Ohio University

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Journal of JU YI for the Fall of 2010

JU YI

1. Sept.29, 2010- Oct.5, 2010:

Prepared my presentation on Wednesday (Oct.6, 2010)

This week I read '**R12 methods in explicitly correlated molecular electronic structure theory**' by Wim Klopper. After reading the paper, I searched MP2 method,bra-ket notation, and quantum chemistry. Also, again, I read section1(introduction) because I had to explain my section to Yi and Vusi. I had a difficult time understanding the paper because every notation and equation were in physical chemistry. However, I knew that R12 method was better than other methods and the method handled many electron integrals.
I am going to explain section1 of the paper on Wednesday(Oct.6). So, I prepared some powerpoint slides on Latex for my presentation. Also, I looked my group members' powerpoint slides.
Next week, I am going to hopefully finish our paper, and start a new paper.

2. Oct.6, 2010-Oct.13, 2010:

Understanding the pair function $|u_{ij}\rangle$ in R12 method

During this week, I spent time understanding the pair function $|u_{ij}\rangle$. In R12 methods the pair function $|u_{ij}\rangle$ has the form;

$$|u_{ij}\rangle = |v_{ij}\rangle + |w_{ij}\rangle$$
$$|v_{ij}\rangle = \sum_{k<l} C_{ij}^{kl} \hat{Q_{12}} f_{12} \, |kl\rangle$$
$$|w_{ij}\rangle = \sum_{a<b} t_{ij}^{ab} \, |ab\rangle$$

First, I knew that;

- Any function ψ can be written as a sum of complete set of orthonormal function φ.

$$\psi = \sum_i C_i \varphi_i$$
$$|\psi\rangle = \sum_i C_i |\varphi_i\rangle = \sum_i C_i |i\rangle$$

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- In the paper, they used the following notation for one- and many-electron functions:
  - $\Psi, \Psi_N \ldots$: N-electron wavefunction
  - $\Phi, \Phi_k, |\Phi\rangle, |\Phi_i^a\rangle, |\Phi_{ij}^{ab}\rangle \ldots$: Slater determinants

$$\Phi(r_1, r_2) = \varphi_1(r_1)\varphi_2(r_2) - \varphi_2(r_1)\varphi_1(r_2) = \begin{vmatrix} \varphi_1(r_1) & \varphi_2(r_1) \\ \varphi_1(r_2) & \varphi_2(r_2) \end{vmatrix}$$

$$\Phi(r_1, \ldots, r_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(r_1) & \ldots & \varphi_N(r_1) \\ \vdots & \ldots & \vdots \\ \varphi_1(r_N) & \ldots & \varphi_N(r_N) \end{vmatrix}$$

  - $\varphi_k, \varphi_p, \ldots$: orthonormal spin orbitals
  - $i, j, k, \ldots$: occupied spin orbitals
  - $a, b, c, \ldots$: virtual spin orbitals
  - $X_p^q = \langle p|X|q\rangle$, $Y_{rs}^{pq} = \langle rs|Y|pq\rangle$, $A_{ij} = \langle \varphi_i|\hat{A}|\varphi_j\rangle$

Next, I understood and compared the notation of pair function $|u_{ij}\rangle$ with the notation of Dr.Mohlenkamp.

- N-electrons of Hartree-Fock wavefunction:

$$\Psi_{HF} = A\left[\varphi_1(1)\varphi_2(2)\cdots\varphi_i(i)\cdots\varphi_N(N)\right] = A\prod_{i=1}^{N}\varphi_i(i)$$
$$\text{where } A = -A^T \text{ (antisymmetrizer)}$$

- $\Psi_{HF}(r_1, r_2, \cdots, r_N) = A\prod_{i=1}^{N}\varphi_i(r_i)$
- $\epsilon_j^a\Psi_{HF} = A\prod_{i=1, i\neq j}^{N}\varphi_i(r_i)\varphi_a(r_j)$
- $|a\rangle = \Psi_a = \epsilon_j^a\Psi_{HF}$
  $|ab\rangle = \Psi_{ab} = \epsilon_{ij}^{ab}\Psi_{HF}$
- $|w_{ij}\rangle = \sum_{a<b} t_{ij}^{ab}|ab\rangle = \sum_{a<b} t_{ij}^{ab}\epsilon_{ij}^{ab}\Psi_{HF}$

3. Oct.14, 2010-Oct.20, 2010:

Understanding Hylleraas functional;

$$H[u_{ij}] = \langle u_{ij}|\hat{Q_{12}}(\hat{F}_1 + \hat{F}_2 - \varepsilon_i - \varepsilon_j)\hat{Q_{12}}|u_{ij}\rangle + 2\langle u_{ij}|\hat{Q_{12}}r_{12}^{-1}|ij\rangle \geq \varepsilon_{ij}^{(2)}$$

This week I worked understanding the Hylleraas function.

- Hylleraas functional;

$$H[u_{ij}] = \langle u_{ij}|\hat{Q_{12}}(\hat{F}_1 + \hat{F}_2 - \varepsilon_i - \varepsilon_j)\hat{Q_{12}}|u_{ij}\rangle + 2\langle u_{ij}|\hat{Q_{12}}r_{12}^{-1}|ij\rangle \geq \varepsilon_{ij}^{(2)}$$

  - $\hat{F}$: Fock operators for electrons 1 and 2

$$\hat{F}_i\varphi_i(r) = \varepsilon_i\varphi_i(r)$$

- $\varepsilon_i, \varepsilon_j$: orbital energies of the Hartree-Fock spin-orbitals φ_i and φ_j
- $\varepsilon_{ij} = \left\langle Qu_{ij} | r_{12}^{-1} | \varphi_{ij} \right\rangle, \varphi_{ij} = \varphi_i(r_1)\varphi_j(r_2)$
- MP2 correlation energy separates into pair contributions (Sinanoglu):

$$E_2 = \sum_{i \leq j} \varepsilon_{ij}^{(2)}$$

- $\hat{Q_{12}}$:Strong orthogonality operator, for example

$$\hat{Q_{12}} = (1 - \hat{P}(1))(1 - \hat{P}(2))$$
$$\text{where } \hat{P} = \sum_i |\varphi_i\rangle\langle\varphi_i|$$
$$\hat{P}(1), \hat{P}(2)\text{: Projection operators for electrons 1 and 2}$$

- $|ij\rangle$: two electron determinant containing the two occupied spin orbitals φ_i and φ_j,

$$|ij\rangle = \frac{1}{\sqrt{2}}\{\varphi_i(1)\varphi_j(2) - \varphi_j(1)\varphi_i(2)\}$$

4. Oct.21,2010 - Oct.27, 2010:

Moller-Plesset Perturbation theory(MP)

This week went much more slowly than anticipated. However, I did have a better understanding of some of papers because I studied some of notations and equations during last 4 weeks. This week, I spent much time on the understanding MP-theory (Moller-Plesset Perturbation theory). I need to know Rayleigh-Schrodinger perturbation theory(RS-PT) because MP-theory is a special application of RS-PT. Now, I understood RS-PT. This upcoming week I am going to read 'Note on an approximation tratment for many-electron systems' by Moller and Plesset, 1934. This paper is the main idea of MP.

5. Oct.27,2020 - Nov.3, 2010:

Moller-Plesset Perturbation theory(MP)

This week, I continuously worked understanding the Moller-Plesset Perturbation theory.

- Mller-Plesset perturbation theory (MP) is one of several quantum chemistry post-Hartree-Fock ab initio methods in the field of computational chemistry. It improves on the Hartree-Fock method by adding electron correlation effects by means of Rayleigh-Schrdinger perturbation theory (RS-PT), usually to second (MP2), third (MP3) or fourth (MP4) order. Its main idea was published as early as 1934 by Christian Mller and Milton S. Plesset.
- The MP theory is a special application of Rayleigh-Schrdinger perturbation theory(RS-PT). In RS-PT one considers an unperturbed hamiltonian operator $\hat{H}_0$ to which is added a small perturbation $\hat{V}$:

$$\hat{H} = \hat{H}_0 + \lambda\hat{V} \tag{1}$$

Here λ is an expansion parameter that will be taken as $\lambda = 1$ at the end.

- perturbed energy:

$$E = \lim_{n\to\infty} \sum_{i=0}^{n} \lambda^i E^i \tag{2}$$

- perturbed wavefunction:

$$\Psi = \lim_{n\to\infty} \sum_{i=0}^{n} \lambda^i \Psi^i \tag{3}$$

- Inserting (2) and (3) into (1), and requiring equality for each order of λ, we obtain E^0,E^1,E^2, and $\cdots$.

- The Hamiltonian is partitioned as

$$\hat{H} = \hat{H}_0 + \hat{V}$$

where $\hat{H}_0$ is the Hartree-Fock Hamiltonian

$$\hat{H}_0 = \sum_i F(i) = \sum_i h(i) + V^{HF}(i)$$

and

$$\hat{V} = \sum_{i<j} (r_{ij}^{-1} - V^{HF})$$

is the perturbation. Here, V^{HF} denotes the Coulomb and exchange interaction of electron i with the rest of the electrons in the Hartree-Fock approximation.

- $\hat{H}_0\Psi^0 = E^0\Psi^0 \Rightarrow (\hat{H}_0 - E^0)\Psi^0 = 0$
  $\hat{H}_0\Psi^1 + \hat{V}\Psi^0 = E^0\Psi_1 + E^1\Psi^0 \Rightarrow (\hat{H}_0 - E^0)\Psi^1 = E^1\Psi^0 - \hat{V}\Psi^0$
  $\cdots$
  $E^0 = \langle\Psi^0|\hat{H}_0|\Psi^0\rangle$
  $E^1 = \langle\Psi^0|\hat{V}|\Psi^0\rangle$
  $E^2 = \langle\Psi^0|\hat{V}|\Psi^0 + \Psi^1\rangle$

- The zeroth-order:

$$\hat{H}_0\Psi^0 = E^0\Psi^0$$
$$E^0 = \langle\Psi^0|\hat{H}_0|\Psi^0\rangle = \sum_i \epsilon_i$$

where ϵ_i is the orbital energy for orbital i.

- To first order, the correction to the energy is

$$E^1 = \langle\Psi^0|\hat{V}|\Psi^0\rangle$$
$$= \langle\Psi^0|\sum_{i<j} r_{ij}^{-1}|\Psi^0\rangle - \langle\Psi^0|\sum_i V^{HF}(i)|\Psi^0\rangle$$
$$= \sum_{i<j}\langle ij\|ij\rangle - \sum_i\sum_j\langle ij\|ij\rangle$$

where the

$$\langle ij\|ij\rangle \equiv \langle ij|ij\rangle - \langle ij|ji\rangle \equiv \langle i(1)j(2)|r_{12}^{-1}|i(1)j(2)\rangle - \langle i(1)j(2)|r_{12}^{-1}|j(1)i(2)\rangle$$

- The second sum is just twice the first sum so the final result is

$$E^1 = -\tfrac{1}{2}\sum_{ij}\langle ij\|ij\rangle$$

- This shows that the Hartree-Fock energy is the sum of the zeroth and first oder perturbation energy

$$E^{HF} = E^0 + E^1 = \sum_i \epsilon_i - \frac{1}{2}\sum_{ij}\langle ij\|ij\rangle$$

- The second order correction to the ground state energy depends on the first order correction to the wavefunction.This in turn depends on matrix elements of the perturbation between the unperturbed ground and excited states of $\hat{H}_0$.

$$E^2 = E^S + E^D + E^T + \cdot + E^N$$

- The single excitations contribute

$$E^S = \sum_i \sum_a \frac{|\langle \Psi^0|\hat{V}|\Psi_i^a\rangle|^2}{\epsilon_i - \epsilon_a} = 0$$

because $\langle \Psi^0|\sum_{i<j} r_{ij}^{-1}|\Psi_i^a\rangle = \langle \Psi^0|\sum_i V^{HF}(i)|\Psi_(^a i)\rangle$

- The double excitations contribute

$$E^D = \sum_{i<j}\sum_{a<b}\frac{|\left\langle \Psi^0|\hat{V}|\Psi_{ij}^{ab}\right\rangle|^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

- Because $\sum_i V^{HF}$ is a one electron operator all matrix elements between Ψ^0 and Ψ_{ij}^{ab} vanish and only $\sum_{i<j} r_{ij}^{-1}$ contributes

$$\langle \Psi^0|\sum_{i<j} r_{ij}^{-1}|\Psi_{ij}^{ab}\rangle = \pm\langle ab||ij\rangle$$

- $E^D = \sum_{i<j}\sum_{a<b}\frac{|\langle ab||ij\rangle|^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$
  where

$$\langle ab\|ij\rangle \equiv \langle ab|ij\rangle - \langle ab|ji\rangle \equiv \langle a(1)b(2)|r_{12}^{-1}|i(1)j(2)\rangle - \langle a(1)b(2)|r_{12}^{-1}|j(1)i(2)\rangle$$

- All triple and higher order excitations vanish and so

$$E^T + E^Q + \cdots + E^N = 0$$

- $E^2 = E^D = \sum_{ijab} \frac{|\langle ab||ij\rangle|^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$
- The estimate of the energy to second order is referred to as the MP2 approximation to the energy of the system

$$E^{MP2} = E^0 + E^1 + E^2 = E^{HF} + E^2$$

- A disadvantage is that it is not variational, so the estimate of the correlation energy can be too large.
- An enormous practical advantage is that MP2 is fast, while it is rather reliable in its behavior, and size consistent.

6. Nov.4,2010 - Nov.10, 2010:

Prepare final presentation of Moller-Plesset Perturbation theory(MP)

This week I prepared my group final presentation. My part was the Moller-Plesset(MP) theory. I could understand clearly the zeroth, first, second order MP method during making my presentation part. On Monday, I met my group members-Vusi and Yi. We made power point slides on latex for the final presentation, and we explained our parts. I learned other group members' part. It was helpful to me. This fall, I learned many things for the research and I met good members-Vusi and Yi.

References

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[3]Win Klopper and J. Noga (2003), in *Explicitly correlated wave functions in chemistry and physics: theory and application*,edited by J Rychlewski, pp. 149-183

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[7]Valerio Magnasco (2009),*Methods of Molecular Quantum Mechanics*, pp.133-138

[8]Mller-Plesset perturbation theory, Perturbation theory (quantum mechanics) and Bra-ket notation **From Wikipedia**

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[10]$http://www-theor.ch.cam.ac.uk/people/ross/thesis/node23.html$

[11]$http://www.physics.unlv.edu/\ bernard/phy72103/lectures/lecture2.pdf$