Electronic structure calculations using finite difference time domain method with density functional theory and local density approximation

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Abstract. Density functional theory (DFT) has been used very successful to obtain electronic structures of atoms and molecules. One method to obtain ground state densities and energies using the DFT method is by solving the time-dependent Kohn Sham (TDKS) equation. In this paper we apply the finite difference time domain (FDTD) method to solve the TDKS equation in imaginary time. The FDTD-DFT method is given in this paper and its numerical results for ground states and energies for various atoms and molecules are compared with results from other DFT program.

1. Introdution

After Schrodinger equation was formulated [1], the development of quantum physics increased rapidly. One of the main purposes of quantum physics is to observe the electronic structures of atom and molecule. In a system with only have single particle, the solution of Schrodinger equation can be easily solved analytically. But when the system consists of two or more interacting particle, such as atom and molecule, the analytical solution of Schrodinger equation nearly impossible to solved [2]. The Hartree-Fock method that proposed by Fock [3] with several other methods [4-7] can be used to solve this problem. The exchange interaction of the particles can be calculated exactly using a Hartree-Fock method, but in practical application, this method required very long-time computer calculation [8]. At the same time period where uniform electron gas model proposed by Thomas-Fermi [9], Dirac show that electron exchange interaction can be obtained from local density approximation [10]. Based on these, Hohenberg and Kohn [11] proved that there is some universal density functional which can be used to calculate the interactions between particles and provide a basic foundation on the Density Functional Theory (DFT) method. Hohenberg and Kohn only proved that DFT method can be used to replaced Hartree-Fock method without explaining how to use it.

Application of DFT methods for calculating the electronic structure can be done after Kohn-Sham equation formulated [12], this equation is the exact form of Hohenberg and Kohn theorem [13]. Kohn-Sham formulation is a time-independent static equation that can be used to determine a ground state of the system. Runge and Gross [14] reformulated static Kohn-Sham equation to become time-dependent Kohn-Sham equation. In 1999, more than 2500 papers with DFT topic has been published in Physics and Chemist article [15]. In computational physics and chemistry community, DFT method gives great impact, especially for calculating the electronic structure of atoms and molecules. Some programs like

GAUSSIAN, Firefly, ABINIT, Octopus, and other commercial programs are even developed specifically to the determined electronic structure of the atom and molecule. Each program has different algorithms which have a purpose of speeding up calculations [12] using selection of basis set [16], pseudopotential [17], effective core potential [18], Davidson matrix diagonalization algorithm [19], and others algorithm or numerical methods.

Recently, Finite Difference Time Domain (FDTD) method has been used to solve quantum systems using Schrodinger equation and Hartree-Fock approximation [21-25]. It's shown that the FDTD method gives fairly accurate result in various quantum system calculations. The FDTD method is a general numerical method for solving a differential equation. One of the main advantages of this method is the FDTD method to have a simple algorithm that can be customized with a various condition. In this paper, we calculate electronic structure using the FDTD numerical method with the DFT method in local density approach. The results of various atoms and molecules compared with NIST [26] and Octopus program [27].

2. Theory

The FDTD numerical methods application on various quantum systems using the Schrodinger equation has been fully described by Sudiarta and Geldart [23]. In DFT, the time-dependent Kohn-Sham (TDKS) equation can be solved using FDTD method. The TDKS formula in atomic units ($\hbar = m = 1$) is

$$i\frac{\partial}{\partial t}\varphi_j(\vec{r},t) = \left[-\frac{\nabla^2}{2} + V_s[\rho(\vec{r},t)]\right]\varphi_j(\vec{r},t) \tag{1}$$

the effective potential V_s depends on the core potential, Hartree potential, and exchange-correlation potential. Effective potential can be determined using

$$V_s[\rho(\vec{r},t)] = V(\vec{r},t) + \int \frac{\rho(\vec{r}',\tau)}{|\vec{r}-\vec{r}'|}d^3\vec{r}' + V_{xc}[\rho(\vec{r},t)] \tag{2}$$

where density ρ is total electron density of the system that can be calculeted by

$$\rho(\vec{r},t) = \sum_{i=1}^{N}|\varphi_i^{KS}(\vec{r},t)|^2 \tag{3}$$

The exchange-correlation potential can be calculated using the local density approximation by ignoring correlation factor. In the local density approximation, the total of exchange energy formula is

$$E_x^{LDA}(\rho,\vec{r}) = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\int[\rho(\vec{r})]^{4/3}d\vec{r} \tag{4}$$

exchange potential can be derivate exactly by

$$V_{xc}(\vec{r}) = \frac{\delta E_{xc}[\rho(\vec{r})]}{\delta\rho(\vec{r})} \tag{5}$$

so the exchange potential on the local density approximation has a form

$$V_x^{LDA}(\rho) = -\left[\left(\frac{3}{\pi}\right)\rho(\vec{r})\right]^{1/3} \tag{6}$$

The ground state of the system can be achieved by modifying the TDKS equation into a diffusion equation. This can be done by transforming real-time into imaginary time $\tau = it$ on the TDKS equation. TDKS diffusion equation has the form

$$\frac{\partial\varphi_n(\vec{r},\tau)}{\partial\tau} = \left[\frac{1}{2}\nabla^2 - V_0(\vec{r}) - \int\frac{\rho(\vec{r}',\tau)}{|\vec{r}-\vec{r}'|}d^3\vec{r}' + \left(\frac{3}{\pi}\right)^{\frac{1}{3}}\rho^{\frac{1}{3}}(\vec{r},\tau)\right]\varphi_n(\vec{r},\tau) \tag{7}$$

after a long enough iteration, the system will be in a ground state. Once the orbital of each particle has reached the ground state, the energy value can be determined using

$$E = \sum_n \int \frac{1}{2}\nabla^2\varphi_n(\vec{r})d\vec{r} + \int \rho(\vec{r})V_{core}(\vec{r})d\vec{r} + \frac{1}{2}\iint \frac{\rho(\vec{r_1})\rho(\vec{r_2})}{r_{12}}d\vec{r_1}d\vec{r_2} + E_{xc}[\rho(\vec{r})] \tag{8}$$

3. Numerical methode

The discretization in DFT method can be done using the forward finite difference and the central finite difference scheme in equation (7). The numerical equation result is

$$\varphi_{i,j,k}^{\tau+\Delta\tau} = \alpha\varphi_{i,j,k}^{\tau} + \frac{\beta\Delta\tau}{2}\left\{ \begin{array}{l} \frac{1}{\Delta x^2}\left[\varphi_{(i+1),j,k}^{\tau} - 2\varphi_{i,j,k}^{\tau} + \varphi_{(i-1),j,k}^{\tau}\right] \\ + \frac{1}{\Delta y^2}\left[\varphi_{i,(j+1),k}^{\tau} - 2\varphi_{i,j,k}^{\tau} + \varphi_{i,(j-1),k}^{\tau}\right] \\ + \frac{1}{\Delta z^2}\left[\varphi_{i,j,(k+1)}^{\tau} - 2\varphi_{i,j,k}^{\tau} + \varphi_{i,j,(k-1)}^{\tau}\right] \end{array} \right\} + \frac{\beta\Delta\tau}{2}V_{i,j,k}^{\tau}\varphi_{i,j,k}^{\tau} \tag{9}$$

where α and β is

$$\alpha = \frac{(1 - \frac{\Delta\tau}{2}V_{i,j,k}^{\tau})}{(1 + \frac{\Delta\tau}{2}V_{i,j,k}^{\tau})} \tag{10}$$

$$\beta = \frac{1}{(1 + \frac{\Delta\tau}{2}V_{i,j,k}^{\tau})}$$

electron density $\rho_{i,j,k}^{\tau}$ can be determined by

$$\rho_{i,j,k}^{\tau} = \sum_{i=1}^{N}|\varphi_{i,j,k}^{\tau}|^2 \tag{11}$$

and V^{τ} potential is

$$V_{i,j,k}^{\tau} = (V_{core})_{i,j,k}^{\tau}\rho_{i,j,k}^{\tau} + \sum_{i,j,k}\left[\Delta x^3\frac{\rho_{i',j',k'}^{\tau}}{\sqrt{r_{i,j,k}^2 - r_{i',j',k'}^2}}\right] - \left(\frac{3}{\pi}\rho_{i,j,k}^{\tau}\right)^{\frac{1}{3}} \tag{12}$$

for stability condition, equation (10) must statisfies condition [25]

$$\Delta\tau \le \Delta x / 6 \tag{13}$$

furthermore, the energy value can be calculated using a numerical form of the equation (8)

$$E = \sum_{i,j,k}\left[V_{i,j,k}^{\tau}\rho_{i,j,k}^{\tau} - \frac{\varphi_{i,j,k}^{\tau}}{2}\left\{ \begin{array}{l} \frac{1}{\Delta x^2}\left[\varphi_{(i+1),j,k}^{\tau} - 2\varphi_{i,j,k}^{\tau} + \varphi_{(i-1),j,k}^{\tau}\right] \\ + \frac{1}{\Delta y^2}\left[\varphi_{i,(j+1),k}^{\tau} - 2\varphi_{i,j,k}^{\tau} + \varphi_{i,(j-1),k}^{\tau}\right] \\ + \frac{1}{\Delta z^2}\left[\varphi_{i,j,(k+1)}^{\tau} - 2\varphi_{i,j,k}^{\tau} + \varphi_{i,j,(k-1)}^{\tau}\right] \end{array} \right\}\right] \tag{14}$$

4. Results and discussions

In this paper, we calculate electronic structure of several atoms and molecules using FDTD method with DFT in local density approximation. Coulombic interaction of atoms and molecules were calculated using approach by Sudiarta and Geldart [23] to avoid infinite values at small distances. The result of this work is compared with NIST reference and Octopus program.

4.1. Atom

First of all, in order to validate the results obtained, the FDTD method is applied in Atom Helium system (Z = 2). Two electrons are simulated in the cube with the length of each side is L = 6 a.u.. The size of the simulation box should be large enough so it doesn't affect the ground state of the system. To see the effect of the size of the box, we calculate the ground state energy of the Helium at various grid values. FDTD numerical calculation results are shown in Table 1, as a comparison, Octopus calculation is also included using same parameters.

Table 1. The numerical ground state energy result of the Helium atom in various grid sizes by ignoring the correlation factor (LDA-X) where the NIST reference value is (LSDA-XC) E0 = -2.809599 hartree.

ΔL	T	E_{ext}	E_H	E_x	E_0 (hartee)		
					FDTD	Octopus	| FDTD - NIST |
0.13	2.47511	-6.16050	1.933670	-0.83538	-2.58709	-2.55700	0.222509
0.12	2.52085	-6.23358	1.947581	-0.84088	-2.60603	-2.58240	0.203569
0.11	2.55923	-6.29343	1.959238	-0.84552	-2.62048	-2.59816	0.189119
0.10	2.59032	-6.34190	1.968608	-0.84926	-2.63223	-2.61462	0.177369
0.09	2.61442	-6.37918	1.975051	-0.85185	-2.64156	-2.62442	0.168039

In the FDTD method and other numerical methods that use real space, the sizes of grids and space boundaries are very important. Ideally, to get accurate results, the size of the space boundaries should be as largest as possible (L → ∞) and the size of the grids as smallest as possible (ΔL → 0). This is because when the simulation space is too small, the electrons will interact with the wall of the simulation space. In another hand, when the size of grids is too large, numerical calculations will not give an accurate result and energy cutoff near atom core will large enough.

Table 5.3. The numerical result of ground state energy for several atoms by ignoring the correlation factor (LDA-X) compared with the reference value of NIST (LSDA-XC).

Atom	Octopus	FDTD	NIST
Li	-5.98416011	-6.076681	-7.276402
Be	-11.54349657	-11.735735	-14.295533
B	-18.97425158	-19.503337	-24.058374

The ground state energy of helium atom showed that there is a little difference between FDTD and NIST reference. That's because we can't found LDA-X reference, so we use LSDA-XC where correlation factor is included. Moreover, the difference is due to energy cutoff in the numerical approach that we use on coulomb potentials (Equation 3.32) to avoid the singularity. Although there is some difference, it can be seen that FDTD method give slightly better result than Octopus program on the same parameter. The ground state energy of serveral simple atoms shown in Table 4 by using Δx = Δy = Δz = ΔL = 0.15 at the same sides length (L = 6 a.u.).
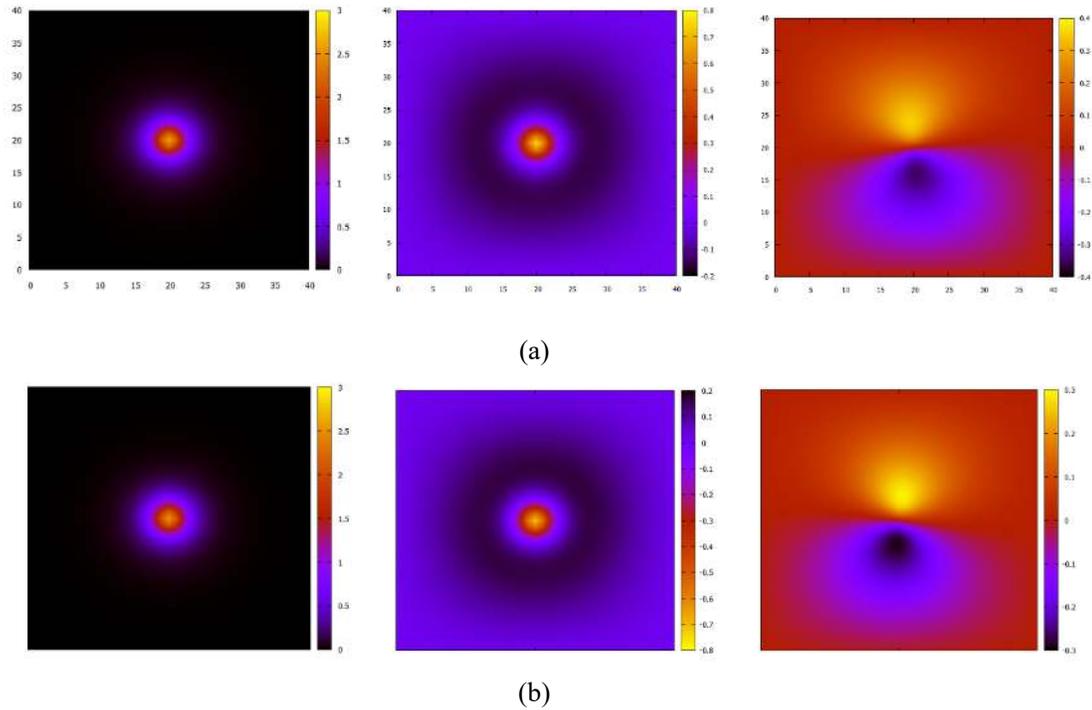
(a)

(b)

Figure 5.1. Kohn-Sham orbital obtained from FDTD (top) and Octopus (bottom) method on Boron atoms (Z = 5) for each electron with spin +1/2.

Besides FDTD method can be used to calculate energy, it also gives a Kohn-Sham orbital directly. The Khon-Sham orbital obtained from FDTD method has a similar contour with the actual atomic orbitals. Figure 5.1 shows each electron with spin +1/2 orbitals for Boron atoms that obtained from FDTD method and Octopus program which resembles the electron configuration of 1s22s22p1. One important thing that we get from the result is Kohn-Sham orbital obtained by the FDTD method does not always reflect the actual electron orbitals. The Kohn-Sham orbital on the FDTD method is a combination of all states at the same (n) energy level. For example, at the energy level with n = 3, sometimes Kohn-Sham orbital has single orbitals configuration (3S1, 3S2, 3P1, etc.), and sometimes it has combination of several l and m (3P1 + 3P2, 3P1 + 3P3, 3P1 + 3P4, etc.) or even combinations between different orbital (3P1 + 3S2, 3S1 + 3P2 + 3D6, etc.).

4.2. Molecule

The ground state of a molecule is interestingly to study. In this paper, we also calculate the electronic structure of simplest molecule system like H2 and HeH+ molecules using FDTD method. Both molecules are selected because they require a small simulation space. The simulation is performed on a cube with a side length L = 10 a.u. and the distance between cores are used is in the equilibrium condition where R = 1.39 on the H2 molecule and R = 1.78 for the HeH$^+$ molecule.
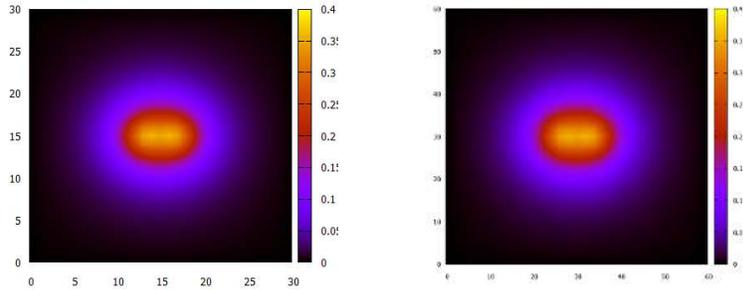
Figure 5.2. Kohn-Sham Orbital before (left) and after (right) interpolation process.

The initial Kohn-Sham orbital that we use taken from interpolation scheme in a larger grid size (Figure 5.2) to faster make calculation process. In addition, the integration on the Coulomb part is solved by parallel using OpenMP [28], it proves that this scheme can speed up the calculation process. The result of numerical calculation of the ground satate energy on H2 and HeH$^+$ molecules is shown in Table. 5.4.

Table 5.4 The numerical result of ground state energy for H2 and HeH$^+$ molecules by ignoring the correlation factor (LDA-X) where the reference value of NIST (LSDA-XC) for H2 molecule is -1.157014 and HeH$^+$ is -2.875109 in atomic unit.

	FDTD	Octopus
$\Delta L = 0.333$ a.u		
H2	-0.954987	-0.92779784
HeH$^+$	-2.355033	-2.18115369
$\Delta L = 0.167$ a.u		
H2	-1.013162	-1.00427504
HeH$^+$	-2.612656	-2.49972321

Using the same parameters, the results of the ground state energy calculations of both molecules show that numerical FDTD methods are consistent with a numerical result on the Octopus program. When compared to reference values using NIST LSDA-XC, FDTD method give slightly better result than Octopus program..
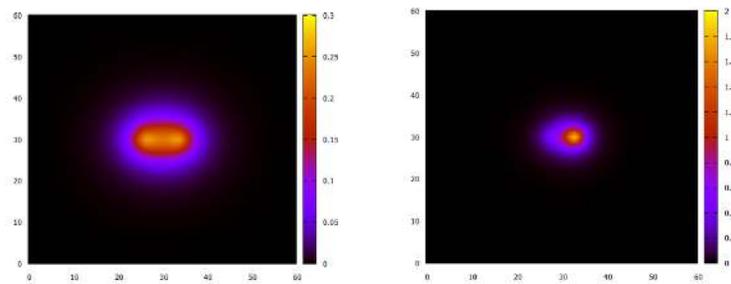

Figure 5.3. Kohn-Sham density obtained from FDTD for H2 (left) and HeH$^+$ (right) molecules.

Besides energy, other parameters that can be observed in this system are density (Figure 5.3). Density can be obtained directly through the Kohn-Sham orbitals resulting from FDTD method. It seems that each atom in the H2 molecule gives the same contribution for density parameter, however for HeH^+ molecule each atom gives a different contribution. That because H2 molecule contains two same atoms (Hydrogen), whereas in the HeH^+ molecule one of them have larger atom than other.

5. Conclusion
The FDTD method with DFT and the local density approximation was successfully applied for calculated electronic structures on several atoms and molecules. The ground state energy result using FDTD method is slightly better than Octopus program. The ground state energy for Helium atom is -2.64156 hartree and for H2 molecule is -1.013162 hartree. The FDTD method was also successfully used to observe the density of H2 and HeH+ molecules. In Kohn-Sham orbital observations, the FDTD method sometimes produces a mixed orbital.

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