

ATOMICITY AND THE SCREENING MECHANISM IN SUPERCONDUCTORS

SOME EFFECTS OF THE ATOMICITY OF A METAL
ON ITS
DIELECTRIC RESPONSE AND ITS SUPERCONDUCTING STATE

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A Thesis
Submitted to the Faculty of Graduate Studies
in Partial Fulfilment of the Requirements
for the Degree
Doctor of Philosophy

McMaster University

May 1968

DOCTOR OF PHILOSOPHY (1968)
(Physics)

McMASTER UNIVERSITY
Hamilton, Ontario

TITLE: Some effects of the atomicity of a metal on its dielectric response and its superconducting state.

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NUMBER OF PAGES: v, 87

SCOPE AND CONTENTS: Although the electronic pairing hypothesis of Bardeen, Cooper and Schrieffer is verified by experiment, the lattice polarisation mechanism for over-screening the repulsion between mates in a pair need not be the sole mechanism.

Alternatives to the lattice polarisation mechanism are discussed and a new approach to electronic polarisation is developed. Propagator formalism is reworked using a charge density propagator to avoid the Dyson equation for the screened potential. The fermi liquid approach to electrons in a metal is avoided, too, because it misses the correlations which give a solid its atomicity. An atomic picture is contrived instead and used to predict what observable features of a superconductor are influenced by atomic correlations.

ACKNOWLEDGEMENTS

I am grateful for the guidance given to me by my supervisors and for the patience and efficiency of Mrs. J. McEwen in typing from a difficult manuscript. The thesis is dedicated to Dr. W. D. Twose who died unexpectedly while I was under his supervision.

PREFACE

"Those who have handled sciences have been either men of experiment or men of dogmas. The men of experiment are like the ant; they only collect and use: the reasoners resemble spiders, who make cobwebs out of their own substance. But the bee takes a middle course, it gathers its material from the flowers of the garden and of the field, but transforms and digests it by a power of its own. Not unlike this is the true business of philosophy; for it neither relies solely or chiefly on the powers of the mind, nor does it take the matter which it gathers from natural history and mechanical experiments and lay it up in the memory as a whole, as it finds it; but lays it up in the understanding altered and digested."

Francis Bacon

Aphorism XCV, *Novum Organum*, 1620

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CHAPTER I

INTRODUCTION

One of the great difficulties of the Bardeen-Cooper-Schrieffer (BCS 57) approach to superconductivity by the pairing hypothesis was to understand why two electrons, which would repel each other in vacuo, are correlated in their motion in a superconducting solid.

Cooper provided the first clue by showing that a pair of electrons excluded from low momentum states by a quiescent fermi sea are unstable against pair formation if there is the slightest trace of attraction between them. The clue to what might cause an attraction, as it turned out, had been given by Fröhlich (F 50) who suggested that overscreening of the electronic charges by the charge density oscillations associated with lattice vibrations could lead to an effective attraction between pairs of electrons.

Now, there is a large body of experimental evidence supporting the pairing hypothesis. This is discussed in standard texts (S 64, R 65). The most dramatic is the phenomenon of two-particle or Josephson tunnelling for which the quantitative agreement with the pairing theory is

more precise than our knowledge of the fundamental constants e and $\hbar$ (L 67).

Measurements of the one particle tunnelling current across a metal-insulator-superconductor have been used to confirm the mechanism of pairing in simple metals (SSW 63); and the remaining question concerns the universality of Fröhlich's mechanism. Many alternative mechanisms have been proposed, but few experiments have been made to test these proposals. In what follows, we give a generalized theory of screening in which the total charge density oscillations screen pair interactions. The coordinates for charge density oscillations need not be purely those for lattice vibrations, and we suggest that one particle tunnelling experiments might be used to examine the mechanism of screening. We do not propose to challenge the pairing hypothesis: we use it, and regard tunnelling as a probe of the low frequency dielectric properties of a metal.

Before arguing a new approach to the pairing mechanism, it is helpful to examine the published literature on other mechanisms, with a view to deciding which provides the most serious challenge to the universality of the Fröhlich mechanism.

CHAPTER II

EXPERIMENTAL APPROACHES TO SCREENING MECHANISMS

The case against the universality of Fröhlich's mechanism is supported by an ipse dixit: "...The situation in metals with incomplete inner shells is radically different. These shells can not be treated as polarizable centres...." (F 66). He is reviewing the scattering of conduction electrons in metals, and has invoked shell closure theorems (CS 35) to justify absorbing the scattering of conduction electrons from closed shells of core electrons into the electron-phonon scattering.

In transition metals, there is a group of one-electron states which does not fit into the core-valence scheme. The tight-binding picture of these states breaks down because core states on different sites overlap. On the other hand, the modified plane wave calculations (D 66, Hu 67) break down because the self-consistent crystalline potential is strong enough to bind an electron in the vicinity of a single site. The open shell effects for such bound states allow small perturbations to excite an electron to a nearby bound state, a process which amounts to deformation of the charge cloud associated with a nuclear site.

The influence of 'transition electrons' on the physical properties of metals is discussed in any magnetism

text. Briefly, there is an approach to magnetic properties based on the assumption that transition metals contain well-localized transition electrons; and a second approach is based on the assumption that transition electrons form an electron fluid with fermi surface obtained from a modified plane wave calculation. Both approaches are limited in scope, but recent work by Hubbard (Hu 63) shows signs of reconciling the two approaches, putting atomic correlations in the fluid.

Eventually, we shall attempt to describe the effects of deformation processes hinted at by Fröhlich in Hubbard's terms, but some experimental evidence must support such a venture. The evidence is of three types:

- (i) observation of the isotope effect on transition temperatures;
- (ii) observation of the relation between transition temperature and the density of one-particle states at the Fermi surface;
- (iii) measurement of the one electron tunnelling current for a metal-insulator-superconductor junction.

First, BCS theory predicts that the transition temperature, T_c , should depend on the average isotopic mass M according to

$$T_c \propto M^{-\alpha}, \quad \alpha_{\text{BCS}} = 1/2 \quad 2.1.$$

Nambu's strong coupling theory with a rigid ion approxima-

tion also suggests an α close to 0.5 (S 64). Experimentally α varies between zero and one half; the system of variation is discussed by Garland (Ga 63). His theoretical explanation for $\alpha \neq 1/2$ is an elaboration of Fröhlich's mechanism: phonons are allowed to scatter electrons between a conduction electron fluid and a transition electron fluid. A similar approach was also made by Kondo (K 62). Two criticisms of their approaches are possible: the first, that the electron fluid picture of transition electrons is of questionable validity; the second, that decreases in α can be produced directly by accounting for processes which do not involve nuclear motion. Indeed, we shall argue that transition electron polarization effects, whether produced by phonon or coulomb scattering, are most likely to give $\alpha \neq 1/2$.

The second set of experimental data is given by Coles (C 64). He notes that the electronic specific heat and the BCS estimate of T_c for an electron fluid increase monotonically with the density of one-electron states at the fermi surface. He shows that in a transition metal series, these two quantities are very poorly correlated towards the end of the series: the electron fluid model does not fit T_c occurrence data.

The third and most germane piece of evidence was obtained by Clark (Cl 67) and Wyatt (Wy 65). Both workers used the theory of the frequency dependence of the super-

conducting gap as developed by Schrieffer, Scalapino and Wilkins (SSW 63). Besides the structure which could be traced to rigid ion phonons, Clark working on thallium and Wyatt working on tantalum noticed structure at frequencies where the simple theory predicted none. In thallium (incomplete p-shell), structure in $\Delta(\omega)$ is most marked around $\hbar\omega \sim 100$ meV, $\hbar\omega \sim 50$ meV and $\hbar\omega \sim 10$ meV. The lowest frequency structure does not disagree with the simple theory; the highest frequency structure has been identified with vibrational and rotational frequencies of interstitial impurity molecules; the structure at intermediate frequencies has not yet been identified, but may be a manifestation of polarisation of the p-shell. In tantalum (incomplete d-shell), the usual phonon structure is observed, but between two frequencies at which phonon structure occurs there is structure which may originate in the normal mode frequencies of d-shell polarisation effects.

We later estimate that this structure should occur at frequencies of the order of fine structure splitting for an incomplete shell, which is in agreement with the fact that the thallium structure occurs at higher frequencies than the tantalum structure. More experimental evidence of the Clark-Wyatt type for transition metal and rare earth superconductors would greatly illuminate the detailed nature of the screening mechanism in these perplexing metals.

CHAPTER III

RECENT THEORIES OF THE SCREENING MECHANISM

Mechanisms for screening the coulomb repulsion between pairs of electrons in a metal have attracted attention for two main reasons. The one is concerned with whether or not fermi liquids are normal or superfluid at very low temperatures; the other concerns the search for high temperature metallic superconductors.

Kohn and Luttinger (KL 65, Lu 66) have examined a mechanism which bears on the question of superfluidity of He-3, nuclear matter and metallic conduction electrons. The objections to their mechanism argued below refer only to the case of electrons. The physical process involved in the Kohn-Luttinger approximation is screening of two-particle interactions by collective particle density effects. In their approximation, there is a discontinuity in the derivative of screened potential with respect to momentum transfer, q . The same type of screening discontinuity is thought to be responsible for the Friedel oscillations of charge density around a screened impurity in a metal (LV 59). The discontinuity also plays a key rôle in the theory of the Kohn effect observed in

the phonon dispersion curves of some metals (WK 62). Using an electron fluid picture with fermi surface adjusted to resemble that found by modified plane wave calculations, Luttinger has investigated what shape of fermi surface gives the highest superconducting transition temperature without phonon effects. His greatest estimate is at least an order of magnitude below observed values of T_c in typical superconductors not showing a perfect isotope effect, $\alpha \neq 1/2$. Also, the theory seems to favour pairing in high angular momentum states, and the main body of experimental evidence for the pairing theory is based on the assumption of singlet s-pairing (S 64).

The question of the possible existence of high temperature metallic superconductors was raised by Geleikman (G 65, 66). He is concerned with a two-fluid model of the electrons in which the repulsion between pairs of electrons in one fluid is screened by charge density oscillations of the other fluid. Geleikman's first attempt to estimate the effect of transition electron polarisation on the two-conduction electron vertex neglected the direct coulomb repulsion between conduction electrons. As might be expected, he overestimated the pairing effect, obtaining $T \sim 300^\circ K$ in contrast to the greatest empirical value $\sim 18^\circ K$ (niobium-tin).

In his second approach to the two-fluid model, he used model wavefunctions to estimate matrix elements

of the coulomb repulsion between conduction and transition electrons. For conduction electrons he used plane waves, for transition electrons, tight-binding wavefunctions made up of spherically averaged atomic d-states. His theory of the two-particle vertex is an approximation to two-band, random-phase-approximation screening. An attempt was made to apply Geleikman's method to niobium, with the following results:

- (i) the electronic density of states for the conduction electrons and transition electrons is required to avoid instabilities against depletion of one band at the expense of the other;
- (ii) when the tight-binding approach is used to estimate the transition density of states, the atomic d-functions for Nb extend to the fifth ring of neighbours in the b.c.c. lattice -- Geleikman's no overlap approximation is quite unjustified.

An attempt to patch up the tight-binding picture by an LCAO approach, mixing d-functions from rings of neighbouring sites into the central d-function, rapidly became a sterile exercise in machine computation, much too lengthy to be completed in view of the questionable physical assumptions inherent in the two-fluid model. However, the investigation of overlap effects in the one-particle LCAO theory of Löwdin (Lö 58) suggested a way of solving overlap problems in the theory of the atomic representation developed in Chapter V. The strongest

conclusion to be drawn from Geleikman's approach seems to be qualitative: that electronic polarization processes are likely to enhance pairing.

The mechanism of screening by polarization of impurities is supported by the experiment of Clark (op. cit. Chapter II). Occurrence data for alloy superconductors also show (M 65) that the addition of non-metallic interstitials to some alloys increases T_c . Three broad classes of impurity processes can be considered:

- (i) excitation of vibrations of a rigid ion impurity;
- (ii) excitation of rotational or vibrational modes of a multinuclear impurity molecule;
- (iii) deformation of incomplete shells of electrons centred at an impurity site.

The first class of process can be quickly absorbed into the rigid ion Fröhlich mechanism by replacing the pure crystal phonon propagators by those for the impure crystal and changing the electron-phonon coupling constants a little. Some work on these lines has been performed by Appel (A 67). Less obviously, the same approach could be used for the second class of process: Ludwig has shown how arbitrary molecular modes affect the phonon density of states in imperfect crystals (L 64).

The third class of process involves both pair forming and pair breaking mechanisms. The former mechanism is an electric transition of the impurity centre, which

couples it to the charge density of the pure crystal electrons; the latter mechanism is a magnetic transition of the impurity centre, which couples it to the pure crystal electronic spin density. The balance between these two mechanisms is an important aspect of the theory of type II superconductors, outside the scope of this thesis.

CHAPTER IV

THE THEORY OF DIELECTRIC RESPONSE

The notation of Baym and Kadanoff (BK 62) is convenient for describing a theory of screening first sketched by Martin and Schwinger (MS 59). The following list of definitions is sufficient to establish units and conventions of sign and phase:

the Hamiltonian for electrons,

$$\hat{H} \equiv \int d^3x \Psi^\dagger(\underline{x}) \left(-\frac{\hbar^2}{2m} \nabla^2 + U_{BG}(\underline{x}) \right) \Psi(\underline{x}) + \frac{1}{2} \iint d^3x d^3y V(\underline{x}, \underline{y}) \Psi^\dagger(\underline{x}) \Psi^\dagger(\underline{y}) \Psi(\underline{y}) \Psi(\underline{x}) \quad 4.1a;$$

average over the grand canonical ensemble,

$$\langle A \rangle \equiv \frac{\text{Trace}[e^{-\beta(\hat{H}-\mu N)} A]}{\text{Trace}[e^{-\beta(\hat{H}-\mu N)}]} \quad 4.1b;$$

Heisenberg field operators on Fock space H of Appendix 2,

$$\begin{aligned} \Psi(1) &= \Psi(\underline{x}_1 t_1) \equiv e^{-\frac{i}{\hbar}(\hat{H}-\mu N)t_1} \Psi(\underline{x}_1) e^{\frac{i}{\hbar}(\hat{H}-\mu N)t_1} \\ \Psi^\dagger(2) &= \Psi^\dagger(\underline{x}_2 t_2) \equiv e^{-\frac{i}{\hbar}(\hat{H}-\mu N)t_2} \Psi^\dagger(\underline{x}_2) e^{\frac{i}{\hbar}(\hat{H}-\mu N)t_2} \end{aligned} \quad 4.1c;$$

the compact notation for integration and spin sum,

$$\begin{aligned}
& \int f(\bar{1}, \bar{2}, \bar{3}, \dots, \bar{n}, p, \dots) g(\bar{1}, \bar{2}, \bar{3}, \dots, \bar{n}, q, \dots) \\
& \equiv \int_{\Omega} d^3x_1 \int_{-\infty}^{+\infty} dt_1 \int_{\Omega} d^3x_2 \int_{-\infty}^{+\infty} dt_2 \dots \int_{\Omega} d^3x_n \int_{-\infty}^{+\infty} dt_n \sum_{\sigma_1 \dots \sigma_n} \\
& f(x_1 t_1, \dots, x_n t_n, x_p t_p \dots) g(x_1 t_1, \dots, x_n t_n, x_q t_q \dots)
\end{aligned}$$

where x refers to position and spin $(\underline{x}, \sigma)$ 4.1d;

the one-particle propagator,

$$G_1(1, 1') \equiv \frac{1}{i} \langle T[\Psi(1) \Psi^\dagger(1')] \rangle \quad 4.1e;$$

the n -particle propagator for $n \geq 2$,

$$\begin{aligned}
G_n(1, 2, \dots, n; 1', 2', \dots, n') & \equiv \left(\frac{1}{i}\right)^n \langle T[\Psi(1) \Psi(2) \dots \Psi(n) \\
& \Psi^\dagger(1') \dots \Psi^\dagger(n')] \rangle \quad 4.1f.
\end{aligned}$$

In the Hamiltonian, $V(1, 2) \equiv \delta(t_1 - t_2) \frac{e^2}{|\underline{x}_1 - \underline{x}_2|}$ is the coulomb repulsion between electrons, U_{BG} is the background potential of charged nuclei. In the grand canonical average β is $(kT)^{-1}$, the inverse of Boltzmann's constant times absolute temperature; and μ is the chemical potential. In the propagators, $T[]$ is the time ordering operation.

The equations of motion for the propagators are

$$\begin{aligned}
\left[\frac{\hbar}{i} \frac{\partial}{\partial t_1} - \frac{\hbar^2}{2m} \nabla_1^2 - \mu + U_{BG}(\underline{x}_1) \right] G_1(1, 1') & = \delta(1 - 1') \\
& - \frac{1}{i} \int V(1, \bar{2}) G_2(1, \bar{2}; 1', \bar{2}^+) \quad 4.2a,
\end{aligned}$$

$$\left[\frac{\hbar}{i} \frac{\partial}{\partial t_1} - \frac{\hbar^2}{2m} \nabla_1^2 - \mu + U_{BG}(\underline{x}_1) \right] G_n(1, 2, \dots, n; 1', 2', \dots, n')$$

$$\begin{aligned}
&= \sum_{m=2}^n [(-1)^{m+1} \delta(1-m') G_{n-1}(2, 3, \dots, n; 1', 2', \\
&\quad \dots (m-1)', (m+1)', \dots, n')] \\
&- \frac{1}{i} \int v(1, \bar{p}) G_{n+1}(\bar{x}_p t_p, 1, 2, \dots, n; \bar{x}_p t_p + \eta, 1', 2', \dots, n')
\end{aligned}$$

4.2b,

where the limit $\eta \rightarrow 0^+$ is intended and the notation

$$G_2(1, 2; 1', 2^+) \equiv \lim_{\eta \rightarrow 0^+} G_2(1, \underline{x}_2 t_2; 1', \underline{x}_2 t_2 + \eta) \quad 4.2c$$

is used as an abbreviation for the limit.

For a grand canonical ensemble, 4.2 is an infinite chain to which three broad classes of approximation procedure have been applied:

- (i) perturbation theory;
- (ii) truncation procedures;
- (iii) use of generating functionals.

The first method, based on an interaction representation and Wick's theorem is described in standard texts (AGD 63). The second method, subject of a review article by Zubarev (Z 60), involves stopping the chain 4.2 after n links. The $(n+1)$ -particle propagator occurring in the n th link of 4.2 is assumed to be factorizable as a product of propagators with particle number $\leq n$. Whatever factorization is assumed, the first n links of 4.2 define every propagator with particle number $\leq n$ as a functional of one of these, say G_1 . The weakness of this method is that the functional form of propagators depends on the factorization of G_{n+1} .

The third approach to 4.2 borrows much from the second approach, but is based on Schwinger's principle of stationary action (Sch 51) using a variation defined by the addition of fictitious potential

$U \equiv \int u(\bar{n}, \bar{n}';) \Psi^\dagger(\bar{n}') \Psi(\bar{n})$ to the Hamiltonian 4.1. Following Kato, Kaboyashi and Namiki (KKN 61), and Blomberg (B 66) the action functional L,

$$L[u] \equiv \sum_{n=1}^{\infty} \frac{1}{n!} G_n(\bar{1}, \bar{2}, \dots, \bar{n}; \bar{1}', \bar{2}', \dots, \bar{n}') u(\bar{1}, \bar{1}') u(\bar{2}, \bar{2}') \dots u(\bar{n}, \bar{n}') \\ = \frac{\text{Trace}[e^{-\beta(\hat{H}-\mu N)} T e^{-\beta U}]}{\text{Trace}[e^{-\beta(\hat{H}-\mu N)}]} \quad 4.3,$$

subject to $\delta L = 0$ is defined. Clearly knowledge of L would give all the propagators by functional derivation. This generating property of L is shared with generating functional G defined by

$$G(1, 1'; u) \equiv \frac{1}{L} \frac{\delta L}{\delta u(1, 1')} \quad 4.4.$$

Functional G has two other congenial properties:

$$\lim_{u \rightarrow 0} G(1, 1'; u) = G_1(1, 1') \quad 4.5;$$

$$\left[\frac{\hbar}{i} \frac{\partial}{\partial t_1} - \frac{\hbar^2}{2m} \nabla_1^2 - \mu + U_{BG}(\underline{x}_1) \right] G(1, 1'; u) \\ = \delta(1-1') - \int u(1, \bar{2}) G(\bar{2}, 1'; u) \\ - \frac{1}{i} \int v(1, \bar{2}) G_2(1, \bar{2}; 1', \bar{2}^+; u) \quad 4.6a.$$

In 4.6, $G_2(u)$ is the two-particle propagator in the

presence of U ; and therefore this equation can be taken as the equation of motion of G_1 in the presence of U . If some truncation of the Zubarev type is performed on the chain of which 4.6 is the first link, $G_2(u)$ can be expressed as some functional of G . Obviously many functionals $G_2[G]$ can be obtained -- there are lots of possible truncations -- but Kadanoff and Baym (KB 61, B 63) have shown how to impose constraints on the choice of functional. They have found a class of approximations which are called conserving and have the properties:

- (i) the rates of absorption of momentum, angular momentum and energy, obtained by integrating the appropriate density in the perturbed system, are equal to the rates of loss computed directly from the probe potential U ;
- (ii) in the special case of U an electromagnetic potential, the response of the system to U , in linear approximation, is gauge-invariant.

By defining a self-energy functional Σ such that 4.6a can be written

$$\begin{aligned} & \left[\frac{\hbar}{i} \frac{\partial}{\partial t_1} - \frac{\hbar^2}{2m} \nabla_1^2 - \mu + U_{BG}(\underline{x}_1) \right] \delta(1, \bar{2}) G(\bar{2}, 1') \\ & = \delta(1, 1') - \int \Sigma(1, \bar{2}) G(\bar{2}, 1') \end{aligned} \quad 4.6b,$$

the Baym-Kadanoff constraints imply the existence of a closed functional $\Phi[G, V]$ such that

$$\Sigma(1, 1'; u) = \frac{\delta \Phi}{\delta G(1, 1'; u)} \quad 4.7.$$

Similar closed functionals Φ have been obtained within the framework of the perturbation theory (AGD 63) where Φ is related to the Helmholtz free energy F .

The theory of screening follows from a change of variable in 4.6. The motivation for the change springs from an examination of the Hartree self-energy,

$$\Sigma_H(1,1'; u) \equiv \frac{\delta(1,1')}{i} \int V(1,\bar{2}) G(\bar{2},\bar{2}^+) \quad 4.8,$$

equal to the potential at point 1 arising from coulomb interactions with the average charge density of the system in the presence of U . The potential difference, $\Sigma_H(u) - \Sigma_H(o)$, is the change in the above coulomb potential as U is switched on. If the potential U is taken to be local and instantaneous,

$$u(n,n') = \delta(n,n') u(n) \quad 4.9,$$

then the average potential change produced by U at point n is

$$w(n) \equiv u(n) + \Sigma_H(n,n; u) - \Sigma_H(n,n; o) \quad 4.10.$$

The inverse permittivity associated with longitudinal potential w is

$$K(n,n') \equiv \lim_{u \rightarrow 0} \frac{\delta w(n)}{\delta u(n')} = \delta(n,n') + i \int V(n,\bar{2}) \langle T[\rho(\bar{2}) \rho(n')] \rangle \quad 4.11,$$

containing the propagator $\langle T[\rho(\bar{2}) \rho(n)] \rangle$ for charge density fluctuations. The screening of potential V by such fluctuations is conveniently described by the

screened two-electron potential,

$$\begin{aligned} V_S(n, n') &\equiv \int V(n, \bar{2}) K(\bar{2}, n') \\ &= V(n, n') + i \int V(n, \bar{2}) \langle T[\rho(\bar{2}) \rho(\bar{3})] \rangle V(\bar{3}, n') \end{aligned} \quad 4.12.$$

By a change of variables, $(u, V) \rightarrow (w, V_S)$, equation of motion 4.6a can be taken to define all propagators as functionals of V_S and G_1 . As in the theory without change of variable, the functionals depend upon some details of a truncation procedure. Before imposing conservation constraints of the Baym-Kadanoff type, 4.6 is reduced to a system of integral equations derived in Appendix 1.

With the definitions

$$M(n, n'; w) \equiv \frac{1}{i} \int V_S(n, \bar{2}) G(n, \bar{3}; w) \Lambda(\bar{3}, n'; \bar{2}) \quad 4.13a$$

for the modified self energy, the triple vertex defined by

$$\Lambda(n, n'; m) \equiv - \frac{\delta G^{-1}(n, n'; w)}{\delta w(m)} \quad 4.13b$$

and the polarisation part

$$Q(n, n'; w) \equiv i \frac{\delta G(n, n^+; w)}{\delta w(n')} = i \int \Lambda(\bar{2}, \bar{2}'; n) G(n', \bar{2}) G(\bar{2}', n') \quad 4.13c,$$

the equation of motion 4.6 becomes

$$\begin{aligned} \int \left[i \frac{\hbar}{i} \frac{\partial}{\partial t_1} - \frac{\hbar^2}{2m} \nabla_1^2 - \mu + \Sigma_H(1, 1; 0) + U_{BG}(1) + w(1) \right] \delta(1, \bar{2}) G(\bar{2}, 1'; w) \\ = \delta(1, 1') - \int M(1, \bar{2}) G(\bar{2}, 1'; w) \end{aligned} \quad 4.14.$$

Self-energy M defined in 4.13 is an implicit functional of $G(w)$ and V_S because Q is a functional of V_S . The asymptotic relation between Σ and M in Appendix 1 restricts M to a functional which is asymptotically equal to a ϕ -derivable Σ .

The following rules tell what form M must have.

Starting from a functional $\Phi[G,V]$ of the Baym-Kadanoff type:

(i) define $\Psi_0[G,V]$ by shrinking any parts of Φ connected to the remainder by only two V-convolutions to δ -functions;

(ii) if $\Phi[G,V]$ is of order n in G and $\Psi_0[G,V]$ is of order m in G, define $\Psi[G,V] = (n) (m)^{-1} \Psi_0[G,V]$;

(iii) if $M(n,n'; w) = \left. \frac{\delta \Psi[G,V]}{\delta G(n,n'; w)} \right|_{V=V_S}$, then the limit

$\Sigma(n,n'; 0) = +\Sigma_H(n,n'; 0) + \lim_{w \rightarrow 0} M(n,n'; w)$ is a Φ -derivable function.

The Hartree terms of the form

$$\Psi_H(G,V) \propto \int \langle \rho(\bar{1}) \rangle V_S(\bar{1}, \bar{2}) \langle \rho(\bar{2}) \rangle \quad 4.15$$

can be shown to vanish identically by an argument which extends one recorded by Abrikosov et al. (AGD 60). The hinge of the argument is the construction of an electric field $\underline{E}(1)$ associated with the average charge density by

$$\text{div}_1 \underline{E}(1) \propto \langle \rho(1) \rangle \quad 4.16.$$

Then 4.15 can be written

$$\begin{aligned} \Psi_H &\propto \int d1 d2 \text{div}_1 \underline{E}(1) V_S(1,2) \langle \rho(2) \rangle \\ &= \int d1 d2 \langle \rho(1) \rangle V_S(1,2) \text{div}_2 \underline{E}(2) \end{aligned} \quad 4.17.$$

The left-hand side of 4.17 can be transformed to give

$$\begin{aligned} \Psi_H &\propto \int d1 d2 [\text{div}_1 (\underline{E}(1) V_S(1,2) \langle \rho(2) \rangle) \\ &\quad - \underline{E}(1) \cdot \text{grad}_1 V_S(1,2) \langle \rho(2) \rangle] \end{aligned} \quad 4.18,$$

whose first term vanishes by writing it as a surface integral over a surface far outside the region where $\langle \rho \rangle$ is not zero. The second term in 4.18 is the negative of the corresponding term from the right-hand side of 4.17:

$$\begin{aligned}\Psi_H &\propto \int d1 d2 \underline{E}(1) \cdot \text{grad}_1 V_S(1,2) \langle \rho(2) \rangle \\ &= \int d1 d2 \underline{E}(1) \cdot \text{grad}_1 V_S(2,1) \langle \rho(2) \rangle;\end{aligned}$$

Ψ_H vanishes if $\text{grad}_1 V_S(1,2) = -\text{grad}_1 V_S(2,1)$. The proof that this last condition is satisfied uses three relations,

$$T[\rho(n)\rho(n')] = T[\rho(n')\rho(n)] \quad 4.19a,$$

$$V(n,n') = V(n',n) \quad 4.19b,$$

$$\text{and} \quad \text{grad}_1 V(1,n) = -\text{grad}_1 V(n,1) \quad 4.19c.$$

Then,

$$\begin{aligned}\text{grad}_1 V_S(2,1) &= \text{grad}_1 V(2,1) + \int dn dn' V(2,n') \langle T[\rho(n')\rho(n)] \rangle \\ &\quad \text{grad}_1 V(n,1) \\ &= -\text{grad}_1 V(1,2) - \int dn dn' \text{grad}_1 V(1,n) \\ &\quad \langle T[\rho(n)\rho(n')] \rangle V(n',2) \\ &= -\text{grad}_1 V_S(1,2).\end{aligned}$$

CHAPTER V

THE ATOMIC PICTURE

An atomic picture for the theory of correlation in narrow energy bands has been presented by Hubbard (Hu 62). If a is the unit of length for interatomic distances in a crystal, A the atomic number, the transformation $(a, A) \rightarrow (\lambda a, \lambda^3 A)$ is referred to as adiabatic scaling by λ . We wish to argue that as λ increases, the adiabatically scaled crystal resembles more and more a set of regularly-spaced, weakly-interacting ions in various states of charge. This conviction suggests a choice of basis for the configuration space H (Appendix 2): a kinematical postulate. The postulate is expressed in the form of an asymptotic condition: in the limit $\lambda \rightarrow \infty$ of adiabatic scaling, the basis functions $|n, Q\rangle$ of H_n converge to the n -electron eigenstates of a system of n interacting electrons centred on a reference ion in the coulomb potential of all the other bare ions. Usually a bare ion is a nucleus: however, perhaps when dealing with transition electrons, the label "bare ion" may refer to a nucleus surrounded by filled shells of tightly bound electrons which partly neutralize the nuclear charge. The coordinates of the reference ion depend on the choice of zero site for generation of a point lattice by application of the space group operators. The standard choice puts the reference ion on the zero site.

As λ varies in the interval $1 \leq \lambda < \infty$, the magnitude of the coulomb potential from the "bare" ions not on the refer-

ence site changes, but the symmetry of this "crystal field" does not change. By labelling the bases of H_n in crystal field multiplets, the variation of λ changes the spacing of multiplet-eigenvalues on the energy axis and changes the radial parts of n -particle wavefunctions, but the degeneracy and angular transformation properties of each multiplet stay constant. The aim of what follows is to exploit the invariance (with respect to choice of zero site for the lattice) of n -electron eigenstates of a crystal in order to construct these eigenstates from the states centred on a reference ion. The possibility of such a construction is anticipated in Davydov's (Da 62) theory of molecular crystals, and the 'multiplicity waves' of Vonsovskii and Svirskii (VS 65) may be discussed as an example of such crystalline eigenstates. The mathematical problems which arise have been examined by Löwdin et al. (Lö 58) for the special case H_1 , and the chapter leans heavily on these earlier investigations.

Suppressing the scaling parameter λ , the notation $|n, Q) = |n, h\Gamma p)$ for the image $j_n(\phi^{h\Gamma p})$ of an n -particle basis function $\phi^{h\Gamma p}$ is convenient,

$$(x_1, x_2, \dots, x_n | n, h\Gamma p) \equiv (0_0, 0_1, 0_2, \dots, \phi^{h\Gamma p}(x_1, x_2, \dots, x_n), 0_{n+1}, \dots)$$

5.1,

where Γ denotes a crystal field multiplet, p is a state in the multiplet subspace and h is the set of additional quantum numbers of the state.

The state $(\alpha|s)|n, h\Gamma p\rangle$ defined by

$$(x_1, x_2, \dots, x_n | (\alpha|s)|n, h\Gamma p) \equiv (\alpha^{-1}(x_1-s), \alpha^{-1}(x_2-s), \dots | n, h\Gamma p)$$

5.2

has two interpretations: interpreted passively, it is the vector $|n, h\Gamma p\rangle$ in a new basis centred on site $(\alpha|s)0$; interpreted actively, it is a new vector obtained by moving the origin of $|n, h\Gamma p\rangle$. The expansion

$$(\alpha|s)|n, h\Gamma p\rangle = \sum_{h'\Gamma'p'} C_{h\Gamma p}^{h'\Gamma'p'} |n, h'\Gamma'p'\rangle \quad 5.3$$

has coefficients

$$\begin{aligned} C_{h\Gamma p}^{h'\Gamma'p'} &\equiv (n, h'\Gamma'p' | (\alpha|s)|n, h\Gamma p) \\ &= \int d^3x (n, h'\Gamma'p' | x) (\alpha^{-1}(x-s) | n, h\Gamma p) \end{aligned} \quad 5.4$$

which also have two interpretations: interpreted passively, they are overlap integrals between atomic states on different sites; interpreted actively, they are the matrix elements of space group operators in the atomic basis.

In the limit $\lambda \rightarrow \infty$, the coefficients 5.4 for $(\alpha|s) \neq (\epsilon|0)$ are expected to vanish, but for any finite λ the overlap integrals do not vanish -- i.e. the states centred on different atomic sites are not orthogonal. The calculation of overlap integrals is a formidable task: for every H_n , and a truncation of the atomic basis after m_n states, in a crystal having $N \sim 10^{20}$ atoms there are Nm_n overlap integrals each involving a slowly converging expansion of wavefunctions for one atom about the centre of another. Drastic approximations are called for and, in order to see features of the theory

that are independent of an approximation, general properties of overlap integrals must be exploited.

The active interpretation supplies the following useful property of overlap integrals: because the crystal Hamiltonian commutes with all the space group operators $(\alpha|s)$, it is possible to find a constant set of transformations of the atomic basis which simultaneously diagonalizes the overlap matrix and the Hamiltonian matrix. The construction of such a constant set is particularly simple for symmorphic space groups.

The crystal momentum transformation,

$$\begin{aligned}
 |n, kh\Gamma p\rangle &\equiv \frac{1}{N} \sum_{\underline{n}} e^{ik \cdot \underline{R}_{\underline{n}}} (\epsilon | \underline{R}_{\underline{n}}) |n, h\Gamma p\rangle \\
 &= e_k |n, h\Gamma p\rangle \\
 \langle n, k' h' \Gamma' p' | &\equiv \frac{1}{N} \sum_{\underline{n}} e^{-ik' \cdot \underline{R}_{\underline{n}}} \langle n, h' \Gamma' p' | (\epsilon | -\underline{R}_{\underline{n}}) \\
 &= \langle n, h' \Gamma' p' | e_k,
 \end{aligned} \tag{5.5a}$$

where e_k is the idempotent for the k -irreducible representation of the group of lattice translations, leads to the following representation of space group operators:

$$\begin{aligned}
 (\alpha | \underline{R}_{\underline{m}}) |n, kh\Gamma p\rangle &= \frac{1}{N} \sum_{\underline{n}} e^{ik \cdot \underline{R}_{\underline{n}}} (\epsilon | \alpha \underline{R}_{\underline{n}} + \underline{R}_{\underline{m}}) (\alpha | o) |n, h\Gamma p\rangle \\
 &= e^{-ik \cdot \underline{R}_{\underline{m}}} e_{\alpha k} (\alpha | o) |n, h\Gamma p\rangle \\
 &= e^{-ik \cdot \underline{R}_{\underline{m}}} \sum_{p' \in \Gamma} \Gamma(\alpha)_{pp'} |n, \alpha kh\Gamma p'\rangle
 \end{aligned} \tag{5.6a}$$

The orthogonality property of idempotents,

$$e_{k+q} e_k = \delta_{q,o} e_k \tag{5.7}$$

shows that the overlap integrals are diagonal in k ,

$$(n, k+q \ h'\Gamma'p' | n, kh\Gamma p) = \delta_{q,0} (n, h'\Gamma'p' | e_k | n, h\Gamma p) .$$

Also, the reduction of 5.6a diagonalizes the overlap matrix exactly because Γ in 5.6a is reduced according to the irreducible representations D_j of the point group $P(k)$ of the group of the wave-vector k ; and using Schur's Lemma together with the fact that e_k commutes with $P(k)$, on a reduced subspace $[|n, khD_j\lambda\rangle, \lambda=1,2,\dots,d_j]$ the operator e_k is a constant multiple of the unit operator,

$$e_k |n, khD_j\lambda\rangle = S_j^h(k) |n, khD_j\lambda\rangle, \quad \lambda=1,2,\dots,d_j \quad 5.8a,$$

where the vectors are linear combinations of $|n, h\Gamma p\rangle$, $p = 1,2,\dots,d_\Gamma$ obtained by the projection operator method of Appendix 4. All the eigenvalues $S_j^h(k)$ of 5.8a are real because the transformed overlap matrix is hermitian,

$$\begin{aligned} (n, h'\Gamma'p' | (e_k | n, h\Gamma p))^* &= (n, h\Gamma p | e_k | n, h'\Gamma'p') \\ &= \text{transpose } (n, h'\Gamma'p' | e_k | n, h\Gamma p) . \end{aligned}$$

The vectors $(S_j^h(k))^{-1/2} |n, khD_j\lambda\rangle$ constitute an orthonormal basis for H_n because

$$\begin{aligned} (n, k'h'D_j'\lambda' | n, khD_j\lambda) &= \delta_{kk'}, (n, h'D_j'\lambda' | e_k | n, hD_j\lambda) \\ &= \delta_{kk'} \delta_{hh'} \delta_{jj'} \delta_{\lambda\lambda'} S_j^h(k) \end{aligned}$$

or

$$\begin{aligned} (n, k'h'D_j'\lambda' | (S_j^{h'}(k'))^{-1/2} (S_j^h(k))^{-1/2} | n, khD_j\lambda) \\ = \delta_{kk'} \delta_{hh'} \delta_{jj'} \delta_{\lambda\lambda'} \end{aligned} \quad 5.9a.$$

And this new basis has the property that the representation of the space group carried by the set $[|n, \alpha khD_j\lambda\rangle, \lambda=1,2,\dots$

$d_j, |\alpha k \epsilon \text{ star of } k|$, i.e. the induced representation from an irreducible allowable representation of the group of the wave-vector k , is irreducible. Therefore, the Hamiltonian for the crystal is a multiple of the unit operator on the subspace spanned by the above set of vectors:

$$\hat{H}|n, \alpha k h D_j \lambda\rangle = E_j^h(k) |n, \alpha k h D_j \lambda\rangle \quad 5.10.$$

Following Löwdin (Lö 58), one can consider the matrix elements of the crystal Hamiltonian in the new basis as the matrix elements of a 'pseudo-hamiltonian'

$$\begin{aligned} \hat{H}'(k) &= (e_k)^{-1/2} \hat{H}(e_k)^{-1/2} \\ &= \frac{\hat{H}}{e_k} \end{aligned} \quad 5.11a$$

in the (non orthonormal) basis derived from the atomic basis by crystal momentum transformation.

The argument proceeding from 5.5a to 5.9a can be reproduced, mutatis mutandis, for asymmorphic space groups. Complications originate from the overlap of states centred on different atoms in the same unit cell. The unit cell of the point lattice (p.l.) is described by the zero vector 0 , and $z-1$ imprimitive vectors $(\epsilon|\tau)0$. A state $|n, h\Gamma p\rangle$ centred on the zero site can be translated to $(\epsilon|\tau)|n, h\Gamma p\rangle$ centred on another site in the unit cell. For convenience, the original state on the zero site is denoted $|n, h\Gamma p\rangle \equiv (\epsilon|0)|n, h\Gamma p\rangle$ in the modified crystal momentum transformation, T_k , defined by

$$\begin{aligned}
|n, kh\Gamma p) &\equiv \frac{1}{Nz} \sum_{p.l.} e^{ik \cdot R_{\underline{n}} + \tau} (\epsilon | R_{\underline{n}} + \tau) |n, h\Gamma p) \\
&= e_k \frac{1}{z} \sum_{\tau} e^{ik \cdot \tau} (\epsilon | \tau) |n, h\Gamma p) \equiv T_k |n, h\Gamma p) \quad 5.5b.
\end{aligned}$$

The action of space group transformations on these crystal momentum eigenstates is clearly

$$\begin{aligned}
(\alpha | v_{\alpha + R_{\underline{m}}}) |n, kh\Gamma p) &= \bar{e}^{ik \cdot R_{\underline{m}}} e_{\alpha k} (\alpha | v_{\alpha}) \frac{1}{z} \sum_{\tau} e^{ik \cdot \tau} (\epsilon | \tau) |n, h\Gamma p) \\
&= \bar{e}^{ik \cdot R_{\underline{m}}} \bar{e}^{ik \cdot v_{\alpha}} e_{\alpha k z} \frac{1}{z} \sum_{\tau} e^{i\alpha k \cdot \tau} (\epsilon | \tau) (\alpha | 0) |n, h\Gamma p) \quad 5.6b,
\end{aligned}$$

which shows that the set $[|n, \alpha kh\Gamma p), p=1,2,\dots,d_{\Gamma} | \alpha \in \text{star of } k]$ carry a (reducible) representation of the space group. The reduction of this representation is performed by first reducing the allowable representation of $L_1(k)$ (Appendix 3) carried by $[|n, kh\Gamma p), p=1,2,\dots,d_{\Gamma}]$ according to the irreducible representations D_j of the point group $P(k)$ of the wave-vector k contained in Γ (Appendix 4).

The overlap matrix after such a reduction is diagonal in k (5.7); and because the transformation operator $T_k = \frac{1}{z} \sum_{\tau} e^{ik \cdot \tau} (\epsilon | \tau) e_k$ commutes with $P(k)$ on a subspace generated by $[|n, khD_j \lambda), \lambda=1,2,\dots,d_j]$ the operator is a multiple of the unit operator:

$$T_k |n, khD_j \lambda) = S_j^h(k) |n, khD_j \lambda) \quad 5.8b.$$

Thus, the orthogonal basis for H_n which simultaneously diagonalizes the crystal Hamiltonian and the overlap matrix is obtained as in the case of symmorphic space groups,

$$\begin{aligned}
(n, k' h' D_j \lambda' | (S_j^{h'}(k'))^{-1/2} (S_j^h(k))^{-1/2} |n, khD_j \lambda) \\
= \delta_{kk'} \delta_{hh'} \delta_{jj'} \delta_{\lambda\lambda'} \quad 5.9b.
\end{aligned}$$

In the orthonormal basis, the Hamiltonian is diagonal (5.10) and the matrix elements of such a crystal Hamiltonian in the k -subspace of the orthonormal basis 5.9 may be considered to be the matrix elements of a pseudo-Hamiltonian between the un-normalized crystal momentum eigenstates 5.5 of the same k :

$$\begin{aligned} \hat{H}'(k) &\equiv (e_k \frac{1}{Z} \sum_{\tau} e^{ik \cdot \tau} (\epsilon | \tau))^{-1/2} \hat{H} (e_k \sum_{\tau} e^{ik \cdot \tau} (\epsilon | \tau))^{-1/2} \\ &= \frac{\hat{H}}{(e_k \frac{1}{Z} \sum_{\tau} e^{ik \cdot \tau} (\epsilon | \tau))} \end{aligned} \quad 5.11b.$$

In the limit of large adiabatic scaling, the eigenvalues S in 5.8 are fixed by the asymptotic condition:

$$\begin{aligned} \lim_{\lambda \rightarrow \infty} S_j^h(k) &= \frac{1}{NZ} \sum_{\underline{n}} \sum_{\tau} e^{ik \cdot R_{\underline{n}} + \tau} (n, hD_{j\mu} | (\epsilon | R_{\underline{n}} + \tau) | n, hD_{j\mu}) \Big|_{\lambda=\infty} \\ &= \frac{1}{NZ} \sum_{\underline{n}} \sum_{\tau} e^{ik \cdot R_{\underline{n}} + \tau} \delta_{\tau,0} \delta_{\underline{n},0} \\ &= \frac{1}{NZ} \text{ independent of } h, j, k \end{aligned} \quad 5.12.$$

Therefore, the pseudo-Hamiltonian 5.11 in the crystal momentum basis 5.5 is ill-defined, since Nz is allowed to become thermodynamically large. For finite λ , $H'(k)$ shows 'dispersion' in k -space, when $S_j^h(k)$ varies with k , of an unusual type.

The reduction of multiplet $[|n, h\Gamma_p\rangle, p=1,2,\dots,d_{\Gamma}]$ by the method of Appendix 4 yields a new basis $[|n, h\bar{\Gamma}_p\rangle, p=1,2,\dots,d_{\Gamma}]$ for the multiplet which has the property that the matrices $\bar{\Gamma}(\alpha)_{pp'}$, for $\alpha \in P(k)$ are block diagonal sums of $D_j(\alpha)$ matrices. If α is not a member of $P(k)$, then the

block diagonal form for the $\bar{\Gamma}$ matrix no longer holds. On the $\bar{\Gamma}$ multiplet, the crystal momentum operator 5.5 is a block diagonal sum of multiples of the identity operator on the D_j subspaces of $\bar{\Gamma}$:

$$e_k \frac{1}{Z} \sum_{\tau} e^{ik \cdot \tau} (\epsilon | \tau) | n, kh\bar{\Gamma}p) = S_p^h(k) | n, kh\bar{\Gamma}p) ,$$

$$S_p^h(k) = S_j^h(k) \text{ if } | n, kh\bar{\Gamma}p) \in [| n, khD_j \mu) , \mu=1,2,\dots,d_j]$$

5.13.

The transformation properties of the S_p are:

$$\begin{aligned} S^h(\alpha k)_p &= \frac{1}{Nz} \sum_{\underline{n}} \sum_{\underline{\tau}} e^{i\alpha k \cdot (R_{\underline{n}} + \tau)} (n, h\bar{\Gamma}p | (\epsilon | R_{\underline{n}} + \tau) | n, h\bar{\Gamma}p) \\ &= \frac{1}{Nz} \sum_{\underline{n}} \sum_{\underline{\tau}} e^{ik \cdot (R_{\underline{n}} + \tau)} \sum_{p', p''} (n, h\bar{\Gamma}p | (\alpha | o)^{-1} | n, h\bar{\Gamma}p') \\ &\quad (n, h\bar{\Gamma}p' | (\epsilon | R_{\underline{n}} + \tau) | n, h\bar{\Gamma}p'') \\ &\quad (n, h\bar{\Gamma}p'' | (\alpha | o) | n, h\bar{\Gamma}p) \\ &= \sum_{p'} \Gamma(\alpha^{-1})_{pp'} S_{p'}^h(k) \Gamma(\alpha)_{p'p} \end{aligned}$$

5.14.

In order to perform the summations over the p.l. to evaluate S_p , it is convenient to arrange lattice points in rings about the zero point, indexing the rings $|n=0,1,2,\dots$ outwards. For the m th ring, a representative point $R_m + \tau_m$ is chosen and a function

$$T_m(\alpha) = \begin{cases} \frac{1}{P_m} & \text{if } \alpha(R_m + \tau_m) \text{ is a lattice point} \\ 0 & \text{if } \alpha(R_m + \tau_m) \text{ is not a lattice point} \end{cases}$$

5.15

with P_m equal to the number of distinct elements $\alpha \in P(o)$ for which $\alpha(R_m + \tau_m) = R_m + \tau_m$. Using definition 5.15 and property 5.14, a compact expression for $S^h(k)_p$ can be written:

$$\begin{aligned}
 S^h(k)_p &= \frac{1}{Nz} \sum_m \sum_{\alpha \in P(o)} T_m(\alpha) e^{ik \cdot \alpha(R_m + \tau_m)} \\
 &\quad (n, h\Gamma p | (\epsilon | \alpha R_m + \alpha \tau_m) | n, h\Gamma p) \\
 &= \frac{1}{Nz} \sum_m \sum_{p'} \sum_{\alpha \in P(o)} T_m(\alpha) e^{i\alpha^{-1} k \cdot (R_m + \tau_m)} \\
 &\quad \Gamma(\alpha^{-1})_{pp'} \Gamma(\alpha)_{p'p} (n, h\Gamma p' | (\epsilon | R_m + \tau_m) \\
 &\quad | n, h\Gamma p') \\
 &= \frac{1}{Nz} \sum_m \sum_{p'} \zeta^m(\Gamma k)_{pp'} (n, h\Gamma p' | (\epsilon | R_m + \tau_m) | n, h\Gamma p')
 \end{aligned}$$

5.16.

For every ring of neighbours, only one translation operator needs to be considered; and the structure factor matrix

$$\zeta^m(\Gamma k)_{pp'} = \sum_{\alpha \in P(o)} T_m(\alpha) e^{i\alpha^{-1} k \cdot (R_m + \tau_m)} \Gamma(\alpha^{-1})_{pp'} \Gamma(\alpha)_{p'p}$$

5.17

is clearly independent of the scaling parameter λ because the k space scales adiabatically with the reciprocal parameter $1/\lambda$. The matrix elements of the translation operator, however, depend on λ , though the asymptotic condition requires that only negative powers of λ appear in any power series expansion of such a matrix element. Before suggesting

approximation procedures for evaluating matrix elements in 5.16, one further general feature of the atomic picture can be studied: the effect of zeros of $S_j^h(k)$ on the transformation 5.9.

Because T_k is idempotent, its eigenvalues may be identically zero. The zeros lead to singularities in 5.9, which can be avoided by adding a small positive number η and understanding 5.9 as a limit:

$$\begin{aligned} \lim_{\eta \rightarrow 0^+} \langle n, k'h'D_j \lambda' | (S_j^{h'}(k') + \eta)^{-1/2} (S_j^h(k) + \eta)^{1/2} | n, khD_j \lambda \rangle \\ = \delta_{kk'} \delta_{hh'} \delta_{jj'} \delta_{\lambda\lambda'} \end{aligned} \quad 5.9c.$$

The operator expansion A2.17 takes the form

$$\begin{aligned} \hat{O} &= \lim_{\eta \rightarrow 0^+} \sum_{nkh\Gamma p} \sum_{n'k'h'\Gamma'p'} \langle n, kh\Gamma p | (T_k + \eta)^{-1/2} \hat{O} \\ &\quad (T_k + \eta)^{-1/2} | n', k'h'\Gamma'p' \rangle (T_k + \eta)^{-1/2} | n, kh\Gamma p \rangle \\ &\quad \langle n', k'h'\Gamma'p' | (T_k + \eta)^{-1/2} \\ &= \lim_{\eta \rightarrow 0^+} \sum_v \sum_{v'} \langle v | (S_v + \eta)^{-1} \hat{O} (S_v + \eta)^{-1} | v' \rangle | v \rangle \langle v' | \\ &= \lim_{\eta \rightarrow 0^+} \sum_{vv'} \langle v | (S_v + \eta)^{-1} \hat{O} (S_v + \eta)^{-1} | v' \rangle X_{vv'} \end{aligned} \quad 5.18$$

where $v = n, kh\Gamma p$ is an abbreviation and the operators $X_{vv'}$ differ from the basic operators of type A2.15 by scalar terms. To avoid confusion with correctly normalized basic operators, the X's above are called d-mons--a term introduced by Anderson (An 62) to describe correlated electronic

modes in transition metals.

As a function of λ

$$S_j^h(k) = S_v(\lambda) = \frac{1}{Nz} \prod_i \left(1 - \frac{\lambda_v^{(i)}}{\lambda}\right)^{g_i} \quad 5.19$$

where $\lambda_v^{(i)}$ is a root of order g_i of $S_v(\lambda) = 0$. The troublesome limits in 5.18 can be cast into the form of complex integrals in the λ -plane by continuing 5.19. The result is

$$\lim_{\eta \rightarrow 0^+} (S_v(\lambda) + \eta)^{-1} |v\rangle_\lambda = \frac{1}{2\pi i} \lim_{\eta \rightarrow 0^+} \oint_c dz (S_v(z) + \eta)^{-1} |v\rangle_z \frac{1}{z - \lambda} \quad 5.20$$

where c is a contour surrounding the point λ , and no other singularities of the integrand. For finite η , c is taken to be a circle of vanishingly small radius about λ . If λ coincides with a solution of $S_v(\lambda) = 0$, the limit $\eta \rightarrow 0^+$ of the integral diverges. However, by permuting the order of integrating around c and following the η -limit, the left-hand side of 5.20 is well defined in H_n . For if λ coincides with $\lambda^{(i)}$, a zero of order g_i for S_v ,
 $S_v^{+1}(z) = a_v^{-1}(z) (z - \lambda^{(i)})^{+g_i},$

$$\begin{aligned} \lim_{\eta \rightarrow 0^+} (S_v(\lambda) + \eta)^{-1} |v\rangle_\lambda &= \frac{1}{2\pi i} \oint_c dz \frac{1}{(z - \lambda)^{g_i + 1}} a_v(z) |v\rangle_z \\ &= \frac{1}{g_i!} \lim_{z \rightarrow \lambda} \frac{\partial^{g_i}}{\partial z^{g_i}} [a_v(z) |v\rangle_z] \quad 5.21; \end{aligned}$$

and the transformation 5.9 is well-defined at the zero of S if the limit 5.21 belongs to H_n for some n . The key result

of this section may be stated as a Theorem: the limit on the right-hand side of 5.21 is a real scalar multiple of the vector $|v\rangle_\lambda$. The essence of the proof is contained in the simplest case, $g_i=1$,

$$S_v^{-1}(\lambda) |v\rangle_\lambda = \lim_{z \rightarrow \lambda} \left[\frac{da_v(z)}{dz} |v\rangle_z + a_v(z) \frac{d}{dz} |v\rangle_z \right] \quad 5.22.$$

clearly, the reality of $S_v(\lambda)$ for real λ implies that $a_v(z)$ and $a_v'(z)$ are also real for real values of z . The second term on the right-hand side of 5.22 is not obviously well-defined, but by defining $|v\rangle_z$ to be a solution of the equation

$$\begin{aligned} \sum_{j=1}^n -\frac{\hbar^2}{2m} \nabla_j^2 - \sum_{n,\tau} \frac{z^3 A e^2}{|x_j - z R_n - z\tau|} (t; x_1 s_1, \dots, x_n s_n | v)_z \\ + \frac{1}{2} \sum_{i,j} \frac{e^2}{|x_i - x_j|} |v\rangle_z = \frac{\hbar}{i} \frac{\partial}{\partial t} (t; x_1 s_1, \dots, x_n s_n | v)_z \quad 5.23, \end{aligned}$$

where A is the ionic charge, the ket $\lim_{z \rightarrow \lambda} \frac{d}{dz} |v\rangle_z$ may be understood to be a solution of the equation

$$\begin{aligned} \left(\sum_{j=1}^n -\frac{\hbar^2}{2m} \nabla_j^2 - \sum_{n,\tau} \frac{\lambda^3 A e^2}{|x_j - \lambda R_n - \lambda\tau|} + \frac{1}{2} \sum_{i,j} \frac{e^2}{|x_i - x_j|} \right. \\ \left. - \frac{\hbar}{i} \frac{\partial}{\partial t} \right) (t; x_1 s_1, \dots, x_n s_n | \lim_{z \rightarrow \lambda} \frac{d}{dz} |v\rangle_z \\ = \sum_{j=1}^n \left(- \sum_{n,\tau} \frac{d}{d\lambda} \frac{\lambda^3 A e^2}{|x_j - \lambda R_n - \lambda\tau|} \right) (t; x_1 s_1, \dots, x_n s_n | v)_\lambda \quad 5.24. \end{aligned}$$

The inhomogeneous term on the right of 5.24 consists of a space group scalar acting on $|v\rangle_\lambda$, and by Schur's Lemma is

a complex multiple of $|v\rangle_\lambda$. Because for real λ the operator is a real function, then the right-hand side of 5.24 is a real multiple of $|v\rangle_\lambda$. The Green's function for the homogeneous equation of 5.24 is the same as that for 5.23 in the limit $z \rightarrow \lambda$. Therefore, the solution of 5.24 can be written

$$\begin{aligned} \lim_{z \rightarrow \lambda} \frac{d}{dz} |v\rangle_z &= \sum_v |v'\rangle \langle v'| \alpha_1(v) |v\rangle \\ &= |v\rangle \alpha_1(v), \text{ where } \alpha_1 \text{ is a real number} \end{aligned} \quad 5.25.$$

To complete the proof for all g_i , induction on the order of differentiation in 5.21 is required:

$$\begin{aligned} \lim_{z \rightarrow \lambda} \frac{\partial^n}{\partial z^n} [a_v(z) |v\rangle_z] &= \beta_n(v) |v\rangle_\lambda \quad \text{implies that} \\ \lim_{z \rightarrow \lambda} \frac{\partial^{n+1}}{\partial z^{n+1}} [a_v(z) |v\rangle_z] &= \beta_{n+1}(v) |v\rangle_\lambda, \beta \text{'s real scalars.} \end{aligned}$$

The induction is proved by a slight generalization of the proof 5.22 to 5.25, $\beta_n(v) = \left(\frac{d}{d\lambda} + \alpha_1(v)\right)^n a_v(\lambda)$.

In order that the vector 5.21 be well-defined in H_n , it is only required to show that the scalar α_1 of 5.25 (and generalizations, β , of it) are bounded. Acting on a vector $|v\rangle \in H_n$, the operator derivative with respect to λ of the one-particle potential of the ions can be written

$$\begin{aligned} \frac{d}{d\lambda} \sum_{i=1}^n \sum_{\underline{n}, \tau} \frac{-Ae^2}{|x_i + \lambda R_{\underline{n}} + \lambda \tau|} &= +Ae^2 \lambda^3 \sum_{i=1}^n \sum_{\underline{n}, \tau} \frac{(\lambda R_{\underline{n}} + \lambda \tau + x_i) \cdot (R_{\underline{n}} + \tau)}{|x_i + \lambda R_{\underline{n}} + \lambda \tau|^3} \\ &\quad - 3Ae^2 \lambda^2 \sum_{i=1}^n \sum_{\underline{n}, \tau} \frac{1}{|x_j + \lambda R_{\underline{n}} + \lambda \tau|} \end{aligned} \quad 5.26.$$

For each i in the sum 5.26, a Taylor series about $x_i=0$ can be developed:

$$Ae^2\lambda^3 \sum_{\underline{n}, \tau} \left[\frac{(R_{\underline{n}}+\tau) \cdot (\lambda R_{\underline{n}} + \lambda \tau + x)}{|\lambda R_{\underline{n}} + \lambda \tau + x|^3} - \frac{3}{\lambda |\lambda R_{\underline{n}} + \lambda \tau + x|} \right] =$$

$$Ae^2\lambda^3 \sum_{\underline{n}, \tau} \left[\frac{-2}{\lambda^2 |R_{\underline{n}} + \tau|^3} - \frac{5x^\mu (R_{\underline{n}} + \tau)_\mu}{\lambda^3 |R_{\underline{n}} + \tau|^3} + \frac{6x^\mu x^\nu}{\lambda^4 |R_{\underline{n}} + \tau|^3} \right.$$

$$\left. \left(\frac{3(R_{\underline{n}} + \tau)_\mu (R_{\underline{n}} + \tau)_\nu}{|R_{\underline{n}} + \tau|^2} - \delta_{\mu\nu} \right) + O\left(\frac{x^\mu x^\nu x^\kappa}{\lambda^5}\right) \right]$$

The first term of this series is proportional to the Madelung constant, M_0 . The higher order terms involve 'generalized Madelung constants',

$$M_p \equiv \frac{1}{a^{p+1}} \sum_{\underline{n}, \tau} \frac{1}{|R_{\underline{n}} + \tau|^{p+1}},$$

$$M_p^{\mu_1 \mu_2 \dots \mu_q} \equiv \frac{1}{a^{p+1}} \sum_{\underline{n}, \tau} \frac{(R_{\underline{n}} + \tau)_{\mu_1} (R_{\underline{n}} + \tau)_{\mu_2} \dots (R_{\underline{n}} + \tau)_{\mu_q}}{|R_{\underline{n}} + \tau|^{p+q+1}},$$

which are of order zero in the lattice distance a , and converge to a value which depends only on the Bravais class of the lattice.

The following atomic integrals,

$$I_{\mu_1 \mu_2 \dots \mu_q}^q \equiv (v | \sum_{i=1}^n x_i^{\mu_1} x_i^{\mu_2} \dots x_i^{\mu_q} | v)$$

converge because $|v\rangle$ vanishes outside a finite volume.

Hence, the expression for $\alpha_1(v)$,

$$\alpha_1(v) = -Ae^2\lambda^3 \left[\frac{2M_0}{\lambda^2 a} + \frac{5M_1^\mu}{\lambda^3 a^2} I_\mu^1 + \frac{6}{\lambda^4 a^3} (M_3^{\mu\nu} - 3M_2^{\mu\nu}) I_{\mu\nu}^2 + \dots \right]$$

5.27

is finite for any finite number of terms. The fact that all the terms in 5.27 are finite does not prove that the series converges. However, 5.27 does show that $T_k \alpha_1(v) |v\rangle$ is the null vector of space H so long as $|v\rangle$ is confined to a finite volume. By similar arguments $T_k \beta_n(v) |v\rangle$ is the null vector of space H.

One cannot be absolutely certain that the only zeros of S are isolated and of finite order at the thermodynamic limit. However, for large finite N, truncation of 5.16 with polynomial approximations for the overlap matrix elements yields an approximation for S in the form of a finite polynomial in ascending powers of $1/\lambda$. The zeros of such a polynomial are, of course, isolated and of finite order in the complex λ -plane.

If the α 's and β 's have the form 5.27, cancellation is possible in 5.18:

$$\lim_{\eta \rightarrow 0^+} \frac{1}{S_j^{h(k)+\eta}} T_k |n, hD_j \lambda\rangle = \begin{cases} |n, hD_j \lambda\rangle, & S \neq 0 \\ |n, 0\rangle, & S = 0 \end{cases} \quad 5.28.$$

Thus, the matrix elements coupling $\hat{O}$ to the d-mons X are ionic matrix elements. By analyzing the time development of d-mons, a picture of the kinematics of electrons in solids very similar to Hubbard's (Hu 62) is obtained with-

out making strong dynamical assumptions about the Hamiltonian $\hat{H}$.

The equal-time commutation relations for d-mons are

$$[X_{\nu\nu}, X_{\mu\mu}]_{\eta_p} = \delta_{\nu,\mu} S_{\mu} X_{\nu\mu} + \eta_p \delta_{\mu,\nu} S_{\nu} X_{\mu\nu}, \quad 5.29,$$

where $\eta_p = \pm 1$. Whatever the value of λ , the Heisenberg operators for d-mons are given by

$$\begin{aligned} X_{\nu\nu}(t) &\equiv e^{-\frac{i}{\hbar} \hat{H}t} X_{\nu\nu} e^{\frac{i}{\hbar} \hat{H}t} \\ &= e^{-\frac{i}{\hbar} (E_{\nu} - E_{\nu})t} X_{\nu\nu}, \end{aligned}$$

and they obey the unequal time commutation relations

$$\begin{aligned} [X_{\nu\nu}(t_1), X_{\mu\mu}(t_2)]_{\eta_p} &= \delta_{\nu,\mu} S_{\mu} e^{\frac{i}{\hbar} E_{\mu}(t_1-t_2)} e^{-\frac{i}{\hbar} \hat{H}t_1} X_{\nu\mu} e^{\frac{i}{\hbar} \hat{H}t_2} \\ &+ \eta_p \delta_{\mu,\nu} S_{\nu} e^{\frac{i}{\hbar} E_{\nu}(t_1-t_2)} e^{-\frac{i}{\hbar} \hat{H}t_2} X_{\mu\nu} e^{\frac{i}{\hbar} \hat{H}t_1} \end{aligned} \quad 5.30.$$

The energies E_{ν} appearing in 5.30 are those for the ion in a crystal field appropriate to the λ which appears in $\hat{H}$.

The average of unequal time commutation relations with respect to any statistical operator ρ commuting with $\hat{H}$ is a function only of the time difference $t_1 - t_2$:

$$\langle [X_{\mu\mu}(t_1), X_{\nu\nu}(t_2)]_{\eta_p} \rangle_{\rho} \equiv \sum_{\phi \in H} (\phi | \rho [X_{\mu\mu}(t_1), X_{\nu\nu}(t_2)]_{\eta_p} | \phi) \quad 5.31;$$

and in the atomic basis

$$\langle [X_{\mu\mu}, (t_1), X_{\nu\nu}, (t_2)]_{\eta_p} \rangle_{\rho} = e^{-\frac{i}{\hbar} (E_{\nu} - E_{\mu}) (t_1 - t_2)} \delta_{\mu\nu} \delta_{\nu\mu} S_{\mu} S_{\nu} (\rho_{\mu} + \eta_p \rho_{\nu}) \quad 5.32.$$

This last result is needed to fix the Green's functions of Chapter VI.

The matrix elements $\rho_{\nu} = (n, hD_j \lambda | \rho | n, hD_j \lambda)$ are ionic averages. The k -dependence of 5.32 comes entirely from the eigenvalues S .

The location of zeros of S_{ν} is of some importance. One can distinguish two types. The first can be located by symmetry alone and is called 'true'. Such zeros arise when all the matrix elements $(n, hD_j p | (\epsilon | R_{\underline{m}} + \tau_{\underline{m}}) | n, hD_j p)$ in the series 5.16 vanish. The second type of zero is called 'accidental' and arises when the series of non-zero terms 5.16 converges to zero instead of unity.

When evaluating matrix elements $(n, hD_j p | (\epsilon | R_{\underline{m}} + \tau_{\underline{m}}) | n, hD_j p)$, several orientations of coordinate axes may be used. Under a change of axes by rotation-inversion $\alpha \in P(\underline{k})$, the ket $(\epsilon | R_{\underline{m}} + \tau_{\underline{m}}) | n, hD_j p)$ transforms as $D_{\underline{v}} \otimes D_j$, the tensor product of irreducible representation D_j with the (reducible) vector representation made up of 3×3 matrices which describe operation α in a Cartesian coordinate system. The reduction of $D_{\underline{v}} \otimes D_j$ according to $[D_j]$, irreducible representations of the point group $P(\underline{k})$ gives

$$D_v \otimes D_j \cong \oplus_j C_v^{j*} \otimes_j D_j, \quad 5.33.$$

The bra $(n, hD_j p |$ transforms under change of axes as D_j^* , the representation conjugate to D_j . Clearly, the condition that $(n, hD_j p | (\epsilon | R_m + \tau_m) | n, hD_j p)$ vanishes identically for all m is $C_v^{j*} \otimes_j = 0$. This condition is independent of λ and, therefore, true zeros are not isolated in the complex λ -plane. However, $S^{-1/2}$ is still defined on the domain of S ($=1$): it may be extended beyond this domain by letting $T_k S^{-1/2}$ be the zero operator, so that 5.28 is valid. The accidental zeros of S are isolated, and can be treated by the method 5.20 to 5.27. They depend on what atoms occupy the Bravais lattice sites, and what approximation is used to build the correlated atomic states. Their relevance is to be compared with that of accidental degeneracies: they are neglected, knowing that if they arise the operator expansion 5.18 loses a few terms.

The true zeros can be located by symmetry, and are therefore independent of the type of atom on the lattice site provided that a change of atom does not lead to a different Bravais Lattice.

CHAPTER VI

DIELECTRIC RESPONSE IN THE ATOMIC PICTURE

The inverse permittivity and screened potential of 4.17 and 4.18 contain the Green's function for the charge density

$$\begin{aligned} D(x_1, x_2; t_1 - t_2 = \tau) &\equiv \langle T(\rho(1)\rho(2)) \rangle \\ &= \theta_+(\tau) \langle \rho(x_1, \tau) \rho(x_2) \rangle + \theta_-(\tau) \langle \rho(x_2) \rho(x_1, \tau) \rangle \end{aligned} \quad 6.1,$$

where the θ -functions, defined by

$$\begin{aligned} \theta_+(\tau) &\equiv 1 \text{ if } \tau \geq 0, 0 \text{ otherwise} \\ \theta_-(\tau) &\equiv 1 \text{ if } \tau \leq 0, 0 \text{ otherwise,} \end{aligned} \quad 6.2$$

can be represented as integrals in the complex plane:

$$\theta_{\pm}(\tau) = \frac{1}{2\pi i} \oint_{C^{\pm}} dz e^{-iz\tau} \left(\frac{1}{z+i\epsilon} - \frac{1}{z-i\epsilon} \right) \quad 6.3$$

where ϵ is a positive infinitesimal, C^+ is the real z -axis $-\infty$ to $+\infty$ closed by the semicircle at infinity in the lower z -plane, C^- is the real z -axis $-\infty$ to $+\infty$ closed by the semicircle at infinity in the upper z -plane.

The statistical averaging, $\langle, \rangle$, over a grand canonical ensemble at temperature $T = \frac{1}{k\beta}$, chemical potential μ and with grand potential $Q(\beta, \mu)$ admits the following boundary condition on correlation functions:

$$\begin{aligned}
\langle \rho(x_1, \tau) \rho(x_2) \rangle &\equiv \frac{1}{Q(\beta, \mu)} \text{Tr} [e^{-\beta(H - \mu N)} e^{-\frac{i}{\hbar} \tau H} \rho(x_1) e^{\frac{i}{\hbar} \tau H} \rho(x_2)] \\
&= \frac{1}{Q} \text{Tr} [\rho(x_1, \tau + i\hbar\beta) e^{-\beta(H - \mu N)} \rho(x_2)] \\
&= \langle \rho(x_2) \rho(x_1, \tau + i\hbar\beta) \rangle
\end{aligned} \tag{6.4}$$

where Tr denotes the trace operation in H, and its value is not altered by cyclic permutation of operator factors of its argument.

Equation 6.1 may be continued to the complex τ -plane by extending the definition of time ordering to complex times. For this purpose the notation

$$\begin{aligned}
D^>(x_1, x_2; \tau) &\equiv \langle \rho(x_1, \tau) \rho(x_2) \rangle \\
D^<(x_1, x_2; \tau) &\equiv \langle \rho(x_2) \rho(x_1, \tau) \rangle
\end{aligned} \tag{6.5}$$

is convenient. The definitions

$$\begin{aligned}
D(x_1, x_2; \tau) &\equiv \begin{cases} D^{(1)}(x_1, x_2; \tau) & \text{if } \text{Re}\tau \geq 0 \\ D^{(2)}(x_1, x_2; \tau) & \text{if } \text{Re}\tau < 0 \end{cases} \\
D^{(1)}(x_1, x_2; \tau) &\equiv \begin{cases} D^<(x_1, x_2; \tau) & \text{if } \text{Im}\tau \geq 0 \\ D^>(x_1, x_2; \tau) & \text{if } \text{Im}\tau < 0 \end{cases} \\
D^{(2)}(x_1, x_2; \tau) &\equiv \begin{cases} D^<(x_1, x_2; \tau) & \text{if } \text{Im}\tau \geq 0 \\ D^>(x_1, x_2; \tau) & \text{if } \text{Im}\tau < 0 \end{cases}
\end{aligned}$$

6.6,

which are contrived by continuing $\theta_+(\tau)$ to the lower τ -plane and $\theta_-(\tau)$ to the upper τ -plane in 6.1 and 6.3, yield a periodic boundary condition for D when 6.4 is invoked:

$$D(x_1, x_2; \tau) = D(x_1, x_2; \tau + i\hbar\beta) \quad 6.7.$$

Therefore, in the complex time interval $[(\text{Re}\tau, 0), (\text{Re}\tau, \hbar\beta)]$, D can be Fourier analysed according to

$$D(x_1, x_2; \tau) = \sum_{\nu} e^{-i \cdot \frac{2\pi\nu}{i\hbar\beta} \tau} D(x_1, x_2; \omega_{\nu}) \quad 6.8$$

where ν runs over the integers and $\omega_{\nu} \equiv \frac{2\pi\nu}{i\hbar\beta}$. The inverse transformation

$$D(x_1, x_2; \omega_{\nu}) = \frac{1}{\hbar\beta} \int_{(\text{Re}\tau, 0)}^{(\text{Re}\tau, \hbar\beta)} d\tau e^{+i\omega_{\nu}\tau} D(x_1, x_2; \tau) \quad 6.9$$

obviously depends on $\text{Re}\tau$. Nevertheless, the analytic continuation of D from the real τ -axis such that 6.7 is valid can be made with the aid of the Fourier transforms of $D^{\lessgtr}$:

$$D^{\lessgtr}(\omega) \equiv \int_{-\infty}^{+\infty} d\tau e^{i\omega\tau} D^{\lessgtr}(\tau) \quad 6.10.$$

From 6.6

$$\begin{aligned} D(\tau - i\hbar\beta) &= D^>(\tau - i\hbar\beta) \\ &= \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} e^{-i\omega(\tau - i\hbar\beta)} D^>(\omega) \\ &= \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} e^{-i\omega\tau} e^{-\hbar\beta\omega} D^>(\omega) \end{aligned} \quad 6.11a,$$

and also

$$\begin{aligned} D(x_1, x_2; \tau) &= D^<(\tau) \\ &= \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} e^{-i\omega\tau} D^<(\omega) \end{aligned} \quad 6.11b.$$

The periodic boundary condition 6.7, therefore, is equivalent to

$$D^>(\omega) = e^{\hbar\omega\beta} D^<(\omega) \quad 6.12,$$

which may be written in terms of a spectral density A:

$$A(x_1, x_2; \omega) \equiv \int_{-\infty}^{+\infty} d\tau e^{i\omega\tau} \langle [\rho(x_1, \tau), \rho(x_2)]_- \rangle \quad 6.13a;$$

$$D^<(\omega) = f(\omega) A(\omega) \quad 6.13b;$$

$$D^>(x_1, x_2; \omega) = [1-f(\omega)] A(x_1, x_2; \omega) \quad 6.13c;$$

$$f(\omega) \equiv (e^{\hbar\omega\beta} - 1)^{-1}, \text{ the Bose statistical factor,} \quad 6.13d.$$

In 6.9,

$$\begin{aligned} D(x_1, x_2; \omega_v) &= \frac{1}{\hbar\beta} \int_{(\text{Re}\tau, 0)}^{(\text{Re}\tau, \hbar\beta)} d\tau e^{i\omega_v\tau} \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} e^{-i\omega\tau} D^<(x_1, x_2; \omega) \\ &= \frac{1}{\hbar\beta i} \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \frac{e^{i(\omega_v - \omega)\text{Re}\tau}}{(\omega_v - \omega)} \\ &\quad (e^{-\omega_v - \omega}\hbar\beta - 1) f(\omega) A(x_1, x_2; \omega) \\ &= \frac{1}{\hbar\beta i} \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} e^{i(\omega_v - \omega)\text{Re}\tau} \frac{A(x_1, x_2; \omega)}{\omega_v - \omega} \quad 6.14. \end{aligned}$$

The integral operator which appears in 6.14,

$$I(a) = \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \frac{1}{a - \omega} \quad 6.15$$

can be continued to the complex a-plane as follows:

(i) for $a \in$ lower half plane,

$$I_l(a) = \lim_{\varepsilon \rightarrow 0^+} \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \left[\frac{1}{a - i\varepsilon - \omega} + \frac{i}{2} \delta(a - \omega) \right] \quad 6.16a;$$

(ii) for $a \in$ upper half plane,

$$I_u(a) = \lim_{\epsilon \rightarrow 0^+} \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \left[\frac{1}{a+i\epsilon-\omega} - \frac{i}{2} \delta(a-\omega) \right]. \quad 6.16b.$$

Such continuations allow 6.14 to be written

$$D(x_1, x_2; \omega_v) = \begin{cases} D^l(x_1, x_2; \omega_v) \equiv \frac{1}{\hbar\beta i} \lim_{\epsilon \rightarrow 0^+} \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \\ e^{i(\omega_v - \omega) \text{Re}\tau} \frac{A(\omega)}{\omega_v - i\epsilon - \omega} + \frac{A(\omega_v)}{2\hbar\beta} \text{ if } v > 0 \\ D^u(x_1, x_2; \omega_v) \equiv \frac{1}{\hbar\beta i} \lim_{\epsilon \rightarrow 0^+} \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \\ e^{i(\omega_v - \omega) \text{Re}\tau} \frac{A(\omega)}{\omega_v + i\epsilon - \omega} - \frac{A(\omega_v)}{2\hbar\beta} \text{ if } v < 0 \end{cases} \quad 6.17a$$

$$e^{i(\omega_v - \omega) \text{Re}\tau} \frac{A(\omega)}{\omega_v + i\epsilon - \omega} - \frac{A(\omega_v)}{2\hbar\beta} \text{ if } v < 0$$

6.17b.

The case $v=0$ can be considered directly by inspection of 6.9. The result is

$$D(x_1, x_2; \omega_0) = D(x_1, x_2; \text{Re}\tau) \quad 6.17c.$$

Returning to 6.8, it is clear that this equation defines an analytic continuation of $D(\tau)$ compatible with 6.6 and 6.7 and given explicitly by

$$D(x_1, x_2; \tau) = \frac{1}{\hbar\beta i} \sum_v e^{-i\omega_v \text{Im}\tau} \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} e^{i\omega \text{Re}\tau} \frac{A(x_1, x_2; \omega)}{\omega_v - \omega} \quad 6.18$$

if the spectral density $A(\omega)$ is known in a form which allows analytic continuation in the complex ω -plane. The foregoing method can be generalized to all types of double-time temperature Green's functions: the case

$G_1(l, l') = \frac{1}{i} \langle T(\psi(l)\psi^\dagger(l')) \rangle$ treated, e.g., by Baym and Mermin (BM 61) has a boundary condition different from 6.7 but their method has been adapted to D here with few changes.

$$\text{Taking } \rho(x) = \rho_e(x) + \rho_i(x) \quad 6.19,$$

where $\rho_e(x) = \psi^\dagger(x)\psi(x)$ is the charge density for electrons and $\rho_i(x)$ the charge displacement operator for nuclei, the spectral density is

$$\begin{aligned} A(x_1, x_2; \omega) = & \int_{-\infty}^{+\infty} d\tau e^{i\omega\tau} [\langle [\rho_e(x_1, \tau), \rho_e(x_2)]_- \rangle \\ & + \langle [\rho_i(x_1, \tau), \rho_i(x_2, 0)]_- \rangle \\ & + \langle [\rho_e(x_1, \tau), \rho_i(x_2)]_- \rangle + \langle [\rho_i(x_1, \tau), \rho_e(x_2)]_- \rangle] \end{aligned} \quad 6.20.$$

The first term under the integral is the spectral density, A_e , for electrons; the second term is the spectral density, A_i for bare nuclear vibrations; the last two terms are spectral densities of electron-nuclear correlations. The latter cannot be ignored: they are the correlations responsible for the success of the rigid-ion approximation in non-transition metals.

Before examining the electron-nuclear interactions, it is helpful to see how the spectral density A_e is influenced by the atomicity of the solid. Without using the crystal momentum eigenstates, the atomic operator expansion

for A_e takes the form

$$\begin{aligned}
 A_e(x_1, x_2; \omega) &= \int_{-\infty}^{+\infty} d\tau e^{i\omega\tau} \sum_{\phi} \sum_{\nu} e^{i \frac{E_{\phi} - E_{\nu}}{\hbar} \tau} e^{-\beta E_{\phi} - \beta \mu N_{\phi}} \\
 &\quad (\phi | \rho(x_1) | \nu) (\nu | \rho(x_2) | \phi) - \text{c.c.} \\
 &= \frac{1}{i} \sum_{\phi} \sum_{\nu} \delta(\omega - \frac{E_{\phi} - E_{\nu}}{\hbar}) F_1(x_1, x_2) - \delta(\omega - \frac{E_{\nu} - E_{\phi}}{\hbar}) \\
 &\quad F_1(x_2, x_1)
 \end{aligned}$$

$$\text{where } F_1(x_1, x_2) = e^{-\beta E_{\phi} - \beta \mu N_{\phi}} (\phi | \rho(x_1) | \nu) (\nu | \rho(x_2) | \phi) \quad 6.21.$$

Besides being real, A_e satisfies the reflection principle

$$A_e(x_1, x_2; \omega) = -A_e(x_2, x_1; -\omega) \quad 6.22.$$

The frequencies appearing in 6.21 are transition frequencies for many particle states for which F is large--i.e., $N_{\nu} = N_{\phi} \sim N z A$ from the fact that the number of electrons must on average neutralize the background charge. Unfortunately the behaviour of these atomic states under λ -scaling is difficult to predict. The states $|\alpha\rangle$ with particle number $N_{\alpha} \sim A$, on the other hand, change very little under λ -scaling: they are tightly localized for $\lambda \gg 1$, and extend a little as $\lambda \rightarrow 1$. The energy levels for these states are the same as those for an atom in a strong crystal field, and the spacing between levels is sensitive to shell closure effects. Using atomic spectroscopy as a guide, the energy difference

between closed shells is about 5eV [in Hg^+ , $^1P_1 - ^1S_0 = 6.67\text{eV}$]. An open shell configuration has energy differences as low as 0.01eV, 0.1eV being typical [in Ni^+ there are 26 terms of the $3d^8 4s 4p^1$ configuration between 3.2 and 4.6 eV above lowest term of $3d^8 4s ns$]. The general trend for energy differences between terms in an open shell configuration is that as l increases from p to d to f the term differences decrease.

The term differences for states having $\nu N Z A$ electrons can be related to the term differences for νA -electron states of the same Hamiltonian. Let $|\alpha_1\rangle$ and $|\alpha_2\rangle$ be states which have $N_{\alpha_1} \nu N_{\alpha_2} \nu A$ and

$$\begin{aligned}\hat{H}|\alpha_1\rangle &= E_{\alpha_1}|\alpha_1\rangle \\ \hat{H}|\alpha_2\rangle &= E_{\alpha_2}|\alpha_2\rangle \\ x_{\alpha_1, \alpha_2} &\equiv |\alpha_1\rangle\langle\alpha_2| \\ [\hat{H}, x_{\alpha_1, \alpha_2}]_- &= (E_{\alpha_1} - E_{\alpha_2}) x_{\alpha_1, \alpha_2}\end{aligned}\quad 6.23.$$

If $|\nu\rangle$ is a state having $N_\nu \nu N Z A$, the action of x_{α_1, α_2} on $|\nu\rangle$ is defined by

$$\begin{aligned}(x_{N_{\alpha_1}+1}, x_{N_{\alpha_1}+2}, \dots, x_{N_\nu} | (\alpha_1 | \nu) &\equiv \hat{A} \int d^3x_1 \dots d^3x_{N_{\alpha_1}} \\ &(\alpha_1 | x_1, \dots, x_{N_{\alpha_1}}) (x_1, \dots, x_{N_\nu} | \nu)\end{aligned}\quad 6.24a$$

$$(x_1, \dots, x_{N_v}, \dots, x_{N_v+N_{\alpha_2}} | \alpha_2 | v') = \hat{A} (x_1, \dots, x_{N_v} | v')$$

$$(x_{N_v+1}, \dots, x_{N_v+N_{\alpha_2}} | d_2) \quad 6.24b,$$

where $\hat{A}$ is the antisymmetrizer. Using 6.23 and 6.24, if

$$\hat{H} | v \rangle = E_v | v \rangle,$$

then $\hat{H} X_{\alpha_1, \alpha_2} | v \rangle = (E_v - E_{\alpha_2} + E_{\alpha_1}) X_{\alpha_1, \alpha_2} | v \rangle \quad 6.25,$

which tells us that $X_{\alpha_1, \alpha_2} | v \rangle$ is an eigenstate, and its eigenvalue differs from that of $| v \rangle$ by an ionic term difference.

The next difficult question to arise is: what ionic term differences occur with greatest weight in the term differences for NZA electron states? Some arguments of Hubbard's serve as a guide. By scaling interatomic distances by λ' , but not increasing the nuclear charge -- λ' -scaling -- the electronic states of the neutral crystal are expected to become those for a weakly interacting assembly of regularly spaced ions whose average charge is zero.

The lowest energy states of such an assembly are composed of ions whose net charge deviates only a little from zero. For an ion with large negative charge can lose electrons from high energy orbitals to orbitals of lower energy on neighbouring ions; and an ion with large positive charge has low energy orbitals which can be populated by electrons from neighbours. The energetics favouring

charge equalization processes is enhanced by shell closure: a closed shell ion with more than A electrons does not easily gain an electron against the shell closure gap in the level density, nor does a closed shell ion with less than A electrons yield up an electron since the energy level density for a transition to an orbital in a higher shell on a neighbouring atom shows a shell closure gap. Therefore, the configurations of ions in the large λ' assembly are predominantly those with electron numbers lying between the two closed shell numbers which bracket A .

In the event of A 's coinciding with a closed shell number, the variation of numbers of electrons on different ions is expected to be very small indeed. Such a situation is one to which the tight binding approximation might be applied to most of the electronic levels.

The state of the large λ' assembly is a tensor product of ionic states on different sites. When the product is λ' -scaled to the physical crystal, the tensor factors will be of the form $|\alpha_1\rangle$, $|\alpha_2\rangle$, etc., and these are the configurations for which contraction 6.21a does not vanish. If $|\alpha_2\rangle$ violates the bracketting condition on electron number, its 'strength' as factor in an $\sqrt{N}Z_A$ -electron state is likely to be small.

The nuclear spectral density A_i , the dynamical structure factor for inelastic neutron scattering experi-

ments, presents few new problems. The remaining difficulty is the assessment of the importance of nuclear-electron correlations, the effects which are responsible for the success of the rigid ion approximation in simple metals. The main concern is to discover what these correlations do to the propagation frequencies for the total charge density at wave-vector $\underline{k}$, $T_{\underline{k}} \rho(x) T_{\underline{k}}$.

The nuclear part of this charge density propagates at one of the bare phonon frequencies $\omega_o(\underline{k})$. The electronic part propagates at d-mon frequencies. As a crude approximation, only one of the phonon frequencies, and only the lowest d-mon frequency are considered, together with a term representing phonon-d-mon coupling:

$$\omega(\underline{k}) \begin{pmatrix} T_{\underline{k}} \rho_i(x) T_{\underline{k}} \\ (\mu | T_{\underline{k}} \rho_e(x) T_{\underline{k}} | \nu) X_{\mu\nu} \\ \vdots \end{pmatrix} = \begin{pmatrix} \omega_o(\underline{k}), \lambda(\underline{k}) \dots \\ \lambda^*(\underline{k}), \omega_{\mu\nu} \dots \\ \vdots \end{pmatrix} \begin{pmatrix} T_{\underline{k}} \rho_i(x) T_{\underline{k}} \\ (\mu | T_{\underline{k}} \rho_e(x) T_{\underline{k}} | \nu) X_{\mu\nu} \\ \vdots \end{pmatrix}$$

where $\omega_{\mu\nu} = \frac{E_\mu - E_\nu}{\hbar}$ is an atomic transition frequency. The eigenfrequencies and eigenvectors of this truncated dynamical equation are

$$\omega(\underline{k})^\pm = \frac{1}{2} [(\omega_o(\underline{k}) + \omega_{\mu\nu}) \pm \sqrt{(\omega_o(\underline{k}) - \omega_{\mu\nu})^2 + 4|\lambda(\underline{k})|^2}]$$

$$\rho_{\underline{k}}^\pm = u_{\underline{k}}^\pm T_{\underline{k}} \rho_i(x) T_{\underline{k}} + v_{\underline{k}}^\pm X_{\mu\nu} (\mu | T_{\underline{k}} \rho_e(x) T_{\underline{k}} | \nu)$$

where

$$u_{\underline{k}}^\pm = \frac{\lambda(\underline{k})}{((\omega_o - \omega^\pm)^2 + \lambda^2)^{1/2}}, \quad v_{\underline{k}}^\pm = \frac{\omega_o - \omega^\pm}{((\omega_o - \omega^\pm)^2 + \lambda^2)^{1/2}}$$

6.26.

A simple metal has $\omega_{\mu\nu} \gg \omega_0(\underline{k})$, $\omega^+ \sim \omega_0 + \frac{2|\lambda|^2}{(\omega_0 - \omega_{\mu\nu})}$, $u^+ \sim 1$ -- the + mode is a renormalized phonon in which the nuclear motion is appreciable. However, if $\omega_{\mu\nu} \sim \omega_0(\underline{k})$, nuclear and electronic motion is mixed. The mixing of these motions can be seen to quench the isotope effect, which for a simple BCS model has an exponent

$$\alpha = \frac{\partial \ln \bar{\omega}}{\partial \ln M} \quad 6.27,$$

where $\bar{\omega}$ is an average frequency for the propagation of charge density. Only the nuclear coordinates depend on the isotopic mass M ; $\bar{\omega}_0 \propto M^{-1/2}$. Therefore, in the presence of mode mixing

$$\begin{aligned} \alpha &= \frac{1}{2} \left(\frac{\partial \ln \bar{\omega}_+}{\partial \ln M} + \frac{\partial \ln \bar{\omega}_-}{\partial \ln M} \right) = \frac{1}{2} \frac{\partial \ln \bar{\omega}_+ \bar{\omega}_-}{\partial \ln M} \\ &= \frac{1}{2} \frac{\partial \ln \bar{\omega}_+ \bar{\omega}_-}{\partial \ln \bar{\omega}_0} \frac{\partial \ln \bar{\omega}_0}{\partial \ln M} = -\frac{1}{2} \left[\frac{1}{2} \frac{\partial \ln \bar{\omega}_+ \bar{\omega}_-}{\partial \ln \bar{\omega}_0} \right] \end{aligned} \quad 6.28,$$

where $\bar{\omega}_0$, $\bar{\omega}_+$, $\bar{\omega}_-$ are averages over $\underline{k}$ of the bare phonon, predominantly phonon, and predominantly d-mon modes, respectively; and $\left[\frac{1}{2} \frac{\partial \ln \bar{\omega}_+ \bar{\omega}_-}{\partial \ln \bar{\omega}_0} \right]$ is the quenching factor,

Q . The expression for Q in the two-frequency model 6.26 is

$$Q = \frac{1}{2} \frac{2\bar{\omega}_0 \omega_{\mu\nu}}{\bar{\omega}_0 \omega_{\mu\nu} - |\lambda|^2} \quad 6.29,$$

which shows how the isotope effect is influenced by the appearance of low frequency electronic transitions: for $\omega_{\mu\nu}$ very large (a simple metal) $Q \sim 1$, whereas if $\omega_{\mu\nu} \sim \bar{\omega}_0$, Q is less than one and may even be negative. Certainly quenching

is in accord with experiment, but a negative isotope effect has not been reported. Nor is it clear that when strong coupling effects and more than one d-mon frequency are included the negative Q survives.

CHAPTER VII
PROPAGATORS IN A SUPERCONDUCTOR

The theory of conserving approximations with screening can be developed in terms of the transpose of the exact one-particle propagator,

$$\begin{aligned}\bar{G}_1(1', 1) &\equiv \frac{1}{i} \langle T[\psi^+(1')\psi(1)] \rangle \\ &= -G_1(1, 1')\end{aligned}\quad 7.1.$$

Nambu (N 60) noticed that these two equivalent forms could be put together in terms of two-component field operators:

$$\Psi(\underline{x}, t, \sigma) = \Psi(x) = \begin{pmatrix} \psi(\underline{x}, t, \sigma) \\ \psi^+(\underline{x}, -t, -\sigma) \end{pmatrix} \quad 7.2a;$$

$$\Psi^+(\underline{x}, t, \sigma) = \Psi^+(x) = [\psi^+(\underline{x}, t, \sigma), \psi(\underline{x}, -t, -\sigma)] \quad 7.2b.$$

The one particle propagator for this field is the 2x2 matrix

$$\underline{G}_1(1, 1') \equiv \frac{1}{i} \begin{pmatrix} \langle T[\psi(\underline{x}_1', t_1', \sigma)\psi^+(\underline{x}_1, t_1, \sigma)] \rangle, \\ \langle T[\psi(\underline{x}_1', t_1', \sigma)\psi(\underline{x}_1, -t_1, -\sigma)] \rangle \\ \langle T[\psi^+(\underline{x}_1', -t_1', -\sigma)\psi^+(\underline{x}_1, t_1, \sigma)] \rangle, \\ \langle T[\psi^+(\underline{x}_1', -t_1', -\sigma)\psi(\underline{x}_1, -t_1, -\sigma)] \rangle \end{pmatrix}$$

$$= \begin{pmatrix} G_1(1,1')_{\sigma\sigma}, & F_1(1,1')_{\sigma,-\sigma} \\ F_2(1,1')_{\sigma,-\sigma}, & -\bar{G}_1(1',1)_{-\sigma,-\sigma} \end{pmatrix}$$

7.3a.

If the statistical operator commutes with the number operator at the thermodynamic limit, the off-diagonal elements of 7.3a vanish. However, the equation of motion for $\underline{G}_1$ in a Φ -derivable approximation admits solutions in which the F's are non-zero. Two remarks greatly simplify the presentation of conserving approximations for $\underline{G}_1$. First, the two component field is associated with a representation of the electronic charge by the matrix

$$e \begin{pmatrix} 1, & 0 \\ 0, & -1 \end{pmatrix} = e \underline{1}^3.$$

Secondly, the F's are related by the symmetry relation

$$F_1(1,1')_{\sigma,-\sigma} = F_2(1,1')_{-\sigma,\sigma}^*,$$

which follows from the relation between the matrix elements of the field operator ψ and its adjoint ψ^+ . Then the equation of motion for $\underline{G}_1$ takes the form

$$\begin{aligned} \left[\frac{\hbar}{i} \frac{\partial}{\partial t} - \frac{\hbar^2}{2m} \nabla_1^2 + U_{BG}(\underline{x}_1) - \mu \right] \underline{G}_1(1,1') &= \underline{1} \delta(1-1') \\ &- \frac{1}{i} \int e \underline{1}^3 V(1,2) e \underline{1}^3 \langle T[\psi^+(2)\psi(2) \psi(1)\psi^+(1')] \rangle \end{aligned}$$

7.3b,

where the appearance of the electric charge appears explicitly in the pair potential. A solution of 7.3b in the

form

$$\begin{aligned} & \left[\frac{\hbar}{i} \frac{\partial}{\partial t} - \frac{\hbar^2}{2m} \nabla_1^2 + U_{BG}(\underline{x}_1) - \mu \right] \underline{G}_1(1, 1') \\ & = \underline{1} \delta(1-1') - \int \underline{M}(1, \bar{2}; \underline{G}, V_S) \underline{G}(\bar{2}, 1') \end{aligned}$$

is conserving if the self energy functional $\underline{M}[\underline{G}, V_S]$ is Ψ -derivable in the following sense. Given a Ψ -derivable approximation for the one-component case,

$$M(n, n') = \frac{\delta \Psi}{\delta G_1(n, n')} ,$$

the corresponding $\underline{M}(n, n')$ is obtained from M by replacing each vertex e by $e \underline{1}_3$ and each propagator G_1 by $\underline{G}_1$. The simplest approximation for $\underline{M}$ is therefore

$$\underline{M}(1, 1') = e \underline{1}_3 \frac{1}{i} V_S(1, 1') \underline{G}(1, 1') e \underline{1}_3 \quad 7.4.$$

Nambu's equation (S 64) is derived from this approximation.

The appearance of finite off-diagonal elements F can be related to pairing by considering a model Hamiltonian, $\hat{H}_M$, in which pairing terms appear explicitly:

$$\begin{aligned} \hat{H}_M = & \sum_{\sigma} \int d^3x \psi^+(\underline{x}\sigma) \left[-\frac{\hbar^2}{2m} \nabla^2 \right] \psi(\underline{x}\sigma) \\ & + \frac{1}{2} \sum_{\sigma} \int d^3x_1 d^3x_2 [\Delta(\underline{x}_1, \underline{x}_2) \psi^+(\underline{x}, \sigma) \psi^+(\underline{x}_2, -\sigma) \\ & + \Delta^*(\underline{x}_1, \underline{x}_2) \psi(\underline{x}_2, -\sigma) \psi(\underline{x}_1, \sigma)] \end{aligned} \quad 7.5,$$

where $\Delta(\underline{x}_1, \underline{x}_2)$ is a pairing amplitude, antisymmetric in $(\underline{x}_1, \underline{x}_2)$. The equation of motion for the field operators under the action of Hamiltonian $\hat{H}_M$ is

$$\begin{aligned}
[\hat{H}_M, \begin{pmatrix} \psi(\underline{y}, \tau) \\ \psi^+(\underline{y}, -\tau) \end{pmatrix}]_- &= [\hat{H}_M, \Psi(\underline{y}, \tau)]_- \\
&= \int d^3x \begin{pmatrix} \frac{\hbar^2}{2m} \nabla_y^2 \delta(\underline{y}, -\underline{x}), -\Delta(\underline{y}, \underline{x}) \\ \Delta^*(\underline{y}, \underline{x}), \frac{\hbar^2}{2m} \nabla_y^2 \delta(\underline{y}, -\underline{x}) \end{pmatrix} \begin{pmatrix} \psi(\underline{x}, \tau) \\ \psi^+(\underline{x}, -\tau) \end{pmatrix}
\end{aligned}$$

7.6,

and since $\hat{H}_M$ is not diagonal for the two-component field operator Ψ , its associated Green's function is not diagonal.

The tunnelling experiments cited by Schrieffer (S 64) which reveal so dramatically the rôle of phonons in establishing the superconducting state of simple metals may be used to search for d-mon effects in transition metals. The interpretation of such experiments depends on the fact that the single-particle tunnelling current across a metal-insulator-superconductor junction is proportional the spectral density for G_{11} at frequency $\omega = \frac{eV}{\hbar}$, where V is the potential difference for the junction. The source of phonon effects in the $G_{11}(\omega)$ spectrum is the spectral density for V_s in approximation 7.4. Since d-mon effects also appear in the spectral density for V_s , their effect on tunnelling should be very similar to that of phonons.

It is by no means clear that approximation 7.4 is accurate: higher order approximations for $\underline{M}$ may contribute additional spectral effects observable in tunnelling.

However, the strong correlation between experimental tunnelling data and inelastic scattering data for simple metals serves to suggest that the additional spectral effects are small. Theoretically, the corrections to 7.4 involve making a vertex correction

$$M(1,1') = \frac{1}{i} \int V_S(1,\bar{2}) G(1,\bar{2}') \Lambda(\bar{2},\bar{2}'; 1')$$

before changing to the two-component field. For a simple model of a metal Migdal (M58) has shown that corrections to Λ are of order electron mass $\div$ nuclear mass.

The experimental evidence cited in Chapter III for charge density propagation at other than phonon frequencies does not establish unambiguously that d-mon effects are present in tantalum and thallium. First, impurity effects have not been precluded strictly; secondly, vertex corrections for a complicated metal need not strictly comply with Migdal's model. More detailed observations are needed; and those observations which would bear most heavily on the question of whether d-mon effects are important are outlined in the conclusion.

Nothing has been said about the coupling of charge density modes to Bloch electron states. It is difficult to make a rigorous analysis of such coupling, but two facts suggest that the coupling to mixed phonon-d-mon modes is not very different from electron-phonon coupling in simple metals. The first is that electron-phonon coupling does not vary by more than an order of magnitude in differ-

ent simple metals with different rigid ion cores: hence, a deformable core 'intermediate' between two closed shell 'rigid' cores is expected to have electron-mixed-mode coupling similar to the rigid cores whose electron numbers bracket the number of electrons on the deformable core. Secondly, the plasma model of a metal described, for example, by Pines (P 63) has electron-plasmon coupling $\sim g_{ep} \cdot (\frac{\omega_o}{\omega_D})^{1/2}$ where g_{ep} is the average electron-ion matrix element, ω_o is the plasmon frequency and ω_D is a Debye frequency for ionic vibrations. If the d-mon frequencies are taken to be 'plasmons with atomic correlations incorporated', and $\omega_o = \omega_{\mu\nu}$ is only a few times greater than ω_D , then the electron-d-mon coupling does not differ by more than an order of magnitude from typical electron-ion coupling terms.

CHAPTER VIII

CONCLUSIONS

In one sense at least, d-mon effects have already been observed in the spin-spin correlation function of a ferromagnet both above and below the curie temperature by inelastic neutron scattering (for example, Lowde et al. (Lo67)). The atomic interpretation of this type of data is coupling of a spin-carrying $\underline{k}$ -independent d-mon to a $\underline{k}$ -dependent phonon. However, the d-mons with which we are concerned here do not carry spin.

The quenching of the isotope effect, and the tunnelling data for tantalum and thallium have natural explanations in the theory of plasma-like d-mons in the spectral form for V_s , but the following extra experimental information would be very helpful.

First, careful monitoring of impurity content in tunnelling experiments on different samples of tantalum and thallium. Secondly, corresponding experiments on rare earth superconductors: the unfilled f-shell should admit d-mon propagation at even lower frequencies than transition metals.

Unfortunately transition metals are usually con-

taminated with chemically similar metals in the same transition group. It is therefore possible that even sample-independent tunnelling structure may result from localized vibrational modes in the phonon density of states for an impure metal with light, chemically similar impurities which persist through all stages of purification.

Fortunately transition metals are often type II superconductors which admit magnetic fields into the bulk of the metal. Tunnelling into a transition metal in the presence of a magnetic field should reveal whether observed frequencies come from impurities or from d-mons. The nuclear vibrations of impurities change very little in a magnetic field. On the other hand, the electronic multiplets with electron-number νA are split approximately as an atomic multiplet is split in the Zeeman effect. Because the magnetic field in a superconductor is highly inhomogeneous, electronic multiplets on different atomic sites are split into different Zeeman levels. Therefore, the oscillator strength of a d-mon is distributed over one range of frequencies around the ionic transition frequency of an unmagnetized ion: such a spreading of oscillator strengths should be observable at high flux densities if the oscillator frequencies for charge density fluctuations contain an appreciable d-mon contribution. The predominantly d-mon frequencies should be smeared by a magnetic

field.

Besides tunnelling, there may be other experiments which would yield information on the spectral density associated with the inverse permittivity. The passage of charged particles through metals, and the microwave optical properties of transition metals might bear examination in the atomic picture.

APPENDIX 1

CONSISTENT APPROXIMATIONS IN THE THEORY OF SCREENING

The equation of motion 4.6 can be written in the form

$$\int G_0^{-1}(1, \bar{2}) G(\bar{2}, 1'; u) = \delta(1-1') - \int u(1, \bar{2}) G(\bar{2}, 1') - \int \Sigma(1, \bar{2}) G(\bar{2}, 1')$$

where $G_0^{-1}(1, 2) \equiv \left[\frac{\hbar}{i} \frac{\partial}{\partial t_1} - \frac{\hbar^2}{2m} \nabla_1^2 + U_{BG}(\underline{x}_1) \right] \delta(1, 2)$

and Σ is a functional of G and V A1.1.

By defining the inverse of the generating functional as

$$\int G^{-1}(1, \bar{2}) G(\bar{2}, 1') \equiv \delta(1-1'),$$

the following expression for the self-energy functional is obtained:

$$G^{-1}(1, 2) = G_0^{-1}(1, 2) + \Sigma(1, 2) + u(1, 2) \quad \text{....A1.2.}$$

Following Kadanoff and Baym (KB 61), the linear response function L is defined by

$$L(1, 2; 1', 2') \equiv \lim_{u \rightarrow 0} \frac{\delta G(1, 1'; u)}{\delta u(2, 2')} ;$$

and by using the generating property of the functional G ,

$$\lim_{u \rightarrow 0} \frac{\delta^{n-1}}{\delta u(2,2') \delta u(3,3') \dots \delta u(n,n')} G(1,1'; u) \\ = G_n(2,3,\dots,n,1; 2',3',\dots,n',1'),$$

$$L \text{ can be written } L(1,2; 1',2') = G_2(1,2; 1',2')$$

$$= G_1(1,1') G_1(2,2') \dots \text{Al.3.}$$

Kadanoff and Baym showed that an approximation $G_2 = G_2[G_1]$ is conserving iff $G_2(1,2; 1',2') = G_2(2,1; 2',1')$. By virtue of Al.3, this condition may be taken as a symmetry requirement on L,

$$L(1,2; 1',2') = L(2,1; 2',1') \dots \text{Al.4.}$$

The equation of motion for L follows from

$$\frac{\delta \Sigma(1,1')}{\delta u(2,2')} = \int \frac{\delta \Sigma(1,1')}{\delta G(\bar{3},\bar{3}')} \frac{\delta G(\bar{3},\bar{3}')}{\delta u(2,2')} \dots \text{Al.5.}$$

Substituting Al.2 on the left-hand side of Al.5, and the definition of L on the right-hand side,

$$-\delta(1-2)\delta(1'-2') - \frac{\delta G^{-1}(1,1')}{\delta u(2,2')} = \int \frac{\delta \Sigma(1,1')}{\delta G(\bar{3},\bar{3}')} L(\bar{3},2; \bar{3}',2').$$

$$\text{Now using } \delta G^{-1}(1,1') = - \int G^{-1}(1,\bar{2}) \delta G(\bar{2},\bar{2}') G^{-1}(\bar{2}',1') \\ \dots \text{Al.6,}$$

$$-\delta(1-2)\delta(1'-2') + \int \bar{G}^{-1}(1,\bar{3}) L(\bar{3},2; \bar{3}',2') G^{-1}(\bar{3}',1') \\ = \int \frac{\delta \Sigma(1,1')}{\delta G(\bar{3},\bar{3}')} L(\bar{3},2; \bar{3}',2'),$$

or more compactly

$$\int L^{-1}(1, \bar{3}; 1', \bar{3}') L(\bar{3}, 2; \bar{3}', 2') \equiv \int \{G^{-1}(1, \bar{3}) G^{-1}(\bar{3}', 1') - \frac{\delta \Sigma(1, 1')}{\delta G(\bar{3}, \bar{3}')} \} L(\bar{3}, 2; \bar{3}', 2') = \delta(1-2) \delta(1'-2') \quad \dots \text{Al.7.}$$

Clearly L satisfies the symmetry requirement Al.4 if L^{-1} does, which allows Al.4 to be expressed in the form

$$\frac{\delta \Sigma(1, 1')}{\delta G(3, 3')} = \frac{\delta \Sigma(3, 3')}{\delta G(1, 1')},$$

an irrotationality condition which implies the existence of a closed functional $\Phi[G]$ such that

$$\Sigma(1, 1') = \frac{\delta \Phi[G]}{\delta G(1, 1')} \quad \dots \text{Al.8.}$$

As a check on the method, we note that Abrikosov, Gor'kov and Dzyaloshinski (AGD 63) have been able to prove the Ward-Pitaevski identities starting from a constraint of the form Al.8.

For a theory with screening, we consider the case $u(1, 1') = u(1) \delta(1-1')$ and define

$$\begin{aligned} w(1) &\equiv u(1) + \Sigma_H(1, 1; u) - \Sigma_H(1, 1; 0) \\ K(1, 1') &\equiv \frac{\delta w(1')}{\delta u(1)} \quad \dots \text{Al.9} \\ V_s(1, 1') &\equiv \int V(1, \bar{2}) \frac{\delta w(1')}{\delta u(\bar{2})} \end{aligned}$$

Under this change of variable, the equation of motion for G becomes

$$\int G_O^{-1}(1, \bar{2}) G(\bar{2}, 1') = \delta(1-1') - w(1) G(1, 1') - \int \Sigma_H(1, \bar{2}; 0) G(\bar{2}, 1') \\ - \frac{1}{i} \int V(1, \bar{2}) \frac{\delta w(\bar{3})}{\delta u(2)} \frac{\delta}{\delta w(\bar{3})} G(1, 1') \quad \dots A1.10.$$

By defining

$$G_O^{-1}(1, 1'; w) \equiv G_O^{-1}(1, 1') - w(1) \delta(1, 1') \\ M(1, 2; w) \equiv \frac{1}{i} \int V_S(1, \bar{3}) \frac{\delta}{\delta w(\bar{3})} \delta(1, 2) \quad \dots A1.11,$$

A1.10 can be written in the form

$$\int G_O^{-1}(1, \bar{2}; w) G(\bar{2}, 1') = \delta(1-1') - \int \Sigma_H(1, \bar{2}; 0) G(\bar{2}, 1') \\ - \int M(1, \bar{2}; w) G(\bar{2}, 1') \quad \dots A1.12.$$

Comparing with the definition of G^{-1} ,

$$G_O^{-1}(1, 2; w) + \Sigma_H(1, 2; 0) + M(1, 2; w) = G^{-1}(1, 2; w) \quad \dots A1.13;$$

and because $\lim_{u \rightarrow 0} w = 0$, the limits of A1.13 and A1.2 are equal,

$$\Sigma(1, 1'; 0) = \Sigma_H(1, 1'; 0) + M(1, 1'; 0) \quad \dots A1.14.$$

The introduction of quantities Λ and Q allows A1.10 to be written as a system of equations:

$$\Lambda(1, 1'; 2) = - \frac{\delta G^{-1}(1, 1'; w)}{\delta w(2)} \quad \dots A1.15. \\ Q(1, 1') = i \frac{\delta G(1, 1^+)}{\delta w(1')}$$

First, M defined in A1.11 is written

$$\begin{aligned} M(1,2) &= \frac{1}{i} \int V_S(1,\bar{3}) \frac{\delta}{\delta w(\bar{3})} G^{-1}(1,\bar{4}) G(\bar{4},2) \\ &= \int V_S(1,\bar{3}) \Lambda(1,\bar{4}; \bar{3}) G(\bar{4},2) \quad \dots \text{A1.16a.} \end{aligned}$$

Secondly, A1.6 gives the relation between Q and Λ from A1.15,

$$\begin{aligned} Q(1,1') &= -i \int G(1,\bar{2}) \frac{\delta G^{-1}(\bar{2},\bar{2}')}{\delta w(1')} G(\bar{2}',1') \\ &= \int G(1,\bar{2}) \Lambda(\bar{2},\bar{2}'; 1') G(\bar{2}',1') \quad \dots \text{A1.16b.} \end{aligned}$$

Finally, V_S can be written, using A1.9, as

$$V_S(1,1') = V(1,1') + \int V(1,\bar{2}) Q(\bar{2},\bar{2}') V_S(\bar{2}',1') \quad \dots \text{A1.16c.}$$

The system A1.16 contains three equations and four unknown functionals of G , clearly a situation calling for a further constraint. The method of approximation which we use begins by regarding V_S as a fixed function.

We then ask what constraints on $M[G]_{V_S \text{ fixed}}$ give a Φ -derivable approximation to Σ via A1.14.

The question can be answered quite simply through the intermediary of a quasi-linear response function $\mathcal{L}$,

$$\mathcal{L}(1,2; 1',2') \equiv \frac{\delta G(1,1'; w)}{\delta w(2,2')} \quad \dots \text{A1.17,}$$

related to L by the equation

$$\mathcal{L}(1,2; 1',2') = \int \mathcal{L}(1,\bar{3}; 1',\bar{3}') \frac{\delta w(\bar{3},\bar{3}')}{\delta u(2,2')} , \text{ or using A1.9,}$$

$$L(1,2; 1',2') = \mathcal{L}(1,2; 1',2') + \int \mathcal{L}(1,\bar{3}; 1',\bar{3}') \frac{\delta \Sigma_H(\bar{3},\bar{3}')}{\delta G(\bar{4},\bar{4}')} \\ L(\bar{4},2; \bar{4}',2').$$

By introducing the inverse $\mathcal{L}^{-1}$, the relation between $\mathcal{L}$ and L becomes

$$\int \left\{ \mathcal{L}^{-1}(1,\bar{3}; 1',\bar{3}') - \frac{\delta \Sigma_H(1,1')}{\delta G(\bar{3},\bar{3}')} \right\} L(\bar{3},2; \bar{3}',2') \\ = \delta(1-2)\delta(1'-2') \quad \dots \text{Al.18.}$$

Recalling that an approximation is conserving if L obeys the symmetry constraint Al.4, a sufficient condition for a conserving approximation is clearly

$$\mathcal{L}^{-1}(1,3; 1',3') = \mathcal{L}^{-1}(3,1; 3',1') \quad \dots \text{Al.19.}$$

To establish an equation of motion for $\mathcal{L}$, definition Al.17 is written

$$\mathcal{L}(1,2; 1',2') = - \int G(1,\bar{3}) \frac{\delta G^{-1}(\bar{3},\bar{3}')}{\delta w(2,2')} G(\bar{3}',1');$$

and with the aid of Al.11 and Al.13,

$$\mathcal{L}(1,2; 1',2') = G(1,2)G(1',2') + \int G(1,\bar{3}) \frac{\delta M(\bar{3},\bar{3}')}{\delta w(2,2')} G(\bar{3}',1') \\ = G(1,2)G(1',2') + \int G(1,\bar{3}) \frac{\delta M(\bar{3},\bar{3}')}{\delta G(\bar{4},\bar{4}')} G(\bar{3}',1') \\ \mathcal{L}(\bar{4},2; \bar{4}',2').$$

By performing convolutions with G^{-1} , the equation of motion for $\mathcal{L}$ becomes

$$\int \mathcal{L}^{-1}(1, \bar{3}; 1', \bar{3}') \mathcal{L}(\bar{3}, 2; \bar{3}', 2') = \delta(1-2) \delta(1'-2')$$

where

$$\mathcal{L}^{-1}(1, 3; 1', 3') \equiv G^{-1}(1, 3) G^{-1}(1', 3') - \left. \frac{\delta M(1, 1')}{\delta G(3, 3')} \right|_{V_S \text{ const}}$$

.... A1.20.

The symmetry requirement A1.19 is satisfied if

$$\left. \frac{\delta M(1, 1')}{\delta G(3, 3')} \right|_{V_S} = \left. \frac{\delta M(3, 3')}{\delta G(1, 1')} \right|_{V_S}, \text{ an irrotationality condition}$$

implying the existence of a closed functional $\Psi[G, V_S]$ such that

$$M(1, 1') = \frac{\delta \Psi}{\delta G(1, 1')} \quad \text{.... A1.21.}$$

Because the variational derivative above is linear, the asymptotic relation A1.14 can be written formally as

$$\lim_{u_f, w \rightarrow 0} \frac{\delta}{\delta G(1, 1')} \{ \Phi = \Phi_H[G, V] + \Psi[G, V_S] \} \quad \text{.... A1.22.}$$

The relation between A1.22 and the expansion of free energy in perturbation theory can be understood in the language of skeleton diagrams (No 62). The rules must take account of the possibility of double counting the Hartree contribution Φ_H to the total. We therefore remove the Hartree term from an expansion of the free energy before skeletizing:

(i) shrink the subdiagrams, which can be disconnected from a given diagram by cutting a fermion line in two places, to a point;

(ii) shrink the subdiagrams, which can be disconnected from a given diagram by cutting an interaction line in two places, to a point;

(iii) remove the Hartree term from $F - F_0 = \Sigma \text{diag}[G_1^{(0)}, V]$;

(iv) sum over the contracted (skeleton) diagrams, replacing each $G_1^{(0)}$ by a G , and each V by a V_s .

A more complete description of the effect of this prescription on the Hartree term is given in Chapter IV.

APPENDIX 2

SECOND QUANTIZED OPERATORS

Second quantization of the Schrodinger field was first described by Fock (F 32); modern accounts are given by Berezin (Be 66), Schweber (Sc 61) and Kastler (Ka 61, Chapter 3). Following the treatment of the latter author, we devote this appendix to a description of configuration space H and the field operators ψ^+ , ψ which act upon it. The purpose is twofold: (i) to introduce notation and terminology free from ambiguity; (ii) to distinguish between kinematical and dynamical aspects of second-quantized fields.

Symbols Ω and σ denote respectively the three-dimensional Euclidean space associated with the volume of the crystal and the two dimensional Hilbert space spanned by $s_z = \pm 1/2$ spin wavefunctions of an electron. The n -tuples of $(\underline{x}, s) \in (\Omega \times \sigma)$ are denoted $(\underline{x}_1 s_1, \underline{x}_2 s_2, \dots, \underline{x}_n s_n) \in (\Omega \times \sigma)^{x_n}$ and by assumption the 0-tuple is the field K of complex numbers. The infinitely differentiable functions $f_n: (\Omega \times \sigma)^{x_n} \rightarrow K$ for any fixed n form a vector space, H_n , with the following definitions:

(i) addition of elements, $(f_n + g_n)(\underline{x}_1 s_1, \dots, \underline{x}_n s_n) \equiv f_n(\underline{x}_1 s_1, \dots, \underline{x}_n s_n) + g_n(\underline{x}_1 s_1, \dots, \underline{x}_n s_n);$

(ii) scalar multiplication by $\lambda \in K$, $(\lambda f_n)(\underline{x}_1 s_1, \dots, \underline{x}_n s_n) \equiv \lambda f_n(\underline{x}_1 s_1, \dots, \underline{x}_n s_n)$;

(iii) the zero function 0_n has value $0 \in K$ for all values of its arguments;

(iv) the inner product $(f_n, g_n) \equiv \sum_{s_1 s_2 \dots s_n} \int d^3 x_1 d^3 x_2 \dots d^3 x_n f_n(\underline{x}_1 s_1, \dots, \underline{x}_n s_n) g(\underline{x}_1 s_1, \dots, \underline{x}_n s_n)$.

.... A2.1.

The space H_n carries a representation of the permutation group of n objects, S_n , representing $\pi \in S_n$ according to $\pi \cdot f_n(\underline{x}_1 s_1, \underline{x}_2 s_2, \dots, \underline{x}_n s_n) \equiv f_n(\underline{x}_{\pi(1)} s_{\pi(1)}, \underline{x}_{\pi(2)} s_{\pi(2)}, \dots,$

$\underline{x}_{\pi(n)} s_{\pi(n)})$ A2.2.

Denoting the signature of π by $\chi(\pi)$, the idempotent A_n ,

$$A_n \equiv \frac{1}{n!} \sum_{\pi \in S_n} \chi(\pi) \pi \quad \dots A2.3,$$

can be represented on H_n , and has eigenvalue +1 or 0. (The former only when f_n is antisymmetric in all pairs of its n arguments.)

The configuration space H of Fock is the direct sum of all H_n 's, $H = \bigoplus_{n=0}^{\infty} H_n$, defined as follows: elements of H are sequences whose members are non-zero at only a finite number of places, $f = (f_0, f_1, \dots, f_n, \dots)$, $f_n \in H_n$

.... A2.4a ;

addition and scalar multiplication are defined as in H_n , component by component; the zero sequence is the sequence of zero functions $(0, 0_1, 0_2, \dots)$; and the inner product is

$$(f, g) \equiv f_0 * g_0 + \sum_{n=1}^{\infty} (f_n, g_n) \quad \dots A2.4b .$$

Space H_n can be embedded in H by the mapping j_n ,

$$j_n: H_n \rightarrow H, \quad j_n(f_n) = (0, 0_1, 0_2, \dots, 0_{n-1}, f_n, 0_{n+1}, \dots) \quad \dots \text{A2.5} ;$$

and we can define an antisymmetrizer $\hat{A}$ such that

$$\hat{A} j_n(f_n) = j_n(A_n f_n), \quad A f = (f_0, f_1, A_2 f_2, \dots, A_n f_n, \dots) \quad \dots \text{A2.6.}$$

Anticipating that n -particle wavefunctions should belong to

H_n , we introduce a number operator N by

$$N f = (0, f_1, 2f_2, 3f_3, \dots, n f_n, \dots) \quad \dots \text{A2.7}$$

$$\zeta(N) f = (\zeta(0) f_0, \zeta(1) f_1, \zeta(2) f_2, \dots, \zeta(n) f_n, \dots)$$

where ζ is a function expressible as a power series.

Using the distribution $\delta(\underline{x} - \underline{x}')$, the operator-valued distributions P and C are defined on H by

$$P(\underline{x}s) f = (0, P(\underline{x}s) f_0, P(\underline{x}s) f_1, \dots, P(\underline{x}s) f_{n-1}, \dots) \quad \dots \text{A2.8a}$$

$$C(\underline{x}s) f = (C(\underline{x}s) f_1, C(\underline{x}s) f_2, C(\underline{x}s) f_3, \dots, C(\underline{x}s) f_{n+1}, \dots) \quad \dots \text{A2.8b}$$

where the product distribution P and the contraction distribution C are defined to be

$$\begin{aligned} P: H_n \rightarrow H_{n+1}, \quad P(\underline{x}s) f_n(\underline{x}_2 s_2, \dots, \underline{x}_{n+1} s_{n+1}) \Big|_{\underline{x}_1 s_1} \\ \equiv \delta_{s s_1} \delta(\underline{x} - \underline{x}_1) f_n(\underline{x}_2 s_2, \dots, \underline{x}_{n+1} s_{n+1}) \quad \dots \text{A2.9a} \end{aligned}$$

$$\begin{aligned} C: H_n \rightarrow H_{n-1}, \quad C(\underline{x}s) f_n(\underline{x}_1 s_1, \dots, \underline{x}_n s_n) \\ \equiv \sum_{s_1} \int d^3 x_1 \delta_{s s_1} \delta(\underline{x} - \underline{x}_1) f_n(\underline{x}_1 s_1, \dots, \underline{x}_n s_n) \quad \dots \text{A2.9b.} \end{aligned}$$

The product and contraction are bona fide operators on H only after 'smoothing' with a test function $g(\underline{x}s) \in H_1$:

$$\begin{aligned}
P(g) &\equiv \int d^3x \, g(\underline{x}s) P(\underline{x}s), \quad P(g) f_n(\underline{x}_2 s_2, \dots, \underline{x}_{n+1} s_{n+1}) \\
&= g(\underline{x}_1 s_1) f_n(\underline{x}_2 s_2, \dots, \underline{x}_{n+1} s_{n+1}) \quad \dots \text{A2.10a}
\end{aligned}$$

$$\begin{aligned}
C(g) &\equiv \int d^3x \, g(\underline{x}s) C(\underline{x}s), \quad C(g) f_n(\underline{x}_1 s_1, \dots, \underline{x}_n s_n) \\
&= \int d^3x_1 g(\underline{x}_1 s_1) f_n(\underline{x}_1 s_1, \dots, \underline{x}_n s_n) \quad \dots \text{A2.10b}
\end{aligned}$$

The following commutation relations between $\hat{A}$, P , C , and $\zeta(N)$ can easily be verified:

$$\zeta(N) \hat{A} - \hat{A} \zeta(N) = 0 \quad \dots \text{A2.11a}$$

$$\zeta(N) P(\underline{x}s) - P(\underline{x}s) \zeta(N+1) = 0 \quad \dots \text{A2.11b}$$

$$\zeta(N+1) C(\underline{x}s) - C(\underline{x}s) \zeta(N) = 0 \quad \dots \text{A2.11c}$$

From definitions A2.7 and A2.9, for $f \in j_n(H_n)$

$$\begin{aligned}
(n+1) \hat{A} C(\underline{x}s) \hat{A} \hat{A} P(\underline{x}' s') \hat{A} f + n \hat{A} P(\underline{x}' s') \hat{A} \hat{A} C(\underline{x}s) \hat{A} f \\
= \delta_{ss'}, \delta(\underline{x} - \underline{x}') \hat{A}
\end{aligned}$$

which can readily be extended to the whole of H ,

$$\begin{aligned}
\hat{A} C(\underline{x}s) \hat{A}^2 P(\underline{x}' s') \hat{A} (N+1) + \hat{A} P(\underline{x}' s') \hat{A}^2 C(\underline{x}s) \hat{A} (N) \\
= \delta_{ss'}, \delta(\underline{x} - \underline{x}') \hat{A}.
\end{aligned}$$

This last operator equality on H takes the form of the canonical anticommutation relations

$$[\psi(\underline{x}, s), \psi^+(\underline{x}' s')]_+ = \delta_{ss'}, \delta(\underline{x} - \underline{x}') \hat{A} \quad \dots \text{A2.12a}$$

$$\begin{aligned}
[\psi^+(\underline{x}s), \psi^+(\underline{x}' s')]_+ = [\psi(\underline{x}s), \psi(\underline{x}' s')]_+ = 0 \\
\dots \text{A2.12b}
\end{aligned}$$

on H if the field operators ψ , ψ^+ are defined by

$$\psi(\underline{x}s) \equiv \hat{A} C(\underline{x}s) \hat{A}^{-1} N^{1/2} = (N+1)^{1/2} \hat{A} C(\underline{x}s) \hat{A}^{-1} \dots A2.13a$$

$$\psi^+(\underline{x}'s') \equiv N^{1/2} \hat{A} P(\underline{x}'s') \hat{A}^{-1} = \hat{A} P(\underline{x}'s') \hat{A}^{-1} (N+1)^{1/2}$$

.... A2.13b

The definition A2.13 is not the only way of obtaining relations A2.12 on a vector space. Indeed, A2.12 may be represented on spaces not isomorphic to H . The relevance of these representations inequivalent to A2.13 on H is debatable, and we explicitly avoid saying more than that H and A2.13 define a particular representation of A2.12.

The construction of Fock space was contrived with the aim of describing systems containing an indefinite number of particles. A correspondence principle relating quantum-mechanical operators to second-quantized operators on H was devised in such a way that the second-quantized hamiltonian H acting on $j_n(H_n)C H$ coincides with the quantum-mechanical hamiltonian operator $H_{q.m}$ for a definite number of particles n . The correspondence principle for the limit $n \rightarrow \infty$ $H_{q.m}$ is summarized by:

- (i) for each one-particle operator $\sum_{i=1}^{N \rightarrow \infty} F_1(\underline{x}_i s_i)$ in $H_{q.m}$, put a term $\sum_s \int d^3x \psi^+(\underline{x}s) F_1(\underline{x}s) \psi(\underline{x}s)$ in H ;
- (ii) for any n -particle operators $\sum_{i_1=1}^{N \rightarrow \infty} \sum_{i_2 \neq i_1}^{N \rightarrow \infty} \dots$

$\sum_{i_n \neq i_{n-1} :: \dots \neq i_1}^{N \rightarrow \infty} F_n(\underline{x}_{i_1} s_{i_1}, \dots, \underline{x}_{i_n} s_{i_n})$ of $H_{q.m}$ put

$$\sum_{s_1} \sum_{s_2} \dots \sum_{s_n} \int d^3x_1 \dots \int d^3x_n \psi^+(\underline{x}_1 s_1) \psi^+(\underline{x}_2 s_2) \dots \psi^+(\underline{x}_n s_n)$$

$F_n(\underline{x}_1 s_1, \dots, \underline{x}_n s_n) \psi(\underline{x}_n s_n) \dots \psi(\underline{x}_1 s_1)$ in H .

It is usually supposed that practically all the dynamical features of a system may be obtained from a truncated Hamiltonian with no operators for $n \geq 3$. For example, the truncated Hamiltonian for a system of electrons neutralized by a background potential U_{BG} is

$$\begin{aligned}
 H = & \sum_s \int d^3x \, \psi^\dagger(\underline{x}s) \left\{ -\frac{\hbar^2}{2m} \nabla^2 + U_{BG}(\underline{x}) \right\} \psi(\underline{x}s) \\
 & + \frac{1}{2} \sum_{ss'} \int d^3x \int d^3x' \, \psi^\dagger(\underline{x}s) \psi^\dagger(\underline{x}'s') V(\underline{x}s, \underline{x}'s') \psi(\underline{x}'s') \psi(\underline{x}s) \\
 & \dots \text{A2.14}
 \end{aligned}$$

The use of a truncated Hamiltonian, whether classical, quantum-mechanical or second-quantized, to estimate the time evolution of states is a dynamical postulate. In solid state physics, the usual way of handling a Hamiltonian such as A2.14 is through the single-particle picture: the elements $f_1 \in H_1$, over which $\psi^\dagger, \psi$ are tested, are solutions of the Schrodinger equation for a single particle moving in the potential U_{BG} . Single-particle dynamics can be described on any Fock space H , and does not depend on the choice of basis for H_n , $n > 1$.

Kinematical postulates refer to the limiting behaviour of bases $\{f_n^{(p)}\}_{p=1}^\infty$ for spaces H_n . An example of such a postulate is the asymptotic condition of Lehmann Symanzik and Zimmermann (LSZ 55) used in relativistic quantum field theory and described, for example, in a simple-minded way by Bjorken and Drell (BD 65). In Chapter V we introduce

an asymptotic condition: that in the limit of large atomic separation $f_n^{(p)}$ are linear combinations of n -particle states of ions in a vanishingly small crystal field.

The introduction of bases $\{f_n^{(p)}\} \subset H_n$ allows any operator defined on H to be expanded in terms of a set $\{X\}$ of basic operators defined by

$$X^{mp,nq} \equiv |m,p\rangle\langle n,q| \quad \dots A2.15$$

which act on elements of H according to

$$X^{mp,nq} f' = |m,q\rangle \sum_{s_1 s_2 \dots s_n} \int d^3 x_1 \dots d^3 x_n f_n^{(p)*}(\underline{x}_1 s_1 \dots \underline{x}_n s_n) f'_n(\underline{x}_1 s_1, \dots, \underline{x}_n s_n) \quad \dots A2.16$$

The expansion of an operator $\hat{O}$ defined on H takes the form

$$\hat{O} = \sum_{mp} \sum_{nq} |mp\rangle\langle mp| \hat{O} |nq\rangle\langle nq| = \sum_{mp,nq} (mp|\hat{O}|nq) X^{mp,nq} \quad \dots A2.17$$

The expansion can also be performed for an operator-valued distribution such as ψ^+ :

$$\psi^+(\underline{x}s) = \sum_{mp} \sum_{nq} (mp|N^{1/2} \hat{A} \delta_{ss'} \delta(\underline{x}-\underline{x}') \hat{A}|nq) X^{mp,nq} \quad \dots A2.18$$

$$\sum_{mp} \sum_{nq} (n+1)^{1/2} \delta_{m,n+1} (mp|A \delta_{ss'} \delta(\underline{x}-\underline{x}')|nq) X^{mp,nq}$$

Whenever the number operator N commutes with the Hamiltonian, any vector of $j_n(H_n) \subset H$, an eigenfunction of N , is a linear combination of eigenfunctions of H also in N . Thus the operator expansion A2.18 has the simplified form

$$\hat{H} = \sum_n (\sum_{p,q} (np|\hat{H}|nq) X^{np,nq}) \quad \dots A2.19.$$

A common way to obtain bases for H_n , $n \geq 2$, when a basis $[f_1^{(p)}]$ for H_1 is known is to use tensor products:

$$\begin{aligned} f_2^{(p_1 \times p_2)} \in H_2, f_2^{(p_1 \times p_2)}(\underline{x}_1 s_1, \underline{x}_2 s_2) \\ \equiv f_1^{(p_1)}(\underline{x}_1 s_1) f_1^{(p_2)}(\underline{x}_2 s_2) \\ f_n^{(p_1 \times \dots \times p_n)} \in H_n, f_n^{(p_1 \times \dots \times p_n)}(\underline{x}_1 s_1, \dots, \underline{x}_n s_n) \\ \equiv f_1^{(p_1)}(\underline{x}_1 s_1) \dots f_1^{(p_n)}(\underline{x}_n s_n) \end{aligned}$$

.... A2.20.

The action of A_n on tensors in H_n is

$$\begin{aligned} A_n f_n^{(p_1 \times \dots \times p_n)}(\underline{x}_1 s_1, \dots, \underline{x}_n s_n) \\ = \frac{1}{n!} \det[f_1^{(p_1)}(\underline{x}_1 s_1) \dots f_1^{(p_n)}(\underline{x}_n s_n)] \end{aligned}$$

.... A2.21

and the action $\psi^+(f_1^{(p)})$ is

$$\begin{aligned} (\psi^+(f_1^{(p)}) f_n^{(p_1 \times \dots \times p_n)})(\underline{x}s, \underline{x}_1 s_1, \dots, \underline{x}_n s_n) \\ = \sqrt{n+1} A f_1^{(p)}(\underline{x}s) \frac{1}{n!} \det[f_1^{(p_1)}(\underline{x}_1 s_1) \dots f_1^{(p_n)}(\underline{x}_n s_n)] \\ = \sqrt{n+1} \frac{1}{(n+1)!} \frac{n(n-1)!}{n!} \det[f_1^{(p)}(\underline{x}s) f_1^{(p_1)}(\underline{x}_1 s_1) \dots f_1^{(p_n)}(\underline{x}_n s_n)] \\ = \sqrt{n+1} A f_{n+1}^{(p \times p_1 \times \dots \times p_n)}(\underline{x}s, \underline{x}_1 s_1, \dots, \underline{x}_n s_n) \end{aligned}$$

.... A2.22.

The kinematical postulate leading to a self-consistent field theory of the Hartree-Fock type involves choosing a one-particle basis parametrized by an additional 'potential' added to the one-particle potential of the Hamiltonian. Then, for $n \geq 2$, variation principles in space of tensor products, for example $\delta(p_1 \times p_2 \times \dots \times p_n | H | q_1 \times \dots \times q_n)$ $= \delta_{p_1 q_1} \delta_{p_2 q_2} \dots \delta_{p_n q_n}$ where δ denotes variation of the additional 'potential', give tensor product bases for H_n whose elements are approximate eigenstates of H . There are many different approximation schemes of this type, variously emphasizing symmetry principles in the choice of linear combinations of tensors (Slater determinants) or machine facilities. In Chapter V, the general theory of the atomic picture common to all approximation schemes is studied; and for such a purpose exact n -particle eigenstates of H are postulated. Exact eigenstates lead to an even simpler form of A2.19,

$$\hat{H} = \sum_n (\sum_Q (n, Q | \hat{H} | n, Q) x^{nQ, nQ}) \quad \dots \text{A2.23}$$

where the capital Q labelling the state is a reminder that f_n^Q contains the exact n -body correlation effects.

APPENDIX 3

REPRESENTATIONS OF CRYSTALLOGRAPHIC SPACE GROUPS

Crystallographic space groups are of infinite order but because they possess finitely generated invariant abelian subgroups, their representation theory is straightforward.

The method of construction of representations relies on Frobenius' induction (Lo 59) from a one-dimensional representation of $\mathfrak{U}$, invariant abelian subgroup of lattice translations. These one-dimensional representations take the form

$$(\epsilon | R_{\underline{n}}) \rightarrow e^{i \underline{k} \cdot R_{\underline{n}}} \equiv \Delta_{\underline{k}}[(\epsilon | R_{\underline{n}})] \quad \dots A3.1,$$

where $\underline{k}$ is a three vector defined modul a reciprocal lattice vector.

The process of induction is described by Lomont (Lo 59) and in two collections of lecture notes:

G. W. Mackey, The Theory of Group Representations, Univ. of Chicago, 1955;

A. J. Coleman, Induced Representations with Applications to the Symmetric and Full Linear Groups, Uppsala Univ., 1963.

The process provides a route to the collection of all

irreducible representations of a crystallographic space group; and what follows is a sketch of the main features of the route.

Given a representation of $\mathcal{J}$, $\Delta_{\underline{k}}$, the representation defined by

$$(\epsilon | R_{\underline{n}}) \rightarrow \Delta_{\underline{k}}[(\alpha | t)(\epsilon | R_{\underline{n}})(\alpha | t)^{-1}] = \Delta_{\alpha^{-1}\underline{k}}[(\epsilon | R_{\underline{n}})] \quad \dots A3.2$$

for some $(\alpha | t) \in G$, the space group, is said to be G-conjugate to $\Delta_{\underline{k}}$. The collection of unitarily inequivalent representations in a G-conjugacy class is called the star of $\Delta_{\underline{k}}$, a typical member of the class.

The subgroup $G_{\underline{k}} \subset G$ for which $\Delta_{\alpha^{-1}\underline{k}} \stackrel{\sim}{=} \Delta_{\underline{k}}$ is called the group of the wave-vector $\underline{k}$, where ' $\stackrel{\sim}{=}$ ' denotes unitary equivalence. From A3.2, $G_{\underline{k}} \supset \mathcal{J}$ for all $\underline{k}$; and therefore any irreducible representation of $G_{\underline{k}}$, when restricted to $\mathcal{J}$, is a representation of $\mathcal{J}$. An irreducible representation of $G_{\underline{k}}$ with dimension m which under restriction gives the m -fold direct sum of $\Delta_{\underline{k}}$ is called allowable. The process of induction onto G from each irreducible allowable representation of $G_{\underline{k}}$ yields an irreducible representation of G ; and, moreover, inducing from only one $G_{\underline{k}}$ in every star yields every irreducible representation of G only once. Therefore, to display all irreducible representations of G , it is sufficient to construct irreducible allowable representations of $G_{\underline{k}}$.

The point group of the wave-vector $\underline{k}$, $P_{\underline{k}}$, is the collection of rotations (proper or improper) α for which

$\Delta_{\underline{k}}$ and $\Delta_{\alpha}^{-1}\underline{k}$ are inequivalent. Its order is the order of the star of $\underline{k}$. The irreducible allowable representations, Γ^i , of $G_{\underline{k}}$ correspond one-to-one to irreducible representations, D^i , of $P_{\underline{k}}$. The correspondence is given by

$$\Gamma^i[(\alpha|\underline{v}(\alpha)+\underline{R}_{\underline{n}})] = e^{i\underline{k}\cdot\underline{R}_{\underline{n}}} e^{i(\underline{k}-\alpha^{-1}\underline{k})\cdot\underline{v}(\alpha)} D^i(\alpha) \quad \dots A3.3,$$

where $(\alpha|\underline{v}(\alpha) + \underline{R}_{\underline{n}}) \in G_{\underline{k}}$ and $\underline{v}(\alpha)$ is a fraction of a primitive translation.

APPENDIX 4

REDUCTION OF SOME REDUCIBLE REPRESENTATIONS

In the theory of the atomic picture, it is necessary to reduce the irreducible representation Γ of the crystallographic point group, P_O , to a form which, when restricted to $P_{\underline{k}}$ (see Appendix 3) for some $\underline{k}$, is a block diagonal sum of irreducible representations of $P_{\underline{k}}$.

Using the characters of Γ and the irreducible characters of $P_{\underline{k}}$, it is easy to see what irreducible representations of $P_{\underline{k}}$ appear in the direct sum, and how many times each appears (Lo 59). The projection operator method described by Lomont tells how to perform the decomposition by choosing suitable linear combinations of states in the Γ multiplet. What follows is a description of how to make this choice.

Given that irreducible representation D^i of $P_{\underline{k}}$ appears m_i times in Γ , the matrices $D = \sum_i m_i D_i$, a block diagonal sum form a reducible representation of $P_{\underline{k}}$ unitarily equivalent to the restriction of Γ to $P_{\underline{k}}$. The following operator

$$X = \frac{1}{g_{\underline{k}}} \sum_{\alpha \in P_{\underline{k}}} \Gamma(\alpha) D^*(\alpha) \quad \dots A4.1$$

where $D^*(\alpha) = D(\alpha^{-1})$ and $g_{\underline{k}}$ is the order of $P_{\underline{k}}$ takes a state in the Γ multiplet to a linear combination of states in the multiplet, is unitary, and performs the required reduction. To verify this assertion, the identity

$$\Gamma(\beta) X = X D(\beta) \quad \dots A4.2$$

is used to show that $X^{-1} \Gamma(\beta) X = X^{-1} X D(\beta) = D(\beta)$.

The proof of identity A4.2 is

$$\begin{aligned} \Gamma(\beta) X &= \frac{1}{g_{\underline{k}}} \sum_{\alpha} \Gamma(\beta) \Gamma(\alpha) D(\alpha^{-1} \beta^{-1} \beta) = \frac{1}{g_{\underline{k}}} \sum_{\alpha} \Gamma(\beta \alpha) D(\beta \alpha)^{-1} D(\beta) \\ &= X D(\beta). \end{aligned}$$

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