RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 45, NUMBER 19 15 MAY 1992-I

## Rapid Communications

# Energy versus free-energy conservation in first-principles molecular dynamics

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(Received 14 January 1992; revised manuscript received 26 February 1992)

In applying first-principles molecular dynamics to metals, a fictitious temperature is usefully assigned to the electronic (Fermi-Dirac) occupation functions. This avoids instabilities associated with fluctuations in these occupations during the minimization of the energy density functional. Because these occupations vary with the ionic motion, they give rise to an extra contribution in addition to the usual Hellmann-Feynman forces. If this extra force is omitted, energy is not conserved. We point out, however, that ionic kinetic energy plus electronic free energy *is* conserved, and argue that this yields a sensible and realistic conservative dynamics.

The Hohenberg-Kohn theorem of density-functional theory[1] (DFT) was generalized to finite temperatures $T_{\mathrm{el}}$ in 1965 by Mermin.[2] Although this was an important result, practical applications have been rare. Recently, however, the interest in applications of finite-temperature DFT has been renewed[3] in the context of first-principles molecular dynamics (FPMD).[4-6] This method combines a density-functional calculation of forces and stresses with a classical molecular dynamics for the ionic motion.

The first and most common FPMD scheme is the Car-Parrinello[4] (CP) method. The original formulation for semiconductors used (quite appropriately) was the $T_{\mathrm{el}}=0$ DFT energy, even when the ionic temperature $T_I$ was as large as 1000 K. However, more recent applications to metals benefit by using $T_{\mathrm{el}}>0$ Fermi-Dirac occupations $f_i$ for electron orbitals[6] (single-particle wave functions $\psi_i$ and energies $\varepsilon_i$). The reason does not have much to do with the possible nonzero temperature of the simulation. Instead, the motivation is to avoid discontinuous changes in the orbital occupations when these states cross the Fermi level, a feature which does not plague a semiconductor calculation.

Recently developed FPMD algorithms[7-9] perform self-consistent calculations at every MD time step and these time steps are at least 1 order of magnitude larger than in the CP method. This strategy retains the difficulty of reaching self-consistency in the presence of a small gap: Because of the Fermi surface sharpness in the zero-temperature formalism, state occupancies oscillate and may enter an endless loop rather than converging to a self-consistent solution. The natural way to resolve this difficulty is to allow partial occupations of the Kohn-Sham orbitals. This is a practical and effective procedure which can be traced back in the literature of conventional electronic structure calculations,[10] and has also proved effective when combined with CP types of approaches.[6]

Pedersen and Jackson[11] have recently noticed that when the $T_{\mathrm{el}}>0$ formulas are used in the computation of the Kohn-Sham charge density $\rho$ and in the eigenvalue sum term $(E_B)$ of the total energy,

$$E_B=\sum_i \varepsilon_i f_i\,, \tag{1}$$

$$\rho(r)=\sum_i |\psi_i(r)|^2 f_i \tag{2}$$

(where $\psi_i$ and $\varepsilon_i$ are eigenvectors and eigenvalues), then there is a difficulty in the calculation of the force $\mathbf{F}_\alpha$ acting on the $\alpha$ ion. In order to conserve the total dynamical energy $E=K_I+U$ along the classical ionic trajectory, one must take the total derivative of the Kohn-Sham energy $U=U[\rho(\mathbf{r})]$ by atomic position, including changes in $U$ caused by changes in the occupancy $f_i$. Since the Kohn-Sham functional with variable occupations is not variational with respect to these occupation numbers $(\partial U/\partial f_i\neq 0)$, a new term arises in the forces. The true energy-conserving force $\mathbf{F}'_\alpha$ which appears in the Lagrange or Hamilton equations of motion is

$$\mathbf{F}'_\alpha \equiv -\nabla_\alpha U = \mathbf{F}_\alpha - \sum_i \frac{\partial U}{\partial f_i} \frac{\partial f_i}{\partial(\varepsilon_i - \mu)} \nabla_\alpha(\varepsilon_i - \mu) , \quad (3)$$

where $\mathbf{F}_\alpha$ is the force that would have been found if occupations had been held fixed, and which obeys (in an exact calculation) the Hellmann-Feynman theorem. The last term above vanishes in a $T_{\mathrm{el}}=0$ semiconductor calculation (because $\partial f/\partial \varepsilon = 0$), but at $T_{\mathrm{el}} > 0$ is a new term in the force.

The question then arises whether it is either necessary or worthwhile to use the energy-conserving form (3) when performing FPMD. In this paper we offer the answer "no." We find a plausible argument for using the Hellmann-Feynman part $\mathbf{F}_\alpha$ alone, and we find a good conservation law to replace $K_I + U$. Specifically, the quantity conserved when Hellmann-Feynman forces are used in $K_I + \Omega$, where $\Omega$ is the Mermin free energy[12]

$$\Omega = U - T_{\mathrm{el}} S , \quad (4)$$

$$S = -k_B \sum_i [f_i \ln f_i + (1 - f_i) \ln(1 - f_i)] . \quad (5)$$

Here $U$ is the ordinary DFT energy, except with the $T_{\mathrm{el}} > 0$ modifications of Eqs. (1) and (2). Mermin's formulation of DFT for $T_{\mathrm{el}} > 0$ generalizes the Hohenberg-Kohn-Sham theorems of $T_{\mathrm{el}}=0$ DFT by showing that the true charge density $\rho(\mathbf{r})$ at $T_{\mathrm{el}} > 0$ is the one which minimizes $\Omega$ and that the minimum value of $\Omega$ [i.e., when $\Omega$ is stationary with respect to both $\rho(\mathbf{r})$ and $f_i$] is the exact thermodynamic free energy. The property of being stationary with respect to $f_i$ makes the gradient of the free energy just equal to the Hellmann-Feynman forces,

$$\mathbf{F}_\alpha = -\nabla_\alpha \Omega . \quad (6)$$

That is, the extra piece of $\mathbf{F}'_\alpha$ disappears when the entropy term is included. This establishes the simple conservation law $K_I + \Omega$ for the Hellmann-Feynman forces.

Our proposal differs from the "pseudoenergy" trick of Pederson and Jackson.[11] Their proposal is meant to keep the Kohn-Sham functional variational even in the presence of fractional occupations and is strictly a $T_{\mathrm{el}}=0$ formulation. Since the Mermin functional maps into the Kohn-Sham at $T_{\mathrm{el}}=0$, it is not obvious that these two approaches are equivalent; however, both schemes eliminate the same undesirable instabilities, one at $T_{\mathrm{el}}=0$ and the other (Mermin) at $T_{\mathrm{el}}$ necessarily finite.

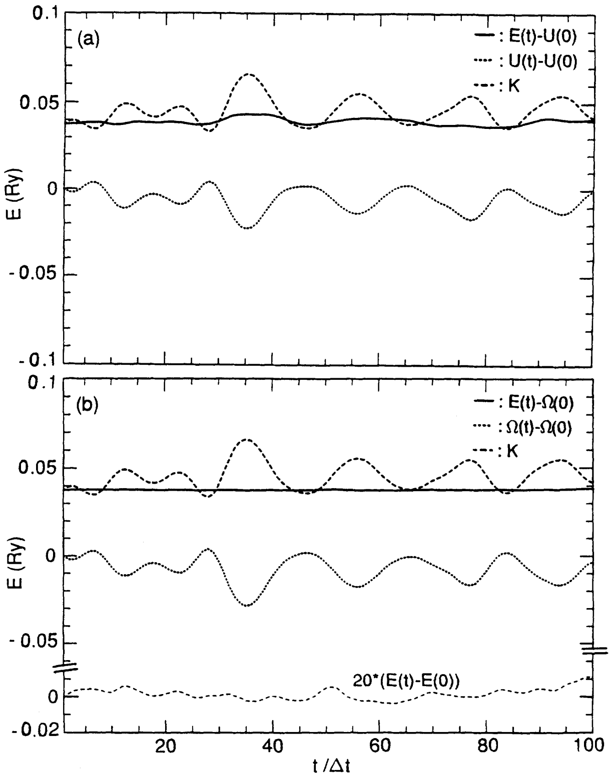

FIG. 1. Kinetic ($K_I$) (dashed lines), and changes in "potential" (dotted lines) and total (solid lines) energies ($E$) for a heated bcc solid of Li described by a supercell containing 16 atoms equilibrated at $T_I \sim 350$ K (lattice constant $a = 3.023$ Å). In (a), $E(t) = K_I(t) + U(t)$, where $U$ is the Kohn-Sham energy [except with the $T_{\mathrm{el}} > 0$ modifications of Eqs. (1) and (2)], while in (b) $E(t) = K_I(t) + \Omega(t)$, where $\Omega(t)$ is the Mermin free energy. The lowest dashed line in (b) shows the noise and drift in the total energy magnified 20 times. The time steps are equal to 200 a.u.

Figure 1 is a numerical demonstration of these conclusions. We have calculated classical trajectories for a heated solid of bcc Li equilibrated at $T_I = 350$ K. The algorithm and its parameters are the same as those described in previous publications.[7,13] The solid was described by a supercell containing 16 atoms (with periodic boundary conditions). If the ions had been stationary in the perfect bcc lattice, and only the $\Gamma$ point of the Brillouin zone had been sampled, then there would have been six degenerate states at the Fermi level and only one electron to be shared among them. When the ions are thermally displaced from the equilibrium position, the degeneracy between the states is removed and, at $T_I = 350$ K, a splitting $\delta\varepsilon \leq 10^{-2}$ eV is produced among them. If one of these states is fully occupied while the others are empty, then, for a fixed arrangement of atoms, the self-consistent cycle enters in the endless loop previously described. To achieve self-consistency in this example we have introduced partial occupations corresponding to $T_{\mathrm{el}} = 600$ K in the distribution function $f_i$.

The dynamics has been generated by calculating self-consistent Hellmann-Feynman forces $-\nabla_\alpha \Omega$. We have plotted in Fig. 1(a) the kinetic energy and the changes in potential ($U$) and total energies ($E = K_I + U$) as functions of time. The fluctuations in the total energy depend directly on the temperature $T_{\mathrm{el}}$ of the electronic system. $T_{\mathrm{el}}$ may be, but does not have to be, related to the average ionic temperature $T_I = (2/3k_B)K_I$. $T_{\mathrm{el}}$ can be chosen arbitrarily provided it eliminates instabilities within the self-consistency algorithm. In this example the fluctuations of $E$ are approximately equal to 10% of the average ionic kinetic energy and therefore not negligible. They could be decreased by lowering the electronic temperature, but only up to a certain point, because below $T_{\mathrm{el}} \approx 150$ K the self-consistent cycle becomes unstable. Figure 1(b) displays the enforcement of the new conservation law ($E = K_I + \Omega$) associated with the Hellmann-Feynman forces. The data were generated in the same run which produced Fig. 1(a), except that now $\Omega$ includes the entropy contribution.

Finally, it is appropriate to ask whether there is any reason to accept the realism of trajectories governed by the Hellmann-Feynman algorithm as opposed, for example, to trajectories which conserve $K_I + U$. Naively it might appear that the latter is the correct conserved energy. However, the additional (non-Hellmann-Feynman) force $\mathbf{F}' - \mathbf{F}$ derives from the variation of the $T_{\mathrm{el}} > 0$ occupation numbers with particle displacement. This does not represent correctly the actual microscopic dynamics. The actual time evolution of electron occupancies is described by a time-dependent Schrödinger equation; the Born-Oppenheimer (adiabatic) approximation changes this to a sequence of time-independent Schrödinger equations. An additional statistical hypothesis enters when the occupancy is chosen to be $f_i(T_{\mathrm{el}})$. There is no reason to believe that the Kohn-Sham $U$ with statistical occupancies $f_i$ correctly describes the true nonadiabatic evolution of electronic wave functions. However, if a statistical temperature dependence is forced by practical necessity, then both thermodynamics and the Mermin theorem[2] tell us that it is the free energy $\Omega$ rather than the internal energy $U$ whose minimization fixes the equilibrium behavior. Therefore, $-\nabla_\alpha \Omega$ should indeed be the right way to calculate the force.

*Note added.* After our manuscript was submitted, we learned of work by Weinert and Davenport,[14] which offers a somewhat different justification for use of the Mermin functional, and also offers a recipe to build alternative functionals for use with other occupancies than Fermi-Dirac.

This work was supported in part by the Division of Materials Sciences, U.S. Department of Energy, under Contract No. DE-AC02-76CH00016, and by a grant of computational time at the National Energy Research Supercomputer Center (NERSC), Livermore, CA. J.L.M. acknowledges a computer time grant from the Minnesota Supercomputer Institute.

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