquad \text{(III.3.33)}$$

with the band indices and the parametric dependence suppressed.

CHAPTER IV

THE MATRIX ELEMENTS OF THE ELECTRON-PHONON INTERACTION IN THE ADIABATIC MODEL

IV.1 The Expectation Values of the Total Hamiltonian for the System of Electrons and Nuclei.

Within the framework of the Adiabatic Model of a system of electrons and nuclei, the Hamiltonian operator acting upon one of the product states gives,

$$H(x,R)\,\mathfrak{T}(x;R) =$$

$$= \left\{ \frac{-\hbar^2}{2M} \sum_{R_n} \nabla^2_{R_n} + \sum_i \left(h_e(\vec{x}_i;R) - \frac{1}{2} v_e(\vec{x};R) \right) \right\} \Psi_e(x;R)\,\Phi_n(R) = \qquad \text{(IV.1.1a)}$$

$$= \Psi_e(x;R) \left(\frac{-\hbar^2}{2M} \right) \sum_{R_n} \nabla^2_{R_n} \Phi_n(R) + \Phi_n(R) \sum_i \left(h_e(\vec{x}_i;R) - \frac{1}{2} v_e(\vec{x}_i;R) \right) \Psi_e(x;R) +$$

$$+ \Phi_n(R) \left(\frac{-\hbar^2}{2M} \right) \sum_{R_n} \nabla^2_{R_n} \Psi_e(x;R) + \left(\frac{-\hbar^2}{2M} \right) \sum_{R_n} \left(\vec{\nabla}_{R_n} \Psi_e(x;R) \right) \cdot \left(\vec{\nabla}_{R_n} \Phi_n(R) \right) . \qquad \text{(IV.1.1b)}$$

The expectation value of the Hamiltonian in this state is,

$$\left\langle \Psi_e \Phi_n \middle| H \middle| \Psi_e \Phi_n \right\rangle =$$

$$= \int \Phi_n^*(R) \left\{ \sum_{R_n} \left(\frac{-\hbar^2}{2M} \right) \nabla_{R_n}^2 + \mathcal{E}_e(R) \right\} \Phi_n(R) \, d^{3N}R \; +$$

$$+ \int \Psi_e^*(x;R) \left\{ \sum_{R_n} \left(\frac{-\hbar^2}{2M} \right) \nabla_{R_n}^2 \right\} \Psi_e(x;R) \, d^{3N}x \; . \qquad \text{(IV.1.2)}$$

In evaluating (IV.1.2) we implicitly assume that each factor of the product eigenstates belongs to an orthonormal set:

$$\int \Psi_{e,1}^*(x;R) \, \Psi_{e,2}(x;R) \, d^{3N}x = \delta_{1,2} \; ; \qquad \text{(IV.1.3a)}$$

$$\int \Phi_{n,\xi}^*(R) \, \Phi_{n,\eta}(R) \, d^{3N}R = \delta_{\xi,\eta} \; . \qquad \text{(IV.1.3b)}$$

In equation (IV.1.2), the dependence of the total energy of the electronic system upon the nuclear coordinates is written explicitly as

$$\mathcal{E}_e(R) = \mathcal{E}_e(\vec{R}_1, \vec{R}_2, \ldots, \vec{R}_n) =$$

$$= \int \Psi_e^*(x;R) \left\{ \sum_i \left(h_e(\vec{x}_i, R) - \frac{1}{2} v_e(\vec{x}_i, R) \right) \right\} \Psi_e(x;R) \, d^{3N}x \, . \qquad \text{(IV.1.4)}$$

The dependence of $\mathcal{E}_e(R)$ upon the nuclear coordinates determines the energy spectrum of the nuclear system. This dependence is determined itself by the equilibrium-position nuclear coordinates which are themselves functions of the ground-state electronic configuration.

When the eigenstates of the system of electrons are approximated by single determinants in an independent-particle formalism, the electronic ground-state and the equilibrium-position nuclear coordinates are determined in the following way:

The ground-state electronic configuration is determined by Fermi energy, ϵ_F. This Fermi energy, ϵ_F, is the minimal single-particle eigenvalue for which there exists a function,

$$F(k_x, k_y, k_z) - \epsilon_F(k_x, k_y, k_z) = 0 \quad , \qquad \text{(IV.1.5)}$$

defining a surface in k-space whose volume includes exactly N points. The surface determined by ϵ_F is the Fermi Surface.

The Fermi energy, the Fermi surface, and the total energy of the electronic system are all parametric functions of the nuclear coordinates. The equilibrium nuclear positions are defined as those for which the total energy of the electronic ground-state is stationary under variations of the nuclear coordinates:

$$\frac{d}{dR_{n,i}}\left(\mathcal{E}_{e,q}(R)\right) = \frac{d}{dR_{n,i}}\left\{ \left\langle \Psi_{e,q}(R) \,|\, H_e(R) \,|\, \Psi_{e,q}(R) \right\rangle \right\} = 0 \qquad \text{(IV.1.6)}$$

for all $R_{n,i}$.

The expansion of the total energy of the electronic system in a Taylor series about the equilibrium-position nuclear coordinates gives

$$\mathcal{E}_e(R) = \mathcal{E}_{e,g}(R^o) + \sum_{m,i\,;\,n,j} \left(\mathcal{E}_g''(R^o)\right)_{m,i;n,j} \frac{\delta R_{m,i}\, \delta R_{n,j} + \dots}{2} \qquad \text{(IV.1.7)}$$

through terms quadratic in the variations of the nuclear coordinates. Thus it is observed that the non-vanishing terms in equation (IV.2) are $\mathcal{E}_g(R^o)$ and terms quadratic in the nuclear coordinates and momenta, and the traditional harmonic-oscillator nuclear eigenfunctions obtain. Equation (IV.1.2) may be rewritten as

$$\langle \Psi_e \Phi_n | H | \Psi_e \Phi_n \rangle =$$

$$\mathcal{E}_g(R^o) + \sum_n \int \Phi_n^*(R) \left\{ \left(\frac{-\hbar^2}{2M}\right) \nabla^2_{R_n} + \frac{M\omega_n^2}{2}\, \delta R_n^2 \right\} \Phi_n(R)\, d^{3N}R \quad , \text{(IV.1.8)}$$

where

$$\omega_n^2 = \left(\frac{d^2\, \mathcal{E}_g(R)}{dR_n^2}\right)_{R^o} - \frac{\hbar^2}{2M} \int \Psi^*_{e,g}(x\,;R)\, \nabla^2_{R_n}\, \Psi_{e,g}(x\,;R)\, d^{3N}x \qquad \text{(IV.1.9)}$$

the frequencies, ω_n, in equations (IV.1.8) and (IV.1.9) are the normal mode vibrational frequencies, $\omega(\vec{q},s)$ — the phonon frequencies. We shall assume henceforth that the problem of diagonalizing the matrix for the nuclear Hamiltonian has been solved and that the phonon frequencies have been determined. (Strictly speaking, the frequencies which obtain from the diagonalization of the matrix in equation (IV.1.8) should be designated the "un-renormalized normal mode frequencies," — $\omega^o(\vec{q},s)$; for the terms linear in δR which connect excited electronic configurations to the ground-state, through the electron-phonon interactions, will influence the phonon spectrum.)

It is to be observed that no non-vanishing matrix elements obtain from the last term in equation (IV.1.1b),

$$\frac{-\hbar^2}{2M}\sum_{R_n}\left(\vec{\nabla}_{R_n}\Psi_e(x;R)\right)\cdot\left(\vec{\nabla}_{R_n}\Phi_n(R)\right)\ , \tag{IV.1.10}$$

for the expectation value of H(x,R) in the ground-state. The nuclear eigenfunctions are approximated by the harmonic oscillator functions determined by the nuclear Hamiltonian in equation (IV.1.8),

$$\left(\frac{-\hbar^2}{2M}\nabla^2_{R_n}+\frac{M\omega_n^2}{2}\delta R_n^2\right)\Phi_{n,\eta}(R)=\eta\hbar\omega_n\Phi_{n,\eta}(R)\ . \tag{IV.1.11}$$

These eigenfunctions are each of a distinct parity, and therefore the factor which involves the nuclear coordinates, in the ground-state expectation value of the operator in (IV.1.10), vanishes:

$$\frac{-\hbar^2}{2M}\int\Phi^*_{n,\gamma}(R)\left(\vec{\nabla}_{R_n}\Phi_{n,\gamma}(R)\right)d^{3N}R=0\ . \tag{IV.1.12}$$

The only non-vanishing matrix elements which obtain from expression (IV.1.10) are those which connect different electronic configurations <u>and</u> different eigenstates.

The expectation value of the operator (IV.1.10) between states which differ in both the nuclear and the electronic configurations is

$$\frac{-\hbar^2}{2M}\sum_{R_n}\left\langle \Psi_{e,1}\,\Phi_{n,\xi}\,\middle|\,\frac{d\Psi_{e,2}}{dR_n}\,\frac{d\Phi_{n,\eta}}{dR_n}\right\rangle =$$

$$= \frac{-\hbar^2}{2M}\sum_{R_n}\left\{\int \Psi^*_{e,1}(x;R)\,\vec{\nabla}_{R_n}\,\Psi_{e,2}(x;R)\,d^{3N}x\right\} \bullet$$

$$\times\left\{\int \Phi_{n,\xi}(R)\,\vec{\nabla}_{R_n}\,\Phi_{n,\eta}(R)\,d^{3N}R\right\} . \qquad \text{(IV.1.13)}$$

It is these matrix elements, (IV.1.13), which are traditionally associated with the electron-phonon interactions. These non-adiabatic terms are designated the "double-derivative" terms because they involve the derivative with respect to the nuclear coordinates acting separately upon the nuclear eigenfunction and upon the electronic eigenfunction. The problem of calculating the matrix elements of the electron-phonon interactions involves evaluating the integrals in the double-derivative terms.

IV.2 Evaluation of the Non-Adiabatic Terms Involving the Double Derivatives.

The factor in the non-adiabatic double-derivative terms which involves the nuclear eigenfunctions,

$$\frac{i\hbar}{2M}\int \Phi^{*}_{n,\xi}(R)\,\vec{\nabla}_{R_n}\,\Phi_{n,\eta}(R)\,d^{3N}R\ , \tag{IV.2.1}$$

can be evaluated directly. The variations of the nuclear coordinates from their equilibrium values are assumed to be small, — this is the justification for truncating the expansion of $\mathcal{E}_e(R)$, equation (IV.1.7) at the terms quadratic in δR. Accordingly, these variations are henceforth described in terms of the normal mode coordinates, $Q_{\vec{q},s}$:

$$\vec{R}_m = \vec{R}^o_m + \vec{\delta R}_m\ , \tag{IV.2.2a}$$

$$\vec{\delta R}_m = \sum_{\vec{q},s} Q_{\vec{q},s}\, e^{i\vec{q}\cdot\vec{R}^o_m}\,\vec{\epsilon}_{\vec{q},s}\ , \tag{IV.2.2b}$$

and the momenta are also expressed as,

$$-i\hbar\vec{\nabla}_{\vec{R}_m} = \vec{P}_{R_m} = \sum_{\vec{q},s} P_{q,s}\, e^{i\vec{q}\cdot\vec{R}^o_m}\,\vec{\epsilon}_{\vec{q},s}\ . \tag{IV.2.2c}$$

The matrix element (IV.2.1) taken between harmonic oscillator nuclear eigenfunctions, associated with the phonon of wave vector $\vec{q}$ is, then,

$$\left\langle \Phi_{n,\xi}(\vec{q},s) \,\middle|\, \vec{P}_{R_m} \,\middle|\, \Phi_{n,\eta}(\vec{q},s) \right\rangle = i \sqrt{\frac{\hbar\omega(\vec{q},s)\, M\eta_{\vec{q}}}{2N}} \left(\delta(\eta-1,\eta) - \delta(\eta+1,\eta)\right) . \tag{IV.2.3}$$

In equation (IV.2.3) the number η_q, which specifies the energy level of the $\vec{q}$-th harmonic oscillator is assumed to specify the number of phonons present of wave vector $\vec{q}$ and band index s. Thus from equation (IV.2.3) it is observed that, because of the delta functions $\delta(\eta-1,\eta)$, $\delta(\eta+1,\eta)$, the double-derivative matrix elements connect nuclear eigenstates which differ in the number of phonons present by one; and thus the factor of the double-derivative term which involves the transition of the electronic state $\Psi_{e,1}(\vec{x};R)$ to the state $\Psi_{e,2}(x;R)$,

$$\frac{i\hbar}{2M} \int \Psi^*_{e,2}(x;R)\, \vec{\nabla}_{R_n}\, \Psi_{e,1}(x;R)\, d^{3N}x \ , \tag{IV.2.4}$$

is associated with the absorption or emission of a single phonon. Such is in keeping with the conceptual model of the electron-phonon interactions.

The difficulties which have heretofore obstructed the development of a formal analysis of the electron-phonon interactions have obtained from the difficulties (or impossibilities) of calculating the derivatives of the electronic eigenfunctions with respect to the nuclear coordinates:

$$\frac{d}{dR_n}\left(\Psi_e(x;R)\right) \quad . \qquad \text{(IV.2.5)}$$

Within the framework of an independent-particle model when the electronic eigenfunctions are approximated by States Determinants,

$$\Psi_e(x;R) = \sqrt{\frac{1}{N}}\,\det\left|\,\psi_{\vec{k}}(\vec{x}_{\vec{k}};R)\,\right| \quad , \qquad \text{(IV.2.6)}$$

the problem of calculating the derivatives in (IV.2.5) reduces to that of determining the derivatives of the single-particle electron orbitals with respect to the nuclear coordinates:

$$\frac{d}{dR_n}\left(\psi_{\vec{k}}(\vec{x}_k;R)\right) \quad . \qquad \text{(IV.2.7)}$$

To demonstrate the difficulties which have, in the past, prevented the calculation of the electron-phonon interactions, three examples of crystalline electronic eigenfunctions will be considered briefly: those for the "free-electron" model of solids; those for the "tight-binding" approximation; and, those for the "almost free electron" model.

For the "free-electron" model of solids, the eigenfunctions for the electrons are plane waves:

$$\psi_{\vec{k}}(\vec{x}_k;R) = \sqrt{\frac{1}{V}}\, e^{i\vec{k}\cdot\vec{x}} \,, \qquad \text{(IV.2.8)}$$

where the wave vectors, $\vec{k}$, are restricted to points in the Brillouin Zone. In this model, the derivatives of $\psi_k(\vec{x}_k;R)$ are all zero,

$$\frac{d}{dR_n}\left(\psi_{\vec{k}}(\vec{x}_k;R)\right) = \sqrt{\frac{1}{V}}\,\frac{d(e^{i\vec{k}\cdot\vec{x}})}{dR_n} = 0 \;. \qquad \text{(IV.2.9)}$$

This result would imply that there are no electron-phonon interactions. Such conclusion is, in fact, the correct one for the "free-electron" model. The plane wave states, (IV.2.8), are the eigenfunctions for electrons moving in a lattice which has no crystalline potential,

$$v_e(\vec{x};R) = 0 \qquad \text{(IV.2.10a)}$$

or

$$h_e(\vec{x};R) = -\frac{\hbar^2}{2M}\nabla_x^2 \,, \qquad \text{(IV.2.10b)}$$

and which are therefore impervious to any variation of nuclear coordinates.

A second approximation to the electronic eigenstates in crystalline solids which is often quite useful is the "tight-binding" approximation. In this model, the electronic eigenfunctions are taken to be Bloch series of the free atom orbitals:

$$\psi_{\vec{k}}(\vec{x}_{\vec{k}};R) = \sqrt{\frac{1}{N}}\sum_{R_p} e^{i\vec{k}\cdot\vec{R}_p}\,\varphi_{atom}(\vec{x}_k-\vec{R}_p) \;. \qquad \text{(IV.2.11)}$$

In equation (IV.2.11) the wave vector $\vec{k}$ is again in the first Brillouin Zone, the function φ is an eigenfunction for the free atom whose nuclei make up the lattice, and the vectors $\vec{R}_p$ determine the perfect lattice nuclear positions. In this model the derivatives of the electronic eigenfunctions with respect to the nuclear coordinates obtain straightforwardly:

$$\frac{d}{dR_n}\left(\psi_{\vec{k}}(\vec{x}_{\vec{k}};R)\right) = \sqrt{\frac{1}{N}}\, e^{i\vec{k}\cdot\vec{R}_n}\left(i\vec{k}\cdot\hat{e}(\delta\vec{R}_n)\,\varphi(\vec{x}_k-\vec{R}_n) - \hat{e}(\delta\vec{R}_n)\cdot\vec{\nabla}_x\,\varphi(\vec{x}_k-\vec{R}_n)\right) . \tag{IV.2.12}$$

However, the tight-binding functions of equation (IV.2.11) are quite poor approximations to the crystalline eigenfunctions of the conduction electrons in metals. The usefulness of the tight-binding approximation is restricted to the inner-shell, or valence-band, electrons in metals, or to insulating solids. Therefore, the derivatives of the eigenfunctions in equation (IV.2.12) are not valid to describe the electron-phonon interactions in normal metals, despite their ease of derivation.

A third approximation often used to describe the electrons in crystalline solids is the "almost-free electron" model. For such, the eigenfunctions are represented by lattice Fourier series:

$$\psi_{\vec{k}}(\vec{x}_k;R) = \sum_i \frac{a(\vec{k}+\vec{K}_i)\, e^{i(\vec{k}+\vec{K}_i)\cdot\vec{x}_k}}{\sqrt{V}} . \tag{IV.2.13}$$

The coefficients $a(\vec{k}+\vec{K}_i)$ in equation (IV.2.13) are determined variationally from the solutions of the secular determinant,

$$\det \left| (h - \varepsilon)_{\vec{k}+\vec{K}_i,\, \vec{k}+\vec{K}_j} \right| = 0 \ . \qquad \text{(IV.2.14)}$$

There are, two immediate problems which arise when using this model to analyse the electron-phonon interactions. First, in order to represent the eigenfunctions accurately in the region near the nucleus (where the potential undergoes the greatest change when the nuclear coordinates change), a very large number of terms must be included in the Fourier series (IV.2.13). Second, the dependence of these eigenfunctions upon the nuclear coordinates is all contained implicitly in the variational coefficients $a(\vec{k}+\vec{K}_i)$. In order to calculate the derivatives of these functions with respect to the nuclear coordinates it would be necessary to solve the variational problem completely for the changed set of nuclear coordinates, say,

$$\vec{R}^o_1, \vec{R}^o_2, \vec{R}^o_3, \ldots, \vec{R}^o_m + \delta\vec{R}_m, \ldots, \vec{R}^o_{N-1}, \vec{R}^o_N \ , \qquad \text{(IV.2.15)}$$

and then to take the limit

$$\lim_{\delta R_m \to 0} \left\{ \frac{\psi(\vec{x}_k; R^o + \delta R_m) - \psi_{\vec{k}}(\vec{x}_k; R^o)}{\delta R_m} \right\} = \frac{d}{dR_m} \left(\psi_k(\vec{x}_k; R) \right) . \qquad \text{(IV.2.16)}$$

The plane wave representation, equation (IV.2.13), is either an inaccurate or a very clumsy representation of the perfect lattice eigenfunctions. Even if only a few terms are included in the lattice Fourier series,

$$\psi_{\vec{k}}(\vec{x}_k;R^\circ) \simeq \sum_{i=0}^{5} \frac{a(\vec{k}+\vec{K}_i)\, e^{i(\vec{k}+\vec{K}_i)\cdot\vec{x}_k}}{\sqrt{V}} , \qquad \text{(IV.2.17)}$$

such that the matrix which generates the secular determinant for the perfect lattice is a 5 X 5 matrix, for the case of the deformed lattice the matrix becomes of the order of $(5 \times 10^{23}) \times (5 \times 10^{23})$ because the translational symmetry of the lattice is destroyed, and there are then non-vanishing matrix elements between all plane waves

$$\left(h(\vec{x},R+\delta R) - \epsilon\right)_{\vec{k}+\vec{K}_j,\,\vec{k}+\vec{K}_i} . \qquad \text{(IV.2.18)}$$

The solution of such a variational problem presents a formidable problem and, of course, still carries with it the sickness inherent to the "almost-free electron" model.

As has been explained in Chapter III, the most accurate eigenfunctions for the electrons in crystalline solids are the A.P.W. variational eigensolutions:

$$\psi_{\vec{k}}(\vec{x}_k;R) = \sqrt{\frac{1}{A_k}} \sum_i a(\vec{k}+\vec{K}_i)\, \psi_{\vec{k}+\vec{K}_i}(\vec{x}_k;R) , \qquad \text{(IV.2.19)}$$

where

$$\psi_{\vec{k}+\vec{K}_i}(\vec{x}_k;R) = \frac{e^{i(\vec{k}+\vec{K}_i)\cdot\vec{x}_k}}{\sqrt{V}} + \sqrt{\frac{1}{N}}\sum_{\vec{R}_p} e^{i\vec{k}\cdot\vec{R}_p}\,\varphi_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_p) \ . \tag{IV.2.20}$$

In equations (IV.2.19) and (IV.2.20) the variational coefficients, $a(\vec{k}+\vec{K}_i)$, and the functional form of the tight-binding components,

$$\varphi^{(\epsilon)}_{\vec{k}+\vec{K}_i}(\vec{x}_k) = \psi^{(\epsilon)}_{\vec{k}+\vec{K}_i}(\vec{x}_k) - \frac{e^{i(\vec{k}+\vec{K}_i)\cdot\vec{x}_k}}{\sqrt{V}} \ , \tag{IV.2.21}$$

are determined by the eigenvalue, $\epsilon(\vec{k})$. The constant, $A(k)$, in equation (IV.2.19) is simply the normalization factor; the eigenfunctions are normalized, such that

$$\int |\psi_k(\vec{x}')|^2 \, d\vec{x}' = 1 \ , \tag{IV.2.22a}$$

$$\sum_i |a(\vec{k}+\vec{K}_i)|^2 = 1 \ . \tag{IV.2.22b}$$

The derivative of the A.P.W. eigenfunction with respect to the nuclear coordinates is

$$\frac{d}{dR_m}\left(\psi_{\vec{k}}(\vec{x}_k;R)\right) \equiv \lim_{\delta R_m \to 0}\left\{\frac{\psi(\vec{x}_k;R+\delta R_m) - \psi_{\vec{k}}(\vec{x}_k;R^{o})}{\delta R_m}\right\}$$

(continued)

$$= \lim_{\delta R_m \to 0} \left\{ \frac{1}{A(k)} \sum_i \left[\sum_{\vec{k}'} \frac{a(\vec{k}'+\vec{K}_i;R+\delta R_m) - a(\vec{k}+\vec{K}_i;R^\circ)}{\delta R_m} \right] \psi_{\vec{k}+\vec{K}_i}(\vec{x}_k;R^\circ) \right\}$$

$$+ \frac{1}{A(k)} \sum_i \frac{a(\vec{k}+\vec{K}_i)\, e^{i\vec{k}\cdot\vec{R}_m}}{\sqrt{N}} \Big(i(\vec{k}+\vec{K}_i) \cdot \hat{e}(\overrightarrow{\delta R}_m)\, \varphi_{\vec{k}+\vec{K}_i}(\vec{x}_k-\vec{R}_m) +$$

$$- \hat{e}(\overrightarrow{\delta R}_m) \cdot \vec{\nabla}_x\, \varphi_{\vec{k}+\vec{K}_i}(\vec{x}_k-\vec{R}_m) \Big) +$$

$$+ \frac{1}{A(k)} \sum_i a(\vec{k}+\vec{K}_i) \sqrt{\frac{1}{N}} \sum_{R_p} e^{i\vec{k}\cdot\vec{R}_p} \frac{d}{d\epsilon} \left(\varphi_{\vec{k}+\vec{K}_i}(\vec{x}_k-\vec{R}_p) \right) \frac{d\epsilon(R_p)}{dR_m} \ . \qquad \text{(IV.2.23)}$$

There are several observations to be made concerning equation (IV.2.23). The function appearing on the first line of that equation,

$$\psi(\vec{x}_k;R+\delta R_m) \ , \qquad \text{(IV.2.24)}$$

is understood to be the function which reduces to the perfect lattice eigenfunction $\psi_k(\vec{x}_k;R^\circ)$ in the limit as $\overrightarrow{\delta R}_m$ vanishes:

$$\lim_{\delta R_m \to 0} \psi(\vec{x}_k;R_m+\delta R_m) = \psi_{\vec{k}}(\vec{x}_k;R^\circ) \ . \qquad \text{(IV.2.25)}$$

The index k appears only on the electronic variable $\vec{x}_k$ in the function on the left hand side of equation (IV.2.25). That function has no index $\vec{k}$, for, as the eigenfunction of the deformed lattice, it does <u>not</u> transform irreducibly as the $\vec{k}$-th (or any other) representation of the translation group of the perfect lattice.

It will be shown in the next chapter that neither the A.P.W. eigenvalues, $\epsilon(k)$, nor the variational coefficients which obtain from them, $a(\vec{k}+\vec{K}_i)$, have a non-vanishing derivative with respect to the nuclear coordinates:

$$\frac{d}{dR_m}\left(\epsilon(\vec{k};R)\right) = 0 \qquad \text{(IV.2.26)}$$

and

$$\frac{d}{dR_m}\left(a(\vec{k}'+\vec{K}_i;R)\right) = 0 \ . \qquad \text{(IV.2.27)}$$

In order to prove the first of these assertions, equation (IV.2.26), it is necessary to set up the matrix for the deformed lattice,

$$\left(h_e(\vec{x};R+\delta R_m) - \epsilon\right)_{\vec{k}'+\vec{K}_j,\vec{k}+\vec{K}_i} \ , \qquad \text{(IV.2.28)}$$

and to solve for the zeroes of the $(10^{25}) \times (10^{25})$ secular determinant which it generates. This will be done in Chapter V. In order to prove the assertion that the variational coefficients are also adiabatic to first order in δR_m, equation (IV.2.27), it is necessary to invert that secular equation and to solve for its eigenfunctions. This will also be done in Chapter V.

For the present, using equations (IV.2.26) and (IV.2.27), the derivative sought is,

$$\frac{d}{dR_m}\left(\psi_{\vec{k}}(\vec{x}_k;R)\right) = \sqrt{\frac{1}{A}}\sum_i \frac{a(\vec{k}+\vec{K}_i)\,e^{i\vec{k}\cdot\vec{R}_m}}{\sqrt{N}}$$

$$\times\left(i(\vec{k}+\vec{K}_i)\cdot\hat{e}(\overrightarrow{\delta R}_m)\,\varphi_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m) - \hat{e}(\overrightarrow{\delta R}_m)\cdot\vec{\nabla}\varphi_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m)\right)$$

(IV.2.29)

IV.3 The Electron-Phonon Vertex Function by the A.P.W. Formalism.

In the independent-particle formalism, the non-adiabatic terms in Frohlich's Hamiltonian,

$$\sum_{\substack{\vec{k}\\ \vec{k}'}} \sum_{\vec{q}} D(\vec{k}',\vec{k},\vec{q})\, c^{+}_{\vec{k}'}\, c_{\vec{k}} \left(a_{\vec{q}} - a^{+}_{-\vec{q}}\right) , \qquad \text{(IV.3.1)}$$

involve the vertex function $D(\vec{k}',\vec{k})$. Within the framework of the Adiabatic Model, andusing Slater determinants as eigenfunctions for the electronic system, this vertex function has the following form:

$$D(\vec{k}',\vec{k},\vec{q}) = \left(\frac{\hbar^{3}\, \omega(\vec{q})\, n_{\vec{q}}}{8NM}\right)^{1/2} \int \psi^{*}_{\vec{k}'}(\vec{x};R)\, \frac{d}{dQ_{\vec{q}}} \left(\psi_{\vec{k}}(\vec{x};R)\right) d\vec{x} \ , \qquad \text{(IV.3.2)}$$

where equations (IV.2.3) and (IV.2.4) have been combined. In equation (IV.3.2) the derivative of the electronic eigenfunction is with respect to the normal mode $Q_{\vec{q}}$. Because the variations of the nuclear coordinates are written such that

$$\vec{R}_{m} = \vec{R}^{o}_{m} + \sum_{\vec{q},s} Q_{\vec{q},s}\, \vec{\epsilon}_{s}(\vec{q})\, e^{i\vec{q}\cdot\vec{R}^{o}_{m}} , \qquad \text{(IV.3.3)}$$

these derivatives are related simply by the chain rule:

$$\frac{d}{dQ_{\vec{q},s}} = \sum_{R_m} \frac{d\vec{R}_{m}}{dQ_{\vec{q},s}}\, \frac{d}{dR_{m}} = \sum_{R_m} \vec{\epsilon}_{s}(\vec{q})\, e^{i\vec{q}\cdot\vec{R}_{m}}\, \frac{d}{dR_{m}} \ . \qquad \text{(IV.3.4)}$$

Therefore, the vertex function $D(\vec{k}', \vec{k}, \vec{q})$ will involve the factor,

$$\int \psi^*_{\vec{k}'}(\vec{x};R) \frac{d}{dR_m} \left(\psi_k(\vec{x};R)\right) d\vec{x} \ , \tag{IV.3.5}$$

which equals, by substituting in equation (IV.2.29),

$$\sqrt{\frac{1}{A(\vec{k})\ A(\vec{k})}} \sum_i \sum_j \left(a^*(\vec{k}'+\vec{K}_j)\ a(\vec{k}+\vec{K}_i) \frac{e^{i\vec{k}\cdot\vec{R}_m}}{\sqrt{N}} \right)$$

$$\times \int \left[\left(\frac{e^{-i(\vec{k}'+\vec{K}_j)\cdot\vec{x}}}{\sqrt{V}} + \sqrt{\frac{1}{N}} \sum_{R_p} e^{-i\vec{k}'\cdot\vec{R}_p} \varphi^*_{\vec{k}+\vec{K}_j}(\vec{x}-\vec{R}_p) \right) \right.$$

$$\left. \times \left(i(\vec{k}+\vec{K}_i) - \vec{\nabla}_x \right) \varphi_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m) \cdot \hat{e}(\delta\vec{R}_m) \right] d\vec{x} \ . \tag{IV.3.6}$$

Equation (IV.3.6) involves four integrals which are evaluated one by one:

$$\frac{e^{i\vec{k}\cdot\vec{R}_m}}{\sqrt{N}} \left(\int \frac{e^{-i(\vec{k}'+\vec{K}_j)\cdot\vec{x}}}{\sqrt{V}} \varphi_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m)\ d\vec{x} \right) i(\vec{k}+\vec{K}_i)\cdot\hat{e}(\delta\vec{R}_m)$$

$$= e^{i(\vec{k}-\vec{k}')\cdot\vec{R}_m} \sqrt{\frac{1}{NV}} \left(\int \varphi_{\vec{k}+\vec{K}_i}(\vec{x}')\ e^{-i(\vec{k}'+\vec{K}_j)\cdot\vec{x}'}\ d\vec{x}' \right) i(\vec{k}+\vec{K}_i)\cdot\hat{e}(\delta\vec{R}_m) \tag{IV.3.7}$$

In equation (IV.3.7) the variable of integration has been transformed as

$$\vec{x}' = \vec{x} - \vec{R}_m \ , \tag{IV.3.8}$$

which leaves the integral over the volume of the entire crystal unchanged:

$$\frac{-e^{i\vec{k}\cdot\vec{R}_m}}{\sqrt{N}}\left(\int \frac{e^{-i(\vec{k}+\vec{K}_j)\cdot\vec{x}}}{\sqrt{V}}\, \vec{\nabla}_x\, \varphi_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m)\, d\vec{x}\right)\cdot \hat{e}(\delta\vec{R}_m)$$

$$= \frac{-e^{i\vec{k}\cdot\vec{R}_m}}{\sqrt{N}}\, \hat{e}(\delta\vec{R}_m)\cdot\left(\left.\frac{e^{-i(\vec{k}+\vec{K}_j)\cdot\vec{x}}}{\sqrt{V}}\, \varphi_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m)\, \hat{e}(\vec{x})\right|_{\text{surface}}\right.$$

$$\left. + \ i(\vec{k}'+\vec{K}_j)\int e^{-i(\vec{k}'+\vec{K}_j)\cdot\vec{x}}\, \varphi_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m)\, d\vec{x}\right)$$

$$= e^{i(\vec{k}-\vec{k}')\cdot\vec{R}_m}\sqrt{\frac{1}{NV}}\left(\int \varphi_{\vec{k}+\vec{K}_i}(\vec{x}')\, e^{-i(\vec{k}'+\vec{K}_j)\cdot\vec{x}'}\, d\vec{x}'\right) i(\vec{k}'+\vec{K}_j)\cdot\hat{e}(\delta\vec{R}_m). \tag{IV.3.9}$$

In evaluating the integral equation (IV.3.9) the surface term which obtained from the integration by parts was discarded because the tight-binding components are all zero on the surface of every cell. The transformation (IV.3.8) was also used,

$$\frac{e^{i\vec{k}\cdot\vec{R}_m}}{\sqrt{N}}\sqrt{\frac{1}{N}}\sum_{R_p} e^{i\vec{k}'\cdot\vec{R}_p}\left(\int \varphi^*_{\vec{k}'+\vec{K}_j}(\vec{x}-\vec{R}_p)\, \varphi_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m)\, d\vec{x}\right) i(\vec{k}+\vec{K}_i)\cdot\hat{e}(\delta\vec{R}_m)$$

(continued)

$$= \frac{e^{i(\vec{k}-\vec{k}')\cdot\vec{R}_m}}{N}\left(\int \varphi^{*}_{\vec{k}'+\vec{K}_j}(\vec{x}')\,\varphi_{\vec{k}+\vec{K}_i}(\vec{x})\,d\vec{x}\right) i(\vec{k}+\vec{K}_i)\cdot\hat{e}(\overrightarrow{\delta R}_m)\ . \qquad \text{(IV.3.10)}$$

The non-overlapping property of the tight-binding components,

$$\varphi^{*}_{\vec{k}'}(\vec{x}-\vec{R}_p)\,\varphi_{\vec{k}}(\vec{x}-\vec{R}_m) = 0 \quad \text{if} \quad \vec{R}_p \neq \vec{R}_m\ , \qquad \text{(IV.3.11)}$$

has been used to simplify the integrals in equation (IV.3.10),

$$\frac{-e^{i\vec{k}\cdot\vec{R}_m}}{N}\sum_{R_p} e^{-i\vec{k}'\cdot\vec{R}_p}\left(\int \varphi^{*}_{\vec{k}'+\vec{K}_j}(\vec{x}-\vec{R}_p)\left(\vec{\nabla}\varphi_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m)\right)d\vec{x}\right)\cdot\hat{e}(\overrightarrow{\delta R}_m)$$

$$= \frac{-e^{i(\vec{k}-\vec{k}')\cdot\vec{R}_m}}{N}\left(\int \varphi^{*}_{\vec{k}'+\vec{K}_j}(\vec{x})\left(\vec{\nabla}\varphi_{\vec{k}+\vec{K}_i}(\vec{x}')\right)d\vec{x}'\right)\cdot\hat{e}(\overrightarrow{\delta R}_m). \qquad \text{(IV.3.12)}$$

Combining equations (IV.3.7), (IV.3.9), (IV.3.10), and (IV.3.12) gives

$$e^{i(\vec{k}-\vec{k}')\cdot\vec{R}_m}\sum_i\sum_j\left(\frac{a^{*}(\vec{k}'+\vec{K}_j)\,a(\vec{k}+\vec{K}_i)}{\sqrt{A(\vec{k}')\,A(\vec{k})}}\right)$$

$$\Bigg\{ i(\vec{k}+\vec{K}_i-\vec{k}'-\vec{K}_j)\cdot\hat{e}(\overrightarrow{\delta R}_m)\sqrt{\frac{1}{N}}\int e^{-i(\vec{k}'+\vec{K}_j)\cdot\vec{x}'}\,\varphi_{\vec{k}+\vec{K}_i}(\vec{x}')\,d\vec{x}' +$$

$$+\ i(\vec{k}+\vec{K}_i)\cdot\hat{e}(\overrightarrow{\delta R}_m)\,\frac{1}{N}\int \varphi^{*}_{\vec{k}'+\vec{K}_j}(\vec{x}')\,\varphi_{\vec{k}+\vec{K}_i}(\vec{x}')\,d\vec{x}' +$$

(continued)

$$+ \hat{e}(\delta\vec{R}_m) \cdot \frac{1}{N} \int \varphi^*_{\vec{k}'+\vec{K}_j}(\vec{x}') \left(\vec{\nabla}\varphi_{\vec{k}+\vec{K}_i}(\vec{x}')\right) d\vec{x}' \Bigg\} . \qquad \text{(IV.3.13)}$$

Transforming this expression into a derivative with respect to the normal mode $Q_{\vec{q}}$ involves the summation over R_m as in equation (IV.3.4), which gives

$$\sum_{R_m} e^{i(\vec{k}-\vec{k}')\cdot\vec{R}_m} \vec{\epsilon}_s(\vec{q})\, e^{i\vec{q}\cdot\vec{R}_m} = N\, \delta(\vec{k}-\vec{k}'+\vec{q}+\vec{K}_\ell)\, \vec{\epsilon}_s(\vec{q}) . \qquad \text{(IV.3.14)}$$

Thus there obtains, as expected, the selection rule for the conservation of lattice pseudo-momentum.

Therefore, the vertex function is

$$D(\vec{k}',\vec{k},\vec{q}) = \delta(\vec{k}-\vec{k}'+\vec{q}+\vec{K}_\ell) \sum_i \sum_j \left(\frac{a^*(\vec{k}'+\vec{K}_j)\, a(\vec{k}+\vec{K}_i)}{\sqrt{A(\vec{k}')\, A(\vec{k})}} \right)$$

$$\Bigg\{ i(\vec{k}+\vec{K}_i-\vec{k}'-\vec{K}_j)\cdot\vec{\epsilon}_s(\vec{q}) \sqrt{\frac{N}{V}} \int e^{-i(\vec{k}'+\vec{K}_j)\cdot\vec{x}}\, \varphi_{\vec{k}+\vec{K}_i}(\vec{x})\, d\vec{x}$$

$$+ i(\vec{k}+\vec{K}_i)\cdot\vec{\epsilon}_s(\vec{q}) \int \varphi^*_{\vec{k}'+\vec{K}_j}(\vec{x})\, \varphi_{\vec{k}+\vec{K}_i}(\vec{x})\, d\vec{x} +$$

$$- \vec{\epsilon}_s(\vec{q}) \int \varphi^*_{\vec{k}'+\vec{K}_j}(\vec{x}) \left(\vec{\nabla}\varphi_{\vec{k}'+\vec{K}_i}(\vec{x})\right) d\vec{x} \Bigg\} \left(\frac{\hbar^3\, \omega(\vec{q})\, n_q}{8NM} \right)^{1/2} . \qquad \text{(IV.3.15)}$$

There are several observations to be made of this vertex function. First, it does display a term which has the form,

$$D(\vec{k},\vec{q}) \sim |\vec{q}|\, C \cong |\vec{q}| \left(\int e^{-i(\vec{k}+\vec{q})\cdot\vec{x}} \varphi_{\vec{k}}(\vec{x})\, d\vec{x} \right) , \qquad \text{(IV.3.16)}$$

as in the Frohlich Hamiltonian. Furthermore, because this term enters with the coefficients,

$$a^{*}(\vec{k}+\vec{q})\; a(\vec{k}) \;, \qquad \text{(IV.3.17)}$$

which are usually the largest Fourier amplitudes in the eigenfunctions, this term will expectedly contribute strongly to the electron-phonon interactions. Second, the transverse phonons enter the normal processes,

$$\vec{k} - \vec{k}' + \vec{q} = 0 \;, \qquad \text{(IV.3.18a)}$$

as well as the Umklapp processes,

$$\vec{k} - \vec{k}' + \vec{q} = K_{\ell} \;. \qquad \text{(IV.3.18b)}$$

The interactions involving the transverse modes enter all three terms in equation (IV.3.15). Even an eigenfunction involving only a single plane wave admits the interactions with the transverse modes through the matrix elements,

$$i\vec{k} \cdot \vec{\epsilon}_{s}(\vec{q}) \int \varphi^{*}_{\vec{k}+\vec{q}}(\vec{x})\, \varphi_{\vec{k}}(\vec{x})\, d\vec{x} \;. \qquad \text{(IV.3.19)}$$

CHAPTER V

THE ENERGY BAND PROBLEM FOR A DEFORMED LATTICE

V.1 The Matrix Elements for the Band Energies when a Single Nucleus is Displaced.

Although the lattice deformations which correspond to the presence of phonons are the normal mode configurations of the nuclei, we shall consider the energy band problem for the case of a single nucleus displaced slightly from its equilibrium position. The lattice deformations of the normal modes (or of any other deformation) can be expressed as lattice Fourier series of such single displacements.

We shall follow the procedure discussed in Chapter III for the A.P.W. method. We shall use a muffin-tin potential,

$$V(\vec{x}) = V(r) \qquad r \le r_s \qquad \text{(V.1.1a)}$$

$$V(\vec{x}) = V(r_s) \qquad r \ge r_s \ , \qquad \text{(V.1.1b)}$$

and shall use, initially, the same potential within the A.P.W. sphere about the displaced nucleus as that for the perfect lattice. It will be shown below that this is the correct muffin-tin potential to use. In Chapter VI the variations of the self-consistent potential are discussed extensively.

A few remarks concerning the drawing of the radius of the inscribed A.P.W. sphere are in order.

Because the A.P.W. sphere remains centered about the nucleus when it is displaced, it is important that the sphere be drawn so as not to intersect the Wigner-Seitz cell boundaries or to overlap into the next cell. This is effected by drawing the radius of the A.P.W. sphere somewhat smaller than the minimum distance from the center of the cell to the cell boundary: i.e., smaller than the radius of "touching spheres."

It is not especially important exactly how much smaller than the maximum allowable value the radius be set, for the validity and accuracy of the A.P.W. method is independent of the size of the A.P.W. sphere, so long as it remains inscribed within the Wigner-Seitz cell. To investigate the electron-phonon interactions by analyzing the differences of the solutions to the energy band problem for the deformed lattice and for the perfect lattice it is required only that the A.P.W. spheres be sufficiently small that they do not intercept the cell boundaries when displaced by the normal mode lattice deformations. In order to estimate the extent of maximum variation of the inter-atomic distance, the mean variation of the nuclear excursions in the Debye limit, where the amplitudes of adjacent nuclei are 180 degrees out of phase with one another, can be calculated from the Virial theorem:

$$V_{\text{ave}} = \frac{M^2\,\omega^2}{2}\left\langle \Delta x^2 \right\rangle = \frac{1}{2}E \ , \qquad \text{(V.1.2)}$$

which, for the Debye limit gives

$$\left\langle \Delta x^2 \right\rangle = \frac{\hbar}{M^2\,\omega_D} = \frac{\hbar^2}{MkT_D} \ , \qquad \text{(V.1.3)}$$

where the identity,

$$\hbar\omega_D \equiv kT_D \ , \qquad \text{(V.1.4)}$$

has been used. For the metals Lithium and Sodium the values of M and T are, respectively, 11.6×10^{-24}, 38.2×10^{-24} gms, 430, 150 deg. K.

For these metals the mean excursion, $\sqrt{\left\langle (\Delta x)^2 \right\rangle}$ is 2.6×10^{-9} cm for Li, and 2.4×10^{-9} cm for Na. Their nearest-neighbor distances in the perfect lattice are, respectively, 5.713×10^{-8} cm and 6.914×10^{-8} cm. Thus it is observed that the interatomic distance between adjacent atoms changes by only a few percent when the lattice undergoes a normal mode distortion.

Therefore, it suffices to draw the A.P.W. sphere radius slightly smaller, say 5% - 10%, than half the nearest neighbor distance.

To analyse the solution to the energy band problem when one nucleus is displaced from its equilibrium position we parallel the discussion of the A.P.W. method as in Section III.

First we examine the variational calculation for the case where the trial functions inside the A.P.W. sphere are matched onto a single plane wave at the sphere radius.

Let the equilibrium position of the displaced nucleus be given by $\vec{R}_m$. The position of this nucleus after displacement is $\vec{R}_m + \vec{\delta R}_m$, which now specifies also the center of the A.P.W. sphere in the $\vec{R}_m$-th cell. Inside the $\vec{R}_m$-th cell the trial functions for the A.P.W. problem are written using the coordinate system having its origin at $\vec{R}_m + \vec{\delta R}_m$. Because the coordinate systems for the equilibrium position- and displaced-atom problems are related by the equation,

$$\vec{r}\,' = \vec{r} - \vec{\delta R}_m \quad . \tag{V.1.5}$$

The plane wave component of the solutions can be written

$$e^{i\vec{k}\cdot\vec{r}} = e^{i\vec{k}\cdot\vec{\delta R}_m}\, e^{i\vec{k}\cdot\vec{r}\,'} \tag{V.1.6a}$$

$$= e^{i\vec{k}\cdot\vec{\delta R}_m} \sum_{e} i^{\ell}(2\ell+1) \sum_{m=-\ell}^{\ell} \frac{(\ell-|m|)!}{(\ell+|m|)!} P_{\ell}^{|m|}(\cos\theta_k)\, e^{-im\varphi_k}$$

$$\times P_{\ell}^{|m|}(\cos\theta')\, e^{im\varphi'}\, j_{\ell}(kr') \quad . \tag{V.1.6b}$$

The primes in equations (V.1.6a), (V.1.6b) designate coordinates measured from the origin centered at the displaced nucleus. The trial A.P.W. functions inside the A.P.W. sphere involve the solutions to the radial equation,

$$\left(\frac{-1}{(r')^2} \frac{d}{dr'} \left(r'^2 \frac{d}{dr'} \right) + \frac{\ell(\ell+1)}{(r')^2} + v(r') - \epsilon \right) u_\ell(r') = 0 \; . \qquad \text{(V.1.7)}$$

The trial functions inside the A.P.W. sphere are matched on to the plane waves, $e^{i\vec{k}\cdot\vec{r}}$ at the displaced sphere surface such that

$$\psi_{\vec{k}}(\vec{x}) = e^{i\vec{k}\cdot\vec{\delta R}_m} \sum_{\ell} i^{\ell}(2\ell+1) \sum_{m=-\ell}^{\ell} \frac{(\ell-|m|)!}{(\ell+|m|)!} P_\ell^{|m|}(\cos\theta_k)\, e^{-im\varphi_k}$$

$$\times P_\ell^{|m|}(\cos\theta')\, e^{im\varphi} \frac{j_\ell(kr_s)}{u_\ell^{\epsilon}(r_s)} u_\ell^{\epsilon}(r') \quad \text{for} \quad r' \le r_s \; . \qquad \text{(V.1.8)}$$

It is to be observed that, aside from the relabelling of the spatial coordinates with primes, this expression is identical with that for the trial function in the perfect lattice except for the factor,

$$e^{i\vec{k}\cdot\vec{\delta R}_m} \; . \qquad \text{(V.1.9)}$$

(Note that the angles which designate the point in k-space, θ_k, and φ_k, are the same for the displaced nucleus as in the perfect lattice.) Thus it is obvious that the eigenvalues which determine the solutions to the integral equation,

$$\int \psi_k^*(\vec{x}) \left(h_e(\vec{x};R+\delta R) - \epsilon(\vec{k})\right) \psi_k^\epsilon(\vec{x})\, d\vec{x} = 0 \ , \qquad (V.1.10)$$

are the same for the displaced nucleus as for the perfect lattice. The explicit expression for the integral above in the displaced nucleus case is,

$$\left(h_e(\vec{x};R+\delta R) - \epsilon\right)_{kk} =$$

$$= e^{-i\vec{k}\cdot\vec{\delta R}_m} \left(\left(k^2 - \epsilon(k)\right) \left(1 - \frac{4\pi r_s^3}{\Omega}\right) + \frac{4\pi r_s^2}{\Omega} \sum_\ell (2\ell+1) \left(j_\ell(k r_s)\right)^2 \frac{u_\ell^{\epsilon'}(r_s)}{u_\ell^{\epsilon}(r_s)} \right) e^{i\vec{k}\cdot\vec{\delta R}_m}$$

$$= \left(\left(k^2 - \epsilon(k)\right) \left(1 - \frac{4\pi r_s^2}{\Omega}\right) + \frac{4\pi r_s^2}{\Omega} \sum_\ell (2\ell+1) \left(j_\ell(k r_s)\right)^2 \frac{u_\ell^{\epsilon'}(r_s)}{u_\ell^{\epsilon}(r_s)} \right) , \qquad (V.1.11)$$

which is identical to $\left(h_e(\vec{x};R^o) - \epsilon(k)\right)_{kk}$, as given in expression (III. 3.17) Although the eigenvalue, $\epsilon(k)$, remains invariant in this special case where the eigenfunction is the plane wave, $e^{i\vec{k}\cdot\vec{x}}$, outside the A.P.W. sphere, the eigenfunction which belongs to it is, of course, changed. The atomic-like part of the eigenfunction is now centered about $\vec{R}_m + \vec{\delta R}_m$, and the eigenfunction is no longer periodic in the lattice. However, inside the A.P.W. sphere, the functional form (or shape) of the eigenfunction is still the same, for the functional form of the eigenfunction there is determined by the eigenvalue, ϵ. Since the eigenvalue, ϵ, remains constant, the radial functions,

$$u_\ell^\epsilon(r) \ , \qquad (V.1.12)$$

and their relative admixtures inside the sphere remain fixed also.

The analysis above can be made more general by varying the trial functions outside the displaced A.P.W. sphere so as to admit other plane waves of the form

$$e^{i(\vec{k}+\vec{K}_j)\cdot\vec{r}'}\,, \tag{V.1.13}$$

where $\vec{K}_j$ is a vector of the reciprocal lattice, just as is done for the perfect lattice.

Following the technique used in equations (V.1.6) through (V.1.10), the matrix element between the trial functions which join continuously onto the plane waves $e^{i\vec{k}\cdot\vec{x}'}$ and $e^{i(\vec{k}+\vec{K}_j)\cdot\vec{x}'}$, respectively, is

$$\begin{aligned}\Bigl(h_e(x;\vec{R}_m+\vec{\delta R}_m)-\epsilon\Bigr)_{\vec{k},\vec{k}+\vec{K}_j} &= \\ &= \frac{4\pi r_s^2}{\Omega}\Biggl(-\Bigl(\vec{k}\cdot(\vec{k}+\vec{K}_j)-\epsilon\Bigr)\frac{j_1(K_j\, r_s)}{|K_j|}+ \\ &\quad+\sum_{\ell=0}^{\infty}(2\ell+1)\,P_\ell\Bigl(\cos\theta^{k}_{k+K_j}\Bigr)j_\ell(kr_s)\,j_\ell(|\vec{k}+\vec{K}_j|\,r_s\;\frac{u_\ell^{\epsilon\,\prime}(r_s)}{u_\ell^{\epsilon}(r_s)}\Biggr)e^{i\vec{K}_j\cdot\vec{\delta R}_m}\,.\end{aligned} \tag{V.1.14}$$

Equation (V.1.13) is observed to be identical to the matrix element of

$$\Bigl(h_e(\vec{x};R^{\circ})-\epsilon\Bigr)_{\vec{k},\vec{k}+\vec{K}_j} \tag{V.1.15}$$

except for the factor

$$e^{i\vec{K}_j \cdot \vec{\delta R}_m} \quad . \tag{V.1.16}$$

The A.P.W. eigenvalue for the deformed lattice is again ascertained by the zeroes of the secular determinant:

$$\det \left| (h - \epsilon)_{ij} \right| = 0 \quad , \tag{V.1.17}$$

just as for the perfect lattice. The rows and columns of the secular determinant are specified by the wave vectors of the plane waves entering the trial functions, such that

$$(h - \epsilon)_{ij} = \int \psi^*_{\vec{k}+\vec{K}_i}(\vec{x}) \left(h_e(\vec{x};\vec{R}_m + \vec{\delta R}_m) - \epsilon \right) \psi_{\vec{k}+\vec{K}_j}(\vec{x})\, d\vec{x} \ . \tag{V.1.18}$$

Therefore, the difference between the secular determinants for the displaced nucleus and for the perfect lattice is only that every matrix element for the former case in the $\vec{K}_j$-th column is multiplied by the factor

$$e^{i\vec{K}_j \cdot \vec{\delta R}_m} \quad , \tag{V.1.19}$$

and every element of the $\vec{K}_i$-th row by the factor

$$e^{-i\vec{K}_i \cdot \vec{\delta R}_m} \quad .$$

Now the theory of determinants establishes that, if, every element of a given row, or column, is multiplied by a constant, c, then the value of the determinant is changed by the same constant. Thus the values of the A.P.W. determinental function are altered by only a factor, and the values of the band energy, $\epsilon(k)$, for which the determinant vanishes are unchanged.

This is not altogether an expected result: the eigenvalue of the function which satisfies the Schrodinger equation explicitly inside the A.P.W. sphere and which is represented by the lattice Fourier series

$$\sum_{\vec{K}_i} a(\vec{k}+\vec{K}_i)\, e^{i(\vec{k}+\vec{K}_i)\cdot\vec{x}} \tag{V.1.20}$$

between the sphere and the cell boundary is invariant under small translations of the muffin-tin potential. Moreover, the eigenfunction which belongs to this eigenvalue is changed only to the extent that it is centered about the displaced sphere.

Although this result is not a property of the complete variational solution to the eigenvalue problem for an electron in a deformed lattice, it will be useful when expanding by minors the secular determinant for the full variational problem. In the next section, it will be shown that the eigenvalues for this problem are invariant up to terms quadratic in the variations of the nuclear coordinates.

V.2 The Solution to the Variational Eigenvalue Problem for an Electron in a Deformed Lattice: Expansion of the Secular Determinant.

The argument above does not completely dispose of the problem of the variation of the one-electron eigenvalues under lattice deformations. When the lattice is deformed by a translation of the $\vec{R}_m$-th nucleus, the one-electron Hamiltonian no longer has the translational symmetry of the perfect lattice. The plane waves in expression (V.1.20) transform irreducibly in the perfect lattice and therefore comprise a complete set of trial functions for that case. However, they do not form a complete set of trial functions for the general aperiodic lattice; and for the case under investigation, the set,

$$\sum_{k'} \sum_{K_j} e^{i(\vec{k}' + \vec{K}_j) \cdot \vec{x}} \tag{V.2.1}$$

must be used as trial functions in the region between the A.P.W. sphere and the cell boundary.

The A.P.W. matrix elements between such trial functions will be similar to that given by equation (V.1.14). However, because the matrix element is taken between two functions of different periodicity in the lattice, the integral over the entire volume of the crystal will have its lowest order term linear in $\vec{\delta R}_m$. For the matrix element between the $(\vec{k}' + \vec{K}_j)$-th and the $(\vec{k}+\vec{K}_i)$-th trial functions, this is,

$$\int_{\mathrm{Vol}} \psi^*_{k'+K_j}(\vec{x})\left(h_e(\vec{x};\vec{R}+\delta\vec{R}_m) - \epsilon\right)\psi_{\vec{k}+\vec{K}_i}(\vec{x})\,\frac{d^3x}{V}$$

$$= \int_{\mathrm{Vol}} \psi^*_{k'+\vec{K}_j}(\vec{x})\left(h_e(\vec{x},R^o) - \epsilon\right)\psi_{\vec{k}+\vec{K}_i}(\vec{x})\,\frac{d^3x}{V} +$$

$$- \int_{\substack{R_m\text{-th}\\ \text{cell}}} \psi^*_{\vec{k}'+\vec{K}_j}(\vec{x})\left(h_e(\vec{x};R^o) - \epsilon\right)\psi_{\vec{k}+\vec{K}_i}(\vec{x})\,\frac{d^3x}{V} +$$

$$+ \int_{\substack{R_m\text{-th}\\ \text{cell}}} \psi^*_{\vec{k}'+\vec{K}_j}(\vec{x})\left(h_e(\vec{x};\vec{R}+\delta\vec{R}_m) - \epsilon\right)\psi_{\vec{k}+\vec{K}_i}(\vec{x})\,\frac{d^3x}{V}\ . \qquad (V.2.2)$$

The first integral in equation (V.2.2) can be written as the sum,

$$\sum_{\vec{R}_p} \frac{e^{i(\vec{k}-\vec{k}')\cdot\vec{R}_p}}{N\Omega} \int_{\Omega} \psi^*_{\vec{k}'+\vec{K}_j}(\vec{x})\left(h_e(\vec{x},R^o) - \epsilon\right)\psi_{\vec{k}+\vec{K}_i}(\vec{x})\,d^3x\ , \qquad (V.2.3)$$

where in (V.2.3) has been used the translational property of the Bloch functions,

$$\psi_{\vec{k}+\vec{K}_i}(\vec{x}+\vec{R}_p) = e^{i\vec{k}\cdot\vec{R}_p}\,\psi_{\vec{k}+\vec{K}_i}(\vec{x})\ , \qquad (V.2.4)$$

and where the integration is over the volume, Ω, of the Wigner-Seitz cell. The first orthogonality relation for the representatives of the irreducible representations of finite groups is,

$$\sum_{T} D^{\alpha}_{ij}(T)^{*}\, D^{\beta}_{k\ell}(T) = \frac{g}{n_{\alpha}}\, \delta_{ik}\, \delta_{j\ell}\, \delta_{\alpha\beta} \,, \qquad (\text{V}.2.5)$$

where g is the order of the group, and n_{α} the dimensionality of the α-th irreducible representation. For the representatives of the lattice translation group, this relation is,

$$\sum_{R_p} e^{i(\vec{k}-\vec{k}')\cdot\vec{R}_p} = N\, \delta(\vec{k}-\vec{k}') \ . \qquad (\text{V}.2.6)$$

Therefore, the expression (V.2.3) is zero when $\vec{k}' \neq \vec{k}$ as is presently the case — the exceptional case having been analysed in the last section. The remaining two integrals in equation (V.2.2) can be combined by using the results of the analysis of the last section as expressed in equation (V.1.14). Using (V.1.14), equation (V.2.2) becomes,

$$\Big(h_e(R+\delta R_m) - \epsilon\Big)_{\vec{k}'+\vec{K}_j,\, \vec{k}+\vec{K}_i} = \frac{4\pi r_s^2}{N\Omega} \Bigg\{ -\Big((\vec{k}'+\vec{K}_j)\cdot(\vec{k}+\vec{K}_i) - \epsilon\Big) \frac{j_1\Big(|\vec{k}+\vec{K}_i-\vec{k}-\vec{K}_j|\, r_s\Big)}{|\vec{k}+\vec{K}_i-\vec{k}'-\vec{K}_j|} +$$

$$+ \sum_{\ell=0}^{\infty} (2\ell+1)\, P_\ell\left(\cos\theta_{\vec{k}'+\vec{K}_j}^{\vec{k}+\vec{K}_i}\right) j_\ell(|\vec{k}+\vec{K}_i|\, r_s)\, j_\ell(|\vec{k}'+\vec{K}_j|\, r_s)\ \times$$

$$\times \frac{u_\ell^{\epsilon'}(r_s)}{u_\ell^{\epsilon}(r_s)} \Bigg\} \left(e^{i(\vec{k}+\vec{K}_i-\vec{k}'-\vec{K}_j)\cdot\delta\vec{R}_m} - 1 \right) =$$

$$= \frac{1}{N} \Big(h_e(R_0) - \epsilon\Big)_{\vec{k}'+\vec{K}_j,\, \vec{k}+\vec{K}_i} \left(e^{i(\vec{k}+\vec{K}_i-\vec{k}'-\vec{K}_j)\cdot\delta\vec{R}_m} - 1 \right) . \qquad (\text{V}.2.7)$$

By expanding the exponent in equation (V.2.7) such that

$$e^{i(\vec{k}+\vec{K}_i-\vec{k}'-\vec{K}_j)\cdot\vec{\delta R}_m} \cong 1 + i(\vec{k}+\vec{K}_i-\vec{k}'-\vec{K}_j)\cdot\vec{\delta R}_m + \ldots \; , \qquad \text{(V.2.8)}$$

the matrix element in equation (V.2.2) and equation (V.2.7) can be expressed as

$$i(\vec{k}+\vec{K}_i-\vec{k}'-\vec{K}_j)\cdot\frac{\vec{\delta R}_m}{N}(h_e-\epsilon)_{\vec{k}'+\vec{K}_j,\,\vec{k}+\vec{K}_i} \; . \qquad \text{(V.2.9)}$$

Because there are now matrix elements connecting all trial functions, the A.P.W. secular determinant will be of the order of $10^{23} \times 10^{23}$. This determinant must now be solved as a function of the trial band energy, ϵ, and its zeroes will render the eigenvalues to the full variational problem of the electron in a deformed lattice.

For purposes of mathematical convenience, the $10^{23} \times 10^{23}$ secular determinant will be written in terms of sub-determinants labelled by their respective k-vectors in the first Brillouin Zone of the perfect lattice; i.e., the element

$$(h-\epsilon)_{k,k} \; , \qquad \text{(V.2.10)}$$

will be understood to stand for the full determinant of

$$\begin{pmatrix} (h-\epsilon)_{k,k} & (h-\epsilon)_{k,k+K_i} & (h-\epsilon)_{k,k+K_j} & \cdots \\ (h-\epsilon)_{k+K_i,k} & (h-\epsilon)_{k+K_i,k+K_j} & (h-\epsilon)_{k+K_i,k+K_j} & \cdots \\ \vdots & & & \end{pmatrix} , \qquad \text{(V.2.11)}$$

and similarly for the element,

$$(h - \epsilon)_{k',k} \quad . \qquad (V.2.12)$$

Also for purposes of convenience, the k-vector of the state whose eigenvalue in the perfect lattice is $\epsilon(\vec{k})$ will be relabelled k_o. The rows and columns of the $10^{23} \times 10^{23}$ secular determinant will be labelled by the k-vectors of the trial functions, beginning with $\vec{k}_o$. The A.P.W. secular determinant now has the form,

$$
|D(\epsilon)| =
\begin{vmatrix}
(h-\epsilon)_{k_0,k_0} & -i(\vec{k}_0-\vec{k}_1)\cdot\dfrac{\overrightarrow{\delta R}_m}{N}(h-\epsilon)_{k_0,k_1} & -i(\vec{k}_0-\vec{k}_2)\cdot\dfrac{\overrightarrow{\delta R}_m}{N}(h-\epsilon)_{k_0,k_2} & \cdots \\
-i(\vec{k}_1-\vec{k}_0)\cdot\dfrac{\overrightarrow{\delta R}_m}{N}(h-\epsilon)_{k_1,k_0} & (h-\epsilon)_{k_1,k_1} & -i(\vec{k}_1-\vec{k}_2)\cdot\dfrac{\overrightarrow{\delta R}_m}{N}(h-\epsilon)_{k_1,k_2} & \cdots \\
-i(\vec{k}_2-\vec{k}_0)\cdot\dfrac{\overrightarrow{\delta R}_m}{N}(h-\epsilon)_{k_2,k_0} & -i(\vec{k}_2-\vec{k}_1)\cdot\dfrac{\overrightarrow{\delta R}_m}{N}(h-\epsilon)_{k_2,k_1} & (h-\epsilon)_{k_2,k_2} & \cdots \\
-i(\vec{k}_3-\vec{k}_0)\cdot\dfrac{\overrightarrow{\delta R}_m}{N}(h-\epsilon)_{k_3,k_0} & -i(\vec{k}_3-\vec{k}_1)\cdot\dfrac{\overrightarrow{\delta R}_m}{N}(h-\epsilon)_{k_3,k_1} & \cdots & \\
-i(\vec{k}_4-\vec{k}_0)\cdot\dfrac{\overrightarrow{\delta R}_m}{N}(h-\epsilon)_{k_4,k_0} & \cdots & & \\
\vdots & & &
\end{vmatrix}
$$

(V.2.13) THE A.P.W. SECULAR DETERMINANT FOR THE DEFORMED LATTICE, $\vec{R}_m = \vec{R}^{\circ}_m + \overrightarrow{\delta R}_m$.

This determinant must now be solved to ascertain its zeroes. The determinant is evaluated directly by expanding in the minors of the first row,

$$D(\epsilon) = \sum_{j=0}^{N} D_{0,j} \, \mathrm{cof}(D_{0,j}) \ , \qquad \text{(V.2.14)}$$

where

$$D_{0,j} = (h - \epsilon)_{\vec{k}_0,\vec{k}_j} \ , \qquad \text{(V.2.15)}$$

and $\mathrm{cof}(D_{0,j})$ is the cofactor of the $(\vec{k}_0,\vec{k}_j)$-th element. Explicitly,

$$
\begin{aligned}
D(\epsilon) = {} & (h-\epsilon)_{k_0,k_0} \prod_{j=1}^{N} (h-\epsilon)_{k_j,k_j} \; + \\
& - (\vec{k}_1-\vec{k}_0) \cdot \frac{\vec{\delta R}_m}{N} (h-\epsilon)_{k_0,k_1}{}^{2} \left[\prod_{\substack{j=1 \\ j\neq 1}}^{N} (h-\epsilon)_{k_j,k_j} + \text{terms } 0(\delta R_m^2 \text{ and higher}) + \ldots \right] + \\
& - (\vec{k}_2-\vec{k}_0) \cdot \frac{\vec{\delta R}_m}{N} (h-\epsilon)_{k_0,k_2}{}^{2} \left[\prod_{\substack{j=1 \\ j\neq 2}}^{N} (h-\epsilon)_{k_j,k_j} + \text{terms } 0(\delta R_m^2 \text{ and higher}) + \ldots \right] + \\
& - (\vec{k}_3-\vec{k}_0) \cdot \frac{\vec{\delta R}_m}{N} (h-\epsilon)_{k_0,k_3}{}^{2} \left[\prod_{\substack{j=1 \\ j\neq 3}}^{N} (h-\epsilon)_{k_j,k_j} + \text{terms } 0(\delta R_m^2 \text{ and higher}) + \ldots \right] + \\
& + \ldots + \\
& - (\vec{k}_N-\vec{k}_0) \cdot \frac{\vec{\delta R}_m}{N} (h-\epsilon)_{k_0,k_N}{}^{2} \left[\prod_{\substack{j=1 \\ j\neq N}}^{N} (h-\epsilon)_{k_j,k_j} + \text{terms } 0(\delta R_m^2 \text{ and higher}) + \ldots \right] + \\
& \qquad + (h-\epsilon)_{k_0,k_0} \left[\text{terms } 0(\delta R_m^2 \text{ and higher}) + \ldots \right]
\end{aligned}
$$

(V.2.16) EXPANSION OF THE A.P.W. SECULAR DETERMINANT BY MINORS

Collecting similar terms and keeping only the terms of lowest order in δR_m, this determinantal function of energy is,

$$D(\epsilon) = \left(\prod_{j=1}^{N} (h-\epsilon)_{k_j,k_j}\right)\left[(h-\epsilon)_{k_0,k_0} - \sum_{j=1}^{N} \frac{|(h-\epsilon)_{k_j,k_0}|^2 - \left((\vec{k}_j-\vec{k}_0)\cdot\delta\vec{R}_m/N\right)^2}{(h-\epsilon)_{k_j,k_j}}\right]$$
$$+ (h-\epsilon)_{k_0,k_0}\left[\text{terms in } |\delta R_m|^2\right] . \qquad \text{(V.2.17)}$$

The second set of terms involving $(h-\epsilon)_{k_0,k_0}$ obtain because the diagonal term, $\prod_{j=1}^{N} (h-\epsilon)_{k_j,k_j}$ is not the full cofactor of $(h-\epsilon)_{k_0,k_0}$, and there must be included additional terms at least of order $(\delta R_m)^2$. It can easily be shown that, if the columns are interchanged, these additional terms involving $(h-\epsilon)_{k_0,k_0}$ have the same form as the first set in equation (V.2.17),

$$\left(\prod_{\substack{j=0\\ j\neq\ell}}^{N} (h-\epsilon)_{k_j,k_j}\right)\left[(h-\epsilon)_{k_\ell,k_\ell} - \sum_{j=\ell+1}^{N} \frac{\left((h-\epsilon)_{k_j,k_\ell}\,(\vec{k}_j-\vec{k}_\ell)\cdot\delta R_m/N\right)^2}{(h-\epsilon)_{k_j,k_j}}\right] . \qquad \text{(V.2.18)}$$

This formal similarity is to be expected, for the secular determinant now includes all states. The set of zeroes for the secular determinant will be the set of all variational eigenvalues, $\epsilon(k_\ell)$, and there will be some 10^{23} such zeroes (not all distinct) as required by the number of states in the Brillouin Zone.

This can be observed by explicitly expanding the principal minor,

$$(h-\epsilon)_{k_0,k_0}\Bigg\{-\left[\sum_{j=2}^{N}\frac{\left((h-\epsilon)_{k_1,k_j}\,(\vec{k}_j-\vec{k}_1)\cdot\overrightarrow{\delta R}_m/N\right)^2}{(h-\epsilon)_{k_j,k_j}}\right]\prod_{j=2}^{N}(h-\epsilon)_{k_j,k_j}+$$

$$+(h-\epsilon)_{k_1,k_1}\Bigg\{-\left[\sum_{j=3}^{N}\frac{\left((h-\epsilon)_{k_2,k_j}\,(\vec{k}_j-\vec{k}_2)\cdot\overrightarrow{\delta R}_m/N\right)^2}{(h-\epsilon)_{k_j,k_j}}\right]\prod_{j=3}^{N}(h-\epsilon)_{k_j,k_j}+$$

$$+(h-\epsilon)_{k_2,k_2}\Bigg\{-\left[\sum_{j=4}^{N}\frac{\left((h-\epsilon)_{k_3,k_j}\,(\vec{k}_j-\vec{k}_3)\cdot\overrightarrow{\delta R}_m/N\right)^2}{(h-\epsilon)_{k_j,k_j}}\right]\prod_{j=4}^{N}(h-\epsilon)_{k_j,k_j}+$$

$$+(h-\epsilon)_{k_3,k_3}\Bigg\{-\left[\sum_{j=5}^{N}\frac{\left((h-\epsilon)_{k_4,k_j}\,(\vec{k}_j-\vec{k}_4)\cdot\overrightarrow{\delta R}_m/N\right)^2}{(h-\epsilon)_{k_j,k_j}}\right]\prod_{j=5}^{N}(h-\epsilon)_{k_j,k_j}+$$

$$+\ldots+$$

$$+(h-\epsilon)_{k_{N-2},k_{N-2}}\Bigg\{-\left((h-\epsilon)_{k_{N-1},k_N}\,(\vec{k}_{N-1}-\vec{k}_N)\circ\overrightarrow{\delta R}_m/N\right)^2$$

$$+(h-\epsilon)_{k_{N-1},k_{N-1}}\Bigg\{(h-\epsilon)_{k_N,k_N}\underbrace{\Bigg\}\Bigg\}\Bigg\}\Bigg\}\cdots\Bigg\}}_{N}$$

(V.2.19) THE EXPANSION OF THE PRINCIPAL MINOR IN THE A.P.W. SECULAR DETERMINANT.

Note that, in the explicit expansion of the principal minor given in (V.2.19), each left-handed curly bracket is enclosed within other such brackets, and these curly brackets are not closed from the right until after the N-th term.

By combining terms symbolically, this principal minor can be written as,

$$(h-\epsilon)_{k_0,k_0}\left\{\prod_{j=1}^{N}(h-\epsilon)_{k_j,k_j} + \right.$$
$$\left. -\sum_{\ell=1}^{N}\left[\sum_{j=\ell+1}^{N}\frac{\left((h-\epsilon)_{k_\ell,k_j}\,(\vec{k}_j-\vec{k}_\ell)\cdot\vec{\delta R}_m/N\right)^2}{(h-\epsilon)_{k_j,k_j}}\prod_{\substack{j=1\\ j\neq\ell}}^{N}(h-\epsilon)_{k_j,k_j}\right]\right\} . \qquad \text{(V.2.20)}$$

Taking cognizance of this formal similarity the expansion of the secular determinant by minors which retains only the lowest-order non-vanishing terms in δR_m is,

$$D(\epsilon) = \frac{1}{N}\sum_{\ell=0}^{N}\left\{\left(\prod_{\substack{j=0\\ j\neq\ell}}^{N}(h-\epsilon)_{k_j,k_j}\right)\right.$$
$$\left.\left[(h-\epsilon)_{k_\ell,k_\ell}-\frac{1}{N}\sum_{j=\ell+1}^{N}\frac{\left((h-\epsilon)_{k_j,k_\ell}\,(\vec{k}_j-\vec{k}_\ell)\cdot\vec{\delta R}_m\right)^2}{(h-\epsilon)_{k_j,k_j}}\right]\right\} . \qquad \text{(V.2.21)}$$

Note that equation (V.2.21) involves a sum of N terms which are only <u>formally</u> equivalent. The terms in the curly brackets are quite different in value states for which the wave vectors, $\vec{k}_\ell$, are quite different. Note also that matrix elements involving <u>every</u> state appear either at "diagonal" elements,

$$(h - \epsilon)_{k_r,k_r} , \qquad \text{(V.2.22)}$$

or, as "off-diagonal" elements involving the incremental change of the nuclear coordinates,

$$(h - \epsilon)_{k_j,k_r} (\vec{k}_j - \vec{k}_r) \cdot \delta\vec{R}_m \quad . \qquad \text{(V.2.23)}$$

There are N(N-1)/2 elements of the form of (V.2.23), and it is to be observed that each one appears in equation (V.2.21) exactly once.

Although equation (V.2.21) has a form which superficially appears rather asymmetric, it is in fact entirely symmetric and the same for any particular state k_r. This can be seen easily if, for the case where the variation of the band energy, $\epsilon(\vec{k}_r)$ is under investigation the r-th and zeroth rows and columns in the A.P.W. determinant are interchanged. These two operations leave the value of the secular determinant invariant, and if the wave vectors, $\vec{k}_r$ and $\vec{k}_0$ designating those two states have their indices exchanged, the expansion of the determinant by minors has again the form of equation (V.2.21).

However, if the state, k_r, is under investigation, the matrix elements in the sum in equation (V.2.21) which pertain to the variation of the band energy, $\epsilon(\vec{k}_r)$ are only those for which $(h - \epsilon)_{k_r,k_r}$ appears inside the square brackets and those terms involving $(h-\epsilon)_{k_j,k_r}(\vec{k}_j-\vec{k}_r)\cdot\vec{\delta R}_m$. The other terms pertain properly to the solutions for the variations of the other eigenvalues, $\epsilon(\vec{k}_j)$. Therefore, such other terms will be neglected initially. It will be demonstrated below that in the neighborhood of the zeroes of interest, — those for $\epsilon(\vec{k}_r)$, — these additional terms in the sum are of the order $|\delta R|^4$.

Thus we seek the zeroes of the function,

$$F\left(\epsilon(k_0)\right)=\prod_{j=1}^{N}(h-\epsilon)_{k_j,k_j}\left[(h-\epsilon)_{k_0,k_0}-\right.$$
$$\left.-\frac{1}{N}\sum_{j=1}^{N}\frac{|(h-\epsilon)_{k_j,k_0}|^2\left((\vec{k}_j-\vec{k}_0)\cdot\vec{\delta R}_m\right)^2}{(h-\epsilon)_{k_j,k_j}}\right]. \tag{V.2.24}$$

It is to be observed that this function has many zeroes. Because the electronic energy spectrum admits many degeneracies, every value of ϵ which equals a degenerate eigenvalue for the perfect lattice,

$$\epsilon=\epsilon^{o}_{k_j}=\epsilon^{o}_{k_\ell}, \tag{V.2.25}$$

renders a zero for $F\left(\epsilon(k_0)\right)$ on account of the factor,

$$\prod_{j=1}^{N}(h-\epsilon)_{k_j,k_j}. \tag{V.2.26}$$

Plainly such zeroes correspond simply to the variational eigenvalues for the perfect lattice, and accordingly are disregarded. The value of ϵ of interest is that one which determines the zero of the second factor,

$$F\left(\epsilon(k_0)\right) = \left[(h-\epsilon)_{k_0,k_0} - \frac{1}{N}\sum_{j=1}^{N} \frac{|(h-\epsilon)_{k_j,k_0}|\left((\vec{k}_j-\vec{k}_0)\cdot\vec{\delta R}_m\right)^2}{(h-\epsilon)_{k_j,k_j}}\right] . \quad (V.2.27)$$

There are two points to be noted about equation (V.2.27).

First, this equation, whose zeroes determine the change in the eigenvalue, $\epsilon(k_0)$, is not a perturbation theoretical result. Although equation (V.2.27) has the form of the equation for the second order change in the eigenvalue according to the perturbation formalism, there is no expansion parameter, λ, which appears in an expression for the Hamiltonian,

$$h = h_0 + \lambda\sigma \quad , \qquad (V.2.28)$$

and in terms of which the eigenvalue is expanded. Equation (V.2.27) obtains from the expansion of the exponent,

$$e^{i(\vec{k}-\vec{k}')\cdot\vec{\delta R}_m} \simeq 1 + i(\vec{k}-\vec{k}')\cdot\vec{\delta R}_m + \ldots \quad , \qquad (V.2.29)$$

and is simply a Taylor series expansion in

$$\frac{|\delta R_m|}{|R^{\circ}_m|} \quad . \qquad (V.2.30)$$

Second, equation (V.2.27) states that the variation in the one-electron energy, $\epsilon(k_0)$ is quadratic in δR_m.

V.3 Evaluation of the Expanded Secular Determinant.

We shall first investigate the zeroes of the energy function,

$$F\left(\epsilon(k_0)\right) = \prod_{j=1}^{N} (h-\epsilon)_{k_j,k_j} \left((h-\epsilon)_{k_0,k_0} - \frac{1}{N} \sum_{j=1}^{N} \frac{\left(|(h-\epsilon)_{k_j,k_0}|(\vec{k}_j-\vec{k}_0)\cdot \overrightarrow{\delta R}_m \right)^2}{(h-\epsilon)_{k_j,k_j}} \right). \tag{V.3.1}$$

Observe again that the values of ϵ for which,

$$\epsilon = \epsilon^{o}(k_j) \;, \tag{V.3.2}$$

cause the function to vanish for any degenerate state, $\vec{k}_j$, correspond simply to the eigenvalues of the imperturbed problem and are therefore disregarded.

The problem now is to calculate the factor,

$$(h-\epsilon)_{k_0,k_0} - \frac{1}{N} \sum_{j=1}^{N} \frac{\left(|(h-\epsilon)_{k_j,k_0}|(\vec{k}_j-\vec{k}_0)\cdot \overrightarrow{\delta R}_m \right)^2}{(h-\epsilon)_{k_j,k_j}} \;, \tag{V.3.3}$$

and to ascertain its zeroes. To do this, first the sum over $\vec{k}$-vector is transformed into an integral over the energy variable ϵ',

$$\sum_{k_j} \longrightarrow \frac{V}{(2\pi)^3} \int k^2 \, dk \, d\Omega = V \int d\Omega \int_{-\infty}^{\infty} d\epsilon' \, g(\epsilon') \;, \tag{V.3.4}$$

by using the Jacobian of the transformation which defines the density of states:

$$g(\epsilon') = \frac{2}{(2\pi)^3}\oint_{\epsilon(k')} \frac{1}{|\mathrm{grad}_{k'}\,\epsilon(k')|}\,dS\ . \qquad (V.3.5)$$

Note that the energy which enters equations (V.3.4) and (V.3.5) as a running variable in the integration over all states is the eigenvalue of the perfect lattice:

$$\epsilon' = \int \psi^*_{\vec{k}'}(\vec{x})\,h(\vec{x})\,\psi_{\vec{k}'}(\vec{x})\,d^3x\ . \qquad (V.3.6)$$

Using this identity, the sum in expression (V.3.3) is written,

$$\frac{1}{N}\sum_{j=1}^{N}\frac{\left(|(h-\epsilon)_{\vec{k}_j,\vec{k}_0}|\,(\vec{k}_j-\vec{k}_0)\cdot\delta\vec{R}_m\right)^2}{(h-\epsilon)_{k_j,k_j}}$$

$$= V\int d\Omega\int_{-\infty}^{\infty}\frac{d\epsilon'\,g(\epsilon')\left(|(h-\epsilon)_{\vec{k}_j,\vec{k}_0}|\,(\vec{k}_j-\vec{k}_0)\cdot\delta\vec{R}_m\right)^2}{(\epsilon'-\epsilon)}\ . \qquad (V.3.7)$$

The problem now resolves into that of determining the behaviour of the integral in equation (V.3.7) as a function of ϵ (<u>not</u> of ϵ' — which is integrated out). For convenience we introduce the symbol,

$$|D(\epsilon,\epsilon')|^2 = \left(|(h-\epsilon)_{k_j,k_0}|\,(\vec{k}_j-\vec{k}_0)\cdot\delta\vec{R}_m\right)^2\ . \qquad (V.3.8)$$

The integral in (V.3.7),

$$\int d\epsilon' \, \frac{g(\epsilon') \, |D(\epsilon', \epsilon)|^2}{(\epsilon' - \epsilon)} \, , \qquad \text{(V.3.9)}$$

has poles at each value of ϵ for which for some state, $\vec{k}$,

$$\epsilon = \epsilon' \equiv \epsilon^{o}(\vec{k}') \; . \qquad \text{(V.3.10)}$$

However, the entire integral is itself multiplied by the product,

$$\prod_{j=1}^{N} (h - \epsilon)_{k_j, k_j} = \prod_{j=1}^{N} \left(\epsilon'(k_j) - \epsilon \right) \, , \qquad \text{(V.3.11)}$$

which serves to eliminate all such poles as specified by (V.3.10) except that for $\vec{k}' = \vec{k}_0$. Therefore, we solve the integral considering the pole at $\epsilon^{o}(k_0)$ only.

In order to evaluate the integral (V.3.9), the variable ϵ' is transformed into the complex plane,

$$\epsilon' = \epsilon'_r + i \, \epsilon'_i \; . \qquad \text{(V.3.12)}$$

In order to evaluate the integral in the complex plane, the contour of integration must be chosen and the convergence of the integrand at infinity assured. The contour of integration must be chosen so as to avoid any singularities or branch cuts pertinent to the integrand. Because the function $|D(\epsilon')|^2$ has only isolated singularities, the contour will be determined by the singularities of $g(\epsilon')$.

The density-of-states function $g(\epsilon')$ is an extremely complicated function, and to find its general form is impossible using known mathematical methods. However, because the integral (V.3.9) has the form of a dispersion relation,

$$\int_0^{\infty} \frac{F(z)\,dz}{z-a} , \tag{V.3.13}$$

the value of the integral will be determined by the values of the integrand in the neighborhood of the singularity, $\epsilon(k_0)$. Therefore, we expand energy dispersion curve about the singularity as,

$$\epsilon(\vec{k}') = \epsilon(\vec{k}_0) + \frac{\hbar^2}{2m^*} |\vec{k}' - \vec{k}_0|^2 + \dots . \tag{V.3.14}$$

This parabolic fitting of the energy bands admits the density-of-state function,

$$g(\epsilon') = \frac{(2m^*)^{3/2}}{2\pi^2 \hbar^3} \epsilon'^{1/2} . \tag{V.3.15}$$

Now because $g(\epsilon')$ involves a non-integral power of ϵ', its phase in the complex plane is arbitrary, and it possesses a branch cut running from the origin to infinity. We choose the branch cut to be the positive real axis and add in infinitesimal imaginary part to $\epsilon(\vec{k}_0)$ so as to move the pole of the integrand off the real axis,

$$\epsilon(\vec{k}_0) \rightarrow \epsilon(\vec{k}_0) + i\delta . \tag{V.3.16}$$

The contour is taken as in Figure 3. Now because the integrand goes to infinity at least as fast as $\epsilon'^{1/2}$, we use the limiting procedure,

$$\frac{g(\epsilon')\,|D(\epsilon')|^2}{(\epsilon' - \epsilon_0 + i\delta)} = \lim_{\mu \to 0} \frac{g(\epsilon')\,|D(\epsilon')|^2}{(\epsilon' - \epsilon_0 + i\delta)}\, e^{-\mu|\epsilon'|} \; . \tag{V.3.17}$$

The value of the integral is then,

$$f(\epsilon') = \frac{\pi}{\sin\frac{3\pi}{2}} \left(\underset{\mu \to 0}{\text{Residue of}} \; \frac{g(\epsilon')\,|D(\epsilon')|^2}{(\epsilon' - \epsilon_0 + i\delta)}\, e^{-\mu|\epsilon'|} \right) , \tag{V.3.18}$$

which equals,

$$f(\epsilon') = -\pi\, g(\epsilon_0)\,|D(\epsilon_0)|^2 \; . \tag{V.3.19}$$

Therefore, we have acquired the evaluation of the energy function in equation (V.3.1) as,

$$F\Big(\epsilon(k_0)\Big) = \prod_{j=1}^{N} (h-\epsilon)_{k_j,k_j} \Bigg[(h)_{k_0,k_0} - \epsilon_0 + {} - \frac{V\pi g(\epsilon_0)}{N} \int d\Omega \left((h-\epsilon_0)^2_{k_j^{\epsilon_0},k_0} \, (\vec{k}_j^{\,\epsilon_0} - \vec{k}_0) \cdot \delta\vec{R}_m \right)^2 \Bigg] \, . \tag{V.3.20}$$

The superscripts, ϵ_0, over the k-vectors, $\vec{k}_j$, in the angular integral in (V.3.20) serve to specify that the integration involves only states of wave vector, $\vec{k}_j$, for which

$$\epsilon(\vec{k}_j) = \epsilon_o = \epsilon(\vec{k}_0) \quad . \qquad \text{(V.3.21)}$$

In general, the angular integral in equation (V.3.20) is very complicated.

The equation (V.3.20) still does not specify for which value of ϵ_o the zeroes will obtain. There still remains a complicated transcendental equation in ϵ_o. We solve for the zero iteratively.

Using the eigenfunctions which belong to the perfect lattice eigenvalue,

$$\epsilon^o(k_0) = \int \psi^{\epsilon^o *}_{\vec{k}_0}(\vec{x})\, h(\vec{x})\, \psi^{\epsilon^o}_{\vec{k}_0}(\vec{x})\, d\vec{x} \quad , \qquad \text{(V.3.22)}$$

and recalling that,

$$\int \psi^{\epsilon^o *}_{\vec{k}_0}(\vec{x}) \left(h(\vec{x}) - \epsilon^o(k_0)\right) \psi^{\epsilon^o}_{\vec{k}_0}(\vec{x})\, d^3x = 0 \quad , \qquad \text{(V.3.23)}$$

it is observed that a shift is the eigenvalue such that

$$\epsilon_o = \epsilon(\vec{k}_0) = \epsilon^o(\vec{k}_0) + \pi V\, g\left(\epsilon^o(k_0)\right) \int d\Omega \left|D(\epsilon^o)\right|^2 \quad , \qquad \text{(V.3.24)}$$

will determine a zero.

Furthermore, when this value for ϵ_o is used in the next interaction, the variation of the eigenfunctions is,

$$\psi^{\epsilon}_{\vec{k}_0}(x) = \psi^{\epsilon^o}_{\vec{k}_0}(x) + \frac{d\psi^{\epsilon}_{\vec{k}_0}(x)}{d\epsilon}\, \delta\epsilon \qquad \text{(V.3.25a)}$$

$$= \psi^{\epsilon^{o}}_{\vec{k}}(x) + \frac{d\psi^{\epsilon}_{k}(\vec{x})}{d\epsilon} O(\delta R_{m})^{2} . \qquad \text{(V.3.25b)}$$

Therefore, the further correction of the eigenvalue ϵ_o which obtains from the next iteration is of order,

$$(\delta R_{m})^{4} ,$$

and is for that reason neglected.

Returning now to equation (V.2.17) in order to reconsider the additional terms in $(h - \epsilon)_{\vec{k}_0,\vec{k}_0}$ which obtained from the expansion of the cofactor of $(h - \epsilon)_{\vec{k}_0,\vec{k}_0}$:

$$(h - \epsilon)_{k_0,k_0} \left[\text{terms in } (\delta R_{m})^{2} \right] . \qquad \text{(V.3.26)}$$

Plainly, at the value of ϵ determined by equation (V.3.24), these terms in (V.3.26) differ from zero only in orders of,

$$(\delta R_{m})^{4} ,$$

and we are justified in consistently neglecting them.

V. 4 The Eigenfunctions for the Deformed Lattice.

In order to evaluate the factor in the electron-phonon "double-derivative" matrix elements involving the electronic eigenfunctions, it is necessary to determine the eigenfunctions for the deformed lattice. If the single-particle eigenfunctions for the deformed lattice are written as

$$\psi^{\epsilon}_{\vec{k}}(\vec{x};\vec{R}+\overrightarrow{\delta R}_m) \ , \tag{V.4.1}$$

then the derivatives of the electronic eigenfunctions with respect to the nuclear coordinates are

$$\lim_{\delta R_m \to 0} \left\{ \frac{\psi^{\epsilon}_{\vec{k}}(\vec{x};\vec{R}+\overrightarrow{\delta R}_m) - \psi^{\epsilon}_{\vec{k}}(\vec{x};R^{o})}{\delta R_m} \right\} \ . \tag{V.4.2}$$

In both (V.4.1) and (V.4.2) the eigenfunctions for the deformed lattice are indexed with the eigenvalue, ϵ, to which they belong and also with the wave vector, $\vec{k}$, which serves to specify the eigenstate to which the function reduces in the equilibrium-position nuclear coordinates. It should be clearly understood that the eigenfunctions for the deformed lattice are <u>not</u> periodic in the lattice. The eigenfunction in (V.4.1) does not transform irreducibly as the k-th (or any other) representation of the lattice translation group.

In Sections V.2 and V.3 it was established that the eigenvalues for the band energies in the deformed lattice are adiabatic through terms linear in the nuclear displacements,

$$\epsilon(\vec{k};\vec{R}+\delta\vec{R}) = \epsilon^{o}(k;R^{o}) + O(\delta R^{2}) \quad , \qquad \text{(V.4.3)}$$

provided the wave vector, $\vec{k}$, does not designate a point on the Brillouin zone boundary.

Therefore, to invert the A.P.W. secular determinant in order to ascertain the eigenvectors which belong to its respective zeroes the same trial functions are used as in the previous sections. In all but the $\vec{R}_m$-th cell the A.P.W. eigenfunctions are used,

$$\psi^{\epsilon^{o}}_{\vec{k}}(\vec{x};R^{o}) = \sqrt{\frac{1}{A}}\left(\sqrt{\frac{1}{V}}\sum_{i} a^{\epsilon^{o}}(\vec{k}+\vec{K}_i)\, e^{i(\vec{k}+\vec{K}_i)\cdot\vec{x}} + \right.$$

$$\left. + \sqrt{\frac{1}{N}}\sum_{\substack{R_p \\ \neq R_m}} e^{i\vec{k}\cdot\vec{R}_p}\, \varphi^{\epsilon^{o}}_{\vec{k}}(\vec{x}\cdot\vec{R}_p)\right) \quad . \qquad \text{(V.4.4)}$$

In equation (V.4.4), A is a normalizing factor, and $\varphi^{\epsilon^{o}}_{\vec{k}}(\vec{x}\cdot\vec{R}_p)$ is the equilibrium-position tight-binding component belonging to the equilibrium-position eigenvalue, $\epsilon^{o}(\vec{k}_o)$. The functions in equation (V.4.4) are recognizably of the form of the equilibrium-position A.P.W. eigenfunctions. In the $\vec{R}_m$-th cell, the trial functions are

$$\psi^{\epsilon^{o}(\vec{k})}(\vec{x};R+\delta R_{m}) = \sqrt{\frac{1}{A}}\sum_{i} a^{\epsilon^{o}}(\vec{k}+\vec{K}_{i})\,\frac{e^{i(\vec{k}+\vec{K}_{i})\cdot\vec{x}}}{\sqrt{V}} \qquad \text{(V.4.5a)}$$

outside the displaced A.P.W. sphere: $|\vec{x}| \geq r'_{s}$, and

$$\begin{aligned}\psi^{\epsilon^{o}(\vec{k})}(\vec{x};R+\delta R_{m}) &= \sum_{i} a^{\epsilon^{o}}(\vec{k}+\vec{K}_{i})\,\psi^{\epsilon^{o}}_{\vec{k}+\vec{K}_{i}}(\vec{x}-\overrightarrow{\delta R}_{m};R^{o})\,e^{i(\vec{k}+\vec{K}_{i})\cdot\overrightarrow{\delta R}_{m}} + \\ &= \sqrt{\frac{1}{A}}\sum_{i} a(\vec{k}+\vec{K}_{i})\left(\frac{e^{i(\vec{k}+\vec{K}_{i})\cdot(\vec{x}-\overrightarrow{\delta R}_{m})}}{\sqrt{V}} + \right. \\ &\quad \left. + \frac{e^{i(\vec{k}+\vec{K}_{i})\cdot\vec{R}_{m}}}{\sqrt{N}}\,\varphi^{\epsilon^{o}}_{\vec{k}+\vec{K}_{i}}(\vec{x}-\vec{R}_{m}-\overrightarrow{\delta R}_{m})\right)e^{i(\vec{k}+\vec{K}_{i})\cdot\overrightarrow{\delta R}_{m}},\end{aligned} \qquad \text{(V.4.5b)}$$

inside the displaced A.P.W. sphere:

$$|\vec{x}| \leq r'_{s} \ .$$

Thus the trial functions employed are the A.P.W. functions for the perfect lattice generated by the eigenvalue, $\epsilon^{o}(\vec{k}_{o})$, in all but the $\vec{R}_{m}$-th cell. In the $\vec{R}_{m}$-th cell, the trial functions are the same combinations of plane waves as for the eigenfunction belonging to $\epsilon^{o}(\vec{k}_{o})$ in the perfect lattice,

$$\sum_{i} a^{\epsilon^{o}}(\vec{k}+\vec{K}_{i})\,e^{i(\vec{k}+\vec{K}_{i})\cdot\vec{x}}\ , \qquad \text{(V.4.6)}$$

and the tight-binding components are displaced rigidly — as specified by the energy parameter —

$$\sum_i a^{\epsilon^0}(\vec{k}+\vec{K}_i)\, e^{i(\vec{k}+\vec{K}_i)\cdot\vec{R}_m+\delta\vec{R}_m}\, \varphi^{\epsilon^0}_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m-\delta\vec{R}_m)\ , \qquad (V.4.7)$$

which vanish smoothly at the displaced A.P.W. sphere radius because of the factors,

$$e^{i(\vec{k}+\vec{K}_i)\cdot\delta\vec{R}_m}\ . \qquad (V.4.8)$$

Labelling these trial functions by their respective wave vectors, $\vec{k}'$, the eigenfunctions for the deformed lattice will be

$$\psi^{\epsilon}(\vec{x};R+\delta R) = \sum_{\vec{k}'} x_{k'}\, \psi_{\vec{k}'}(\vec{x};\vec{R}^{0}+\delta\vec{R}_m)\ . \qquad (V.4.9)$$

The Hamiltonian for the deformed lattice operating upon this eigenfunction renders the equation

$$h(\vec{x};R+\delta R_m)\ \psi^{\epsilon}(\vec{x};R+\delta R_m) = \epsilon\sum_{\vec{k}'} x_{k'}\, \psi_{\vec{k}'}(\vec{x};\vec{R}+\delta\vec{R}_m)\ . \qquad (V.4.10)$$

Multiplying both sides of equation (V.4.10) by $\Psi^{*}_{k''}(\vec{x};R+\delta R_m)$ from the left and integrating over the entire volume of the crystal renders the matrix elements

$$\sum_{k'}\Big(h(R+\delta R_m)\Big)_{k'',k'} x_{k'} = \epsilon\sum_{k'} x_{k'}\, \delta_{k'',k'}\ . \qquad (V.4.11)$$

Now, because the eigenvalue, ϵ, has already been ascertained by the procedure developed in the previous two sections, the determinant of the matrix of equation (V.4.11) vanishes:

$$\det \left| \left(h(R+\delta R) - \epsilon \right)_{k'', k'} \right| = 0 \quad . \tag{V.4.12}$$

Therefore, the set of equations (V.4.11) which determine the coefficients, $x_{k'}$, are redundant. For each eigenvalue $\epsilon(R+\delta R)$ one equation is eliminated in the following way.

Suppose that the energy eigenvalue whose eigenfunction is sought is that which equals $\epsilon^{o}(\vec{k}_o)$ in the limit of the perfect lattice:

$$\lim_{\delta R \to 0} \left(\epsilon(R+\delta R) \right) = \epsilon^{o}(k_o) \quad . \tag{V.4.13}$$

Assuming that

$$x_{k_o} = 1 \quad , \tag{V.4.14}$$

and labelling the elements of the determinant such that the $(h-\epsilon)_{k_o, k'}$ row is the first row, and the $(h-\epsilon)_{k'', k_o}$ column is the first column, the matrix of the coefficients is exactly that appearing in the determinant in equation (V.2.13), except that both the explicit value of the parameter, ϵ, and the functional form of the trial functions inside the A.P.W. sphere are set by the predetermined value of the eigenvalue $\epsilon^o(\vec{k}_o)$.

Using the assumption (V.4.14), and discarding as redundant the equation which generates the first row of the determinant, there remains the $(N-1) \times N$ matrix given by equation (V.4.15).

$$\begin{pmatrix} & (h-\epsilon^{\circ})_{k_1,k_1}\, x_1 & -i(\vec{k}_1-\vec{k}_2)\cdot\frac{\vec{\delta R}_m}{N}(h-\epsilon^{\circ})_{k_1,k_2}\, x_2 & -i(\vec{k}_1-\vec{k}_3)\cdot\frac{\vec{\delta R}_m}{N}(h-\epsilon)_{k_1,k_3}\, x_3 & \cdots \\ -i(\vec{k}_2-\vec{k}_1)\cdot\frac{\vec{\delta R}_m}{N}(h-\epsilon^{\circ})_{k_2,k_1}\, x_1 & & (h-\epsilon^{\circ})_{k_2,k_2}\, x_2 & \cdots & \\ -i(\vec{k}_3-\vec{k}_1)\cdot\frac{\vec{\delta R}_m}{N}(h-\epsilon^{\circ})_{k_3,k_1}\, x_1 & & -(\vec{k}_3-\vec{k}_2)\cdot\frac{\vec{\delta R}_m}{N}(h-\epsilon^{\circ})_{k_3,k_2}\, x_2 & \cdots & \\ -i(\vec{k}_4-\vec{k}_1)\cdot\frac{\vec{\delta R}_m}{N}(h-\epsilon^{\circ})_{k_4,k_1}\, x_1 & & \cdots & & \\ \vdots & & & & \end{pmatrix} = \begin{pmatrix} -i(\vec{k}_1-\vec{k}_0)\cdot\frac{\vec{\delta R}_m}{N}(h-\epsilon^{\circ})_{k_1,k_0} \\ -i(\vec{k}_2-\vec{k}_0)\cdot\frac{\vec{\delta R}_m}{N}(h-\epsilon^{\circ})_{k_2,k_0} \\ \vdots \\ -i(\vec{k}_N-\vec{k}_0)\cdot\frac{\vec{\delta R}_m}{N}(h-\epsilon^{\circ})_{k_N,k_0} \end{pmatrix}$$

(V.4.15): The Matrix of the Coefficients of the Eigenfunction in the Deformed Lattice

The coefficient x_{k_ℓ} is determined by Kramer's Rule:

$$x_{k_\ell} = \frac{|D'(\vec{k}_\ell)|}{\Delta} \;, \tag{V.4.16}$$

where $D'(\vec{k}_\ell)$ represents the determinant of the associated matrix on the left hand side of equation (V.4.15) when the $\vec{k}_\ell$-th column has been replaced by the column matrix on the right hand side, and where Δ represents the discriminant, or the determinant of the matrix on the left hand side. Both these determinants are evaluated by expanding by minors and retaining only the terms of lowest orders in δR_m.

The discriminant, Δ, is identical in form to $D(\epsilon^o)$ except that it involves one fewer factor and term in its series,

$$\Delta(\epsilon^o) = \frac{1}{N}\sum_{\ell=1}^{N}\left\{\left(\prod_{\substack{j=1\\ j\neq\ell}}^{N}(h-\epsilon^o)_{k_j,k_j}\right)\right.$$

$$\left.\times\left[(h-\epsilon^o)_{k_\ell,k_\ell} - \frac{1}{N}\sum_{j=\ell+1}\frac{\left((h-\epsilon^o)_{k_\ell,k_j}(\vec{k}_j-\vec{k}_\ell)\cdot\delta\vec{R}_m\right)^2}{(h-\epsilon^o)_{k_j,k_j}}\right]\right\}. \tag{V.4.17}$$

The associated determinant for, say, $\vec{k}_1$ is

$$D'(\vec{k}_1) = \frac{1}{N}\sum_{\ell=2}^{N}\left\{\left(\prod_{\substack{j=2\\ j\neq\ell}}^{N}(h-\epsilon^{o})_{k_j,k_j}\right)\left(i(\vec{k}_1-\vec{k}_0)\cdot\frac{\overrightarrow{\delta R}_m}{N}(h-\epsilon^{o})_{k_1,k_0}\right)\right.$$

$$\left.\times\left[(h-\epsilon^{o})_{k_\ell,k_\ell}-\frac{1}{N}\sum_{j=\ell+1}^{N}\frac{\left((h-\epsilon^{o})_{k_\ell,k_j}(\vec{k}_j-\vec{k}_\ell)\cdot\overrightarrow{\delta R}_m\right)^2}{(h-\epsilon^{o})_{k_j,k_j}}\right]\right\}. \tag{V.4.18}$$

Discarding now all but the terms of lowest order in δR, the expression for the discriminant becomes simply,

$$\Delta = \prod_{j=1}^{N}(h-\epsilon^{o})_{k_j,k_j}\ , \tag{V.4.19}$$

and the associated determinant for the $\vec{k}_1$-th coefficient becomes

$$|D'(\vec{k}_1)| = i(\vec{k}_1-\vec{k}_0)\cdot\frac{\overrightarrow{\delta R}_m}{N}(h-\epsilon^{o})_{k_1,k_0}\prod_{j=2}^{N}(h-\epsilon^{o})_{k_j,k_j}\ . \tag{V.4.20}$$

In general, it can be seen easily that the associated determinant for the $\vec{k}_1$-th coefficient is, through terms linear in δR,

$$|D'(\vec{k}_\ell)| = i(\vec{k}_\ell-\vec{k}_0)\cdot\frac{\overrightarrow{\delta R}_m}{N}(h-\epsilon^{o})_{k_\ell,k_0}\prod_{\substack{j=1\\ j\neq\ell}}^{N}(h-\epsilon^{o})_{k_j,k_j} \tag{V.4.21}$$

provided $\ell \neq 0$. Therefore, using Kramer's Rule, equation (V.4.16), the coefficient x_ℓ is

$$x_\ell = i(\vec{k}_\ell - \vec{k}_0) \cdot \frac{\vec{\delta R}_m}{N} \frac{(h-\epsilon^o)_{k_\ell, k_0}}{(h-\epsilon^o)_{k_\ell, k_\ell}} . \qquad \text{(V.4.22)}$$

There are two observations to be made concerning this result for x_ℓ.

First, the coefficient x_ℓ displays a singularity when the state $\vec{k}_\ell$ is degenerated in energy with the state $\vec{k}_0$; or

$$\epsilon^o(\vec{k}_\ell) = \int \psi^*_{\vec{k}_\ell}(\vec{x})\, h(\vec{x})\, \psi_{\vec{k}_\ell}(\vec{x})\, d\vec{x} = \epsilon^o = \epsilon^o(\vec{k}_0) \quad . \qquad \text{(V.4.23)}$$

However, the eigenfunction for the deformed lattice is determined by the sum over all states $\vec{k}_\ell$,

$$\psi^{\epsilon^o}(\vec{x}; R + \delta R) = \sum_{\vec{k}_j} x_{\vec{k}_j} \psi^{\epsilon^o}_{\vec{k}_j}(\vec{x}; R + \delta R) \quad . \qquad \text{(V.4.24)}$$

If the summation over $\vec{k}_j$ is transformed into an integration over $\epsilon'(\vec{k}_j)$ in the complex energy plane, as in Section V.3, the singularities of equation (V.4.22) serve to specify that the states which mix into the deformed lattice eigenfunction significantly are those belonging to the same energy eigenvalue.

Second, and more important, equation (V.4.22), and therefore, also equation (V.4.23), involves the factor N in the denominator. Now it was originally assumed that x_{k_0} was unity. Therefore, the ratio of magnitudes of all other coefficients to the first one is

$$\frac{x_{k_\ell}}{x_{k_0}} \sim O\left(\frac{1}{N}\right) \ll 1 \ . \tag{V.4.25}$$

It is thus justifiable to neglect all but the first and overwhelmingly largest component of the eigenfunction.

Therefore, the eigenfunction for the deformed lattice which belongs to the eigenvalue

$$\epsilon^{o}(\vec{k};R+\delta R_m)$$

is

$$\psi^{\epsilon^{o}(\vec{k})}(\vec{x};R+\delta R_m) =$$

$$= \sqrt{\frac{1}{A}} \sum_{i} a^{\epsilon^{o}}(\vec{k}+\vec{K}_i) \left(\frac{e^{i(\vec{k}+\vec{K}_i)\cdot\vec{x}}}{\sqrt{V}} + \sqrt{\frac{1}{N}} \sum_{\substack{\vec{R}_p \\ \neq R_m}} e^{i\vec{k}\cdot\vec{R}_p} \varphi^{\epsilon^{o}}_{\vec{k}}(\vec{x}-\vec{R}_p) + \right.$$

$$\left. + \frac{e^{i(\vec{k}+\vec{K}_i)\cdot(\vec{R}_m+\delta\vec{R}_m)}}{\sqrt{N}} \varphi^{\epsilon^{o}}_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m-\delta\vec{R}_m) \right) . \tag{V.4.26}$$

The derivatives of the one-electron crystalline eigenfunctions follow directly from equation (V.4.26).

Using again the approximation for the exponent

$$e^{i(\vec{k}+\vec{K}_i)\cdot\delta\vec{R}_m} \cong 1 + i(\vec{k}+\vec{K}_i)\cdot\delta\vec{R}_m \ , \qquad \text{(V.4.27)}$$

there obtains

$$\psi^{\epsilon^o(\vec{k})}(\vec{x};R^o+\delta R_m) - \psi^{\epsilon^o}_{\vec{k}}(\vec{x};R^o) =$$

$$= \sum_i a_i^{\epsilon^o}(\vec{k}+\vec{K}_i)\, e^{i\vec{k}\cdot\vec{R}_m}\Big[\Big(\varphi^{\epsilon^o}_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m-\delta\vec{R}_m) - \varphi^{\epsilon^o}_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m)\Big)$$

$$+ i(\vec{k}+\vec{K}_i)\cdot\delta\vec{R}_m\, \varphi^{\epsilon^o}_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m-\delta\vec{R}_m)\Big] \ . \qquad \text{(V.4.28)}$$

Using the fundamental definition of the differential calculus,

$$\lim_{\delta R_m\to 0}\Big[\varphi^{\epsilon^o}_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m-\delta\vec{R}_m) - \varphi^{\epsilon^o}_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m)\Big]\Big/\delta\vec{R}_m =$$

$$= -\vec{\nabla}_{\vec{x}}\, \varphi^{\epsilon^o}_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m)\cdot\hat{e}(\delta\vec{R}_m) \ . \qquad \text{(V.4.29)}$$

The second term in equation (V.4.28) admits the simple limit

$$\lim_{\delta R_m\to 0}\Big[i(\vec{k}+\vec{K}_i)\cdot\delta\vec{R}_m\, \varphi^{\epsilon^o}_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m-\delta\vec{R}_m)\Big]\Big/\delta\vec{R}_m =$$

$$= i(\vec{k}+\vec{K}_i)\cdot\hat{e}(\delta\vec{R}_m)\, \varphi^{\epsilon^o}_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m) \ . \qquad \text{(V.4.30)}$$

In both equations (V.4.29) and (V.4.30) the symbol,

$$\hat{e}(\delta\vec{R}_m) \; , \tag{V.4.31}$$

represents the unit vector in the direction of $\delta\vec{R}_m$.

Therefore, the derivative sought is given by,

$$\frac{d}{dR_m} \psi_{\vec{k}}(\vec{x};R) \equiv$$

$$\equiv \lim_{\delta R_m \to 0} \frac{\left[\psi^{\epsilon^o}(k;R^o+\delta R_m)(\vec{x};R^o+\delta R_m) - \psi^{\epsilon^o}_{\vec{k}}(k;R^o)(\vec{x};R^o)\right]}{\delta R_m}$$

$$= \frac{e^{i\vec{k}\cdot\vec{R}_m}}{\sqrt{N}} \sum_i a^{\epsilon^o}(\vec{k}+\vec{K}_i)\Big(i(\vec{k}+\vec{K}_i)\cdot\hat{e}(\delta\vec{R}_m)\, \varphi^{\epsilon^o}_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m) +$$

$$- \vec{\nabla}_{\vec{x}}\left(\varphi^{\epsilon^o}_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m)\right)\cdot\hat{e}(\delta\vec{R}_m)\Big) \; . \tag{V.4.32}$$

This is exactly the result which was used in Chapter IV, and which was to be proven.

CHAPTER VI

THE CRYSTALLINE POTENTIAL IN A DEFORMED LATTICE

VI.1 The Problem of the Self-Consistency of the Crystalline Potential in a Deformed Lattice.

The energy band problem for a deformed lattice is not completely solved with the development of the energy eigenvalues for the deformed lattice and of the eigenfunctions which belong to them. The accurate solution to every many-electron problem using the single-particle formalism requires that the potential used to describe the field of the electrons be self-consistent. If the single-particle Hamiltonian, $h(\vec{x})$, which involves the electronic potential, $v_e(\vec{x})$, admits the eigenfunctions, $\psi(\vec{x})$, then these eigenfunctions must regenerate $v_e(\vec{x})$; or, if,

$$h(\vec{x})\ \psi(\vec{x}) = \left(-\nabla^2 - \frac{2Z}{|\vec{x}|} + v_e(\vec{x})\right)\ \psi(\vec{x}) = \epsilon\ \psi(\vec{x}) \quad , \qquad \text{(VI.1.1)}$$

then, the set,

$$\{\psi(\vec{x})\} \rightarrow v_e(\vec{x}) \quad . \qquad \text{(VI.1.2)}$$

This aspect of the many-electron problem was discussed extensively in Chapter III. The problem of self-consistency is now addressed for the case of a deformed lattice.

First, the self-consistency of a muffin-tin lattice is considered.

It has been shown in Chapter V, that the band energy eigenvalues for a muffin-tin lattice are adiabatic through terms linear in the nuclear displacements:

$$\epsilon(\vec{k};R+\vec{\delta R}_m) = \epsilon^o(\vec{k};R^o) + O(\delta R_m^2) \quad . \qquad \text{(VI.1.2)}$$

Since the terms of order higher than linear are systematically neglected in this analysis, the band energies for the deformed lattice are ordered exactly as for the perfect lattice. Because the spin of the electron allows each state to be doubly occupied, the N/2 states of lowest energies for the deformed lattice will have the same band energies as for the perfect lattice and will be identically occupied.

Therefore, the Fermi Surface is invariant under first-order variations of the nuclear coordinates. This phenomenon is illustrated schematically in Figure 4.

The electronic potential is developed from the one-electron eigenfunctions by the equation (VI.1.3):

$$v_e(\vec{x};\vec{R}_1,\vec{R}_2,\ldots,\vec{R}_N) = v_e(\vec{x};R)$$

$$= \sum_{\vec{k}=0}^{\vec{k}_F}\left(\int |\psi_{\vec{k}}(\vec{x};R)|^2 \frac{1}{|\vec{x}-\vec{x}'|}\, d\vec{x}'\right)$$

$$- \frac{3}{2\pi^2}\left(\sum^{k_F} 3\pi^2 |\psi_{\vec{k}}(\vec{x};R)|^2\right)^{1/3} , \qquad (VI.1.3)$$

as discussed in Chapter III. For the perfect lattice, the eigenfunctions which enter equation (VI.1.3) are, of course, the set,

$$\left\{\psi_{\vec{k}}(\vec{x};R^{o})\right\} , \qquad (VI.1.4)$$

and for the deformed lattice, the functions used are the set,

$$\left\{\psi^{\epsilon^{o}(\vec{k})}(\vec{x};R+\delta R_m)\right\} . \qquad (VI.1.5)$$

In Chapter V it was shown that the solutions for the deformed lattice are identical to those for the perfect lattice in all except the $\vec{R}_m$-th cell, and that in the $\vec{R}_m$-th cell the eigenfunctions are,

$$\psi^{\epsilon^{o}(\vec{K})}(\vec{x};R+\delta R_m) = \sqrt{\frac{1}{A}}\sum_i a^{\epsilon^{o}}(\vec{k}+\vec{K}_i)\,\frac{e^{i(\vec{k}+\vec{K}_i)\cdot\vec{x}}}{\sqrt{V}} , \qquad (VI.1.6)$$

outside the displaced A.P.W. sphere:

$$|\vec{x}'| \geq r_s' \ ,$$

and

$$\psi^{\epsilon^o(\vec{k})}(\vec{x};R+\delta R_m) = \sum_i a(\vec{k}+\vec{K}_i)\,\psi^{\epsilon^o}_{\vec{k}+\vec{K}_i}(\vec{x}-\delta\vec{R}_m;R^o)\,e^{i(\vec{k}+\vec{K}_i)\cdot\delta\vec{R}_m}$$

$$= \sqrt{\frac{1}{A}}\sum_i a(\vec{k}+\vec{K}_i)\left(\frac{e^{i(\vec{k}+\vec{K}_i)\cdot\vec{x}}}{\sqrt{V}} + \frac{e^{i(\vec{k}+\vec{K}_i)\cdot\vec{R}_m+\delta\vec{R}_m}}{\sqrt{N}}\,\varphi^{\epsilon^o}_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m-\delta\vec{R}_m)\right), \quad \text{(VI. 1.7)}$$

inside the displaced A.P.W. sphere:

$$|\vec{x}'| \leq r_s' \ .$$

For the movement, the effect of the charge densities in neighboring cells will be neglected; only the charge within the $\vec{R}_m$-th cell will be considered when generating the potential in that cell. In order to develope the potential for the displaced A.P.W. sphere, the eigenfunctions are written as,

$$\psi^{\epsilon^o(\vec{k})}(\vec{x};R+\delta R_m) = \psi^{\epsilon^o}_{\vec{k}}(\vec{x};R^o) + \left(\frac{d\psi^{\epsilon^o(k)}}{dR_m}\right)_{R_m^o} \delta R_m \ . \quad \text{(VI.1.8)}$$

Using the results of the last Chapter, equation (V.4.32), the eigenfunction in equation (VI.1.8) is written,

$$\psi^{\epsilon^0(\vec{k})}(\vec{x};R+\delta R_m) = \psi^{\epsilon^0}_{\vec{k}}(\vec{x};R^0) + \sqrt{\frac{1}{A}}\sum_i a^{\epsilon^0}(\vec{k}+\vec{K}_i) \times \frac{e^{i\vec{k}\cdot\vec{R}_m}}{\sqrt{N}}\left(i(\vec{k}+\vec{K}_i)\cdot\varphi^{\epsilon^0}_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m;R^0) - \vec{\nabla}_x\left(\varphi^{\epsilon^0}_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m;R^0)\right)\cdot\right)\delta\vec{R}_m \;. \qquad \text{(VI.1.9)}$$

When the eigenfunctions in equation (VI.1.9) are used in the equation for the crystalline potential, (VI. 1.3), there obtain the following expressions for the Coulomb term,

$$\left(v_e(\vec{x})\right)_{\text{Coulomb}} = \sum_{\vec{k}=0}^{\vec{k}_F}\left(\int\left|\psi^{\epsilon^0(k)}(\vec{x}')\right|^2 \frac{1}{|\vec{x}-\vec{x}'|}\,d\vec{x}'\right)$$

$$= \sum_{\vec{k}=0}^{k_F}\left(\int\left|\psi^{\epsilon^0(k)}(\vec{x}';R+\delta R_m)\right|^2 \frac{1}{|\vec{x}-\vec{x}'|}\,d\vec{x}'\right). \qquad \text{(VI.1.10)}$$

Substituting in equation (VI.1.9), this becomes,

$$\left(v_e(\vec{x};R^0+\delta R_m)\right)_{\text{Coulomb}} = \sum_{\vec{k}=0}^{\vec{k}_F}\left(\int\left|\psi^{\epsilon^0(k)}_{\vec{k}}(\vec{x}';R^0)\right|^2 \frac{}{|\vec{x}-\vec{x}'|}\,d\vec{x}' + \left|\psi^{\epsilon^0 *}_{\vec{k}}(\vec{x}';R^0)\right.\right.$$

(continued)

$$\times\Bigg(\sqrt{\frac{1}{A}}\sum_i a^{\epsilon^0}(\vec{k}+\vec{K}_i)\Bigg)\frac{e^{i\vec{k}\cdot\vec{R}_m}}{\sqrt{N}}\Big(i(\vec{k}+\vec{K}_i)-\vec{\nabla}_{x'}\Big)\,\varphi^{\epsilon^0}_{\vec{k}+\vec{K}_i}(\vec{x}'-\vec{R}_m;R^0)\cdot\delta\vec{R}_m\Bigg)\frac{1}{|\vec{x}-\vec{x}'|}\,d\vec{x}'$$

$$+\int\Bigg(\Bigg(\sqrt{\frac{1}{A}}\sum_i a^{\epsilon^0}(\vec{k}+\vec{K}_i)^*\,\frac{e^{-i\vec{k}\cdot\vec{R}_m}}{\sqrt{N}}\Big(-i(\vec{k}+\vec{K}_i)-\vec{\nabla}_{x'}\Big)\,\varphi^*_{\vec{k}+\vec{K}_i}(\vec{x}'-\vec{R}_m;R^0)\cdot\delta\vec{R}_m\Bigg)$$

$$\times\,\psi_k^{\epsilon^0(\vec{k})}(\vec{x}';R^0)\,\frac{1}{|\vec{x}-\vec{x}'|}\,d\vec{x}'\;. \qquad \text{(VI.1.11)}$$

The first term in equation (VI.1.11) is recognized as simply the potential for the perfect lattice, $v_e(\vec{x};R^0)_{\text{Coulomb}}$. The other terms will be examined one by one. The equilibrium position eigenfunction is,

$$\sqrt{\frac{1}{A}}\sum_i a^{\epsilon^0}(\vec{k}+\vec{K}_i)\left(\frac{e^{i(\vec{k}+\vec{K}_i)\cdot\vec{x}}}{\sqrt{V}}+\sqrt{\frac{1}{N}}\sum_{\vec{R}_p}e^{i\vec{k}\cdot\vec{R}_p}\,\varphi^{\epsilon^0}_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_p)\right)\;. \qquad \text{(VI.1.12)}$$

Therefore, as in Chapter IV, there obtain eight distinct integral expressions to evaluate:

<u>(i.a)</u> $$\frac{1}{A}\sum_i\sum_j\left(a^*(\vec{k}+\vec{K}_j)\,a(\vec{k}+\vec{K}_i)\,e^{i\vec{k}\cdot\vec{R}_m}\,i(\vec{k}+\vec{K}_i)\cdot\delta\vec{R}_m\right)$$

$$\times\sqrt{\frac{1}{VN}}\int e^{-i(\vec{k}+\vec{K}_j)\cdot\vec{x}'}\,\varphi_{\vec{k}+\vec{K}_i}(\vec{x}'-\vec{R}_m)\,\frac{1}{|\vec{x}-\vec{x}'|}\,d\vec{x}'$$

<u>(ii.a)</u> $$\frac{1}{A}\sum\sum\left(a^{*}(\vec{k}+\vec{K}_j)\; a(\vec{k}+\vec{K}_i)\; e^{i\vec{k}\cdot\vec{R}_m}\; i(\vec{k}+\vec{K}_i)\cdot\delta\vec{R}_m\right)$$

$$\times\frac{1}{N}\sum_{R_p} e^{-i\vec{k}\cdot\vec{R}_p}\int\varphi^{*}_{\vec{k}+\vec{K}_j}(\vec{x}'-\vec{R}_p)\;\varphi_{\vec{k}+\vec{K}_i}(\vec{x}'-\vec{R}_m)\;\frac{1}{|\vec{x}-\vec{x}'|}\,d\vec{x}'$$

<u>(iii.a)</u> $$-\frac{1}{A}\sum_i\sum_j\left(a^{*}(\vec{k}+\vec{K}_j)\; a(\vec{k}+\vec{K}_i)\; e^{i\vec{k}\cdot\vec{R}_m}\;\delta\vec{R}_m\right)\cdot$$

$$\times\sqrt{\frac{1}{VN}}\int e^{-i(\vec{k}+\vec{K}_j)\cdot\vec{x}'}\left(\vec{\nabla}_{x'}\left(\varphi_{\vec{k}+\vec{K}_i}(\vec{x}'-\vec{R}_m)\right)\right)\frac{1}{|\vec{x}-\vec{x}'|}\,d\vec{x}'$$

<u>(iv.a)</u> $$-\frac{1}{A}\sum_i\sum_j\left(a^{*}(\vec{k}+\vec{K}_j)\; a(\vec{k}+\vec{K}_i)\; e^{i\vec{k}\cdot\vec{R}_m}\;\delta\vec{R}_m\right)\cdot$$

$$\times\frac{1}{N}\sum_{R_p} e^{-i\vec{k}\cdot\vec{R}_p}\int\varphi^{*}_{\vec{k}+\vec{K}_j}(\vec{x}'-\vec{R}_p)\left(\vec{\nabla}_{x'}\left(\varphi_{\vec{k}+\vec{K}_i}(\vec{x}'-\vec{R}_m)\right)\right)\frac{1}{|\vec{x}-\vec{x}'|}\,d\vec{x}'$$

<u>(i.b)</u> $$-\frac{1}{A}\sum_i\sum_j a^{*}(\vec{k}+\vec{K}_j)\; a(\vec{k}+\vec{K}_i)\; e^{-i\vec{k}\cdot\vec{R}_m}\; i(\vec{k}+\vec{K}_j)\cdot\delta\vec{R}_m$$

$$\times\sqrt{\frac{1}{VN}}\int\varphi^{*}_{\vec{k}+\vec{K}_j}(\vec{x}'-\vec{R}_m)\; e^{i(\vec{k}+\vec{K}_i)\cdot\vec{x}'}\;\frac{1}{|\vec{x}-\vec{x}'|}\,d\vec{x}'$$

$$\underline{\text{(ii.b)}}\quad -\frac{1}{A}\sum_{i}\sum_{j}\left(a^{*}(\vec{k}+\vec{K}_j)\, a(\vec{k}+\vec{K}_i)\, e^{-i\vec{k}\cdot\vec{R}_m}\, i(\vec{k}+\vec{K}_j)\cdot\delta\vec{R}_m\right)$$

$$\times\frac{1}{N}\sum_{R_p} e^{-i\vec{k}\cdot\vec{R}_p}\int\varphi^{*}_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m)\,\varphi_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_p)\,\frac{1}{|\vec{x}-\vec{x}'|}\,d\vec{x}'$$

$$\underline{\text{(iii.b)}}\quad -\frac{1}{A}\sum_{i}\sum_{j}\left(a^{*}(\vec{k}+\vec{K}_j)\, a(\vec{k}+\vec{K}_i)\, e^{-i\vec{k}\cdot\vec{R}_m}\;\delta\vec{R}_m\right)\cdot$$

$$\times\sqrt{\frac{1}{VN}}\left(\vec{\nabla}_{x'}\left(\varphi^{*}_{\vec{k}+\vec{K}_j}(\vec{x}'-\vec{R}_m)\right)\right) e^{i(\vec{k}+\vec{K}_i)\cdot\vec{x}'}\,\frac{1}{|\vec{x}-\vec{x}'|}\,dx'$$

$$\underline{\text{(iv.b)}}\quad -\frac{1}{A}\sum_{i}\sum_{j}\left(a^{*}(\vec{k}+\vec{K}_j)\, a(\vec{k}+\vec{K}_i)\, e^{-i\vec{k}\cdot\vec{R}_m}\;\delta\vec{R}_m\right)\cdot$$

$$\times\frac{1}{N}\sum_{R_p}\int\left(\vec{\nabla}_{x'}\left(\varphi^{*}_{\vec{k}+\vec{K}_j}(\vec{x}'-\vec{R}_m)\right)\right)\varphi_{\vec{k}+\vec{K}_i}(\vec{x}'-\vec{R}_p)\,\frac{1}{|\vec{x}-\vec{x}'|}\,d\vec{x}' \qquad \text{(VI.1.13)}$$

In the expressions (i.a) - (iv.b) above, the superscript $\epsilon^{0}(\vec{k})$ has been omitted. The sum of these eight integrals can be simplified in the following way.

Integrating the expression (iii.a) by parts, as was done in Chapter IV, renders the equation,

$$- \delta\vec{R}_m \cdot \int e^{-i(\vec{k}+\vec{K}_j)\cdot\vec{x}'} \left(\vec{\nabla}_{x'}\left(\varphi_{\vec{k}+\vec{K}_i}(\vec{x}'-\vec{R}_m)\right)\right) \frac{1}{|\vec{x}-\vec{x}'|}\, d\vec{x}'$$

$$= - e^{-i(\vec{k}+\vec{K}_j)\cdot\vec{x}'} \varphi_{\vec{k}+\vec{K}_i}(\vec{x}'-\vec{R}_m) \frac{1}{|\vec{x}-\vec{x}'|}\Bigg|_s +$$

$$- i(\vec{k}+\vec{K}_j)\cdot\delta\vec{R}_m \int e^{-i(\vec{k}+\vec{K}_j)\cdot\vec{x}'} \varphi_{\vec{k}+\vec{K}_i}(\vec{x}'-\vec{R}_m) \frac{1}{|\vec{x}-\vec{x}'|}\, d\vec{x}' +$$

$$- \delta\vec{R}_m \cdot \vec{\nabla}_x \int e^{-i(\vec{k}+\vec{K}_j)\cdot\vec{x}'} \varphi_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m) \frac{1}{|\vec{x}-\vec{x}'|}\, d\vec{x}' \,. \qquad \text{(VI.1.14)}$$

The surface term in equation (VI.1.14) vanishes because the tight-binding functions, $\varphi_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m)$, are zero outside the A.P.W. sphere. Because of the minus sign in (iii.a), the expressions (i.a) and (iii.a) can be combined to give,

$$\frac{1}{A}\sum_i \sum_j \left(a(\vec{k}+\vec{K}_i)\, a^*(\vec{k}+\vec{K}_j)\, e^{i\vec{k}\cdot\vec{R}_m}\, i(\vec{K}_i-\vec{K}_j)\cdot\delta\vec{R}_m\right)$$

$$\times \sqrt{\frac{1}{VN}} \int e^{-i(\vec{k}+\vec{K}_j)\cdot\vec{x}'} \varphi_{\vec{k}+\vec{K}_i}(\vec{x}'-\vec{R}_m) \frac{1}{|\vec{x}-\vec{x}'|}\, d\vec{x}' +$$

$$- \frac{1}{A}\sum_i \sum_j \left(a(\vec{k}+\vec{K}_i)\, a^*(\vec{k}+\vec{K}_j)\, e^{i\vec{k}\cdot\vec{R}_m}\right)$$

(continued)

$$\times\ \delta\vec{R}_m \cdot \vec{\nabla}_x\left(\sqrt{\frac{1}{VN}}\int e^{-i(\vec{k}+\vec{K}_j)\cdot\vec{x}'}\ \varphi_{\vec{k}+\vec{K}_i}(\vec{x}'-\vec{R}_m)\ \frac{1}{|\vec{x}-\vec{x}'|}\ d\vec{x}'\right) \tag{VI.1.15}$$

Similarity, (i.b) and (iii.b) can be combined to give,

$$\frac{1}{A}\sum_i\sum_j\left(a^*(\vec{k}+\vec{K}_j)\ a(\vec{k}+\vec{K}_i)\ e^{-i\vec{k}\cdot\vec{R}_m}\ i(\vec{K}_i-\vec{K}_j)\cdot\delta\vec{R}_m\right)$$

$$\times\left(\sqrt{\frac{1}{VN}}\int e^{i(\vec{k}+\vec{K}_j)\cdot\vec{x}'}\ \varphi^*_{\vec{k}+\vec{K}_j}(\vec{x}'-\vec{R}_m)\ \frac{1}{|\vec{x}-\vec{x}'|}\ d\vec{x}'\right)$$

$$-\frac{1}{A}\sum_i\sum_j\left(a^*(\vec{k}+\vec{K}_j)\ a(\vec{k}+\vec{K}_i)\ e^{-i\vec{k}\cdot\vec{R}_m}\right)$$

$$\times\left(\delta\vec{R}_m\cdot\vec{\nabla}_x\sqrt{\frac{1}{VN}}\int e^{i(\vec{k}+\vec{K}_i)\cdot\vec{x}'}\ \varphi^*_{\vec{k}+\vec{K}_j}(\vec{x}'-\vec{R}_m)\ \frac{1}{|\vec{x}-\vec{x}'|}\ d\vec{x}'\right) . \tag{VI.1.16}$$

By using the non-overlapping property of the tight-binding components,

$$\varphi^*_{k'}(\vec{x}-\vec{R}_m)\ \varphi_k(\vec{x}-\vec{R}_p) = 0 \qquad \text{if} \qquad \vec{R}_m \neq \vec{R}_p\ , \tag{VI.1.17}$$

the expressions (ii.a) and (ii.b) can be combined to give,

$$\frac{1}{A}\sum_i\sum_j\left(a^*(\vec{k}+\vec{K}_j)\ a(\vec{k}+\vec{K}_i)\ i(\vec{K}_i-\vec{K}_j)\cdot\delta\vec{R}_m\right)$$

(continued)

$$\times \frac{1}{N}\int \varphi^{*}_{\vec{k}+\vec{K}_j}(\vec{x}'-\vec{R}_m)\,\varphi_{\vec{k}+\vec{K}_i}(\vec{x}'-\vec{R}_m)\,\frac{1}{|\vec{x}-\vec{x}'|}\,d\vec{x}' \quad . \text{(VI.1.18)}$$

Similarly, integrating (iv.b) by parts and adding the result to (iv.a) renders,

$$-\frac{1}{A}\sum\sum\left(a^{*}(\vec{k}+\vec{K}_j)\;a(\vec{k}+\vec{K}_i)\right) ,$$

$$\times\ \delta\vec{R}_m\cdot\vec{\nabla}_x\left(\frac{1}{N}\int \varphi^{*}_{\vec{k}+\vec{K}_j}(\vec{x}'-\vec{R}_m)\,\varphi_{\vec{k}+\vec{K}_i}(\vec{x}'-\vec{R}_m)\,\frac{1}{|\vec{x}-\vec{x}'|}\,d\vec{x}'\right) . \quad \text{(VI.1.19)}$$

Combining (VI.1.15), (VI.1.16), (VI.1.18), and (VI.1.19) gives,

$$v_e(\vec{x};R+\delta R)_{\text{Coulomb}} = v_e(\vec{x};R^{\circ})_{\text{Coulomb}} +$$

$$+\sum_{k=0}^{k_F}\left\{\frac{1}{A(k)}\sum_{i}\sum_{j}\left(a^{*}(\vec{k}+\vec{K}_j)\;a(\vec{k}+\vec{K}_i)\right)\right.$$

$$\times\left[i(\vec{K}_i-\vec{K}_j)\cdot\delta\vec{R}_m\sqrt{\frac{1}{VN}}\int\left(e^{-i(\vec{k}+\vec{K}_j)\cdot\vec{x}'}\;\varphi_{\vec{k}+\vec{K}_i}(\vec{x}')\right.\right.$$

$$\left.-\,e^{i(\vec{k}+\vec{K}_j)\circ\vec{x}'}\;\varphi^{*}_{\vec{k}+\vec{K}_i}(\vec{x}')\right)\cdot\left(\frac{1}{|(\vec{x}-\vec{x}'-\vec{R}_m)|}\right)d\vec{x}' +$$

$$-\,\delta\vec{R}_m\cdot\vec{\nabla}_x\sqrt{\frac{1}{VN}}\int\left(e^{-i(\vec{k}+\vec{K}_j)\circ\vec{x}'}\;\varphi_{\vec{k}+\vec{K}_i}(\vec{x}')\right.$$

$$+ e^{i(\vec{k}+\vec{K}_j)\cdot\vec{x}'}\, \varphi^*_{\vec{k}+\vec{K}_i}(\vec{x}')\Bigg)\cdot\left(\frac{1}{|\vec{x}-\vec{x}'-\vec{R}_m|}\right)d\vec{x}' +$$

$$- i(\vec{K}_i-\vec{K}_j)\cdot\delta\vec{R}_m \frac{1}{N}\int \varphi^*_{\vec{k}\pm\vec{K}_j}(\vec{x}')\,\varphi_{\vec{k}+\vec{K}_i}(x')\,\frac{1}{|\vec{x}-\vec{x}'-\vec{R}_m|}\,d\vec{x}' +$$

$$- \delta\vec{R}_m\cdot\vec{\nabla}_x\frac{1}{N}\int\varphi^*_{\vec{k}+\vec{K}_j}(\vec{x}')\,\varphi_{\vec{k}+\vec{K}_i}(\vec{x}')\,\frac{1}{|\vec{x}-\vec{x}'-\vec{R}_m|}\,d\vec{x}'\Bigg]\Bigg\} . \qquad \text{(VI.1.20)}$$

In equation (VI.1.20) there has been used the property that the A.P.W. variational coefficients, $a(\vec{k}+\vec{K}_i)$ are conventionally taken as pure real,

$$a^*(\vec{k}+\vec{K}_i) = a(\vec{k}+\vec{K}_i) \quad , \qquad \text{(VI.1.21)}$$

and the dummy variables of integration have been transformed as,

$$\vec{x}' = \vec{x}'' - \vec{R}_m \quad . \qquad \text{(VI.1.22)}$$

The exchange potential is derived similarly,

$$v_e(\vec{x};R+\delta R)_{\text{exchange}} = -\frac{3}{2\pi^2}\left\{\sum_{k=0}^{k_F} 3\pi^2\,|\,\psi_k(\vec{x};R+\delta R)\,|^2\right\}^{1/3}$$

$$= -\frac{3}{2\pi^2}\left\{3\pi^2\sum_{k=0}^{k_F}\left|\,\psi_{\vec{k}}(\vec{x};R^o) + \frac{d\psi_{\vec{k}}(\vec{x})}{dR_m}\,\delta R_m\right|^2\right\}^{1/3} . \qquad \text{(VI.1.23)}$$

A given term in the sum is examined. As before, there is a single term,

$$|\psi_{\vec{k}}(\vec{x};R^{\circ})|^{2} \ , \qquad \text{(VI.1.24)}$$

representing the perfect lattice eigenstates and eight terms linear in δR_m attributable to the variation of the eigenfunctions. These are as follows:

$$\frac{1}{A}\sum_{i}\sum_{j}\left(a^{*}(\vec{k}+\vec{K}_j)\ a(\vec{k}+\vec{K}_i)\right)$$

$$\times\left\{ i(\vec{k}+\vec{K}_i)\circ\vec{\delta R}_m\ \frac{e^{-i(\vec{k}+\vec{K}_j)\cdot(\vec{x}-\vec{R}_m}}{\sqrt{VN}}\ \varphi_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m) + \right.$$

$$+\ i(\vec{k}+\vec{K}_i)\cdot\vec{\delta R}_m\ \frac{1}{N}\ \varphi^{*}_{\vec{k}+\vec{K}_j}(\vec{x}-\vec{R}_m)\ \varphi_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m) +$$

$$-\ \vec{\delta R}_m\cdot\left(\vec{\nabla}\varphi_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m)\right)\frac{e^{-i(\vec{k}+\vec{K}_j)\cdot(\vec{x}-\vec{R}_m)}}{\sqrt{VN}} +$$

$$-\ \vec{\delta R}_m\circ\left(\vec{\nabla}\varphi_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m)\right)\frac{1}{N}\ \varphi^{*}_{\vec{k}+\vec{K}_j}(\vec{x}-\vec{R}_m) +$$

$$-\ i(\vec{k}+\vec{K}_j)\cdot\vec{\delta R}_m\ \frac{e^{+i(\vec{k}+\vec{K}_i)\cdot(\vec{x}-\vec{R}_m)}}{\sqrt{VN}}\ \varphi^{*}_{\vec{k}+\vec{K}_j}(\vec{x}-\vec{R}_m) +$$

$$\left. \begin{aligned} & -i(\vec{k}+\vec{K}_j)\circ\delta\vec{R}_m \frac{1}{N}\varphi^*_{\vec{k}+\vec{K}_j}(\vec{x}-\vec{R}_m)\,\varphi_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m) + \\ & -\delta\vec{R}_m\circ\left(\vec{\nabla}\varphi^*_{\vec{k}+\vec{K}_j}(\vec{x}-\vec{R}_m)\right)\frac{e^{i(\vec{k}+\vec{K}_i)\cdot(\vec{x}-\vec{R}_m)}}{\sqrt{VN}} \\ & -\delta\vec{R}_m\cdot\left(\vec{\nabla}\varphi^*_{\vec{k}+\vec{K}_j}(\vec{x}-\vec{R}_m)\right)\frac{1}{N}\varphi_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m) \end{aligned} \right\} . \qquad \text{(VI.1.25)}$$

Plainly the fourth and eight terms in equation (VI.1.25) can be combined as,

$$-\delta\vec{R}_m\cdot\vec{\nabla}\frac{1}{N}\left(\varphi^*_{\vec{k}+\vec{K}_j}(\vec{x}-\vec{R}_m)\,\varphi_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m)\right) . \qquad \text{(VI.1.26)}$$

Uisng the identity,

$$\begin{aligned} e^{i(\vec{k}+\vec{K})\cdot\vec{x}}\left(\vec{\nabla}\varphi_k(\vec{x}-\vec{R}_m)\right) &= \vec{\nabla}\left(e^{i(\vec{k}+\vec{K})\cdot\vec{x}}\varphi_k(\vec{x}-\vec{R}_m)\right) \\ &\quad -i(\vec{k}+\vec{K})\,e^{i(\vec{k}+\vec{K})\cdot\vec{x}}\varphi_k(\vec{x}-\vec{R}_m) , \end{aligned} \qquad \text{(VI.1.27)}$$

the third term becomes,

$$\begin{aligned} & -\delta\vec{R}_m\cdot\vec{\nabla}\left(\frac{e^{-i(\vec{k}+\vec{K}_j)\cdot(\vec{x}-\vec{R}_m)}}{\sqrt{VN}}\varphi_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m)\right) + \\ & -i(\vec{k}+\vec{K}_j)\cdot\delta\vec{R}_m\frac{e^{i(\vec{k}+\vec{K}_j)\circ(\vec{x}-\vec{R}_m)}}{\sqrt{VN}}\varphi_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m) , \end{aligned} \qquad \text{(VI.1.28)}$$

and a similar expression obtains for the seventh term,

$$- \overrightarrow{\delta R}_m \cdot \vec{\nabla}\left(\frac{e^{i(\vec{k}+\vec{K}_i)\cdot(\vec{x}-\vec{R}_m)}}{\sqrt{VN}} \, \varphi^*_{\vec{k}+\vec{K}_j}(\vec{x}-\vec{R}_m)\right) +$$

$$+ \, i(\vec{k}+\vec{K}_i)\cdot\overrightarrow{\delta R}_m \, \frac{e^{i(\vec{k}+\vec{K}_i)\cdot(\vec{x}-\vec{R}_m)}}{\sqrt{VN}} \, \varphi^*_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m) \; . \qquad \text{(VI.1.29)}$$

The second and sixth and the first and fifth terms may be also combined to give a simple result. Combining all eight terms gives,

$$\frac{1}{A(k)} \sum_i \sum_j \left(a^*(\vec{k}+\vec{K}_j) \, a(\vec{k}+\vec{K}_i)\right)$$

$$\times \left\{ i(\vec{K}_i-\vec{K}_j)\cdot\overrightarrow{\delta R}_m \left(\frac{e^{-i(\vec{k}+\vec{K}_j)\cdot(\vec{x}-\vec{R}_m)}}{\sqrt{VN}} \, \varphi_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m) + \right.\right.$$

$$\left. + \frac{e^{i(\vec{k}+\vec{K}_i)\cdot(\vec{x}-\vec{R}_m)}}{\sqrt{VN}} \, \varphi^*_{\vec{k}+\vec{K}_j}(\vec{x}-\vec{R}_m) + \frac{1}{N} \varphi^*_{\vec{k}+\vec{K}_j}(\vec{x}-\vec{R}_m) \, \varphi_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m)\right)$$

$$- \overrightarrow{\delta R}_m \cdot \vec{\nabla}\left(\frac{1}{N} \varphi^*_{\vec{k}+\vec{K}_j}(\vec{x}-\vec{R}_m) \, \varphi_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m) + \right.$$

$$\left.\left. + \frac{e^{-i(\vec{k}+\vec{K}_j)\cdot(\vec{x}-\vec{R}_m)}}{\sqrt{VN}} \, \varphi_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m) + \frac{e^{i(\vec{k}+\vec{K}_i)\cdot(\vec{x}-\vec{R}_m)}}{\sqrt{VN}} \, \varphi^*_{\vec{k}+\vec{K}_j}(\vec{x}-\vec{R}_m)\right) \right\}$$

$$\text{(VI.1.30)}$$

Using the form of the eigenfunction, $\psi_{\vec{k}}(\vec{x};R^{\circ})$ itself, and of the trial functions, $\psi_{\vec{k}+\vec{K}_i}(\vec{x};R^{\circ})$, equation (VI.1.30) can be put in the form,

$$\begin{aligned}
&\Bigg\{\frac{1}{A}\sum_{i}\sum_{j}\Big(a^{*}(\vec{k}+\vec{K}_j)\,a(\vec{k}+\vec{K}_i)\,i(\vec{K}_i-\vec{K}_j)\cdot\overrightarrow{\delta R}_m\Big)\\
&\qquad\times\Big(\psi^{*}_{\vec{k}+\vec{K}_j}(\vec{x}-\vec{R}_m)\,\psi_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m)-\frac{1}{V}\,e^{i(\vec{K}_i-\vec{K}_j)\cdot(\vec{x}-\vec{R}_m)}\Big)\Bigg\}+\\
&\qquad-\Bigg\{\frac{1}{A}\sum_{i}\sum_{j}\Big(a^{*}(\vec{k}+\vec{K}_j)\,a(\vec{k}+\vec{K}_i)\Big)\\
&\qquad\times\overrightarrow{\delta R}_m\cdot\vec{\nabla}\Big(\psi^{*}_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m)\,\psi_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m)-\frac{1}{V}\,e^{i(\vec{K}_i-\vec{K}_j)\cdot(\vec{x}-\vec{R}_m)}\Big)\Bigg\}\,.
\end{aligned}\tag{VI.1.31}$$

Similarly, equation (VI.1.20) can be put in the form,

$$\begin{aligned}
&\Bigg\{\frac{1}{A}\sum_{i}\sum_{j}\Big(a^{*}(\vec{k}+\vec{K}_j)\,a(\vec{k}+\vec{K}_i)\,i(\vec{K}_i-\vec{K}_j)\cdot\overrightarrow{\delta R}_m\Big)\\
&\qquad\times\Bigg(\int\psi^{*}_{\vec{k}+\vec{K}_j}(\vec{x}')\,\psi_{\vec{k}+\vec{K}_i}(\vec{x}')\,\frac{1}{|\vec{x}-\vec{R}_m-\vec{x}'|}\,d\vec{x}'\,+\\
&\qquad-\frac{1}{V}\int e^{i(\vec{K}_i-\vec{K}_j)\cdot\vec{x}'}\,\frac{1}{|\vec{x}-\vec{R}_m-\vec{x}'|}\,d\vec{x}'\Bigg)\Bigg\}+
\end{aligned}$$

(continued)

$$-\left\{\frac{1}{A}\sum_{i}\sum_{j} a^{*}(\vec{k}+\vec{K}_{j})\,a(\vec{k}+\vec{K}_{i})\right.$$

$$\times\ \delta\vec{R}_{m}\cdot\vec{\nabla}_{x}\left(\int \psi^{*}_{\vec{k}+\vec{K}_{j}}(\vec{x}')\,\psi_{\vec{k}+\vec{K}_{i}}(\vec{x}')\,\frac{1}{|\vec{x}-\vec{R}_{m}-\vec{x}'|}\,d\vec{x}'\ +\right.$$

$$\left.\left.-\ \frac{1}{V}\int e^{i(\vec{K}_{i}-\vec{K}_{j})\cdot\vec{x}'}\,\frac{1}{|\vec{x}-\vec{R}_{m}-\vec{x}'|}\,d\vec{x}'\right)\right\}. \tag{VI.1.32}$$

When the expressions (VI.1.31) and (VI.1.32) are combined and summed over all the states within the Fermi surface,

$$\sum_{\vec{k}=0}^{k_{F}}\ , \tag{VI.1.33}$$

it is observed that the crystalline potential for the deformed lattice is <u>not</u> simply the same potential for the perfect lattice but displaced "rigidly" by $\delta\vec{R}_{m}$. To demonstrate this difference clearly, the following Fourier amplitudes of the charge densities and of the Coulomb and exchange potentials are defined:

$$\left(\rho_{e}(\vec{x})\right)_{\vec{k}+\vec{K}_{j};\vec{k}+\vec{K}_{i}} = \frac{1}{A}\,a^{*}(\vec{k}+\vec{K}_{j})\,a(\vec{k}+\vec{K}_{i})\,\psi^{*}_{\vec{k}+\vec{K}_{j}}(\vec{x};R)\,\psi_{\vec{k}+\vec{K}_{i}}(\vec{x};R). \tag{VI.1.34}$$

$$\left(v_{e}(\vec{x}-\vec{R}_{m};R)_{\text{Coulomb}}\right)_{\vec{k}+\vec{K}_{j};\vec{k}+\vec{K}_{i}} =$$

$$= \frac{1}{A}\,a^{*}(\vec{k}+\vec{K}_{j})\,a(\vec{k}+\vec{K}_{i})\int \psi^{*}_{\vec{k}+\vec{K}_{j}}(\vec{x}')\,\psi_{\vec{k}+\vec{K}_{i}}(\vec{x}')\,\frac{1}{|\vec{x}-\vec{x}'-\vec{R}_{m}|}\,d\vec{x}'$$

(continued)

$$= \int \left(\rho_e(\vec{x}';R) \right)_{\vec{k}+\vec{K}_j;\vec{k}+\vec{K}_i} \frac{1}{|\vec{x}-\vec{R}_m-\vec{x}'|} \, d\vec{x}' \qquad \text{(VI.1.35)}$$

$$\left(v_e(\vec{x}-\vec{R}_m;R)_{\text{exchange}} \right)_{\vec{k}+\vec{K}_j;\vec{k}+\vec{K}_i} =$$

$$= \left(\frac{1}{A} a^*(\vec{k}+\vec{K}_j)\, a(\vec{k}+\vec{K}_i)\, \psi^*_{\vec{k}+\vec{K}_j}(\vec{x}-\vec{R}_m)\, \psi_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m) \right)^{1/3} =$$

$$= \left(\left(\rho(\vec{x}-\vec{R}_m;R) \right)_{\vec{k}+\vec{K}_j,\vec{k}+\vec{K}_i} \right)^{1/3} . \qquad \text{(VI.1.36)}$$

From these it can be seen that the expression for the electronic crystalline potential is,

$$v_e(\vec{x};R) = \sum_{k=0}^{k_F} \left(\sum_{i,j} \int \left(\rho(\vec{x}';R) \right)_{\vec{k}+\vec{K}_i,\vec{k}+\vec{K}_j} \frac{1}{|\vec{x}-\vec{x}'|} \, d\vec{x}' \right) +$$

$$- \frac{3}{2\pi^2} \left\{ 3\pi^2 \sum_{k=0}^{k_F} \left(\sum_{i,j} \rho(\vec{x};R)_{\vec{k}+\vec{K}_j;\vec{k}+\vec{K}_i} \right) \right\}^{1/3} , \qquad \text{(VI.1.37)}$$

where the variable has been changed as,

$$\vec{x} = \vec{x}_1 - \vec{R}_m \; . \qquad \text{(VI.1.38)}$$

There is also now defined the plane-wave charge density: that part of the charge density attributable to the plane wave components of the eigenfunctions; or,

$$\left(\rho_e(\vec{x};R:P.-W.)\right)_{\vec{k}+\vec{K}_j;\vec{k}+\vec{K}_i} = \frac{1}{A}\, a^*(\vec{k}+\vec{K}_j)\; a(\vec{k}+\vec{K}_i)\, \frac{e^{i(\vec{K}_i-\vec{K}_j)\cdot\vec{x}}}{\sqrt{V}} . \tag{VI.1.39}$$

Substituting equations (VI.1.37) and (VI.1.39) into the expressions for the potential for the deformed lattice (VI.1.31) and (VI.1.32) gives, for the Coulomb term,

$$\begin{aligned} v_e(\vec{x};R+\vec{\delta R}_m)_{\text{Coulomb}} = \sum_{k=0}^{k_F} \sum_{i,j} \Bigg\{ & \int \left(\rho_e(\vec{x}';R^o)\right)_{\vec{k}+\vec{K}_j;\vec{k}+\vec{K}_i} \frac{1}{|\vec{x}-\vec{x}'|}\, d\vec{x}' + \\ & + i(\vec{K}_i-\vec{K}_j)\cdot\vec{\delta R}_m \int \bigg(\left(\rho_e(\vec{x}';R^o)\right)_{\vec{k}+\vec{K}_j;\vec{k}+\vec{K}_i} - \\ & - \rho_e(\vec{x}';R^o;P.-W.)_{\vec{k}+\vec{K}_j;\vec{k}+\vec{K}_i} \bigg) \cdot \frac{1}{|\vec{x}-\vec{x}'|}\, d\vec{x}' + \\ & - \vec{\delta R}_m \cdot \vec{\nabla}_x \int \bigg(\left(\rho_e(\vec{x}';R^o)\right)_{\vec{k}+\vec{K}_j;\vec{k}+\vec{K}_i} - \\ & - \rho_e(\vec{x}';R^o;P.-W.)_{\vec{k}+\vec{K}_j;\vec{k}+\vec{K}_i} \bigg) \cdot \frac{1}{|\vec{x}-\vec{x}'|}\, d\vec{x}' \Bigg\} , \end{aligned} \tag{VI.1.40}$$

and for the exchange term,

$$\begin{aligned} v_e(\vec{x};R+\vec{\delta R}_m)_{\text{exchange}} = -\frac{3}{2\pi^2} \Bigg\{ & 3\pi^2 \sum_{k=0}^{k_F} \sum_{i,j} \bigg(\left(\rho_e(\vec{x};R^o)\right)_{\vec{k}+\vec{K}_j,\vec{k}+\vec{K}_i} + \\ & + i(\vec{K}_i-\vec{K}_j)\cdot\vec{\delta R}_m \bigg(\left(\rho_e(\vec{x};R^o)\right)_{\vec{k}+\vec{K}_j,\vec{k}+\vec{K}_i} - \end{aligned}$$

(continued)

$$
\begin{aligned}
&- \Big(\rho_e(\vec{x};R^\circ : P.-W.)\Big)_{\vec{k}+\vec{K}_j,\vec{k}+\vec{K}_i}\Big) + \\
&- \overrightarrow{\delta R}_m \circ \vec{\nabla}_x \Bigg(\Big(\rho_e(\vec{x};R^\circ)\Big)_{\vec{k}+\vec{K}_j,\vec{k}+\vec{K}_i} - \\
&- \Big(\rho_e(\vec{x};R^\circ : P.-W.)\Big)_{\vec{k}+\vec{K}_j,\vec{k}+\vec{K}_i}\Bigg)\Bigg)\Bigg\}^{1/3} .
\end{aligned}
\tag{VI.1.41}
$$

Together equations (VI.1.40) and (VI.1.41) comprise the electronic potential for the deformed lattice:

$$
v_e(\vec{x};R+\delta R_m) = v_e(\vec{x};R+\delta R_m)_{\text{Coulomb}} + v_e(\vec{x};R+\delta R_m)_{\text{exchange}} . \tag{VI.1.42}
$$

Having derived this potential for the $\vec{R}_m$-th cell of the deformed lattice, it is next required to examine the energy eigenvalues which it admits. It will be shown that this deformed potential admits eigenvalues identical to those calculated in Chapter V through terms linear in δR_m. In short, the deformation of the potential only produces changes in the energy eigenvalues of order $(\delta R_m)^2$ and higher.

It is necessary, then, to set up the entire A.P.W. variational problem for the deformed lattice using the new electronic potential generated by the deformed lattice eigenfunctions. In order to establish that this new potential does not alter the variational eigenvalues by terms less than quadratic in δR_m, — i.e., is self-consistent, — it must be shown only that there are no non-vanishing diagonal matrix elements between the perfect lattice trial functions.

As stated at the beginning of this chapter it is initially assumed that the deformation of the crystalline potential is confined to the $\vec{R}_m$-th cell. The potential in all other cells is assumed to be identical with that of the perfect lattice. In the $\vec{R}_m$-th cell, the A.P.W. trial functions are of the form,

$$\begin{aligned}\psi_{\vec{k}+\vec{K}_i}(\vec{x};\vec{R}_m) &= \frac{e^{i(\vec{k}+\vec{K}_i)\cdot\vec{x}}}{\sqrt{V}} + \frac{e^{i(\vec{k}-\vec{R}_m)}}{\sqrt{N}}\,\varphi_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m) + \\ &+ i(\vec{k}\cdot\overrightarrow{\delta R}_m)\,\frac{e^{i(\vec{k}\cdot\vec{R}_m)}}{\sqrt{N}}\,\varphi_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m) \\ &- \frac{e^{i(\vec{k}\circ\vec{R}_m)}}{\sqrt{N}}\,\overrightarrow{\delta R}_m\circ\vec{\nabla}_x\,\varphi_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m)\ . \qquad \text{(VI.1.43)}\end{aligned}$$

Because the investigation is of the terms linear in change in the potential (VI.1.40), (VI.1.41), (or VI.1.42) from that used in Chapter V, the matrix elements involving the last two sets of terms in equation (VI.1.43) will be neglected.

Recognizeably, the terms in equations (VI.1.41) and (VI.1.42) which are

$$-\sum_{k=0}^{k_F}\left\{\sum_{i,j}\left(\left(\rho(\vec{x};R^{o})\right)_{\vec{k}+\vec{K}_i;\vec{k}+\vec{K}_j} - \overrightarrow{\delta R}_m\cdot\vec{\nabla}_x\ \rho(\vec{x};R^{o})_{\vec{k}+\vec{K}_j;\vec{k}+\vec{K}_i}\right)\right\}, \qquad \text{(VI.1.44)}$$

represent simply the rigidly translated potential; i.e., the rigid-ion model potential for the deformed lattice. These terms generate the potential used in Chapter V. There must now be added to the diagonal elements of the A.P.W. matrix terms involving,

$$\sum_{i,j}\left(\overrightarrow{\delta R}_m \cdot \vec{\nabla}_x \int \left(\rho(\vec{x}';R^\circ;P-W)\right)_{\vec{k}+\vec{K}_i;\vec{k}+\vec{K}_j} \frac{1}{|\vec{x}-\vec{x}'|}\, d\vec{x}' + \right.$$

$$\left. -\frac{1}{3}\, \overrightarrow{\delta R}_m \cdot \vec{\nabla}_x \left(\rho(\vec{x};R^\circ;P-W)\right)_{\vec{k}+\vec{K}_i;\vec{k}+\vec{K}_j}\right) , \tag{VI.1.45}$$

and terms involving,

$$\sum_{i,j} i(\vec{K}_i-\vec{K}_j)\cdot \overrightarrow{\delta R}_m \left(\int \left(\rho(\vec{x}';R^\circ)\right)_{\vec{k}+\vec{K}_i,\vec{k}+\vec{K}_j} - \left(\rho(\vec{x}';R^\circ;P-W)\right)_{\vec{k}+\vec{K}_i,\vec{k}+\vec{K}_j}\right)$$

$$\times \frac{1}{|\vec{x}-\vec{x}'|}\, d\vec{x}' +$$

$$-\frac{1}{3}\left(\left(\rho(\vec{x};R^\circ)\right)_{\vec{k}+\vec{K}_j,\vec{k}+\vec{K}_i} - \left(\rho(\vec{x};R^\circ;P-W)\right)_{\vec{k}+\vec{K}_i,\vec{k}+\vec{K}_j}\right) . \tag{VI.1.46}$$

In both equations (VI.1.45) and (VI.1.46) the functional change in the exchange potential which is linear in δR_m has been expressed in the expansion,

$$(1+\varepsilon)^{1/3} \simeq 1 + \frac{1}{3}\,\varepsilon + \dots \; . \tag{VI.1.47}$$

Now, to show that there are no non-vanishing diagonal matrix elements involving either (VI.1.45) or (VI.1.46), there will be used the following properties of the Bloch functions which are used as the A.P.W. trial functions. Under the operation of inversion of the spatial coordinates,

$$\vec{x}' = -\vec{x} \ , \qquad \text{(VI.1.48)}$$

the trial functions become,

$$\psi_{\vec{k}+\vec{K}_i}(-\vec{x}) = e^{-i(\vec{k}+\vec{K}_i)\cdot\vec{x}} \, u_{\vec{k}+\vec{K}}(-\vec{x}) \ . \qquad \text{(VI.1.49)}$$

Because this function transforms as the $(-\vec{k})$-th representation of the lattice translation group, the phase of the periodic orbital can be chosen such that,

$$u_{\vec{k}+\vec{K}}(-\vec{x}) = u^{*}_{\vec{k}+\vec{K}_i}(\vec{x}) \ , \qquad \text{(VI.1.50)}$$

provided that the lattice has a center of inversion. Thus, there obtains the property,

$$\psi_{\vec{k}+\vec{K}_i}(-\vec{x}) = \psi^{*}_{\vec{k}+\vec{K}_i}(\vec{x}) \ . \qquad \text{(VI.1.51)}$$

(A moment's scruting of the A.P.W. trial functions as given by equation (III.12) or (III.13) and comparison of them with the plane wave, $e^{i(\vec{k}+\vec{K}_i)\cdot\vec{x}}$, will suffice to show that the A.P.W. trial functions already satisfy this relationship.) Also will be used the property that the A.P.W. variational coefficients can be made real:

$$a^{*}(\vec{k}+\vec{K}_j) = a(\vec{k}+\vec{K}_j) \ . \qquad \text{(VI.1.52)}$$

Taking the Coulomb term in equation (VI.1.45) between the state,

$$\psi_{\vec{k}'+\vec{K}_\ell}(\vec{x}) \ ,$$

gives,

$$\sum_{i,j} a(\vec{k}+\vec{K}_j)\, a(\vec{k}+\vec{K}_i)$$

$$\delta\vec{R}_m \cdot \int d\vec{x}\ |\psi_{\vec{k}'+\vec{K}_\ell}(\vec{x})|^2\, \vec{\nabla}_x \int d\vec{x}'\ \psi^*_{\vec{k}+\vec{K}_j}(\vec{x}')\, \psi_{\vec{k}+\vec{K}_i}(\vec{x}')\, \frac{1}{|\vec{x}-\vec{x}'|} \ . \qquad \text{(VI.1.53a)}$$

Now substituting both variables of integration as

$$\vec{x}'' = -\vec{x}$$

and

$$\vec{x}''' = -\vec{x}'$$

gives

$$\sum_{i,j} a(\vec{k}+\vec{K}_j)\, a(\vec{k}+\vec{K}_i)$$

$$\delta\vec{R}_m \cdot \int d\vec{x}''\, |\psi_{\vec{k}'+\vec{K}_\ell}(\vec{x}'')|^2 \left(-\vec{\nabla}_{x''} \int d\vec{x}'''\ \psi_{\vec{k}+\vec{K}_j}(\vec{x}''')\, \psi^*_{\vec{k}+\vec{K}_i}(\vec{x}''')\, \frac{1}{|\vec{x}''-\vec{x}'''|}\right) . \qquad \text{(VI.1.53b)}$$

Interchanging the dummy indices, i and j, in (VI.1.53b) renders an expression identical to (VI.1.53a) but of opposite sign because of the minus sign which entered on account of the odd parity of the gradient operator:

$$\vec{\nabla}_{-\vec{x}} = -\vec{\nabla}_{\vec{x}} \ . \qquad \text{(VI.1.54)}$$

A similar analysis can be made of the exchange terms in equation (VI.1.45). Therefore, there are no non-vanishing diagonal matrix elements involving the linear changes in the electronic potential which are associated with a gradient of the electron density:

$$\int d\vec{x}\, |\psi_{\vec{k}'+\vec{K}_\ell}(\vec{x})|^2 \, \vec{\delta R}_m \cdot \vec{\nabla}_x \left(\int \psi^*_{\vec{k}+\vec{K}_j}(\vec{x}')\, \psi_{\vec{k}+\vec{K}_i}(\vec{x}')\, \frac{1}{|\vec{x}-\vec{x}'|}\, d\vec{x}' + \right.$$

$$\left. - \frac{1}{3}\, \psi^*_{\vec{k}+\vec{K}_j}(\vec{x})\, \psi_{\vec{k}+\vec{K}_i}(\vec{x}) \right) = 0 \; . \qquad \text{(VI.1.55)}$$

The functional changes in the potential represented by expression (VI.1.46) admit similar treatment. Considering the diagonal element between the state, $\psi_{\vec{k}'+\vec{K}_\ell}(\vec{x})$ again, there are terms of the form,

$$\sum_{i,j} \left(a(\vec{k}+\vec{K}_j)\, a(\vec{k}+\vec{K}_i)\, i\,(\vec{K}_i-\vec{K}_j) \cdot \vec{\delta R}_m \right)$$

$$\int d\vec{x}\, |\psi_{\vec{k}'+\vec{K}_\ell}(\vec{x})|^2 \int d\vec{x}'\, \psi^*_{\vec{k}+\vec{K}_j}(\vec{x}')\, \psi_{\vec{k}+\vec{K}_i}(\vec{x}')\, \frac{1}{|\vec{x}-\vec{x}'|} \; . \qquad \text{(VI.1.56a)}$$

By changing both the variables of integration as was done in expression (VI.1.53a), and using the property of the Bloch functions expressed in equation (VI.1.51) there obtains,

$$\sum_{i,j} \left(a(\vec{k}+\vec{K}_j)\, a(\vec{k}+\vec{K}_i)\, i\,(\vec{K}_i-\vec{K}_j) \cdot \vec{\delta R}_m \right)$$

(continued)

$$\times \int d\vec{x}'' \, |\psi_{\vec{k}'+\vec{K}_\ell}(\vec{x}'')|^2 \int d\vec{x}''' \, \psi_{\vec{k}+\vec{K}_j}(\vec{x}''') \, \psi^*_{\vec{k}+\vec{K}_i}(\vec{x}''') \frac{1}{|\vec{x}''-\vec{x}'''|} \, . \tag{VI.1.56b}$$

If the indices, i and j are interchanged in (VI.1.56b), there obtains the negative of (VI.1.56a), and therefore, the sum of half of both vanishes. Again, a similar treatment of the exchange terms in equation (VI.1.46) demonstrates that the diagonal matrix elements of those terms also vanish.

Thus it has been shown that the functional changes in the electronic potential in the $\vec{R}_m$-th cell which developes from the eigenfunctions for the deformed lattice have no non-vanishing diagonal matrix elements linear in δR_m. Therefore, this deformed lattice potential which can be quite different from the perfect-lattice electronic potential, admits the same eigenvalues as did the potential used in the previous iteration up to terms quadratic in δR_m:

$$\left(v_e(\vec{x};R+\delta R_m)\right)_{1^{st}\text{-iteration}} \longrightarrow \epsilon^o(\vec{k}) + O(\delta R_m)_1^2$$

and

$$\left(v_e(\vec{x};R+\delta R_m)\right)_{2^{nd}\text{-iteration}} \longrightarrow \epsilon^o(\vec{k}) + O(\delta R_m)_1^2 + O(\delta R_m)_2^2 \, . \tag{VI.1.57}$$

Therefore, within the criterion for self-consistency that there be no change in the eigenvalues linear in δR_m between the i-th and the (i+1)-th iterations, the eigenfunctions for the deformed lattice determined in Chapter V,

$$\psi^{\epsilon(\vec{k})}(\vec{x}_k; R+\delta R_m) = \sqrt{\frac{1}{A(k)}}\sum_i \left(a^{\epsilon^\circ(\vec{k})}(\vec{k}+\vec{K}_i)\right)$$

$$\times\left\{\frac{e^{i(\vec{k}+\vec{K}_i)\cdot\vec{x}}}{\sqrt{V}} + \sqrt{\frac{1}{N}}\sum_{R_p \neq R_m} e^{i(\vec{k}+\vec{K}_i)\cdot\vec{R}_p}\,\varphi^{\epsilon^\circ(\vec{k})}_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_p) +\right.$$

$$\left. + \sqrt{\frac{1}{N}}\, e^{i(\vec{k}+\vec{K}_i)\cdot\vec{R}_m}\left(i(\vec{k}+\vec{K}_i)\cdot\delta\vec{R}_m - \delta\vec{R}_m\circ\vec{\nabla}_x\right)\varphi^{\epsilon^\circ(\vec{k})}_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m)\right\},$$

(VI.1.58)

are self-consistent, and therefore, the proper ones to use to determine the derivative terms,

$$\frac{d}{dR_m}\left(\psi_{\vec{k}}(\vec{x}_k; R)\right),$$

for the electron-phonon interaction matrix elements.

VI.2 Further Remarks Upon Self-Consistency. The Phenomenon of Shielding.

In the previous section, it was demonstrated that the eigenvalues for the band energies in the deformed lattice, which were calculated in Chapter V, Section 3,

$$\epsilon(\vec{k};R+\delta R_m) = \epsilon^{0}(\vec{k}) + O(\delta R_m^2) \ , \qquad \text{(VI.2.1)}$$

are self-consistent through orders linear in δR_m. The eigenfunctions for the deformed muffin-tin lattice which belong to these eigenvalues are

$$\begin{aligned}\psi^{\epsilon(\vec{k})}(\vec{x}_k;R+\delta R_m) = {} & \sqrt{\frac{1}{A(k)}}\sum_i a^{\epsilon(\vec{k})}(\vec{k}+\vec{K}_i) \times \\ & \times\left\{\frac{e^{i(\vec{k}+\vec{K}_i)\cdot\vec{x}}}{\sqrt{V}} + \sqrt{\frac{1}{N}}\sum_{R_p\neq R_m} e^{i\vec{k}\cdot\vec{R}_p}\,\varphi^{\epsilon(\vec{k})}_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_p) + \right. \\ & \left. + \frac{e^{i\vec{k}\cdot\vec{R}_m}}{\sqrt{N}}\left(i(\vec{k}+\vec{K}_i)\cdot\delta\vec{R}_m - \delta\vec{R}_m\cdot\vec{\nabla}\right)\varphi^{\epsilon(\vec{k})}_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m)\right\} . \qquad \text{(VI.2.2)}\end{aligned}$$

The crystalline potential which is generated by the eigenfunctions in equation (VI.2.2) is

$$\begin{aligned}v_e(\vec{x};R+\delta R_m) = v_e(\vec{x};R^{o}) - \Big(&\vec{\nabla}v_e(\vec{x};R^{o})\cdot\delta\vec{R}_m \\ &- \vec{\nabla}v_e(\vec{x};R^{o};\text{P.-W.})\cdot\delta\vec{R}_m\Big) . \qquad \text{(VI.2.3)}\end{aligned}$$

In equation (VI.2.3) the symbol, $v_e(\vec{x};R^\circ;P.-W.)$, represents the plane-wave potential given by

$$\begin{aligned} v_e(\vec{x};R^\circ;P.-W.) &= \sum_{\vec{k}=0}^{k_F} \left\{ \sum_{i,j} \frac{a(\vec{k}+\vec{K}_i)\, a(\vec{k}+\vec{K}_j)}{A(k)\, V} \times \left(\int e^{i(\vec{K}_i-\vec{K}_j)\cdot\vec{x}'} \frac{1}{|\vec{x}-\vec{x}'|}\, d\vec{x}' \right) \right\} + \\ &\quad - \frac{3}{2\pi^2} \left\{ 3\pi^2 \sum_{\vec{k}=0}^{k_F} \left(\sum_{i,j} \frac{a(\vec{k}+\vec{K}_i)\, a(\vec{k}+\vec{K}_j)}{A(k)\, V} e^{i(\vec{K}_i-\vec{K}_j)\cdot\vec{x}} \right) \right\}^{1/3} \\ &= \sum_{\vec{k}=0}^{k_F} \left\{ \sum_{i,j} \left(\int \left(\rho(\vec{x}';R^\circ;P.-W.)\right)_{\vec{k}+\vec{K}_j,\vec{k}+\vec{K}_i} \frac{1}{|\vec{x}-\vec{x}'|}\, d\vec{x}' \right) \right\} + \\ &\quad - \frac{3}{2\pi^2} \left\{ 3\pi^2 \sum_{\vec{k}=0}^{k_F} \left(\sum_{i,j} \left(\rho(\vec{x};R^\circ;P.-W.)\right)_{\vec{k}+\vec{K}_j,\vec{k}+\vec{K}_i} \right) \right\}^{1/3} . \end{aligned} \tag{VI.2.4}$$

This phenomenon of the deformed lattice that the plane-wave component of the charge density is impervious to the motion of the nucleus while the tight-binding components is translated rigidly with it, is represented schematically in Figure 5.

The eigenfunctions represented by equation (VI.2.2) obtained for the muffin-tin lattice when it was assumed that the electronic potential for the deformed lattice was

$$v_e(\vec{x};R+\delta R_m) \cong v_e(\vec{x};R^\circ) - \vec{\nabla} v_e(\vec{x};R^\circ)\cdot \delta R_m \ , \tag{VI.2.5}$$

i.e. neglecting the imperviousness of the plane-wave component of the charge density, and when it was assumed that the deformation of the crystalline potential was restricted to the $\vec{R}_m$-th cell. So long as the variation of the crystalline potential is assumed to be restricted to the $\vec{R}_m$-th cell, and the variations in other cells is neglected such that

$$v_e(\vec{x};R+\delta R_m) = v_e(\vec{x};R^o) \quad , \tag{VI.2.6}$$

if $\vec{x}$ lies in any but the $\vec{R}_m$-th cell, then the corrections to the eigenfunctions, (VI.2.2) attributable to the differences between the potentials (VI.2.4) and (VI.2.5) will be of order (1/N), as determined in a manner identical with the analysis of Section V.4. Therefore, the eigenfunctions in equation (VI.2.2) are the correct ones for the deformed muffin-tin lattice provided that the criterion for self-consistency is not less than (1/N):

$$\left| \Big(\psi(\vec{x}_k;R+\delta R_m)\Big)_{2^{nd}\text{-iteration}} - \Big(\psi(\vec{x}_k;R+\delta R_m)\Big)_{1^{st}\text{-iteration}} \right| \le \delta \; , \tag{VI.2.7}$$

and

$$\delta > \frac{1}{N} \; , \tag{VI.2.8}$$

for all values of $\vec{x}_k$.

The reason for this relative smallness of the corrections to the eigenfunctions can be understood quite simply.

The crystalline eigenfunctions are of unit modulus when integrated over a single Wigner-Seitz cell:

$$\int_{\Omega} | \psi_k(\vec{x};R)|^2 \, d\vec{x} = 1 \quad . \qquad \text{(VI.2.9)}$$

In order to adjust the modulus of the eigenfunction to maintain normalization throughout a lattice of N unit cells, the orbital is divided by $\sqrt{N}$. It is for this reason that the plane-wave components are multiplied by

$$\sqrt{\frac{1}{V}} = \sqrt{\frac{1}{N\Omega}} \quad , \qquad \text{(VI.2.10)}$$

and the Bloch sum of non-overlapping tight-binding components by $N^{-1/2}$,

$$\sqrt{\frac{1}{N}} \sum_{R_p} e^{i\vec{k}\cdot\vec{R}_p} \varphi_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_p) \quad . \qquad \text{(VI.2.11)}$$

The eigenfunctions for the perfect lattice are eigenstates of the perfect-lattice Hamiltonian, $h_e(\vec{x};R^0)$, and are orthogonal over the volume of the perfect lattice. So long as the variations of the potential are restricted to a single cell, the non-vanishing matrix elements of the Hamiltonian between such states will be of order N^{-1}:

$$\int_V \psi^*_{\vec{k}'}(\vec{x}) \, h_e(\vec{x};R+\delta R_m) \, \psi_{\vec{k}}(\vec{x}) \, d\vec{x} = \epsilon_k \, \delta_{k',k'} - \int_{\Omega R_m} \psi^*_{\vec{k}'}(\vec{x}) \, h_e(\vec{x};R^0) \, \psi_{\vec{k}}(\vec{x}) \, d\vec{x} +$$

$$+ \int_{\Omega R_m} \psi^*_{k'}(\vec{x}) \, h_e(\vec{x};\vec{R}_m + \vec{\delta R}_m) \, \psi_k(\vec{x}) \, d\vec{x} = 0 + O\left(\frac{1}{N} \epsilon_k \, \delta R_m\right). \qquad \text{(VI.2.12)}$$

In the derivation of the eigenvalues of the band energies for the deformed lattice in Chapter V, the muffin-tin model of the lattice was used because it was necessary to analyse explicitly the matrix elements,

$$(h_e - \epsilon)_{\vec{k}'+\vec{K}_j,\vec{k}+\vec{K}_i} , \qquad \text{(VI.2.13)}$$

in the deformed lattice. Also, in the discussion of the previous section the muffin-tin lattice was used and the deformation was restricted to a single unit cell.

However, the analysis of both sections of this chapter has been almost completely general. Nowhere was necessary to the discussion of the self-consistency of either the eigenvalues or the eigenstates the fact that the assumed eigenfunctions for the deformed lattice, equation (VI.2.2), had obtained from a muffin-tin model, or the fact that the deformation had been restricted to a single unit cell. For the argument for the self-consistency of both the band energies and the eigenfunctions was necessary only the vanishing of the diagonal matrix elements of the functional variations of the electronic potential. To demonstrate that such matrix elements vanish it was required to use the property of the charge density of the perfect lattice that

$$\left(\rho_e(\vec{x})\right)_{\vec{k}+\vec{K}_i,\vec{k}+\vec{K}_j} = \frac{1}{A(k)}\, a(\vec{k}+\vec{K}_i)\, a(\vec{k}+\vec{K}_j)\, \psi^*_{\vec{k}+\vec{K}_i}(\vec{x})\, \psi_{\vec{k}+\vec{K}_j}(\vec{x}) =$$

$$= \left(\rho_e(-\vec{x})\right)^*_{\vec{k}+\vec{K}_j,\vec{k}+\vec{K}_i} , \qquad \text{(VI.2.14)}$$

which property depends not at all upon the restrictions of the muffin-tin model. The potential due to the electrons in the lattice is given generally by equation (VI.1.3)

$$v_e(\vec{x};R) = \sum_{\vec{k}=0}^{k_F}\left(\int |\psi_{\vec{k}}(\vec{x}';R)|^2 \frac{1}{|\vec{x}-\vec{x}'|}\, d\vec{x}'\right)$$

$$-\frac{3}{2\pi^2}\left(3\pi^2 \sum_{\vec{k}}^{k_F} |\psi_{\vec{k}}(\vec{x};R)|^2\right)^{1/3} =$$

$$= \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \Big(v_e(r;R)\Big)_{\ell,m} P_{\ell}^{|m|}(\cos\theta)\, e^{im\varphi} \ . \qquad \text{(VI.2.15)}$$

The criteriae of self-consistency require that, in the fully general analysis, each term in the series in equation (VI.2.14) develope from the eigenfunctions of the nuclear configuration under consideration:

$$\left| \Big(v_e(r;R)\Big)_{\ell,m \ \underset{\text{iteration}}{\text{i-th}}} - \Big(v_e(r;R)\Big)_{\ell,m \ \underset{\text{iteration}}{\text{(i+1)-th}}} \right| \le \delta(\text{s.c.}) \ , \qquad \text{(VI.2.16)}$$

for all r, and for all ℓ,m, where δ(s.c.) is some small number taken as the criterion of self-consistency for the potential. Plainly the problem of the self-consistency of the muffin-tin potential is included in the general problem the self-consistent field. For the muffin-tin model, the potential is required to satisfy the inequality

$$\left| v(r;R)_{\ell=0 \atop \substack{\text{i-th} \\ \text{iteration}}} - v(r;R)_{\ell=0 \atop \substack{\text{(i+1)-th} \\ \text{iteration}}} \right| \leq \delta(\text{s.c.}) \ , \qquad \text{(VI.2.17)}$$

for all r inside the A.P.W. sphere, the potential being arbitrarily taken as constant in the rest of the cell.

A procedure for solving the problem for the complete potential in a deformed lattice is as follows:

Taking the general solutions for the perfect lattice which obtain from the complete potential of the perfect lattice,

$$\psi_{\vec{k}}(\vec{x}_k;R^o) = \sqrt{\frac{1}{A(k)}} \sum_i a^{\epsilon(k)}(\vec{k}+\vec{K}_i) \times$$
$$\times \left(\frac{e^{i(\vec{k}+\vec{K}_i)\cdot\vec{x}}}{\sqrt{V}} + \sqrt{\frac{1}{N}} \sum_{\vec{R}_p} e^{i\vec{k}\cdot\vec{R}_p} \varphi_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_p) \right), \qquad \text{(VI.2.18)}$$

a potential for the deformed lattice which would be used for the first iteration would be taken as identical as for the perfect lattice in all but the $\vec{R}_m$-th cell and in the $\vec{R}_m$-th cell would be constructed using equation (VI.2.3). As argued in the previous chapter and section, the solutions for this deformed lattice would differ from equation (VI.2.17) only in the R_m-th cell when they would be

$$\psi(\vec{x}_k; R + \delta R_m) = \psi_{\vec{k}}(\vec{x}_k; R^{o}) + \sqrt{\frac{1}{A(k)}} \sum_i \frac{a^{\epsilon}(\vec{k}+\vec{K}_i)}{\sqrt{N}} e^{i\vec{k}\cdot\vec{R}_m} \times$$

$$\times \left(i(\vec{k}+\vec{K}_i)\cdot\delta\vec{R}_m \, \varphi_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m) - \delta\vec{R}_m \cdot \vec{\nabla} \varphi_{\vec{k}+\vec{K}_i}(\vec{x}-\vec{R}_m) \right) +$$

$$+ \text{ terms } O\left(\frac{1}{N}\right) \qquad \text{(VI.2.19)}$$

through terms linear in δR_m. Now on the next iteration, the potential which is regenerated by the solutions (VI.2.19) will manifest certain multipole moments which will alter the potential in cells other than the $\vec{R}_m$-th. The solutions to the variational problem for the eigenfunctions in these other cells will differ from the functions in equation (VI.2.18) by terms of the order

$$\sim \frac{1}{|\vec{R}_e - \vec{R}_m|^{p \geq 2}} O\left(\frac{1}{N}\right) . \qquad \text{(VI.2.20)}$$

The correction terms in (VI.2.20) will be included in the next and each subsequent iteration until the criterion of self-consistency is satisfied. Obviously the magnitude of these correction terms will be largest in the cells adjacent or near to the $\vec{R}_m$-th cell. The correction to the total charge density which arises from these terms will produce additional multipole moments which will diminish the magnitude of such moments due to the changed charge density in the $\vec{R}_m$-th cell in cells distant from both. This is simply the phenomenon of shielding and obtains naturally and directly from the property of self-consistency.

VI.3 The Virtues of the A.P.W. Method and the Vices of the Rigid-Ion Model.

The conclusions of the last two sections hold much significance for evaluating a common approximation for the electron-phonon interactions. As was discussed at some length in Chapter IV, the direct evaluation of the matrix elements for the electron-phonon interactions from the "double-derivative" terms in the Adiabatic Model has been heretofore inaccessible because of the difficulties in calculating accurately the derivatives of the electronic eigenfunctions,

$$\frac{d}{dR_{m,i}}\left(\psi_{\vec{k}}(\vec{x}_k;R)\right) . \qquad (VI.3.1)$$

An alternate development of the theory which has been widely used [36] is as follows.

The crystalline potential which enters the electronic Hamiltonian

$$\begin{aligned} h_e(\vec{x};R) &= -\nabla^2 - \sum_{\vec{R}_p} \frac{2Z}{|\vec{x}-\vec{R}_p|} + v_e(\vec{x};R) \\ &= -\nabla^2 + u(\vec{x};R) \ , \qquad (VI.3.2) \end{aligned}$$

is recognizably a function of the nuclear coordinates, $R=\{R_1,R_2,\ldots,R_N\}$. It is assumed that this potential can be expanded in a Taylor series about its equilibrium-position value, such that

$$u(\vec{x};R) = u(\vec{x};R^o) + \sum_{R_m} \sum_i \left(\frac{du(\vec{x};R)}{dR_{m,i}}\right)_{R^o} \delta R_{m,i} + \dots , \qquad \text{(VI.3.3)}$$

and that the terms linear in $\delta R_{m,i}$ do not vanish. The electron-phonon interactions are then assumed to obtain from the linear terms in (VI.3.3) considered as perturbations:

$$D(\vec{k}',k) = \delta R_{m,i} \int \psi^*_{\vec{k}}(\vec{x}';R) \left(\frac{d}{dR_{m,i}} u(\vec{x}';R)\right)_{R^o} \psi_{\vec{k}}(\vec{x}';R)\, d\vec{x}' . \qquad \text{(VI.3.4)}$$

The expansion in terms of nuclear coordinates in equation (VI.3.3) and equation (3.4) is usually transformed into one in terms of normal mode coordinates, Q_q, as in Chapter IV.

Although the original work in which the matrix elements of equation (VI.3.4) were derived involved lengthy arguments to justify their equivalence with the "double-derivative" terms, the validity of equation (VI.3.4) is easily established for the case where the function $\psi_{\vec{k}}(\vec{x};R)$ is an eigenfunction of the one-electron Hamiltonian (by no means a traditionally common circumstance):

$$h_e(\vec{x};R)\, \psi_{\vec{k}}(\vec{x};R) = \epsilon_{\vec{k}}(R)\, \psi_{\vec{k}}(\vec{x};R) . \qquad \text{(VI.3.5)}$$

Now equation (VI.3.5) is not only an eigenvalue equation for the Hamiltonian operator of the electronic coordinates acting upon the electronic eigenstate $\psi_{\vec{k}}(\vec{x};R)$, it is also a parametric equation in the 3N parametric functions $R_{m,i}$.

As such it may be differentiated with respect to any one of these parametric variables to give

$$\left(\frac{dh_e(\vec{x};R)}{dR_{m,i}}\right)\psi_{\vec{k}}(\vec{x};R) + h_e(\vec{x};R)\left(\frac{d}{dR_{m,i}}\psi_{\vec{k}}(\vec{x};R)\right) =$$

$$= \left(\frac{d\,\epsilon_{\vec{k}}(R)}{dR_{m,i}}\right)\psi_{\vec{k}}(\vec{x};R) + \epsilon_{k}(R)\left(\frac{d}{dR_{m,i}}\psi_{\vec{k}}(\vec{x};R)\right) \quad .(\text{VI}.3.6)$$

Multiplying equation (VI.3.6) from the left by $\psi_{\vec{k}'}(\vec{x};R)$ and integrating out the electronic coordinates gives

$$\int \psi_{\vec{k}}(\vec{x};R)\left(\frac{d}{dR_{m,i}}h_e(\vec{x};R)\right)\psi_{\vec{k}}(\vec{x};R)\,d\vec{x} =$$

$$= \left(\epsilon_{k}(R) - \epsilon_{k'}(R)\right)\int \psi_{\vec{k}}(\vec{x};R)\left(\frac{d}{dR_{m,i}}\psi_{\vec{k}}(\vec{x};R)\right)d\vec{x} \;.\; (\text{VI}.3.7)$$

The integral on the left band side of equation (VI.3.7) is recognized as the term multiplying $\delta R_{m,i}$ in the matrix element (VI.3.4). The terms on the right hand side of (VI.3.7) are simply the "double-derivative" terms multiplied by $(\epsilon_{\vec{k}} - \epsilon_{\vec{k}'})$. The conservation of energy requires that this energy difference be equal to that of the phonon absorbed or emitted,

$$\epsilon_{\vec{k}} - \epsilon_{\vec{k}'} = \hbar\omega_{\vec{q}} \quad . \qquad (\text{VI}.3.8)$$

Multiplying both sides of equation (VI.3.7) by the normal mode coordinate Q_q and substituting equation (VI.3.8) for the energy difference gives

$$Q_q \int \psi^*_{\vec{k}'}(\vec{x};R)\left(\frac{d}{dR_{m,i}} h_e(\vec{x};R)\right) \psi_{\vec{k}}(\vec{x};R)\, d\vec{x} =$$

$$= \sqrt{\frac{\hbar}{2NM\omega(q)}} \int \psi^*_{\vec{k}'}(\vec{x};R)\left(\frac{d}{dR_{m,i}} h_e(\vec{x};R)\right) \psi_{\vec{k}}(\vec{x};R)\, d\vec{x} =$$

$$= \sqrt{\frac{\hbar\omega(q)}{2NM}} \int \psi^*_{\vec{k}'}(\vec{x};R)\left(\frac{d}{dR_{m,i}} \psi_{\vec{k}}(\vec{x};R)\right) d\vec{x} \ . \qquad \text{(VI.3.9)}$$

This is exactly the identity between the two forms of the electron-phonon matrix elements which was to be demonstrated.

In order to use the matrix elements of equation (VI.3.4) for the electron-phonon interactions, it is necessary to evaluate the derivatives

$$\frac{d}{dR_{m,i}}\left(h_e(\vec{x};R)\right) = \frac{d}{dR_{m,i}}\left(u(\vec{x};R)\right) \ . \qquad \text{(VI.3.10)}$$

It is often assumed that the crystalline potential is simply a superposition of free-atom or free-ion potentials

$$u(\vec{x};R) = \sum_{\vec{R}_p} V_{atom}(\vec{x}-\vec{R}_p) \ , \qquad \text{(VI.3.11)}$$

and furthermore, it is often assumed as well that the derivatives of the crystalline potential with respect to the nuclear coordinates is given by

$$\frac{d}{dR_{m,i}}\Big(u(\vec{x};R)\Big) = -\vec{\nabla}_i\, V_{atom}(\vec{x}-\vec{R}_m) \ . \qquad \text{(VI.3.12)}$$

This is the Rigid-Ion Model [37, 38]. This model has been widely used albeit with no justification beyond the ad hoc assumption given by equation (VI.3.12).

The discussion of this Chapter has established that the Rigid-Ion assumption, (VI.3.12), is incorrect, and that even if the crystalline potential were accurately represented by (VI.3.11), the derivative with respect to the nuclear coordinate $R_{m,i}$ would be

$$\frac{d}{dR_{m,i}}\Big(u(\vec{x};R)\Big) \neq -\vec{\nabla}_i\, u(\vec{x}-\vec{R}_m)$$

$$= -\vec{\nabla}_i\, u(\vec{x}-\vec{R}_m) + \vec{\nabla}_i\, v_e(\vec{x}-\vec{R}_m;\text{P.-W.}) \ , \qquad \text{(VI.3.13)}$$

as derived in Section VI.1.

There are additional advantages to using the "double-derivative" terms as developed from the A.P.W. eigenfunctions. In Chapters IV and V it was shown that the derivative of the electronic eigenfunctions were given by

$$\frac{d}{dR_{m,i}}\left(\psi_{\vec{k}}(\vec{x}_k;R)\right) = \sqrt{\frac{1}{A(k)}}\sum_{j} a^{\varepsilon(k)}(\vec{k}+\vec{K}_j) \times$$

$$\times \frac{e^{i\vec{k}\cdot\vec{R}_m}}{\sqrt{N}}\left((\vec{k}+\vec{K}_j)_i\, \varphi_{\vec{k}+\vec{K}_j}(\vec{x}-\vec{R}_m) - \vec{\nabla}_i\, \varphi_{\vec{k}+\vec{K}_j}(\vec{x}-\vec{R}_m)\right) , \tag{VI.3.14}$$

neglecting additional corrections which are of the order of (1/N)-times smaller than these above. However, if the matrix elements using the <u>correct</u> derivative of the crystalline potential is calculated,

$$\frac{d}{dR_{m,i}}\left(u(\vec{x};R)\right) = \lim_{\delta R_{m,i}\to 0}\left(u(\vec{x};R^{o}+\delta R_{m,i}) - u(\vec{x};R^{o})\right)\Big/\delta R_{m,i} , \tag{VI.3.15}$$

when developing the correct potential for the deformed lattice,

$$u(\vec{x};R+\delta R_{m,i}) , \tag{VI.3.16}$$

all of these small corrections must be included. This is because the potential involves the sum over all N electronic eigenstates of terms representing the potential due to to each an electron in a deformed-lattice eigenstate,

$$v_e(\vec{x};R+\delta R_{m,i}) = \sum_{k=0}^{k_F}\left\{\int |\psi^*_{\vec{k}}(\vec{x}';R+\delta R_{m,i})|^2 \frac{1}{|\vec{x}-\vec{x}'|}d\vec{x}'\right\} + $$

$$- \frac{3}{2\pi^2}\left\{3\pi^2 \sum_{k=0}^{k_F} |\psi_{\vec{k}}(\vec{x};R+\delta R_{m,i})|^2\right\}^{1/3} . \tag{VI.3.17}$$

In short, the matrix elements which obtain directly from the "double-derivative" terms involve single terms while those which obtain from the variations of the crystalline potential involves series of N such terms for which the cumulative effects of small corrections are not necessarily negligeable. Therefore to calculate the electron-phonon interaction matrix elements using equation (VI.3.1) is formidable more difficult than to use the derivatives of the one-electron eigenstates directly.

APPENDIX

EXPERIMENTAL OBSERVATION OF THE ELECTRON-PHONON INTERACTIONS

Although the electron-phonon interaction dominate all of the transport theory of metals, and are of crucial importance for many other phenomena, there exists no direct way to observe or to measure experimentally the electron-phonon interaction matrix elements,

$$D(\vec{k},\vec{q},\epsilon) \quad ,$$

the derivation of which has been the entirety of this analysis. Every experimental observation of phenomena related to the electron-phonon interactions involves a complicated average of these transition matrix elements over either part of or the whole of the Fermi surface.

One property of metals which is related directly to the electron-phonon interactions is the electrical resistivity. The temperature-dependent part of the electrical resistivity of pure metals is caused by the scattering of electrons by thermally excited phonons. The derivation of the formulae for the electrical resistivity for the various ranges of temperatures is extremely complicated. It involves assumptions concerning the validity of a Boltzmann type distribution function, and some (usually clumsy) approximate solution to a Boltzmann transport equation.

The derivation of the formula for the high-temperature resistivity of pure metals will not be repeated here because such is not the subject of this analysis. The derivation performed by H. Jones in Volume XIX of the Encyclopedia of Physics gives [11].

$$\rho_L = \frac{1}{\sigma} = 4.776 \times 10^{-2} \left(\frac{T}{M_A \, \Theta_D^2 \, \Omega^{1/3}} \right) \left(\frac{C}{\epsilon_F} \right)^2 \qquad (A.1)$$

for the high-temperature resistivity, where M_A is the atomic weight, Θ_D the Debye temperature and Ω the atomic volume in cubic Angstroms. The resistivity is then given in practical units, ohms-cm. The constant C is the average of

$$\hat{e}(\delta\vec{R}) \cdot \int \psi^*_{\vec{k}'}(\vec{x}) \frac{d\vec{u}(\vec{x};R)}{dR} \psi_k(\vec{x}) \, d\vec{x} \qquad (A.2)$$

taken over the entirety of the Fermi surface.

For Lithium, the conductivity at 300°K is $\sigma^{-1} = 4.44 \times 10^{-8}$ ohm-cm., [39] , $M_A = 6.94$, $\Omega^{1/3} = 2.775 \text{Å}$, $\Theta_D = 430^\circ K$ [40] . Substituted into equation (A.1), these require that the ratio C/ϵ_F be

$$\frac{C}{\epsilon_F} = 0.105 \ . \qquad (A.3)$$

To perform the integral in (A.2) a number of additional approximations to the potential and the wave functions of Lithium have been admitted. First, the eigenfunctions for the states on the Fermi surface are approximated by the tight-binding component plus the single plane-wave in the first Brillouin Zone which designates that state. This approximation was motivated by an examination of the variational coefficients for the eigenfunctions in three special directions near the Fermi surface: $\Delta(0,5/4,0)$, $\Sigma(3/4,3/4,0)$, $\Lambda(3/4,3/4,3/4)$. At each of these points, an inversion of the A.P.W. secular determinant at the value of the energy for which the determinant vanished demonstrated that the variational coefficient which multiplied the component

$$\psi_{\vec{k}}^{\epsilon_F}(\vec{x}) \;,$$

was of the magnitude 0.95 to 0.99:

$$a^{\epsilon_F}(\vec{k}_F) \simeq 0.95 - 0.99 \;; \qquad \text{(A.4)}$$

while the next and other variational coefficients, were no larger than a few percent and diminished rapidly with the magnitude of $\vec{K}$,

$$a^{\epsilon_F}(\vec{k}_F + \vec{K}_i) \le 0.05 \;. \qquad \text{(A.5)}$$

Second, the Fermi surface was assumed to be spherical. In fact the Fermi surface for Lithium is slightly aspherical; however, the greatest difference which is between the lengths of the wave vectors or the Fermi surface in the Δ, (0,1,0) and Σ, (1,1,0) directions is only on the order of 4%. The magnitude of the k-vector for the Fermi surface was taken to be the weighted average of the magnitudes of k_F in the three special directions, Δ, Σ, and Λ.

Third, the number of ℓ-wave components to the eigenfunctions were restricted to two: $\ell=0$; $\ell=1$. When performing the A.P.W. variational calculation for the band energies, thirteen values of ℓ were used: $\ell=0$ to $\ell=12$. However, when the A.P.W. eigenfunctions belonging to the Fermi energy were integrated out and normalized, the relative magnitudes of the ℓ-th components for the eigenfunctions approximated by the tight-binding component plus a single plane-wave were given by the following coefficients.

$$\begin{array}{lll} \ell=0 & & 0.65537 \\ \ell=1 & & 0.31018 \\ \ell=2 & & 0.03234 \\ \left.\begin{array}{c}\ell=3\\ \text{to}\\ \ell=12\end{array}\right\} & < & 0.001\ . \end{array} \tag{A.6}$$

The relative size of these components is shown graphically in Figure 67

Fourth, the approximation of the eigenfunction by a function involving a single plane-wave in the regions between the A.P.W. spheres and the cell boundaries greatly simplifies the calculation of the variation of the crystalline potential,

$$\frac{du}{dR}(\vec{x};R)\ . \tag{A.7}$$

In Chapter VI it was shown that the differences between this derivative and the simple gradient of the potential,

$$-\vec{\nabla}_x u(\vec{x};R) \quad , \tag{A.8}$$

arose from the rigidity of the plane-wave charge density,

$$\rho_e(\vec{x};R;P.-W.) \quad . \tag{A.9}$$

It was shown that the potential for the deformed lattice is generated by an altered charge density where the variation of the charge density are given by

$$\frac{d}{dR_i}\Big(\rho_e(\vec{x};R)\Big) = -\vec{\nabla}_i\Big(\rho_e(\vec{x};R)\Big) + \vec{\nabla}_i\Big(\rho_e(\vec{x};R;P.-W.)\Big) \quad . \tag{A.10}$$

However, from the definition of the plane-wave charge density (VI. 2.14) it is clear that the plane-wave charge density for a crystal whose eigenfunctions require only a single plane-wave is a constant, and in such case the second correcting term on the right hand side of equation (A.10) vanishes. Therefore, in this case we are justified in approximating

$$\frac{d}{dR_i}\Big(u(\vec{x};R)\Big) \cong -\vec{\nabla}_i\Big(u(\vec{x};R)\Big) \quad . \tag{A.11}$$

The calculations for the transition matrix elements of Lithium used the results of the energy band and Fermi surface calculations on Lithium which have been reported previously the Quarterly Progress Report No. 53 of The Solid State and Molecular Theory Group [41] . The potential used to calculate the gradient which enters the transition matrix elements is tabulated in that article. For the calculation of the eigenfunctions on the Fermi surface, a modification of the program developed by the Rudge and reported in No. 59 the Quarterly Progress Reports [42] was used. A further program was written which integrated out and normalized the A.P.W. eigenfunctions, which calculated and stored the gradient of the muffin-tin potential, and which numerically integrated out the matrix elements (A.2).

The calculated value of the constant C is

$$C = 0.03669 \text{ ryd.} \tag{A.12}$$

in A.P.W. units, Rydbergs. The value of the Fermi energy was calculated previously as

$$\epsilon_F = 0.2989 \text{ ryd.} \tag{A.13}$$

Together these give a ratio of

$$\frac{C}{\epsilon_F} = 0.1223 \ . \tag{A.14}$$

Comparing these results, (A.3) and (A.14) renders

	measured	calculated
$\frac{C}{\epsilon_F}$	0.105	0.122

(A.15)

The calculated value of the ratio is observed to be on the order of 18%. This error is considerably greater than that introduced by any (or all) of the various approximations:

i.) the single-plane wave eigenfunction;

ii.) the restriction of the eigenfunction to the $\ell=0$ and $\ell=1$ components;

iii.) the use of the simple gradient for the variation of the potential.

The probable source of the largest portion of this error is the inaccuracies in the potential used. As was emphasized in earlier chapters, the proper potential which must be used is that one generated by its own eigenfunctions (together with the nuclear potential), i.e., the self-consistent potential. For the calculations on Lithium the potential used was simply the spherical portion of the superposed atomic potentials

$$u(\vec{x};R) \simeq \sum_{\vec{R}_p} V_{\text{atomic}}(\vec{x}-\vec{R}_p) \quad . \tag{A.16}$$

This potential probably manifests a larger gradient over much of the cell than would the correct self-consistent potential, and such may well be the major source of error in (A.15).

ACKNOWLEDGMENTS

The author acknowledges the supervision and assistance of Professor George F. Koster during the two years in which this dissertation was written.

Credit and thanks go also to W. E. Rudge for use of his programs for calculating the A. P. W. crystalline eigenfunctions.

The numerical calculations were performed on the M.I.T. Computation Center's I. B. M. 7094 digital computor.

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Biographical Note

The author was born in 1934 in California. He holds a Batchelor's degree from the University of California at Berkeley and one of Master of Science from the Massachusetts Institute of Technology.

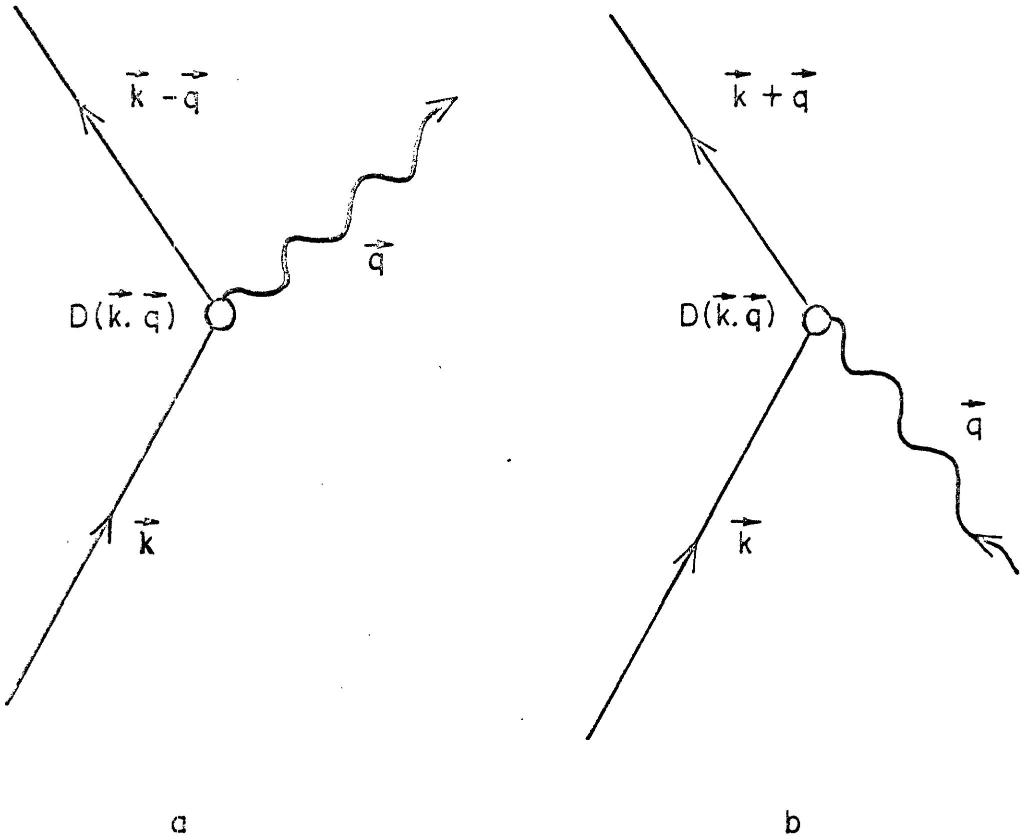
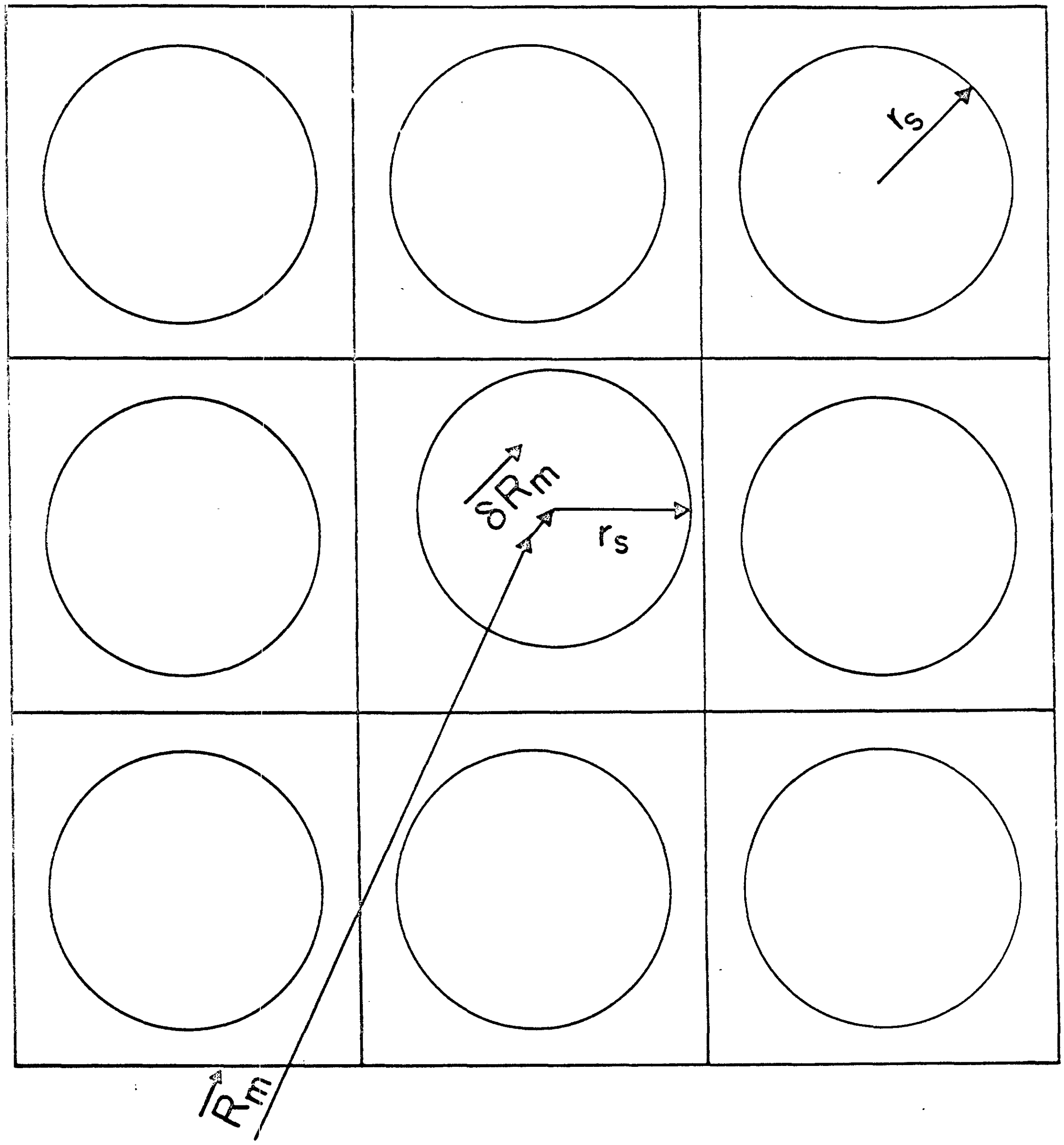
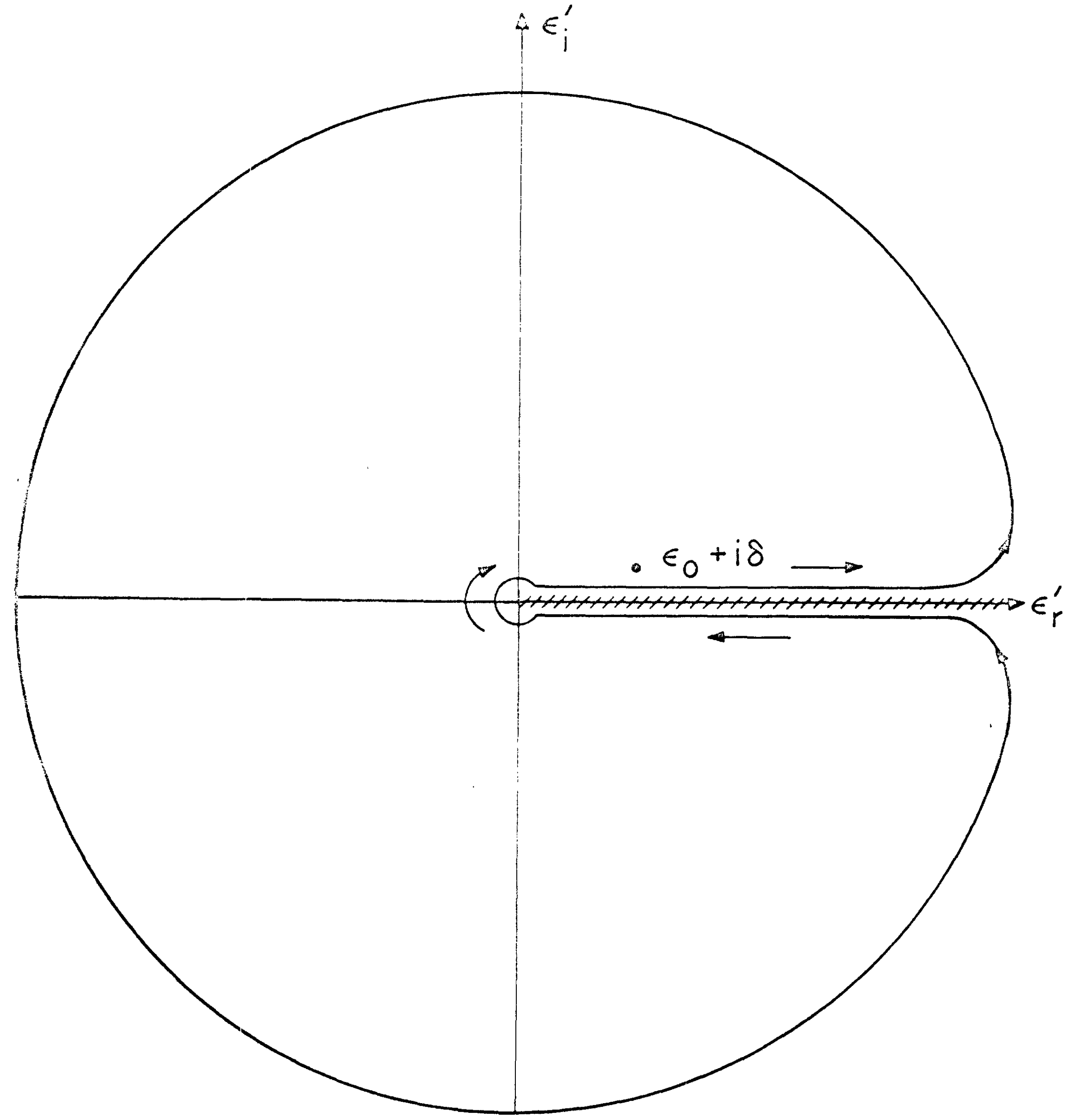


Figure 1 The Fundamental Processes Involving Electrons & Phonons : Emission (a) & Absorption (b) Determined by the Vertex Function $D(\vec{k}_1\vec{q})$



Schematic Representation of the Deformed Muffin-tin Lattice Where the $\vec{R}_m$-th Nucleus is Translated to $\overrightarrow{R_m} + \overrightarrow{\delta R_m}$.



Contour Used for Integrating out

$$\frac{g(\epsilon')\left(\xi(\epsilon',\epsilon_0)\right)^2 e^{-\mu|\epsilon'|}}{(\epsilon'-\epsilon_0+i\delta)}$$

and

$$\frac{g(\epsilon')\left(D(\epsilon',\epsilon_0)\right)^2}{\left((\epsilon'-\epsilon_0+i\delta)^2-\omega_q^2\right)}$$

in the Complex Energy Plane.

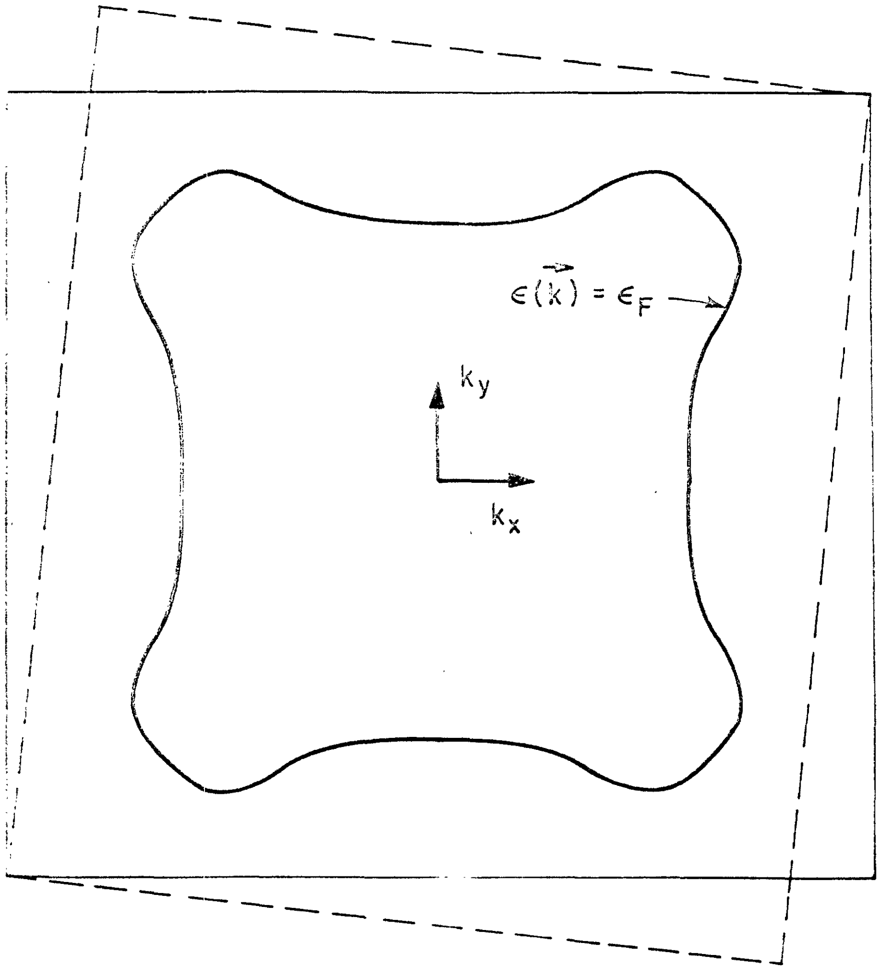


Figure 4 Schematic Representation of the Invariance of a Fermi Surface which does not intersect the Brillomin Zone Boundaries under a Lattice Deformation

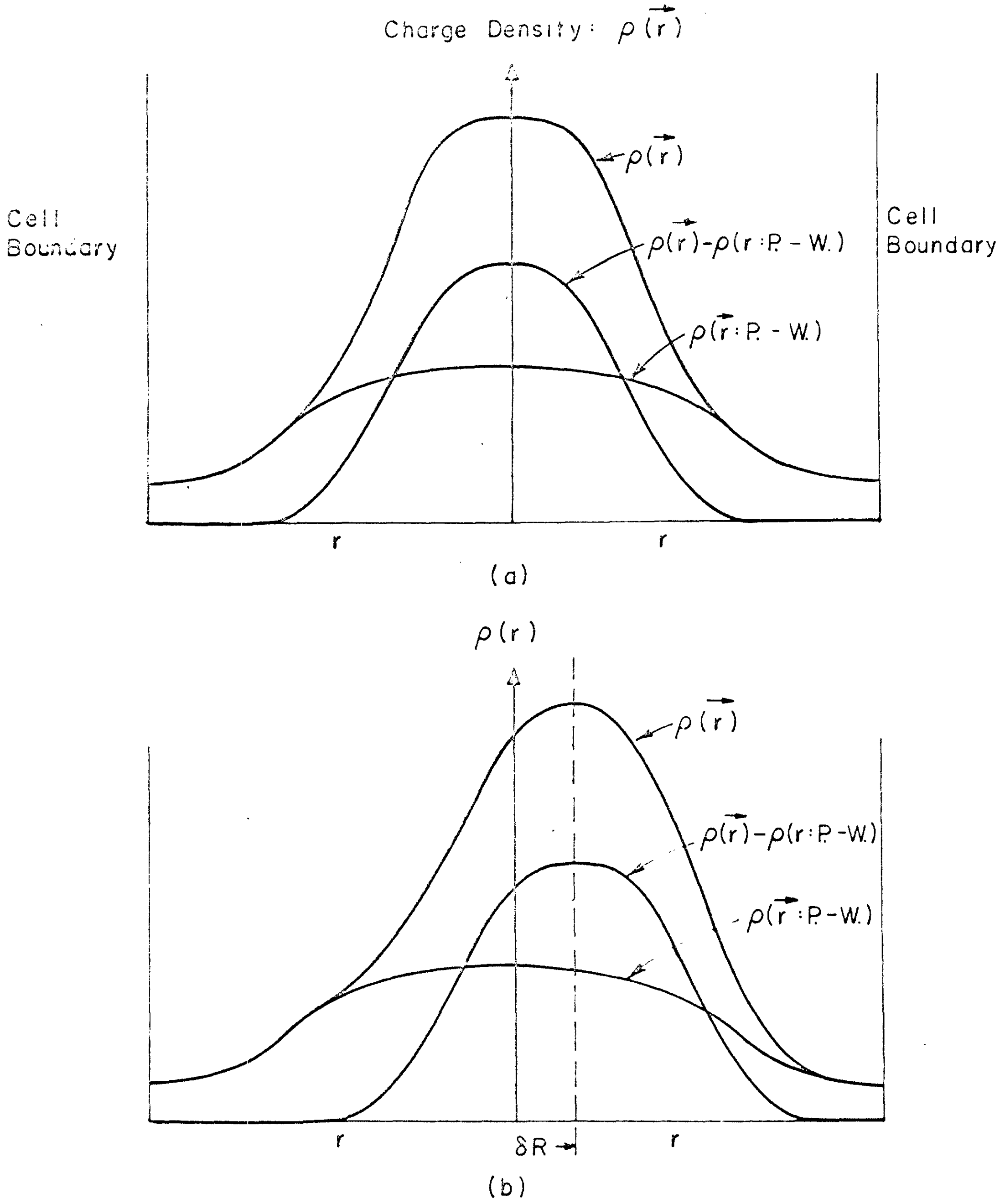
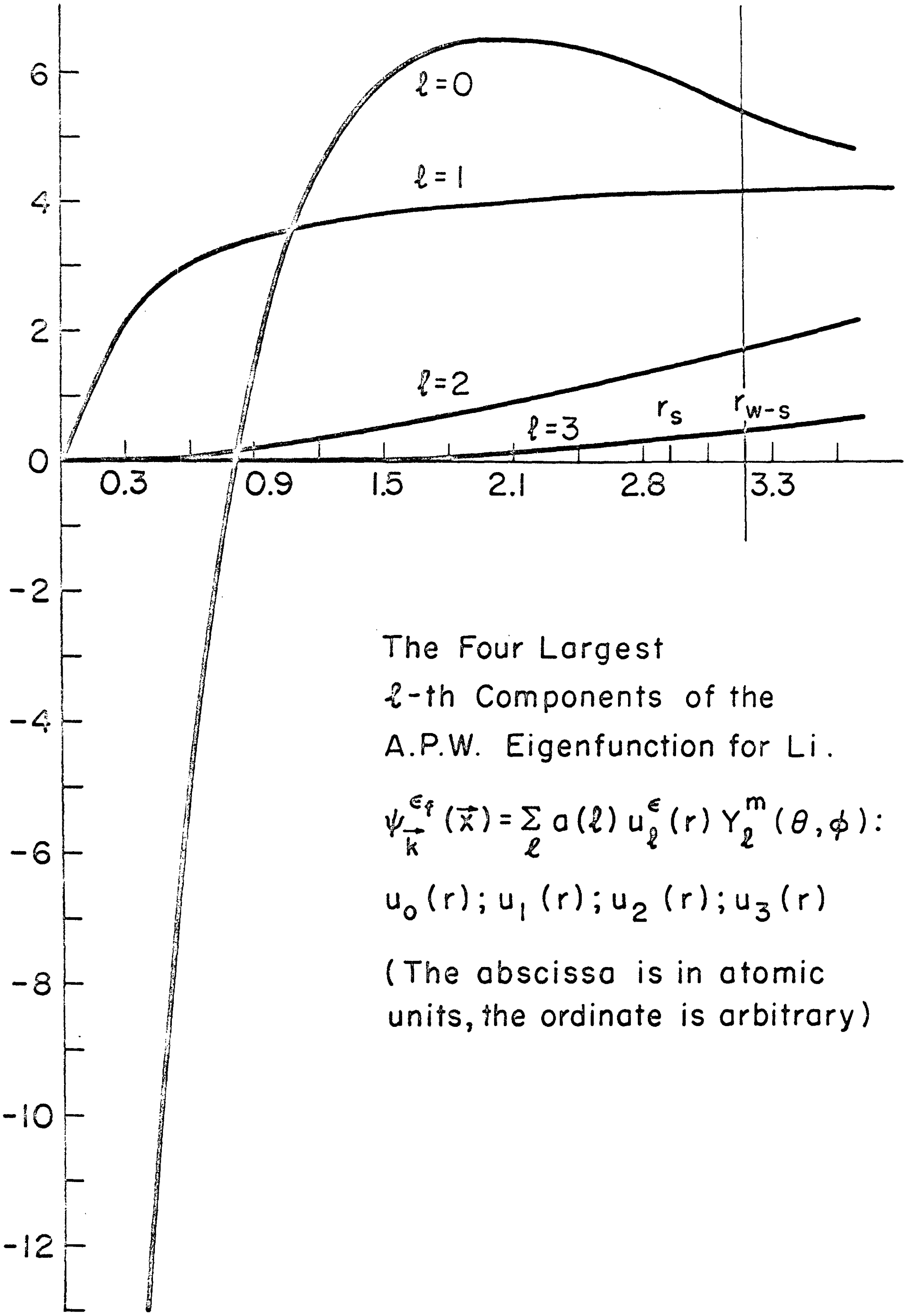


Figure 5 Electronic Charge Densities in the Perfect & Deformed Lattices



The Four Largest ℓ-th Components of the A.P.W. Eigenfunction for Li.

$\psi_{\vec{k}}^{\epsilon_f}(\vec{x}) = \sum_{\ell} a(\ell)\, u_{\ell}^{\epsilon}(r)\, Y_{\ell}^{m}(\theta,\phi)$:

$u_0(r); u_1(r); u_2(r); u_3(r)$

(The abscissa is in atomic units, the ordinate is arbitrary)