Molecular Dynamics and *ab Initio* Total Energy Calculations

In a recent Letter,[1] Car and Parrinello described a molecular-dynamics approach to total-energy calculations that allows global minimization of the total energy to be achieved with respect to both electronic and ionic coordinates. In this Comment, we shall briefly describe a number of modifications we have made to Car and Parrinello's method that can significantly increase the speed of the computation.

Car and Parrinello write the equation of motion (EOM) for the electronic state $\phi_{n\mathbf{k}}$ as

$$\mu \ddot{\phi}_{n\mathbf{k}}(\mathbf{r},t) = -\frac{\partial E}{\partial \phi_{n\mathbf{k}}(\mathbf{r},t)} + \sum_{n'} \Delta^{\mathbf{k}}_{nn'} \phi_{n'\mathbf{k}}(\mathbf{r},t), \tag{1}$$

where E is the total energy, $\Delta^{\mathbf{k}}_{nn'}$ are the Lagrange multipliers for the constraints of orthogonality and normalization, and μ is a fictitious mass. Car and Parrinello used the Verlet algorithm[2] to integrate the EOM and an iterative method to orthogonalize the wave functions.[3] On removal of the Lagrange multipliers for the orthogonality constraints and replacement of $\Delta^{\mathbf{k}}_{nn}$ by $\lambda_{n\mathbf{k}}$, the energy eigenvalue of the state, the EOM for the coefficient of the plane wave $\exp[i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}]$ becomes

$$\mu \ddot{c}_{n,\mathbf{k}+\mathbf{G}} = -[|\mathbf{k}+\mathbf{G}|^2 + V_{\mathbf{G}=0} - \lambda_{n\mathbf{k}}] C_{n,\mathbf{k}+\mathbf{G}} - \sum_{\mathbf{G}' \neq \mathbf{G}} V_{\mathbf{G}-\mathbf{G}'} C_{n,\mathbf{k}+\mathbf{G}'}, \tag{2}$$

where $\hbar^2/2m+1$. This is an oscillator equation with frequency $\omega = [(|\mathbf{k}+\mathbf{G}|^2 + V_{\mathbf{G}=0} - \lambda_{n\mathbf{k}})/\mu]^{1/2}$. An analytic integration of the EOM gives the coefficient $C_{n,\mathbf{k}+\mathbf{G}}$ at the next time step as

$$C_{n,\mathbf{k}+\mathbf{G}}(\Delta t) = 2\cos(\omega\Delta t) C_{n,\mathbf{k}+\mathbf{G}}(0) - C_{n,\mathbf{k}+\mathbf{G}}(-\Delta t) - 2[1-\cos(\omega\Delta t)] \frac{\sum_{\mathbf{G}'\neq\mathbf{G}} V_{\mathbf{G}-\mathbf{G}'} c_{n,\mathbf{k}+\mathbf{G}'}/\mu}{\omega^2}, \tag{3}$$

where $C_{n,\mathbf{k}+\mathbf{G}}(0)$ and $C_{n,\mathbf{k}+\mathbf{G}}(-\Delta t)$ are the values of the coefficient at the present and previous time steps, respectively. We orthogonalize the wave functions at the end of each time step by the Gram-Schmidt procedure.

When the Verlet algorithm is used to integrate the EOM, the time step Δt must be kept short enough to accommodate the most rapidly oscillating plane waves. We bypass this restriction by integrating the oscillator EOM analytically. The value of Δt is then limited by the largest time step that can be taken before updating of the final term in (2). This value can be significantly longer than the value at which the Verlet algorithm becomes unstable if the Hamiltonian is dominated by the diagonal components. In Fig. 1 we present the results of *ab initio* calculations of the total energy for an eight-atom cell of germanium in the diamond structure using 4096 plane waves. The convergence of the total energy to its ground-state value is shown for the old method (open diamonds) and new method (full diamonds) for performing the electron dynamics. The length of the time steps with the exact EOM could be increased to 6 times the value at which the Verlet algorithm became unstable and gives convergence in roughly $\frac{1}{10}$ the number of time steps.

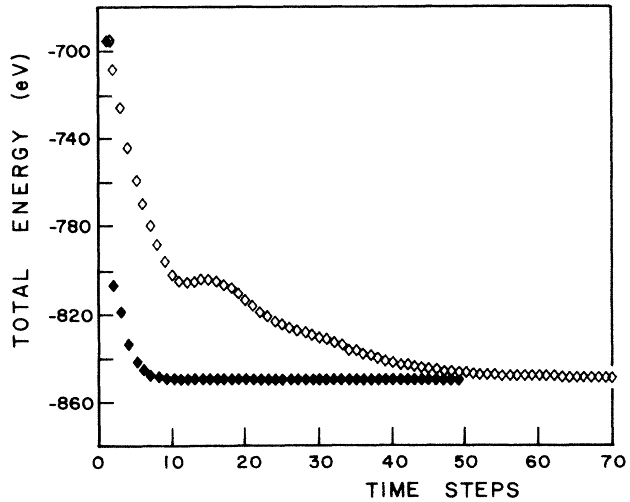

FIG. 1. Evolution of the total energy for an eight-atom cell of germanium in the diamond structure.

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

[2] L. Verlet, Phys. Rev. **159**, 98 (1967).

[3] R. Car, private communication.