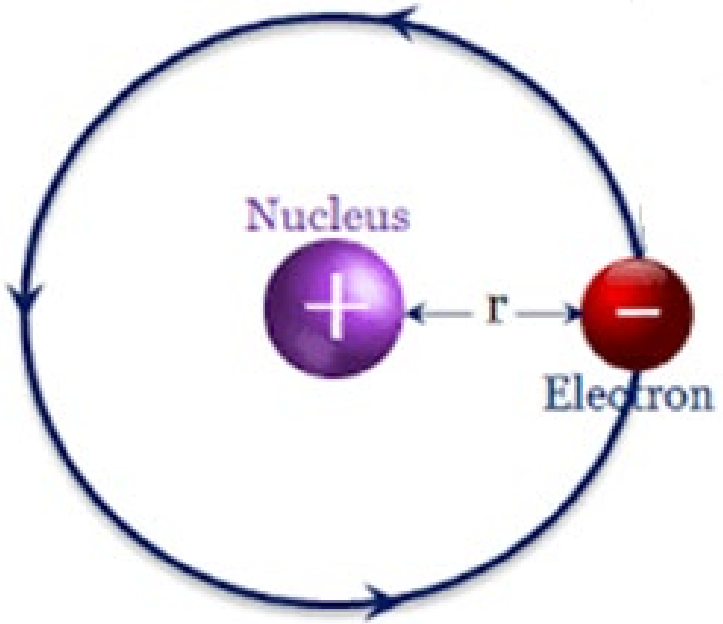
For the electron in H atom

$$\left[-\frac{1}{2}\nabla^2 + V(\mathbf{r})\right]\psi_n(\mathbf{r}) = E_n\psi_n(\mathbf{r})$$

Here, we don't consider the motion of proton. Why ?

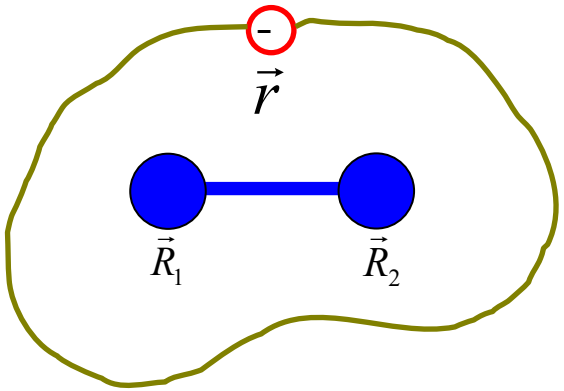
➔ Born-Oppenheimer approximation



For the electron in H_2^+

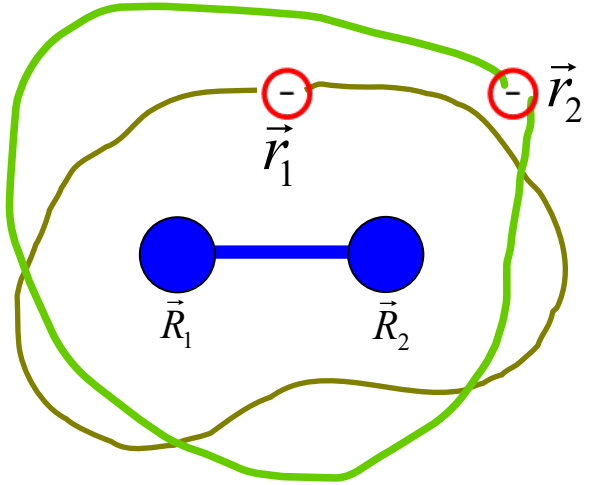
$$\left[-\frac{1}{2}\nabla^2 + V(\vec{r})\right]\psi(\vec{r}) = E\psi(\vec{r})$$

$$V(\vec{r}) = \frac{1}{|\vec{r} - \vec{R}_1|} + \frac{1}{|\vec{r} - \vec{R}_2|}$$



The equation for the two electron in H_2 ?

Hamiltonian for the two electrons



$$\hat{H} = \left(-\frac{1}{2}\frac{\partial}{\partial \vec{r}_1^{\,2}} - \frac{1}{2}\frac{\partial}{\partial \vec{r}_2^{\,2}} + V(\vec{r}_1) + V(\vec{r}_2) \right) + \frac{1}{\left|\vec{r}_1 - \vec{r}_2\right|}$$

Hamiltonian for N electrons

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

- Question !!, why do we have the factor $1/2$?
- It may contain the SOC and many other terms. But we are mainly interested in the calculation of the electron-electron correlation.
- Note the symbol for the one-body operator

$$\hat{h}(\mathbf{r}) = -\frac{1}{2}\nabla^2 + V(\mathbf{r}) \text{ , and then } \hat{H}_N = \sum_{i=1}^{N}\hat{h}(\mathbf{r}_i) + \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

Schrodinger equation for N identical Fermion

$$\hat{H}_N \Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = E\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)$$

- Note that X_i collectively denotes the position coordinate and the spin.
- Fundamental antisymmetric nature of the identical Fermion state function

$$\Psi(\mathbf{x}_2, \mathbf{x}_1, \ldots, \mathbf{x}_N) = -\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)$$

Slater Determinant

- We assume that the many-body wave function can be constructed by the determinant of N distinct one-body orbital.

$$\Psi(\mathbf{x}_1,\mathbf{x}_2,...,\mathbf{x}_N)=\mathbf{SD}\left[\psi_1,\psi_2,...,\psi_N\right]=\frac{1}{\sqrt{N}}\begin{vmatrix}\psi_1(\mathbf{x}_1) & \psi_1(\mathbf{x}_2) & ... & \psi_1(\mathbf{x}_N)\\ \psi_2(\mathbf{x}_1) & \psi_2(\mathbf{x}_2) & ... & \psi_2(\mathbf{x}_N)\\ ... & ... & ... & ...\\ \psi_N(\mathbf{x}_1) & \psi_N(\mathbf{x}_2) & ... & \psi_N(\mathbf{x}_N)\end{vmatrix}$$

- The orthonormal one-body orbital

$$\left\langle\psi_n(\mathbf{x})\middle|\psi_m(\mathbf{x})\right\rangle=\left\langle\sigma_n\middle|\sigma_m\right\rangle\int\psi_n^*(\mathbf{r})\psi_m(\mathbf{r})d^3\mathbf{r}=\delta_{n,m}$$

Note

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

Orbital index. The name for N distinct functions

Particle index. The name for N identical partic

Slater Determinant

- If the spin index looks uncomfortable, we may first proceed with the theory without spin degree of freedom.

$$\Psi(\mathbf{x}_1,\mathbf{x}_2,...,\mathbf{x}_N)=\mathbf{SD}\left[\psi_1,\psi_2,...,\psi_N\right]=\frac{1}{\sqrt{N!}}\begin{vmatrix}\psi_1(\vec{r}_1) & \psi_1(\vec{r}_2) & ... & \psi_1(\vec{r}_N)\\ \psi_2(\vec{r}_1) & \psi_2(\vec{r}_2) & ... & \psi_2(\vec{r}_N)\\ ... & ... & ... & ...\\ \psi_N(\vec{r}_1) & \psi_N(\vec{r}_2) & ... & \psi_N(\vec{r}_N)\end{vmatrix}$$

- The orthonormal one-body orbital

$$\left\langle\psi_n(\mathbf{x})\middle|\psi_m(\mathbf{x})\right\rangle=\int\psi_n^*(\mathbf{r})\psi_m(\mathbf{r})d^3\mathbf{r}=\delta_{n,m}$$

Variational Search for the N orbitals.

- Search for the N orbital which minimize the energy expectation

$$E = \left\langle \Psi(\mathbf{x}_1,\ldots,\mathbf{x}_N) \middle| \hat{H}_N \middle| \Psi(\mathbf{x}_1,\ldots,\mathbf{x}_N) \right\rangle$$

- Under the constraint. $\int \psi_n^*(\mathbf{r})\psi_m(\mathbf{r})d^3\mathbf{r} = \delta_{n,m}$

- We needs N Langrangian multiplier to implement the constraint.

Euler-Langrange equation

$$\tilde{E} = \left\langle \Psi(\mathbf{x}_1,\ldots,\mathbf{x}_N) \middle| \hat{H}_N \middle| \Psi(\mathbf{x}_1,\ldots,\mathbf{x}_N) \right\rangle - \sum_n \varepsilon_n \left(\int \psi_n^*(\mathbf{r}) \psi_n(\mathbf{r}) d^3\mathbf{r} - 1 \right)$$

- Find the N orbital which minimize the energy expectation

Show that

I. With the Slater determinant wavefunction

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = \mathbf{SD}\left[\psi_1, \psi_2, \ldots, \psi_N\right]$$

II. We have

$$E = \left\langle \Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N) \middle| \hat{H}_N \middle| \Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N) \right\rangle = \left\langle \Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N) \middle| \sum_{i=1}^{N} \hat{h}(\mathbf{r}_i) + \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{1}{\left|\mathbf{r}_i - \mathbf{r}_j\right|} \middle| \Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N) \right\rangle$$

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

$$+ \frac{1}{2} \sum_{\lambda=1}^{N} \sum_{\mu=1}^{N} \iint \frac{\psi_\lambda^*(\mathbf{r}_1) \psi_\mu^*(\mathbf{r}_2) \psi_\lambda(\mathbf{r}_1) \psi_\mu(\mathbf{r}_2)}{\left|\mathbf{r}_1 - \mathbf{r}_2\right|} d^3\vec{r}_1 d^3\vec{r}_2 - \frac{1}{2} \sum_{\lambda=1}^{N} \sum_{\mu=1}^{N} \iint \frac{\psi_\lambda^*(\mathbf{r}_1) \psi_\mu^*(\mathbf{r}_2) \psi_\lambda(\mathbf{r}_2) \psi_\mu(\mathbf{r}_1)}{\left|\mathbf{r}_1 - \mathbf{r}_2\right|} d^3\vec{r}_1 d^3\vec{r}_2$$

Two-body energy : Coulomb energy

III. Two parts of the two-body energy. The Coulomb energy

$$\frac{1}{2}\sum_{\lambda=1}^{N}\sum_{\mu=1}^{N}\iint\frac{\psi_\lambda^*(\mathbf{r}_1)\psi_\mu^*(\mathbf{r}_2)\psi_\lambda(\mathbf{r}_1)\psi_\mu(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}d^3\vec{r}_1 d^3\vec{r}_2=\frac{1}{2}\sum_{\lambda=1}^{N}\sum_{\mu=1}^{N}\iint\frac{|\psi_\lambda(\mathbf{r}_1)|^2|\psi_\mu(\mathbf{r}_2)|^2}{|\mathbf{r}_1-\mathbf{r}_2|}d^3\vec{r}_1 d^3\vec{r}_2$$

$$=\frac{1}{2}\iint\frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}d^3\vec{r}_1 d^3\vec{r}_2$$

IV. Can we call it the density, the one-body density ? Later, we define it more rigorously

$$\rho(\mathbf{r})=\sum_{\lambda=1}^{N}\psi_\lambda^*(\mathbf{r})\psi_\lambda(\mathbf{r})$$

Two-body energy : Coulomb energy

V. The density

$$\int \rho(\mathbf{r}) d^3\vec{r} = \sum_{\lambda=1}^{N} \int \psi_\lambda^*(\mathbf{r}) \psi_\lambda(\mathbf{r}) d^3\vec{r} == ???$$

VI. Do you like the name “Coulomb energy” ?

$$\frac{1}{2} \iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d^3\vec{r}_1 d^3\vec{r}_2$$

Two-body energy : Exchange energy

III. Two parts of the two-body energy. The exchange energy

$$-\frac{1}{2}\sum_{\lambda=1}^{N}\sum_{\mu=1}^{N}\iint\frac{\psi_{\lambda}^{*}(\mathbf{r}_1)\psi_{\mu}^{*}(\mathbf{r}_2)\psi_{\lambda}(\mathbf{r}_2)\psi_{\mu}(\mathbf{r}_1)}{|\mathbf{r}_1-\mathbf{r}_2|}d^3\vec{r}_1 d^3\vec{r}_2$$

IV. Recover the spin degree of freedom

$$-\frac{1}{2}\sum_{\lambda=1}^{N}\sum_{\mu=1}^{N}\iint\frac{\psi_{\lambda}^{*}(\mathbf{r}_1)\psi_{\mu}^{*}(\mathbf{r}_2)\psi_{\lambda}(\mathbf{r}_2)\psi_{\mu}(\mathbf{r}_1)}{|\mathbf{r}_1-\mathbf{r}_2|}\left\langle s_1=s_\lambda\middle|s_1=s_\mu\right\rangle\left\langle s_2=s_\mu\middle|s_1=s_\lambda\right\rangle d^3\vec{r}_1 d^3\vec{r}_2$$

V. Non-zero exchange energy only between the orbital with the same spin.

Euler-Langrange equation

$$\tilde{E} = \left\langle \Psi(\mathbf{x}_1,...,\mathbf{x}_N) \middle| \hat{H}_N \middle| \Psi(\mathbf{x}_1,...,\mathbf{x}_N) \right\rangle - \sum_n \varepsilon_n \left(\int \psi_n^*(\mathbf{r}) \psi_n(\mathbf{r}) d^3\mathbf{r} - 1 \right)$$

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

$$+ \frac{1}{2} \sum_{\lambda=1}^{N} \sum_{\mu=1}^{N} \iint \frac{\psi_\lambda^*(\mathbf{r}_1) \psi_\mu^*(\mathbf{r}_2) \psi_\lambda(\mathbf{r}_1) \psi_\mu(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d^3\vec{r}_1 d^3\vec{r}_2 - \frac{1}{2} \sum_{\lambda=1}^{N} \sum_{\mu=1}^{N} \iint \frac{\psi_\lambda^*(\mathbf{r}_1) \psi_\mu^*(\mathbf{r}_2) \psi_\lambda(\mathbf{r}_2) \psi_\mu(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} d^3\vec{r}_1 d^3\vec{r}_2$$

$$- \sum_n \varepsilon_n \left(\int \psi_n^*(\mathbf{r}) \psi_n(\mathbf{r}) d^3\mathbf{r} - 1 \right)$$

$$\frac{\delta \tilde{E}}{\delta \psi_\lambda^*} = 0$$

Euler-Langrange equation

$$\frac{\delta \tilde{E}}{\delta \psi_\lambda^*} = 0$$

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

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

$$\left(-\frac{1}{2}\nabla^2 + V(\mathbf{r}) + V_H(\mathbf{r})\right)\psi_\lambda(\mathbf{r}) - \int \Omega(\mathbf{r},\mathbf{r}')\psi_\lambda(\mathbf{r}')d^3\vec{r}' = \varepsilon_\lambda\psi_\lambda(\mathbf{r})$$

Euler-Langrange equation

I. Coulomb potential. It is local multiplicative

$$V_H(\mathbf{r}) = \sum_{\mu=1}^{N} \int \frac{\psi_\mu^*(\mathbf{r}')\psi_\mu(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3\mathbf{r}' = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3\mathbf{r}'$$

II. The action of the exchange potential, a non-local interaction

$$-\int \Omega(\mathbf{r},\mathbf{r}')\psi_\lambda(\mathbf{r}') d^3\vec{r}' = -\sum_{\mu=1}^{N} \int \frac{\psi_\mu^*(\mathbf{r}')\psi_\mu(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} \psi_\lambda(\mathbf{r}') d^3\vec{r}$$

Hatree-Fock self-consistent field

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

Compare the following two energies

$$E=\left\langle\Psi(\mathbf{x}_1,\ldots,\mathbf{x}_N)\middle|\hat{H}_N\middle|\Psi(\mathbf{x}_1,\ldots,\mathbf{x}_N)\right\rangle$$
$$=\sum_{\lambda=1}^{N}\int\psi_\lambda^*(\mathbf{r})\left(-\frac{1}{2}\nabla^2+V(\mathbf{r})\right)\psi_\lambda(\mathbf{r})d^3\vec{r}$$
$$+\frac{1}{2}\sum_{\lambda=1}^{N}\sum_{\mu=1}^{N}\iint\frac{\psi_\lambda^*(\mathbf{r}_1)\psi_\mu^*(\mathbf{r}_2)\psi_\lambda(\mathbf{r}_1)\psi_\mu(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}d^3\vec{r}_1d^3\vec{r}_2$$
$$-\frac{1}{2}\sum_{\lambda=1}^{N}\sum_{\mu=1}^{N}\iint\frac{\psi_\lambda^*(\mathbf{r}_1)\psi_\mu^*(\mathbf{r}_2)\psi_\lambda(\mathbf{r}_2)\psi_\mu(\mathbf{r}_1)}{|\mathbf{r}_1-\mathbf{r}_2|}d^3\vec{r}_1d^3\vec{r}_2$$

Versus

$$\sum_{\lambda=1}^{N}\varepsilon_\lambda$$

Show that

$$\sum_{\lambda=1}^{N}\varepsilon_\lambda = E - \frac{1}{2}\sum_{\lambda=1}^{N}\sum_{\mu=1}^{N}\iint \frac{\psi_\lambda^*(\mathbf{r}_1)\psi_\mu^*(\mathbf{r}_2)\psi_\lambda(\mathbf{r}_1)\psi_\mu(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}d^3\vec{r}_1 d^3\vec{r}_2 + \frac{1}{2}\sum_{\lambda=1}^{N}\sum_{\mu=1}^{N}\iint \frac{\psi_\lambda^*(\mathbf{r}_1)\psi_\mu^*(\mathbf{r}_2)\psi_\lambda(\mathbf{r}_2)\psi_\mu(\mathbf{r}_1)}{|\mathbf{r}_1-\mathbf{r}_2|}d^3\vec{r}_1 d^3\vec{r}_2$$

Electronic Structure Theories

$$\left(-\frac{1}{2}\nabla^2 + V(\mathbf{r}) + V_H(\mathbf{r})\right)\psi_\lambda(\mathbf{r}) - \int \Omega(\mathbf{r},\mathbf{r}')\psi_\lambda(\mathbf{r}')d^3\vec{r}' = \varepsilon_\lambda\psi_\lambda(\mathbf{r})$$

Theories have been developed for this non-local potential function.

Hatree-Fock is one of them. Very preliminary one.

Electronic Structure Theories

$$\left(-\frac{1}{2}\nabla^2 + V(\mathbf{r}) + V_H(\mathbf{r})\right)\psi_\lambda(\mathbf{r}) - \int \Omega(\mathbf{r},\mathbf{r}')\psi_\lambda(\mathbf{r}')d^3\vec{r}' = \varepsilon_\lambda\psi_\lambda(\mathbf{r})$$

In the Kohn-Sham prescription of the density functional theory, it is believed that there might be some local function that can work

$$\Omega(\mathbf{r},\mathbf{r}') = V_{xc}(\mathbf{r})\delta(\mathbf{r}'-\mathbf{r})$$

Exchange-correlation potential.

$$\left(-\frac{1}{2}\nabla^2 + V(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r})\right)\psi_\lambda(\mathbf{r}) = \varepsilon_\lambda\psi_\lambda(\mathbf{r})$$

NOTE & Discussion

$$\hat{H}_N \Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = E\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)$$

$$\left(-\frac{1}{2}\nabla^2 + V(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r}) \right) \psi_\lambda(\mathbf{r}) = \varepsilon_\lambda \psi_\lambda(\mathbf{r})$$

How can we find this local multiplicative potential ???

Physical implication of the ex-corr potential

$$\left(-\frac{1}{2}\nabla^2 + V(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r})\right)\psi_\lambda(\mathbf{r}) = \varepsilon_\lambda \psi_\lambda(\mathbf{r})$$