

Ab-initio mixed-basis molecular dynamics simulation applied to carbon microclusters

Y. Maruyama ^a, H. Kamiyama ^b, K. Ohno ^a and Y. Kawazoe ^a

^aInstitute for Materials Research, Tohoku University, 2 - 1 - 1 Katahira, Sendai 980, Japan

^bAomori Public College, 153 - 4 Goushi-Zawa, Yamazaki, Aomori 030, Japan

The electronic structures of carbon microclusters C_3 , C_{60} are simulated by means of *ab-initio* molecular dynamics using mixed-basis which consists of both plane waves and atomic orbitals, incorporating all electrons (and full-potential) into calculation. The present method powerfully supports the use of localized electron orbitals including 1s core with considerably limited requirement of basis functions as compared with the standard approach using only pseudopotentials.

1. Introduction

The Car-Parrinello (CP) method[1] and the related simulated annealing approach of *ab-initio* molecular dynamics simulations are powerful tools to investigate the electronic and atomic structures and vibrational modes of variety of systems. These approaches combined with the local density approximation (LDA), the pseudopotentials and the expansion in terms of plane waves (PW's) of the electronic states have successfully been applied to the covalent semiconductors such as silicon.

However, it is pointed out that there are several problems in these methods. The main problem is in the case of treating localized electron orbitals; it would be necessary to use quite a large number of PW's to describe the localized orbitals and much longer computational time to achieve a good convergence of the expansion-coefficients. Sometimes, to preserve the Born-Oppenheimer (BO) surface may not be so easy in the original CP approach which uses only PW's.

Recently, a ultrasoft pseudopotential, which can reduce the number of PW's to 1/5 - 3/10 as compared with the norm-conserving pseudopotential, has been proposed by Vanderbilt.[2] To overcome the problems mentioned above, this potential has been applied to some systems includ-

ing first-row and transition-metal elements.[3,4] However, there still remain the sensitive problems such as how to choose a cutoff radius r_c . Especially, in the case of light atoms which has strong covalent bonds like carbon the molecular environment is quite different from the atomic environment. Therefore, it seems necessary to take account of the influence from the core region, but it is very hard to deal with the asymmetric region near nucleus.

The main interest of our work is to treat the system of light atoms like carbon correctly, and to perform *ab-initio* molecular dynamics simulation, and so we apply *mixed-basis approach* to expand wave functions. This scheme uses not only PW's but also atomic orbitals (AO's), and then makes it possible to handle strongly localized electron orbitals, even 1s core, without using any pseudopotentials. The present work is the first attempt to apply the mixed-basis to the *ab-initio* full-potential molecular dynamics simulation of carbon microclusters.

2. Mixed-basis approach in the Car-Parrinello formalism

For the dynamics of electrons, we use the usual steepest decent (SD) method having the first derivative with respect to t so as to keep the electronic states near the BO surface at each time step. In order to orthogonalize different electronic levels, here we adopt the Gram-Schmidt orthogonalization and the Payne algorithm[5] for the

*Acknowledgements: This research has been supported in part by Partnership Program with IBM Japan Co. Ltd. The authors are very grateful to Sumitomo Metal Industry, Ltd. for the use of NEC SX-2A supercomputer.

choice of the Lagrange multiplier associated with the orthogonal condition. On the other hand, we treat the atomic motion by the classical Newton equation as in the original CP formalism. Such choices, however, should not be regarded as any specific feature of the mixed-basis approach; the reader should note that the mixed-basis approach is basically applicable to any other algorithms of *ab-initio* simulations mentioned above.

Historically speaking, the mixed-basis approach in the band calculation was developed in order to handle the spatial locality and asymmetry of the *d*-orbitals correctly. In the present work we use PW's and Slater type atomic orbitals (AO's) to expand all kinds of the wave functions including 1s core. In the mixed-basis formalism, atomic bases are not orthogonal to the PW's. Therefore, we start from the modified CP equation which guarantees the orthogonality;

$$\mu S \dot{\Psi}_i = -(H - \Psi_i^\dagger H \Psi_i S) \Psi_i, \quad (1)$$

$$M_m \ddot{\mathbf{R}}_m = -\partial E / \partial \mathbf{R}_m, \quad (2)$$

where μ denotes the fictitious "mass" for electron wave functions, while M_m represents the real nucleus mass of the *m*th atom, S denotes the overlap matrix of the wave functions; H and E denote the Hamiltonian of the electrons and the total energy of the system, respectively.

The distinguishing feature of the present equations with the mixed-basis approach from those with the earlier PW approach is the presence of the overlap matrix S in Eq.(1), which is due to the fact that the bases are not mutually orthogonal. Introducing the lower half triangular matrix U which satisfies $S = UU^\dagger$ and is constructed in the Choleski decomposition,[6] and writing $U^\dagger \Psi_i = \Phi_i$ and $H' = U^{-1} H U^{\dagger-1}$, we finally have:

$$\mu \dot{\Phi}_i = -(H' - \Phi_i^\dagger H' \Phi_i) \Phi_i. \quad (3)$$

Once we adopt this representation, the main algorithm for updating the wave function Φ_i is the same as the original PW approach. To evaluate the charge density one needs to trace the wave functions to those in the original nondiagonal frame via the relation $\Psi_i = U^{\dagger-1} \Phi_i$.

The effective one-electron Hamiltonian reads

$$H = T + V, \quad T = -\frac{1}{2} \nabla^2,$$

$$V(\mathbf{r}) = -\sum_m \frac{Z_m}{|\mathbf{r} - \mathbf{R}_m|} + \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + V^{ec}(\mathbf{r}), \quad (4)$$

where we use the atomic unit (a.u.), $\hbar = m_e = e = 1$. In Eq.(5), Z_m and \mathbf{R}_m denote, respectively, the atomic number and the position of the *m*th atom, $\rho(\mathbf{r})$ is the total electron density and $V^{ec}(\mathbf{r})$ the exchange-correlation potential which is evaluated in real space under the local density approximation. In our formalism, we evaluate $\rho(\mathbf{r})$ directly in real space from the expansion-coefficients determined at the previous step. In this paper we neglect the freedom of spin.

In the present formalism of the atomic dynamics, the spatial derivatives of the total energy basically reads

$$\begin{aligned} \frac{\partial E}{\partial \mathbf{R}_m} &= \frac{\partial(\sum_i \Psi_i^\dagger T \Psi_i)}{\partial \mathbf{R}_m} + \int \frac{\partial \rho}{\partial \mathbf{R}_m} V d\mathbf{r} \\ &+ \frac{\partial}{\partial \mathbf{R}_m} \sum_{n(\neq m)} \frac{Z_n Z_m}{|\mathbf{R}_n - \mathbf{R}_m|} - Z_m \int \rho(\mathbf{r}) \frac{\partial}{\partial \mathbf{R}_m} \frac{d\mathbf{r}}{|\mathbf{R}_m - \mathbf{r}|}. \end{aligned} \quad (5)$$

The first two terms represent the variational forces involving all the derivatives of AO's which depend explicitly on \mathbf{R}_m , while the sum of the last two terms represents the Hellmann-Feynman force which already exists in the original CP method using only PW's. Although the core orbitals do not affect the interatomic forces significantly, we may not neglect the first two terms (variational forces) in Eq.(5) when the electronic states deviate from the BO surface. In order to keep the electronic states as close to the BO surface as possible, our simulation performs at each time step one extra-loop for the electronic SD calculation without updating the atomic positions.

3. Simulation Results

3.1. C₃

For the simulation of C₃ we use three 1s and nine 2p AO's neglecting the spin, with four AO's locating on each atomic site, and 485 PW's. For

all computation, we use a RISC workstation, IBM RS6000/530 with 32MB main memory, where one basic loop takes about 64 seconds in CPU time. The cutoff energy of the PW's corresponds to about 4.3 a.u. = 8.7 Ryd. We assume the following two initial atomic positions; [a] linear with the same bond length of 2.55 a.u. = 1.35 Å and [b] triangular with the same bond length of 2.84 a.u. = 1.50 Å. To integrate temporal sequences, we use Verlet's algorithm in the second derivatives in Eq.(2). The basic time step Δt we adopt here is 4.0 a.u. ($= 9.6 \times 10^{-17}$ sec), while we assume $\mu=50$ a.u.

Figure 1 shows the time sweep of the three interatomic distances obtained on condition [b]. From this figure, we observe a damping oscillation towards the optimal linear structure with the same bond lengths, 1.31 Å, which should be compared with 1.29 Å determined by localized orbital approach by Terakura et al.[7] The experimental value of the bond length deduced by equating $\hbar^2/4md^2$ with 0.4244cm^{-1} is 1.287 Å.[8] We may see that the final stable structure is not the triangular structure but the optimal linear structure obtained in both conditions and this result also agrees with the experiment.

The existence of this damping in the oscillation is due to the SD algorithm in Eq.(1) or (3) Therefore, strictly speaking, it is hard to say that the frequencies of these oscillations are only due to Hellmann-Feynman force. These oscillations are expected to correspond to the physical vibrational motions, since these should be originated from characteristic vibrational mode. As reference data, we show the presently calculated data below. The initial vibration wavenumber around triangular structure which can be estimated from Figure 1 is $2.9 \times 10^3\text{cm}^{-1}$. The vibration wavenumbers around the linear structure are $1.2 \times 10^3\text{cm}^{-1}$ and $2.1 \times 10^3\text{cm}^{-1}$ and these correspond to a symmetric and asymmetric stretch mode, respectively. The present results agree well with experimental values[9,10] of 1225cm^{-1} and 2040cm^{-1} .

3.2. C₆₀

In the case of C₆₀, the size of system and the computation become much bigger than that of

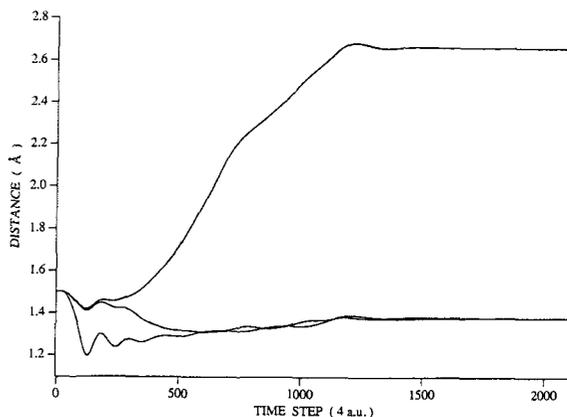


Figure 1. Atomic motion starting from the triangular C₃.

C₃. Therefore, we confine ourselves to optimizing the structure of C₆₀ and to checking its structural stability around the experimentally known values.

For C₆₀, we use 60 1s, 60 2s and 180 2p AO's locating on each atomic site, and 2969 PW's. This number of PW's corresponds to the energy cutoff of 7 Ryd. This energy cutoff is much smaller than that of the conventional plane wave pseudopotential (PP)scheme. (The conventional pp scheme requires about 30000 PW's; 30 Ryd in this system.) For the computation, we have used NEC SX-2A supercomputer (at Sumitomo Metal Industry, Ltd.), with which we achieved 99% vector operation ratio, where one basic loop takes about 660 seconds in CPU time.

We assume the initial atomic distances in two ways; 1.45 Å for the single bond length and 1.53 Å for the double bond length. Experimental values are 1.40 Å and 1.46 Å, respectively, and these initial bond lengths correspond to about 4% longer ones. The basic time step Δt we adopt here is 8.0 a.u. ($= 1.92 \times 10^{-16}$ sec), while we assume $\mu=200$ a.u.

First, we show the estimated electron-charge density on a plane cutted at the center of C₆₀ in Fig.2 in logarithmic scale. One may see the strongly localized 1s core electrons in the vicinity of atomic positions and covalent bonds with directional qualities. This figure indicates the effectiveness of the present approach.

Second, we show the distribution of obtained 90 bond lengths between the nearest neighbour atoms in 100 steps in Figure 3. There are two broad bands which correspond to single and double bond lengths. This means that kinetic energy of nuclear system is still so high at this time that the system have not yet converged to the final stable structure. In this simulation we calculated 150 steps to check the stability of C_{60} . We confirmed that the assumed structure of C_{60} have been very stable during the optimization process.

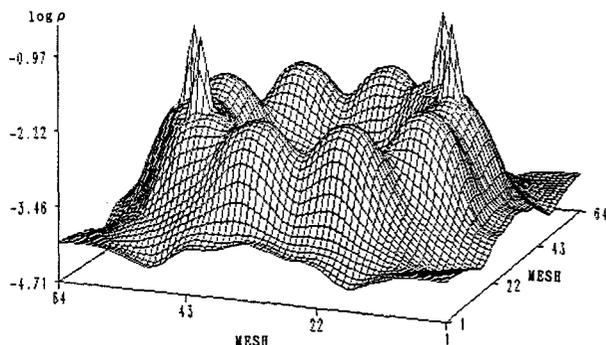


Figure 2. Electron density distribution of C_{60} at the central plane.

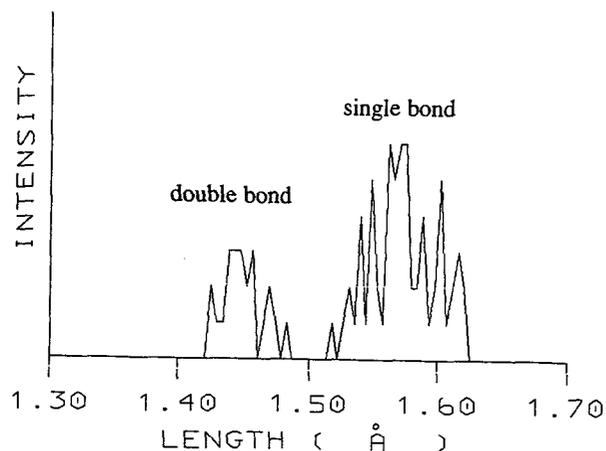


Figure 3. Histogram of the C-C bond lengths of C_{60}

4. Conclusion

The present mixed-basis approach for the *ab-initio* molecular dynamics makes it possible to calculate the system which has localized electron orbitals. We have shown a good agreement with experiments for a small system of C_3 . For C_{60} , we have confirmed the structural stability.

Although the present scheme takes longer computational time than PP scheme in calculating Hamiltonian matrix elements, when the system size becomes much bigger, it would have an advantage of the computation because of its limited requirement of basis functions.

REFERENCES

1. R. Car and M. Parrinello, Phys. Rev. Lett. **55**(1985)2471.
2. D. Vanderbilt, Phys. Rev. **B41**(1990)7892.
3. C. Lee, D. Vanderbilt, K. Laasonen, R. Car and M. Parrinello, Phys. Rev Lett.**69** (1992) 462.
4. A. Pasquarello, K. Laasonen, R. Car, C. Lee and D. Vanderbilt, Phys. Rev Lett.**69** (1992) 1982.
5. M. P. Teter, M. C. Payne and D. C. Allan, Phys. Rev. **B40** (1989) 12255.
6. K. M. Ho, C. Elsässer, C. T. Chan and M. Fähnle, J. Phys. **C4**, (1992) 5189.
7. K. Terakura, T. Hoshino and T. Asada, in: *Microclusters*, edited by S. Sugano, Y. Nishina and S. Ohnishi, [Springer Series in Materials Science Vol.4] Springer Verlag, Berlin, (1987) 257.
8. W. Weltner, Jr. and D. McLeod, Jr., J. Chem. Phys. **45**, (1966) 3096.
9. K. W. Chang and W. R. M. Graham, J. Chem. Phys. **77**, (1982) 4300.
10. D.L. Eaton, Porous Glass Support Material, US Patent No. 3 904 422 (1975).