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FIRST-PRINCIPLES MOLECULAR DYNAMICS CALCULATION OF SELENIUM CLUSTERS

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The equilibrium structures of small selenium clusters are obtained via first-principle molecular dynamics calculations based on the linearized-augmented-plane-wave (LAPW) method. Resulting equilibrium structures show a good agreement with experimental data and other first-principle calculations.

Keywords: First-principle; MD; LAPW; non-orthogonal basis set; selenium cluster; stable structure

1. INTRODUCTION

The LAPW method [1, 2] in the framework of density-functional-theory (DFT) [3] has been utilized for electronic structure calculations of various materials and have provided many satisfactory results. One of the significant features of using the LAPW basis set is its ability to deal with a wide range of elements in the periodic table. In particular, first-row elements and transition metals are difficult to treat with usual plane-wave basis approaches, due to the localized nature of valence electrons. Secondly, all-electron full-potential version of LAPW (FLAPW) method provide very accurate information on the band structure, total energy, cohesive energy and other valuable quantities.

Recent developments of the atomic force calculation in the LAPW method [4, 5, 6, 7, 8] enables us to calculate realistic atomic forces. Consequently, predictions of the stable structures and dynamical properties become possible in *ab-initio*. However, most of the force calculations based on

the LAPW basis set has been performed for nearly symmetric lattice structures and for static systems.

One of the bottlenecks associated with performing dynamical calculations is due to the rather low performance of a usual LAPW programming code. We have developed highly vectorized LAPW code in the framework of projector approach proposed by Goedecker and Maschke [6, 7]. In fact, our code shows about 94% vector ratio when executed on a vector computer. Secondly, in the LAPW force representation usually makes use of the fact that core states are self-consistent with the potential in each Muffin-Tin (MT) spheres. This means that the re-calculation of the radial wave functions in each MT-spheres is needed to calculate the atomic forces at every time steps when atoms move. However, this process increases remarkably the task for the convergence of the electronic state to its new ground state. Because of this, we have implemented our LAPW based molecular-dynamics (LAPW-MD) code with the fully-relaxed core states at their initial atomic configuration.

In this paper we will mainly discuss technical problems of the first principle molecular-dynamics simulation with the LAPW basis sets. As a test calculation, we have performed molecular-dynamics calculation of small selenium clusters and obtained their stable structures. Generally, valence electrons in a cluster system are more localized near the constituent atoms than in perfect crystals. So the LAPW basis sets are expected to represent such localized states efficiently. Comparisons with experimental data and other calculations are also discussed. Throughout this paper, we have used Hartree atomic units.

2. CALCULATION

The first-principle molecular-dynamics which we have carried out in the present work differs from the one in Car-Parrinello (CP)'s framework. We have used an extrapolation scheme in updating the wave functions so as to maintain the system in a finite thickness of Born-Oppenheimer (BO) surface. Such extrapolation scheme was first proposed by Arias *et al.* [9] with a conjugate gradient (CG) method. We have adopted the same extrapolation scheme but with a preconditioned steepest descent (PSD) method [10], because the CG method is too time-consuming to apply for the LAPW method on which the present molecular dynamics simulation is based. This extrapolation scheme allows us to use a larger MD time step by about 10 times than that used in a usual CP's method, so that the time spent for updating the overlap matrix is decreased in an effective sense.

The PSD method for non-orthogonal basis such as LAPW basis can be formulated as follows [11]. Expanding a wave function $\psi_i(\mathbf{r})$ in terms of non-orthogonal basis sets $\phi_G(\mathbf{r})$

$$\psi_i(\mathbf{r}) = \sum_G c_i(\mathbf{G}) \phi_G(\mathbf{r}), \quad (1)$$

the SD equation

$$\hat{H}\psi_i(\mathbf{r}) = (E_i - \epsilon_i)\psi_i(\mathbf{r}), \quad (2)$$

can be written in the matrix form:

$$\mathbf{S}\hat{\mathbf{C}}_i = -(\mathbf{H} - \epsilon_i\mathbf{S}) \cdot \mathbf{C}_i, \quad (3)$$

where \mathbf{C}_i , \mathbf{H} and \mathbf{S} are the i 'th eigenvector, Hamiltonian matrix and overlap matrix, respectively. This equation is expressed alternatively as

$$\hat{\mathbf{C}}'_i = -(\mathbf{H}' - \epsilon_i) \cdot \mathbf{C}'_i \quad (4)$$

where the \mathbf{C}'_i and \mathbf{H}' are defined by

$$\mathbf{C}_i \equiv \mathbf{U}\mathbf{C}_i, \mathbf{H}' \equiv \mathbf{U}^{\dagger-1}\mathbf{H}\mathbf{U}^{-1}. \quad (5)$$

Here \mathbf{U} is the upper half triangle matrix which is determined by Choleski decomposition [12] of the overlap matrix \mathbf{S} . Equation (4) has the same form as when orthogonal basis sets are used instead of non-orthogonal basis sets. We have applied the SD method with preconditioned procedure proposed by Teter *et al.* [10] to a more general case of non-orthogonal basis sets, and have successfully obtained a good convergence rate and stability of eigenvectors. The preconditioned SD equation applicable to non-orthogonal basis sets is written as follows,

$$\hat{\mathbf{C}}'_i = -\mathbf{K}' \cdot (\mathbf{H}' - \epsilon_i) \cdot \mathbf{C}'_i \quad (6)$$

where $\mathbf{K}' \equiv \mathbf{U}\mathbf{K}\mathbf{U}^{-1}$, and \mathbf{K} is preconditioning operator as described in Ref [10].

After quenching the electronic state to BO surface, we can evaluate the forces acting on each atom. The expression for atomic forces in the LAPW method, derived by Yu *et al.* [8] has been used. The atomic forces consist of two contributions. The first term is the electrostatic force, namely the bare Hellmann-Feynman force, and the second term is the incomplete basis set (IBS) correction usually called the Pulay's force [13,14]. In the latter, they have used the radial Schrödinger's equation to simplify the force representation. This technic has been used in the calculation of the matrix elements of Hamiltonian in the conventional scheme [15], but not in the Goedecker and Maschke's scheme which we have used in the present work. As mentioned earlier, such simplification might increase the computational task when we require the dynamics calculation of our main interest. Then we have calculated the IBS correction terms in a direct manner without using radial Schrödinger's equation. Details of the calculation is summarized in Appendix.

We have employed the frozen-core approximation throughout the present calculation. Core states are treated fully-relativistically without spin-orbit interactions.

3. RESULTS

We have carried out the *ab-initio* MD simulation of Se_2 and Se_3 clusters with the method described above. In cases when the system contains a few electrons, spin configuration becomes important [16]. Therefore we have used the local-spin-density approximation (LSDA) with the von Barth-Hedin's exchange-correlation potential [17]. The face-centered-cubic supercell with the dimension of 20 Å were used for Se_2 and Se_3 clusters. The cut-off energy of the LAPW basis set was taken as 4 a.u., which corresponds to about 750 LAPW's. Only a Γ point in the Brillouin zone was considered as k point sampling, since the larger unit cell makes k -point sampling unimportant in insulators and semi-conductors. For the calculation in MT spheres, we have used 201 points radial mesh with a logarithmic step size of 0.044. The radius of the MT sphere was chosen to be $R = 2.0$ a.u. The spherical harmonics expansion was truncated at $l_{\text{max}} = 8$, which is used to expand the wave function, charge density and potentials.

Initial configuration of each clusters was set as follows. For the Se_2 , bond length of 4.02 a.u. was chosen. For the Se_3 , isosceles triangle with bond length of 4.5 a.u. and bond angle of 80° was chosen. At first, we have obtained the ground state in their initial configuration and fully-relaxed core states.

The MD simulation with the time step of 50 a.u. has been carried out, in which quenching of the electronic state with use of PSD method was repeated by 6 times in average at each MD step. This quenching procedure maintains the deviation of electronic states from BO surface within $10^{-9}/(\text{band})$. Initial atomic velocities were set to be zero. In order to search for a stable structure of clusters, the artificial damping force proportional to the atomic velocity was added into the original Newtonian equation,

$$M_I \frac{d^2 \mathbf{R}_I}{dt^2} = \mathbf{F}_I - \eta M_I \frac{d\mathbf{R}_I}{dt} \quad (7)$$

where the M_I , \mathbf{R}_I and η are the atomic mass, atomic position and damping coefficient, respectively. We have adopted 0.005 a.u. for η in all present calculations.

The stable structures of Se_2 and Se_3 obtained are shown in Table I. Our results show a good agreement with the experiment and other first-principle calculations. We have obtained the ground state of triplet-state for Se_2 and singlet-state for Se_3 in their stable structures. For Se_3 , to our knowledge there is no experimental data about stable structures. Theoretically it is known that there are two stable structures about Se_3 , one of which is an isosceles triangle (C_{2v} symmetry) and the other is a regular triangle (D_{3h} symmetry). In the present simulation the latter structure was obtained.

To investigate the effect of re-calculation of the core states, we have carried out two different simulations for Se_3 . First, we have performed a simulation for 480 steps with the frozen-core approximation and obtained the nearly stable structure. Figure 1 shows the time evolution of three bond length obtained by this calculation. Second, we have re-calculated the core

TABLE I The bond length l and bond angles α of the stable structures for Se_2 and Se_3 clusters

		$l [\text{a.u.}]$	$\alpha [\text{deg.}]$
Se_2	present work	4.19	
	experiment ^a	4.10	
	other calc. ^b	4.16	
Se_3	present work	4.47	60.0
	other calc. ^c	4.46	60.0

^aReference 18

^bReference 20

^cReference 19

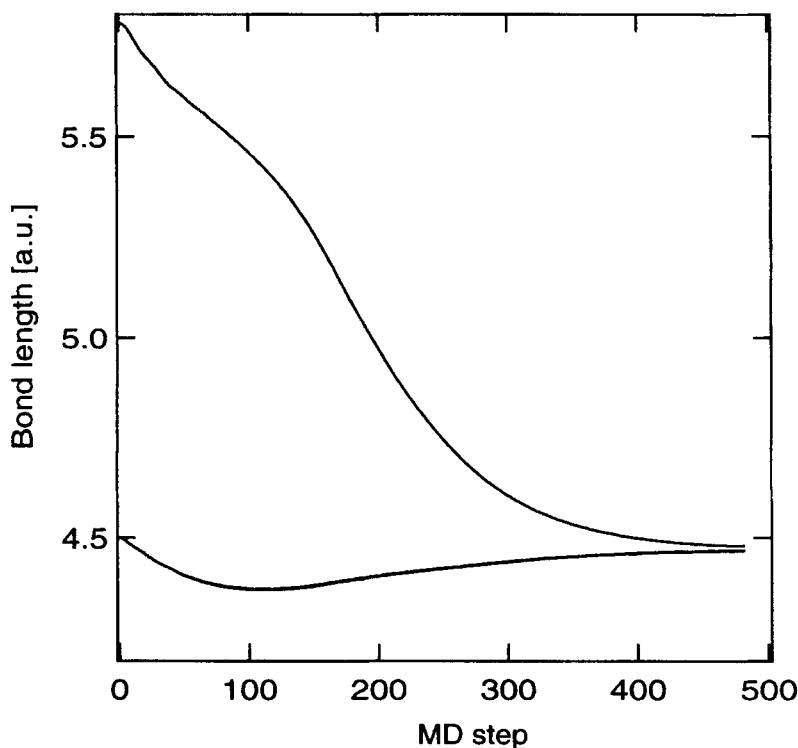


FIGURE 1 Time evolution of the bond length of Se_3 (first run).

states with this geometry, and then we have continued the MD simulation with such updated core states for another 80 steps. The time evolution of bond length during this run is shown in Fig. 2.

In this latter simulation, we have altered the damping coefficient η to 0.001 to accelerate the speed of finding its stable structure. Figures 3 and 4 show the time evolution of eigenvalues of first run and second run, respectively.

From these separate simulations, we have found that the effect of changes of core states is small enough to be negligible for the selenium clusters.

4. CONCLUSIONS

We have implemented the first-principle molecular-dynamics calculation with the LAPW basis set. We have shown that the preconditioned steepest descent method used in conjunction with the wave function extrapolation scheme can be satisfactory extended to the case of the non-orthogonal basis

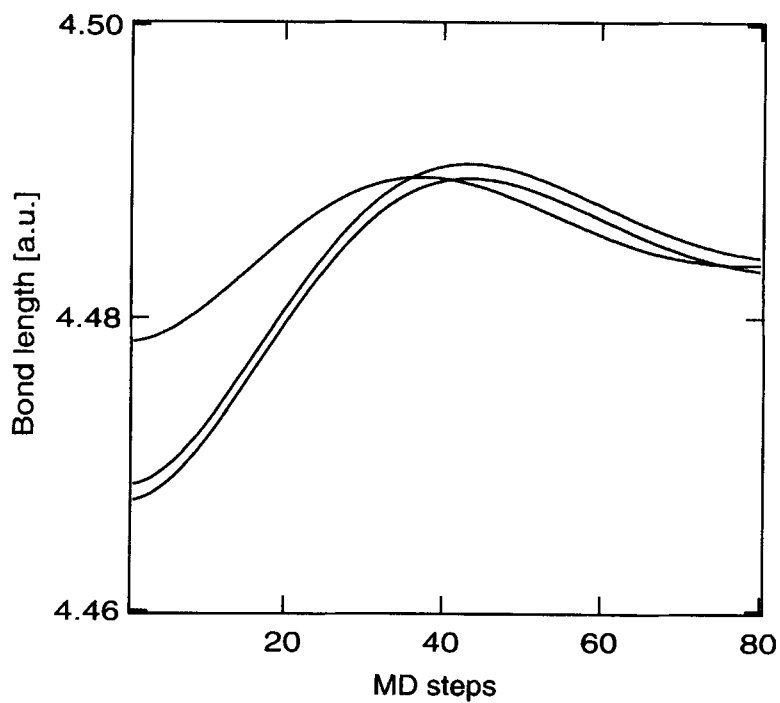


FIGURE 2 Time evolution of the bond length of Se_3 (second run).

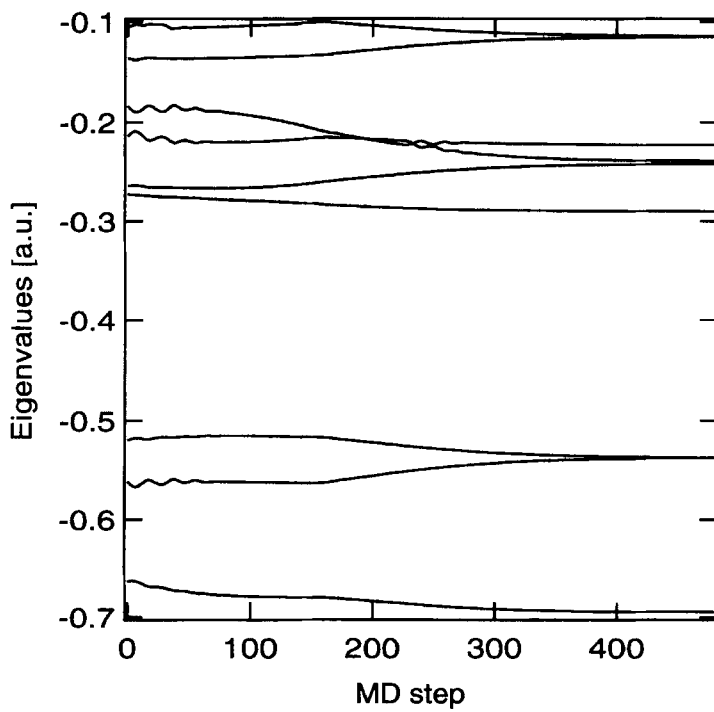


FIGURE 3 Time evolution of the eigenvalues of Se_3 (first run).

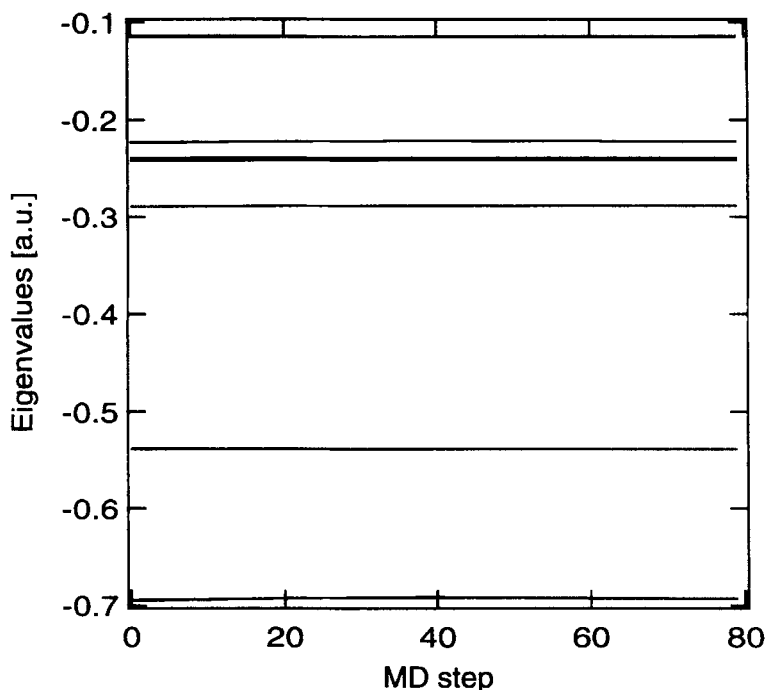


FIGURE 4 Time evolution of the eigenvalues of Se_3 (second run).

sets. When it is applied to small selenium clusters, we have obtained the stable structures for Se_2 and Se_3 in an excellent agreement with the experimental data and the other first-principle calculations.

It is to be noted that our LAPW-MD code will work more efficiently on parallel-super computer, because the calculation of the charge density and potential in each MT-sphere is made possible mutually independently.

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Those who are interested in the programme code of the *ab-initio* molecular dynamics simulation developed in the present work, please contact Y.Hiwatari at the e-mail address: hiwatari@hiwa003.s.kanazawa-u.ac.jp.

APPENDIX: DETAILS OF IMPLEMENTATION OF THE FORCE CALCULATION

We have employed the force representation derived by Yu *et al.* [8] with a little modification. In their paper, IBS correction term consist of few parts. The modification which we have made in the present work is about the term

$$\langle \phi_G | (H_{MT} - \varepsilon_i) | \phi_{G'} \rangle, \quad (8)$$

where H_{MT} is a spherical part of the Hamiltonian. In the original work of Yu *et al.*, this term was combined with the radial Schrödinger's equations to simplify the representation and make sure that this should be Hermite. However, as mentioned earlier in this paper, this simplification requires that the core states must be self-consistent with potential at every time steps.

Our modification is based on a rather straightforward calculation of this term part by part. H_{MT} consists of two terms, kinetic energy operator $-(1/2)\nabla^2$ and spherical potential $V_{SP}(r)$. When we represent the LAPW basis function $\phi_G(\mathbf{r})$ as

$$\phi_G(\mathbf{r}) = \sum_{lm} [p_{lm}^{1*}(\mathbf{G})R_l^1(r) + p_{lm}^{2*}(\mathbf{G})R_l^2(r)] Y_{lm}(\hat{\mathbf{r}}), \quad (9)$$

the kinetic energy operator term of Eq. 8 is calculated as follows,

$$\begin{aligned} \langle \phi_G | -\frac{1}{2}\nabla^2 | \phi_{G'} \rangle = & -\frac{1}{2} \sum_{lm} \sum_{\kappa, \kappa'} p_{lm}^{\kappa}(\mathbf{G}) p_{lm}^{\kappa'*}(\mathbf{G}') \left[-l(l+1) \int R_l^{\kappa} R_l^{\kappa'} dr \right. \\ & \left. + R_l^{\kappa}(R) \frac{\partial R_l^{\kappa'}}{\partial r} R^2 - \int \frac{\partial R_l^{\kappa}}{\partial r} \frac{\partial R_l^{\kappa'}}{\partial r} r^2 dr \right]. \end{aligned} \quad (10)$$

where p_{lm}^{1*}, p_{lm}^{2*} are the projector operator as described in Ref. [6,7] and R_l^1 and R_l^2 are the solution of radial Schrödinger's equation and its energy derivative, respectively.

However, the second term of Eq. 10 does not satisfy the Hermite condition. Then we equate the $\kappa = 2, \kappa' = 1$ term with $\kappa = 1, \kappa' = 2$ term in the second term of Eq. 10 to assure the Hermiteness. The other terms, $\langle \mathbf{G} | V_{SP} | \mathbf{G}' \rangle$ and $\langle \mathbf{G} | \epsilon_i | \mathbf{G}' \rangle$, are calculated by direct integration.

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