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INTERATOMIC INTERACTIONS IN METALS ^(1,2)

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Résumé. — On développe une théorie des propriétés de cohésion des métaux qui, bien qu'inapplicable aux métaux de transition, terres rares et actinides, est cependant valable pour les autres métaux quelle qu'en soit la composition et la structure. Deux points sont à la base de cette théorie ; d'une part une nouvelle formulation du problème à N corps, d'autre part la méthode du pseudo-potential pour tenir compte des couches profondes des ions. Lorsqu'on développe l'énergie exacte en puissances du pseudo-potential et que l'on garde les termes principaux, on obtient une formule approchée pour l'énergie de cohésion qui contient explicitement les forces entre les atomes deux par deux. On montre que ces forces ne sont ni ioniques ni covalentes mais de caractère spécifiquement métallique.

Abstract. — A theory of the cohesive properties of metals is developed which, though inapplicable to transition, rare earth, and actinide metals, holds otherwise for arbitrary composition and structure. The theory is based on two ingredients, a new dielectric formulation of the many-body problem and the pseudo-potential method for dealing with the ion cores. When the exact energy is expanded in powers of the pseudo-potential and the dominant terms retained, there results an approximate formula for the cohesive energy explicitly containing pairwise central forces between the atoms. It is proved that these forces are neither ionic nor covalent but specifically metallic in character.

I. Introduction. — In the early history of the theory of metals, calculation of the cohesive energy of a metal was of central concern. Apart from a very considerable development of the theory of the electron gas, recent effort, both experimental and

theoretical, has been focussed primarily on properties of one-electron character. In the present work, we have returned to the study of the cohesive properties of metals.

Difficulties in the way of such studies are twofold :

a) Even for the electron gas (i.e., a uniform background of positive charge instead of atoms) we

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have a theory accurate only at electron densities higher than normal [1]. The most advanced work thus far, that of Hubbard [2] is still of uncertain accuracy at normal electron densities.

b) The intricacies introduced by the presence of atoms has been regarded as almost insuperable thus far.

We get around difficulty (a) by observing that it applies only to volume dependent properties. It is largely irrelevant for structural changes at constant volume. The simplification made possible by the use of the pseudo-potential introduced by Phillips and Kleinman [3], and its weakness [4], largely eliminate difficulty (b).

Accordingly, in this talk, we outline a theory of the cohesive energy based on the following ingredients :

(1) The dielectric formulation of the many-body problem [5] modified so that it starts out from the Hartree approximation rather than from free electrons [5].

(2) The replacement of the actual atomic potential by the pseudo-potential, and the application of self-consistent perturbation theory to the latter.

Each of these features of the theory will be presented and discussed but not derived here. We shall use the structure so developed to show the existence of and give approximate formulae for interatomic forces without regard for atomic constitution or arrangement. A proof will then be indicated that these forces are neither ionic nor covalent in character.

II. Dielectric formulation of the many-body problem. — Nozières and Pines [5] prove that the total energy $E(e^2)$ of a gas of N electrons in volume Ω is given by

$$E(e^2) = E(0) - \int_0^{e^2} \frac{d\lambda}{\lambda} \sum_q \left[\frac{\hbar}{2\pi} \int_0^\infty d\omega \operatorname{Im} \frac{1}{\epsilon(q, \omega; \lambda)} - \frac{Nv_q}{2\Omega} \right]; \quad (1)$$

where $E(0)$ is the free-electron energy, $\epsilon(q, \omega; \lambda)$ is the dielectric function of the electron gas for wavenumber q , frequency ω , and value λ of the electron charge squared, and where v_q is the Fourier transform of the Coulomb interaction, $4\pi e^2/q^2$. Equation (1) furnishes a rapid means of approximate calculation of the energy once an approximate dependence of the dielectric function on λ , q and ω is established. However, despite the appearance in the integral over λ of small values of λ , the charge squared can never be treated as small, and it is necessary to go to infinite order of perturbation theory to obtain the lowest satisfactory approximation to the dielectric function [5]. But then all distinction from perturbation theory is lost, and the analysis has no advantage over the beautiful work of Hubbard [2], who established an equation equivalent to (1) by perturbation theory,

obtained explicit results for the electron gas and treated electrons in a crystal as well. Hubbard found it convenient, if not essential, to start his perturbation analysis of the crystal from the Hartree problem. We therefore have derived an exact formula analogous to (1) and holding for non-uniform systems as well by starting out from the Hartree approximation rather than the free particle problem; indeed we have found it impossible to generalize (1) to nonuniform systems by starting out directly from the latter problem.

We consider a collection of N electrons and nuclei (charges Z_i , $\sum_i Z_i = N$) fixed in arbitrary positions within volume Ω . Because no restriction is made as to composition or atomic arrangements we encompass alloys, crystals, amorphous solids, and liquids in the present treatment.

The generalization of eq. (1) proceeds by introducing a parameter ξ , $0 \leq \xi \leq 1$ into the functional dependence of the energy on the wavefunction. For $\xi = 0$, the energy has the factorized form of the Hartree theory; for $\xi = 1$, it has the exact form. At intermediate values of ξ , it has a mixed form which requires a fairly deep study of the time evolution and statistical mechanics of systems governed by such an energy function. All that can be done, however, leading to a generalization of existing self-consistent field theory. One can then introduce the dielectric function in the usual way, express the derivative of the energy with respect to ξ in terms of the dielectric function and arrive at the desired result :

$$E(1) = E(0) - \frac{\hbar}{2\pi} \int_0^1 d\xi \operatorname{tr} \int_0^\infty d\omega \operatorname{Im} \{ (\epsilon - \mathbf{I}) \cdot [\mathbf{I} + \xi(\epsilon - \mathbf{I})]^{-1} \} - \sum_q \frac{Nv_q}{2\Omega}. \quad (2)$$

In eq. (2) $E(1)$ is the exact ground-state energy, and $E(0)$ is the ground-state energy in the Hartree-approximation. The dielectric function ϵ is regarded as a matrix with respect to the wavenumber q of the linear response of the system to a perturbing external potential of wavenumber q'

$$(\epsilon)_{qq'} = \epsilon(q, q', \omega; \xi), \quad (3)$$

and \mathbf{I} is the unit matrix.

If one simplifies to the case of the electron gas, ϵ is diagonal in q . One can then expand ϵ in powers of ξ . Keeping only the $\xi = 0$ value of ϵ in the integrand (i.e., the Hartree or RPA value of ϵ) gives Hubbard's result immediately. It is not difficult to work out the term in ϵ linear in ξ ; including it in the integrand still permits the integral over ξ to be carried out. The resulting integrals over q and ω are now in the process of numerical computation. It is evident that the parameter ξ can be used as the systematic ordering parameter lacking in Hubbard's theory and that the

results of the numerical calculations now in progress will give us some idea of the convergence of the procedure at ordinary metallic densities.

III. The pseudo-potential. — The preceding result, eq. (2), contains the contribution of all electrons in the metal to the total energy. However, there are atoms for which a clear separation between core and valence electrons is possible [7]. The wave functions of the former are largely unaffected by the state of aggregation and can be presumed known from the solution of the isolated atom problem. As Phillips and Kleinman have shown, it is then possible systematically to ignore the existence of the core electrons, replacing the requirement of orthogonality between valence and core wave functions by a fictitious additive potential, the repulsive potential [8]. Thus, the influence upon the valence electrons of a single nucleus plus its core electrons, an ion core, may be represented by a one-electron pseudo-potential.

The exact form of the pseudo-potential is complicated, being nonlocal and eigenvalue-dependent in character. However, the pseudo-potential is not unique [4], and a selection from among the family of allowable pseudo-potentials may be made on the basis of convenience. In the following, we shall suppose the pseudo-potential to be local and eigenvalue independent, our investigations being mainly exploratory in character. Although we shall not specify the pseudo-potential in detail, what we have in mind is a potential which is properly Coulombic outside the core and flat inside the core (See fig. 1). The cut-off radius and well depth can

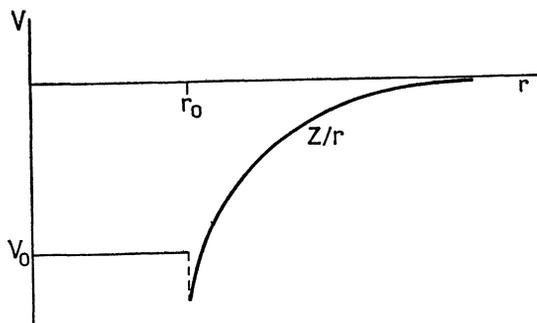


FIG. 1. — A schematic plot of the pseudo-potential V as a function of radius r . Outside the core, $r > r_0$, V is the potential of a point ion having the charge of the core (Z/r). Inside the core, $r < r_0$, V is flat ($V = V_0$).

then be determined by fitting to the lowest s -level and p -levels of a single valence electron outside the core, as determined from atomic spectra. N. Wisner has determined a few such potentials and finds that, as one could expect, the higher levels are well fitted also. A few values of the parameters he obtains are given in the table.

The effect of the repulsive potential is largely to

TABLE

PSEUDO-POTENTIAL PARAMETERS

ATOM	$-V_0(Ry)$	$r_0(a_0)$	IONIC RADIUS (a_0)
Na	0.424	2.1	1.9
K	0.435	3.2	2.5
Rb	0.451	4.6	2.8
Cs	0.410	5.5	3.2

cancel the strong attractive potential inside the core. Further, the attractive Coulomb tail outside the core is screened in the self-consistent theory of the type constructed here [9]. The net potential acting on the valence electrons is therefore weak, i.e., gives rise to band gaps small compared to the Fermi energy. One can treat the sum of the pseudo-potentials associated with each ion core as a perturbation upon the electron gas, provided one does self-consistent perturbation theory.

IV. Interatomic interactions. — No essential changes in the dielectric formulation of § II is required by the introduction the pseudo-potential; eq. (2) still holds. We now suppose the pseudo-potential to be a perturbation and make a power series expansion of each of the two terms in eq. (2) in the pseudo-potential. That means (i) doing self-consistent perturbation theory to get the Hartree energy $E(0)$ in powers of the pseudo-potential, and (ii) similarly expanding the dielectric function $\epsilon(q, q', \omega, \xi)$. Some findings of Phillips [10] and of Phillips and Kleinman [11] in another context can be used as a basis for arguing that the contribution to the energy of the terms arising from the expansion of ϵ are significantly smaller than those arising from the expansion of the Hartree energy. We therefore neglect them in the present investigation, and expand only the Hartree energy. We arrive finally at the result that the total energy of the metal is approximately equal to the exact energy of the electron gas (which depends on electron density only) plus the first few terms of the expansion of the Hartree energy.

Apart from one or two subtleties we cannot dwell on here, the expansion of the Hartree energy is straightforward. Provided the band gaps in a crystal of similar composition are small compared to the Fermi energy, as they are for the simple metals, one can terminate the expansion after second order, with the result

$$\begin{aligned}
 E = E_0 - \frac{1}{3} NE_F \\
 + \sum_l U_l + N \sum_l \bar{u}_l \\
 + \frac{1}{2} \sum_{l''} U_{l''}.
 \end{aligned}
 \tag{4}$$

The first line in (4) contains E_0 , the exact energy of the electron gas, and the only other term dependent solely on electron density (E_F is the free-electron Fermi energy). The second line contains terms dependent both on electron density and composition but not on atomic arrangement. In the second line, \bar{u}_i is the spatial average of that portion of the pseudo-potential of ion-core "l", $v_l(r - r_i)$, differing from the point ion potential

$$-z_l e^2 / |r - r_i|.$$

U_i is the net interaction energy of each ion-core with its own screening cloud

$$U_i = -\frac{1}{2} \sum'_q (1 - 1/\epsilon(q)) \frac{4\pi z_l^2(q) e^2}{\Omega q^2}. \quad (5)$$

In (5) $\epsilon(q)$ is the static dielectric function of the electron gas for wavenumber q , and $z_l(q)$ is the ratio of the Fourier transform of the pseudo-potential to that of the point ion potential. We note parenthetically that

$$z_l(q \rightarrow 0) = z_l, \quad (6)$$

the charge on the ion core. The last line in (4) contains the desired interatomic interactions:

$$U_{ll'} = \sum_q \frac{4\pi e^2}{\Omega q^2} [z_l z_{l'} - z_l(q) z_{l'}(q) + z_l(q) z_{l'}(q) / \epsilon(q)] \times e^{iq \cdot r_{ll'}} \quad (8)$$

It is derived on the assumption that the ion cores do not come in contact; otherwise, a term of the Born-Mayer type would have to be added to (7).

Eq. (7) corresponds to central forces, generally repulsive. Noncentral forces can be only of three-body and higher type, and, arising from higher orders of perturbation theory, can be expected to be of order $x = \frac{4\pi e^2 z_l^2(q)}{\epsilon(q) q^2 E_F}$ smaller. For the important q in (7), x is ordinarily small, i.e., ≤ 0.1 , for the simple metals. Thus we expect (7) to give the interatomic forces in the simple metals to something like 10% accuracy. In the small core limit, i.e., point ions, (7) reduces to the screened Coulomb interaction [12].

The expression (7) for $U_{ll'}$ is simple enough to hope that quantitative answers to such questions as why the various metallic elements crystallize in the structures they do may be forthcoming soon. In any event, calculations are under way.

V. Nature of the interactions. — The types of interatomic interactions familiar in nonmetallic substances are Born-Mayer repulsions, van der Waals attractions, ionic bonds, and covalent bonds. The first two, requiring completely localized charged distributions are evidently not present in the metals except possibly for core-core interactions. It seems possible at least that the metallic bonds derived in the last section in the entity $U_{ll'}$ may be

partially ionic and/or covalent in character. We have proved, however, that they are not.

An atom has ionic character if, as it moves through the aggregation of atoms under consideration, it transports a net charge. Similarly, a covalent bond exists between two atoms if, as the pair moves through the aggregation, it transports a net charge different from the sum of the net charges transported by each atom moving independently.

The electron density $n(r)$ in our metal may be expanded self-consistently in a power series in the pseudo-potential, just as the energy was, with the result

$$n(r) = n_0(r) + \sum_l n_l(r) + \sum_{l,m} n_{lm}(r) + \sum_{l,m,n} n_{lmn}(r) + \dots \quad (8)$$

In (8) $n_0(r)$ is the free electron density N/Ω , $n_l(r)$ is the contribution to the charge density of the l^{th} ion core, $n_{lm}(r)$ the contribution of the pair of ion cores lm , etc... Conservation of charge (i.e., normalization) requires that

$$\int d^3r n_l(r) = \int d^3r n_{lm}(r) = 0, \text{ etc...} \quad (9)$$

Thus, the total number of electrons associated specifically with any cluster of ion cores must be zero. That does not prove the absence of covalent or ionic character, however. It may be possible that $n_l(r)$ or $n_{lm}(r)$, e.g., goes to a constant value $n_l(\infty)$ or $n_{lm}(\infty)$ at large distances from core l or cores l and m and that consequently there is a net fraction of an electron $-\Omega n_l(\infty)$ or $-\Omega n_{lm}(\infty)$ localized in the vicinity of a cluster which is transported with the cluster and yet neutralized by the asymptotic part so that (9) is satisfied. The problem of ascertaining the existence of ionic or covalent character thus reduces to studying the asymptotic behavior of the electron density associated with a cluster of ion cores.

We have been able to prove rigorously (within the Hartree approximation) that the only order of perturbation theory in which a nonvanishing contribution to the asymptotic part of the electron density occurs is the first order. In all other orders, the asymptotic part vanishes exactly. Further, in first order the amount of electron charge localized about each ion core is exactly sufficient to neutralize the ion core. We have proved, therefore, that atoms in metals have no ionic character and that covalent bonds do not exist in metals. The interatomic interactions of the last section therefore are neither ionic nor covalent but specifically metallic in nature.

As one increases the strength of the pseudo-potential, one might expect that the area of the Fermi surface might ultimately decrease towards zero so that one passes over to an insulator. The perturbation theory used here no longer converges,

and ionic and covalent character become possible. What happens as the area of the Fermi surface decreases is that the range of distance over which metallic screening occurs increases. Thus in a semimetal with a very small Fermi surface, one might have a net charge in a covalent bond localized on an-atomic scale which is surrounded by a neutralizing cloud with a radius of order a hundred atomic separations. Thus in principle, the theorem

holds for semimetals, but because of the long screening radius there is a greater resemblance to an insulator than to a metal as regards ionic or covalent character.

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