Chapter 7: Introduction to Many-body Theory

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1 Introduction

$$H = T + V = -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}) \tag{1}$$

若 N 个粒子间无相互作用 $(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N)$

$$H = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla_i^2 + \sum_{i=1}^{N} v(\vec{r}_i) \tag{2}$$

若粒子间存在相互作用 $V(\vec{r}_i, \vec{r}_j)$

$$H = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla_i^2 + \sum_{i=1}^{N} v_{\text{ext}}(\vec{r}_i) + \frac{1}{2}\sum_{i\neq j}^{N} v(\vec{r}_i, \vec{r}_j) \tag{3}$$

Example: N-Electrons Atom (N 个电子的原子)

$$v_{\text{ext}}(\vec{r}) = v_{\text{ext}}(r) = -\frac{Z}{r} \tag{4}$$

$$v(\vec{r}, \vec{r}') = \frac{e^2}{|\vec{r} - \vec{r}'|} \tag{5}$$

猜测多体的薛定谔方程为

$$H\Psi_n(\vec{r}_1, \cdots, \vec{r}_N) = E_n\Psi_n(\vec{r}_1, \cdots, \vec{r}_N) \tag{6}$$

但上面这个式子并不准确，因为自旋也会起作用，令 $x_i = \vec{r}_i, \xi$

$$H\Psi_n(x_1, \cdots, x_N) = E_n\Psi_n(x_1, \cdots, x_N) \tag{7}$$

根据全同性原理，交换两粒子位置，波函数对称或反对称。

- 对于费米子，波函数反对称

$$\Psi_n(x_1, \cdots, x_i, \cdots, x_j, \cdots, x_N) = -\Psi_n(x_1, \cdots, x_j, \cdots, x_i, \cdots, x_N) \tag{8}$$

- 对于玻色子，波函数对称

$$\Psi_n(x_1, \cdots, x_i, \cdots, x_j, \cdots, x_N) = \Psi_n(x_1, \cdots, x_j, \cdots, x_i, \cdots, x_N) \tag{9}$$

体系能量

$$E = \langle\Psi| H |\Psi\rangle \tag{10}$$

$$T = \int \mathrm{d}\vec{r}_1 \cdots \mathrm{d}\vec{r}_N \Psi^\dagger(x_1, \cdots, x_N) \left(-\frac{\hbar^2}{2m}\right) \sum_{i=1}^{N} \nabla_i^2 \Psi(x_1, \cdots, x_N) \tag{11}$$

$$V_{\text{ext}} = \int \mathrm{d}\vec{r}_1 \cdots \mathrm{d}\vec{r}_N \Psi^\dagger(x_1, \cdots, x_N) \sum_{i=1}^{N} v_{\text{ext}}(\vec{r}_i) \Psi(x_1, \cdots, x_N) \tag{12}$$

$$V = \int \mathrm{d}\vec{r}_1 \cdots \mathrm{d}\vec{r}_N \Psi^\dagger(x_1, \cdots, x_N) \frac{1}{2} \sum_{i \neq j}^{N} v(\vec{r}_i, \vec{r}_j) \Psi(x_1, \cdots, x_N) \tag{13}$$

密度算符

$$\hat{\rho}(\vec{r}) = \sum_{i=1}^{N} \delta(\vec{r} - \vec{r}_i) \tag{14}$$

体系密度

$$\rho(\vec{r}) = \langle\Psi| \hat{\rho}(\vec{r}) |\Psi\rangle = \int \mathrm{d}\vec{r}_1 \cdots \mathrm{d}\vec{r}_N \Psi^\dagger(x_1, \cdots, x_N) \sum_{i=1}^{N} \delta(\vec{r} - \vec{r}_i) \Psi(x_1, \cdots, x_N) \tag{15}$$

根据全同性原理，交换两个电子波函数不变

$$\rho(\vec{r}, \xi) = N \int \mathrm{d}\vec{r}_2 \cdots \mathrm{d}\vec{r}_N \Psi^\dagger(\vec{r}, \xi, x_2, \cdots, x_N) \Psi(\vec{r}, \xi, x_2, \cdots, x_N) \tag{16}$$

2 Noninteracting Homogeneous System 无相互作用的均匀系统

对于无相互作用的系统

$$v_{\text{ext}}(\vec{r}) = 0 \tag{17}$$

$$v(\vec{r}, \vec{r}') = 0 \tag{18}$$

$$H = -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla_i^2 \tag{19}$$

$$-\frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla_i^2 \Psi(x_1, \cdots, x_N) = E \Psi(x_1, \cdots, x_N) \tag{20}$$

上式可以得到严格解，分离变量，$\psi_n(x)$ 表示第 x 个粒子处于第 n 个轨道

$$\Psi(x_1, \cdots, x_N) = \psi_{n_1}(x_1) \cdots \psi_{n_N}(x_N) \tag{21}$$

显而易见 $\psi_n(x)$ 满足

$$-\frac{\hbar^2}{2m} \nabla_i^2 \psi_n(x) = \varepsilon_n \psi_n(x) \tag{22}$$

则

$$E = \sum_{i=1}^{N} \varepsilon_{n_i} \tag{23}$$

轨道

$$\psi_i = \frac{1}{\sqrt{V}} e^{i\vec{k}_i \cdot \vec{r}} \chi_i(\xi) \tag{24}$$

交换两个粒子，Eq.(21) 不满足对称性，因此我们需要将 Ψ 对称化

- 对于费米子
$$\Psi(x_1,\cdots,x_N) = \frac{1}{\sqrt{N!}}\sum_P(-1)^P P[\psi_{n_1}(x_1)\cdots\psi_{n_N}(x_N)] \tag{25}$$
P 是交换次数，总交换数是 $N!$。

- 对于玻色子
$$\Psi(x_1,\cdots,x_N) = \frac{1}{\sqrt{N!}}\sum_P P[\psi_{n_1}(x_1)\cdots\psi_{n_N}(x_N)] \tag{26}$$

接下来先讨论费米子

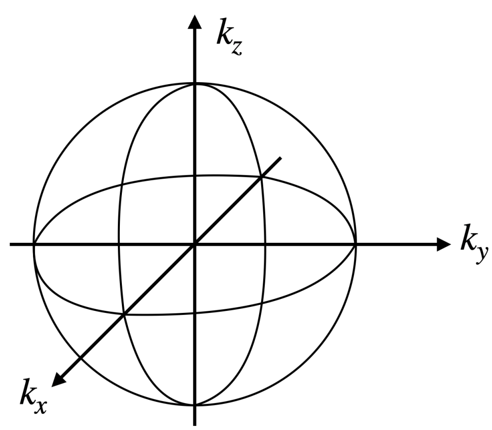
$$\begin{aligned}\Psi(x_1,\cdots,x_N) =& \frac{1}{\sqrt{N!}}\sum_P(-1)^P P[\psi_{n_1}(x_1)\cdots\psi_{n_N}(x_N)] \\ =& \frac{1}{\sqrt{N!}}\begin{vmatrix}\psi_{n_1}(x_1) & \psi_{n_1}(x_2) & \cdots & \psi_{n_1}(x_N) \\ \psi_{n_2}(x_1) & \psi_{n_2}(x_2) & \cdots & \psi_{n_2}(x_N) \\ & & \cdots & \\ \psi_{n_N}(x_1) & \psi_{n_N}(x_2) & \cdots & \psi_{n_N}(x_N)\end{vmatrix}\end{aligned} \tag{27}$$

交换行列式第 i 列和第 j 列，行列式差个负号。若 $\psi_i(x)=\psi_j(x)$，则 $\Psi=0$，这也正是泡利不相容原理 (Pauli exclusion Principle)：在费米子组成的系统中，不能有两个或两个以上的粒子处于完全相同的状态。波函数分为空间部分和自旋部分

$$\psi_i(x) = \psi_i(\vec{r})\chi_i(\xi) = \frac{1}{\sqrt{V}}e^{i\vec{k}_i\cdot\vec{r}}\chi_i(\xi) = \frac{1}{\sqrt{V}}\exp(ik_{ix}x+ik_{iy}y+ik_{iz}z)\chi_i(\xi) \tag{28}$$

$$\varepsilon_i = \frac{\hbar^2}{2m}\left(k_{ix}^2+k_{iy}^2+k_{iz}^2\right) = \frac{\hbar^2}{2m}\vec{k}_i^2 \tag{29}$$

若 $\vec{k}_i=\vec{k}_j, \chi_i(\xi)=\chi_j(\xi)$，则 $\Psi=0$。即相同动量可以填充两个电子，一个自旋向上，一个自旋向下，想象有一个球，电子由内向外填充，这就是著名的费米球 (Fermi sphere)。费米球中存在一个最大半径，称为费米波矢 (Fermi wavevector)，记作 F_k；对应的动量称为费米动量 (Fermi momentum)，记作 $p_F=\hbar k_F$；对应的能量称为费米能 (Fermi energy)，记作 $\varepsilon_F=\frac{\hbar^2k_F^2}{2m}$。



k_F 由密度 n 决定，接下来推导 n 与 k_F 的关系。粒子数

$$N = 2\sum_{\vec{k}}\theta(k_F-k) \tag{30}$$

其中 $\theta(x)$ 是 Heaviside step function

$$\theta(x)=\begin{cases}1 & x\geq 0\\ 0 & x<0\end{cases} \tag{31}$$

当体积 $V\to\infty$ 时，和化为积分的形式

$$\sum_{\vec{k}}\to\frac{V}{(2\pi)^3}\int \mathrm{d}\vec{k} \tag{32}$$

$$\begin{aligned}N=&2\frac{V}{(2\pi)^3}\int \mathrm{d}\vec{k}\theta(k_F-k)\\ =&2\frac{V}{(2\pi)^3}\int_0^{k_F}k^2\mathrm{d}k\int_0^{\pi}\sin\theta\mathrm{d}\theta\int_0^{2\pi}\mathrm{d}\phi\\ =&2\frac{V}{(2\pi)^3}4\pi\int_0^{k_F}k^2\mathrm{d}k=\frac{V}{3\pi^2}k_F^3\end{aligned} \tag{33}$$

体系密度

$$n=\frac{N}{V}=\frac{1}{3\pi^2}k_F^3 \tag{34}$$

由于粒子从内层开始填充，故体系处于基态。体系能量（设无粒子相互作用）

$$E=T=2\sum_{\vec{k}}\theta(k_F-k)\frac{\hbar^2}{2m}k^2=\frac{\hbar^2}{2m}\frac{2V}{(2\pi)^3}4\pi\int_0^{k_F}k^4\mathrm{d}k=\frac{V}{5\pi^2}\frac{\hbar^2}{2m}k_F^5=N\frac{3}{5}\varepsilon_F=N\bar{t} \tag{35}$$

$\bar{t}=\frac{3}{5}\varepsilon_F$ 也称为平均单粒子能量。定义体系压强

$$P=-\frac{\mathrm{d}E}{\mathrm{d}V}\bigg|_N=-\frac{3}{5}N\frac{\mathrm{d}\varepsilon_F}{\mathrm{d}V}\bigg|_N=-\frac{3}{5}N\frac{\mathrm{d}}{\mathrm{d}V}\left(\frac{\hbar^2k_F^2}{2m}\right) \tag{36}$$

$$n=\frac{N}{V}=\frac{1}{3\pi^2}k_F^3\quad\Rightarrow\quad k_F=\left(3\pi^2\frac{N}{V}\right)^{\frac{1}{3}} \tag{37}$$

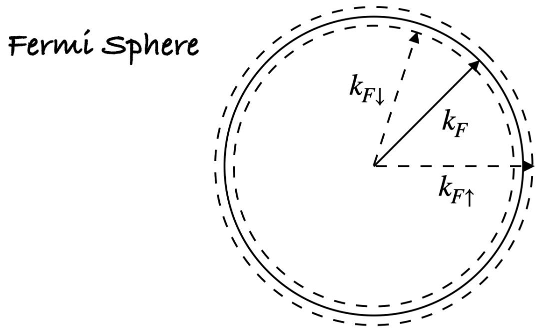
$$P=-\frac{3}{5}N\frac{\mathrm{d}}{\mathrm{d}V}\left(\frac{\hbar^2k_F^2}{2m}\right)=\frac{1}{5}\frac{\hbar^2}{m}\left(3\pi^2\right)^{\frac{2}{3}}n^{\frac{5}{3}} \tag{38}$$

现在讨论玻色子。玻色子不存在泡利不相容原理，只需使波函数对称且体系能量最低，显然

$$\Psi(x_1,\cdots,x_N)=\psi_0(x_1)\cdots\psi_0(x_N) \tag{39}$$

这是一个很著名的现象——玻色-爱因斯坦凝聚 (Bose-Einstein condensation)。在三维空间中的无限深势阱中所有粒子均处于基态，三个方向 L 都趋于无穷大时，在热力学极限下讨论压强，$V\to\infty$，$N\to\infty$，$N/V=$ finite，所有粒子的动量均为 0，因此压强 $P=0$，系统无响应。

3 Magnetic Susceptibility of Ideal Electrons Gas 理想电子（费米子）气体的磁化率



费米波矢 k_F 对应费米能量 $\varepsilon_F = \frac{\hbar^2 k_F^2}{2m}$。取自然单位制令 $\hbar = 1$，加磁场，磁场与电子磁矩耦合，自旋向上与自旋向下的两个费米球分离。磁矩逆着磁场，费米能量增加 $\mu_B B$；磁矩顺着磁场，费米能量减少 $\mu_B B$。$k_{F\downarrow}$ 和 $k_{F\uparrow}$ 显然由磁场决定。极端情况

- 当 $B = 0$ 时，$k_{F\downarrow} = k_{F\uparrow}$
- 当 $B \to \infty$ 时，$k_{F\downarrow} = 0$

设加一个很小的磁场，使两个费米球分开很小的距离，讨论磁化率

$$\varepsilon_{F\uparrow} - \mu_B B = \varepsilon_{F\downarrow} + \mu_B B \tag{40}$$

得到

$$k_{F\uparrow} = \sqrt{k_{F\downarrow}^2 + 4m\mu_B B} \tag{41}$$

又

$$n_\uparrow = \frac{N_\uparrow}{V} = \frac{1}{6\pi^2} k_{F\uparrow}^3 \tag{42}$$

$$n_\downarrow = \frac{N_\downarrow}{V} = \frac{1}{6\pi^2} k_{F\downarrow}^3 \tag{43}$$

$$\frac{N_\uparrow + N_\downarrow}{V} = \frac{1}{6\pi^2}\left(k_{F\uparrow}^3 + k_{F\downarrow}^3\right) = \frac{1}{3\pi^2} k_F^3 \tag{44}$$

磁化强度

$$M = \mu_B (N_\uparrow - N_\downarrow) \tag{45}$$

磁化率

$$\begin{aligned}\chi =& \frac{\partial M}{\partial B}\bigg|_{B\to 0} = \frac{M}{B}\bigg|_{B\to 0} = \frac{\mu_B V (n_\uparrow - n_\downarrow)}{B}\bigg|_{B\to 0} \\ =& \mu_B V \frac{1}{6\pi^2}\left(k_{F\uparrow}^3 - k_{F\downarrow}^3\right)\frac{1}{B}\bigg|_{B\to 0} \\ =& \mu_B V \frac{1}{6\pi^2}\left[\left(k_{F\downarrow}^2 + 4m\mu_B B\right)^{\frac{3}{2}} - k_{F\downarrow}^3\right]\frac{1}{B}\bigg|_{B\to 0}\end{aligned} \tag{46}$$

当 $x \to 0$ 时，$(1+x)^{\frac{3}{2}} = 1 + \frac{3}{2}x$

$$\begin{aligned}
\chi =& \mu_B V \frac{1}{6\pi^2} \left[\left(k_{F\downarrow}^2 + 4m\mu_B B\right)^{\frac{3}{2}} - k_{F\downarrow}^3 \right] \frac{1}{B} \bigg|_{B\to 0} \\
=& \mu_B V \frac{1}{6\pi^2} \left(k_{F\downarrow}^3 \frac{3}{2} \frac{4m\mu_B B}{k_{F\downarrow}^2} \right) \frac{1}{B} \bigg|_{B\to 0} \\
=& \mu_B V \frac{1}{6\pi^2} k_{F\downarrow}^3 \frac{6m\mu_B}{k_{F\downarrow}^2} \bigg|_{B\to 0} \\
=& \mu_B^2 V \frac{mk_F}{\pi^2} = \frac{3\mu_B^2 V n}{2\varepsilon_F}
\end{aligned} \tag{47}$$

磁化率 χ 是正数，称为 Pauli 顺磁性，目前在实验上已经得到很好地验证。

4 Fermi Gas Model for Nuclei

原子核由中子和质子构成，中子和质子的自旋都是 $\frac{1}{2}$，因此中子和质子都是费米子，中子和质子的分布形成一个费米球。接下来我们讨论核的 von Weizsäcker 模型。N 是中子 (neutrons) 数，Z 是质子 (protons) 数，核子数 $A = N + Z$。将中子和质子看成一种粒子的两个态，将这种态称为同位旋 (isospin)，我们利用该观点来建立核模型。

在前面对自由电子气体的讨论中我们得到 (这里的 N 是电子数)

$$\frac{N}{V} = \frac{1}{3\pi^2} k_F^3 \tag{48}$$

现在我们有自旋和同位旋两个自由度，一共有四种态。讨论特殊情况，设 $N = Z = \frac{A}{2}$

$$n = \frac{A}{V} = \frac{2}{3\pi^2} k_F^3 \tag{49}$$

质子和中子并不是完全简并的，因为质子间存在库伦相互作用，而中子间不存在库伦相互作用，库伦相互作用使能量增大。定义束缚能 (binding energy of nuclei)，束缚能是将所有质子中子束缚在一起与它们在无穷远位置的能量差。

$$B(Z, A) = \left[ZM_p + NM_n - M(A, Z)\right] c^2 \tag{50}$$

另一种写法

$$B(Z, A) = a_{\rm v} A - a_{\rm s} A^{\frac{2}{3}} - a_{\rm c} \frac{Z^2}{A^{\frac{1}{3}}} - a_{sy} \frac{(N-Z)^2}{A} + B_{\rm p} \tag{51}$$

接下来解释各项。假设 $n = \frac{A}{V}$ 为一定值

1. Volumn energy $\sim V \sim A \quad \Rightarrow \quad a_{\rm v} A$
2. Surface energy $\sim S \sim V^{\frac{2}{3}} \sim A^{\frac{2}{3}} \quad \Rightarrow \quad a_{\rm s} A^{\frac{2}{3}}$

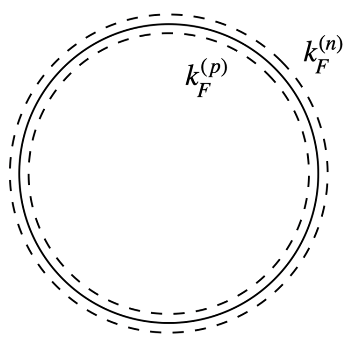
3. Coulomb energy

$$
\begin{aligned}
U =& e^2 \iint \mathrm{d}\vec{r}\mathrm{d}\vec{r}' \frac{\rho_z(\vec{r})\rho_z(\vec{r}')}{|\vec{r}-\vec{r}'|} \\
\doteq& e^2\rho_z^2 \iint \mathrm{d}\vec{r}\mathrm{d}\vec{r}' \frac{1}{|\vec{r}-\vec{r}'|} \qquad \text{近似 } \rho_z(\vec{r}) = \frac{Z}{V} = \rho_Z \\
=& e^2\rho_z^2 \int \mathrm{d}\vec{r}'' \frac{1}{r''} \int \mathrm{d}\vec{r}' \qquad \text{令 } \vec{r}'' = \vec{r}-\vec{r}' \qquad \mathrm{d}\vec{r}'' = \mathrm{d}\vec{r} \\
=& e^2\rho_z^2 \int \mathrm{d}\vec{r}\frac{1}{r} \int \mathrm{d}\vec{r}' \\
=& e^2\rho_z^2 V 4\pi \int \mathrm{d}r \frac{1}{r} r^2 = e^2\rho_z^2 V 4\pi \int_0^{r_0 (r_0\to\infty)} r\mathrm{d}r \\
=& e^2\rho_z^2 V 2\pi r_0^2 \\
=& e^2 2\pi \left(\frac{3}{4\pi}\right)^{\frac{2}{3}} n\frac{Z^2}{A^{\frac{1}{3}}} \sim \frac{Z^2}{A^{\frac{1}{3}}} \qquad \Rightarrow \qquad a_\mathrm{c}\frac{Z^2}{A^{\frac{1}{3}}}
\end{aligned} \tag{52}
$$

4. Symmetry energy

令 $\lambda = \frac{N-Z}{A} \ll 1$，又 $N+Z=A$，则

$$
Z = \frac{A}{2}(1-\lambda) \qquad N = \frac{A}{2}(1+\lambda) \tag{53}
$$



$$
T_n = \frac{3}{5} N \varepsilon_F^{(n)} = \frac{3}{5} N \frac{1}{2M_n} \left[k_F^{(n)}\right]^2 \hbar^2 \tag{54}
$$

$$
T_p = \frac{3}{5} Z \varepsilon_F^{(p)} = \frac{3}{5} Z \frac{1}{2M_p} \left[k_F^{(p)}\right]^2 \hbar^2 \tag{55}
$$

假定 $M_n = M_p = m$，讨论 T 与 $T_{\lambda=0}$ 的区别

$$
\begin{aligned}
T =& T_n + T_p = \frac{3}{5}\hbar^2 \frac{1}{2m} \left\{ N\left[k_F^{(n)}\right]^2 + Z\left[k_F^{(p)}\right]^2 \right\} \\
=& \frac{3}{5} V^{-\frac{2}{3}} \hbar^2 \frac{1}{2m} \left(3\pi^2\right)^{\frac{2}{3}} \left(N^{\frac{5}{3}} + Z^{\frac{5}{3}}\right) \\
=& cV^{-\frac{2}{3}} \left(N^{\frac{5}{3}} + Z^{\frac{5}{3}}\right) \\
=& cV^{-\frac{2}{3}} \left(\frac{A}{2}\right)^{\frac{5}{3}} \left[(1-\lambda)^{\frac{5}{3}} + (1+\lambda)^{\frac{5}{3}}\right]
\end{aligned} \tag{56}
$$

$$
\begin{aligned}
T-T_{\lambda=0} =& cV^{-\frac{2}{3}}\left(\frac{A}{2}\right)^{\frac{5}{3}}\left[(1-\lambda)^{\frac{5}{3}}+(1+\lambda)^{\frac{5}{3}}-2\right] \\
=& cV^{-\frac{2}{3}}\left(\frac{A}{2}\right)^{\frac{5}{3}}\left(1-\frac{5}{3}\lambda+\frac{\frac{5}{3}\cdot\frac{2}{3}}{2}\lambda^2+1+\frac{5}{3}\lambda+\frac{\frac{5}{3}\cdot\frac{2}{3}}{2}\lambda^2-2\right) \\
\sim& A^{\frac{5}{3}}V^{-\frac{2}{3}}\lambda^2 = A^{\frac{5}{3}}V^{-\frac{2}{3}}\frac{(N-Z)^2}{A^2} = n^{\frac{2}{3}}\frac{(N-Z)^2}{A} \\
\sim& \frac{(N-Z)^2}{A} \qquad \Rightarrow \qquad a_{sy}\frac{(N-Z)^2}{A}
\end{aligned}
\tag{57}
$$

5. Pairing energy B_p，不考虑别的原因，odd-odd 比 even-even, odd-even, even-odd 中子质子数的组合能量低，更稳定。这是核物理中的性质，不讨论。

6. 核势对中子和质子的影响一样，不考虑。

5 Thomas-Fermi Theory

$$
H=-\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla_i^2+\sum_{i=1}^{N}v_{\text{ext}}(\vec{r}_i)+\frac{1}{2}\sum_{i\neq j}^{N}v(\vec{r}_i,\vec{r}_j) \tag{58}
$$

接下来讨论多电子原子基态能量、第一激发态能量、密度分布等问题。以 Na 原子为例，电子数 $N=11$。核的库伦势

$$
v_{\text{ext}}(\vec{r})=v_{\text{ext}}(r)=-\frac{Z}{r} \tag{59}
$$

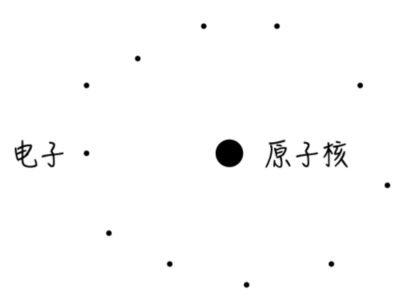
电子的相互作用势

$$
v(\vec{r},\vec{r}')=\frac{e^2}{|\vec{r}-\vec{r}'|} \tag{60}
$$

求解薛定谔方程的本征态和本征能

$$
H\Psi_n=E_n\Psi_n \tag{61}
$$

目前唯一能严格解的是氢原子，但我们可以用近似的方法解钠原子。



电子密度分布

$$
\rho(\vec{r}) \tag{62}
$$

核密度分布

$$
\rho_{\text{ext}}(\vec{r})=Z\delta(\vec{r}) \tag{63}
$$

将电子看成经典的，则电子分布满足经典电动力学，满足 Poisson Equation

$$
\nabla^2V_{\text{eff}}(\vec{r})=-4\pi\left[\rho(\vec{r})-\rho_{\text{ext}}(\vec{r})\right] \tag{64}
$$

原子核不存在时，体系密度均匀，可以使用 Fermi sphere。想象原子核 Z 连续变化，电子被吸引到原子核附近，得到近似均匀体系 (quasi-homogeneous system)。对于均匀体系

$$\rho = \frac{1}{3\pi^2} k_F^3 \tag{65}$$

类似地，对于近似均匀体系

$$\rho(\vec{r}) = \frac{1}{3\pi^2} k_F^3(\vec{r}) \tag{66}$$

体系能量守恒

$$\frac{1}{2m} k_F^2(\vec{r}) + v_{\text{eff}} = \mu \quad \text{(constant)} \tag{67}$$

$$\rho(\vec{r}) = \frac{1}{3\pi^2} \left\{ 2 \left[\mu - v_{\text{eff}}(\vec{r}) \right] \right\}^{\frac{3}{2}} \tag{68}$$

有效势

$$v_{\text{eff}}(\vec{r}) = -\int \frac{\rho_{\text{ext}}(\vec{r}')}{|\vec{r} - \vec{r}'|} \mathrm{d}r' + \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} \mathrm{d}r' = v_{\text{ext}}(\vec{r}) + v_H(\vec{r}) \tag{69}$$

其中 v_H 是 Hartree potential

$$\begin{aligned} \nabla^2 v_{\text{eff}}(\vec{r}) =& -\nabla^2 \int \frac{\rho_{\text{ext}}(\vec{r}')}{|\vec{r} - \vec{r}'|} \mathrm{d}r' + \nabla^2 \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} \mathrm{d}r' \\ =& -\int \rho_{\text{ext}}(\vec{r}) \left(\nabla^2 \frac{1}{|\vec{r} - \vec{r}'|} \right) \mathrm{d}\vec{r}' + \int \rho(\vec{r}) \left(\nabla^2 \frac{1}{|\vec{r} - \vec{r}'|} \right) \mathrm{d}\vec{r}' \\ =& 4\pi \int \rho_{\text{ext}}(\vec{r}) \delta(\vec{r} - \vec{r}') \mathrm{d}\vec{r}' - 4\pi \int \rho(\vec{r}) \delta(\vec{r} - \vec{r}') \mathrm{d}\vec{r}' \end{aligned} \tag{70}$$

满足 Poisson equation。故

$$v_{\text{eff}}(\vec{r}) = v_{\text{ext}}(\vec{r}) + v_H(\vec{r}) = -\int \frac{\rho_{\text{ext}}(\vec{r}')}{|\vec{r} - \vec{r}'|} \mathrm{d}r' + \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} \mathrm{d}r' \tag{71}$$

先考察 $v_{\text{ext}}(\vec{r})$

$$\rho_{\text{ext}}(\vec{r}) = Z\delta(\vec{r}) \tag{72}$$

$$v_{\text{ext}}(\vec{r}) = -Z \int \frac{\delta(\vec{r} - \vec{r}')}{|\vec{r} - \vec{r}'|} \mathrm{d}\vec{r}' = -\frac{Z}{r} \tag{73}$$

接下来看 $v_H(\vec{r})$

$$\begin{aligned} \nabla^2 v_H(\vec{r}) =& \nabla^2 \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} \mathrm{d}r' = -4\pi\rho(\vec{r}) \\ =& -4\pi \frac{1}{3\pi^2} \left\{ 2[\mu - v_{\text{eff}}(\vec{r})] \right\}^{\frac{3}{2}} \\ =& -\frac{8\sqrt{2}}{3\pi^2} \left[\mu - v_H(\vec{r}) - v_{\text{ext}}(\vec{r}) \right]^{\frac{3}{2}} \end{aligned} \tag{74}$$

即

$$\nabla^2 v_H(\vec{r}) = -\frac{8\sqrt{2}}{3\pi^2} \left[\mu - v_H(\vec{r}) - v_{\text{ext}}(\vec{r}) \right]^{\frac{3}{2}} \tag{75}$$

接下来解 $v_H(\vec{r})$。定义 Screening function

$$\varphi(\vec{r}) = \frac{1}{v_{\text{ext}}(\vec{r})} \left[v_{\text{ext}}(\vec{r}) + v_H(\vec{r}) - \mu \right] \tag{76}$$

$$\begin{aligned} \nabla^2 [\varphi(\vec{r}) v_{\text{ext}}(\vec{r})] =& \nabla^2 v_{\text{ext}}(\vec{r}) + \nabla^2 v_H(\vec{r}) \\ =& 4\pi\rho_{\text{ext}}(\vec{r}) - 4\pi\rho(\vec{r}) \\ =& -4\pi\rho(\vec{r}) \end{aligned} \tag{77}$$

故

$$\nabla^2 v_H(\vec{r}) = -\frac{8\sqrt{2}}{3\pi^2}\left[-\varphi(\vec{r})v_{\text{ext}}(\vec{r})\right]^{\frac{3}{2}} = -4\pi\rho(\vec{r}) = \nabla^2[\varphi(\vec{r})v_{\text{ext}}(\vec{r})] \tag{78}$$

即

$$\nabla^2[\varphi(\vec{r})v_{\text{ext}}(\vec{r})] = -\frac{8\sqrt{2}}{3\pi^2}\left[-\varphi(\vec{r})v_{\text{ext}}(\vec{r})\right]^{\frac{3}{2}} \tag{79}$$

$$\nabla^2[\frac{1}{r}\varphi(\vec{r})] = \frac{8\sqrt{2}}{3\pi^2}Z^{\frac{1}{2}}\left[\frac{1}{r}\varphi(\vec{r})\right]^{\frac{3}{2}} \tag{80}$$

设体系处于球对称

$$\nabla^2 = \frac{1}{r}\frac{\mathrm{d}^2}{\mathrm{d}r^2}r \tag{81}$$

$$\frac{\mathrm{d}^2}{\mathrm{d}r^2}\varphi(r) = \frac{8\sqrt{2}}{3\pi^2}Z^{\frac{1}{2}}\frac{1}{\sqrt{r}}[\varphi(r)]^{\frac{3}{2}} \tag{82}$$

这是非线性常微分方程，无严格解。

$$\frac{1}{2m}k_F^2(\vec{r}) + v_{\text{eff}} = \mu \quad \text{(constant)} \tag{83}$$

我们讨论极端情况 $Z = N, V \to \infty, k_F(r) \to 0, v_{\text{eff}}(r) \to 0$，则 $\mu = 0$。

$$\varphi(\vec{r}) = 1 + \frac{1}{v_{\text{ext}}(\vec{r})}\left[v_H(\vec{r}) - \mu\right] = 1 + \frac{v_H(r)}{v_{\text{ext}}(r)} = 1 - \frac{r}{Z}v_H(r) \tag{84}$$

$$\varphi(r=0) = 1 \qquad\qquad \varphi(r\to\infty) = 0 \;\Rightarrow\; v_H(r\to\infty) = \frac{Z}{r} \tag{85}$$

$$\begin{aligned} v_H(r) &= \int \frac{\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}\mathrm{d}\vec{r}' \qquad\qquad (r\to\infty, r\gg r') \\ &= \int \frac{\rho(\vec{r}')}{r}\mathrm{d}\vec{r}' = \frac{1}{r}\int \rho(\vec{r}')\mathrm{d}\vec{r}' = \frac{N}{r} = \frac{Z}{r} \end{aligned} \tag{86}$$

令 $x = \alpha r$，

$$\alpha = 4\left(\frac{2Z}{9\pi^2}\right)^{\frac{1}{3}} \tag{87}$$

则

$$\frac{\mathrm{d}^2}{\mathrm{d}x^2}\varphi(x) = x^{-\frac{1}{2}}[\varphi(x)]^{\frac{3}{2}} \tag{88}$$

边界条件

$$\varphi(x=0) = 1 \qquad\qquad \varphi(x\to\infty) = 0 \tag{89}$$

当 $x\to\infty$ 时，令 $\varphi(x) = ax^b$，代入 Eq.(88) 得

$$ab(b-1)x^{b-2} = a^{\frac{3}{2}}x^{\frac{3}{2}b-\frac{1}{2}} \tag{90}$$

$$\begin{cases} b-2 = \frac{3}{2}b - \frac{1}{2} \\ ab(b-1) = a^{\frac{3}{2}} \end{cases} \qquad \Rightarrow \qquad \begin{cases} a = 144 \\ b = -3 \end{cases} \tag{91}$$

$$\varphi(x) \underset{x\to\infty}{=} \frac{144}{x^3} \tag{92}$$

当 $r\to\infty$ 时

$$v_{\text{eff}}(r) = v_H(r) + v_{\text{ext}}(r) = \varphi(r)v_{\text{ext}}(r) \sim -\frac{Z}{r^4} \tag{93}$$

$$\rho(r) = \frac{2^{\frac{3}{2}}}{3\pi^2}\left[-v_{\text{eff}}(r)\right]^{\frac{3}{2}} \sim r^{-6} \tag{94}$$

实际上在原子中，$\rho(r) \sim e^{-3r}$ $(r \to \infty)$，虽然我们得到的结果与严格解有区别，但仍是一个很好的结果。

当 $x \to 0$ 时，令 $\varphi(x) = 1 + cx$

$$v_H(r=0) = \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|}\mathrm{d}\vec{r}' = \int \frac{\rho(\vec{r}')}{r'}\mathrm{d}\vec{r}' \tag{95}$$

$$v_H(r) + v_{\text{ext}}(r) = \varphi(r)v_{\text{ext}}(r) \tag{96}$$

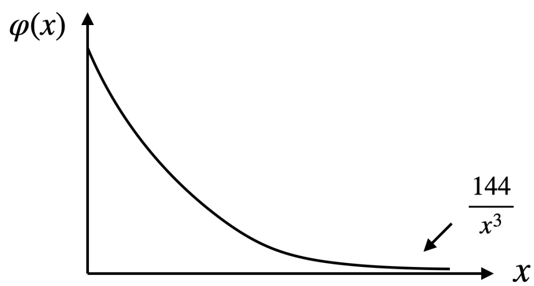
$$v_H(r=0) + v_{\text{ext}}(r \to 0) = (1 + c\alpha r)v_{\text{ext}}(r \to 0) \tag{97}$$

$$v_H(r=0) - \frac{Z}{r} = (1 + c\alpha r)\left(-\frac{Z}{r}\right) \tag{98}$$

得到

$$c = -\frac{1}{\alpha Z}v_H(r=0) < 0 \tag{99}$$

$$\varphi(r) = 1 + cx == 1 - \frac{1}{\alpha Z}v_H(0)x = 1 - \frac{r}{Z}v_H(0) \tag{100}$$



Thomas-Fermi 理论后续仍有发展，我们这里只简单地列出人名：Thomas(1927)-Fermi(1927)-Dirac(1928)-von Weizsäcker(1935)。

6 Hartree Theory

$$H = \sum_{i=1}^{N}\left(-\frac{\hbar^2}{2m}\right)\nabla_i^2 + \sum_{i=1}^{N} v_{\text{ext}}(\vec{r}_i) + \frac{1}{2}\sum_{i \neq j}^{N} v(\vec{r}_i, \vec{r}_j) \tag{101}$$

$$H\Psi_n = E_n\Psi_n \tag{102}$$

符号简化，令

$$h_i = \left(-\frac{\hbar^2}{2m}\right)\nabla_i^2 + v_{\text{ext}}(\vec{r}_i) \tag{103}$$

$$v_{ij} = v(\vec{r}_i, \vec{r}_j) \tag{104}$$

则

$$H = \sum_{i=1}^{N} h_i + \frac{1}{2}\sum_{i \neq j}^{N} v_{ij} \tag{105}$$

解基态的薛定谔方程，设 $x = \vec{r}, \xi$，Hartree 近似

$$\Psi_H(x_1, \cdots, x_N) = \psi_1(x_1)\cdots\psi_N(x_N) \tag{106}$$

这个近似有个很大的缺陷，即 Ψ 不满足对称性，而满足对称性的式子是我们之后要讨论的 Hartree-Fork 理论。Anyway，我们先来看 Hartree 理论。波函数归一

$$\int \Psi_H^\dagger(x_1,\cdots,x_N)\Psi_H(x_1,\cdots,x_N)\mathrm{d}x_1\cdots\mathrm{d}x_N = 1 \tag{107}$$

假设自旋部分自动求和

$$\int \Psi_H^\dagger(x_1,\cdots,x_N)\Psi_H(x_1,\cdots,x_N)\mathrm{d}\vec{r}_1\cdots\mathrm{d}\vec{r}_N = \prod_{i=1}^{N}\int \psi_i^\dagger(x_i)\psi_i(x_i)\mathrm{d}\vec{r}_i = 1 \tag{108}$$

体系密度

$$\begin{aligned}\rho(\vec{r}) &= \int \Psi_H^\dagger(x_1,\cdots,x_N)\sum_{i=1}^{N}\delta(\vec{r}-\vec{r}_i)\Psi_H(x_1,\cdots,x_N)\mathrm{d}\vec{r}_1\cdots\mathrm{d}\vec{r}_N \\ &= \sum_{i=1}^{N}|\psi_i(x)|^2 = \sum_{i=1}^{N}|\phi_i(\vec{r})\chi_i(\xi)|^2 = \sum_{i=1}^{N}|\phi_i(\vec{r})|^2\end{aligned} \tag{109}$$

$\psi_i \to \delta\psi_i$，用变分原理导出 ϕ_i 满足的方程，引入 Lagrange 乘子

$$\delta\bar{H} - \sum_{i=1}^{N}\varepsilon_i\delta\int|\phi_i(\vec{r})|^2\mathrm{d}\vec{r} = \delta\bar{H} - \sum_{i=1}^{N}\varepsilon_i\left[\int\delta\phi_i^\dagger(\vec{r})\phi_i(\vec{r})\mathrm{d}\vec{r} + \int\phi_i^\dagger(\vec{r})\delta\phi_i(\vec{r})\mathrm{d}\vec{r}\right] = 0 \tag{110}$$

计算 $\bar{H}$

$$\begin{aligned}\bar{H} &= \langle\Psi_H|\,H\,|\Psi_H\rangle \\ &= \langle\Psi_H|\sum_{i=1}^{N}h_i + \frac{1}{2}\sum_{i\neq j}^{N}v_{ij}\,|\Psi_H\rangle \\ &= \left\langle\prod_{l=1}^{N}\phi_l(\vec{r}_l)\right|\sum_{i=1}^{N}h_i + \frac{1}{2}\sum_{i\neq j}^{N}v_{ij}\left|\prod_{m=1}^{N}\phi_m(\vec{r}_m)\right\rangle \\ &= \sum_{i=1}^{N}\left\langle\prod_{l=1}^{N}\phi_l(\vec{r}_l)\right|h_i\left|\prod_{m=1}^{N}\phi_m(\vec{r}_m)\right\rangle + \frac{1}{2}\sum_{i\neq j}^{N}\left\langle\prod_{l=1}^{N}\phi_l(\vec{r}_l)\right|v_{ij}\left|\prod_{m=1}^{N}\phi_m(\vec{r}_m)\right\rangle \\ &= \sum_{i=1}^{N}\langle\phi_i(\vec{r}_i)|\,h_i\,|\phi_i(\vec{r}_i)\rangle + \frac{1}{2}\sum_{i\neq j}^{N}\langle\phi_i(\vec{r}_i)\phi_j(\vec{r}_j)|\,v_{ij}\,|\phi_i(\vec{r}_i)\phi_j(\vec{r}_j)\rangle \\ &= \sum_{i=1}^{N}\langle\phi_i(\vec{r})|\,h(\vec{r})\,|\phi_i(\vec{r})\rangle + \frac{1}{2}\sum_{i\neq j}^{N}\langle\phi_i(\vec{r})\phi_j(\vec{r}')|\,v(\vec{r},\vec{r}')\,|\phi_i(\vec{r})\phi_j(\vec{r}')\rangle\end{aligned} \tag{111}$$

计算 $\delta\bar{H}$

$$\begin{aligned}\delta\bar{H} =&\sum_{i=1}^{N}\int\left\{[\delta\phi_i^\dagger(\vec{r})]h(\vec{r})\phi_i(\vec{r})+\phi_i^\dagger(\vec{r})h(\vec{r})[\delta\phi_i(\vec{r})]\right\}\mathrm{d}\vec{r}\\&+\frac{1}{2}\sum_{i\neq j}^{N}\iint\{[\delta\phi_i^\dagger(\vec{r})]\phi_j^\dagger(\vec{r}')\phi_i(\vec{r})\phi_j(\vec{r}')+\phi_i^\dagger(\vec{r})[\delta\phi_j^\dagger(\vec{r}')]\phi_i(\vec{r})\phi_j(\vec{r}')\\&+\phi_i^\dagger(\vec{r})\phi_j^\dagger(\vec{r}')[\delta\phi_i(\vec{r})]\phi_j(\vec{r}')+\phi_i^\dagger(\vec{r})\phi_j^\dagger(\vec{r}')\phi_i(\vec{r})[\delta\phi_j(\vec{r}')]\}v(\vec{r},\vec{r}')\mathrm{d}\vec{r}\mathrm{d}\vec{r}'\\=&2\sum_{i=1}^{N}\int[\delta\phi_i^\dagger(\vec{r})]h(\vec{r})\phi_i(\vec{r})\mathrm{d}\vec{r}\\&+\sum_{i\neq j}^{N}\iint\{[\delta\phi_i^\dagger(\vec{r})]\phi_j^\dagger(\vec{r}')\phi_i(\vec{r})\phi_j(\vec{r}')+\phi_i^\dagger(\vec{r})\phi_j^\dagger(\vec{r}')[\delta\phi_i(\vec{r})]\phi_j(\vec{r}')\}v(\vec{r},\vec{r}')\mathrm{d}\vec{r}\mathrm{d}\vec{r}'\\=&\sum_{i=1}^{N}\int\delta\phi_i^\dagger(\vec{r})\left[h(\vec{r})\phi_i(\vec{r})+\sum_{j\neq i}^{N}\int|\phi_j(\vec{r}')|^2\phi_i(\vec{r})v(\vec{r},\vec{r}')\mathrm{d}\vec{r}'\right]\mathrm{d}\vec{r}+C.C.\end{aligned} \tag{112}$$

$$\begin{aligned}&\delta\bar{H}-\sum_{i=1}^{N}\varepsilon_i\delta\int|\phi_i(\vec{r})|^2\mathrm{d}\vec{r}=\delta\bar{H}-\sum_{i=1}^{N}\varepsilon_i\left[\int\delta\phi_i^\dagger(\vec{r})\phi_i(\vec{r})\mathrm{d}\vec{r}+\int\phi_i^\dagger(\vec{r})\delta\phi_i(\vec{r})\mathrm{d}\vec{r}\right]\\=&\sum_{i=1}^{N}\int\delta\phi_i^\dagger(\vec{r})\left[h(\vec{r})\phi_i(\vec{r})+\sum_{j\neq i}^{N}\int|\phi_j(\vec{r}')|^2\phi_i(\vec{r})v(\vec{r},\vec{r}')\mathrm{d}\vec{r}'-\varepsilon_i\phi_i(\vec{r})\right]\mathrm{d}\vec{r}+C.C.=0\end{aligned} \tag{113}$$

即

$$\left[h(\vec{r})+\sum_{j\neq i}^{N}\int|\phi_j(\vec{r}')|^2v(\vec{r},\vec{r}')\mathrm{d}\vec{r}'-\varepsilon_i\right]\phi_i(\vec{r})=0 \tag{114}$$

令

$$v_H^i(\vec{r})=\sum_{j\neq i}^{N}\int|\phi_j(\vec{r}')|^2v(\vec{r},\vec{r}')\mathrm{d}\vec{r}' \tag{115}$$

v_H 是 orbital-dependent Hartree potential。

$$h_i=-\frac{\hbar^2}{2m}\nabla_i^2+v_{\mathrm{ext}}(\vec{r}_i) \tag{116}$$

我们得到 orbital-dependent Hartree equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2+v_{\mathrm{ext}}(\vec{r})+v_H^i(\vec{r})-\varepsilon_i\right]\phi_i(\vec{r})=0 \tag{117}$$

为了解这个方程，可以先给定某些固定的轨道，先丢掉 v_H^i，将方程的解代入 Eq.(115) 得到 v_H^i，再将 v_H^i 代回原方程继续求解，反复多次迭代，直到前后两次迭代得到的解的精度在想要的范围内。

Hartree 理论可以再做进一步简化。将求和号拿入积分号中

$$\begin{aligned}v_H^i(\vec{r})&=\int\sum_{j\neq i}^{N}|\phi_j(\vec{r}')|^2v(\vec{r},\vec{r}')\mathrm{d}\vec{r}'\\&=\int\left[\sum_{j}^{N}|\phi_j(\vec{r}')|^2v(\vec{r},\vec{r}')-|\phi_i(\vec{r}')|^2v(\vec{r},\vec{r}')\right]\mathrm{d}\vec{r}'\\&=\int\left[\rho(\vec{r}')-|\phi_i(\vec{r}')|^2\right]v(\vec{r},\vec{r}')\mathrm{d}\vec{r}'\end{aligned} \tag{118}$$

假设电子数很多，$|\psi_i(\vec{r})|^2 \ll \rho(\vec{r})$，则

$$v_H(\vec{r}) \doteq \int \rho(\vec{r}')v(\vec{r},\vec{r}')\mathrm{d}\vec{r}' \tag{119}$$

这也称作平均场近似，此时 v_H 不再依赖 i，我们平时说的 Hartree equation 一般是指下式

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + v_{\mathrm{ext}}(\vec{r}) + v_H(\vec{r})\right]\phi_i(\vec{r}) = \varepsilon_i\phi_i(\vec{r}) \tag{120}$$

7 Hartree-Fock Theory

Hartree 中波函数

$$\Psi_H(x_1,\cdots,x_N) = \psi_1(x_1)\cdots\psi_N(x_N) \tag{121}$$

不满足对称性，将它对称化

$$\begin{aligned}\Psi_{HF}(x_1,\cdots,x_N) =& \frac{1}{\sqrt{N!}}\sum_{k_1,\cdots,k_N}\varepsilon_{k_1,\cdots,k_N}[\psi_1(x_1)\cdots\psi_N(x_N)]\\ =& \frac{1}{\sqrt{N!}}\begin{vmatrix}\psi_1(x_1) & \psi_1(x_2) & \cdots & \psi_1(x_N)\\ \psi_2(x_1) & \psi_2(x_2) & \cdots & \psi_2(x_N)\\ & & \cdots & \\ \psi_N(x_1) & \psi_N(x_2) & \cdots & \psi_N(x_N)\end{vmatrix}\end{aligned} \tag{122}$$

$$\psi_i(x_j) = \phi_i(\vec{r}_j)\chi_i(\xi_j) \tag{123}$$

波函数归一化，自旋部分自动求和

$$\int \Psi_H^\dagger(x_1,\cdots,x_N)\Psi_H(x_1,\cdots,x_N)\mathrm{d}\vec{r}_1\cdots\mathrm{d}\vec{r}_N = 1 \tag{124}$$

假设有 2 个粒子

$$\begin{aligned}\Psi_{HF}(x_1,x_2) =& \frac{1}{\sqrt{2}}\begin{vmatrix}\phi(\vec{r}_1)\chi_\alpha(\xi_1) & \phi(\vec{r}_2)\chi_\alpha(\xi_2)\\ \phi(\vec{r}_1)\chi_\beta(\xi_1) & \phi(\vec{r}_2)\chi_\beta(\xi_2)\end{vmatrix}\\ =& \frac{1}{\sqrt{2}}\phi(\vec{r}_1)\phi(\vec{r}_2)[\chi_\alpha(\xi_1)\chi_\beta(\xi_2) - \chi_\beta(\xi_1)\chi_\alpha(\xi_2)]\end{aligned} \tag{125}$$

这是我们最熟悉的波函数，波函数空间部分对称，自旋部分反对称。

$$\begin{aligned}&\int |\Psi_{HF}|^2\mathrm{d}\vec{r}_1\mathrm{d}\vec{r}_2\\ =&\frac{1}{2}\int \mathrm{d}\vec{r}_1\mathrm{d}\vec{r}_2|\phi(\vec{r}_1)|^2|\phi(\vec{r}_2)|^2[\chi_\alpha^\dagger(\xi_1)\chi_\beta^\dagger(\xi_2) - \chi_\beta^\dagger(\xi_1)\chi_\alpha^\dagger(\xi_2)][\chi_\alpha(\xi_1)\chi_\beta(\xi_2) - \chi_\beta(\xi_1)\chi_\alpha(\xi_2)] = 1\end{aligned} \tag{126}$$

满足归一化条件。

$$H = \sum_{i=1}^{N} h_i + \frac{1}{2}\sum_{i\neq j}^{N} v_{ij} \tag{127}$$

计算 $\bar{H}$

$$\begin{aligned}\bar{H} =& \langle\Psi_{HF}|\, H\, |\Psi_{HF}\rangle\\ =& \langle\Psi_{HF}|\sum_{i=1}^{N} h_i\,|\Psi_{HF}\rangle + \langle\Psi_{HF}|\,\frac{1}{2}\sum_{i\neq j}^{N} v_{ij}\,|\Psi_{HF}\rangle\\ =& \bar{H}_1 + \bar{H}_2\end{aligned} \tag{128}$$

$$
\begin{aligned}
&\bar{H}_1 = \langle \Psi_{HF} | \sum_{i=1}^{N} h_i \, |\Psi_{HF}\rangle \\
&= \sum_{i=1}^{N} \frac{1}{N!} \int \mathrm{d}\vec{r}_1 \cdots \mathrm{d}\vec{r}_N \sum_{k'_1,\cdots,k'_N} \varepsilon_{k'_1,\cdots,k'_N} \psi^\dagger_{k'_1}(x_1) \cdots \psi^\dagger_{k'_N}(x_N) h_i \sum_{k_1,\cdots,k_N} \varepsilon_{k_1,\cdots,k_N} \psi_{k_1}(x_1) \cdots \psi_{k_N}(x_N) \\
&= \sum_{i=1}^{N} \frac{1}{N!} \sum_{k'_1,\cdots,k'_N} \sum_{k_1,\cdots,k_N} \varepsilon_{k'_1,\cdots,k'_N} \varepsilon_{k_1,\cdots,k_N} \int \mathrm{d}\vec{r}_1 \cdots \mathrm{d}\vec{r}_N \psi^\dagger_{k'_1}(x_1) \cdots \psi^\dagger_{k'_N}(x_N) h_i \psi_{k_1}(x_1) \cdots \psi_{k_N}(x_N) \\
&= \sum_{i=1}^{N} \frac{1}{N!} \sum_{k'_1,\cdots,k'_N} \sum_{k_1,\cdots,k_N} \varepsilon_{k'_1,\cdots,k'_N} \varepsilon_{k_1,\cdots,k_N} \delta_{k'_1 k_1} \cdots \delta_{k'_{i-1} k_{i-1}} \delta_{k'_{i+1} k_{i+1}} \cdots \delta_{k'_N k_N} \int \mathrm{d}\vec{r}_i \psi^\dagger_{k'_i}(x_i) h(\vec{r}_i) \psi_{k_i}(x_i) \qquad (129) \\
&= \sum_{i=1}^{N} \frac{1}{N!} \sum_{k_1,\cdots,k_N} |\varepsilon_{k_1,\cdots,k_N}|^2 \int \mathrm{d}\vec{r}_i \psi^\dagger_{k_i}(x_i) h(\vec{r}_i) \psi_{k_i}(x_i) \\
&= \sum_{i=1}^{N} \frac{1}{N!} \sum_{k_1,\cdots,k_N} \int \mathrm{d}\vec{r} \phi^\dagger_{k_i}(\vec{r}) h(\vec{r}) \phi_{k_i}(\vec{r}) = \sum_{i=1}^{N} \frac{1}{N!} (N-1)! \sum_{j=1} \int \mathrm{d}\vec{r} \phi^\dagger_j(\vec{r}) h(\vec{r}) \phi_j(\vec{r}) \\
&= \sum_{j=1} \int \mathrm{d}\vec{r} \phi^\dagger_j(\vec{r}) h(\vec{r}) \phi_j(\vec{r}) = \sum_{i=1} \int \mathrm{d}\vec{r} \phi^\dagger_i(\vec{r}) h(\vec{r}) \phi_i(\vec{r})
\end{aligned}
$$

$$
\begin{aligned}
&\bar{H}_2 = \langle \Psi_{HF} | \frac{1}{2} \sum_{i \neq j}^{N} v_{ij} | \Psi_{HF} \rangle \\
=&\frac{1}{2} \sum_{i \neq j}^{N} \frac{1}{N!} \sum_{k'_1,\cdots,k'_N} \sum_{k_1,\cdots,k_N} \varepsilon_{k'_1,\cdots,k'_N} \varepsilon_{k_1,\cdots,k_N} \int \mathrm{d}\vec{r}_1 \cdots \mathrm{d}\vec{r}_N \psi^\dagger_{k'_1}(x_1) \cdots \psi^\dagger_{k'_N}(x_N) v_{ij} \psi_{k_1}(x_1) \cdots \psi_{k_N}(x_N) \\
=&\frac{1}{2} \sum_{i \neq j}^{N} \frac{1}{N!} \sum_{k'_1,\cdots,k'_N} \sum_{k_1,\cdots,k_N} \varepsilon_{k'_1,\cdots,k'_{i-1},k'_i,k'_{i+1},\cdots,k'_{j-1},k'_j,k'_{j+1},\cdots,k'_N} \varepsilon_{k_1,\cdots,k_{i-1},k_i,k_{i+1},\cdots,k_{j-1},k_j,k_{j+1}\cdots k_N} \\
&\delta_{k'_1 k_1} \cdots \delta_{k'_{i-1} k_{i-1}} \delta_{k'_{i+1} k_{i+1}} \cdots \delta_{k'_{j-1} k_{j-1}} \delta_{k'_{j+1} k_{j+1}} \cdots \delta_{k'_N k_N} \int \mathrm{d}\vec{r}_i \mathrm{d}\vec{r}_j \psi^\dagger_{k'_i}(x_i) \psi^\dagger_{k'_j}(x_j) v_{ij} \psi_{k_i}(x_i) \psi_{k_j}(x_j) \\
=&\frac{1}{2} \sum_{\substack{i \neq j \\ (\text{spin } i = \text{spin } j)}}^{N} \frac{1}{N!} \sum_{k_1,\cdots,k_N} |\varepsilon_{k_1,\cdots,k_N}|^2 \int \mathrm{d}\vec{r}_i \mathrm{d}\vec{r}_j \\
&\left[\psi^\dagger_{k_i}(x_i) \psi^\dagger_{k_j}(x_j) v_{ij} \psi_{k_i}(x_i) \psi_{k_j}(x_j) - \psi^\dagger_{k_j}(x_i) \psi^\dagger_{k_i}(x_j) v_{ij} \psi_{k_i}(x_i) \psi_{k_j}(x_j) \right] \\
=&\frac{1}{2} \sum_{i \neq j}^{N} \frac{1}{N!} \sum_{k_1,\cdots,k_N} \int \mathrm{d}\vec{r}_i \mathrm{d}\vec{r}_j \left[\psi^\dagger_{k_i}(x_i) \psi^\dagger_{k_j}(x_j) v_{ij} \psi_{k_i}(x_i) \psi_{k_j}(x_j) - \psi^\dagger_{k_j}(x_i) \psi^\dagger_{k_i}(x_j) v_{ij} \psi_{k_i}(x_i) \psi_{k_j}(x_j) \right] \\
=&\frac{1}{2} \sum_{i \neq j}^{N} \frac{1}{N!} \int \mathrm{d}\vec{r}_i \mathrm{d}\vec{r}_j \sum_{k_1,\cdots,k_N} \left[\psi^\dagger_{k_i}(x_i) \psi^\dagger_{k_j}(x_j) v_{ij} \psi_{k_i}(x_i) \psi_{k_j}(x_j) - \psi^\dagger_{k_j}(x_i) \psi^\dagger_{k_i}(x_j) v_{ij} \psi_{k_i}(x_i) \psi_{k_j}(x_j) \right] \\
=&\frac{1}{2} \sum_{i \neq j}^{N} \frac{1}{N!} \int \mathrm{d}\vec{r}_1 \mathrm{d}\vec{r}_2 (N-2)! \sum_{m \neq n} \left[\psi^\dagger_m(x_1) \psi^\dagger_n(x_2) v \psi_m(x_1) \psi_n(x_2) - \psi^\dagger_n(x_1) \psi^\dagger_m(x_2) v \psi_m(x_1) \psi_n(x_2) \right] \\
=&\frac{1}{2} \int \mathrm{d}\vec{r}_1 \mathrm{d}\vec{r}_2 \sum_{m \neq n} \left[\psi^\dagger_m(x_1) \psi^\dagger_n(x_2) v(\vec{r}_1, \vec{r}_2) \psi_m(x_1) \psi_n(x_2) - \psi^\dagger_n(x_1) \psi^\dagger_m(x_2) (\vec{r}_1, \vec{r}_2) \psi_m(x_1) \psi_n(x_2) \right] \\
=&\frac{1}{2} \sum_{i \neq j} \int \mathrm{d}\vec{r} \mathrm{d}\vec{r}' \left[\psi^\dagger_i(\vec{r}) \psi^\dagger_j(\vec{r}') v(\vec{r}, \vec{r}') \psi_i(\vec{r}) \psi_j(\vec{r}') - \psi^\dagger_j(\vec{r}) \psi^\dagger_i(\vec{r}') (\vec{r}, \vec{r}') \psi_i(\vec{r}) \psi_j(\vec{r}') \right] \\
=&\frac{1}{2} \sum_{i \neq j} \int \mathrm{d}\vec{r} \mathrm{d}\vec{r}' v(\vec{r}, \vec{r}') |\phi_i(\vec{r}) \phi(\vec{r}')|^2 - \frac{1}{2} \sum_{\substack{i \neq j \\ (\text{spin } i = \text{spin } j)}} \int \mathrm{d}\vec{r} \mathrm{d}\vec{r}' v(\vec{r}, \vec{r}') \phi^\dagger_i(\vec{r}) \phi^\dagger_j(\vec{r}') \phi_j(\vec{r}) \phi_i(\vec{r}')
\end{aligned}
\tag{130}
$$

故

$$
\begin{aligned}
\bar{H} =& \sum_{i=1} \int \mathrm{d}\vec{r} \phi^\dagger_i(\vec{r}) h(\vec{r}) \phi_i(\vec{r}) + \frac{1}{2} \sum_{i \neq j} \int \mathrm{d}\vec{r} \mathrm{d}\vec{r}' v(\vec{r}, \vec{r}') |\phi_i(\vec{r}) \phi(\vec{r}')|^2 \\
&- \frac{1}{2} \sum_{\substack{i \neq j \\ (\text{spin } i = \text{spin } j)}} \int \mathrm{d}\vec{r} \mathrm{d}\vec{r}' v(\vec{r}, \vec{r}') \phi^\dagger_i(\vec{r}) \phi^\dagger_j(\vec{r}') \phi_j(\vec{r}) \phi_i(\vec{r}') \\
=& \bar{H}_{\text{Hartree}} + \bar{H}_{\text{exchange}}
\end{aligned}
\tag{131}
$$

$$
\delta \bar{H} = \delta \bar{H}_{\text{Hartree}} + \delta \bar{H}_{\text{exchange}} \tag{132}
$$

计算 $\delta\bar{H}_{\text{exchange}}$

$$\begin{aligned}
\delta\bar{H}_{\text{exchange}} =& -\frac{1}{2}\sum_{\substack{i\neq j\\ (\text{spin } i=\text{spin } j)}}\int\left[\delta\phi_i^\dagger(\vec{r})\phi_j^\dagger(\vec{r}')\phi_j(\vec{r})\phi_i(\vec{r}')+\phi_i^\dagger(\vec{r})\delta\phi_j^\dagger(\vec{r}')\phi_j(\vec{r})\phi_i(\vec{r}')\right.\\
&\left.+\phi_i^\dagger(\vec{r})\phi_j^\dagger(\vec{r}')\delta\phi_j(\vec{r})\phi_i(\vec{r}')+\phi_i^\dagger(\vec{r})\phi_j^\dagger(\vec{r}')\phi_j(\vec{r})\delta\phi_i(\vec{r}')\right]v(\vec{r},\vec{r}')\mathrm{d}\vec{r}\mathrm{d}\vec{r}'\\
=& -\sum_{\substack{i\neq j\\ (\text{spin } i=\text{spin } j)}}\int\left[\delta\phi_i^\dagger(\vec{r})\phi_j^\dagger(\vec{r}')\phi_j(\vec{r})\phi_i(\vec{r}')+\phi_i^\dagger(\vec{r})\phi_j^\dagger(\vec{r}')\delta\phi_j(\vec{r})\phi_i(\vec{r}')\right]v(\vec{r},\vec{r}')\mathrm{d}\vec{r}\mathrm{d}\vec{r}'\\
=& -\sum_{i=1}^{N}\delta\phi_i^\dagger(\vec{r})\sum_{\substack{j\neq i\\ (\text{spin } i=\text{spin } j)}}\int\phi_j^\dagger(\vec{r}')\phi_j(\vec{r})\phi_i(\vec{r}')v(\vec{r},\vec{r}')\mathrm{d}\vec{r}\mathrm{d}\vec{r}'+C.C
\end{aligned} \tag{133}$$

$$\begin{aligned}
&\delta\bar{H}-\sum_{i=1}^{N}\varepsilon_i\delta\int|\phi_i(\vec{r})|^2\mathrm{d}\vec{r}\\
=&\delta\bar{H}_{\text{Hartree}}-\sum_{i=1}^{N}\varepsilon_i\left[\int\delta\phi_i^\dagger(\vec{r})\phi_i(\vec{r})\mathrm{d}\vec{r}+\int\phi_i^\dagger(\vec{r})\delta\phi_i(\vec{r})\mathrm{d}\vec{r}\right]+\delta\bar{H}_{\text{exchange}}\\
=&\sum_{i=1}^{N}\int\mathrm{d}\vec{r}\delta\phi_i^\dagger(\vec{r})\left\{\left[h(\vec{r})+v_H^i(\vec{r})-\varepsilon_i\right]\phi_i(\vec{r})-\sum_{\substack{j\neq i\\ (\text{spin } j=\text{spin } i)}}\int\phi_j^\dagger(\vec{r}')\phi_j(\vec{r})\phi_i(\vec{r}')v(\vec{r},\vec{r}')\mathrm{d}\vec{r}'\right\}+C.C.\\
=&0
\end{aligned} \tag{134}$$

则

$$\left[h(\vec{r})+v_H^i(\vec{r})-\varepsilon_i\right]\phi_i(\vec{r})-\sum_{\substack{j\neq i\\ (\text{spin } j=\text{spin } i)}}\int\phi_j^\dagger(\vec{r}')\phi_j(\vec{r})\phi_i(\vec{r}')v(\vec{r},\vec{r}')\mathrm{d}\vec{r}'=0 \tag{135}$$

我们前面已经定义过 $v_H^i(\vec{r})$

$$v_H^i(\vec{r})=\sum_{j\neq i}^{N}\int|\phi_j(\vec{r}')|^2v(\vec{r},\vec{r}')\mathrm{d}\vec{r}' \tag{136}$$

令

$$v_{\text{xi}}(\vec{r})\phi_i(\vec{r})=-\sum_{\substack{j\neq i\\ (\text{spin } j=\text{spin } i)}}\int\phi_j^\dagger(\vec{r}')\phi_j(\vec{r})\phi_i(\vec{r}')v(\vec{r},\vec{r}')\mathrm{d}\vec{r}' \tag{137}$$

则

$$\left[h(\vec{r})+v_H^i(\vec{r})+v_{\text{xi}}(\vec{r})-\varepsilon_i\right]\phi_i(\vec{r})=0 \tag{138}$$

我们来分析 Eq.(138)

$$\begin{aligned}
v_H^i(\vec{r})\phi_i(\vec{r})=&\sum_{j\neq i}^{N}\int\mathrm{d}\vec{r}'|\phi_j(\vec{r}')|^2v(\vec{r},\vec{r}')\phi_i(\vec{r})\\
=&\sum_{\substack{j\neq i\\ (\text{spin } j=\text{spin } i)}}^{N}\int\mathrm{d}\vec{r}'|\phi_j(\vec{r}')|^2v(\vec{r},\vec{r}')\phi_i(\vec{r})+\sum_{\substack{j\neq i\\ (\text{spin } j\neq\text{spin } i)}}^{N}\int\mathrm{d}\vec{r}'|\phi_j(\vec{r}')|^2v(\vec{r},\vec{r}')\phi_i(\vec{r})
\end{aligned} \tag{139}$$

则

$$\begin{aligned}
&\left[v_H^i(\vec{r}) + v_{\text{xi}}(\vec{r})\right]\phi_i(\vec{r}) \\
=&\sum_{\substack{j\neq i \\ (\text{spin } j=\text{spin } i)}}^{N} \int \mathrm{d}\vec{r}'|\phi_j(\vec{r}')|^2 v(\vec{r},\vec{r}')\phi_i(\vec{r}) + \sum_{\substack{j\neq i \\ (\text{spin } j\neq\text{spin } i)}}^{N} \int \mathrm{d}\vec{r}'|\phi_j(\vec{r}')|^2 v(\vec{r},\vec{r}')\phi_i(\vec{r}) \\
&- \sum_{\substack{j\neq i \\ (\text{spin } j=\text{spin } i)}} \int \phi_j^\dagger(\vec{r}')\phi_j(\vec{r})\phi_i(\vec{r}')v(\vec{r},\vec{r}')\mathrm{d}\vec{r}' \\
=&\sum_{\substack{j \\ (\text{spin } j=\text{spin } i)}}^{N} \int \mathrm{d}\vec{r}'|\phi_j(\vec{r}')|^2 v(\vec{r},\vec{r}')\phi_i(\vec{r}) + \sum_{\substack{j \\ (\text{spin } j\neq\text{spin } i)}}^{N} \int \mathrm{d}\vec{r}'|\phi_j(\vec{r}')|^2 v(\vec{r},\vec{r}')\phi_i(\vec{r}) \\
&- \sum_{\substack{j \\ (\text{spin } j=\text{spin } i)}} \int \phi_j^\dagger(\vec{r}')\phi_j(\vec{r})\phi_i(\vec{r}')v(\vec{r},\vec{r}')\mathrm{d}\vec{r}' \\
=&\sum_{j}^{N} \int \mathrm{d}\vec{r}'|\phi_j(\vec{r}')|^2 v(\vec{r},\vec{r}')\phi_i(\vec{r}) - \sum_{\substack{j \\ (\text{spin } j=\text{spin } i)}} \int \mathrm{d}\vec{r}'\phi_j^\dagger(\vec{r}')\phi_j(\vec{r})\phi_i(\vec{r}')v(\vec{r},\vec{r}') \\
=&\left[v_H(\vec{r}) + \tilde{v}_{\text{xi}}(\vec{r})\right]\phi_i(\vec{r})
\end{aligned} \tag{140}$$

Orbital-dependent Hartree equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + v_{\text{ext}}(\vec{r}) + v_H(\vec{r}) + \tilde{v}_{\text{xi}}(\vec{r})\right]\phi_i(\vec{r}) = \varepsilon_i\phi_i(\vec{r}) \tag{141}$$

与 Hartree equation 类似，我们通过迭代的方法解 Eq.(141)。