Møller-Plesset Perturbation theory

- Møller and Plesset suggested to use the self-consistently converged solution of the Hatree-Fock equation as the starting point of the perturbation expansion. They suggest to reformulate the zero-th order problems in terms of Hatree-Fock SCF fields.

Møller-Plesset Perturbation theory

- Suppose we have the N orthonormal orbitals as the solution to the equation

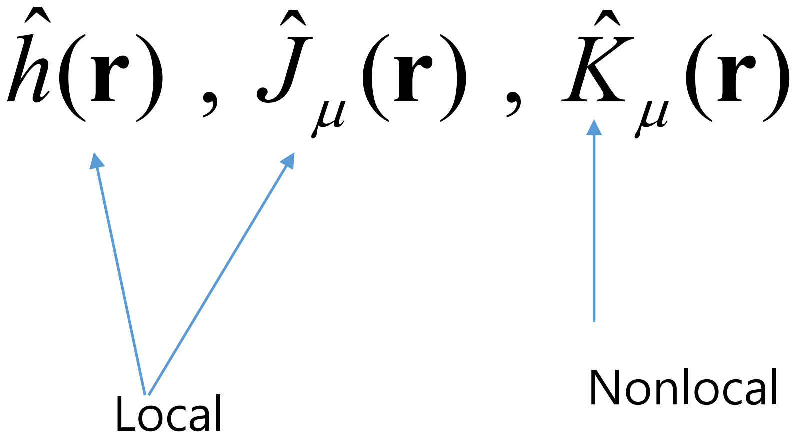
$$\left(-\frac{1}{2}\nabla^2+V(\mathbf{r})\right)\psi_\lambda(\mathbf{r})+\left(\sum_{\mu=1}^{N}\int\frac{\psi_\mu^*(\mathbf{r}_2)\psi_\mu(\mathbf{r}_2)}{|\mathbf{r}-\mathbf{r}_2|}d^3\vec{r}_2\right)\psi_\lambda(\mathbf{r})-\sum_{\mu=1}^{N}\int\frac{\psi_\mu^*(\mathbf{r}_2)\psi_\lambda(\mathbf{r}_2)\psi_\mu(\mathbf{r})}{|\mathbf{r}-\mathbf{r}_2|}d^3\vec{r}_2=\varepsilon_\lambda\psi_\lambda(\mathbf{r})$$

- Define the following operators, $\hat{h}$, $\hat{J}$, $\widehat{K}$

$$\hat{h}(\mathbf{r})=-\frac{1}{2}\nabla^2+V(\mathbf{r})$$

$$\hat{J}_\mu(\mathbf{r})\psi(\mathbf{r})=\int\frac{\psi_\mu^*(\mathbf{r}_2)\psi_\mu(\mathbf{r}_2)}{|\mathbf{r}-\mathbf{r}_2|}d^3\vec{r}_2\psi(\mathbf{r})$$

$$\hat{K}_\mu(\mathbf{r})\psi(\mathbf{r})=-\int\frac{\psi_\mu^*(\mathbf{r}_2)\psi(\mathbf{r}_2)}{|\mathbf{r}-\mathbf{r}_2|}d^3\vec{r}_2\psi_\mu(\mathbf{r})$$



$$\hat{h}(\mathbf{r})\ ,\ \hat{J}_\mu(\mathbf{r})\ ,\ \hat{K}_\mu(\mathbf{r})$$

Local

Nonlocal

$$\hat{K}_{\mu}(\mathbf{r})\psi_{\lambda}(\mathbf{r}) = -\int \frac{\psi_{\mu}^{*}(\mathbf{r}_2)\psi_{\lambda}(\mathbf{r}_2)}{\left|\mathbf{r}-\mathbf{r}_2\right|} d\mathbf{x}_2 \psi_{\mu}(\mathbf{r}) = -\int \frac{\psi_{\mu}^{*}(\mathbf{r}_2)\psi_{\lambda}(\mathbf{r}_2)}{\left|\mathbf{r}-\mathbf{r}_2\right|} d\mathbf{x}_2 \left\langle \sigma_{\mu} \middle| \sigma_{\lambda} \right\rangle \psi_{\mu}(\mathbf{r})$$

Note

The inner product includes the spin part.

For the Hatree-Fock SCF fields

- With the N orthonormal orbitals as the so

$$\left(\hat{h}(\mathbf{r})+\sum_{\mu=1}^{N}\hat{J}_{\mu}(\mathbf{r})+\sum_{\mu=1}^{N}\hat{K}_{\mu}(\mathbf{r})\right)\psi_{\lambda}(\mathbf{r})=\varepsilon_{\lambda}\psi_{\lambda}(\mathbf{r})$$

- For the product state of two particle

$$\left(\hat{h}(\mathbf{r}_1)+\sum_{\mu=1}^{N}\hat{J}_{\mu}(\mathbf{r}_1)+\sum_{\mu=1}^{N}\hat{K}_{\mu}(\mathbf{r}_1)+\hat{h}(\mathbf{r}_2)+\sum_{\mu=1}^{N}\hat{J}_{\mu}(\mathbf{r}_2)+\sum_{\mu=1}^{N}\hat{K}_{\mu}(\mathbf{r}_2)\right)\psi_{\lambda}(\mathbf{r}_1)\psi_{\xi}(\mathbf{r}_2)=(\ldots)\psi_{\lambda}(\mathbf{r}_1)\psi_{\xi}(\mathbf{r}_2)$$

$$\varepsilon_{\lambda}+\varepsilon_{\xi}$$

For the Hatree-Fock SCF fields

- The Slater Determinant of SCF N orbitals

$$|\Psi(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N)\rangle = \frac{1}{\sqrt{N!}}\begin{vmatrix} \psi_1(\mathbf{x}_1) & \psi_1(\mathbf{x}_2) & \ldots & \psi_1(\mathbf{x}_N) \\ \psi_2(\mathbf{x}_1) & \psi_2(\mathbf{x}_2) & \ldots & \psi_2(\mathbf{x}_N) \\ \ldots & \ldots & \ldots & \ldots \\ \psi_N(\mathbf{x}_1) & \psi_N(\mathbf{x}_2) & \ldots & \psi_N(\mathbf{x}_N) \end{vmatrix}$$

- Show that

$$\sum_{i=1}^{N}\left(\hat{h}(\mathbf{r}_i)+\sum_{\mu=1}^{N}\hat{J}_\mu(\mathbf{r}_i)+\sum_{\mu=1}^{N}\hat{K}_\mu(\mathbf{r}_i)\right)|\Psi\rangle = \left(\sum_{\lambda=1}^{N}\varepsilon_\lambda\right)|\Psi\rangle$$

Hamiltonian

- The zero-th order

$$\hat{H}_N^{(0)} = \sum_{i=1}^{N}\left(\hat{h}(\mathbf{r}_i) + \sum_{\mu=1}^{N} \hat{J}_\mu(\mathbf{r}_i) + \sum_{\mu=1}^{N} \hat{K}_\mu(\mathbf{r}_i) \right)$$

- The full Hamiltonian

$$\hat{H}_N = \sum_{i=1}^{N} \hat{h}(\mathbf{r}_i) + \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\frac{1}{\left|\mathbf{r}_i - \mathbf{r}_j\right|}$$

- Perturbation