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.

Density-functional energies and forces with Gaussian-broadened fractional occupations

C. Elsässer and M. Fähnle

Max-Planck-Institut für Metallforschung, Institut für Physik, Heisenbergstrasse 1, D-70569, Stuttgart, Germany

C. T. Chan and K. M. Ho

Ames Laboratory and Department of Physics, Iowa State University, Ames, Iowa 50011

(Received 20 January 1994)

It is demonstrated that the Gaussian-broadening scheme for the explicit inclusion of fractional occupation numbers in density-functional calculations of crystals, as originally given by Fu and Ho [Phys. Rev. B **28**, 5480 (1983)], contains an additional term to the total energy which makes the energy functional variational and exactly cancels a correction to the density-functional forces originating from changes in the occupation numbers.

I. INTRODUCTION

For the determination of microscopic and macroscopic properties of condensed matter from first principles the density-functional theory in the local-density approximation¹ is used by a large community of researchers with considerable success. This has been stressed in a recent paper by Weinert and Davenport,² who elucidated a way to find variational energy functionals for the calculation of the most important quantity of the density-functional theory, the total energy.

For crystalline solids total energies and forces are obtained via self-consistent-field band calculations involving integrations over $\mathbf{k}$ vectors of Bloch functions in the first Brillouin zone. These integrations are commonly approximated by summations over a finite set of sampling $\mathbf{k}$ points. For insulating systems at zero temperature the occupation of the Bloch states can be fixed to two or zero electrons per spin-degenerate state. In metals a fractional occupation of states at the sampling $\mathbf{k}$ points close to the Fermi energy is commonly introduced to mimic the properties of the Fermi surface. Quite often used schemes are the linear tetrahedron method³ or fictive temperature broadening schemes such as the Fermi broadening discussed in Ref. 2, or the Gaussian broadening given by Fu and Ho.⁴

Weinert and Davenport² gave a general way to obtain additional terms $\Delta E[\rho]$ to the total energy $\tilde{E}[\rho]$ which yield variational density functionals $E_0[\rho] = \tilde{E}[\rho] + \Delta E[\rho]$ for energies with fractional occupations, and the corresponding forces $\mathbf{F}_\alpha = -\frac{\delta E_0}{\delta \mathbf{r}_\alpha}$. They derived explicit ex-

pressions using the Fermi function:

$$f_i = \frac{2}{e^{\beta(\varepsilon_i - \mu)} + 1} \quad (1.1)$$

for the occupation numbers f_i of electronic states with energies ε_i in a system with the chemical potential μ . The broadening parameter $\beta = (k_B T)^{-1}$ can formally be related to a temperature T of the system, the corresponding variational energy functional $E_0[\rho]$ to the thermodynamic free energy F or the grand potential Ω . However, as Weinert and Davenport pointed out themselves, “no physical significance is necessarily given to the ‘inverse temperature’ β or to the form of ΔE .”² This leaves the choice open for different distribution functions as well, such as the complementary error function

$$f_i = \frac{2}{\sqrt{\pi}} \int_{-\infty}^{\frac{\mu - \varepsilon_i}{\Delta}} \exp[-x^2] dx \quad (1.2)$$

used in the Gaussian-broadening method.⁴ But in Ref. 2 the authors conjecture whether “any simple functional form of ΔE for Gaussian broadening can be found, since no simple functional form for the inverse function to the complementary error function exists.”

In Sec. II of this paper we show that the Gaussian-broadening method, as given in Ref. 4, leads to a variational energy functional, in which the additional term ΔE can be identified, and that no correction term originating from changes in the occupation numbers needs to be included in the corresponding forces. A direct derivation of ΔE following Ref. 2 is sketched in Sec. III.

II. THE ENERGY FUNCTIONAL IN THE GAUSSIAN-BROADENING METHOD

The total energy per unit cell of a crystal can be calculated by the formula:⁴

$$\begin{aligned} \bar{E}[\rho] = E_S + E_{\text{Ewald}} + \alpha Z - \Omega_c \sum_{\mathbf{G}} \rho^*(\mathbf{G}) V_{Hx}^{\text{in}}(\mathbf{G}) \\ + \frac{1}{2} \Omega_c \sum_{\mathbf{G} \neq 0} \frac{8\pi |\rho(\mathbf{G})|^2}{|\mathbf{G}|^2} + \Omega_c \sum_{\mathbf{G}} \rho^*(\mathbf{G}) \epsilon_{xc}(\mathbf{G}) \quad . \end{aligned} \quad (2.1)$$

In the context of the present paper the only interesting term, which explicitly contains occupation numbers, is the first one, E_S . For the meaning of all others we kindly refer the reader to Refs. 4 and 6. E_S is the sum of eigenvalues over all occupied Bloch states:

$$E_S = \Omega_c \sum_{n\mathbf{k}} f_{n\mathbf{k}} \epsilon_{n\mathbf{k}} \quad , \quad (2.2)$$

where Ω_c is the volume of the unit cell, $\epsilon_{n\mathbf{k}}$ and $f_{n\mathbf{k}}$ are the eigenvalue and the occupation number, respectively, of a Bloch state in the n th band with the wave vector $\mathbf{k}$. The occupation numbers fulfill the requirement that each unit cell contains Z electrons:

$$Z = \sum_{n\mathbf{k}} f_{n\mathbf{k}} \quad . \quad (2.3)$$

Note that up to here the $\mathbf{k}$ are discrete quantum numbers, and the $f_{n\mathbf{k}}$ are integer numbers (2 or 0).

A real macroscopic crystal ($\approx 10^{23}$ unit cells) can be imagined as an infinite system and approximated by a unit cell with periodic boundary conditions. Then the wave vector $\mathbf{k}$ is a continuous quantity, and the sum E_S can be replaced by an integral E_B :

$$E_B = \int_{-\infty}^{\mu} \epsilon \mathcal{D}(\epsilon) d\epsilon \quad , \quad (2.4)$$

the band energy of the system, where $\mathcal{D}(\epsilon)$ is the density of states. The chemical potential μ (Fermi energy ϵ_F at $T = 0$ K) is determined to fulfill the requirement of having the correct number of electrons in the unit cell:

$$Z = \int_{-\infty}^{\mu} \mathcal{D}(\epsilon) d\epsilon \quad . \quad (2.5)$$

Equations (2.4) and (2.5) for E_B and Z are accurate in principle but the exact shape of $\mathcal{D}(\epsilon)$, which formally is a sum of δ functions for all possible Bloch states, is unknown. Hence the aim is to find an approximation for $\mathcal{D}(\epsilon)$. A reasonable way is to choose a finite set of sampling $\mathbf{k}$ points in the first Brillouin zone and to broaden the δ function of each state artificially, for instance, by a Gaussian function with a finite width parameter Δ :

$$\mathcal{D}(\epsilon) = \sum_{n\mathbf{k}} \frac{2}{\Delta\sqrt{\pi}} \exp \left[-\frac{(\epsilon - \epsilon_{n\mathbf{k}})^2}{\Delta^2} \right] \quad . \quad (2.6)$$

The integral E_B is then reduced again to a sum ϑ , but now over only the sampling $\mathbf{k}$ points. Inserting Eq. (2.6) in Eq. (2.5) and comparing with Eq. (2.3) the occupation numbers, which are no longer integer but fractional, are thus given by the complementary error function:

$$f_{n\mathbf{k}} = \frac{2}{\Delta\sqrt{\pi}} \int_{-\infty}^{\mu} \exp \left[-\frac{(\epsilon - \epsilon_{n\mathbf{k}})^2}{\Delta^2} \right] d\epsilon \quad . \quad (2.7)$$

Inserting Eq. (2.6) in Eq. (2.4) we get

$$E_B = E_S + \Delta E \quad , \quad (2.8)$$

where E_S is just given by Eq. (2.2), and ΔE is an additional term given by

$$\Delta E = - \sum_{n\mathbf{k}} \frac{2\Delta}{\sqrt{\pi}} \frac{1}{2} \exp \left[-\frac{(\mu - \epsilon_{n\mathbf{k}})^2}{\Delta^2} \right] \quad . \quad (2.9)$$

In the following we show that ΔE of Eq. (2.9) is just the term that makes the energy functional, according to Ref. 2, variational with respect to fractional occupation numbers. The variation of E_B is given by

$$\begin{aligned} \delta E_B = \delta E_S + \delta \Delta E = \sum_{n\mathbf{k}} \delta f_{n\mathbf{k}} \epsilon_{n\mathbf{k}} + \sum_{n\mathbf{k}} f_{n\mathbf{k}} \delta \epsilon_{n\mathbf{k}} \\ + \delta \Delta E \quad . \end{aligned} \quad (2.10)$$

With Eq. (2.9) for ΔE we get

$$\begin{aligned} \delta \Delta E = \sum_{n\mathbf{k}} (\mu - \epsilon_{n\mathbf{k}}) \\ \times \frac{2}{\Delta\sqrt{\pi}} \exp \left[-\frac{(\mu - \epsilon_{n\mathbf{k}})^2}{\Delta^2} \right] (\delta \mu - \delta \epsilon_{n\mathbf{k}}) \quad . \end{aligned} \quad (2.11)$$

The variation of the occupation numbers of Eq. (2.7) yields

$$\delta f_{n\mathbf{k}} = \frac{2}{\Delta\sqrt{\pi}} \exp \left[-\frac{(\mu - \epsilon_{n\mathbf{k}})^2}{\Delta^2} \right] (\delta \mu - \delta \epsilon_{n\mathbf{k}}) \quad . \quad (2.12)$$

Comparing Eq. (2.11) and Eq. (2.12) and using Eq. (2.3) we finally get

$$\delta \Delta E = - \sum_{n\mathbf{k}} \delta f_{n\mathbf{k}} \epsilon_{n\mathbf{k}} \quad (2.13)$$

and for the band energy

$$\delta E_B = \sum_{n\mathbf{k}} f_{n\mathbf{k}} \delta \epsilon_{n\mathbf{k}} \quad . \quad (2.14)$$

Hence we have shown that ΔE is just the additional term that cancels all first-order variations due to fractional occupation numbers and makes the energy functional $E_0[\rho]$ variational.² In fact, Eq. (2.14) holds for any arbitrary broadening function $f_{n\mathbf{k}}$ (see the Appendix). However, in spite of its variational property, it is not granted that the energy functional with few sampling $\mathbf{k}$ points and a finite broadening approximates the “physical” func-

tional with continuous $\mathbf{k}$ vectors and zero broadening well. Therefore, test calculations for the convergence of considered physical quantities, for instance, the total energy of a crystal, with respect to the number of $\mathbf{k}$ points and the broadening width are necessary (see, e.g., Fig. 3 in Ref. 4).

From E_0 the atomic forces can be calculated directly with the Gaussian as well as with the Fermi broadening scheme according to

$$\mathbf{F}_\alpha = -\frac{\delta E_0}{\delta \mathbf{r}_\alpha} . \quad (2.15)$$

An important simplification for the calculation of forces arises from the use of E_0 instead of $\tilde{E}$ for any finite set of sampling $\mathbf{k}$ vectors, namely, that there is no contribution originating from changes $\delta f_{n\mathbf{k}}$. The formalism to calculate such contributions, when using $\tilde{E}$ [Eq. (2.1)], was described in Refs. 5 and 6, but based on the experience in Ref. 5, "that the term due to the change in occupation has a negligible effect," the contributions were neglected since then. Fortunately this was the correct thing to do because, by using the Gaussian broadening with E_B instead of E_S , $\tilde{E}$ is replaced by E_0 .

However in Ref. 7, in the case of the calculation of forces on Pd atoms surrounding an interstitial H atom in Pd_nH supercells ($n = 4, 8, 16$, and 32) (Tables 3–5 in Ref. 7), force contributions originating from $\delta f_{n\mathbf{k}}$ [last term of Eq. (17) in Ref. 6] were included in an approximate way in the mistaken expectance to get more accurate results. But in the Pd_{32}H supercells, when the amounts of the forces were very small (less than about 0.01 Ry/a.u.), a slow, long-range decay behavior of the forces was found, which could not be understood satisfactorily. The reanalysis of our data yields that the $\delta f_{n\mathbf{k}}$ contributions are of similar size as the forces $\mathbf{F}_\alpha$ themselves, and sometimes with a different sign, thus obscuring the amounts and directions of the forces on the different neighbor shells of Pd atoms around the H atom. By omitting the $\delta f_{n\mathbf{k}}$ contributions according to the perceptions of the present paper the resulting forces $\mathbf{F}_\alpha$ show a decay behavior of shorter range. The reanalyzed data for Pd_nH , together with new results for Nb_nH supercells ($n = 2, 4, 8$, and 16), will be presented in a forthcoming publication.⁸

Needs *et al.*⁹ argued that using the Gaussian-broadening scheme with E_B according to Eq. (2.4) for total-energy calculations of crystals should be inconsistent with the corresponding Schrödinger equation for the electronic Bloch states. Instead of E_B they recommend to use E_S of Eq. (2.2) with the occupation numbers of Eq. (2.7). Thus ΔE , which makes the energy functional variational, is omitted. The consistency of the energy functional E_0 and the Schrödinger equation can be demonstrated for the Gaussian broadening in the same way as Gillan recently showed it for the Fermi broadening.¹⁰ With the argumentations in Refs. 2 and 10 and the present paper we think that their objection is disproved.

III. DERIVATION OF ΔE IN THE WAY OF WEINERT AND DAVENPORT

In this short section we rederive ΔE of Eq. (2.9) following the way described by Weinert and Davenport.² According to the Eqs. (8)–(10) in Ref. 2 we need the occupation numbers f_i as functions of the eigenvalues ε_i ,

$$f_i = f_i(\varepsilon_i) , \quad (3.1)$$

and the inverse function,

$$\varepsilon_i = \mathcal{F}_i(f_i) . \quad (3.2)$$

The additional energy term ΔE is then given by

$$\Delta E = \sum_i \int^{f_i} \mathcal{F}_i(\tilde{f}_i) d\tilde{f}_i . \quad (3.3)$$

In the Gaussian-broadening method no simple analytical expression exists for the inverse function of the complementary error function [Eq. (1.2)]. However, the problem can be circumvented¹¹ with a substitution of the integration over f_i in Eq. (3.3) by an integration over the ε_i obeying Eq. (3.1) and Eq. (3.2):

$$\Delta E = \sum_i \int^{\varepsilon_i} \tilde{\varepsilon}_i \frac{df_i}{d\tilde{\varepsilon}_i} d\tilde{\varepsilon}_i . \quad (3.4)$$

Integrating by parts and choosing the integration constant $C_0 = \mu Z$ for number-conserving changes we finally obtain again ΔE according to Eq. (2.9).

IV. SUMMARY

In this paper we have shown that the density-functional energy with the Gaussian broadening⁴ is variational with respect to fractional occupation numbers. In the calculation of forces contributions due to changes in the occupation numbers vanish completely. The relation to a recent paper of Weinert and Davenport² has been illustrated, and an energy term ΔE for the Gaussian broadening, which is as simple as for the Fermi broadening,² has been derived.

ACKNOWLEDGMENTS

One of the authors (C.E.) would like to thank J. Furthmüller and K. Hummler for helpful discussions. This work was supported by the NATO Collaborative Research Grant No. 910439. The Ames Laboratory is operated for the U.S. Department of Energy by the Iowa State University under Contract No. W-7405-ENG-82.

APPENDIX

In this appendix, the validity of Eq. (2.14) for any broadening function $\mathcal{F}(x)$, which decays reasonably fast around $x = 0$, is shown for E_B of Eq. (2.4), with $\mathcal{D}$ given by [cf. Eq. (2.6)]:

$$\mathcal{D}(\varepsilon) = \sum_i \mathcal{F}(\varepsilon - \varepsilon_i) \quad , \quad (\text{A1})$$

and the f_i defined by [cf. Eq. (2.7)]:

$$f_i = \int_{-\infty}^{\mu} \mathcal{F}(\varepsilon - \varepsilon_i) d\varepsilon \quad . \quad (\text{A2})$$

Consider some variation with respect to a parameter λ , e.g., a displacement of atoms, that causes the ε_i and μ to change. The change in E_B is then

$$\begin{aligned} \frac{\partial E_B}{\partial \lambda} &= \sum_i \frac{\partial}{\partial \lambda} \int_{-\infty}^{\mu} \varepsilon \mathcal{F}(\varepsilon - \varepsilon_i) \\ &= \sum_i \int_{-\infty}^{\mu} \varepsilon \left(-\frac{\partial}{\partial \varepsilon} \mathcal{F}(\varepsilon - \varepsilon_i) \right) \frac{\partial \varepsilon_i}{\partial \lambda} d\varepsilon \\ &\quad + \sum_i \frac{\partial \mu}{\partial \lambda} \mu \mathcal{F}(\mu - \varepsilon_i) \quad . \end{aligned} \quad (\text{A3})$$

Integrating by parts and using Eq. (2.5) with

$$\frac{\partial Z}{\partial \lambda} = 0 \quad (\text{A4})$$

we finally obtain

$$\frac{\partial E_B}{\partial \lambda} = \sum_i f_i \frac{\partial \varepsilon_i}{\partial \lambda} \quad (\text{A5})$$

for any “well-behaved” broadening function $\mathcal{F}(x)$.

¹ P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, *ibid.* **140**, A1133 (1965).

² M. Weinert and J. W. Davenport, Phys. Rev. B **45**, 13 709 (1992).

³ G. Lehmann and M. Taut, Phys. Status Solidi B **54**, 469 (1972).

⁴ C.-L. Fu and K. M. Ho, Phys. Rev. B **28**, 5480 (1983).

⁵ K. M. Ho, C.-L. Fu, and B. N. Harmon, Phys. Rev. B **28**, 6687 (1983).

⁶ K. M. Ho, C. Elsässer, C. T. Chan, and M. Fähnle, J. Phys.

Condens. Matter **4**, 5189 (1992).

⁷ C. Elsässer, K. M. Ho, C. T. Chan and M. Fähnle, J. Phys. Condens. Matter **4**, 5207 (1992).

⁸ C. Elsässer, M. Fähnle, L. Schimmele, C. T. Chan, and K. M. Ho (unpublished).

⁹ R. J. Needs, R. M. Martin, and O. H. Nielsen, Phys. Rev. B **33**, 3778 (1986).

¹⁰ M. J. Gillan, J. Phys. Condens. Matter **1**, 689 (1989).

¹¹ J. Furthmüller (private communication).