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Virial Theorem in Self-Consistent-Field Calculations*

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(Received 3 November 1970)

An incorrect application of the virial theorem in earlier papers by the author led to an erroneous calculation of the pressure in lithium metal when Kohn and Sham's exchange potential was used. The correct form of the virial theorem with local exchange and correlation potentials is derived, and a value quite close to zero is obtained for the pressure in lithium at normal density. Calculations with the author's recently proposed potential function are unaffected by the discovery of the error.

In a paper[1] describing a modification of the Kohn-Sham exchange-potential function, it was stated that poor results are obtained for the calculated density of lithium metal when the Kohn-Sham exchange is used. This is not correct. The error arose through a misapplication of the virial theorem. We wish to correct the error and make some additional comments.

The virial theorem for a solid with fixed atomic nuclei may be written as

$$PV = -V\frac{\partial \mathcal{E}}{\partial V} = \frac{2}{3}(\mathcal{T} - \mathcal{U}). \tag{1}$$

In this formula $\mathcal{T}$ is the expectation value of the electron kinetic energy, and $\mathcal{U}$ is the virial of Clausius:

$$\mathcal{U} = -\tfrac{1}{2}\int |\Phi|^2 (\textstyle\sum_i \vec{r}_i\cdot\nabla_i + \sum_\alpha \vec{r}_\alpha\cdot\nabla_\alpha) U\, d^{3N}r, \tag{2}$$

where the $\vec{r}_i$'s are electron coordinates, the $\vec{r}_\alpha$'s are the positions of the nuclei, and U is the potential energy operator including all Coulomb interactions. Following Slater,[2] the electron part of the virial and the kinetic energy can be combined and transformed with the aid of the Schrödinger equation into a surface integral:

$$\frac{2}{3}(\mathcal{T} - \mathcal{U}_e) = \sum_{ij}\frac{\hbar}{12m}\int [(\nabla_j\Phi^*)(\vec{r}_i\circ\nabla_i\Phi) - \Phi^*\nabla_j(\vec{r}_i\cdot\nabla_i\Phi) + \text{c.c.}]\cdot d\vec{S}_j\, d^{3(N-1)}r. \tag{3}$$

In simple crystals which are symmetric with respect to inversion about each atomic site, the nuclear part of the virial will be zero, so calculating the pressure involves only evaluating the right-hand side of (3). This is what was done in all of our calculations, and we thereby avoided determining the pressure from the difference of two very large numbers, as in (1), or from a numerical differentiation of the total energy.

The case of self-consistent fields differs somewhat from the above for the exchange-correlation energy (but not for the other parts of the total energy). The exchange-correlation energy is assumed to have the simple form[3]

$$\mathcal{U}_{xc} = \int \rho\epsilon_{xc}(\rho)\, d^3r. \tag{4}$$

The contribution to the pressure from this term is[4]

$$P_{xc} = -\frac{\partial}{\partial V}\int \rho\epsilon_{xc}(\rho)\, d^3r = \frac{1}{V}\int \rho^2\frac{d\epsilon_{xc}}{d\rho}\, d^3r. \tag{5}$$

The right-hand side of (5) is not in the form of a virial but may be changed with an integration by parts to

$$P_{xc}V = -\frac{1}{3}\int \rho\vec{r}\cdot\nabla\frac{d(\rho\epsilon_{xc})}{d\rho}\, d^3r + \frac{1}{3}\int \rho^2\frac{d\epsilon_{xc}}{d\rho}\,\vec{r}\cdot d\vec{S}. \tag{6}$$

The volume integral now has the required form, and an additional surface integral has been pro-

duced. It is this surface term which was overlooked. Again, it is possible to convert the kinetic energy and the electron part of the virial into a surface integral. The final result is

$$PV=\sum_i \frac{\hbar^2}{12m}\int [(\nabla\phi_i^*)\vec{r}\cdot\nabla\phi_i - \phi_i^*\nabla(\vec{r}\cdot\nabla\phi_i)+\text{c.c.}]\cdot d\vec{S} + \frac{1}{3}\int \rho^2 \frac{d\epsilon_{xc}}{d\rho}\,\vec{r}\cdot d\vec{S} + \frac{1}{3}\sum_\alpha \vec{r}_\alpha\cdot\nabla_\alpha u_\alpha(\vec{r}_\alpha), \quad (7)$$

where the ϕ_i's are one-electron wave functions, and the u_α's are the potential functions for the nuclei. As noted above, the nuclear term will vanish in simple cases.

When the Kohn-Sham exchange potential is used in the one-electron self-consistent-field equations for lithium metal at normal density, the resulting wave functions give +105 kbar for the first term on the right-hand side of (7). The second term on the right-hand side of (7), which was omitted in Ref. 1, gives −97 kbar for the exchange part. The correlation contribution is somewhat uncertain. Nozières and Pines's[5] formula for the correlation energy of the free-electron gas gives −11 kbar as the contribution to the pressure. The final result −3 kbar may be compared to the known bulk modulus for lithium, 123 kbar, which indicates a calculated zero-pressure lattice parameter that is correct to about 1%.

The calculated pressure with the modified potential function proposed in Ref. 1 is −6 kbar at normal density which, given the uncertainties in the correlation correction used in Kohn-Sham's scheme, is about as good as the result in the preceding paragraph. With the modified potential function, the second term on the right-hand side of (7) vanishes, and the whole of the calculated pressure comes from the first term. Thus, the one-electron wave functions must differ noticeably from those calculated with the Kohn-Sham potential even though the final estimates of the pressure are close. This may also be inferred from the potential functions shown in Fig. 1 of Ref. 1.

If the exchange part of (4) is multiplied by $\frac{3}{2}$, the Slater exchange potential[6] is obtained in the one-electron equations, and the exchange term in (7) is also altered. On the basis of some unpublished $\vec{k}\cdot\vec{p}$ calculations, it appears that in this case the calculated pressure will be about −55 kbar before any correction is made for correlation. This is clearly poorer than the pressure obtained with the Kohn-Sham exchange.

In addition to the calculations for iron with the modified potential function reported in Ref. 1, a similar one has now also been done using the Kohn-Sham exchange. At normal density, the first term on the right-hand side of (7) is +622 kbar, and the exchange part of the second term is −305 kbar. The free-electron correlation[5] pressure is −56 kbar. The sum of these, 261 kbar, is about 15% of the bulk modulus, so the calculated zero-pressure density will be rather poorer than in the case of lithium. It is generally believed that the free-electron estimate of the correlation energy is inappropriate for narrow bands such as the *d* bands in iron, so it is not surprising that the calculated pressure is quite a bit too large. The computed pressure is 43 kbar when the modified potential function is used. Thus, the modified potential appears to account fairly well for correlation in a circumstance where the free-electron gas model does not.

The author wishes to acknowledge that L. J. Sham had pointed out the likelihood of an error in the calculation for lithium metal with the Kohn-Sham potential.

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*Work performed under the auspices of the U. S. Atomic Energy Commission.

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