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Energy theorems in constrained density-functional theory

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Abstract. The virial theorem is derived within a density-functional framework for enclosed many-electron systems subjected to external constraints. The scaling relations for the density and the energy density functionals for enclosed systems are defined, and a scheme for enforcing the virial theorem on the solution of a constrained density-functional calculation is proposed. The Hellmann–Feynman theorem for this case is also discussed.

1. Introduction

The virial and the Hellmann–Feynman theorems are regarded as two of the most powerful quantum-mechanical theorems applicable to molecules and solids. For reviews, see for example Marc and McMillan (1985) and Deb (1973). Although these two energy theorems were originally derived using the wavefunction theory, in recent years they have been reinvestigated within the framework of density-functional theory (DFT) (Hohenberg and Kohn 1964, Kohn and Sham 1965). The latter provides an alternative description of electronic structure using the single-particle density (March and Deb 1987) as the basic variable instead of the many-particle wavefunction and has thus established itself as a conceptually simple and practically useful tool in several branches of physics (Dreizler and Providencia 1985) and chemistry (Parr 1983). Further interesting problems connected with charge and magnetisation fluctuations in solids (Dederichs *et al* 1984) have also recently been encompassed by a density-functional approach compatible with arbitrary constraints imposed on the density (Dederichs *et al* 1984, Westhaus 1983). In the conventional DFT, the Hellmann–Feynman and virial theorems (Averill and Painter 1981, Ghosh and Parr 1985, Levy and Perdew 1985) have been shown to retain their usual forms while the present work aims at investigating the nature and scope of these two theorems in the context of DFT for constrained systems.

The constrained density-functional formalism discussed by Dederichs *et al* (1984) has an important bearing on the recently proposed bistability model for cerium impurities by Schluter and Varma (1982, 1983) and its subsequent discussion by Bringer (1983). In constrained DFT, one might have the physical constraint imposing the density to be restricted to a certain volume or region and integrated to a certain value; also, the expectation value of a certain suitable operator might be constrained to possess a particular value. Since the solution of a density-functional scheme for a constrained case

differs from that of the unconstrained one, important differences are likely to appear in the energy theorems as well.

In wavefunction theory, the virial theorem (VT) can be derived, following Slater (1933), through manipulations of the Schrödinger equation with the virial operator directly. The alternative route follows the scaling procedure of Fock (1930) and the variational property of the energy (Lowdin 1959). In DFT too, one arrives at the VT either by explicit consideration (Slater 1972) of the Kohn–Sham (KS) type single-particle equation (Kohn and Sham 1965) or using the scaling property (Szasz *et al* 1975) of the energy density functionals. The density-functional version of the VT also follows in a general manner (Ghosh and Parr 1985) from the scaling properties of the energy density functionals and the Euler equation without recourse to any explicit forms of the functionals. The last method of derivation has the advantage over the variational method when approximate functionals are used since, for such cases, the minimum property of the functional is not guaranteed. The Euler equation has, however, been proved to be rigorously valid (Langreth 1984) without using the variational property, even for approximate functionals.

For enclosed systems, i.e. for finite volume constraint, in wavefunction theory, the VT has been derived using the Schrödinger equation approach by Cottrell and Paterson (1951). The scaling approach in this connection has however received rather little attention (Fernandez and Castro 1982). For enclosed systems, in DFT too, the VT has been employed to obtain expressions for pressure (Lieberman 1971, Janak 1974, Heine 1980, Godwal *et al* 1983). General derivations of VT using DFT for constrained systems have, however, not been studied. In what follows, we present in § 2 a density-functional derivation of VT when the net density $\rho(\mathbf{r})$ or an orbital density (e.g. the f-orbital density $\rho_f(\mathbf{r})$) is constrained. The derivations are based on (i) the KS equation, (ii) the scaling property of the energy functionals and the variational principle, and (iii) the scaling property and the Euler equation. Section 3 discusses the Hellmann–Feynman theorem in the presence of constraints. The effect of other constraints on the VT is discussed and an optimum scale parameter is obtained in § 4 to enforce the VT in such cases. Finally we offer a few concluding remarks in § 5 and discuss the scaling relations of the density functionals corresponding to an enclosed system in the Appendix.

2. Density-functional theory and the virial theorem for constrained systems

The density-functional description of a many-electron system characterised by an external potential $v(\mathbf{r})$ is concerned with the energy expressed as a unique functional of the electron density $\rho(\mathbf{r})$, i.e.

$$E[\rho] = T[\rho] + \int v(\mathbf{r})\rho(\mathbf{r}) \, d\mathbf{r} + J[\rho] + U_{xc}[\rho] + V_{nn} \quad (1)$$

where $T[\rho]$ is the kinetic energy (KE), $J[\rho]$ the classical Coulomb energy given by

$$J[\rho] = \frac{1}{2} \iint d\mathbf{r} \, d\mathbf{r}' \, \rho(\mathbf{r})\rho(\mathbf{r}')/|\mathbf{r} - \mathbf{r}'| \quad (2)$$

$U_{xc}[\rho]$ the exchange–correlation (XC) energy functionals and V_{nn} is the nuclear repulsion contribution. (Atomic units are used throughout.)

The simplest constraint imposed on density is that its integral within a volume V (e.g. a sphere of radius a) equals N , the number of electrons. This corresponds to the minimisation of the functional

$$E[\rho] - \mu \left(\int_V \rho(\mathbf{r}) \, d\mathbf{r} - N \right)$$

resulting in the Euler equation

$$\delta E / \delta \rho - \mu = 0 \quad (3)$$

which can be solved for the density and hence the energy. Alternatively, one can solve the KS equations, viz.

$$[-\frac{1}{2}\nabla^2 + v_{\text{eff}}(\mathbf{r})]\psi_i = \varepsilon_i \psi_i \quad (4a)$$

$$v_{\text{eff}}(\mathbf{r}) = v(\mathbf{r}) + \int d\mathbf{r}' \rho(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'| + \delta E_{\text{xc}} / \delta \rho \quad (4b)$$

which are obtained from equations (1) and (3) by replacing $T[\rho]$ by $T_s[\rho]$, the latter being the KE of a system of non-interacting particles of density $\rho(\mathbf{r})$, and incorporating the contribution $(T - T_s)$ into the xc term, i.e. $E_{\text{xc}} = U_{\text{xc}} + (T - T_s)$.

The constraint might also restrict the f-orbital density alone of a rare-earth metal, viz.

$$\int_V \rho_f(\mathbf{r}) \, d\mathbf{r} = N_f \quad (5)$$

here N_f is the number of f electrons within the volume V . The VT within the density-functional framework can now be derived in three alternative ways.

2.1. Kohn–Sham equation and the virial theorem

To derive the VT from the KS equation (4), we pre-multiply the latter by ψ_i^* and operate with $\mathbf{r} \cdot \nabla$ to obtain

$$\begin{aligned} (\mathbf{r} \cdot \nabla \psi_i^*) (-\frac{1}{2}\nabla^2 + v_{\text{eff}})\psi_i + \psi_i^* [\mathbf{r} \cdot \nabla (-\frac{1}{2}\nabla^2 + v_{\text{eff}})]\psi_i + \psi_i^* v_{\text{eff}}(\mathbf{r} \cdot \nabla \psi_i) \\ = (\mathbf{r} \cdot \nabla \psi_i^*) \varepsilon_i \psi_i + \psi_i^* \varepsilon_i (\mathbf{r} \cdot \nabla \psi_i). \end{aligned} \quad (6)$$

Making use of the complex conjugate of equation (4) into the third term of equation (6), one obtains

$$-\frac{1}{2}\psi_i^* (\mathbf{r} \cdot \nabla) \nabla^2 \psi_i + \psi_i^* (\mathbf{r} \cdot \nabla v_{\text{eff}})\psi_i + \frac{1}{2}(\mathbf{r} \cdot \nabla \psi_i) \nabla^2 \psi_i^* = 0. \quad (7)$$

Using the identity

$$-[\psi_i^* (\mathbf{r} \cdot \nabla) \nabla^2 \psi_i] + (\mathbf{r} \cdot \nabla \psi_i) \nabla^2 \psi_i^* = 2\psi_i^* \nabla^2 \psi_i - \nabla \cdot [\psi_i^{*2} \nabla (\mathbf{r} \cdot \nabla \psi_i / \psi_i^*)] \quad (8)$$

in equation (7) and integrating one obtains

$$\int \psi_i^* \nabla^2 \psi_i \, d\mathbf{r} + \int \psi_i^* (\mathbf{r} \cdot \nabla v_{\text{eff}})\psi_i \, d\mathbf{r} - \frac{1}{2} \int_S d\mathbf{s} \cdot [\psi_i^{*2} \nabla (\mathbf{r} \cdot \nabla \psi_i / \psi_i^*)] = 0. \quad (9)$$

Now, the last term within the brackets can be rewritten as

$$[\psi_i^{*2} \nabla (\mathbf{r} \cdot \nabla \psi_i / \psi_i^*)] = \psi_i^* \nabla (\mathbf{r} \cdot \nabla \psi_i) - (\mathbf{r} \cdot \nabla \psi_i) \nabla \psi_i^* \quad (10)$$

of which the first term on the RHS vanishes at the surface; thus, the only contribution of

the surface integral term in equation (9) comes from the last term of equation (10), leading to

$$-2 \left(-\frac{1}{2} \int \psi_i^* \nabla^2 \psi_i \, d\mathbf{r} \right) + \int \rho_i(\mathbf{r} \cdot \nabla v_{\text{eff}}) \, d\mathbf{r} + \frac{1}{2} \int_S d\mathbf{s} \cdot (\mathbf{r} \cdot \nabla \psi_i) \nabla \psi_i^* = 0. \quad (11)$$

Following Cottrell and Paterson (1951) and McLellan (1974), we now use the dimensionless scaled coordinates, viz. $\mathbf{r} = a\omega$, i.e. $(x, y, z) = (a\omega_1, a\omega_2, a\omega_3)$, and the boundary condition for ψ_i to obtain the result

$$(\mathbf{r} \cdot \nabla \psi_i) = -a(\partial \psi_i / \partial a)_r. \quad (12)$$

Now, multiplying the KS equation (4) by $(\partial \psi_i / \partial a)$ and its derivative with respect to a by ψ_i^* and using the complex conjugate of the KS equation, we obtain

$$(\partial \varepsilon_i / \partial a) = -\frac{1}{2} \int [\psi_i^* \nabla^2 (\partial \psi_i / \partial a) - (\partial \psi_i / \partial a) \nabla^2 \psi_i^*] \, d\mathbf{r} + \int \psi_i^* (\partial v_{\text{eff}} / \partial a) \psi_i \, d\mathbf{r} \quad (13)$$

which, on using the Green theorem and the boundary condition, simplifies to

$$(\partial \varepsilon_i / \partial a) = \frac{1}{2} \int_S d\mathbf{s} \cdot (\nabla \psi_i^*) (\partial \psi_i / \partial a) + \int \psi_i^* (\partial v_{\text{eff}} / \partial a) \psi_i \, d\mathbf{r}. \quad (14)$$

Replacing the surface integral of equation (11) using equations (12) and (14), one obtains

$$2 \left[-\frac{1}{2} \int \psi_i^* \nabla^2 \psi_i \, d\mathbf{r} \right] - \int \rho_i(\mathbf{r} \cdot \nabla v_{\text{eff}}) \, d\mathbf{r} + a(\partial \varepsilon_i / \partial a) - a \int \psi_i^* (\partial v_{\text{eff}} / \partial a) \psi_i \, d\mathbf{r} = 0. \quad (15)$$

Summation over the orbitals leads to

$$2T_s - \int_0^a \rho(\mathbf{r})(\mathbf{r} \cdot \nabla v_{\text{eff}}) \, d\mathbf{r} + a \sum_i (\partial \varepsilon_i / \partial a) - a \int_0^a \rho(\mathbf{r})(\partial v_{\text{eff}} / \partial a) \, d\mathbf{r} = 0. \quad (16)$$

Now, in KS theory, the energy E is given by

$$E = \sum_i \varepsilon_i - \int_0^a \rho(\mathbf{r}) v_{\text{eff}}(\mathbf{r}) \, d\mathbf{r} + V_{\text{ks}} \quad (17)$$

where the energy term V_{ks} is given by $V_{\text{ks}} = E[\rho] - T_s[\rho]$ and $v_{\text{eff}} = (\delta V_{\text{ks}} / \delta \rho)$. Differentiating (17) with respect to a , we obtain

$$(\partial E / \partial a) = \sum_i (\partial \varepsilon_i / \partial a) - \int_0^a \rho(\mathbf{r})(\partial v_{\text{eff}} / \partial a) \, d\mathbf{r} - \int_0^a (\partial \rho / \partial a) v_{\text{eff}} \, d\mathbf{r} + \int_0^a (\delta V_{\text{ks}} / \delta \rho) (\partial \rho / \partial a) \, d\mathbf{r} \quad (18)$$

where the boundary condition that the density and the potential energy density vanish at the boundary $r = a$ has been used. Using equation (18), equation (16) becomes

$$2T_s - \int_0^a \rho(\mathbf{r})(\mathbf{r} \cdot \nabla v_{\text{eff}}) d\mathbf{r} + a(\partial E/\partial a) = 0 \quad (19)$$

which gives the virial theorem

$$2T_s + 2(T - T_s) + V + a(\partial E/\partial a) = 0 \quad (20a)$$

i.e.

$$2T + V + a(\partial E/\partial a) = 0 \quad (20b)$$

where V is the potential energy given by $V[\rho] = E[\rho] - T[\rho]$. This follows from the scaling properties of the density functionals (Szasz *et al* 1975) and the derivation of Ghosh and Parr (1985).

When additional constraints are imposed (e.g. the second moment of the f-orbital density at the impurity site), i.e.

$$\gamma \left(\int_0^a r^2 \rho_f(\mathbf{r}) d\mathbf{r} - \langle r^2 \rangle_f \int_0^a \rho_f(\mathbf{r}) d\mathbf{r} \right) \quad (21)$$

is added to the energy functional, leading to a parabolic potential $\gamma(r^2 - \langle r^2 \rangle_f)$ in the KS equation for the f orbital, an extra contribution will arise from the second term of equation (19), resulting in

$$2T_s - \int_0^a \rho(\mathbf{r})(\mathbf{r} \cdot \nabla v_{\text{eff}}) d\mathbf{r} - 2\gamma \langle r^2 \rangle_f + a(\partial E/\partial a) = 0 \quad (22a)$$

i.e.

$$2T + V - 2\gamma \langle r^2 \rangle_f + a(\partial E/\partial a) = 0 \quad (22b)$$

instead of the conventional form of the virial theorem given by equation (20). It may be noted here that if the density and the energy components are calculated through the Kohn–Sham scheme, it is easier to use equations (19) and (22a) since T_s and v_{eff} are directly obtained during the calculation. Although equations (20) and (22b) represent compact forms, it is difficult to obtain $T[\rho]$ and $V[\rho]$ in a KS calculation.

2.2. Virial theorem from the Euler equation for density

While the Kohn–Sham scheme is the most widely used one in DFT, the more general equation for density is the Euler equation (3) rewritten as

$$\delta T/\delta \rho + \delta V/\delta \rho = \mu. \quad (23)$$

It is now of interest to obtain the virial theorem from this equation, irrespective of any specific forms of the energy functionals, using only the scaling properties of the kinetic and potential energy functionals.

For a functional $F[\rho]$ with the scaling property (see Appendix for the definition of scaling for constrained systems, equation (A4))

$$F_\zeta \equiv F_\zeta[\rho_\zeta, a/\zeta] = \zeta^k F[\rho, a] \quad (24)$$

one can easily show, following the derivation of Ghosh and Parr (1985) (see the Appendix of this paper), that

$$\int_0^a \rho(\mathbf{r}) [\mathbf{r} \cdot \nabla(\delta F/\delta \rho)] d\mathbf{r} = - \left(\int_0^b d\mathbf{r} (\partial \rho_\zeta / \partial \zeta) (\partial F_\zeta / \delta \rho_\zeta) \right) \Big|_{\zeta=1}. \quad (25)$$

Using equation (A8) of the Appendix, equation (25) becomes

$$\begin{aligned} & \int_0^a \rho(\mathbf{r}) [\mathbf{r} \cdot \nabla(\delta F/\delta \rho)] d\mathbf{r} \\ &= -(\delta F_\zeta / \delta \zeta) \Big|_{\zeta=1} - (a/\zeta) (\partial F_\zeta / \partial a) \Big|_{\zeta=1} + a \int_0^a d\mathbf{r} (\delta F/\delta \rho) (\partial \rho / \partial b) \Big|_{\zeta=1} \\ &= -kF - a(\partial F/\partial a) + a \int_0^a d\mathbf{r} (\partial F/\partial \rho) (\delta \rho / \delta a). \end{aligned} \quad (26)$$

Now, the scaled functionals (equations (A4) and (24)) for the kinetic and potential energy components (Szasz *et al* 1975, Levy *et al* 1985) become

$$T_\zeta \equiv T_\zeta[\rho_\zeta, a/\zeta] = \zeta^2 T[\rho, a] \quad (27a)$$

$$V_\zeta \equiv V_\zeta[\rho_\zeta, a/\zeta] = \zeta V[\rho, a]. \quad (27b)$$

Operating the Euler equation (23) with the virial operator ($\mathbf{r} \cdot \nabla$), integrating after multiplication with $\rho(\mathbf{r})$ and using equations (26) and (27), one obtains the result:

$$2T + V + a(\partial E/\partial a) - a \int_0^a d\mathbf{r} [(\delta T/\delta \rho) + (\delta V/\delta \rho)] (\partial \rho / \partial a) = 0. \quad (28)$$

The last term of equation (28) vanishes on account of the Euler equation (23) resulting in the ∇T (20). In the presence of the constraint (21), the additional term of equation (22) appears.

2.3. Virial theorem, the scaling procedure and the energy minimisation

The scaled energy E_ζ can be written, using equation (27), as

$$E_\zeta = \zeta^2 T[\rho] + \zeta V[\rho] \quad (29)$$

which gives

$$(dE_\zeta/d\zeta) = 2\zeta T[\rho] + V[\rho]. \quad (30)$$

Now considering the scaled energy as $E_\zeta[b, \rho_\zeta(b(\zeta, a), \zeta)]$, equation (A8) gives

$$(dE_\zeta/d\zeta) = (\partial E_\zeta / \partial \zeta)_b - (a/\zeta) (\partial E_\zeta / \partial a)_\zeta. \quad (31)$$

Assuming the energy to be minimum, i.e. the condition

$$(\partial E_\zeta / \partial \zeta)_b = \int_0^b d\mathbf{r} [(\partial \rho_\zeta / \partial \zeta)_a + (a/\zeta) (\partial \rho_\zeta / \partial a)_\zeta] (dE_\zeta / \delta \rho_\zeta)_b = 0 \quad (32)$$

and using equations (30) and (31), one obtains

$$2\zeta T[\rho] + V[\rho] + \zeta a(\partial T/\partial a) + a(\partial V/\partial a) = 0. \quad (33)$$

If the minimum corresponds to the value $\zeta = 1$, one has the virial theorem (20).

Although the two earlier derivations require the density to satisfy the KS or Euler equations exactly, the variational derivation shows that even an approximate density would satisfy the VT if optimised with respect to scaling during the energy minimisation.

The optimum scale factor corresponds to the minimum of the scaled energy and is obtained from equation (33) as

$$\zeta_0 = -\{V[\rho] + a(\partial V/\partial a)\}/\{2T[\rho] + a(\partial T/\partial a)\}. \quad (34)$$

That the corresponding scaled density $\rho_{\zeta_0}(\mathbf{r}; b_0)$ where $b_0 = a/\zeta_0$ will satisfy the virial theorem, although $\rho(\mathbf{r})$ does not, can easily be proved. Thus, differentiation of equation (29) at constant ζ gives

$$(\partial E_{\zeta}/\partial a) = \zeta^2(\partial T[\rho]/\partial a) + \zeta(\partial V[\rho]/\partial a). \quad (35)$$

Now multiplying equation (33) with ζ ($=\zeta_0$), one has

$$2\zeta_0^2 T[\rho] + \zeta_0 V[\rho] + \zeta_0^2 a(\partial T/\partial a) + \zeta_0 a(\partial V/\partial a) = 0 \quad (36)$$

which can be rewritten, using equation (35) for $\zeta = \zeta_0$, as

$$2\zeta_0^2 T[\rho] + \zeta_0 V[\rho] + a(\partial E_{\zeta_0}/\partial a) = 0 \quad (37a)$$

or

$$2T_{\zeta_0} + V_{\zeta_0} + b(\partial E_{\zeta_0}/\partial b) = 0 \quad (37b)$$

proving the VT for scaled energy components.

In solids, it is often very important to ensure that the density satisfies the VT (especially in connection with the calculation of pressure, etc.) and equation (34) would be useful.

3. Hellmann–Feynman theorem for constrained systems

The Hellmann–Feynman (HF) theorem, in wavefunction theory, expresses the energy derivative as

$$(\partial E/\partial \lambda) = \langle \psi | (\partial H/\partial \lambda) | \psi \rangle \quad (38)$$

where λ is a parameter characterising the Hamiltonian H . If λ appears only in the single-particle potential $v(\mathbf{r})$, equation (38) simplifies to

$$(\partial E/\partial \lambda) = \int d\mathbf{r} \rho(\mathbf{r}) [\partial v(\mathbf{r})/\partial \lambda]. \quad (39)$$

In DFT, equation (39) follows directly from the energy functional

$$E[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) v(\mathbf{r}) + F[\rho] \quad (40)$$

and the Euler equation (see also equations (3) and (23))

$$\delta E/\delta \rho = v(\mathbf{r}) + \delta F/\delta \rho = \mu. \quad (41)$$

Differentiating equation (40) with respect to λ , and using equation (41), one obtains

$$\begin{aligned} (\partial E/\partial \lambda) &= \int d\mathbf{r} \rho(\mathbf{r}) [\partial v(\mathbf{r})/\partial \lambda] + \int d\mathbf{r} v(\mathbf{r}) [\partial \rho(\mathbf{r})/\partial \lambda] + \int d\mathbf{r} (\delta F/\delta \rho) [\partial \rho(\mathbf{r})/\partial \lambda] \\ &= \int d\mathbf{r} \rho(\mathbf{r}) [\partial v(\mathbf{r})/\partial \lambda] + \mu \int d\mathbf{r} [\partial \rho(\mathbf{r})/\partial \lambda] \\ &= \int d\mathbf{r} \rho(\mathbf{r}) [\partial v(\mathbf{r})/\partial \lambda]. \end{aligned} \quad (42)$$

The HF theorem for constrained systems (Epstein 1974, 1980) can also be easily obtained through the KS equation. The energy functional corresponding to the KS equation (4) is given by equation (17), which on differentiation yields

$$(\partial E/\partial \lambda) = \sum_i (\partial \varepsilon_i/\partial \lambda) - \int d\mathbf{r} v_{\text{eff}}[\partial \rho(\mathbf{r})/\partial \lambda] - \int d\mathbf{r} \rho(\mathbf{r})[\partial v_{\text{eff}}/\partial \lambda] \\ + \int d\mathbf{r} (\delta V/\delta \rho)[\partial \rho(\mathbf{r})/\partial \lambda] + \int d\mathbf{r} \rho(\mathbf{r})[\partial v(\mathbf{r})/\partial \lambda]. \quad (43)$$

Now, from the KS equation (4), one can write

$$\sum_i \varepsilon_i = -\frac{1}{2} \sum_i \langle \psi_i^* | \nabla^2 | \psi_i \rangle + \int d\mathbf{r} v_{\text{eff}}(\mathbf{r}) \rho(\mathbf{r}) \quad (44)$$

which gives

$$\sum_i (\partial \varepsilon_i/\partial \lambda) = -\frac{1}{2} \sum_i \int_S ds \cdot [\psi_i^* \nabla(\partial \psi_i/\partial \lambda) - (\partial \psi_i/\partial \lambda) \nabla \psi_i^*] \\ + \int d\mathbf{r} \rho(\mathbf{r}) (\partial v_{\text{eff}}/\partial \lambda). \quad (45)$$

Therefore, the HF theorem for the constrained DFT is

$$(\partial E/\partial \lambda) = \int_0^a d\mathbf{r} \rho(\mathbf{r}) (\partial v/\partial \lambda) - \frac{1}{2} \sum_i \int_S ds \cdot [\psi_i^* \nabla(\partial \psi_i/\partial \lambda) - (\partial \psi_i/\partial \lambda) \nabla \psi_i^*]. \quad (46)$$

The surface integral, however, vanishes for the boundary condition $\psi_i(a) = 0$ and therefore equation (46) reduces to equation (39). For periodic boundary conditions with $\psi_i(a) \neq 0$, this term might contribute in general.

If the parameter λ is $\langle r^2 \rangle_f$ corresponding to the constraint (21), the corresponding HF theorem (39) gives

$$(\partial E/\partial \langle r^2 \rangle_f) = \gamma. \quad (47)$$

The HF theorem is obeyed by the exact solution of the KS equation or the Euler equation for density but it can also be satisfied by suitable variational solutions. Now if $\rho(\mathbf{r})$ is such a variationally obtained density satisfying the HF theorem but not the VT, a proper scaled density $\rho_\zeta(\mathbf{r})$ with a scale factor $\zeta (= \zeta_0)$ of equation (34) would satisfy the VT. It is however to be seen how far the HF theorem would be applicable with this scaled density.

4. Discussion

The analysis of the scaling procedure discussed in § 2 can be directly employed in the constrained density-functional calculations. When a constraint of the form (21) is used, the resulting density satisfies equation (22) instead of the actual VT (20). However, the density $\rho_f(\mathbf{r})$ obtained through the constraint (21) can be forced to satisfy the VT of equation (20) by scaling with the scale factor of equation (34).

In order to ensure that the new scaled density $\rho_f(\zeta, \mathbf{r})$ is the solution of interest, the constraint should be imposed on the scaled density (see Parr and Ghosh (1986) for an analogous algorithm used for improving the Thomas–Fermi theory), i.e. equation (21) should be replaced by

$$\gamma \left((1/\zeta^2) \int_0^a r^2 \rho_f(\mathbf{r}) \, d\mathbf{r} - \langle r^2 \rangle_f \int_0^a \rho_f(\mathbf{r}) \, d\mathbf{r} \right) \quad (48)$$

with $\zeta (= \zeta_0)$ of equation (34).

Thus the modified KS scheme can be implemented as follows. First, using a trial density or potential, the KS equation is solved with a trial value of the Lagrange parameter γ , the scale factor is determined from equation (34) and equation (48) is checked. If not obeyed, the calculation is repeated with other values of γ until the expression of equation (48) vanishes. The scaled f-orbital density is now obtained using the scale factor and equation (A1). The calculations are repeated until the self-consistency in density is reached. Clearly, the constraint (21) is satisfied by the scaled f-orbital density and, using the scale factor, the scaled energy can be obtained using, for example, equation (29). Also the VT is automatically satisfied.

Thus the energy can be calculated for a desired value of $\langle r^2 \rangle_f$. It is however simpler to obtain the energy as a function of the $\langle r^2 \rangle_f$ values. For the trial γ the self-consistent density is first obtained and the scaled f-orbital density as well as the scaled energy are then calculated. The value of $\langle r^2 \rangle_f$ to which this particular γ and the energy corresponds is obtained by equating equation (48) to zero. Repeated calculations with varying values of γ provide the energy as a function of $\langle r^2 \rangle_f$.

5. Concluding remarks

The VT has been derived here within a density-functional framework for enclosed systems as well as for cases where only the f-orbital density is restricted. The effect of other constraints in a density-functional calculation has been discussed with regard to the VT. The scaling relations for the density and the energy density functionals in enclosed systems are defined and employed for obtaining the VT. While the derivation from the KS equation is straightforward, the scaling approach provides several interesting new relationships. This does not seem to have been pointed out earlier even in connection with wavefunction theory. The scaling procedure is shown to be especially useful in providing a means for imposing the VT on a density which otherwise does not obey it.

The discussion presented here is of importance in connection with the bistability model of Schluter and Varma (1982, 1983) who had chosen hydrogenic trial densities in the calculation. This corresponds to using the constraint that the expectation value $\langle r^2 \rangle_f$ evaluated with the f-orbital density yields the desired value. The HF theorem for systems subjected to constraints is important in the work of Dederichs *et al* (1984). Although not discussed here, other constraints like magnetisation, etc., would be of interest and can be handled in an analogous manner.

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Appendix. Scaling relations of density functionals for enclosed systems

In this appendix, we define the scaling procedure for an enclosed system (e.g. within a sphere of radius a). Let the density $\rho(\mathbf{r})$ be scaled by a scale factor ζ to yield the scaled density $\rho_\zeta(\mathbf{r})$, i.e.

$$\rho_\zeta(\mathbf{r}) = \zeta^3 \rho(\zeta \mathbf{r}). \quad (\text{A1})$$

The normalisation and the boundary conditions of the original density given by

$$\int_0^a d\mathbf{r} \rho(\mathbf{r}) = N \quad \text{and} \quad \rho(\mathbf{r}) = 0 \quad \text{for} \quad r \geq a \quad (\text{A2})$$

are preserved by the scaled density as

$$\int_0^b d\mathbf{r} \rho_\zeta(\mathbf{r}) = N \quad \text{and} \quad \rho_\zeta(\mathbf{r}) = 0 \quad \text{for} \quad r \geq b \quad (\text{A3})$$

where $b = a/\zeta$.

The scaling of an energy functional $F[\rho]$ is now defined as

$$F[\rho] = \int_0^a d\mathbf{r} f(\mathbf{r}, \rho(\mathbf{r}))$$

$$F_\zeta \equiv F_\zeta[\zeta, a] \equiv F_\zeta[\rho_\zeta, b] = \int_0^b d\mathbf{r} f(\mathbf{r}, \rho_\zeta(\mathbf{r})). \quad (\text{A4})$$

Clearly, for the scaled functional, one has the derivative

$$(dF_\zeta/d\zeta) = \int_0^b d\mathbf{r} (\partial\rho_\zeta/\partial\zeta) (\delta F_\zeta/\delta\rho_\zeta)_b + (\partial F_\zeta/\partial b)_{\rho_\zeta} (\partial b/\partial\zeta). \quad (\text{A5})$$

Now, one can easily write for a spherically symmetric system

$$(\partial F_\zeta/\partial b)_{\rho_\zeta} = 4\pi b^2 f(b, \rho_\zeta(b)). \quad (\text{A6})$$

Alternatively, one can consider F_ζ as $F_\zeta[\rho_\zeta(\mathbf{r}, b), b]$ and write

$$(\partial F_\zeta/\partial b)_\zeta = (\partial F_\zeta/\partial b)_{\rho_\zeta} + \int_0^b d\mathbf{r} (\partial\rho_\zeta/\partial b)_\zeta (\delta F_\zeta/\delta\rho_\zeta)_b. \quad (\text{A7})$$

Using equation (A7), equation (A5) becomes

$$(dF_\zeta/\partial\zeta) = \int_0^b d\mathbf{r} (\partial\rho_\zeta/\partial\zeta) (\delta F_\zeta/\delta\rho_\zeta)_b - (a/\zeta) (\partial F_\zeta/\partial a)$$

$$+ (a/\zeta^2) \int_0^b d\mathbf{r} (\partial\rho_\zeta/\partial b) (\delta F_\zeta/\delta\rho_\zeta)_b. \quad (\text{A8})$$

Alternatively, using equation (A6), equation (A5) can be written as

$$(dF_\zeta/d\zeta) = \int_0^b d\mathbf{r} (\partial\rho_\zeta/\partial\zeta) (\delta F_\zeta/\delta\rho_\zeta) - (a/\zeta^2) 4\pi b^2 f(b, \rho_\zeta(b)) \quad (\text{A9})$$

which is valid for spherically symmetric systems. Results other than equations (A5) and (A9) are, however, not restricted to spherical enclosures alone and can be extended to

arbitrary surfaces provided the deformation considered is isotropic and can therefore be characterised by one single scaling parameter.

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