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In a recent paper [1], M C Payne has analysed the method originally introduced by two of us to perform molecular dynamics simulations with interatomic forces derived directly from the electronic ground state [2]. However the equations quoted in [1] do not correspond entirely to the original procedure. For this reason we have decided to write a joint comment in order to outline the differences and explain the consequences.

We restate briefly the terms of the discussion. In a molecular dynamics simulation, classical trajectories for the nuclei (or the ions in a pseudopotential formulation) are obtained by solving the set of Newton's equations of motion that can be derived from the Lagrangian

$$\mathcal{L}_I = K_I - \Phi(\{R_I\}) \tag{1}$$

Here $K_I = \sum_I \frac{1}{2} M_I \dot{R}_I^2$ is the kinetic energy of the ions and $\Phi(\{R_I\})$ is their potential energy. M_I and R_I are ionic masses and positions, respectively. According to the Born–Oppenheimer approximation Φ is related to the instantaneous electronic ground state, i.e. within density-functional theory:

$$\Phi(\{R_I\}) = \min_{\{\psi_i\}} E[\{\psi_i\}, \{R_I\}] \tag{2}$$

Here E is the Kohn–Sham energy functional and $\{\psi_i\}$ are a set of occupied orthonormal single-particle orbitals in terms of which the ground-state electronic charge density is $n(r) = \sum_I |\psi_I(r)|^2$. The term E contains the ground-state quantum energy of the electrons as well as the Coulomb energy of the ions. Since the Lagrangian $\mathcal{L}_I$ does not depend explicitly on time the total internal energy $U_I = K_I + \Phi(\{R_I\})$ is a constant of motion.

Rather than solving equation (2) and Newton's equations for the ions separately, a generalized purely classical Lagrangian was introduced in [2] for both electronic and ionic degrees of freedom:

$$\mathcal{L}_{eI} = K_e + K_I - E[\{\psi_I\}, \{R_I\}] + \sum_{ij} \Lambda_{ij} \left(\int dr \, \psi_I^*(r) \psi_j(r) - \delta_{ij} \right) \tag{3}$$

where $K_e = \mu \int d\mathbf{r} \mid \dot{\psi} \mid^2$ is a classical kinetic energy term associated with the electronic degrees of freedom $\{\psi_I(\mathbf{r})\}$, μ is a parameter that controls the timescale of the electronic motion and Λ_{ij} are Lagrangian multipliers that impose the orthonormality constraints between the orbitals. From equation (3) one derives the equations of motion:

$$\mu \ddot{\psi}_i = -H\psi_i + \sum_i \Lambda_{ij}\psi_j$$

$$M_I \ddot{R}_I = -\frac{\partial E}{\partial R_I}.$$

$$(4)$$

Here H is the single-particle Kohn–Sham Hamiltonian [3], and

$$\Lambda_{ij} = H_{ij} - \mu \int d\mathbf{r} \, \dot{\psi}_I^*(\mathbf{r})\dot{\psi}_j(\mathbf{r}). \qquad (5)$$

The orthonormality constraints are holonomic and the total internal energy $U_{eI} = K_e + K_I + E[\{\psi_I\}, \{\mathbf{r}_I\}]$ is a constant of motion for the trajectories generated by equations (4). In order to reproduce the physical ionic trajectories with equations (4), the fictitious electron dynamics must be characterized by frequencies much larger than those of the ions. In this case the coupling between the two subsystems (i.e. electrons and ions) is weak and, if the electrons were initially at rest in the ground state, they will follow adiabatically the ionic motion, remaining very close to the instantaneous ground state. In such a case the fictitious classical system (3) provides an efficient tool to perform MD simulations for the ions with forces that obey equation (2) without explicitly solving it at every time step. This implies that the energy $U_I' = K_I + E[\{\psi_I\}, \{\mathbf{r}_I\}]$ is approximately constant and very close to U_I. The smallest electronic frequency is of the order of $(E_g/\mu)^{\frac{1}{2}}$ [4], where E_g is the energy gap in the single-particle electronic spectrum. Since μ is a disposable parameter, one can always dynamically decouple electrons and ions for an insulating system ($E_g > 0$). When this occurs electrons and ions are not in thermal equilibrium. This is a metastable situation. However the time needed for energy equipartition between electrons and ions is larger than physical ionic relaxation times. This allows one to perform meaningful statistical averages.

Here we prove this point numerically by performing a test run on a system consisting of 16 silicon atoms with periodic boundary conditions and a plane-wave energy cut-off of 6 Ry. The ionic system was equilibrated at $T \sim 390$ K with the electrons in the ground state. The system was then allowed to evolve freely under the action of equations (4), which were numerically integrated by using the Verlet algorithm and by imposing the orthonormality constraints as discussed in [5]. In figure 1(a) we plot K_I, $E[\{\psi_I\}, \{\mathbf{r}_I\}]$ and their sum U_I'. On the scale of the picture $U_I' \approx$ constant. However if we enlarge the scale by two orders of magnitude as in figure 1(b), U_I' shows some variations. These are exactly compensated by K_e, leading to constant U_{eI} within numerical accuracy. The variations in U_I' are much smaller than the typical variations in either K_I or $E[\{\psi_I\}, \{\mathbf{r}_I\}]$. No canonical drift in U_I' is observed. This corresponds to a metastable situation in which the temperature of the electrons is much smaller than that of the ions. The lifetime of this metastable state is much longer than typical ionic relaxation times. Indeed we have continued the run for a much longer time than is shown in figure 1 and we have not observed any appreciable drift in U_I'. During the entire run K_e remained very small with no canonical drift. Since K_e measures
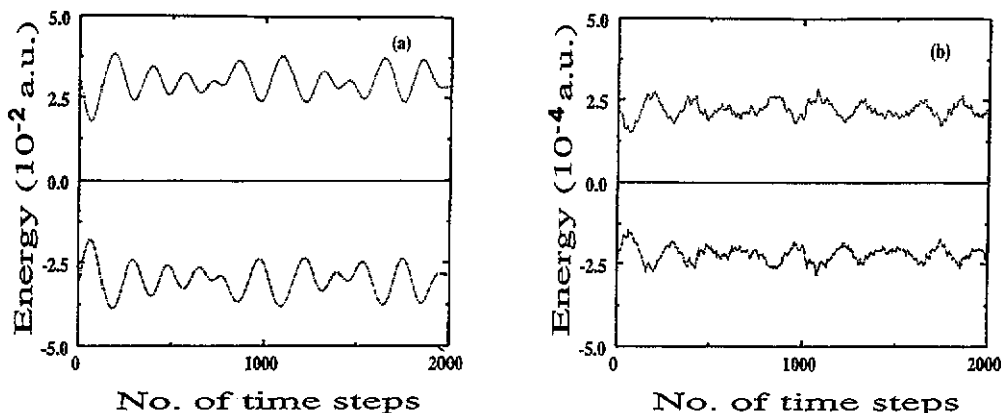
Figure 1. Time variation of electronic and ionic properties for a segment of 2000 time steps of a much longer run ($\Delta t = 7$ au, $\mu = 300$ au). (a) K_I (broken curve), $E[\{\psi_I\}, \{r_I\}]$ (chain curve), U_I' (full curve); (b) K_e (broken curve), U_I' (chain curve), U_{eI} (full curve). The parameters E, U_I', U_{eI} are measured relative to the initial value $U_{eI} = -61.62887$ au.

the deviation from the Born–Oppenheimer surface, this implies that during the run $U_I'(\{r_I\}) \approx \Phi(\{r_I\})$. We have checked numerically that this was the case. The smallness of K_e ensures adequate evaluation of the ionic forces.

The results shown in figure 1 illustrate a number of features of the Car–Parrinello method which should be noted. Firstly, the kinetic energy of the electrons is not a simple fraction of the kinetic energy of the ions as would be expected if the electrons were continuously in the instantaneous ground state. Instead the kinetic energy of the electrons shows small fluctuations on a timescale shorter than that of the ionic motion. The magnitude of these fluctuations represent the error in the electronic configuration, i.e. the distance of the electrons from the Born–Oppenheimer surface. The magnitude of these fluctuations is of the order of 2.5×10^{-5} au. Although these are extremely small, the crucial point is how these errors vary with time. This is where the equations of motion play a critical role. Provided that the timescales of the electronic and ionic systems are well separated this error remains bounded and does not increase continuously with time, at least over the timescale of a typical simulation. The second point is that a molecular dynamics calculation differs qualitatively from a simulation performed using empirical potentials. The kinetic energy of the electrons is part of the conserved total energy of the complete dynamical system in a molecular dynamics calculation. If the kinetic energy of the electrons varies with time then the energy of the ionic system would also have to vary in order to keep the total energy of the system constant. As clearly illustrated in figure 1(b) the effect of the variation in the kinetic energy of the electrons during the molecular dynamics simulation is to produce fluctuations of the order of 0.5% of the kinetic ionic energy in the total energy of the ionic system. The canonical drift is at least two orders of magnitude smaller. This is comparable with the canonical drift of conventional MD simulations. In this case, however, the instantaneous fluctuations are much smaller because they are related only to the finite time step used in the numerical integration of the equations of motion. Finally, the ionic trajectories in the molecular dynamics simulation will be modulated by the fluctuations in the electronic system. Provided that the timescales of these modulations are much shorter than ionic timescales it is expected that the average

forces acting on the ions and consequently the ionic trajectories will be accurate. In metals and other systems where $E_g \approx 0$, part of the electronic frequency spectrum will always overlap with the ionic modes. At variance with the behaviour illustrated above, this leads to much faster equilibrium and consequent departure from the BO surface. In this case, as discussed in [6], systematic electron minimizations are needed to maintain the system close to the BO surface. In addition, energy will have to be continuously supplied to the ionic degrees of freedom to make up for the energy which has been transferred to the electronic degrees of freedom. This can be done dynamically using two Nosé thermostats, one attached to the ions and the other to the electrons [7].

In [1] the equations of motion for the electrons are:

$$\mu \ddot{\psi}_i = -H\psi_i + \Lambda_i \psi_i \tag{6}$$

where

$$\Lambda_i = H_{ii} . \tag{7}$$

These equations are different from equations (4) and (5) and cannot be derived from the Lagrangian (3). As discussed in [1], they do not lead to a conservative dynamics. In addition, the Lagrangian multipliers given in (7) do not preserve orthonormality, which is enforced by a Gram–Schmidt or a similar orthonormalization procedure. As a consequence, even in the case of insulators, equations (6) do not guarantee that the electrons will remain for a long time close to the ground state when coupled to ionic motion. In order to obtain physical ionic trajectories, in all cases (insulators and metals) the dynamics must be supplemented with systematic electronic minimizations.

Since the electrons are never exactly in the ground state it is important to estimate the error in the ionic trajectories. It is well known that Hellman–Feynman (HF) forces are very sensitive even to small departures from the BO surface. The analysis in [1], based on a perturbative approach, shows that the error in the HF forces oscillates when using second-order equations for the electron dynamics. Instead, it is single-signed when using first-order equations, as for example in the steepest descent minimization approach. One has to ensure that the oscillating error averages out in a time shorter than typical ionic timescales. The perturbative analysis of [1] is strictly valid only for short time evolution. On a longer timescale one has to rely either on numerical tests or on sophisticated mathematical arguments that discuss the stability of complex dynamical systems [8]. An alternative way to perform molecular dynamics simulations based on efficient conjugate gradients minimization for the electrons to the BO surface has been recently proposed [9].

Acknowledgments

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