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UMI®
ON ELECTRONIC INTERACTIONS
IN THE FREE-ELECTRON MODEL INCLUDING EXCHANGE

by

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A THESIS
SUBMITTED TO THE FACULTY
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY IN PHYSICS

Approved May 15, 1953
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Houston, Texas
May, 1953
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Introduction

A. Nature of the Problem

Out of the free-electron theory there has developed an one-electron approximation known as the band approximation or energy-band method. It is the Hartree-Fock approximation with the added assumption that each one-electron function extends over the entire solid and has equal amplitude at equivalent atoms. Consequently, the one-electron wave functions have the form

$$\psi_k(r) = u_k(r) e^{i \vec{k} \cdot \vec{r}}$$  \hspace{1cm} (1)

where $u_k(r)$ has the translational periodicity of the lattice.

Clearly, the free-electron theory is contained as a special case.

The difficulties associated with obtaining rigorous Hartree-Fock solutions of the form (1), as well as the presumed complexity of the resultant $\psi_k(x)$, are in sharp contrast to the simplicity and attendant mathematical tractability of the free-electron theory.

Experiment and theory reveal, however, that the free-electron picture, at least in certain cases, provides a reasonably good working model.

In particular, the Sommerfeld law of linear temperature dependence for the electronic specific heat has received striking confirmation.

Theoretically, the Hartree-Fock solution for the wave function (ground state) associated with $\vec{k} = 0$ in the case of sodium has been shown on two occasions (Wigner and Seitz, 1933, 1934; Löwdin, 1951) by quite different techniques to be effectively flat over the bulk, by far, of the volume of the crystal.
Further, employing group theoretical methods and using the basic cellular assumption of the Wigner-Seitz method, it has been shown (Von der Lage and Bethe, 1947) that along six symmetry axes in $\mathbf{k}$ space (the axis including $\mathbf{k}=(0,0,\frac{2\pi}{a})$ and its equivalents), the energy as a function of $\mathbf{k}$ in the first Brillouin zone of sodium is essentially the same as for free electrons, deviations occurring only at the very corners of the rhombododecahedron where the symmetry axes concerned intersect the surface of the first Brillouin zone.

The plane-wave approximation to the Hartree-Fock solutions has been used, in fact, by every investigator who has calculated a cohesive energy by the Wigner-Seitz method, for the Coulomb self-energy, mean Fermi energy, exchange energy, and, in particular, the correlation energy (a large contribution), all of which are free electron evaluations, have either in toto or in part been used in the calculations with considerable success (Kuhn and Van Vleck, 1950; Herring, 1951).

Slater (1953) has recently leveled sharp criticism at the Wigner-Seitz method, referring to Wigner's correlation energy calculation as a poor approximation to the "true" correlation energy and to the excellent results for sodium as obtained by Wigner and Seitz as probably fortuitous.

In weighing the first criticism it must be remembered that what Wigner calculated was not the energy difference between the "true" energy and that obtained with a rigorous solution in the form of a single determinant of the Hartree-Fock equations, but the energy of interaction of free electrons as justified by the flatness of the $\mathbf{k}=0$ wave function in conjunction with the fact that in the Wigner-Seitz method, the higher energy one-electron functions are all assumed to be of the form $\psi_{\mathbf{k}} = \psi_{\mathbf{k}=0} e^{ik\mathbf{r}}$. 
The Wigner-Seitz method is essentially a free-electron theory.

With regard to Slater's second criticism, we consider that even if the good results for the cohesive energy are partially accidental (which has certainly not been demonstrated conclusively) there is, nonetheless, a real compensation in the gain in simplicity and pictorial representation offered by the Wigner-Seitz method in comparison to the more rigorous, elaborate, but conceptually difficult method used by Löwdin (1951).

The cohesive energy is only one of many interesting considerations with regard to metals that arise involving the conduction electrons. There are problems of x-ray emission and absorption, magnetic and optical phenomena, the electronic specific heat, electrical and thermal conductivities, thermoelectric effects, etc., basically associated with excited states, the density of energy levels, and transitions between states.

All these have been considered in varying degrees of approximation, but almost without exception, the electronic interactions have been neglected primarily due to lack of techniques for handling such a complication.

With regard to excited states, a possible rigorous approach would be through the construction of total wave functions as linear superpositions of determinantal wave functions, each determinant referring to a particular configuration of one electron states. The difficulties in carrying through such a program are clearly tremendous.

For these reasons it is of interest to consider the possibility of employing a plane-wave approximation to the Hartree-Fock solution, at least for some of the simple metals, as a starting point in an attempt to deal with the effects of electronic interactions on some of the phenomena listed above.
However, within the realm of the Hartree-Fock approximation, and in efforts to progress beyond it, inadequacies and divergences arise when it is assumed that a determinant of plane-wave single particle functions, i.e. free electrons in an approximation including exchange, provides an adequate representation for the solution of the Hartree-Fock equations.

For one-electron functions of the form \( \psi_k(r) \), the exchange energy of an electron in the state \( k \), as obtained by summing the exchange interactions with all remaining electrons of the assemblage, is a function of \( k \), \( E_{EX}(k) \), hence the usual distribution function of Fermi-Dirac statistics is modified even if the electrons are free except for their mutual electrostatic interaction.

Introducing exchange into the free-electron picture, one may write, for temperature \( T \),

\[
E(k) = \frac{\hbar^2}{2m} k^2 + E_{EX}(k) \\
= \frac{\hbar^2}{2m} k^2 - \sum_{k' \neq k} \mathcal{f}(k', T) \frac{e^2 e}{k' + k} \int \frac{d^3k_1 d^3k_2}{(\hbar^2 - k_1^2)}
\]

where \( \mathcal{f}(k, T) \), the distribution function, is always equal to or less than unity and must satisfy the relation

\[
\kappa = \frac{N}{k} = \sum_{k} G \mathcal{f}(k, T)
\]
with $N$ and $V$ the total number of electrons and total volume respectively, and $G$ is a degeneracy parameter.

For temperature $T = 0$, with

$$f(k, T = 0) = \begin{cases} 
1 & |k| \leq k_f \\
0 & |k| > k_f 
\end{cases}$$

and $G = 2$, Dirac (1930) first obtained

$$E_{\text{ex}}(k) = -\frac{e^2}{\hbar} \left( k_f + \frac{k_f^2 - k^2}{2k} \log \left| \frac{k + k_f}{k - k_f} \right| \right)$$

which possesses a logarithmically divergent derivative with respect to $k$ at $k = k_f$, hence the energy level density at $k = k_f$ is zero.

Assuming the functional form of $f(k, T)$ to be the same as that of the Fermi-Dirac distribution, Bardeen (1936) obtained an approximate solution of the equations (*) and found that the level density at the Fermi surface decreased logarithmically with decreasing temperature, i.e., with decreasing total energy of the system. As a result, the electronic specific heat for free electrons at constant volume tends to zero with temperature as $\gamma T / |\log T|$ in contradistinction to the Sommerfeld linear law $C_v = \gamma T$. 
The correlation energy for free electrons (1) (Wigner, 1934; Ufford, 1941; Macke, 1950) represents a correction for at least one of the inadequacies of the plane-wave assumption for the Hartree-Fock solution, and Wigner (1938) conjectured that the inclusion of the correlations between electrons of opposed spin would tend to increase the level density at the Fermi surface thus increasing the specific heat and thereby restoring agreement between the calculated and observed behavior.

An application of the Rayleigh-Schrödinger perturbation method using the simple kinetic energy operator as unperturbed Hamiltonian, the mutual Coulomb potential as perturbation, and the usual plane-wave

(1) The term "correlation energy" as used for free electrons arises from the fact that in the approximation taking account of exchange, the probability density distribution for pairs of electrons

\[ \rho(r_1, r_2) = \int \text{*} \psi^*(\vec{r}_1) \psi(\vec{r}_2) \, d\vec{r}_3 \, d\vec{r}_4 \ldots d\vec{r}_n \]

where \( \psi(\vec{r}) = (N! \frac{-i\hbar}{2}) \det \psi_1(\vec{r}_1), \psi_2(\vec{r}_2), \ldots, \psi_N(\vec{r}_N) \)

\[ \psi_i(\vec{r}) = \sqrt{\frac{1}{V}} e^{i \vec{r} \cdot \vec{s}_i} \]

\( \alpha \in \frac{1}{V^2} \) i.e. independent of \( V \), the separation between electrons, hence, in this approximation opposed spin electrons are completely independent - no statistical correlations exist among them.

For electrons with parallel spins, a statistical correlation does exist, and, in accord with the Pauli exclusion principle as evidenced by the determinantal form of the total wave function, the probability of finding two electrons with parallel spins at the same point in space is zero.
determinant of unit multiplicity as ground state, leads to a logarithmic divergence in the second order approximation (Ufford, 1941; Heisenberg, 1947; Macke, 1950).

This divergence led Heisenberg to ascribe special properties to the electrons in an encircling spherical energy band at the Fermi surface. This concept is basic for his theory of superconductivity.

Macke interpreted the divergence as being indicative of the importance of the summations occurring in the higher order approximations. Restricting the matrix elements appearing in the summations of the Rayleigh-Schrodinger perturbation series to transitions involving predominantly the electrons on the Fermi surface (small momentum changes), he was able to obtain a convergent expression for the resulting infinite series.

The correlation energy (energy in addition to the first order energy which includes exchange) obtained in this way compares remarkably well with the Wigner calculation for free electrons.

Another divergence occurs in Landsberg's (1949) calculation of the soft x-ray emission band, \( L_{III} \), of sodium using a theory proposed by Skinner (1946) to account for a low intensity tail evidenced on the long wavelength side of the band. The divergence encountered is stronger than the logarithmic divergence of the perturbation calculations but is a direct parallel in the sense that Landsberg used plane-wave determinantal wave functions assuming these to be a reasonable approximation for sodium on the basis of the arguments presented earlier in this report.

In lieu of a better wave function, Landsberg introduced into the integrals defining the matrix elements the functions \( e^{-\lambda r_{12}/r_{12}} \), where \( r_{12} \) is the distance between two electrons, in place of \( \lambda r_{12} \); the Coulomb dependence on separation distance. Through forcing convergence in this manner, and selecting the arbitrary parameter \( \lambda = 1.2 \times 10^8 \) cm\(^{-1} \),
he was able to match satisfactorily the experimentally determined band
shape including a reasonable length for the tail.

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The success of the insertion of the exponential into the matrix
elements was interpreted by Landsberg as suggestive of long range elec-
tronic correlations coexistent with known short range correlations (pre-
sumably involved in the Wigner calculation) neither of which is present
in the one-electron approximation underlying the calculation. \(-\lambda \sqrt{2}\)

It occurred to Wohlfarth (1950) that an exponential, \(e^{-\lambda}\),
i ntroduced into the exchange integral for free electrons would remove the
infinity in the slope of \(E_{\text{ex}}(k)\) at the Fermi surface.

Wohlfarth assumed that with the removal of this divergence the
electronic specific heat would have its usual linear temperature depend-
ence at all temperatures except for a residual decrease in the Sommerfeld
\(\gamma\), depending on \(\lambda\). On this basis he found that the ratio of the
Sommerfeld specific heat to the specific heat calculated with inclusion
of the modified exchange energy approached for large \(\lambda\), a value close
to unity as the temperature \(T \to 0\). In the limit \(\lambda \to \infty\), the ratio
for \(T = 0\) is unity; however, for \(\lambda = 1.2 \times 10^8 \text{cm}^{-1}\), the value chosen
by Landsberg for the x-ray study, the ratio is only 8% above unity and
the density of states curve has very nearly normal form (thereby justifying
the starting assumption).(1)

(1) We have calculated the total exchange energy for sodium using the
plane-wave approximation with exponential inserted as in Wohlfarth's
study and find, using the above value for \(\lambda\), the free electron value
without exponential reduced by a factor \(7 \times 10^{-3}\).
The device was viewed as an empirical method for estimating correlation while retaining a one-electron character for the total wave function. Again, as Landsberg had done, the correlations supposedly taken into account by the exponential were considered as of a different nature from those considered by Wigner.

Wolfarth went further in that he actually elevated the device to the level of a screened potential, \( e^2 = -\frac{\lambda \nu_2}{\nu_2} \), for he pointed out that the method was still unsatisfactory for calculating cohesive energies of metals; the screening term would affect the Coulomb as well as the exchange energy term appearing in the total energy expression.

Bohm and Pines (1950) were led independently to the concept of an effective screened Coulomb force in a study, both classical (published) and quantum-mechanical (unpublished) of the interaction of charges in an electron gas of high density.

In a preliminary note they reported a screening radius

\[ \Lambda^{-1} = \left( \frac{\hbar k_F}{m} \right) \left( \frac{m}{4\pi n_0 e^2} \right)^{1/2} \]

where \( e \) and \( m \) are the electron charge and mass respectively and \( n_0 \) the electron density. For sodium, \( k_F = \frac{2}{3} \times 10^9 \text{ cm}^{-1} \) and \( \Lambda = 10^{-8} \text{ cm} \), which they note as being in agreement with the screening radius adopted empirically by Landsberg and Wolfarth.

In a recent review article, Mott (1952) comments that the term \( e^{-\lambda \nu_2} \) is thought to represent the screening of the interaction between any two electrons due to all the other electrons, and that although
it is not known how to include the screening in the present theory, a similar term appears naturally in the case of the interaction of the electrons with a dissolved atom in an alloy.

Mott reports that Lee-Whiting (unpublished) has extended Landsberg's calculations to the x-ray absorption spectrum and to the finite lifetime of electrons above the Fermi distribution; a screening constant was used and a method obtained for calculating it, according to Mott, which led to the same result given by Bohm and Pines.

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In Macke's paper (1950), referred to above, the summation technique for the perturbation series which led to a correlation energy in agreement with the only previous estimate available, was also employed in carrying out a variational calculation wherein the trial wave function was written in formal analogy to that which would result from a first order perturbation calculation using a screened potential and the plane-wave ground state determinant as the zeroth order wave function.

The results of applying $\delta E = 0$ led, in Macke's hands, to an expression of the correlation energy identical, term for term, to that of the perturbation calculation; the Coulomb and exchange energy remain unmodified. The resultant screening radius is not constant, depending, in a rather involved way, on momenta involved in the transitions.

Macke discussed the screening function as arising from polarization of the continuous distribution of positive charge, implicitly contained in the plane-wave approximation, in analogy to the Debye theory of electrolytes.

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It is clear from the foregoing that there is much confliction of interpretation and use of the screening term:

1. Landsberg modified off-diagonal Coulomb matrix elements formed with plane waves to avoid a divergence;

2. Wohlfarth modified part of the diagonal element associated with the ground state but gave a hybrid interpretation in terms of long distance correlations;

3. Bohm and Pines (as well as Mott) look upon the concept as a real screening effect and not as a device to enable more satisfactory calculations to be made within the domain of the plane-wave one-electron approximation.

B. Purpose, Conjectures and Principal Results of Investigation

We have investigated the concept of electronic screening from the standpoint of achieving a uniform and consistent interpretation for the purpose of providing a technique for dealing, in first approximation at least, with the effects of electronic interactions while retaining the relative simplicity of the one-electron picture and, in particular, the plane-wave approximation to the Hartree-Fock solutions.

Our study has led us to conjecture that a consistent interpretation of the screening term may be found in its use as a variational function along the lines of the calculation by Macke.

Also, we have been led to hypothesize the existence of a uniform screening function to be employed in the calculations using plane-wave determinants of all off-diagonal Coulomb matrix elements occurring in probability coefficients of wave expansions or in transition probabilities.
We stress the exception of diagonal elements, i.e., the screening exponential is interpreted by us purely as a device with no physical interpretation as a real screened potential.

Hence, we are in disagreement with Wohlfarth's use of the exponential in the calculation of exchange energy.

Further, there is no problem of the proper use of the screening term in the calculation of cohesive energy for with the use of it one determines correlation energy and, in fact, is led effectively to Wigner's result which is always contained in final evaluations of the cohesive energy by the Wigner-Seitz method.

Thus, the screening term may be viewed as "estimating" electronic correlations provided we use as operational definition the actual calculation of the correlation energy itself.

As a consequence, we do not distinguish between long and short range correlations, as do Landsberg and Wohlfarth, in accord with our non-physical interpretation of the screening term.

In Chapter II, Section 2, we point out reasons why Macke's screening function cannot be applied consistently to all types of transitions.

In Chapter II, Section 3, we present our modification of the variational calculation. We have obtained a new screening function of general applicability and with it a new expression for the correlation energy.

With the modification one may obtain straightforwardly an infinity of types of trial wave functions by continuing the formal perturbation expansion of the wave function to higher orders.

Insofar as its dependence on electron density, \( k_F \), \( \hbar \), \( m \) and \( e \) is concerned, our screening function is identical to that obtained from the Bohm-Fines screening radius.
We have evaluated our general screening function. In the domain of importance to questions of divergence, we find, for sodium, numerical agreement with the value empirically obtained by Landsberg in the L\textsubscript{III} emission band study.

The screening function's dependence on electron density (or Fermi level) leads to a curve which effectively predicts the breadth of x-ray emission bands. The results are in agreement with Skinner's experimental observations.

Therefore, within the range of validity of the calculations involved, we have a partial confirmation of our conjectures.

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We should like to conclude this introduction with a sincere expression of appreciation to Professor W. V. Houston for the readiness with which he has made accessible his knowledge of fundamental quantum-mechanical interpretations and methods. With pleasure, we acknowledge his many comments and valuable criticisms on the basic ideas and methods underlying this work.
Chapter I

The Hartree-Fock and Plane-Wave Approximation for Solids

The Hamiltonian operator for a solid consisting of $N$ electrons in a preformed space lattice of $N$ positively charged ions is assumed to exist in the sense that characteristic values $\Xi$ and associated characteristic functions $\Psi(\vec{r})$ exist for the resultant Schrödinger equation

$$\mathcal{H} \Psi(\vec{r}) = \left\{ -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla_i^2 + \sum_{i<j}^{N} V_{ij} + \sum_{i}^{N} \frac{e^2}{\epsilon R_{ij}} \right\} \Psi(\vec{r})$$

$$(1.1)$$

$$= \left\{ \sum_{i=1}^{N} \frac{\hbar^2}{2m} \nabla_i^2 + \sum_{i<j}^{N} V_{ij} + \frac{1}{\epsilon} \sum_{i}^{N} \frac{e^2}{R_{ij}} \right\} \Psi(\vec{r})$$

$$= \Xi \Psi(\vec{r})$$

with specified boundary conditions.

In this equation, $\vec{r}_i$ is the position vector for electron $i$ of charge $e$ and mass $m$, $V_{ij} = |\vec{r}_i - \vec{r}_j|$, the separation distance between electrons $i$ and $j$, $V_i = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}$, the mutual potential energy of the ions, $\sum_{i}^{N} V_{i}$ the reciprocal potential energy of ion $\lambda$ and electron $i$, and $\Psi(\vec{r}) = \Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$ where $\vec{r}_i$ includes both space, $\vec{r}_i$, and spin, $S_i$, coordinates of electron $i$.

All thermal vibrations of the ions as well as all magnetic interactions, spin-spin forces and relativistic effects among the electrons have been omitted.
The total energy of the ground state of the electron assemblage is given by the lowest characteristic value $\mathcal{E}_0$ of the equation

$$\sum_\alpha \mathcal{V}(\mathbf{r}_\alpha) = \mathcal{E} \Psi(\mathbf{r})$$

for antisymmetrical functions $\Psi(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$.

The one-electron approximation known as the Hartree-Fock-Dirac approximation arises from the assumption that

$$\Psi(\mathbf{r}) = \det \{ \chi_1(\mathbf{r}_1), \chi_2(\mathbf{r}_2), \ldots, \chi_N(\mathbf{r}_N) \} \tag{1.2}$$

where $\chi_i(\mathbf{r}_i)$ is a function involving the variables $\mathbf{r}_i$ of only one electron and the symbol $\det \{ \}$ denotes a determinant made up of these one electron functions with the elements appearing along the diagonal contained in the brackets $\{ \}$. The Hartree-Fock-Dirac system of simultaneous, non-linear, partial differential equations determining the $\chi_i(\mathbf{r}_i)$ is deduced from the general fact that the functions $\chi_i(\mathbf{r}_i)$ which give the best approximation $\mathcal{E}_0'$ of the lowest energy $\mathcal{E}_0$ are determined by the variation principle $\delta \mathcal{E} = 0$ with

$$\mathcal{E} = \frac{\int \Psi^*(\mathbf{r}) \sum_\alpha \mathcal{V}(\mathbf{r}_\alpha) \Psi(\mathbf{r}) \, d\mathbf{r}}{\int \Psi^* \Psi \, d\mathbf{r}} \tag{1.3}$$

$$= \frac{\langle \Psi, \sum_\alpha \mathcal{V}(\mathbf{r}_\alpha) \Psi \rangle}{\langle \Psi, \Psi \rangle}$$

where $\int \ldots \, d\mathbf{r}$ implies integration over all space variables $(\mathbf{r}, \mathbf{r}_1, \ldots, \mathbf{r}_N)$ and summations over all spin variables $(s_1, s_2, \ldots, s_N)$. 

Assuming the \( \psi_{\xi}(\overline{x}_i) \) ortho-normal, i.e.

\[
(\psi_{\xi}(\overline{x}_i), \psi_{\eta}(\overline{x}_j)) = \delta_{\xi \eta} = \begin{cases} 
1 & \xi = \eta \\
0 & \xi \neq \eta 
\end{cases}
\]  
(1.4)

Insertion of Eqn. (1.2) into (1.3) yields

\[
E = \sum_{\xi=1}^{N} \int \psi_{\xi}^{*}(\overline{x}_i) \frac{\partial}{\partial \overline{x}_i} \psi_{\xi}(\overline{x}_i) \, d\overline{x}_i + \sum_{\xi, \eta=1}^{N} \frac{1}{2} \frac{1}{v_{12}} \left[ \psi_{\xi}^{*}(\overline{x}_i) \psi_{\eta}^{*}(\overline{x}_j) \psi_{\eta}(\overline{x}_j) \psi_{\xi}(\overline{x}_i) \right] \, d\overline{x}_i d\overline{x}_j 
\]  
(1.5)

Application of the variation principle \( \delta E = 0 \) results in the system of the Hartree-Fock-Dirac differential equations:

\[
\frac{\partial}{\partial \overline{x}_i} \psi_{\xi}(\overline{x}_i) + \sum_{\lambda=1}^{N} \varepsilon^2 \int \frac{\psi_{\lambda}^{*}(\overline{x}_2) \psi_{\lambda}(\overline{x}_2)}{v_{12}} \, d\overline{x}_2 \cdot \psi_{\xi}(\overline{x}_i) = 0
\]  
(1.6)

\[
+ \sum_{\lambda=1}^{N} \varepsilon^2 \int \frac{\psi_{\lambda}^{*}(\overline{x}_2) \psi_{\xi}(\overline{x}_2)}{v_{12}} \, d\overline{x}_2 \cdot \psi_{\lambda}(\overline{x}_i)
\]

\[
+ \sum_{\lambda=1}^{N} \frac{\varepsilon^2}{2 \varepsilon_{\lambda}} \psi_{\lambda}(\overline{x}_i) = 0
\]

\( \xi = 1, 2, \ldots, N \).
The $\lambda_2$ are Lagrangian multipliers which for a non-degenerate system may be taken as $\lambda_2 = 0 \ (\lambda \neq \beta)$, 

$$\lambda_2 = \epsilon_\xi \left[ \text{sometimes referred to as the energy parameter of the equation} \right].$$

The energy parameter $\epsilon_\xi$ for $\psi_\xi(\vec{r}_i)$ is the negative of the energy required to remove the electron in the state $\psi_\xi$ from the solid when $\psi_\xi(\vec{r}) = u_\xi (\vec{r}) e^{-i \epsilon_\xi \phi}$.

Also $\epsilon_\xi = \epsilon_\xi (\vec{k})$ and $\epsilon_\xi (\vec{k'}) - \epsilon_\xi (\vec{k})$ is the energy required to change the state of an electron from $\psi_\xi(\vec{r}_i)$ to $\psi_\xi(\vec{r}_j)$ (Seitz, 1940).

Assuming separability of spin, i.e.

$$\psi_\xi (\vec{r}_i) = \psi_\xi (\vec{r}_i) \eta_0 (\vec{r}_i) \quad (1.7)$$

where we take $\eta_0 (\vec{r}_i) = \delta_0 \delta_i$ we obtain for the total energy:

$$E = \frac{1}{\epsilon} \int \psi_\xi^* (\vec{r}) \frac{\delta}{\delta \psi_\xi (\vec{r})} \psi_\xi (\vec{r}) \ dr_i, \quad (1.8)$$

$$+ \frac{1}{\alpha \beta} \psi_\xi (\vec{r}) \psi_\beta (\vec{r})$$

$$+ \frac{1}{\epsilon} \int \epsilon e^2 \left[ \frac{1}{r_{\lambda 2}^{1/2}} \frac{1}{r_{\lambda 2}^{1/2}} \right] \ dr_i \ dr_j, \quad (1.8)$$

$$+ \frac{1}{\epsilon} \int \epsilon e^2 \left[ \frac{\psi_\xi^* (\vec{r}) \psi_\xi (\vec{r}) \psi_\xi (\vec{r}) \psi_\xi (\vec{r})}{r_{\lambda 2}^{1/2}} \ dr_i \ dr_j, \quad (1.8)$$
where

\[ \sum_{\xi}^{(1)} \equiv \text{all occupied electron states} \]

\[ \sum_{\xi \neq \lambda}^{(2)} \equiv \text{all pairs of occupied electron states} \]

\[ \sum_{\xi \neq \lambda}^{(3)} \equiv \text{all pairs of electron states occupied by electrons with mutually parallel spins.} \]

The assumption of separability of space and spin functions leads to the so-called Hartree-Fock approximation (the title is sometimes given to what we have termed the Hartree-Fock-Dirac approximation).

The Hartree-Fock differential equations are of two types, depending on whether the one-particle state is singly or doubly occupied (Brillouin, 1933, 1934).

Assuming the \[ \psi_\xi \] are equal in pairs with spins opposed, a ground state of unit multiplicity is obtained, and is the usual assumption for the normal state of all simple solids.

If we assume that \[ \psi_\xi (\vec{r}_1) = -\frac{1}{\sqrt{2}} \psi_\xi (\vec{r}_1) \], then Eqn. (1.8), reduces to

\[
E_{\text{plane waves}} = \frac{\sum}{K} \int \psi^*_{\xi} (\vec{r}) \frac{\sqrt{m}}{\hbar} \psi_{\xi} (\vec{r}) \, d\vec{r}
+ \sum_{\alpha, \beta} V_{\alpha, \beta} + \frac{N}{2V} \int \frac{e^2}{1r_{1,2}^2} \, d\vec{r}_{1,2}
- \sum_{K_1, K_2} \frac{e^2}{K_1, K_2 \sqrt{V}} \int \frac{e^{i(K_1 - K_2) \cdot \vec{r}_{1,2}}}{1r_{1,2}^2} \, d\vec{r}_{1,2}
\]  

(1.9)
The free electron model would assume the positive ionic charge of the lattice smeared out and that

\[ \sum_{\alpha \neq \beta} V_{\alpha \beta} + \frac{N}{2V} \int \frac{e^2}{|r_1 - r_2|} \, dr_2 + \sum_{\alpha, i} V_{\alpha i} = W \quad (1.10) \]

where \( W \) is a constant. The exchange energy would not be present in the simplest theory.

In the plane wave approximation to the Hartree-Fock equations one may consider the electrons as bound by an average potential determined by the lattice-lattice, electron-electron, and lattice-electron potentials. Exchange energy, as seen in Eqn. (1.9) would be present. This is the model referred to as free electrons including exchange.
Chapter II

Perturbation and Variational Determinations of the Correlation Energy for Free Electrons

Section 1. Perturbation Calculation

Our discussion of the perturbation calculation will be restricted effectively to consideration of the assumptions and technique which enables summation over the second and all higher orders of the perturbation series for the energy $E$ leading to a convergent expression.

We refer the reader to Heisenberg (1947) and Macke (1950) for details regarding the zeroth and first order energies.

The matrix elements $C_{on} = C_{on}^* = C_{no}$ linking the ground state

$$\mathcal{F}_0 (\hat{x}) = (N!)^{-\frac{1}{2}} \det \left\{ \frac{\psi_i (\hat{x}_i)}{\hat{p}_i}, \frac{\psi_j (\hat{x}_j)}{\hat{p}_j}, \ldots, \frac{\psi_n (\hat{x}_n)}{\hat{p}_n} \right\}$$

where (1)

$$\psi_i (\hat{x}_i) = V^{-\frac{1}{2}} \frac{e^{\frac{i}{\hbar} \hat{p}_i \cdot \hat{x}_i}}{\sigma \sqrt{2\pi}^N}$$

$\sigma = 1, 2, V =$ volume, and the momenta $\hat{p}_i^z, z = 1, 2, \ldots, N/2$ filling a Fermi sphere of radius $\hat{D}$, each $\hat{p}_i^z$ doubly occupied, and the excited states with no less and no more than two particles outside the Fermi sphere (all other matrix elements with $\mathcal{F}_0^-$ vanish) are given by

$$C_{on} = \left( \mathcal{F}_0, \sum_{i<j}^N \frac{\varepsilon_i^2 - \varepsilon_j^2}{\hat{p}_i^z \hat{p}_j^z} \mathcal{F}_n \right)$$

$$= \frac{e^2 \hbar^2}{\pi RV} \left\{ \frac{\delta_{i,j} \delta_{i',j'} \delta_{i,j} \delta_{i',j'}}{\hat{q}^2} - \frac{\delta_{i,j} \delta_{i',j'} \delta_{i,j} \delta_{i',j'}}{\left( \hat{p}_i^z \hat{p}_j^z + \hat{q}^2 \right)^2} \right\}$$

$(1)$ The $\hat{p}$ notation, $\vec{p} = \hbar \vec{k}$ will be used interchangeably with the $\vec{k}$ notation.
wherein momentum and spin are conserved; thus, (Fig. 2.1),

\[ \vec{p}_1' - \vec{p}_1 = \vec{p}_2' - \vec{p}_2 = \vec{q} \]  

(2.3)

and spin conservation is read from the \( \mathcal{S} \) -functions in (2.2).

The \( \frac{1}{2} q^2 \) term is present for both parallel and opposed spin interaction whereas the second term is non-zero only for parallel spin interaction (exchange contribution to matrix elements).

The second order energy

\[ E_2^0 = - \sum_m \frac{1}{E_m - E_0} \]  

(2.4)

becomes in the continuum approximation

\[ E_2^0 = - \frac{N^2 \alpha \chi_{ex}}{8 \pi^3 \rho^3} \int \frac{dq^2 dp_1 dp_2}{q^2 (p^2 - p_2 + q^2)} \cdot \left\{ \frac{1}{q^4} - \frac{1}{2q^2(p^2 - p_2 + q^2)} \right\} \]  

(2.5a)

where

\[ m(E_m - E_0) = q^2 (p^2 - p_2 + q^2) \]

and

\[ \chi = \frac{4m \alpha}{\hbar D} = \frac{2}{\pi} \left( \frac{4}{\pi} \right)^{1/2} \frac{\beta}{2a_H} \]

(2.5b)

\[ = \frac{332}{2} \frac{\beta}{2a_H} = \frac{1}{3} \frac{\beta}{2a_H} \]
Fig. 2.1

\[ \mathbf{p}' - \mathbf{p} = \mathbf{p}_2 - \mathbf{p}_2' = \mathbf{q} \]

\[ |\mathbf{p}_1| \leq D \quad \quad |\mathbf{p}_2| \leq D \]

\[ |\mathbf{p}_1 + \mathbf{q}| > D \quad |\mathbf{p}_2 - \mathbf{q}| > D \]

\[ 0 \leq |\mathbf{q}| \leq 2D \]
with $\alpha_n$ the Bohr radius for hydrogen and

$$\frac{4\pi}{3} r_s^3 = \frac{1}{N}$$

the volume per electron (for monovalent solids, $r_s = r_s^0$, the radius of the Wigner-Seitz sphere).

The $\epsilon_{ex}$ is defined by the total exchange energy $\mathcal{E}_{ex} = -N\epsilon_{ex}$ thus

$$\epsilon_{ex} = \frac{916}{r_s^0}$$

with $r_s^0$ expressed in Bohr radii.

The expression (2.5) diverges as $\int_0^{\infty} \frac{d\theta}{\theta^2}$. Clearly the $\frac{1}{\theta^2}$ term is the dominant term of the quantity in brackets occurring in the integrand of $\mathcal{E}_{ex}^0$. The divergence is to be associated with small $\theta$ hence with the electron states on the surface of the Fermi sphere. The physical interpretation is that the Coulomb potential through its $\frac{1}{\theta^2}$ dependence, is extremely far-reaching and leads to an overwhelming predominance of small angle deflections, small momentum change, small $\theta$.

We assume, with Macke, that the higher order energy terms may be estimated by taking all matrix elements and energy differences associated with the intermediate transitions to be the same. Therefore we have

$$\epsilon_{m_n} = \epsilon_{m_n, n_2} = \cdots = \epsilon_{n_{s-1}, n_s} = \epsilon_{n_s, 0} = \frac{e^2}{\pi N^2 \theta^2}$$

$$\epsilon_{m_1}^0 - \epsilon_0^0 = \epsilon_{m_s}^0 - \epsilon_0^0 = \cdots = \epsilon_{n_{s-1}}^0 - \epsilon_0^0 = \epsilon_{n_s}^0 - \epsilon_0^0$$

(2.6)

with exchange in these orders of approximation to be treated as a correction.
On this basis,

\[
K^{(s+1)} = (-1)^s \sum_{m_1, \ldots, m_s} \frac{b_{m_0} b_{m_1} b_{m_2} \ldots b_{m_s}}{(k_{m_0}^0 - E_0^0)(k_{m_1}^0 - E_0^0) \ldots (k_{m_s}^0 - E_0^0)}
\]

(2.7)

becomes, in the continuum approximation,

\[
E^{(s+1)} = (-1)^s 2^{2s-1} m^s \left( \frac{\hbar}{2m} \right)^{s+1} \left( \frac{e^2 \hbar^2}{\pi N} \right)^{s+1} 
\]

(2.8a)

\[
\int \frac{dq^7}{q^{2s+2}} \frac{dp_0 dp_1 dp_2 \ldots dp_s}{(k_0 - \vec{p}_i + q) \cdot q \ldots (k_s - \vec{p}_s + q) \cdot q}
\]

\[
= \frac{N \epsilon_{\text{ex}}}{2p^4} \int \frac{dq^7}{4\pi q^2} \int \frac{dp_0}{\pi} \left\{ - \frac{k \cdot p}{q^2} \int \frac{dp_i}{q \cdot \Delta} \right\}^s
\]

(2.9a)

where

\[
\Delta \cdot q = q \cdot (\vec{p}_0 - \vec{p}_i + q)
\]

and the momenta are restricted by

\[
|\vec{p}_o| \leq P ; \quad |\vec{p}_i| \leq P ; \quad |\vec{p}_o + q| > P
\]

\[
|\vec{p}_i - q| > P \quad \text{for } i = 1, 2, \ldots, s.
\]
With this form for $F^{(S+1)}$, Macke was enabled to obtain an expression for the correlation energy:

$$\sum_{S=1}^{\infty} F^{(S+1)} = -NE_{\text{corr}}.$$

$$= -\frac{NE_{ex}}{2P^4} \int \frac{dq^*}{4\pi q^2} \int \frac{dP^*}{q^2 + \frac{\hbar P^*}{\pi}}$$

(2.10)

which we shall use later for comparison purposes.

The exchange correction has been estimated by Macke to be of the order of $1/4$ to $1/5$ of the correlation energy (2.10) with opposite sign.

Section 2. Variational Calculation

A trial wave function may be calculated, in general, through the use of a simpler Schrödinger equation - simpler through selection of the potential function - which may even possess certain symmetry characteristics equivalent to the more intractable Schrödinger equation. The inclusion of one or more arbitrary parameters in the potential function leads to their inclusion in the characteristic functions which then possess
the flexibility for a variational calculation of the original Schrödinger

equation.

Macke formed a trial wave function through starting with the same
unperturbed Hamiltonian and writing the wave function as the first order
perturbation solution of the Schrödinger equation with perturbing potential

$$\sum_{ij} e^2 e^{-\frac{r_{ij}}{\mu}} / r_{ij}$$

(2.11)
in place of the Coulomb potential. In (2.11), $\mu$ is independent of $\vec{r}$
but otherwise unrestricted.

Thus

$$\Phi(\vec{x}) = \Psi_0(\vec{x}) - \sum_{n \neq 0} \frac{S_{n0}}{E_n - E_n^0} \Psi_n(\vec{x})$$

(2.12)

where

$$S_{n0} = \left( \Psi_n, \sum_{ij} e^2 / r_{ij} e^{-\frac{r_{ij}}{\mu}} \Psi_0 \right)$$

(2.13)

$$= S_{n0}^* = S_{0n} = \frac{e^2 \hbar^2}{2m} \left\{ \frac{\delta_0 \delta_0' \delta_0 \delta_0'}{(\mu^2 + q^2)} - \frac{\delta_0 \delta_0'}{\mu^2 + (p^2 + q^2)^2} \right\}$$

Inserting (2.12) into

$$\kappa = \frac{\langle \Phi | H | \Phi \rangle}{\langle \Phi | \Phi \rangle}$$

(2.14)

where $H$ is the total Hamiltonian including the ordinary Coulomb potential,
and retaining terms to the second order in $S_{n0}$, there results (1)

$$
E = E_0 + E_{oo} + \sum_{n \neq 0} \frac{S_{nn0} - S_{nnm} - \Delta_{nn0}}{E_n - E_0} 
+ \sum_{n \neq m \neq 0} \frac{S_{nnmm} S_{mn0}}{(E_n - E_0)(E_m - E_0)}
$$

(2.15)

Employing the summation equation (2.9a)

$$
E_{core} = \frac{N\hbar^2 E_n}{\pi^3 P^3} \int \frac{d\rho^{-} d\rho^{+} d\rho^{-}}{q^2 (P^{-} - \rho^{+} + q)}
$$

(2.16)

$$
\left\{ -\frac{2}{q^2(\mu^2 + q^2)} + \frac{1}{(\mu^2 + q^2)^2} + \frac{1}{(\mu^2 + q^2)^2 q^{2\pi}} \int \frac{d\rho^{-}}{q^2 (\rho^{-} - \rho^{+} + q)} \right\}
$$

Excepting $E_{oo}$, the exchange terms of the $E'$s and $S'$s are neglected. Setting $\delta E = 0$, Macke found

$$
\mu^2 = \frac{\hbar P}{\pi} \int \frac{d\rho^{-}}{q^2 (\rho^{-} - \rho^{+} + q)}
$$

(2.17)

(1) Note that $E_0$ and $E_{oo}$ which contains the Coulomb and exchange energies are not affected due to the form of the trial function $\hat{E}(\vec{r})$.  

Substituting (2.17) for $\mu^2$ in (2.16) one obtains identically Eqn. (2.10), the correlation energy calculated by the perturbation method. This is a striking result and a credit to Macke’s ingenuity.

In full,

$$\mu^2 = \frac{\mathcal{K} P \int \frac{d\rho^1}{q^2 (\vec{p}_0 - \vec{p}_2 + q)}}{1}$$  \hfill (2.18)

with $|\vec{p}_0| < P; |\vec{p}_2| < P; |\vec{p}_0 + q| > P; |\vec{p}_2 - q| > P$

and $q^2$ restricted to the range $(0, 2P)$, and we obtain\(^{(1)}\)

$$\mu^2 = \mathcal{K} P \int \left[ P + Z + g/2 \right.$$

$$+ \frac{\left[ p^2 - (z_0 + g)^2 \right]}{q} \log (z_0 + p + q) \left. \right]$$

$$- \frac{\left[ p^2 - z_0^2 \right]}{q} \log (z + p)$$

$$+ 2 (z_0 + g/2) \log (z_0 + g/2) \right] \left[ \right.$$\hfill (2.19)

wherein $z_0 = \vec{p}_0 \cdot \vec{g}/q$.

\(^{(1)}\) Set $\mathcal{K} = \lambda$, $Z_0 = x - g/4$ to compare with Macke’s $\frac{\mathcal{D}}{g} \frac{d}{x+g}$. The second term in Macke’s expression should have a (+) sign, not (-).
We wish to consider this variational calculation from two aspects:

(1) the possibility of employing the screening function for the calculation of matrix elements in general;

(2) the possibility of extending the formal perturbation expansion for the trial function to higher orders to obtain different classes of trial functions.

With regard to the first consideration, the difficulty in attempting to extend the range of application of \( \mu \) resides in its dependence on \( \mathcal{Z}_0 \), the projection of \( \mathcal{P}_0 \) in the direction of \( \mathcal{G} \).

We have encountered divergences in \( \mu \) for configurations in momentum space associated with energy conservative transitions. The basic reason is clear, for we may write

\[
\mu^2 = \frac{m \varepsilon P}{\pi} \int \frac{d\mathcal{P}_2}{\Delta \mathcal{E}}
\]

since

\[
\Delta \mathcal{E} = m^{-1} (\mathcal{P}_2^2 + \mathcal{P}_2' - \mathcal{P}_0^2 - \mathcal{P}_2) = m^{-1} \mathcal{G} \cdot (\mathcal{P}_0 - \mathcal{P}_2 + \mathcal{G}) = m^{-1} \mathcal{G} \cdot (\mathcal{P}_0 - \mathcal{P}_2') = m^{-1} \mathcal{G} (\mathcal{Z}_0 - \mathcal{Z}_2')
\]

In the perturbation calculation, \( \mathcal{Z}_0 \) never enters the range of variation of \( \mathcal{Z}_2' \), thus \( \Delta \mathcal{E} \neq 0 \) for all finite (with the exception of one limiting point since the lower limit of \( \mathcal{Z}_0 \) equals the upper limit of \( \mathcal{Z}_2' \) but this isolated case is inconsequential). The divergence coupled with
a real ambiguity in assigning $\bar{\mathbf{Z}}_0$ and $\bar{\mathbf{Z}}_2$ in transition configurations other than those of the perturbation calculation (where it makes no difference which vector is taken as $\vec{F}$ or $\vec{F}_Z$) render Macke's screening function incapable of general applicability beyond the perturbation calculation.

New trial wave functions may be formed by writing the formal perturbation expansion for $\mathbf{Z}(x)$, Eqn. (2.12), to orders higher than the first. An important difference arises through the appearance of matrix elements of the type $\mathbf{S}_{nilj}$, $\mathbf{nilj} \neq 0$, linking intermediate states. Unless the intermediate transitions are so restricted that $\mathbf{Z}_0 \neq \mathbf{Z}_2$ then the same difficulties which we have been considering above occur within the calculation itself, for the associated screening functions retain their dependence on $\mathbf{Z}_0$ and in the same manner as above.(1) No such difficulty occurs with the use of the "first order" wave function (2.12) since the $\mathbf{S}_{nilj}$, $\mathbf{nilj} \neq 0$, do not appear.

---

(1) This is the case since the $\mathbf{Z}_2$ obtained with the new trial functions are expressed in terms of powers of $\int \frac{d\phi}{\phi}$. 
Section 3. On a Modification of the Variational Calculation: A New Screening Function and Expression for the Correlation Energy

In passing to the continuum approximation and employing only the first terms of the matrix elements $S_{nn}$ and $C_{nn}$ one obtains for the terms

$$
\sum_{n \neq 0} \frac{S_{nn}S_{nn} - S_{nn}C_{nn} - C_{nn}S_{nn}}{E_n - E_0} \tag{3.1}
$$

of the total energy $E$ (Eqn. 2.16)

$$
\frac{N \xi E_W}{8\pi^3 p^3} \int \frac{d\mathbf{q} \cdot d\mathbf{p} \cdot d\mathbf{p}'}{(\mathbf{p} - \mathbf{q} + \mathbf{q}' \cdot \mathbf{q}') \cdot q^2 (q^2 + q'^2)} \left\{ \frac{\mathbf{q} \cdot \mathbf{q}'}{q^2(q^2 + q'^2)} + \frac{1}{(q^2 + q'^2)^2} \right\} \tag{3.2}
$$

wherein we now write $\nu$ for the screening function.

For the term

$$
\sum_{n \neq m \neq 0} \frac{S_{nm}S_{mn}}{(E_n - E_0)(E_m - E_0)} \tag{3.3}
$$

occurring in $E$ (2.16), we resort to the expression for $E$ (Eqns. 2.8a and 2.9a) from which one properly obtains

$$
\frac{N \xi E_W}{8\pi^3 p^3} \left( \frac{1}{\pi} \right) \int \frac{d\mathbf{q} \cdot d\mathbf{p} \cdot d\mathbf{p}'}{q \cdot (\mathbf{p} - \mathbf{q} + \mathbf{q}') \cdot (\mathbf{p} - \mathbf{q}')} \left\{ \frac{1}{q^2(q^2 + q'^2)} \right\} \tag{3.4}
$$
The two expressions (3.2) and (3.4) when combined yield

\[ E_{\text{corr}}(\gamma) = \frac{N \hbar E_{\text{ex}}}{8 \pi^3 \rho^3} \int \frac{dq^2 dp^2 dp^2}{q^2 (p_0^2 - p^2 + q^2)} \]

\[ \cdot \left\{ \frac{-2}{q^2(\gamma^2 + q^2)} + \frac{1}{(\gamma^2 + q^2)^2} \right\} \]

\[ + \frac{\hbar \rho}{\pi} \int \frac{dp^2}{q^2 (p_0^2 - p^2 + q^2)} \left( \frac{1}{q^2(\gamma^2 + q^2)^2} \right) \right\} \]

(3.5)

and this is the most general result for if \( \gamma^2 \) is not restricted to any particular set of variables, then \( \gamma^2 \) may be a function of \( \vec{p} \) as well as \( \vec{p} \), and \( \vec{q} \). Macke’s \( E_{\text{corr}}(\mu) \) results if we assume \( \gamma^2 \) independent of \( \vec{p} \), but dependent on \( \vec{p} \) and \( \vec{q} \), for \( (\gamma^2 + q^2)^{-2} \) may be taken out of the integrand of the \( \vec{p} \) integration, expression (2.17) results and \( \gamma^2 \rightarrow \mu^2 \).

Clearly, if the \( \vec{z} \) dependence (due to Macke’s assumption that \( \gamma^2 \) depends on \( \vec{p} \) ) is objectionable in the quest for a screening function of general validity, then we shall restrict \( \gamma^2 \) to be at most a function of \( \vec{q} \), i.e. \( \gamma^2 \rightarrow \beta^2(\vec{q}) \).
With this restriction, (3.5) becomes

\[ K_{\text{corr.}}(\beta) = \frac{N\lambda E_{\text{ex}}}{8\pi^3 p^3} \int dq^- . \]  

\[ (3.6) \]

\[ \left\{ \left[ \frac{-2}{q^2(\beta^2+q^2)} + \frac{1}{(\beta^2+q^2)^2} \right] \int \frac{dp_0^- dp_\perp^-}{q^\cdot (p_0^- - \vec{p}_\perp + \vec{q})} \right. \]

\[ + \frac{1}{q^2(\beta^2+q^2)^2} K_P \int \frac{dp_0^- dp_\perp^- dp_\perp^+}{q^\cdot (p_0^- - \vec{p}_\perp + \vec{q}) q^\cdot (p_0^- - \vec{p}_\perp + \vec{q})} \left\} \]

Forming \( \delta K_{\text{corr.}} = 0 \), we obtain

\[ \frac{\beta^2}{(\beta^2+q^2)} \int \frac{dp_0^- dp_\perp^-}{q^\cdot (p_0^- - \vec{p}_\perp + \vec{q})} \]

\[ - \frac{1}{(\beta^2+q^2)} K_P \int \frac{dp_0^- dp_\perp^- dp_\perp^+}{(q^\cdot (p_0^- - \vec{p}_\perp + \vec{q}) q^\cdot (p_0^- - \vec{p}_\perp + \vec{q})} \]
Thus

$$\beta^2 = \frac{\cal{K}P}{\cal{I}} \frac{\int \frac{dp_0 \, dp_i \, dp_j}{q \cdot (\vec{p}_0 - \vec{p}_i + q) \cdot (\vec{p}_0 - \vec{p}_j + q)}}{\int \frac{dp_0 \, dp_i}{q \cdot (\vec{p}_0 - \vec{p}_i + q)}}$$ \hspace{1cm} (3.8)

$$= \frac{\cal{K}P}{\cal{I}} \frac{\int \frac{dp_0}{(\int \frac{dp_0}{q \cdot \Delta}})^2}{\int dp_0 (\int \frac{dp_0}{q \cdot \Delta}})$$ \hspace{1cm} (3.9)

$$\Delta = \vec{p}_0 - \vec{p}_i + \vec{q}$$

Since

$$\frac{i}{\lambda} \int \frac{dp_0}{q \cdot \Delta} = \mu^2 / \cal{K}P$$

where $\mu$ is Macke's screening function, we have

$$\beta^2 = \frac{\int \mu^4 dp_0}{\int \mu^2 dp_0}$$ \hspace{1cm} (3.10)
Substituting $\beta^2$ back into (3.6) we have for the correlation energy

$$E_{\text{corr.}} = E(\beta)_{\text{min.}}$$

$$= -\frac{N\kappa E_{\text{ex}}}{8\pi^3 R^3} \int \frac{dq^7}{q^7 \cdot q^7}.$$  

$$\left( \int \frac{dp_0 \cdot dp_1}{q \cdot \Delta} \right)^2$$

$$\left( \int \frac{dp_0 \cdot dp_1}{q \cdot \Delta} \right)^2 \frac{\int \frac{dp_0 \cdot dp_1}{q \cdot \Delta} \left[ q^2 + \frac{\kappa P}{\pi} \int \frac{dp_1}{q \cdot \Delta} \right]}$$

which may be compared to Eqn. (2.10).

The difficulties discussed in Section 2 above with regard to the use of new trial wave functions formed by extension of the formal perturbation expansion to higher orders do not arise with the use of our modification. Thus, we have an infinity of trial functions ordered
according to order of approximation of a perturbation expansion.
Chapter III

Application of General Screening Function to
Soft X-Ray Emission Band Studies

The soft x-ray emission band of sodium has a pronounced tail extending a little more than one electron volt past the expected low-energy limit of the band. Similar long wave length tails are a prominent feature of \( L_{III} \) emission bands of other light metals.

Skinner (1946) proposed that the tail arose from level broadening due to the short lifetime of the state with a vacancy in the conduction band since due to the interactions of the electrons in the band, an Auger transition will occur whereby a conduction electron from a higher level faces into the vacant level and the excess energy is used to raise a second conduction electron to a level above the Fermi surface.

Landsberg (1949) used Skinner's model in the calculation of the \( L_{III} \) band shape for sodium.

The interaction perturbation was assumed to be the difference between the ordinary Coulomb interaction which occurs in the complete Hamiltonian and the single coordinate potentials which occur in the Hartree-Fock Hamiltonian.

Assuming normalized plane-wave determinants as suitable approximations for initial and final states, the single-coordinate potentials contribute not at all to the matrix elements determining the transition probabilities and one obtains the pure Coulomb matrix elements, \( \mathcal{C}_{\mathbf{f}} = \frac{4\pi e^2}{\nu_0^2} \) (neglecting parallel spin interactions), where \( \mathbf{q} = \mathbf{\mathbf{k}} - \mathbf{k}' \) (conservation of momentum) with \( \mathbf{k}' \) specifying the vacancy left by the radiating electron, \( \mathbf{k} \) the state from which an electron falls into the hole, and \( \mathbf{k}_2, \mathbf{k}'_2 \) the initial and final states of the electron which jumps above the Fermi level (see Fig. 4.1a).
\[ \vec{b}_2' - \vec{b}_2 = \vec{b}_1 - \vec{b}_1' = \vec{q} \]

\[ |\vec{b}_1'| < R_F \]
\[ |\vec{b}_2| \leq R_F \]

\[ |\vec{b}_1| > |\vec{b}_1'| \]
\[ |\vec{b}_2 + \vec{q}| > R_F \]

\[ 0 \leq |\vec{q}| \leq 2R_F \]
Ignoring degeneracies, Landsberg used ordinary time dependent perturbation theory to calculate the total probability of an electron making a transition in time \( t \) into the vacancy specified by \( \vec{k}' \), which is held fixed through the calculation.

As noted in our introduction, this transition probability diverged. The divergence is as \( \int \frac{d\omega}{\omega} \) rather than \( \int \frac{d\omega}{\omega} \) of the perturbation calculation.

In our work we have considered the total transition probability for excitation out of the ground state \( \gamma_0 \), that is

\[
P_{\text{TOTAL}} = \sum_{n \neq 0} \frac{1}{(\omega_n^0 - \omega_0^0)^2}
\]

(24.1)

We find that this also diverges as \( \int \frac{d\omega}{\omega} \), thus there is no basis for distinction between the perturbation and transition probability divergences in terms of electronic interactions.

To overcome this divergence, Landsberg introduced the function \( e^{-\lambda'k'^2/\nu'k'^2} \) in place of \( e^{-\lambda k^2/\nu k^2} \) in calculating the matrix elements. A convergent total probability for transition into \( \vec{k}' \), \( P(k';\lambda) \), resulted, hence a finite half-width \( \Delta(k';\lambda) \) for all levels associated with \( \vec{k}' \) since \( \Delta(k';\lambda) \sim k' P(k';\lambda) \).

Choosing \( \lambda' \) such that \( \Delta(0,\lambda') \approx 1/k', \lambda' = \frac{1}{16\pi \nu''^2} \), a new density of states \( N(E)dE \) was obtained through considering the effects of broadening of levels on the free-electron density of states \( \sim E^{1/2}dE \).

For \( L_{III} \) transitions, \( N(E) \) predominantly determines the shape of the emission band. Landsberg's modified \( N(E) \) reproduces quite satisfactorily the shape, including tail, of the emission band (ignoring in this discussion a slight anomaly experimentally observed near the Fermi level -see Skinner (1946)).
For all $k'$ in the band, $\Delta(k') \leq \Delta(0)$, thus the lifetime of a vacancy is a minimum at the bottom of the conduction band in accord with the model proposed by Skinner. Further, $\Delta(k) \to 0$ as $k \to k_F$ (Fermi level), the broadening is zero at the Fermi level since only electrons of higher energy can fall into the vacancy; thus, there is no loss of sharpness at the Fermi level.

In brief, the theory and results appear consistent with experiment. It is thus with considerable interest that we apply one general screening function to the x-ray calculation. The justification for extending the use of the screening function to calculation of the matrix elements determining the transition probabilities may be found at the very basis of the time-dependent perturbation calculations. This is most clearly seen to first order of approximation in the adiabatic time-dependent calculation. Starting with the ground state $E_0$ (non-degenerate state) one finds upon allowing the Coulomb interaction to build up gradually that the time dependent wave function has eased into the form

$$\Phi(x,t) = \sum_{m=0}^{\infty} \frac{\mathcal{C}_m(t)}{E_0 - E_m} \varphi_m(x)$$

(4.2)

where the $\mathcal{C}_m(t)$ are effectively the ordinary Coulomb matrix elements $\mathcal{C}_m$, independent of time, due to the assumed gradual change of potential with time. However, the total transition probability diverges (vide Eqn. 4.1 and discussion), and the entire method of attack is invalidated.
If the variational method employing the screening function (Chapter II and Introduction) has any significance at all, it is that to the first order, a divergence-free, improved (certainly energywise) wave function is obtained by calculating the matrix elements which enter the first order perturbation expansion for the wave function using a screening function, i.e. $\mathcal{C}_{\gamma 0} \Rightarrow S_{\gamma 0}$

But these are the matrix elements determining the transition probabilities, hence we may calculate them using a screening function whenever they occur.

To this end we use the evaluation of the screening function for small $\gamma$, which is the important range with regard to divergences, employing the following approximations (\mathcal{E} space notation):

\[
\int \frac{d\vec{k}_2}{q^2 (k_0 - \vec{k}_2 + \vec{q})} = 2\hbar \int k_\perp \sqrt{k^2 - (z_0 + q/2)^2} \log \frac{z_0 + q/2 + k_\perp}{z_0 + q/2} \]

\[
\int \frac{d\vec{k}_2 \cdot d\vec{k}_1}{q^2 (k_0 - \vec{k}_1 + \vec{q})} \approx \frac{8\pi}{3} \left(1 - \log 2\right) \hbar^4 k_\perp^3 q \quad (4.3)
\]
and

\[
\int dk_0 \int \frac{dk_1}{q \cdot \Delta} \int \frac{dk_2}{q \cdot \Delta}
\]

\[
\approx 8\pi^2 \hbar^5 k_F^4 \left\{ \frac{1}{2} - 2 \left( \frac{2}{3} \log 2 - \frac{1}{6} \right) + \int_0^1 \left( \log \frac{t+1}{t} \right)^2 dt \right\}
\]

(4.5)

\[
\therefore \quad k_F^2 \beta^2 \left( \frac{\beta^2}{\hbar^2} \right) = \frac{\hbar k_F}{\pi \hbar} \frac{\int dk_0 \left( \int \frac{dk_1}{q \cdot \Delta} \right)^2}{\int dk_0 \left( \int \frac{dk_1}{q \cdot \Delta} \right)}
\]

(4.6)

\[
= 8\pi \hbar k_F^2
\]
For sodium, \( \beta_3 = 3.96 \alpha_H \)
\[
K = \frac{2}{\pi} \left( \frac{4}{9\pi} \right)^{\frac{1}{3}} \frac{\beta_3}{\alpha_H} = 1.31
\]
and
\[
K_F = 0.914 \times 10^8 \text{ cm}^{-1}
\]
thus
\[
\lambda_K = 0.97 \times 10^8 \text{ cm}^{-1}
\]
(4.7)
which is to be compared with the empirical value of \( \lambda \) chosen by Landsberg
\[
\lambda = 1.2 \times 10^8 \text{ cm}^{-1}
\]
Beyond numerical agreement, our screening function offers much more in its dependence on \( K \) and \( K_F^2 \).

Following Landsberg's derivation of the half-width \( \Delta(k) \), we obtain for the bottom of the conduction band \( k = 0 \), the half-width in e.V.

\[
\Delta(0) = 8.36 \left\{ \log \frac{K_F^2 + \beta^2}{\beta^2} - \frac{K_F^2}{K_F^2 + \beta^2} \right\} \text{ e.V. (4.8)}
\]
Since \( \beta k_F \sim K K_F^2 \)

\[
\Delta(0) = 8.36 \left\{ \log \frac{1 + K}{K} - \frac{1}{1 + K} \right\} \text{ e.V. (4.9)}
\]
and using \( K \sim \beta_3/3 \) with \( \beta_3 \) expressed in Bohr radii, we have

\[
\Delta(0) = 8.36 \left\{ \log \frac{3 + \beta_3}{\beta_3} - \frac{3}{3 + \beta_3} \right\} \text{ e.V. (4.10)}
\]
Half Width for $k = 0$

$\Delta(\theta)$ in eV

VS

1) $k$ (dimensionless)

2) $s_S = \frac{3}{n^{1/3}}$ (Bohr RADIUS)

($n =$ number of valence electrons per atom)

$\Delta(\theta)$ in eV

$\theta$

$S_S (a_h)$

Fig. 4.2
expressed completely in terms of the radius of the sphere equivalent in volume to the volume per electron, or, in monovalent solids, the Wigner-Seitz sphere radius
\[
\frac{4\pi}{3} (\frac{1}{3} a_m) ^3 = \frac{V}{N}
\]
which is a measure of ionic separation.

In Fig. 4.2 we have plotted \(A(0)\) as a function of \(K\) and \(\rho_s\).

Since \(A(0)\) is a measure of the length of tail, we are led, for example, to predict a longer tail for lithium than exists for sodium.

There is an interesting interpretation of the behavior of \(A(0)\) in its dependence on \(\rho_s\): as electron density decreases or ionic separation increases, the Fermi level decreases, the energy difference between the level for \(K=0\) and the Fermi level decreases, the instability of the state with a vacancy at \(K=0\) is lessened, the lifetime of the hole increases, the breadth of the level decreases.

According to Skinner's observations (Skinner 1939, 1946), the length of the tail increases with increasing number of valence electrons per atom which we interpret as increasing Fermi level. This is in accord with our results, since \(K \propto K^{-1}\) and for a decrease in \(K\) we find an increase in \(A(0)\) (Eqn. (4.9) and Fig. 4.2).

The screening function also decreases with decreasing volume per electron or increasing ionic separation and vanishes for infinite dilation of the lattice or infinite dilution of the electron gas. This is due to the fact that \(K=2 \alpha \frac{1}{\rho_s^2}\) thus
\[
\beta_{uv} = \frac{\rho_s}{\rho_s^2} = 1 = \frac{n^{1/3}}{2}
\]
where \(n\) is the number of valence electrons per atom.

Correspondingly, with increase in \(\rho_s\) there is an increase in correlation energy.
Literature Cited


1934. Ibid. No. 159.


1934. Ibid. 46: 509
