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Full-potential Mixed-basis Simulated Annealing Calculation of C_{60}*

Yutake MARUYAMA[a], Hiroshi KAMIYAMA[b], Kaoru OHNO[a] and Yoshiyuki KAWAZOE[a]

[a] *Institute for Materials Research, Tohoku University, 2 - 1 - 1 Katahira, Sendai 980, Japan*
[b] *Aomori Public College, 153 - 4 Goushi-Zawa, Yamazaki, Aomori 030, Japan*

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A new class of small carbon clusters called Fullerene, e.g. C_{60} discovered in 1985, is one of the most interesting nanoscale materials at present because of its unique shape and physical and chemical properties. In this paper, the electronic structure and the structural stability of the C_{60} microcluster are examined by means of dynamical simulated annealing. We apply mixed-basis fomalism in order to describe wave functions including accurately core and valence orbitals. The basis set of this scheme consists of both plane waves and atomic orbitals, incorporating all electrons and full-potential into calculation. The present method is superior to the standard approach using the plane wave expansion and a pseudopotential, with respect that strongly localized electron orbitals like 1s and 2p can be described with considerably limited number of basis functions.

KEYWORDS: C_{60}, mixed-basis, simulated annealing, electronic structure

1. Introduction

A fundamentally new kind of carbon cluster, C_{60}, discovered by Kroto and Smalley[1], and the other larger size carbon microclusters (C_{70}, C_{84}, etc.) are called Fullerenes and have been studied extensively with much current interests because of their unique shapes, and moreover their physically and chemically peculiar properties; i.e. these microclusters have cage structures. Especially, C_{60} is most stable and has a soccer-ball shape. It is, therefore, a challenging theme to study the relationship between the electronic structure and the structural stability of C_{60}.

Basically, simulated annealing scheme is used for total-energy minimization of a complicated system which has so many degrees of freedom. The dynamical simulated annealing which is represented by Car-Parrinello (CP) method[2] and the related simulated annealing approaches such as the conjugate gradients are powerful tools to investigate both the electronic and atomic structures. These approaches combined with the local density approximation (LDA), the pseudopotentials, and the expansion of the electron wave functions in terms of plane waves (PW's), have successfully been applied to the covalent semiconductors such as silicon.

However, it has been 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, it is not easy to preserve the system on the Born-Oppenheimer (BO) surface in the usual approach which uses only PW's.

Recently, an ultrasoft pseudopotential, which can reduce the number of PW's to $1/5 \sim 3/10$ as compared with the norm-conserving pseudopotential, has been proposed by Vanderbilt[3]. To overcome the problems mentioned above, this new theoretical technique has been applied to some systems including first-row and transition-metal elements[4,5]. However, there still remain some sensitive problems such as how to choose cutoff radius r_c and how to solve core correction problem. Especially, in the case of light atoms with strong covalent bonds like carbon, the molecular environment is quite different from the atomic environment; it seems necessary to take account of the influence in the core region, although it is hard to deal with the asymmetric region near nucleus.

The main interest of this work is to treat the system of light atoms like carbon accurately, and to obtain the stable structure which reflects the correct potential of C_{60} by performing the simulated annealing, and so we apply *mixed-basis approach* to expand wave functions. This scheme uses not only PW's but also atomic orbitals (AO's) to make 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* simulated annealing calculation of C_{60}.

2. Mixed-basis approach in the dynamical simulated annealing formalism

For the dynamics of electronic system, we use the usual steepest descent (SD) method having the first derivative with respect to t in the basic time-evolution equation 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[6] for the 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 usual 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* dynamic simulations.

Historically speaking, the mixed-basis approach in the band calculation was developed in order to handle ac-

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curately the spatial locality and asymmetry of the d-orbitals[7]. They applied the mixed-basis not to treat the core wave functions but only to expand the valence wave functions, therefor they used a pseudopotential in their formalism. In the present work, we use PW's and Slater type atomic orbitals (STO) to expand the total wave functions including 1s core. In the mixed-basis formalism, different basis sets are not orthogonal each other. Therefore, we start from the modified CP equation which guarantees the orthogonality;

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

$$M_m \ddot{\mathbf{R}}_m = -\frac{\partial E}{\partial \mathbf{R}_m}, \tag{2}$$

where μ denotes the fictitious friction constant for the time evolution of electron wave functions, M_m the real nucleus mass of the mth atom, $\mathbf{R}_m$ the position of the mth atom, S the overlap matrix of the wave functions, H and E the Hamiltonian of the electrons and the total energy of the system, respectively.

The distinct feature of the present equations of the mixed-basis approach from those of the usual plane wave approach is the presence of the overlap matrix S in eq.(1), which is due to the fact that the plane waves and the atomic orbitals are not mutually orthogonal. Introducing the lower half triangular matrix U which satisfies $S = UU^\dagger$ and is constructed by the Choleski decomposition[7], and writing $U^\dagger \Psi_i = \Phi_i$ and $H' = U^{-1} H U^{\dagger -1}$, we finally have:

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

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 reconvert 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

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

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

where we use the atomic unit (a.u.), such that $\hbar = m_e = e = 1$. In eq.(4), Z_m denotes the atomic number of the mth atom, $\rho(\mathbf{r})$ the total electron density and $V^{ec}(\mathbf{r})$ is 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 and simply multiply a factor 2 to every state.

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

$$\frac{\partial E}{\partial \mathbf{R}_m} = \frac{\partial(\sum_i \Psi_i^\dagger T \Psi_i)}{\partial \mathbf{R}_m} + \int \frac{\partial \rho}{\partial \mathbf{R}_m} V d\mathbf{r}$$

$$+ \frac{\partial}{\partial \mathbf{R}_m} \sum_{n(\neq m)} \frac{Z_n Z_m}{|\mathbf{R}_n - \mathbf{R}_m|} - Z_m \int \rho(\mathbf{r}) \frac{\partial}{\partial \mathbf{R}_m} \frac{d\mathbf{r}}{|\mathbf{R}_m - \mathbf{r}|}. \tag{5}$$

The first two force terms involve all the derivatives of AO's which depend explicitly on $\mathbf{R}_m$; these terms are called the variational force or Pulay force, and the sum of the last two terms represent the Coulomb forces between nuclei, and between electron cloud and nucleus.

According to the Hellmann-Feynman theorem, physically accurate forces can only be calculated when the wave functions are very close to the BO surface, and in this situation only, the first two terms become negligible, and the last two terms are identified with the Hellmann-Feynman force. The usual plane wave expansion has only the sum of the last two terms, because the plane wave basis set does not depend on the atomic positions. In the mixed-basis approach, we have to preserve the first two terms in eq.(5), variational force, when the electronic states deviate from the BO surface. In this paper we neglect these terms because we are not interested in the optimizing procedure itself but only in the final result of the most stable structure. In this case it is known that the variational force is not significant.

3. Simulation procedure and initial conditions

We can divide the simulation procedure mainly into two stages. First, we fit the atomic sites until the electonic states converge well to the eigen wave functions. Second, after getting convergency we release all the constraints of the atomic sites and perform the simulated annealing according to eq.(1) $\sim$ eq.(5). In the first stage, the electronic systems are converged in two ways. Initially, we roughly converge the electronic system by the usual matrix diagonalization with relatively small number of bases, and then we increase the number of bases, and finally obtain the convergence of the system by the SD algorithm. In this convergent stage, we mix the estimated charge distribution with those in the last time step by one to nine at each time step.

The supercell should be chosen as large as possible to keep the independence of the system, although the large supercell makes computaion difficult. In this paper we use the following supercell for an isolated C_{60} cluster. That is, the applied supercell is a simple cubic with a lattice constant 21.3 a.u.(= 11.3Å) and is divided into 64 x 64 x 64 mesh points, where 3 meshs correspond to 1 a.u.(= 0.52918Å). C_{60} has almost a sphere shape of diameter about 13.4 a.u.(= 7.1Å) and then the nearest neighbor atomic distance between different C_{60}'s is 7.9 a.u.(= 4.1Å).

We use totally 300 AO's (each 60 for 1s, 2s, $2p_x$, $2p_y$, and $2p_z$) locating on each atomic site. This AO basis set corresponds to *the minimum basis set* in quantum chemistry. And we use 1365 PW's for the small basis

set and 2969 PW's for the larger basis set. This number of PW's for the larger basis set 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 30,000 PW's with 30 Ryd).

We assume two initial atomic distances; 1.46Å for the single bond length and 1.53Å for the double bond length. Experimental values are 1.40Å and 1.47Å, respectively, and the present initial values are about 4% longer. The basic time step Δt we adopt here is 8.0 a.u. ($= 1.92 \times 10^{-16}$sec), while for the fictitious friction constant we assume μ=200 a.u.

Table 1. Simulation procedure and the number of plane waves.

Diagonalization	1365 PW's	10 steps
SD (atoms fixed)	2969 PW's	30 steps
SD (atoms released)	2969 PW's	90 steps

Table 2. Calculation conditions.

Supercell	s.c. 11.3 × 11.3 × 11.3 Å^3
Initial interatomic distances	single bond = 1.53 Å double bond = 1.47 Å
Time step	Δt = 8.0 a.u.
Fictitious friction constant	μ = 200 a.u.

For the computation, we have mainly used HITAC S3800/380 supercomputer with 3 CPUs (at Hitachi Co.), where one basic loop takes about 17 seconds in CPU time.

4. Results and discussions

First, we show the change of energy levels with time step in Fig.1. As mentioned above, the initial 40 steps are the convergent stages and the rests are the simulated annealing stages. The 60 1s core levels are located at about −11.3 a.u. with good degeneracy, and 120 valence levels are located at about $0 \sim -0.8$ a.u.

Second, we show the electron-charge density distribution on a cross-section across the center of C_{60} 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.

One also see the small charge distribution on the supercell wall. This means that the assumed cell size is not large enough to keep out the interaction between clusters. As a result, the degeneracies of eigenvalues are different from the expected ones (in Fig.3). As is well known, the highest occupied molecular orbital (HOMO) of an isolated C_{60} has a fivefold degeneracy,[8] but in this result, these orbitals split silghtly into threefold and twofold degeneracies. Two plausible arguments are possible for this reasoning. First, the potential should be an isolated one, but our result reflects an influence of crystal

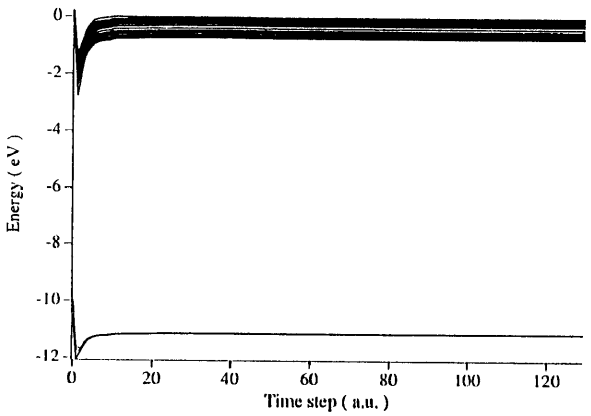

Figure 1. The change of energy levels with time step.

field with the simple cubic symmetry. Second, the plane wave basis set chosen do not span the real space homogeneously. We have numbered the plane waves spherically in reciprocal lattice space to reduce the number of plane waves, although the cubic cutoff is necessary for our choice of the simple cubic supercell.

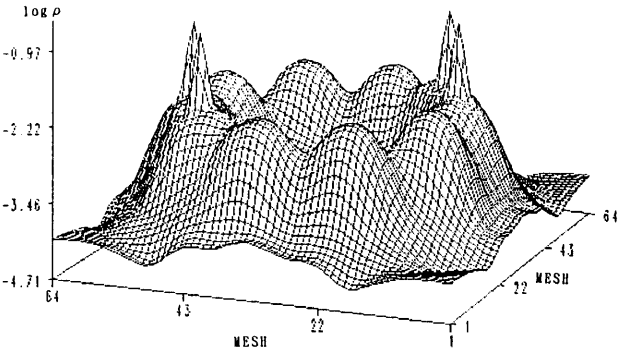

Figure 2. Electron-charge density distribution of C_{60} at the central plane.

C_{60} has 30 double bonds and 60 single bonds. We show the change of 90 bond lengths between the nearest neighbour atoms with time step in Fig.4. In the initial 40 steps the lengths do not change because of the convergent stage. After 40 steps, C_{60} begins to relax and the bond lengths start to change. There are mainly 4 kind of bond lengths and this separation also reflects the infulence of the crystal field with the simple cubic symmetry and the inhomogenety of the plane wave basis set, mentioned above.

However, we can see in Fig.6 that the overall structure of C_{60} certainly approaches to a stable configuration. This figure shows the change of distances between the 60 carbon atoms and the center of C_{60}. We can see all the distances decreasing with time step from the initial structure which we assumed about 4 % larger in length than the experimental values.

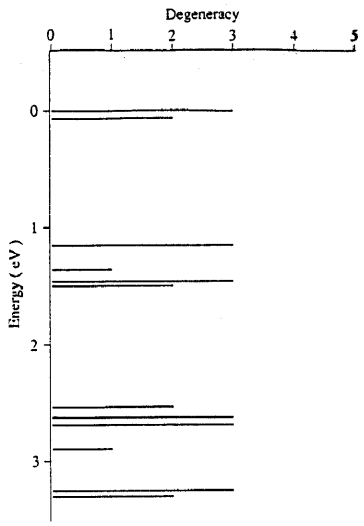

Figure 3. Degeneracies near the HOMO level.

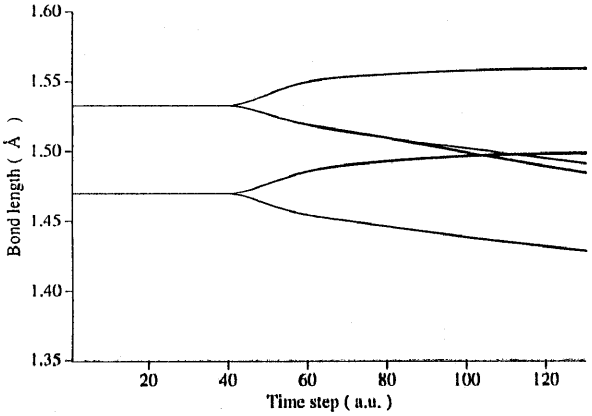

Figure 4. The change of bond lengths with time step.

5. Conclusion

The present mixed-basis approach for the simulated annealing makes it possible to calculate the system which has localized electron orbitals.

In this paper, unfortunately, we could not get the most stable structure of C_{60} because of the limit of the CPU time. Moreover, the supercell is too small to keep the isolation of the system and the plane wave basis set does not span the real space homogeneously in the present simulation. Nevertheless, in this tentative work we make it sure that the C_{60} has a stable structure approximately with the experimentally predicted structure constants. At present we are calculating with refined basis set by getting rid of the inhomogeneity of the PW's. The resul-

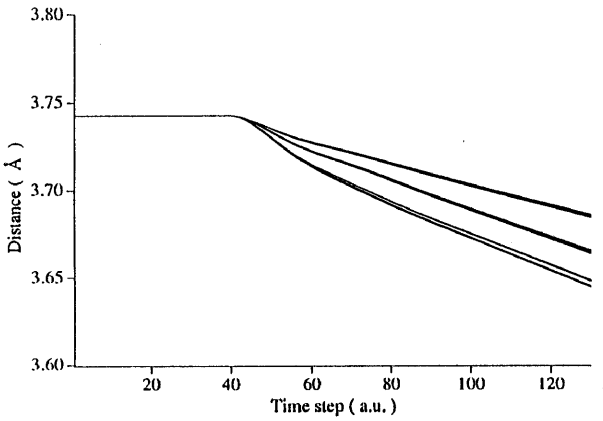

Figure 5. The change of distances between 60 atoms and the center of C_{60} with time step.

ts will appear elsewhere. 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.

Acknowledgements

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