PHYSICAL REVIEW B VOLUME 40, NUMBER 11 15 OCTOBER 1989-I

# First-principles molecular dynamics for metals

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(Received 22 March 1989; revised manuscript received 9 June 1989)

A Car-Parrinello-type first-principles molecular-dynamics approach capable of treating the partial occupancy of electronic states that occurs at the Fermi level in a metal is presented. The algorithms used to study metals are both simple and computationally efficient. We also discuss the connection between ordinary electronic-structure calculations and molecular-dynamics simulations as well as the role of Brillouin-zone sampling. This extension should be useful not only for metallic solids but also for solids that become metals in their liquid and/or amorphous phases.

Recently, Car and Parrinello[1] have proposed a new technique for molecular-dynamics simulations which does not require pair (or other) potentials as input. Rather the ion-ion interactions are calculated in an *ab initio* fashion using the (local)-density-functional theory in conjunction with the Hellmann-Feynman theorem. Most of the systems[2] studied with this method to date have been insulators or semiconductors in their solid phases where there is a gap at the Fermi level. This results in an important simplification because it is known in advance what the occupancy of the various states will be.

We are interested in studying ordinary metals such as sodium or aluminum and have had to contend with the possibility of nearly degenerate states at the Fermi level $E_F$. In addition, in metals it frequently happens that during the course of the calculation a level moves through $E_F$. Therefore some sort of dynamic change in the occupancy of the level is needed. The purpose of this paper is to point out a fairly simple and fast algorithm for including partial occupations of states which we believe will greatly benefit the Car-Parrinello method. The main attractions of the Car-Parrinello approach with pseudopotentials and a plane-wave basis are (i) the ability to calculate forces from first principles, (ii) the simultaneous updating of ionic and electronic coordinates[3] (global simulation instead of a local one), and (iii) the use of iterative diagonalization of the occupied subspace techniques that avoid the need to diagonalize large matrices.

In this paper we describe (a) our technique for calculating the electronic structure of metallic systems with a Car-Parrinello-type approach, (b) an efficient algorithm for calculating the electronic structure during an "electronic quench," and (c) how to carry out molecular dynamics for metals with this first-principles approach.

In brief, our test system is a unit cell of 16 sodium atoms with periodic boundary conditions. The density is taken to be 0.93 g/cm$^3$, which is the experimental density of sodium at its normal melting temperature of 371 °K. Kohn-Sham orbitals are expanded in plane waves with an energy cutoff of 9 Ry, resulting in 1100 plane waves at the sampling $\Gamma$ point. The pseudopotential used here is a seminonlocal one[4] with $s$ nonlocality. This system is an ideal test case for metals since for $\Gamma$ there are six degenerate states (with two electrons in them) at the Fermi level when the atoms are in their perfect bcc positions.

Before starting molecular dynamics (MD), one must "quench" the electrons to the self-consistent ground state for a given configuration of the atoms. If during the MD simulation, the electrons move off the Born-Oppenheimer surface substantially, a quench with the ions frozen will again be necessary. For metals, treating both occupied and unoccupied states by including the Fermi occupations is both physically and computationally desirable: if one does not allow for partial occupation of states near $E_F$, the convergence may be very slow, diverge, or as in Fig. 1, continue to oscillate. In addition, in cases of de-

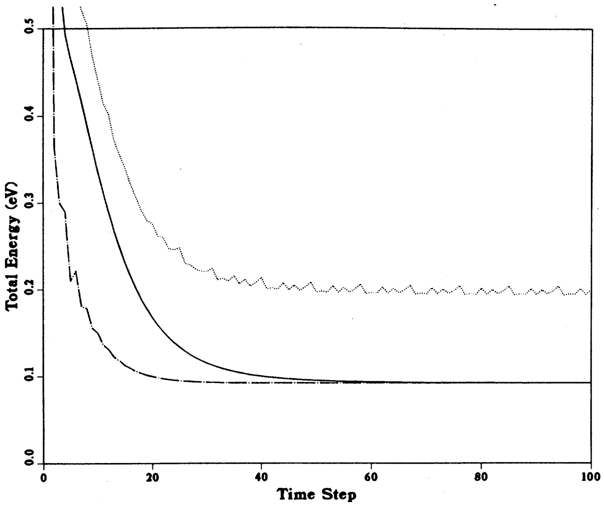

FIG. 1. Various iterative schemes for calculating the total ground-state energy of unit cell of 16-Na atoms. The dashed line shows the total energy using the improved algorithm discussed in the text, the solid line is for the steepest-descent algorithm of Ref. 6, and the dotted line (shifted up by 0.1 eV for clarity) is for the Car-Parrinello steepest descent used according to the original scheme, without diagonalizing the $\Lambda$ matrix and without using the Fermi functions. Note that the last curve does not converge during the 100 time steps.

generacies, not allowing partial occupation can lead to symmetry breaking.

To show how to build in the Fermi-Dirac statistics and reach self-consistency rapidly, we proceed as follows. The problem may be expressed as an iterative way to find the eigenstates and eigenvalues of a Hamiltonian self-consistently. The Kohn-Sham procedure of obtaining single-particle equations with orthonormality constraints is often given as

$$\frac{\delta E}{\delta\psi_i^*}=H\psi_i=\sum_j \lambda_{ij}\psi_j \ . \tag{1}$$

The difficulty in treating metals using Eq. (1) is that the force $\delta E/\delta\psi_i^*$ is apparently zero for an unoccupied state. (The change in density, and hence total energy, is zero for changes in the unoccupied states.) However, the Hamiltonian operator $H$ is a Sturm-Liouville operator with a complete spectrum—both occupied and unoccupied levels—regardless of the occupation numbers $f_i$. The formally correct extension is to take the variation with respect to $f_i\psi_i^*$, i.e.,

$$\frac{\delta E}{\delta(f_i\psi_i^*)}=H\psi_i=\sum_j \lambda_{ij}\psi_j \ . \tag{1$'$}$$

This distinction is important in treating metals since now the "virtual" force $\delta E/\delta(f_i\psi_i^*)$ is independent of $f_i$ and is well defined for both the occupied and unoccupied states. This same connection between the wave functions and the operator $H$ underlies the calculation of metals in standard electronic-structure methods.

Assigning an occupation $f_i$ to a state $\psi_i$ is not meaningful unless the $\Lambda(=\lambda_{ij})$ matrix is diagonalized and its eigenvectors are used to do a proper unitary transformation of the $\psi$'s. If $U\,(=u_{ij})$ is the matrix of the eigenvectors of $\Lambda$, then the correct eigenstates are given by

$$\psi_i'=\sum_j u_{ij}^{\dagger}\psi_j \tag{2}$$

and the weights $f_i$ should be assigned to these new states. We use a Fermi function

$$f_i=\frac{w_i}{1+\exp[(\varepsilon_i-E_F)/k_BT]} \tag{3}$$

to determine the weights near $E_F$, where $\varepsilon_i$ is the $i$th eigenvalue of the $\Lambda$ matrix, $w_i$ is a weight factor to account for the Brillouin-zone summation, and $k_BT$ is a thermal width typically 1–2 mH. We also note that in the most general case, the Kohn-Sham total energy expression with weight $f_i$ assigned to $\psi_i$ (rather than $\psi_i'$) may not even be variational. For the special case when the $f_i$'s are independent of $i$, it can be shown that the states $\{\psi_i\}$ yield the correct density. If, however, eigenvalues fall near $E_F$ or if there are accidental or near-accidental degeneracies present during the MD simulation, then partial occupations should be used. While the occupation numbers can be thought of as another set of constraints that enter the Lagrangian of Ref. 1, implementing them in such an approach is difficult both in practice and principle.

We have also devised an updating scheme for the electronic coordinates, which runs faster than the reported algorithms[1,5,6] for a number of test cases. This extension of the steepest-descent algorithm of Ref. 6 gives the updated electronic coefficients, $C_i(\mathbf{G})$, as

$$C_i^{t+\Delta t}(\mathbf{G})=C_i^t(\mathbf{G})-\left[\frac{\beta_1[1-\exp(-\omega^2 n\Delta t)]+\beta_2[1-\exp(-\omega^2\Delta t)]}{\omega^2}\right]\left[\frac{\delta E}{\delta C_i^{t*}(\mathbf{G})}-\lambda_{ii}C_i^t(\mathbf{G})\right] . \tag{4}$$

Here, $\omega^2=\omega^2(\mathbf{G})$ represents a diagonal as defined in Ref. 5 (except there is no $\mu$), the $\beta$'s can be thought of as parameters to mix the two steepest-descent solutions, and $\Delta t$ and $n\,\Delta t$ are two different time steps. The trick here is to add two (or more) steepest-descent-type solutions using different time steps during an electronic quench. The smaller (larger) time step controls the descents in the initial (final) stages of the iterative scheme. The important point is that the time step in an electronic quench does not have any physical meaning and hence can be manipulated effectively to suit the optimization process; Eq. (4) is only one way of improving the scheme proposed in Ref. 6.

During the quench, we also mix the new density that is calculated from the new (updated, orthonormalized using the Gram-Schmidt process and transformed) coefficients with the density from the previous time step. In Fig. 1, we compare this method to direct steepest descent and also to the case without self-consistent partial occupations for a typical electronic quench of the 16-Na-atom unit cell. The algorithm of Payne *et al.*[5] fails to converge here even with the correct self-consistent partial occupations and hence is not shown. For these 16-Na atoms near their perfect bcc positions and using only the $\Gamma$ point, there are unoccupied states around $E_F$. The correct self-consistent solution cannot be obtained if integral occupations are used starting from our initial state. As shown in Fig. 1, there are oscillations in the total energy that do not go away even after 100 time steps, while with the correct occupations the quench is completed within 40–50 time steps. Our improved steepest descent also saves about 40–50 % in computer time compared to the direct steepest suggested in Ref. 6 for the present case.

To make the connection between electronic-structure calculations and MD simulations, we invoke the Born-Oppenheimer approximation. If we define a Lagrangian consisting of the ionic kinetic energy and a potential given by the ground-state electronic total energy as a function of the ionic coordinates, then clearly the total energy of the electrons and (classical) ions is conserved. The resulting equations of motion of the ions (with the forces given via the Hellmann-Feynman theorem) will generate the physical trajectories if the Born-Oppenheimer approximation is valid. (If it is not valid, both electronic and ions must be treated quantum mechanically and then the Hellmann-Feynman theorem cannot be used to obtain the forces.) As is the case in any microcanonical MD simulation, the degree to which the total energy is actually conserved depends on how accurately the various equations are solved numerically.

In our approach to first-principles MD, we demand that the electrons are on the Born-Oppenheimer surface (BOS); *any* numerical technique (e.g., fictitious dynamics,[1] perturbation expansions, or second variations) that yields the instantaneous ground-state electron wave functions can be used to update the electronic degrees of freedom. In practice, during the MD simulation we calculate the $\Lambda$ matrix ($\equiv\langle\psi_j|H|\psi_i\rangle$) and then use the diagonal elements to determine $E_F$ and the partial occupations $\{f_i\}$. If needed, one can diagonalize the $\Lambda$ matrix and make the unitary transform as done during the quench, but we find it faster and more convenient to avoid this since the off-diagonal elements of the $\Lambda$ matrix are small. There is no density mixing during the MD runs. Finally, we use the Verlet algorithm[7] (or other algorithms such as Beeman[8]) to update (extrapolate) both the ionic and the electronic coordinates.

In Fig. 2 we show a typical MD run for the 16-Na-atom unit cell. To extrapolate the electron wave functions, we used a fictitious electronic mass $\mu=100$ and $\Delta t=5$ (in atomic units; see also Ref. 1 for details pertaining to $\mu$). The simulation was started with the atoms near the perfect bcc positions and the partial occupancies were $\approx\frac{1}{3}$ for each of the six nearly degenerate states near $E_F$ at $\Gamma$. After 800 time steps—during which the occupations change continually due to crossings at $E_F$—each $f_i$ changed by about 0.1 for these six states. The total energy is conserved although, since the system is not yet in equilibrium, the kinetic energy (i.e., the temperature) of the ions dropped by about 120 K and the Kohn-Sham potential energy increased. This simulation shows that it is possible to carry out MD calculations using Car-Parrinello-type techniques for systems without gaps in their electronic band structure at $E_F$ with little or no increases in the computational time.

Formally, we consider the evolution of the BOS electrons to be determine by the *real* time-dependent Schrödinger equation rather than by a fictitious Lagrangian: The wave functions at times $t$ and $t_0$ are related by the (unitary) time evolution operator $U(t,t_0)$

$$|\psi(t)\rangle=U(t,t_0)|\psi(t_0)\rangle\ , \tag{5}$$

where $U(t,t_0)$ satisfies

$$\frac{d}{dt}U(t,t_0)=-\frac{i}{\hbar}H(t)U(t,t_0)\ , \tag{6}$$

$$U(t_0,t_0)=1\ , \tag{7}$$

$$U(t,t_0)=1-\frac{i}{\hbar}\int_{t_0}^{t}H(t')U(t',t_0)dt'\ . \tag{8}$$

If $H$ were independent of time, Eq. (8) would reduce to the familiar $\exp(-iHt/\hbar)$. In the present case, $H$ does depend on time through the implicit dependence on the time-dependent wave functions and the ionic positions. If changes in occupation numbers are handled consistently—a necessary condition—then in principle the electrons evolving via Eqs. (5)–(8) will remain on the BOS. Approximations to the integral equation for $U(t,t_0)$ clearly involve the virtual force of Eq. (1′). Our formulation suggests that new efficient algorithms taking into account the physics underlying Eqs. (5)–(8) are possible; we are currently investigating some.

Molecular-dynamics simulations for metals can also be done treating only the (discrete) occupied states, but then when the occupations of the electronic states change, there is a rather rapid rise of the electrons off the BOS and the total energy is no longer conserved. This is demonstrated in Fig. 2 where the total energy for a MD run with identical initial conditions, but considering the "occupied subspace only," is also shown. (Systems that do not have nearly degenerate states at $E_F$ may not show such large changes during times possibly orders of magnitude longer.) The increase is easily understood from Eqs. (5)–(8): Including only the occupied states requires that the wave functions change *discontinuously* as levels cross $E_F$ whereas the true time evolution given by $U(t,t_0)$ is

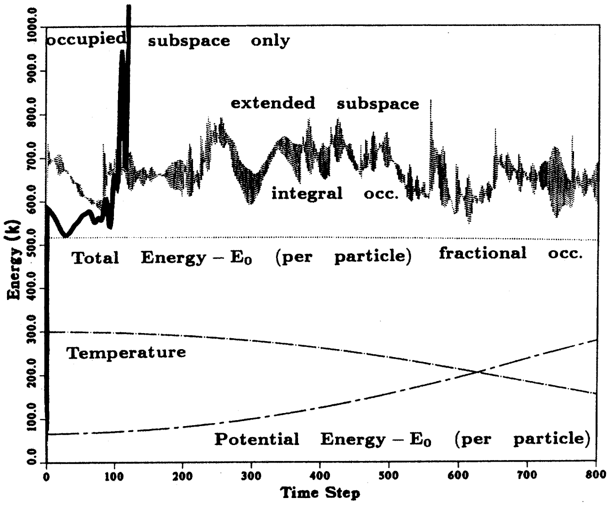

FIG. 2. Total energies per particle (relative to $E_0=-74\,700$ K) for typical microcanonical MD runs of the 16-Na unit cell using either the "extended subspace" (extra unoccupied electronic levels included) with (a) fractional and (b) integral occupations, or (c) the "occupied subspace only" (only the states occupied at $t=0$ are included in the simulations). Also shown for case (a) are the temperature (starting at 300 °K) and the Kohn-Sham potential energy. All runs had the same initial conditions, same total energy at the first time step, and were not quenched during the MD runs. Note that the total energy (a) is conserved for fractional occupations, (b) fluctuates about an average (higher) energy for integral occupations, and (c) goes off scale for the "occupied subspace only." Clearly (c) requires frequent quenches while for (a) no quenches are necessary during the time interval shown.

continuous. These discontinuities necessitate more frequent quenches; in cases were the symmetry of the states differ, even a quench will not recover the correct states since the occupied and unoccupied states belong to orthogonal representations. Including Fermi-Dirac occupations and unoccupied states as suggested here greatly reduces such problems.

Finally, we point out the role of Brillouin-zone sampling in these types of calculations. Since the underlying assumption in any first-principles MD method is the validity of the Born-Oppenheimer approximation, one is in principle doing a standard electronic-structure calculation at each time step to get the electronic density which in turn defined the forces on the ions. As is well known from general symmetry arguments, the wave functions for a system consisting of $N$ unit cells with periodic boundary conditions are labeled by $N$ distinct $k$ points in the first Brillouin zone. Thus there is a one-to-one relationship between the number of $k$ points sampled and the *total* number of unit cells (and atoms) in the system, i.e., $k$-point sampling is a form of finite-size scaling *but with constraints* on the ionic configuration. Since the internal order (or disorder) does not enter into the symmetry arguments, these comments are applicable to models of crystalline and amorphous solids, as well as liquids, that use finite-size cells with periodic boundary conditions.

For example, consider a large unit cell and the single $k$ point $\Gamma$. If there are an even number of electrons in the cell, then except possibly for degeneracies, the discrete one-particle density of states (DOS) will have a gap at $E_F$ (an insulator). By increasing either the number of atoms in the unit cell or the number of $k$ points, one is effectively changing the total number of atoms in the system, and not surprisingly, the DOS also. For the case of the $\Gamma$ point and a 54-atom unit cell of Na atoms at their perfect bcc positions, there will be a gap ($\sim 1$ eV) at $E_F$. (For the 16-atom cell there are degenerate levels at $E_F$.) Obviously, one should not conclude from the 54-atom cell that Na is an insulator, but rather that the DOS obtained from small $k$-point samplings must be interpreted with care. General experience, however, has shown that $k$-point samplings which are inadequate for a faithful representation of the DOS can still provide accurate integral properties such as total energies and charge densities. The accuracy of ensemble averages (calculated as temporal averages) depends on the accuracy of the spatial ($k$-point) averages for each time step, except in the special case that temporal and spatial averages are equivalent. In a strongly diffusing system, i.e., a liquid, this last assumption may be satisfied well enough that reasonable DOS can be obtained from small ($\sim 100-1000$-atom) systems; where there is no diffusion (both crystalline and amorphous solids), accurate DOS may be difficult to obtain in this way.

In conclusion, we have presented an extension of the Car-Parrinello ideas to systems with partially occupied electronic states, both for the electronic quench and molecular dynamics. As we have pointed out, there is a direct connection between these types of methods and standard electronic-structure calculations; thus both, in principle, should give identical answers. An independent approach for calculating the (occupied) electronic states for metals has recently been proposed,[9] but that paper does not consider the MD aspects of the technique. We have demonstrated that our proposed method works in practice for a test case that has all the difficulties associated with partially occupied near-degenerate states at the Fermi level. The results of a MD simulation for a 54-atom unit cell of sodium will be reported elsewhere.[10]

We thank R. E. Watson, P. B. Allen, J. Q. Broughton, and R. Car for useful discussions and R. Car and M. Parrinello for kindly providing their program. This work was supported by the Division of Materials Sciences, U. S. Department of Energy, under Contract No. DE-AC02-76CH00016 and by a grant of computer time at the National Magnetic Fusion Energy Computing Center, Livermore, California.

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