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THE EQUATION OF STATE OF A CRYSTAL AT ZERO TEMPERATURE

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The pressure within the crystalline lattice is represented with the aid of perturbation theory as a sum of a kinetic pressure, determined from the value of the wave function and its derivatives at the boundary of the unit cell, and a Coulomb pressure, derived from the Coulomb (chiefly exchange and correlation) interaction between cells in such a way that interactions within the cells are eliminated.

IN the Thomas-Fermi approximation method, the pressure of a metal at absolute zero is expressed in terms of the electron density at the boundary of the neutral cell in such a way that inaccuracies in the determination of the energy of the electrons within are eliminated. The goal of the present paper is to derive for the pressure an exact quantum mechanical expression having this same advantage. The Coulomb interaction is not completely omitted, but use is made of only the Coulomb interaction between the cells, the greater part of which, except in the case of ionic crystals, consists of exchange and correlation effects.

This formula can be derived with the aid of an expression for the quantum mechanical stress tensor (see [1,2]). It would seem profitable also to derive it directly, using ordinary perturbation theory to transform the equation

$$p = -\partial(E_e + E_n)/\partial V,$$

where E_e is the eigenvalue for the ground state of the electrons and E_n is the Coulomb energy of the nuclei (the nuclei are regarded as stationary).

Before carrying out the calculations, let us formulate the result. We shall introduce the notation (see [3]):

$$\gamma(x'|\,x) = N\int \Psi^*(x', x_2, \ldots, x_N)\,\Psi(x, x_2, \ldots, x_N)\,dx_2\ldots dx_N \tag{2}$$

— the first-order density matrix; $\gamma(x) = \gamma(x\,|\,x)$ — the mean electron density; and

$$\Gamma(x_1, x_2) = \tfrac{1}{2}N(N-1)\int |\Psi(x_1, x_2, x_3, \ldots, x_N)|^2 dx_3\ldots dx_N \tag{2'}$$

— the second-order electron density.

Here, Ψ is the normalized wave function. The quantities $\gamma(x)$, $\gamma(x'|\,x)$, and $\Gamma(x_1, x_2)$ possess, in contradistinction to Ψ, a direct physical significance; they contain no arbitrary phase factors and are independent of the crystal volume chosen as a basis, so that they can equally well be applied to an infinite crystal (and to infinite N).

For simplicity, we shall consider the average pressure under isotropic compression. Let us choose a substance having cells of the Brillouin zone type; i.e., such that all points on the boundary between adjacent cells are equidistant from the centers of the neighboring cells. The cell may contain several nuclei. We assume that the cells are identical and can be formed from one another by displacements and rotations which preserve the lattice structure. Under these conditions, the pressure is

$$p = p_{\mathrm{kin}} + p_{\mathrm{Coul}},$$

where p_{kin} is the average value of the quantity

$$p_{\mathrm{kin}}(x) = \frac{\hbar^2}{2m}\left[\frac{\partial^2\gamma(x'|x)}{\partial n'\partial n} - \frac{1}{2}\frac{\partial^2\gamma(x'|x)}{\partial n'^2} - \frac{1}{2}\frac{\partial^2\gamma(x'|x)}{\partial n^2}\right]_{x'=x} \tag{4}$$

over the surface of the cell (with weight equal to the distance between centers of neighboring cells). In this expression $\partial/\partial n$ is the derivative with respect to the variable x along the normal to the boundary, and $\partial/\partial n'$ is the corresponding derivative with respect to x'.

The Coulomb portion of the pressure is equal to the work done by the Coulomb forces between the cells as the latter are displaced by uniform expansion, divided by the change in volume. We assume that for uniform expansion in all directions by a factor $1 + \epsilon$ the change in cell volume is $\delta\omega = 3\epsilon\omega$, and that the displacement vector for the g-th cell $\delta\mathbf{R}_g = \epsilon\mathbf{R}_g$, where $\mathbf{R}_g$ is the radius vector of its center. Making use of the identical nature of the cells, we find it natural to write the Coulomb contribution to the pressure in the form

$$p_{\mathrm{Coul}} = \frac{1}{6\omega}\sum_{g\neq 0}\mathbf{F}_{0g}(\mathbf{R}_g - \mathbf{R}_0), \tag{5}$$

where $\mathbf{F}_{0g}$ is the total (taking the nuclei into account) repulsive Coulomb force between the cells:

$$\mathbf{F}_{0g} = \int\limits_{\omega_0} d\mathbf{r}_1 \int\limits_{\omega_g} d\mathbf{r}_2 \rho(\mathbf{r}_1, \mathbf{r}_2) e^2 (\mathbf{r}_2 - \mathbf{r}_1) / |\mathbf{r}_2 - \mathbf{r}_1|^3, \tag{6}$$

$$\begin{aligned} \rho(\mathbf{r}_1, \mathbf{r}_2) = {} & 2\Gamma(\mathbf{r}_1, \mathbf{r}_2) - \sum_{\omega_0} Z_h \delta(\mathbf{r}_1 - \mathbf{R}_h) \gamma(\mathbf{r}_2) \\ & - \sum_{\omega_g} \gamma(\mathbf{r}_1) Z_{h'} \delta(\mathbf{r}_2 - \mathbf{R}_{h'}) \\ & + \sum_{\omega_0} \sum_{\omega_g} Z_h \delta(\mathbf{r}_1 - \mathbf{R}_h) Z_{h'} \delta(\mathbf{r}_2 - \mathbf{R}_{h'}). \end{aligned} \tag{7}$$

Here, the radius vector $\mathbf{R}_h$ runs over the nuclei of the cell ω_0, Z_h is the charge, while the quantities $\mathbf{R}_{h'}$ and $\mathbf{Z}_{h'}$ refer to the nuclei of the cell ω_g. The function $\rho(\mathbf{r}_1, \mathbf{r}_2)$ can be written in the form

$$\rho(\mathbf{r}_1, \mathbf{r}_2) = [2\Gamma(\mathbf{r}_1, \mathbf{r}_2) - \gamma(\mathbf{r}_1)\gamma(\mathbf{r}_2)] + \rho(\mathbf{r}_1)\rho(\mathbf{r}_2), \tag{8}$$

$$\rho(\mathbf{r}) = \gamma(\mathbf{r}) - \sum Z_h \delta(\mathbf{r} - \mathbf{R}_h). \tag{9}$$

The first term in (8) gives the exchange, or, more exactly, the exchange-correlation portion of the Coulomb interaction, and the second gives the classical portion.

Since the cells are neutral in the mean and nearly spherical, the classical part of the interaction usually, except in the case of ionic crystals, makes an extremely small (numerically) contribution to the force and the pressure; the exchange part can, however, contribute significantly.

In the single-electron approximation, in which the wave function is represented by a single determinant, Eqs. (2), (2′), and (4) assume the following forms

$$\gamma(\mathbf{r}) = \sum |\psi_i(\mathbf{r})|^2, \tag{10}$$

$$2\Gamma(\mathbf{r}_1, \mathbf{r}_2) - \gamma(\mathbf{r}_1)\gamma(\mathbf{r}_2) = -|\gamma^+(\mathbf{r}_1|\mathbf{r}_2)|^2 - |\gamma^-(\mathbf{r}_1|\mathbf{r}_2)|^2, \tag{11}$$

$$p_{\mathbf{kin}}(\mathbf{r}) = \frac{\hbar^2}{2m} \sum_i \left(\frac{\partial \psi_i^*}{\partial n} \frac{\partial \psi_i}{\partial n} - \frac{1}{2} \psi_i^* \frac{\partial^2 \psi_i}{\partial n^2} - \frac{1}{2} \psi_i \frac{\partial^2 \psi_i^*}{\partial n^2} \right). \tag{12}$$

Here the ψ_i are the normalized single-electron wave functions;

$$\gamma^+(\mathbf{r}_1|\mathbf{r}_2) = \sum^+ \psi_i^*(\mathbf{r}_1)\psi_i(\mathbf{r}_2), \quad \gamma^-(\mathbf{r}_1|\mathbf{r}_2) = \sum_i^- \psi_i^*(\mathbf{r}_1)\psi_i(\mathbf{r}_2) \tag{13}$$

are the sums over ψ_i, referred to positive and negative spin orientation, respectively.

We turn now to the derivation of Eqs. (3) — (7). We must, in accordance with Eq. (1), find the change in the energy of the system for a uniform expansion by a factor $1 + \epsilon$. We note first that the nuclei can be regarded as strongly bound to the centers of the cells, and that only the cells as a whole take part in the expansion. Of course, such an expanded state will not, generally speaking, be an equilibrium one for the given volume (nor will the state produced by a uniform increase in the separation of the nuclei); it will, however, differ only infinitesimally from the equilibrium state, so that there will be only a second-order difference in energy.

In order that the boundaries may be neglected, we shall choose as usual a certain large volume Ω of the crystal, containing N electrons. At the boundaries of Ω the wave function ψ is assumed to be periodic in the coordinates of each electron; we accordingly refer the Coulomb energy of the nuclei and its variation under deformation to the volume Ω. The volume after expansion by the factor $1 + \epsilon$ is designated by Ω' and the eigenfunction in Ω' is denoted Ψ'. If the separation of all of the nuclei is increased uniformly, we can establish a correspondence between the points of Ω and those of Ω'; then, multiplying the equation for Ψ' by Ψ^* and the equation for Ψ^* by Ψ', subtracting, and integrating over all of the variables, we obtain the virial theorem.

We shall now do the same thing, establishing the correspondence between Ω and Ω' in another fashion. Let us construct about the displaced centers of the cells new cells of the same size. Let the sum of these cells be Ω''. The volume Ω' consists of Ω'' plus the sum of the gaps between the cells. We now establish a correspondence not between Ω' and Ω, but between Ω'' and Ω: we refer the centers of the new cells to those of the original cells, and then correlate each point in Ω'' with the point in Ω which is similarly situated relative to the center of the corresponding cell. Thus, to a single point located on the boundary of a cell in Ω there correspond two points in Ω'', lying on either side of the intercell gap, so that the function Ψ', continuous in Ω', can now be regarded as discontinuous in Ω''. The values of Ψ' in the spaces between the cells need not be considered at all, since no integration is performed over these regions.

The equation for Ψ has the form

$$\begin{aligned} E_{\mathbf{e}} \Psi = {} & - \sum_{i=1}^{N} \frac{\hbar^2}{2m} \Delta_i \Psi - \sum_{i=1}^{N} \sum_h \frac{e^2 Z_h}{|\mathbf{r}_i - \mathbf{R}_h|} \Psi \\ & + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \Psi. \end{aligned} \tag{14}$$

In order that the boundary of Ω have no effect, we must in the last summation include not only the distances separating all of the points $\mathbf{r}_i$ and $\mathbf{r}_j$ within Ω, but also all of the distances between these points and their images as produced by a parallel displacement through Ω; correspondingly, in the sum over the nuclei we must take account, not only of the $\mathbf{R}_h$ within Ω, but of a whole infinite lattice as well. (If desired, a factor $\exp(-\kappa\,|\mathbf{r}_i - \mathbf{r}_j|)$ can be introduced to give convergence, and κ allowed to go to zero in the final result.)

The equation for Ψ' within Ω'', if the same coordinates are introduced in Ω'' as in Ω, is written in the form

$$E'_{\mathbf{e}}\,\Psi' = -\sum_{i=1}^{N}\frac{\hbar^2}{2m}\Delta_i\Psi' - \sum_{i=1}^{N}\sum_{h}\frac{e^2 Z_h}{|\mathbf{r}_i - \mathbf{R}_h|'}\Psi' + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|'}\Psi'. \tag{15}$$

Here $|\mathbf{r}_i - \mathbf{R}_h|' = |\mathbf{r}_i - \mathbf{R}_h|$ if the coordinates $\mathbf{r}_i$ and the nucleus $\mathbf{R}_h$ are situated in the same cell, and $|\mathbf{r}_i - \mathbf{R}_h|' = |\mathbf{r}_i - \mathbf{R}_h + \epsilon(\mathbf{R}_g - \mathbf{R}_{g'})|$, if $\mathbf{r}_i$ and $\mathbf{R}_h$ lie in different cells having centers $\mathbf{R}_g$ and $\mathbf{R}_{g'}$; the quantities $|\mathbf{r}_i - \mathbf{r}_j|'$ behave analogously. In contradistinction to the virial theorem, no coefficient need be used here in the Laplacian, since the correspondence between Ω'' and Ω at each point preserves the scale.

As noted above, we multiply the equation for Ψ' by Ψ^* and that for Ψ^* by Ψ', subtract, sum over all spins, and integrate over all coordinates. In the left-hand part, as a result of the normalization of Ψ, we obtain the desired difference $E'_e - E_e$ to a high order of accuracy.

On the right, we first consider some Coulomb term, say the term due to the interaction between the first and second electron:

$$\iint\cdots\int\left[\frac{e^2}{2\,|\mathbf{r}_1 - \mathbf{r}_2|'} - \frac{e^2}{2\,|\mathbf{r}_1 - \mathbf{r}_2|}\right]\Psi^*\Psi'\,dx_1\cdots dx_N,$$

summation over all of the spins being understood. To a high order of accuracy, Ψ' can be replaced by Ψ. Further, the same contribution is provided by all of the terms involving $|\mathbf{r}_i - \mathbf{r}_j|$, $N(N-1)$ in all. Integrating first over the variables $x_3, \ldots,$ x_N, and then over x_1 and x_2, we obtain

$$\iint\left[\frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|'} - \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}\right]\Gamma(\mathbf{r}_1, \mathbf{r}_2)\,d\mathbf{r}_1\,d\mathbf{r}_2.$$

We break up the range of integration over $\mathbf{r}_1$ and $\mathbf{r}_2$ into cells, and represent this integral in the form of a double summation:

$$\sum_{g}\sum_{g'}\int_{\omega_g}\int_{\omega_{g'}} d\mathbf{r}_1\,d\mathbf{r}_2\,\Gamma(\mathbf{r}_1, \mathbf{r}_2)\left[\frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|'} - \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}\right].$$

Terms with $g = g'$ go to zero, in accordance with what has been said above; terms with $g \neq g'$, in view of the symmetry of Γ, are symmetrical in g and g'. As a result, the integral takes on the form of a sum over all possible combinations of g and g':

$$\sum_{g\neq g'}\int_{\omega_g}\int_{\omega_{g'}} d\mathbf{r}_1\,d\mathbf{r}_2\,2\Gamma(\mathbf{r}_1, \mathbf{r}_2)\left[\frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|'} - \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}\right].$$

The difference within the square brackets is evidently, to a high order of accuracy

$$\frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2 + \varepsilon(\mathbf{R}_g - \mathbf{R}_{g'})|} - \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \approx -\frac{e^2(\mathbf{r}_1 - \mathbf{r}_2)\,\varepsilon(\mathbf{R}_g - \mathbf{R}_{g'})}{|\mathbf{r}_1 - \mathbf{r}_2|^3}$$

and the double-summation term under consideration equals

$$\varepsilon\mathbf{F}'_{gg'}(\mathbf{R}_g - \mathbf{R}_{g'}),$$

where $\mathbf{F}'_{gg'}$ is that part of the force $\mathbf{F}_{gg'}$ which corresponds to the first term in Eq. (7). In exactly the same way, the second Coulomb term in Eq. (15) yields the second and third terms of (7). The change in E_n yields the fourth term in Eq. (7). Referring everything to a single cell and dividing by the change in volume, we obtain Eq. (5), exactly.

Let us now consider a term with a given Laplacian Δ_i. Integrating first over $d\mathbf{r}_i$, we obtain

$$-\frac{\hbar^2}{2m}\int(\Psi^*\Delta_i\Psi' - \Psi'\Delta_i\Psi^*)\,d\mathbf{r}_i = -\sum_{g}\frac{\hbar^2}{2m}\int_{\omega_g}(\Psi^*\Delta_i\Psi' - \Psi'\Delta_i\Psi^*)\,d\mathbf{r}_i = -\sum_{g}\frac{\hbar^2}{2m}\oint_{S_g} dS\left(\Psi^*\frac{\partial\Psi'}{\partial n} - \Psi'\frac{\partial\Psi^*}{\partial n}\right),$$

with $\partial/\partial n$ the derivative with respect to the exterior normal to the surface of the cell S_g. If the function Ψ', together with its derivatives, were continuous, then, owing to periodicity, the sum would go to zero: the integral over each boundary between neighboring cells would appear twice, first for one cell and then for the other, with opposite signs. Because of the discontinuous nature of Ψ' in Ω'', there remains for each boundary a difference between two nearly, but not precisely, equal integrals. The width of the inter-cell gap $\delta = \epsilon\,|\mathbf{R}_g - \mathbf{R}'_g|$; the discontinuities in Ψ' and $\partial\Psi'/\partial n$ are therefore equal, respectively, to $\delta\,\partial\Psi'/\partial n$ and $\delta\,\partial^2\Psi'/\partial n^2$, and the sum with which we are concerned becomes

$$-\sum_{S_{g,g'}}\frac{\hbar^2}{2m}\delta\int_{S'_{gg'}} ds\left(\frac{\partial\Psi'}{\partial n}\frac{\partial\Psi^*}{\partial n} - \Psi^*\frac{\partial^2\Psi'}{\partial n^2}\right).$$

We can now replace Ψ' by Ψ with high-order accuracy. Integrating over all of the remaining variables, with the exception of dx_i, and taking account of the fact that all of the terms with $i = 1,$ $2, \ldots$ yield the same contribution, we obtain the contribution to $E'_e - E_e$:

$$-\sum_{S_{g,g'}}\frac{\hbar^2}{2m}\delta\int_{S_{g,g'}} ds\left[\frac{\partial^2\gamma(x'|x)}{\partial n'\partial n} - \frac{\partial^2\gamma(x'|x)}{\partial n^2}\right]_{x'=x}.$$

Here δdS is the element of volume of the gap, so that the remaining factor can be regarded as the pressure; this is, however, inconvenient, because of the complexity of the expression thus derived.

Repeating the same argument for the functions Ψ'^* and Ψ, instead of for Ψ' and Ψ^*, we obtain the complex-conjugate expression, in which the Coulomb terms, being real, are unchanged. Taking the half-sum, we obtain, exactly, Eq. (4).

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