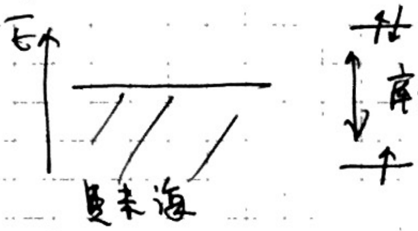
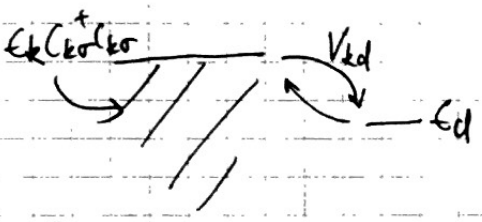
Lecture 5 金属中的局域磁矩.   教材 Chap. 7



1) 基本图象与模型.

模型：单杂质 Anderson 模型.

$$H=\sum_{k\sigma} c_{k\sigma}^{\dagger}c_{k\sigma}\epsilon_k+\sum_{\sigma} c_{d\sigma}^{\dagger}c_{d\sigma}\epsilon_d+\sum_{k\sigma}V_{kd}\left(c_{k\sigma}^{\dagger}c_{d\sigma}+h.c.\right)+U n_{d\uparrow}n_{d\downarrow}.$$



$$H_d=\sum_{\sigma}\epsilon_d c_{d\sigma}^{\dagger}c_{d\sigma}+U\hat{n}_{d\uparrow}\hat{n}_{d\downarrow}$$

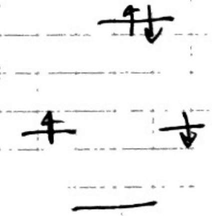
$$\hat{n}_d=\hat{n}_{d\uparrow}+\hat{n}_{d\downarrow}$$

$n_d=0$: $E=0$ $n_d=1$: $c_{d\uparrow}^{\dagger}|0\rangle$ or $c_{d\downarrow}^{\dagger}|0\rangle$ $E=\epsilon_d$.

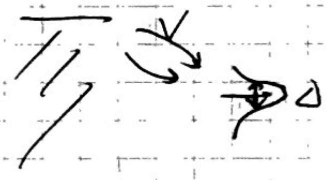
$n_d=2$: $c_{d\uparrow}^{\dagger}c_{d\downarrow}^{\dagger}|0\rangle$. $n_{d\uparrow}=n_{d\downarrow}=1$, $E=2\epsilon_d+U$.

$$U=\langle dd|V_{ee}|dd\rangle=\int d\vec{r}_1 d\vec{r}_2\,|\varphi_d(\vec{r}_1)|^2|\varphi_d(\vec{r}_2)|^2\frac{e^2}{|\vec{r}_1-\vec{r}_2|}$$ (屏蔽)库仑势.

$V_d=0$:



$V_d\neq 0$:



$c_{d\sigma}^{\dagger}|0\rangle$ 不再是本征态，寿命有限 $\Leftrightarrow$ 能级展宽.

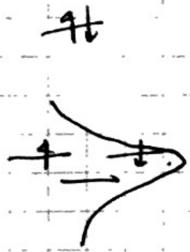
费米黄金法则 $$\frac{1}{\tau}=2\pi\frac{|V_{kd}|^2N(\epsilon_d)}{\hbar}\triangleq\frac{2\Delta}{\hbar}.$$

Δ: ~~[illegible]~~ d-k 杂化(hybridization)能量尺度. $\Delta\sim\pi\frac{|V_{kd}|^2N(\epsilon_d)}{\hbar}$

* 弱杂化: $U\gg|\epsilon_d|\gg\Delta$. 局域磁矩.

图像近似成立.

* 强杂化: $U\gg\Delta\gg|\epsilon_d|$



磁矩加入费米面.

* 无磁性: $U<\Delta$

2) 平均场近似.

相互作用项: $U n_{d\uparrow} n_{d\downarrow} = U c_{d\uparrow}^{\dagger} c_{d\uparrow} c_{d\downarrow}^{\dagger} c_{d\downarrow}$.

假设: 基态波函数为 Slater 行列式态 (Hatree-Fock; 平均场).

$\langle U n_{d\uparrow} n_{d\downarrow} \rangle$ 用 Wick 定理展开:

$= U \langle c_{d\uparrow}^{\dagger} c_{d\uparrow} c_{d\downarrow}^{\dagger} c_{d\downarrow} \rangle$.

$\langle c_{d\uparrow}^{\dagger} c_{d\downarrow} \rangle = 0$: 由于自旋旋转对称性/自旋守恒

因此只有 $\langle c_{d\uparrow}^{\dagger} c_{d\uparrow} \rangle \langle c_{d\downarrow}^{\dagger} c_{d\downarrow} \rangle$ 一种拆分方法.

[平均场近似 $\langle c^{\dagger} c \rangle \neq 0$ (序参量) 往往由对称性决定]

* 平均场分解:

$$\hat{H} = \sum_{k\sigma} \epsilon_k c_{k\sigma}^{\dagger} c_{k\sigma} + \sum_{\sigma} \epsilon_d c_{d\sigma}^{\dagger} c_{d\sigma} + \sum_{k\sigma} V_{kd} (c_{k\sigma}^{\dagger} c_{d\sigma} + h.c.) + U n_{d\uparrow} n_{d\downarrow}$$

$$\approx \sum_{k\sigma} \epsilon_k c_{k\sigma}^{\dagger} c_{k\sigma} + \sum_{\sigma} \epsilon_d c_{d\sigma}^{\dagger} c_{d\sigma} + \sum_{k\sigma} V_{kd} (c_{k\sigma}^{\dagger} c_{d\sigma} + h.c.) + U \langle \hat{n}_{d\uparrow} \rangle \hat{n}_{d\downarrow} + U \langle \hat{n}_{d\downarrow} \rangle \hat{n}_{d\uparrow}$$

$$\underbrace{- U \langle \hat{n}_{d\uparrow} \rangle \langle \hat{n}_{d\downarrow} \rangle}$$ 仅改变能量零点, 可先不考虑.

$$\left[\begin{array}{l} \hat{A}\hat{B} \approx \langle A \rangle \hat{B} + \hat{A} \langle B \rangle - \langle A \rangle \langle B \rangle, \\ \langle \hat{A}\hat{B} \rangle = \langle R.H.S. \rangle \end{array}\right]$$

$$= \sum_{k\sigma} \epsilon_k c_{k\sigma}^{\dagger} c_{k\sigma} + \sum_{\sigma} E_{d\sigma} c_{d\sigma}^{\dagger} c_{d\sigma} + \sum_{k\sigma} V_{kd} (c_{k\sigma}^{\dagger} c_{d\sigma} + h.c.) = \hat{H}_{MF}$$

w/ $E_{d\sigma} = \epsilon_d + U \langle \hat{n}_{d\bar{\sigma}} \rangle$.

$\boxed{n_{d\uparrow} \neq n_{d\downarrow}: \text{自旋守恒/对称性破缺} \quad \text{假设破缺在z方向}}$

3) 对角化 $\hat{H}_{MF}$:

假设 $\hat{H}_{MF} = \sum_{n\sigma} \epsilon_{n\sigma} c_{n\sigma}^{\dagger} c_{n\sigma}$

w/ $c_{n\sigma} = \sum_{k} \langle n\sigma | k\sigma \rangle c_{k\sigma} + \langle n\sigma | d\sigma \rangle c_{d\sigma}$.

$$[\hat{H}_{MF}, c_{n\sigma}^{\dagger}] = \epsilon_{n\sigma} c_{n\sigma}^{\dagger} = \epsilon_{n\sigma} \left(\sum_{k} \langle k\sigma | n\sigma \rangle c_{k\sigma}^{\dagger} + \langle d\sigma | n\sigma \rangle c_{d\sigma}^{\dagger} \right).$$

$$[\hat{H}_{MF}, c_{n\sigma}^{\dagger}] = [\hat{H}_{MF}, \sum_{k} \langle k\sigma | n\sigma \rangle c_{k\sigma}^{\dagger} + \langle d\sigma | n\sigma \rangle c_{d\sigma}^{\dagger}]$$

$$= \sum_{k} \langle k\sigma | n\sigma \rangle (\epsilon_k c_{k\sigma}^{\dagger} + V_{k\sigma} c_{d\sigma}^{\dagger}) + \langle d\sigma | n\sigma \rangle (E_{d\sigma} c_{d\sigma}^{\dagger} + \sum_{k} V_{kd} c_{k\sigma}^{\dagger})$$

$$= \sum_{k} (\langle k\sigma | n\sigma \rangle \epsilon_k + \langle d\sigma | n\sigma \rangle V_{kd}) c_{k\sigma}^{\dagger} + \left(\sum_{k} \langle k\sigma | n\sigma \rangle V_{k\sigma} + \langle d\sigma | n\sigma \rangle E_{d\sigma} \right) c_{d\sigma}^{\dagger}$$

对比二者, 得到

$$\begin{cases} \epsilon_{n\sigma} \langle k\sigma | n\sigma \rangle = \epsilon_k \langle k\sigma | n\sigma \rangle + V_{kd} \langle d\sigma | n\sigma \rangle & ① \\ \epsilon_{n\sigma} \langle d\sigma | n\sigma \rangle = E_{d\sigma} \langle d\sigma | n\sigma \rangle + \sum_{k} V_{kd} \langle k\sigma | n\sigma \rangle & ② \end{cases}$$

可由此求解本征值 $\epsilon_{n\sigma}$:

$$① \Rightarrow \langle k\sigma | n\sigma \rangle = \frac{V_{kd}}{\epsilon_{n\sigma} - \epsilon_k} \langle d\sigma | n\sigma \rangle.$$

代入②，消去 $\langle k\sigma|n\sigma\rangle$，可得

$$(\epsilon_{n\sigma}-\epsilon_{d\sigma})\langle d\sigma|n\sigma\rangle=\sum_k V_{kd}\langle k\sigma|n\sigma\rangle=\sum_k\frac{V_{kd}^2}{\epsilon_{n\sigma}-\epsilon_k}\langle d\sigma|n\sigma\rangle$$

$$\therefore\quad \epsilon_{n\sigma}=\epsilon_{d\sigma}+\sum_k\frac{V_{kd}^2}{\epsilon_{n\sigma}-\epsilon_k}.$$

4) 格林函数 $G_{dd\sigma}(\omega)$.

我们先计算 $G_{dd\sigma}(\omega_n)=-\int_0^\beta d\tau\, e^{i\omega_n\tau}\, T_\tau\langle c_{d\sigma}(\tau)c_{d\sigma}^\dagger(0)\rangle$.

自由费米子：$G_{nn\sigma}(\omega_n)=-\int_0^\beta d\tau\, e^{i\omega_n\tau}\, T_\tau\langle c_{n\sigma}(\tau)c_{n\sigma}^\dagger(0)\rangle$

$$=\frac{1}{i\omega_n-\epsilon_n}.$$

$$G_{dd\sigma}(\omega_n)=-\int_0^\beta d\tau\, e^{i\omega_n\tau}\sum_{nm}T_\tau\langle c_{n\sigma}(\tau)c_{m\sigma}^\dagger(0)\rangle\langle d\sigma|n\sigma\rangle\langle m\sigma|d\sigma\rangle$$

$$=\sum_{nm}\delta_{nm}\frac{1}{i\omega_n-\epsilon_n}\langle d\sigma|n\sigma\rangle\langle m\sigma|d\sigma\rangle$$

$$=\sum_n\frac{1}{i\omega_n-\epsilon_n}\langle d\sigma|n\sigma\rangle\langle n\sigma|d\sigma\rangle.$$

可由①②将 ϵ_n；$\langle d\sigma|n\sigma\rangle$ 解出代入即得.

另外一种比较简捷的计算方法：

对于二次型 Hamiltonian： $\hat H_{MF}=\sum_{n\sigma}\epsilon_{n\sigma}c_{n\sigma}^\dagger c_{n\sigma}$.

$$G_{n\sigma;m\sigma'}(\omega_n)=\frac{1}{i\omega_n-\epsilon_n}\delta_{nm}\delta_{\sigma\sigma'}.$$

对应单体 Hamiltonian： $\hat H_{MF}=\sum_{n\sigma,m\sigma'}c_{n\sigma}^\dagger\langle n\sigma|\hat h_{MF}|m\sigma'\rangle c_{m\sigma'}$

$$\langle n\sigma|\hat h_{MF}|m\sigma'\rangle=\epsilon_{n\sigma}\delta_{nm}\delta_{\sigma\sigma'}$$

令 $\hat G(\omega_n)=\dfrac{1}{i\omega_n-\hat h_{MF}}=\sum_{n\sigma}\dfrac{|n\sigma\rangle\langle n\sigma|}{i\omega_n-\epsilon_{n\sigma}}$

$$G_{n\sigma;m\sigma'}(\omega_n)=\langle n\sigma|\hat G(k,i\omega_n)|m\sigma'\rangle$$

$$\boxed{\begin{array}{l}\text{一般地，对二次型 } \hat H=\sum_{\alpha}c_\alpha^\dagger\langle\alpha|\hat h|\beta\rangle c_\beta\\ \hat G(\omega_n)^{-1}=i\omega_n-\hat h\end{array}}$$

例：$G_{dd,\sigma}(\omega_n)=\langle d\sigma|\hat G(i\omega_n)|d\sigma\rangle=\sum_{n\sigma}\dfrac{|\langle d\sigma|n\sigma\rangle|^2}{i\omega_n-\epsilon_{n\sigma}}$.

求解 $\hat G(\omega_n)^{-1}=i\omega_n-\hat h_{MF}$:

w/ $\hat h_{MF}=\sum_{k\sigma}|k\sigma\rangle\epsilon_k\langle k\sigma|+\sum_\sigma|d\sigma\rangle\epsilon_{d\sigma}\langle d\sigma|+\sum_{k\sigma}(|k\sigma\rangle V_{kd}\langle d\sigma|+h.c.)$

~~$\therefore\ \langle k\sigma|\hat G(\omega_n)^{-1}|k\sigma\rangle=G_{k\sigma}(\omega_n)^{-1}=i\omega_n-\epsilon_k.$~~

~~$\hat G(\omega_n)(i\omega_n-\hat h_{MF})$~~

利用 $(i\omega_n - \hat h_{MF})\cdot \hat G(\omega_n) = 1$ (#)

记: $\langle \vec k\sigma|\hat G(\omega_n)|\vec k'\sigma'\rangle = \delta_{\sigma\sigma'}\delta_{\vec k\vec k'} G_{k\sigma}(\omega_n)$

$\langle \vec k\sigma|\hat G(\omega_n)|d\sigma'\rangle = \delta_{\sigma\sigma'} G_{kd,\sigma}(\omega_n)$

$\langle d\sigma|\hat G(\omega_n)|d\sigma'\rangle = \delta_{\sigma\sigma'} G_{dd,\sigma}(\omega_n)$

∴ $\langle \vec k\sigma|\#|\vec k\sigma\rangle = 1$

$\Rightarrow (i\omega_n - \epsilon_k)G_{k\sigma}(\omega_n) - V_{kd}G_{kd\sigma}(\omega_n) = 1$

$\langle \vec k\sigma|\#|d\sigma\rangle = 0$

$\Rightarrow (i\omega_n-\epsilon_k)G_{kd\sigma}(\omega_n) - V_{kd}G_{dd\sigma}(\omega_n) = 0$ ①

$\langle d\sigma|\#|d\sigma\rangle = 1$

$\Rightarrow (i\omega_n - \tilde\epsilon_{d\sigma})G_{dd\sigma}(\omega_n) - \sum_k V_{kd}G_{kd\sigma}(\omega_n) = 1$ ②

① $\Rightarrow G_{kd\sigma}(\omega_n) = \frac{V_{kd}}{i\omega_n-\epsilon_k}G_{dd\sigma}(\omega_n)$.

代入②, $\Rightarrow$

$$(i\omega_n - \tilde\epsilon_{d\sigma})G_{dd\sigma}(\omega_n) = \sum_k V_{kd}G_{kd\sigma}(\omega_n)+1$$
$$= \sum_k \frac{V_{kd}^2}{i\omega_n-\epsilon_k}G_{dd\sigma}(\omega_n)+1$$

∴ $$G_{dd,\sigma}(\omega_n) = \frac{1}{i\omega_n - \tilde\epsilon_{d\sigma} - \sum_k \frac{V_{kd}^2}{i\omega_n-\epsilon_k}}$$

$$[G_{dd\sigma}(\omega_n)]^{-1} = i\omega_n - \tilde\epsilon_{d\sigma} - \sum_k \frac{V_{kd}^2}{i\omega_n-\epsilon_k}$$

$$[G^{ret}_{dd\sigma}(\omega)]^{-1} = \omega - \tilde\epsilon_{d\sigma} - \sum_k\frac{V_{kd}^2}{\omega-\epsilon_k+i0^+}.$$

5) 自能修正.

Motivation: 自由费米子 $G(\omega_n) = i\omega_n - \epsilon$.

故令 $\Sigma_{d\sigma}(\omega_n) = \sum_k \frac{V_{kd}^2}{i\omega_n-\tilde\epsilon_{d\sigma}}$.

$\Sigma^{ret}_{d\sigma}(\omega) = \sum_k \frac{V_{kd}^2}{\omega-\epsilon_k+i0^+}$.

实部代表能量修正: $\mathrm{Re}\,\Sigma = \frac{1}{V}\int\frac{d^3k}{(2\pi)^3}\mathcal{P}\frac{V_{kd}^2}{\omega-\epsilon_k}$.

虚部代表(寿命)$^{-1}$或能级展宽:

$$\mathrm{Im}\,\Sigma^{ret}_{d\sigma}(\omega) = \sum_k V_{kd}^2(-i\pi)\delta(\omega-\epsilon_k)$$
$$= -i\pi\langle V_{kd}^2\rangle_{FS}N(\omega).$$

忽略掉 $\mathrm{Re}\,\Sigma$，忽略 $\mathrm{Im}\,\Sigma$ 的 ω- dependence:

$$G^{ret}_{dd,\sigma}(\omega) = \frac{1}{\omega - E_{d\sigma} + i\pi\Delta}$$

$$\text{w/ } \Delta = \pi \langle V_{kd}^2\rangle_{FS} N(E_{d\sigma}).$$

谱函数 $$A_{dd}(\omega) = -\frac{1}{\pi}\mathrm{Im}\,G^{ret}_{dd,\sigma}(\omega) = \frac{1}{\pi}\frac{\Delta}{(\omega - E_{d\sigma})^2 + \Delta^2}.$$

$\rho_{d\sigma}(\omega)$. 能量为 ω 时的态密度.

6) 自洽方程，

$$\begin{aligned}\langle n_{d\sigma}\rangle &= \langle c^\dagger_{d\sigma} c_{d\sigma}\rangle \\ &= \sum_{nm}\langle c^\dagger_{n\sigma} c_{m\sigma}\rangle \langle d\sigma|n\sigma\rangle\langle m\sigma|d\sigma\rangle \\ &= \sum_n \langle c^\dagger_{n\sigma} c_{n\sigma}\rangle\, |\langle d\sigma|n\sigma\rangle|^2 \\ &= \sum_n f(\epsilon_{n\sigma})\, |\langle d\sigma|n\sigma\rangle|^2. \qquad f(x) = \frac{1}{1+e^{\beta x}}.\end{aligned}$$

$$A_{d\sigma}(\omega) = \sum_n |\langle d\sigma|n\sigma\rangle|^2 \delta(\omega - \epsilon_{n\sigma})$$

$$\cancel{\therefore \langle n_{d\sigma}\rangle = \int_{-\infty}^{\infty} d\omega\, f(\epsilon_{n\sigma})\, \ldots \sum_n \delta(\omega - \epsilon_{n\sigma})\, |\langle d\sigma|n\sigma\rangle|^2}$$

$$\cancel{= \int_{-\infty}^{\infty} d\omega\, f(\omega)\, A(\omega)}$$

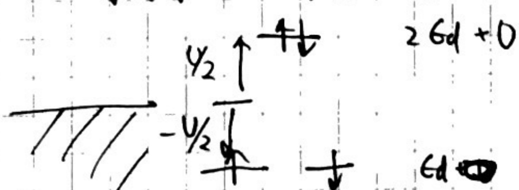
$$\begin{aligned}\therefore \langle n_{d\sigma}\rangle &= \int_{-\infty}^{\infty} d\omega \sum_n \delta(\omega - \epsilon_{n\sigma}) f(\omega)\, |\langle d\sigma|n\sigma\rangle|^2 \\ &= \int_{-\infty}^{\infty} d\omega\, f(\omega)\, A_{d\sigma}(\omega).\end{aligned}$$

$T=0$: $\beta = \infty$. $f(\omega) = \begin{cases}1, & \omega<0\\ 0, & \omega>0\end{cases}$. （假设 $\mu = 0$）.

$$\begin{aligned}\langle n_{d\sigma}\rangle &= \int_{-\infty}^{0}\frac{d\omega}{\pi}\frac{\Delta}{(\omega - \epsilon_d - U\langle n_{d-\sigma}\rangle)^2 + \Delta^2} \\ &= \frac{1}{\pi}\cot^{-1}\left(\frac{\epsilon_d + U\langle n_{d-\sigma}\rangle}{\Delta}\right).\end{aligned}$$

$$\begin{cases}\langle n_{d\uparrow}\rangle = \dfrac{1}{\pi}\cot^{-1}\left(\dfrac{\epsilon_d + U\langle n_{d\downarrow}\rangle}{\Delta}\right)\\[2ex] \langle n_{d\downarrow}\rangle = \dfrac{1}{\pi}\cot^{-1}\left(\dfrac{\epsilon_d + U\langle n_{d\uparrow}\rangle}{\Delta}\right).\end{cases}$$

有没有 $\langle n_{d\uparrow}\rangle \neq \langle n_{d\downarrow}\rangle$ 的解?



令 $\epsilon_d = -U/2$: $2\epsilon_d + U = U/2$

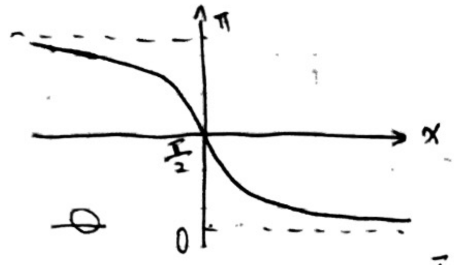
这时最容易出现局域磁矩.

~~若 $\Delta \ll |\epsilon_d| = \frac{U}{2}$~~

$$\cancel{\cot^{-1}\left(\frac{\epsilon_d + U\langle n_{d\sigma}\rangle}{\Delta}\right) \approx \pi - \frac{\Delta}{\epsilon_d + U\langle n_{d\sigma}\rangle} = \pi - \frac{\Delta}{U}\frac{1}{\langle n_{d\sigma}\rangle - \frac{1}{2}}}$$

~~若 $\langle n_{d\uparrow}\rangle - \frac{1}{2}$ 为有限值 $\Rightarrow \langle n_{d\downarrow}\rangle \approx \frac{1}{\pi}\left(\pi - \frac{\Delta}{U}\frac{1}{\langle n_{d\uparrow}\rangle - \frac{1}{2}}\right)$~~

$\cot^{-1} x$,



- $\langle n_{d\sigma}\rangle = \frac{1}{\pi}\cot^{-1}\Big[\underbrace{\frac{U}{\Delta}\big(\langle n_{d-\sigma}\rangle - \frac{1}{2}\big)}_{x}\Big]$

$\langle n_{d\sigma}\rangle - \frac{1}{2} > 0$: $x \to +\infty$. $\cot^{-1}(x) \to 0$ $\langle n_{d-\sigma}\rangle \to 0$

$\langle n_{d\sigma}\rangle - \frac{1}{2} < 0$: $x \to -\infty$ $\cot^{-1}(x) \to \pi$ $\langle n_{d-\sigma}\rangle \to 1$.

$\langle n_{d\uparrow}\rangle \approx 1$ $\langle n_{d\downarrow}\rangle \approx 0$ 是一组解.

事实上，此时（$\epsilon_d = -U/2$）有粒子/空穴对称性，$\Rightarrow n_{d\uparrow} + n_{d\downarrow} = 1$.

令 $n_{d\uparrow} = \frac{1}{2} + x$; $n_{d\downarrow} = \frac{1}{2} - x$.

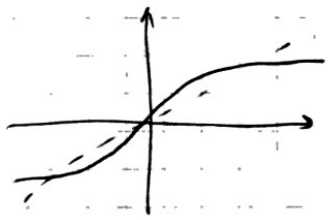
$$\frac{1}{2} + x = \frac{1}{\pi}\cot^{-1}\Big[\frac{U}{\Delta}\big(\tfrac{1}{2} - x - \tfrac{1}{2}\big)\Big]$$

$$= \frac{1}{\pi}\cot^{-1}\big(-\frac{U}{\Delta}x\big).$$

$$\therefore\ x = -\frac{1}{2} + \frac{1}{\pi}\cot^{-1}\big(-\frac{U}{\Delta}x\big)$$

$$= \frac{1}{\pi}\Big[\cot^{-1}\big(-\frac{U}{\Delta}x\big) - \frac{\pi}{2}\Big]$$

$$= \frac{1}{\pi}\tan^{-1}\big(\frac{U}{\Delta}x\big).$$



- $x=0$ 总是一个解.

$\frac{U}{\Delta} > 1$：有三个解.

两解对应 $\langle n_{d\uparrow}\rangle \neq \langle n_{d\downarrow}\rangle$ 有局域磁矩

$\frac{U}{\Delta} < 1$：一个解.

无局域磁矩.

7) 平均场与变分法.

* $T=0$: 以 Hartree-Fock 为例.

$$\hat{H} = \int d\vec{r}\, \hat{\psi}^+(\vec{r}) \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right] \hat{\psi}(\vec{r}) + \frac{1}{2}\int d\vec{r}\, d\vec{r}'\, \hat{\psi}^+(\vec{r})\hat{\psi}^+(\vec{r}') \frac{e^2}{|\vec{r}-\vec{r}'|} \hat{\psi}(\vec{r}')\hat{\psi}(\vec{r})$$

变分方程: $\cancel{\frac{\delta HF}{\delta\phi_\alpha^*(\vec{r})}}$ $\frac{\delta}{\delta\phi_\alpha^*(\vec{r})}\left[\langle HF|\hat{H}|HF\rangle - \sum_{\alpha\in A}\epsilon_\alpha \int d\vec{r}\, |\phi_\alpha(\vec{r})|^2\right] = 0$

$$\Rightarrow \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}) + \sum_{\beta\in A}\int d\vec{r}'\, \phi_\beta^*(\vec{r}')\phi_\beta(\vec{r}')\frac{e^2}{|\vec{r}-\vec{r}'|}\right]\phi_\alpha(\vec{r}) - \sum_{\beta\in A}\int d\vec{r}'\, \phi_\beta^*(\vec{r}')\phi_\alpha(\vec{r}')\phi_\beta(\vec{r})\frac{e^2}{|\vec{r}-\vec{r}'|} = \epsilon_\alpha \phi_\alpha(\vec{r}).$$

对应 $\hat{H}_{MF} = \int d\vec{r}\, \hat{\psi}^+(\vec{r})\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\hat{\psi}(\vec{r})$

$$+ \int d\vec{r}\, d\vec{r}'\, \langle\hat{\psi}^+(\vec{r})\hat{\psi}(\vec{r})\rangle \frac{e^2}{|\vec{r}-\vec{r}'|}\hat{\psi}^+(\vec{r}')\hat{\psi}(\vec{r}')$$

$$+ \int d\vec{r}\, d\vec{r}'\, \langle\hat{\psi}^+(\vec{r})\hat{\psi}(\vec{r}')\rangle \frac{e^2}{|\vec{r}-\vec{r}'|}\hat{\psi}^+(\vec{r}')\hat{\psi}(\vec{r})$$

假设 $\hat{H}_{MF} = \sum_\alpha \epsilon_\alpha C_\alpha^+ C_\alpha$, $\quad C_\alpha^+ = \int d\vec{r}\, \phi_\alpha(\vec{r})\hat{\psi}^+(\vec{r})$.

$$[\hat{H}_{MF}, C_\alpha^+] = \epsilon_\alpha C_\alpha^+ = \epsilon_\alpha \int d\vec{r}\, \phi_\alpha(\vec{r})\hat{\psi}^+(\vec{r}).$$

另一方面, $[\hat{H}_{MF}, C_\alpha^+] = [\hat{H}_{MF}, \int d\vec{r}\, \phi_\alpha(\vec{r})\hat{\psi}^+(\vec{r})]$

$$= \cancel{\int d\vec{r}\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\phi_\alpha(\vec{r})}$$

$$= \int d\vec{r}\, \hat{\psi}^+(\vec{r})\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\phi_\alpha(\vec{r})$$

$$+ \sum_{\beta\in A}\int d\vec{r}'\, \phi_\beta^*(\vec{r}')\phi_\beta(\vec{r}')\frac{e^2}{|\vec{r}-\vec{r}'|}\hat{\psi}^+(\vec{r})\phi_\alpha(\vec{r})$$

$$+ \sum_{\beta\in A}\int d\vec{r}'\, \phi_\beta^*(\vec{r})\phi_\beta(\vec{r}')\frac{e^2}{|\vec{r}-\vec{r}'|}\phi_\alpha(\vec{r})\hat{\psi}^+(\vec{r}').$$

要求 $\hat{\psi}^+(\vec{r})$ 前系数相等, 即得到前述变分方程.

8) $T>0$: 基态波函数 $\to Z = \mathrm{tr}(e^{-\beta H_{MF}})$

H_{MF}: 变分 Hamiltonian.

例: $H_{MF} = \sum_{k\sigma}\epsilon_k C_{k\sigma}^+ C_{k\sigma} + \sum_\sigma \epsilon_d C_{d\sigma}^+ C_{d\sigma} + \sum_{k\sigma} V_{kd}(C_{k\sigma}^+ C_{d\sigma} + h.c.)$

$$+ U\eta_{d\uparrow} n_{d\downarrow} + U\eta_{d\downarrow} n_{d\uparrow}$$

这里 $\eta_{d\sigma}$ 相当于平均场分解中的 $\langle n_{d\sigma}\rangle$, 但我们把它们看成变分参数.

考虑 $Z = \mathrm{tr}(e^{-\beta\hat{H}}) = \mathrm{tr}(e^{-\beta(\hat{H}-\hat{H}_{MF})}e^{-\beta\hat{H}_{MF}})$

$$= \frac{\mathrm{tr}[e^{-\beta(\hat{H}-\hat{H}_{MF})}e^{-\beta\hat{H}_{MF}}]}{\mathrm{tr}(e^{-\beta\hat{H}_{MF}})}\mathrm{tr}(e^{-\beta\hat{H}_{MF}})$$

$$= \langle e^{-\beta(\hat{H}-\hat{H}_{MF})}\rangle_{MF} Z_{MF} \qquad w/\ Z_{MF} = \mathrm{tr}(e^{-\beta\hat{H}_{MF}})$$

$$\geq e^{-\beta\langle\hat{H}-\hat{H}_{MF}\rangle_{MF}} Z_{MF}. \quad 因 \langle e^{-x}\rangle \geq e^{-\langle x\rangle}.$$

考虑 $F = -\frac{1}{\beta} \ln Z$. $\qquad F_{MF} = -\frac{1}{\beta} \ln Z_{MF}$

$\therefore F \leq F_{MF} + \langle H - H_{MF} \rangle_{MF}$.

自变分计算步骤:

$$H_{MF} = H_{MF}(\eta_{d\sigma}).$$

计算 $F_{MF} + \underbrace{\langle H - H_{MF} \rangle_{MF}}$

$$\| $$

$$\langle U \hat{n}_{d\uparrow} \hat{n}_{d\downarrow} - U \eta_{d\uparrow} \hat{n}_{d\downarrow} - U \eta_{d\downarrow} \hat{n}_{d\uparrow} \rangle_{MF}$$

变分: 令 $\frac{\partial F_{MF} + \langle H - H_{MF} \rangle_{MF}}{\partial \eta_{d\sigma}} = 0$

即可推出自洽方程.