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Ab initio molecular-dynamics simulations of Si clusters using the higher-order finite-difference-pseudopotential method

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We perform *ab initio* molecular-dynamics simulations using the *higher-order* finite-difference-pseudopotential (FDP) method to calculate the interatomic forces. Our approach is compared to molecular-dynamics-simulation calculations where the forces are calculated using a plane-wave basis. The ground-state structures of small silicon clusters obtained from the FDP simulation are in excellent agreement with those of the plane-wave method. The FDP method is performed completely in real space, and is easier to implement than methods based on a plane-wave expansion.

A common approach to electronic structural calculations utilizes *ab initio* pseudopotentials coupled with a plane-wave basis.[1] The smooth nature of the pseudopotentials and pseudo-wave-functions often leads to rapidly converging plane-wave expansions. For localized systems, plane waves or Fourier expansions are not readily applicable. In this case, often a large supercell is introduced to retain an "artificial periodicity." While the combination of supercells, pseudopotentials, and a plane-wave basis can be a very useful approach, the combination does have certain limitations. For example, the plane-wave basis may have to replicate large regions of the supercell where the wave function vanishes. This can result in the need for a large number of plane waves. Moreover, the supercell geometry may allow significant interactions between localized systems in neighboring cells, if the cell is not made sufficiently large.

A method[2,3] which solves the Kohn-Sham equation[4] directly on a grid in real space has recently been introduced, which avoids many of these problems. Within this method, a *higher-order* finite-difference method has been combined with the pseudopotential method. The combination of the smooth pseudopotentials and a higher-order expansion for the kinetic-energy operator (∇^2) allows one to perform accurate and efficient electronic calculations, completely in real space. This method eliminates the use of supercells for localized systems, and avoids problems with electrostatic divergences associated with charged systems. In previous papers,[2,3] this finite-difference-pseudopotential (FDP) method has been shown to yield accurate eigenvalues, charge densities, and bond lengths of several diatomic molecules. However, this method remains untested with respect to some key issues. Specifically, will this method prove to be useful for performing molecular-dynamics simulations?

Here we illustrate the implementation of Hellmann-Feynman forces for use in *ab initio* molecular dynamics within the FDP method. The discretization of the wave function on a real space grid may not be conducive to "well-behaved" forces. Consider the case of an isolated atom. Suppose we place this atom at the origin of the grid, and then displace this atom along some arbitrary direction. We would find that the symmmetry of degenerate states may be broken by such a displacement. This symmetry breaking occurs because the expansion of the wave function on the grid no longer preserves the original symmetry. Although the differences between degenerate orbitals are small, such differences might have a significant effect on the interatomic forces.

We have focused our first applications on silicon clusters. Structures of small silicon clusters have been calculated using simulated annealing via pseudopotentials with a plane-wave basis.[5] We compare the results of such simulations with the FDP method to compute interatomic forces, and assess the accuracy of this approach.

In both the plane-wave-pseudopotential and the FDP approaches, we use the local-density approximation (LDA).[4] The total ground-state energy within the LDA is

$$E_{\text{tot}}=T[\rho]+E_{e\text{-}i}(\mathbf{R}_a,[\rho])+E_{\text{Hart}}[\rho]+E_{\text{xc}}[\rho]+E_{i\text{-}i}(\mathbf{R}_a), \tag{1}$$

where $T[\rho]$ is the kinetic energy, $E_{e\text{-}i}(\mathbf{R}_a,[\rho])$ is the ionic potential energy, $E_{\text{Hart}}[\rho]$ is the Hartree potential energy, $E_{\text{xc}}[\rho]$ is the exchange-correlation energy,[6] $E_{i\text{-}i}(\mathbf{R}_a)$ is the interionic core-interaction energy, $\rho(\mathbf{r})=\sum_n^{\text{occupied states}}|\psi_n(\mathbf{r})|^2$ is the ground-state valence-charge density, and $\psi_n(\mathbf{r})$ are the ground-state wave functions. In Eq. (1), the contributions from the electron-ion and ion-ion interactions are the only two parts that have explicit dependence on the nuclear coordinates. Since the Hellmann-Feynman[7] theorem asserts that the first-order change in the wave functions does not contribute to the forces, only the $E_{e\text{-}i}$ and $E_{i\text{-}i}$ terms are relevant. The total force F_a^α on an atom located at $\mathbf{R}_a$ in the α direction for a finite system is

$$F_a^\alpha=-\frac{dE_{\text{tot}}}{dR_a^\alpha}=-\frac{\partial E_{e\text{-}i}}{\partial R_a^\alpha}-\frac{\partial E_{i\text{-}i}}{\partial R_a^\alpha}\,. \tag{2}$$

The interionic core interaction is simply the point-charge interaction under the frozen-core approximation. It is the direct pair summation of Coulomb interactions for an isolated system, and an Ewald summation[8] for a periodic system. The nonlocal ionic pseudopotential describing the interactions between valence electrons and pseudoionic cores may be separated into a local potential and a Kleinman and Bylander[9] form of a nonlocal pseudopotential in *real space*,[2,3,10]

$$V_{\text{ion}}(\mathbf{r})\psi_n(\mathbf{r})=\sum_a V_{\text{loc}}(|\mathbf{r}_a|)\psi_n(\mathbf{r}) + \sum_{a,n,lm} G^a_{n,lm}u_{lm}(\mathbf{r}_a)\Delta V_l(r_a), \tag{3}$$

$$G^a_{n,lm}=\frac{1}{\langle \Delta V^a_{lm}\rangle}\int u_{lm}(\mathbf{r}_a)\Delta V_l(r_a)\psi_n(\mathbf{r})d^3r, \tag{4}$$

and $\langle \Delta V^a_{lm}\rangle$ is the normalization factor,

$$\langle \Delta V^a_{lm}\rangle=\int u_{lm}(\mathbf{r}_a)\Delta V_l(r_a)u_{lm}(\mathbf{r}_a)d^3r, \tag{5}$$

where $\mathbf{r}_a=\mathbf{r}-\mathbf{R}_a$, and the u_{lm} are the atomic pseudopotential wave functions of the angular-momentum quantum number l,m from which the l-dependent ionic pseudopotential $V_l(r)$ is generated. $\Delta V_l(r)=V_l(r)-V_{\text{loc}}(r)$ is the difference between the l component of the ionic pseudopotential and the local ionic potential.

The energy from the electron-ion interaction, $E_{e\text{-}i}$, can be obtained by using Eq. (3) as

$$E_{e\text{-}i}=\sum_a \int \rho(\mathbf{r})V_{\text{loc}}(r_a)d^3r+\sum_{a,n,lm}\langle \Delta V^a_{lm}\rangle[G^a_{n,lm}]^2, \tag{6}$$

where the sum on n is over the occupied states. Combining Eqs. (2) and (6), one can get an expression for the force,

$$F^\alpha_a=\int \rho(\mathbf{r})\frac{\partial V_{\text{loc}}(r_a)}{\partial r^\alpha_a}d^3r+2\sum_{n,lm}\langle \Delta V^a_{lm}\rangle G^a_{n,lm}\frac{\partial G^a_{n,lm}}{\partial r^\alpha_a} - \frac{\partial E_{i\text{-}i}}{\partial R^\alpha_a}\,. \tag{7}$$

The force from the electronic contribution comprises two parts. The first term at the right-hand side of Eq. (7) is the contribution from the local ionic potential, and the second term is from the nonlocal potential. Within our finite-difference procedure, the integrations are replaced by a direct summation over the grid points.

As a first test, we have calculated the interatomic forces for a silicon diatomic molecule. The method of Troullier and Martins[10] was used to construct the nonlocal pseudopotentials using the exchange-correlation functional of Ceperley and Alder.[11] Nonlocal pseudopotentials were generated from the atomic s and p valence-electronic states using a cutoff radius of 2.5 a.u. The higher angular momentum components in the wave function are negligible. The computational details of our calculation are as in our previous work:[2,3] The grid spacing used in this calculation is $h=0.75$ a.u. The wave functions are forced to vanish outside a cutoff radius of 6.8 a.u. The kinetic-energy operator is expanded up to twelfth order in h for our higher-order finite-difference expansion.[2,12]

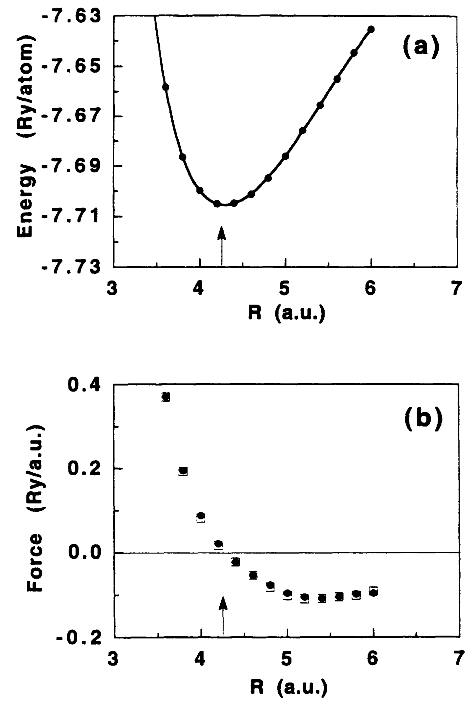

FIG. 1. (a) Total energy of the Si_2 molecule vs bond length. The calculated points have been fit to a sixth-order polynomial. (b) Forces at the calculated points from both the derivative of the curve in (a) (open squares) and from the calculation of the Hellmann-Feynman expression in Eq. (7) (filled circles).

The force on an atom can be calculated either from the numerical derivative of the total energy with respect to the displacement of an atom, or from the evaluation of the explicit Hellmann-Feynman expression of Eq. (7). We display the total energy of the Si_2 molecule versus the bond length in Fig. 1(a). To test the accuracy of Eq. (7) within the FDP method, we determined the interatomic force for the silicon diatomic molecule numerically by differentiating a sixth-order polynomial fit to the energy versus bond length at the calculated points. We show the calculated forces together with the results of a Hellmann-Feynman explicit calculation of Eq. (7) in Fig. 1(b). The forces from both procedures agree with each other within 10^{-3} Ry/a.u. The difference comes mainly from the errors in the polynomial fit. We applied the same test to a Si_3 cluster, and obtained results as accurate as for the diatomic molecule.

Ab initio molecular-dynamics simulations have been implemented using the interatomic forces obtained from the FDP method. We have used such simulations to determine the structures of small Si clusters. Specifically, we employ Langevin molecular dynamics to perform a simulated annealing. Our results are compared to similar calculations using a plane-wave basis in the determination of forces. Langevin dynamics is a very useful tool in the study of dynamic and structural properties of clusters.[13,14] In this method, particles are considered to move in a viscous medium. Within this medium, the particles experience a rapidly fluctuating

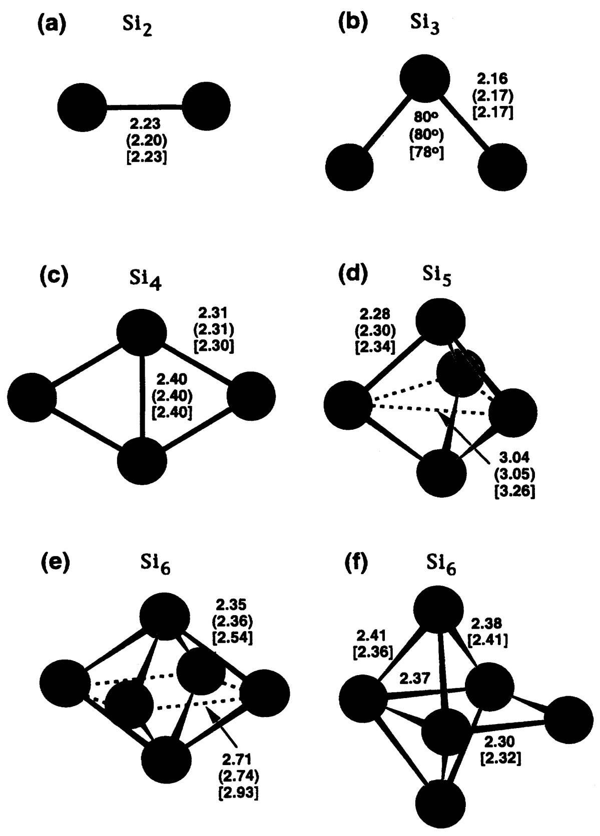

FIG. 2. Comparison of the structures of small Si clusters with previous studies. The values in parentheses are from a plane-wave-pseudopotential calculation (Ref. 5). Those in square brackets are from a Hartree-Fock calculation (Ref. 16). The bond lengths are in Å.

random force. The random forces simulate a heat bath with an adjustable temperature; the work done by the random forces is dissipated by the medium. If the viscosity coefficient of the medium is set to zero, the Langevin simulation reduces to a microcanonical simulation, i.e., the total energy is conserved when the viscosity is set to zero.

For Si_n, $2<n\leq 6$, we start the simulation from a random atomic configuration at an initial temperature of about 3000 K. The cluster is then annealed to 300 K by using a linear annealing schedule with a temperature step of about 500 K. The equations of motion are integrated using the algorithm given in Ref. 15 and a time step of 300 a.u. ($\approx 7\times 10^{-15}$ sec). The system is equilibrated for about 50 time steps at each temperature. The final structure is obtained from a steepest-descent relaxation of the configuration at 300 K. The ground-state structures of Si_2-Si_6 clusters are shown in Fig. 2. Results from pseudopotential calculations using a plane-wave basis[5] and Hartree-Fock calculations[16,17] are also given in the figure. The FDP method gives nearly identical structures for these small Si clusters when compared to the other methods. Bond-length differences between the results of the FDP method and that of the plane-wave-pseudopotential method are typically less than 1%. Since LDA bond lengths often vary by ~1–2 % from experiment, this accuracy is quite satisfactory.

We illustrate here the Langevin molecular-dynamics simulation for the Si_6 cluster in detail. The binding energy per atom for the Si_6 cluster during the annealing is plotted versus the annealing time in Fig. 3. The initial and final temperatures correspond to 3000 and 300 K, respectively. The initial structure and some typical structures, which appeared during the simulation, have been inserted into Fig. 3. These results are similar to the simulation[5] using a plane-wave basis. As in the previous studies,[5,17,18] we find two structures which are quasidegenerate in energy for the ground state of Si_6. One is a tetragonal bipyramid [Fig. 2(e)], and the other is an edge-capped trigonal bipyramid [Fig. 2(f)]. Both structures have singlet electronic ground states. The edge-capped trigonal bipyramid structure is about 7.4 meV/atom lower than that of the tetragonal bipyramid structure. This energy difference is almost the same as a previous Hartree-Fock result of about 7.2 meV/atom.[17] The energy difference is so small that it is problematic as to the "real" ground-state structure. Recent Raman-spectrum measurements[19] have suggested that the ground-state structure of a Si_6 cluster is a tetragonal bipyramid.

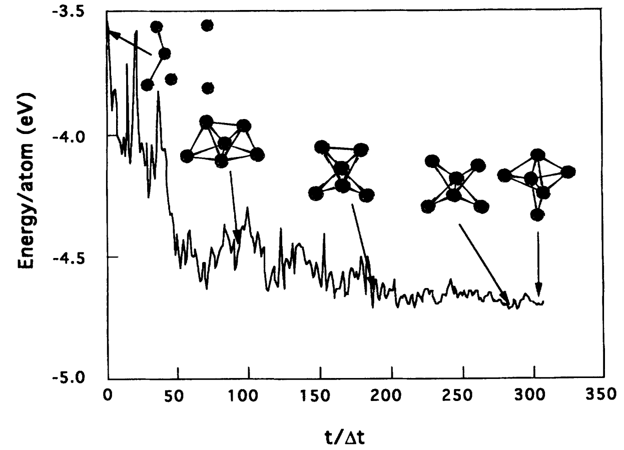

FIG. 3. Binding energy per atom during a Langevin molecular-dynamics annealing from ~3000 to ~300 K for a Si_6 cluster. The initial structure and some typical structures during the simulation are also shown. Bonds are drawn for interatomic distances smaller than 2.6 Å.

There is another issue that needs to be addressed with respect to *ab initio* molecular dynamics: conservation of energy. If the energy is not conserved, e.g., owing to poorly converged forces or errors introduced by the discretization of the wave functions, the dynamics of the system of interest may not be well replicated. We have tested the energy conservation for a Si_6 cluster. We started the simulation at a temperature of 3000 K. After thermalizing the system, we turned off the Langevin heat bath. We then examined the fluctuations in the kinetic energy E_k, potential energy E_p, and total energy E_t $(=E_k+E_p)$ over a time span of 100 time steps. By examining the standard deviations from the mean values, we obtained a measure of the quality of our energy conservation. We found $\sigma_{E_t}\approx 6\times 10^{-4}$ eV/atom and $\sigma_{E_p}=\sigma_{E_k}\approx 1\times 10^{-2}$ eV/atom, and there was no apparent drift present in the total energy. The standard deviation of the total energy is roughly two orders of magnitude smaller than that of kinetic energy and potential energy:

($\sigma_{E_t}/\sigma_{E_p}=6\times10^{-2}$). To assess the accuracy of the FDP results, a similar molecular-dynamics simulation was carried out using a plane-wave basis. The standard deviations of σ_{E_p}, σ_{E_k}, and σ_{E_t} were found to agree within a few percent between both simulations. The energy cutoff used in the plane-wave simulation was 18 Ry. The Hamiltonian matrix size was $\sim 8000\times 8000$, which is about the same as that in the FDP simulation.

In conclusion, we have implemented the molecular-dynamics simulations using the FDP method. We have demonstrated that the FDP method can predict accurate ground-state structures of clusters. We have shown that the FDP approach gives comparable accuracy to methods using a plane-wave basis. However, the FDP method is easier to implement, and all operations can be performed in real space.

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