A Density Functional Study for Hydrogen Bond Energy by Employing Real Space Grids

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In order to examine the efficiency of a nobel real space grid method for density functional theory (DFT) calculations, the hydrogen bond energy of the water dimer was computed. It was demonstrated that the real space grid augmented by double grid near the atomic core can yield a realistic hydrogen bond energy curve of the water dimer.

Density functional theory (DFT) has recently emerged as an effcient approach for the electronic structure calculations in the field of chemistry as well as physics.[1,2] It was suggested that DFT can yield results of comparable accuracy to MP2 calculations for a series of small molecules with less expense.[3] It is therefore desirable to develop more efficient way to accomplish the DFT calculations. A planewave basis coupled with a pseudopotential is known as a successful method for such calculations.[4] In recent years, a method that employs a grid in real space and finite-difference method to solve the Kohn-Sham equation has been introduced.[5,6] The real space finite-difference approach has several advantages compared with planewave basis. First of all, it can treat non-periodic systems such as clusters or charged systems as well as semi-periodic systems. Secondly, it is straightforward to augment basis functions only near the atomic core region where the pseudopotentials vary rapidly. The third is that one can drastically reduce the number of fast fourier transformations (FFT), because only the total electron density must be transformed by FFT and it becomes more amenable to parallel implementations. Finally it should be stressed that the real space grid method is identical to the planewave basis approach when it is applied to a periodic system except that the Hamiltonian operation is done in the real space.

A drawback of the real space grid is that the relative position of an atom with respect to grid points will seriously affect the results of the computations unless the grid spacing is narrow enough. That is because a pseudopotential varies so rapidly near the atomic center that the grid points could not represent accurately the variation of the pseudopotentials. One of the promising ways to conquer this problem is to prepare extremely narrow grid points near the atomic core region, which leads to a high degree of accuracy; however, it causes the increase of the computational cost as well as computer storage. Recently Ono and Hirose proposed a quite simple and efficient double-grid technique that requires only a modest increase of computational cost without a loss of accuracy in the framework of the real space finite-difference method.[7] It has been shown that the real space finite-difference method can yield potential energy curves of the chemical bonds efficiently;[5,6] however, it is still unknown whether the method is adequate for the calculation of potential energies of weakly bound systems or not. In this Letter we calculate the hydrogen bond energy of the water dimer by using the real space grid method reinforced by the double grid proposed by Ono and Hirose and examine the accuracy of the method. The results of the computations will be compared with those of DFT calculations by Gaussian 94.[8]

The Kohn-Sham equation for the orbital φ_i with eigenvalue ε_i of the system can be written as

$$\left[-\frac{1}{2}\nabla^2 + \int \frac{\rho(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + v_{ps}(\mathbf{r}) + v_{xc}(\mathbf{r})\right]\varphi_i = \varepsilon_i\varphi_i \ ,$$

where the first term inside the parenthesis is the kinetic energy operator, the second is the Hartree potential, the third is the pseudopotentials of the atoms, and the fourth is the exchange and correlation functional, respectively. In our calculations we employed the fourth-order finite-difference scheme to express the kinetic energy operator of Eq. (1).[5] The Hartree potential is computed by the method in reference 9 to remove the periodic image of the potential. The non-local atomic pseudopotentials are separated into a local potential and a Kleinman-Bylander form in real space.[10] The double grid technique was applied to non-local part of the pseudopotential only near the atomic core region, where the dense grid spacing is one-fifth of the coarse grid spacing h. The h is set at 0.287 au in this work. The exchange and correlation interactions are estimated by local density approximations (LDA). The functional used in this work is that proposed by Perdew and Zunger.[11]

In order to compute the interaction energy of the water dimer, the molecules are placed in a cubic simulation box of size 18.4 au. In Figure 1 the geometry of the hydrogen bonded water dimer is presented. Hydrogen bond energy curve is generated by varying the R(O-O) distance in Figure 1 with other geometrical parameters fixed. As was pointed out in reference 12, the potential energy surface of the system is very flat with respect to internal coordinates; therefore, these constraints have practically no effect on the binding energy. The interaction energy ΔE_{int} is calculated by the equation,

$$\Delta E_{int} = E_{dim} - 2\cdot E_{mono} \ ,$$

where E_{dim} is the potential energy of the dimer and E_{mono} is that of monomer. To examine the validity of the calculations, the results are compared with experimental value[13] and those of DFT calculations by Gaussian 94 with the same exchange and

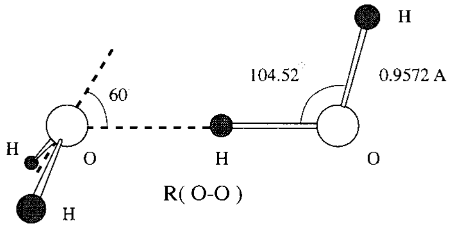

Figure 1. Geometry of the hydrogen bonded water dimer.

correlation functional. Two sets of gaussian basis functions are employed. One is the correlation-consistent polarized valence orbital basis set of double zeta quality (cc-pVDZ).[14] Another is that augmented by diffuse functions(AUG-cc-pVDZ).

The results are presented in Figure 2. The experimental value (+ mark) indicates the optimal O-O distance and the hydrogen bond energy of the water dimer. In reference 12, it is shown that the O-O distance and the interaction energy optimized by the MP2 calculation agrees with the experimental value within 0.1 a.u. and 0.1 kcal/mol difference, respectively. In this sense, the experimental value can be considered to be highly reliable as well as the MP2 calculation. As for the DFT calculation of Gaussian 94 with cc-pVDZ basis functions, the hydrogen bond energy is overestimated and the optimal O-O length is underestimated significantly as compared with experimental value. The introduction of the diffuse type basis functions greatly improves the behavior of the potential energy curve(AUG-cc-pVDZ). Though the stable O-O distance varies scarecely, the depth of the hydrogen bond energy curve becomes very shallow. This work also overestimates the binding energy and underestimates the O-O distance as compared with the experimental value; however, the differences are not so serious. There may be several reasons why the energy difference between this work and the Gaussian 94(AUG-cc-pVDZ) is significant where the O-O distance is short. With regard to the accuracy of the numerical calculations, the Gaussian 94 will be superior to this work because the spatial integrations of the Gaussian functions are much more accurate than that of real space grids though the double grid technique has been introduced. The other origin of the discrepancy may be attributed to the fact that the real space grids are sufficiently prepared outside the atomic core regions. As has been shown in Figure 2, the augmentation of the diffuse type orbitals is essential for the calculation of hydrogen bond energy in the Gaussian 94. Spatially localized atomic basis functions are not adequate to describe realistic behavior of the wavefunctions far from the atomic core region. The planewave basis has the same advantage because of its delocalized nature. As a result it would be valid to say that the real space grid method can yield a realistic hydrogen bond energy in comparable accuracy with the Gaussian 94. As for the computational cost of the real space grid method, it increases as the square of the number of atoms in the system ($O(N^2)$), while that of the localized atomic orbital basis approach scales in $O(N^4)$ when no symmetry is assumed. Therefore, this method becomes advantageous as the number of atoms increases. From these calculations it was demonstrated that the real space and finite difference method coupled with the pseudo-potentials is adequate for the calculations of rather weak interactions such as hydrogen bond energy within the Kohn-Sham DFT scheme. Further it is expected that the method will be successfully applied to the ab initio molecular dynamics simulations[15] where the hydrogen bond energy will play an essential role.

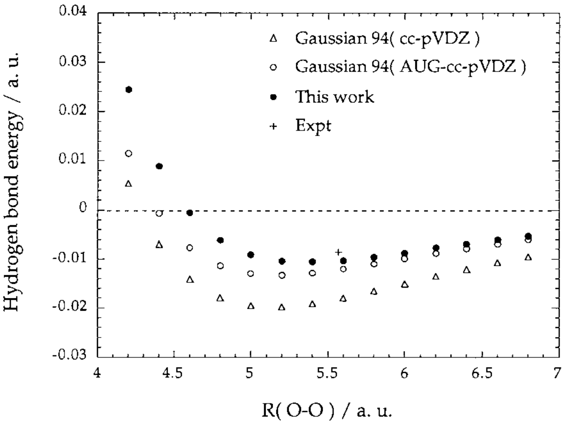

Figure 2. Hydrogen bond energy curves as a function of O-O distance.

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