Application of Density Functional Heaviside-Fermi Level Operator Formalism to Large Molecules and Nanoscale Materials

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An efficient and real space method is proposed for calculating the electron densities in nonperiodic, nanoscale systems using Cartesian coordinates in three dimensions. Instead of solving Schrödinger eigenvalue problems, "Heaviside-Fermi level operator" method (density matrix method) is used in an iterative procedure, with a separable nonlocal form of pseudopotential and a fast method for solving Poisson's equation. Example calculations of the electronic structures for C_2 and O_2 di-atomic molecules are presented. The present method can be applied for the tight-binding (TB) parametrizations and they are used for the calculations of large scale systems.
Key Words: Finite element method, density functional theory, density matrix, nonlocal pseudopotential, large molecule

1. INTRODUCTION

Significant progress has been made in the last decade in the computational materials science by density functional theory (DFT) [1-10]. The DFT uses the density of a many-electron system as the fundamental quantity to be calculated rather than the wave functions. The plane wave basis allows us to use the efficient FFT algorithm in three-dimensional (3D) Cartesian coodinates for periodic and non-periodic systems using the supercell technique, which has certain limitations and difficulties. In the present study, an efficient and real space method is proposed for calculating the electron densities in nonperiodic, nanoscale systems using Cartesian coordinates in three dimensions [1-8]. Specifically, we use the discrete variable representations (DVR) scheme in the whole stages of the present formulations, so-called the finite element method (FEM). Instead of solving Schrödinger eigenvalue problems, "Heaviside-Fermi level operator" method (density matrix DM method) is used in an iterative procedure. A separable nonlocal form of Haman, Schlüter and Chiang (HSC) pseudopotential [11] and a fast method for solving Poisson's equation are also used for performing efficient calculations. Example calculations of the electronic structures for C_2 and O_2 diatomic molecules are presented. For large molecules, one can perform much faster calculations by using the TB parametrizations derived from the present DF-FEM-DM method.

2. PRINCIPLE OF CALCULATIONS

In the present study, a new approach [7] is used to calculate the electronic density within the density functional theory (DFT) in real space that bypasses solving the Kohn-Sham (KS) equation. In the standard treatments, the kinetic energy operators in the Hamiltonian are replaced by the finite difference operators as:

$$-\frac{\hbar^2}{2m}\left[\sum_{n_x=-N}^{N} Cn_x\Psi\left(x_i+n_xh_x, y_j, z_k\right)+\sum_{n_y=-N}^{N} Cn_y\Psi\left(x_i, y_j+n_yh_y, z_k\right) + \sum_{n_z=-N}^{N} Cn_z\Psi\left(x_i, y_j, z_k+n_zh_z\right)\right]$$
$$+\left[V_{ion}\left(x_i, y_j, z_k\right)+V_H\left(x_i, y_j, z_k\right)+V_{xc}\left(x_i, y_j, z_k\right)\right]\Psi\left(x_i, y_j, z_k\right)$$
$$=E\Psi\left(x_i, y_j, z_k\right).$$

(1)

In the above eq.(1), V_{ion}, V_H and V_{xc} are the ionic, Hartree and exchange correlation potentials, respectively.

The key ingredient of this approach is the combined use of the finite element method (FEM) and the Heaviside-Fermi level operator using a pseudopotential treatment [11]. In this approach the electron density is expressed as

$$\rho(\mathbf{r})=\sum_\sigma\sum_i|\psi_{\sigma i}(\mathbf{r})|^2=\sum_\sigma\langle\mathbf{r}|H\left(E_F-H_\sigma[\rho,\xi]\right)|\mathbf{r}\rangle,$$

(2)

where

$$H\left(E_F-H_\sigma\right)=\lim_{Ne\to\infty}\sum_{n=0}^{Ne}a_n\left(E_F\right)T_n\left(H_\sigma\right).$$

(3)

In the above eq.(2), ξ denotes the spin porlarization, $\xi=\left(\rho^+-\rho^-\right)/\rho$, and E_F the Fermi energy.

In the present formulation, the normalized (scaled) quantities are used

$$a_0\left(E_F\right)=-\frac{1}{\pi}\left(\phi_{E_F}-\pi\right), \quad a_n\left(E_F\right)=-\frac{2}{\pi n}\sin\left(n\phi_{E_F}\right)$$

(4)

$$\phi_{E_F}=\cos^{-1}\left(\overline{E}_F\right), \quad \overline{E}_F=\frac{E_F-\overline{H}}{\Delta H}, \quad \overline{H}_\sigma=\frac{H_\sigma-\overline{H}}{\Delta H}$$

(5)

$$\overline{H}=\frac{E_{max}+E_{min}}{2}, \quad \Delta H=\frac{E_{max}-E_{min}}{2}.$$

(6)

To derive the electrostatic Coulomb potentials, we use a fast method with the fast Fourier transform (FFT's) for nonperiodic systems without having to enlarge the system. The procedure is to transform the static potential so that the boundary condition of Poisson's equation is of the Dirichlet type: The electro-static Coulomb potential outside the electronic densities region is expanded in terms of the multiple electric moments Q_{lm} as

$$\phi_>(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' = 4\pi \sum_{lm} \frac{Q_{lm}}{2l+1} \frac{Y_{lm}(\theta,\phi)}{r^{l+1}}, \quad (7)$$

$$Q_{lm} = \int Y_{lm}^*(\theta,\phi) r^l \rho(\mathbf{r}) d\mathbf{r}, \quad (8)$$

where $Y_{lm}(\theta,\phi)$ are sherical harmonics. Then, the electric potential in the meshed space is solved as follows:

$$\nabla^2\phi = -4\pi\rho \quad (9)$$

$$\phi(\mathbf{r})\big|_{boundary} = \phi_0(\mathbf{r}) \quad (10)$$

The remaining potential $\delta\phi(\mathbf{r})$ resulting from the charge density difference between the true charge density $\rho(\mathbf{r})$ and $\rho_0(\mathbf{r})$ (originating from $\phi_0(\mathbf{r})$) is calculated by using the FFT:

$$\delta\phi(\mathbf{r}) = \phi(\mathbf{r}) - \phi_0(\mathbf{r}) \quad (11)$$

$$\delta\phi(\mathbf{r}) = \rho(\mathbf{r}) + \frac{1}{4\pi}\nabla^2\phi_0(\mathbf{r}) \quad (12)$$

$$\delta\phi(\mathbf{r}) = \sum_{nmk} \hat{\delta\phi}_{nmk} \sin\frac{n\pi x}{N_x\Delta x} \sin\frac{m\pi y}{N_y\Delta y} \sin\frac{k\pi z}{N_z\Delta_z}, \quad (13)$$

$$\delta\rho(\mathbf{r}) = \sum_{nmk} \hat{\delta\rho}_{nmk} \sin\frac{n\pi x}{N_x\Delta x} \sin\frac{m\pi y}{N_y\Delta y} \sin\frac{k\pi z}{N_z\Delta z},$$

where

$$\hat{\delta\phi}_{nmk} = 4\pi \frac{\hat{\delta\rho}_{nmk}}{p_x^2(n) + p_y^2(m) + p_z^2(k)}. \quad (14)$$

$$\phi(\mathbf{r}) = \delta\phi(\mathbf{r}) + \phi_0(\mathbf{r}) \quad (15)$$

$$\phi_0(\mathbf{r}) = 4\pi Q_{00} Y_{00} \frac{1}{r} erf(\frac{r}{r_0}) + 4\pi \sum_{lm} \frac{Q_{lm}}{2l+1} \frac{Y_{lm}(\theta,\phi)}{r^{l+1}} \left[erf(\frac{r}{r_0}) \right]^{l+3} \quad (16)$$

In the discrete variable representation (DVR), the HSC pseudopotential can be discretized in the separable nonlocal form [11,12] as

$$V_{ps}^{DVR} = V_{loc} + \sum_{k,l,m} \frac{\Delta V_l |\tilde{f}_k lm\rangle\langle \tilde{f}_k lm| \Delta V_l}{\Delta V_l(r_k)}, \quad (17)$$

$$\Delta V_l(r_k) = \langle \tilde{f}_k | \Delta V_l | \tilde{f}_k \rangle. \quad (18)$$

Here, it should be noted that the above eqs.(17) and (18) are evaluated by using the interpolation function $\tilde{f}_k$ with Gaussian integration weight ω_k and orthonormal pseudo wave functions $\varphi_k(\mathbf{r})$ as

$$\tilde{f}_k = \frac{1}{\sqrt{w_k}} \sum_{k=0}^{N-1} \varphi_k^*(r_i)\varphi_k(r), \quad (19)$$

$$\varphi_k(r) = \frac{1}{r}\sqrt{\frac{2}{N\Delta r}} \sin\left(\frac{\pi k r}{N\Delta r}\right). \quad (20)$$

The total energy of the system can be given in the standard formula

$$E_v[\rho_v] = \sum_\sigma \sum_n^{N_v^\sigma} \varepsilon_{\sigma,n} - \sum_\sigma \int d\vec{r} \rho_v^\sigma \left[\tfrac{1}{2}\phi_v + \upsilon_{xc,\sigma}(\rho,\xi) - \varepsilon_{xc}(\rho,\xi)\right]$$
$$+ \sum_\sigma \int dr \rho_v^\sigma \left[\varepsilon_{xc}(\rho,\xi) - \varepsilon_{xc}(\rho_c,0) + \frac{1}{2}\sum_{i\neq j} \frac{Z_{ci}Z_{cj}}{R_{ij}}\right]. \quad (21)$$

where the first term, one-electron energy, is calculated by using the FEM and Heaviside density matrix method.

$$\sum_\sigma \sum_n^{N_v^U} \varepsilon_{\sigma,n} = \sum_\sigma \int d\vec{r} \left\langle \vec{r} \left| H_\sigma[\rho_v,\xi] h(E_F - H_\sigma[\rho_v,\xi]) \right| \vec{r} \right\rangle \quad (22)$$

3. RESULTS AND DISCUSSIONS

The dimension of mesh spacing used for the FEM analysis is shown in Fig.1, for diatomic molecules like C_2 and O_2. The uniform grid spacings of h=0.2~0.4a.u ($h_x=h_y=h_z=h$) are used.

Fig.1b shows the electrostatic Coulomb potential, due to uniform charge distributions of two spherical regions of our test calculations in FEM. For the finer meshs than $h \cong 0.5$, one can get fairly good agreement of the electrostatic potentials compared with the results of the exact calculations (dot-dashed curve).

We compare in Fig.2 the electronic charge densities $\rho(r)$ and one-electron energy eigenvalues calculated by FEM for electrons in a box (rectangular parallelepiped) of $13a_0 \times 13a_0 \times 15a_0$ dimension, with those by the exact calcultions. One can see in Figs.2a and 2b that the FEM calcultions are in good agreement with trhe exact calculations.

We present in Table 1 the calculated spectroscopic constants for diatomic molecules C_2 and O_2 by the present method in comparison with those of other calculations and experimental results. The present calculation results of equilibrium bond lengths, binding energies D_e (the energy difference between the dimers at the equilibrium and their constituent atoms) and vibrational frequencies ω_e are in good agreement with other calculations. However, the binding energies are substantially larger than the experimental values. This overbinding may result from the crudeness of the mesh spacing or inadequacies in the LDA and the pseudopotential sued in the present calculations.
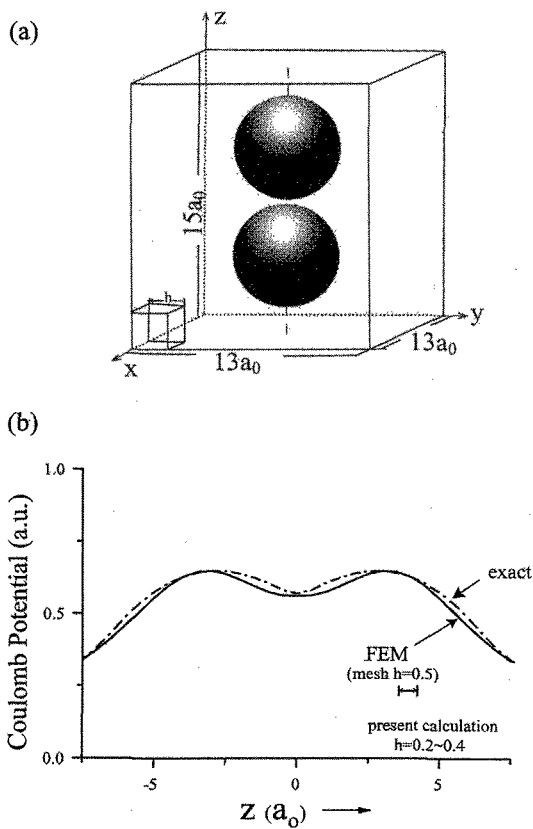
(a)

(b)

Fig.1 Dimensions of mesh spacing used for the FEM analysis (a); and calculated electrostatic Coulomb potential by FEM with h=0.5 (solid curve).
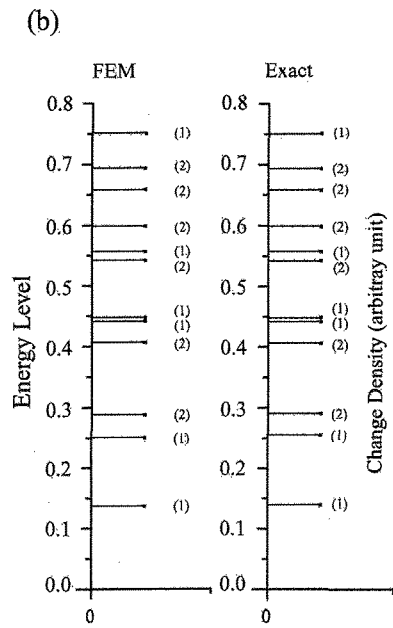
(b)

Fig.2 The electronic charge densities $\rho(\mathbf{r})$ calculated by FEM with the uniform mesh of h=0.5 for electrons confined in the box of $13a_0 \times 13a_0 \times 15a_0$ are presented in (a), in comparison with those of the exact calculations. The energy eigenvalues are shown in b), in comparison with the exact values. The numbers in parentheses are the degeneracy of the corresponding eigenstates.
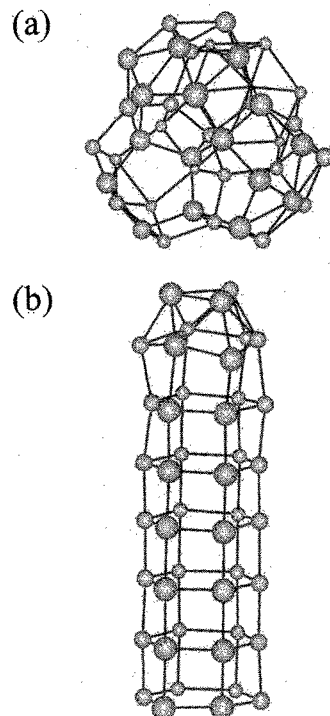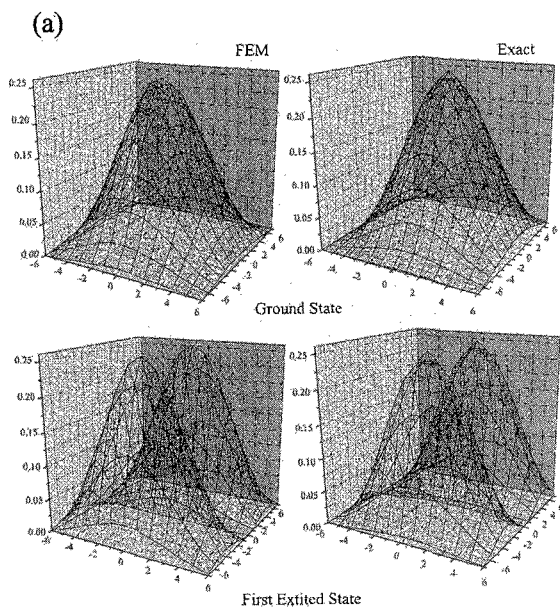
(a)

(b)

Fig.3 Atomic configurations of Si_{45} clusters, stable (a) and metastable (b) structures.

In Fig.3, we present the calculated atomic configurations of Si_{45} clusters, stable tetrahedron

(a)

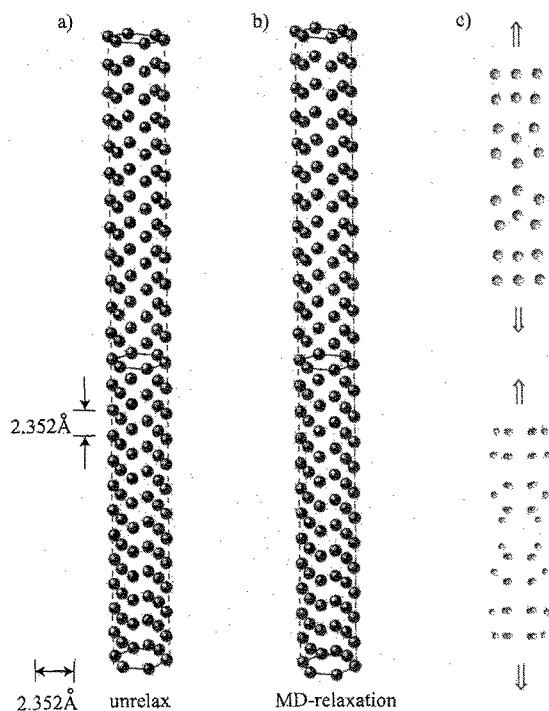structure (a), and metastable structure of stacked benzen

Fig.4 Quasi-1D structure of $(Si_6)_n$ nanotube: (a) unrelaxed, (b) relaxed, and locally stretched (c) structures. All structures are relaxed under the condition that uppermost and lowest 6-membered rings are fixed.

Table.1 Spectroscopic Constants for Diatomic Molecules C_2 and O_2

	C_2	O_2
	r_e(au)	
Experiment	2.35	2.28
present	2.44	2.40
Other method[a]	2.343	2.39
	D_e(ev)	
Experiment	6.3	5.2
present	8.3	8.55
Other method[a]	8.2	8.5
	ω_e(cm^{-1})	
Experiment	1860	1580
present	1920	1620
Other method[a]	1923	1625

a) D. J. Kouri, Y. Huang and D. K. Hoffman, J. Phys. Chem., **100** (1996) 7903; Experimantal results are from Ref.15.

-like rings (b). The structures of the Si_{45} clusters have been studied extensively in conjunction with the chemical reactivity e.g., with ammonia and methanol molecules [13]. In view of the stability of the stacked benzene-like rings, we have calculated the atomic structures of $(Si_6)_n$ "nanotube", under the condition that the uppermost and lowest 6-membered rings are fixed, and presented the results in Fig.4. One can see that there are little differences between the unrelaxed (Fig.4a) and relaxed

(4b) structures respectively, indicating the stability of the " nanotube" structures. Fig. 4c shows the stretched atomic configuration (about 10%) under tension and the electronic conversions from sp^2 to sp^3 hybrids can be observed in the heavily distorted region. We have also found that the tensile strength of "Si nanotube" is sufficiently high ~100GPa, comparable to the compressive strength of carbon nanotube.

We are currently studying the electronic transport properties of "Si nanotubes", as in the recent calculations of nanoelectromechanical effects of carbon nanotubes [14].

4. CONCLUSIONS

The new DF-FEM-DM method is presented for calculating the electronic structures in nonperiodic, polyatomic systems using Cartesian coordinates in three dimensions. The density matrix method and spin-density-functional theory are used, rather than solving the Schrödinger eigenvalue problem. A fast method for solving Poisson's equation in nonperiodic systems, and a separable nonlocal form of norm conserving pseudopotentials (with no spurious states and no PW cut-off problem) have been employed. Example calculations are presented for small di-atomic molecules like C_2 and O_2. The present scheme also allows us to derive the tight-binding (TB) parameters which can be applied to calculations of the large scale systems.

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