

Simplification of total-energy and pressure calculations in solids

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In addition to presenting an expression for the pressure which is valid for all treatments of exchange and correlation, we derive a new relation for the kinetic energy of the cores which, in the muffin-tin approximation, leads to an algebraic cancellation of various core contributions to the pressure. Thus, numerical difficulties associated with total-energy and pressure calculations are greatly reduced.

INTRODUCTION

Calculations of the total energy and pressure-volume relation for solids are of considerable current interest. In addition to providing a means of studying phase stability and finding compressibilities, a comparison of predicted and measured lattice constants offers a way of checking the approximations (muffin-tin approximation and approximations for exchange and correlation effects) used in most energy-band calculations.

Two contributions are made in this paper. In Sec. I, we show that Slater's¹ derivation of the expression for the pressure can be generalized to apply to any treatment of exchange and correlation. Straightforward application of this pressure expression involves serious numerical difficulties arising from cancellation between very large kinetic- and potential-energy contributions from the core states.

The main point of this paper is that, at least in the muffin-tin approximation, the pressure expression can be rewritten so that this cancellation is effected algebraically. This largely eliminates the numerical difficulties usually associated with these calculations. The muffin-tin approximation is discussed in Sec. II, and a new expression for the kinetic energy of the cores is developed in Sec. III; this expression can be used to check the accuracy of the core calculation. In Sec. IV, it is used to simplify the pressure and total-energy expressions.

I. TOTAL ENERGY AND PRESSURE

The total energy of a solid with the nuclei frozen is given by^{1,2} (all quantities in atomic units)

$$E = T + U + E_{xc} \tag{1}$$

Here T is given by

$$T = \sum_i \int \psi_i^* (-\nabla^2) \psi_i d^3r, \tag{2}$$

where the ψ_i 's are the solutions of an effective one-electron Schrödinger equation, and the sum extends over all occupied electron states.

The potential energy U in Eq. (1) is given by

$$U = -2Z \sum_{\mathbf{R}} \int d^3r \frac{\rho(\vec{r})}{|\vec{r} - \mathbf{R}|} + \int d^3r d^3r' \times \frac{\rho(\vec{r}) \rho(\vec{r}')}{|\vec{r} - \vec{r}'|} + Z^2 \sum'_{\mathbf{R} \neq \mathbf{R}'} \frac{1}{|\mathbf{R} - \mathbf{R}'|}, \tag{3}$$

where $\rho(\vec{r})$ is the electron charge density,

$$\rho(\vec{r}) = \sum_i |\psi_i(\vec{r})|^2. \tag{4}$$

The first term in Eq. (3) is the Coulomb interaction between the electrons and the nuclei, the second term is the Coulomb interaction of the electrons with each other, and the last term is the Coulomb interaction of the nuclei with each other.

The final term E_{xc} in Eq. (1) is the exchange-correlation contribution to the total energy; it is defined as the difference between the exact total energy of the system and $T + U$ as given by Eqs. (2) and (3). The general form of this term is not known, although a number of approximations for it have been suggested.^{3,4}

Variation of the total energy with respect to the electron charge density leads to an effective one-electron Schrödinger equation of the form

$$[-\nabla^2 + V(\vec{r})] \psi_i = \epsilon_i \psi_i, \tag{5}$$

where

$$V(\vec{r}) = \frac{\delta U}{\delta \rho(\vec{r})} + \frac{\delta E_{xc}}{\delta \rho(\vec{r})} = -2Z \sum_{\mathbf{R}} \frac{1}{|\vec{r} - \mathbf{R}|} + \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3r' + \mu_{xc}(\vec{r}) \tag{6}$$

and

$$\mu_{xc}(\vec{r}) \equiv \frac{\delta E_{xc}}{\delta \rho(\vec{r})}$$

is the exchange-correlation contribution to the effective one-electron potential.

An expression for the pressure may be obtained, following Slater,¹ by operating on Eq. (5) with $(\vec{r} \cdot \nabla)$, multiplying by ψ_i^* , and integrating over all space. Using the conjugate of Eq. (5) to reexpress the term $\psi_i^* (V - \epsilon_i)(\vec{r} \cdot \nabla) \psi_i$, we find

$$\int d^3r [\psi_i^* (\vec{r} \cdot \nabla) \nabla^2 \psi_i - (\nabla^2 \psi_i^*) \vec{r} \cdot \nabla \psi_i] \\ = \int \psi_i^* \psi_i (\vec{r} \cdot \nabla) V d^3r .$$

Using Gauss's theorem, noting that all surface integrals vanish because the wave functions vanish sufficiently far outside the crystal, and summing over occupied states, one obtains

$$2T = \int \rho (\vec{r} \cdot \nabla) V d^3r . \quad (7)$$

To obtain an expression for the pressure, one substitutes Eq. (6) into (7), carries out the differentiation term by term, and identifies the pressure from the total force on the nuclei. These manipulations are described in detail in Slater's paper,¹ and lead to the result

$$3P\mathcal{V} = 2T + U - \int \rho (\vec{r} \cdot \nabla) \mu_{xc} d^3r , \quad (8)$$

where \mathcal{V} is the volume of the crystal. This result is exact and completely general, whereas Slater's derivation applies only to the $X\alpha$ method.

A simplification of the exchange-correlation contribution to the pressure can be made for those cases where the exchange-correlation energy is taken to be of the form

$$E_{xc} = \int \rho \epsilon_{xc}(\rho) d^3r . \quad (9)$$

Among others, this approximation applies to the $X\alpha$ method³ and the local-density scheme of Kohn and Sham.⁴ One has

$$\mu_{xc} = \frac{d}{d\rho} [\rho \epsilon_{xc}(\rho)] \Big|_{\rho=\rho(\vec{r})} .$$

The fact that μ_{xc} depends on position only through its dependence on the charge density $\rho(\vec{r})$ allows us to integrate the exchange-correlation term in Eq. (8) by parts, obtaining

$$3P\mathcal{V} = 2T + U - 3 \int \rho (\epsilon_{xc} - \mu_{xc}) d^3r . \quad (10)$$

The $X\alpha$ method³ has the interesting property that the exchange-correlation term in Eq. (10) is numerically equal to E_{xc} as given by Eq. (9).

The major practical difficulty in the use of Eq. (10) to obtain pressure-volume relations from energy-band calculations becomes apparent when we recognize that both T and U contain very large contributions from the electronic core states, which are highly localized around the nuclei. These contributions very nearly cancel each other, since the pressure is zero at the equilibrium volume, and serious numerical difficulties involving differences of large numbers are thus inherent in the use of Eq. (10). However, it is possible, at least within the muffin-tin approximation, to isolate those core contributions to T and U which cancel each other in Eq. (10), which greatly simplifies the calculation of the pressure-volume relation. Before exhibiting this result, we first describe the muffin-tin approximation.

II. MUFFIN-TIN APPROXIMATION

In the muffin-tin approximation, the electron charge density in each unit cell is replaced by its spherical average within the inscribed sphere (the muffin tin, of radius R) and by a constant ρ_0 in the interstitial region between the inscribed sphere and the unit-cell boundaries. To ensure charge neutrality,

$$Z_{\text{out}} = \rho_0 \Omega_0 = Z - 4\pi \int_0^R r^2 \rho(r) dr , \quad (11)$$

where

$$\Omega_0 = \Omega - \frac{4}{3} \pi R^3 \quad (12)$$

is the interstitial volume, and Ω is the volume of the unit cell. The electron-charge density is taken to be the same in each of the N unit cells of the crystal.

The potential energy U given in Eq. (2) becomes

$$U = N \left(-2Z \sum_{\vec{R}} \int_{\Omega} d^3r \frac{\rho(r)}{|\vec{r} - \vec{R}|} \right. \\ \left. + \sum_{\vec{R}} \int_{\Omega} d^3r \int_{\Omega} d^3r' \frac{\rho(r)\rho(r')}{|\vec{r} - \vec{r}' - \vec{R}|} + Z^2 \sum_{\vec{R}}' \frac{1}{|\vec{R}|} \right) , \quad (13)$$

where all integrations extend over one unit cell. These integrals are now broken up into integrals over the muffin tins, within which the charge density is spherically symmetric, and integrals over the interstitial regions, where the charge density is constant. For crystals of cubic symmetry (and others of lower symmetry, provided the unit cell is not too anisotropic in shape), angular integrations of quantities such as $|\vec{r} - \vec{R}|^{-1}$ give simply $|\vec{R}|^{-1}$. Using this result, and adding and subtracting ρ_0 from the charge density inside the muffin tin, one can eventually put U into the form

$$u \equiv U/N = -8\pi Z \int_0^R r \rho(r) dr + 2(4\pi)^2 \\ \times \int_0^R dr r \rho(r) \int_0^r dr' r'^2 \rho(r') \\ - \frac{1}{2} C \frac{Z_{\text{out}}^2}{a} , \quad (14)$$

where a is the lattice constant, and C , which is a different constant for each crystal lattice, is given by

$$C = \frac{4\pi a^3}{\Omega_0^2} \left[\frac{\Omega^2 A}{2\pi a^3} - \frac{6\Omega + 4\Omega_0}{5} \left(\frac{R}{a} \right)^2 \right] . \quad (15)$$

The constant A , defined by

$$\frac{A}{a} = \frac{1}{\Omega} \int \frac{d^3r}{r} - \sum' \frac{1}{R} , \quad (16)$$

can be evaluated for any lattice by the Ewald method; values for A for the cubic lattices have been given by Coldwell-Horsfall and Maradudin,⁵ and the resulting values of C are given in Table I.

TABLE I. Values of A from Ref. 5; values of C from Eq. (15).

Lattice	A	C
sc	2.8372976	3.1166857
bcc	3.639240	4.085521
fcc	4.5848756	4.8320664

The one-electron potential in each unit cell which results from varying $U + E_{xc}$ with respect to the charge density $\rho(r)$ is

$$V(r) = \begin{cases} 0, & r > R; \\ -\frac{2Z}{r} + 8\pi \int_0^r \left(\frac{r'^2}{r} - r' \right) \rho(r') dr' \\ \quad + 8\pi \int_0^R r \rho(r) dr \\ \quad + C \frac{Z_{\text{out}}}{a} + \mu_{xc}(r) \\ \quad - \mu_{xc}(\rho_0), & r < R. \end{cases} \quad (17)$$

This is exactly the same as the muffin-tin potential which would have been obtained from the charge density using the method of Slater and de Cicco.⁶

Note that

$$(\vec{r} \cdot \nabla)V = r \frac{dV}{dr} = \frac{2Z}{r} - 8\pi \int_0^R r'^2 \rho(r') dr' \\ + (\vec{r} \cdot \nabla) \mu_{xc}(r), \quad r < R$$

so that we can rewrite Eq. (14) as

$$u = -4\pi \int_0^{R^-} dr r^2 \rho(r) (\vec{r} \cdot \nabla)V(r) \\ + 4\pi \int_0^{R^-} dr r^2 \rho(r) (\vec{r} \cdot \nabla) \mu_{xc}(r) \\ - \frac{1}{2} C \frac{Z_{\text{out}}^2}{a}. \quad (18)$$

The integrations in this expression go out to just inside the muffin-tin radius, and so do not include any contributions from the discontinuity in $V(r)$.

III. CORE STATES

We define a core state as any state which is localized around the nucleus and has negligible amplitude at and beyond the muffin-tin radius. The usual method of obtaining T for the core consists in multiplying the Schrödinger equation, Eq. (5), by ψ^* for each core state, integrating over the unit cell, and then summing over all core states:

$$t_c = T_c/N = \sum \epsilon_c - \int_{\Omega} \rho_c(r) V(r) d^3r, \quad (19)$$

where $\rho_c(\vec{r})$ is the core charge density.

However, another expression exists for t_c . It is obtained, just as in Eq. (7), by operating on the Schrödinger equation for a core state with $(\vec{r} \cdot \nabla)$, multiplying by ψ_c^* , and integrating over the unit cell. Integrals involving core states taken over the surface of the unit cell will vanish, because the core states have negligible amplitude there, and we have immediately

$$2t_c = \int_{\Omega} \rho_c(r) (\vec{r} \cdot \nabla) V d^3r \\ = 4\pi \int_0^R r^3 \rho_c(r) \frac{dV}{dr} dr. \quad (20)$$

Equations (19) and (20) furnish a fairly stringent test of the accuracy of the core-state calculation: it must be true that

$$\sum \epsilon_c - \int_{\Omega} \rho_c(r) V(r) d^3r \\ = \frac{1}{2} \int_{\Omega} \rho_c(r) (\vec{r} \cdot \nabla) V(r) d^3r. \quad (21)$$

IV. PRESSURE AND TOTAL ENERGY

A considerable simplification of Eq. (10) for the pressure results if we use Eq. (20) for t_c , instead of Eq. (19), and evaluate the potential energy u from Eq. (18). If we use the subscript v to denote the valence contributions to all quantities, we have

$$3P\Omega = 2t_v - 4\pi \int_0^{R^-} dr r^3 \rho_v(r) \frac{dV}{dr} - \frac{1}{2} C \frac{Z_{\text{out}}^2}{a} \\ + 4\pi \int_0^{R^-} dr r^3 \rho(r) \frac{d\mu_{xc}}{dr} \\ - 3 \int_{\Omega} \rho(\epsilon_{xc} - \mu_{xc}) d^3r. \quad (22)$$

The use of Eq. (20) for t_c results in an algebraic cancellation of part of the potential energy u , so that the quantities remaining in Eq. (22) are several orders of magnitude smaller than t or u themselves. This cancellation essentially eliminates the numerical difficulties ordinarily associated with pressure calculations.

A final practical expression for the pressure is obtained by inserting

$$t_v = \sum \epsilon_v - \int_{\Omega} \rho_v(r) V(r) d^3r \quad (23)$$

into Eq. (22), and integrating the term involving $d\mu_{xc}/dr$ by parts:

$$3P\Omega = 2 \sum \epsilon_v - 4\pi \int_0^{R^-} dr r \rho_v(r) \frac{d}{dr} [r^2 V(r)] \\ - \frac{1}{2} C \frac{Z_{\text{out}}^2}{a} \\ - 3Z_{\text{out}} [\epsilon_{xc}(\rho_0) - \mu_{xc}(\rho_0)] \\ - 4\pi R^3 \rho(R) [\epsilon_{xc}(R) - \mu_{xc}(R)]. \quad (24)$$

For a given one-electron potential $V(r)$, this expression involves only the valence-state energies and the valence charge density; the core states enter only through their contribution to $V(\vec{r})$.

Liberman⁷ has also given an expression for the pressure from which the core states have largely been eliminated; however, his expression involves integrals of the valence-state wave functions over

the surface of the unit cell, which he approximates by integrals over the Wigner-Seitz sphere. Equation (24), on the other hand, involves only a single integral over the muffin tin, which can be performed without approximation.

A simplification of the expression for the total energy also results from using Eq. (20) for t_c . From Eq. (1),

$$E/N = -2\pi \int_0^R dr r^3 \rho_c(r) \frac{dV}{dr} + t_v - 4\pi \int_0^{R^-} dr r^3 dr^3 \rho_v(r) \frac{dV}{dr} + 4\pi \int_0^{R^-} dr r^3 \rho(r) \frac{d\mu_{xc}}{dr} - \frac{1}{2} C \frac{Z_{\text{out}}^2}{a} + \int_0 \rho \epsilon_{xc} d^3r .$$

Using Eq. (23) for t_v and integrating $d\mu_{xc}/dr$ by parts,

$$E/N = -2\pi \int_0^R dr r^3 \rho_c(r) \frac{dV}{dr} + \sum \epsilon_v - 4\pi \int_0^{R^-} dr r^2 \rho_v(r) \frac{d}{dr} [rV(r)] - \frac{1}{2} C \frac{Z_{\text{out}}^2}{a} + Z_{\text{out}} \epsilon_{xc}(\rho_0) + 4\pi \int_0^R dr r^2 \rho(r) (4\epsilon_{xc} - 3\mu_{xc}) - 4\pi R^3 \rho(R) [\epsilon_{xc}(R) - \mu_{xc}(R)] . \quad (25)$$

The advantage of this expression is that the entire core contribution, which is a major part of the total energy, is lumped into the first term. This term can be related to simple integrals over the core-state wave functions as follows: The potential is spherically symmetric, so the core-state wave functions have the form

$$\psi_i = \frac{P_i(r)}{r} Y_L(\hat{r}) , \quad (26)$$

where $Y_L(\hat{r})$ is a spherical harmonic, and the radial equation for P_i is

$$\frac{dP_i}{dr} - \frac{(l+1)P_i}{r} = Q_i \quad (27)$$

$$\frac{dQ_i}{dr} + (l+1) \frac{Q_i}{r} = (V - \epsilon_i)P_i .$$

Multiply the second of these equations by P_i , integrate over the muffin tin, and integrate $P_i Q_i'$ by parts to find

$$4\pi \int_0^R V P_i^2 dr - \epsilon_i = -4\pi \int_0^R Q_i^2 dr .$$

Now sum over core states, and compare to Eq. (21):

$$\begin{aligned} \sum \epsilon_c - 4\pi \int_0^R r^2 \rho_c(r) V(r) dr \\ = 2\pi \int_0^R dr r^3 \rho_c(r) \frac{dV}{dr} \\ = 4\pi \sum_i \int_0^R Q_i^2 dr . \end{aligned} \quad (28)$$

Thus, the core contribution to the total energy per unit cell, the first term in Eq. (25), is

$$\begin{aligned} -2\pi \int_0^R dr r^3 \rho_c(r) \frac{dV}{dr} \\ = -4\pi \sum_i \int_0^R Q_i^2 dr . \end{aligned} \quad (29)$$

Use of Eqs. (25) and (29) make it somewhat easier to find the total energy to the necessary accuracy.

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