PHYSICAL REVIEW B VOLUME 24, NUMBER 12 15 DECEMBER 1981

Virial theorem in the density-functional formalism: Forces in H_2

F. W. Averill* and G. S. Painter

Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

(Recieved 29 June 1981)

The virial expression valid in density-functional theory contains an integral over the gradient of the effective exchange-correlation potential. The significance of this term in correcting the noninteracting kinetic and electrostatic energies is discussed in this work. From the gradient integral in the local density approximation an expression is derived for the kinetic-energy part of the exchange-correlation energy density, and its connection with the derivation of von Barth and Williams is discussed. To illustrate the application of these developments to the molecular case, results are presented from Gaussian-orbital cluster calculations for H_2. In this study the forces in the dimer are calculated using the Hellmann-Feynman and virial theorems, and results are compared with the force obtained by direct interpolation from the binding-energy curve. The usefulness of the various methods for calculating the force is discussed.

In the density-functional formalism of Hohenberg, Kohn, and Sham[1,2] (HKS) the ground-state energy can be written as a functional of the density $n(\vec{r})$ in the form

$$E[n(\vec{r})]=T_s[n(\vec{r})]+U_{es}+E_{xc}[n(\vec{r})]\ , \tag{1}$$

where $T_s[n(\vec{r})]$ is the kinetic energy of a noninteracting electron system with the same density as the interacting one, U_{es} is the classical electrostatic energy, and $E_{xc}[n(\vec{r})]$, by definition, is the exchange-correlation energy functional. It is easily shown, e.g., by following the procedure described by Slater,[3] that the electrostatic form of the Hellmann-Feynman theorem[4] is rigorously satisfied in density-functional theory (see also Ref. 5). In atomic units

$$-\frac{\partial E}{\partial X_p}=\int n(\vec{r})\frac{\partial}{\partial X_p}\left[\frac{Z_p}{|\vec{r}-\vec{R}_p|}\right]d\vec{r}-\sum_{q\neq p}\frac{\partial}{\partial X_p}\left[\frac{Z_pZ_q}{|\vec{R}_p-\vec{R}_q|}\right]\ . \tag{2}$$

The Hellmann-Feynman theorem is obeyed by *local* density functionals as well, provided the only implicit X_p dependence in E_{xc} is that of $n(\vec{r})$.[6]

In terms of exact quantities T and U (the exact kinetic and potential energies, respectively, of the *interacting* system), the virial theorem can be written in the force form[3]

$$-\sum_p \vec{R}_p\cdot\vec{\nabla}_pE=2T+U\ . \tag{3}$$

These exact energies are those making up the universal functional $F[n]=\langle\psi\,|\,T+U\,|\,\psi\rangle$, and it is this functional which Kohn and Sham[2] decomposed to *define* $E_{xc}[n]$. From the definition in Eq. (1), E_{xc} contains the exchange and correlation energy of both kinetic and potential origin. Though the amount of each is not known, the relation between the parts can be written

$$E_{xc}=T_{xc}+U_{xc}\ , \tag{4}$$

where T_{xc} and U_{xc} are defined by

$$\begin{aligned}T&=T_s+T_{xc}\ ,\\ U&=U_{es}+U_{xc}\ .\end{aligned} \tag{5}$$

To obtain a working form of the virial theorem in terms of the quantities defined in the density-functional formalism, two approaches can be considered. Firstly, T and U in Eq. (3) could be expressed in terms of T_s and U_{es} using Eq. (5); this will be addressed later in connection with the local-density approximation (LDA). Alternatively, the HKS one-electron equations can be used to evaluate $\sum_p\vec{R}_p\cdot\vec{\nabla}_pE$ with the result taken as an expression of the force form of the virial theorem valid in density-functional theory. Subsequently, it will be shown that these two procedures yield the same result in the LDA.

Again, following the generalized procedure of

Slater,[3] it is straightforward to show that for an arbitrary cluster of atoms in the density-functional formalism an exact virial relation of complete generality is obtained:

$$-\sum_{p}\vec{R}_p\cdot\vec{\nabla}_p E = 2T_s+U_{\text{es}} - \int n(\vec{r})\vec{r}\cdot\vec{\nabla}v_{\text{xc}}(\vec{r})d\vec{r}\,, \tag{6}$$

where $v_{\text{xc}}(\vec{r})$ is the effective exchange-correlation potential function. This reduces to the expression derived by Janak[7] for the pressure in a solid if the left-hand side of Eq. (6) (which holds for arbitrary displacements of the nuclei) is restricted to homogeneous volume changes. Janak discussed the value of this relation in reducing numerical problems associated with pressure calculations for solids.

The significance of the gradient integral in Eq. (6) is clear from the definitions of T_s and U_{es}. It must be just the proper combination of exchange and correlation energies in the kinetic- and potential-energy channels to give the correct interacting quantities as represented by Eq. (3). To see that this is valid, consider the energy functional of Eq. (1). For each displacement of the nuclei, this functional attains its minimum, which is the ground state for the correct density, in the external potential of the nuclei. Thus, the left-hand sides of Eqs. (3) and (6) may be equated. It then follows that

$$-\int n(\vec{r})\vec{r}\cdot\vec{\nabla}v_{\text{xc}}(\vec{r})d\vec{r}=2(T-T_s)+U-U_{\text{es}}\,. \tag{7}$$

From the definition of Eq. (5),

$$-\int n(\vec{r})\vec{r}\cdot\vec{\nabla}v_{\text{xc}}(\vec{r})d\vec{r}=2T_{\text{xc}}+U_{\text{xc}}\,, \tag{8}$$

i.e., the gradient integral represents just the proper combination of exchange-correlation corrective terms to produce the sum characteristic of the *interacting* electron system $2T+U$ on the right-hand side of Eq. (6).

In the local-density approximation, the effective exchange-correlation potential becomes

$$\begin{aligned} v_{\text{xc}}(\vec{r}) &= \frac{\partial}{\partial n(\vec{r})}[n(\vec{r})\epsilon_{\text{xc}}(n(\vec{r}))] \\ &\equiv \mu_{\text{xc}}(\vec{r})\,, \end{aligned} \tag{9}$$

where $\epsilon_{\text{xc}}(n(r))$ is the exchange-correlation energy density derived from electron-gas calculations. The potential $\mu_{\text{xc}}(\vec{r})$ depends on $\vec{r}$ implicitly through $n(\vec{r})$ alone. From this, it is easily shown that in the LDA

$$-\int n(\vec{r})\vec{r}\cdot\vec{\nabla}\mu_{\text{xc}}(n(\vec{r}))d\vec{r}=-3\int n(\vec{r})[\epsilon_{\text{xc}}(n(\vec{r}))-\mu_{\text{xc}}(n(\vec{r}))]d\vec{r}\,. \tag{10}$$

Now using Eq. (4) to replace U_{xc}, Eq. (8) becomes [with the LDA replacement of $v_{\text{xc}}(\vec{r})$ by $\mu_{\text{xc}}(n(\vec{r}))$]

$$-\int n(\vec{r})\vec{r}\cdot\vec{\nabla}\mu_{\text{xc}}(n(\vec{r}))d\vec{r}=T_{\text{xc}}+E_{\text{xc}}\,. \tag{11}$$

From this, a kinetic-energy density $t_{\text{xc}}(n(\vec{r}))$ is defined which gives the kinetic contribution to the exchange-correlation energy in Eq. (4), i.e., Eq. (11) can be written

$$-\int n(\vec{r})\vec{r}\cdot\vec{\nabla}\mu_{\text{xc}}(n(\vec{r}))d\vec{r}=-\int n(\vec{r})[t_{\text{xc}}(n(\vec{r}))+\epsilon_{\text{xc}}(n(\vec{r}))]d\vec{r}\,. \tag{12}$$

Identifying this with Eq. (10), an expression for $t_{\text{xc}}(n(\vec{r}))$ is obtained:

$$t_{\text{xc}}(n(\vec{r}))=3\mu_{\text{xc}}(n(\vec{r}))-4\epsilon_{\text{xc}}(n(\vec{r}))\,, \tag{13}$$

defining the exchange-correlation contribution to the kinetic energy of the homogeneous *interacting* electron gas in the LDA. This expression has also been derived by von Barth[8] from considerations that $\epsilon_{\text{xc}}(n(\vec{r}))$ satisfies the virial theorem. This analysis is discussed by Williams, Kübler, and Gelatt[9] and by Williams and von Barth.[10] Thus, the t_{xc} derived directly or through Eq. (6) are equivalent in the LDA.

It is interesting to observe that for the statistical ($X\alpha$ or $\rho^{1/3}$) exchange model,

$$\mu_{\text{xc}}(n(\vec{r}))=\tfrac{4}{3}\,\epsilon_{\text{xc}}(n(\vec{r}))\,, \tag{14}$$

so that $t_{\text{xc}}(n(\vec{r}))=0$. It is then readily apparent that Slater's demonstration that the $X\alpha$ model satisfies the virial theorem is valid, for he included all exchange-correlation contributions in the potential-energy term and used T_s as the kinetic energy. In this case, Eq. (6) reduces to

TABLE I. Total energy and forces (in a.u.) in $X\alpha$ and GL models, using a $[8s\,3p/4s\,3p]$ Gaussian basis. The forces are determined from the virial expression F_V, the Hellmann-Feynman theorem F_{HF}, and differentiation of E, F_E.

Bond	$X\alpha$				GL			
length	E	F_v	F_{HF}	F_E	E	F_V	F_{HF}	F_E
1.20	−1.0576	0.1295	0.1326	0.1290	−1.1455	0.1232	0.1265	0.1229
1.30	−1.0671	0.0656	0.0681	0.0653	−1.1545	0.0594	0.0621	0.0592
1.40	−1.0712	0.0198	0.0219	0.0193	−1.1580	0.0137	0.0161	0.0133
1.50	−1.0714	−0.0132	−0.0112	−0.0136	−1.1576	−0.0192	−0.0169	−0.0194
1.60	−1.0688	−0.0369	−0.0349	−0.0376	−1.1544	−0.0428	−0.0405	−0.0433

$$-\sum_p \vec{R}_p\cdot\vec{\nabla}_p E = 2T_s + U_{\mathrm{es}} + U_{\mathrm{xc}} = 2T_s + U\ , \qquad (15)$$

as derived by Slater.

Relative to the number of force calculations in Hartree-Fock and configuration-interaction molecular studies, rather little attention has been directed to this important problem in applications of the LDA to molecules. In the remainder of this paper, some results are given of a study of the force in the H_2 molecule employing some of the previous developments for the virial and Hellmann-Feynman theorems.

Calculation of the force from the Hellmann-Feynman theorem requires well-converged solutions determining the density $n(\vec{r})$ in Eq. (2), and the integral in the expression must be evaluated with precision. The calculation is more difficult than that required for the total energy, since the latter obeys a minimum principle, whereas the force does not. To remove the problem of sensitivity of the electrostatic potential to the density representation, a Gaussian basis set was adopted for this study. In this basis, the electrostatic (r_{12}^{-1}) interactions are evaluated analytically. The problem of achieving a high degree of convergence remains; however, for the light atoms good Gaussian basis sets are available, and procedures for extending the basis to improve convergence are well known. In this study, computational procedures were developed for solving the spin-polarized one-electron equations and evaluating the total energy and electrostatic forces. The integral algorithms of McMurchie and Davidson[11] were used to evaluate the overlap and Coulomb integrals and matrix elements, and exchange-correlation-dependent terms were evaluated numerically using three-dimensional (Diophantine) numerical sampling.[12] In this study, a contracted $[8s\,3p/4s\,3p]$ Gaussian basis set was used for the dimer calculations, where one s function was that of the free H atom. This $1s$ atomic solution was obtained from the cluster calculation in a single-site mode, using exponents from the $8s$ Gaussian basis set for hydrogen given by Clementi and Mehl.[13] In this atomic calculation, all Gaussian functions were free, so the resulting eigenvector defines the minimum energy within the prescribed eight-Gaussian basis set. The supplementary basis orbitals are those corresponding to the most diffuse (three) s Gaussians of the atomic basis. A limited total-energy optimization in the dimer calculation served to define the exponents of the three p Gaussians in the molecular basis. These uncontracted s and p Gaussians provide the variational freedom[14] for the molecular states to respond to the environment.

In Tables I and II, results are presented for two

TABLE II. Comparison of calculated and experimental equilibrium separation (R_e in a.u.), binding energy (E_B in eV), and vibrational frequency (ω in cm^{-1}).

		$X\alpha$		GL	
	Experiment (Ref. 18)	This work	DCS (Ref. 19)	This work	LCMTO (Ref. 20)
R_e	1.40	1.46	1.46	1.44	1.44
E_B	4.75	3.59	3.59	4.76	4.76
ω	4400	4110	4110	4227	4200

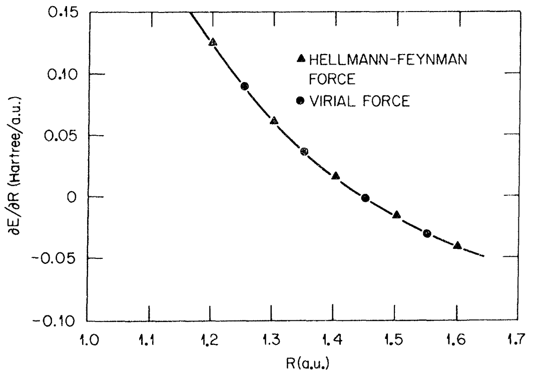

FIG. 1. Force on the hydrogen nucleus in the H_2 dimer as a function of internuclear separation in the LSDA of GL (Ref. 15). The virial force (dots) is calculated from Eq. (6) and the Hellmann-Feynman force (triangles) from Eq. (2).

popular exchange-correlation models, the $X\alpha$ with $\alpha=0.7$ and the local spin-density approximation (LDSA) of Gunnarsson and Lundqvist[15] (GL). A summary of force calculations by three different methods appears in Table I.[16] The quantity F_V is the force determined from the virial theorem, Eq. (6), and F_{HF} is the Hellmann-Feynman force, Eq. (2). The third force F_E is determined by differentiation of a Lagrange polynomial fit to the total energy dependence on internuclear separation.[17] All three forces in each exchange-correlation model are seen to be consistent with one another, with F_E and F_V being in best agreement. The accuracy of Eq. (6) for determining the "virial" force is apparent from these results. The forces F_{HF} and F_V in the GL model are plotted as a function of internuclear separation in Fig. 1.

Spectroscopic parameters calculated with the two exchange-correlation models are compared with experiment and with results from other works in Table II. The $X\alpha$ results are from Dunlap, Connolly, and Sabin,[19] who treated the total energy as a functional of $n(\vec{r})$ and $\tilde{n}(\vec{r})$ (charge fit density). Similarly, the results obtained using the GL model are in excellent accord with those reported by Gunnarsson, Harris, and Jones using the linear-combination-of-muffin-tin-orbitals (LCMTO) approach.[20] Since the same method was used in the present calculation for both $X\alpha$ and GL models, it can be definitively stated that the differences between the $X\alpha$ and GL models in Table II are due to the treatment of exchange and correlation alone, and not ascribable to methodology.

The relative convergence rates of the kinetic and total energies, eigenvalues, and forces are apparent from Table III. For the various basis sets noted, calculations were carried out at the equilibrium separation using the $X\alpha$ model. In this case, Eq. (14) holds (for the exact solution) and at equilibrium $2T_s+U\ =\ 0$, i.e., $-U/T_s$ converges to 2.0. Comparison of E and T_s (especially with the small basis sets) shows the behavior expected in that E obeys a minimum principle, whereas T_s does not. This would favor determination of F_E were it not for the necessity to carry out total-energy calculations for (in principle) arbitrary displacements in each coordinate for each of the N atoms in the cluster. On the other hand, F_V and F_{HF} are evaluated at a single separation, but the expression from which the virial force is determined, Eq. (6), does not obey a variational principle (e.g., in the $X\alpha$ case F_V is determined from $2T_s+U=E+T_s$), although the convergence is considerably more rapid than that of F_{HF}. The computation of F_V is

TABLE III. Convergence of total energy E, kinetic energy T_s, eigenvalue $\epsilon_{1\sigma_g}$, and virial and Hellmann-Feynman forces (F_V and F_{HF}, respectively) with basis size in H_2. The $X\alpha$ exchange-correlation model is used; all quantities in a.u.

Basis set	E	T_s	$\epsilon_{1\sigma_g}$	F_V	F_{HF}
1s	−0.9985	0.6739	−0.4116	−0.2231	+ 0.1889
2s	−1.0614	1.0017	−0.3441	−0.0411	+ 0.0760
3s	−1.0685	1.0643	−0.3422	−0.0029	+ 0.0573
4s	−1.0688	1.0704	−0.3428	+ 0.0011	+ 0.0598
5s	−1.0688	1.0702	−0.3428	+ 0.0010	+ 0.0597
(4s,1p)	−1.0716	1.0719	−0.3405	+ 0.0003	+ 0.0091
(4s,2p)	−1.0717	1.0722	−0.3405	+ 0.0003	+ 0.0060
(4s,3p)	−1.0717	1.0722	−0.3403	+ 0.0003	+ 0.0023
(4s,4p)	−1.0718	1.0722	−0.3403	+ 0.0003	+ 0.0002
(4s,3p,1d)	−1.0718	1.0721	−0.3403	+ 0.0002	+ 0.0020

further restricted to systems of particular symmetry.[21] On the other hand, F_{HF} can be calculated for systems of arbitrary symmetry at a single separation and is conceptually useful in its connection with the gradient of the classical electrostatic potential at the nucleus. The difficulties in converging F_{HF} are well known.[22] A first-order error in the wave function, which gives a second-order error in the total energy, produces an error of first order in F_{HF}.[4] The requirement for large basis sets to describe accurately F_{HF} is a consequence of polarization effects in the bond density. Since F_{HF} is computed as the difference between the force of nuclear repulsion (exactly represented) and the force of attraction between electrons and nuclei, a precise representation of the electronic density shifts is required. Studies in the present approach are under way to explore the usefulness of force calculations based on the valence part of the electronic density. A novel approach for circumventing the limitations of the Hellmann-Feynman force calculation by treating a valence-only energy functional has also been recently suggested.[23]

The authors are grateful to S. B. Trickey, J. W. Mintmire, A. R. Williams, and J. Harris for helpful comments. One of us (F.W.A.) also benefitted from a visit with the Quantum Theory Project, University of Florida, and acknowledges useful discussions with colleagues there. This research was sponsored by the Division of Materials Sciences, U.S. Department of Energy, under Contract No. W-7405-eng-26 with the Union Carbide Corporation. The work of one of us (F.W.A.) was partially supported by Oak Ridge Associated Universities.

---

*Permanent address: Judson College, Elgin, Illinois 60120.

[1] P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).

[2] W. Kohn and L. J. Sham, Phys. Rev. 136, A1133 (1965).

[3] J. C. Slater, J. Chem. Phys. 57, 2389 (1972).

[4] J. O. Hirschfelder and W. J. Meath, Adv. Chem. Phys. 12, 3 (1967).

[5] R. A. Harris and D. F. Heller, J. Chem. Phys. 62, 3601 (1975).

[6] For example, a position-dependent scaling parameter α in a generalized $X\alpha$ scheme would necessitate corrective terms (see Ref. 3).

[7] J. F. Janak, Phys. Rev. B 9, 3985 (1974).

[8] U. von Barth, quoted in Ref. 9.

[9] A. R. Williams, J. Kübler, and C. D. Gelatt, Jr., Phys. Rev. B 19, 6094 (1979).

[10] U. von Barth and A. R. Williams (unpublished). We are grateful to Art Williams for sending excerpts from this work prior to publication.

[11] L. E. McMurchie and E. R. Davidson, J. Comput. Phys. 26, 218 (1978).

[12] See, for example, F. W. Averill and D. E. Ellis, J. Chem. Phys. 59, 6412 (1973).

[13] E. Clementi and J. W. Mehl, IBM Research Report No. RJ883 (1971).

[14] R. D. Bardo and K. Ruedenberg, J. Chem. Phys. 59, 5956 (1973).

[15] O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B 13, 4274 (1976).

[16] The potential function $\mu_{\mathrm{xc}}^{\pm}$ of Ref. 15 was derived directly from their calculations for the homogeneous spin-polarized electron liquid. The result differs slightly from that defined by Eq. (9), and differences of a few percent occur in evaluating the gradient of Eq. (6). Using Eq. (9) and the GL exchange-correlation energy density represented as

$$\epsilon_{\mathrm{xc}}(r_s,\zeta)=\epsilon_{\mathrm{xc}}^{P}(r_s)+[\epsilon_{\mathrm{xc}}^{F}(r_s)-\epsilon_{\mathrm{xc}}^{P}(r_s)]f(\zeta)\ ,$$

where r_s and ζ are usual electron-gas parameters for density and spin polarization $[\zeta=(n_+-n_-)/n]$ and

$$f(\zeta)=\frac{[(1+\zeta)^{4/3}+(1-\zeta)^{4/3}-2]}{(2^{4/3}-2)}\ ,$$

$$\mu_{\mathrm{xc}}^{\pm}=\frac{\partial}{\partial n_{\pm}}(n\epsilon_{\mathrm{xc}}^{P})+\left[\frac{\partial}{\partial n_{\pm}}(n\epsilon_{\mathrm{xc}}^{F})-\frac{\partial}{\partial n_{\pm}}(n\epsilon_{\mathrm{xc}}^{P})\right]f(\zeta)$$

$$+(\epsilon_{\mathrm{xc}}^{F}-\epsilon_{\mathrm{xc}}^{P})g^{\pm}(\zeta)\ ,$$

where

$$\frac{\partial}{\partial n_{\pm}}(n\epsilon_{\mathrm{xc}}^{i})=-\tfrac{4}{3}a_i r_s^{-1}$$

$$-C_i\ln(1+1/X_i)\ ,\quad i=P,F$$

and

$$g^{\pm}(\zeta)=\pm\frac{4}{3}\frac{[(1+\zeta)^{1/3}-(1-\zeta)^{1/3}](1\mp\zeta)}{(2^{4/3}-2)}\ .$$

Here

$$\epsilon^{i}_{\mathrm{xc}}(r_s) = -a_i r_s^{-1} - C_i[(1+X_i^3)\ln(1+1/X_i) + X_i/2 - X_i^2 - \tfrac{1}{3}], \qquad i=P,F$$

and

$$X_i = r_s/r_i,$$

$$a_p = 3/2\pi(9\pi/4)^{1/3},$$

$$a_F = 2^{1/3}a_p .$$

Fit parameters are given as $C_p -0.0666$, $C_F=0.0406$, $r_p = 11.4$, and $r_F=15.9$, defining ϵ_{xc} and μ_{xc} in rydbergs. The potential in this form was used in the present calculations.

[17] Instabilities can occur with polynomial fits; however, our experience indicates such representations for binding-energy curves are sufficiently well behaved for force determinations.

[18] K. P. Huber, in *American Institute of Physics Handbook*, edited by D. E. Gray (McGraw-Hill, New York, 1972), Sec. 7g.

[19] B. I. Dunlap, J. W. D. Connolly, and J. R. Sabin, J. Chem. Phys. 71, 4993 (1979).

[20] O. Gunnarsson, J. Harris, and R. O. Jones, Phys. Rev. B 15, 3027 (1977).

[21] Since the virial expression [e.g., Eq. (6)] defines a sum over atoms and coordinates on the left-hand side, a meaningful force F_p^i can be extracted only if $R_p^i = \pm R_m^j$ and $F_p^i = \pm F_m^j$ ($i=x$, y, or z) for each $m=1,\ldots,N$ and $j=x$, y, or z, for which $R_m^j F_m^j \neq 0$.

[22] See, for example, B. J. Rosenberg and I. Shavitt, J. Chem. Phys. 63, 2162 (1975).

[23] J. Harris, R. O. Jones, and J. E. Müller (unpublished). We are grateful to these authors for this information prior to publication.