

ON THE QUANTUM-MECHANICAL CALCULATIONS OF THE PRESSURE IN SOLIDS

G. M. GANDEL'MAN and E. S. PAVLOVSKIĬ

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A quantum-mechanical formula which is a generalization of the virial theorem is derived, for the pressure in a solid at zero temperature. A more detailed examination is made of the application of this formula in the approximation of spherical cells.

INTRODUCTION

IN the treatment of solid substances the usual problem is the calculation of the energy of cohesion in the normal state, and also the determination of the compressibility curve, i.e., the dependence of the pressure on the density. The pressure at a prescribed density is calculated (at zero temperature) as the derivative of the energy of the substance with respect to its volume,

$$p = -dE/dV. \quad (1)$$

Thus to determine the pressure in a given state one must know the energy also in a neighboring state, which is a considerable inconvenience. As is well known (cf. e.g., reference 1), in the Thomas-Fermi statistical method one can calculate the pressure directly in terms of the Thomas-Fermi potential or in terms of the density of electrons at the boundary of a cell in the given state, without differentiation. But the Thomas-Fermi method does not give negative pressures and for this reason does not describe the cohesion of solids. Inclusion of exchange and quantum corrections gives a zero pressure at a finite density, but in a region in which these effects cannot be treated as corrections.

A quantum-mechanical approach to the calculation of the energy and the pressure not only gives the fact of the cohesion of solids and the correct order of magnitude of the cohesion energy, but also can give a number of features of the compressibility curve that are caused by changes of the structure of the electron shells during compression. An example of this is the phase transition observed in cesium, for which Sternheimer² has proposed an explanation in terms of a calculation. In connection with this there is the interesting question of how one can express the pressure in terms of the quantum-mechanically described state of a solid. Feynman³ has considered an analogous problem. He found the forces with

which the nuclei in a molecule can be held at a prescribed distance in terms of the wave function of the electrons in a stationary state (with the prescribed position of the nuclei).

The problem of the pressure in a solid is much more complicated. This is due to the fact that in molecules the electron wave functions vanish at infinity together with their derivatives, whereas in the case of a solid one considers either an infinite body with a given density or else a body of a fixed finite volume (in a sense that will be stated later) with a prescribed pressure on its surface, so that the system is not closed.

It would be possible to express the pressure in terms of the quantum-mechanical stress tensor,⁴ part of which is due to the electric interaction (the electromagnetic tensor). This part has to be included, despite the electric neutrality of the atoms taken as a whole, since although the mean electric field (and the total electric volume force) acting on an atom is zero, it nevertheless contributes to the surface forces, to the pressure. This is expressed by the fact that the electric field appears quadratically in the electromagnetic tensor. The necessity of taking the electromagnetic tensor into account brings with it a number of difficulties; because of this we shall not derive the formula for the pressure in terms of the stress tensor.

DERIVATION OF THE QUANTUM-MECHANICAL FORMULA FOR THE PRESSURE

The energy of a solid body in which the nuclei are regarded as fixed at the points R_α ($\alpha = 1, 2, \dots, N$, where N is the number of nuclei) is given by the following formula:

$$\hat{E} = \int \Psi^*(q) \hat{H} \Psi(q) dq + E_{NN},$$

$$E_{NN} = \frac{1}{2} \sum_{\beta \neq \alpha} Z^2 e^2 / |R_\alpha - R_\beta|, \quad (2)$$

where \hat{H} is the Hamiltonian of the system of elec-

trons (relativistic effects are everywhere neglected):

$$\hat{H}(q) = -\frac{\hbar^2}{2m} \sum_i \Delta_i - Ze^2 \sum_{i,\alpha} \frac{1}{|r_i - R_\alpha|} + \frac{e^2}{2} \sum_{i,k+i} \frac{1}{r_{ik}}. \quad (3)$$

The summation over i is taken over all electrons; q is the set of space and spin coordinates of all the electrons. In the stationary state determined from the condition that the energy be a minimum, $\Psi(q)$ satisfies the Schrödinger equation

$$\hat{H}(q)\Psi(q) = E_0\Psi(q) \quad (4)$$

and the normalization condition

$$\int \Psi^*(q)\Psi(q) dq = 1. \quad (4a)$$

Strictly speaking the integrals in Eqs. (2) and (4a) must be extended over an infinite volume, but in this case we would have to include in the system considered also the body that bounds the volume. We shall replace it by a rigid wall, and at the boundary of the volume V shall postulate the boundary condition $\Psi = 0$. Thus the concept of the volume of the body is sharply defined. Now we can assume that the integrals in Eqs. (2) and (4a) are taken over the volume V .

The energy (2) depends on a parameter, on the volume V or, what is the same thing, on the average internuclear distance R_0 . For the calculation of the pressure we differentiate the energy with respect to this parameter. In doing so we note that when R_0 changes there are changes of the wave function and of the volume of integration

$$\frac{dE}{dR_0} = \int \left(\frac{\partial \Psi^*(q)}{\partial R_0} \hat{H} \Psi(q) + \Psi^* \hat{H} \frac{\partial \Psi}{\partial R_0} \right) dq + \int \Psi^* \frac{\partial \hat{H}}{\partial R_0} \Psi dq + \frac{dE_{NN}}{dR_0} + \frac{\partial E}{\partial R_0}.$$

Here in the last term $\partial/\partial R_0$ denotes differentiation with constant Ψ and H (with respect to the "upper limit"). In the first integral we add and subtract $(\partial\Psi/\partial R_0)(\hat{H}\Psi)^*$, and then use the Schrödinger equation (4). We get

$$\frac{dE}{dR_0} = E_0 \left\{ \frac{\partial}{\partial R_0} \int \Psi^* \Psi dq + \int \frac{\partial}{\partial R_0} (\Psi^* \Psi) dq \right\} + \int \Psi^* \frac{\partial \hat{H}}{\partial R_0} \Psi dq + \frac{dE_{NN}}{dR_0} + \int \left[\Psi^* \hat{H} \frac{\partial \Psi}{\partial R_0} - \frac{\partial \Psi}{\partial R_0} (\hat{H}\Psi)^* \right] dq.$$

The expression in curly brackets is equal to zero because of the preservation of the normalization (4a) under the change of volume. Accordingly we have

$$\frac{dE}{dR_0} = \int \Psi^* \frac{\partial \hat{H}}{\partial R_0} \Psi dq + \frac{dE_{NN}}{dR_0} + \int \left[\Psi^* \hat{H} \frac{\partial \Psi}{\partial R_0} - \frac{\partial \Psi}{\partial R_0} (\hat{H}\Psi)^* \right] dq. \quad (5)$$

Equation (5) differs from the Feynman formula³ by the last term, which arises because of the fact that the system considered here is not closed. It is not hard to convince oneself that for a finite volume of the body this term does not vanish, as it would for a free molecule. Equation (5) is convenient in that it contains only quantities of the same order of magnitude as the quantity dE/dR_0 that is being calculated. The larger terms of the order of E/R_0 are automatically excluded. In calculating the pressure p directly from Eq. (1) by first calculating the energy $E(V)$ as a function of the volume and then differentiating with respect to V one would have to find small differences of large quantities, since the energy of compression (or the energy of cohesion) is much smaller than the total energy E of the body. For practical purposes, however, formula (5) is unsuitable, because the region near the surface of the body makes substantial contributions to all the integrals although the region itself can be made arbitrarily small in comparison with the whole volume of the body. This is due to the fact that $\partial\Psi/\partial R_0$ and $\partial H/\partial R_0$ are proportional near the surface to the linear dimensions of the body. To prove this let us write the boundary condition $\Psi = 0$ at the surface of the body, $r = R$, for a variation of R_0 :

$$\Psi + \delta R_0 \partial \Psi / \partial R_0 = 0 \text{ at } r = R + \delta R,$$

from which we get on the boundary

$$\frac{\partial \Psi}{\partial R_0} = - \frac{\partial \Psi}{\partial r} \frac{\partial R}{\partial R_0} = - \frac{\partial \Psi}{\partial r} \frac{R}{R_0}. \quad (6)$$

The proof is similar for $\partial H/\partial R_0$.

Thus, although the formula (5) is correct, it cannot be used in practice because of the finite contribution of the region near the surface of the body. Just to make this situation clearer, we have considered a body of finite volume, and not an infinite body with a prescribed density. In the following section a formula for the pressure will be obtained that is free from this shortcoming.

GENERALIZATION OF THE VIRIAL THEOREM

As is well known, the virial theorem $E + E_K = 0$ holds in the quantum mechanics of a stationary system of particles interacting by the Coulomb law; E and E_K are respectively the total energy and kinetic energy of the system. The usual way of proving this theorem is to introduce into the formula for the energy a scale factor λ , and then set the derivative of the energy with respect to the parameter λ equal to zero for $\lambda = 1$, because of the stationary property of the system (the energy must be a minimum for $\lambda = 1$).

By exactly the same method we obtain in this section a generalization of the virial theorem for a quantum-mechanical system of nuclei and electrons in a stationary state with a prescribed finite value of its volume V (the nuclei, as before, are regarded as fixed); this theorem provides a possibility of calculating the pressure.

We shall start from the Hartree-Fock (H-F) approximation, which we are going to use in what follows. The theorem so obtained can, however, be extended to a more general case without difficulty.

We write down the energy in the H-F approximation:^{5,6}

$$\begin{aligned}
 E = & -2 \frac{\hbar^2}{2m} \sum_{k=1}^{ZN/2} \int \psi_k^*(r) \Delta \psi_k(r) dr - 2Ze^2 \sum_k \sum_{\alpha} \int \frac{|\psi_k(r)|^2}{|r - R_{\alpha}|} dr \\
 & + 2e^2 \sum_{i,k} \int \frac{1}{r_{12}} |\psi_i(r_1)|^2 |\psi_k(r_2)|^2 dr_1 dr_2 \\
 & - e^2 \sum_{i,k} \int \frac{1}{r_{12}} \psi_i^*(r_1) \psi_k(r_1) \psi_k^*(r_2) \psi_i(r_2) dr_1 dr_2 + E_{\text{NN}} \\
 \equiv & E_k + E_{eN} + E_{ee} + A_{ee} + E_{\text{NN}}. \quad (7)
 \end{aligned}$$

Here $\psi_i(\mathbf{r})$ are the spatial parts of the one-electron wave functions from which the Fock determinant is constructed. Equation (7) is written for the case in which there is a pair of electrons with opposite spins for each spatial state ψ_i (this means that ferromagnetic substances are excluded from this treatment). The summation over i and k is taken over all different spatial functions; the summation over the spins has already been done.

The requirement that the energy be a minimum with respect to arbitrary variations of the ψ_i that preserve the orthonormality of the system of functions ψ_i leads to the system of H-F equations (λ_{ik} are variation parameters):

$$\begin{aligned}
 & \left(-\frac{\hbar^2}{2m} \Delta - \sum_{\alpha} \frac{Ze^2}{|r - R_{\alpha}|} + 2e^2 \sum_i \int \frac{|\psi_i(r')|^2}{|r - r'|} dr' \right) \psi_k(r) \\
 & - e^2 \sum_i \int \frac{\psi_i^*(r') \psi_i(r) \psi_k(r')}{|r - r'|} dr' = \sum_i \lambda_{ki} \psi_i(r). \quad (8)
 \end{aligned}$$

To derive the virial theorem we take as the unit of length the average internuclear distance R_0 and introduce a changed form of the wave functions:

$$\rho = r/R_0, \quad \psi_i(r) = R_0^{-3/2} \varphi_i(\rho).$$

Here it must be remembered that the $\varphi_i(\rho)$ have further dependence on R_0 as a parameter. We express the energy E in terms of the φ_k :

$$\begin{aligned}
 E = & -2 \frac{\hbar^2}{2m R_0^2} \sum_k \int \varphi_k^* \Delta_{\rho} \varphi_k d\rho - \frac{2Ze^2}{R_0} \sum_{k,\alpha} \int \frac{|\varphi_k(\rho)|^2}{|\rho - R_{\alpha}/R_0|} d\rho \\
 & + \frac{2e^2}{R_0} \sum_{i,k} \int \frac{1}{\rho_{12}} |\varphi_i(\rho_1)|^2 |\varphi_k(\rho_2)|^2 d\rho_1 d\rho_2 \\
 & - \frac{e^2}{R_0} \sum_{i,k} \int \frac{1}{\rho_{12}} \varphi_i^*(\rho_2) \varphi_k(\rho_2) \varphi_k^*(\rho_1) \varphi_i(\rho_1) d\rho_1 d\rho_2 \\
 & + \frac{Z^2 e^2}{2R_0} \sum_{\alpha, \beta \neq \alpha} \left| \frac{R_{\alpha}}{R_0} - \frac{R_{\beta}}{R_0} \right|^{-1}. \quad (7a)
 \end{aligned}$$

There are corresponding changes in the H-F equations. Let us differentiate Eq. (7a) with respect to R_0 . Here, just as in the preceding section, we make use of the H-F equations for φ_k , first adding and subtracting a term

$$2 \frac{\hbar^2}{2m R_0^2} \sum_k \int \frac{\partial \varphi_k}{\partial R_0} \Delta_{\rho} \varphi_k^* d\rho,$$

in E_k . We note that in the differentiation there is no need to take into account the dependence of R_{α}/R_0 on R_0 , since the change of the mutual distribution of the nuclei with a change of R_0 occurs in second order. We get:

$$\begin{aligned}
 \frac{dE}{dR_0} = & -\frac{1}{R_0} (2E_k + E_{eN} + E_{ee} + A_{ee} + E_{\text{NN}}) \\
 & - \frac{\hbar^2}{m R_0^2} \sum_k \int \left(\varphi_k^* \Delta_{\rho} \frac{\partial \varphi_k}{\partial R_0} - \frac{\partial \varphi_k}{\partial R_0} \Delta_{\rho} \varphi_k^* \right) d\rho \\
 & + 2 \sum_{i,k} \int d\rho \left(\lambda_{ki} \frac{\partial \varphi_k^*}{\partial R_0} \varphi_i + \lambda_{ki}^* \frac{\partial \varphi_k}{\partial R_0} \varphi_i^* \right).
 \end{aligned}$$

The last term is equal to zero, as is easily seen if we recall the self-adjoint property of the matrix λ_{ki} and the preservation of the orthonormality of the functions φ_k under the change of volume. Using Eq. (1) and the relation $V \sim R_0^3$, we get the virial theorem in the following form

$$3pV = E_k + E + \frac{\hbar^2}{m R_0} \sum_k \int \left(\varphi_k^* \Delta_{\rho} \frac{\partial \varphi_k}{\partial R_0} - \frac{\partial \varphi_k}{\partial R_0} \Delta_{\rho} \varphi_k^* \right) d\rho. \quad (9)$$

In Eq. (9), unlike Eq. (5), the contribution of the region near the surface of the body can obviously be made arbitrarily small as the number of cells N goes to infinity, since the boundary conditions on the φ_k are fixed for a value of ρ that does not depend on R_0 . The origin of the last term in Eq. (9) is the same as for Eq. (5). Let us transform this term to a more convenient form. To do this we break up the integral with respect to ρ over the entire volume into a sum of integrals over the individual cells V_{α} and note that the integrand can be put in the form of the divergence of a vector. Accordingly the volume integral over

V_α can be reduced to an integral over the surface S of the cell:

$$3\rho V = E_\kappa + E + \frac{\hbar^2}{mR_0} \sum_{k, \alpha} \oint_{S_\alpha} \left(\varphi_k^* \nabla_\rho \frac{\partial \varphi_k}{\partial R_0} - \frac{\partial \varphi_k}{\partial R_0} \nabla_\rho \varphi_k^* \right)_n dS, \quad (10)$$

By means of the boundary conditions the derivatives of φ_k with respect to R_0 on the cell surfaces that appear in Eq. (10) can always be expressed in terms of the values of the functions themselves and their derivatives at the boundary, in a manner similar to the way this was done in the preceding section [Eq. (6)]. This will be done concretely a bit later [cf. Eq. (12)] for the Bloch conditions in the Wigner-Seitz method of spherical cells.

In concluding this section we remark that the extension of the result of Eq. (9) or Eq. (10) obtained in the H-F approximation to the general case is trivial. We give the result:

$$3\rho V = E_\kappa + E + \frac{\hbar^2}{2mR_0} \sum_i \int \left(\Phi^*(\rho) \Delta_{\rho_i} \frac{\partial \Phi}{\partial R_0} + \frac{\partial \Phi}{\partial R_0} \Delta_{\rho_i} \Phi^* \right) d\rho,$$

$$E_\kappa = - \frac{\hbar^2}{2mR_0^2} \sum_i \int \Phi^*(\rho) \Delta_{\rho_i} \Phi d\rho =$$

$$- \frac{\hbar^2}{2m} \sum_i \int \Psi^*(q) \Delta_i \Psi(q) dq,$$

$$E = \int \Psi^*(q) \hat{H} \Psi(q) dq + E_{\text{NN}},$$

$$\Phi(\rho) = R_0^{3n/2} \Psi(q), \quad \rho = q/R_0.$$

The summation is taken over all electrons; n is the number of electrons.

THE PRESSURE IN THE WIGNER-SEITZ APPROXIMATION

Ordinarily calculations of the energy of cohesion of solids are made by means of the spherical cell method of Wigner and Seitz.⁷ In this case the parameter R_0 is the radius of a cell. At the boundary of the cell $\rho = 1$. The wave function φ_k of an electron with the quasi-momentum \mathbf{k} obeys the Bloch conditions, which in the case of spherical cells take the form⁸

$$\varphi_k(\rho, \pi - \theta) = \exp\{-2ikR_0 \cos \theta\} \varphi_k(\rho, \theta),$$

$$\frac{\partial \varphi_k(\rho, \pi - \theta)}{\partial \rho} = - \exp\{-2ikR_0 \cos \theta\} \frac{\partial \varphi_k(\rho, \theta)}{\partial \rho} \text{ at } \rho = 1. \quad (11)$$

Here θ is the angle between the quasi-momentum \mathbf{k} and the radius vector \mathbf{r} . Differentiating the expressions (11) with respect to R_0 , let us substitute them in Eq. (10), first breaking the integral in Eq. (10) into two identical integrals and replacing θ by $(\pi - \theta)$ in one of them.

After this we use the conditions (11) and their complex conjugates. We get

$$3\rho v = E_\kappa + E + \frac{\hbar^2}{mR_0} \sum_k \int ik \cos \theta \left\{ \left(\varphi_k^* \frac{\partial \varphi_k}{\partial \rho} - \frac{\partial \varphi_k^*}{\partial \rho} \varphi_k \right) \right\}_{\rho=1} d\Omega. \quad (12)$$

Here E and E_κ are the total and kinetic energies belonging on the average to one cell, and v is the volume of a cell. For the case of the simple boundary conditions $\varphi_k = 0$ or $\partial \varphi_k / \partial \rho = 0$ at $\rho = 1$ the last term in Eq. (12) is zero.

Equation (12) can be written in terms of the ψ_k :

$$3\rho v = E_\kappa + E + \frac{\hbar^2 R_0^3}{m} \sum_k \int ik \cos \theta \left| \left(\psi_k^* \frac{\partial \psi_k}{\partial r} - \frac{\partial \psi_k^*}{\partial r} \psi_k \right) \right|_{r=R_0} d\Omega. \quad (12a)$$

In the cell method the wave function ψ_k is written in the form of a series

$$\psi = \sum_l A_l(k) R_l(E, r) P_l(\cos \theta). \quad (13)$$

R_l satisfies the radial Schrödinger equation with the potential $U(r)$. The function (13) must satisfy the Bloch conditions; this gives an infinite system of homogeneous equations for the A_l , which in practice is broken off at a finite number of equations and unknowns; by equating the determinant of the system to zero one can find the eigenvalue E for a given R_0 .⁸

After the functions ψ_k are found, the total energy E and the kinetic energy E_κ are found by calculating integrals [cf. Eq. (7)]. Here in the spherical-cell approximation all the integrals except the exchange integral reduce to integrals over the individual cells. In the calculation of the exchange integral, however, the interaction of several neighboring cells is important, and this leads to well known difficulties in the practical use of Eq. (12).

We note that the solution of the one-electron Schrödinger equation (14) (sic) with the boundary conditions (11) gives the functions ψ_k approximately, because the system of H-F equations does not break up exactly into separate equations of the type of Eq. (14). The H-F equations can be reduced to the form (14) by means of the modification of the H-F approximation proposed by Slater,⁹ with subsequent introduction of an effective potential $U(r)$ that is the same for all electrons. It is most expedient to use for $U(r)$ the statistical Thomas-Fermi potential.

The formula (12), which it is most convenient to use, was derived by applying one-electron functions of the Bloch type in the H-F method (to each spatial function satisfying the Bloch conditions there corresponds a pair of electrons with opposite spins).

Therefore the question arises as to the accuracy of the H-F approximation as applied to a metal. It is well known that for the case of an unfilled band, when the H-F method does not coincide with the Heitler-London method, the H-F method can be extremely inaccurate at small densities of the substance because of the neglect of the effect of Coulomb correlation between the electrons.^{6,10} Therefore calculation of the cohesion energy by the H-F method without the introduction of correlation corrections can give incorrect results. In spite of this we can hope for good accuracy of the H-F approximation in the calculation of the pressure in compressed substances. In any case, however, it is always necessary to estimate the importance of correlation effects.

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