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Orthogonalized Plane Wave Method and Total Energy of a Metal

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We analyze a method for the computation of the total energy of a metal, proposed by Harrison and based upon the following approximations: (a) the self-consistent potential, (b) a second-order perturbation expansion, with a pseudopotential derived from the orthogonalized-plane-wave method. It is shown that the total energy can always be expressed as a sum of terms, each of them being a simple generalization of terms already known from more elementary calculations. The main effect of orthogonalizing the conduction electrons to the core is in increasing the ionic charge. These results are shown for two forms of the total energy. The first one is suitable for computations on the reciprocal lattice and contains a self-energy term, an Ewald's electrostatic term, and a second-order perturbation term; in the second one, a short-range pair interaction between ions is exhibited, the form of which is explicitly given.

I. INTRODUCTION

The calculation of metallic properties has long been hindered by the problem of the choice of a suitable potential for the one-electron Hamiltonian. It was believed that the effective potential acting on a conduction electron was small but one could not think of a potential being at the same time small and realistic.

For simplicity we can start with the quasifree-electron approximation in which the potential is purely phenomenological. Its matrix elements are unknown, so that the formulas obtained cannot be easily compared with experiments.

On the other hand, one can pick a more realistic (but no longer small) potential. The relationship between the shape of the potential and the numerical values obtained is then obscured by the complex numerical work which has to be performed.

The introduction of the orthogonalized-plane-wave (OPW) method simplified the situation by giving a theoretical basis to the quasifree-electron scheme. It also gave a practical means of getting a small potential out of a realistic (and large) potential.

The two points of view seemed, then, to be reconciled when in a recent article, Harrison[1] pointed out that approximating the non-Hermitian pseudopotential of the OPW method by a real potential could not be justified. A second-order perturbation expansion of the total energy leads in fact to terms which were not expected from the simplified theory.

We intend to show in the present paper that the above-mentioned terms can be, in fact, rearranged in such a way that their physical origin appears more clearly. The total energy of the electron-plus-ion system is then expressed as a sum of three terms, each of them being a generalization of its quasifree-electron equivalent. One is a volume dependent term which is a kind of self-energy of the individual ions, the second a purely electrostatic energy term, and the third an interaction energy expressed as a second-order perturbation term.

It is also well known (see, for instance, Refs. 2 and 3) that with a real potential, a second-order perturbation expansion leads to an expression of the total energy as a sum of pair interactions between ions. Such a result is also true with a pseudopotential,[1] and we shall derive here the explicit form of this pair-interaction function. We shall prove that in this respect the OPW method is also a generalization of simpler models and that the interaction is still a short-range one.

In the first section of this paper we shall calculate the one-electron energy with a second-order perturbation expansion. The total energy of the system will be deduced in the second part, while the pair interaction function as well as a remark on the self-consistency of the method will be given in the third part. Though the calculations of the two first parts could be done with a large variety of pseudopotentials, we shall use from the beginning a special one which is nearly the same as Harrison's[1] because it seems to be the most natural way to introduce in the last section the pair-interaction function.

Let us at last remark that the above-mentioned results have been obtained with the help of a perturbation expansion, the convergence of which will not be discussed here.

II. CALCULATION OF THE ONE-ELECTRON ENERGIES

We shall here calculate the eigenvalues of the one-electron Hamiltonian with OPW and perturbation methods.

Let

$$H=T+V \tag{2.1}$$

be a Hamiltonian whose eigenfunctions are one-electron wave functions. T is the kinetic energy operator with eigenfunctions. $|\mathbf{k}\rangle=e^{i\mathbf{k}\cdot\mathbf{r}}$ and eigenvalues $E_{\mathbf{k}}$.

V is a self-consistent Hartree potential; that is to say, the real distribution of all the electrons of the metal has been taken into account in V. This potential is small far from the ions but cannot be thought of as a perturbation in their immediate vicinity.

The spirit of the OPW method is to take advantage of the knowledge of a certain, incomplete, set of eigen-

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[1] W. A. Harrison, Phys. Rev. **129**, 2503 (1963).
[2] M. A. Ruderman and C. Kittel, Phys. Rev. **96**, 99 (1954).
[3] M. H. Cohen, J. Phys. Radium **23**, 643 (1962).

functions of Eq. (2.1) (the $|c\rangle$ functions with eigenvalues E_c) so as to find more easily the remaining eigenfunctions $|\psi_{\mathbf{k}}\rangle$ (with eigenvalues $\mathcal{E}_{\mathbf{k}}$).

One can express the orthogonality of $|\psi_k\rangle$ to any $|c\rangle$ function by writing that it has the form

$$|\psi_{\mathbf{k}}\rangle=(1-P)|\varphi_{\mathbf{k}}\rangle, \tag{2.2}$$

where P is the projection operator on the $|c\rangle$ functions:

$$P=\sum_c |c\rangle\langle c|. \tag{2.3}$$

From Eqs. (2.1) and (2.2), we get

$$\{T+V-\sum_c(E_c-\mathcal{E}_{\mathbf{k}})|c\rangle\langle c|\}|\varphi_{\mathbf{k}}\rangle \equiv (T+V+V_{\mathbf{k}})|\varphi_{\mathbf{k}}\rangle=\mathcal{E}_{\mathbf{k}}|\varphi_{\mathbf{k}}\rangle. \tag{2.4}$$

The definition of $|\varphi_{\mathbf{k}}\rangle$ through Eq. (2.2) is not unique for we can add to $|\varphi_{\mathbf{k}}\rangle$ any function of the form $\sum_c \alpha_c|c\rangle$ without changing $|\psi_{\mathbf{k}}\rangle$. We shall use this indeterminacy to transform Eq. (2.3) into an eigenfunction problem with a small pseudopotential.

Let us first divide V into two parts in the following way. Its first part V_1 will be a sum of nonoverlapping potentials centered on every nucleus,

$$V_1=\sum_{\mathbf{R}_i} v_1(\mathbf{r}-\mathbf{R}_i).$$

$v_1(\mathbf{r}-\mathbf{R})$ is chosen to be zero for $|\mathbf{r}-\mathbf{R}_i|>r_0$ where r_0 is smaller than the inscribed sphere in the atomic cell. It includes all the important and rapidly varying part of V in this sphere, that is to say all the part of V which arises from the ion which stands at the center of the sphere.

V_2 is the remaining part of the potential, which we shall assume to be small everywhere.

We shall now choose $|\varphi_{\mathbf{k}}\rangle$ such that for any permissible variation of $|\varphi_{\mathbf{k}}\rangle$

$$\delta\langle\varphi_k|V_1+V_{\mathbf{k}}|\varphi_{\mathbf{k}}\rangle=0.$$

One easily gets

$$H_1|\varphi_{\mathbf{k}}\rangle\equiv\{T+(1-P)V_1+V_2\}|\varphi_{\mathbf{k}}\rangle=\mathcal{E}_{\mathbf{k}}|\varphi_{\mathbf{k}}\rangle. \tag{2.5}$$

Actually the $|c\rangle$ functions are those of the core electrons localized in the vicinity of every nucleus. If $u(\mathbf{r})$ has no amplitude near any nucleus, we have $P|u\rangle=0$. Furthermore, any $|\psi_{\mathbf{k}}\rangle$ has a small amplitude in the same region, so that the functions $c(\mathbf{r})$ form a nearly complete set of functions for functions localized near any nucleus. In other words, P acts more or less as a sum of square wells centered on every nucleus with a depth which is nearly 1 at the center and 0 outside.

Equation (2.5) now defines a pseudopotential $W=(1-P)V_1+V_2$ with the two following properties:

(a) From the above, we see that W is small, for $(1-P)$ is small where V_1 is important and vice versa, and V_2 is always small. We can thus perform a perturbation expansion with W.

(b) W is not Hermitian. W contains the product of two Hermitian operators so that its adjoint $W^\dagger$ is given by

$$W^\dagger=V_2+V_1(1-P). \tag{2.6}$$

With Eq. (2.5), the perturbation expansion[4] is readily performed and one gets

$$\mathcal{E}_{\mathbf{k}}=E_{\mathbf{k}}+\langle\mathbf{k}|W|\mathbf{k}\rangle+\sum_{\mathbf{q}\neq0}\frac{\langle\mathbf{k}|W|\mathbf{k}+\mathbf{q}\rangle\langle\mathbf{k}+\mathbf{q}|W|\mathbf{k}\rangle}{E_{\mathbf{k}}-E_{\mathbf{k}+\mathbf{q}}} \tag{2.7}$$

and

$$|\varphi_{\mathbf{k}}\rangle=(1+a_{\mathbf{k}})|\mathbf{k}\rangle+\sum_{\mathbf{q}\neq0}|\mathbf{k}+\mathbf{q}\rangle\frac{\langle\mathbf{k}+\mathbf{q}|W|\mathbf{k}\rangle}{E_{\mathbf{k}}-E_{\mathbf{k}+\mathbf{q}}};$$

$$|\psi_{\mathbf{k}}\rangle=(1-P)|\varphi_{\mathbf{k}}\rangle. \tag{2.8}$$

Formulas (2.7) and (2.8) are not the usual ones in two respects:

(a) The numerator of (2.7) is not a squared modulus.

(b) We want $|\psi_{\mathbf{k}}\rangle$ to be normalized to unity so that $a_{\mathbf{k}}$ will not be zero.

We shall first transform (2.7) by introducing the potential $W^\dagger$ which has to be a first-order quantity as well as W. Let us note that

$$\langle\mathbf{k}+\mathbf{q}|W^\dagger|\mathbf{k}\rangle-\langle\mathbf{k}+\mathbf{q}|W|\mathbf{k}\rangle=\langle\mathbf{k}+\mathbf{q}|[P,V_1]|\mathbf{k}\rangle =\langle\mathbf{k}+\mathbf{q}|[P,((V+T)-(T+V_2))]|\mathbf{k}\rangle. \tag{2.9}$$

As $H=T+V$ and $P=\sum_c|c\rangle\langle c|$ are commuting operators, and $|\mathbf{k}\rangle$ and $|\mathbf{k}+\mathbf{q}\rangle$ are eigenfunctions of T, Eq. (2.9) gives

$$\langle\mathbf{k}+\mathbf{q}|W^\dagger|\mathbf{k}\rangle-\langle\mathbf{k}+\mathbf{q}|W|\mathbf{k}\rangle =-\langle\mathbf{k}+\mathbf{q}|P|\mathbf{k}\rangle(E_{\mathbf{k}}-E_{\mathbf{k}+\mathbf{q}}) -\langle\mathbf{k}+\mathbf{q}|[P,V_2]|\mathbf{k}\rangle. \tag{2.10}$$

We shall now suppose that V_2 is very slowly varying in the region where P is not zero. If this is the case, V_2 can be replaced by a constant in $[P,V_2]$ so that the last term of (2.10) is zero.

Equation (2.10) enables us to transform (2.7). Furthermore, it tells us that any matrix element of P has to be considered as a first-order term as well as those of W or $W^\dagger$.

With Eqs. (2.7) and (2.10) one gets

$$\mathcal{E}_{\mathbf{k}}=E_{\mathbf{k}}+\langle\mathbf{k}|W|\mathbf{k}\rangle+\sum_{\mathbf{q}\neq0}\frac{|\langle\mathbf{k}+\mathbf{q}|W|\mathbf{k}\rangle|^2}{E_{\mathbf{k}}-E_{\mathbf{k}+\mathbf{q}}} -\sum_{\mathbf{q}\neq0}\langle\mathbf{k}|P|\mathbf{k}+\mathbf{q}\rangle\langle\mathbf{k}+\mathbf{q}|W|\mathbf{k}\rangle. \tag{2.11}$$

A further simplification will appear if one makes use

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[4] Throughout this article we shall suppose that the system is enclosed in a box of volume L^3 so that the eigenstates are discrete, and the perturbation expansion can be performed in the usual way. We shall adopt here the atomic unit system: $\hbar=m=e=1$. For the Fourier transform we shall use the definition

$$V(\mathbf{q})=[1/L^3]\int e^{+i\mathbf{q}\cdot\mathbf{r}}V(\mathbf{r})d\mathbf{r},$$

so that we have $V(\mathbf{q})=\langle\mathbf{k}+\mathbf{q}|V|\mathbf{k}\rangle$.

of the closure relation

$$\sum_{\mathbf{q}}|\mathbf{k}+\mathbf{q}\rangle\langle\mathbf{k}+\mathbf{q}|=1\,. \tag{2.12}$$

We get

$$-\sum_{\mathbf{q}\neq0}\langle\mathbf{k}|P|\mathbf{k}+\mathbf{q}\rangle\langle\mathbf{k}+\mathbf{q}|W|\mathbf{k}\rangle=\langle\mathbf{k}|P|\mathbf{k}\rangle\langle\mathbf{k}|W|\mathbf{k}\rangle -\langle\mathbf{k}|P[(1-P)V_1+V_2]V|\mathbf{k}\rangle; \tag{2.13}$$

because of the relation $P^2=P$, the term $P(1-P)V_1$ cancels out and we get

$$\mathcal{E}_{\mathbf{k}}=E_{\mathbf{k}}+\{1+\langle\mathbf{k}|P|\mathbf{k}\rangle\}\langle\mathbf{k}|W|\mathbf{k}\rangle-\langle\mathbf{k}|PV_2|\mathbf{k}\rangle +\sum_{\mathbf{q}\neq0}\frac{|\langle\mathbf{k}+\mathbf{q}|W|\mathbf{k}\rangle|^2}{E_{\mathbf{k}}-E_{\mathbf{k}+\mathbf{q}}}. \tag{2.14}$$

Equation (2.14) is not the classical result of the perturbation theory because of the $-\langle\mathbf{k}|PV_2|\mathbf{k}\rangle$ and $\langle\mathbf{k}|P|\mathbf{k}\rangle\langle\mathbf{k}|W|\mathbf{k}\rangle$ terms. This is not important because we have to keep in mind that it is the total energy of the system and not $\mathcal{E}_{\mathbf{k}}$ which has a physical meaning. Indeed we shall see in the next section that the presence of those terms is necessary in order to express the total energy in a simple manner.

Let us now normalize $|\psi_{\mathbf{k}}\rangle$. From Eq. (2.8) we get

$$|\psi_{\mathbf{k}}\rangle=|k\rangle(1+a_{\mathbf{k}}-\langle\mathbf{k}|P|\mathbf{k}\rangle)+\sum_{\mathbf{q}\neq0}|\mathbf{k}+\mathbf{q}\rangle \times\left\{\frac{\langle\mathbf{k}+\mathbf{q}|W|\mathbf{k}\rangle}{E_{\mathbf{k}}-E_{\mathbf{k}+\mathbf{q}}}-(1+a_{\mathbf{k}})\langle\mathbf{k}+\mathbf{q}|P|\mathbf{k}\rangle\right\}, \tag{2.15a}$$

so that we must have $a_{\mathbf{k}}=\langle\mathbf{k}|P|\mathbf{k}\rangle$.

As $|\psi_{\mathbf{k}}|$ is a first-order wave function and $\langle\mathbf{k}|P|\mathbf{k}\rangle$ a first-order quantity, we shall neglect $a_{\mathbf{k}}\langle\mathbf{k}+\mathbf{q}|P|\mathbf{k}\rangle$ in the right-hand member so that $|\psi_{\mathbf{k}}\rangle$ reads

$$|\psi_{\mathbf{k}}\rangle=|\mathbf{k}\rangle+\sum_{\mathbf{q}\neq0}|\mathbf{k}+\mathbf{q}\rangle \times\left\{\frac{\langle\mathbf{k}+\mathbf{q}|W|\mathbf{k}\rangle}{E_{\mathbf{k}}-E_{\mathbf{k}+\mathbf{q}}}-\langle\mathbf{k}+\mathbf{q}|P|\mathbf{k}\rangle\right\}. \tag{2.15b}$$

The origin of the nonzero value of $a_{\mathbf{k}}$ is the following. From Eq. (2.8) and from the definition of P, $|\psi_{\mathbf{k}}\rangle$ has a very small amplitude near any nucleus. This means that the effect of orthogonalizing $|\psi_{\mathbf{k}}\rangle$ to the core functions leads to a repulsion of a charge $a_{\mathbf{k}}$ from the vicinity of the nuclei. $|\varphi_{\mathbf{k}}\rangle$ has then to be renormalized so that $|\psi_{\mathbf{k}}\rangle$ is a proper wave function. We shall see in the next section that this repulsion explains also the existence of the extra terms of (2.14).

III. CALCULATION OF THE TOTAL ENERGY

In this section, we shall express the total energy as a sum of three terms, each of which has a simple physical meaning. The first one will depend only on the number of conduction electrons and ions and not on the shape of the crystalline lattice; it will contain the energy of the free electrons plus a self-energy of the ions. The second one will represent the electrostatic energy of a metal idealized as a lattice of positive charges embedded in a uniform cloud of electrons, the density of which is such that the total charge will be equal to zero. The last one will be the difference between the actual energy and the first two terms and will appear as a second-order perturbation term in which a matrix element of the bare potential is multiplied on one side by a matrix element of the dressed potential.

In order to obtain such a result, we shall explain first what is the physical origin of the various contributions to the total energy E_{tot}, and what are the terms we take into account in the potential V. Keeping in mind the structure of the expression we are looking for, we shall first rearrange the electrostatic terms of E_{tot} in order to eliminate some expressions which could not be obtained with the desired accuracy. To go one step further we shall need to explain what part of V enters into V_1 and V_2 and how we get the Hartree potential. The final formulas will then be obtained after some very simple calculations that we shall briefly summarize.

A. The Total Energy

The total energy E_{tot} of the metal contains the following terms

$$E_{\text{tot}}=\sum_i\mathcal{U}_i+\sum_{k<k_F}\mathcal{E}_{\mathbf{k}}-\frac{1}{2}\int\rho(\mathbf{r})U(\mathbf{r})d\mathbf{r} +\frac{1}{2}\int\rho_{\text{ion}}(\mathbf{r})V_{\text{ion}}(\mathbf{r})d\mathbf{r}, \tag{3.1}$$

where $\mathcal{U}_i$ is the ion self-energy.

$\rho(\mathbf{r})$ is the charge density at the point $\mathbf{r}$ of the conduction electrons and $U(\mathbf{r})$ is the corresponding potential given by

$$\Delta U(\mathbf{r})+4\pi\rho(\mathbf{r})=0\,.$$

The minus sign in front of the corresponding term arises because the conduction electron interaction energy $\frac{1}{2}\int\rho(\mathbf{r})U(\mathbf{r})d\mathbf{r}$ has been counted twice in the Hartree procedure.

$\rho_{\text{ion}}(\mathbf{r})$ is the charge density of the ions, $V_{\text{ion}}(\mathbf{r})$ the related potential, and $\frac{1}{2}\int\rho_{\text{ion}}(\mathbf{r})V_{\text{ion}}(\mathbf{r})d\mathbf{r}$ the ion interaction energy. We must not forget that the ion which stands at R_i does not interact with the potential it creates itself. To remind us of this fact and of the special meaning of the related integral, we shall write $\tilde{V}_{\text{ion}}$ for the potential instead of V_{ion}.

$\mathcal{E}_{\mathbf{k}}$ is the electron energy, given by (2.14). This energy has been expressed with the help of a potential V, the nature of which we shall now discuss.

B. Form of $V(r)$

Let us explain what terms are contained in $V(\mathbf{r})$. First comes a term L involving all the non-Coulomb features of the potential. It can represent, for example,

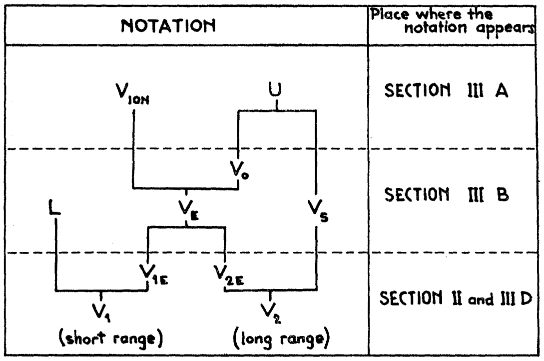

FIG. 1. Summary of the different ways the potential has been separated in Secs. II and III as well as the relationship between the different notations.

the exchange interaction between the $|c\rangle$ and the $|\psi\rangle$ electrons. L is a sum of interactions localized around each ion.

$$L=\sum_{\mathbf{R}}\ell(\mathbf{r}-\mathbf{R}), \tag{3.2}$$

where ℓ is a short-range potential.

Then we have a Coulomb term V_E corresponding to the potential due to the nuclei, the $|c\rangle$ electrons and a sum of plane waves $\sum_{k<k_F}|\mathbf{k}\rangle$. The total charge ρ_E which generated V_E is then zero. As the $|c\rangle$ electrons are in the vicinity of the nuclei ρ_E is well represented by point-charges, $-Z$ localized on each crystalline site imbedded in a uniform charge $+Z$, where Z is the valence of the ions.

The rest of V is a Coulomb potential V_S, which arises from the difference in charge density between the actual electrons and the plane waves. It thus includes the effects of (a) the orthogonalization procedure of the OPW method and (b) the second-order perturbation method.

V_S is thus a Hartree potential. It is, of course, the most involved term of this theory, but it has already been shown by Harrison[1] that such a term could be calculated without difficulty.

It has to be emphasized that V_E and V_S are real potentials and not operators in contradistinction to L and P. Their Fourier transforms

$$V_E(\mathbf{q})=\langle\mathbf{k}+\mathbf{q}|V_E|\mathbf{k}\rangle;\quad V_S(\mathbf{q})=\langle\mathbf{k}+\mathbf{q}|V_S|\mathbf{k}\rangle \tag{3.3}$$

are thus independent of $\mathbf{k}$.

C. Rearrangement of Terms

It is clear that some manipulation will now be necessary in order to obtain the above-mentioned form for the total energy. Indeed one can notice that the notation is quite different in Secs. A and B above, and still not the same as in Sec. II. This unhappy feature is due to the very nature of our problem, and our task is now to match together different parts of E_{tot} or V. As this is not an easy matter, we think it useful to summarize in Fig. 1 how the different terms which enter V are grouped in the subsections of Sec. III.

The first thing we need to do is make a transformation of the electrostatic part of (3.1). Let ρ_0 be the charge density due to the plane waves $\sum_{k<k_F}|\mathbf{k}\rangle$, and V_0, the related potential. From the definition of V_S and V_E we have

$$U(\mathbf{r})=V_0(\mathbf{r})+V_S(\mathbf{r}),\quad \tilde{V}_E(\mathbf{r})=V_0(\mathbf{r})+\tilde{V}_{\text{ion}}(\mathbf{r}), \tag{3.4a}$$

or

$$\rho(\mathbf{r})=\rho_0(\mathbf{r})+\rho_S(\mathbf{r}),\quad \rho_E(\mathbf{r})=\rho_0(\mathbf{r})+\rho_{\text{ion}}(\mathbf{r}). \tag{3.4b}$$

By making use of Eqs. (3.4) the last two terms of (3.1) may be written as

$$\frac{1}{2}\int\rho_E(\mathbf{r})\tilde{V}_E(\mathbf{r})d\mathbf{r}-\frac{1}{2}\int\rho_S(\mathbf{r})V_S(\mathbf{r})d\mathbf{r}$$
$$-\int\rho_0(\mathbf{r})[V_E(\mathbf{r})+V_S(\mathbf{r})]d\mathbf{r}. \tag{3.5}$$

As ρ_0 has only one Fourier component (for $q=0$) the three terms of (3.5) are

(a) the self-energy of the charge ρ_E,

(b) $$-\frac{1}{2}\int\rho_S(\mathbf{r})V_S(\mathbf{r})d\mathbf{r}=-(L^3/2)\sum_{\mathbf{q}}\rho_S(\mathbf{q})V_S(-\mathbf{q}), \tag{3.6}$$

where $\rho_S(q)$ and $V_S(q)$ are the Fourier transforms of $\rho_S(\mathbf{r})$ and $V_S(\mathbf{r})$, and

(c) $$-\int\rho_0(\mathbf{r})[V_E(\mathbf{r})+V_S(\mathbf{r})]d\mathbf{r}=-\sum_{k<k_F}\langle\mathbf{k}|V_E+V_S|\mathbf{k}\rangle. \tag{3.7}$$

This term cancels out $\sum_{k<k_F}\langle\mathbf{k}|V_E+V_S|\mathbf{k}\rangle$ which comes from the first-order perturbation term of $\mathcal{E}_{\mathbf{k}}$ in (3.1). As we shall now see, this cancellation greatly simplifies the calculation of V_S.

D. Form of V_1, V_2, and V_S

We have now to separate V into V_1 and V_2. As we want V_1 to include all that part of V which varies rapidly near the nucleus, V_1 contains L plus the potential V_{1E} created inside the sphere of radius r_0 by the part of ρ_E which lies in it. Moreover, r_0 is chosen in such a way that this sphere is substantially bigger than the region of the space where $|c\rangle$ is not zero.

V_2 is thus formed of V_S plus V_{2E}, the remaining part of V_E. From the definition of r_0 it is apparent that V_{2E} is practically constant in the region where P effectively acts as it was supposed in the last section when asserting that $[P,V_2]=0$. We shall now calculate V_S and prove that the same is true for it.

Let us first remark that

$$\rho_S(\mathbf{r})=\sum_{k<k_F}(\psi_{\mathbf{k}}^*(\mathbf{r})\psi_{\mathbf{k}}(\mathbf{r})-1) \tag{3.8}$$

does not contain any zero-order terms. (See Eq. 2.15b.)

We also point out that ρ_S and V_S are now combined in such a way in (3.1) and (3.6) that *it is sufficient to know them to first order.* [This was not the case in the primitive form of (3.1) and explains why we needed to cancel out (3.7) by another part of the total energy at this stage of the calculation.]

From Eq. (2.15b) we get now $\rho_S(\mathbf{q})$ up to first order

$$\rho_S(\mathbf{q})=\frac{1}{L^3}\sum\nolimits_{k<k_F}\left[\frac{\langle\mathbf{k}+\mathbf{q}|W|\mathbf{k}\rangle}{E_{\mathbf{k}}-E_{\mathbf{k}+\mathbf{q}}}+\frac{\langle\mathbf{k}-\mathbf{q}|W|\mathbf{k}\rangle^*}{E_{\mathbf{k}}-E_{\mathbf{k}+\mathbf{q}}}-(\langle\mathbf{k}+\mathbf{q}|P|\mathbf{k}\rangle+\langle\mathbf{k}|P|\mathbf{k}-\mathbf{q}\rangle)\right] \tag{3.9}$$

and with the help of the Poisson equation we obtain

$$V_S(\mathbf{q})=\sum\nolimits_{k<k_F}\left[\frac{\langle\mathbf{k}+\mathbf{q}|(1-P)V_1+V_{2E}|\mathbf{k}\rangle}{E_{\mathbf{k}}-E_{\mathbf{k}+\mathbf{q}}}+\frac{\langle\mathbf{k}-\mathbf{q}|(1-P)V_1+V_{2E}|\mathbf{k}\rangle^*}{E_{\mathbf{k}}-E_{\mathbf{k}-\mathbf{q}}}-(\langle\mathbf{k}+\mathbf{q}|P|\mathbf{k}\rangle+\langle\mathbf{k}|P|\mathbf{k}-\mathbf{q}\rangle)\right]\Bigg/\left\{\frac{q^2L^3}{4\pi}-\sum\nolimits_{k<k_F}\left[\frac{1}{E_{\mathbf{k}}-E_{\mathbf{k}+\mathbf{q}}}+\frac{1}{E_{\mathbf{k}}-E_{\mathbf{k}-\mathbf{q}}}\right]\right\}. \tag{3.10}$$

For large q the denominator is proportional to q^2 while the numerator certainly goes to zero as $1/q^2$ and more likely as $1/q^4$. Thus by Fourier transform, for short distances $V_S(\mathbf{r})$ is a constant, which proves that $[P,V_S]$ could be neglected in (2.10).

One has still to show that we were consistent when writing in Sec. II that any matrix element of V_2 was small. From (3.10) it is now apparent that $\langle\mathbf{k}+\mathbf{q}|V_2|\mathbf{k}\rangle$ is small whenever $V_{2E}(\mathbf{q})$ is, and from the definition of V_{2E} the latter is true for large q, but when q goes to zero $V_{2E}(\mathbf{q})$ is proportional to $1/q^2$. $\langle\mathbf{k}+\mathbf{q}|V_2|\mathbf{k}\rangle$ will nevertheless be small because if we put together the two V_{2E} terms of V_2, a q^2 factor will appear which will remove the $1/q^2$ divergency.

We can now obtain the total energy in the proposed form by splitting (3.1) as follows.

E. Final Form of the Total Energy

a. The Structure Independent Terms

We can easily prove that the following terms do not depend on the relative positions of the ions, but only on the total volume of the system.

$$E_0=\sum\nolimits_i \mathcal{U}_i+\sum\nolimits_{k<k_F}\{E_{\mathbf{k}}+\langle\mathbf{k}|L|\mathbf{k}\rangle-\langle\mathbf{k}|PV_1|\mathbf{k}\rangle+\langle\mathbf{k}|P|\mathbf{k}\rangle\langle\mathbf{k}|(1-P)V_1|\mathbf{k}\rangle\}. \tag{3.11}$$

Indeed the $|c\rangle$ functions for two different crystalline sites do not overlap, and V_1 is, as L, a sum of nonoverlapping potentials centered on the same sites.

$$V_1=\sum\nolimits_{\mathbf{R}_i} v(\mathbf{r}-\mathbf{R}_i). \tag{3.12}$$

We thus obtain, for example,

$$\langle\mathbf{k}|PV_1|\mathbf{k}\rangle\equiv\sum\left\{\int\frac{e^{-i\mathbf{k}(\mathbf{r}-\mathbf{R}_i)}}{\sqrt{L^3}}c(\mathbf{r}-\mathbf{R}_i)d(\mathbf{r}-\mathbf{R}_i)\times\int c^*(\mathbf{r}'-\mathbf{R}_i)v_1(\mathbf{r}'-\mathbf{R}_i)\frac{e^{i\mathbf{k}(\mathbf{r}'-\mathbf{R}_i)}}{\sqrt{L^3}}d(\mathbf{r}'-\mathbf{R}_i)\right\},$$

where the summation runs over all the sites R_i and all the $|c\rangle$ functions centered on this site. Such an expression clearly depends only on the total volume L^3 and certainly not on the relative positions of the ions, and so will be the case for (3.11).

b. The Electrostatic Interaction Term

The following terms will now be put together:

$$E_{\mathrm{es}}=\frac{1}{2}\int\rho_E(\mathbf{r})\tilde{V}_E(\mathbf{r})d\mathbf{r}-\sum\nolimits_{k<k_F}\{\langle\mathbf{k}|PV_{2E}|\mathbf{k}\rangle-\langle\mathbf{k}|P|\mathbf{k}\rangle\langle\mathbf{k}|V_{2E}|\mathbf{k}\rangle\}. \tag{3.13}$$

We prove in Appendix A that

$$\rho_1(\mathbf{r})\equiv-\sum\nolimits_{\mathbf{q}}e^{-i\mathbf{q}\cdot\mathbf{r}}\sum\nolimits_{k<k_F}\frac{\langle\mathbf{k}|P|\mathbf{k}+\mathbf{q}\rangle}{L^3}$$

may be interpreted as a sum of point charges localized on the ionic sites $\mathbf{R}_i$ and that we can write

$$-\sum\nolimits_{k<k_F}\{\langle\mathbf{k}|PV_{2E}|\mathbf{k}\rangle-\langle\mathbf{k}|P|\mathbf{k}\rangle\langle\mathbf{k}|V_{2E}|\mathbf{k}\rangle\}=\int\rho_1(\mathbf{r})V_{2E}(\mathbf{r})d\mathbf{r}=\alpha\int\rho_E(\mathbf{r})\tilde{V}_E(\mathbf{r})d\mathbf{r}, \tag{3.14}$$

with

$$\alpha=[\langle\mathbf{k}|P|\mathbf{k}\rangle]_{\mathrm{av}}=\sum\nolimits_{k<k_F}\langle\mathbf{k}|P|\mathbf{k}\rangle/\sum\nolimits_{k<k_F}\langle\mathbf{k}|\mathbf{k}\rangle. \tag{3.15}$$

The electrostatic term E_{es} can then be written as

$$E_{\mathrm{es}}=\tfrac{1}{2}(1+2\alpha)\int\rho_E(\mathbf{r})\tilde{V}_E(\mathbf{r})d\mathbf{r}\simeq\tfrac{1}{2}(1+\alpha)^2\int\rho_E(\mathbf{r})\tilde{V}_E(\mathbf{r})d\mathbf{r}. \tag{3.16}$$

Equation (3.16) has a simple physical meaning. From

(3.15) and (2.15a) α is the mean value of the total charge repelled by the ions in the course of orthogonalization of all the $|\psi_k\rangle$ functions to the $|c\rangle$ functions. As far as electrostatic energy is concerned, we see that this fact appears in the presence of an additional charge of opposite sign $-\alpha Z$ localized on each ion counterbalanced by the charge αZ uniformly spread on the whole crystal.

c. The Second-Order Perturbation Term

The terms which have not been taken into account are now the following:

$$E_p=\frac{L^3}{2}\sum_{\mathbf{q}}\rho_S(\mathbf{q})V_S(-\mathbf{q})+\sum_{k<k_F}\left(\sum_{\mathbf{q}\neq 0}\frac{|\langle\mathbf{k}+\mathbf{q}|W|\mathbf{k}\rangle|^2}{E_{\mathbf{k}}-E_{\mathbf{k}+\mathbf{q}}}+\langle\mathbf{k}|P|\mathbf{k}\rangle\langle\mathbf{k}|V_S|\mathbf{k}\rangle-\langle\mathbf{k}|PV_S|\mathbf{k}\rangle\right). \tag{3.17}$$

With the value of $\rho_S(\mathbf{q})$ (3.9) and $V_S(\mathbf{q})$ (3.10), it is readily found that E_p can also be written

$$E_p=\tfrac{1}{2}\sum_{k<k_F}\sum_{\mathbf{q}\neq 0}\left\{\frac{\langle\mathbf{k}|V_1(1-P)+V_{2E}|\mathbf{k}+\mathbf{q}\rangle\langle\mathbf{k}+\mathbf{q}|(1-P)V_1+V_{2E}+V_S|\mathbf{k}\rangle}{E_{\mathbf{k}}-E_{\mathbf{k}+\mathbf{q}}}\right.$$
$$\left.+\frac{\langle\mathbf{k}|V_1(1-P)+V_{2E}+V_S|\mathbf{k}+\mathbf{q}\rangle\langle\mathbf{k}+\mathbf{q}|(1-P)V_1+V_{2E}|\mathbf{k}\rangle}{E_{\mathbf{k}}-E_{\mathbf{k}+\mathbf{q}}}\right\}. \tag{3.18}$$

Formula (3.18) is analogous to the perturbation term obtained with a small Hermitian potential. We have indeed the product of two matrix elements, one corresponding to the bare potential, and the second to the bare adjoint potential plus the screening term (that is to say, W itself).

It is now apparent that the total energy given by this second-order perturbation expansion can be regarded as a generalization of the ordinary result obtained by using a small potential instead of a pseudopotential W.

Indeed, the new terms which appear in (3.11), (3.16), or (3.18) are a consequence either of the repulsion of the conduction electrons by the core electrons or of the use of a non-Hermitian potential.

We can thus conclude that in this respect, the OPW method gives a theoretical basis to the quasifree-electron model.

IV. GENERAL REMARKS AND CONCLUSION

A. Self-Consistency of the Total Energy Expression

We used a perturbation expansion of $\mathcal{E}_{\mathbf{k}}$ in order to obtain the total energy of the system. For a given $\mathbf{q}$, it is clear that $\mathcal{E}_{\mathbf{k}}$ diverges when $E_{\mathbf{k}}=E_{\mathbf{k}+\mathbf{q}}$; so it does not stand to reason that (3.2) is the correct value of the energy.

One can nevertheless prove[5] that.

(a) for any given $\mathbf{q}$, the summation on $k<k_F$ leads to a converging expression for the energy (3.18). The total energy is thus a sum of finite expressions.

(b) (3.2) is the correct value of the energy up to the second order if (and only if) the Fermi surface is not deformed by the first-order term of the perturbation expansion.

We have then to show that $\langle\mathbf{k}|W|\mathbf{k}\rangle$ is independent of the direction of $\mathbf{k}$ for $|\mathbf{k}|=k_F$.

Indeed

$$\langle\mathbf{k}|W|\mathbf{k}\rangle=\langle\mathbf{k}|V_E+V_S|\mathbf{k}\rangle+\langle\mathbf{k}|L-PV_1|\mathbf{k}\rangle. \tag{4.1}$$

V_E and V_S being Coulomb potentials, the first term is k-independent. We shall now replace in P the index c by the double index $(\mathbf{R}_i,t)$, where t specifies all the quantum numbers of the related wave function. $t(\mathbf{r}-\mathbf{R}_i)$ has the form $Y_l^m(\theta,\varphi)P_{nl}(\mathbf{r}-\mathbf{R}_i)$. As L and V_1 are functions of $(\mathbf{r}-\mathbf{R})$ only, by expanding $|\mathbf{k}\rangle$ in spherical Bessel functions, and summing on the index m, one readily proves that the last term of (4.1) is a function of $|\mathbf{k}|$ only. We have thus correctly calculated the total energy up to second-order terms in the last section.

B. Pair Interactions and Range of Forces

It has already been noticed[3,5] that a second-order perturbation expansion with a real potential leads for the total energy to an expression which can be interpreted as a sum of pair interactions. Harrison[1] derived the same result for his pseudopotential but did not write down the explicit form of the interaction function.

We think it is worthwhile to give this formula here and to comment on its principal features. We shall first rewrite in our own notation the pair-interaction function derived by Harrison from E_p, and shall afterwards add the contribution of E_S to get it in its final form.

a. Form of the E_p Term

Let us first notice that in E_p the term $\mathbf{q}=0$ is excluded from the summation; for $\mathbf{q}\neq 0$, $V_E(\mathbf{q})$ is just the

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[5] A. Blandin and R. Pick, Physique de la Matière Condensée (to be published).

Fourier transform of the *potential produced by the ionic charge density*. With the help of this remark and of formulas (3.10), (3.12), and (3.17), it is easily shown that we can write

$$E_p=\textstyle\sum_{\mathbf{q}\neq 0}|S(\mathbf{q})|^2E(\mathbf{q}),\quad V_S(\mathbf{q})=S(\mathbf{q})v_S(\mathbf{q}),\tag{4.2}$$

where

$$S(\mathbf{q})=\textstyle\sum_{\mathbf{R}i}e^{-i\mathbf{q}\cdot\mathbf{R}_i},\tag{4.3}$$

$$E(\mathbf{q})=\tfrac{1}{2}\textstyle\sum_{k<k_F}\dfrac{\langle\mathbf{k}|\ell-o^\dagger-(4\pi Ze^{-i\mathbf{q}\cdot\mathbf{r}}/q^2L^3)|\mathbf{k}+\mathbf{q}\rangle\langle\mathbf{k}+\mathbf{q}|\ell-o+[-(4\pi Z/q^2L^3)+v_S(\mathbf{q})]e^{i\mathbf{q}\cdot\mathbf{r}}|\mathbf{k}\rangle}{E_\mathbf{k}-E_{\mathbf{k}+\mathbf{q}}}+\text{c.c.},\tag{4.4}$$

$$v_S(\mathbf{q})=\frac{1}{H(\mathbf{q})}\textstyle\sum_{k<k_F}\left\{\left[\dfrac{\langle\mathbf{k}+\mathbf{q}|\ell-o-(4\pi Ze^{i\mathbf{q}\cdot\mathbf{r}}/q^2L^3)|\mathbf{k}\rangle}{E_\mathbf{k}-E_{\mathbf{k}+\mathbf{q}}}+\dfrac{\langle\mathbf{k}|\ell-o^\dagger-(4\pi Ze^{-i\mathbf{q}\cdot\mathbf{r}}/q^2L^3)|\mathbf{k}-\mathbf{q}\rangle}{E_\mathbf{k}-E_{\mathbf{k}-\mathbf{q}}}\right]\right.$$
$$\left.-\textstyle\sum_t[\langle\mathbf{k}+\mathbf{q}|t\rangle\langle t|\mathbf{k}\rangle+\langle\mathbf{k}|t\rangle\langle t|\mathbf{k}-\mathbf{q}\rangle]\right\},\tag{4.5}$$

$$\langle\mathbf{k}+\mathbf{q}|o|\mathbf{k}\rangle=\textstyle\sum_t\langle\mathbf{k}+\mathbf{q}|t\rangle\langle t|v_1|\mathbf{k}\rangle,\quad\langle\mathbf{k}+\mathbf{q}|o^\dagger|\mathbf{k}\rangle=\sum_t\langle\mathbf{k}+\mathbf{q}|v_1|t\rangle\langle t|\mathbf{k}\rangle,\tag{4.6}$$

$$H(\mathbf{q})=\frac{q^2L^3}{4\pi}-\textstyle\sum_{k<k_F}\left(\dfrac{1}{E_\mathbf{k}-E_{\mathbf{k}+\mathbf{q}}}+\dfrac{1}{E_\mathbf{k}-E_{\mathbf{k}-\mathbf{q}}}\right)=\dfrac{q^2L^3}{4\pi}-\dfrac{k_FL^3}{4\pi^2}g\left(\dfrac{q}{2k_F}\right),\tag{4.7}$$

$$g(x)=1+\frac{1-x^2}{2x}\log\frac{1+x}{|1-x|}.\tag{4.8}$$

E_p can thus be expressed as

$$E_p=\textstyle\sum_{\mathbf{R}i,\mathbf{R}j}\sum_{\mathbf{q}\neq 0}e^{i\mathbf{q}\cdot(\mathbf{R}_i-\mathbf{R}_j)}E(\mathbf{q})$$
$$=E_{p,0}+\textstyle\sum_{\mathbf{R}i,\mathbf{R}j\neq\mathbf{R}i}\mathcal{F}_1(\mathbf{R}_i-\mathbf{R}_j),\tag{4.9}$$

which defines $\mathcal{F}_1(\mathbf{r})$ by its Fourier transform.

Though it shows up a pair interaction, (4.9) is not in itself so useful a formula as (4.2); one can see that $E(\mathbf{q})$ diverges as $1/q^2$ when q goes to zero, and decreases very rapidly for q tending to infinity. As long as summations are performed on the reciprocal lattice, (4.2) converges quickly because $E(\mathbf{q})$ is already a small quantity for the smallest $\mathbf{q}$ compatible with $S(\mathbf{q})\neq 0$. On the other hand, for large distances $\mathcal{F}_1(\mathbf{r})$ falls off as $1/r$ so that the summation on the direct lattice cannot be done without much difficulty. This is unimportant in fact because all these difficulties will disappear when we add the pair interaction terms which come from E_S.

b. The Pair-Interaction Function

It may seem surprising to devote this whole subsection to the addition to (4.2), of a term which is readily seen to be

$$\tfrac{1}{2}\textstyle\sum_{\mathbf{R}i,\mathbf{R}i\neq\mathbf{R}i}\left(\sum_{\mathbf{q}\neq 0}-\dfrac{4\pi Z}{L^3q^2}[-Z-2P(\mathbf{q})]e^{i\mathbf{q}\cdot(R_i-R_j)}\right),\tag{4.10}$$

where

$$P(\mathbf{q})=\textstyle\sum_{k<k_F}\{\sum_t\langle\mathbf{k}+\mathbf{q}|t\rangle\langle t|\mathbf{k}\rangle\}.\tag{4.11}$$

In fact this addition is not easy to perform if we wish to obtain a result that we can easily compare with those of simpler theories. We have to remove all the divergencies which come from the $1/q^2$ character of the Coulomb potential when q goes to zero. We already noticed in Sec. III D that such a removal could be done on V_2. This will also be possible for the pair-interaction function.

We first separate all the terms which contribute to (4.4) and (4.10). We then notice that every time there exists a diverging term, we can group it with one or two other ones such that the sum is no longer divergent. After this rearrangement is performed, the total expression is easily brought into the following form:

$$E_{\text{tot}}=\mathcal{E}_0+\mathcal{E}_{\text{int}}=\mathcal{E}_0+\tfrac{1}{2}\textstyle\sum_{\mathbf{R}i,\mathbf{R}j\neq\mathbf{R}i}\mathcal{F}(\mathbf{R}_i-\mathbf{R}_j),\tag{4.12}$$

where $\mathcal{E}_0$ is a self-energy of the ions and $\mathcal{F}(\mathbf{R}_i-\mathbf{R}_j)$ is given by

$$\mathcal{F}(\mathbf{R}_i-\mathbf{R}_j)=\textstyle\sum_{\mathbf{q}\neq 0}e^{i\mathbf{q}\cdot(\mathbf{R}_i-\mathbf{R}_j)}\mathcal{E}(\mathbf{q})$$
$$=\textstyle\sum_{\mathbf{q}\neq 0}e^{i\mathbf{q}\cdot(\mathbf{R}_i-\mathbf{R}_j)}\left[2b(\mathbf{q})+\dfrac{|-Z-P(\mathbf{q})+A(\mathbf{q})+A^*(-\mathbf{q})|^2}{H(\mathbf{q})}\right],\tag{4.13}$$

with

$$b(\mathbf{q})=\textstyle\sum_{k<k_F}\dfrac{|\langle\mathbf{k}+\mathbf{q}|\ell-o|\mathbf{k}\rangle|^2}{E_\mathbf{k}-E_{\mathbf{k}+\mathbf{q}}},\tag{4.14}$$

$$A(\mathbf{q})=\textstyle\sum_{k<k_F}\dfrac{\langle\mathbf{k}+\mathbf{q}|\ell-o|\mathbf{k}\rangle}{E_\mathbf{k}-E_{\mathbf{k}+\mathbf{q}}}.\tag{4.15}$$

The following comments may be made on Eq. (4.13):

(1) Three kinds of terms appear in $\mathcal{E}(\mathbf{q})$: (a) the ionic charge $-Z$; (b) the "additional charge due to the orthogonalization procedure": $-P(\mathbf{q})$; (c) all the non-Coulomb terms of the potential, which are in $A(\mathbf{q})$ and $b(\mathbf{q})$.

One easily realizes that the existence of the (c) terms is not only related to the use of an OPW method but also to the presence of a non-Coulomb part L in the original potential V. Thus, even if we make the very crude approximation that the Hartree potential is small enough so that V by itself can be thought of as a perturbing potential, both terms which appear in (c) will still be present in $\mathcal{E}(\mathbf{q})$.

(2) $\mathcal{E}(\mathbf{q})$ is continuous for $q=0$. The term $q\neq 0$ need no longer be discarded in the summation (4.13).

(3) The first derivatives of $\mathcal{E}(\mathbf{q})$ are also continuous for $q=0$. Then for large distances, $\mathcal{F}(\mathbf{r})$ no longer falls off as $1/r$. The asymptotic form of $f(\mathbf{r})$ is now related to the infinite derivative of $H(\mathbf{q})$ [and presumably of $A(\mathbf{q})$ and $b(\mathbf{q})$] for $|\mathbf{q}|=2k_F$. If we assume that $A(\mathbf{q})$ and $b(\mathbf{q})$ are less singular than (or have the same singularity as) $H(\mathbf{q})$, then $f(\mathbf{r})$ will have the asymptotic form $C\cos|2k_F r|/r^3$, where C is a constant related to the behavior of $\mathcal{E}(\mathbf{q})$ for $|\mathbf{q}|\simeq 2k_F$. This result is a generalization of what was obtained with the approximation mentioned in (1.a) when the term L is also neglected.[6] [This means: $P(\mathbf{q})=A(\mathbf{q})=b(\mathbf{q})=0$.]

(4) In (4.13), a $|P(\mathbf{q})|^2/H(\mathbf{q})$ term has been added so that a more symmetrical formula appears. This is the same kind of approximation we made in adding an α^2 term in (3.16). On the other hand, since $\mathcal{F}(\mathbf{r})$ describes a short-range interaction, the approximation of $\rho_1(\mathbf{r})$ by a sum of point charges (which was adequate as long as an important part of Sec. III came from the interaction of distant charges) may be too crude for small values of $\mathbf{r}$. In other words, for such distances, we cannot approximate $P(\mathbf{q})$ by αZ, as we implicitly did in comment (1).

C. Conclusion

We have now succeeded in proving the following statements. To third-order terms:

(a) The OPW method does not bring any fundamental modification to the quasifree-electron scheme.

(b) Apart from a constant, the total energy of the metal may be written as a sum of two terms.

The first term is of an electrostatic nature and represents the self-energy of ions, whose charge has been increased by the OPW orthogonalization, embedded in a compensating field of opposite charge.

The second term comes from the perturbation theory and is expressed, as usual, as a product of the matrix element of a bare potential by the corresponding matrix element of the dressed potential.

(c) The total energy of the metal can also be written as a sum of pair interactions. This two-body force has a short-range and an asymptotic oscillating behavior.

On the other hand, throughout this paper we emphasized that part of the total energy which depends upon the structure of the crystal and more or less neglected the self-energy term which is a function of its volume. The above formulas then are only useful for the study of some properties of metals such as crystal structure, elastic constants at constant volume. They can also be generalized to binary alloys, giving then the effective chemical interaction between the different kinds of ions, and therefore their ordered structure. These, and some other applications, have been reviewed by Harrison.[7]

If it turns out that the second-order perturbation method proposed by Harrison[1] leads, for many metals, to numerical results in good agreement with experiment, then the above formulas will allow one to investigate the influence of the new terms arising from the OPW method on this agreement.

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APPENDIX

Let us define the following charge density:

$$\begin{aligned}\rho_1(\mathbf{r})&\equiv-\textstyle\sum_{k<k_F}\sum_c\dfrac{\langle\mathbf{k}|c\rangle}{L^3}c^*(\mathbf{r})\dfrac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{L^3}}\\&=-\textstyle\sum_{\mathbf{q}}e^{-i\mathbf{q}\cdot\mathbf{r}}\sum_{k<k_F}\dfrac{\langle\mathbf{k}|P|\mathbf{k}+\mathbf{q}\rangle}{L^3},\end{aligned}\tag{A1}$$

where $c(\mathbf{r})$ is the wave function of the state $|c\rangle$.

$\rho_1(\mathbf{r})$ is real $[\rho_1(\mathbf{q})=\rho_1^*(-\mathbf{q})]$ and has the mean value

$$\rho_{1,0}\equiv[\rho_1(\mathbf{q})]_{q=0}=-\frac{1}{Nv}\textstyle\sum_{k<k_F}\langle\mathbf{k}|P|\mathbf{k}\rangle,\tag{A2}$$

where v is the atomic volume.

The charge density $\rho_1(\mathbf{r})-\rho_{1,0}$ is of the same nature as ρ_E; indeed, the mean value of that charge is zero and, from (A1), $\rho_1(\mathbf{r})$ is a sum of negative charges localized around the nuclear sites, the charge near every nucleus being the same and equal to $v\rho_{1,0}$. We

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[6] A. Blandin, paper contributed to the session on Solid Solutions at the A.I.M.E. Meeting, Cleveland, October 1963 (unpublished).

[7] W. A. Harrison, Phys. Rev. **129**, 2512 (1963).

can then write $\rho_1(\mathbf{r})-\rho_{1,0}=\alpha\rho_E$ so that

$$-\textstyle\sum_{k<k_F}\{\langle\mathbf{k}|PV_{2E}|\mathbf{k}\rangle-\langle\mathbf{k}|P|\mathbf{k}\rangle\langle\mathbf{k}|V_{2E}|\mathbf{k}\rangle\}$$

$$=-\textstyle\sum_{k<k_F}\sum_{q\neq0}\langle\mathbf{k}|P|\mathbf{k}+\mathbf{q}\rangle\langle\mathbf{k}+\mathbf{q}|V_{2E}|\mathbf{k}\rangle$$

$$=\alpha\int V_{2E}(\mathbf{r})\rho_E(\mathbf{r})d\mathbf{r}. \qquad \text{(A3)}$$

On the other hand, $V_{2E}(\mathbf{r})$ is exactly of the same nature as $\tilde{V}_E$ [see Eq. (3.4a)] and the interaction of $\rho_E(\mathbf{r})$ with $[\tilde{V}_E(\mathbf{r})-V_{2E}(\mathbf{r})]$ is just a self-energy term which could be added to (3.11), but is so small that it can be neglected. We can thus identify (A3) with

$$\alpha\int\rho_E(\mathbf{r})\tilde{V}_E(\mathbf{r})d\mathbf{r}. \qquad \text{(A4)}$$

Finally from (A2) and from the definition of ρ_0 given in Sec. III C we find that

$$\alpha=\textstyle\sum_{k<k_F}\langle\mathbf{k}|P|\mathbf{k}\rangle/\sum_{k<k_F}\langle\mathbf{k}|\mathbf{k}\rangle=[\langle\mathbf{k}|P|\mathbf{k}\rangle]_{\text{av}}. \qquad \text{(A5)}$$

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Spin-Wave Interaction in the Itinerant-Electron Model of Ferromagnetism*

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Using a simple itinerant-electron model of ferromagnetism with exchange interaction and Coulomb repulsion between band electrons, spin waves, and their interactions are discussed. In the random-phase approximation, we obtained the diagonal elements of spin-wave interactions which reduce to Dyson's result in the limit of localized electrons for our model. A diagrammatical interpretation of the result is also given. When the band with down spin is partially filled and that with up spin empty, the spin-wave interaction consists of the part arising from the modified exchange interaction, the part due to the electron kinetic energy and the Coulomb repulsion, and the part which involves both of these effects. Among these, the second seems to be rather small. For small values of the wave vectors of the spin waves involved, the spin-wave interaction depends on the wave vectors in the same way as in Dyson's result. The modification on the exchange interaction is such that the short-range part of the original exchange interaction is suppressed, whereas the long-range part remains unaffected. This arises from electron (hole) exchanges, and cancels in the limit of localized electrons.

I. INTRODUCTION

SINCE Dyson's theory[1] on the spin-wave interactions of the Heisenberg spin system appeared, this problem has been a subject of many investigations.[2] However, the experimental test of these theories did not appear until recently. Experiments have been performed on ferromagnetic metals such as[3] Ni and[4] permalloy to determine the temperature dependence of spin-wave frequencies which arise from spin-wave interactions. In the low-temperature region, they obtained the spin-wave frequency which decreases with the temperature as $T^{5/2}$, in agreement with Dyson's result. However, its magnitude, which is proportional to the square of the range of exchange interactions, is too large and requires the range of exchange interactions of about eight times the lattice constant to fit the above mentioned theoretical result. There are other evidences[5] which indicate the existence of long-range exchange interactions. However, it was pointed out that such a long-range exchange interaction is inconsistent with other experimental evidence.[4] It has been suggested that the itinerant character of electrons in these metals may be important.[6]

On the other hand this problem is also of theoretical interest as another example in which interactions among elementary excitations play a major role.[1,2,7] Although the property of elementary excitations in many-body systems has been a subject of numerous investigations, not much work has been done on the problem of interactions among them, which are essential in understanding the temperature dependence of energies of ele-

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