PHYSICAL REVIEW B VOLUME 45, NUMBER 23 15 JUNE 1992-I

Brief Reports

Brief Reports are accounts of completed research which, while meeting the usual **Physical Review** *standards of scientific quality, do not warrant regular articles. A Brief Report may be no longer than four printed pages and must be accompanied by an abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

Fractional occupations and density-functional energies and forces

M. Weinert and J. W. Davenport
Department of Physics 510A, Brookhaven National Laboratory, Upton, New York 11973

(Received 4 February 1992)

The explicit inclusion of fractional occupation numbers in density-functional calculations is shown to require an additional term to make the energy functional variational. The contribution from this term to the density-functional force exactly cancels the correction term depending on changes in the occupation number. For occupation numbers obeying a Fermi distribution, the resulting functional is identical in form to the grand potential; other choices for the form of the occupation numbers will result in different functionals. These terms, although numerically small, should be included in practical calculations that allow for fractional occupation numbers.

I. INTRODUCTION

Density-functional theory[1,2] in the local-density approximation is quite successful in predicting properties of materials. An important ingredient in this success is the ability to calculate a variational total energy. The existence of different variational functionals is by now well known,[3,4] as is the procedure for calculating[5-8] the associated density-functional forces. Most of these derivations assume either fixed integral occupation numbers,[5,6] or else that variable occupation numbers will not alter the form of the energy functional.[7,8] Fractional occupation numbers are formally introduced via the grand potential of finite-temperature thermodynamics.[2,9]

In practical calculations, variable occupation numbers are often introduced even for finite systems. (A band calculation with finite **k**-point sampling is still formally a finite system, but with periodic boundary conditions.) This procedure has the advantage that the calculations for metallic systems typically coverage more rapidly, and that a broadening of each level crudely mimics larger systems or better **k**-point sampling, although since these systems are finite, the grand potential is formally not applicable. It is important to emphasize, however, that finite-temperature density-functional theory is the fundamental basis for treating *infinite* electronic systems at physical temperatures $T > 0$.

In this paper, we demonstrate that by explicitly including variable occupation numbers, an additional term is required to make the standard total-energy functional properly variational. Moreover, when this term is included, there is no correction term to the density-functional force due to changes in occupation number. For occupation numbers satisfying a Fermi distribution, the variational total-energy functional is identical in form to the grand potential; for other choices of the occupation numbers, however, the form will be different. Although these results are straightforward, they help clarify and correct various statements made in the literature concerning density-functional total energies and forces. Computational evidence for the existence of these terms can be found in standard electronic-structure calculations,[8] as well as in a recent first-principles molecular-dynamics investigation[10] that used the grand potential of finite-temperature density-functional theory[2,9] directly. Thus, the results of this paper are also of practical importance.

II. ENERGY FUNCTIONALS

Consider the energy functional[1-4]

$$\tilde{E}[n]=\tilde{T}_s[n]+U[n]+E_{\mathrm{xc}}[n] , \tag{1}$$

where $n(\mathbf{r})$ is either the input, n_{in}, or output, n_{out}, density. The Coulomb energy is

$$U[n]=\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} - \sum_{\nu} Z_\nu \int d\mathbf{r}\frac{n(\mathbf{r})}{|\mathbf{r}-\mathbf{R}_\nu|}+\frac{1}{2}\sum_{\nu,\nu'}\frac{Z_\nu Z_{\nu'}}{|\mathbf{R}_\nu-\mathbf{R}_{\nu'}|} , \tag{2}$$

E_{ex} is the exchange-correlation energy, and the "kinetic" energy is given by

$$\tilde{T}_s[n]=\sum_i f_i \varepsilon_i - \int d\mathbf{r}\, n(\mathbf{r})\, v_{\mathrm{eff}}[n_{\mathrm{in}}] , \tag{3}$$

where $v_{\mathrm{eff}}[n_{\mathrm{in}}]$ is the effective single-particle potential. The difference between these equations and those previously given[3,4] is that the (possibly) fractional occupation numbers f_i have been explicitly included in the eigenvalue sum. This functional $\tilde{E}$ includes both the standard Kohn-Sham functional[1,2] E_{KS} (for $n \equiv n_{\text{out}}$) and the modified functional[3,4] (for $n \equiv n_{\text{in}}$), and at the exact density n_0, $E_{\text{KS}}[n_0]=\tilde{E}[n_0]$. When the occupation numbers are fixed, then $\tilde{E}$ is variational (stationary) for either choice of n, as shown previously. Here we will demonstrate that including the occupation numbers explicitly requires that an additional term be added to the energy functional.

Expanding n about the exact density n_0, it is easy to show that, to first order, the Coulomb and exchange terms are

$$U[n_0+\delta n]+E_{\text{xc}}[n_0+\delta n] = U[n_0]+E_{\text{xc}}[n_0]+\int d\mathbf{r}\, \delta n(\mathbf{r}) v_{\text{eff}}[n_0] \ , \tag{4}$$

and the kinetic-energy term is

$$\tilde{T}_s[n_0+\delta n]= \tilde{T}_s[n_0]-\int d\mathbf{r}\, \delta n(\mathbf{r}) v_{\text{eff}}[n_0]+\sum_i \delta f_i\, \varepsilon_i \ . \tag{5}$$

Thus, for a given density n, the density functional is

$$\tilde{E}[n_0+\delta n]=\tilde{E}[n_0]+\sum_i \delta f_i \varepsilon_i + O(\delta^2) \ . \tag{6}$$

All first-order terms vanish, i.e., the functional is stationary, except for the term depending on the change in occupation numbers. If $\delta f_i \neq 0$, this term will be nonzero since the eigenvalues ε_i are not all equal to the same constant, although numerically it may be quite small.

To generate a proper variational functional, we must add a term $\Delta E[n]$ such that

$$\Delta E[n_0+\delta n]=\Delta E[n_0]-\sum_i \delta f_i\, \varepsilon_i + O(\delta^2) \ . \tag{7}$$

The form of this correction will depend on the functional form of the occupation numbers. A sufficient condition is that there exists a function $\mathcal{F}(f_i)=\varepsilon_i$. Then ΔE is given as the integral of $\mathcal{F}$ with respect to f_i.

Consider a Fermi function form for the occupation numbers (we will discuss other choices later):

$$f_i=\frac{1}{e^{\beta(\varepsilon_i-\mu)}+1} \ , \tag{8}$$

where μ is determined either by numerical conservation or the chemical potential of the system. Although it is natural to make the additional correspondence $\beta^{-1}=k_B T$, this identification is not necessary. The inverse function $\mathcal{F}$ is easily found to be

$$\mathcal{F}(f_i)=\frac{1}{\beta}\ln\left[\frac{1-f_i}{f_i}\right]+\mu \ . \tag{9}$$

Integrating this term with respect to f_i, we obtain

$$\begin{aligned}\Delta E &= \frac{1}{\beta}\sum_i \int df_i \left[\ln\left[\frac{f_i}{1-f_i}\right]-\beta\mu\right] \\ &= \frac{1}{\beta}\sum_i \int df_i [\ln f_i - \ln(1-f_i)-\beta\mu] \\ &= \frac{1}{\beta}\sum_i [f_i \ln f_i + (1-f_i)\ln(1-f_i)] - \mu \sum_i f_i + C_0 \ ,\end{aligned} \tag{10}$$

where C_0 is a constant of integration which determines the reference energy. For number conserving changes, we choose $C_0=\mu N$, and then $\mu(N-\sum_i f_i)=0$:

$$\Delta E=\frac{1}{\beta}\sum_i [f_i \ln f_i + (1-f_i)\ln(1-f_i)] \ . \tag{10$'$}$$

Allowing the possibility of non-number-conserving changes, we choose $C_0=0$ and then

$$\Delta E=\frac{1}{\beta}\sum_i [f_i \ln f_i + (1-f_i)\ln(1-f_i)] - \mu\sum_i f_i \ . \tag{10$''$}$$

Thus, a term of the form given in Eqs. (10′) or (10″) is required to make the energy functional properly variational when variable occupation numbers are permitted.

The form of Eq. (10′) for number conserving variations is the same[11] as the entropy contribution to the free energy for noninteracting particles, $-TS_s[n]$. When non-number-conserving changes are also included, Eq. (10″), the resulting energy functional is identical in form to the grand potential of finite-temperature thermodynamics, i.e., $E_0[n]=\tilde{E}[n]+\Delta E=\Omega[n]$.[2,9] The interpretation proposed in this paper—that ΔE is a consequence of defining a proper variational functional—has the advantage that no physical significance is necessarily given to the "inverse temperature" β or to the form of ΔE. Thus, $E_0[n]$ can be used in situations (such as finite systems) where the concept of temperature is problematic.

III. FORCES

In density-functional theory, the force on atom α is given as the derivative of the (variational) energy functional $E_0=\tilde{E}+\Delta E$ with respect to a displacement $\delta\tau_\alpha$:

$$\mathbf{F}_\alpha=-\frac{\delta E_0}{\delta \tau_\alpha} \ . \tag{11}$$

The derivation of the force follows in much the same manner as the demonstration of the variational nature of the energy functional. The result is

$$\begin{aligned}\mathbf{F}_\alpha = \mathbf{F}^\alpha_{\text{HF}} - \sum_i f_i &\left[\left\langle \frac{\delta\psi_i}{\delta\tau_\alpha}\right|(H-\varepsilon_i)\left|\psi_i\right\rangle \right. \\ &\left. + \left\langle \psi_i \right|(H-\varepsilon_i)\left|\frac{\delta\psi_i}{\delta\tau_\alpha}\right\rangle\right] \\ &- \sum_i \frac{\delta f_i}{\delta\tau_\alpha}\varepsilon_i - \frac{\delta}{\delta\tau_\alpha}\Delta E \ .\end{aligned} \tag{12}$$

The first term $\mathbf{F}_{\text{HF}}$ is the standard Hellmann-Feynman[12] result, i.e., the classical electrostatic force due to all the charges in the system. The second term—the "Pulay" force—contains the corrections[13,14] that depend on details of the calculations: In an exact calculation, as well as in some other special cases, these terms vanish.[6,13,14] (This contribution is also known as the "incomplete basis set" force.)

The third term depends on the changes in occupation numbers. While the existence of this term has been realized previously,[7,8] it has either been neglected or assumed to vanish. Indeed, if all the states are occupied with fixed occupations ($f_i \equiv 1$), then this terms does vanish. If, however, changes in occupation are allowed, either because of level crossings or "thermal" effects, then formally this term is not identically equal to zero, in complete analogy with Eq. (6).[15]

By differentiating either Eq. (10′) (and using number conservation, $\mu \sum \delta f_i = 0$) or Eq. (10″), the correction term coming from ΔE is easily found to be

$$-\frac{\delta \Delta E}{\delta \tau_\alpha} = \sum_i \frac{\delta f_i}{\delta \tau_\alpha} \varepsilon_i \; . \tag{13}$$

This term exactly cancels the third term and hence the proper density-functional force is equal to only the Hellmann-Feynman and Pulay forces,

$$\mathbf{F}_\alpha = \mathbf{F}^\alpha_{\mathrm{HF}} - \sum_i f_i \left[\left\langle \frac{\delta \psi_i}{\delta \tau_\alpha} \middle| (H - \varepsilon_i) \middle| \psi_i \right\rangle + \left\langle \psi_i \middle| (H - \varepsilon_i) \middle| \frac{\delta \psi_i}{\delta \tau_\alpha} \right\rangle \right] . \tag{14}$$

IV. DISCUSSION

The results of the preceding sections demonstrate that there are no correction terms to the density-functional force due to changes in the occupation numbers *if* the proper variational energy functional E_0 is used. This is a formal statement that is independent of such calculational parameters as **k**-point sampling, etc. An equivalent statement is that the line integral of the Hellmann-Feynman and Pulay forces is given by differences of the functional $E_0 = \tilde{E} + \Delta E$, when variable occupation numbers are allowed.

This restatement is relevant to first-principles molecular-dynamics (MD) methods.[16,17] In these methods, the ionic motion is treated classically, and the potential-energy surface is defined by the density-functional (Kohn-Sham) energy as a function of the ionic positions $\{R_I\}$. The Lagrangian for Born-Oppenheimer (adiabatic) dynamics can be written as[17,18]

$$\mathcal{L}_{\mathrm{BO}} = \sum_I \tfrac{1}{2} M_I \dot{R}_I^2 - E[n, \{R_I\}] \; . \tag{15}$$

The force of the ions is then determined using the Hellmann-Feynman forces. (In principle, the Pulay forces also must be included. However, most of these calculations to date have used plane waves and pseudopotentials; for a plane-wave basis, the Pulay forces vanish identically.[6,13] If the Pulay terms are nonzero, as for example in a linearized plane-wave calculation,[8] then they must be included also.) The total energy, defined as the sum of the kinetic energy of the ions and the potential energy E, is a conserved quantity, if and only if the force is the derivative of the potential energy. Thus, if Hellmann-Feynman (plus Pulay) forces are used, then the correct energy functional to use in Eq. (15) is $E = E_0$.

In MD calculations, the changes in occupation number between time steps are finite and will depend on the parameter β^{-1}; to get reasonable conservation of energy, the calculation parameters should be chosen so that all δf_i are small. The optimum values will depend on the time step and the number and energy separation of states near μ. Similar considerations also hold for the self-consistency process itself with fixed ionic positions (the changes δf_i between interations determine the rate of approach to the self-consistent value of the energy), and for standard density-functional calculations in which the force is used to relax the atomic positions.

Another approach, followed by Wentzcovitch, Martins, and Allen[10] (WMA), uses the finite-temperature formalism of Mermin[9] to introduce fractional occupations and a term of the form of Eq. (10). The use of the grand potential[2,9] has appeal in that it provides a physical interpretation of the form of Eq. (10), albeit for noninteracting particles. WMA found significant improvement in energy conservation during MD runs, even though the electrons and ions were at different "temperatures" and the grand potential is not formally applicable to finite systems. Based on the discussion above, and the discussion in Ref. 10, it is clear that this observed improvement comes about because the force and the potential energy are now consistent.[19]

The analysis presented here takes as a starting ansatz the commonly used assumptions of an energy functional of the form of Eq. (1) and variable occupation numbers, and then derives the additional terms required to make the functional variational. Although the functionals E_0 and Ω are identical in form, the underlying assumptions are different. By not associating physical significance to β, and the corresponding "temperature" T, one is not tied to the particular functional form of the grand potential. Instead, one can define a variational functional given a particular choice for the form of f_i. Common computational alternatives to the Fermi function form for f_i are interpolation schemes (e.g., linear tetrahadron and Fourier fits) and Gaussian broadening of each level. The interpolation schemes implicitly assign fractional occupations; unfortunately, the form of ΔE will depend on details of the calculations, including **k**-point sets and the band structure itself. For Gaussian broadening, the occupation numbers are related to the complementary error function, $\mathrm{erfc}[(\varepsilon_i - \mu)/\alpha]$. A simple calculation shows that ΔE as given in Eq. (10) will not yield a variational energy for Gaussian broadening. It is not obvious that any simple functional form of ΔE for Gaussian broadening can be found, since no simple functional form for the inverse function to erfc exists. (An infinite series expansion of the inverse, $\mathcal{I}$, can be defined from reversion of the infinite series representation of the error function, but is not useful in practice since it leads to an infinite series for ΔE. Reasonable numerical approximations, however, may still be possible.) On the other hand, Fermi broadening, which corresponds to broadening each level with a function $[f_i=\int^{\mu}d\varepsilon g_i(\varepsilon_i)]$

$$g_i(\varepsilon)=\frac{1}{4k_BT}\operatorname{sech}^2\frac{\varepsilon-\varepsilon_i}{2k_BT}\ , \tag{16}$$

is at least as simple to use in calculations and plots as a Gaussian, but has the advantage that a simple and practical variational functional for the energy can be defined.

In conclusion, we have demonstrated that if fractional (variable) occupation numbers are allowed, then an additional term is required in the energy functional in order for it to be variational. When this term is included, the density-functional force is equal to the Hellmann-Feynman (+ Pulay) force only; no correction terms due to changes in occupation numbers exist. If the occupation numbers are chosen to have the functional form of a Fermi distribution, then the proper variational energy functional is identical in form to the grand potential of finite-temperature density-functional theory,[2,9] but no physical significance such as temperature or entropy need or should be associated with this term. Although the numerical effects of this term may be small, they do exist and should be included in practical calculations that make use of fractional occupation numbers.

ACKNOWLEDGMENTS

We thank P. B. Allen and R. M. Wentzcovitch for a copy of Ref. 10 prior to publication. This work was supported under contract No. DE-AC02-76CH00016 with the Division of Materials Sciences, U.S. Department of Energy.

---

[1] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, Phys. Rev. **140**, A1130 (1965).

[2] A. K. Rajagopal, in *Advances in Chemical Physics,* edited by I. Prigogine and S. A. Rice (Wiley, New York, 1980), Vol. 41, pp. 59–193.

[3] J. Harris, Phys. Rev. B **31**, 1770 (1985).

[4] M. Weinert, R. E. Watson, and J. W. Davenport, Phys. Rev. B **32**, 2115 (1985).

[5] J. Ihm, A. Zunger, and M. L. Cohen, J. Phys. C **12**, 4409 (1979); **13**, 3095(E) (1980).

[6] P. Bendt and A. Zunger, Phys. Rev. Lett. **50**, 1684 (1983).

[7] K. M. Ho, C. L. Fu, and B. N. Harmon, Phys. Rev. B **28**, 6687 (1983).

[8] R. Yu, D. Singh, and H. Krakauer, Phys. Rev. B **43**, 6411 (1991).

[9] N. D. Mermin, Phys. Rev. **137**, A1441 (1965).

[10] R. M. Wentzcovitch, J. L. Martins, and P. B. Allen (unpublished).

[11] J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (Wiley, New York, 1940), pp. 109–126.

[12] H. Hellmann, *Einführung in die Quantumchemie* (Deuticke, Leipzig, 1937), p. 285; R. P. Feynman, Phys. Rev. **56**, 340 (1939).

[13] A. C. Hurley, Proc. R. Soc. London, Ser. A **226**, 170 (1954); **226**, 179 (1954).

[14] P. Pulay, Mol. Phys. **17**, 197 (1969).

[15] If changes in occupation are allowed because of level crossings and $T=0$, then $f_i[\delta\tau_\alpha]$ may be discontinuous, i.e., $\delta f_i/\delta\tau_\alpha$ can be infinite, and the functional derivatives are not defined. To treat this case, a limiting process of $T\rightarrow 0$ should be used, and then the analysis given here holds, although the range in $|\delta\tau_\alpha|$ for which it is valid will depend on the value of β.

[16] R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).

[17] G. W. Fernando, G. X. Qian, M. Weinert, and J. W. Davenport, Phys. Rev. B **40**, 7985 (1989).

[18] In methods such as Ref. 16 that use fictitious dynamics, an additional term corresponding to the "kinetic energy" of these fictitious degrees of freedom is added to the Lagrangian. This term will also give a contribution to the conserved energy.

[19] A different approach in which the occupation numbers f_i are treated as variational parameters is discussed in M. R. Pederson and K. A. Jackson, Phys. Rev. B **43**, 7312 (1991). Since the first-order terms proportional to δf_i vanish by construction, the total energy and (Hellmann-Feynman) forces are consistent.