

AB INITIO HARTREE-FOCK CALCULATIONS OF SOME DIATOMIC MOLECULES INVOLVING GROUP IV SEMICONDUCTORS

Ata Özmat

Department of Physics, Yeditepe University



Introduction

Hartree-Fock method is an ab initio method which does not require any data but fundamental knowledge of complex system such as molecules to calculate total energy of respective molecules by solving Schrödinger equation instead of performing experiments. While doing that, calculation speed of computer has to be used. In this project, total energies of some diatomic molecules of group IV elemental and compound semiconductors are calculated. They are C(diamond) SiC(silicon carbide) and Si(silicon). Moreover, an approximation is performed to find interatomic distance and dissociation energy of C diatomic molecule.

Many-Body System

For a many-body system such as an element or a molecule containing higher atomic number then Z=2, solution of Schrödinger equation for the system is extremely difficult and needs an advanced treatment. Hamiltonian of this kind of system can be represented by Born-Oppenheimer approximation which neglects motion of nuclei since they are less mobile than electrons.

$$\hat{H}_{BO} = -\frac{1}{2}\sum_{i=1}^N \nabla_i^2 + \frac{1}{2}\sum_{i,j=1; i\neq j}^N \frac{1}{|r_i - r_j|} - \sum_{n=1}^K \sum_{i=1}^N \frac{Z_n}{|r_i - R_n|}$$

Wavefunction needs a special treatment too. It has to be antisymmetric and normalized. It needs to contain permutation of n-electron system. This wavefunction is written in a determinant called the Slater Determinant. Each element in this determinant is spin orbital which is a product of molecular orbital and spin function of each electron in the system.

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \cdots & \chi_N(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \cdots & \chi_N(\mathbf{x}_2) \\ \vdots & \vdots & & \vdots \\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \cdots & \chi_N(\mathbf{x}_N) \end{vmatrix}.$$

Hartree-Fock Method

Each molecular orbital is constructed by a basis set. Hartree-Fock method does not offer an exact solution. This problem is caused by variational calculation. Variational calculation gives an iterative method through calculation of the wavefunction.

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$$\psi_i = \sum_{\mu=1}^N c_{\mu i} \phi_{\mu}$$

$c_{\mu i}$ is molecular orbital expansion coefficient which obtainedby variational calculation and ϕ_{μ} is basis function. Basis functions are special functions constructed to mathematically represent molecular orbitals in linear combinations. STO-3G, 6-31G and 6-31G** are the basis functions used in this project. Roothaan-Hall equations give a solution for energy calculation. In fact, it is a representation of Hartree-Fock method. It contains the Fock Matrix, $F_{\mu\nu}$, that is the Hamiltonian for this method.

$$\sum_{\nu=1}^N (F_{\mu\nu} - \epsilon_i S_{\mu\nu}) c_{\nu i} = 0 \quad \mu = 1, 2, \dots, N$$

$F_{\mu\nu}$ is expressed by Hamiltonian of a single electron in the first term and two-electron repulsion integral in the second term

$$F_{\mu\nu} = H_{\mu\nu}^{core} + \sum_{\lambda=1}^N \sum_{\sigma=1}^N P_{\lambda\sigma} \left[(\mu\nu|\lambda\sigma) - \frac{1}{2}(\mu\lambda|\nu\sigma) \right]$$

Roothaan-Hall equations can be expressed for different spins occupying the same orbital by assigning slightly different molecular orbital to each spin. Then, each equation is doubled in number. This is called unrestricted Hartree-Fock method(UHF). Otherwise, it is the restricted Hartree-Fock method(RHF). An advanced method in the family Hartree-Fock method is Møller-Plesset perturbation theory(MP). It is the many-body version of perturbation theory. In this project, second-order of Møller-Plesset perturbation theory (MP2) is used.

$$E^{(2)} = \sum_j^{occ} \sum_i^{<i} \sum_a^{virt} \sum_b^{<b} (\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j)^{-1} |(ij||ab)|^2$$

Results

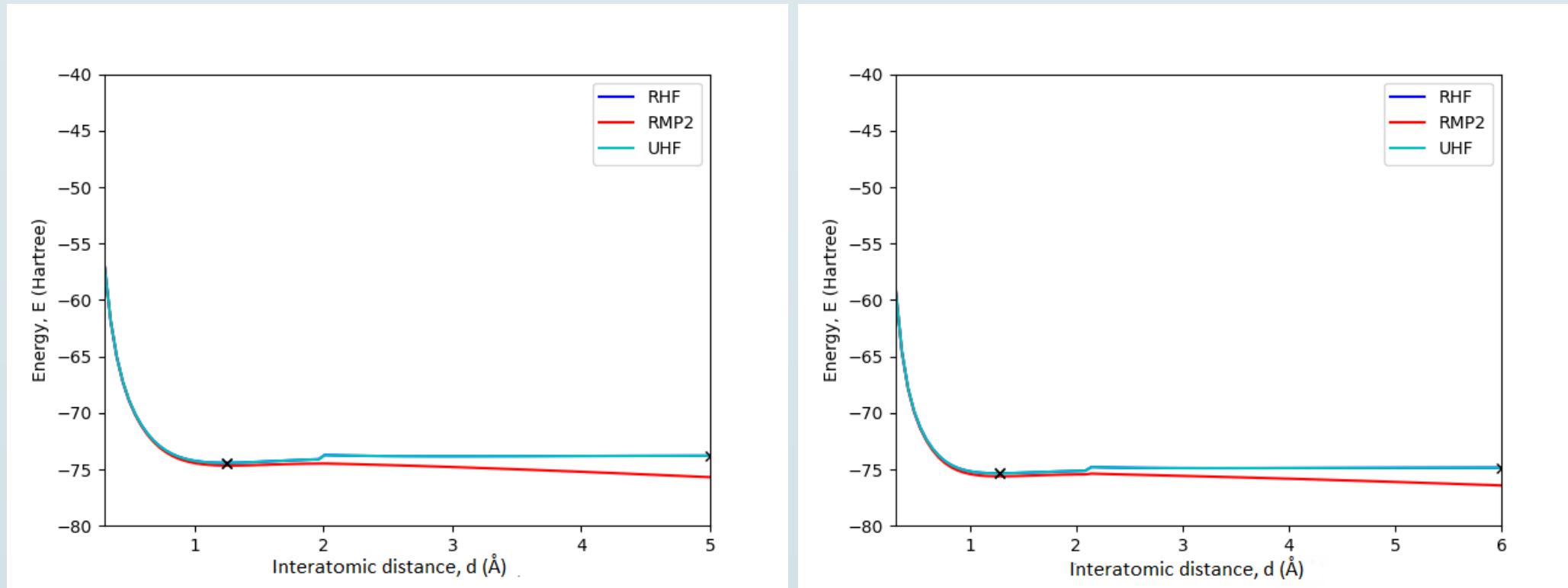
Total energies (in unit of hartree) of diatomic molecules of C(diamond), SiC and Si are calculated by HF and MP2 with STO-3G, 6-31G and 6-31G** basis sets. HF-limit is the lower bound of variational method. In other words, this value is where the calculation with basis set of maximum accuracy converges to. Percentage errors for the calculations with the most advanced basis set are no more than 2% which is acceptable.

Basis Set	HF	MP2
STO-3G	-74.31543321633097	-74.60170708
6-31G	-75.28764779567433	-75.56380829
6-31G**	-75.30478401785325	-75.63989476
HF-limit	-75.77 ± 0.03	

Basis Set	HF	MP2
STO-3G	-318.9390974420726	-318.94414016
6-31G	-320.87166204520844	-320.92331359
6-31G**	-320.4690950115624	-320.61646889
HF-limit ^a	-326.6471	

Basis Set	HF	MP2
STO-3G	-570.8571609523077	-571.04476776
6-31G	-577.6036049654211	-577.7473778
6-31G**	-577.6784880265851	-577.83158984
HF-limit ^a	-577.7811	

Interatomic distance and dissociation energy of C diatomic molecule is calculated with a different method. In a range of chosen interatomic distance of the molecule, total energy of the molecule is calculated on so many points. Therefore, interatomic distance is found on equilibrium position. Further, dissociation energy is found substracting the calculated energy on the furthest point in the range from the calculated energy on the equilibrium position.



The figure at left is calculated by STO-3G. The one on the right is calculated by 6-31G. There is no significant different seen from the graphs. However, the following figure shows the difference.

Basis Set	Interatomic distance, d (Å)	Dissociation energy (hartree)
STO-3G	1.2494	0.629
6-31G	1.2787	0.498
Reference	1.54 ^a	0.555 ^b

For interatomic distance, percentage error is 16.97% - 18.87%. For dissociation energy, it is 10.27% - 13.45%. Accuracy of these calculations is not satisfying.

Conclusion

Total energy calculations of HF and MP2 are quite accurate due to the lower bound of variational calculation. Besides experimental data, ab initio method is quite favorable for this calculation. UHF has to be performed by different softwares. Because, the results obtained by UHF are quite same with the results obtained by RHF. For interatomic distance and dissociation energy calculation, a different approach has to be used in order to get acceptable results with proper errors. It needs a further research. Computational limitation is such restrictive handicap that extremely long durations of calculations obstruct more accurate and more complicated calculations. It can be overcome by using a fster programming language or computer. Otherwise, a faster method is needed.

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