第五章　关联

5.1　单电子近似的理论基础

5.2　费米液体理论

5.3　强关联体系

多电子体系(After Born-Oppenheimer 绝热近似)：

$$\hat{H}=\sum_i -\frac{\hbar^2}{2m}\nabla_i^2+\frac{1}{2}\sum_{i\neq j}\frac{1}{4\pi\varepsilon_0}\frac{e^2}{|\vec{r}_i-\vec{r}_j|}-\sum_{i,n}\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{|\vec{r}_i-\vec{R}_n|} \nearrow \sum V_i$$

$$\hat{H}\Phi=E\Phi$$

关联：电子—电子相互作用

弱：单电子近似， 电子平均场

5.1 单电子近似的理论基础

单电子近似着眼于任何 用N个单电子波函数 $\phi_j(q_j)$

构建N电子系统总体波函数

$\Phi(q_1,q_2,\dots,q_N)$

1. Hartree方程(1928)

连乘积形式： $\Phi\left(\phi_{q_1}\dots\phi_{q_N}\right)=\phi_1(\vec{r}_1)\phi\left(\vec{r}_2\right)\cdots\phi_N\left(\vec{r}_N\right)$

$$E=\langle H\rangle=\sum_j\int\phi_j^*\left(\vec{r}_1\right)\left(-\frac{\hbar^2}{2m}\vec{\nabla}_1^2+V_j\left(\vec{r}_j\right)\right)\phi_j\left(\vec{r}_1\right)d\vec{r}_1$$

$$+\frac{e^2}{8\pi\varepsilon_0}\sum_{j'\neq j}\sum\iint\left|\phi_j\left(\vec{r}_1\right)\right|^2\frac{1}{\left|\vec{r}_1-\vec{r}_2\right|}\left|\phi_{j'}\left(\vec{r}_2\right)\right|^2d\vec{r}_1d\vec{r}_2$$

按变分原理，$\{\phi_j(q_j)\}$ 的选取E达到极小

$$\delta\left[\langle H\rangle-\sum_{j=1}^{N}\varepsilon_j\left(\langle\phi_i|\phi_j\rangle-1\right)\right]=0$$

ε_j : *Lagrang*乘子

正交归一条件 $\int\phi_j^*(\vec{r})\phi_{j'}(\vec{r})d\vec{r}=\delta_{jj'}$

单电子方程

$$\left[-\frac{\hbar^2}{2m}\nabla^2+V(\vec{r})+\frac{e^2}{4\pi\varepsilon_0}\sum_{(j'\neq j)}\int\frac{\left|\phi_{j'}(\vec{r}\,')\right|^2}{\left|\vec{r}-\vec{r}\,'\right|}d\vec{r}\,'\right]\times\phi_j(\vec{r})=\varepsilon_j\phi_j(\vec{r})$$

$$\left[-\frac{\hbar^2}{2m}\nabla^2+V(\vec{r})+\frac{e^2}{4\pi\varepsilon_0}\sum_{j'\neq j}\int\frac{\left|\phi_{j'}(\vec{r}\,')\right|^2}{\left|\vec{r}-\vec{r}\,'\right|}d\vec{r}\,'\right]\times\phi_j(\vec{r})=\varepsilon_j\phi_j(\vec{r})$$

动能　原子核对电子形成的势能　其余N-1个电子对j电子的库仑作用能

自洽求解，H_2, He计算与实验相符。

26个电子的Fe原子，运算要涉及10^{76}个数，对称简化10^{53}个

→整个太阳系没有足够物质打印这个数据表！

2. 凝胶模型(jellium model)

为突出探讨相互作用电子系统的哪些特征是区别于不计其相互作用者，可人为地简化假定电子是沉浸在空间密度持恒的正电荷背景之中(不考虑离子的周期性)。

正电荷的作用体现于在相互作用电子体系的**Hamiltonian**中出现一个维持系统聚集的附加项 $V_{\oplus}$

金属体系，设电子波函数：　$\phi_j(\vec{r})=\frac{1}{\sqrt{\Omega}}\exp(i\vec{k}_j\cdot\vec{r})$

Ω为体系总体积

Hartree方程中的势：

$$V + \sum_{j'\neq j}\frac{1}{4\pi\varepsilon_0}\int\frac{e}{\left|\vec{r}-\vec{r}_j{}'\right|}\left|\frac{1}{\sqrt{\Omega}}\exp\left(i\vec{k}_{j'}\cdot\vec{r}_{j'}\right)\right|^2 d\vec{r}_j{}'$$

$$= V_\oplus + \frac{1}{4\pi\varepsilon_0}\frac{e}{\Omega}\sum_{j'}\int\frac{d\vec{r}_{j'}}{\left|\vec{r}-\vec{r}_j{}'\right|} - \frac{1}{4\pi\varepsilon_0}\frac{e}{\Omega}\int\frac{d\vec{r}_j}{\left|\vec{r}-\vec{r}_j\right|}$$

第二项是全部电子在r处形成的势，与 $V_\oplus$相抵消

第三项是须扣除的自作用，与j有关，但如取r为计算原点：

$$\frac{1}{4\pi\varepsilon_0}\frac{e}{\Omega}\int\frac{d\vec{r}_j}{\left|\vec{r}_j\right|} = \frac{1}{\varepsilon_0\Omega}\int r_j dr_j \xrightarrow{\Omega\to\infty} 0$$

所以对凝胶模型，Hartree方程： $\left[-\frac{\hbar^2}{2m}\nabla^2 + E\left(\vec{K}\right)\right]\phi_K\left(\vec{r}\right) = 0$

相互作用→没有相互作用　　　　电子＋正电荷背景→自由电子气

3. Hartree-Fock方程(1930)

Hartree方程不满足Pauli不相容原理

电子：费米子　　单电子波函数f：→N电子

体系的总波函数：

$$\Phi=(N!)^{-\frac{1}{2}}\begin{vmatrix} f_1(r_1s_1) & \cdots & f_1(r_Ns_N) \\ \vdots & \ddots & \vdots \\ f_N(r_1s_1) & \cdots & f_N(r_Ns_N) \end{vmatrix}$$

不涉及自旋—轨道耦合时：　$f_j=\psi_j(\vec{r}_j)\chi_j(s_j)$

N电子体系能量期待值：

$$E=\langle H\rangle=\sum_j\int\Psi_j^*(\vec{r})\left(-\frac{\hbar^2}{2m}\nabla^2+U^{ion}(\vec{r})\right)\Psi_j(\vec{r})d\vec{r}$$

$$+\frac{e^2}{8\pi\varepsilon_0}\sum_{jj'}\iint\left|\Psi_j(\vec{r})\right|^2\frac{1}{\left|\vec{r}-\vec{r}'\right|}\left|\Psi_{j'}(\vec{r}')\right|^2d\vec{r}d\vec{r}'$$

$$-\frac{e^2}{8\pi\varepsilon_0}\sum_{j'j}\iint d\vec{r}d\vec{r}'\frac{1}{\left|\vec{r}-\vec{r}'\right|}\Psi_j^*(\vec{r})\Psi_j(\vec{r}')\Psi_{j'}^*(\vec{r}')\Psi_{j'}(\vec{r})\delta_{sjsj'}$$

1. 第二项j, j’可以相等，自相互作用
2. 自相互作用严格相消（通过第二，三项）
3. 第三项为交换项，同自旋电子

通过变分：

$$\delta\left[\langle H\rangle-\sum_{jj'}\lambda_{jj'}\left(\int\Psi_j^*\Psi_{j'}d\vec r-\delta_{jj'}\right)\right]=0$$

么正变换：

$$\phi_j=\sum_{j'}u_{jj'}\Psi_{j'}\rightarrow\lambda\rightarrow\varepsilon$$

单电子方程：

$$\left[-\frac{\hbar^2}{2m}\nabla^2+U^{ion}(\vec r)+\frac{e^2}{4\pi\varepsilon_0}\sum_{j'}\int\frac{\left|\phi_j(\vec r\,')\right|^2}{\left|\vec r-\vec r'\right|}d\vec r'-\frac{e^2}{4\pi\varepsilon_0}\sum_{j'}\int d\vec r d\vec r'\frac{\phi_j^*(\vec r\,')\phi_j(\vec r\,')}{\left|\vec r-\vec r'\right|}\delta s_{sj,sj'}\right]\phi_j(\vec r)=\varepsilon_j\phi_j(\vec r)$$

与Hartree方程的差别：第三项对全体电子，第四项新增，交换作用项。求和只涉及与j态自旋平行的j’态，是电子服从Fermi统计的反映。

4. Koopmann定理（1934)

$$\varepsilon_j=\int\phi_j^*(\vec r)\varepsilon_j\phi_j(\vec r)d\vec r=\langle\Phi_N|H_N|\Phi_N\rangle-\langle\Phi_{N-1}|H_{N-1}|\Phi_{N-1}\rangle$$

单电子轨道能量等于N电子体系从第j个轨道上取走一个电子并保持N－1个电子状态不不变的总能变化值。

推广：系统中一个电子由状态j转移到态i而引起系统能量的变化

$\varepsilon_i - \varepsilon_j$　　　　$E \neq \sum \varepsilon_j$

5. 交换空穴(Fermi hole)

将H-F方程改写为：

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + U^{ion}(\vec{r}) + \frac{e^2}{4\pi\varepsilon_0}\int d\vec{r}\,'\frac{\rho(\vec{r}\,') - \rho_j^{HF}(\vec{r},\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\right]\phi_j(\vec{r}) = \varepsilon_j\phi_j(\vec{r})$$

其中： $\rho(\vec{r}\,') \equiv \sum_j^N |\phi_j(\vec{r}\,')|^2$　全体电子在$\vec{r}\,'$位的密度

$$\rho_j^{HF}(\vec{r},\vec{r}\,') \equiv \sum_{\substack{j' \\ spin\,//}} \frac{\phi_{j'}^*(\vec{r}\,')\phi_j(\vec{r}\,')\phi_{j'}(\vec{r})\phi_j^*(\vec{r})}{\phi_j^*(\vec{r})\phi_j(\vec{r})}$$　交换电荷密度

$\vec{r} = \vec{r}\,'$　时，$\rho_j^{HF}(\vec{r},\vec{r}\,') = \rho(\vec{r})$

$\rho_j^{HF}(\vec{r},\vec{r}\,')$对全空间的积分恰好等于一个电子电量：

$$\int \rho_j^{HF}(\vec{r},\vec{r}\,')d\vec{r}\,' = \sum_{\substack{j'\\ spin\,//}} \frac{\phi_j^*(\vec{r})\phi_{j'}(\vec{r})}{\phi_j^*(\vec{r})\phi_j(\vec{r})}\int \phi_j^*(\vec{r}\,')\phi_{j'}(\vec{r}\,')d\vec{r}\,'$$

$$= \sum_{\substack{j'\\ spin\,//}} \frac{\phi_j^*(\vec{r})\phi_{j'}(\vec{r})}{\phi_j^*(\vec{r})\phi_j(\vec{r})}\delta_{jj'} = 1$$

在*HF*方程中合理地扣除被研究电子与全体电子互作用中的自身作用。ρ_j^{HF}依赖于j，难直接用于求解固体多电子问题。

引入平均交换电荷密度： $\bar{\rho}^{HF}(\vec{r},\vec{r}\,') = \dfrac{1}{N}\sum_j \rho_j^{HF}(\vec{r},\vec{r}\,')$

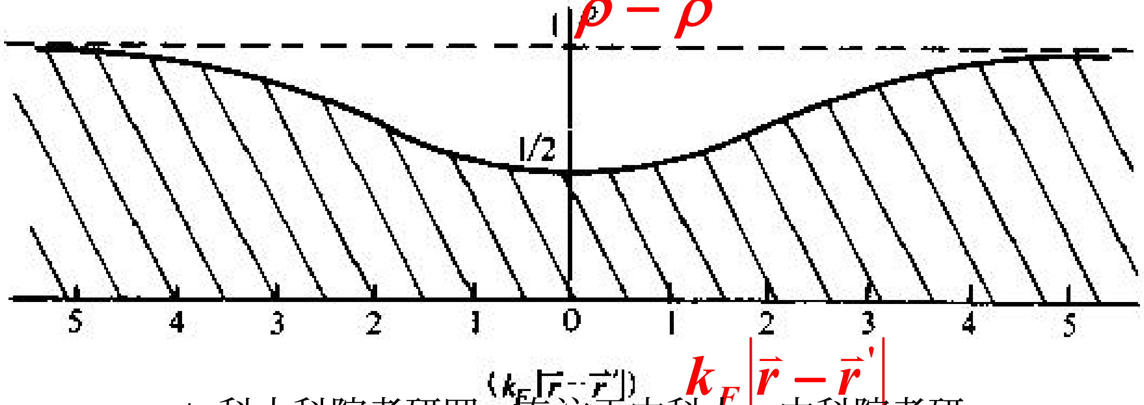
定性讨论：假设

$$\phi_j = \frac{1}{\sqrt{\Omega}}\exp(i\vec{k}_j\cdot\vec{r})$$

$$\bar{\rho}^{HF}(\vec{r},\vec{r}\,') = \frac{N}{\Omega}\frac{9}{2}\frac{\left[k_F|\vec{r}-\vec{r}\,'|\cos k_F|\vec{r}-\vec{r}\,'| - \sin k_F|\vec{r}-\vec{r}\,'|\right]^2}{\left[k_F|\vec{r}-\vec{r}\,'|\right]^6}$$

$$k_F^6 = (3\pi^2\rho)^2,\ \rho = \frac{N}{\Omega}$$

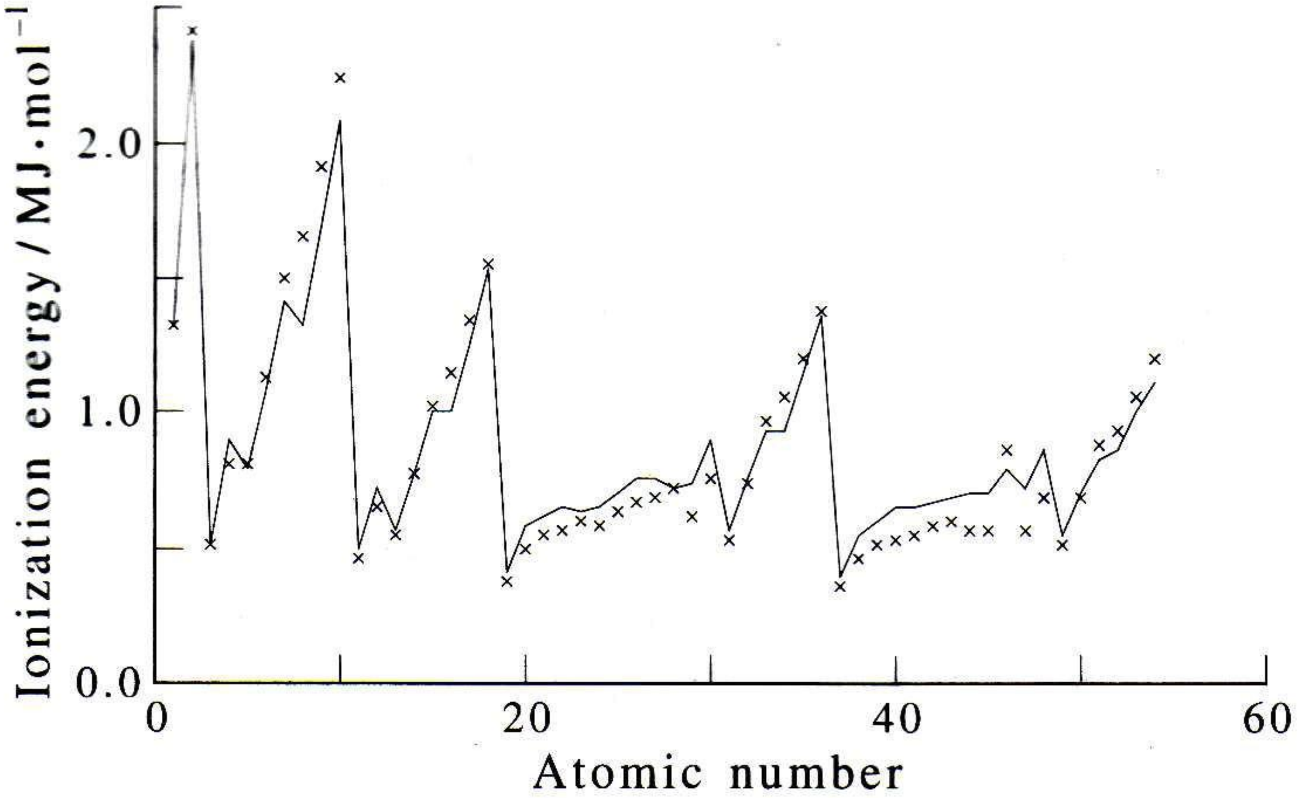
Fermi hole:与某电子自旋相同的其余邻近电子在围绕该电子形成总量为1的密度亏欠域



$\rho - \bar{\rho}^{HF}$

$k_F|\vec{r}-\vec{r}\,'|$

举例：利用HF方程和Koopmann定理研究原子的电离能



6. Slater's X*a* 方法

HF方法的缺点：

- HF方程仅考虑了交换作用，没有考虑关联，许多体系不能正确描述（金属）
- 对原子/分子体系计算量不算大，但对固体计算量就很大：

$$[-\frac{1}{2}\nabla^2 + V^{ext}(\vec{r}) + \int \frac{\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} d^3r']\varphi_i(\vec{r}) - \boxed{[\sum_j \delta(s_i,s_j)\int \frac{\varphi_j^*(\vec{r}\,')\varphi_i(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} d^3r']}\varphi_j(\vec{r}) = \varepsilon_i\varphi_i(\vec{r})$$

Nonlocal exchange term

用平均的局域（交换）势替代HF方程中的非局域交换势：

$$V^{ex}(r) = -\alpha \frac{3}{2\pi}[3\pi^2\rho(r)]^{1/3}, \quad \alpha = 0.66 \sim 1 \text{ for most systems}$$

$X\alpha$

7. 密度泛函理论(Density functional theory)

(1) Thomas-Fermi-Dirac Model

- energy as a function of the one electron density, ρ
- nuclear-electron attraction, electron-electron repulsion

$$V_{NE}[\rho] = \sum_A Z_A \int \frac{\rho}{r_A} d\tau \quad J[\rho] = \int \frac{\rho(1)\rho(2)}{r_{12}} d\tau_1 d\tau_2$$

- Thomas-Fermi approximation for the kinetic energy

$$T[\rho] = c\int \rho^{5/3} d\tau \quad c = \frac{3}{10}(3\pi^2)^{2/3}$$

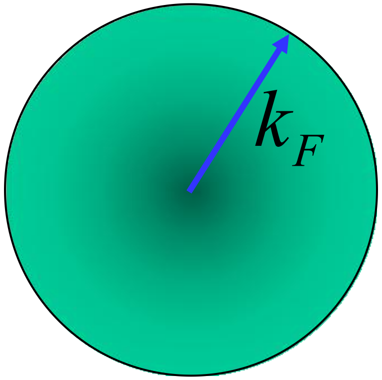
- Slater approximation for the exchange energy

$$K[\rho] = c\int \rho^{4/3} d\tau \quad c = -\frac{9\alpha}{8}\left(\frac{3}{\pi}\right)^{1/3} \quad \alpha = 0.66 \sim 1$$

Thomas-Fermi Model

- **Thomas-Fermi model (semiclassical): 1927**

- **Electron density of a uniform electron gas:**



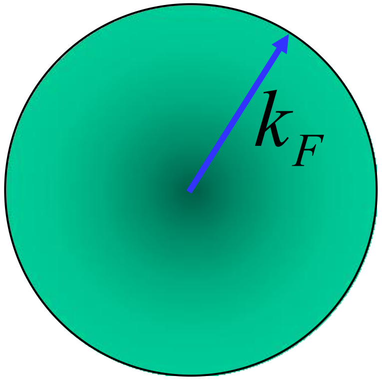
$$n = \frac{2}{(2\pi)^3}(\text{volume of Fermi sphere}) = \frac{2}{(2\pi)^3}\frac{4}{3}\pi k_F^3$$

- **Fermi wavevector and electron kinetic energy of a uniform electron gas**

$$k_F = (3\pi^2 n)^{1/3}$$

$$T = \frac{(\hbar k)^2}{2m} = \frac{\hbar^2[3\pi^2 n]^{2/3}}{2m}$$

Thomas-Fermi Model



$$T = \frac{(\hbar k)^2}{2m} = \frac{\hbar^2 [3\pi^2 n]^{2/3}}{2m}$$

- **We may assume that the kinetic energy of the electron gas depends on the local electron density:**

$$T(\vec{r}) = \frac{(\hbar k)^2}{2m} = \frac{\hbar^2 [3\pi n^2(\vec{r})]^{2/3}}{2m}$$

- **The total kinetic energy of electrons in the system is therefore a functional of electron density:**

$$T = \int T(\vec{r}) n(\vec{r}) d^3 r = C \int [n(\vec{r})]^{5/3} d^3 r$$

(2) The Hohenberg-Kohn Theorem

In 1964, Hohenberg and Kohn proved that

> "For molecules with a nondegenerate ground state, the ground-state molecular energy, wave function and all other molecular electronic properties are uniquely determined by the ground-state electron probability density $\rho_0(x, y, z)$, namely, $E_0 = E_0[\rho_0]$."
>
> *Phys. Rev. 136, 13864 (1964)*

Density functional theory (DFT) attempts to calculate E_0 and other ground-state molecular properties from the ground-state electron density ρ_0.

Proof:

The electronic Hamiltonian is

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{n}\nabla_i^2 + \sum_{i=1}^{n}\upsilon(\vec{r}_i) + \sum_{j}\sum_{i>j}\frac{1}{r_{ij}}$$

$$\upsilon(\vec{r}_i) = -\sum_{\alpha}\frac{Z_\alpha}{r_{i\alpha}}$$

$$\hat{H}\psi_0 = E_0\psi_0$$

In DFT, $\upsilon(\vec{r}_i)$ is called the external potential acting on electron i, since it is produced by charges external to the system of electrons.

Once the external potential $\upsilon(\vec{r}_i)$ and the number of electrons n are specified, the electronic wave functions and allowed energies of the molecule are determined as the solutions of the electronic Schrödinger equation.

Now we need to prove that the ground-state electron probability density $\rho_0(\vec{r})$

determines $\left\{\begin{array}{l}\text{the external potential (except for an arbitrary additive constant)}\\ \text{the number of electrons.}\end{array}\right.$

a) Since $\boxed{\int \rho_0(\vec{r})d\vec{r} = n, \;\; \rho_0(\vec{r})}$ determines the number of electrons.

b) To see that $\rho_0(\vec{r})$ determines the external potential $\upsilon(\vec{r}_i)$, we suppose that this is false and that there are two external potentials υ_a and υ_b (differing by more than a constant) that each give rise to the same ground-state electron density ρ_0.

Let

$$\hat{H}_a = -\frac{1}{2}\sum_{i=1}^{n}\nabla_i^2 + \sum_{i=1}^{n}\upsilon_a(\vec{r}_i) + \sum_j\sum_{i>j}\frac{1}{r_{ij}}$$

$$\hat{H}_b = -\frac{1}{2}\sum_{i=1}^{n}\nabla_i^2 + \sum_{i=1}^{n}\upsilon_b(\vec{r}_i) + \sum_j\sum_{i>j}\frac{1}{r_{ij}}$$

$$\hat{H}_a\psi_{0,a} = E_{0,a}\psi_{0,a}$$

$$\hat{H}_b\psi_{0,b} = E_{0,b}\psi_{0,b}$$

$\psi_{0,a}, E_{0,a}$: the exact ground-state wave function and energy of $\hat{H}_a$

$\psi_{0,b}, E_{0,b}$: the exact ground-state wave function and energy of $\hat{H}_b$

Since $\hat{H}_a$ and $\hat{H}_b$ differ by more than a constant,

$\psi_{0,a}$ and $\psi_{0,b}$ must be different functions.

Proof:

Assume $\psi_{0,a} = \psi_{0,b}$, thus

$$\left.\begin{aligned}\hat{H}_a\psi_{0,a} &= E_{0,a}\psi_{0,a}\\ \hat{H}_b\psi_{0,a} &= E_{0,b}\psi_{0,a}\end{aligned}\right\} \Rightarrow \left(\hat{H}_a - \hat{H}_b\right)\psi_{0,a} = \left(E_{0,a} - E_{0,b}\right)\psi_{0,a}$$

$$\left(\sum_{i=1}^{n}\left[\upsilon_a(\vec{r}_i) - \upsilon_b(\vec{r}_i)\right]\right)\psi_{0,a} = \left(E_{0,a} - E_{0,b}\right)\psi_{0,a}$$

thus $\sum_{i=1}^{n}\left[\upsilon_a(\vec{r}_i) - \upsilon_b(\vec{r}_i)\right]$ = a constant, which contradicts the given information.

If the ground state is nondegenerate, then there is only one normalized function, the exact ground-state wave function ψ_0, that gives the exact ground state energy E_0 for a given Hamiltonian $\hat{H}$.

According to the variation theorem, suppose that ϕ is any normalized well-behaved trial variation function.

If $\phi \neq \psi_0$, then $\langle \phi | \hat{H} | \phi \rangle > E_0$

Now use $\psi_{0,b}$ as a trial function with the Hamiltonian $\hat{H}_a$, then

$$\begin{aligned} E_{0,a} &< \langle \psi_{0,b} | \hat{H}_a | \psi_{0,b} \rangle \\ &= \langle \psi_{0,b} | \hat{H}_a + \hat{H}_b - \hat{H}_b | \psi_{0,b} \rangle \\ &= \langle \psi_{0,b} | \hat{H}_a - \hat{H}_b | \psi_{0,b} \rangle + \langle \psi_{0,b} | \hat{H}_b | \psi_{0,b} \rangle \end{aligned}$$

Substituting $\hat{H}_a - \hat{H}_b = \sum_{i=1}^{n} \left[\upsilon_a(\vec{r}_i) - \upsilon_b(\vec{r}_i) \right]$ gives

$$E_{0,a} < \left\langle \psi_{0,b} \left| \sum_{i=1}^{n} \left[\upsilon_a(\vec{r}_i) - \upsilon_b(\vec{r}_i) \right] \right| \psi_{0,b} \right\rangle + E_{0,b}$$

Let $B(r_i)$ be a function of the spatial coordinates x_i, y_i, z_i of electron i, then

$$\left\langle \psi \left| \sum_{i=1}^{n} B(\vec{r}_i) \right| \psi \right\rangle = \int \psi^* \sum_{i=1}^{n} B(\vec{r}_i) \psi d\tau$$

$$= \sum_{i=1}^{n} \int |\psi|^2 B(\vec{r}_i) d\tau$$

$$= \int n|\psi|^2 B(\vec{r}_i) d\tau$$

$$= \int \rho(r) B(r) dr$$

Using the above result, we get

$$E_{0,a} < \int \rho_{0,b}(\vec{r})[\upsilon_a(\vec{r}) - \upsilon_b(\vec{r})] d\vec{r} + E_{0,b}$$

Similarly, if we go through the same reasoning with a and b interchanged, we get

$$E_{0,b} < \int \rho_{0,a}(\vec{r})[\upsilon_b(\vec{r}) - \upsilon_a(\vec{r})] d\vec{r} + E_{0,a}$$

By hypothesis, the two different wave functions give the same electron density: $\rho_{0,a} = \rho_{0,b}$. Putting $\rho_{0,a} = \rho_{0,b}$ and adding the above two inequalities yield

$$\boxed{E_{0,a} + E_{0,b} < E_{0,b} + E_{0,a}}$$

This result is false, so our initial assumption that two different external potentials could produce the same ground-state electron density must be false. Hence, the ground-state electron probability density ρ_0 determines the external potential (to within an additive constant that simply affects the zero level of energy) and also determines the number of electrons.

"For systems with a nondegenerate ground state, the ground-state electron probability density $\rho_0(\vec{r})$ determines the ground-state wave function and energy, and other properties"

$$E_0 = E_\upsilon[\rho_0]$$

v emphasizes the dependence of E_0 on the external potential $\upsilon(\vec{r})$, which differs for different molecules.

$$E_0 = \langle \psi_0 | \hat{H} | \psi_0 \rangle = \bar{T}[\rho_0] + \bar{V}_{Ne}[\rho_0] + \bar{V}_{ee}[\rho_0]$$

$$\bar{V}_{Ne}[\rho_0] = \left\langle \psi_0 \middle| \sum_{i=1}^{n} \upsilon(\vec{r}_i) \middle| \psi_0 \right\rangle = \int \rho_0(\vec{r})\upsilon(\vec{r})d\vec{r}$$

However, the functionals $\bar{T}[\rho_0]$ and $\bar{V}_{ee}[\rho_0]$ are unknown.

E_0 is also written as

$$E_0 = E_\upsilon[\rho_0] = \int \rho_0(\vec{r})\upsilon(\vec{r})d\vec{r} + F[\rho_0]$$

$$F[\rho_0] = \bar{T}[\rho_0] + \bar{V}_{ee}[\rho_0]$$

The functional $F[\rho_0]$ is independent of the external potential.

(3) The Hohenberg-kohn variational theorem

"For every trial density function $\rho_{tr}(\vec{r})$ that satisfies $\int \rho_{tr}(\vec{r})d\vec{r} = n$ and $\rho_{tr}(\vec{r}) \geq 0$ for all $\vec{r}$, the following inequality holds: $E_0 \leq E_{\upsilon}[\rho_{tr}]$, where E_0 is the true ground–state energy."

Proof:

Let $\rho_{tr}(\vec{r})$ satisfy that $\int \rho_{tr}(\vec{r})d\vec{r} = n$ and $\rho_{tr}(\vec{r}) \geq 0$. By the Hohenberg-Kohn theorem, $\rho_{tr}(\vec{r})$ determines the external potential υ_{tr}, and this in turn determines the wave function ψ_{tr} that corresponds to the density $\rho_{tr}(\vec{r})$.

Let us use the wave function ψ_{tr} as a trial variation function for the molecule with Hamiltonian $\hat{H}$. According to the variation theorem

$$\left\langle \psi_{tr} \middle| \hat{H} \middle| \psi_{tr} \right\rangle = \left\langle \psi_{tr} \middle| \hat{T} + \hat{V}_{ee} + \sum_{i=1}^{n} \upsilon(\vec{r}_i) \middle| \psi_{tr} \right\rangle$$

$$\geq E_0 = E_\upsilon[\rho_0]$$

Since the left hand side of this inequality can be rewritten as

$$\overline{T}[\rho_{tr}] + \overline{V}_{ee}[\rho_{tr}] + \int \rho_{tr} \upsilon(\vec{r}) d\vec{r} = E_\upsilon[\rho_{tr}]$$

One gets $E_\upsilon[\rho_{tr}] \geq E_\upsilon[\rho_0]$

Hohenberg and Kohn proved their theorems only for nondegenerate ground states. Subsequently, Levy proved the theorems for degenerate ground states.

(4) The Kohn-Sham method

沈吕九

If we know the ground-state electron density $\rho_0(\vec{r})$, the Hohenberg-Kohn theorem tells us that it is possible in principle to calculate all the ground-state molecular properties from ρ_0 , without having to find the molecular wave function.

1965, Kohn and Sham devised a practical method for finding $\rho_0(\vec{r})$ and for finding E_0 from $\rho_0(\vec{r})$. [*Phys. Rev., 140, A 1133 (1965)*]. Their method is capable, in principle, of yielding exact results, but because the equations of the Kohn-Sham (KS) method contain an unknown functional that must be approximated, the KS formation of DFT yield approximate results.

Kohn and Sham considered a fictitious reference system s of n noninteracting electrons that each experience the same external potential $\upsilon_s(\vec{r}_i)$ that makes the ground-state electron probability density $\rho_s(\vec{r})$ of the reference system equal to the exact $\rho_0(\vec{r})$ of the molecule we are interested in: $\rho_s(\vec{r}) = \rho_0(\vec{r})$.

Since the electrons do not interact with one another in the reference system, the Hamiltonian of the reference system is

$$\hat{H}_s = \sum_{i=1}^{n}\left[-\frac{1}{2}\nabla_i^2 + \upsilon_s(\vec{r}_i)\right] = \sum_{i=1}^{n}\hat{h}_i^{KS}$$

where $\hat{h}_i^{KS}$ is the one-electron Kohn-Sham Hamiltonian.

Thus, the ground-state wave function $\psi_{s,0}$ of the reference system is:

$$\psi_{s,0} = \left| u_1 u_2 \cdots u_n \right|, \quad u_i = \theta_i^{KS}(\vec{r}_i)\sigma_i$$

$$\hat{h}_i^{KS}\theta_i^{KS} = \varepsilon_i^{KS}\theta_i^{KS}$$

σ_i is a spin function (either α or β)

ε_i^{KS} 's are Kohn-Sham orbital energies.

For convenience, the zero subscript on ρ is omitted hereafter.

Define $\Delta\overline{T}[\rho]$ and $\Delta\overline{V}_{ee}[\rho]$ as follows:

$$\Delta\overline{T}[\rho] = \overline{T}[\rho] - \overline{T}_s[\rho]$$

$$\Delta\overline{V}_{ee}[\rho] = \overline{V}_{ee}[\rho] - \frac{1}{2}\iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2$$

$\Delta\overline{T}$ is the difference in the average ground-state electronic kinetic energy between the molecule and the reference system of noninteracting electrons.

The quantity $\frac{1}{2}\iint \rho(\vec{r}_1)\rho(\vec{r}_2) r_{12}^{-1} d\vec{r}_1 d\vec{r}_2$ is the classical expression (in atomic units) for the electrostatic interelectronic repulsion energy.

Remember that $E_\upsilon[\rho] = \int \rho(\vec{r})\upsilon(\vec{r})d\vec{r} + \overline{T}[\rho] + \overline{V}_{ee}[\rho]$

With the above definitions, $E_\upsilon[\rho]$ can be written as

$$E_\upsilon[\rho] = \int \rho(\vec{r})\upsilon(\vec{r})d\vec{r} + \overline{T}_s[\rho] + \frac{1}{2}\iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 + \Delta\overline{T}[\rho] + \Delta\overline{V}_{ee}[\rho]$$

Define the exchange-correlation energy functional $E_{XC}[\rho]$ by

$$E_{XC}[\rho] = \Delta\overline{T}[\rho] + \Delta\overline{V}_{ee}[\rho]$$

Now we have

$$E_0 = E_\upsilon[\rho] = \underbrace{\int \rho(\vec{r})\upsilon(\vec{r})d\vec{r} + \overline{T}_s[\rho] + \frac{1}{2}\iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2}_{} + \underbrace{E_{XC}[\rho]}_{}$$

The first three terms on the right side are easy to evaluate from ρ and they make the main contributions to the ground-state energy.

The fourth quantity E_{XC} is a relatively small term, but is not easy to evaluate accurately. The key to accurate KS DFT calculation of molecular properties is to get a good approximation to E_{XC}

Now we need explicit equations to find the ground-state electron density ρ.

Since the fictitious system of noninteracting electrons is defined to have the same electron density as that in the ground state of the molecule: $\rho_s = \rho_0$, it is readily proved that

$$\rho = \rho_s = \sum_{i=1}^{n} \left|\theta_i^{KS}\right|^2$$

$$\left(\text{Using } \rho_s = \left\langle \psi_s \middle| \sum_{i=1}^{n} \delta\left(\vec{r} - \vec{r}_i\right) \middle| \psi_s \right\rangle \text{ and } \psi_s = \left|u_1 u_2 \cdots u_n\right| \right)$$

$$\overline{T}_s = -\frac{1}{2}\left\langle \psi_s \middle| \sum_{i=1}^{n} \nabla_i^2 \middle| \psi_s \right\rangle = -\frac{1}{2}\sum_{i=1}^{n}\left\langle \theta_i^{KS}(1) \middle| \nabla_1^2 \middle| \theta_i^{KS}(1) \right\rangle$$

Thus E_0 becomes

$$E_0 = -\sum_{\alpha} Z_\alpha \int \frac{\rho(\vec{r}_1)}{r_{1\alpha}} d\vec{r}_1 - \frac{1}{2}\sum_{i=1}^{n}\left\langle \theta_i^{KS}(1) \middle| \nabla_1^2 \middle| \theta_i^{KS}(1) \right\rangle$$

$$+\frac{1}{2}\iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 + E_{XC}[\rho]$$

The Hohenberg-Kohn variational theorem tell us that we can find the ground-state energy by varying ρ (subject to the constraint $\int \rho \mathrm{dr} = n$) so as to minimize the functional $E_\upsilon[\rho]$. Equivalently, instead of varying ρ, we can vary the KS orbitals θ_i^{KS}. Thus, the Kohn-Sham orbitals are those that minimize the above energy expression subject to the orthonormality constraint:

$$\hat{h}^{KS}(1)\theta_i^{KS}(1) = \varepsilon_i^{KS}\theta_i^{KS}(1)$$

$$\hat{h}^{KS}(1) = -\frac{1}{2}\nabla_1^2 - \sum_\alpha \frac{Z_\alpha}{r_{1\alpha}} + \int \frac{\rho(\vec{r}_2)}{r_{12}} d\vec{r}_2 + \upsilon_{XC}(1)$$

with the exchange-correlation potential υ_{XC} defined by

$$\upsilon_{XC}(\vec{r}) = \frac{\delta E_{XC}[\rho(\vec{r})]}{\delta\rho(\vec{r})}$$

(If $E_{XC}[\rho(\vec{r})]$ is known, its functional derivative υ_{XC} is also known.)

The KS operator $\hat{h}^{KS}(1)$ is the same as the HF operator except that the exchange operators in the HF operator are replaced by $\upsilon_{XC}(\vec{r})$, which handles the effects of both exchange and electron correlation.

(5) Local density approximation

$$\text{LDA:} \qquad E^{xc}[\rho] = \int \rho(\vec{r})\varepsilon^{xc}(\rho)d\vec{r}$$

Compare to uniform electron gas result:

$$\text{Jellium model:} \; E^{xc} = \int \rho\varepsilon^{xc}(\rho)d\vec{r}$$

(High density limit)

$$\varepsilon^{xc} = \frac{E^{xc}}{N} = -\frac{0.916}{r_s} + 0.0622\ln(r_s) - 0.096 + o(r_s)$$

$$\frac{1}{\rho} = \frac{4}{3}\pi r_s^3$$

The Perdew-Zunger Parameterization And the Uniform Electron Gas Result

- **Let's compare the PZ parameterization with the uniform electron gas result for r_s <<1**

Uniform Electron gas result :

$$\frac{E^{xc}}{N} = -\frac{0.916}{r_s} + 0.0622\ln(r_s) - 0.096 + o(r_s)\ (\mathrm{Ry})$$

$$\boxed{\frac{1}{\rho} = \frac{4}{3}\pi r_s^3}$$

PZ parameterization :

$$\varepsilon^{ex}(r_s) = -\frac{0.916}{r_s}: \quad \text{The uniform electron gas result}$$

$$\varepsilon^{corr}(r_s) = 0.0622\ln(r_s) - 0.096 + \boxed{[0.004\ln(r_s) - 0.0232]r_s}; \qquad r_s < 1$$

Quantum Monte Carlo result of Ceperley and Alder

The Perdew-Zunger Parameterization of The Exchange-Correlation Energy (LDA)

$$E^{xc}[\rho] = \int \rho(\vec{r})\varepsilon^{xc}(\rho)d\vec{r}$$

- **Perdew and Zunger's parameterization of Ceperley and Alder result:**

$$\varepsilon^{xc}(r_s) = \varepsilon^{ex}(r_s) + \varepsilon^{corr}(r_s)$$

$$\boxed{\frac{1}{\rho} = \frac{4}{3}\pi r_s^3}$$

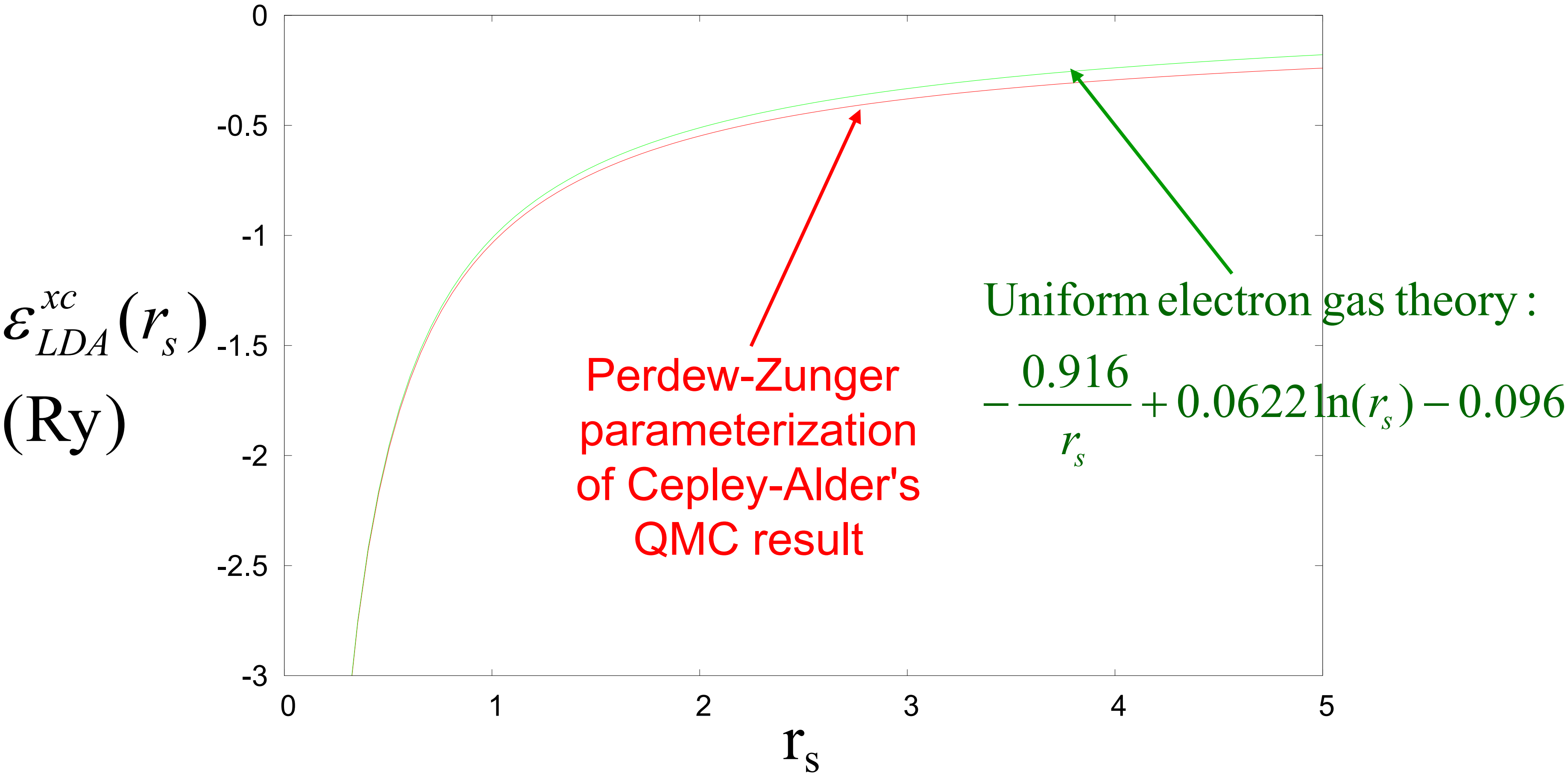
$$\varepsilon^{ex}(r_s) = -\frac{0.916}{r_s}:\quad \text{The uniform electron gas result}$$

$$\varepsilon^{corr}(r_s) = -\frac{0.2846}{(1+1.0529r_s^{1/2}+0.3334r_s)};\qquad r_s > 1$$

$$\varepsilon^{corr}(r_s) = 0.0622\ln(r_s) - 0.096 + [0.004\ln(r_s) - 0.0232]r_s;\qquad r_s < 1$$

P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

Exchange And Correlation Energies: LDA vs. Uniform Electron Gas



Perdew-Zunger parameterization of Cepley-Alder's QMC result

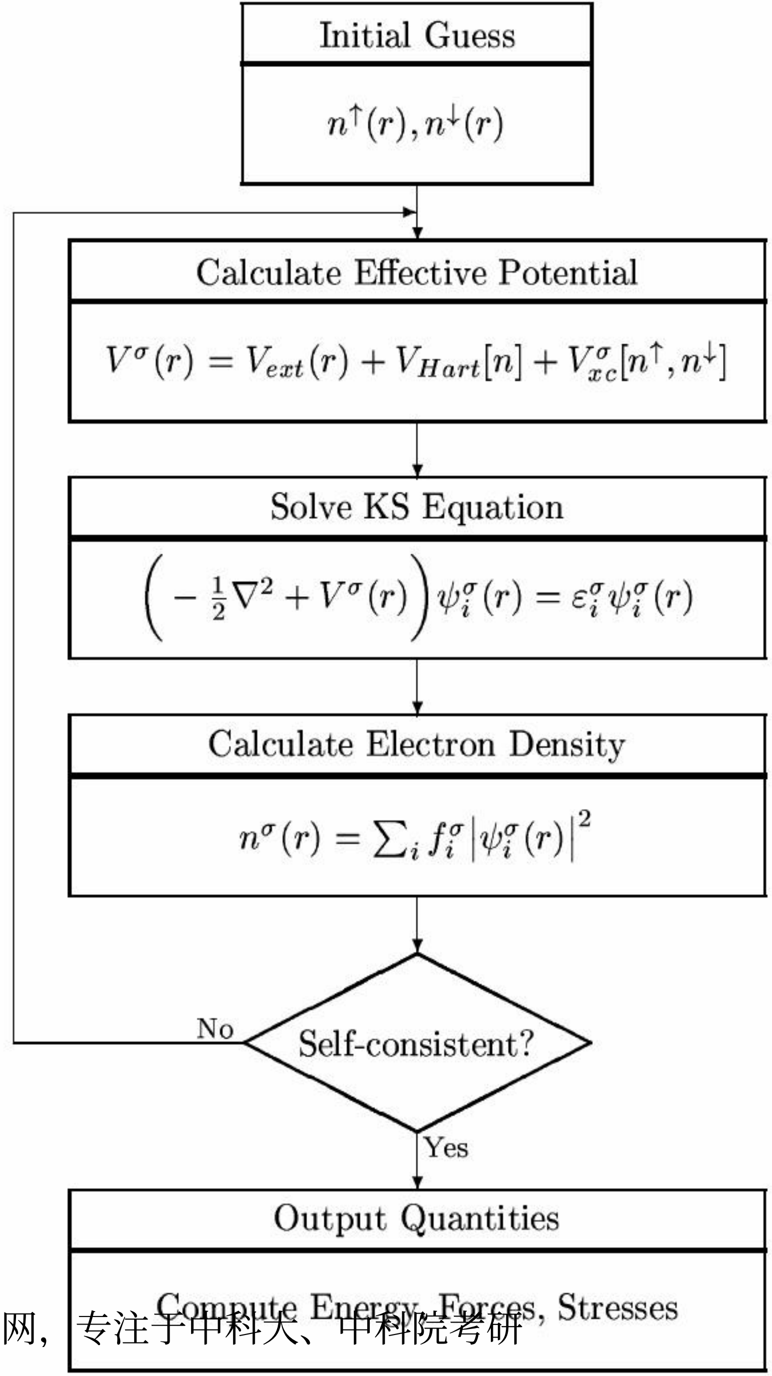
Uniform electron gas theory :

$$-\frac{0.916}{r_s}+0.0622\ln(r_s)-0.096$$

But electrons in real solids is not a uniform electron gas!

Flow Chat

$$(-\frac{1}{2}\nabla^2 + V^H + V^{xc} + V^{ext})\varphi_i(r) = \varepsilon_i\varphi_i(r)$$



Initial Guess

$n^{\uparrow}(r), n^{\downarrow}(r)$

Calculate Effective Potential

$V^{\sigma}(r) = V_{ext}(r) + V_{Hart}[n] + V^{\sigma}_{xc}[n^{\uparrow}, n^{\downarrow}]$

Solve KS Equation

$\left(-\frac{1}{2}\nabla^2 + V^{\sigma}(r)\right)\psi^{\sigma}_i(r) = \varepsilon^{\sigma}_i\psi^{\sigma}_i(r)$

Calculate Electron Density

$n^{\sigma}(r) = \sum_i f^{\sigma}_i \left|\psi^{\sigma}_i(r)\right|^2$

Self-consistent?

Output Quantities

Compute Energy, Forces, Stresses

Local Density Approximation: A unexpected success

- **Local density approximation is exact for a uniform electron gas**

- **But for any realistic material system, the charge density is far from uniform**

- **Kohn and Sham were careful enough to point this out**

Kohn and Sham did not expect that LDA would be useful for calculating the properties of real materials: "***we do not expect an accurate description of the chemical bonding***" *(by LDA)*.

- **It is still not well understood why LDA works extremely well for a wide variety of material systems**

- **The success of LDA is UNEXPECTED**

Comments on the DFT methods:

(1) The KS equations are solved in a self-consistent fashion, like the HF equations.

(2) The computation time required for a DFT calculation formally scales the third power of the number of basis functions.

(3) There is no DF molecular wave function.

(4) The KS orbitals can be used in qualitative MO discussions, like the HF orbitals.

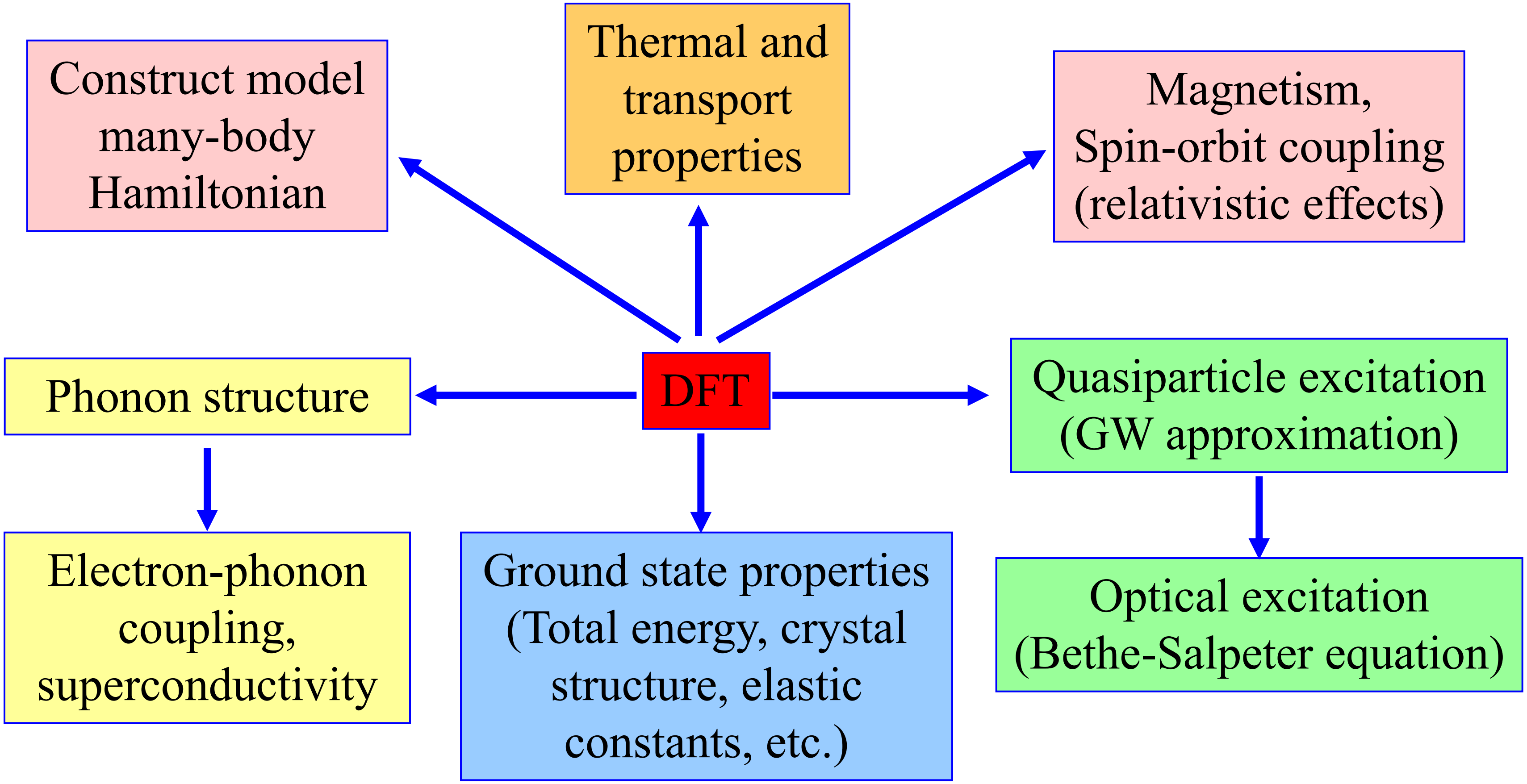
(5) Koopmans' theorem doesn't hold here, except ε_i^{KS} (HOMO) $= -IP$ (HOMO)

(6) Various approximate functionals $E_{XC}\left[\rho(\vec{r})\right]$ are used in molecular DF calculations. The functional E_{XC} is written as the sum of an exchange-energy functional E_X and a correlation-energy functional E_C :

$$E_{XC} = E_X + E_C$$

(7) Nowadays KS DFT methods are generally believed to be better than the HF method, and in most cases they are even better than MP2.

Material Properties Studied



Construct model many-body Hamiltonian

Thermal and transport properties

Magnetism, Spin-orbit coupling (relativistic effects)

Phonon structure

DFT

Quasiparticle excitation (GW approximation)

Electron-phonon coupling, superconductivity

Ground state properties (Total energy, crystal structure, elastic constants, etc.)

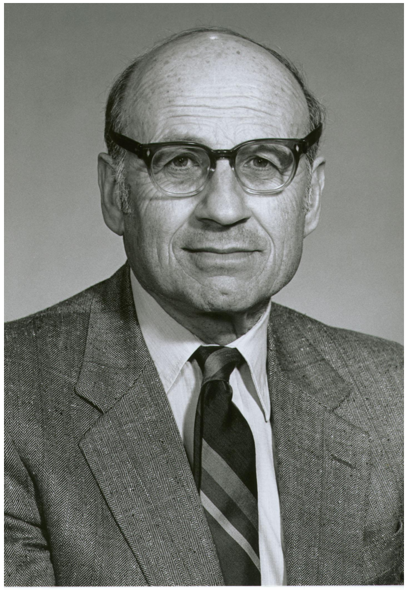
Optical excitation (Bethe-Salpeter equation)

The Nobel Prize in Chemistry 1998

Kungliga
Svenska Vetenskapsakademien
har den 13 oktober 1998 beslutat
att med det
NOBELPRIS
som detta år tillerkännes den
som gjort den viktigaste kemiska
upptäckten eller förbättringen
med ena hälften belöna
Walter Kohn
för hans utveckling av täthets-
funktionalteorin

STOCKHOLM DEN 10 DECEMBER 1998

Jan S. Nilsson Erling Norrby



Walter Kohn (1923-)

"for his development of the density-functional theory "

密度泛函理论新进展

理论、方法与应用

- 理论体系

  交换相关泛函、含时密度泛函、动力学平均场、密度泛函微扰理论

- 数值方法

  基组、格点、线性标度

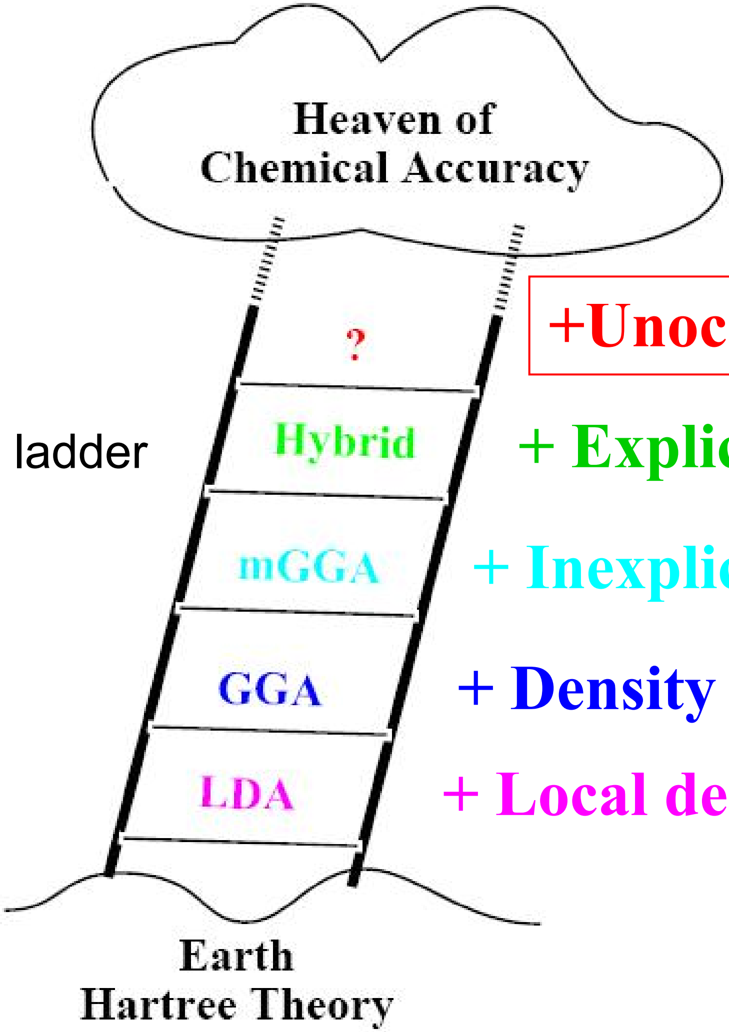
- 应用

  物理、化学、生物、材料、纳米科学、光谱学

Part I: 理论体系

交换相关泛函

jacob's ladder



+Unoccupied orbital information

+ Explicit occupied orbital information

+ Inexplicit occupied orbital information

+ Density gradient

+ Local density

Perdew PRL2003

局域密度近似(LDA)

$$E_{xc}^{LSDA}[\rho^{\alpha},\rho^{\beta}] = \int dr\rho(r)\epsilon_{xc}(\rho^{\alpha}(r),\rho^{\beta}(r))$$

- LDA *underestimates* Ec but *overestimates* Ex, resulting in unexpectedly good values of Exc.

- The LDA has been applied in, calculations of band structures and total energies in solid-state physics.

- In quantum chemistry,it is much less popular, because *it fails to provide results that are accurate enough* to permit a quantitative discussion of the chemical bond in molecules.

广义梯度近似(GGA)

- Any real system is spatially inhomogeneous, it has a spatially *varying density n(r),* it would clearly be useful to also include information on the rate of this variation in the functional.
- In this approximation ,one tries to systematically calculate gradient-corrections of general functions of n(r) and ∇n(r)

$$E_{xc}^{GGA}[n]=\int d^3r f\left(n(r),\nabla n(r)\right)$$

- *Different* GGAs differ in the choice of the function f(n,∇n).

Alex D. Becke
“一切都是合法的”　　剑宗
John P. Perdew
一定的物理规律（如标度关系和渐进行为）为基础，PBE　　气宗

- GGAs used in quantum chemistry typically proceed by fitting parameters to test sets of selected molecules.

- Nowadays the most popular GGAs are PBE in physics, and BLYP in chemistry.

- *Current* GGAs seem to give *reliable* results for all main types of chemical bonds (covalent, ionic, metallic and hydrogen bridge).

Meta-GGA

- In addition to the density and its derivatives, Meta-GGAs depend also on the Kohn-Sham *kinetic-energy density*:

$$\tau(\vec{r}) = \frac{\hbar^2}{2m} \sum_i |\nabla \phi_i(\vec{r})|^2$$

- So that Exc can be written as Exc [n(r), ∇n(r), τ (r)]. The additional degree of freedom provided by τ is used to satisfy additional constraints on Exc.
- Meta-GGAs have given favorable results, even when compared to the best GGAs.
- The full potential of this type of approximation is only beginning to be explored systematically.

Hybrid Functionals

- Common hybrid functional mix a fraction of Hartree-Fock exchange into the DFT exchange functional.

$$E_{xc}^{B3} = E_{xc}^{LDA} + a(E_x^{exact} - E_x^{LDA}) + b\,\Delta E_x^{GGA} + c\,\Delta E_c^{GGA}$$

$a = 0.20, b = 0.72, c = 0.81$ (Becke, 1993)

B3PW91, B3LYP

B3LYP is the main working-horse in computational chemistry

$$E_{xc}^{0} = E_{xc}^{DFT} + a(E_x^{exact} - E_x^{DFT}) \quad \text{(Perdew,1998)}$$

$a = 0.25$ PBE0

LDA: Slater exchange
Vosko-Wilk-Nusair correlation, etc

GGA: Exchange: B88, PW91, PBE, OPTX, HCTH, etc
Correlations: LYP, P86, PW91, PBE, HCTH, etc

Hybrid GGA: B3LYP, B3PW91, B3P86, PBE0,
B97-1, B97-2, B98, O3LYP, etc

Meta-GGA: VSXC, PKZB, TPSS, etc

Hybrid meta-GGA: τHCTHh, TPSSh, BMK, etc

自相互作用修正(SIC)

- Describing the behavior of many electrons interacting via coulombs’law:

$$U[n]=\frac{1}{2}\int d^3r\int d^3r'\frac{n(\vec{\mathbf{r}})n(\vec{\mathbf{r}}')}{|\vec{\mathbf{r}}-\vec{\mathbf{r}}'|}$$

- It will vanish for one electron system because of the self-interaction in it.
- So we have:

$$\langle\hat{V}_{ee}\rangle=U[n]-NU\left[\frac{n}{N}\right],$$

Fermi and Amaldi 1934(the first version of SIC)

- Now it becomes:

$$E_{xc}^{approx,SIC}[n_{\uparrow},n_{\downarrow}]=E_{xc}^{approx}[n_{\uparrow},n_{\downarrow}]-\sum_{i,\sigma}(E_H[n_{i\sigma}]+E_{xc}^{approx}[n_{i\sigma},0])$$

- This correction can be applied on top of any approximate density functional, and ensures that the resulting corrected functional satisfies:

$$E_{xc}^{approx,SIC}[n^{(1)},0]=-E_H[n^{(1)}]$$

for a one-electron system.

Optimized Effective Potential (OEP)

- Since orbital functionals depend on the density only implicitly, we can not directly calculate the functional derivative via orbitals $\phi_i[n]$.

- In the case of kinetic-energy functional, we use the Kohn-Sham scheme to minimize E[n].

- In the case of orbital expressions for Exc, the corresponding indirect scheme is known as the *optimized effective potential.*

- The minimization of the orbital functional with respect to the density is achieved by repeated application of the chain rule for functional derivatives:

$$v[n](\vec{r}) = \frac{\delta E_{xc}^{orb}[\{\phi_i\}]}{\delta n(\vec{r})}$$

$$= \int d^3r' \int d^3r'' \sum_i [\frac{\delta E_{xc}^{orb}[\{\phi_i\}]}{\delta \phi_i(\vec{r'})} \frac{\delta \phi_i(\vec{r'})}{\delta v_s(\vec{r''})} \frac{\delta v_s(\vec{r''})}{\delta n(\vec{r})} + c.c]$$

- Further evaluation of Eq. above gives rise to an integral equation that determines the belonging to the chosen orbital functional $v_{xc}[n]$

$$E_{xc}[\{\phi_i[n]\}]$$

- *KLI*(Krieger, Li and Iafrate) approximation to solve the full OEP integral equation. The application of the OEP methodology to the Fock term is as known as the *EXX* (extra-exchange method).

GW近似

- 以自能代替密度泛函局域近似中的交换关联能
- 固体能隙问题

$$E_g = \epsilon_{N+1}(N+1) - \epsilon_N(N)$$

- 准粒子方程

$$H'\Psi_i(r) + \int \Sigma(r, r'; E_i)\Psi_i(r')d^3r' = E_i\Psi_i(r)$$

- 零级近似，plasmon-pole模型，自洽

含时密度泛函

- Runge-Gross定理
- 作用量泛函

$$A = \int_{t_0}^{t_1} dt < \Psi(t)|i\frac{\partial}{\partial t} - \hat{H}(t)|\Psi(t) >$$

- TDKS方程

$$i\frac{\partial \psi_j(x)}{\partial t} = (-\frac{\nabla^2}{2} + v_{ks}[n](x))\psi_j(x)$$

TDDFT中的线性响应

- 外场微扰

$$v_{ext}(x) = v_0(r) + v_1(r,t)\Theta(t-t_0)$$

- 一阶密度响应

$$n_1(x) = \int d^4x\chi(x,x')v_1(x')$$

- KS响应函数

$$\chi_{ks}(r,r';\omega) = \sum_{j,k}(f_k - f_j)\frac{\phi_j(r)\phi_k^*(r)\phi_j^*(r')\phi_k(r')}{\omega - (\epsilon_j - \epsilon_k) + i\eta}$$

TDDFT中的线性响应

- 线性响应方程

$$n_1(x) = \int d^4x' \chi_{ks}(x, x') v_{ks,1}(x')$$

$$v_{ks,1}(x) = v_1(x) + v_H(x) + \int d^4x' \frac{\delta v_{XC}(x)}{\delta n(x')}[n_0] n_1(x')$$

- 交换相关核，绝热局域密度近似

$$v_{XC}^{ALDA}[n](x) = v_{XC}^{unif}(n(x)) = \frac{d}{d\rho}(\rho \epsilon_{xc}^{hom}(\rho))|_{\rho=n(x)}$$

L(S)DA+U

- Mott绝缘体，Hubbard模型
- Anisimov et al.： Stoner I -->Hubbard U
- 轨道序：

$$E^{U}[\{n\}] = \frac{1}{2}\sum_{\{\gamma\}}(U_{\gamma_1\gamma_3\gamma_2\gamma_4} - U_{\gamma_1\gamma_3\gamma_4\gamma_2})n_{\gamma_1\gamma_2}n_{\gamma_3\gamma_4}$$

- Dudarev et al.：惩罚泛函

$$\frac{(U-J)}{2}\sum_{\sigma}(\sum_{m_1} n^{\sigma}_{m_1,m_1} - \sum_{m_1,m_2} n^{\sigma}_{m_1,m_2}n^{\sigma}_{m_2,m_1})$$

动力学平均场理论

- 量子多体问题局域动力学（把点阵模型映射到自洽的量子杂质模型）
- 冻结空间涨落，考虑局域量子涨落
- Hubbard模型哈密顿量

$$H=-\sum_{<ij>,\sigma} t_{ij}(c_{i\sigma}^{+}c_{j\sigma}^{+}+c_{j\sigma}^{+}c_{i\sigma}^{+})+U\sum_{i} n_{i\uparrow}n_{i\downarrow}$$

- 单格点动力学

$$S_{eff}=-\int_0^\beta\int_0^\beta d\tau'\sum_\sigma c_{0\sigma}^{+}(\tau)\mathcal{G}_0^{-1}(\tau-\tau')c_{0\sigma}(\tau')$$

$$+U\int_0^\beta d\tau n_{0\uparrow}(\tau)n_{0\downarrow}(\tau)$$

- 自洽方程

$$\mathcal{G}_0(i\omega_n)^{-1} = i\omega_n + \mu + G(i\omega_n)^{-1} - R[G(i\omega_n)]$$

- Anderson杂质模型
- DFT-DMFT

流密度泛函理论

- 处理任意强度磁场下相互作用电子体系（1987）
- 一套规范不变且满足连续性方程的自洽方程组
- 交换相关能量不仅依赖于电荷密度还依赖于顺磁流密度
- 原子分子对磁场的响应，自发磁化，磁场中的二维量子点，造新的交换相关近似

相对论性密度泛函理论

- 量子电动力学的单粒子方程：Dirac方程

$$h_D = c\boldsymbol{\alpha}\cdot\mathbf{p} + (\boldsymbol{\beta}-1)c^2 + V(r)$$

- Dirac-Coulomb（DC）哈密顿量

$$H = \sum_i h_D(r_i) + \sum_{i>j}\frac{1}{r_{ij}}$$

- Dirac-Coulomb-Breit（DCB）哈密顿量

$$g_{ij}^{CB} = \frac{1}{r_{ij}} - \frac{1}{2}\left(\frac{(\alpha_i\cdot\alpha_j)}{r_{ij}} + \frac{(\alpha_i\cdot r_{ij})(\alpha_j\cdot r_{ij})}{r_{ij}^3}\right)$$

相对论性密度泛函理论

- **相对论情形的HK定理，四分量Dirac-Kohn-Sham（DKS）方程，数值旋量基组，缩并Gaussian型旋量基组**
- 两分量准相对论方法
  - **Breit-Pauli**近似 $(p/mc)^2$
  - **ZORA**近似 $E/(2mc^2 - V)$
- 有效核势（**ECP**）方法

密度泛函微扰理论

- 晶格振动理论
- 线性响应-->Hessian矩阵，2n+1定理

$$\left\{\begin{array}{l} \triangle n(r) = 4\, Re \sum_{n=1}^{N/2} \Psi_n^*(r) \triangle \Psi_n(r) \\ (H_{SCF} - \epsilon_n)| \triangle \Psi_n >= -(\triangle V_{SCF} - \triangle \epsilon_n)|\Psi_n > \end{array}\right.$$

$$\begin{aligned} E_{el}^{(2)} &= \sum_{k,n}[< \Psi_{k,n}^{(1)}|H^{(0)} - \epsilon_{k,n}^{(0)}|\Psi_{k,n}^{(1)} > + < \Psi_{k,n}^{(1)}|V^{(1)}|\Psi_{k,n}^{(0)} > \\ &+ < \Psi_{k,n}^{(0)}|V^{(1)}|\Psi_{k,n}^{(1)} >] + \sum_{k,n} < \Psi_{k,n}^{(0)}|V^{(2)}|\Psi_{k,n}^{(0)} > \\ &+ \frac{1}{2} \int \frac{\delta^2 E_{xc}}{\delta n(r) \delta n(r')} n^{(1)}(r) n^{(1)}(r') \end{aligned}$$

- 冻声方法，分子动力学谱分析方法

几何Berry位相

- 电介质极化，介电常数
- 偶极矩-->宏观极化；流-->极化变化
- 电荷密度（波函数的模）；流（波函数的位相）
- 零电场情况下，任意两个晶体态之间的极化变化对应着 一个几何量子位相
- 晶格振动、铁电、压电效应、自发极化、静态介电张量、电子介电常数。。。
- 不如传统的微扰理论方法普适，但实现简单、计算量小

Part II:数值方法

数值离散方法

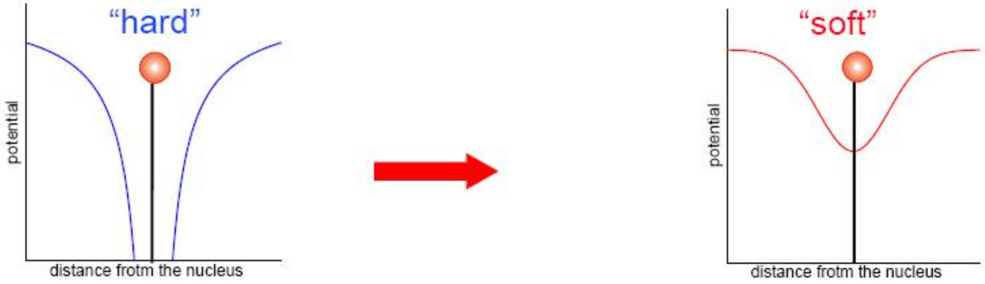
- 基组展开
  - LCAO基组（Gaussian基组、数值基组）
- 实空间网格

平面波基组：从OPW到PP

- 平面波展开
- 正交化平面波（OPW）

$$|\chi_{k+G} >= |k+G> - \sum_c |\phi_c >< \phi_c|k+G>$$

- 赝势（PP）方法
  - 经验赝势
  - 模守恒赝势
  - 超软赝势



Muffin-tin势场与分波方法

- Muffin-tin势场近似
  - 缀加平面波（APW）
  - 格林函数方法（KKR）
- 线性化方法
  - LAPW
  - LMTO
- 分波方法的发展
  - FP-LAPW
  - third-generation MTO, NMTO, EMTO

平面波基组：从USPP到PAW

- 投影缀加波（PAW）方法
- 赝波函数空间

$$\tau = 1 + \sum_i \left(|\phi_i> - |\tilde{\phi}_i> \right) < \tilde{p}_i|$$

- USPP or PAW? (VASP, ABINIT, ...)

实空间网格

- 简单直观
- 允许通过增加网格密度系统地控制计算收敛精度
- 线性标度
- 可以方便的通过实空间域分解实现并行计算
- 处理某些特殊体系（带电体系、隧穿结。。。）

有限差分

- 从微分到差分

$$\frac{\partial^2\Psi}{\partial x^2} = \sum_{n=-N}^{N} C_n \Psi(x_i + nh, y_j, z_k) + O(h^{2N+2})$$

- 提高FD方法的计算效率
  - 对网格进行优化，如曲线网格（适应网格）和局部网格优化（复合网格）
  - 结合赝势方法
  - 多尺度（multiscale）或预处理（preconditioning）

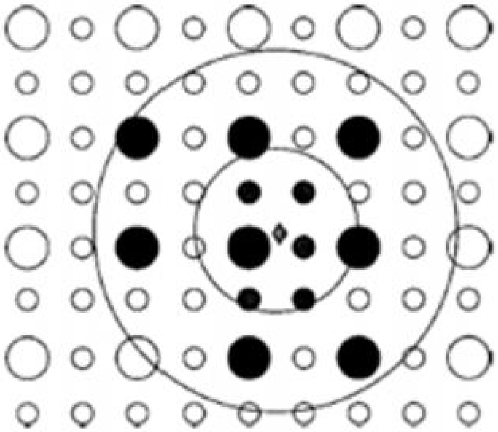
有限元

- 变分方法
- 处理复杂的边界条件
- 矩阵稀疏程度及带状结构往往不如有限差分好
- 广义的本征值问题

多分辨网格上的小波基组

- 多分辨分析

$$V_N = V_M \oplus W_{M+1} \oplus \cdots \oplus W_N$$



- 半取样（semicardinal）基组

线性标度与量子力学中的局域性

- “近视原理”
- 局域化的Wannier函数或密度矩阵
  - 绝缘体：指数衰减，能隙越大衰减越快
  - 金属：零温下按幂率衰减，在有限温度下可出现指数衰减
- 局域区域
- 线性标度系数，crossover

线性标度算法

- 分治方法
- 费米算符展开和费米算符投影方法
- 直接最小化方法
  - 密度矩阵最小化

$$\Omega = Tr[(3F^2 - 2F^3)(H - \mu I)]$$

  - 轨道最小化

$$\Omega = Tr[(2I - S)(H - \mu S)]$$

  - 优基组密度矩阵最小化

线性标度算法

- 基于格林函数的递归方法
- 脱离轨道的（orbital-free,OF）算法
- 对角化以外的线性标度
  - 构造有效哈密顿量的算法
  - 几何优化与分子动力学
  - TDDFT

Part III:应用

物理学：强相关体系

- 模型哈密顿量
- LDA++
- 电子结构：CrO_2
- 点阵动力学: 钚

化学：弱作用体系

- 松散堆积的软物质、惰性气体、生物分子和聚合物，物理吸附、Cl+HD反应
- 用传统的密度泛函理论处理弱作用体系
- 一个既能产生vdW相互作用系数又能产生总关联能的非局域泛函：无缝的（seamless）方法
- GW近似
- 密度泛函加衰减色散（DFdD）

生命科学：生物体系

- 困难（尺寸问题、时间尺度）
- QM/MM方法（饱和原子法、冻结轨道法）
- 简单势能面方法
  - 线性同步过渡（LST ）
  - 二次同步过渡（QST ）
- 完全的分子动力学
  - 并行复制动力学（parallel replica dynamics）
  - 超动力学（hyperdynamics, metadynamics）
  - 温度加速的动力学（temperature accelerated dynamics ）
  - 快速蒙特卡罗（on-the-fly kineric Monte Carlo）方法

纳米和材料科学：输运性质及其他

- 输运：非平衡态第一性原理模拟
- 材料力学：运动学Monte Carlo（KMC）--> 点阵气体和元胞自动机 --> 连续方程的有限差分有限元求解

光谱学：激发态和外场

- 系综密度泛函理论
- 考虑系统对称性，用求和方法计算多重态激发能
- 多体微扰理论，GW近似Bethe-Salpeter方程
- TDDFT，线性响应

一些计算软件

- Gaussian, DMol3, Q-Chem, ADF, SIESTA
- VASP, CASTEP,ABINIT, PWSCF, CPMD
- Octopus
- BigDFT

5.2 费米液体理论

1. 费米体系

费米温度： $T_F = \frac{1}{k_B}\lim_{T\to 0}\mu$ μ：化学势

均匀的无相互作用的三维系统，费米温度：

$$T_F = \frac{\varepsilon_F}{k_B} = \frac{1}{2mk_B}(3\pi^2 n)^{2/3}$$

费米简并系统：费米子系统的温度通常运运低于费米温度

室温下金属中的传导电子

费米温度给出了系统中元激发存在与否的标度

在费米温度以下，系统的性质由数目有限的低激发态决定。

有相互作用和无相互作用的简并费米子系统中，低激发态的性质具有较强的对应性。

2. 费米液体

金属中电子通常是可迁移的，称为电子气， 电子动能：

$$E_k = \frac{3}{5}\varepsilon_F = \frac{3}{5}\frac{\hbar^2}{2m}(\frac{3\pi^2 N}{V})^{2/3} \propto n^{2/3}$$

电子势能：

$$E_P = \sum_{ij}\frac{e^2}{r_{ij}} \propto n^{1/3}$$

在高密度下，电子动能为主，自由电子气模型是较好的近似。在低密度下，电子之间的势能或关联变得越来越重要，电子可能由于这种关联作用进入液相甚至晶相。

较强关联下，电子系统被称为电子液体或费米液体或**Luttinger液体(1D)**

$$\text{无相互作用的粒子} \xrightarrow{\text{绝热方式}} \text{电子－电子相互作用}$$

$$\text{单电子态} \xrightarrow{?} \text{多电子本征态}$$

从单电子态出发描述体系真正状态是否是好近似?

相互作用：(1)单电子能级分布变化(势的变化);(2)电子散射导致某一态上有限寿命(驰豫时间)

3. 朗道费米液体理论

单电子图象不是一个正确的出发点，但只要把电子改成准粒子或准电子，就能描述费米液体。准粒子遵从费米统计，准粒子数守恒，因而费米面包含的体积不发生变化。

假设激发态用动量 $\vec{p}$ 表示

$E = E_g + \sum_{\vec{p}} \varepsilon(p) n_{\vec{p}}$　$n_{\vec{p}}$为准粒子分布函数，E_g为基态能量。

系统的熵：$S = -k_B \sum_{\vec{p}} [n_{\vec{p}} \ln n_{\vec{p}} + (1-n_{\vec{p}}) \ln(1-n_{\vec{p}})]$

在平衡态下，$n_{\vec{p}}$服从费米分布　$n_{\vec{p}} = \dfrac{1}{e^{[\varepsilon(p)-\mu]/k_B T}+1}$

$\varepsilon(p)$与温度有关

朗道费米液体理论的适用条件：

(1). 必须有可明确定义的费米面存在

在平衡态下， $n_{\vec{p}}$ 服从费米分布 $n_{\vec{p}} = \dfrac{1}{e^{[\varepsilon(p)-\mu]/k_B T}+1}$

$\varepsilon(p)$ 与温度有关

$n(k) = Z(k)\theta[\mu-\varepsilon(k)]+\Phi(k)$ $\Phi(k)$ 是一个连续变化函数。

物理图象：一个准粒子 可以看作由一个裸粒子 (比例为 $Z(k_F)$) 加上周围其他元激发的贡献 (比例 $(1-Z(k_F))$), 对应的占据率为 $\Phi(k)$

$m \rightarrow m^* = \dfrac{m}{Z} \Rightarrow$ 正常费米液体要求： $0 < Z(k_F) \le 1$

$Z(k_F) = 0$：准粒子图象失效

(2). 准粒子有足够长的寿命

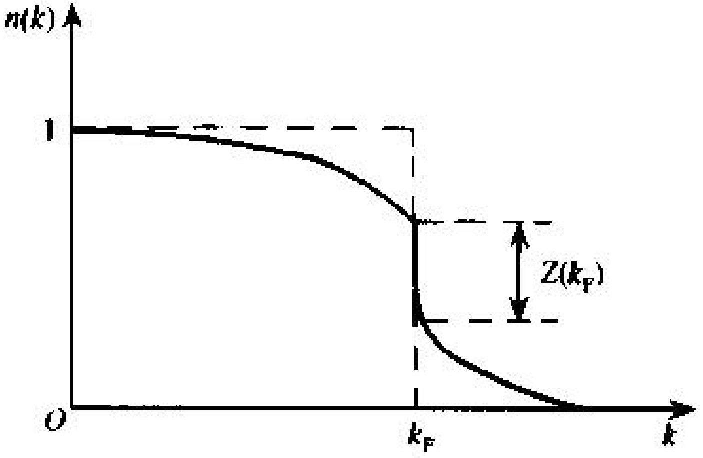


图 12.2 费米液体(实线)和非相互作用费米气体(虚线)量子态的平均占据率

Fermi Liquid Theory

First of all, What is Fermi Liquid ? If a system is described by the following Hamiltonian, it is called Fermi Liquid :

$$H=\sum_{\vec{k}}\varepsilon_0(\vec{k})n(\vec{k})+\frac{1}{2V}\sum_{\vec{k},\vec{k}'}f(\vec{k},\vec{k}')n(\vec{k})n(\vec{k}')$$

where $n(\vec{k})=C^{+}(\vec{k})C(\vec{k})$ is the number operator in momentum space

(1) The theory is non-trivial because of the quartic interaction

(2) However, the single-particle picture might work under some assumptions

Consider a system with 4 fermion interaction. The most general Hamiltonian is :

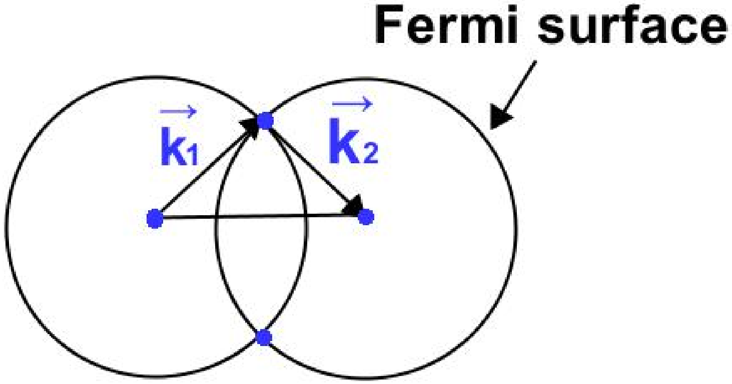
$$H=\sum_{\vec{k}}\varepsilon_0(\vec{k})n(\vec{k})+\sum_{\vec{k}_i}V(\vec{k}_i)\ \delta(\vec{k}_1+\vec{k}_2-\vec{k}_3-\vec{k}_4)\times C^{+}(\vec{k}_1)C^{+}(\vec{k}_2)C(\vec{k}_3)C(\vec{k}_4)$$

In weak coupling, some interactions are more important than the other – by space argument. Take 2D electron gas as an example. In the weak coupling and low temperature limit, only electrons very close to the Fermi surface is important.

$$V(\vec{k}_i)\ \rightarrow\ V(\theta_1,\ \theta_2,\ \theta_3,\ \theta_4)$$

Due to momentum conservation, not all angles $(\theta_1,\ \theta_2,\ \theta_3,\ \theta_4)$ are free

Take $(\theta_1,\ \theta_2)$ as independent parameter first. For given $\vec{k}_1, \vec{k}_2$, the other two momenta $\vec{k}_3, \vec{k}_4$ are completely fixed. However, if $\vec{k}_1 + \vec{k}_2 = 0$, the allowed phase space is enlarged to the whole Fermi surface. Thus, we expect this kind of interaction would dominate over the others.



$$\Delta(\vec{k}, \vec{k}') \bullet \psi^+(\vec{k})\psi^+(-\vec{k})\psi(\vec{k})\psi(-\vec{k})$$

BCS scattering

Note that this argument is only appropriate in weak coupling limit !

On the other hand, if we take $(\theta_1,\ \theta_3)$ as independent parameter, there is another kind of interaction would dominate the others (by similar argument)

$$F(\vec{k},\vec{k}') \bullet \ \psi^{+}(\vec{k})\psi(\vec{k})\psi^{+}(\vec{k}')\psi(\vec{k}')$$ forward scattering

Thus, in weak coupling, we expect these two interactions are the most important ones.

(1) For repulsive interaction, it can be shown that the BCS interaction can be safely ignored → Fermi Liquid !
(2) For attractive interaction, the instability is triggered ……
The system is better described by BCS theory !

Now we are ready to write down the Fermi Liquid Theory in more familiar form

In weak coupling and at low temperature, the density is not far from the free Fermi distribution. Thus, define the density variation

$$\Delta n(\vec{k}) = n(\vec{k}) - \Theta(\vec{k}_F - \vec{k})$$

Rewrite H in terms of $\Delta n(\vec{k})$

$$H = \sum_{\vec{k}} \Theta(\vec{k}_F - \vec{k})\ \varepsilon_0(\vec{k}) + \varepsilon_0(\vec{k})\Delta n(\vec{k}) + \frac{1}{2V}\sum_{\vec{k},\vec{k}'} f(\vec{k},\vec{k}')\Theta(\vec{k}_F - \vec{k})\Theta(\vec{k}_F - \vec{k}')$$

$$+\frac{1}{V}\sum_{\vec{k},\vec{k}'}\Theta(\vec{k}_F - \vec{k}')f(\vec{k},\vec{k}')\Delta n(\vec{k}) + \frac{1}{2V}\sum_{\vec{k},\vec{k}'} f(\vec{k},\vec{k}')\Delta n(\vec{k})\Delta n(\vec{k}')$$

Bare energy : $E_0 = \sum_{\vec{k}} \Theta(\vec{k}_F - \vec{k})\ \varepsilon_0(\vec{k}) + \frac{1}{2V} \sum_{\vec{k},\vec{k}'} \Theta(\vec{k}_F - \vec{k})\Theta(\vec{k}_F - \vec{k}') f(\vec{k},\vec{k}')$

It is only a constant. Will ignore it later.

quasi-particle spectrum :

$H_1 = \sum_{\vec{k}} \varepsilon(\vec{k})\Delta n(\vec{k})$ where $\varepsilon(\vec{k}) = \varepsilon_0(\vec{k}) + \frac{1}{V} \sum_{\vec{k}' < \vec{k}_F} f(\vec{k},\vec{k}')$

Finally , quasi-particle interactions

$$H_2 = \frac{1}{2V} \sum_{\vec{k},\vec{k}'} f(\vec{k},\vec{k}')\Delta n(\vec{k})\Delta n(\vec{k}')$$

Collecting all terms, the Hamiltonian is

$$H = \sum_{\vec{k}} \varepsilon(\vec{k})\Delta n(\vec{k}) + \frac{1}{2V} \sum_{\vec{k},\vec{k}'} f(\vec{k},\vec{k}')\Delta n(\vec{k})\Delta n(\vec{k}')$$

Now use mean-field approximation , we can solve the quasti-particle distribution self-consistently.

$$H_{MF}=\sum_{\vec{k}}\varepsilon(\vec{k})\Delta n(\vec{k})+\frac{1}{2V}\sum_{\vec{k},\vec{k}'}f(\vec{k},\vec{k}')<\Delta n(\vec{k}')>\Delta n(\vec{k})\times 2$$

$$=\sum_{\vec{k}}[\varepsilon(\vec{k})+\frac{1}{V}\sum_{\vec{k}'}f(\vec{k},\vec{k}')<\Delta n(\vec{k}')>]\,\Delta n(\vec{k})$$

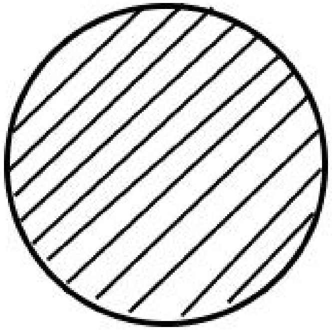
It becomes a quadratic theory and the mean-field dispersion is :

$$E(\vec{k})=\varepsilon(\vec{k})+\frac{1}{V}\sum_{\vec{k}'}f(\vec{k},\vec{k}')<\Delta n(\vec{k}')>$$

Make use of the MF dispersion , we obtain the self-consistent equation :

$$\Delta n(\vec{k})=\frac{1}{e^{\beta[E(\vec{k})-\mu]}+1}-\Theta(\vec{k}_F-\vec{k})\ ,\ \beta=\frac{1}{k_BT}$$

Simple Picture for Fermi Liquid

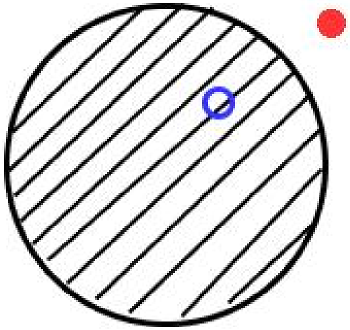


Free theory :

$$\varepsilon_0(\vec{k}) = \frac{\vec{k}^2}{2m}$$

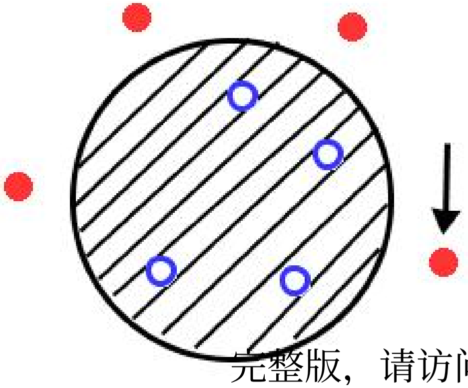
→

Now , add in the particle-particle interaction.



One quasi-particle :

$$\varepsilon(\vec{k}) = \frac{\vec{k}^2}{2m} + \frac{1}{V}\sum_{\vec{k}'} f(\vec{k},\vec{k}')\,\Theta(\vec{k}_F - \vec{k}')$$



Many quasi-particles present :

$$E(\vec{k}) = \varepsilon(\vec{k}) + \frac{1}{V}\sum_{\vec{k}'} f(\vec{k},\vec{k}') < \Delta n(\vec{k}') >$$

Many interesting properties :

(1) Effective mass m^* :

$$\frac{m^*}{m} = 1 + \frac{1}{3}F_1 \quad , \quad 2N(0)f(\vec{k},\vec{k}') = \sum_l F_l P_l(\cos\theta)$$

(2) Specific heat :   Linear temperature dependence

$$C_v = \frac{1}{3} m^* k_F k_B{}^2 T$$

(3) Sound velocity :

$$\left[\frac{v_1}{v_1(0)}\right] = \frac{1+F_0}{1+\frac{1}{3}F_1}$$

(4) Spin susceptibility :

$$\frac{\chi}{\chi_0} = \frac{1+\frac{1}{3}F_1}{1+\frac{1}{4}Z_0}$$

Compare with Curie susceptibility

$$\chi(T) \sim \frac{1}{T} \ !$$

朗道费米液体理论是处理相互作用费米子体系的唯象理论。
在相互作用不是很强时，理论对三维液体正确。
二维情况下，多大程度上成立不知道。
一维情况下，不成立。→luttinger液体

一维：低能激发为自旋为1/2的电中性自旋子和无自旋荷电为$\pm e$ 的波色子的激发。

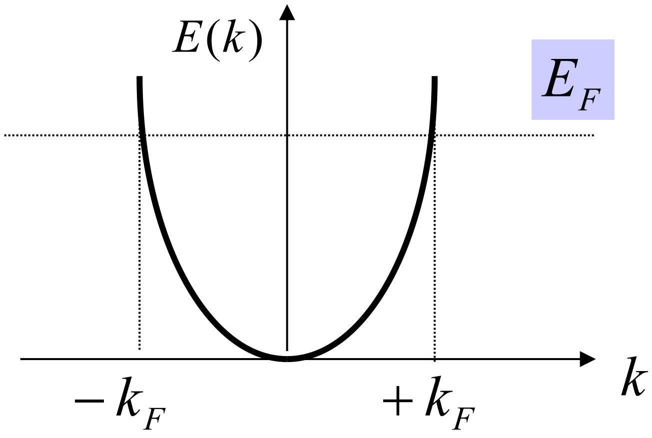
非费米液体行为：与费米液体理论预言相偏离的性质

THE PHYSICS OF LUTTINGER LIQUIDS

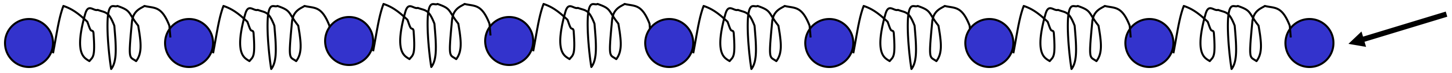
THE LUTTINGER LIQUID: INTERACTING SYSTEM OF 1D ELECTRONS AT LOW ENERGIES

- FERMI SURFACE HAS ONLY TWO POINTS

failure of Landau´s Fermi liquid picture



- ELECTRONS FORM A HARMONIC CHAIN AT LOW ENERGIES



Coulomb + Pauli interaction

collective excitations are vibrational modes

REMARKABLE PROPERTIES

- Absence of electron-like quasi-particles
  (only collective bosonic excitations)
- Spin-charge separation
  (spin and charge are decoupled and propagate with different velocities)
- Absence of jump discontinuity in the momentum distribution at $\pm k_F$
- Power-law behavior of various correlation functions and transport quantities. The exponent depends on the electron-electron interaction

OUTLINE

- What is a Fermi liquid, and why the Fermi liquid concept breaks in 1D
- The Tomonaga-Luttinger model
  - The TL-Hamiltonian and its bosonization
  - Diagonalization
  - Bosonic fields and electron operators
  - Local density of states
- Tunneling into a Luttinger liquid
- Luttinger liquid with a single impurity
- Physical realizations of Luttinger liquids

LITERATURE

- H.J. Schulz, G. Cuniberti and P. Pieri
  Fermi liquids and Luttinger liquids, cond-mat/9807366

- K. Flensberg
  Lecture notes on the one-dimensional electron gas and the theory of Luttinger liquids

- J. von Delft and H. Schoeller
  Bosonization for beginners refermionization for experts, cond-mat/9805275

- J. Voit
  One-dimensional Fermi liquids, Rep. Prog. Phys. 58, 977 (1995)

SHORTLY ABOUT FERMI LIQUIDS

Landau 1957-1959

Low energy excitations of a system of interacting particles described in terms of ``quasi-particles`` (single-particle excitations)

- Key point: quasi-particles have same quantum numbers as the corresponding non-interacting system (adiabatic continuity)

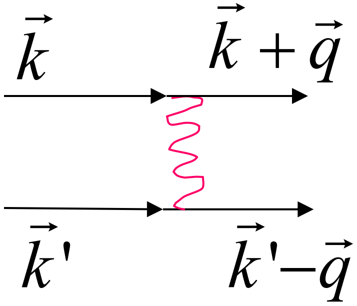
⇓

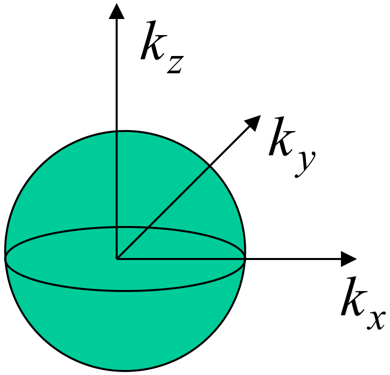
  - Start from appropriate noninteracting system
  - Renormalization of a set of parameters (e.g. effective mass)

- Also collective excitations occur (e.g. zero sound) at finite energies

FERMI LIQUIDS II

Effect of Coulomb interaction is to induce a finite life-time τ





Pauli exclusion principle

- only states within kT around Fermi sphere available
- quasiparticle states near Fermi sphere scatter only weakly

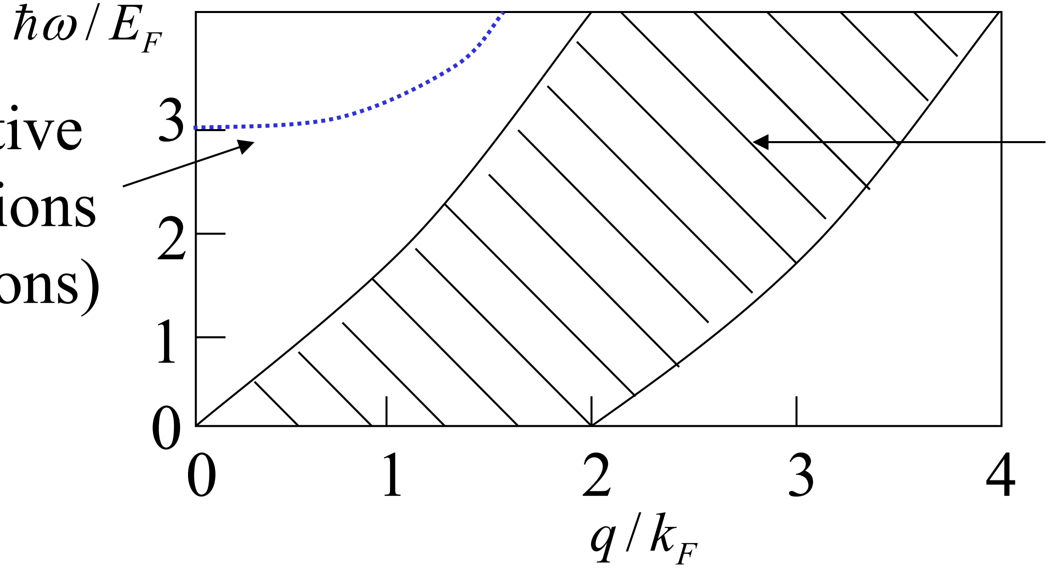
$$\tau_k^{-1} \to 0 \quad \text{when} \quad k \to k_F$$

3D

QUASI-PARTICLE PICTURE IS APPLICABLE IN 3D

FERMI LIQUIDS III

- DISPERSION OF EXCITATIONS IN 3D

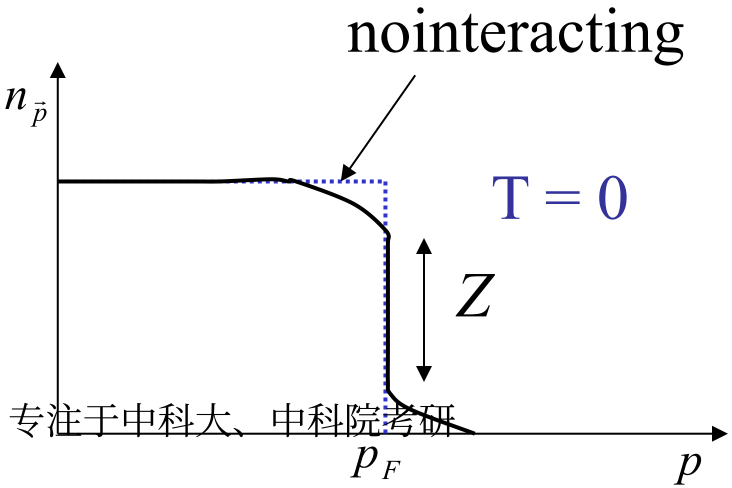


collective excitations (plasmons)

single-particle excitations

- Finite jump in momentum distribution

Z quasi-particle weight



LIFETIME OF ``QUASI-PARTICLES´´

Fermi´s golden rule yields for the lifetime τ

$$\tau_k^{-1} = \frac{2\pi}{\hbar} 2 \frac{1}{\Omega^2} \sum_{\vec{k}'\vec{q}} \left| \frac{V(q)}{\varepsilon(\vec{q}, \varepsilon_{\vec{k}+\vec{q}} - \varepsilon_{\vec{k}})} \right|^2 \delta(\varepsilon_{\vec{k}} + \varepsilon_{\vec{k}'} - \varepsilon_{\vec{k}+\vec{q}} - \varepsilon_{\vec{k}'-\vec{q}})$$

screened Coulomb interaction

spin

energy conservation

$$\times \left\{ n_F(\xi_{\vec{k}'})[1 - n_F(\xi_{\vec{k}+\vec{q}})][1 - n_F(\xi_{\vec{k}'-\vec{q}})] - [1 - n_F(\xi_{\vec{k}'})] n_F(\xi_{\vec{k}+\vec{q}}) n_F(\xi_{\vec{k}'-\vec{q}}) \right\}$$

$\xi_k = \varepsilon_k - \mu$

scattering out of state k

scattering into state k

In 3D an integration over angular dependence takes care of δ-function

$$\tau_k^{-1} \approx \frac{|V|^2 \rho^3}{\hbar} \int_{-\infty}^{0} d\xi \int_{0}^{\infty} d\xi' \theta(\xi_k + \xi - \xi') = \frac{|V|^2 \rho_k^3 \xi_k^2}{2\hbar}$$

$\tau_k \to \infty, k \to k_F$

$T = 0$

LIFETIME OF ``QUASI-PARTICLES´´ II

What about the lifetime τ in 1D?

In 1D k, k' are scalars. Integration over k' yields

$$\tau_k^{-1} \approx \frac{2}{\hbar}\int \frac{dq}{|q|}\left|\frac{V_1(q)}{\varepsilon(q)}\right| n_F(\varepsilon_{k+q})[1-n_F(\varepsilon_{k+q})][1-2n_F(\varepsilon_k)]$$

formally, it diverges
at small q
but we can insert a
small cut-off

- At small T

$$n_F(\varepsilon)[1-n_F(\varepsilon)] \to k_B T\delta(\varepsilon-\varepsilon_F)$$

$$1-2n_F(\varepsilon) \approx (\varepsilon-\varepsilon_F)/2k_BT$$

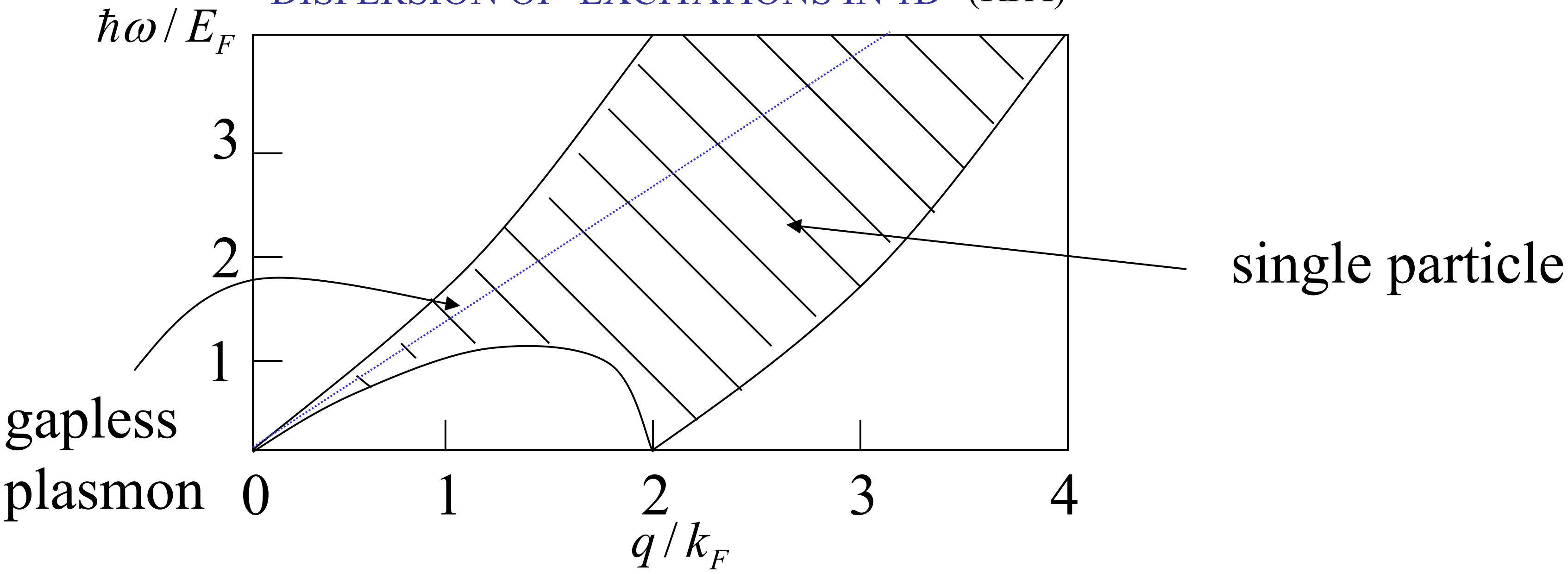
$$\rightarrow \quad \tau^{-1}/(\varepsilon-\varepsilon_F) \approx \begin{cases} 1/(\varepsilon-\varepsilon_F), & q\approx 0 \\ \text{const}, & q\approx 2k_F \end{cases}$$

i.e., this ratio cannot be made arbitrarily small as in 3D

BREAKDOWN OF LANDAU THEORY IN 1D

- $(\varepsilon - \varepsilon_F)\tau$ no longer diverges at k_F (no angular integration over direction of $\vec{k}'$ as in 3D)
- collective excitations are plasmons with $\omega_{1D} = \mathrm{v}|\mathrm{k}|$

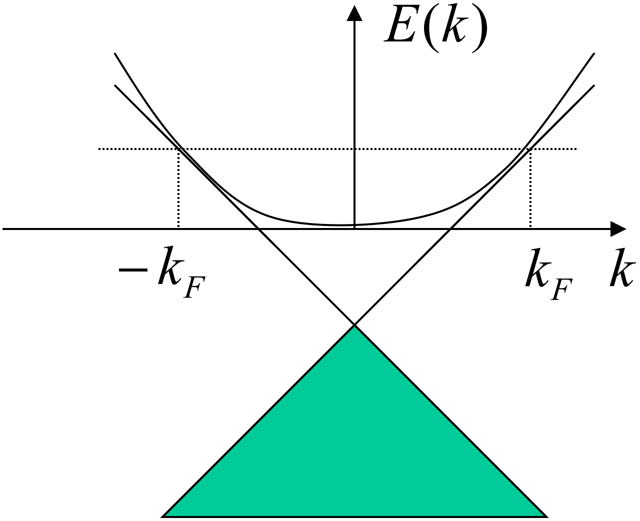
DISPERSION OF EXCITATIONS IN 1D (RPA)



COLLECTIVE AND SINGLE-PARTICLE EXCITATION NON DISTINCT

THE TOMONAGA-LUTTINGER MODEL

EXACTLY SOLVABLE MODEL FOR INTERACTING
1D ELECTRONS AT LOW ENERGIES



Assumptions:

- Only small momenta exchanges are included
- Dispersion relation is linearized near E_F
(both collective and single-particle excitations have linear dispersion)
- Model becomes exact when linearized branches extend from $(-\infty,\infty)$

TOMONAGA-LUTTINGER HAMILTONIAN

$$\boxed{H = H_0 + H_{\text{int}}}$$

free part

interaction

- Free part

$$H_0 = \sum_k \xi_k c_k^+ c_k , \qquad \xi_k = \varepsilon_k - \mu = (|k| - k_F)\hbar \mathrm{v}_\mathrm{F}$$

c_k, c_k^+ fermionic annihilation/creation operators

$$\{c_k, c_{k'}^+\} = \delta_{k,k'},\ \{c_k, c_{k'}\} = 0,\ \{c_k^+, c_{k'}^+\} = 0$$

- Introduce right moving $k > 0$, and left moving k < 0 electrons

$$c_k = c_{Rk}\theta(k) + c_{Lk}\theta(\text{-}k)$$

$$\Rightarrow\ H_0 = \hbar \mathrm{v}_\mathrm{F} \sum_k k(c_{Rk}^+ c_{Rk} - c_{Lk}^+ c_{Lk}) - (N_R + N_L)\hbar k_F \mathrm{v}_\mathrm{F}$$

TL HAMILTONIAN II

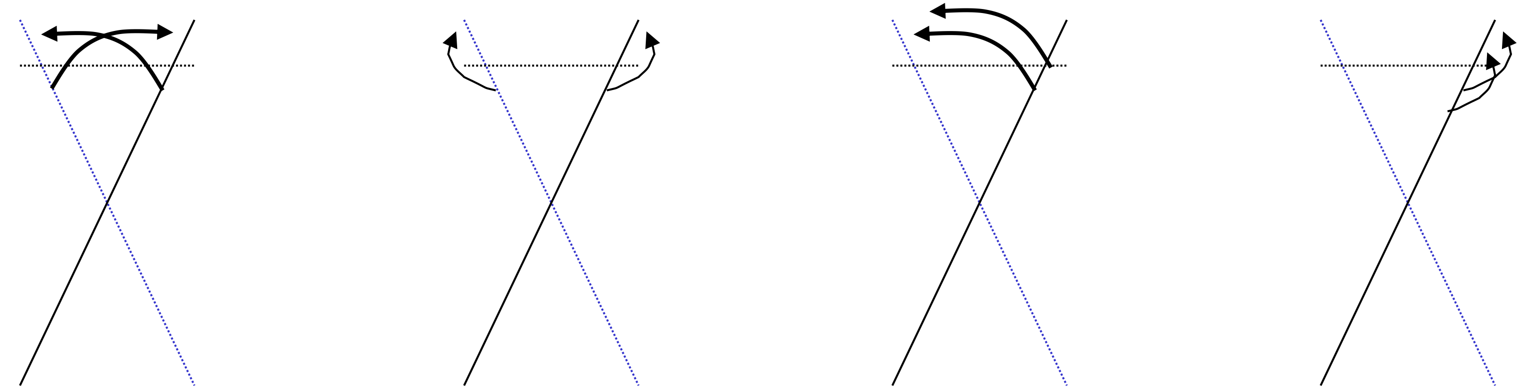
$$H = H_0 + H_{\text{int}}$$

free part

interaction

- Interactions

$$H_{\text{int}} = \frac{1}{L}\sum_{k,k',q\neq 0} V(q)\, c^{+}_{k} c^{+}_{k'} c_{k'-q} c_{k+q} \rightarrow H_2 + H_4$$

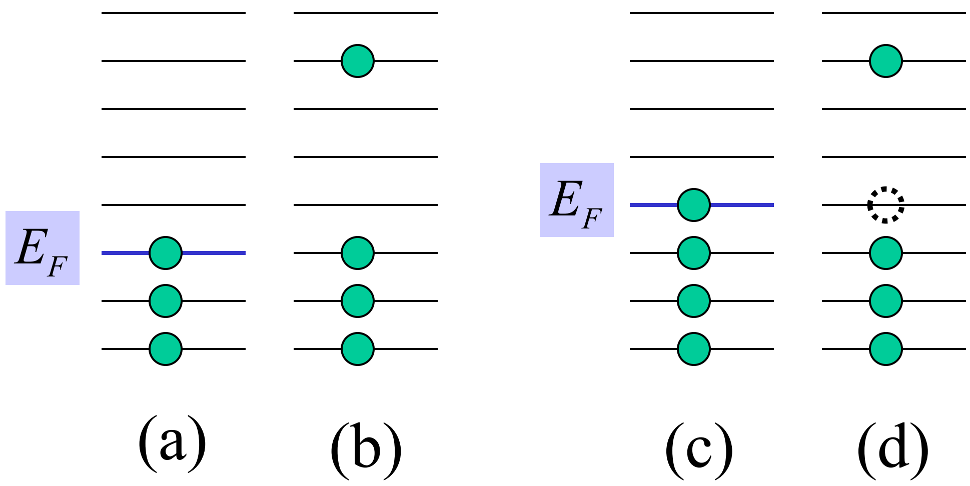


backscattering g_1 forward g_2 umklapp g_3 forward g_4

BOSONIZATION

BOSONIZATION: EXPRESS FERMIONIC HAMILTONIAN IN TERMS OF BOSONIC OPERATORS

⟺ construct bosonic Hamiltonian with the same spectrun



(a) and (b) have same spectrum but different ground state

EXCITED STATE CAN BE WRITTEN IN TERMS OF CHARGE EXCITATIONS, OR BOSONIC ELECTRON-HOLE EXCITATIONS

STEP 1

WHICH OPERATORS DO THE JOB?

Introduce the density operators (create excitation of momentum *q*)

$$\rho_R(q) = \sum_{k>0} c_k^+ c_{k+q}, \qquad \rho_L(q) = \sum_{k<0} c_k^+ c_{k+q}$$

and consider their commutation relations

$$[\rho_R(q), \rho_R(-q')] = \delta_{q,q'} \frac{Lq}{2\pi}$$

$$[\rho_L(q), \rho_L(-q')] = -\delta_{q,q'} \frac{Lq}{2\pi}$$

$$[\rho_R(q), \rho_L(-q')] = 0$$

nearly bosonic
commutation relations

STEP 1: PROOF

Consider e.g. $[\rho_R(q),\rho_R(-q)]$

$$[\rho_R(q),\rho_R(-q)] = \sum_{k,k'>0}[c_k^+ c_{k+q}, c_{k'}^+ c_{k'-q}]$$

$$= \sum_{k,k'>0}(c_k^+ c_{k+q} c_{k'}^+ c_{k'-q} - c_{k'}^+ c_{k'-q} c_k^+ c_{k+q})$$

algebra of
fermionic operators

$$= \sum_{k,k'>0}(c_k^+ c_{k'-q}\delta_{k+q,k'} - c_{k'}^+ c_{k+q}\delta_{k,k'-q})$$

$$= \sum_{k>0}\theta(k+q)(c_k^+ c_k - c_{k+q}^+ c_{k+q})$$

$n_k = c_k^+ c_c$

occupation operator

$$= \sum_{k>0}\theta(k+q)(n_k - n_{k+q})$$

$n_k \to \langle n_k \rangle = 1$

$if \quad k << k_F$

$$\cong \frac{L}{2\pi}\int_0^q dk = \frac{Lq}{2\pi}$$

STEP 2

Examine now $[H_0, \rho_R(q)] = -q\hbar \mathrm{v}_\mathrm{F} \rho_R(q)$

$$[H_0, \rho_L(q)] = q\hbar \mathrm{v}_\mathrm{F} \rho_L(q)$$

STATES CREATED BY ρ_R ARE EIGENSTATES OF H_0 WITH ENERGY $\hbar \mathrm{v}_\mathrm{F} q$

BOSONIZED HAMILTONIAN

$$H_0 = \frac{\pi\hbar \mathrm{v}_\mathrm{F}}{L} \sum_{q>0} (\rho_R(-q)\rho_R(q) + \rho_L(-q)\rho_L(q)) + \frac{\hbar \mathrm{v}_\mathrm{F}\pi}{L}(N_R^2 + N_L^2)$$

and

$$H_2 = \sum_{q\neq 0} g_2(q)(\rho_R(q)\rho_L(-q) + \rho_L(q)\rho_R(-q))$$

$$H_4 = \sum_{q\neq 0} g_4(q)(\rho_L(q)\rho_L(-q) + \rho_R(q)\rho_R(-q))$$

interactions

STEP 2: PROOF

Example: $[H_0, \rho_R(q)] = -q\hbar \mathrm{v}_{\mathrm{F}} \rho_R(q)$

$$
\begin{aligned}
[H_0, \rho_R(-q)] &= \hbar \mathrm{v}_{\mathrm{F}} \sum_{k,k'>0} k [c_k^+ c_k, c_{k'}^+ c_{k'+q}] \\
&= \hbar \mathrm{v}_{\mathrm{F}} \sum_{k,k'>0} k (c_k^+ c_{k'+q} \delta_{k'k} - c_{k'}^+ c_k \delta_{k,k'+q}) \\
&= \hbar \mathrm{v}_{\mathrm{F}} \sum_{k,k'>0} k (c_k^+ c_{k+q} - c_{k-q}^+ c_k \theta(k-q)) \\
&= -\hbar \mathrm{v}_{\mathrm{F}} q \rho_R(q) + \hbar \mathrm{v}_{\mathrm{F}} \sum_{0<k<-q} (k+q) c_k^+ c_{k+q} \approx -q\hbar \mathrm{v}_{\mathrm{F}} \rho_R(q)
\end{aligned}
$$

STEP 3

Introduce the bosonic operators

$$a_q = \sqrt{\frac{2\pi}{qL}}\rho_R(q), \quad a_q^+ = \sqrt{\frac{2\pi}{qL}}\rho_R(-q)$$

$$b_q = \sqrt{\frac{2\pi}{qL}}\rho_L(-q), \quad b_q^+ = \sqrt{\frac{2\pi}{qL}}\rho_L(q)$$

$$[a_q, a_q^+] = [b_q, b_q^+] = \delta_{q,q'}$$

$$[a_q, a_{q'}] = [b_q, b_{q'}] = 0$$

yielding

$$H = \hbar \mathrm{v}_\mathrm{F} \sum_{q>0} q\left(1 + \frac{g_4}{\pi\hbar \mathrm{v}_\mathrm{F}}(q)\right)(a_q^+ a_q + b_q^+ b_q) + \frac{1}{\pi}\sum_{q>0} q g_2(q)(a_q b_q + a_q^+ b_q^+)$$

DIAGONALIZATION

$$E(q) = \hbar q \mathrm{v}(q), \quad \mathrm{v} = \mathrm{v}_\mathrm{F}\sqrt{\left(1 + \frac{g_4(q)}{2\pi\hbar \mathrm{v}_\mathrm{F}}\right)^2 - \left(\frac{g_2(q)}{2\pi\hbar \mathrm{v}_\mathrm{F}}\right)^2}$$

SPIN-CHARGE SEPARATION

If we include spin, it gets slightly more complicated ... and interesting

$$H_0 = \frac{\pi \hbar \mathrm{v}_\mathrm{F}}{L} \sum_{\sigma, q \neq 0} (\rho_{R\sigma}(-q)\rho_{R\sigma}(q) + \rho_{L\sigma}(-q)\rho_{L\sigma}(q))$$

and interaction (satisfying SU2 symmetry)

$$H_{\mathrm{int}} = \frac{\mathrm{V}}{L} \sum_{\sigma\sigma', q} (\rho_{R\sigma}(q)\rho_{L\sigma'}(-q) + R \leftrightarrow L)$$

Introduce the spin and charge densities $\rho = \rho_\downarrow + \rho_\uparrow, \quad \sigma = \sigma_\downarrow + \sigma_\uparrow$

Hamiltonian decouple in two independent spin and charge parts, with excitations propagating with velocities v_ρ, and $\mathrm{v}_\sigma = \mathrm{v}_F$

SPACE REPRESENTATION

Long wavelength limit (interactions $g_4(q) \approx 0, \quad g_2(q) = V_2$)

Appropriate linear combinations Π, θ of the field ρ(x) can be defined. Then one finds

$$H = \frac{\mathrm{v}_\rho}{2} \int dx \, [g\Pi^2(x) + \frac{1}{g} \partial_x \vartheta(x)^2]$$

where

$$g = \sqrt{\frac{1 - V_2 / \pi\hbar \mathrm{v}_\mathrm{F}}{1 + V_2 / \pi\hbar \mathrm{v}_\mathrm{F}}}, \qquad \mathrm{v}_\rho = \mathrm{v}_\mathrm{F} \sqrt{1 - (V_2 / \pi\hbar \mathrm{v}_\mathrm{F})^2}$$

Luttinger parameter $g < 1$ repulsive interaction

BOSONIC REPRESENTATION OF Ψ

Fermionic operator $\Psi(x)=\frac{1}{\sqrt{L}}\sum_k c_k e^{ikx}\approx\Psi_R(x)+\Psi_L(x)$

Where e.g. Ψ_R

- decreases the number of electrons by one
- displaces the boson configuration for that state

Express ψ in the form of a bosonic displacement operator *B*

- from $[\Psi_\eta(x),\rho_\eta(x')]=\delta(x\text{-}x')$ $\eta=R,L$

$$[e^B,\rho_\eta(x')]=[B,\rho_\eta(x')]e^B$$

if $[B,\rho_\eta]$ a *c*-number

BOSONIZATION IDENTITY

$\Psi_{R,L}(x)\approx U_{R,L}\,e^{\pm ik_F x}\,e^{-i\vartheta_{R,L}(x)}$ U ladder operator, ϑ bosonic

LOCAL DENSITY OF STATES

i) Local density of states at $x = 0$

$$\rho(\varepsilon) = \frac{1}{\nu\hbar}\int_{-\infty}^{+\infty} dt\, e^{i\varepsilon t/\hbar}\left\langle\left\{\Psi(0,t),\Psi^{+}(0,0)\right\}\right\rangle +$$

ν density of states of non-interacting system

$$\rho(\varepsilon) = \frac{v_{\mathrm{F}}}{v\Gamma((g+1/g)/2)}\left(\frac{|\varepsilon|}{\varepsilon_c}\right)^{\frac{1}{2}(g+1/g-2)}$$

at $T = 0$

ε_c cut-off energy

Γ gamma function

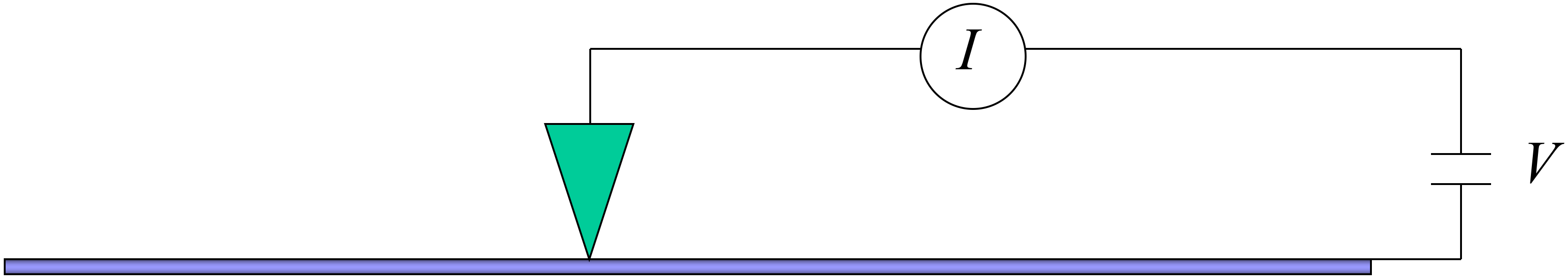
ii) Local density of states at the end of a Luttinger liquid

$$\rho_{\mathrm{end}}(\varepsilon) = \frac{v_{\mathrm{F}}}{v\Gamma(g/2)}\left(\frac{|\varepsilon|}{\varepsilon_c}\right)^{(1/g-1)}$$

at $T = 0$

MEASURING THE LDOS

Measurement of the local density of states by tunneling



$$H = H_1 + H_2 + H_T$$

coupling

system 2

system 1

$$H_T = \sum_{kp} (t_{kp} c^+_{2p} c_{1k} + t^*_{kp} c^+_{1k} c_{2p}) \equiv H_{21} + H_{12}$$

See e.g. carbon nanotube experiment by Bockrath *et al*. Nature, **397**, 598 (1999)

MEASURING THE LDOS II

Tunneling current can be evaluated by use of Fermi´s golden rule

$$I_{21} = e(\Gamma_{21} - \Gamma_{12})$$

$$\Gamma_{21} = \frac{2\pi}{\hbar} \sum_{f_{21}} \left| \langle f_{21} | H_T | i \rangle \right|^2 \delta(E_i - E_{f_{21}}) e^{-\beta E_i}$$

Γ_{ij} tunneling rate i to j

$f_{21} = c_2^+ c_1$

- t_{kp} constant ⟶ $I = \frac{1}{eR} \int d\varepsilon [n_F(\varepsilon - \mu_1) - n_F(\varepsilon - \mu_2)] \rho_1(\varepsilon) \rho_2(\varepsilon)$

$R = \hbar / (2\pi |t|^2 \nu_1 \nu_2 e^2)$

$$I = \frac{1}{eR} \int_0^V d\varepsilon \rho_{LL}(\varepsilon) \rho_{LL}(\varepsilon) \approx V^{(g+1/g-1)}$$

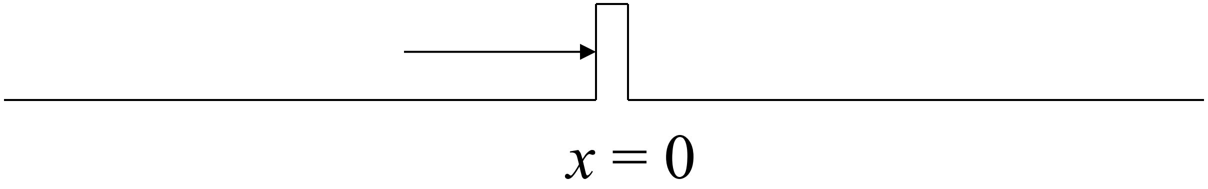
LL to LL

$$I = \frac{1}{eR} \int_0^V d\varepsilon \rho_{LL}(\varepsilon) \approx V^{(g+1/g)/2}$$

LL to metal

SINGLE IMPURITY

Weak link



Again tunneling current can be evaluated by use of Fermi´s golden rule

However, now is tunneling from the end of a LL

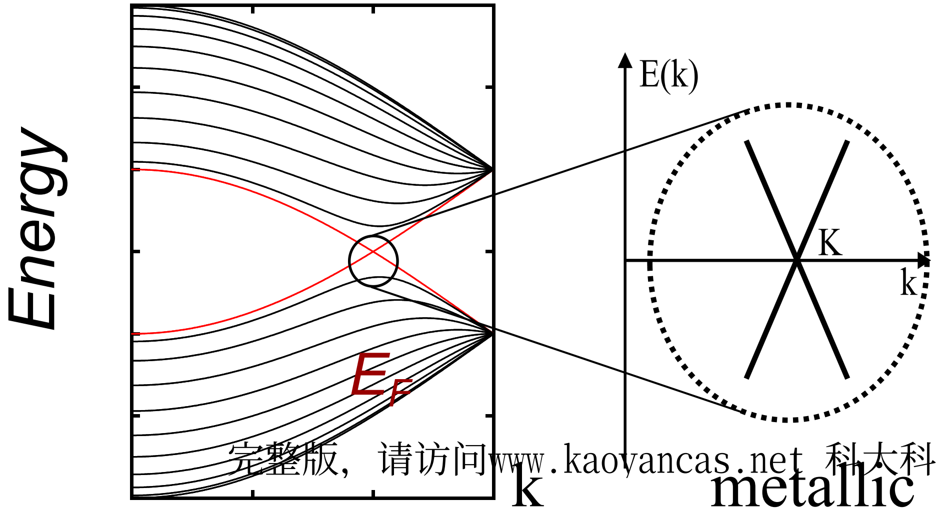
$$I = \frac{1}{eR}\int_0^V d\varepsilon \rho_{\text{end}}(\varepsilon)\rho_{\text{end}}(\varepsilon) \approx V^{(2/g-1)}$$

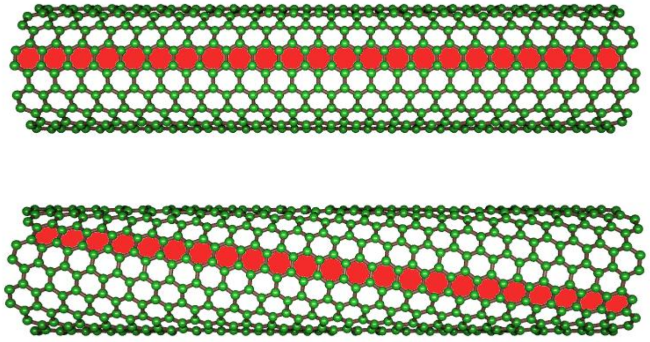
end to end

Charge density wave is pinned at the impurity

PHYSICAL REALIZATIONS

- Semiconducting quantum wires
- Edge states in fractional quantum Hall effect
- Single-walled metallic carbon nanotubes





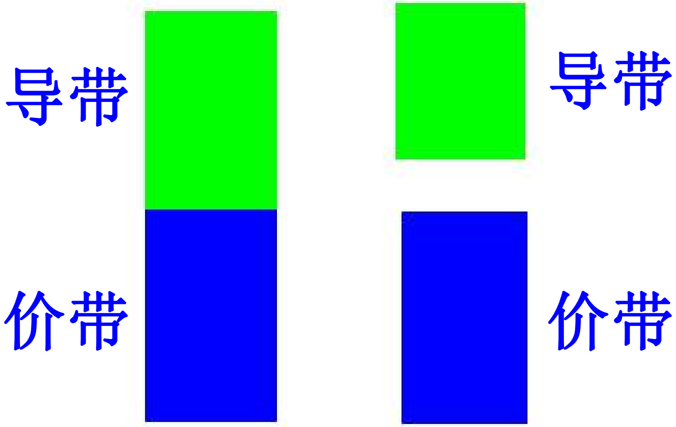
metallic 1D conductor with 2 linear bands

5.3　强关联体系

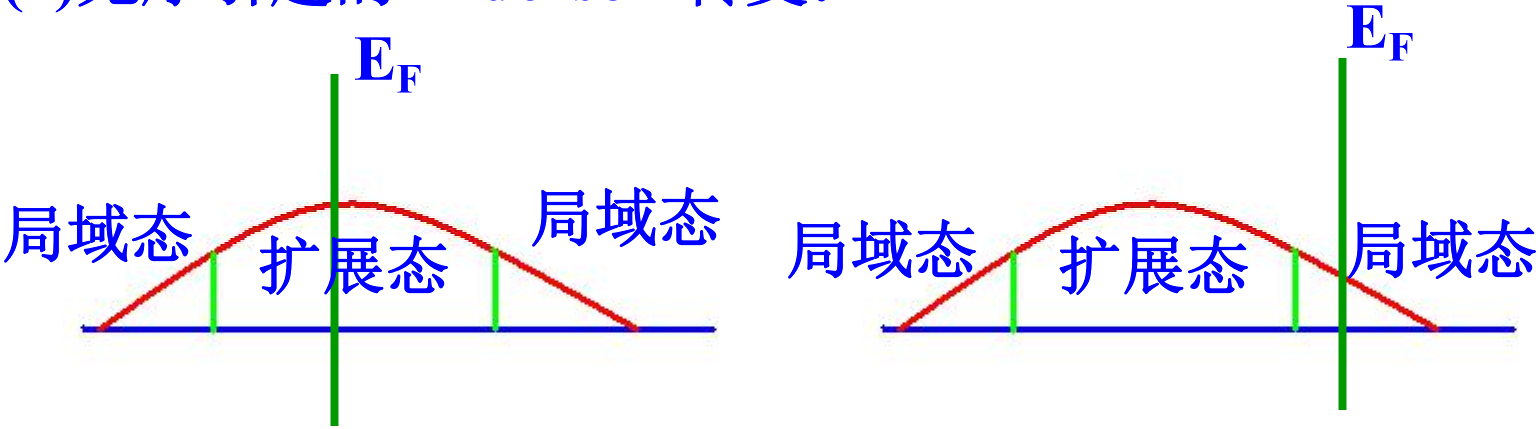
1. 窄能带现象

金属与绝缘体之分：

(1)能带框架下的区分：



(2)无序引起的Anderson 转变：



(3)电子间关联导致的Mott金属－绝缘体转变

(a).MnO:5个3d→未满3d带；O^{2-} 2p是满带不与3d能带重叠

能带论→MnO的3d带将具有金属导电性

实际上，MnO是绝缘体！

(b).ReO3:能带论→绝缘体。实际上是金属。

(c). 一些过渡金属氧化物当温度升高时会从绝缘体→金属

f电子或d电子波函数的分布范围是否和近邻产生重叠，是电子离域还是局域化的基本判据

l壳层体积与Winger-Seitz元胞体积的比值：

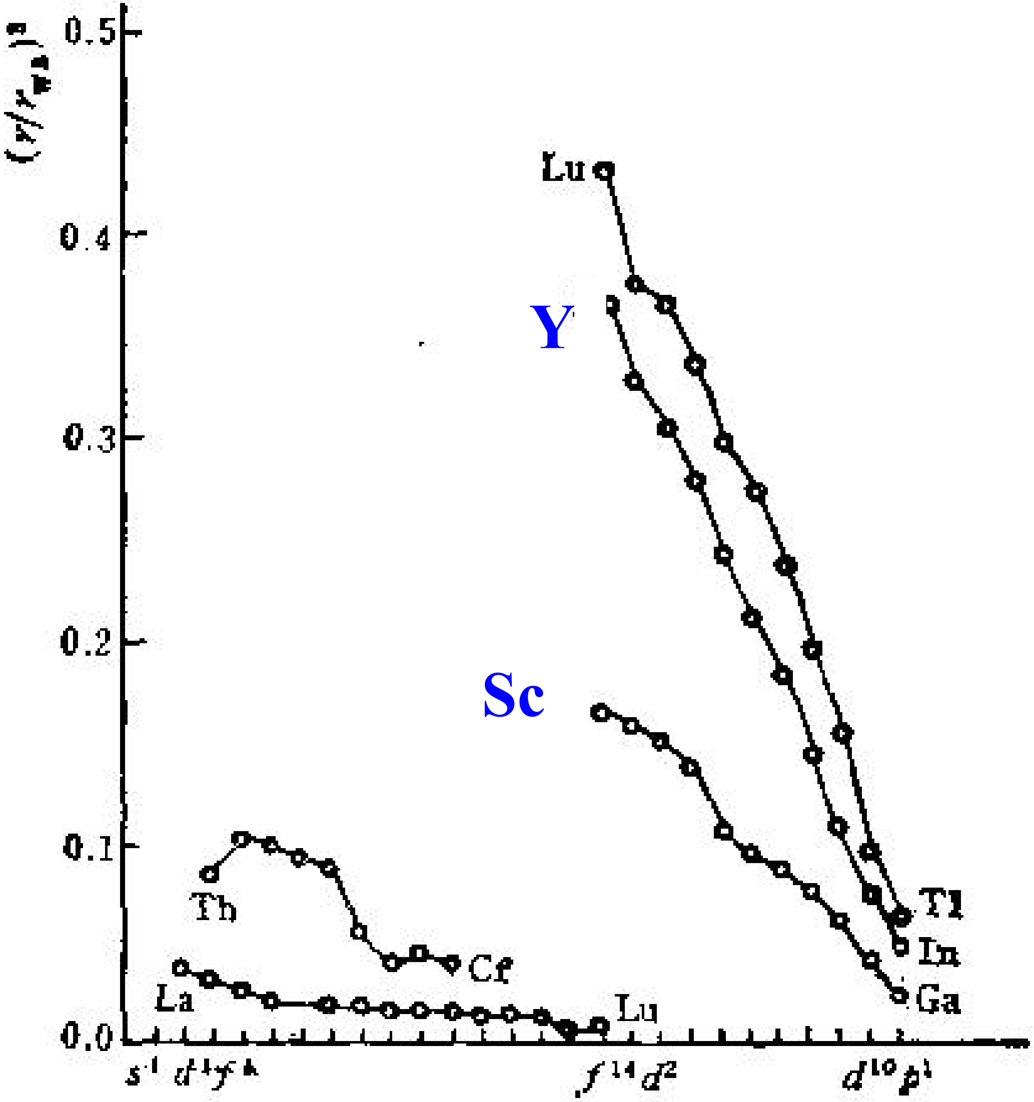
4f最小，5f次之，3d,4d,5d…

多电子态的局域化强度的顺序：

4f>5f>3d>4d>5d

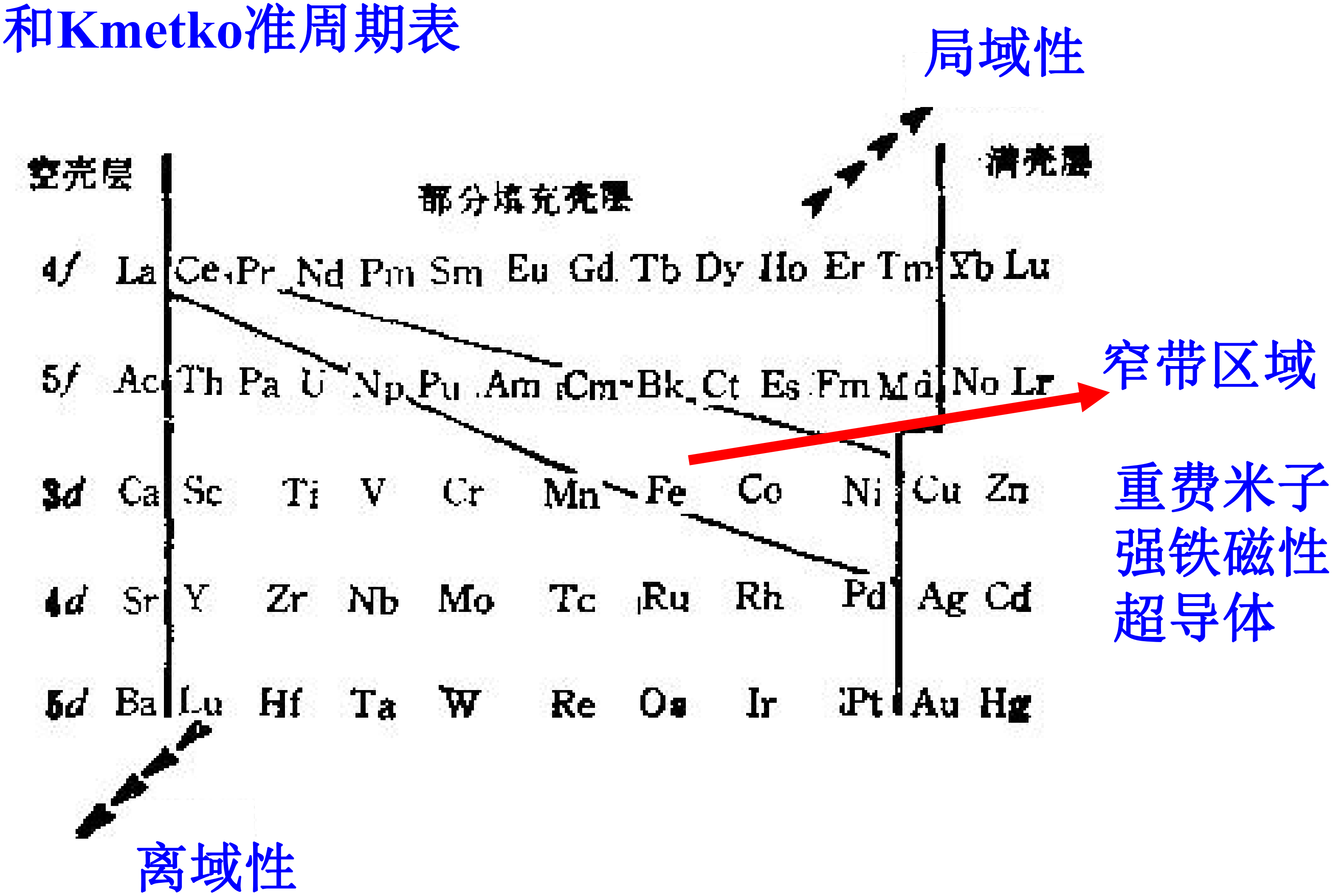
→ 能带宽度上升

另外，从左往右穿过周期表，部分填充壳层的半径逐步降低，关联重要性增加。



4f，5f元素和3d,4d,5d元素的壳层体积与Winger-Seitz元胞体积的比值

Smith和Kmetko准周期表



局域性

窄带区域

重费米子
强铁磁性
超导体

离域性

图1.2.3 稀土、锕系和过渡金属的f和d轨道局域化趋势的准周期表

另一类窄带现象：来自能带中的近自由电子与溶在晶格中具有3d,5f或4f壳层电子的溶质原子相互作用

Friedel与Anderson

稀土元素或过渡金属化合物中的能隙不可能仅用“电荷转移能”、“杂化能隙”、“有效库仑相关能”三者之一来描述，而应该说三者同时发挥作用。

稀土化合物部分存在混价“mixed valence”。混价的作用导致在Fermi面附近存在非常窄的能带(部分填充f能带或f能级），电子可以在4f能级和离域化能带之间转移，对固体基态性质产生显著影响。

2. 窄能带现象的理论模型

选择经验参数的模型Hamilton量方法

Hubbard模型和Anderson模型

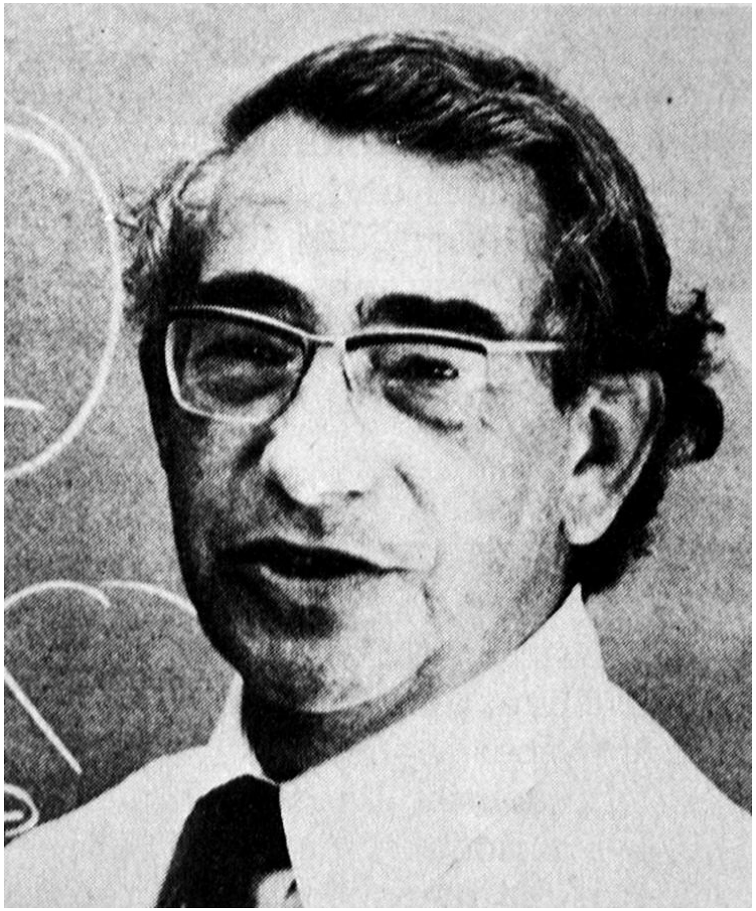
The Hubbard Model

From simple quantum mechanics to many-particle interaction in solids

-a short introduction

Historical facts

- Hubbard Model was first introduced by John Hubbard in 1963.
- Who was Hubbard? He was born in 1931 and died 1980. Theoretician in solid state physics, field of work: Electron correlation in electron gas and small band systems. He worked at the A.E.R.E., Harwell, U.K., and at the IBM Research Labs, San José, USA.



Picture taken from: Physics Today, Vol. 34, N°4, 1981

What, in general, is the HM?

- Hubbard model is a quantum theoretical model for many-particle interaction in and with a periodic lattice
- It is based on an interaction Hamitonian, some transformations and assumptions to be able to treat certain problems (e.g. magnetic behaviour and phase transitions) with solid state theory

Quantum mechanics

- **Basics:**
  - Schrödinger equation $$\underbrace{\left(-\frac{\hbar^2}{2m}\nabla^2+V(\vec{r})\right)}_{H}\psi=i\hbar\frac{\partial}{\partial t}\psi=E\psi$$
  - Expectation values $$A=\left\langle\varphi\middle|\hat{A}\middle|\varphi\right\rangle \; or \; A=\int\varphi^*\hat{A}\varphi du$$
  - Orthonormality and closure relation

$$\psi_k^*(\vec{r}',t)\psi_l(\vec{r},t)=\delta_{kl}\delta(\vec{r}'-\vec{r}) \qquad \int\psi(\vec{r},t)\psi(\vec{r},t)d^3r=1$$

  - The bra-ket notation $$\underbrace{\psi_k(\vec{r},t)}_{real\ space\ fct.}=\left\langle\vec{r}\middle|\underbrace{\psi_k(t)}_{state\ fct.}\right\rangle \qquad \left\langle k\middle|l\right\rangle=\delta_{kl}$$

Basis transformation, mathematically

- **A basis transformation can be simply performed:**

$$\begin{aligned} A &= 1 \cdot A \\ &= \sum_{\alpha} |k_\alpha\rangle\langle k_\alpha| A \end{aligned}$$

- **An equation is transformed the same way:**

$$\begin{aligned} A|\psi\rangle &= A \cdot 1|\psi\rangle \\ &= A\sum_\alpha |k_\alpha\rangle\langle k_\alpha|\psi\rangle \\ &= \sum_\alpha \psi_{k_\alpha} A|k_\alpha\rangle \end{aligned}$$

Single particle equations

- **Particle in a potential:**

$$\underbrace{\left(-\frac{\hbar^2}{2m}\nabla^2+V(\vec{r})\right)}_{H}\psi = i\hbar\frac{\partial}{\partial t}\psi = E\psi$$

  - **Periodic potentials:** $V(\vec{r}) = V(\vec{r}+n\vec{R})$

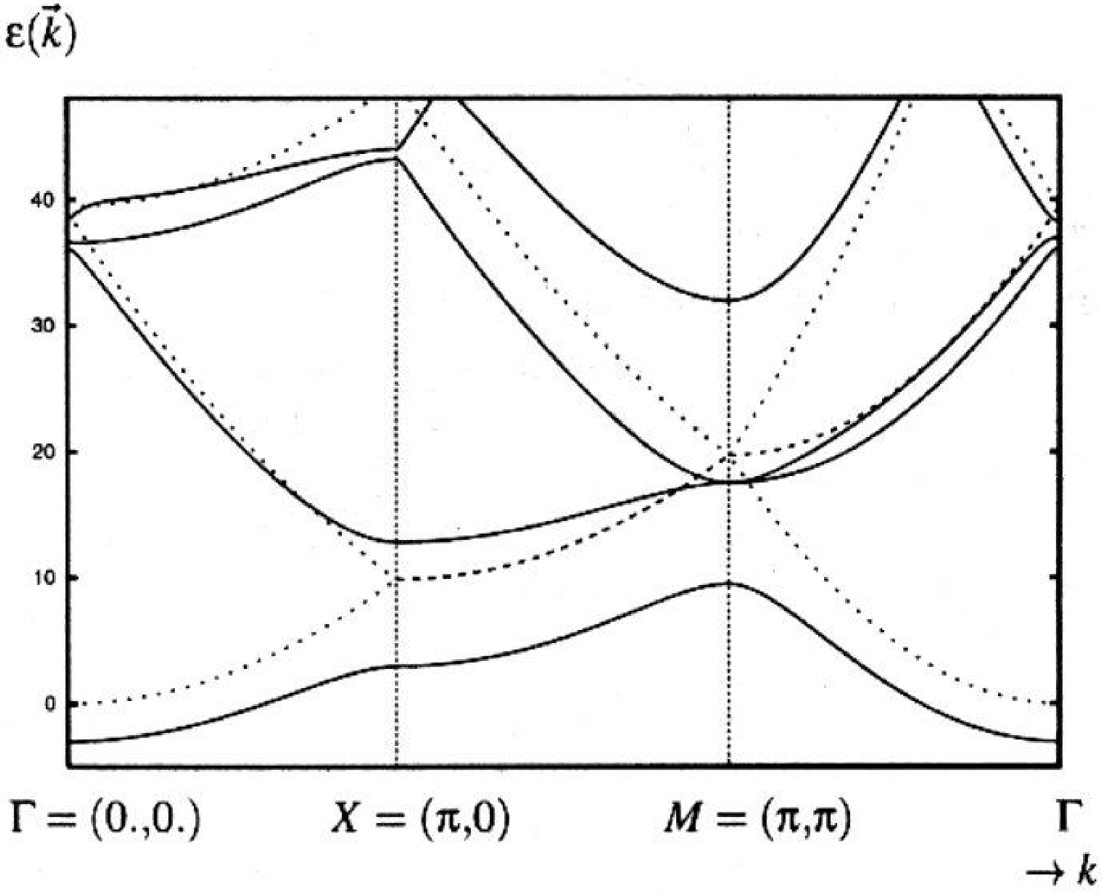
- **Solution for weak coupling to potential: Bloch wave**

$$\psi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{V}}\exp\left(i\vec{k}\vec{r}\right)u_{\vec{k}}(\vec{r})$$

Single particle equations

- **Dispersion relation for free electrons (dashed line):** $\varepsilon^{(0)}(\vec{k}) = \frac{\hbar^2 k^2}{2m}$

- **Dispersion relation for Bloch electrons (quasi-free)(solid line): The energies at $\vec{k} = \vec{G}$ are *no longer degenerated.* Two eigenenergies at those points.**



Graph from Gerd Czycholl, „Theoretische Festkörperphysik", Vieweg-Verlag

Single particle equations

- Stronger lattice potential: coupling to lattice points occurs; a modified Bloch wave is used, e.g. **Wannier states** resulting from the *Tight-Binding-Model*:

$$\psi_{n\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}} \exp(i\vec{k}\vec{R}) w_n(\vec{r} - \vec{R})$$

- Wannier states produce an orthonormal base of localized states; atomic wavefunctions would also be localized, but they are not orthonormal.

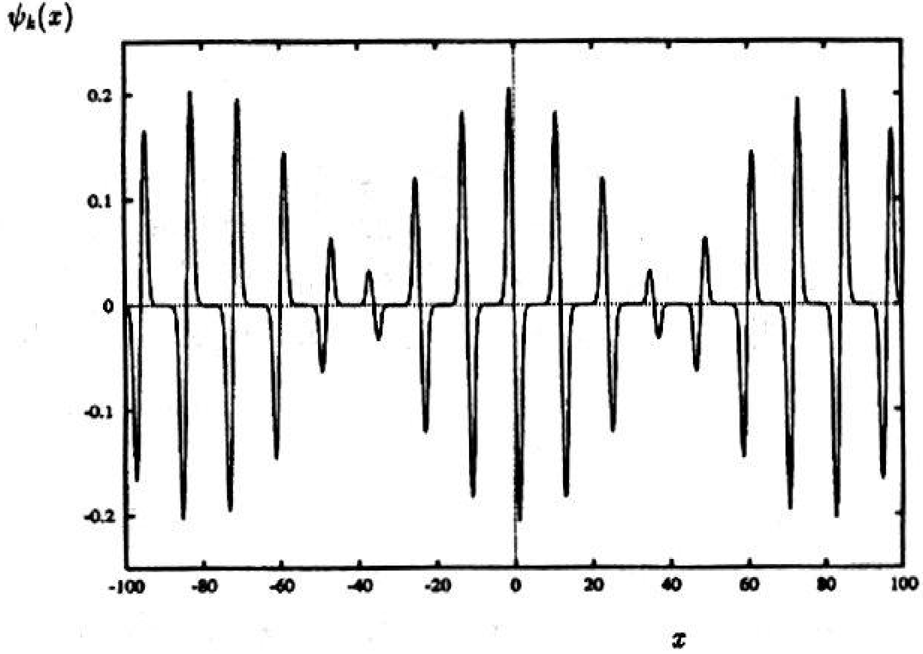
Comparison between the two new wavefunctions

$$\psi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{V}} \exp\left(i\vec{k}\vec{r}\right) u_{\vec{k}}(\vec{r})$$

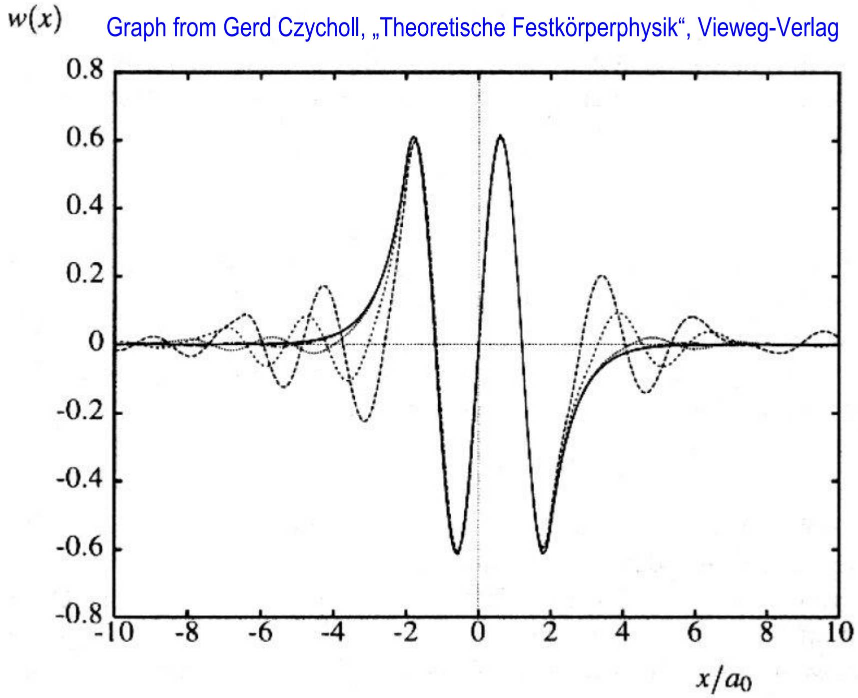
$$\psi_{n\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}} \exp(i\vec{k}\vec{R}) w_n(\vec{r} - \vec{R})$$

Bloch wavefunction

Graph from Gerd Czycholl, „Theoretische Festkörperphysik“, Vieweg-Verlag



Graph from Gerd Czycholl, „Theoretische Festkörperphysik“, Vieweg-Verlag



Wannier wavefunction (w-part)

Wavefunction for many particles

- Wavefunction is not simply the product of all single particle wavefunctions;
  1. **Particles can not be differed**
  2. **Fermions must obey Pauli principle**
- Ansatz: Slaterdeterminante

$$\left|\psi_{k_1\ldots k_{N_e}}(1\ldots N_e)\right\rangle = \frac{1}{\sqrt{N_e!}}\det\begin{pmatrix} \left|k_1\right\rangle^{(1)} & \cdots & \left|k_1\right\rangle^{(N_e)} \\ \vdots & \ddots & \vdots \\ \left|k_{N_e}\right\rangle^{(1)} & \cdots & \left|k_{N_e n}\right\rangle^{(N_e)} \end{pmatrix}$$

Second Quantization for Fermions

- **Creation and distruction operators create or destroy states:**

$$c_{k_\alpha}\left|\ldots 1\ldots 0\ldots \underbrace{0}_{\alpha}\ldots 1\ldots\right\rangle = 0$$

$$c_{k_\alpha}\left|\ldots 1\ldots 0\ldots \underbrace{1}_{\alpha}\ldots 1\ldots\right\rangle = \pm\left|\ldots 1\ldots 0\ldots \underbrace{0}_{\alpha}\ldots 1\ldots\right\rangle$$

$$c_{k_\alpha}^{+}\left|\ldots 1\ldots 0\ldots \underbrace{0}_{\alpha}\ldots 1\ldots\right\rangle = \pm\left|\ldots 1\ldots 0\ldots \underbrace{1}_{\alpha}\ldots 1\ldots\right\rangle$$

$$c_{k_\alpha}^{+}\left|\ldots 1\ldots 0\ldots \underbrace{1}_{\alpha}\ldots 1\ldots\right\rangle = 0$$

Second Quantization

- The operators fulfill the commutator relation:

$$\left[c_{k_\alpha}, c_{k_\alpha}\right]_+ = c_{k_\alpha} c_{k_\alpha} + c_{k_\alpha} c_{k_\alpha} = 0 = \left[c^+_{k_\alpha}, c^+_{k_\alpha}\right]_+$$

$$\left[c_{k_\alpha}, c^+_{k_\beta}\right]_+ = \delta_{\alpha\beta} = \begin{cases} 1 & for\, \alpha = \beta \\ 0 & else \end{cases}$$

- This is a must, otherwise one would disturb closure relation and orthonormality of wavefunctions described by second quantization

Hamiltonian for many particles

- **Summation over all single particles Hamiltonians + interaction Hamiltonian:**

$$H = H_0 + H_1 \text{ with } H_0 = \sum_{i=1}^{N_e} \frac{\vec{p}_i^{\,2}}{2m} + V(\vec{r}_i) \text{ and } H_1 = \sum_{i<j} u(\vec{r}_i - \vec{r}_j)$$

- **interaction potential u is the repulsive Coulomb interaction**

$$u(\vec{r}_i - \vec{r}_j) = \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

Operators in second quantization

$$A^{(1)} = \sum_{i=1}^{N_e} A^{(1)}(\vec{r}_i)$$

$$A^{(1)} = \sum_{i=1}^{N_e} \underbrace{\sum_{\alpha=1}^{\infty} |k_\alpha\rangle^{(i)(i)}\langle k_\alpha|}_{1} A^{(1)}(\vec{r}_i) \underbrace{\sum_{\beta=1}^{\infty} |k_\beta\rangle^{(i)(i)}\langle k_\beta|}_{1}$$

$$A^{(1)} = \sum_{i=1}^{N_e}\sum_{\alpha=1}^{\infty} |k_\alpha\rangle^{(i)(i)}\langle k_\alpha| A^{(1)}(\vec{r}_i)\sum_{\beta=1}^{\infty} |k_\beta\rangle^{(i)(i)}\langle k_\beta|$$

$$= \sum_{\alpha,\beta=1}^{\infty}\langle k_\alpha|A^{(1)}(\vec{r})|k_\beta\rangle \underbrace{\sum_{i=1}^{N_e}|k_\alpha\rangle^{(i)(i)}\langle k_\beta|}_{=c^{+}_{k_\alpha}c_{k_\beta}}$$

$$A^{(1)} = \sum_{\alpha,\beta=1}^{\infty} A^{(1)}_{k_\alpha,k_\beta}\, c^{+}_{k_\alpha} c_{k_\beta}$$

Operators in second quantization

$$A^{(2)} = \frac{1}{2}\sum_{i\neq j} A^{(2)}\left(\vec{r}_i, \vec{r}_j\right)$$

$$\begin{aligned}
A^{(2)} &= \frac{1}{2}\sum_{i\neq j}\sum_{\alpha,\beta,\gamma,\delta} \left|k_\alpha\right\rangle^{(i)(i)}\left\langle k_\alpha\right\|k_\beta\rangle^{(j)(j)}\left\langle k_\beta\right|A^{(2)}\left(\vec{r}_i,\vec{r}_j\right)\left|k_\gamma\right\rangle^{(j)(j)}\left\langle k_\gamma\right\|k_\delta\rangle^{(i)(i)}\left\langle k_\delta\right| \\
&= \frac{1}{2}\sum_{i\neq j}\sum_{\alpha,\beta,\gamma,\delta} \left|k_\alpha\right\rangle^{(i)}\left|k_\beta\right\rangle^{(j)(i)}\left\langle k_\alpha\right|^{(j)}\left\langle k_\beta\right|A^{(2)}\left(\vec{r}_i,\vec{r}_j\right)\left|k_\gamma\right\rangle^{(j)}\left|k_\delta\right\rangle^{(i)(j)}\left\langle k_\gamma\right|^{(i)}\left\langle k_\delta\right| \\
&= \frac{1}{2}\sum_{\alpha,\beta,\gamma,\delta} A^{(2)}_{k_\alpha k_\beta, k_\gamma k_\delta}\sum_{i\neq j}\left|k_\alpha\right\rangle^{(i)}\left|k_\beta\right\rangle^{(j)(j)}\left\langle k_\gamma\right|^{(i)}\left\langle k_\delta\right| \\
A^{(2)} &= \frac{1}{2}\sum_{\alpha,\beta,\gamma,\delta=1}^{\infty} A^{(2)}_{k_\alpha k_\beta, k_\gamma k_\delta}\, c^{+}_{k_\alpha} c^{+}_{k_\beta} c_{k_\gamma} c_{k_\delta}
\end{aligned}$$

Hamiltonian in second quantization

- Is transformed like the one-particle operator $A^{(1)}$ and the two-particle operator $A^{(2)}$

$$H = \sum_{i=1}^{N_e} \underbrace{\frac{p_i^2}{2m} + V(\vec{r}_i)}_{t} + \sum_{i<j} u\left(\vec{r}_i - \vec{r}_j\right)$$

$$\longleftrightarrow H = \sum_{k_\alpha k_\beta} t_{k_\alpha k_\beta} c^+_{k_\alpha} c_{k_\beta} + \frac{1}{2} \sum_{k_\alpha k_\beta k_\gamma k_\delta} u_{k_\alpha k_\beta, k_\gamma k_\delta} c^+_{k_\alpha} c^+_{k_\beta} c_{k_\gamma} c_{k_\delta}$$

Hamiltonian in second quantization

- Now: Matrix element $u_{k_\alpha k_\beta ,k_\gamma k_\delta}$ must be determined. Herefore, a wavefunction has to be chosen.
  - Example: Bloch-wave

$$
\begin{aligned}
H &= \sum_{n\vec{k}\sigma} \Big[\varepsilon_n(\vec{k})\, c^{+}_{n\vec{k}\sigma} c_{n\vec{k}\sigma} \\
&\quad + \frac{1}{2} \sum_{(n_1\vec{k}_1\sigma_1)\ldots(n_4\vec{k}_4\sigma_4)} u_{(n_1\vec{k}_1\sigma_1)(n_2\vec{k}_2\sigma_2),(n_3\vec{k}_3\sigma_{34})(n_4\vec{k}_4\sigma_4)}\, c^{+}_{n_1\vec{k}_1\sigma_1} c^{+}_{n_2\vec{k}_2\sigma_2} c_{n_3\vec{k}_3\sigma_3} c_{n_4\vec{k}_4\sigma_4} \Big]
\end{aligned}
$$

Coming closer to Hubbard...

Evaluation of matrix elements with <u>Wannier wave functions</u>:

$$H=\sum_{k_\alpha k_\beta} t_{k_\alpha k_\beta} c^+_{k_\alpha} c_{k_\beta} + \frac{1}{2}\sum_{k_\alpha k_\beta k_\gamma k_\delta} u_{k_\alpha k_\beta, k_\gamma k_\delta} c^+_{k_\alpha} c^+_{k_\beta} c_{k_\gamma} c_{k_\delta}$$

→

$$\begin{aligned} H &= \sum_{n\vec{R}, n'\vec{R}', \sigma} t_{n\vec{R}, n'\vec{R}'} c^+_{n\vec{R}\sigma} c_{n'\vec{R}'\sigma} \\ &+ \frac{1}{2}\sum_{\sigma\sigma'} \sum_{(n_1\vec{R}_1)\ldots(n_4\vec{R}_4)} u_{(n_1\vec{R}_1)(n_2\vec{R}_2),(n_3\vec{R}_3)(n_4\vec{R}_4)} c^+_{n_1\vec{R}_1\sigma} c^+_{n_2\vec{R}_2\sigma'} c_{n_3\vec{R}_3\sigma'} c_{n_4\vec{R}_4\sigma} \end{aligned}$$

Final Assumptions

- **Now: only direct neighbor interactions, restriction to one band.**

$$E_0 = t_{\vec{R},\vec{R}}\,; \quad t = t_{\vec{R},\vec{R}+\vec{\Delta}}$$

$$U = u_{\vec{R}\vec{R},\vec{R}\vec{R}} = \iint \left|w(\vec{r})\right|^2 \left|w(\vec{r}\,')\right|^2 \frac{e^2}{\left|\vec{r}-\vec{r}\,'\right|} d^3r\,d^3r'$$

$$V = u_{\vec{R}\vec{R}+\vec{\Delta},\vec{R}+\vec{\Delta}\vec{R}} = \iint \left|w(\vec{r})\right|^2 \left|w(\vec{r}\,'-\vec{\Delta})\right|^2 \frac{e^2}{\left|\vec{r}-\vec{r}\,'\right|} d^3r\,d^3r'$$

$$X = u_{\vec{R}\vec{R},\vec{R}\vec{R}+\vec{\Delta}} = \iint w^*(\vec{r})\,w(\vec{r}-\vec{\Delta}) \left|w(\vec{r}\,')\right|^2 \frac{e^2}{\left|\vec{r}-\vec{r}\,'\right|} d^3r\,d^3r'$$

Meaning of matrix elements

- t: **single particle hopping**
- U: **Hubbard-U**, describes onsite-Coulomb interaction
- V: Nearest-neighbor (density) interaction
- X: conditional hopping interaction

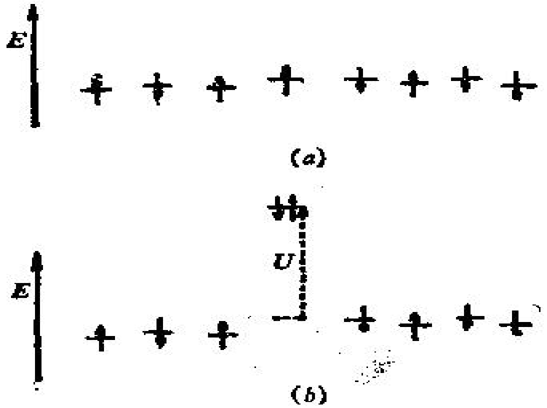


图1.2.5 Hubbard 相关能 U 的说明

(a) 每个局域态上有一个电子；(b) 同一座位上有两个电子引起的能量增加 U

The Hubbard Models

- simple Hubbard model

$$H = \sum_{\vec{R}\sigma} \sum_{\vec{\Delta} n.n.} t c^{+}_{\vec{R}\sigma} c_{\vec{R}+\vec{\Delta}\sigma} + U \sum_{\vec{R}} c^{+}_{\vec{R}\uparrow} c_{\vec{R}\uparrow} c^{+}_{\vec{R}\downarrow} c_{\vec{R}\downarrow}$$

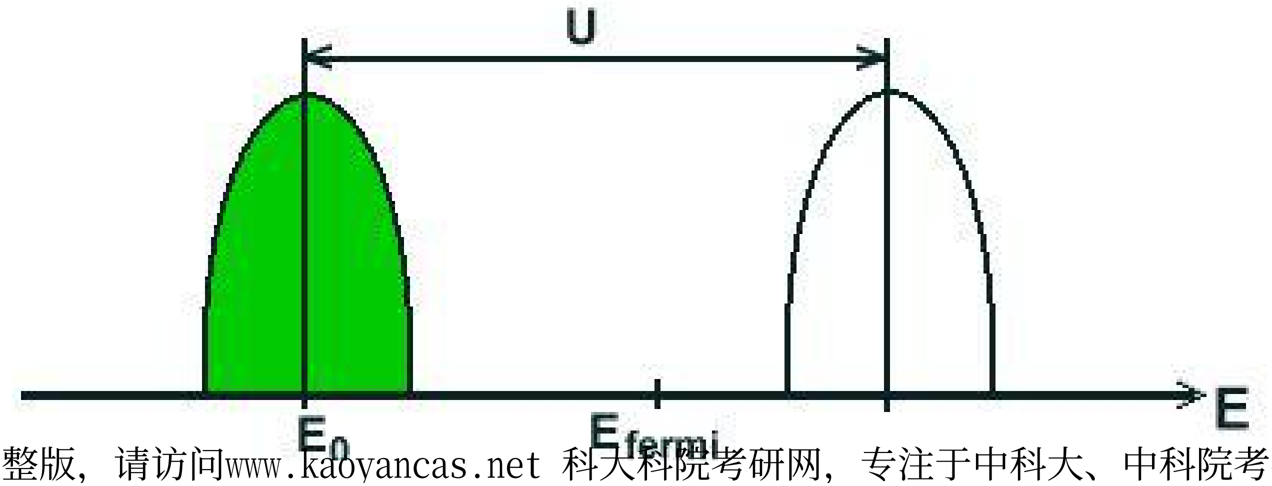
- extended Hubbard model

$$H_{ext} = H + \tfrac{1}{2} V \sum_{\vec{R}\vec{\Delta}} \sum_{\sigma\sigma'} c^{+}_{\vec{R}\sigma} c_{\vec{R}\sigma} c^{+}_{\vec{R}\sigma'} c_{\vec{R}\sigma'}$$

- and any combination of matrix elements...

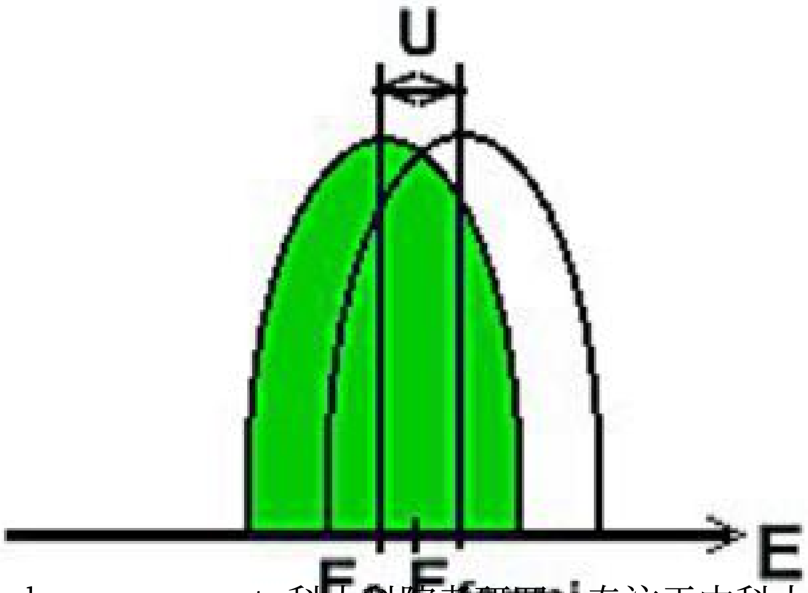
Mott-Hubbard transition, insulating (Mott) phase

Case 1: Strong coupling, **U/t >> 1**: Mott insulating state for a half-filled system. The density of states (available states for adding or removing particle) consits of 2 "*Hubbard bands*" at E_0 and E_0+U. The system is insulating if E_{fermi} is between the bands. This phase is antiferromagnetic, remember the Heisenberg term.

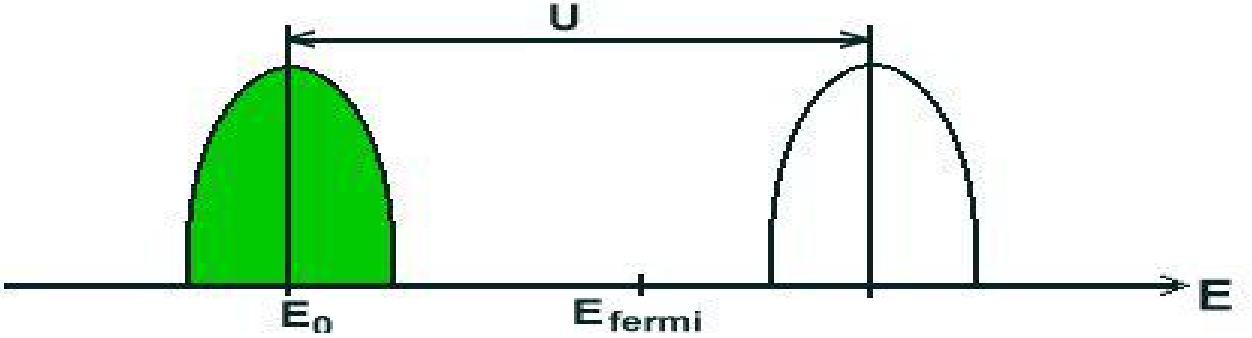


Mott-Hubbard transition, metallic phase

Case 2: t/U>>1, **weak coupling**: Gap disappears, density of states unchanged to simple tight-binding; the Fermi energy now lies in the band middle and the system is metallic. This transition from insulating to metallic due to changes in U/t is called ***Mott-Hubbard transition.***



Mott-Hubbard transition



$T\uparrow$,下*Hubbard* 带的 $e\rightarrow$ 上*Hubbard* 带，形成电子一空穴对 激子：

$$V=-\frac{e^2}{4\pi\varepsilon_0\varepsilon r}$$

$T\uparrow\uparrow$，上*Hubbard* 带上有足够多电子，屏蔽作用使电子一空穴对 减为：

$$V=-\frac{e^2}{4\pi\varepsilon_0\varepsilon r}e^{-k_0 r}$$

当电子浓度到达临界值，使屏蔽长度 $1/k_0$短于电子一空穴对的尺度a_0：

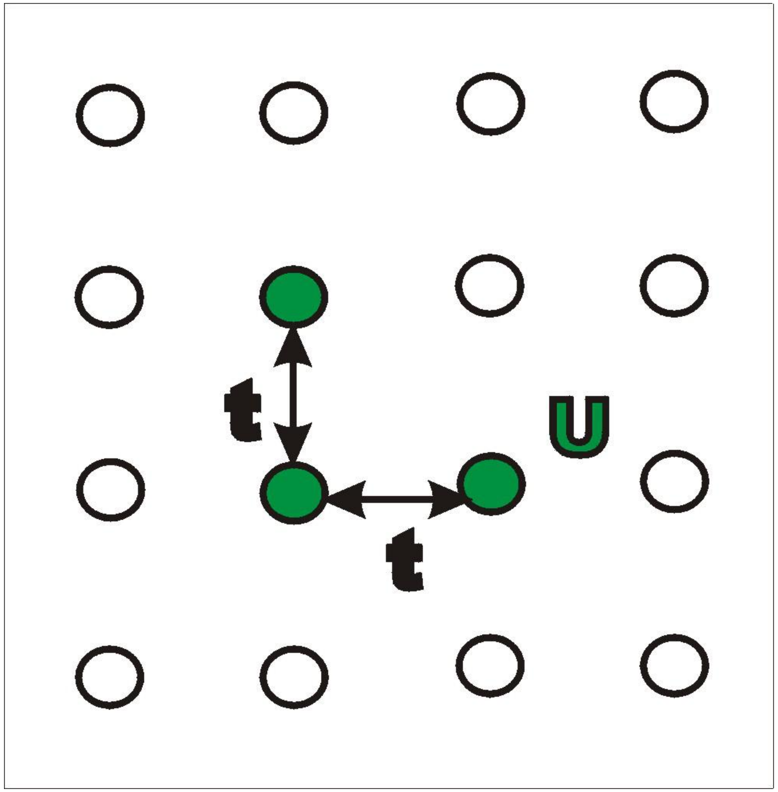
$a_0k_0>1$

时，束缚解除，电导率急剧增加，过渡到金属态

Some Examples...

Let's look at the following case:

<u>2D square lattice, the band we restrict to is half filled</u>



$t, U \neq 0$

Antiferromagnetism for half-filling

$$H=\sum_{\vec{R}\sigma}\sum_{\vec{\Delta}n.n.}tc^{+}_{\vec{R}\sigma}c_{\vec{R}+\vec{\Delta}\sigma}+U\sum_{\vec{R}}c^{+}_{\vec{R}\uparrow}c_{\vec{R}\uparrow}c^{+}_{\vec{R}\downarrow}c_{\vec{R}\downarrow}$$

U/t>>1, strong coupling: Spin-spin interaction expected (direct exchange interaction, RKKY interaction, super-exchange interaction): virtual hopping is introduced, treated as perturbation. Calculation and operator relations yield as only dynamical part

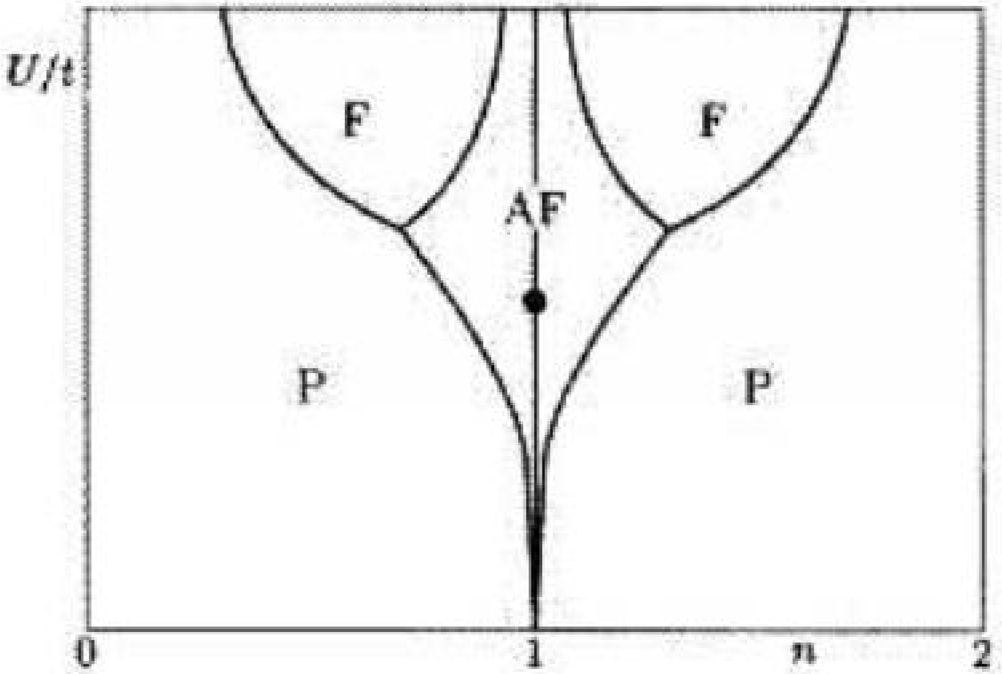
$$H'=\frac{2t^2}{\underbrace{U}_{>0}}\sum_{\vec{R}\vec{\Delta}}\vec{S}_{\vec{R}}\vec{S}_{\vec{R}+\vec{\Delta}}=J\sum_{\vec{R}\vec{\Delta}}\vec{S}_{\vec{R}}\vec{S}_{\vec{R}+\vec{\Delta}}$$

This is exactly the **Heisenberg Hamiltonian** for antiferromagnetic exchange coupling with coupling constant J.

Dependence of phases on U/t and n (where n=number of electrons/lattice site)

- **The following graph is shown without any warranty: (Perturbation theory can not be applied in the mid region of U/t)**

Graph from P. Fazekas, Electron correlation and magnetism



Limits of the model

- The Hamiltonian is in principle applicable for every solid state problem; often, a screened potential instead of the unscreened Coulomb potential is used

- Up to now, the problem is to find calculable wavefunctions; the problem is often not analytically solvable. The advantage of the Hamiltonian, not to be restricted to very special conditions, is the disadvantage during the calculation

Conclusions

- Hubbard Model is derived from many-fermion Hamiltonian
- Is a powerful model to describe phases in terms of interactions

Graphs taken from:

Theoretische Festkörperphysik / Gerd Czycholl.
- Braunschweig ; Wiesbaden : Vieweg, 2000

Lecture notes on electron correlation and magnetism / Patrik Fazekas.
- Singapore : World Scientific, 1999

Thanks to Gerd Czycholl for writing the book „Theoretische Festkörperphysik“

Hubbard处理干净系统的，Anderson模型则被用来处理包含杂质的系统。近藤Hamilton量：

$H=\sum_{k\delta} E(\vec{k})n_{\vec{k}\delta}+J\vec{S}\cdot\vec{s}$　$\vec{S}$:杂质的局域自旋

$\vec{s}=\sum_{kk'} c^{+}_{k\sigma}\sigma_{\sigma\sigma'}c_{k'\sigma'}$　为自由电子在杂质附近的局域自旋密度

J为$\vec{S}$与$\vec{s}$间的交换作用积分。

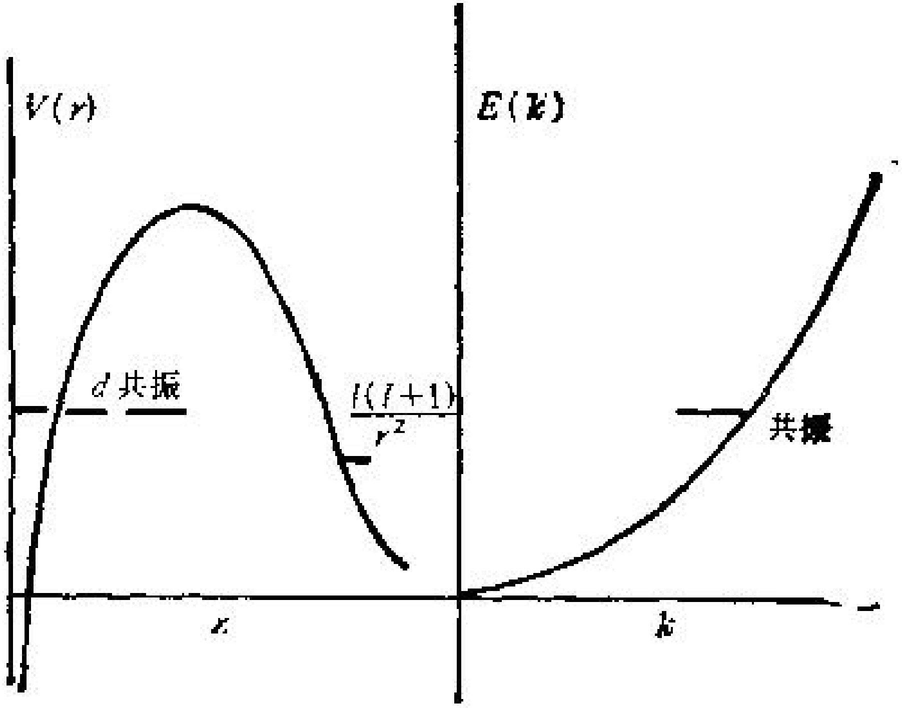
这一理论对$\vec{S}$的存在未加论证。

引入在位相关能U,并为描述杂质原子引入附加轨道ϕ_d，它处于自由电子的$Fermi$面附近，其占据数为$n_{d\sigma}$，产生数符为$c^{+}_{d\sigma}$，

Anderson　Hamilton :

$$H=\sum_{k\delta}E(\vec{k})n_{\vec{k}\delta}+U\hat{n}_{d\uparrow}\hat{n}_{d\downarrow}+E_d(\hat{n}_{d\uparrow}+\hat{n}_{d\downarrow})+\sum_{k\delta}V_{dk}(C^{+}_{d\delta}C_{k\delta}+c.c.)$$

$d-k$隧穿项 V_{dk} ：使局域轨道 ϕ_d通过离心力势垒的隧穿　过程进入 $Friedel$共振态



由于穿过离心力势垒的隧道效应所引起的d电子共振

共振宽度：$\Delta = \pi(V_{dk}^2)\rho(E_d)$　ρ为态密度。

如$E_d < E_F$，　$\Delta / U < \pi$，共振态将分裂

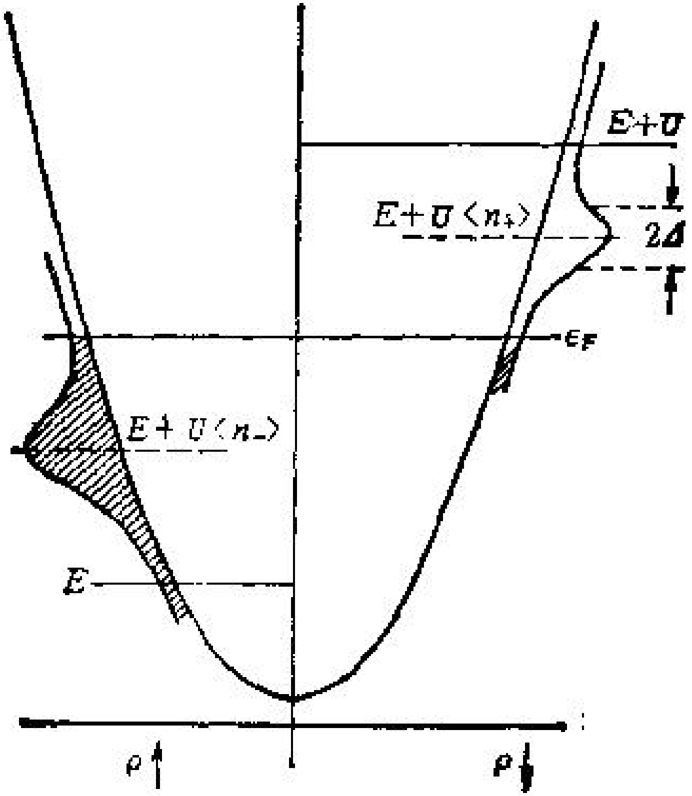


图1.2.7　磁性引起的能级自旋劈裂

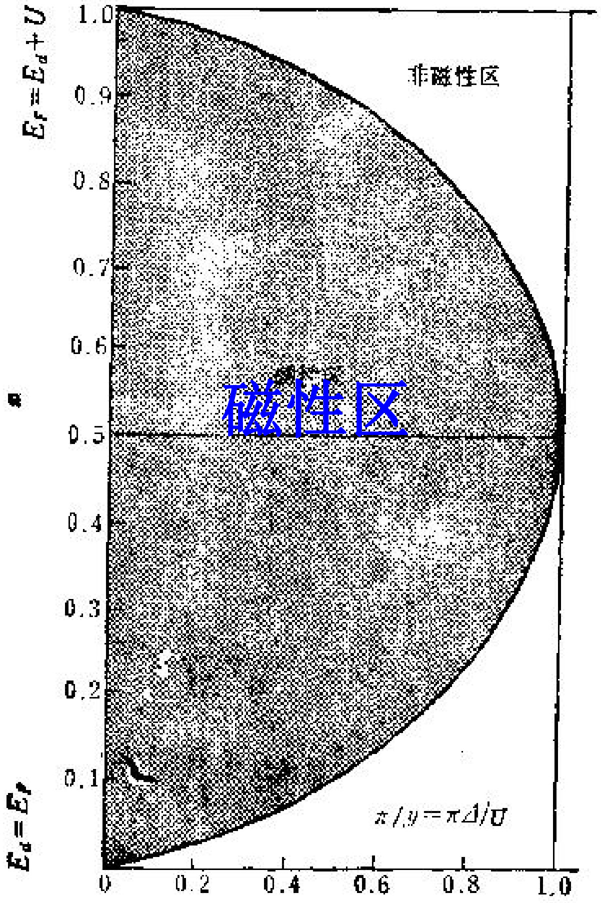


图1.2.8　Anderson 模型的磁性区域

局域态ϕ_d与被散射的自由电子态 相混合：

虽不存在局域束缚电子 态，却存在局域磁距。

*Anderson*与*Kondo*等效：

$$J=\frac{2\Delta}{\pi}\left(\frac{1}{E_d}-\frac{1}{E_d+U}\right)$$