a mechanism to dominate at all temperatures. Both the dislocation model and the "vacancy" model of Peart and Askill can account for a small correlation factor. However, the authors are somewhat more disposed toward the dislocation model, particularly since it can explain the analogous thermomigration and electromigration observed in γ-Fe.[51] Low values for D_{02} and Q_2 also find an easy explanation in the dislocation model. The weakness of this hypothesis is the need to postulate an extensive dislocation network formed during the phase transformation and unexpectedly stable under

annealing treatment. Until there is direct experimental observation to the contrary, we are inclined to hold to this explanation, although the single vacancy, divacancy model[21] is also still a possibility.

ACKNOWLEDGMENTS

Pressure Calculations and the Virial Theorem for Modified Hartree-Fock Solids and Atoms*

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(Received 23 September 1968)

An expression for the pressure of a Hartree-Fock-Slater solid is derived. It is shown that for this expression only those forms of the local exchange potential that are rigorously derived from the variational principle will give meaningful results in pressure calculations.

I. INTRODUCTION

IN a large number of the calculations made for the electronic energy levels of atoms and solids, a modified form of the Hartree-Fock equations is used. The modification is generally that of replacing the nonlocal Hartree-Fock exchange terms, which are difficult to calculate, by a local exchange potential $V_{ex}(r)$, which is proportional to the $\frac{1}{3}$ power of the local electron density $\rho(r)$, or $V_{ex}(r) = C[\rho(r)]^{1/3}$. In the Kohn-Sham approximation,[1] C is $(3/\pi)^{1/3}$, and in the Slater approximation[2] it is larger by $\frac{3}{2}$.

The present paper treats the problem of calculating pressure for a system described by the modified Hartree-Fock equations and, in particular, considers just what bearing the derivation of the one-electron exchange term has on the rigorously correct formulation of the pressure.

It will be shown that the pressure of a solid may be determined by the modified Hartree-Fock method, using a form of the virial theorem in which $PV = \frac{2}{3}T + \frac{1}{3}U$. The terms P, V, T, and U are, respectively, pressure, volume, average kinetic, and potential energy for the solid. For the case of free atoms, $2T = -U$.

It will also be shown that this theorem can give meaningful results only when applied to those cases in which the one-electron eigenvalue equations have been derived from the expression for the total energy, using the variational principle rigorously. This is so in the case of the Kohn-Sham approximation, and consequently results of calculations using this approximation obey the virial theorem. In the case of Slater exchange, an approximation is made in the application of the variational principle, and as a result the thermodynamic states obtained are not the true equilibrium states for the modified Hartree-Fock system, so that calculations based on the Slater approximation do not obey the virial theorem.

II. CALCULATION OF ENERGY AND PRESSURE

Consider a system of a very large volume V, containing N electrons. The total energy of this system for the modified form of the Hartree-Fock equations may be written as

$$E = \int_0^V -\sum_i \psi_i(\mathbf{r}_i)_1 \tfrac{1}{2}\nabla^2 \psi_i(\mathbf{r}_1)d\mathbf{r}_1 + \tfrac{1}{2}\sum_i\sum_j \int_0^V \frac{\psi_i^*(\mathbf{r}_1)\psi_i(\mathbf{r}_1)\psi_j(\mathbf{r}_2)\psi(\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2}{|\mathbf{r}_1-\mathbf{r}_2|} - \frac{1}{2}\frac{3}{\pi}\left(\frac{3\pi^2}{4}\right)^{1/3}\int_0^V [\sum_{i(\uparrow)} \psi_i^*(\mathbf{r}_1)\psi_i(\mathbf{r}_1)]^{4/3}d\mathbf{r}_1$$

$$-\frac{1}{2}\frac{3}{\pi}\left(\frac{3\pi^2}{4}\right)^{1/3}\int_0^V [\sum_{i(\downarrow)} \psi_i^*(\mathbf{r}_1)\psi_i(\mathbf{r}_1)]^{4/3}d\mathbf{r}_1 - \sum_i\sum_\alpha Z_\alpha \int_0^V \frac{\psi_1^*(\mathbf{r}_1)\psi_i(\mathbf{r}_1)d\mathbf{r}_1}{|\mathbf{r}_\alpha-\mathbf{r}_1|} + \tfrac{1}{2}\sum_\alpha\sum_\beta \frac{Z_\alpha Z_\beta}{|\mathbf{r}_\alpha-\mathbf{r}_\beta|}. \quad (1)$$

[1] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965); R. Gaspar, Acta Phys. Acad. Sci. Hung. **3**, 263 (1954).
[2] J. C. Slater, Phys. Rev. **81**, 385 (1951).

The first term is the kinetic energy of all the electrons. The second term is the Coulomb repulsion between all electrons. The third and fourth terms are the free-electron approximation to the electron exchange interaction for spin-up and spin-down states, with the sums over only the same spins. The fifth term is the interaction between all electrons and nuclei. The last term is the interaction between all nuclei. The nuclei are assumed to be stationary. The wave functions $\psi_1(\mathbf{r})$, $\cdots, \psi_N(\mathbf{r})$ for the N electrons are the usual one-particle functions satisfying the Bloch conditions, and may be written in the form

$$\psi_i(\mathbf{r}) = \sum_K \frac{A_K e^{i(\mathbf{K}+\mathbf{k}_i)\cdot\mathbf{r}}}{V^{1/2}}, \qquad (2)$$

where $\mathbf{K}$ is a vector in the reciprocal-lattice space of the unit crystallographic cell and $\mathbf{k}_i$ is the wave vector of the ith electron satisfying the periodic boundary conditions. In order to calculate the pressure from the energy, it will be convenient to define a reduced coordinate system where

$$\boldsymbol{\tau} = \mathbf{r}/V^{1/3} \quad \text{and} \quad \mathbf{K} + \mathbf{k}_i = \mathbf{g}_i.$$

Because $\mathbf{g}_i$ is expressed in terms of the reciprocal lattice, it leads to a dimensionless quantity in $(\mathbf{g}_i\cdot\mathbf{r})$, which is proportional to $|\boldsymbol{\tau}|$. Then the one-particle wave functions may be written as

$$\psi_i(\mathbf{r}) = \phi_i(\boldsymbol{\tau},A)/V^{1/2}, \qquad (3)$$

where

$$\phi_i(\boldsymbol{\tau},A) = \sum_{g_i} A_{g_i} e^{i\mathbf{g}_i\cdot\boldsymbol{\tau}}. \qquad (4)$$

The term A represents the set of A_{g_i}, and $\phi(\boldsymbol{\tau},A)$ represents the set of $\phi_i(\boldsymbol{\tau},A)$. The expression for the total energy in terms of the reduced coordinate system then becomes

$$E = \sum_i -\frac{1}{V^{2/3}}\int_0^1 \phi_i^*(\boldsymbol{\tau}_1,A)_1 \tfrac{1}{2}\nabla^2\phi_i(\boldsymbol{\tau}_1,A)d\boldsymbol{\tau}_1 + \tfrac{1}{2}\sum_i\sum_j \int_0^1\int_0^1 \frac{\phi_i^*(\boldsymbol{\tau}_1,A)\phi_i(\boldsymbol{\tau}_1,A)\phi_j^*(\boldsymbol{\tau}_2,A)\phi_j(\boldsymbol{\tau}_2,A)d\boldsymbol{\tau}_1 d\boldsymbol{\tau}_2}{V^{1/3}|\tau_1-\tau_2|}$$

$$-\frac{1}{2}\frac{3}{\pi}\left(\frac{3\pi^2}{4}\right)^{1/3}\int_0^1 \frac{[\sum_{i(\uparrow)}\phi_i^*(\boldsymbol{\tau}_1,A)\phi_i(\boldsymbol{\tau}_1,A)]^{4/3}}{V^{1/3}}d\boldsymbol{\tau}_1 + \text{spin-down exchange term}$$

$$-\sum_i\sum_\alpha Z_\alpha \int_0^1 \frac{\phi_i^*(\boldsymbol{\tau}_1,A)\phi_i(\boldsymbol{\tau}_1,A)d\boldsymbol{\tau}_1}{V^{1/3}|\tau_\alpha-\tau_1|} + \tfrac{1}{2}\sum_\alpha\sum_\beta \frac{Z_\alpha Z_\beta}{V^{1/3}|\tau_\alpha-\tau_\beta|}. \qquad (5)$$

We will now review the application of the variational principle to the total energy (5) to show its relationship to the proper calculation of pressure of an equilibrium solid.

To determine the equilibrium state for a given volume, the variational principle is applied along with the constraint that the number of electrons in each state $\int\phi_i\phi_i d\tau$ remains fixed. The term $-\mu_i$ is the Lagrange multiplier for each state. Then

$$\delta E = \sum_i \int_0^1 \left(\frac{\partial E}{\partial\phi_i^*}\right)_{V,\phi_j}\delta\phi_i^* d\tau + \sum_i\int_0^1 \left(\frac{\partial E}{\partial\phi_i}\right)_{V,\phi_j}\delta\phi_i d\tau \quad (6)$$

and

$$-\sum_i \mu_i\delta\int_0^1 \phi_i^*\phi_i d\tau = 0, \qquad (7)$$

where $\delta\phi_i$ is an infinitesimal variation in the wave function about the equilibrium configuration at a fixed volume, and $(\partial E/\partial\phi_i)_{V,\phi_j}$ represents the partial derivative of the energy with respect to the ith-electron wave function holding the volume and the remaining wave functions ϕ_j constant.

Combining (6) and (7), we may write

$$\sum_i \left[\left(\frac{\partial E}{\partial\phi_i^*}\right)_V - \mu_i\phi_i\right]\delta\phi_i^* + \text{c.c.} = 0, \qquad (8)$$

which leads to the set of one-electron Schrödinger equations which must be solved self-consistently.

$$\left\{-\frac{1}{V^{2/3}}\frac{\nabla^2}{2} + \sum_j\int_0^1 \frac{\phi_j^*(\boldsymbol{\tau}_2)\phi_j(\boldsymbol{\tau}_2)d\boldsymbol{\tau}_2}{V^{1/3}|\tau_1-\tau_2|}\right.$$

$$-\frac{2}{\pi}\left(\frac{3\pi}{4}\right)^{1/3}\frac{[\sum_{i(\uparrow)}\phi_i(\boldsymbol{\tau}_1)\phi_i(\boldsymbol{\tau}_1)]^{1/3}}{V^{1/3}}$$

$$\left.-\sum_\alpha\frac{Z_\alpha}{V^{1/3}|\tau_\alpha-\tau_1|} - \mu_i\right\}\phi_i(\boldsymbol{\tau}_1) = 0. \qquad (9)$$

The exchange term is for electrons with the same spin directions as $\phi_i(\boldsymbol{\tau},A)$ and has been derived previously.[1] μ_i is seen to be the one-electron eigenvalue.

In applying the variational principle to the total energy in (5), to obtain (9) the partial derivative of the total local exchange energy V_{ex} with respect to the wave function is taken. If instead of taking the partial derivative, the averaged exchange energy is taken, then

$$\frac{2V_{ex}\phi_i(\tau)}{\sum_{i(\uparrow)}\phi_i^*(\tau)\phi_i(\tau)}$$

$$= -\frac{3}{\pi}\left(\frac{3\pi^2}{4}\right)^{1/3}[\sum_{i(\uparrow)}\phi_i^*(\tau)\phi_i(\tau)]^{1/3}\phi_i(\tau),$$

which results in a set of one-electron equations which

are identical to (9) except that the exchange term is larger by $\frac{3}{2}$. This is the Slater approximation to exchange. This procedure does not satisfy the variational principle as has been pointed out by others.[2,3] What has been done by taking the averaged exchange is equivalent to the case in thermodynamics in which one minimized the molar free energy rather than the partial molar free energy. This leads to the calculation of wave functions and eigenvalues which are not the lowest energy states of the original energy expression (5). Consequently, these wave functions and eigenvalues will result in energies or pressures that are not the correct equilibrium values for this energy expression.

In order to derive an expression for the pressure let us consider a system at $T=0°K$ which undergoes an infinitesimal change in volume, dV. In Eq. (5), the energy is a function only of the volume V and $\phi(\tau,A)$. We may then write the change in energy as

$$dE=\left(\frac{\partial E}{\partial V}\right)_\phi dV+\sum_i \int_0^1 \left(\frac{\partial E}{\partial \phi_i{}^*}\right)_{V,\phi_j} d\phi_i{}^* d\tau$$

$$+\sum_i \int_0^1 \left(\frac{\partial E}{\partial \phi_i}\right)_{V,\phi_j} d\phi_i d\tau, \quad (10)$$

where $(\partial E/\partial V)_\phi$ is the partial derivative holding all ϕ's constant, and $d\phi_i$ represents a change in the wave function in going reversibly between two equilibrium states separated by the infinitesimal volume dV. It is not to be confused with $\delta\phi_i$. However, $(\partial E/\partial \phi_i)_{V,\phi_j}$ is the same quantity in both (8) and (6).

Since

$$(\partial E/\partial \phi_i{}^*)_{V,\phi_j}-\mu_i\phi_i=0,$$

then substituting in (10),

$$dE=\left(\frac{\partial E}{\partial V}\right)_\phi dV+\sum_i \mu_i \int_0^1 \phi_i{}^* d\phi_i d\tau+\sum_i \mu_i \int_0^1 \phi_i d\phi_i{}^* d\tau,$$

$$dE=\left(\frac{\partial E}{\partial V}\right)_\phi dV+\sum_i \mu_i d\int \phi_i{}^*\phi_i d\tau, \quad (11)$$

where $d\int(\phi_i{}^*\phi_i)d\tau=dn_i$ is the change in the number of electrons in the ith state for a change in volume of dV, and is not to be confused with $\delta\langle\phi_i\phi_i\rangle$ of Eq. (7).

Following conventional notation,[4] we define the pressure P as

$$P=-(\partial E/\partial V)_\phi.$$

Then (11) becomes

$$dE=-pdV+\sum_i^n \mu_i dn_i.$$

This expression is formally identical to the change in energy during a reversible process of a system of N chemical species. It also shows that we may consider each electron in each eigenstate to be equivalent to a distinct chemical species, and that their one-electron eigenvalues are then equal to their chemical potentials.

For the case of electrons, dn_i can only be 0 or ± 1, and will depend on the occupation number of the state. At $0°K$ $dn_i=0$ and $dE=-PdV$, unless an occupied energy state crosses an unoccupied state, in which case the equilibrium condition to be satisfied at constant volume is

$$\sum_{i=1}^N \mu_i dn_i=0.$$

This is simply the general condition of equilibrium for chemical reactions in homogeneous systems, and the promotion of an electron from one eigenstate to another is formally equivalent to the conversion of one chemical species to another.

We may write (5) in the following familiar concise notation:

$$E=T+U,$$

$$U=U_{ee}+U_{ex}+U_{en}+U_{nn}.$$

Then by straightforward differentiation of (5),

$$-V(\partial E/\partial V)_\phi=\tfrac{2}{3}T+\tfrac{1}{3}U \quad (12)$$

and

$$PV=\tfrac{2}{3}T+\tfrac{1}{3}U. \quad (13)$$

This formalism may be applied to solids or liquids. In the case of the latter, each crystallographic unit cell can be considered to be made up of a very large number of disordered atoms, i.e., liquid. Expressions similar to (12) have been derived by others, but to the author's knowledge, not explicitly for the present case.

If (13) were applied to cases in which the wave functions were not correctly minimized by the variational principle, then spurious thermodynamic properties will be calculated, as will be demonstrated in Sec. III, by making calculations for the free atom.

III. APPLICATION TO ATOMS

The formalism of Sec. II may be extended to atoms by considering the case in which the lattice parameter becomes large but not necessarily infinite, and all electrons are localized on isolated atoms and so do not interact with neighbors. The large lattice parameter allows the solution of the Schrödinger equation to be extended far enough away from the nucleus so as to go to zero at large distances and satisfy the atomic boundary condition of the wave function. In this limit $PV \to 0$ and we obtain the well-known result $2T=-U$. This result may be derived rigorously for an atom[5] using the varia-

[3] R. D. Cowan et al., Phys. Rev. 144, 5 (1966).
[4] H. B. Callen, Thermodynamics (John Wiley & Sons, Inc., New York, 1960).

[5] V. Fock, Z. Physik 63, 1930 (1930); W. Kauzmann, Quantum Chemistry (Academic Press Inc., New York, 1957).

TABLE I. Results of atomic calculations for $E=\frac{3}{3}T+\frac{1}{3}U$.[a]

Kohn-Sham	Slater	Slater'
	Aluminum	
−480.694	−480.458	−497.372
−0.309×10⁻³	5.638	−0.214×10⁻³
	Argon	
−1049.035	−1048.714	−1077.130
−0.397×10⁻³	9.472	−0.992×10⁻⁴
	Krypton	
−5493.729	−5493.039	−5582.900
−0.1251+10⁻²	29.952	−0.192×10⁻²
	Xenon	
−14 447.306	−14 446.355	−14 618.707
−0.293×10⁻²	57.447	−0.403×10⁻²

[a] All units are in Ry.

tional principle, in which case it can be shown that $2T=-U$ only if the wave function is minimized for the energy expression.

Using the programs of Herman and Skillman,[6] atomic calculations were made for the total energy E, and $\frac{3}{3}T+\frac{1}{3}U$ for the atom using the two forms of the exchange. These results are shown in the first two columns of Table I. In these calculations, we have not used the tail correction for the atomic potential proposed by Herman and Skillman. It is seen for the isolated atom that to within the order of numerical accuracy the calculations made with Kohn-Sham exchange obey the virial theorem and those made with the Slater exchange do not because the wave functions are not correctly minimized.

Inasmuch as the Slater exchange is so widely used, it is worthwhile to ask the question: For what total energy expression are the wave functions generated by the one-electron Slater exchange equations the correctly minimized ones? This can be shown for the expression of the total energy in which the exchange energy has been increased by $\frac{2}{3}$. Calculating the pressure as before, the results are shown in the last column of Table I labeled

Slater'. In this model, the exchange term is rigorously derivable from the total energy by the variational method and obeys the virial theorem, but the total energy is now much lower than even the Hartree-Fock energies. This is, of course, due to the fact that the Coulomb interaction in the exchange integral is now $\frac{3}{2}$ larger than the same term in Hartree-Fock calculations.

IV. SUMMARY

The chief purpose of this paper has been to call attention to the need for internal self-consistency in the calculation of those thermodynamic properties of the solid such as pressure which depend extremely sensitively upon the balance of energies. As an example, a PV of 0.1 Ry in solid aluminum at normal density results in a pressure of approximately 130 kbar. Consequently, it is crucial that the correct equilibrium state be calculated by the proper application of the variational principle to the total energy expression when deriving the one-electron equations.

It is of interest to note that a similar problem arises in molecular quantum mechanics[7] wherein calculations of molecular energy are made as a function of internuclear separation, usually using approximate wave functions. In order not to obtain spurious results for bond-force constants, it is necessary to force the wave functions to obey the virial theorem by introducing a variational parameter and requiring the wave functions to minimize the total energy expression. This function will generally not be the correct wave function for for the Hamiltonian which is the Hartree-Fock function, but it will minimize the energy as is required by the variational principle.

ACKNOWLEDGMENT

[6] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Inc., Englewood Cliffs, N. J., 1963).

[7] M. L. Benston and B. Kirtman, J. Chem. Phys. **44**, 119 (1966); P. Phillipson, *ibid.* **44**, 633 (1966).