

Chapter 1: Phase in Quantum Mechanics

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$$i\hbar \frac{\partial}{\partial t} |\psi\rangle = H(t) |\psi\rangle \quad (1)$$

$$|\psi(t)\rangle = |\psi(t)| e^{i\phi(t)} \quad (2)$$

1 Berry's Phase

H 不含时

$$H |n\rangle = E_n |n\rangle \quad (3)$$

E_n 是本征值, $|n\rangle$ 是本征态。本征态构成正交完备基, 可以用来展开

$$|\psi(t)\rangle = \sum_n c_n(t) |n\rangle \quad (4)$$

$$c_n(t) = \langle n | \psi(t) \rangle \quad (5)$$

$$|\psi(t)\rangle = \sum_n \langle n | \psi(t) \rangle |n\rangle = \sum_n |n\rangle \langle n | \psi(t) \rangle \quad (6)$$

得到单位算符 $\sum_n |n\rangle \langle n| = 1$ 。将 $|\psi\rangle(t)$ 代入薛定谔方程

$$i\hbar \frac{\partial}{\partial t} \sum_n c_n(t) |n\rangle = H \sum_n c_n(t) |n\rangle = \sum_n c_n(t) H |n\rangle = \sum_n c_n(t) E_n |n\rangle \quad (7)$$

将 $\langle m|$ 作用在方程两边

$$i\hbar \frac{\partial}{\partial t} \sum_n c_n(t) \langle m | n \rangle = \sum_n c_n(t) E_n \langle m | n \rangle \quad (8)$$

$$i\hbar \frac{\partial}{\partial t} c_m(t) = E_m c_m(t) \quad (9)$$

$$i\hbar \frac{1}{c_m(t)} \frac{\partial}{\partial t} c_m(t) = E_m \quad (10)$$

$$\int_0^t i\hbar \frac{1}{c_m(t')} \frac{\partial}{\partial t'} c_m(t') dt' = \int_0^t E_m dt' \quad (11)$$

$$i\hbar |\ln c_m(t) - \ln c_m(0)| = E_m(t)t \quad (12)$$

$$c_m(t) = c_m(0) e^{-i \frac{E_m(t)}{\hbar} t} \quad (13)$$

$$|\psi(t)\rangle = \sum_n c_n(t) |n\rangle = \sum_n c_n(0) e^{-i \frac{E_n(t)}{\hbar} t} |n\rangle \quad (14)$$

设 $|\psi(t)\rangle$ 在一个态上演化

$$c_n(t=0) = \delta_{n,m} \quad (15)$$

$$|\psi(t)\rangle = \sum_n \delta_{n,m} e^{-i \frac{E_n(t)}{\hbar} t} |n\rangle = e^{-i \frac{E_m(t)}{\hbar} t} |m\rangle \quad (16)$$

Slow varying Hamiltonian

$$H(t=0) |n(t=0)\rangle = E_n(t=0) |n(t=0)\rangle \quad (17)$$

当 $H(t) = H$ 时,

$$|\psi(t)\rangle = e^{-i \frac{E_n}{\hbar} t} |n\rangle \quad (18)$$

当 $H(t)$ 含时时, 近似

$$|\psi(t)\rangle \doteq \exp \left[-\frac{i}{\hbar} \int_0^t E_n(t') dt' + i\gamma_n(t) \right] |n(t)\rangle = c_n(t) |n(t)\rangle \quad (19)$$

$$H(t) |\psi(t)\rangle = i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle \quad (20)$$

$$H(t) c_n(t) |n(t)\rangle = i\hbar \frac{\partial}{\partial t} c_n(t) |n(t)\rangle = i\hbar \dot{c}_n(t) |n(t)\rangle + i\hbar c_n(t) |\dot{n}(t)\rangle = E_n(t) c_n(t) |n(t)\rangle \quad (21)$$

$$\dot{c}_n(t) = c_n(t) \left[-\frac{i}{\hbar} E_n(t) + i\dot{\gamma}_n(t) \right] \quad (22)$$

代入 Eq.(21)

$$E_n(t) c_n(t) |n(t)\rangle = E_n(t) c_n(t) |n(t)\rangle - \hbar \dot{\gamma}_n(t) c_n(t) |n(t)\rangle + i\hbar c_n(t) |\dot{n}(t)\rangle \quad (23)$$

即

$$\dot{\gamma}_n(t) |n(t)\rangle = i |\dot{n}(t)\rangle \quad (24)$$

哈密顿量依赖时间往往是通过形式 $H(t) = H(\vec{R}(t))$

$$H(\vec{R}(t)) |n(\vec{R}(t))\rangle = E_n(\vec{R}(t)) |n(\vec{R}(t))\rangle \quad (25)$$

$$|\dot{n}(\vec{R}(t))\rangle = \frac{d}{dt} \vec{R}(t) \cdot \nabla_{\vec{R}} |n(\vec{R}(t))\rangle \quad (26)$$

$$\dot{\gamma}_n(t) |n(\vec{R}(t))\rangle = i \frac{d}{dt} \vec{R}(t) \cdot \nabla_{\vec{R}} |n(\vec{R}(t))\rangle = i \frac{d}{dt} \vec{R}(t) \cdot |\nabla_{\vec{R}} n(\vec{R}(t))\rangle \quad (27)$$

将 $\langle n(\vec{R}(t)) |$ 作用在方程两边

$$\dot{\gamma}_n(t) = i \langle n(\vec{R}(t)) | \nabla_{\vec{R}} n(\vec{R}(t)) \rangle \cdot \dot{\vec{R}}(t) \quad (28)$$

$$\begin{aligned} \gamma_n(t) &= i \int_0^t \langle n(\vec{R}(t')) | \nabla_{\vec{R}} n(\vec{R}(t')) \rangle \cdot \dot{\vec{R}}(t') dt' \\ &= i \int_{\vec{R}(0)}^{\vec{R}(t)} \langle n(\vec{R}(t')) | \nabla_{\vec{R}} n(\vec{R}(t')) \rangle d\vec{R}(t') \\ &= i \int_0^t \langle n(t') | \dot{n}(t') \rangle dt' \end{aligned} \quad (29)$$

代入近似解

$$|\psi(t)\rangle \doteq \exp\left[-\frac{i}{\hbar} \int_0^t E_n(t') dt'\right] \exp\left[-\int_0^t \langle n(t') | \dot{n}(t') \rangle dt'\right] |n(t)\rangle \quad (30)$$

$$\alpha_n(t) = -\frac{1}{\hbar} \int_0^t E_n(t') dt' \quad (31)$$

$$\gamma_n(t) = i \int_0^t \langle n(t') | \dot{n}(t') \rangle dt' \neq 0 \quad (32)$$

$\alpha_n(t)$ 被称为动力学因子 (Dynamic phase factor), $\gamma_n(t)$ 被称为几何因子 (Geometry phase factor), 也叫 Berry's Phase。

给定一特殊情况, $\vec{R}(0) = \vec{R}(T), H(0) = H(T)$, T 时刻

$$\gamma_n(T) = i \int_0^T \langle n(\vec{R}(t')) | \nabla_{\vec{R}} n(\vec{R}(t')) \rangle \cdot d\vec{R}(t') \quad (33)$$

环路积分

$$\gamma_n(C) = i \oint_C \langle n(\vec{R}) | \nabla_{\vec{R}} n(\vec{R}) \rangle \cdot d\vec{R} \quad (34)$$

2 Adiabatic Condition 绝热条件

我们已经得到

$$|\psi(t)\rangle \doteq \exp\left[-\frac{i}{\hbar} \int_0^t E_n(t') dt'\right] \exp\left[-\int_0^t \langle n(t') | \dot{n}(t') \rangle dt'\right] |n(t)\rangle \quad (35)$$

那么上述近似在什么情况下是一个好的近似? $H(t)$ 变化缓慢 (极端情况 $H(t) = H$)。

假定

$$|\psi(0)\rangle = |m\rangle \quad (36)$$

即 $|\psi\rangle$ 在态 $|m\rangle$ 上演化。当 $t \leq 0$ 时, $H(t) = H(0)$; 当 $t > 0$ 时, $H(t)$ 含时。

$$H(0) |m\rangle = E_m(0) |m\rangle \quad (37)$$

将 $|\psi\rangle$ 用一组正交完备积 $|l\rangle$ 展开

$$|\psi(t)\rangle = \sum_l c_l(t) |l(t)\rangle \quad (38)$$

其中

$$c_l(t) = a_l(t) \exp\left[-\frac{i}{\hbar} \int_0^t E_l(t') dt'\right] \quad (39)$$

将 $|\psi(t)\rangle$ 代入薛定谔方程 $i\hbar \frac{\partial}{\partial t} |\psi\rangle = H |\psi\rangle$

$$\begin{aligned} & i\hbar \sum_l \left\{ \dot{a}_l \exp\left[-\frac{i}{\hbar} \int_0^t E_l(t') dt'\right] |l\rangle - \frac{i}{\hbar} a_l E_l \exp\left[-\frac{i}{\hbar} \int_0^t E_l(t') dt'\right] |l\rangle + a_l \exp\left[-\frac{i}{\hbar} \int_0^t E_l(t') dt'\right] |\dot{l}\rangle \right\} \\ & = \sum_l a_l \exp\left[-\frac{i}{\hbar} \int_0^t E_l(t') dt'\right] H(t) |l\rangle = \sum_l a_l \exp\left[-\frac{i}{\hbar} \int_0^t E_l(t') dt'\right] E_l |l\rangle \end{aligned} \quad (40)$$

即

$$i\hbar \sum_l \left\{ \dot{a}_l \exp\left[-\frac{i}{\hbar} \int_0^t E_l(t') dt'\right] |l\rangle + a_l \exp\left[-\frac{i}{\hbar} \int_0^t E_l(t') dt'\right] |\dot{l}\rangle \right\} = 0 \quad (41)$$

将 $\langle n|$ 作用在方程左右两边

$$\sum_l \dot{a}_l(t) \exp\left[-\frac{i}{\hbar} \int_0^t E_l(t') dt'\right] \delta_{n,l} + \sum_l a_l(t) \exp\left[-\frac{i}{\hbar} \int_0^t E_l(t') dt'\right] \langle n(t)|\dot{l}(t)\rangle = 0 \quad (42)$$

即

$$\dot{a}_n(t) \exp\left[-\frac{i}{\hbar} \int_0^t E_n(t') dt'\right] + \sum_l a_l(t) \exp\left[-\frac{i}{\hbar} \int_0^t E_l(t') dt'\right] \langle n(t)|\dot{l}(t)\rangle = 0 \quad (43)$$

$$\dot{a}_n(t) = -a_n(t) \langle n(t)|\dot{n}(t)\rangle - \sum_{l(\neq n)} a_l(t) \exp\left\{\frac{i}{\hbar} \int_0^t [E_n(t') - E_l(t')] dt'\right\} \langle n(t)|\dot{l}(t)\rangle \quad (44)$$

由于我们讨论的是 $|\psi(0)\rangle = |m\rangle$, 当 $|n\rangle = |m\rangle$ 时

$$\dot{a}_m(t) = -a_m(t) \langle m(t)|\dot{m}(t)\rangle - \sum_{l(\neq m)} a_l(t) \exp\left\{\frac{i}{\hbar} \int_0^t [E_m(t') - E_l(t')] dt'\right\} \langle m(t)|\dot{l}(t)\rangle \quad (45)$$

好的近似要求对于任意 $n \neq m$, $a_n(t)$ 都很小, 同样 $\dot{a}_n(t)$ 也很小

$$\begin{aligned} \dot{a}_n(t) &= -a_n(t) \langle n(t)|\dot{n}(t)\rangle - \sum_{l(\neq n)} a_l(t) \exp\left\{\frac{i}{\hbar} \int_0^t [E_n(t') - E_l(t')] dt'\right\} \langle n(t)|\dot{l}(t)\rangle \\ &= -a_n(t) \langle n(t)|\dot{n}(t)\rangle - \sum_{l(\neq n,m)} a_l(t) \exp\left\{\frac{i}{\hbar} \int_0^t [E_n(t') - E_l(t')] dt'\right\} \langle n(t)|\dot{l}(t)\rangle \\ &\quad - a_m(t) \exp\left\{\frac{i}{\hbar} \int_0^t [E_n(t') - E_m(t')] dt'\right\} \langle n(t)|\dot{m}(t)\rangle \end{aligned} \quad (46)$$

当 $n, l \neq m$ 时, $a_n(t)$ 和 $a_l(t)$ 是小量, 因此第一项和第二项是小量, 而 $a_m(t)$ 是大量, 因此要求 $\langle n|\dot{m}\rangle$ 是小量。

由于 $\langle n|\dot{m}\rangle$ 的量纲是 $[\frac{1}{T}]$, 不能形容大小, 因此我们需要寻找参数组成一个无量纲量, 如

$$\left| \frac{\langle n|\dot{m}\rangle \hbar}{E_n - E_m} \right| \ll 1 \quad (47)$$

可以将它等价写成

$$\left| \frac{\hbar \langle n|\dot{H}|m\rangle}{(E_n - E_m)^2} \right| \ll 1 \quad (48)$$

即“绝热条件”。

接下来证明二者等价:

$$H(t) |n(t)\rangle = E_n(t) |n(t)\rangle \quad (49)$$

对时间求导

$$\dot{H}(t) |n(t)\rangle + H(t) |\dot{n}(t)\rangle = \dot{E}_n(t) |n(t)\rangle + E_n(t) |\dot{n}(t)\rangle \quad (50)$$

将 $\langle m|$ 作用在方程两边

$$\langle m(t)|\dot{H}(t)|n(t)\rangle + H(t) \langle m(t)|\dot{n}(t)\rangle = \dot{E}_n(t) \langle m(t)|n(t)\rangle + E_n(t) \langle m(t)|\dot{n}(t)\rangle \quad (51)$$

即

$$\langle m(t)|\dot{H}(t)|n(t)\rangle + E_m \langle m(t)|\dot{n}(t)\rangle = E_n(t) \langle m(t)|\dot{n}(t)\rangle \quad (52)$$

$$\langle m(t)|\dot{H}(t)|n(t)\rangle = [E_n(t) - E_m(t)] \langle m(t)|\dot{n}(t)\rangle \quad (53)$$

$$\langle m(t) | \dot{n}(t) \rangle = \frac{\langle m | \dot{H} | n \rangle}{E_n - E_m} \quad (54)$$

证毕。

$$\begin{aligned} \dot{a}_m(t) &= -a_m(t) \langle m | m \rangle (t) \dot{m}(t) - \sum_{l(\neq m)} a_l(t) \exp \left\{ \frac{i}{\hbar} \int_0^t [E_m(t') - E_l(t')] dt' \right\} \langle m(t) | \dot{l}(t) \rangle \\ &= -a_m(t) \langle m(t) | \dot{m}(t) \rangle \quad (\text{第二项是小量}) \end{aligned} \quad (55)$$

$$\ln a_m(t') \Big|_0^t = - \int_0^t \langle m(t') | \dot{m}(t') \rangle dt' \quad (56)$$

$$a_m(t) = \exp \left[- \int_0^t \langle m(t') | \dot{m}(t') \rangle dt' \right] a_m(0) \quad (57)$$

$$\begin{aligned} |\psi(t)\rangle &= \sum_n a_n(t) \exp \left[- \frac{i}{\hbar} \int_0^t E_n(t) dt' \right] |n(t)\rangle \\ &= a_m(t) \exp \left[- \frac{i}{\hbar} \int_0^t E_m(t) dt' \right] |m(t)\rangle \quad (n \neq m \text{ 都是小量}) \\ &= a_m(t) e^{i\alpha_m(t)} |m(t)\rangle \end{aligned} \quad (58)$$

$$|\psi(t)\rangle = e^{i[\alpha_m(t) + \gamma_m(t)]} |m(t)\rangle \quad (59)$$

Example

已知

$$H(\vec{B}(t)) = -\mu_B \vec{\sigma} \cdot \vec{B}(t) \quad (60)$$

$$\vec{B}(t) = (B_1 \cos 2\omega_0 t, B_1 \sin 2\omega_0 t, B_0) \quad (61)$$

绝热条件成立，求几何因子。

$$\begin{aligned} H(t) &= -\mu_B [B_x \sigma_x + B_y \sigma_y + B_z \sigma_z](t) \\ &= -\mu_B \left(B_x \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} + B_y \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} + B_z \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \right) (t) \\ &= -\mu_B \begin{bmatrix} B_0 & B_1 e^{-i2\omega_0 t} \\ B_1 e^{i2\omega_0 t} & -B_0 \end{bmatrix} \end{aligned} \quad (62)$$

求解方程

$$H(t) |\psi_{\pm}(t)\rangle = E_{\pm} |\psi_{\pm}(t)\rangle \quad (63)$$

得到本征矢和本征值

$$|\psi_{-}(t)\rangle = \begin{bmatrix} \cos \theta \\ \sin \frac{\theta}{2} e^{-i2\omega_0 t} \end{bmatrix} \quad E_{-}(t) = -\mu_B \sqrt{B_0^2 + B_1^2} \quad (64)$$

$$|\psi_{+}(t)\rangle = \begin{bmatrix} -\sin \theta \\ \cos \frac{\theta}{2} e^{i2\omega_0 t} \end{bmatrix} \quad E_{+}(t) = \mu_B \sqrt{B_0^2 + B_1^2} \quad (65)$$

$$\theta = \tan^{-1} \frac{B_1}{B_0} \quad (66)$$

假定 $|\psi(t)\rangle$ 在 $|\psi_{-}(t)\rangle$ 上演化

$$|\psi(t=0)\rangle = |\psi_{-}(t=0)\rangle \quad (67)$$

$$\begin{aligned}
\gamma_-(t) &= i \int_0^t \langle \psi_-(t') | \dot{\psi}_-(t') \rangle dt' \\
&= i \int_0^t \begin{bmatrix} \cos \theta & \sin \frac{\theta}{2} e^{i2\omega_0 t'} \end{bmatrix} \begin{bmatrix} 0 \\ -i2\omega \sin \frac{\theta}{2} e^{-i2\omega_0 t'} \end{bmatrix} dt' \\
&= i \int_0^t (-2i)\omega_0 \sin^2 \frac{\theta}{2} dt' \\
&= 2\omega_0 t \sin^2 \frac{\theta}{2}
\end{aligned} \tag{68}$$

$$\begin{aligned}
|\psi(t)\rangle &= \exp[i\gamma_-(t)] \exp\left[-\frac{i}{\hbar} \int_0^t E_-(t') dt'\right] |\psi_-(t)\rangle \\
&= \exp\left[i2\omega_0 t \sin^2 \frac{\theta}{2}\right] \exp\left[\frac{i}{\hbar} \mu_B \sqrt{B_0^2 + B_1^2} t\right] |\psi_-(t)\rangle
\end{aligned} \tag{69}$$

$$|\psi(T)\rangle = \exp[i\pi(1 - \cos \theta)] \exp\left[\frac{i}{\hbar} \mu_B \sqrt{B_0^2 + B_1^2} T\right] |\psi_-(t)\rangle \tag{70}$$

几何因子

$$\gamma(t) = \pi(1 - \cos \theta) \tag{71}$$

3 Effective field and Degeneracy point

$$\begin{aligned}
\gamma_n(C) &= \oint_C i \langle n(\vec{R}) | \nabla_{\vec{R}} n(\vec{R}) \rangle \cdot d\vec{R} \\
&= - \oint_C \vec{A}_n(\vec{R}) \cdot d\vec{R} \\
&= - \iint_S [\nabla_{\vec{R}} \times \vec{A}_n(\vec{R})] \cdot d\vec{S} \\
&= - \iint_S \vec{B}_n(\vec{R}) \cdot d\vec{S}
\end{aligned} \tag{72}$$

其中

$$\vec{A}_n(\vec{R}) = i \langle n(\vec{R}) | \nabla_{\vec{R}} n(\vec{R}) \rangle \vec{A}_n(\vec{R}) \tag{73}$$

$$\vec{B}_n(\vec{R}) = \nabla_{\vec{R}} \times \vec{A}_n(\vec{R}) \tag{74}$$

$\vec{A}_n(\vec{R})$ 为矢势 (vector potential), $\vec{B}_n(\vec{R})$ 为有效场。由于 $\vec{A}_n(\vec{R})$ 是实数, 接下来证明 $\langle n(\vec{R}) | \nabla_{\vec{R}} n(\vec{R}) \rangle$ 是纯虚数。即证明

$$\langle n(\vec{R}) | \nabla_{\vec{R}} n(\vec{R}) \rangle = - \langle n(\vec{R}) | \nabla_{\vec{R}} n(\vec{R}) \rangle^\dagger \tag{75}$$

已知

$$\langle n(\vec{R}) | n(\vec{R}) \rangle = 1 \tag{76}$$

方程两边作用 $\nabla_{\vec{R}}$

$$\begin{aligned}
\nabla_{\vec{R}} \langle n(\vec{R}) | n(\vec{R}) \rangle &= \langle \nabla_{\vec{R}} n(\vec{R}) | n(\vec{R}) \rangle + \langle n(\vec{R}) | \nabla_{\vec{R}} n(\vec{R}) \rangle \\
&= \langle n(\vec{R}) | \nabla_{\vec{R}} n(\vec{R}) \rangle^\dagger + \langle n(\vec{R}) | \nabla_{\vec{R}} n(\vec{R}) \rangle = 0
\end{aligned} \tag{77}$$

因此

$$\langle n(\vec{R}) | \nabla_{\vec{R}} n(\vec{R}) \rangle = - \langle n(\vec{R}) | \nabla_{\vec{R}} n(\vec{R}) \rangle^\dagger \tag{78}$$

即

$$\langle n(\vec{R}) | \nabla_{\vec{R}} n(\vec{R}) \rangle = i \operatorname{Im} \langle n(\vec{R}) | \nabla_{\vec{R}} n(\vec{R}) \rangle \quad (79)$$

$$\gamma_n(C) = -\operatorname{Im} \oint_C \langle n(\vec{R}) | \nabla_{\vec{R}} n(\vec{R}) \rangle \cdot d\vec{R} \quad (80)$$

$$\vec{A}_n(\vec{R}) = \operatorname{Im} \langle n(\vec{R}) | \nabla_{\vec{R}} n(\vec{R}) \rangle \quad (81)$$

$$\begin{aligned} \vec{B}_n(\vec{R}) &= \nabla_{\vec{R}} \times \vec{A}_n(\vec{R}) = \nabla_{\vec{R}} \times \operatorname{Im} \langle n(\vec{R}) | \nabla_{\vec{R}} n(\vec{R}) \rangle \\ &= \operatorname{Im} \nabla_{\vec{R}} \times \langle n(\vec{R}) | \nabla_{\vec{R}} n(\vec{R}) \rangle \end{aligned} \quad (82)$$

接下来证明 $\vec{B}_n(\vec{R})$ 另外一种形式:

$$\vec{B}_n(\vec{R}) = \operatorname{Im} \sum_{m(\neq n)} \frac{\langle n(\vec{R}) | \nabla_{\vec{R}} H | m(\vec{R}) \rangle \times \langle m(\vec{R}) | \nabla_{\vec{R}} H | n(\vec{R}) \rangle}{[E_n(\vec{R}) - E_m(\vec{R})]^2} \quad (83)$$

证明如下

$$\begin{aligned} \vec{B}_n(\vec{R}) &= \operatorname{Im} \nabla_{\vec{R}} \times \langle n(\vec{R}) | \nabla_{\vec{R}} n(\vec{R}) \rangle \\ &= \operatorname{Im} \left[\langle \nabla_{\vec{R}} n(\vec{R}) | \times | \nabla_{\vec{R}} n(\vec{R}) \rangle + \langle n(\vec{R}) | \nabla_{\vec{R}} \times \nabla_{\vec{R}} n(\vec{R}) \rangle \right] \end{aligned} \quad (84)$$

其中

$$\nabla_{\vec{R}} \times \nabla_{\vec{R}} n(\vec{R}) = 0 \quad (85)$$

当 \vec{v} 不是纯虚数或实数时, $\vec{v} \times \vec{v}^\dagger \neq 0$

$$\begin{aligned} \vec{B}_n(\vec{R}) &= \operatorname{Im} \left[\langle \nabla_{\vec{R}} n(\vec{R}) | \times | \nabla_{\vec{R}} n(\vec{R}) \rangle \right] \\ &= \operatorname{Im} \left[\langle \nabla_{\vec{R}} n(\vec{R}) | \left(\sum_m | m(\vec{R}) \rangle \langle \vec{R} | \right) \times | \nabla_{\vec{R}} n(\vec{R}) \rangle \right] \\ &= \operatorname{Im} \sum_m \left[\langle \nabla_{\vec{R}} n(\vec{R}) | m(\vec{R}) \rangle \times \langle m(\vec{R}) | \nabla_{\vec{R}} n(\vec{R}) \rangle \right] \\ &= \operatorname{Im} \left[\sum_{m(\neq n)} \langle \nabla_{\vec{R}} n(\vec{R}) | m(\vec{R}) \rangle \times \langle m(\vec{R}) | \nabla_{\vec{R}} n(\vec{R}) \rangle + \langle \nabla_{\vec{R}} n(\vec{R}) | n(\vec{R}) \rangle \times \langle n(\vec{R}) | \nabla_{\vec{R}} n(\vec{R}) \rangle \right] \\ &= \operatorname{Im} \sum_{m(\neq n)} \langle \nabla_{\vec{R}} n(\vec{R}) | m(\vec{R}) \rangle \times \langle m(\vec{R}) | \nabla_{\vec{R}} n(\vec{R}) \rangle \end{aligned} \quad (86)$$

又由于我们需要证明

$$\vec{B}_n(\vec{R}) = \operatorname{Im} \sum_{m(\neq n)} \frac{\langle n(\vec{R}) | \nabla_{\vec{R}} H | m(\vec{R}) \rangle \times \langle m(\vec{R}) | \nabla_{\vec{R}} H | n(\vec{R}) \rangle}{[E_n(\vec{R}) - E_m(\vec{R})]^2} \quad (87)$$

即证

$$\frac{\langle m | (\nabla_{\vec{R}} H) | n \rangle}{E_n - E_m} = \langle m | \nabla_{\vec{R}} | n \rangle \quad (88)$$

由

$$H | n \rangle = E_n(\vec{R}) | n \rangle \quad (89)$$

方程两边作用 $\nabla_{\vec{R}}$

$$(\nabla_{\vec{R}} H) | n \rangle + H \nabla_{\vec{R}} | n \rangle = \nabla_{\vec{R}} E_n(\vec{R}) | n \rangle + E_n(\vec{R}) \nabla_{\vec{R}} | n \rangle \quad (90)$$

方程两边作用 $\langle m|$

$$\langle m|(\nabla_{\vec{R}}H)|n\rangle + \langle m|H\nabla_{\vec{R}}|n\rangle = \langle m|\nabla_{\vec{R}}E_n(\vec{R})|n\rangle + \langle m|E_n(\vec{R})\nabla_{\vec{R}}|n\rangle \quad (91)$$

由于 Hamilton 是厄米的, 又由于 $\nabla_{\vec{R}}E_n(\vec{R})$ 与内积空间无关

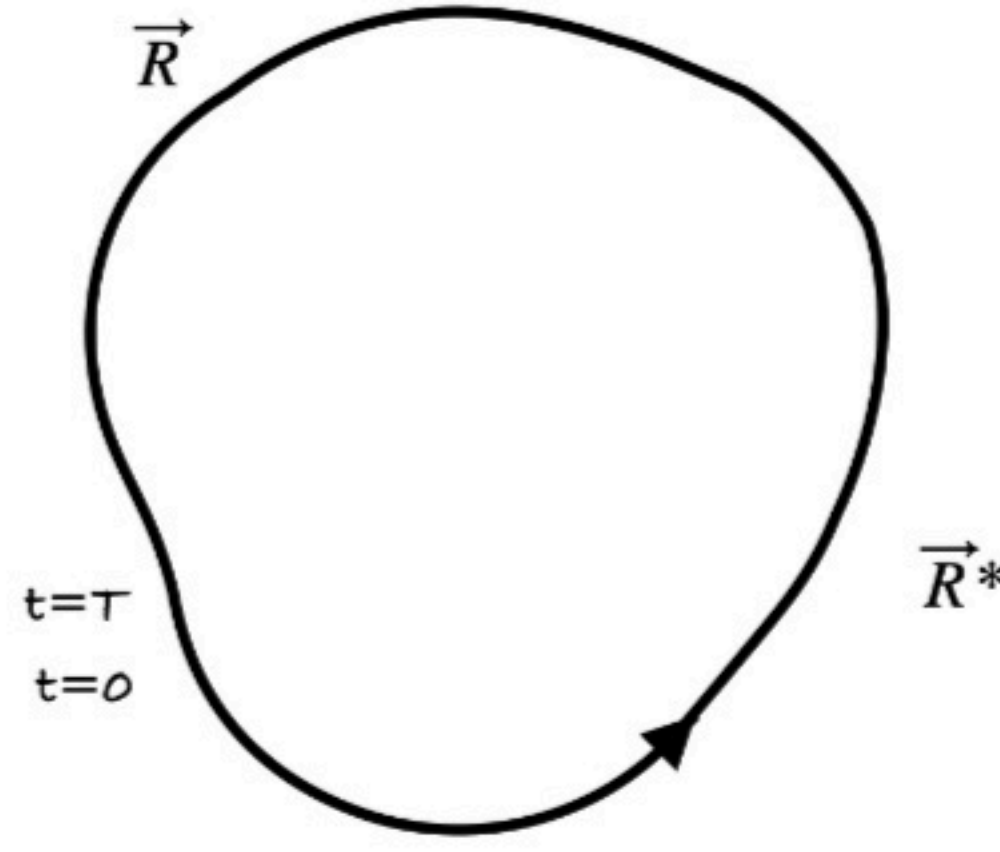
$$\langle m|(\nabla_{\vec{R}}H)|n\rangle + \langle m|E_m(\vec{R})\nabla_{\vec{R}}|n\rangle = \langle m|E_n(\vec{R})\nabla_{\vec{R}}|n\rangle \quad (92)$$

即

$$\langle m|(\nabla_{\vec{R}}H)|n\rangle = (E_n - E_m)\langle m|\nabla_{\vec{R}}|n\rangle \quad (93)$$

$$\langle m|(\nabla_{\vec{R}}H)|n\rangle^\dagger = (E_n - E_m)\langle m|\nabla_{\vec{R}}|n\rangle^\dagger \quad (94)$$

证毕。



假定 $\vec{R}(0) = \vec{R}(T)$, $H(0) = H(T)$, 在 \vec{R} 空间中有一点 \vec{R}^* , \vec{R}^* 不在环上但接近环, 假定 \vec{R}^* 有两个态 $|m\rangle$ 和 $|n\rangle$, $|m\rangle$ 和 $|n\rangle$ 简并且 $|m\rangle \neq |n\rangle$ 。

$$H(\vec{R}^*)|m(\vec{R}^*)\rangle = E_m(\vec{R}^*)|m(\vec{R}^*)\rangle \quad (95)$$

$$H(\vec{R}^*)|n(\vec{R}^*)\rangle = E_n(\vec{R}^*)|n(\vec{R}^*)\rangle \quad (96)$$

$$E_m(\vec{R}^*) = E_n(\vec{R}^*) = E(\vec{R}^*) \quad (97)$$

只考虑简并态 $|m\rangle$ 和 $|n\rangle$, 记为 $|+\rangle$ 和 $|-\rangle$ 。

$$\vec{B}_+(\vec{R}) = \text{Im} \frac{\langle +|\nabla_{\vec{R}}H|-\rangle \times \langle -|\nabla_{\vec{R}}H|+\rangle}{[E_+(\vec{R}) - E_-(\vec{R})]^2} \quad (98)$$

$$\vec{B}_-(\vec{R}) = \text{Im} \frac{\langle -|\nabla_{\vec{R}}H|+\rangle \times \langle +|\nabla_{\vec{R}}H|-\rangle}{[E_-(\vec{R}) - E_+(\vec{R})]^2} \quad (99)$$

$$H(\vec{R}^*)|\pm(\vec{R}^*)\rangle = E_\pm(\vec{R}^*)|\pm(\vec{R}^*)\rangle = E(\vec{R}^*)|\pm(\vec{R}^*)\rangle \quad (100)$$

普遍情况下

$$H(\vec{R}) = \begin{bmatrix} H_{++}(\vec{R}) & H_{+-}(\vec{R}) \\ H_{-+}(\vec{R}) & H_{--}(\vec{R}) \end{bmatrix} \quad (101)$$

假定

$$H(\vec{R}^*) = \begin{bmatrix} H_{++}(\vec{R}^*) & 0 \\ 0 & H_{--}(\vec{R}^*) \end{bmatrix} = \begin{bmatrix} E(\vec{R}^*) & 0 \\ 0 & E(\vec{R}^*) \end{bmatrix} \quad (102)$$

取 $H(\vec{R}^*) = 0$, 由于 \vec{R}^* 与 \vec{R} 离得很近, $H(\vec{R})$ 可用 \vec{R}^* 展开

$$H(\vec{R}) = a\sqrt{(\vec{R} - \vec{R}^*)^2} + b\vec{\sigma} \cdot (\vec{R} - \vec{R}^*) \quad (103)$$

移动坐标系令 $\vec{R}^* = 0$, 则

$$H(\vec{R}) = aR + b\vec{\sigma} \cdot \vec{R} \quad (104)$$

令 $a = 0, b = 1$, 简化 $H(\vec{R})$ (只要物理本质存在, 如何简化并不重要)

$$H(\vec{R}) = \vec{\sigma} \cdot \vec{R} = \begin{bmatrix} z & x - iy \\ x + iy & -z \end{bmatrix} \quad (105)$$

求 $H(\vec{R})$ 的本征态和本征值

$$H(\vec{R}) = \vec{\sigma} \cdot \vec{R} = \begin{vmatrix} z - E & x - iy \\ x + iy & -z - E \end{vmatrix} = E^2 - (x^2 + y^2 + z^2) = 0 \quad (106)$$

$$E_+ = -E_- = R \quad (107)$$

$$\nabla_{\vec{R}} H(\vec{R}) = \nabla_{\vec{R}} (\vec{\sigma} \cdot \vec{R}) = \vec{\sigma} \quad (108)$$

代回 Eq.(98), 得

$$\vec{B}_{+x}(\vec{R}) = \text{Im} \frac{\langle + | \sigma_y | - \rangle \langle - | \sigma_z | + \rangle}{2R^2} = 0 \quad (109)$$

$$\vec{B}_{+y}(\vec{R}) = \text{Im} \frac{\langle + | \sigma_z | - \rangle \langle - | \sigma_x | + \rangle}{2R^2} = 0 \quad (110)$$

$$\vec{B}_{+z}(\vec{R}) = \text{Im} \frac{\langle + | \sigma_x | - \rangle \langle - | \sigma_y | + \rangle}{2R^2} = \frac{1}{2R^2} \quad (111)$$

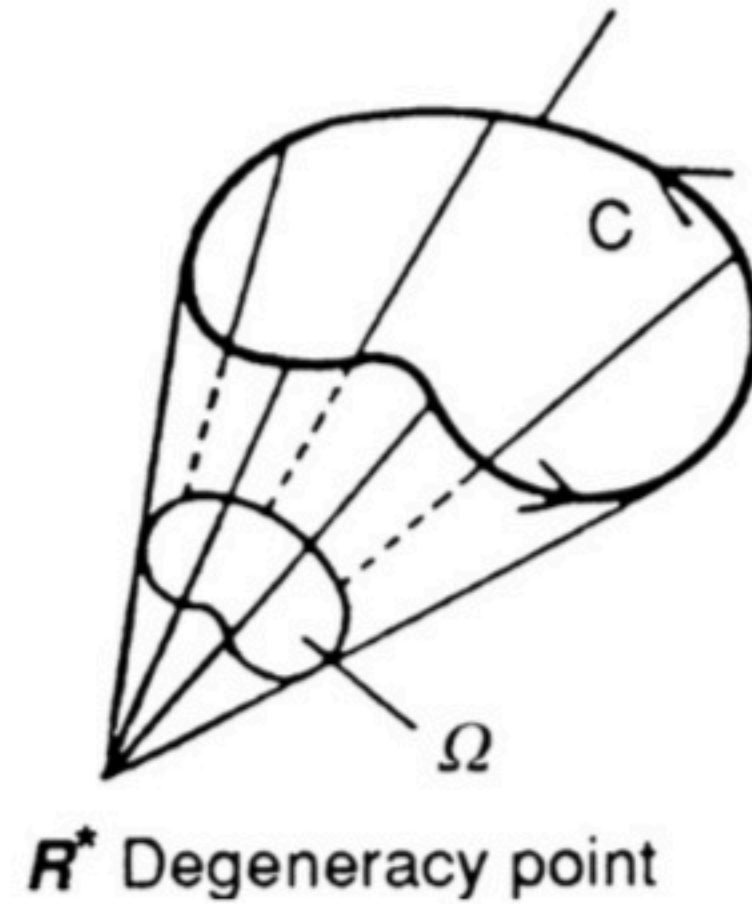
即

$$\vec{B}_+(\vec{R}) = \frac{\vec{R}}{2R^3} \quad (112)$$

这种形式的磁场是由磁单极 $\rho_m(\vec{R}) = -\frac{1}{2}\delta(\vec{R})$ 引起的, 而自然界中并不存在磁单极, 因此也不存在形如上式的磁场。

Anyway, 我们来计算 Berry's phase

$$\gamma_+(C) = -\gamma_-(C) = -\iint_S \vec{B}_+(\vec{R}) \cdot d\vec{S} = -\iint_S \frac{\vec{R}}{2R^3} \cdot d\vec{S} = -\frac{1}{2}\Omega(C) \quad (113)$$



4 Aharanov-Ananda Phase

接下来讨论和 Berry's phase 关系很大的一个概念: Aharanov-Ananda Phase。
哈密顿量变化很慢时,

$$|\psi(t)\rangle \doteq \exp[i\gamma_n(t)] \exp[i\alpha_n(t)] |n(t)\rangle \quad (114)$$

当 $H(T) = H(0)$ 时

$$\begin{aligned} |\psi(T)\rangle &\doteq \exp[i\gamma_n(C)] \exp[i\alpha_n(t)] |n(T)\rangle \\ &= \exp[i\gamma_n(C)] \exp[i\alpha_n(t)] |n(0)\rangle \\ &= \exp[i\gamma_n(C)] \exp[i\alpha_n(t)] |\psi(0)\rangle \end{aligned} \quad (115)$$

$$\alpha_n(t) = -\frac{1}{\hbar} \int_0^t E_n(t') dt' \quad (116)$$

将 $|\phi(t)\rangle$ 写成

$$|\psi(t)\rangle = e^{i\phi} |\psi(0)\rangle \quad (\phi \neq \alpha) \quad (117)$$

接下来讨论 $|\psi(t)\rangle$ 不在一个态上演化。由于 $|\psi(t)\rangle$ 不在一个态上演化, 动力学因子 α 不再写成如上形式, 因此我们需要重新定义动力学因子:

$$\alpha(T) = -\frac{1}{\hbar} \int_0^T dt \langle \psi(x) | H(t) | \psi(t) \rangle \quad (118)$$

因此几何因子

$$\gamma = \phi - \alpha \quad (119)$$

定义

$$|\tilde{\psi}(t)\rangle = e^{-if(t)} |\psi(t)\rangle \quad (120)$$

要求

$$f(T) - f(0) = \phi \quad (121)$$

将 $|\psi(t)\rangle = e^{if(t)} |\tilde{\psi}(t)\rangle$ 代入薛定谔方程

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = i\hbar \frac{\partial}{\partial t} [e^{if(t)} |\tilde{\psi}(t)\rangle] = -\hbar \dot{f}(t) |\psi(t)\rangle + i\hbar e^{if(t)} \frac{\partial}{\partial t} |\tilde{\psi}(t)\rangle = H(t) |\psi(t)\rangle \quad (122)$$

方程两边作用 $\langle \psi(t) |$

$$-\hbar \dot{f}(t) + i\hbar \langle \psi(t) | e^{if(t)} \frac{\partial}{\partial t} |\tilde{\psi}(t)\rangle = -\hbar \dot{f}(t) + i\hbar \langle \tilde{\psi}(t) | \frac{\partial}{\partial t} |\tilde{\psi}(t)\rangle = \langle \psi(t) | H(t) | \psi(t) \rangle \quad (123)$$

方程两边积分 $\int_0^t dt'$

$$f(T) - f(0) = \int_0^t dt' \langle \tilde{\psi}(t') | i \frac{\partial}{\partial t'} |\tilde{\psi}(t')\rangle - \frac{1}{\hbar} \int_0^t dt' \langle \psi(t') | H(t') | \psi(t') \rangle \quad (124)$$

即

$$\phi = \int_0^t dt' \langle \tilde{\psi}(t') | i \frac{\partial}{\partial t'} |\tilde{\psi}(t')\rangle + \alpha \quad (125)$$

故

$$\alpha(T) = -\frac{1}{\hbar} \int_0^T dt \langle \psi(t) | H(t) | \psi(t) \rangle \quad (126)$$

$$\gamma(T) = \int_0^T dt \left\langle \tilde{\psi}(t) \left| i \frac{\partial}{\partial t} \right| \tilde{\psi}(t) \right\rangle \quad (127)$$

当哈密顿量 $H(t) = H$ 时, γ 也不为 0。

假定存在特殊情况 $H(t) = H$, 且 $|\psi(t)\rangle$ 在两个态上演化

$$H |\psi_{\pm}\rangle = E_{\pm} |\psi_{\pm}\rangle \quad (128)$$

设

$$|\psi(0)\rangle = \cos \frac{\theta}{2} |\psi_{-}\rangle + \sin \frac{\theta}{2} |\psi_{+}\rangle \quad (129)$$

$$\begin{aligned} |\psi(t)\rangle &= e^{-\frac{iE_{-}t}{\hbar}} \cos \frac{\theta}{2} |\psi_{-}\rangle + e^{-\frac{iE_{+}t}{\hbar}} \sin \frac{\theta}{2} |\psi_{+}\rangle \\ &= e^{-\frac{iE_{-}t}{\hbar}} \left[\cos \frac{\theta}{2} |\psi_{-}\rangle + e^{-\frac{i(E_{+}-E_{-})t}{\hbar}} \sin \frac{\theta}{2} |\psi_{+}\rangle \right] \end{aligned} \quad (130)$$

在 T 时刻刚好一个周期, 有

$$\frac{(E_{+} - E_{-})T}{\hbar} = 2\pi \quad (131)$$

$$|\psi(T)\rangle = e^{-\frac{iE_{-}T}{\hbar}} \left[\cos \frac{\theta}{2} |\psi_{-}\rangle + \sin \frac{\theta}{2} |\psi_{+}\rangle \right] = e^{-\frac{iE_{-}T}{\hbar}} |\psi(0)\rangle \quad (132)$$

total phase

$$\phi = -\frac{E_{-}T}{\hbar} \quad (133)$$

Dynamic phase

$$\begin{aligned} \alpha &= -\frac{1}{\hbar} \int_0^T \langle \psi(t) | H(t) | \psi(t) \rangle dt \\ &= -\frac{1}{\hbar} \int_0^T \left[\cos \frac{\theta}{2} \langle \psi_{-} | + e^{\frac{i(E_{+}-E_{-})t}{\hbar}} \sin \frac{\theta}{2} \langle \psi_{+} | \right] H(t) \left[\cos \frac{\theta}{2} |\psi_{-}\rangle + e^{-\frac{i(E_{+}-E_{-})t}{\hbar}} \sin \frac{\theta}{2} |\psi_{+}\rangle \right] dt \\ &= -\frac{1}{\hbar} \int_0^T \left(\cos^2 \frac{\theta}{2} E_{-} + \sin^2 \frac{\theta}{2} E_{+} \right) dt \\ &= -\frac{1}{\hbar} \left(\cos^2 \frac{\theta}{2} E_{-} + \sin^2 \frac{\theta}{2} E_{+} \right) T \end{aligned} \quad (134)$$

A-A phase

$$\begin{aligned} \gamma &= \phi - \alpha \\ &= -\frac{E_{-}T}{\hbar} + \frac{1}{\hbar} \left(\cos^2 \frac{\theta}{2} E_{-} + \sin^2 \frac{\theta}{2} E_{+} \right) T \\ &= \frac{1}{\hbar} (E_{+} - E_{-})T \left(\frac{1 - \cos \theta}{2} \right) = \pi(1 - \cos \theta) \neq 0 \end{aligned} \quad (135)$$

当 $|\psi(t)\rangle$ 在一个态上演化时, 即 $\theta = 0$ 或 $\theta = \pi$ 时

$$\gamma = \begin{cases} 0 & \theta = 0 \\ 2\pi & \theta = \pi \end{cases} \quad (136)$$

因此在一般情况下, $\gamma \neq 0$ 。

Example: Quantum Harmonic Oscillator

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 \quad (137)$$

$$E_n = (n + \frac{1}{2})\hbar\omega \quad (138)$$

$$|\psi(t=0)\rangle = \cos \frac{\theta}{2} |\psi_0\rangle + \sin \frac{\theta}{2} |\psi_1\rangle \quad (139)$$

$$\begin{aligned} |\psi(t)\rangle &= e^{-\frac{i\omega t}{2}} \cos \frac{\theta}{2} |\psi_0\rangle + e^{-\frac{i\omega t}{2}} \sin \frac{\theta}{2} |\psi_1\rangle \\ &= e^{-\frac{i\omega t}{2}} \left(\cos \frac{\theta}{2} |\psi_0\rangle + e^{-i\omega t} \sin \frac{\theta}{2} |\psi_1\rangle \right) \end{aligned} \quad (140)$$

又

$$T = \frac{2\pi}{\omega} \quad (141)$$

因此

$$|\psi(T)\rangle = e^{-i\pi} \left(\cos \frac{\theta}{2} |\psi_0\rangle + \sin \frac{\theta}{2} |\psi_1\rangle \right) = e^{-i\pi} |\psi(0)\rangle \quad (142)$$

Total phase

$$\phi = -\pi \quad (143)$$

Dynamic phase

$$\begin{aligned} \alpha &= -\frac{1}{\hbar} \int_0^T \langle \psi(t) | H(t) | \psi(t) \rangle dt \\ &= -\frac{1}{\hbar} \int_0^T \left[\cos \frac{\theta}{2} \langle \psi_0 | + e^{\frac{i\omega t}{2}} \sin \frac{\theta}{2} \langle \psi_1 | \right] H(t) \left[\cos \frac{\theta}{2} |\psi_0\rangle + e^{-\frac{i\omega t}{2}} \sin \frac{\theta}{2} |\psi_1\rangle \right] dt \\ &= -\frac{1}{2} \left(\cos^2 \frac{\theta}{2} + 3 \sin^2 \frac{\theta}{2} \right) \omega T \\ &= -\pi(2 - \cos \theta) \end{aligned} \quad (144)$$

A-A phase

$$\gamma = \phi - \alpha = -\pi + \pi(2 - \cos \theta) = \pi(1 - \cos \theta) \neq 0 \quad (145)$$

当 $|\psi(t)\rangle$ 在一个态上演化时, 即 $\theta = 0$ 或 $\theta = \pi$ 时

$$\gamma = \begin{cases} 0 & \theta = 0 \\ 2\pi & \theta = \pi \end{cases} \quad (146)$$

5 Gauge Invariance of Quantum Mechanics 量子力学中的规范不变性

我们首先来回顾电动力学中的规范不变性。在电动力学中

$$\vec{E} = -\nabla V - \frac{1}{c} \frac{\partial \vec{A}}{\partial t} \quad (147)$$

$$\vec{B} = \nabla \times \vec{A} \quad (148)$$

通过规范变化 (gauge transformation)

$$V \rightarrow V' = V - \frac{1}{c} \frac{\partial \chi}{\partial t} \quad (149)$$

$$\vec{A} \rightarrow \vec{A}' = \vec{A} + \nabla\chi \quad (150)$$

我们得到

$$\vec{E} \rightarrow \vec{E} \quad \vec{B} \rightarrow \vec{B} \quad (151)$$

接下来我们来说明量子力学中的规范不变性。量子力学中的规范不变性指薛定谔方程在规范变化下形式不变。

$$\left[\frac{\vec{p}^2}{2m} + V(\vec{r}, t) \right] \psi(\vec{r}, t) = i\hbar \frac{\partial}{\partial t} \psi(\vec{r}, t) \quad (152)$$

考虑电场与磁场，薛定谔方程写成

$$\left[\frac{1}{2m} \left(\vec{p} - q \frac{\vec{A}}{c} \right)^2 + V(\vec{r}, t) \right] \psi(\vec{r}, t) = i\hbar \frac{\partial}{\partial t} \psi(\vec{r}, t) \quad (153)$$

其中算符 \vec{p} 为正则动量 (canonical momentum), $\vec{p} - q \frac{\vec{A}}{c}$ 为运动动量 (kinetic momentum)。进行规范变化

$$V \rightarrow V' = V - \frac{q}{c} \frac{\partial}{\partial t} \chi \quad (154)$$

$$\vec{A} \rightarrow \vec{A}' = \vec{A} + \nabla\chi \quad (155)$$

在规范变化下，波函数多了一个相位因子

$$\psi \rightarrow \psi' = e^{\frac{iq\chi}{\hbar c}} \psi \quad (156)$$

$$\left[\frac{1}{2m} \left(\vec{p} - q \frac{\vec{A}'}{c} \right)^2 + V'(\vec{r}, t) \right] \psi'(\vec{r}, t) = i\hbar \frac{\partial}{\partial t} \psi'(\vec{r}, t) \quad (157)$$

接下来证明规范变化后的薛定谔方程与变化前的薛定谔方程等价。

$$\begin{aligned} & \left(\vec{p} - q \frac{\vec{A}'}{c} \right) f(\vec{r}, t) e^{\frac{iq\chi(\vec{r}, t)}{\hbar c}} \\ &= \left(\frac{\hbar}{i} \nabla - q \frac{\vec{A} + \nabla\chi}{c} \right) f(\vec{r}, t) e^{\frac{iq\chi(\vec{r}, t)}{\hbar c}} \\ &= \left[\frac{\hbar}{i} \nabla f(\vec{r}, t) \right] e^{\frac{iq\chi(\vec{r}, t)}{\hbar c}} + \frac{q}{c} \nabla\chi f(\vec{r}, t) e^{\frac{iq\chi(\vec{r}, t)}{\hbar c}} - q \frac{\vec{A}}{c} f(\vec{r}, t) e^{\frac{iq\chi(\vec{r}, t)}{\hbar c}} - \frac{q}{c} \nabla\chi f(\vec{r}, t) e^{\frac{iq\chi(\vec{r}, t)}{\hbar c}} \\ &= \left[\left(\vec{p} - q \frac{\vec{A}}{c} \right) f(\vec{r}, t) \right] e^{\frac{iq\chi(\vec{r}, t)}{\hbar c}} \end{aligned} \quad (158)$$

$f(\vec{r}, t)$ 为任一函数。用该关系作用 $\psi'(\vec{r}, t)$ 两次，得

$$\left(\vec{p} - q \frac{\vec{A}'}{c} \right)^2 \psi'(\vec{r}, t) = \left[\left(\vec{p} - q \frac{\vec{A}}{c} \right)^2 \psi(\vec{r}, t) \right] e^{\frac{iq\chi}{\hbar c}} \quad (159)$$

$$i\hbar \frac{\partial}{\partial t} \psi'(\vec{r}, t) = i\hbar \frac{\partial}{\partial t} \left[e^{\frac{iq\chi}{\hbar c}} \psi(\vec{r}, t) \right] = \left(-\frac{q}{c} \frac{\partial}{\partial t} \chi \right) \psi'(\vec{r}, t) + e^{\frac{iq\chi}{\hbar c}} i\hbar \frac{\partial}{\partial t} \psi(\vec{r}, t) \quad (160)$$

代入 Eq.(157)，得

$$\left[\frac{1}{2m} \left(\vec{p} - q \frac{\vec{A}}{c} \right)^2 + V(\vec{r}, t) - \frac{q}{c} \frac{\partial}{\partial t} \chi \right] \psi'(\vec{r}, t) = \left(-\frac{q}{c} \frac{\partial}{\partial t} \chi \right) \psi'(\vec{r}, t) + e^{\frac{iq\chi}{\hbar c}} i\hbar \frac{\partial}{\partial t} \psi(\vec{r}, t) \quad (161)$$

$$\left[\frac{1}{2m} \left(\vec{p} - q \frac{\vec{A}}{c} \right)^2 + V(\vec{r}, t) \right] e^{\frac{iq\chi}{\hbar c}} \psi(\vec{r}, t) = e^{\frac{iq\chi}{\hbar c}} i\hbar \frac{\partial}{\partial t} \psi(\vec{r}, t) \quad (162)$$

即

$$\left[\frac{1}{2m} \left(\vec{p} - q \frac{\vec{A}}{c} \right)^2 + V(\vec{r}, t) \right] \psi(\vec{r}, t) = i\hbar \frac{\partial}{\partial t} \psi(\vec{r}, t) \quad (163)$$

证毕。

$$\vec{p}f(\vec{r}, t)e^{-\frac{iS(\vec{r}, t)}{\hbar}} = (\vec{p} - \nabla S)f(\vec{r}, t)e^{-\frac{iS(\vec{r}, t)}{\hbar}} \quad (164)$$

6 Phase Change due to Scalar Potential $V(t)$ and Vector Potential $\vec{A}(\vec{r})$

在考虑标量势 $V(t)$ 和矢势 $\vec{A}(\vec{r})$ 之前

$$H(t) = H_0(t) \quad (165)$$

$$i\hbar \frac{\partial}{\partial t} \psi_0(\vec{r}, t) = H_0(t) \psi_0(\vec{r}, t) \quad (166)$$

将标量势 $V(t)$ 和矢势 $\vec{A}(\vec{r})$ 分开讨论。

Scalar Potential $V(t)$

$$H(t) = H_0(t) + V(t) \quad (167)$$

$$i\hbar \frac{\partial}{\partial t} \psi(\vec{r}, t) = H(t) \psi(\vec{r}, t) \quad (168)$$

$\psi(\vec{r}, t)$ 和 $\psi_0(\vec{r}, t)$ 的关系

$$\psi(\vec{r}, t) = \psi_0(\vec{r}, t) e^{-\frac{iS(t)}{\hbar}} \quad (169)$$

其中

$$S(t) = \int_{t_0}^t V(t') dt' \quad (170)$$

接下来证明这一关系。

将 $\psi(\vec{r}, t)$ 代入薛定谔方程

$$\begin{aligned} \text{LHS} &= i\hbar \frac{\partial}{\partial t} \psi(\vec{r}, t) = i\hbar \frac{\partial}{\partial t} \left[\psi_0(\vec{r}, t) e^{-\frac{iS(t)}{\hbar}} \right] \\ &= i\hbar \frac{\partial}{\partial t} \psi_0(\vec{r}, t) e^{-\frac{iS(t)}{\hbar}} + \psi_0(\vec{r}, t) e^{-\frac{iS(t)}{\hbar}} \frac{\partial}{\partial t} S(t) \\ &= [H_0(t) + V(t)] \psi_0(\vec{r}, t) e^{-\frac{iS(t)}{\hbar}} \\ &= H \psi(\vec{r}, t) = \text{RHS} \end{aligned} \quad (171)$$

证毕。

Vector Potential $\vec{A}(\vec{r})$

$$H_0(t) \sim \psi_0(\vec{r}, t) \quad i\hbar \frac{\partial}{\partial t} \psi_0(\vec{r}, t) = H_0(t) \psi_0(\vec{r}, t) \quad (172)$$

考虑 $\vec{A}(\vec{r})$

$$H(t) \sim \psi(\vec{r}, t) \quad i\hbar \frac{\partial}{\partial t} \psi(\vec{r}, t) = H(t) \psi(\vec{r}, t) \quad (173)$$

$\psi(\vec{r}, t)$ 和 $\psi_0(\vec{r}, t)$ 的关系

$$\psi(\vec{r}, t) = \psi_0(\vec{r}, t) e^{-\frac{iS(\vec{r})}{\hbar}} \quad (174)$$

其中 Dirac factor

$$S(\vec{r}) = -\frac{q}{c} \int_{\vec{r}_0}^{\vec{r}} \vec{A}(\vec{r}') \cdot d\vec{r}' \quad (175)$$

接下来证明这一关系。

$$H_0 = \frac{\vec{p}^2}{2m} \quad (176)$$

$$\vec{p} e^{-\frac{iS(\vec{r})}{\hbar}} = e^{-\frac{iS(\vec{r})}{\hbar}} (-i\hbar) \nabla \left[-\frac{iS(\vec{r})}{\hbar} \right] = e^{-\frac{iS(\vec{r})}{\hbar}} \frac{q}{c} \nabla \int_{\vec{r}_0}^{\vec{r}} \vec{A}(\vec{r}') \cdot d\vec{r}' = e^{-\frac{iS(\vec{r})}{\hbar}} \frac{q}{c} \vec{A}(\vec{r}) \quad (177)$$

由 Eq.(164) 可得

$$\left[\vec{p} - \frac{q}{c} \vec{A}(\vec{r}) \right] f(\vec{r}, t) e^{-\frac{iS(\vec{r})}{\hbar}} = [\vec{p} f(\vec{r}, t)] e^{-\frac{iS(\vec{r})}{\hbar}} \quad (178)$$

作用两次

$$\frac{1}{2m} \left[\vec{p} - \frac{q}{c} \vec{A}(\vec{r}) \right]^2 \psi_0(\vec{r}, t) e^{-\frac{iS(\vec{r})}{\hbar}} = \frac{1}{2m} [\vec{p}^2 \psi_0(\vec{r}, t)] e^{-\frac{iS(\vec{r})}{\hbar}} \quad (179)$$

代入薛定谔方程

$$\text{LHS} = i\hbar \frac{\partial}{\partial t} \psi(\vec{r}, t) = i\hbar \frac{\partial}{\partial t} \left[\psi_0(\vec{r}, t) e^{-\frac{iS(\vec{r})}{\hbar}} \right] = i\hbar \left[\frac{\partial}{\partial t} \psi_0(\vec{r}, t) \right] e^{-\frac{iS(\vec{r})}{\hbar}} \quad (180)$$

$$\text{RHS} = H \psi(\vec{r}, t) = \frac{1}{2m} \left[\vec{p} - \frac{q}{c} \vec{A}(\vec{r}) \right]^2 \psi_0(\vec{r}, t) e^{-\frac{iS(\vec{r})}{\hbar}} = \frac{1}{2m} [\vec{p}^2 \psi_0(\vec{r}, t)] e^{-\frac{iS(\vec{r})}{\hbar}} \quad (181)$$

由 LHS = RHS 得

$$i\hbar \frac{\partial}{\partial t} \psi_0(\vec{r}, t) = \frac{\vec{p}^2}{2m} \psi_0(\vec{r}, t) \quad (182)$$

证毕。

General Case

$$H_0(t) \sim \psi_0(\vec{r}, t) \quad (183)$$

将两种情况结合起来

$$H(t) \sim \psi(\vec{r}, t) \quad (184)$$

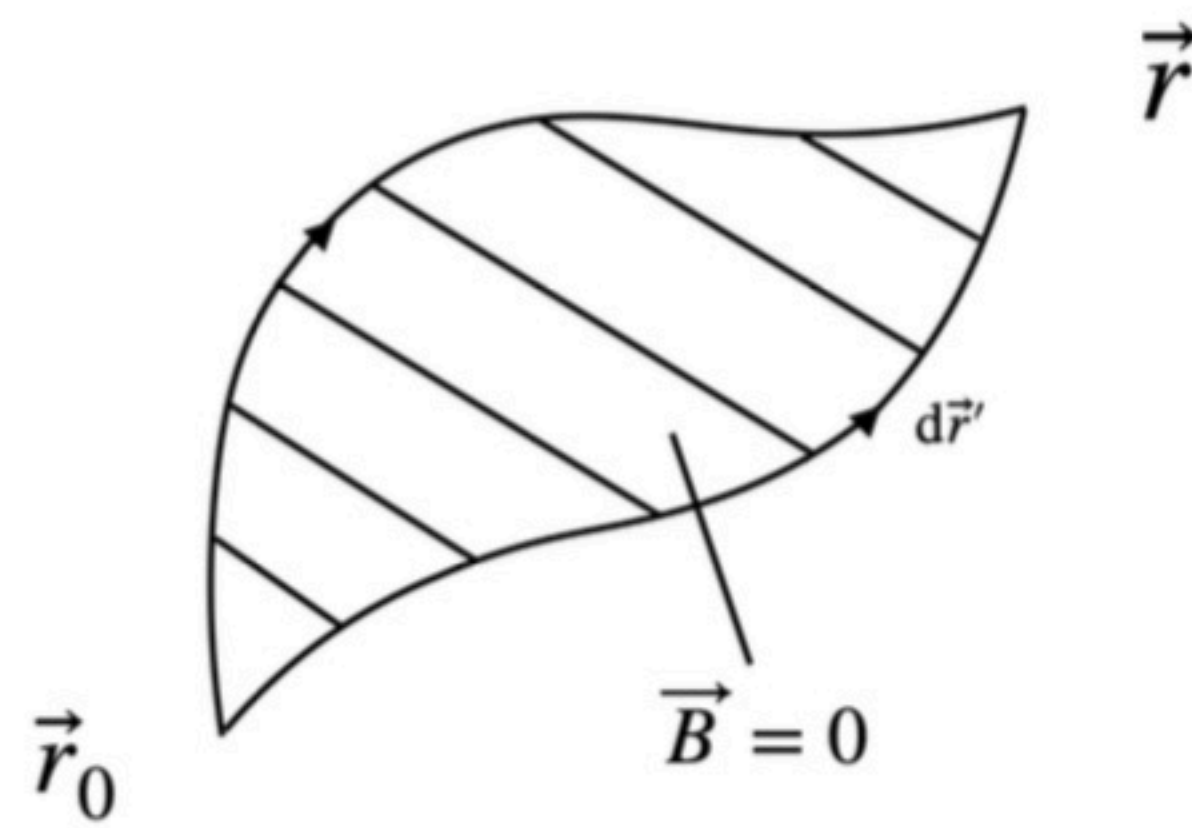
$$\psi(\vec{r}, t) = \psi_0(\vec{r}, t) e^{-\frac{iS(\vec{r}, t)}{\hbar}} \quad (185)$$

其中

$$S(\vec{r}, t) = \int_{t_0}^t V(t') dt' - \frac{q}{c} \int_{\vec{r}_0}^{\vec{r}} \vec{A}(\vec{r}') \cdot d\vec{r}' \quad (186)$$

$\int_{\vec{r}_0}^{\vec{r}} \vec{A}(\vec{r}') \cdot d\vec{r}'$ 可能依赖路径, 接下来我们来研究什么情况下 $\int_{\vec{r}_0}^{\vec{r}} \vec{A}(\vec{r}') \cdot d\vec{r}'$ 与路径有关。

(1) 图中区域 $\vec{B}(\vec{r}) = 0$



$$\nabla \times \vec{A}(\vec{r}) = \vec{B}(\vec{r}) = 0 \quad (187)$$

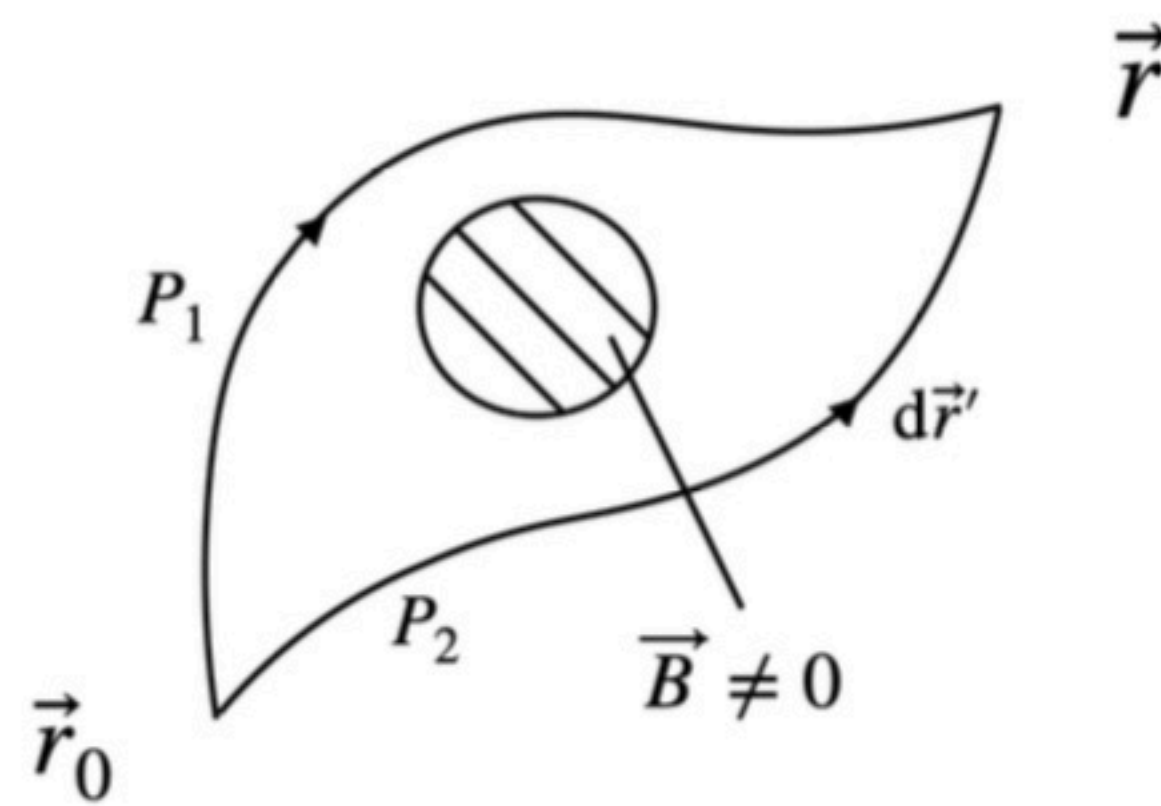
因此 \vec{A} 可以写成

$$\vec{A}(\vec{r}) = \nabla \chi(\vec{r}) \quad (188)$$

$$\int_{\vec{r}_0}^{\vec{r}} \vec{A}(\vec{r}') \cdot d\vec{r}' = \int_{\vec{r}_0}^{\vec{r}} \nabla \chi(\vec{r}') \cdot d\vec{r}' = 0 \quad (189)$$

与路径无关

(2) 图中区域 $\vec{B}(\vec{r}) \neq 0$



$$\begin{aligned} \int_{\vec{r}_0(P_1)}^{\vec{r}} \vec{A}(\vec{r}') \cdot d\vec{r}' + \int_{\vec{r}(P_2)}^{\vec{r}_0} \vec{A}(\vec{r}') \cdot d\vec{r}' &= \oint \vec{A}(\vec{r}') \cdot d\vec{r}' \\ &= \iint_S [\nabla \times \vec{A}(\vec{r}')] \cdot d\vec{S} = \iint_S \vec{B}(\vec{r}') \cdot d\vec{S} = \Phi \neq 0 \end{aligned} \quad (190)$$

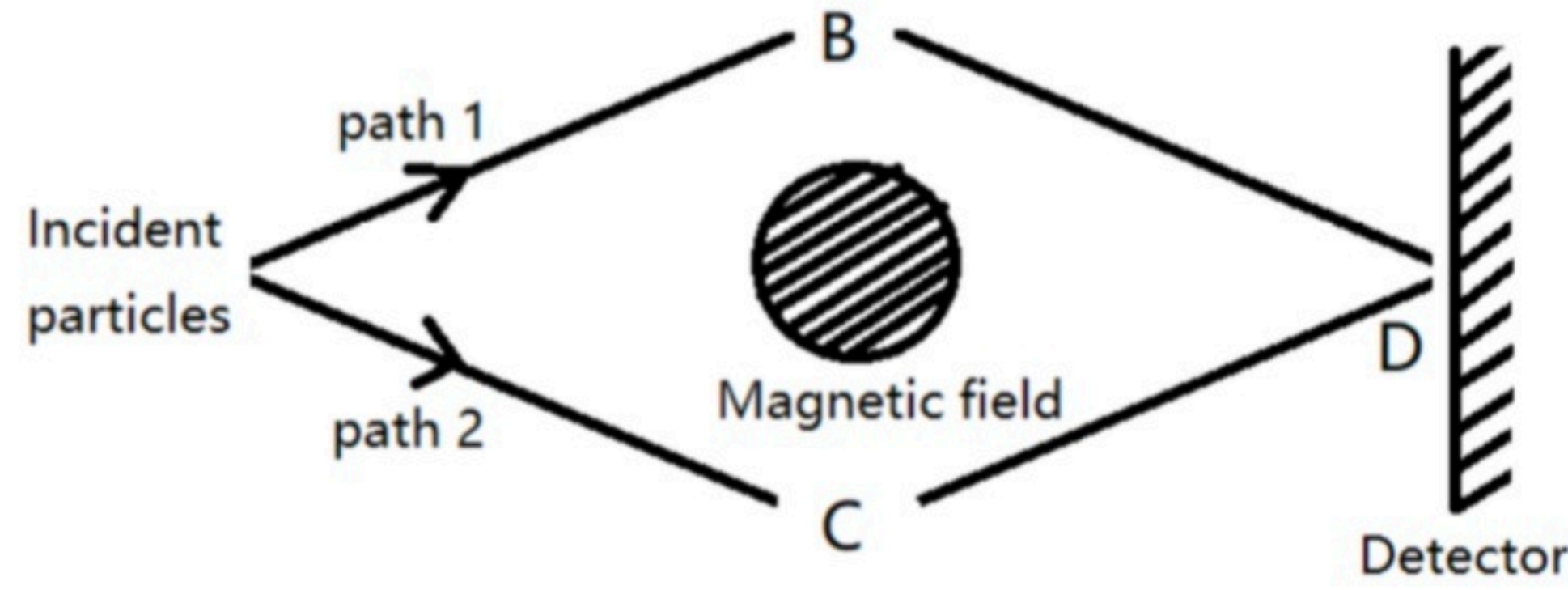
故

$$\int_{\vec{r}_0(P_1)}^{\vec{r}} \vec{A}(\vec{r}') \cdot d\vec{r}' \neq \int_{\vec{r}_0(P_2)}^{\vec{r}} \vec{A}(\vec{r}') \cdot d\vec{r}' \quad (191)$$

积分与路径有关。

7 Aharanov-Bohm Effect

Magnetic A-B Effect Experiment(1959)



设在路径 A-B-D 中, $|\psi_2| \ll |\psi_1|$; 在路径 A-C-D 中, $|\psi_1| \ll |\psi_2|$ 。

当 $\vec{B} = 0$ 时

$$\psi_0(\vec{r}, t) \sim \psi_1(\vec{r}, t) + \psi_2(\vec{r}, t) \quad (192)$$

当 $\vec{B} \neq 0$ 时

$$\begin{aligned} \psi(\vec{r}, t) &\sim \exp\left[\frac{iq}{\hbar c} \int_{\vec{r}_0}^{\vec{r}} \vec{A}(\vec{r}') \cdot d\vec{r}'\right] \psi_0(\vec{r}, t) \\ &= \exp\left[\frac{iq}{\hbar c} \int_{\vec{r}_0(P_1)}^{\vec{r}} \vec{A}(\vec{r}') \cdot d\vec{r}'\right] \psi_1(\vec{r}, t) + \exp\left[\frac{iq}{\hbar c} \int_{\vec{r}_0(P_2)}^{\vec{r}} \vec{A}(\vec{r}') \cdot d\vec{r}'\right] \psi_2(\vec{r}, t) \\ &= \exp\left[\frac{iq}{\hbar c} \int_{\vec{r}_0(P_1)}^{\vec{r}} \vec{A}(\vec{r}') \cdot d\vec{r}'\right] \left\{ \psi_1(\vec{r}, t) + \psi_2(\vec{r}, t) \exp\left[\frac{iq}{\hbar c} \left(\int_{\vec{r}_0(P_2)}^{\vec{r}} - \int_{\vec{r}_0(P_1)}^{\vec{r}} \right) \vec{A}(\vec{r}') \cdot d\vec{r}' \right] \right\} \\ &= \exp\left[\frac{iq}{\hbar c} \int_{\vec{r}_0(P_1)}^{\vec{r}} \vec{A}(\vec{r}') \cdot d\vec{r}'\right] \left\{ \psi_1(\vec{r}, t) + \psi_2(\vec{r}, t) \exp\left[-\frac{iq}{\hbar c} \oint \vec{A}(\vec{r}') \cdot d\vec{r}'\right] \right\} \\ &\sim \psi_1(\vec{r}, t) + \psi_2(\vec{r}, t) \exp\left(-\frac{iq}{\hbar c} \Phi\right) \end{aligned} \quad (193)$$

$$\begin{aligned} |\psi(\vec{r}, t)|^2 &= \left[\psi_1^\dagger(\vec{r}, t) + \psi_2^\dagger(\vec{r}, t) e^{\frac{iq}{\hbar c} \Phi} \right] \left[\psi_1(\vec{r}, t) + \psi_2(\vec{r}, t) e^{-\frac{iq}{\hbar c} \Phi} \right] \\ &= |\psi_1|^2 + |\psi_2|^2 + \psi_1^\dagger \psi_2 e^{-\frac{iq}{\hbar c} \Phi} + \psi_1 \psi_2^\dagger e^{\frac{iq}{\hbar c} \Phi} \\ &= |\psi_1|^2 + |\psi_2|^2 + 2|\psi_1 \psi_2| \cos\left(\phi_1 - \phi_2 + \frac{q\Phi}{\hbar c}\right) \end{aligned} \quad (194)$$

Φ 和 \vec{B} 有关

$$\delta\phi = \frac{q\Phi}{\hbar c} \quad (195)$$

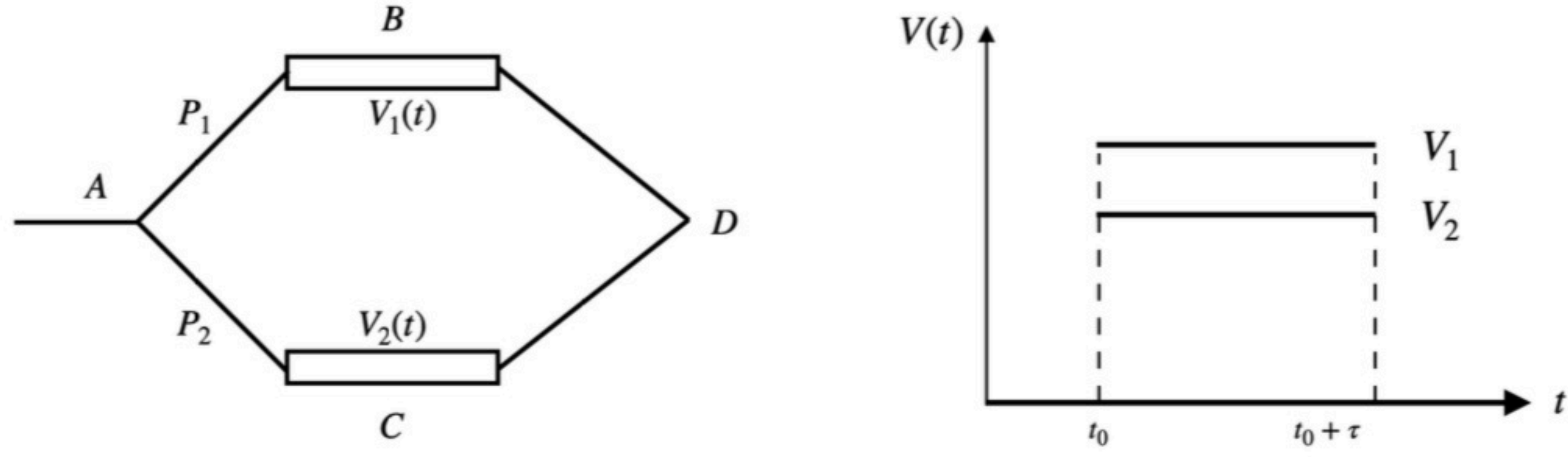
当经过一个周期即

$$\frac{q\Delta\Phi}{\hbar c} = 2\pi \quad (196)$$

$$\Delta\Phi = \frac{2\pi\hbar c}{q} \quad (197)$$

在经典电动力学中, \vec{A} 无物理意义, 而在量子力学中 \vec{A} 能够显现出来, 即 A-B 效应。

Electric Aharonov-Bohm Effect



设在路径 A-B-D 中, $|\psi_2| \ll |\psi_1|$; 在路径 A-C-D 中, $|\psi_1| \ll |\psi_2|$ 。

当 $V_1(t) = 0, V_2(t) = 0$ 时

$$\psi_0(\vec{r}, t) \sim \psi_1(\vec{r}, t) + \psi_2(\vec{r}, t) \quad (198)$$

当 $V_1(t) \neq 0, V_2(t) \neq 0$ 时

$$\begin{aligned} \psi(\vec{r}, t) &\sim \exp\left[\frac{i}{\hbar} \int_{(P_1)}^t V(t') \cdot dt'\right] \psi_1(\vec{r}, t) + \exp\left[\frac{i}{\hbar} \int_{(P_1)}^t V(t') \cdot dt'\right] \psi_2(\vec{r}, t) \\ &\sim \psi_1(\vec{r}, t) + \psi_2(\vec{r}, t) \exp\left\{i \left[\int_{(P_2)}^t V(t') \cdot dt' - \int_{(P_1)}^t V(t') \cdot dt' \right] \frac{1}{\hbar}\right\} \end{aligned} \quad (199)$$

设 $V_1(t), V_2(t)$ 是如上图的函数

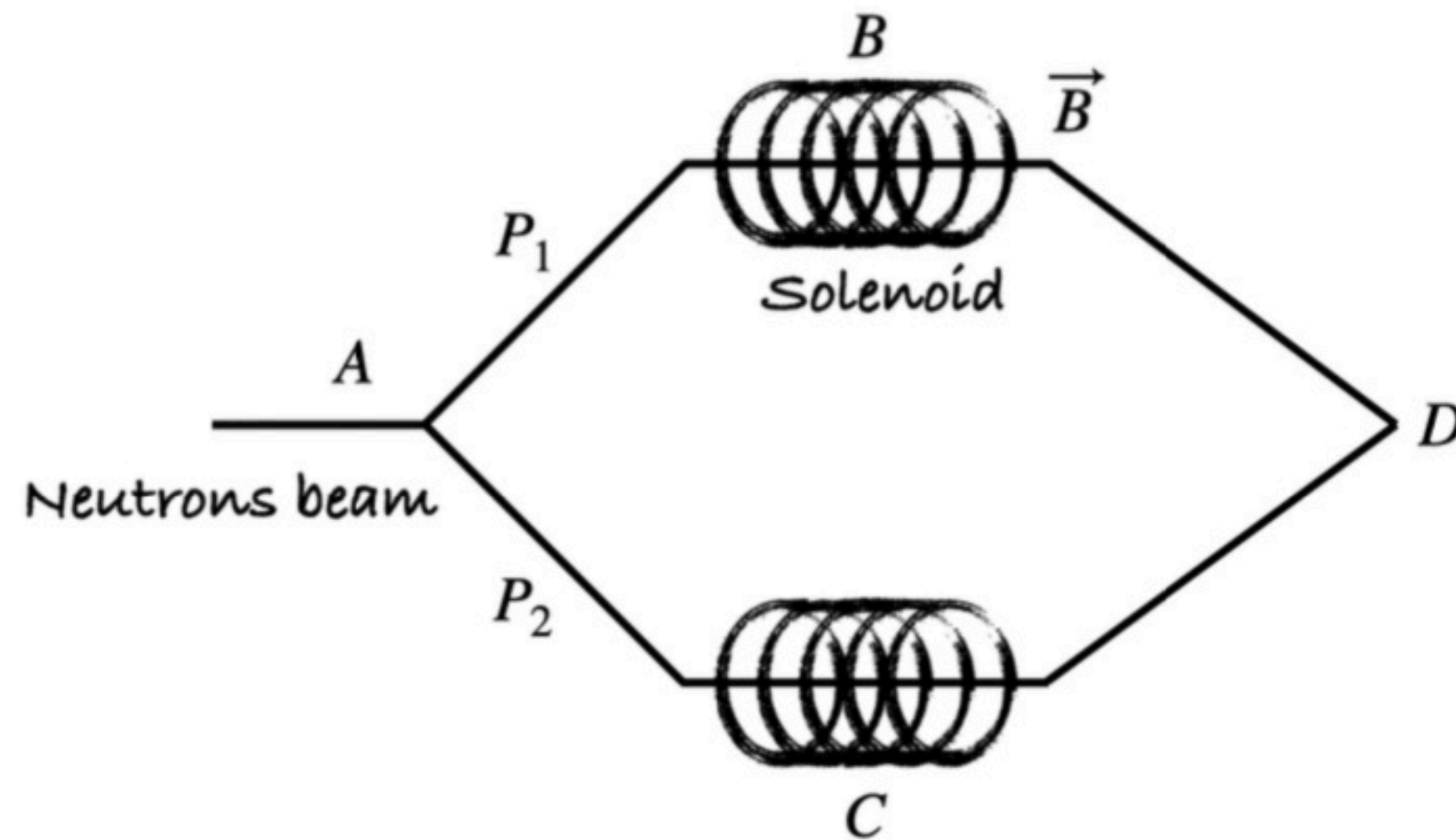
$$\begin{aligned} \psi(\vec{r}, t) &\sim \psi_1(\vec{r}, t) + \psi_2(\vec{r}, t) \exp\left[i (V_2 - V_1) \frac{\tau}{\hbar}\right] \\ &= \psi_1(\vec{r}, t) + \psi_2(\vec{r}, t) e^{-\frac{i\Delta V\tau}{\hbar}} \quad (\Delta V = V_1 - V_2) \end{aligned} \quad (200)$$

$$\begin{aligned} |\psi(\vec{r}, t)|^2 &= \left[\psi_1^\dagger(\vec{r}, t) + \psi_2^\dagger(\vec{r}, t) e^{\frac{i\Delta V\tau}{\hbar}} \right] \left[\psi_1(\vec{r}, t) + \psi_2(\vec{r}, t) e^{-\frac{i\Delta V\tau}{\hbar}} \right] \\ &= |\psi_1|^2 + |\psi_2|^2 + \psi_1^\dagger \psi_2 e^{-\frac{i\Delta V\tau}{\hbar}} + \psi_1 \psi_2^\dagger e^{\frac{i\Delta V\tau}{\hbar}} \\ &= |\psi_1|^2 + |\psi_2|^2 + 2|\psi_1 \psi_2| \cos\left(\phi_1 - \phi_2 + \frac{\Delta V\tau}{\hbar}\right) \end{aligned} \quad (201)$$

$$\Delta\phi = \frac{\Delta V\tau}{\hbar} \quad (202)$$

由于存在技术上的困难, 目前在实验中还未观察到这一现象。

Scalar Aharonov-Bohm Effect Experiment(1992)



$$H = \frac{\vec{p}^2}{2m} - \vec{\mu} \cdot \vec{B} = \frac{p^2}{2m} - \mu_B \vec{\sigma} \cdot \vec{B} \quad (203)$$

$$V = \mu_B \vec{\sigma} \cdot \vec{B} \quad (204)$$

假设

$$\vec{B}_1 = \hat{e}_z B \quad \vec{B}_2 = 0 \quad (205)$$

则

$$\Delta V = \mu_B B \sigma \quad (206)$$

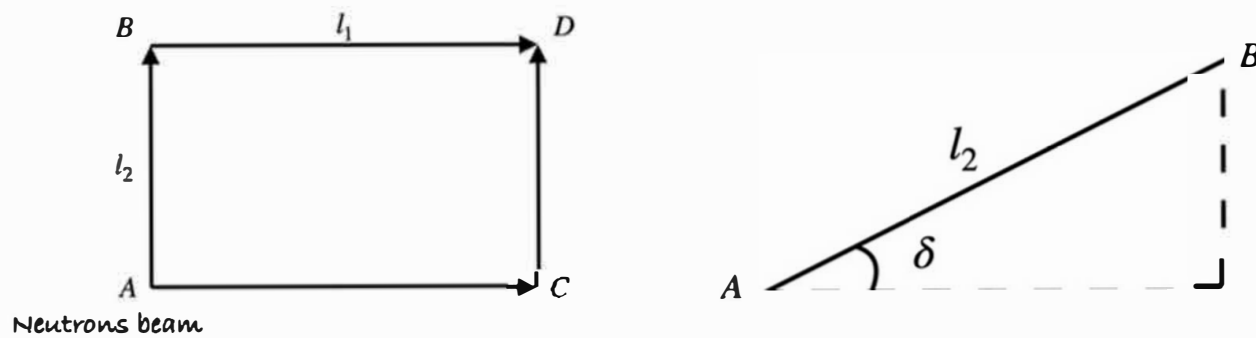
在 $t_0 \rightarrow t_0 + \tau$ 加磁场 \vec{B} , 观察到

$$\Delta \phi = \frac{\Delta V \tau}{\hbar} \quad (207)$$

8 Gravitationally Induced Phase

Experiment(1975)

引力和量子力学是相洽的吗? 我们来设计一个实验观察引力在量子力学中的表现。



将 BD 边抬高

$$\Delta V = m_n g l_2 \sin \delta \quad (208)$$

如果这个势能能够在量子力学中表现出来且被观察到, 那么会引起的相位变化

$$\Delta \phi = \frac{\Delta V T}{\hbar} \quad (209)$$

设中子速度 \vec{v}

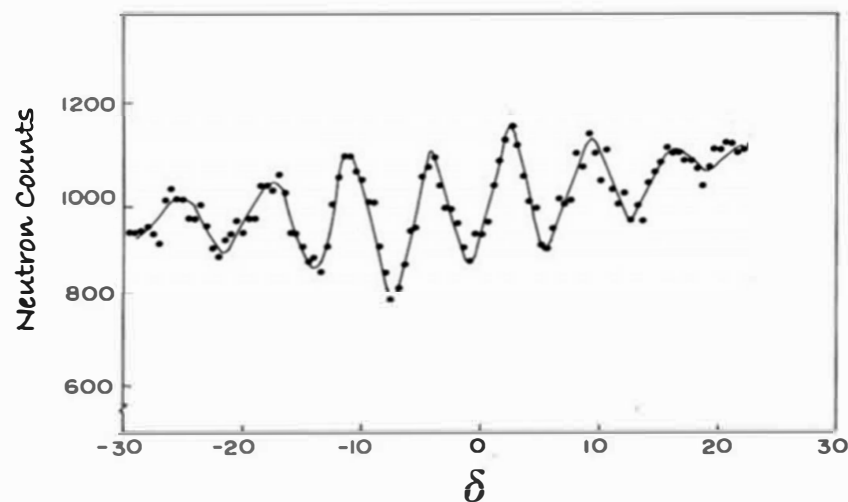
$$T = \frac{l_1}{v} = \frac{l_1}{\hbar/m_n \lambda} = \frac{l_1 m_n \lambda}{\hbar} \quad (210)$$

则

$$\Delta \phi = \frac{\Delta V T}{\hbar} = \frac{m_n^2 g l_1 l_2 \lambda \sin \delta}{\hbar^2} \quad (211)$$

若 $\hbar \rightarrow 0$, 则 $\Delta \phi \rightarrow \infty$, 无任何效应。因此这是纯粹的量子力学效应。

实验中 $l_1 l_2 = 10 \text{ cm}^2$, $\lambda = 1.42 \text{ \AA}$, 实验结果证实了引力效应可以在量子力学中观察到。



Chapter 2: Path Integral Formalism of Quantum Mechanics

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1 Definition of Propagator

Time Independent Case

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = H |\psi(t)\rangle \quad (1)$$

H 不含时，波函数可以写成 (t' 是 t 之前的任意一个时间点)

$$|\psi(t)\rangle = \exp\left[-\frac{i}{\hbar} H(t-t')\right] |\psi(t')\rangle \quad (2)$$

将 $\langle \vec{r} |$ 作用在方程两边

$$\langle \vec{r} | \psi(t) \rangle = \langle \vec{r} | \exp\left[-\frac{i}{\hbar} H(t-t')\right] |\psi(t')\rangle \quad (3)$$

单位算符 $\int d\vec{r}' |\vec{r}'\rangle \langle \vec{r}'| = 1$ 作用在方程右边

$$\langle \vec{r} | \psi(t) \rangle = \int d\vec{r}' \langle \vec{r} | \exp\left[-\frac{i}{\hbar} H(t-t')\right] |\vec{r}'\rangle \langle \vec{r}' | \psi(t') \rangle \quad (4)$$

$$\psi(\vec{r}, t) = \langle \vec{r} | \psi(t) \rangle \quad (5)$$

$$\psi(\vec{r}, t) = \int d\vec{r}' \langle \vec{r} | \exp\left[-\frac{i}{\hbar} H(t-t')\right] |\vec{r}'\rangle \psi(\vec{r}', t') = \int d\vec{r}' K(\vec{r}, t; \vec{r}', t') \psi(\vec{r}', t') \quad (6)$$

在物理上， $K(\vec{r}, t; \vec{r}', t')$ 被称为传播子 (propagator)，在数学上是 Kernel 或 Green's function。定义

$$K(\vec{r}, t; \vec{r}', t') = \langle \vec{r} | \exp\left[-\frac{i}{\hbar} H(t-t')\right] |\vec{r}'\rangle \quad (7)$$

当 $t = t'$ 时

$$K(\vec{r}, t; \vec{r}', t') = \langle \vec{r} | \vec{r}' \rangle = \delta(\vec{r} - \vec{r}') \quad (8)$$

假定 H 存在一系列本征态和相应的本征值

$$H |n\rangle = E_n |n\rangle \quad (9)$$

$|n\rangle$ 构成完备基，存在单位算符

$$|n\rangle \langle n| = 1 \quad (10)$$

$$\begin{aligned}
K(\vec{r}, t; \vec{r}', t') &= \langle \vec{r} | \exp \left[-\frac{i}{\hbar} H(t - t') \right] | \vec{r}' \rangle \\
&= \sum_n \sum_{n'} \langle \vec{r} | n \rangle \langle n | \exp \left[-\frac{i}{\hbar} H(t - t') \right] | n' \rangle \langle n' | \vec{r}' \rangle \\
&= \sum_n \sum_{n'} \psi_n(\vec{r}) \delta_{n,n'} \psi_{n'}^\dagger(\vec{r}') \exp \left[-\frac{i}{\hbar} E_n(t - t') \right] \\
&= \sum_n \psi_n(\vec{r}) \psi_n^\dagger(\vec{r}') e^{-\frac{i}{\hbar} E_n(t-t')} \\
&= \sum_n \left[\psi_n(\vec{r}) e^{-\frac{i}{\hbar} E_n t} \right] \left[\psi_n(\vec{r}') e^{-\frac{i}{\hbar} E_n t'} \right]^\dagger \\
&= \sum_n \psi_n(\vec{r}, t) \psi_n^\dagger(\vec{r}', t')
\end{aligned} \tag{11}$$

Example: The Free Particle

$$H = -\frac{\hbar^2}{2m} \nabla^2 \tag{12}$$

自由粒子的解是平面波

$$\psi_{\vec{p}}(\vec{r}, t) = \frac{1}{(2\pi\hbar)^{3/2}} \exp \left[\frac{i}{\hbar} \left(\vec{p} \cdot \vec{r} - \frac{p^2}{2m} t \right) \right] \tag{13}$$

其传播子

$$\begin{aligned}
K(\vec{r}, t; \vec{r}', t') &= \int \psi_{\vec{p}}(\vec{r}, t) \psi_{\vec{p}}^\dagger(\vec{r}', t') d\vec{p} \\
&= \frac{1}{(2\pi\hbar)^3} \int d\vec{p} \exp \left[\frac{i\vec{p}}{\hbar} (\vec{r} - \vec{r}') - \frac{ip^2}{2m\hbar} (t - t') \right]
\end{aligned} \tag{14}$$

由于

$$d\vec{p} = dp_x dp_y dp_z \tag{15}$$

且 dp_x, dp_y, dp_z 等价

$$\begin{aligned}
&\int_{-\infty}^{\infty} dp_x \exp \left[\frac{i}{\hbar} p_x (x - x') - \frac{i}{2m\hbar} p_x^2 (t - t') \right] \\
&= \int_{-\infty}^{\infty} dp_x \exp \left\{ \left[-\frac{i}{2m\hbar} (t - t') \right] \left(p_x^2 - 2mp_x \frac{x - x'}{t - t'} \right) \right\} \\
&= \int_{-\infty}^{\infty} dp_x \exp \left\{ \left[-\frac{i}{2m\hbar} (t - t') \right] \left[\left(p_x - m \frac{x - x'}{t - t'} \right)^2 - m^2 \frac{(x - x')^2}{(t - t')^2} \right] \right\} \\
&= \exp \left[\frac{im(x - x')^2}{2\hbar(t - t')} \right] \int_{-\infty}^{\infty} dp_x \exp \left\{ \left[-\frac{i}{2m\hbar} (t - t') \right] \left[\left(p_x - m \frac{x - x'}{t - t'} \right)^2 \right] \right\} \\
&= \exp \left[\frac{im(x - x')^2}{2\hbar(t - t')} \right] \int_{-\infty}^{\infty} dp_x \exp \left[-\frac{i}{2m\hbar} (t - t') p_x^2 \right]
\end{aligned} \tag{16}$$

根据 Euler integral

$$\int_{-\infty}^{\infty} dx e^{-\alpha x^2} = \sqrt{\frac{\pi}{\alpha}} \tag{17}$$

$$\int_{-\infty}^{\infty} dp_x \exp \left[\frac{i}{\hbar} p_x (x - x') - \frac{i}{2m\hbar} p_x^2 (t - t') \right] = \exp \left[\frac{im(x - x')^2}{2\hbar(t - t')} \right] \sqrt{\frac{2m\pi\hbar}{i(t - t')}} \tag{18}$$

故

$$K(\vec{r}, t; \vec{r}', t') = \left[\frac{2m\pi\hbar}{i(t-t')} \right]^{\frac{3}{2}} \exp \left[\frac{im(\vec{r} - \vec{r}')^2}{2\hbar(t-t')} \right] \quad (19)$$

General Case

回到前面不含时情况下的波函数

$$\begin{aligned} \psi(\vec{r}, t) &= \int d\vec{r}' \langle \vec{r} | \exp \left[-\frac{i}{\hbar} H(t-t') \right] | \vec{r}' \rangle \psi(\vec{r}', t') \\ &= \int d\vec{r}' \langle \vec{r} | \exp \left[-\frac{i}{\hbar} H(t-t'' + t'' - t') \right] | \vec{r}' \rangle \psi(\vec{r}', t') \\ &= \int d\vec{r}' \langle \vec{r} | \exp \left[-\frac{i}{\hbar} H(t-t'') \right] \exp \left[-\frac{i}{\hbar} H(t'' - t') \right] | \vec{r}' \rangle \psi(\vec{r}', t') \\ &= \int d\vec{r}' \int d\vec{r}'' \langle \vec{r} | \exp \left[-\frac{i}{\hbar} H(t-t'') \right] | \vec{r}'' \rangle \langle \vec{r}'' | \exp \left[-\frac{i}{\hbar} H(t'' - t') \right] | \vec{r}' \rangle \psi(\vec{r}', t') \\ &= \int d\vec{r}' \int d\vec{r}'' K(\vec{r}, t; \vec{r}'', t'') K(\vec{r}'', t''; \vec{r}', t') \psi(\vec{r}', t') \end{aligned} \quad (20)$$

又

$$\psi(\vec{r}, t) = \int d\vec{r}' K(\vec{r}, t; \vec{r}', t') \psi(\vec{r}', t') \quad (21)$$

即

$$K(\vec{r}, t; \vec{r}', t') = \int d\vec{r}'' K(\vec{r}, t; \vec{r}'', t'') K(\vec{r}'', t''; \vec{r}', t') \quad (22)$$

因此

$$K(\vec{r}, t; \vec{r}', t') = \int d\vec{r}_1 \int d\vec{r}_2 \cdots \int d\vec{r}_{N-1} K(\vec{r}, t; \vec{r}_{N-1}, t_{N-1}) K(\vec{r}_{N-1}, t_{N-1}; \vec{r}_{N-2}, t_{N-2}) \cdots K(\vec{r}_1, t_1; \vec{r}', t') \quad (23)$$

2 Equation of Motion for $K(\vec{r}, t; \vec{r}', t')$

前面我们讨论的都是比较熟悉的薛定谔方程里面的东西，接下来我们来研究 $K(\vec{r}, t; \vec{r}', t')$ 的另一个性质，即讨论格林函数 $K(\vec{r}, t; \vec{r}', t')$ 的运动方程。

$$\psi(\vec{r}, t) = \int K(\vec{r}, t; \vec{r}', t') \psi(\vec{r}', t') d\vec{r}' \quad (24)$$

将 $(i\hbar \frac{\partial}{\partial t} - H)$ 算符作用在方程两边

$$0 = \int \left[\left(i\hbar \frac{\partial}{\partial t} - H \right) K(\vec{r}, t; \vec{r}', t') \right] \psi(\vec{r}', t') d\vec{r}' \quad (25)$$

因此我们得到 K 的运动方程

$$\left(i\hbar \frac{\partial}{\partial t} - H \right) K(\vec{r}, t; \vec{r}', t') = 0 \quad (26)$$

传播子代表是 t' 时刻对 t 时刻的影响，也就是说 t 时刻的性质是由 t' 时刻决定的，且 $t > t'$ 。当 $t < t'$ 时，若 $K \neq 0$ ，则代表后面时刻 t' 可以影响前面时刻 t ，这显然是不对的。因此

$$\begin{cases} (i\hbar \frac{\partial}{\partial t} - H) K(\vec{r}, t; \vec{r}', t') = 0 & (t > t') \\ K(\vec{r}, t; \vec{r}', t') = 0 & (t < t') \end{cases} \quad (27)$$

在 $t = t'$ 时, 有奇性 (singular), 即

$$\left(i\hbar\frac{\partial}{\partial t} - H\right) K(\vec{r}, t; \vec{r}', t') = c(\vec{r}, \vec{r}')\delta(t - t') \quad (28)$$

接下来我们来确定 $c(\vec{r}, \vec{r}')$, 两边积分

$$\int_{-\infty}^{\infty} \left(i\hbar\frac{\partial}{\partial t} - H\right) K(\vec{r}, t; \vec{r}', t') dt = \int_{-\infty}^{\infty} c(\vec{r}, \vec{r}')\delta(t - t') dt \quad (29)$$

$$\begin{aligned} \text{LHS} &= \int_{-\infty}^{t'-} \left(i\hbar\frac{\partial}{\partial t} - H\right) K(\vec{r}, t; \vec{r}', t') dt + \int_{t'-}^{t'+} \left(i\hbar\frac{\partial}{\partial t} - H\right) K(\vec{r}, t; \vec{r}', t') dt \\ &\quad + \int_{t'+}^{\infty} \left(i\hbar\frac{\partial}{\partial t} - H\right) K(\vec{r}, t; \vec{r}', t') dt \\ &= \int_{t'-}^{t'+} \left(i\hbar\frac{\partial}{\partial t} - H\right) K(\vec{r}, t; \vec{r}', t') dt = \int_{t'-}^{t'+} i\hbar\frac{\partial}{\partial t} K(\vec{r}, t; \vec{r}', t') dt \\ &= i\hbar K(\vec{r}, t = t'; \vec{r}', t') \end{aligned} \quad (30)$$

当 H 不含时时, $K(\vec{r}, t = t'; \vec{r}', t') = \delta(\vec{r} - \vec{r}')$, 因此

$$\text{LHS} = i\hbar\delta(\vec{r} - \vec{r}') \quad (31)$$

$$\text{RHS} = \int_{-\infty}^{\infty} c(\vec{r}, \vec{r}')\delta(t - t') dt = c(\vec{r}, \vec{r}') \quad (32)$$

由 LHS=RHS 得

$$c(\vec{r}, \vec{r}') = i\hbar\delta(\vec{r} - \vec{r}') \quad (33)$$

则

$$\left(i\hbar\frac{\partial}{\partial t} - H\right) K(\vec{r}, t; \vec{r}', t') = i\hbar\delta(\vec{r} - \vec{r}')\delta(t - t') \quad (34)$$

这就是 $K(\vec{r}, t; \vec{r}', t')$ 的运动方程。

3 Time-dependent Case

前面我们讨论的都是 H 不含时的情况, 接下来我们讨论 H 含时的情况

$$i\hbar\frac{\partial}{\partial t} |\psi(t)\rangle = H(t) |\psi(t)\rangle \quad (35)$$

可以将波函数写成以下形式

$$|\psi(t)\rangle = U(t, t') |\psi(t')\rangle \quad (36)$$

$U(t, t')$ 为演化算符 (evolution operator), 将 $|\psi(t)\rangle$ 代回薛定谔方程得到

$$i\hbar\frac{\partial}{\partial t} U(t, t') = H(t)U(t, t') \quad (37)$$

对波函数作用 $\langle \vec{r} |$

$$\langle \vec{r} | \psi(t) \rangle = \langle \vec{r} | U(t, t') |\psi(t')\rangle = \int d\vec{r}' \langle \vec{r} | U(t, t') | \vec{r}' \rangle \langle \vec{r}' | \psi(t') \rangle \quad (38)$$

即

$$\psi(\vec{r}, t) = \int d\vec{r}' K(\vec{r}, t; \vec{r}', t') \psi(\vec{r}', t') \quad (39)$$

定义普遍情况的传播子

$$K(\vec{r}, t; \vec{r}', t') = \langle \vec{r} | U(t, t') | \vec{r}' \rangle \quad (40)$$

不断重复作用演化算符，可以得到

$$U(t, t') = U(t, t_{N-1})U(t_{N-1}, t_{N-2}) \cdots U(t_1, t') \quad (41)$$

因此

$$\begin{aligned} K(\vec{r}, t; \vec{r}', t') &= \langle \vec{r} | U(t, t') | \vec{r}' \rangle = \langle \vec{r} | U(t, t_{N-1})U(t_{N-1}, t_{N-2}) \cdots U(t_1, t') | \vec{r}' \rangle \\ &= \int d\vec{r}_{N-1} \int d\vec{r}_{N-2} \cdots \int d\vec{r}_1 \langle \vec{r} | U(t, t_{N-1}) | \vec{r}_{N-1} \rangle \langle \vec{r}_{N-1} | U(t_{N-1}, t_{N-2}) | \vec{r}_{N-2} \rangle \cdots \langle \vec{r}_1 | U(t_1, t') | \vec{r}' \rangle \\ &= \int d\vec{r}_{N-1} \int d\vec{r}_{N-2} \cdots \int d\vec{r}_1 K(\vec{r}, t; \vec{r}_{N-1}, t_{N-1}) K(\vec{r}_{N-1}, t_{N-1}; \vec{r}_{N-2}, t_{N-2}) \cdots K(\vec{r}_1, t_1; \vec{r}', t') \end{aligned} \quad (42)$$

很容易发现并验证

$$U^\dagger(t, t') = U(t, t') \quad (43)$$

$$-i\hbar \frac{\partial}{\partial t} U^\dagger(t, t') = H(t)U^\dagger(t, t') \quad (44)$$

$$\langle \psi(t) | \psi(t) \rangle = \langle \psi(t') | U^\dagger(t, t') U(t, t') | \psi(t') \rangle = 1 \quad (45)$$

因此

$$U^\dagger(t, t') U(t, t') = 1 \quad (46)$$

$$U^\dagger(t, t') = U^{-1}(t, t') = U(t, t') \quad (47)$$

因此 U 是么正算符 (unitary operator)

定义

$$|\vec{r}, t\rangle = U^\dagger(t, 0) |\vec{r}\rangle \quad (48)$$

则

$$\langle \vec{r}, t | = \langle \vec{r} | U(t, 0) \quad (49)$$

$$\begin{aligned} K(\vec{r}, t; \vec{r}', t') &= \langle \vec{r} | U(t, t') | \vec{r}' \rangle = \langle \vec{r} | U(t, 0) U(0, t') | \vec{r}' \rangle \\ &= \langle \vec{r} | U(t, 0) U^\dagger(0, t') | \vec{r}' \rangle = \langle \vec{r}, t | \vec{r}', t' \rangle \end{aligned} \quad (50)$$

接下来讨论特殊情况： $H(t)=H$

$$U(t, t') = \exp\left[-\frac{iH(t-t')}{\hbar}\right] \quad (51)$$

$$U(t, 0) = \exp\left(-\frac{iHt}{\hbar}\right) \quad (52)$$

$$\begin{aligned} |\vec{r}, t\rangle &= U^\dagger(t, 0) |\vec{r}\rangle = \exp\left(\frac{iHt}{\hbar}\right) |\vec{r}\rangle = \sum_n \exp\left(\frac{iHt}{\hbar}\right) |n\rangle \langle n | \vec{r} \rangle \\ &= \sum_n \exp\left(\frac{iHt}{\hbar}\right) |n\rangle \psi_n^\dagger(\vec{r}) = \sum_n |n\rangle \exp\left(\frac{iE_n t}{\hbar}\right) \psi_n^\dagger(\vec{r}) \end{aligned} \quad (53)$$

$$\begin{aligned} K(\vec{r}, t; \vec{r}', t') &= \langle \vec{r}, t | \vec{r}', t' \rangle = \sum_n \sum_m \langle m | \exp\left(-\frac{iE_m t}{\hbar}\right) \psi_m(\vec{r}) \exp\left(\frac{iE_n t'}{\hbar}\right) \psi_n^\dagger(\vec{r}') | n \rangle \\ &= \sum_n \exp\left[\frac{iE_n(t'-t)}{\hbar}\right] \psi_n(\vec{r}) \psi_n^\dagger(\vec{r}') = \sum_n \psi_n(\vec{r}, t) \psi_n^\dagger(\vec{r}', t') \end{aligned} \quad (54)$$

与第一节中哈密顿量不含时定义推导得到的传播子一致。

我们来证明一个单位算符

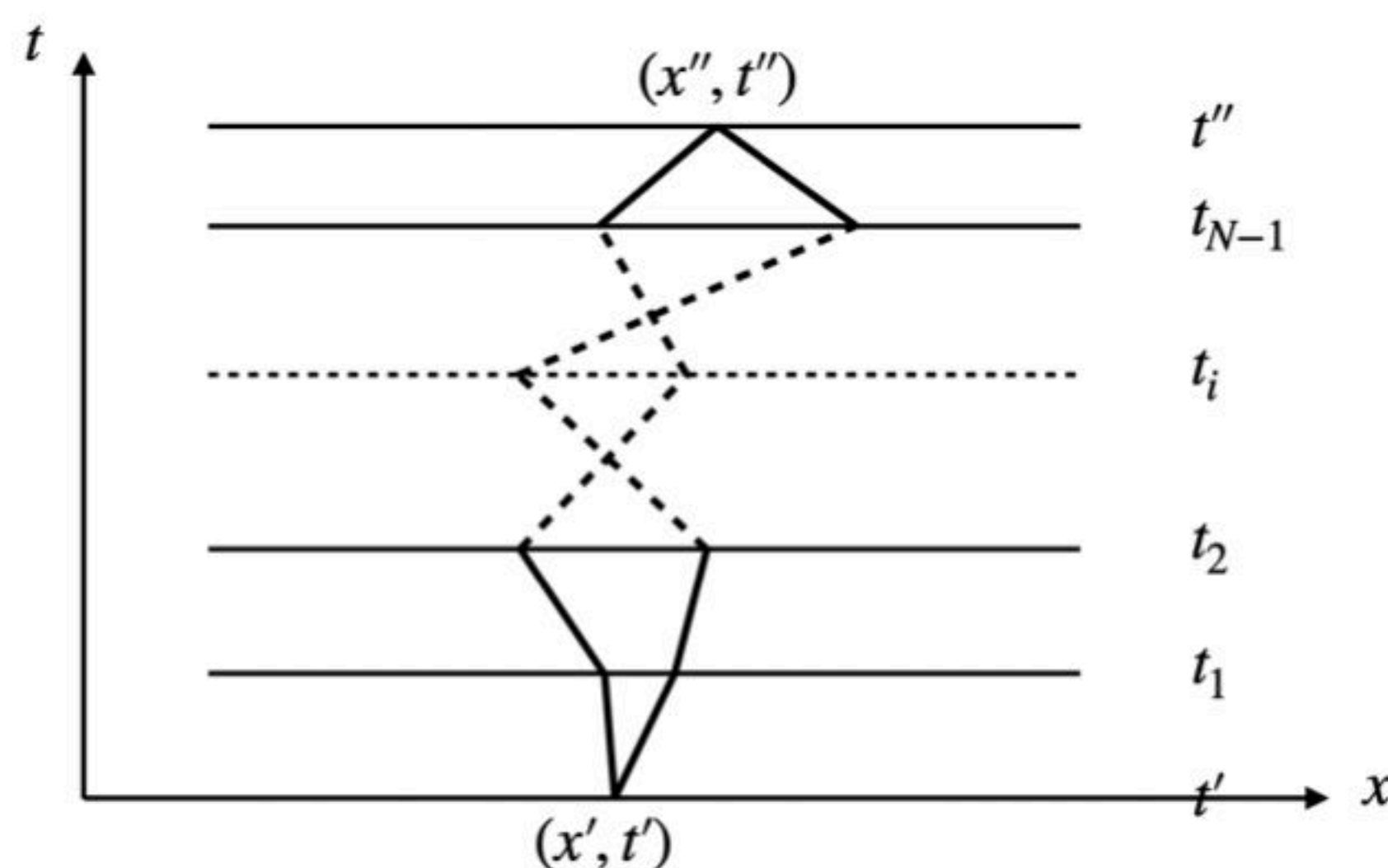
$$\int d\vec{r} |\vec{r}, t\rangle \langle \vec{r}, t| = \int d\vec{r} e^{iHt/\hbar} |\vec{r}\rangle \langle \vec{r}| e^{-iHt/\hbar} = e^{iHt/\hbar} e^{-iHt/\hbar} = 1 \quad (55)$$

$$K(\vec{r}, t; \vec{r}', t') = \langle \vec{r}, t | \vec{r}', t' \rangle = \int d\vec{r}'' \langle \vec{r}, t | \vec{r}'', t'' \rangle \langle \vec{r}'', t'' | \vec{r}', t' \rangle \quad (56)$$

4 Feynman's Formulation of Quantum Mechanics

为了书写方便，我们写成一维形式

$$\begin{aligned} & \langle x'', t'' | x', t' \rangle \\ &= \int dx_{N-1} \int dx_{N-2} \cdots \int dx_1 \langle x'', t'' | x_{N-1}, t_{N-1} \rangle \langle x_{N-1}, t_{N-1} | x_{N-2}, t_{N-2} \rangle \cdots \langle x_1, t_1 | x', t' \rangle \end{aligned} \quad (57)$$



粒子从 (x', t') 以任意一条路径运动到 (x'', t'')

Dirac's Remark

若 $t_2 \rightarrow t_1$

$$\langle x_2, t_2 | x_1, t_1 \rangle \sim \exp \left[\frac{i \int_{t_1}^{t_2} L_{\text{classical}}(x, \dot{x}, t) dt}{\hbar} \right] \quad (58)$$

拉格朗日作用量

$$S(n, n-1) = \int_{t_{n-1}}^{t_n} L_{\text{classical}}(x, \dot{x}, t) dt \quad (59)$$

$$\langle x_n, t_n | x_{n-1}, t_{n-1} \rangle \sim \exp \left[\frac{iS(n, n-1)}{\hbar} \right] \quad (60)$$

设 $\Delta t = t_n - t_{n-1} \rightarrow 0$

$$\begin{aligned} S(n, n-1) &= \int_{t_{n-1}}^{t_n} \left[\frac{m\dot{x}^2}{2} - V(x) \right] dt \\ &= \Delta t \left[\frac{m}{2} \left(\frac{x_n - x_{n-1}}{\Delta t} \right)^2 - V \left(\frac{x_n + x_{n-1}}{2} \right) \right] \end{aligned} \quad (61)$$

我们可以在 $\langle x'', t'' | x', t' \rangle$ 直接放入无穷个积分, 使 Δt 无穷小

$$\begin{aligned}
 & \langle x'', t'' | x', t' \rangle \\
 &= \int dx_{N-1} \int dx_{N-2} \cdots \int dx_1 \langle x'', t'' | x_{N-1}, t_{N-1} \rangle \langle x_{N-1}, t_{N-1} | x_{N-2}, t_{N-2} \rangle \cdots \langle x_1, t_1 | x', t' \rangle \\
 &\sim \int dx_{N-1} \int dx_{N-2} \cdots \int dx_1 \prod_{n=1}^N \exp \left[\frac{i}{\hbar} S(n, n-1) \right] \\
 &= \int D[x(t)] \exp \left[\frac{i}{\hbar} \sum_{n=1}^N S(n, n-1) \right] \\
 &= \int D[x(t)] \exp \left\{ \frac{i}{\hbar} S_N[x(t)] \right\}
 \end{aligned} \tag{62}$$

其中

$$S_N[x(t)] = \sum_{n=1}^N S(n, n-1) = \int_{t'}^{t''} L(x, \dot{x}, t) dt \tag{63}$$

设 $\vec{r}(t_0) = \vec{r}', \vec{r}(t_N) = \vec{r}'', t_0 = t', t_N = t''$, 且 $t_0, t_1, \dots, t_{N-1}, t_N$ 等分

$$\varepsilon = t_j - t_{j-1} \quad j = 1, 2, \dots, N \tag{64}$$

$$S_N[\vec{r}(t)] = \int_{t'}^{t''} L(\vec{r}, \dot{\vec{r}}, t) dt = \varepsilon \sum_{j=1}^N L \left(\frac{\vec{r}_j + \vec{r}_{j-1}}{2}, \frac{\vec{r}_j - \vec{r}_{j-1}}{\varepsilon}, t' + j\varepsilon \right) \tag{65}$$

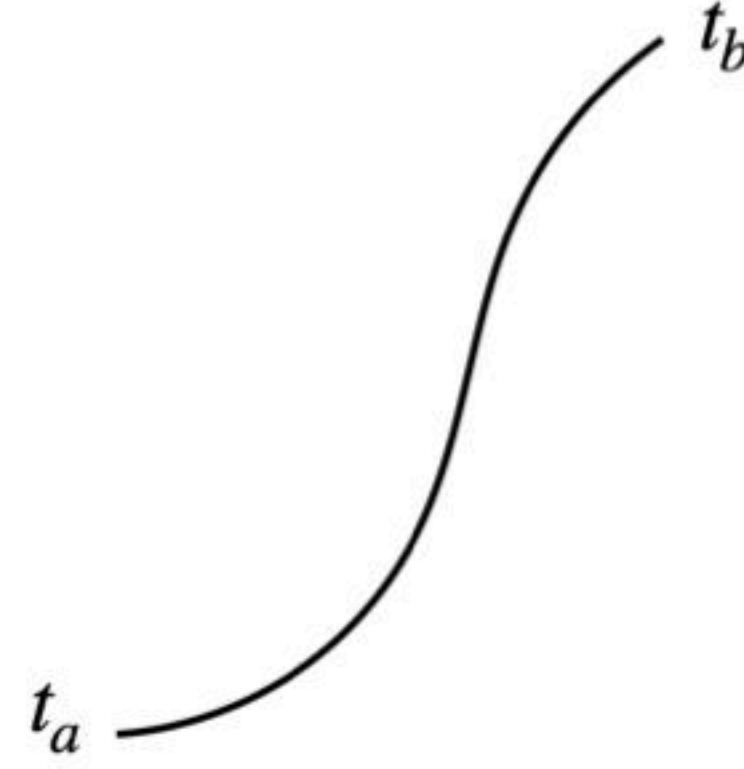
$$K_N(\vec{r}'', t''; \vec{r}', t') = \langle \vec{r}'', t'' | \vec{r}', t' \rangle_N \sim \int D[\vec{r}(t)] \exp \left\{ \frac{i}{\hbar} S_N[\vec{r}(t)] \right\} \tag{66}$$

我们希望

$$K(\vec{r}'', t''; \vec{r}', t') = \lim_{N \rightarrow \infty} K_N(\vec{r}'', t''; \vec{r}', t') \tag{67}$$

Review: Euler-Lagrange Principle

已知一个粒子 t_a 和 t_b 时刻的位置, 它的运动轨迹是使作用量 $S[x(t)]$ 最小的那一条。



根据最小作用量原理

$$\begin{aligned}
 \delta S[x(t)] &= \delta \int_{t_a}^{t_b} L(x, \dot{x}, t) dt \\
 &= \int_{t_a}^{t_b} \left(\frac{\partial L}{\partial x} \delta x + \frac{\partial L}{\partial \dot{x}} \delta \dot{x} \right) dt \\
 &= \int_{t_a}^{t_b} \left(\frac{\partial L}{\partial x} \delta x + \frac{\partial L}{\partial \dot{x}} \frac{d}{dt} \delta x \right) dt \\
 &= \int_{t_a}^{t_b} \left[\frac{\partial L}{\partial x} - \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{x}} \right) \right] \delta x dt + \left[\frac{\partial L}{\partial \dot{x}} \delta x \right]_{t_a}^{t_b} \\
 &= \int_{t_a}^{t_b} \left[\frac{\partial L}{\partial x} - \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{x}} \right) \right] \delta x dt = 0
 \end{aligned} \tag{68}$$

得到 Euler-Lagrange Equation

$$\frac{\partial L}{\partial x} - \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{x}} \right) = 0 \quad (69)$$

Example: 1-D Free Particle

$$L = \frac{1}{2} m \dot{x}^2 \quad (70)$$

代入拉格朗日方程

$$\frac{\partial L}{\partial x} - \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{x}} \right) = 0 \quad (71)$$

得

$$m\dot{x} = \text{constant} \quad (72)$$

$$p = m\dot{x} = m \frac{x'' - x'}{t'' - t'} \quad (73)$$

$$S_N[x(t)] = \int_{t'}^{t''} L(x, \dot{x}, t) dt = \frac{1}{2} \int_{t'}^{t''} m \dot{x}^2 dt = \frac{m}{2} \frac{(x'' - x')^2}{t'' - t'} \quad (74)$$

$$S(x_{j+1}, t_{j+1}; x_j, t_j) = \frac{m}{2} \frac{(x_{j+1} - x_j)^2}{t_{j+1} - t_j} = \frac{m}{2} \frac{(x_{j+1} - x_j)^2}{\varepsilon} \quad (75)$$

由 Dirac's remark 我们知道, 当 $t \rightarrow t'$ 时

$$K(x, t; x', t') = C \exp \left[\frac{iS(x, t; x', t')}{\hbar} \right] = C \exp \left[\frac{im}{2\hbar} \frac{(x - x')^2}{t - t'} \right] \quad (76)$$

接下来我们用初始条件来定 C。当 $t = t'$ 时,

$$K(x, t; x', t') = \delta(x - x') \quad (77)$$

已知积分

$$\lim_{\alpha \rightarrow \infty} e^{-i\alpha x^2} \sqrt{\frac{\alpha}{\pi}} = e^{-i\frac{\pi}{4}} \delta(x) \quad (78)$$

$$\begin{aligned} \lim_{t \rightarrow t'} K(x, t; x', t') &= C \lim_{t \rightarrow t'} \exp \left[\frac{im}{2\hbar} \frac{(x - x')^2}{t - t'} \right] \\ &= C \lim_{t \rightarrow t'} \exp \left[\frac{im}{2\hbar} \frac{(x - x')^2}{t - t'} \right] \sqrt{-\frac{m(x - x')^2}{2\pi\hbar(t - t')}} \sqrt{-\frac{2\pi\hbar(t - t')}{m(x - x')^2}} \\ &= C e^{-i\frac{\pi}{4}} \sqrt{-\frac{2\pi\hbar(t - t')}{m(x - x')^2}} \delta(x - x') = \delta(x - x') \end{aligned} \quad (79)$$

$$C = \sqrt{-\frac{m}{2\pi\hbar(t - t')}} e^{i\frac{\pi}{4}} = \sqrt{-\frac{m}{2\pi\hbar(t - t')}} e^{i\frac{\pi}{2}} = \sqrt{\frac{m}{2\pi i\hbar(t - t')}} \quad (80)$$

$$K(x, t; x', t') = C \exp \left[\frac{im}{2\hbar} \frac{(x - x')^2}{t - t'} \right] = \sqrt{\frac{m}{2\pi i\hbar(t - t')}} \exp \left[\frac{im}{2\hbar} \frac{(x - x')^2}{t - t'} \right] \quad (81)$$

当 $(t - t')$ 为有限大小时, 我们将 t' 到 t 分成无穷等份

$$\begin{aligned} K(x, t; x', t') &= \int dx_1 \int dx_2 \cdots \int dx_{N-1} \left[\frac{m}{2\pi i\hbar(t - t')} \right]^{\frac{N}{2}} \exp \left[\frac{im}{2\hbar\varepsilon} \sum_{j=0}^{N-1} (x_{j+1} - x_j)^2 \right] \\ &= \left[\frac{m}{2\pi i\hbar(t - t')} \right]^{\frac{N}{2}} \int dx_1 \int dx_2 \cdots \int dx_{N-1} \exp \left[\frac{im}{2\hbar\varepsilon} \sum_{j=0}^{N-1} (x_{j+1} - x_j)^2 \right] \end{aligned} \quad (82)$$

根据积分

$$\int_{-\infty}^{\infty} dx_2 \exp[\alpha(x_1 - x_2)^2 + \beta(x_3 - x_2)^2] = \exp\left[\frac{\alpha\beta}{\alpha + \beta}(x_1 - x_3)^2\right] \sqrt{-\frac{\pi}{\alpha + \beta}} \quad (83)$$

于是

$$\begin{aligned} & \int_{-\infty}^{\infty} dx_1 \int_{-\infty}^{\infty} dx_2 \cdots \int_{-\infty}^{\infty} dx_{N-1} \exp\left[\frac{im}{2\hbar\varepsilon} \sum_{j=0}^{N-1} (x_{j+1} - x_j)^2\right] \\ &= \left(\frac{2\hbar}{im}\right)^{\frac{N-1}{2}} \int_{-\infty}^{\infty} dy_1 \int_{-\infty}^{\infty} dy_2 \cdots \int_{-\infty}^{\infty} dy_{N-1} \exp\left[\frac{1}{\varepsilon} \sum_{j=0}^{N-1} (y_{j+1} - y_j)^2\right] \end{aligned} \quad (84)$$

其中 $y = \sqrt{\frac{im}{2\hbar}}x$ 。依次积分，设

$$\alpha_1 = \frac{1}{\varepsilon} \quad \beta = \frac{1}{\varepsilon} \quad \alpha_2 = \frac{\alpha_1\beta}{\alpha_1 + \beta} = \frac{1}{2\varepsilon} \quad \alpha_1 + \beta = \frac{2}{\varepsilon} \quad (85)$$

猜测

$$\alpha_m = \frac{1}{m\varepsilon} \quad (86)$$

则

$$\alpha_{m+1} = \frac{\alpha_m\beta}{\alpha_m + \beta} = \frac{1}{(m+1)\varepsilon} \quad (87)$$

得证。得到普遍表达式

$$\alpha_m + \beta = \frac{1}{m\varepsilon} + \frac{1}{\varepsilon} = \frac{m+1}{m\varepsilon} \quad (88)$$

于是

$$\begin{aligned} & \int_{-\infty}^{\infty} dx_1 \int_{-\infty}^{\infty} dx_2 \cdots \int_{-\infty}^{\infty} dx_{N-1} \exp\left[\frac{im}{2\hbar\varepsilon} \sum_{j=0}^{N-1} (x_{j+1} - x_j)^2\right] \\ &= \left(\frac{2\hbar}{im}\right)^{\frac{N-1}{2}} \int_{-\infty}^{\infty} dy_1 \int_{-\infty}^{\infty} dy_2 \cdots \int_{-\infty}^{\infty} dy_{N-1} \exp\left[\frac{1}{\varepsilon} \sum_{j=0}^{N-1} (y_{j+1} - y_j)^2\right] \\ &= \left(\frac{2\hbar}{im}\right)^{\frac{N-1}{2}} \exp\left[\frac{1}{N\varepsilon}(y - y')^2\right] \sqrt{-\frac{\pi\varepsilon}{2}} \sqrt{-\frac{\pi 2\varepsilon}{3}} \cdots \sqrt{-\frac{\pi m\varepsilon}{m+1}} \cdots \sqrt{-\frac{\pi(N-1)\varepsilon}{N}} \\ &= \left(\frac{2\hbar}{im}\right)^{\frac{N-1}{2}} \exp\left[\frac{im}{2\hbar} \frac{(x - x')^2}{N\varepsilon}\right] (-\pi\varepsilon)^{\frac{N-1}{2}} \frac{1}{\sqrt{N}} \\ &= \exp\left[\frac{im}{2\hbar} \frac{(x - x')^2}{N\varepsilon}\right] \left(-\frac{2\pi\hbar\varepsilon}{im}\right)^{\frac{N-1}{2}} \frac{1}{\sqrt{N}} \end{aligned} \quad (89)$$

整理成

$$\begin{aligned} K(x, t; x', t') &= \left[\frac{m}{2\pi i\hbar(t-t')}\right]^{\frac{N}{2}} \int dx_1 \int dx_2 \cdots \int dx_{N-1} \exp\left[\frac{im}{2\hbar\varepsilon} \sum_{j=0}^{N-1} (x_{j+1} - x_j)^2\right] \\ &= \left(\frac{m}{2\pi i\hbar N\varepsilon}\right)^{\frac{N}{2}} \exp\left[\frac{im}{2\hbar} \frac{(x - x')^2}{N(t-t')}\right] \left(-\frac{2\pi\hbar\varepsilon}{im}\right)^{\frac{N-1}{2}} \frac{1}{\sqrt{N}} \\ &= \sqrt{\frac{m}{2\pi i\hbar(t-t')}} \exp\left[\frac{im}{2\hbar} \frac{(x - x')^2}{N(t-t')}\right] \end{aligned} \quad (90)$$

我们发现，用经典理论导出的结果与量子力学的结果完全一致，量子力学是可以从经典理论中导出的。但量子力学和经典力学的过程完全不同，如量子力学中粒子没有固定路线、算符之间的不对易性、海森堡不确定性原理等，都与经典力学完全不一样。过程中发生了什么使得我们通过经典力学的作用量得到量子力学的结果？

回到一维自由粒子情况

$$K(x, t; x', t') = C \int_{-\infty}^{\infty} dx_1 \int_{-\infty}^{\infty} dx_2 \cdots \int_{-\infty}^{\infty} dx_{N-1} \exp \left[\frac{im}{2\hbar\varepsilon} \sum_{j=0}^{N-1} (x_{j+1} - x_j)^2 \right] \quad (91)$$

从中拿出一个积分

$$\begin{aligned} & \int dx_j \exp \left[\frac{im}{2\hbar\varepsilon} (x_j - x_{j-1})^2 \right] \exp \left[\frac{im}{2\hbar\varepsilon} (x_{j+1} - x_j)^2 \right] \\ &= \int dx_j \exp \left[\frac{im}{2\hbar\varepsilon} (x_j^2 - 2x_j x_{j-1} + x_{j-1}^2) \right] \exp \left[\frac{im}{2\hbar\varepsilon} (x_{j+1}^2 - 2x_{j+1} x_j + x_j^2) \right] \\ &= \exp \left[\frac{im}{2\hbar\varepsilon} (x_{j-1}^2 + x_{j+1}^2) \right] \exp \left[-\frac{im}{\hbar\varepsilon} \left(\frac{x_{j-1} - x_{j+1}}{2} \right)^2 \right] \int_{-\infty}^{\infty} dx_j \exp \left[\frac{im}{\hbar\varepsilon} \left(x_j - \frac{x_{j-1} + x_{j+1}}{2} \right)^2 \right] \end{aligned} \quad (92)$$

已知积分

$$\lim_{\alpha \rightarrow \infty} e^{i\alpha x^2} \sqrt{\frac{\alpha}{\pi}} = e^{\frac{i\pi}{4}} \delta(x) \quad (93)$$

当 $\hbar \rightarrow 0$ 时, 退化到经典理论, 令 $\alpha = \frac{m}{\hbar\varepsilon} \rightarrow \infty$

$$\begin{aligned} \lim_{\hbar \rightarrow 0} \exp \left[\frac{im}{\hbar\varepsilon} \left(x_j - \frac{x_{j-1} + x_{j+1}}{2} \right)^2 \right] &= \lim_{\alpha \rightarrow \infty} \exp \left[i\alpha \left(x_j - \frac{x_{j-1} + x_{j+1}}{2} \right)^2 \right] \sqrt{\frac{\alpha}{\pi}} \sqrt{\frac{\pi}{\alpha}} \\ &= \sqrt{\frac{\pi\hbar\varepsilon}{m}} e^{\frac{i\pi}{4}} \delta \left(x_j - \frac{x_{j-1} + x_{j+1}}{2} \right) \end{aligned} \quad (94)$$

在经典理论中, 积分退化为一点的贡献, 自由粒子的运动路线是一条直线。

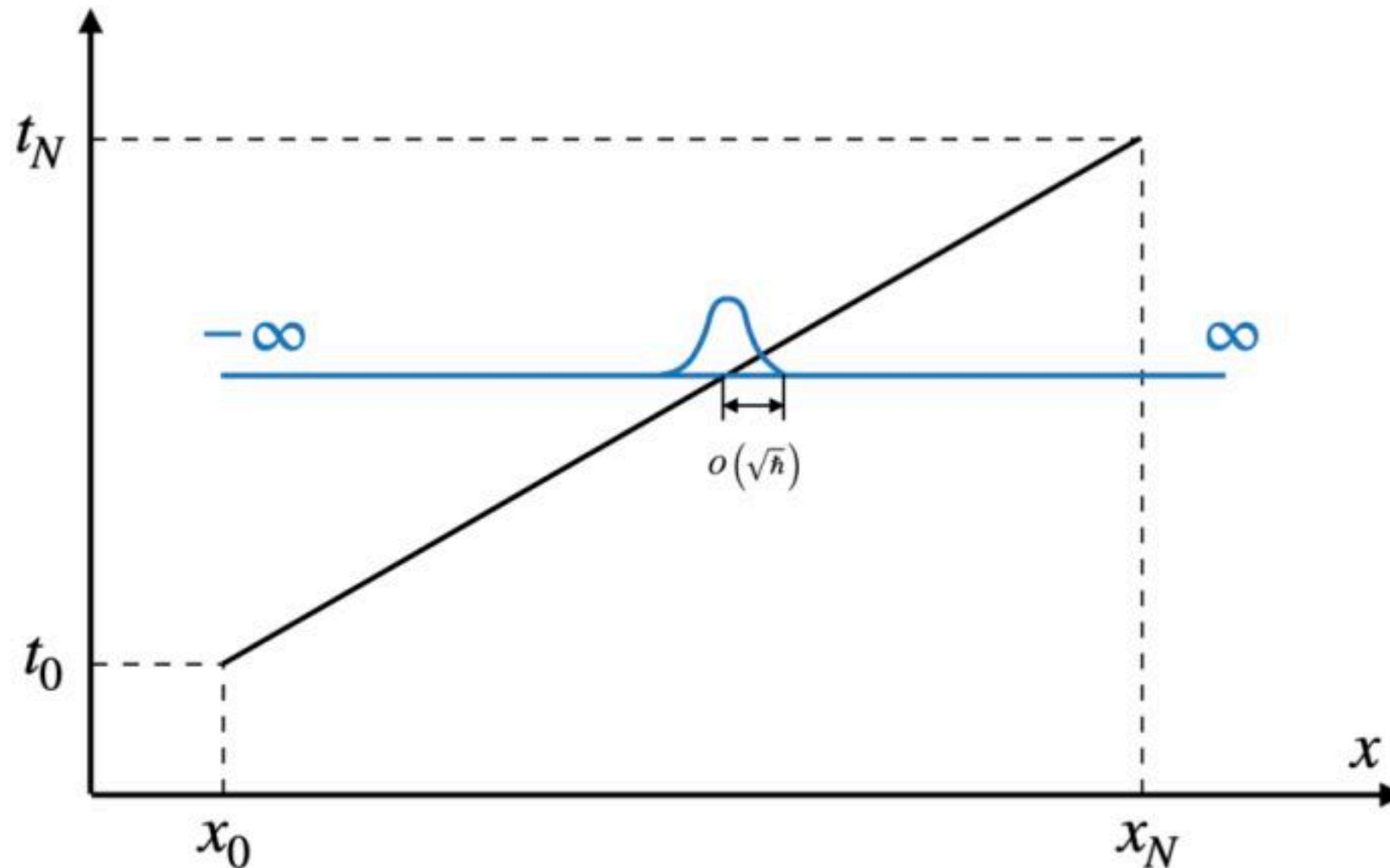
当 \hbar 有限时, Gauss 函数有一个很小的贡献

$$\left(x_j - \frac{x_{j-1} + x_{j+1}}{2} \right)^2 \frac{m}{\varepsilon} \frac{1}{\hbar} \sim O(1) \quad (95)$$

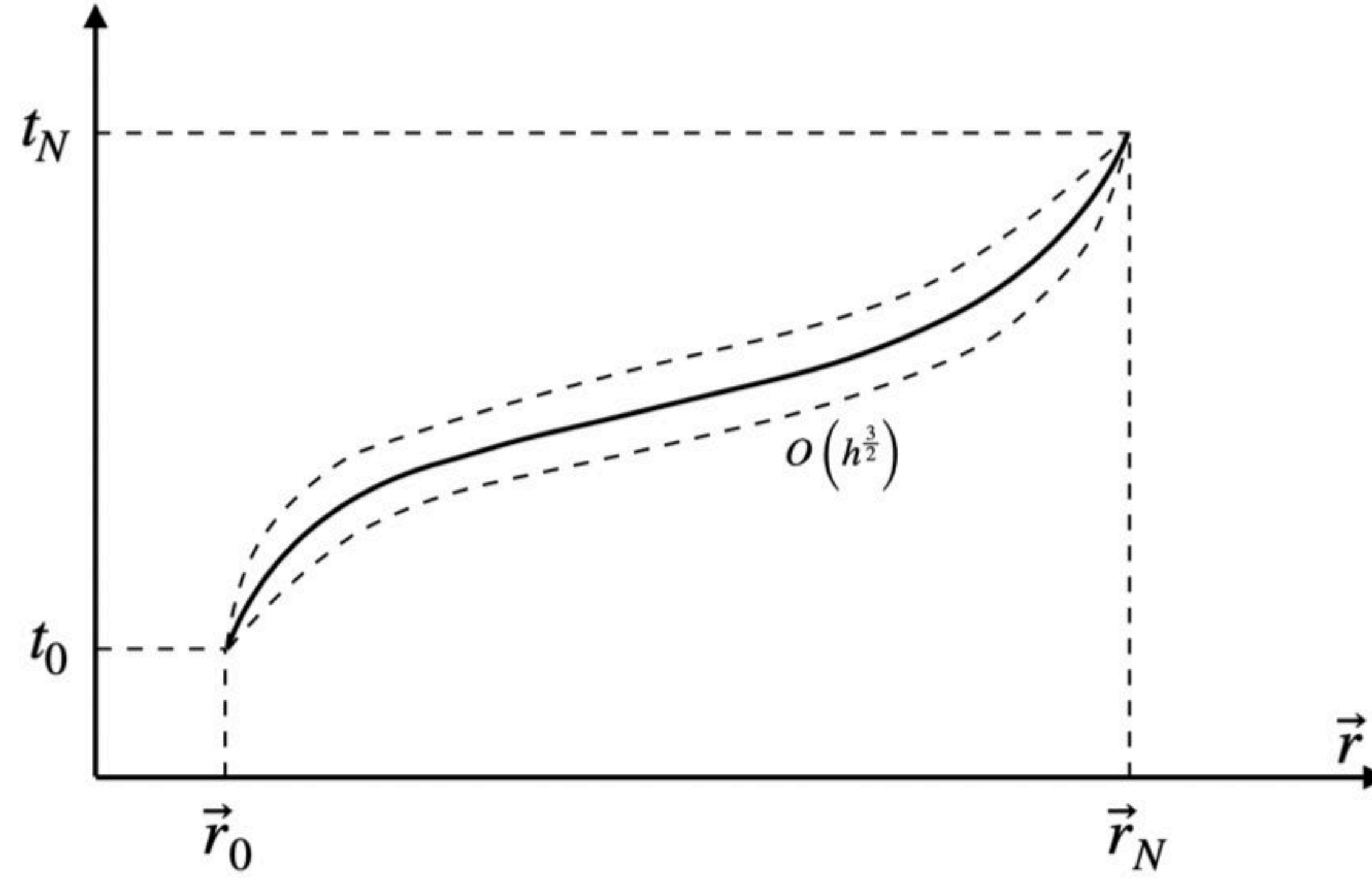
$$\left(x_j - \frac{x_{j-1} + x_{j+1}}{2} \right)^2 \frac{m}{\varepsilon} \sim O(\hbar) \quad (96)$$

$$x_j \sim \frac{x_{j-1} + x_{j+1}}{2} + O(\sqrt{\hbar}) \quad (97)$$

展开宽度的量级是 $\sqrt{\hbar}$ 。



三维情况经典理论下粒子轨迹为一条曲线，而量子力学下有 $\hbar^{\frac{3}{2}}$ 的展开宽度。



5 从 Feynman 路径积分导出传播子

$$\begin{aligned}
& K(\vec{r}', t'; \vec{r}, t) \\
&= \lim_{N \rightarrow \infty} \int \prod_{j=1}^{N-1} d\vec{r}_j \exp \left\{ \frac{i}{\hbar} S_N[\vec{r}(t)] \right\} \\
&= \lim_{N \rightarrow \infty} \int \prod_{j=1}^{N-1} d\vec{r}_j \exp \left[\frac{i}{\hbar} \varepsilon \sum_{j=1}^N L \left(\frac{\vec{r}_j + \vec{r}_{j-1}}{2}, \frac{\vec{r}_j - \vec{r}_{j-1}}{\varepsilon}, t + j\varepsilon \right) \right] \\
&= \lim_{M \rightarrow \infty} \lim_{N-M \rightarrow \infty} \int \prod_{j=1}^{M-1} d\vec{r}_j \prod_{i=M+1}^{N-1} d\vec{r}_i d\vec{r}_M \\
&\quad \exp \left\{ \frac{i}{\hbar} \varepsilon \left[\sum_{j=1}^M L \left(\frac{\vec{r}_j + \vec{r}_{j-1}}{2}, \frac{\vec{r}_j - \vec{r}_{j-1}}{\varepsilon}, t + j\varepsilon \right) + \sum_{i=M+1}^N L \left(\frac{\vec{r}_i + \vec{r}_{i-1}}{2}, \frac{\vec{r}_i - \vec{r}_{i-1}}{\varepsilon}, t + M\varepsilon + i\varepsilon \right) \right] \right\} \quad (98) \\
&= \int d\vec{r}_M \lim_{M \rightarrow \infty} \int \prod_{j=1}^{M-1} d\vec{r}_j \exp \left[\frac{i}{\hbar} \varepsilon \sum_{j=1}^M L \left(\frac{\vec{r}_j + \vec{r}_{j-1}}{2}, \frac{\vec{r}_j - \vec{r}_{j-1}}{\varepsilon}, t + j\varepsilon \right) \right] \\
&\quad \lim_{N-M \rightarrow \infty} \int \prod_{i=1}^{M-1} d\vec{r}_i \exp \left[\frac{i}{\hbar} \varepsilon \sum_{i=M}^M L \left(\frac{\vec{r}_i + \vec{r}_{i-1}}{2}, \frac{\vec{r}_i - \vec{r}_{i-1}}{\varepsilon}, t + M\varepsilon + i\varepsilon \right) \right] \\
&= \int d\vec{r}_M K(\vec{r}', t'; \vec{r}_M, t_M) K(\vec{r}_M, t_M; \vec{r}, t)
\end{aligned}$$

\vec{r}_M 是哑矢量 (dummy index)，用 \vec{r}'' 表示 \vec{r}_M

$$K(\vec{r}', t'; \vec{r}, t) = \int d\vec{r}'' K(\vec{r}', t'; \vec{r}'', t'') K(\vec{r}'', t''; \vec{r}, t) \quad (99)$$

这个方程我们在薛定谔方程中提到过，现在我们从路径积分中导出同样的结果，验证了这一点。

6 Dirac's Remark ($t_2 \rightarrow t_1$)

$$\begin{aligned}\langle x_2, t_2 | x_1, t_1 \rangle &\sim \exp \left[\frac{i}{\hbar} \int_{t_1}^{t_2} L(x, \dot{x}, t) dt \right] \\ &= \exp \left\{ \frac{i}{\hbar} \left[\frac{1}{2} m \frac{(x_2 - x_1)^2}{t_2 - t_1} - (t_2 - t_1) V(x_1) \right] \right\}\end{aligned}\quad (100)$$

在量子力学中我们定义

$$\begin{aligned}\langle x_2, t_2 | x_1, t_1 \rangle &= \langle x_2 | \exp \left[-\frac{i}{\hbar} H(t_2 - t_1) \right] | x_1 \rangle \\ &= \langle x_2 | \exp \left[-\frac{i}{\hbar} (H_0 + V)(t_2 - t_1) \right] | x_1 \rangle\end{aligned}\quad (101)$$

H_0 和 V 在量子力学中具有不对易性, 利用如下关系式

$$\exp[\varepsilon(A + B)] = \exp(\varepsilon A) \exp(\varepsilon B) \left[\exp \left(-\frac{1}{2} \varepsilon^2 [A, B] \right) + O(\varepsilon^3) \right] \quad (102)$$

$$\lim_{\varepsilon \rightarrow 0} \exp[\varepsilon(A + B)] = \exp(\varepsilon A) \exp(\varepsilon B) \quad (103)$$

由于 $(t_2 - t_1) \rightarrow 0$,

$$\begin{aligned}\langle x_2, t_2 | x_1, t_1 \rangle &= \langle x_2 | \exp \left[-\frac{i}{\hbar} H_0(t_2 - t_1) \right] \exp \left[-\frac{i}{\hbar} V(t_2 - t_1) \right] | x_1 \rangle \\ &= \langle x_2 | \exp \left[-\frac{i}{\hbar} H_0(t_2 - t_1) \right] | x_1 \rangle \exp \left[-\frac{i}{\hbar} V(x_1)(t_2 - t_1) \right]\end{aligned}\quad (104)$$

自由粒子的传播子

$$\langle x_2 | \exp \left[-\frac{i}{\hbar} H_0(t_2 - t_1) \right] | x_1 \rangle = \left[\frac{m}{2\pi i \hbar (t_2 - t_1)} \right]^{\frac{1}{2}} \exp \left[\frac{im}{2\hbar} \frac{(x_2 - x_1)^2}{t_2 - t_1} \right] \quad (105)$$

$$\langle x_2, t_2 | x_1, t_1 \rangle = \left[\frac{m}{2\pi i \hbar (t_2 - t_1)} \right]^{\frac{1}{2}} \exp \left\{ \frac{i}{\hbar} \left[\frac{m}{2} \frac{(x_2 - x_1)^2}{t_2 - t_1} - (t_2 - t_1) V(x_1) \right] \right\} \quad (106)$$

当 $t_2 \rightarrow t_1$ 时, Feynman 给出的结果和 Schrödinger 给出的结果一致。

7 从 Feynman 路径积分导出 $t'' - t' = \text{finite}$ 时的传播子

$$\begin{aligned}\langle x'', t'' | x', t' \rangle &= \langle x'' | \exp \left[-\frac{i}{\hbar} H(t'' - t') \right] | x' \rangle \\ &= \langle x'' | \exp \left[-\frac{i}{\hbar} H(t'' - t_{N-1}) \right] \cdots \exp \left[-\frac{i}{\hbar} H(t_{j+1} - t_j) \right] \cdots \exp \left[-\frac{i}{\hbar} H(t_1 - t') \right] | x' \rangle \\ &= \int dx_1 \cdots dx_{N-1} \langle x'' | \exp \left[-\frac{i}{\hbar} H(t'' - t_{N-1}) \right] | x_{N-1} \rangle \cdots \\ &\quad \langle x_{j+1} | \exp \left[-\frac{i}{\hbar} H(t_{j+1} - t_j) \right] | x_j \rangle \cdots \langle x_1 | \exp \left[-\frac{i}{\hbar} H(t_1 - t') \right] | x' \rangle \\ &= \left(\frac{m}{2\pi i \hbar \varepsilon} \right)^{\frac{N}{2}} \int dx_1 \cdots dx_{N-1} \exp \left\{ \sum_{j=1}^{N-1} \left[\frac{im(x_{j+1} - x_j)^2}{2\hbar \varepsilon} - \frac{i}{\hbar} \varepsilon V(x_j) \right] \right\} \\ &= \int D[x(t)] \exp \left\{ \frac{i}{\hbar} \int_{t'}^{t''} \left[\frac{m}{2} \dot{x}^2 - V(x) \right] dt \right\}\end{aligned}\quad (107)$$

根据 Lie-Trotter Formula

$$\exp[it(A+B)] = \lim_{N \rightarrow \infty} \left[\exp\left(\frac{itA}{N}\right) \exp\left(\frac{itB}{N}\right) \right]^N \quad (108)$$

$$\begin{aligned} & \langle x | \exp\left[-\frac{i}{\hbar} H(t-t')\right] | x' \rangle \\ &= \langle x | \exp\left[-\frac{i}{\hbar} (H_0 + V)(t-t')\right] | x' \rangle \\ &= \langle x | \left[\exp\left(-\frac{iH_0\varepsilon}{\hbar}\right) \exp\left(-\frac{iV\varepsilon}{\hbar}\right) \right]^N | x' \rangle \\ &= \int dx_1 \cdots dx_{N-1} \langle x'' | \exp\left(-\frac{iH_0\varepsilon}{\hbar}\right) \exp\left(-\frac{iV\varepsilon}{\hbar}\right) | x_{N-1} \rangle \cdots \langle x_1 | \exp\left(-\frac{iH_0\varepsilon}{\hbar}\right) \exp\left(-\frac{iV\varepsilon}{\hbar}\right) | x' \rangle \\ &= \langle x_N = x | \prod_{j=1}^{N-1} \int_{-\infty}^{\infty} dx_j \exp\left(-\frac{i\varepsilon}{2m\hbar} p^2\right) \exp\left[-\frac{i\varepsilon}{\hbar} V(x)\right] | x_{N-1} \rangle \langle x_{N-1} | \exp\left(-\frac{i\varepsilon}{2m\hbar} p^2\right) \\ & \quad \exp\left[-\frac{i\varepsilon}{\hbar} V(x)\right] | x_{N-2} \rangle \cdots | x_1 \rangle \langle x_1 | \exp\left(-\frac{i\varepsilon}{2m\hbar} p^2\right) \exp\left[-\frac{i\varepsilon}{\hbar} V(x)\right] | x_1 = x' \rangle \\ &= \left(\frac{m}{2\pi i\hbar\varepsilon}\right)^{\frac{N}{2}} \prod_{j=1}^{N-1} \int_{-\infty}^{\infty} dx_j \exp\left[\frac{i}{\hbar} \int_{t'}^t L dt''\right] \end{aligned} \quad (109)$$

$$K(x, t, x', t') = \int D[x(t)] \exp\left[\frac{i}{\hbar} S(t, t')\right] \quad (110)$$

我们可以从 Feynman 路径积分给出量子力学的结果。

8 从 Feynman 路径积分导出传播子的运动方程

已知运动方程

$$i\hbar \frac{\partial}{\partial t} \langle x, t | x', t' \rangle = \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \langle x, t | x', t' \rangle \quad (111)$$

$$\begin{aligned} \langle x, t | x', t' \rangle &\sim \left(\frac{m}{2\pi i\hbar\varepsilon}\right)^{\frac{N}{2}} \prod_{j=1}^{N-1} \int dx_j \exp\left[\frac{i}{\hbar} S(t, t')\right] \\ &= \left[\frac{m}{2\pi i\hbar(t-t_{N-1})}\right]^{\frac{1}{2}} \left(\frac{m}{2\pi i\hbar\varepsilon}\right)^{\frac{N-1}{2}} \prod_{j=1}^{N-1} \int dx_j \exp\left[\frac{i}{\hbar} S(t, t_{N-1})\right] \prod_{n=1}^{N-1} \exp\left[\frac{i}{\hbar} S(n, n-1)\right] \end{aligned} \quad (112)$$

方程左边

$$i\hbar \frac{\partial}{\partial t} \langle x, t | x', t' \rangle = i\hbar \left(-\frac{1}{2}\right) \frac{1}{t-t_{N-1}} \langle x, t | x', t' \rangle - \left[\frac{\partial}{\partial t} S(t, t_{N-1})\right] \langle x, t | x', t' \rangle \quad (113)$$

其中

$$\begin{aligned} \frac{\partial}{\partial t} S(t, t_{N-1}) &= \frac{\partial}{\partial t} \left[(t-t_{N-1}) L\left(\frac{x+x_{N-1}}{2}, \frac{x-x_{N-1}}{t-t_{N-1}}, \frac{t+t_{N-1}}{2}\right) \right] \\ &= \frac{\partial}{\partial t} \left\{ (t-t_{N-1}) \left[\frac{1}{2} m \left(\frac{x-x_{N-1}}{t-t_{N-1}}\right)^2 - V\left(\frac{x+x_{N-1}}{2}\right) \right] \right\} \\ &= -\frac{1}{2} m \left(\frac{x-x_{N-1}}{t-t_{N-1}}\right)^2 - V\left(\frac{x+x_{N-1}}{2}\right) \\ &= -T - V \end{aligned} \quad (114)$$

代回 Eq.(113)

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} \langle x, t | x', t' \rangle &= i\hbar \left(-\frac{1}{2} \right) \frac{1}{t - t_{N-1}} \langle x, t | x', t' \rangle - \left[\frac{\partial}{\partial t} S(t, t_{N-1}) \right] \langle x, t | x', t' \rangle \\ &= \left[i\hbar \left(-\frac{1}{2} \right) \frac{1}{t - t_{N-1}} + \frac{1}{2} m \left(\frac{x - x_{N-1}}{t - t_{N-1}} \right)^2 + V(x) \right] \langle x, t | x', t' \rangle \end{aligned} \quad (115)$$

方程右边

$$\text{RHS} = \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \langle x, t | x', t' \rangle \quad (116)$$

其中

$$\begin{aligned} \frac{\partial}{\partial x} \langle x, t | x', t' \rangle &= \frac{i}{\hbar} \langle x, t | x', t' \rangle \frac{\partial}{\partial x} S(t, t_{N-1}) \\ &= \frac{i}{\hbar} \langle x, t | x', t' \rangle \frac{\partial}{\partial x} \left\{ (t - t_{N-1}) \left[\frac{1}{2} m \left(\frac{x - x_{N-1}}{t - t_{N-1}} \right)^2 - V \left(\frac{x + x_{N-1}}{2} \right) \right] \right\} \\ &= \frac{im}{\hbar} \frac{x - x_{N-1}}{t - t_{N-1}} \langle x, t | x', t' \rangle \end{aligned} \quad (117)$$

$$\begin{aligned} \frac{\partial^2}{\partial x^2} \langle x, t | x', t' \rangle &= \frac{\partial}{\partial x} \left(\frac{im}{\hbar} \frac{x - x_{N-1}}{t - t_{N-1}} \langle x, t | x', t' \rangle \right) \\ &= \left[\frac{im}{\hbar} \frac{1}{t - t_{N-1}} - \frac{m^2}{\hbar^2} \left(\frac{x - x_{N-1}}{t - t_{N-1}} \right)^2 \right] \langle x, t | x', t' \rangle \end{aligned} \quad (118)$$

$$\begin{aligned} \text{RHS} &= \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \langle x, t | x', t' \rangle \\ &= \left[-\frac{i\hbar}{2} \frac{1}{t - t_{N-1}} + \frac{m}{2} \left(\frac{x - x_{N-1}}{t - t_{N-1}} \right)^2 + V(x) \right] \langle x, t | x', t' \rangle \end{aligned} \quad (119)$$

LHS=RHS, 故运动方程得证。即可以通过 Feynman 路径积分导出运动方程。

9 Equivalence of Feynman's Formulation and Schrödinger Function

$$\psi(x, t + \varepsilon) = \int_{-\infty}^{\infty} K(x, t + \varepsilon, y, t) \psi(y, t) dy \quad (120)$$

Dirac's remark 给出, 当 $\varepsilon \rightarrow 0^+$ 时

$$K(x, t + \varepsilon, y, t) = C \exp \left[\frac{i\varepsilon}{\hbar} L \left(\frac{x + y}{2}, \frac{x - y}{\varepsilon}, t \right) \right] = C \exp \left\{ \frac{i\varepsilon}{\hbar} \left[\frac{m}{2} \left(\frac{x - y}{\varepsilon} \right)^2 - V \left(\frac{x + y}{2}, t \right) \right] \right\} \quad (121)$$

代回 Eq.(120)

$$\psi(x, t + \varepsilon) = C \int_{-\infty}^{\infty} \exp \left\{ \frac{i\varepsilon}{\hbar} \left[\frac{m}{2} \left(\frac{x - y}{\varepsilon} \right)^2 - V \left(\frac{x + y}{2}, t \right) \right] \right\} \psi(y, t) dy \quad (122)$$

令 $x = y - \eta$

$$\psi(x, t + \varepsilon) = C \int_{-\infty}^{\infty} d\eta \exp \left\{ \frac{i\varepsilon}{\hbar} \left[\frac{m\eta^2}{2\varepsilon^2} - V \left(x + \frac{\eta}{2}, t \right) \right] \right\} \psi(x + \eta, t) \quad (123)$$

展开

$$\psi(x, t) + \varepsilon \frac{\partial}{\partial t} \psi = C \int_{-\infty}^{\infty} d\eta \exp \left(\frac{im\eta^2}{2\hbar\varepsilon} \right) \exp \left[-\frac{i\varepsilon}{\hbar} V \left(x + \frac{\eta}{2}, t \right) \right] \left[\psi(x, t) + \eta \frac{\partial}{\partial x} \psi + \frac{1}{2} \eta^2 \frac{\partial^2}{\partial x^2} \psi + \cdots \right] \quad (124)$$

由于

$$\frac{m\eta^2}{2\hbar\varepsilon} \sim O(1) \quad \eta \sim O(\sqrt{\varepsilon}) \quad (125)$$

ε 和 η 是小量

$$\psi(x, t) + \varepsilon \frac{\partial}{\partial t} \psi = C \int_{-\infty}^{\infty} d\eta \exp\left(\frac{im\eta^2}{2\hbar\varepsilon}\right) \left[1 - \frac{i\varepsilon}{\hbar} V(x, t)\right] \left[\psi(x, t) + \eta \frac{\partial}{\partial x} \psi + \frac{1}{2} \eta^2 \frac{\partial^2}{\partial x^2} \psi + \cdots\right] \quad (126)$$

已知积分

$$\int_{-\infty}^{\infty} d\eta \exp\left(\frac{im\eta^2}{2\hbar\varepsilon}\right) = \sqrt{\frac{2\pi\hbar\varepsilon i}{m}} \quad (127)$$

$$\int_{-\infty}^{\infty} d\eta \exp\left(\frac{im\eta^2}{2\hbar\varepsilon}\right) \eta = 0 \quad (128)$$

$$\int_{-\infty}^{\infty} d\eta \exp\left(\frac{im\eta^2}{2\hbar\varepsilon}\right) \eta^2 = \frac{\sqrt{\pi}}{2} \left(\frac{2\hbar\varepsilon i}{m}\right)^{\frac{3}{2}} \quad (129)$$

则

$$C \sqrt{\frac{2\pi\hbar\varepsilon i}{m}} = 1 \quad \Rightarrow \quad C = \sqrt{\frac{m}{2\pi\hbar\varepsilon i}} \quad (130)$$

$$C \int_{-\infty}^{\infty} d\eta \exp\left(\frac{im\eta^2}{2\hbar\varepsilon}\right) \eta^2 = \frac{\sqrt{\pi}}{2} \left(\frac{2\hbar\varepsilon i}{m}\right)^{\frac{3}{2}} \sqrt{\frac{m}{2\pi\hbar\varepsilon i}} = \frac{i\hbar\varepsilon}{m} \quad (131)$$

$$\begin{aligned} \psi(x, t) + \varepsilon \frac{\partial}{\partial t} \psi &= C \int_{-\infty}^{\infty} d\eta \exp\left(\frac{im\eta^2}{2\hbar\varepsilon}\right) \left[1 - \frac{i\varepsilon}{\hbar} V(x, t)\right] \left[\psi(x, t) + \eta \frac{\partial}{\partial x} \psi + \frac{1}{2} \eta^2 \frac{\partial^2}{\partial x^2} \psi + \cdots\right] \\ &= \left[1 - \frac{i\varepsilon}{\hbar} V(x, t)\right] \left[\psi(x, t) + \frac{1}{2} \frac{\partial^2}{\partial x^2} \psi(x, t) \frac{i\hbar\varepsilon}{m}\right] \end{aligned} \quad (132)$$

整理得

$$i\hbar \frac{\partial}{\partial t} \psi(x, t) = \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x, t)\right] \psi(x, t) \quad (133)$$

10 Formulation in the Phase Space

$$\begin{aligned}
& K(x, t; x', t') \\
&= \int \prod_{j=1}^{N-1} dx_j \langle x | \exp\left(-\frac{i\varepsilon}{2m\hbar} p^2\right) \exp\left[-\frac{i\varepsilon}{\hbar} V(x)\right] |x_{N-1}\rangle \langle x_{N-1}| \exp\left(-\frac{i\varepsilon}{2m\hbar} p^2\right) \exp\left[-\frac{i\varepsilon}{\hbar} V(x)\right] |x_{N-2}\rangle \cdots \\
&\quad \langle x_1 | \exp\left(-\frac{i\varepsilon}{2m\hbar} p^2\right) \exp\left[-\frac{i\varepsilon}{\hbar} V(x)\right] |x'\rangle \\
&= \int \prod_{j=1}^{N-1} dx_j \prod_{i=1}^N dp_i \langle x | \exp\left(-\frac{i\varepsilon}{2m\hbar} p^2\right) |p_N\rangle \langle p_N| \exp\left[-\frac{i\varepsilon}{\hbar} V(x)\right] |x_{N-1}\rangle \langle x_{N-1}| \exp\left(-\frac{i\varepsilon}{2m\hbar} p^2\right) |p_{N-1}\rangle \\
&\quad \langle p_{N-1}| \exp\left[-\frac{i\varepsilon}{\hbar} V(x)\right] |x_{N-2}\rangle \cdots \langle x_1 | \exp\left(-\frac{i\varepsilon}{2m\hbar} p^2\right) |p_1\rangle \langle p_1| \exp\left[-\frac{i\varepsilon}{\hbar} V(x)\right] |x'\rangle \\
&= \left(\frac{1}{\sqrt{2\pi\hbar}}\right)^{2N} \int \prod_{j=1}^{N-1} dx_j \prod_{i=1}^N dp_i \exp\left(-\frac{i\varepsilon}{2m\hbar} p_N^2\right) \exp\left(\frac{ip_N x_N}{\hbar}\right) \exp\left(-\frac{ip_N x_{N-1}}{\hbar}\right) \exp\left[-\frac{i\varepsilon}{\hbar} V(x_{N-1})\right] \\
&\quad \exp\left(-\frac{i\varepsilon}{2m\hbar} p_{N-1}^2\right) \exp\left(\frac{ip_{N-1} x_{N-1}}{\hbar}\right) \exp\left(-\frac{ip_{N-1} x_{N-2}}{\hbar}\right) \exp\left[-\frac{i\varepsilon}{\hbar} V(x_{N-2})\right] \cdots \\
&\quad \exp\left(-\frac{i\varepsilon}{2m\hbar} p_1^2\right) \exp\left(\frac{ip_1 x_1}{\hbar}\right) \exp\left(-\frac{ip_1 x'}{\hbar}\right) \exp\left[-\frac{i\varepsilon}{\hbar} V(x')\right] \\
&= \left(\frac{1}{\sqrt{2\pi\hbar}}\right)^{2N} \int \prod_{j=1}^{N-1} dx_j \prod_{i=1}^N dp_i \exp\left\{\frac{i\varepsilon}{\hbar} \left[p_i \frac{x_i - x_{i-1}}{\varepsilon} - \frac{p_i^2}{2m} - V(x_{i-1})\right]\right\} \\
&= \left(\frac{1}{\sqrt{2\pi\hbar}}\right)^{2N} \int \prod_{j=1}^{N-1} dx_j \prod_{i=1}^N dp_i \exp\left[\frac{i\varepsilon}{\hbar} (p_i \dot{x} - H)\right] \\
&= \left(\frac{1}{\sqrt{2\pi\hbar}}\right)^{2N} \int \prod_{j=1}^{N-1} dx_j \prod_{i=1}^N dp_i \exp\left(\frac{iS}{\hbar}\right)
\end{aligned} \tag{134}$$

$$K(x, t; x', t') = \int D[x] D[p] \exp\left(\frac{iS}{\hbar}\right) \tag{135}$$

11 从 Feynman 路径积分导出 $K(x, t; x', t') = \delta(x - x')$ ($t \rightarrow t'$)

$$K(x, t; x', t') = \int dx_1 \int dx \cdots \int dx_{N-1} \left(\frac{m}{2\pi i \hbar \varepsilon}\right)^{\frac{N}{2}} \exp\left[\frac{im}{2\hbar\varepsilon} \sum_{j=0}^{N-1} (x_{j+1} - x_j)^2\right] \tag{136}$$

$$\lim_{\varepsilon \rightarrow 0} \exp\left[\frac{im}{2\hbar\varepsilon} (x_{j+1} - x_j)^2\right] = \sqrt{-\frac{2\pi\hbar\varepsilon}{m}} e^{-\frac{i\pi}{4}} \delta(x_{j+1} - x_j) \tag{137}$$

$$\begin{aligned}
K(x, t; x', t') &= \int dx_1 \int dx \cdots \int dx_{N-1} \left(\frac{m}{2\pi i \hbar \varepsilon}\right)^{\frac{N}{2}} \exp\left[\frac{im}{2\hbar\varepsilon} \sum_{j=0}^{N-1} (x_{j+1} - x_j)^2\right] \\
&= \left(\frac{m}{2\pi i \hbar \varepsilon}\right)^{\frac{N}{2}} \left(-\frac{2\pi\hbar\varepsilon}{m}\right)^{\frac{N}{2}} \left(e^{-\frac{i\pi}{4}}\right)^N \int dx_1 \int dx \cdots \int dx_{N-1} \prod_{j=0}^{N-1} \delta(x_{j+1} - x_j) \\
&= (i)^{\frac{N}{2}} \left(e^{-\frac{i\pi}{2}}\right)^{\frac{N}{2}} \delta(x - x') = \delta(x - x')
\end{aligned} \tag{138}$$

12 从 Feynman 路径积分导出 Time-dependent Case 的结论

$$|\psi(t)\rangle = U(t, t') |\psi(t')\rangle \quad (139)$$

$$i\hbar \frac{\partial}{\partial t} U(t, t') = H(t)U(t, t') \quad (140)$$

设 $H(t) = H$ 时的解是

$$U(t, t') = \exp\left[-\frac{iH(t-t')}{\hbar}\right] \quad (141)$$

接下来求 $U(t, t')$ 的形式解

$$dU(t, t') = \frac{1}{i\hbar} H(t)U(t, t')dt \quad (142)$$

$$\int_{t'}^{t''} dU(t, t') = \frac{1}{i\hbar} \int_{t'}^{t''} H(t)U(t, t')dt \quad (143)$$

由于 $U(t', t') = 1$, 得到

$$U(t'', t') - 1 = \frac{1}{i\hbar} \int_{t'}^{t''} H(t)U(t, t')dt \quad (144)$$

$$\begin{aligned} U(t'', t') &= 1 + \frac{1}{i\hbar} \int_{t'}^{t''} H(t_1)U(t_1, t')dt_1 \\ &= 1 + \frac{1}{i\hbar} \int_{t'}^{t''} H(t_1) \left[1 + \frac{1}{i\hbar} \int_{t'}^{t_1} H(t_2)U(t_2, t')dt_2 \right] dt_1 \\ &= 1 + \frac{1}{i\hbar} \int_{t'}^{t''} H(t_1)dt_1 + \left(\frac{1}{i\hbar} \right)^2 \int_{t'}^{t''} dt_1 \int_{t'}^{t_1} dt_2 H(t_1)H(t_2)U(t_2, t') \\ &= \dots \\ &= 1 + \sum_{n=1}^{\infty} \left(\frac{1}{i\hbar} \right)^n \int_{t'}^{t''} dt_1 \int_{t'}^{t_1} dt_2 \dots \int_{t'}^{t_{n-1}} dt_n H(t_1)H(t_2) \dots H(t_n) \\ &= (t'' - t') \exp \left[-\frac{i}{\hbar} \int_{t'}^{t''} dt H(t) \right] \end{aligned} \quad (145)$$

故

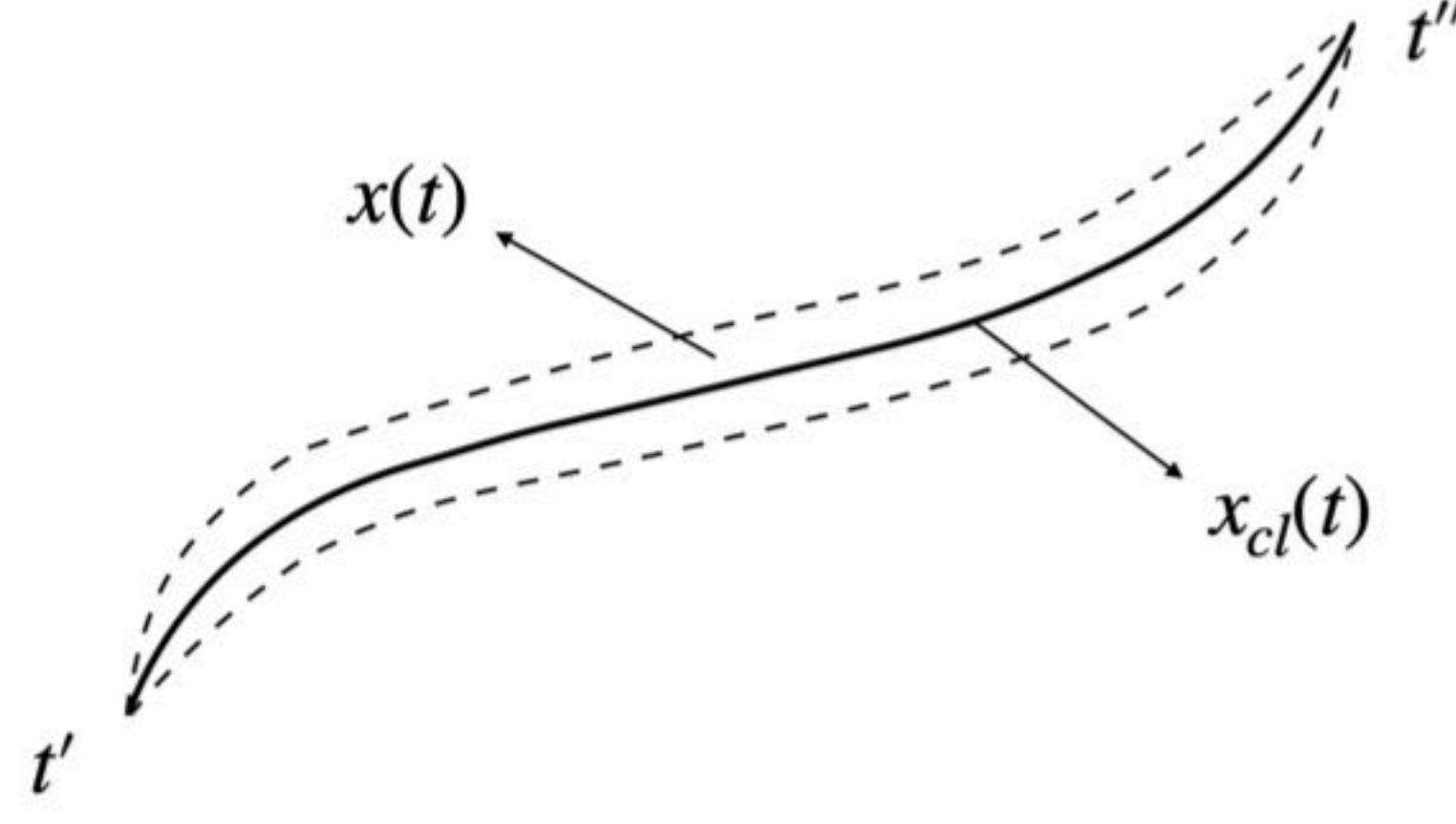
$$U(t, t') = T \exp \left[-\frac{i}{\hbar} \int_{t'}^t dt'' H(t'') \right] \quad (146)$$

13 General Method for Calculating the Propagator (Semiclassical Method)

$$K(x'', t''; x', t') = \int D[x(t)] e^{\frac{i}{\hbar} S} \quad (147)$$

其中

$$S = \int_{t'}^{t''} dt L(x, \dot{x}, t) = \int_{t'}^{t''} dt \left[\frac{1}{2} m \dot{x}^2 - V(x, t) \right] \quad (148)$$



$$x(t) = x_{\text{cl}}(t) + q(t) \quad (149)$$

其中 $q(t)$ 来源于量子涨落 (QM-Fluctuation), 是小量, $x_{\text{cl}}(t)$ 满足

$$\frac{\partial}{\partial t} \left(\frac{\partial L}{\partial \dot{x}_{\text{cl}}} \right) - \frac{\partial L}{\partial x_{\text{cl}}} = 0 \quad (150)$$

$$\dot{x}(t) = \dot{x}_{\text{cl}}(t) + \dot{q}(t) \quad \dot{q}(t') = \dot{q}(t'') \quad (151)$$

$$\begin{aligned} S &= \int_{t'}^{t''} dt \left[\frac{1}{2} m (\dot{x}_{\text{cl}} + \dot{q})^2 - V(x_{\text{cl}} + q, t) \right] \\ &= \int_{t'}^{t''} dt \left[\frac{1}{2} m (\dot{x}_{\text{cl}}^2 + 2\dot{x}_{\text{cl}}\dot{q} + \dot{q}^2) - V(x_{\text{cl}}, t) - \frac{\partial V}{\partial x_{\text{cl}}} q \right] \\ &= S_{\text{cl}} + \int_{t'}^{t''} dt \left[\frac{1}{2} m (2\dot{x}_{\text{cl}}\dot{q} + \dot{q}^2) - \frac{\partial V}{\partial x_{\text{cl}}} q \right] \end{aligned} \quad (152)$$

由于

$$\int_{t'}^{t''} dt \frac{d}{dt} (\dot{x}q) = \int_{t'}^{t''} dt (\ddot{x}q + \dot{x}\dot{q}) = 0 \quad (153)$$

则

$$\dot{x}\dot{q} = -\ddot{x}q \quad (154)$$

$$S = S_{\text{cl}} + \int_{t'}^{t''} dt \left[\frac{1}{2} m (-2\ddot{x}q + \dot{q}^2) - \frac{\partial V}{\partial x_{\text{cl}}} q \right] \quad (155)$$

又

$$m\ddot{x}_{\text{cl}} = -\frac{\partial V}{\partial x_{\text{cl}}} \quad (156)$$

$$S = S_{\text{cl}} + \int_{t'}^{t''} dt \left(\frac{1}{2} m \dot{q}^2 - \frac{1}{2} \frac{\partial^2 V}{\partial x_{\text{cl}}^2} q^2 \right) = S_{\text{cl}} + S_{\text{QM-F}} \quad (157)$$

量子涨落

$$\begin{aligned} S_{\text{QM-F}} &= \int_{t'}^{t''} dt \left(\frac{1}{2} m \dot{q}^2 - \frac{1}{2} \frac{\partial^2 V}{\partial x_{\text{cl}}^2} q^2 \right) \\ &= \frac{m}{2} \int_{t'}^{t''} dt q \left(-\frac{d^2}{dt^2} - \frac{1}{m} \frac{\partial^2 V}{\partial x_{\text{cl}}^2} \right) q \\ &= \frac{m}{2} \int_{t'}^{t''} dt q(t) A(t) q(t) \end{aligned} \quad (158)$$

其中

$$A(t) = -\frac{d^2}{dt^2} - \frac{1}{m} \frac{\partial^2 V}{\partial x_{\text{cl}}^2} = -\frac{d^2}{dt^2} - \omega(t) \quad (159)$$

$$\omega(t) = \frac{1}{m} \frac{\partial^2 V}{\partial x_{\text{cl}}^2} \quad (160)$$

$A(t)$ 是厄米算符

$$A(t)\varphi_n(t) = \lambda_n\varphi_n(t) \quad (161)$$

$\varphi_n(t)$ 构成完备基, 用 $\varphi_n(t)$ 展开 $q(t)$

$$q(t) = \sum_{n=1}^{\infty} a_n \varphi_n(t) = \lim_{N \rightarrow \infty} \sum_{n=1}^N a_n \varphi_n(t) \quad (162)$$

$$\begin{aligned} S_{\text{QM-F}} &= \frac{m}{2} \sum_{n,m} \int_{t'}^{t''} dt a_n a_m \varphi_n(t) A(t) \varphi_m(t) \\ &= \frac{m}{2} \sum_{n,m} a_n a_m \int_{t'}^{t''} dt \varphi_n(t) A(t) \varphi_m(t) \\ &= \frac{m}{2} \sum_{n,m} a_n a_m \lambda_m \int_{t'}^{t''} dt \varphi_n(t) \varphi_m(t) \\ &= \frac{m}{2} \sum_{n,m} a_n a_m \lambda_m \delta_{m,n} T \\ &= \frac{m}{2} \sum_n a_n^2 \lambda_n T \end{aligned} \quad (163)$$

$$\begin{aligned} K(x'', t''; x', t') &= \int D[x(t)] e^{\frac{i}{\hbar} S} \\ &= e^{\frac{i}{\hbar} S_{\text{cl}}} \int D[q(t)] e^{\frac{i}{\hbar} S_{\text{QM-F}}} \\ &= e^{\frac{i}{\hbar} S_{\text{cl}}} \int D[q(t)] \exp\left(\frac{im}{2\hbar} \sum_n a_n^2 \lambda_n T\right) \\ &= e^{\frac{i}{\hbar} S_{\text{cl}}} \pi^N N! \left(\frac{m}{2\pi i \hbar T}\right)^{\frac{N+1}{2}} \int \prod_{n=1}^N da_n \exp\left(\frac{im}{2\hbar} \sum_n a_n^2 \lambda_n T\right) \\ &= e^{\frac{i}{\hbar} S_{\text{cl}}} \pi^N N! \left(\frac{m}{2\pi i \hbar T}\right)^{\frac{N+1}{2}} \left(\frac{2\pi \hbar i}{mT}\right)^{\frac{N}{2}} \frac{1}{\sqrt{\prod_{n=1}^N \lambda_n}} \\ &= e^{\frac{i}{\hbar} S_{\text{cl}}} \pi^N N! \left(\frac{m}{2\pi i \hbar T}\right)^{\frac{1}{2}} T^{-N} \frac{1}{\sqrt{\prod_{n=1}^N \lambda_n}} \end{aligned} \quad (164)$$

Example: 1-D Free Particle

$$\lambda_n = \left(\frac{n\pi}{T}\right)^2 \quad (165)$$

$$\prod_{n=1}^N \lambda_n = \prod_{n=1}^N \left(\frac{n\pi}{T}\right)^2 = (N!)^2 \frac{\pi^{2N}}{T^{2N}} \quad (166)$$

$$\begin{aligned} K(x'', t''; x', t') &= e^{\frac{i}{\hbar} S_{\text{cl}}} \pi^N N! \left(\frac{m}{2\pi i \hbar T}\right)^{\frac{1}{2}} T^{-N} \frac{1}{\sqrt{\prod_{n=1}^N \lambda_n}} \\ &= e^{\frac{i}{\hbar} S_{\text{cl}}} \pi^N N! \left(\frac{m}{2\pi i \hbar T}\right)^{\frac{1}{2}} T^{-N} \frac{T^N}{N! \pi^N} \\ &= \left(\frac{m}{2\pi i \hbar T}\right)^{\frac{1}{2}} e^{\frac{i}{\hbar} S_{\text{cl}}} \end{aligned} \quad (167)$$

Chapter 3: The WKB Approximation

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1 Introduction

薛定谔方程

$$\frac{d^2}{dx^2}\psi(x) + \frac{2m}{\hbar^2} [E - V(x)] \psi(x) = 0 \quad (1)$$

令

$$k^2(x) = \frac{2m}{\hbar^2} [E - V(x)] \quad (2)$$

薛定谔方程可以写成

$$\frac{d^2}{dx^2}\psi(x) + k^2(x)\psi(x) = 0 \quad (3)$$

这是 Sturm-Liouville 方程，是最普遍的二阶微分方程。

当 $V(x) = V$ 时，

$$\psi(x) = Ae^{\pm ikx} \quad (4)$$

受此启发，做近似

$$\psi(x) = A \exp\left[\pm i \int^x k(x') dx'\right] \quad (5)$$

什么时候是好的近似呢？当然是当 $V(x)$ 变化慢的时候，但 $V(x)$ 变化快慢用什么来定义？我们应该把它定量化，接下来解决这个问题。

$$\psi'(x) = A \exp\left[\pm i \int^x k(x') dx'\right] [\pm ik(x)] \quad (6)$$

$$\psi''(x) = A \exp\left[\pm i \int^x k(x') dx'\right] [-k^2(x)] + A \exp\left[\pm i \int^x k(x') dx'\right] [\pm ik'(x)] \quad (7)$$

代入薛定谔方程，得到

$$[-k^2(x) \pm ik'(x) + k^2(x)] \psi(x) = 0 \quad (8)$$

上式在什么情况下成立呢？

$$-k^2(x) \pm ik'(x) + k^2(x) = 0 \quad (9)$$

即

$$\left| \frac{k'(x)}{k^2(x)} \right| \ll 1 \quad (10)$$

$$2k(x)k'(x) = \frac{4m}{\hbar^2} \cdot [E - V(x)]^{\frac{1}{2}} \cdot \frac{1}{2} [E - V(x)]^{-\frac{1}{2}} [-V'(x)] = -\frac{2m}{\hbar^2} V'(x) \quad (11)$$

$$\left| \frac{m}{\hbar^2} \frac{V'(x)}{k^3(x)} \right| \ll 1 \quad (12)$$

即

$$\left| \frac{mV'(X)}{\{2m[E - V(x)]\}^{\frac{3}{2}}} \right| \hbar \ll 1 \quad (13)$$

- 当 $\hbar \rightarrow 0$ 时，为半经典近似，能够很好地满足上述不等式。
- 当 $V'(x)$ 很小，即势能变化缓慢时，能够很好地满足上述不等式。
- 当 $E = V(x)$ 时，是经典和量子的拐点 (dangerous point)，近似可能失败。

得到好的近似的条件后，我们继续解薛定谔方程

$$\frac{d^2}{dx^2} \psi(x) + \frac{2m}{\hbar^2} [E - V(x)] \psi(x) = 0 \quad (14)$$

$$k^2(x) = \frac{2m}{\hbar^2} [E - V(x)] \quad (15)$$

近似解

$$\psi(x) = A \exp \left[\pm i \int^x k(x') dx' \right] \quad (16)$$



当 $x > x_1$ 时，

$$\begin{aligned} \psi(x) &= A_1 \exp \left[i \int_{x_1}^x k(x') dx' \right] + A_2 \exp \left[-i \int_{x_1}^x k(x') dx' \right] \\ &\sim \cos \left[\int_{x_1}^x k(x') dx' + \eta_1 \right] \end{aligned} \quad (17)$$

当 $x < x_2$ 时

$$\begin{aligned} \psi(x) &= A'_1 \exp \left[i \int_{x_2}^x k(x') dx' \right] + A'_2 \exp \left[-i \int_{x_2}^x k(x') dx' \right] \\ &\sim \cos \left[\int_{x_2}^x k(x') dx' - \eta_2 \right] \\ &= \cos \left[\int_{x_1}^x k(x') dx' + \int_{x_2}^{x_1} k(x') dx' - \eta_2 \right] \end{aligned} \quad (18)$$

这两个解本质上是同一个解，比较两解

$$\int_{x_2}^{x_1} k(x') dx' - \eta_2 = n\pi + \eta_1 \quad (19)$$

$$\int_{x_1}^{x_2} k(x') dx' = n\pi - (\eta_1 + \eta_2) \quad n = 0, \pm 1, \pm 2, \dots \quad (20)$$

$$k(x) \sim \sqrt{E - V(x)} \quad (21)$$

由此 Eq.(20) 给出了能量的条件，并显示出能量是分立的，即给出能量的量子化条件。

目前 η_1 和 η_2 仍为未知量，我们需要让近似更进一步。

2 Approximation Including the Next Order

为了得到更精确的解，我们将近似解写成

$$\psi(x) = A(x) \exp \left[\pm i \int^x k(x') dx' \right] \quad (22)$$

接下来我们要做的是确定 $A(x)$ 。

$$\psi'(x) = A'(x) \exp \left[\pm i \int^x k(x') dx' \right] + A(x) \exp \left[\pm i \int^x k(x') dx' \right] [\pm i k(x)] \quad (23)$$

$$\begin{aligned} \psi''(x) &= A''(x) \exp \left[\pm i \int^x k(x') dx' \right] + A'(x) \exp \left[\pm i \int^x k(x') dx' \right] [\pm i k(x)] \\ &\quad + A'(x) \exp \left[\pm i \int^x k(x') dx' \right] [\pm i k(x)] + A(x) \exp \left[\pm i \int^x k(x') dx' \right] [-k^2(x)] \\ &\quad + A(x) \exp \left[\pm i \int^x k(x') dx' \right] [\pm i k'(x)] \\ &= A''(x) \exp \left[\pm i \int^x k(x') dx' \right] + 2A'(x) \exp \left[\pm i \int^x k(x') dx' \right] [\pm i k(x)] \\ &\quad + A(x) \exp \left[\pm i \int^x k(x') dx' \right] [-k^2(x)] + A(x) \exp \left[\pm i \int^x k(x') dx' \right] [\pm i k'(x)] \\ &= -k^2(x) A(x) \exp \left[\pm i \int^x k(x') dx' \right] \end{aligned} \quad (24)$$

即

$$A''(x) + 2A'(x) [\pm i k(x)] + A(x) [\pm i k'(x)] = 0 \quad (25)$$

近似确定 $A(x)$ ，忽略 $A'(x)$

$$2A'(x)k(x) = -A(x)k'(x) \quad (26)$$

$$\frac{A'(x)}{A(x)} = -\frac{1}{2} \frac{k'(x)}{k(x)} \quad (27)$$

$$\int \frac{A'(x)}{A(x)} dx = -\frac{1}{2} \int \frac{k'(x)}{k(x)} dx \quad (28)$$

$$\ln A(x) = -\frac{1}{2} \ln k(x) + \tilde{A} \quad (29)$$

$$A(x) = |k(x)|^{-\frac{1}{2}} \tilde{A} \quad (30)$$

代入 $\psi(x)$ 近似解得

$$\psi(x) = \tilde{A} |k(x)|^{-\frac{1}{2}} \exp \left[\pm i \int^x k(x') dx' \right] \quad (31)$$

当 $E = V(x)$ 即当 $k(x) = 0$ 时， $\psi(x)$ 趋于无穷大，因此进一步近似仍然不够。

3 Semiclassical Expansion

$$\psi(x) = A \exp \left[\frac{i}{\hbar} S(x) \right] \quad (32)$$

$$\psi'(x) = A \exp \left[\frac{i}{\hbar} S(x) \right] \frac{i}{\hbar} S'(x) \quad (33)$$

$$\psi''(x) = A \exp\left[\frac{i}{\hbar} S(x)\right] \left[-\frac{1}{\hbar^2} S'^2(x)\right] + A \exp\left[\frac{i}{\hbar} S(x)\right] \frac{i}{\hbar} S''(x) \quad (34)$$

代入薛定谔方程，得

$$\frac{i}{\hbar} S''(x) - \frac{1}{\hbar^2} S'^2(x) + k^2(x) = 0 \quad (35)$$

即

$$i\hbar S''(x) - S'^2(x) + 2m[E - V(x)] = 0 \quad (36)$$

由此可知 $S(x, \hbar)$ 。当 $\hbar \rightarrow 0$ 时退化为经典理论。设 \hbar 是小量，用 \hbar 做泰勒展开

$$S(x) = S_0(x) + \hbar S_1(x) + \hbar^2 S_2(x) + \cdots = \sum_{n=0}^{\infty} \hbar^n S_n(x) \quad (37)$$

代入薛定谔方程

$$i\hbar[S_0''(x) + \hbar S_1''(x) + \hbar^2 S_2''(x)] - [S_0'(x) + \hbar S_1'(x) + \hbar^2 S_2'(x)]^2 + 2m[E - V(x)] = 0 \quad (38)$$

分别比较 $\hbar^0, \hbar^1, \hbar^2$ 的系数

$$-S_0'^2 + 2m[E - V(x)] = 0 \quad (39)$$

$$iS_0''(x) - 2S_0'(x)S_1'(x) = 0 \quad (40)$$

得到

$$S_0'(x) = \pm \hbar k(x) \quad (41)$$

$$S_0(x) = \pm \hbar \int_{x_0}^x k(x') dx' \quad (42)$$

$$\psi(x) = A \exp\left[\frac{i}{\hbar} S_0(x)\right] = A \exp\left[\pm i \int_{x_0}^x k(x') dx'\right] \quad (43)$$

又 Eq.(40)

$$\frac{iS_0''(x)}{2S_0'(x)} = s_1'(x) \quad (44)$$

解得

$$S_1(x) = \frac{i}{2} \ln |k(x)| \quad (45)$$

$$\begin{aligned} \psi(x) &= A \exp\left\{\frac{i}{\hbar}[S_0(x) + \hbar S_1(x)]\right\} = A \exp\left\{\frac{i}{\hbar}\left[\pm \hbar \int_{x_0}^x k(x') dx' + \hbar \frac{i}{2} \ln |k(x)|\right]\right\} \\ &= A \exp\left[\pm i \int_{x_0}^x k(x') dx' - \frac{1}{2} \ln |k(x)|\right] = A |k(x)|^{-\frac{1}{2}} \exp\left[\pm i \int_{x_0}^x k(x') dx'\right] \end{aligned} \quad (46)$$

用 \hbar 做半经典系统展开是物理学家做的事情，而解微分方程不仅是物理学家做的事情，数学家做得更早，接下来我们讨论数学家在解微分方程上做的工作。

4 Mathematician's Work

WKB(Wentzel-Kramers-Brillouin) 近似又叫 WKBJ 近似，其中“J”代表 Harold Jeffreys。1923 年 Jeffreys 发展出一种近似解线性二阶微分方程解的一般方法，这一类方程包括薛定谔方程。而薛定谔方程本身是在两年后才发展起来的。

$$\frac{d}{dx} \left[p(x) \frac{dy}{dx} \right] + [\lambda^2 q_0(x) + q_1(x)] y = 0 \quad (47)$$

这是最典型的二阶线性微分方程——Sturm-Liouville 方程。薛定谔方程是 Sturm-Liouville 方程的特殊情况 (当 $p(x)$ 和 $q_1(x)$ 是常数时)。1837 年 Liouville 指出 Sturm-Liouville 方程总能化成薛定谔方程的形式。

引入变量

$$t = \int_{x_0}^x \left[\frac{q_0(x')}{p(x')} \right]^{\frac{1}{2}} dx' \quad (48)$$

$$w(x) = [q_0(x)p(x)]^{\frac{1}{4}} y(x) \quad (49)$$

Sturm-Liouville 方程化为

$$\frac{d^2 w}{dt^2} + \lambda^2 w = \left[(q_0 p)^{-\frac{1}{4}} \frac{d^2}{dt^2} (q_0 p)^{\frac{1}{4}} - \frac{q_1}{q_0} \right] w \quad (50)$$

令

$$r(t) = (q_0 p)^{-\frac{1}{4}} \frac{d^2}{dt^2} (q_0 p)^{\frac{1}{4}} - \frac{q_1}{q_0} \quad (51)$$

则

$$\frac{d^2 w}{dt^2} + \lambda^2 w = r(t)w \quad (52)$$

在 Feynman 路径积分中我们已经知道, 这类微分方程总可以写成积分方程的形式

$$w(t) = c_1 \cos \lambda t + c_2 \sin \lambda t + \int_{t_0}^t \frac{\sin \lambda(t-s)}{\lambda} r(s) w(s) ds \quad (53)$$

代入 Eq.(52) 即可验证。

对于薛定谔方程

$$\lambda^2 q_0(x) = \frac{2m}{\hbar^2} [E - V(x)] \quad p(x) = 1 \quad (54)$$

$\lambda \rightarrow 0$ 对应 $\hbar \rightarrow 0$ 即半经典近似。当 $\lambda \rightarrow \infty$ 时

$$|c_1 \cos \lambda t + c_2 \sin \lambda t| \gg \left| \int_{t_0}^t \frac{\sin \lambda(t-s)}{\lambda} r(s) w(s) ds \right| \quad (55)$$

零级近似

$$w(t) = c_1 \cos \lambda t + c_2 \sin \lambda t \quad (56)$$

将

$$t = \int_{x_0}^x \left[\frac{q_0(x')}{p(x')} \right]^{\frac{1}{2}} dx' \quad (57)$$

代入 $w(t)$, 则

$$\begin{aligned} y(x) &= [q_0(x)p(x)]^{-\frac{1}{4}} w(x) \\ &= [q_0 p]^{-\frac{1}{4}} \left\{ c_1 \cos \left[\lambda \int_{x_0}^x \left(\frac{q_0}{p} \right)^{\frac{1}{2}} dx' \right] + c_2 \sin \left[\lambda \int_{x_0}^x \left(\frac{q_0}{p} \right)^{\frac{1}{2}} dx' \right] \right\} \\ &= \sqrt{\frac{\lambda}{k(x)}} \left\{ c_1 \cos \left[\int_{x_0}^x k(x') dx' \right] + c_2 \sin \left[\int_{x_0}^x k(x') dx' \right] \right\} \end{aligned} \quad (58)$$

5 Bound States



当 $x > x_1$ 时

$$\psi(x) \sim \cos \left(\int_{x_1}^x k(x') dx' + \eta_1 \right) \quad (59)$$

当 $x < x_2$ 时

$$\psi(x) \sim \cos \left(\int_{x_2}^x k(x') dx' - \eta_2 \right) \quad (60)$$

$$\int_{x_1}^{x_2} k(x) dx = n\pi - (\eta_1 + \eta_2) \quad (61)$$

给出了能量的量子化条件，其本质上是微分方程的性质。接下来我们来确定 η_1 和 η_2 。

首先定义

$$\kappa(x) = \begin{cases} \frac{1}{\hbar} \sqrt{2m[V(x) - E]} & V(x) > E \\ \frac{1}{\hbar} \sqrt{2m[E - V(x)]} & V(x) < E \end{cases} \quad (62)$$

从 x_1 的方向看，当 $x < x_1$ 时，

$$\psi(x) = A \frac{1}{[\kappa(x)]^{\frac{1}{2}}} \exp \left[- \int_x^{x_1} \kappa(x') dx' \right] \quad (63)$$

当 $x > x_1$ 时，

$$\psi(x) = B \frac{1}{[\kappa(x)]^{\frac{1}{2}}} \cos \left[\int_{x_1}^x \kappa(x') dx' + \tilde{\eta}_1 \right] \quad (64)$$

当 $x = x_1$ 时， $\kappa(x) = 0$ ，此时波函数的解变为无穷大，而这显然不成立。接下来我们来近似求当 $x = x_1$ 时的严格解。当 $x \rightarrow x_1$ 时，做线性展开

$$E - V(x) = - \left. \frac{dV(x)}{dx} \right|_{x_1} (x - x_1) \quad (65)$$

代入薛定谔方程

$$- \frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) + V(x) \psi(x) = E \psi(x) \quad (66)$$

令

$$\xi = \left(- \frac{2m}{\hbar^2} \left. \frac{dV(x)}{dx} \right|_{x_1} \right)^{\frac{1}{3}} (x - x_1) \quad (67)$$

其中 ξ 和 $(x - x_1)$ 同号。薛定谔方程可化为 Airy equation

$$\frac{d^2}{d\xi^2} \psi + \xi \psi = 0 \quad (68)$$

它的解

$$\psi \sim \frac{1}{\sqrt{\pi}} \int_0^\infty \cos \left(\frac{1}{3} u^3 - u\xi \right) du \quad (69)$$

查数学用表可知解的渐进行为。当 $\xi \rightarrow -\infty$ 时，

$$\psi \sim \frac{A}{|\xi|^{\frac{1}{4}}} \exp \left(- \frac{2}{3} |\xi|^{\frac{3}{2}} \right) \quad (70)$$

当 $\xi \rightarrow \infty$ 时，

$$\psi \sim \frac{B}{\xi^{\frac{1}{4}}} \cos \left(\frac{2}{3} \xi^{\frac{3}{2}} - \frac{1}{4} \pi \right) \quad (71)$$

$$\begin{aligned}
\int_{x_1}^x k(x') dx' &= \int_{x_1}^x \frac{1}{\hbar} \sqrt{2m[E - V(x')]} dx' \\
&= \int_0^\xi \frac{1}{\hbar} \sqrt{2m[E - V(x')]} d\xi \left(-\frac{2m}{\hbar^2} \frac{dV(x)}{dx} \Big|_{x_1} \right)^{-\frac{1}{3}} \\
&= \int_0^\xi \xi'^{\frac{1}{2}} d\xi' = \frac{2}{3} \xi^{\frac{3}{2}}
\end{aligned} \tag{72}$$

故

$$\tilde{\eta}_1 = -\frac{1}{4}\pi \tag{73}$$

$$\psi(x) = B \frac{1}{[\kappa(x)]^{\frac{1}{2}}} \cos \left[\int_{x_1}^x \kappa(x') dx' - \frac{1}{4}\pi \right] \tag{74}$$

从 x_2 的方向看, 当 $x > x_2$ 时,

$$\psi(x) = C \frac{1}{[\kappa(x)]^{\frac{1}{2}}} \exp \left[- \int_{x_2}^x \kappa(x') dx' \right] \tag{75}$$

当 $x < x_2$ 时,

$$\psi(x) = D \frac{1}{[\kappa(x)]^{\frac{1}{2}}} \cos \left[\int_x^{x_2} \kappa(x') dx' - \tilde{\eta}_2 \right] \tag{76}$$

令

$$\xi = \left(\frac{2m}{\hbar^2} \frac{dV(x)}{dx} \Big|_{x_2} \right)^{\frac{1}{3}} (x_2 - x) \tag{77}$$

其中 ξ 和 $(x_2 - x)$ 同号。薛定谔方程可化为 Airy equation

$$\frac{d^2}{d\xi^2} \psi + \xi \psi = 0 \tag{78}$$

当 $\xi \rightarrow \infty$ 时,

$$\psi \sim \frac{1}{\xi^{\frac{1}{4}}} \cos \left(\frac{2}{3} \xi^{\frac{3}{2}} - \frac{1}{4}\pi \right) \tag{79}$$

$$\begin{aligned}
\int_x^{x_2} k(x') dx' &= \int_x^{x_2} \frac{1}{\hbar} \sqrt{2m[E - V(x')]} dx' \\
&= \int_\xi^0 \frac{1}{\hbar} \sqrt{2m[E - V(x')]} d\xi \left(-\frac{2m}{\hbar^2} \frac{dV(x)}{dx} \Big|_{x_1} \right)^{-\frac{1}{3}} \\
&= \int_0^\xi \xi'^{\frac{1}{2}} d\xi' = \frac{2}{3} \xi^{\frac{3}{2}}
\end{aligned} \tag{80}$$

故

$$\tilde{\eta}_2 = \frac{1}{4}\pi \tag{81}$$

$$\psi(x) = D \frac{1}{[\kappa(x)]^{\frac{1}{2}}} \cos \left[\int_x^{x_2} \kappa(x') dx' - \frac{1}{4}\pi \right] \tag{82}$$

我们来总结一下, 当 $x > x_1$ 时

$$\psi(x) = B \frac{1}{[\kappa(x)]^{\frac{1}{2}}} \cos \left[\int_{x_1}^x \kappa(x') dx' - \frac{1}{4}\pi \right] \tag{83}$$

当 $x < x_2$ 时

$$\psi(x) = D \frac{1}{[\kappa(x)]^{\frac{1}{2}}} \cos \left[\int_x^{x_2} \kappa(x') dx' - \frac{1}{4}\pi \right] \tag{84}$$

这两个解本质上是同一个解

$$\int_{x_1}^{x_2} \kappa(x') dx' + \int_{x_2}^x \kappa(x') dx' - \frac{1}{4}\pi = n\pi - \left[\int_x^{x_2} \kappa(x') dx' - \frac{1}{4}\pi \right] \quad (85)$$

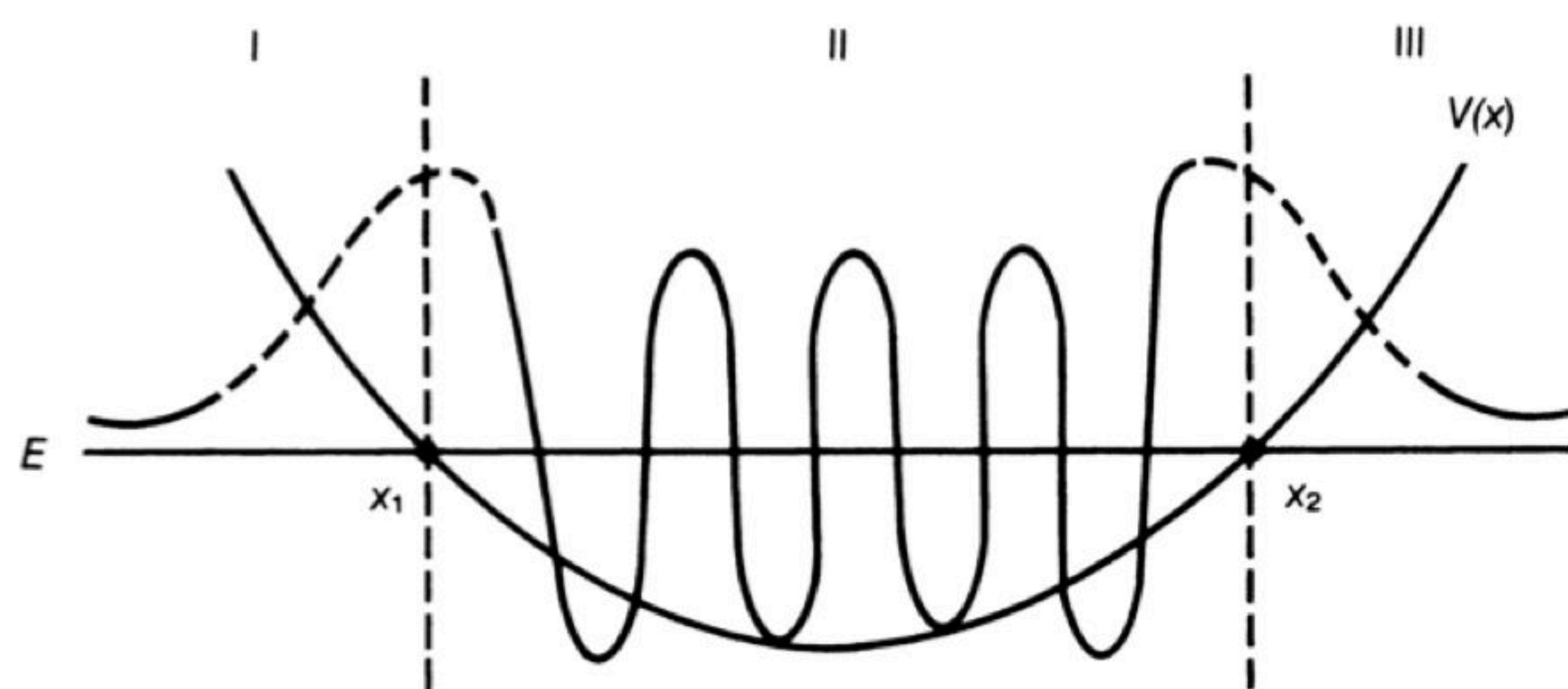
$$\int_{x_1}^{x_2} k(x) dx = n\pi + \frac{1}{2}\pi = \left(n + \frac{1}{2}\right) \pi \quad (86)$$

这也是所谓的玻尔量子化条件。这个式子也可以写成另一种形式

$$p(x) = \hbar k(x) \quad (87)$$

$$\int_{x_1}^{x_2} p(x) dx = \left(n + \frac{1}{2}\right) \pi \hbar \quad (88)$$

$$\oint p(x) dx = (2n + 1) \pi \hbar \quad (89)$$

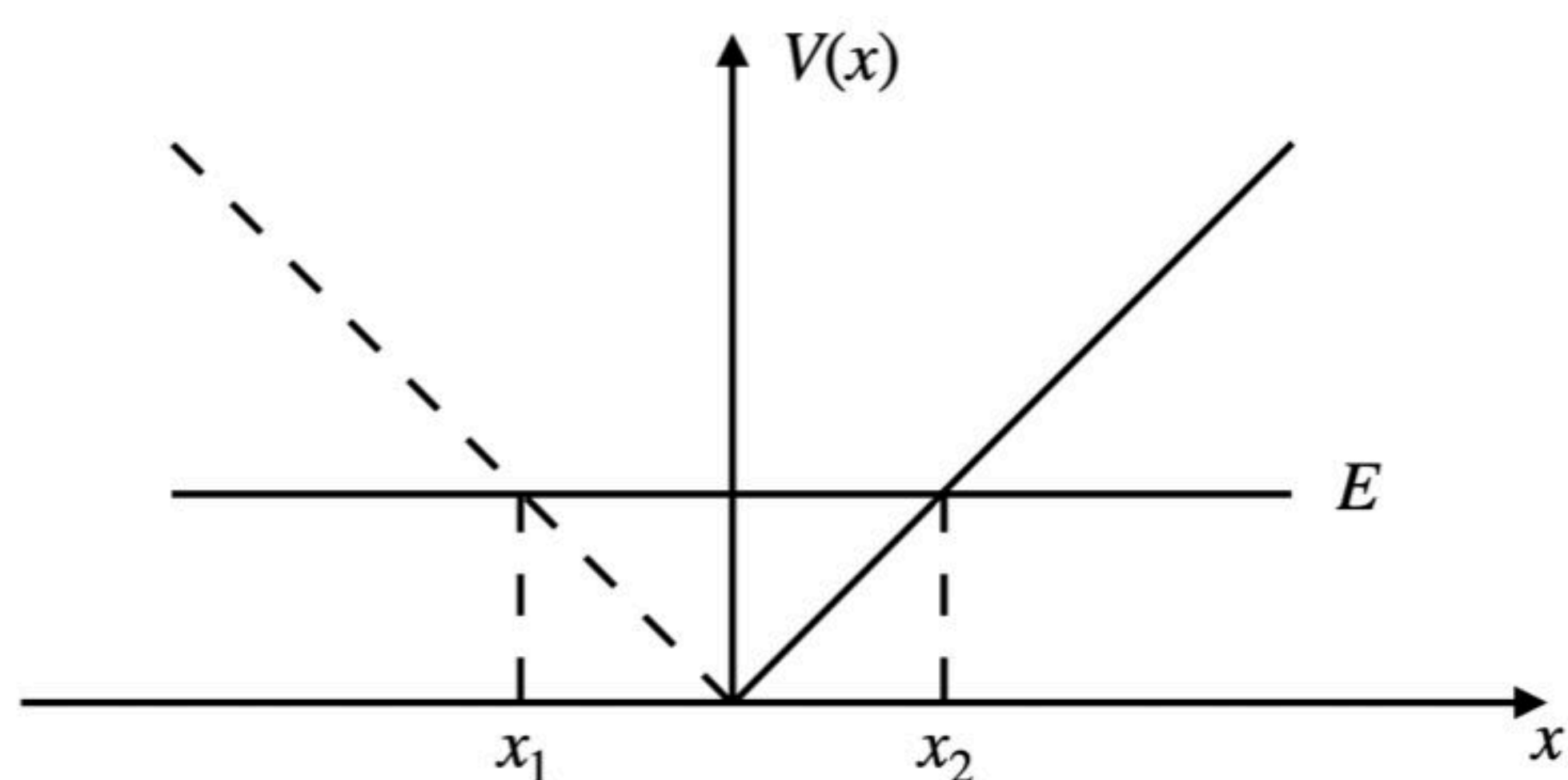


Example: The Energy Spectrum of A Ball Bouncing Up And Down Over A Hard Surface

$$V(x) = \begin{cases} mgx & x > 0 \\ \infty & x < 0 \end{cases} \quad (90)$$

将势阱进行偶延拓 $V(x) = V(-x)$

$$V(x) = mg|x| \quad (91)$$



拐点

$$x_1 = -\frac{E}{mg} \quad x_2 = \frac{E}{mg} \quad (92)$$

根据初始条件， n 只取奇数。量子化条件

$$\int_{-E/mg}^{E/mg} dx \sqrt{2m(E - mg|x|)} = \left(n_{\text{odd}} + \frac{1}{2}\right) \pi \hbar \quad (n_{\text{odd}} = 1, 3, 5, \dots) \quad (93)$$

$$\int_0^{E/mg} dx \sqrt{2m(E - mgx)} = \left(n - \frac{1}{4}\right) \pi \hbar \quad (n = 1, 2, 3, \dots) \quad (94)$$

又

$$\begin{aligned} \int_0^{E/mg} dx \sqrt{2m(E - mgx)} &= \frac{\sqrt{2m}}{\hbar} \int_0^{E/mg} dx \sqrt{E - mgx} \\ &= \frac{\sqrt{2m}}{\hbar} \frac{1}{mg} \frac{2}{3} (E - mgx)^{\frac{3}{2}} \Big|_0^{E/mg} \\ &= \frac{\sqrt{2m}}{mg\hbar} \frac{2}{3} E^{\frac{3}{2}} \end{aligned} \quad (95)$$

$$E_n = \frac{1}{2} \left[3 \left(n - \frac{1}{4} \right) \pi \right]^{\frac{2}{3}} (mg^2 \hbar^2)^{\frac{1}{3}} \quad (96)$$

这个问题不需要任何近似就能分析解决，能量值可以用 Airy function 的零点来表示

$$\text{Ai}(-\lambda_n) = 0 \quad (97)$$

$$E_n = \left(\frac{\lambda_n}{2^{\frac{1}{3}}} \right) (mg^2 \hbar^2)^{\frac{1}{3}} \quad (98)$$

对弹跳球的量子理论处理，看似与现实世界关系不大。但事实证明，这种类型的势能实际上对研究 quark-antiquark bound system (quarkonium) 的能谱具有实际意义。

n	WKB	Exact
1	2.320	2.338
2	4.082	4.088
3	5.517	5.521
4	6.784	6.787
5	7.942	7.944
6	9.021	9.023
7	10.039	10.040
8	11.008	11.009
9	11.935	11.936
10	12.828	12.829

6 Alternate Point of View

从 $x < x_2$ 到 $x > x_2$ ，本质上是同一个解，在实空间无法绕过 $x = x_2$ 这点，而在复空间可以绕过。所以我们接下来要做解析延拓，将解延拓成复变量的形式。



当 $x > x_2$ 时,

$$\psi(x) = \frac{C}{[\kappa(x)]^{\frac{1}{2}}} \exp \left[- \int_{x_2}^x \kappa(x') dx' \right] \quad (99)$$

当 $x < x_2$ 时,

$$\begin{aligned} \psi(x) &= \frac{D}{[\kappa(x)]^{\frac{1}{2}}} \cos \left[\int_x^{x_2} \kappa(x') dx' - \frac{\pi}{4} \right] \\ &\sim \frac{1}{[\kappa(x)]^{\frac{1}{2}}} \left\{ \exp \left[-i \int_{x_2}^x \kappa(x') dx' - i \frac{\pi}{4} \right] + \exp \left[i \int_{x_2}^x \kappa(x') dx' + i \frac{\pi}{4} \right] \right\} \end{aligned} \quad (100)$$

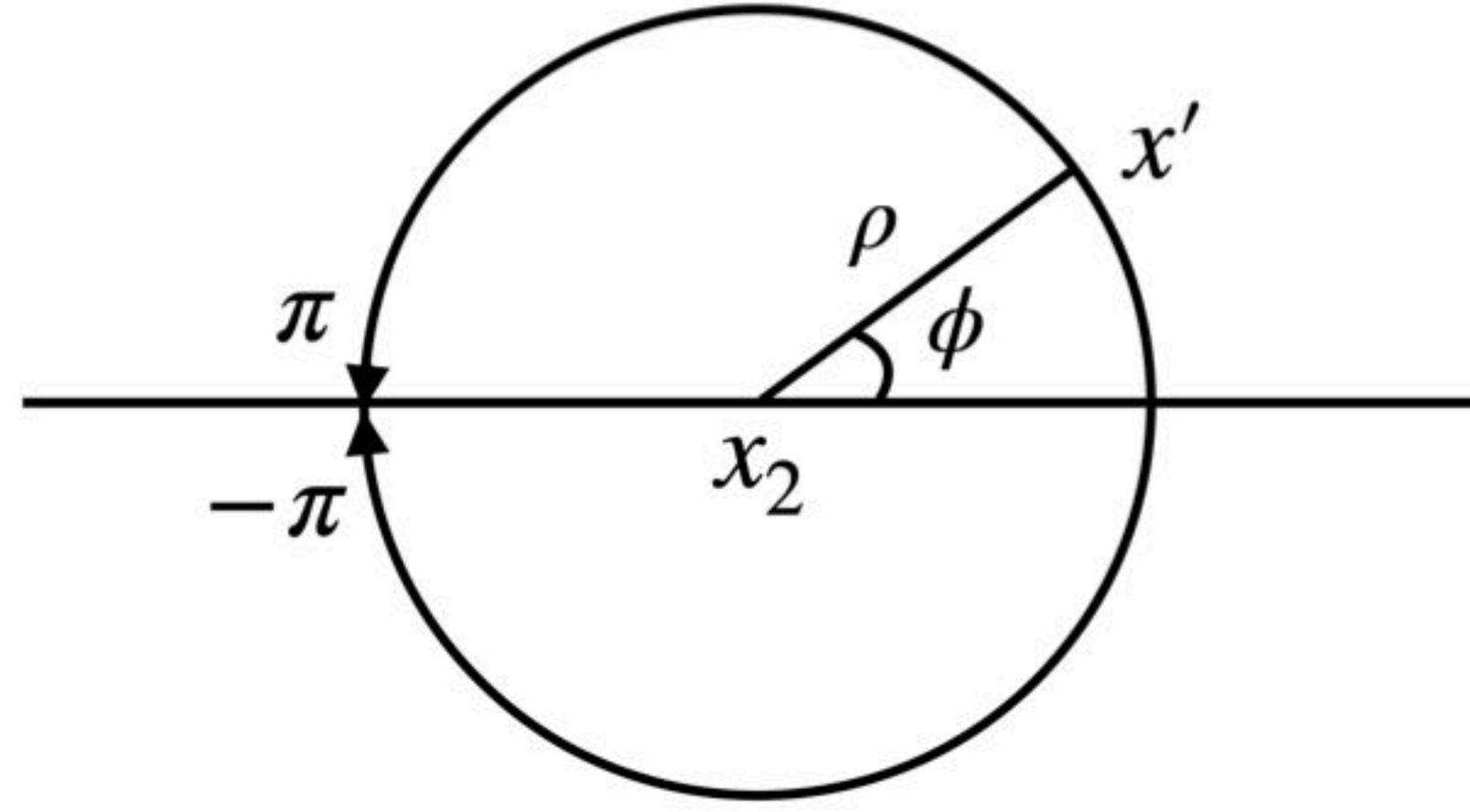
当 $x > x_2$ 时, 在 $x = x_2$ 处作线性展开

$$\kappa(x') \sim \sqrt{x' - x_2} \quad (101)$$

$$\psi(x) \sim \frac{1}{(x - x_2)^{\frac{1}{4}}} \exp \left[- \int_{x_2}^x \sqrt{x' - x_2} dx' \right] \quad (102)$$

当 $x < x_2$ 时,

$$\psi(x) \sim \frac{1}{(x_2 - x)^{\frac{1}{4}}} \left\{ \exp \left[-i \int_{x_2}^x \sqrt{x_2 - x} dx' - i \eta_2 \right] + \exp \left[i \int_{x_2}^x \sqrt{x_2 - x} dx' + i \eta_2 \right] \right\} \quad (103)$$



令

$$x' - x_2 = \rho e^{i\phi} \quad (104)$$

$$k(x') \sim \sqrt{x_2 - x'} \quad (105)$$

则

$$\begin{aligned} - \int_{x_2}^x dx' \kappa(x) &= - \int_{x_2}^x dx' \sqrt{x' - x_2} = - \int_{x_2}^x dx' \sqrt{(x_2 - x') e^{i\pi}} = -i \int_{x_2}^x dx' k(x') \quad (\text{沿 } \pi \text{ 方向延拓}) \\ &= - \int_{x_2}^x dx' \sqrt{(x_2 - x') e^{-i\pi}} = i \int_{x_2}^x dx' k(x') \quad (\text{沿 } -\pi \text{ 方向延拓}) \end{aligned} \quad (106)$$

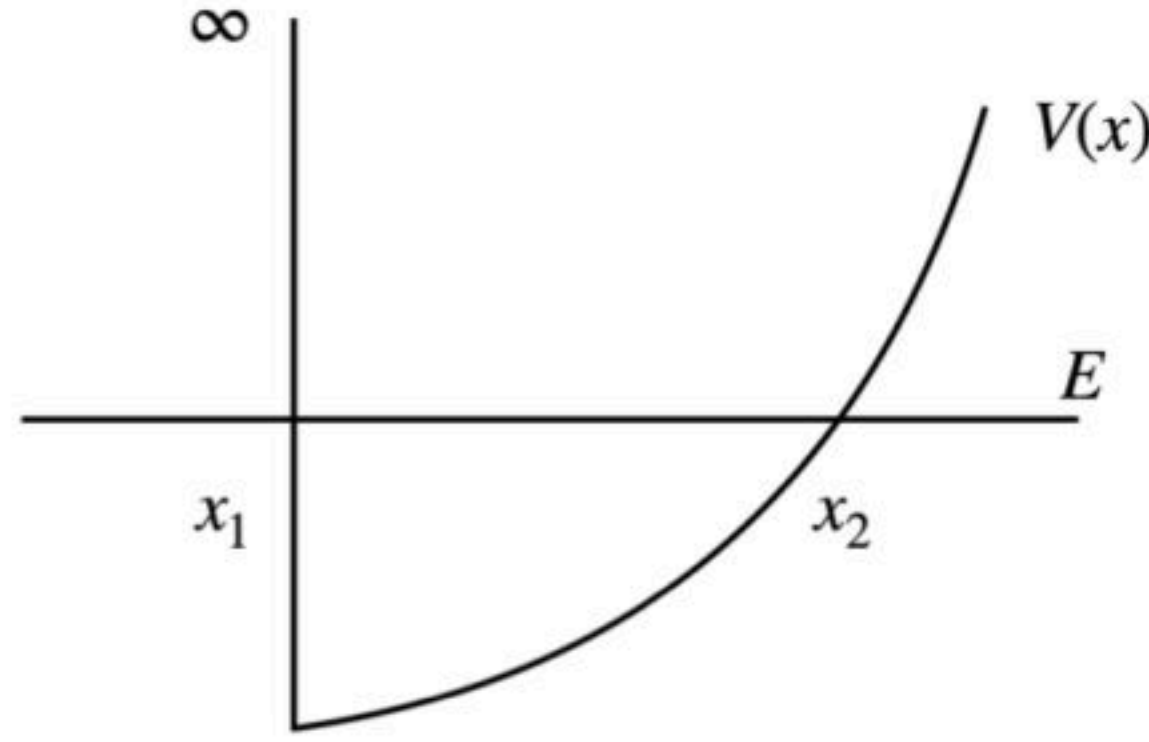
$$\begin{aligned} [\kappa(x)]^{-\frac{1}{2}} &= (x - x_2)^{-\frac{1}{4}} = [(x_2 - x) e^{i\pi}]^{-\frac{1}{4}} = [k(x)]^{-\frac{1}{2}} e^{-i\frac{\pi}{4}} \quad (\text{沿 } \pi \text{ 方向延拓}) \\ &= [(x_2 - x) e^{-i\pi}]^{-\frac{1}{4}} = [k(x)]^{-\frac{1}{2}} e^{i\frac{\pi}{4}} \quad (\text{沿 } -\pi \text{ 方向延拓}) \end{aligned} \quad (107)$$

故

$$\eta_2 = \frac{\pi}{4} \quad (108)$$

7 Other Special Cases

Example 1



$$\psi(x_1) = 0 \quad (109)$$

当 $x > x_1$ 时

$$\psi(x) \sim \sin \left[\int_{x_1}^x k(x') dx' + \eta \right] \quad (110)$$

当 $x \rightarrow x_1$ 时, $\psi(x) \rightarrow 0$, 故 $\eta = 0$ 。

$$\psi(x) \sim \cos \left[\frac{\pi}{2} - \int_{x_1}^x k(x') dx' \right] = \cos \left[\frac{\pi}{2} + \int_x^{x_2} k(x') dx' + \int_{x_2}^{x_1} k(x') dx' \right] \quad (111)$$

当 $x < x_2$ 时

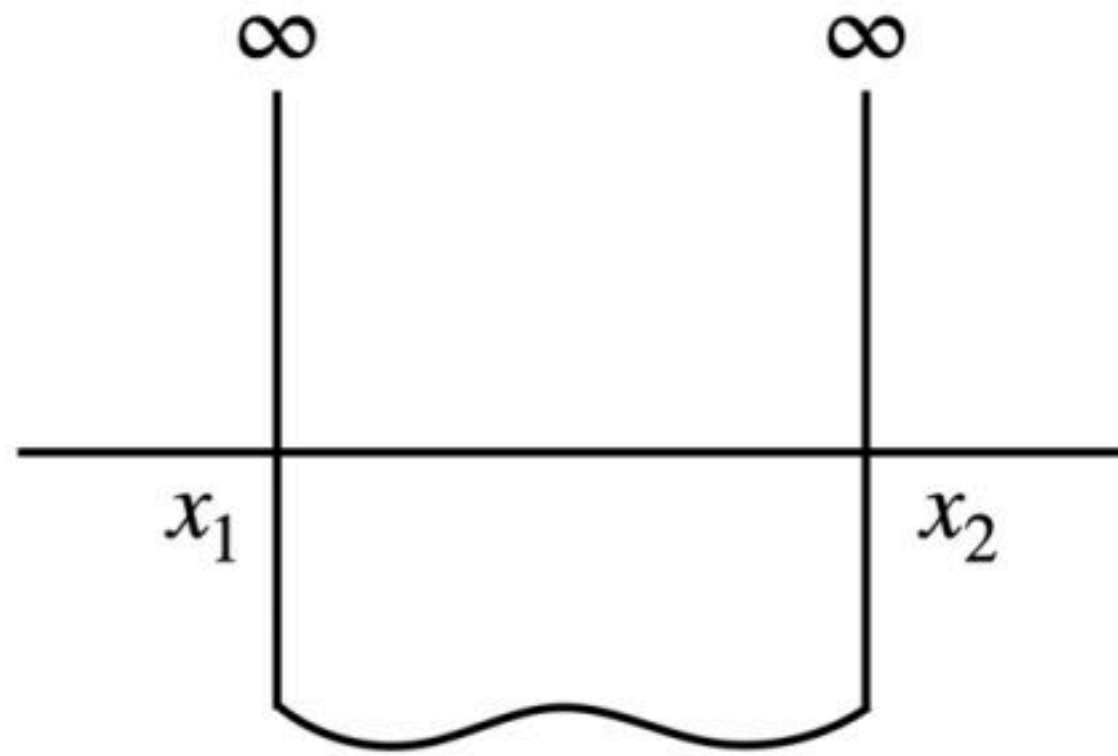
$$\psi(x) \sim \cos \left[\int_{x_2}^x k(x') dx' - \frac{\pi}{4} \right] \quad (112)$$

这两个解本质上是同一个解

$$\int_{x_1}^{x_2} k(x') dx' = \left(n - \frac{1}{4} \right) \pi \quad (113)$$

这和解析延拓的结果完全一致。

Example 2



若用玻尔量子化条件

$$\int_{x_1}^{x_2} k(x') dx' = \left(n + \frac{1}{2} \right) \pi \quad (114)$$

将得到错误的结果, 因为在 x_1 和 x_2 处都不满足 WKB 近似条件, 即 $V(x)$ 变化缓慢。这时我们需要重新讨论, 做特殊处理。

当 $x > x_1$ 时

$$\psi(x) \sim \sin \left[\int_{x_1}^x k(x') dx' \right] \quad (115)$$

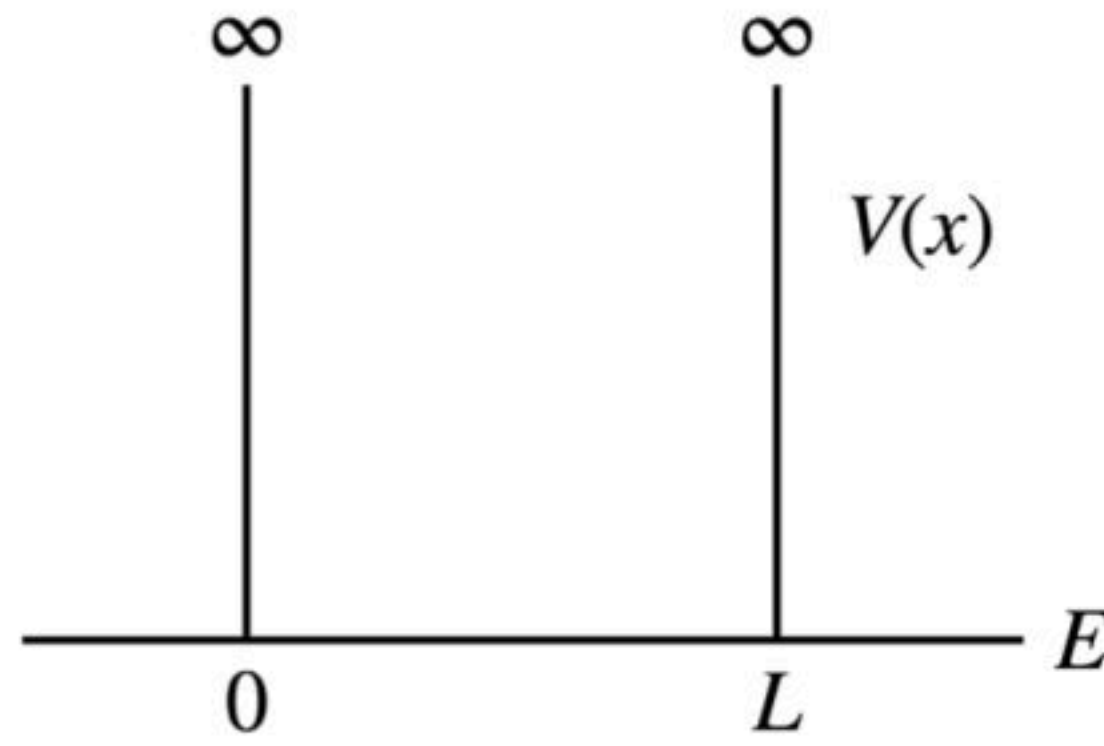
当 $x < x_2$ 时

$$\psi(x) \sim \sin \left[\int_x^{x_2} k(x') dx' \right] = \sin \left[\int_x^{x_1} k(x') dx' + \int_{x_1}^{x_2} k(x') dx' \right] \quad (116)$$

$$\int_{x_1}^{x_2} k(x') dx' = n\pi \quad (117)$$

$$\oint p(x) dx = 2n\pi\hbar = nh \quad (118)$$

这也就是索末菲量子化条件。

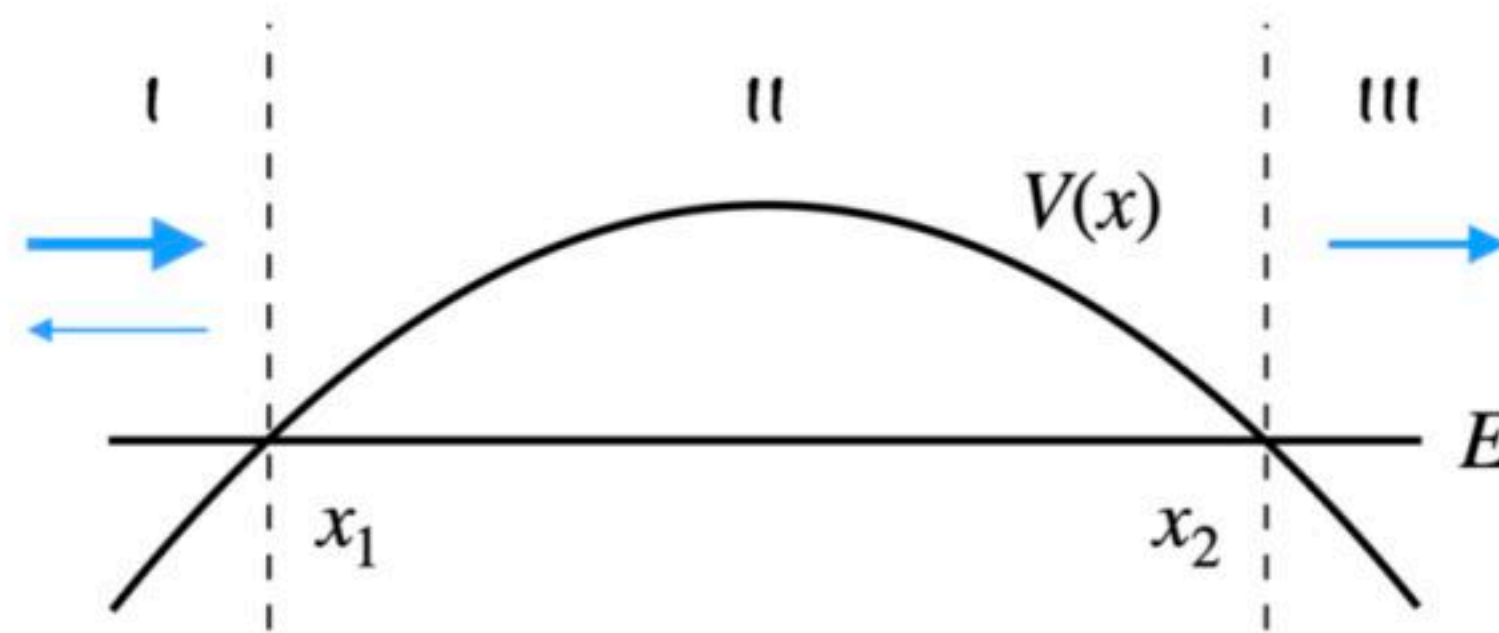


利用索末菲量子化条件

$$2 \int_0^L \sqrt{2mE} dx = nh \quad (119)$$

$$E = \frac{n^2 h^2}{8mL^2} \quad (120)$$

8 tunneling 势垒贯穿



- 在 I 区域

$$\psi(x) = \frac{1}{\sqrt{k(x)}} \cos \left[\int_{x_1}^x k(x') dx' - \frac{\pi}{4} \right] \quad (121)$$

- 在 II 区域

$$\psi(x) = \frac{1}{\sqrt{\kappa(x)}} \exp \left[- \int_{x_1}^x \kappa(x') dx' \right] + c_0 \frac{1}{\sqrt{\kappa(x)}} \exp \left[\int_{x_1}^x \kappa(x') dx' \right] \quad (122)$$

由于 $|c_0| \ll 1$

$$\psi(x) \doteq \frac{1}{\sqrt{\kappa(x)}} \exp \left[- \int_{x_1}^x \kappa(x') dx' \right] \quad (123)$$

- 在 III 区域

$$\psi(x) = \frac{c}{\sqrt{k(x)}} \exp \left[i \int_{x_1}^x k(x') dx' + i \frac{\pi}{4} \right] \quad (124)$$

透射波几率流密度

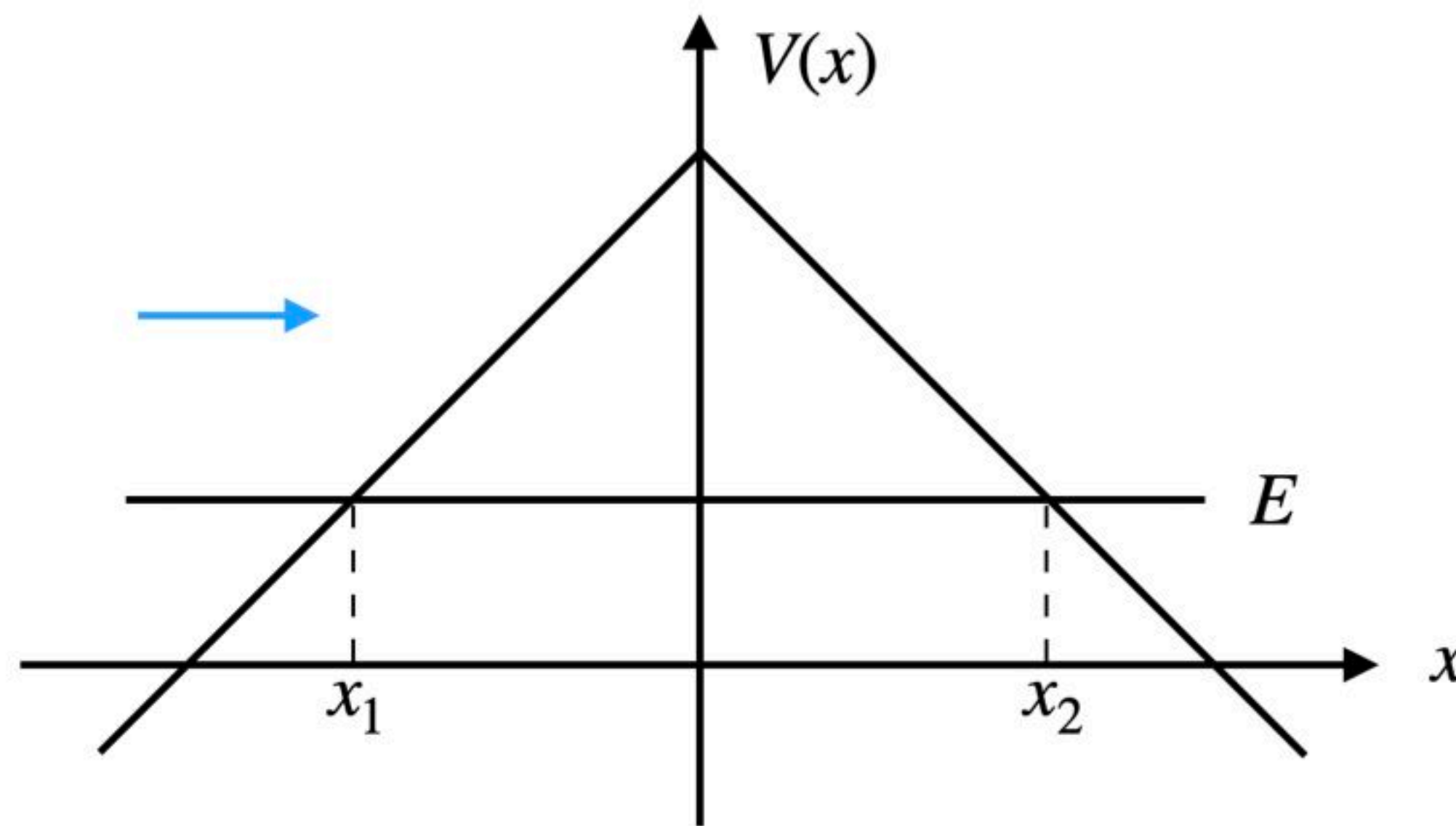
$$J = k(x_2) |\psi(x_2)|^2 \sim \exp \left[-2 \int_{x_1}^{x_2} \kappa(x') dx' \right] \quad (125)$$

隧穿因子 (tunneling factor)

$$T \propto \exp \left[-2 \int_{x_1}^{x_2} \kappa(x) dx \right] = \exp \left\{ -2 \int_{x_1}^{x_2} \frac{1}{\hbar} \sqrt{2m[V(x) - E]} dx \right\} \quad (126)$$

Example

$$V(x) = \begin{cases} V_0 - mgx & x > 0 \\ V_0 + mgx & x < 0 \end{cases} \quad (127)$$

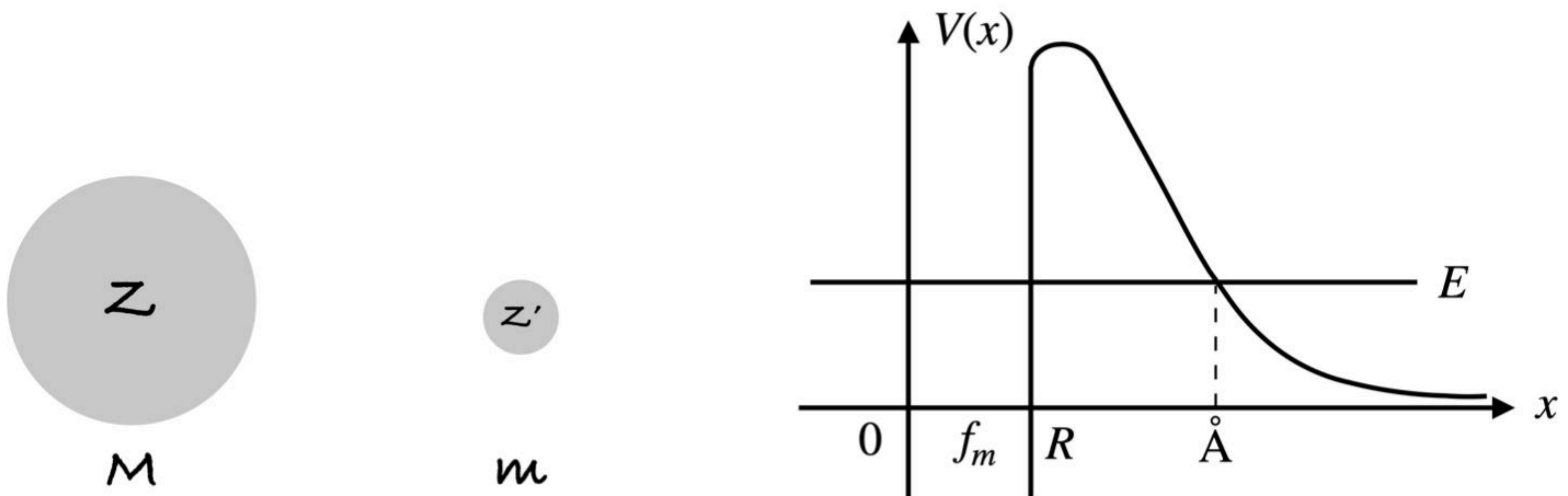


$$T = \exp \left[-2 \int_{x_1}^{x_2} \kappa(x) dx \right] = \exp \left[-4 \int_0^{x_2} \frac{\sqrt{2m}}{\hbar} \sqrt{V_0 - mgx - E} dx \right] = \exp \left[-\frac{8}{3} \sqrt{\frac{2m}{\hbar}} \frac{1}{mg} (V_0 - E)^{\frac{3}{2}} \right] \quad (128)$$

Example: The α Decay of Nuclei

$$V(r) = \frac{ZZ'e^2}{r} \quad (129)$$

$$r_1 \sim f_m \quad r_2 \sim \overset{\circ}{\text{A}} \quad r_2 \gg r_1 \quad (130)$$



这个问题具有球对称性，因此我们只考虑它的径向

$$\psi_{n,l,m}(r, \theta, \phi) = \frac{\chi(r)}{r} Y_{l,m}(\theta, \phi) \quad (131)$$

$$-\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} \chi(r) + \left[\frac{ZZ'e^2}{r} + \frac{l(l+1)}{2\mu r^2} \right] \chi(r) = E \chi(r) \quad (132)$$

有效势

$$V_{\text{eff}}(r) = \frac{ZZ'e^2}{r} + \frac{l(l+1)}{2\mu r^2} \quad (133)$$

$$V(r) = \frac{ZZ'e^2}{r} \quad (134)$$

$$\begin{aligned} T &= \exp \left\{ -2 \int_{r_1}^{r_2} \frac{1}{\hbar} \sqrt{2\mu[V_{\text{eff}}(r) - E]} dr \right\} \\ &= \exp \left\{ -2 \int_{r_1}^{r_2} \frac{1}{\hbar} \sqrt{2\mu \left[\frac{ZZ'e^2}{r} + \frac{l(l+1)}{2\mu r^2} - E \right]} dr \right\} \end{aligned} \quad (135)$$

$$r_2 = \frac{ZZ'e^2}{E} \quad (136)$$

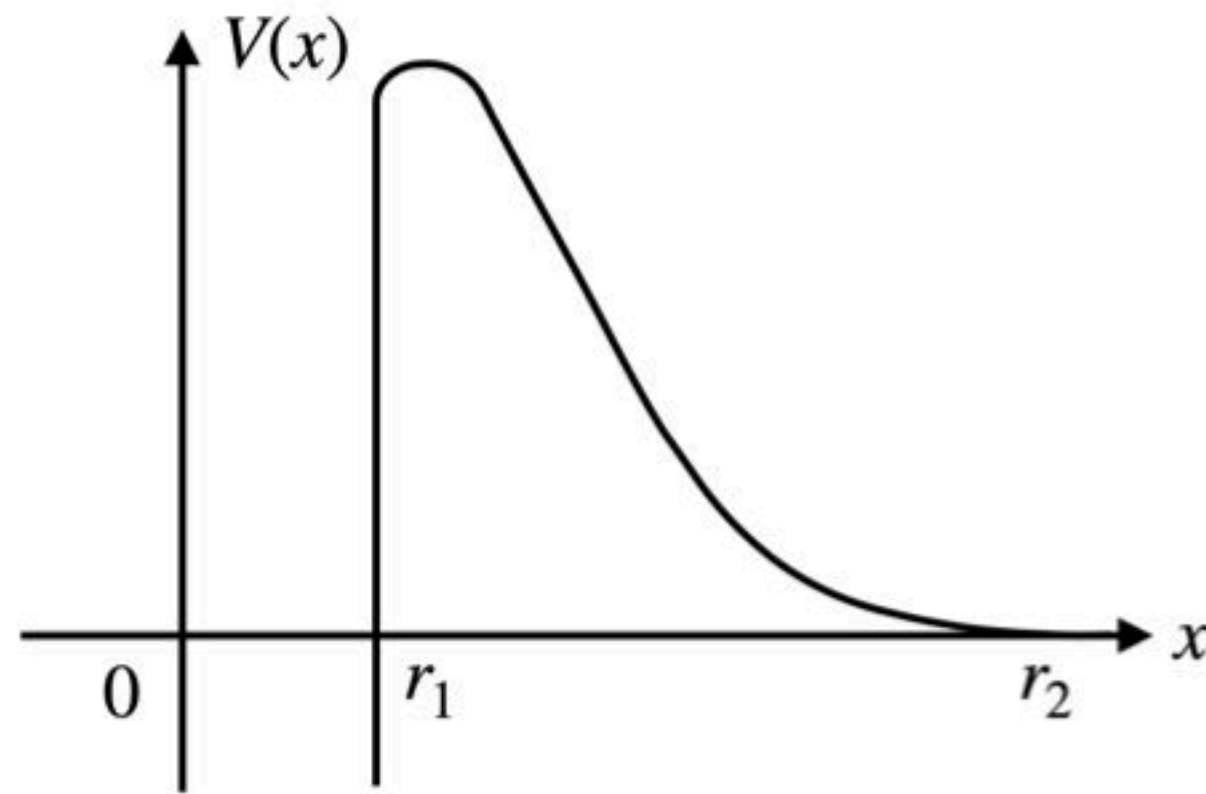
1. $E \neq 0, l = 0$

$$\begin{aligned} \frac{1}{\hbar} \int_{r_1}^{r_2} \sqrt{2\mu[V_{\text{eff}}(r) - E]} dr &= \frac{\sqrt{2\mu}}{\hbar} \int_{r_1}^{r_2} \sqrt{\frac{ZZ'e^2}{r} - E} dr \\ &= \frac{\pi ZZ'e^2}{\hbar \sqrt{\frac{2E}{\mu}}} \left(1 - \frac{2}{\pi} \sin^{-1} \frac{1}{u^{\frac{1}{2}}} \right) - \frac{\sqrt{2\mu ER}}{\hbar} \left(\frac{ZZ'e^2}{ER} - 1 \right)^{\frac{1}{2}} \end{aligned} \quad (137)$$

2. $E = 0, l = 0$

$$T = \exp \left\{ - \int_{r_1}^{r_2} \frac{2}{\hbar} \sqrt{2\mu V(r)} dr \right\} \quad (138)$$

(a) If $V(x)$ has a finite range

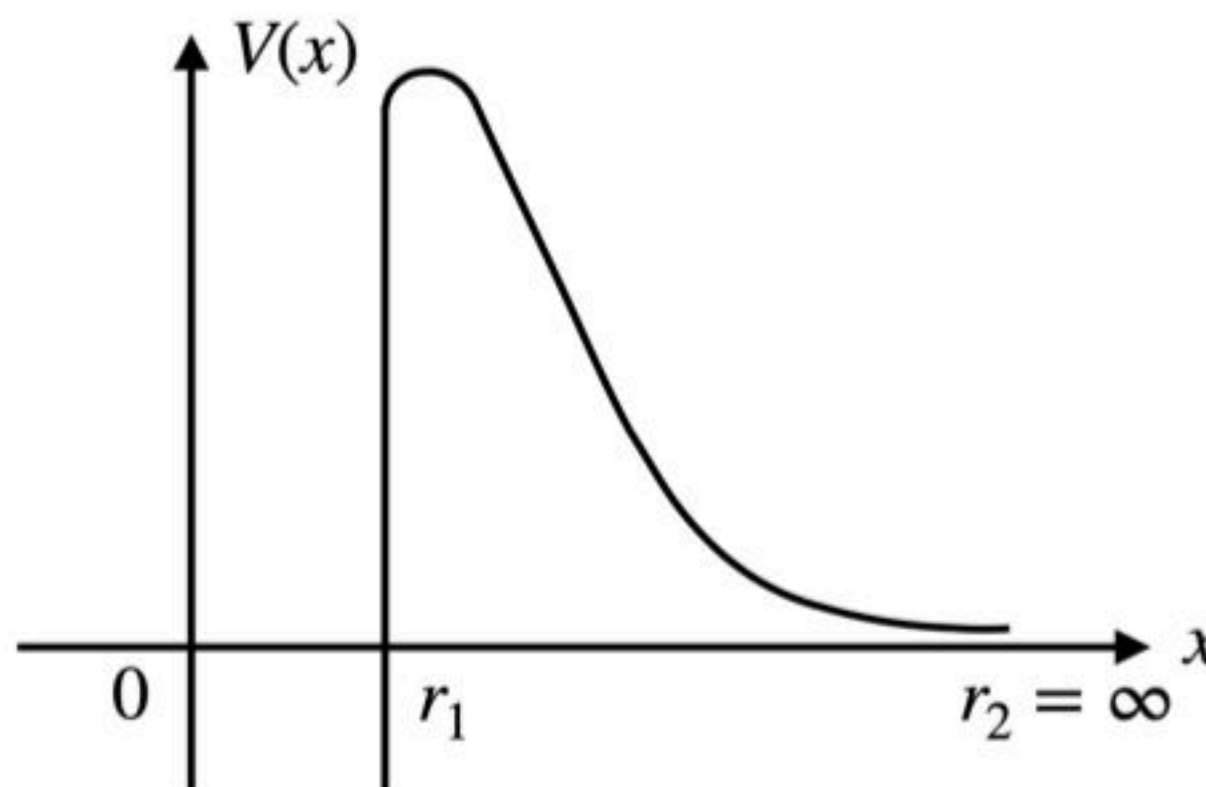


$$\int_{r_1}^{r_2} \frac{2}{\hbar} \sqrt{2\mu V(r)} dr = \text{finite} \quad (139)$$

$$T \neq 0 \quad (140)$$

能发生隧穿。

(b) If $V(x)$ extends to infinity, but falls off faster than $\frac{1}{r^2}$



$$\int_{r_1}^{r_2} \frac{2}{\hbar} \sqrt{2\mu V(r)} dr < \int_{r_1}^{\infty} \frac{2}{\hbar} \sqrt{2\mu \frac{1}{r^{2+\varepsilon}}} dr = \text{finite} \quad (141)$$

$$T \neq 0 \quad (142)$$

能发生隧穿。

(c) If $V(x)$ extends to infinity, but falls off like $\frac{1}{r^2}$

$$\int_{r_1}^{r_2} \frac{2}{\hbar} \sqrt{2\mu V(r)} dr \sim \int_{r_1}^{\infty} \frac{1}{r} dr \rightarrow \infty \quad (143)$$

$$T = 0 \quad (144)$$

不能发生隧穿。

3. $E = 0, l > 0$

$$T = \exp \left\{ -2 \int_{r_1}^{r_2} \frac{1}{\hbar} \sqrt{2\mu \left[\frac{ZZ'e^2}{r} + \frac{l(l+1)}{2\mu r^2} \right]} dr \right\} \quad (145)$$

$$\int_{r_1}^{r_2} \frac{2}{\hbar} \sqrt{2\mu \left[\frac{ZZ'e^2}{r} + \frac{l(l+1)}{2\mu r^2} \right]} dr \geq \int_{r_1}^{r_2} \frac{2}{\hbar} \frac{\sqrt{l(l+1)}}{r} dr \xrightarrow{r_2 \rightarrow \infty} \text{infinity} \quad (146)$$

$$T = 0 \quad (147)$$

不能发生隧穿。

Chapter 5: Rotation And Vibration of Molecules

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2020 年 7 月 19 日

1 Introduction

系统中包含 M 个原子核和 N 个电子，薛定谔方程写为

$$H(\vec{R}_1, \dots, \vec{R}_M; \vec{r}_1, \dots, \vec{r}_N) \psi(\vec{R}_1, \dots, \vec{R}_M; \vec{r}_1, \dots, \vec{r}_N) = E \psi(\vec{R}_1, \dots, \vec{R}_M; \vec{r}_1, \dots, \vec{r}_N) \quad (1)$$

进行符号简化

$$\vec{R} = \vec{R}_1, \dots, \vec{R}_M \quad (2)$$

$$\vec{r} = \vec{r}_1, \dots, \vec{r}_N \quad (3)$$

$$H(\vec{R}, \vec{r}) \psi(\vec{R}, \vec{r}) = E \psi(\vec{R}, \vec{r}) \quad (4)$$

将哈密顿量写成

$$H(\vec{R}, \vec{r}) = H_N(\vec{R}) + H_{el}(\vec{r}) + V(\vec{R}, \vec{r}) \quad (5)$$

其中 $H_N(\vec{R})$ 是核子的哈密顿量， $H_{el}(\vec{r})$ 是电子的哈密顿量， $V(\vec{R}, \vec{r})$ 是核子与电子的相互作用势。

将波函数近似写成

$$\psi(\vec{R}, \vec{r}) \doteq A(\vec{R}) n(\vec{R}, \vec{r}) \quad (6)$$

其中 $A(\vec{R})$ 是核子部分的波函数，忽略电子的影响； $n(\vec{R}, \vec{r})$ 是电子部分的波函数，它很大地依赖于核子的位置， \vec{R} 以参数的形式出现。代入薛定谔方程

$$\left[H_N(\vec{R}) + H_{el}(\vec{r}) + V(\vec{R}, \vec{r}) \right] A(\vec{R}) n(\vec{R}, \vec{r}) = E A(\vec{R}) n(\vec{R}, \vec{r}) \quad (7)$$

电子波函数满足薛定谔方程

$$\left[H_{el}(\vec{r}) + V(\vec{R}, \vec{r}) \right] n(\vec{R}, \vec{r}) = U_n(\vec{R}) n(\vec{R}, \vec{r}) \quad (8)$$

于是

$$\left[H_N(\vec{R}) + U_n(\vec{R}) \right] A(\vec{R}) n(\vec{R}, \vec{r}) = E A(\vec{R}) n(\vec{R}, \vec{r}) \quad (9)$$

方程两边作用 $\int d\vec{r} n^\dagger(\vec{R}, \vec{r})$ ，忽略 $U_n(\vec{R})$ 的影响

$$\left[H_N(\vec{R}) + U_n(\vec{R}) \right] A(\vec{R}) = E A(\vec{R}) \quad (10)$$

这是很常见的一种近似，叫 Born-Oppenheimer approximation，第一步近似是将核子与电子的自由度分开，第二步近似是 $\int d\vec{r} n^\dagger(\vec{R}, \vec{r})$ 作用时将 $U_n(\vec{R})$ 的影响忽略不计。

2 Diatomic Molecule

我们先讨论最简单的分子——双原子分子。重新定义符号

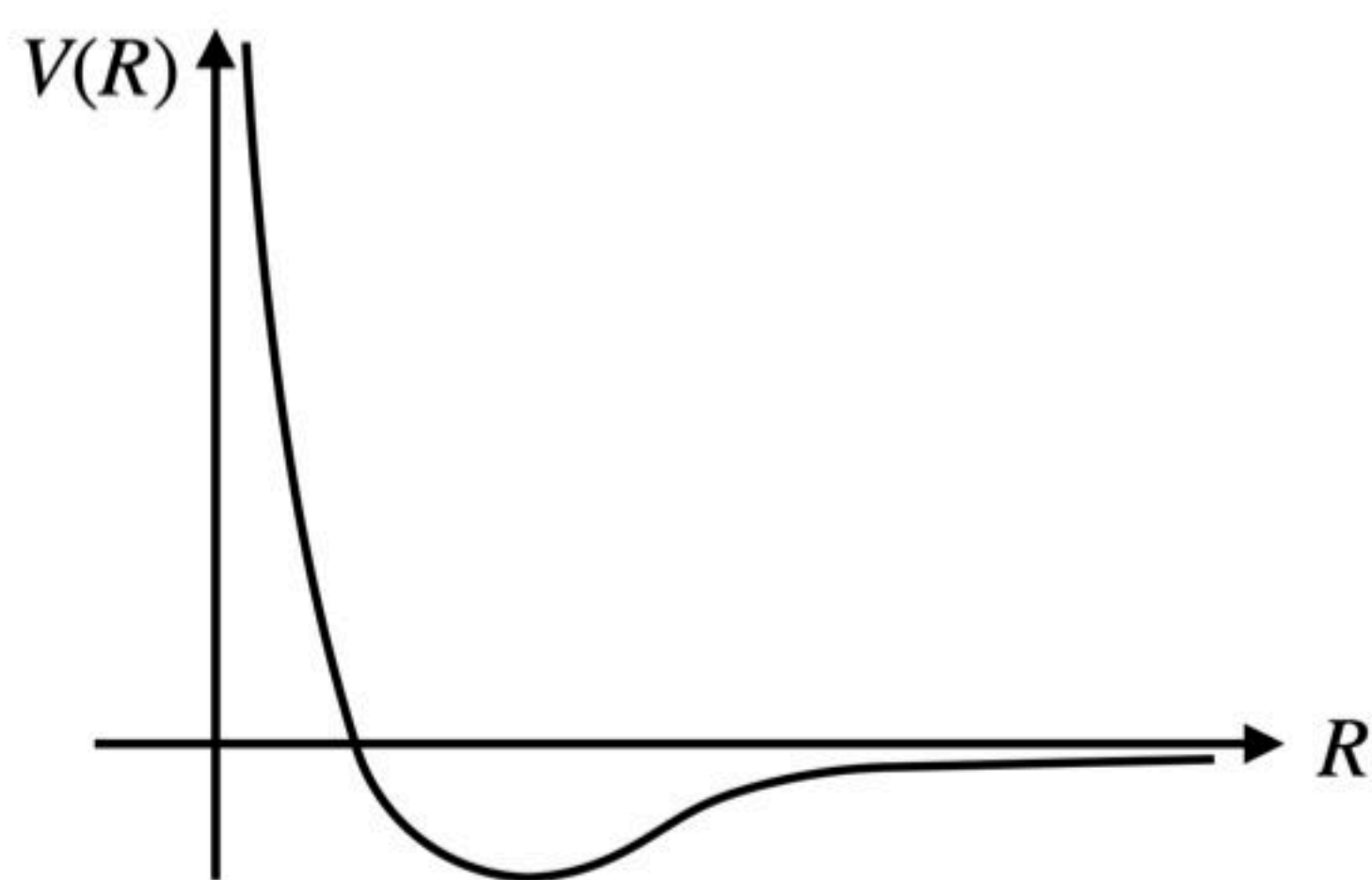
$$A(\vec{R}) = \psi(\vec{R}_1, \vec{R}_2) \quad (11)$$

$$U_n(\vec{R}) = V(\vec{R}) = V(\vec{R}_1 - \vec{R}_2) \quad (12)$$

$$\left[H_N(\vec{R}) + V(\vec{R}_1 - \vec{R}_2) \right] \psi(\vec{R}_1, \vec{R}_2) = E_{\text{total}} \psi(\vec{R}_1, \vec{R}_2) \quad (13)$$

$$\left[-\frac{\hbar^2}{2M_1} \nabla_1^2 - \frac{\hbar^2}{2M_2} \nabla_2^2 + V(\vec{R}) \right] \psi(\vec{R}_1, \vec{R}_2) = E_{\text{total}} \psi(\vec{R}_1, \vec{R}_2) \quad (14)$$

这是一个比较纯粹的数学问题，首先我们要先知道 $V(\vec{R})$ ， $V(\vec{R})$ 是两原子核间的相互作用。由于 $V(0) \rightarrow \infty, V(\infty) \rightarrow 0^-$ ，当 $x \rightarrow \infty$ 时为范德瓦尔斯势 (Vander Waals Potential)。定性画出 $V(\vec{R}) = V(R)$ 的图像



将质心坐标自由度分离

$$\vec{R}_c = \frac{M_1 \vec{R}_1 + M_2 \vec{R}_2}{M_1 + M_2} \quad \vec{R} = \vec{R}_1 - \vec{R}_2 \quad (15)$$

$$\frac{1}{M_1} \nabla_1^2 + \frac{1}{M_2} \nabla_2^2 = \frac{1}{M} \nabla_{\vec{R}_c}^2 + \frac{1}{\mu} \nabla_{\vec{R}}^2 \quad (16)$$

其中

$$M = M_1 + M_2 \quad \mu = \frac{M_1 M_2}{M_1 + M_2} \quad (17)$$

薛定谔方程改写为

$$\left[-\frac{\hbar^2}{2\mu} \nabla_{\vec{R}}^2 + V(\vec{R}) - \frac{\hbar^2}{2M} \nabla_{\vec{R}_c}^2 \right] \psi(\vec{R}_1, \vec{R}_2) = E_{\text{total}} \psi(\vec{R}_1, \vec{R}_2) \quad (18)$$

哈密顿量分成质心坐标部分和相对坐标部分。将 $\psi(\vec{R}_1, \vec{R}_2)$ 分离变量

$$\psi(\vec{R}_1, \vec{R}_2) = f(\vec{R}_c) \Phi(\vec{R}) \quad (19)$$

质心坐标部分薛定谔方程

$$-\frac{\hbar^2}{2M} \nabla_{\vec{R}_c}^2 f(\vec{R}_c) = E_c f(\vec{R}_c) \quad (20)$$

它的解 $f(\vec{R}_c)$ 是平面波，在空间任一点出现概率相等，因此我们对这个方程不感兴趣。相对坐标部分薛定谔方程

$$\left[V(\vec{R}) - \frac{\hbar^2}{2\mu} \nabla_{\vec{R}}^2 \right] \Phi(\vec{R}) = E \Phi(\vec{R}) \quad (21)$$

$$E_{\text{total}} = E_c + E \quad (22)$$

进一步分离变量

$$\Phi(\vec{R}) = \frac{\chi(R)}{R} Y_{L,M}(\theta, \phi) \quad (23)$$

$Y_{L,M}(\theta, \phi)$ 是球谐函数 (spherical harmonic function)。

$$\nabla_{\vec{R}}^2 = \frac{1}{R^2} \frac{\partial}{\partial R} R^2 \frac{\partial}{\partial R} - \frac{\vec{L}^2}{\hbar^2 R^2} = \frac{1}{R} \frac{d^2}{dR^2} R - \frac{\vec{L}^2}{\hbar^2 R^2} \quad (24)$$

$$\vec{L}^2 Y_{L,M}(\theta, \phi) = L(L+1) \hbar^2 Y_{L,M}(\theta, \phi) \quad (25)$$

于是

$$\left[\frac{\hbar^2}{2\mu} \left(-\frac{1}{R} \frac{d^2}{dR^2} R + \frac{L(L+1)}{R^2} \right) + V(\vec{R}) \right] \chi(R) Y_{L,M}(\theta, \phi) = E \chi(R) Y_{L,M}(\theta, \phi) \quad (26)$$

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + \frac{L(L+1)\hbar^2}{2\mu R^2} + V(\vec{R}) \right] \chi(R) = E \chi(R) \quad (27)$$

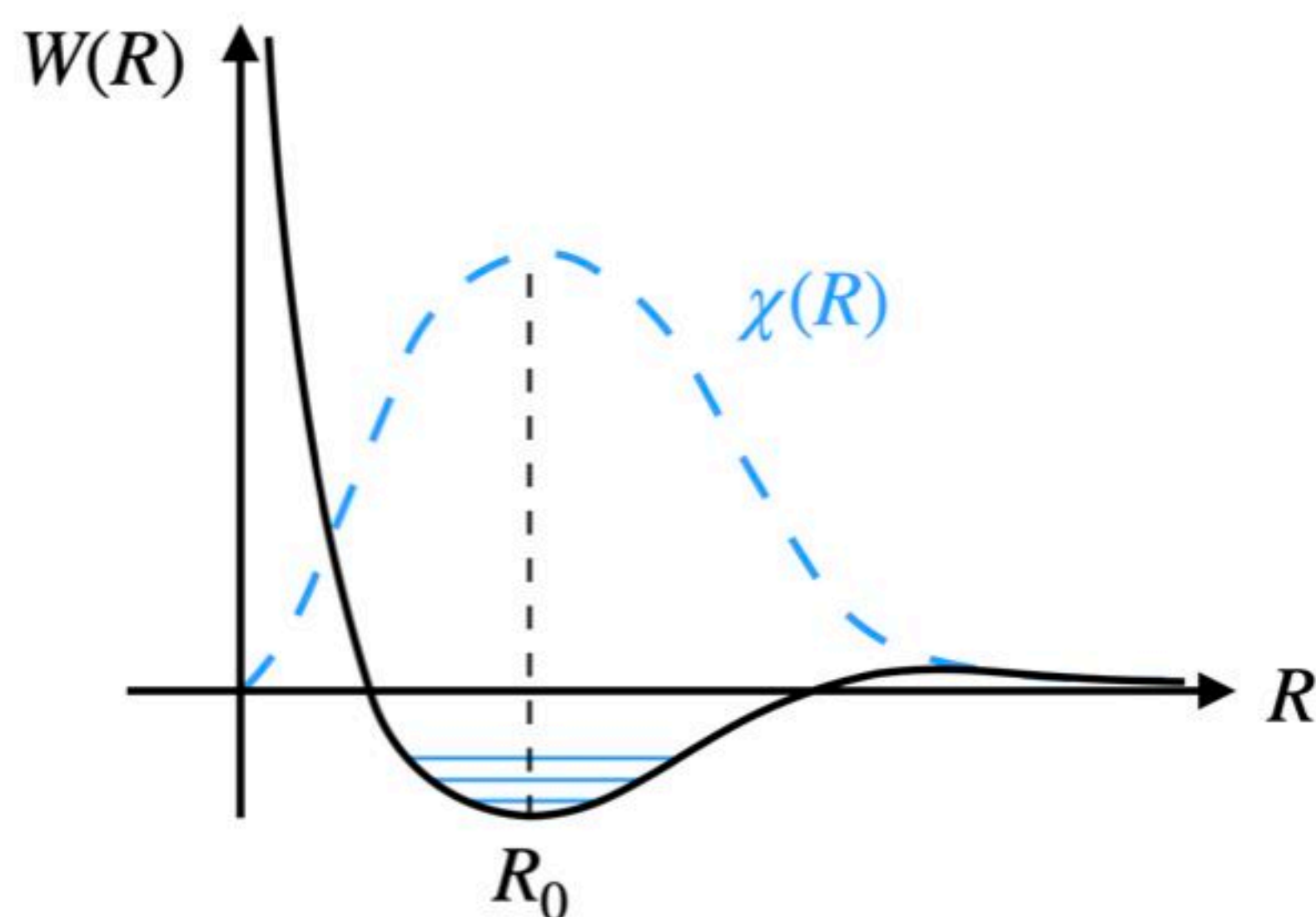
边界条件

$$\chi(\infty) = 0 \quad \chi(0) = 0 \quad (28)$$

定义

$$W(R) = V(R) + \frac{L(L+1)\hbar^2}{2\mu R^2} \quad (29)$$

由于当 $R \rightarrow \infty$ 时, $V(R)$ 的形式是 $(-\frac{\alpha}{R^6})$, 故 $W(R)$ 的图像为



原子核在 R_0 附近振动, 在 $W(R)$ 最小的地方, 原子核出现的几率越大, 即

$$\left. \frac{dW}{dR} \right|_{R_0} = 0 \quad (30)$$

$$\left. \frac{dV}{dR} \right|_{R_0} = \frac{L(L+1)\hbar^2}{\mu R_0^3} \quad (31)$$

将 $W(R)$ 在 R_0 处泰勒展开, 并略去高阶项

$$\begin{aligned} W(R) &= W(R_0) + \left. \frac{dW}{dR} \right|_{R_0} (R - R_0) + \frac{1}{2} W''(R_0) (R - R_0)^2 + \frac{1}{3!} W'''(R_0) (R - R_0)^3 + \dots \\ &= W(R_0) + \frac{1}{2} W''(R_0) (R - R_0)^2 \end{aligned} \quad (32)$$

定义

$$\frac{1}{2} W''(R_0) = \frac{1}{2} \mu \omega_0^2 \quad (33)$$

则

$$W(R) = W(R_0) + \frac{1}{2}\mu\omega_0^2(R - R_0)^2 \quad (34)$$

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + \frac{1}{2}\mu\omega_0^2(R - R_0)^2 \right] \chi(R) = E' \chi(R) \quad (35)$$

其中

$$E' = E - V(R_0) - \frac{L(L+1)\hbar^2}{2\mu R_0^2} \quad (36)$$

令 $\xi = R - R_0$, 进行符号简化

$$-\frac{\hbar^2}{2\mu} \frac{d^2}{d\xi^2} \chi + \frac{1}{2}\mu\omega_0^2 \xi^2 \chi = E' \chi \quad (37)$$

边界条件

$$\chi(R=0) = \chi(\xi = -R_0) = 0 \quad \chi(\xi = \infty) = 0 \quad (38)$$

方程形式与谐振子相同, 而这个边界条件的限制是谐振子所没有的, 因此该方程与谐振子的解不同但相似。谐振子的解

$$\chi(\xi) \propto e^{-\frac{1}{2}\alpha^2 \xi^2} H_\nu(\alpha \xi) \quad (39)$$

其中 $\alpha = \sqrt{\frac{\mu\omega_0}{\hbar}}$ 。本征能量

$$E' = \left(\nu + \frac{1}{2} \right) \hbar\omega_0 \quad \nu = 0, 1, 2, \dots \quad (40)$$

边界条件对解的影响很小, 因为 $R_0 \gg \frac{1}{\alpha}$, 故 $\alpha R_0 \gg 1$, $e^{-\frac{1}{2}\alpha^2 \xi^2} \rightarrow 0$, 很好地近似满足边界条件。将 $E' = (\nu + \frac{1}{2}) \hbar\omega_0$ 代入 Eq.(36)

$$E_{\nu,L} = V(R_0) + \left(\nu + \frac{1}{2} \right) \hbar\omega_0 + \frac{L(L+1)\hbar^2}{2J} \quad (41)$$

其中 $(\nu + \frac{1}{2}) \hbar\omega_0$ 是振动能量, $\frac{L(L+1)\hbar^2}{2J}$ 是转动能量, $J = \mu R_0^2$ 是转动惯量。

Example: Rotation Spectrum of H₂

$$\Psi(\vec{R}_1, \vec{R}_2) = \phi(\vec{R}_1, \vec{R}_2) \chi(S_{1z}, S_{2z}) \quad (42)$$

$\chi(S_{1z}, S_{2z})$ 为自旋部分, 自旋部分暂时与我们讨论的内容无关, 但在后面的多体理论中将指出, 自旋部分是影响波函数的。全同性原理要求, 交换原子核时, 波函数可能不变号, 也可能变号。

$$\Psi(\vec{R}_1, \vec{R}_2) = \pm \Psi(\vec{R}_2, \vec{R}_1) \quad (43)$$

在两粒子自旋为整数时不变号, 这是玻色子 (Boson); 自旋为半整数时变号, 这是费米子 (Fermion)。氢原子核的自旋是 $\frac{1}{2}$, 因此它是费米子。

$$\Psi(\vec{R}_1, \vec{R}_2) = -\Psi(\vec{R}_2, \vec{R}_1) \quad (44)$$

$\chi(S_{1z}, S_{2z})$ 有两种状态, 当它是单态时, 交换两粒子位置波函数变号; 当它是三重态时, 交换两粒子位置不变号。故自旋在全同性原理中起作用。交换两原子核位置

$$\vec{R}_c = \frac{\vec{R}_1 + \vec{R}_2}{2} \rightarrow \vec{R}_c \quad \vec{R} = \vec{R}_1 - \vec{R}_2 \rightarrow -\vec{R} \quad (45)$$

$$R \rightarrow R \quad \theta \rightarrow \pi - \theta \quad \phi \rightarrow \pi + \phi \quad (46)$$

$$Y_{L,M}(\theta, \phi) \rightarrow Y_{L,M}(\pi - \theta, \pi + \phi) = (-1)^L Y_{L,M}(\theta, \phi) \quad (47)$$

- 当 L 是偶数时

$$\Psi(\vec{R}_1, \vec{R}_2) = \frac{\chi_{\nu,L}(R)}{R} Y_{L,M}(\theta, \phi) \chi_0(S_{1z}, S_{2z}) \quad (48)$$

$Y_{L,M}(\theta, \phi)$ 不变号, 则 $\chi_0(S_{1z}, S_{2z})$ 变号, 对应自旋单态。

- 当 L 是奇数时

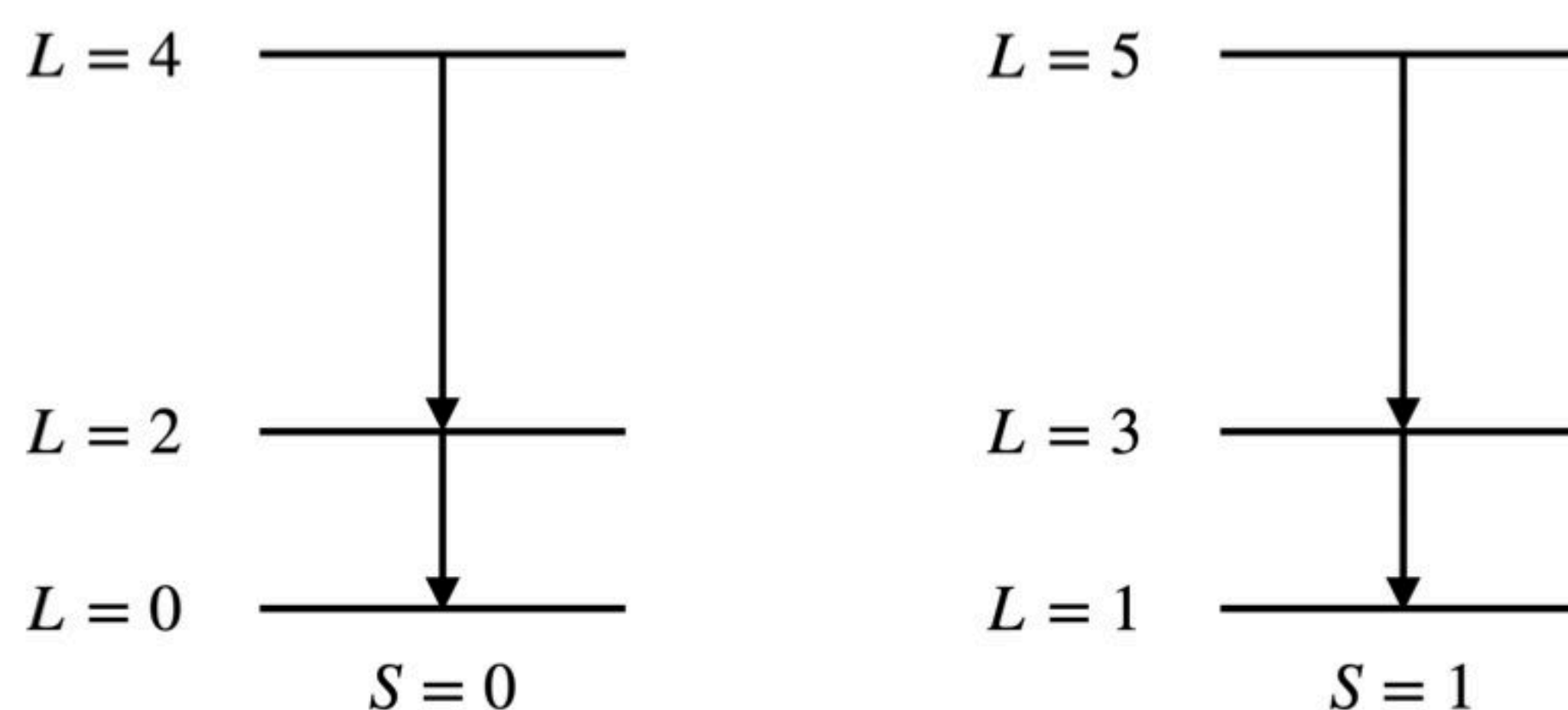
$$\Psi(\vec{R}_1, \vec{R}_2) = \frac{\chi_{\nu,L}(R)}{R} Y_{L,M}(\theta, \phi) \chi_1(S_{1z}, S_{2z}) \quad (49)$$

$Y_{L,M}(\theta, \phi)$ 变号, 则 $\chi_1(S_{1z}, S_{2z})$ 不变号, 对应自旋三重态。

这一点可以通过实验来检验, 因为自旋三重态与自旋单态在自然界中出现的几率是不同的

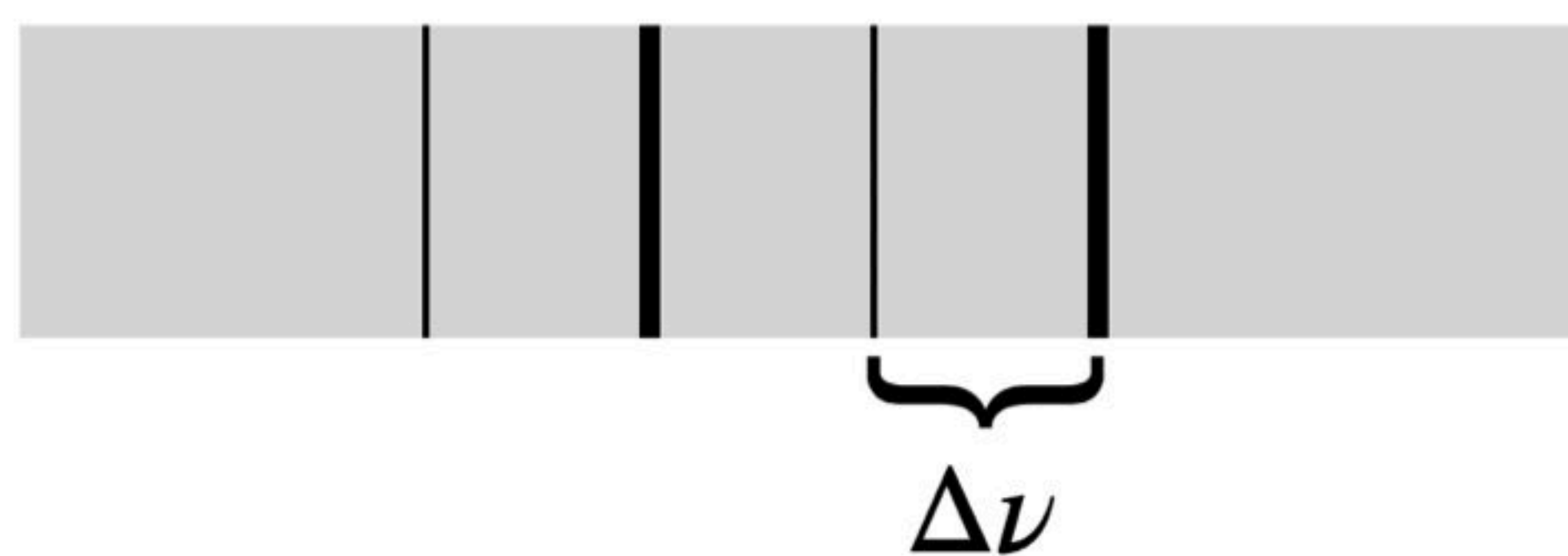
$$(S = 1) : (S = 0) = 3 : 1 \quad (50)$$

三重态氢分子 ($S = 1$) 我们叫正氢 (Orthohydrogen), 单态氢 ($S = 0$) 分子也叫仲氢 (Parahydrogen)。我们来看氢分子的转动谱



为什么两套谱系间不会发生跃迁呢? 因为激光跃迁时不带磁场, 没有东西与自旋耦合, 自旋的自由度是守恒的, $S = 1$ 永远是 $S = 1$, $S = 0$ 永远是 $S = 0$, 因此跃迁永远是 $L \rightarrow L - 2$ 。光谱能量

$$\Delta E = \frac{\hbar^2}{2J} [L(L+1) - (L-2)(L-1)] = \frac{\hbar}{\pi J} + \text{constant} \sim L \quad (51)$$



$$\Delta \nu = (\Delta E|_{L+1} - \Delta E|_L) \frac{1}{\hbar} = \frac{1}{\pi J} \quad (52)$$

Example: Order Estimate of E_e , E_{vib} , E_{rot}

从基态到第一激发态

$$E_e \sim \frac{\hbar^2}{ma^2} \quad (53)$$

a 约为两原子核之间的距离, m 是电子质量。

$$E_{\text{vib}} \sim \hbar \omega_0 \sim \hbar \frac{\hbar \alpha^2}{\mu} = \frac{\hbar^2 \alpha^2}{\mu} \quad (54)$$

$$E_{\text{rot}} \sim \frac{\hbar^2}{J} = \frac{\hbar^2}{\mu R_0^2} \quad (55)$$

令 $\xi = R - R_0 = \frac{1}{x}R_0$, 其中 $x \sim 1 - 10$ 由于 $\alpha\xi \sim 1$, 即 $\alpha \sim \frac{1}{\xi} = \frac{x}{R_0}$, 因此

$$E_{\text{vib}} \sim x^2 \frac{\hbar^2}{\mu R_0^2} \quad (56)$$

比较 E_e 和 E_{vib}

$$E_e \gg E_{\text{vib}} \quad (57)$$

比较 E_{vib} 和 E_{rot}

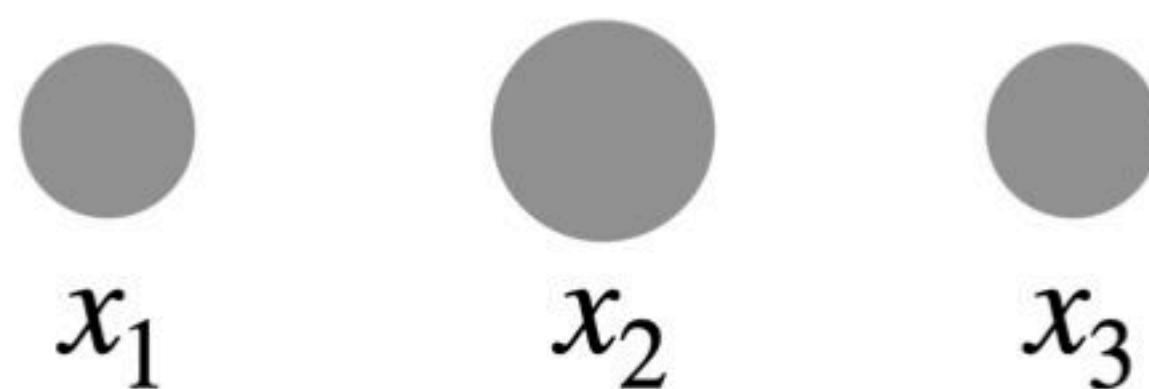
$$E_{\text{vib}} \gg E_{\text{rot}} \quad (58)$$

故

$$E_e \gg E_{\text{vib}} \gg E_{\text{rot}} \quad (59)$$

3 Vibrations of A Linear Triatomic Molecule

排成一条线的三原子分子, 如 CO_2



$$H = -\frac{\hbar^2}{2} \sum_{i=1}^3 \frac{1}{m_i} \frac{\partial^2}{\partial x_i^2} + V(x_1, x_2, x_3) \quad (60)$$

令

$$x_1 - x_2 = \tilde{x}_1 \quad x_3 - x_2 = \tilde{x}_3 \quad (61)$$

$$\left. \frac{\partial V}{\partial \tilde{x}_1} \right|_{\tilde{x}_1^{(0)}} = 0 \quad \left. \frac{\partial V}{\partial \tilde{x}_3} \right|_{\tilde{x}_3^{(0)}} = 0 \quad (62)$$

$$\left. \frac{\partial^2 V}{\partial \tilde{x}_1^2} \right|_{\tilde{x}_1^{(0)}} = k_1^2 \quad \left. \frac{\partial^2 V}{\partial \tilde{x}_3^2} \right|_{\tilde{x}_3^{(0)}} = k_2^2 \quad (63)$$

$$\tilde{x}_1^{(0)} = a_1 \quad \tilde{x}_3^{(0)} = a_2 \quad (64)$$

则

$$\begin{aligned} V(x_1, x_2, x_3) &= V(\tilde{x}_1, x_2, \tilde{x}_3) \doteq V(\tilde{x}_1, \tilde{x}_3) \\ &= V(\tilde{x}_1^{(0)}, \tilde{x}_3^{(0)}) + \left. \frac{\partial V}{\partial \tilde{x}_1} \right|_{\tilde{x}_1^{(0)}} (\tilde{x}_1 - \tilde{x}_1^{(0)}) + \left. \frac{\partial V}{\partial \tilde{x}_3} \right|_{\tilde{x}_3^{(0)}} (\tilde{x}_3 - \tilde{x}_3^{(0)}) \\ &\quad + \frac{1}{2} \left. \frac{\partial^2 V}{\partial \tilde{x}_1^2} \right|_{\tilde{x}_1^{(0)}} (\tilde{x}_1 - \tilde{x}_1^{(0)})^2 + \frac{1}{2} \left. \frac{\partial^2 V}{\partial \tilde{x}_3^2} \right|_{\tilde{x}_3^{(0)}} (\tilde{x}_3 - \tilde{x}_3^{(0)})^2 + \dots \end{aligned} \quad (65)$$

$$\begin{aligned} &= V(\tilde{x}_1^{(0)}, \tilde{x}_3^{(0)}) + \frac{1}{2} \left. \frac{\partial^2 V}{\partial \tilde{x}_1^2} \right|_{\tilde{x}_1^{(0)}} (\tilde{x}_1 - \tilde{x}_1^{(0)})^2 + \frac{1}{2} \left. \frac{\partial^2 V}{\partial \tilde{x}_3^2} \right|_{\tilde{x}_3^{(0)}} (\tilde{x}_3 - \tilde{x}_3^{(0)})^2 \\ &= V(\tilde{x}_1^{(0)}, \tilde{x}_3^{(0)}) + \frac{1}{2} k_1^2 (x_1 - x_2 - a_1)^2 + \frac{1}{2} k_2^2 (x_3 - x_2 - a_2)^2 \end{aligned}$$

$$H = -\frac{\hbar^2}{2} \sum_{i=1}^3 \frac{1}{m_i} \frac{\partial^2}{\partial x_i^2} + \frac{1}{2} k_1^2 (x_1 - x_2 - a_1)^2 + \frac{1}{2} k_2^2 (x_3 - x_2 - a_2)^2 \quad (66)$$

讨论 $k_1 = k_2 = k$, $a_1 = a_2 = a$ 的情况

$$H\Psi(x_1, x_2, x_3) = E\Psi(x_1, x_2, x_3) \quad (67)$$

引入质心坐标

$$M = m_1 + m_2 + m_3 \quad X = \frac{1}{M}(m_1 x_1 + m_2 x_2 + m_3 x_3) \quad (68)$$

$$\xi = x_2 - x_1 - a \quad \eta = x_3 - x_2 - a \quad (69)$$

进行微分变换

$$\frac{\partial}{\partial x_1} = \frac{\partial X}{\partial x_1} \frac{\partial}{\partial X} + \frac{\partial \xi}{\partial x_1} \frac{\partial}{\partial \xi} + \frac{\partial \eta}{\partial x_1} \frac{\partial}{\partial \eta} = \frac{m_1}{M} \frac{\partial}{\partial X} - \frac{\partial}{\partial \xi} \quad (70)$$

$$\frac{\partial}{\partial x_2} = \frac{m_2}{M} \frac{\partial}{\partial X} + \frac{\partial}{\partial \xi} - \frac{\partial}{\partial \eta} \quad (71)$$

$$\frac{\partial}{\partial x_3} = \frac{m_3}{M} \frac{\partial}{\partial X} + \frac{\partial}{\partial \eta} \quad (72)$$

$$\frac{\partial^2}{\partial x_1^2} = \left(\frac{m_1}{M} \frac{\partial}{\partial X} - \frac{\partial}{\partial \xi} \right)^2 = \frac{m_1^2}{M^2} \frac{\partial^2}{\partial X^2} - \frac{2m_1}{M} \frac{\partial^2}{\partial X \partial \xi} + \frac{\partial^2}{\partial \xi^2} \quad (73)$$

$$\frac{\partial^2}{\partial x_2^2} = \left(\frac{m_2}{M} \frac{\partial}{\partial X} + \frac{\partial}{\partial \xi} - \frac{\partial}{\partial \eta} \right)^2 = \frac{m_2^2}{M^2} \frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial \xi^2} - \frac{\partial^2}{\partial \eta^2} + \frac{2m_2}{M} \frac{\partial^2}{\partial X \partial \xi} - \frac{2m_2}{M} \frac{\partial^2}{\partial X \partial \eta} - 2 \frac{\partial^2}{\partial \xi \partial \eta} \quad (74)$$

$$\frac{\partial^2}{\partial x_3^2} = \left(\frac{m_3}{M} \frac{\partial}{\partial X} + \frac{\partial}{\partial \eta} \right)^2 = \frac{m_3^2}{M^2} \frac{\partial^2}{\partial X^2} - \frac{2m_3}{M} \frac{\partial^2}{\partial X \partial \eta} + \frac{\partial^2}{\partial \eta^2} \quad (75)$$

$$\sum_{i=1}^3 \frac{1}{m_i} \frac{\partial^2}{\partial x_i^2} = \frac{1}{M} \frac{\partial^2}{\partial X^2} + \left(\frac{1}{m_1} + \frac{1}{m_2} \right) \frac{\partial^2}{\partial \xi^2} + \left(\frac{1}{m_3} + \frac{1}{m_2} \right) \frac{\partial^2}{\partial \eta^2} - \frac{2}{m_2} \frac{\partial^2}{\partial \xi \partial \eta} \quad (76)$$

薛定谔方程

$$-\frac{\hbar^2}{2} \left[\frac{1}{M} \frac{\partial^2}{\partial X^2} + \left(\frac{1}{m_1} + \frac{1}{m_2} \right) \frac{\partial^2}{\partial \xi^2} + \left(\frac{1}{m_3} + \frac{1}{m_2} \right) \frac{\partial^2}{\partial \eta^2} - \frac{2}{m_2} \frac{\partial^2}{\partial \xi \partial \eta} \right] \Psi + \frac{k^2}{2} (\xi^2 + \eta^2) \Psi = E \Psi \quad (77)$$

分离变量

$$\Psi(x_1, x_2, x_3) = \Phi(X) \tilde{\psi}(\xi, \eta) \quad (78)$$

质心部分是 trivial 的, 我们对此不感兴趣

$$-\frac{\hbar^2}{2M} \frac{\partial^2}{\partial X^2} \Phi(X) = E_c \Phi(X) \quad (79)$$

相对坐标部分

$$-\frac{\hbar^2}{2} \left[\left(\frac{1}{m_1} + \frac{1}{m_2} \right) \frac{\partial^2}{\partial \xi^2} + \left(\frac{1}{m_3} + \frac{1}{m_2} \right) \frac{\partial^2}{\partial \eta^2} - \frac{2}{m_2} \frac{\partial^2}{\partial \xi \partial \eta} \right] \tilde{\Psi}(\xi, \eta) + \frac{k^2}{2} (\xi^2 + \eta^2) \tilde{\Psi}(\xi, \eta) = \tilde{E} \tilde{\Psi}(\xi, \eta) \quad (80)$$

$$E = E_c + \tilde{E} \quad (81)$$

由于 $\frac{\partial^2}{\partial \xi \partial \eta}$ 项的存在, 无法将 $\tilde{\Psi}(\xi, \eta)$ 分离变量, 因此我们需要做一些操作——将 ξ, η 转动, 引入自由度 α , 从而将 $\frac{\partial^2}{\partial \xi \partial \eta}$ 项丢掉。做正交变换

$$\xi' = \xi \cos \alpha + \eta \sin \alpha \quad (82)$$

$$\eta' = -\xi \sin \alpha + \eta \cos \alpha \quad (83)$$

代入相对坐标部分薛定谔方程

$$\left\{ -\frac{\hbar^2}{2} \left(\frac{1}{m_1} + \frac{1}{m_2} \right) \left(\cos^2 \alpha \frac{\partial^2}{\partial \xi'^2} - \sin 2\alpha \frac{\partial^2}{\partial \xi' \partial \eta'} + \sin^2 \alpha \frac{\partial^2}{\partial \eta'^2} \right) \right. \\ \left. + \left(\frac{1}{m_3} + \frac{1}{m_2} \right) \left(\sin^2 \alpha \frac{\partial^2}{\partial \xi'^2} + \sin 2\alpha \frac{\partial^2}{\partial \xi' \partial \eta'} + \cos^2 \alpha \frac{\partial^2}{\partial \eta'^2} \right) \right. \\ \left. - \frac{1}{m_2} \left(\sin 2\alpha \frac{\partial^2}{\partial \xi'^2} + 2 \cos 2\alpha \frac{\partial^2}{\partial \xi' \partial \eta'} - \sin 2\alpha \frac{\partial^2}{\partial \eta'^2} \right) + \frac{k^2}{2} (\xi'^2 + \eta'^2) \right\} \tilde{\Psi} = \tilde{E} \tilde{\Psi} \quad (84)$$

令 $\frac{\partial^2}{\partial \xi' \partial \eta'}$ 项的系数为 0

$$-\left(\frac{1}{m_1} + \frac{1}{m_2} \right) \sin 2\alpha + \left(\frac{1}{m_3} + \frac{1}{m_2} \right) \sin 2\alpha - \frac{2}{m_2} \cos 2\alpha = 0 \quad (85)$$

解得

$$\tan 2\alpha = \frac{2m_1 m_3}{m_2(m_1 - m_3)} \quad (86)$$

Eq.(84) 整理得

$$\left\{ -\frac{\hbar^2}{2} \left[\left(\frac{1}{m_1} + \frac{1}{m_2} \right) \cos^2 \alpha + \left(\frac{1}{m_3} + \frac{1}{m_2} \right) \sin^2 \alpha - \frac{1}{m_2} \sin 2\alpha \right] \frac{\partial^2}{\partial \xi'^2} \right. \\ \left. - \frac{\hbar^2}{2} \left[\left(\frac{1}{m_1} + \frac{1}{m_2} \right) \sin^2 \alpha + \left(\frac{1}{m_3} + \frac{1}{m_2} \right) \cos^2 \alpha + \frac{1}{m_2} \sin 2\alpha \right] \frac{\partial^2}{\partial \eta'^2} + \frac{1}{2} k (\xi'^2 + \eta'^2) \right\} \tilde{\Psi} = \tilde{E} \tilde{\Psi} \quad (87)$$

令

$$\frac{1}{A} = \left(\frac{1}{m_1} + \frac{1}{m_2} \right) \cos^2 \alpha + \left(\frac{1}{m_3} + \frac{1}{m_2} \right) \sin^2 \alpha - \frac{1}{m_2} \sin 2\alpha \quad (88)$$

$$\frac{1}{B} = \left(\frac{1}{m_1} + \frac{1}{m_2} \right) \sin^2 \alpha + \left(\frac{1}{m_3} + \frac{1}{m_2} \right) \cos^2 \alpha + \frac{1}{m_2} \sin 2\alpha \quad (89)$$

则

$$\left(-\frac{\hbar^2}{2A} \frac{\partial^2}{\partial \xi'^2} + \frac{k}{2} \xi'^2 - \frac{\hbar^2}{2B} \frac{\partial^2}{\partial \eta'^2} + \frac{k}{2} \eta'^2 \right) \tilde{\Psi} = \tilde{E} \tilde{\Psi} \quad (90)$$

分离变量

$$\tilde{\Psi}(\xi', \eta') = f(\xi') g(\eta') \quad (91)$$

$$\left(-\frac{\hbar^2}{2A} \frac{\partial^2}{\partial \xi'^2} + \frac{k}{2} \xi'^2 \right) f(\xi') = E_A f(\xi') \quad (92)$$

$$\left(-\frac{\hbar^2}{2B} \frac{\partial^2}{\partial \eta'^2} + \frac{k}{2} \eta'^2 \right) g(\eta') = E_B g(\eta') \quad (93)$$

$$\tilde{E} = E_A + E_B \quad (94)$$

两个方程都是谐振子。定义

$$\omega_A = \sqrt{\frac{k}{A}} \quad \omega_B = \sqrt{\frac{k}{B}} \quad (95)$$

得到能谱

$$E_A = \left(n_A + \frac{1}{2} \right) \hbar \omega_A \quad n_A = 0, 1, 2, \dots \quad (96)$$

$$E_B = \left(n_B + \frac{1}{2} \right) \hbar \omega_B \quad n_B = 0, 1, 2, \dots \quad (97)$$

Example: CO₂ (O=C=O)

对于二氧化碳分子

$$m_1 = m_3 \quad \Rightarrow \quad \cos 2\alpha = 0, \tan 2\alpha = \infty \quad \Rightarrow \quad \alpha = \frac{\pi}{4} \quad (98)$$

$$A = m_1 \quad B = \frac{m_1 + m_2}{2m_1 + m_2} \quad (99)$$

$$\omega_A = \sqrt{\frac{k}{m_1}} \quad \omega_B = \sqrt{\frac{k(2m_1 + m_2)}{m_1 m_2}} \quad (100)$$

$$\begin{aligned} \tilde{\Psi}_0 &\sim \exp\left(-\frac{A\omega_A}{2\hbar}\xi'^2\right) \exp\left(-\frac{B\omega_B}{2\hbar}\eta'^2\right) \\ &= \exp\left[-\frac{A\omega_A}{4\hbar}(\xi + \eta)^2\right] \exp\left[-\frac{B\omega_B}{4\hbar}(-\xi + \eta)^2\right] \\ &= \exp\left[-\frac{A\omega_A}{4\hbar}(x_3 - x_1 - 2a)^2\right] \exp\left[-\frac{B\omega_B}{4\hbar}(x_3 + x_1 - 2x_2)^2\right] \end{aligned} \quad (101)$$

Chapter 6: Variational Principle with Its Application to Two-particle Systems

Chen Huang

2020 年 8 月 2 日

$$1 \quad H\psi = E\psi \Leftrightarrow \bar{H} = \int \psi^\dagger H\psi d\tau$$

$$H\psi = E\psi \Leftrightarrow \bar{H} = \int \psi^\dagger H\psi d\tau \quad (1)$$

其中 $\psi(\vec{r}_1, \dots, \vec{r}_N)$, $d\tau = d\vec{r}_1 \cdots d\vec{r}_N$, 所有变换需满足

$$\int \psi^\dagger \psi d\tau = 1 \quad (2)$$

做虚变化

$$\psi \rightarrow \psi + \delta\psi \quad (3)$$

$$\psi^\dagger \rightarrow \psi^\dagger + \delta\psi^\dagger \quad (4)$$

$$\delta\bar{H} = \bar{H}(\psi + \delta\psi, \psi^\dagger + \delta\psi^\dagger) - \bar{H}(\psi, \psi^\dagger) \sim (\delta\psi)^2 \quad (5)$$

$$\bar{H} = \int \psi^\dagger H\psi d\tau \Rightarrow H\psi = E\psi$$

$$\delta\bar{H} = \delta \int \psi^\dagger H\psi d\tau = 0 \quad (6)$$

由于约束条件

$$\int \psi^\dagger \psi d\tau = 1 \quad (7)$$

引入 Lagrange 乘子

$$\begin{aligned} & \delta\bar{H} - \lambda \delta \int \psi^\dagger \psi d\tau \\ &= \int (\delta\psi^\dagger) H\psi d\tau + \int \psi^\dagger H(\delta\psi) d\tau + \int (\delta\psi^\dagger) H(\delta\psi) d\tau - \lambda \int (\delta\psi^\dagger) \psi d\tau - \lambda \int \psi^\dagger (\delta\psi) d\tau - \lambda \int \delta\psi^\dagger \delta\psi d\tau \\ &= \int (\delta\psi^\dagger) H\psi d\tau + \int \psi^\dagger H(\delta\psi) d\tau - \lambda \int (\delta\psi^\dagger) \psi d\tau - \lambda \int \psi^\dagger (\delta\psi) d\tau \quad (\text{略去高阶项}) \\ &= \int (\delta\psi^\dagger) (H - \lambda) \psi d\tau + \int \psi^\dagger (H - \lambda) (\delta\psi) d\tau = 0 \end{aligned} \quad (8)$$

故

$$H\psi = \lambda\psi \quad H^\dagger \psi^\dagger = \lambda\psi^\dagger \quad (9)$$

$$1 \quad H\psi = E\psi \Leftrightarrow \bar{H} = \int \psi^\dagger H \psi d\tau$$

2

$$H\psi = E\psi \Rightarrow \bar{H} = \int \psi^\dagger H \psi d\tau$$

假设

$$H\psi_\lambda = E_\lambda \psi_\lambda \quad (10)$$

则

$$E_\lambda = \int \psi_\lambda^\dagger H \psi_\lambda d\tau \quad (11)$$

ψ_λ 满足

$$\int \psi_\lambda^\dagger \psi_\lambda d\tau = 1 \quad (12)$$

做虚变化

$$\psi_\lambda \rightarrow \psi_\lambda + \delta\psi_\lambda \quad (13)$$

$$\psi_\lambda^\dagger \rightarrow \psi_\lambda^\dagger + \delta\psi_\lambda^\dagger \quad (14)$$

由于虚变化前后都要满足 Eq.(12)

$$\int (\psi_\lambda^\dagger + \delta\psi_\lambda^\dagger)(\psi_\lambda + \delta\psi_\lambda) d\tau = \int d\tau [\psi_\lambda^\dagger \psi_\lambda + \psi^\dagger(\delta\psi) + (\delta\psi_\lambda^\dagger)\psi_\lambda + (\delta\psi_\lambda^\dagger)(\delta\psi_\lambda)] = 1 \quad (15)$$

$$\int d\tau [\psi^\dagger(\delta\psi) + (\delta\psi_\lambda^\dagger)\psi_\lambda + (\delta\psi_\lambda^\dagger)(\delta\psi_\lambda)] = \int d\tau \delta|\psi_\lambda|^2 + \int d\tau |\delta\psi_\lambda|^2 = 0 \quad (16)$$

接下来看 E_λ

$$E_\lambda \rightarrow E_\lambda + \delta E_\lambda = \int d\tau (\psi_\lambda^\dagger + \delta\psi_\lambda^\dagger) H (\psi_\lambda + \delta\psi_\lambda) \quad (17)$$

$$\begin{aligned} \delta E_\lambda &= \int d\tau [\psi_\lambda^\dagger H(\delta\psi_\lambda) + (\delta\psi_\lambda^\dagger) H \psi_\lambda + (\delta\psi_\lambda^\dagger) H(\delta\psi_\lambda)] \\ &= E_\lambda \int d\tau [\psi_\lambda^\dagger(\delta\psi_\lambda) + (\delta\psi_\lambda^\dagger)\psi_\lambda] + \int d\tau (\delta\psi_\lambda^\dagger) H(\delta\psi_\lambda) \\ &= -E_\lambda \int d\tau |\delta\psi_\lambda|^2 + \int d\tau (\delta\psi_\lambda^\dagger) H(\delta\psi_\lambda) = 0 \end{aligned} \quad (18)$$

$$H\psi_\nu = E_\nu \psi_\nu \quad (19)$$

ψ_ν 构成完备积，用它来展开 ψ_λ

$$\delta\psi_\lambda = \sum_\nu \delta a_\nu \psi_\nu \quad (20)$$

将 $\delta\psi$ 代入 Eq.(18)

$$\delta E_\lambda = -E_\lambda \sum_\nu |\delta a_\nu|^2 + \sum_\nu E_\nu |\delta a_\nu|^2 = 0 \quad (21)$$

当 $\delta a_\nu \neq 0$ 时

$$\frac{\delta E_\lambda}{\delta a_\nu} = 0 \quad (22)$$

对于基态 $E_\lambda = E_0$

$$\delta E_\lambda = -E_0 \sum_\nu |\delta a_\nu|^2 + \sum_\nu E_\nu |\delta a_\nu|^2 \geq -E_0 \sum_\nu |\delta a_\nu|^2 + E_0 \sum_\nu |\delta a_\nu|^2 = 0 \quad (23)$$

$$\frac{\delta^2 E_\lambda}{\delta a_\nu^2} \geq 0 \quad (24)$$

基态中 E_λ 即严格解对应极小值。在 Hilbert 空间中 $\int d\tau |\psi|^2 = 1$ 球面上除严格解外，任何虚变化计算出来的 \bar{H} 总是比严格解大。

General Meaning of Variational Principle

牛顿方程和变分原理可以互相导出

$$\frac{d^2}{dt^2}x = -\frac{\partial V(x)}{\partial x} \Leftrightarrow S = \int_{t_1}^{t_2} L dt \quad (25)$$

同样我们也有

$$H\psi = E\psi \Leftrightarrow \bar{H} = \int \psi^\dagger H\psi d\tau \quad (26)$$

即，微分方程 \Leftrightarrow 变分原理。In general, Sturm-Liouville equation

$$[-P(x)y']' + Q(x)y = \lambda y \quad (27)$$

对应

$$J(y) = \int_a^b [P(x)y'^2 + Q(x)y^2] dx \quad (28)$$

变分条件是 $\int_a^b y^2 dx = 1$, $y(a) = 0$, $y(b) = 0$ 。

2 Ritz Variational Theory

从另一个角度看

$$\int \psi^\dagger H\psi d\tau \geq E_0 \quad (29)$$

其中 E_0 是薛定谔方程真正的本征值。任意波函数 ψ 总能写成

$$\psi = \sum_{n=0}^{\infty} c_n \varphi_n \quad (30)$$

$$H\varphi_0 = E_0\varphi_0 \quad (31)$$

将 $\psi = \sum_{n=0}^{\infty} c_n \varphi_n$ 代入 Eq.(29)

$$\int \psi^\dagger H\psi d\tau = \sum_{n=0}^{\infty} \sum_{n'=0}^{\infty} c_n^\dagger c_{n'} \int \varphi_{n'}^\dagger H\varphi_n d\tau = \sum_{n=0}^{\infty} \sum_{n'=0}^{\infty} c_n^\dagger c_{n'} E_n \delta_{nn'} = \sum_{n=0}^{\infty} |c_n|^2 E_n \geq E_0 \sum_{n=0}^{\infty} |c_n|^2 = E_0 \quad (32)$$

引入试探波函数 $\psi(x_1, \dots, x_N; c_1, \dots, c_N) = \psi(q, c_1, \dots, c_N)$

$$\int |\psi|^2 dq = 1 \quad (33)$$

计算 \bar{H}

$$\bar{H}(c_1, \dots, c_N) = \frac{\int dq \psi^\dagger(q, c_1, \dots, c_N) H\psi(q, c_1, \dots, c_N)}{\int |\psi|^2 dq} \quad (34)$$

$$\delta \bar{H}(c_1, \dots, c_N) = \sum_{i=1}^N \frac{\partial \bar{H}}{\partial c_i} \delta c_i = 0 \quad (35)$$

故

$$\frac{\partial \bar{H}}{\partial c_i} = 0 \quad \text{for} \quad i = 1, 2, 3, \dots \quad (36)$$

Example

$$H = -\frac{1}{2} \frac{d^2}{dx^2} + \frac{k}{2} x^2 \quad (37)$$

用变分原理解 $H\psi(x) = E\psi(x)$, 取试探波函数

$$\psi(x) = ce^{-\lambda x^2} = \left(\frac{2\lambda}{\pi}\right)^{\frac{1}{4}} e^{-\lambda x^2} \quad (38)$$

计算 \bar{H}

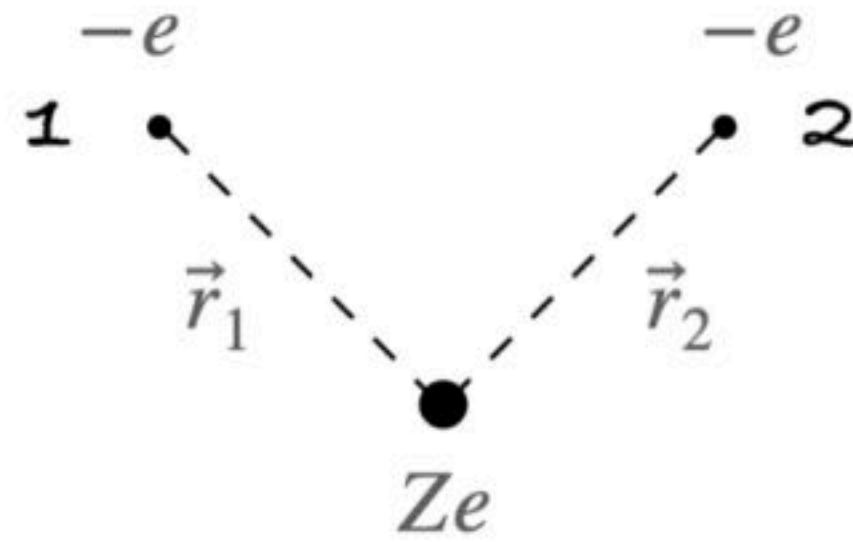
$$\begin{aligned} \bar{H} &= \int \psi^\dagger H \psi dx \\ &= \int \psi^\dagger \left(-\frac{1}{2} \frac{d^2}{dx^2} + \frac{k}{2} x^2 \right) ce^{-\lambda x^2} dx \\ &= \int \left(\frac{2\lambda}{\pi} \right)^{\frac{1}{2}} \left[\left(\frac{k}{2} - 2\lambda^2 \right) x^2 + \lambda \right] e^{-2\lambda x^2} dx \\ &= \frac{\lambda}{2} + \frac{k}{8\lambda} \end{aligned} \quad (39)$$

$$\frac{\partial \bar{H}}{\partial \lambda} = \frac{1}{2} - \frac{k}{8\lambda^2} = 0 \quad (40)$$

得到 $\lambda = \frac{1}{2}\sqrt{k}$, 代回 Eq.(39) 和 Eq.(38), 得

$$\bar{H} = \frac{1}{2}\sqrt{k} \quad (41)$$

$$\psi = \left(\frac{\sqrt{k}}{\pi} \right)^{\frac{1}{4}} e^{-\frac{1}{2}\sqrt{k}x^2} \quad (42)$$

3 He Atom

$$H = -\frac{\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + V(|\vec{r}_1 - \vec{r}_2|) \quad (43)$$

取自然单位制 (natural unit), 令 $e^2 = 1, m = 1, \hbar = 1$

$$H = -\frac{1}{2} (\nabla_1^2 + \nabla_2^2) - \frac{Z}{r_1} - \frac{Z}{r_2} + V(|\vec{r}_1 - \vec{r}_2|) \quad (44)$$

薛定谔方程

$$H(\vec{r}_1, \vec{r}_2) \Psi(\vec{r}_1, \sigma_1; \vec{r}_2, \sigma_2) = E \Psi(\vec{r}_1, \sigma_1; \vec{r}_2, \sigma_2) \quad (45)$$

波函数分为空间部分和自旋部分

$$\Psi(\vec{r}_1, \sigma_1; \vec{r}_2, \sigma_2) = \Psi(\vec{r}_1, \vec{r}_2) \chi(\sigma_1, \sigma_2) = \begin{cases} \Psi(\vec{r}_1, \vec{r}_2) \chi_s(\sigma_1, \sigma_2) & (\text{singlet 单态}) \\ \Psi(\vec{r}_1, \vec{r}_2) \chi_t(\sigma_1, \sigma_2) & (\text{triplet 三重态}) \end{cases} \quad (46)$$

我们最感兴趣的是 He 原子的基态。He 原子基态的两个电子是自旋单态，自旋部分反对称，空间部分对称。令

$$H_0 = -\frac{1}{2} (\nabla_1^2 + \nabla_2^2) - \frac{Z}{r_1} - \frac{Z}{r_2} \quad (47)$$

$$H = H_0 + V(|\vec{r}_1 - \vec{r}_2|) = H_0 + H' \quad (48)$$

First Method: Perturbation Theory

$$H_0 \Psi^{(0)}(\vec{r}_1, \vec{r}_2) = E_0 \Psi^{(0)}(\vec{r}_1, \vec{r}_2) \quad (49)$$

$$\Psi^{(0)}(\vec{r}_1, \vec{r}_2) = \psi_{100}(\vec{r}_1) \psi_{100}(\vec{r}_2) \quad (50)$$

ψ_{100} 是基态 ($n=1, l=0, m=0$) 氢原子薛定谔方程的解，满足

$$\left(-\frac{1}{2} \nabla^2 - \frac{Z}{r} \right) \psi_{100}(\vec{r}) = \varepsilon_0^{(0)} \psi_{100}(\vec{r}) \quad (51)$$

$$\varepsilon_0^{(0)} = -\frac{Z^2}{2n^2} \Big|_{n=1} = -\frac{1}{2} Z^2 \quad (52)$$

$$\psi_{100}(\vec{r}) = \frac{Z^{\frac{3}{2}}}{\sqrt{\pi}} e^{-Zr} \quad (53)$$

在微扰论中，基态 He 原子

$$E_0 = E_0^{(0)} + E_0^{(1)} + E_0^{(2)} + \dots \quad (54)$$

根据之前我们计算的结果

$$E_0^{(0)} = 2\varepsilon_0^{(0)} = -Z^2 \quad (55)$$

接下来计算一级微扰 $E_0^{(1)}$

$$\begin{aligned} E_0^{(1)} &= \langle \Psi^{(0)} | H' | \Psi^{(0)} \rangle \\ &= \int d\vec{r}_1 d\vec{r}_2 \Psi^{(0)\dagger}(\vec{r}_1, \vec{r}_2) H' \Psi^{(0)}(\vec{r}_1, \vec{r}_2) \\ &= \int d\vec{r}_1 d\vec{r}_2 \Psi^{(0)\dagger}(\vec{r}_1, \vec{r}_2) V(|\vec{r}_1 - \vec{r}_2|) \Psi^{(0)}(\vec{r}_1, \vec{r}_2) \\ &= \int d\vec{r}_1 d\vec{r}_2 |\psi_{100}(r_1)|^2 |\psi_{100}(r_2)|^2 V(|\vec{r}_1 - \vec{r}_2|) \\ &= \int d\vec{r}_1 d\vec{r}_2 \left(\frac{z^3}{\pi} \right)^2 e^{-2Z(r_1+r_2)} V(|\vec{r}_1 - \vec{r}_2|) \end{aligned} \quad (56)$$

令

$$V(|\vec{r}_1 - \vec{r}_2|) = \frac{1}{|\vec{r}_1 - \vec{r}_2|} = \frac{1}{r_{12}} \quad (57)$$

$$E_0^{(1)} = \int d\vec{r}_1 d\vec{r}_2 \left(\frac{z^3}{\pi} \right)^2 e^{-2Z(r_1+r_2)} \frac{1}{r_{12}} = \left(\frac{z^3}{\pi} \right)^2 I(Z) \quad (58)$$

其中

$$I(Z) = \int d\vec{r}_1 d\vec{r}_2 e^{-2Z(r_1+r_2)} \frac{1}{r_{12}} = \frac{5\pi^2}{8\lambda^5} \quad (59)$$

代入 Eq.(58) 得到

$$E_0^{(1)} = \frac{5}{8} Z \quad (60)$$

$$E_0 = E_0^{(0)} + E_0^{(1)} = -Z^2 + \frac{5}{8}Z \quad (61)$$

二级微扰

$$E_0^{(2)} = \sum_n' \frac{|\langle 0 | H' | n \rangle|^2}{E_0^{(0)} - E_n^{(0)}} \quad (62)$$

从形式我们可以感觉到非常复杂。

Second Method: Variational Principle

无电子相互作用的波函数

$$\Psi(\vec{r}_1, \vec{r}_2) = \frac{Z^3}{\pi} \exp[-Z(r_1 + r_2)] \quad (63)$$

选取试探波函数是一个非常依靠经验的行为，我们选取这样的试探波函数

$$\Phi(\vec{r}_1, \vec{r}_2, \lambda) = \frac{\lambda^3}{\pi} \exp[-\lambda(r_1 + r_2)] \quad (64)$$

将试探波函数写成以下形式

$$\Phi(\vec{r}_1, \vec{r}_2) = U(r_1)U(r_2) \quad (65)$$

$$U(r) = \sqrt{\frac{\lambda^3}{\pi}} \exp(-\lambda r) \quad (66)$$

计算 \bar{H}

$$\begin{aligned} \bar{H} &= \int d\vec{r}_1 d\vec{r}_2 \Phi^\dagger \left(-\frac{1}{2} \nabla_1^2 - \frac{Z}{r_1} - \frac{1}{2} \nabla_2^2 - \frac{Z}{r_2} + \frac{1}{r_{12}} \right) \Phi \\ &= \int d\vec{r}_1 d\vec{r}_2 U(r_1)U(r_2) \left(-\frac{1}{2} \nabla_1^2 - \frac{Z}{r_1} - \frac{1}{2} \nabla_2^2 - \frac{Z}{r_2} + \frac{1}{r_{12}} \right) U(r_1)U(r_2) \end{aligned} \quad (67)$$

$U(r)$ 是类氢离子的波函数，满足以下微分方程

$$\left(-\frac{1}{2} \nabla^2 - \frac{\lambda}{r} \right) U(r) = -\frac{\lambda^2}{2} U(r) \quad (68)$$

$$\begin{aligned} \bar{H} &= \int d\vec{r}_1 d\vec{r}_2 U(r_1)U(r_2) \left(-\frac{1}{2} \nabla_1^2 - \frac{\lambda}{r_1} - \frac{Z-\lambda}{r_1} - \frac{1}{2} \nabla_2^2 - \frac{\lambda}{r_2} - \frac{Z-\lambda}{r_2} + \frac{1}{r_{12}} \right) U(r_1)U(r_2) \\ &= \int d\vec{r}_1 d\vec{r}_2 \left(-\lambda^2 - \frac{Z-\lambda}{r_1} - \frac{Z-\lambda}{r_2} + \frac{1}{r_{12}} \right) \left(\frac{\lambda^3}{\pi} \right)^2 \exp[-2\lambda(r_1 + r_2)] \end{aligned} \quad (69)$$

类氢原子 $\frac{1}{r}$ 的平均值

$$\int U^2(r) \frac{1}{r} d\vec{r} = \frac{\lambda}{a_0} \quad (70)$$

a_0 是玻尔原子半径，取自然单位制 $a_0 = 1$

$$\int U^2(r) \frac{1}{r} d\vec{r} = \lambda \quad (71)$$

故

$$\bar{H} = -\lambda^2 - 2(Z-\lambda)\lambda + \frac{5}{8}\lambda = \lambda^2 - \left(2Z - \frac{5}{8}\right)\lambda \quad (72)$$

$$\frac{\partial \bar{H}}{\partial \lambda} = 2\lambda - 2Z + \frac{5}{8} = 0 \quad \Rightarrow \quad \lambda = Z - \frac{5}{16} \quad (73)$$

代回 Eq.(72)

$$\bar{H} = \left(Z - \frac{5}{16}\right)^2 - 2\left(Z - \frac{5}{16}\right)^2 = -\left(Z - \frac{5}{16}\right)^2 \quad (74)$$

$$E \leq -\left(Z - \frac{5}{16}\right)^2 = -Z^2 + \frac{5}{8}Z - \frac{25}{256} \quad (75)$$

对比一阶微扰的结论 $E = -Z^2 + \frac{5}{8}Z$ ，变分法得到的结论更精确。最开始我们取的试探波函数是

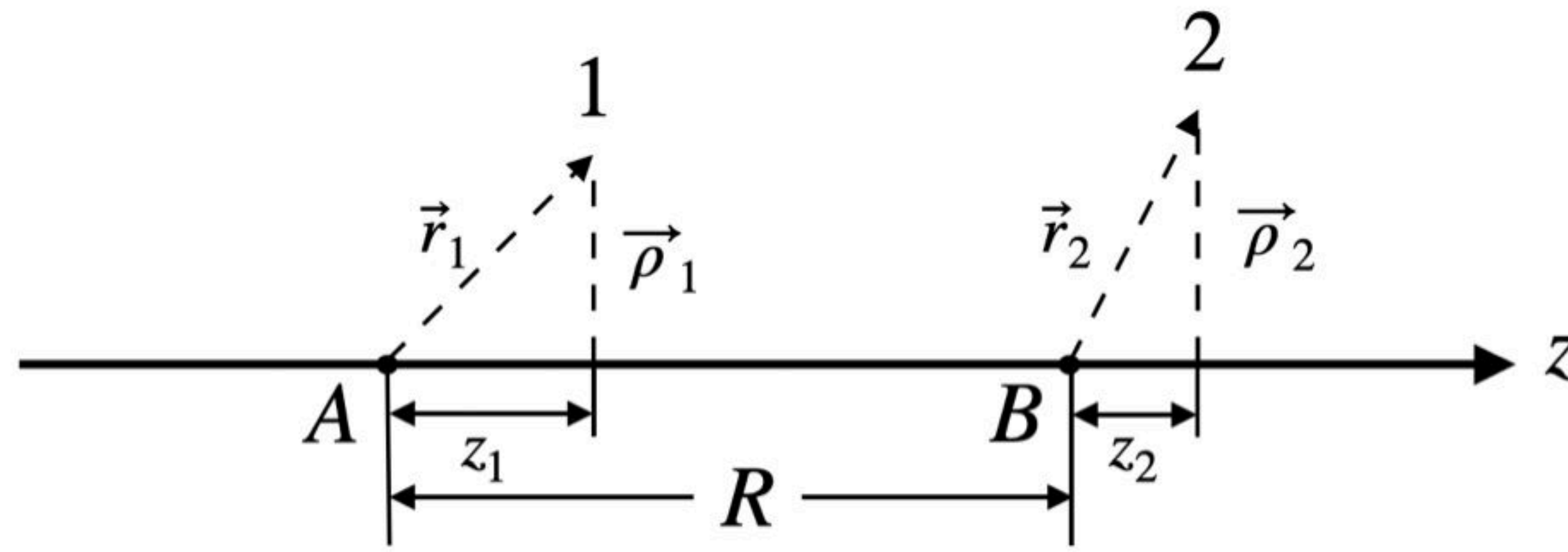
$$\Phi(\vec{r}_1, \vec{r}_2, \lambda) = \frac{\lambda^3}{\pi} \exp[-\lambda(r_1 + r_2)] \quad (76)$$

而我们可以任意多地添加变分参数，必然会使结果更为精确，如

$$\Phi(\vec{r}_1, \vec{r}_2, \lambda) = \frac{\lambda^3}{\pi} \exp[-\lambda(r_1 + r_2)](1 + cr_{12}) \quad (77)$$

目前对 He 最多的变分参数是 499 个，得到的 \bar{H} 精确度是 10^{-6} 。

4 Van der Waals Interaction (Two Hydrogen Atoms)



$$\vec{r} = (\vec{\rho}, z) \quad r^2 = \rho^2 + z^2 \quad (78)$$

$$H = H_0 + H' \quad (79)$$

$$H_0 = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{1}{r_1} - \frac{1}{r_2} \quad (80)$$

$$H' = -\frac{1}{r_{1B}} - \frac{1}{r_{2A}} + \frac{1}{r_{12}} + \frac{1}{R} \quad (81)$$

讨论两个基态氢原子

$$\Phi_0(\vec{r}_1, \vec{r}_2) = \varphi_{100}(\vec{r}_1)\varphi_{100}(\vec{r}_2) \quad (82)$$

令 $R \rightarrow \infty$ ，展开 H'

$$\begin{aligned} \frac{1}{r_{12}} &= \frac{1}{|\vec{r}_1 - \vec{r}_2|} = \frac{1}{\sqrt{(R + z_2 - z_1)^2 + (\vec{\rho}_1 - \vec{\rho}_2)^2}} \\ &= \frac{1}{R} \left[1 + \frac{2(z_2 - z_1)}{R} + \frac{(z_2 - z_1)^2 + (\vec{\rho}_1 - \vec{\rho}_2)^2}{R^2} \right]^{-\frac{1}{2}} \end{aligned} \quad (83)$$

当 $x \rightarrow 0$ 时， $(1+x)^{-\frac{1}{2}} = 1 - \frac{1}{2}x + \frac{3}{8}x^2 - \frac{5}{16}x^3 + \dots$ ，利用这个关系式展开上式 ($R \rightarrow \infty$)

$$\begin{aligned} \frac{1}{r_{12}} &= \frac{1}{R} \left[1 - \frac{(z_2 - z_1)}{R} - \frac{(z_2 - z_1)^2 + (\vec{\rho}_1 - \vec{\rho}_2)^2}{2R^2} + \frac{3(z_2 - z_1)^2}{2R^2} \right] \\ &= \frac{1}{R} \left[1 - \frac{(z_2 - z_1)}{R} + \frac{2(z_2 - z_1)^2 - (\vec{\rho}_1 - \vec{\rho}_2)^2}{2R^2} \right] \end{aligned} \quad (84)$$

$$\frac{1}{r_{1B}} = \frac{1}{\sqrt{(R - z_1)^2 + \rho_1^2}} = \frac{1}{R} \left[1 - \frac{2z_1}{R} + \frac{r_1^2}{R^2} \right]^{-\frac{1}{2}} = \frac{1}{R} \left(1 + \frac{z_1}{R} - \frac{r_1^2}{2R^2} + \frac{3z_1^2}{2R^2} \right) \quad (85)$$

$$\frac{1}{r_{2A}} = \frac{1}{\sqrt{(R+z_2)^2 + \rho_2^2}} = \frac{1}{R} \left[1 + \frac{2z_2}{R} + \frac{r_2^2}{R^2} \right]^{-\frac{1}{2}} = \frac{1}{R} \left(1 - \frac{z_2}{R} - \frac{r_2^2}{2R^2} + \frac{3z_2^2}{2R^2} \right) \quad (86)$$

故

$$\begin{aligned} H' &= -\frac{1}{r_{1B}} - \frac{1}{r_{2A}} + \frac{1}{r_{12}} + \frac{1}{R} \\ &= \frac{1}{R} \left\{ -\left(1 + \frac{z_1}{R} - \frac{r_1^2}{2R^2} + \frac{3z_1^2}{2R^2} \right) - \left(1 - \frac{z_2}{R} - \frac{r_2^2}{2R^2} + \frac{3z_2^2}{2R^2} \right) \right. \\ &\quad \left. + \left[1 - \frac{(z_2 - z_1)}{R} + \frac{2(z_2 - z_1)^2 - (\vec{\rho}_1 - \vec{\rho}_2)^2}{2R^2} \right] + 1 \right\} \\ &= \frac{1}{R} \left[\frac{2(z_2 - z_1)^2 - (\vec{\rho}_1 - \vec{\rho}_2)^2}{2R^2} + \frac{r_1^2 + r_2^2}{2R^2} - \frac{3(z_1^2 + z_2^2)}{2R^2} \right] \\ &= \frac{1}{R^3} (\vec{\rho}_1 \cdot \vec{\rho}_2 - 2z_1 z_2) = \frac{1}{R^3} (\vec{r}_1 \cdot \vec{r}_2 - 3z_1 z_2) \end{aligned} \quad (87)$$

First Method: Perturbation Theory

一级微扰

$$E^{(1)} = \langle 0 | H' | 0 \rangle = \int d\vec{r}_1 d\vec{r}_2 \varphi_{100}^\dagger(r_1) \varphi_{100}^\dagger(r_2) \frac{1}{R^3} (\vec{r}_1 \cdot \vec{r}_2 - 3z_1 z_2) \varphi_{100}(r_1) \varphi_{100}(r_2) = 0 \quad (88)$$

二级微扰

$$E^{(2)} = \sum_n' \frac{|\langle 0 | H' | n \rangle|^2}{E_0 - E_n} \quad (89)$$

二级微扰很难计算，需要先做近似

$$E_0 = -\frac{1}{2} \frac{1}{n^2} \Big|_{n=1} \cdot 2 = -1 \quad (90)$$

$$E_1 = -\frac{1}{2} \frac{1}{n^2} \Big|_{n=2} \cdot 2 = -\frac{1}{4} \quad (91)$$

因此

$$\begin{aligned} E^{(2)} &\geq \sum_n' \frac{|\langle 0 | H' | n \rangle|^2}{E_0 - E_1} = \frac{1}{E_0 - E_1} \sum_n' |\langle 0 | H' | n \rangle|^2 \\ &= \frac{1}{E_0 - E_1} \sum_n' \langle 0 | H' | n \rangle \langle n | H' | 0 \rangle \\ &= \frac{1}{E_0 - E_1} \left(\sum_n \langle 0 | H' | n \rangle \langle n | H' | 0 \rangle - \langle 0 | H' | 0 \rangle \langle 0 | H' | 0 \rangle \right) \\ &= \frac{1}{E_0 - E_1} [\langle 0 | H'^2 | 0 \rangle - (\langle 0 | H' | 0 \rangle)^2] = \frac{1}{E_0 - E_1} \langle 0 | H'^2 | 0 \rangle \end{aligned} \quad (92)$$

$$\begin{aligned} &= \frac{1}{E_0 - E_1} \int d\vec{r}_1 d\vec{r}_2 \frac{1}{R^6} (\vec{r}_1 \cdot \vec{r}_2 - 3z_1 z_2)^2 \Phi_0^\dagger(\vec{r}_1, \vec{r}_2) \Phi_0(\vec{r}_1, \vec{r}_2) \\ &= \frac{1}{E_0 - E_1} \frac{1}{R^6} \int d\vec{r}_1 d\vec{r}_2 [(\vec{r}_1 \cdot \vec{r}_2)^2 - 6\vec{r}_1 \cdot \vec{r}_2 z_1 z_2 + 9z_1^2 z_2^2] |\varphi_{100}(r_1)|^2 |\varphi_{100}(r_2)|^2 \\ &= \frac{1}{E_0 - E_1} \frac{1}{R^6} \int d\vec{r}_1 d\vec{r}_2 (x_1^2 x_2^2 + y_1^2 y_2^2 + 4z_1^2 z_2^2 + 2x_1 x_2 y_1 y_2 - 4x_1 x_2 z_1 z_2 - 4y_1 y_2 z_1 z_2) |\Phi_0(\vec{r}_1, \vec{r}_2)|^2 \\ &= \frac{1}{E_0 - E_1} \frac{6}{R^6} \left(\int d\vec{r}_1 |\varphi_{100}(r_1)|^2 \frac{r_1^2}{3} \right)^2 = \frac{1}{E_0 - E_1} \frac{6}{R^6} = -\frac{8}{R^6} \end{aligned}$$

$$\Delta E = E^{(1)} + E^{(2)} \geq -\frac{8}{R^6} \quad (93)$$

Second Method: Variational Principle

假设

$$\psi(\vec{r}_1, \vec{r}_2) = \varphi_{100}(r_1)\varphi_{100}(r_2)(1 + \lambda H') = \Phi_0(\vec{r}_1, \vec{r}_2)(1 + \lambda H') \quad (94)$$

由于我们假设时并没有将波函数归一化，因此取 \bar{H} 时需要归一化

$$\bar{H} = \frac{\iint d\vec{r}_1 d\vec{r}_2 \psi^\dagger(\vec{r}_1, \vec{r}_2)(H_0 + H')\psi(\vec{r}_1, \vec{r}_2)}{\iint d\vec{r}_1 d\vec{r}_2 |\psi(\vec{r}_1, \vec{r}_2)|^2} \quad (95)$$

令分子为 N ，分母为 D

$$D = \iint d\vec{r}_1 d\vec{r}_2 |\psi(\vec{r}_1, \vec{r}_2)|^2 = \iint d\vec{r}_1 d\vec{r}_2 |\Phi_0(\vec{r}_1, \vec{r}_2)|^2 (1 + \lambda H')^2 = 1 + \lambda^2 \langle 0 | H'^2 | 0 \rangle \quad (96)$$

$$\begin{aligned} N &= \iint d\vec{r}_1 d\vec{r}_2 \psi^\dagger(\vec{r}_1, \vec{r}_2)(H_0 + H')\psi(\vec{r}_1, \vec{r}_2) \\ &= \iint d\vec{r}_1 d\vec{r}_2 \Phi_0^\dagger(\vec{r}_1, \vec{r}_2)(1 + \lambda H')(H_0 + H')(1 + \lambda H')\Phi_0(\vec{r}_1, \vec{r}_2) \\ &= \langle 0 | H_0 + \lambda H_0 H' + H' + \lambda H'^2 + \lambda H' H_0 + \lambda^2 H' H_0 H' + \lambda H'^2 + \lambda^2 H'^3 | 0 \rangle \\ &= E_0 + (2\lambda E_0 + 1) \langle 0 | H' | 0 \rangle + 2\lambda \langle 0 | H'^2 | 0 \rangle + \lambda^2 \langle 0 | H' H_0 H' | 0 \rangle + \lambda^2 \langle 0 | H'^3 | 0 \rangle \\ &= E_0 + 2\lambda \langle 0 | H'^2 | 0 \rangle + \lambda^2 \langle 0 | H' H_0 H' | 0 \rangle \end{aligned} \quad (97)$$

接下来证明 $\langle 0 | H' H_0 H' | 0 \rangle = 0$

$$\begin{aligned} \langle 0 | H' H_0 H' | 0 \rangle &= \langle 0 | \frac{1}{R^3}(x_1 x_2 + y_1 y_2 - 2z_1 z_2) H_0 \frac{1}{R^3}(x_1 x_2 + y_1 y_2 - 2z_1 z_2) | 0 \rangle \\ &= \frac{1}{R^6} \int d\vec{r}_1 d\vec{r}_2 \Phi_0^\dagger(\vec{r}_1, \vec{r}_2)(x_1 x_2 H_0 x_1 x_2 + x_1 x_2 H_0 y_1 y_2 - 2x_1 x_2 H_0 z_1 z_2 + y_1 y_2 H_0 x_1 x_2 + \\ &\quad y_1 y_2 H_0 y_1 y_2 - 2y_1 y_2 H_0 z_1 z_2 - 2z_1 z_2 H_0 x_1 x_2 - 2z_1 z_2 H_0 y_1 y_2 + 4z_1 z_2 H_0 z_1 z_2) \Phi_0(\vec{r}_1, \vec{r}_2) \\ &= \frac{1}{R^6} \int d\vec{r}_1 d\vec{r}_2 \Phi_0^\dagger(\vec{r}_1, \vec{r}_2)(x_1 x_2 H_0 x_1 x_2 + y_1 y_2 H_0 y_1 y_2 + 4z_1 z_2 H_0 z_1 z_2) \Phi_0(\vec{r}_1, \vec{r}_2) \\ &= \frac{6}{R^6} \int d\vec{r}_1 d\vec{r}_2 \Phi_0^\dagger(\vec{r}_1, \vec{r}_2) x_1 x_2 [h_0(\vec{r}_1) + h_0(\vec{r}_2)] x_1 x_2 \Phi_0(\vec{r}_1, \vec{r}_2) \\ &= \frac{12}{R^6} \int d\vec{r}_1 d\vec{r}_2 \Phi_0^\dagger(\vec{r}_1, \vec{r}_2) x_1 x_2 h_0(\vec{r}_1) x_1 x_2 \Phi_0(\vec{r}_1, \vec{r}_2) \\ &= \frac{12}{R^6} \int \varphi_{100}^\dagger(r_1) x_1 h_0(\vec{r}_1) x_1 \varphi_{100}(r_1) d\vec{r}_1 \int \varphi_{100}^\dagger(r_2) x_2^2 \varphi_{100}(r_2) d\vec{r}_2 \\ &= \frac{12}{R^6} A \int \varphi_{100}^\dagger(r_2) x_2^2 \varphi_{100}(r_2) d\vec{r}_2 \end{aligned} \quad (98)$$

其中

$$h_0(\vec{r}) = -\frac{1}{2} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V(r) \quad (99)$$

$$h_0(\vec{r})\varphi_{100}(\vec{r}) = \varepsilon_0 \varphi_{100}(\vec{r}) \quad (100)$$

$$\varepsilon_0 = \frac{1}{2} E_0 = -\frac{1}{2} \frac{1}{n^2} \Big|_{n=1} = -\frac{1}{2} \quad (101)$$

$$\langle r \rangle = \int r |\varphi(r)|^2 d\vec{r} = 4\pi \int r^3 |\varphi(r)|^2 dr = 4 \int_0^\infty r^3 e^{-2r} dr = 4 \cdot \frac{3}{8} = \frac{3}{2} \quad (102)$$

$$\langle r^2 \rangle = \int r^2 |\varphi(r)|^2 d\vec{r} = 4\pi \int r^4 |\varphi(r)|^2 dr = 4 \int_0^\infty r^4 e^{-2r} dr = 4 \cdot \frac{3}{4} = 3 \quad (103)$$

$$\begin{aligned}
A &= \int \varphi_{100}^\dagger(r_1) x_1 h_0(\vec{r}_1) x_1 \varphi_{100}(r_1) d\vec{r}_1 \\
&= \int \varphi_{100}^\dagger(r) x \left[-\frac{1}{2} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V(r) \right] x \varphi_{100}(r) d\vec{r} \\
&= \int \varphi_{100}^\dagger(r) \left[-\frac{1}{2} x \frac{\partial^2}{\partial x^2} x - \frac{1}{2} x^2 \left(\frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + x^2 V(r) \right] \varphi_{100}(r) d\vec{r} \tag{104}
\end{aligned}$$

$$\begin{aligned}
&= \int \varphi_{100}^\dagger(r) \left[-x \frac{\partial}{\partial x} - \frac{1}{2} x^2 \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + x^2 V(r) \right] \varphi_{100}(r) d\vec{r} \\
&= \int \varphi_{100}^\dagger(r) x^2 h_0(\vec{r}) \varphi_{100}(r) d\vec{r} - \int \varphi_{100}^\dagger(r) x \frac{\partial}{\partial x} \varphi_{100}(r) d\vec{r} \\
&\quad \int \varphi_{100}^\dagger(r) x \frac{\partial}{\partial x} \varphi_{100}(r) d\vec{r} = - \int \varphi_{100}^\dagger(r) \frac{r}{3} \varphi_{100}(r) d\vec{r} = -\frac{1}{3} \langle r \rangle \tag{105}
\end{aligned}$$

$$\begin{aligned}
A &= \int \varphi_{100}^\dagger(r) x^2 h_0(\vec{r}) \varphi_{100}(r) d\vec{r} + \frac{1}{3} \langle r \rangle = \frac{1}{3} \varepsilon_0 \int \varphi_{100}^\dagger(r) r^2 \varphi_{100}(r) d\vec{r} + \frac{1}{3} \langle r \rangle \\
&= \frac{1}{3} \varepsilon_0 \langle r^2 \rangle + \frac{1}{3} \langle r \rangle = \frac{1}{3} \left(-\frac{1}{2} \langle r^2 \rangle + \langle r \rangle \right) = \frac{1}{3} \left(-\frac{1}{2} \cdot 3 + \frac{3}{2} \right) = 0 \tag{106}
\end{aligned}$$

故 $\langle 0 | H' H_0 H' | 0 \rangle = 0$

$$N = E_0 + 2\lambda \langle 0 | H'^2 | 0 \rangle \tag{107}$$

$$\bar{H} = \frac{E_0 + 2\lambda \langle 0 | H'^2 | 0 \rangle}{1 + \lambda^2 \langle 0 | H'^2 | 0 \rangle} \tag{108}$$

令

$$q = \langle 0 | H'^2 | 0 \rangle = \frac{6}{R^6} \tag{109}$$

$$\bar{H} = \frac{E_0 + 2\lambda q}{1 + \lambda^2 q} \tag{110}$$

$$\frac{\partial \bar{H}}{\partial \lambda} = \frac{2q(1 + \lambda^2 q) - (E_0 + 2\lambda q) 2\lambda q}{(1 + \lambda^2 q)^2} = 0 \tag{111}$$

解得

$$\lambda = \frac{-E_0 \pm \sqrt{E_0^2 + 4q}}{2q} \tag{112}$$

由于 $\delta H < 0$, 因此我们取 $\lambda = \frac{-E_0 - \sqrt{E_0^2 + 4q}}{2q}$, 代回 Eq.(109)

$$\bar{H} = \frac{E_0 + (-E_0 - \sqrt{E_0^2 + 4q})}{1 + \frac{1}{4q}(E_0 + \sqrt{E_0^2 + 4q})^2} = \frac{-4q\sqrt{E_0^2 + 4q}}{4q + (E_0 + \sqrt{E_0^2 + 4q})^2} \tag{113}$$

这个式子过于复杂, 不好计算, 我们可以做一些近似。当 $x \rightarrow 0$ 时, $\frac{1}{1+x} = 1 - x$, 由于 q 是小量, \bar{H} 化为

$$\bar{H} = \frac{E_0 + 2\lambda q}{1 + \lambda^2 q} \doteq (E_0 + 2\lambda q)(1 - \lambda^2 q) \doteq E_0 + (2\lambda - \lambda^2 E_0)q \tag{114}$$

$$\frac{\partial \bar{H}}{\partial \lambda} = (2 - 2\lambda E_0)q = 0 \Rightarrow \lambda = \frac{1}{E_0} \tag{115}$$

$$\bar{H} = E_0 + \frac{1}{E_0} q \tag{116}$$

因此

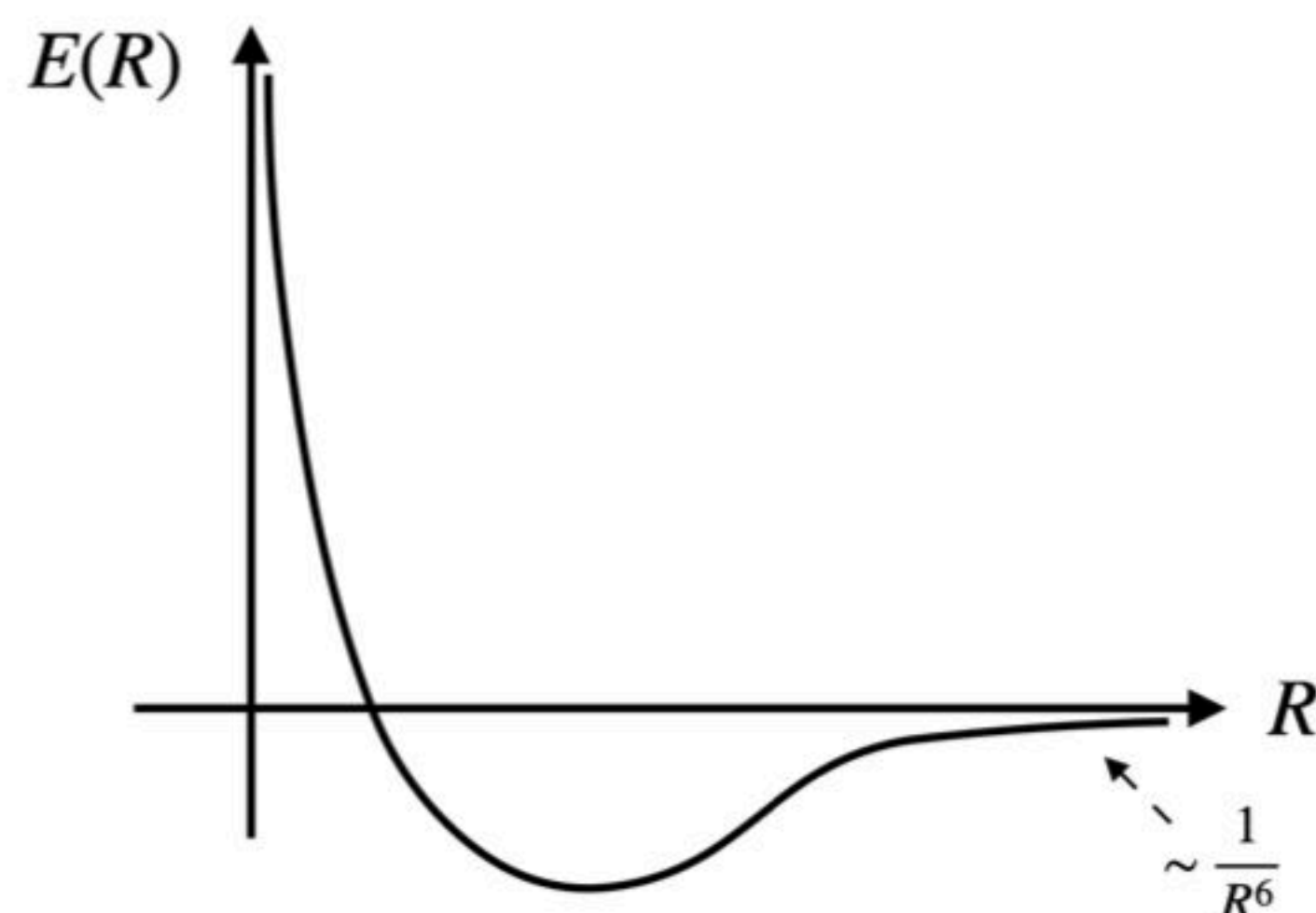
$$\Delta E \leq \frac{1}{E_0} q = \frac{1}{E_0} \langle 0 | H'^2 | 0 \rangle = \frac{1}{E_0} \frac{6}{R^6} = -\frac{6}{R^6} \tag{117}$$

前面我们通过微扰论已经给出结果

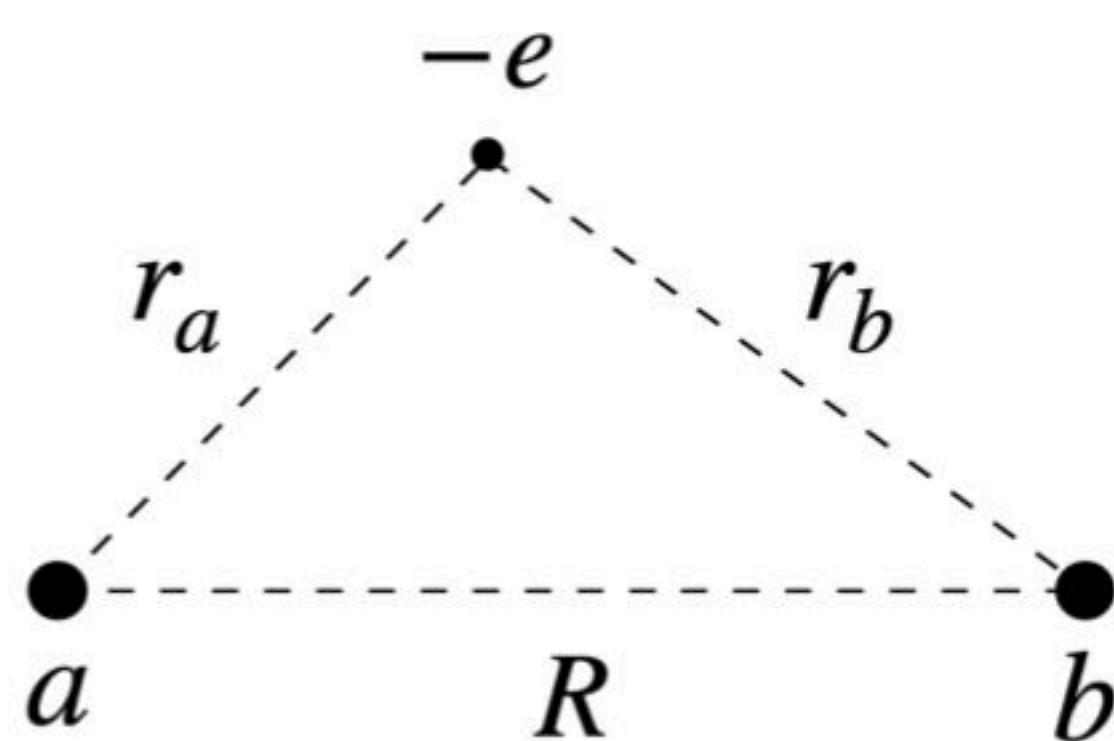
$$\Delta E \geq -\frac{8}{R^6} \quad (118)$$

因此，在自然单位制下

$$-\frac{8}{R^6} \leq \Delta E \leq -\frac{6}{R^6} \quad (119)$$



5 Hydrogen Molecule Ion 氢分子离子



$$H = \frac{1}{R} + H_{\text{el}} \quad (120)$$

电子部分哈密顿量

$$H_{\text{el}} = -\frac{1}{2}\nabla^2 - \frac{1}{r_a} - \frac{1}{r_b} \quad (121)$$

我们的目的是解薛定谔方程

$$H\psi = E\psi \quad (122)$$

或写成

$$H_{\text{el}}\psi = \left(-\frac{1}{2}\nabla^2 - \frac{1}{r_a} - \frac{1}{r_b}\right)\psi = \left(E - \frac{1}{R}\right)\psi \quad (123)$$

根据经验引入变分波函数，用线性组合的方式

$$\psi = c_a \frac{\lambda^{\frac{3}{2}}}{\sqrt{\pi}} e^{-\lambda r_a} + c_b \frac{\lambda^{\frac{3}{2}}}{\sqrt{\pi}} e^{-\lambda r_b} \quad (124)$$

$$\int |\psi|^2 d\vec{r} = 1 \quad (125)$$

根据波函数的对称性

$$c_a = \pm c_b \quad (126)$$

$$\psi_{\pm} = c_a \left(\frac{\lambda^{\frac{3}{2}}}{\sqrt{\pi}} e^{-\lambda r_a} \pm \frac{\lambda^{\frac{3}{2}}}{\sqrt{\pi}} e^{-\lambda r_b} \right) = c_a (\psi_a \pm \psi_b) \quad (127)$$

接下来通过波函数归一化来定参数 c_a

$$\langle \psi_{\pm} | \psi_{\pm} \rangle = c_a^2 \langle \psi_a \pm \psi_b | \psi_a \pm \psi_b \rangle = c_a^2 (\langle \psi_a | \psi_a \rangle + \langle \psi_b | \psi_b \rangle \pm 2 \langle \psi_a | \psi_b \rangle) = c_a^2 (2 \pm 2 \langle \psi_a | \psi_b \rangle) = 1 \quad (128)$$

令

$$J = \langle \psi_a | \psi_b \rangle = \langle \psi_b | \psi_a \rangle = \frac{\lambda^3}{\pi} \int d\vec{r} e^{-\lambda(r_a+r_b)} \quad (129)$$

则

$$c_a = (2 \pm 2J)^{-\frac{1}{2}} \quad (130)$$

$$\psi_{\pm} = (2 \pm 2J)^{-\frac{1}{2}} (\psi_a \pm \psi_b) \quad (131)$$

接下来计算 \bar{H}

$$H = \frac{1}{R} + H_{\text{el}} \quad (132)$$

第一项 $\frac{1}{R}$ trivial, 我们来关注第二项

$$\bar{H}_{\text{el}} = \langle \psi_{\pm} | H_{\text{el}} | \psi_{\pm} \rangle = \frac{1}{2 \pm 2J} \langle \psi_a \pm \psi_b | H_{\text{el}} | \psi_a \pm \psi_b \rangle \quad (133)$$

符号简化, 令 $|a\rangle = |\psi_a\rangle, |b\rangle = |\psi_b\rangle$

$$\begin{aligned} \bar{H}_{\text{el}} &= \frac{1}{2 \pm 2J} \langle a \pm b | H_{\text{el}} | a \pm b \rangle \\ &= \frac{1}{2 \pm 2J} (\langle a | H_{\text{el}} | a \rangle + \langle b | H_{\text{el}} | b \rangle \pm \langle a | H_{\text{el}} | b \rangle \pm \langle b | H_{\text{el}} | a \rangle) \\ &= \frac{1}{1 \pm J} (\langle a | H_{\text{el}} | a \rangle \pm \langle b | H_{\text{el}} | a \rangle) \end{aligned} \quad (134)$$

计算 $H_{\text{el}} |a\rangle$

$$\begin{aligned} H_{\text{el}} |a\rangle &= \left(-\frac{1}{2} \nabla^2 - \frac{1}{r_a} - \frac{1}{r_b} \right) |a\rangle = \left(-\frac{1}{2} \nabla^2 - \frac{1}{r_a} - \frac{1}{r_b} \right) |a\rangle \\ &= \left(-\frac{1}{2} \nabla^2 - \frac{\lambda}{r_a} - \frac{1-\lambda}{r_a} - \frac{1}{r_b} \right) |a\rangle \\ &= \left(-\frac{\lambda^2}{2} - \frac{1-\lambda}{r_a} - \frac{1}{r_b} \right) |a\rangle \end{aligned} \quad (135)$$

则

$$\begin{aligned} \langle a | H_{\text{el}} | a \rangle &= \langle a | \left(-\frac{\lambda^2}{2} - \frac{1-\lambda}{r_a} - \frac{1}{r_b} \right) |a\rangle \\ &= -\frac{\lambda^2}{2} - (1-\lambda) \langle a | \frac{1}{r_a} |a\rangle - \langle a | \frac{1}{r_b} |a\rangle \\ &= -\frac{\lambda^2}{2} - \lambda(1-\lambda) - \kappa \end{aligned} \quad (136)$$

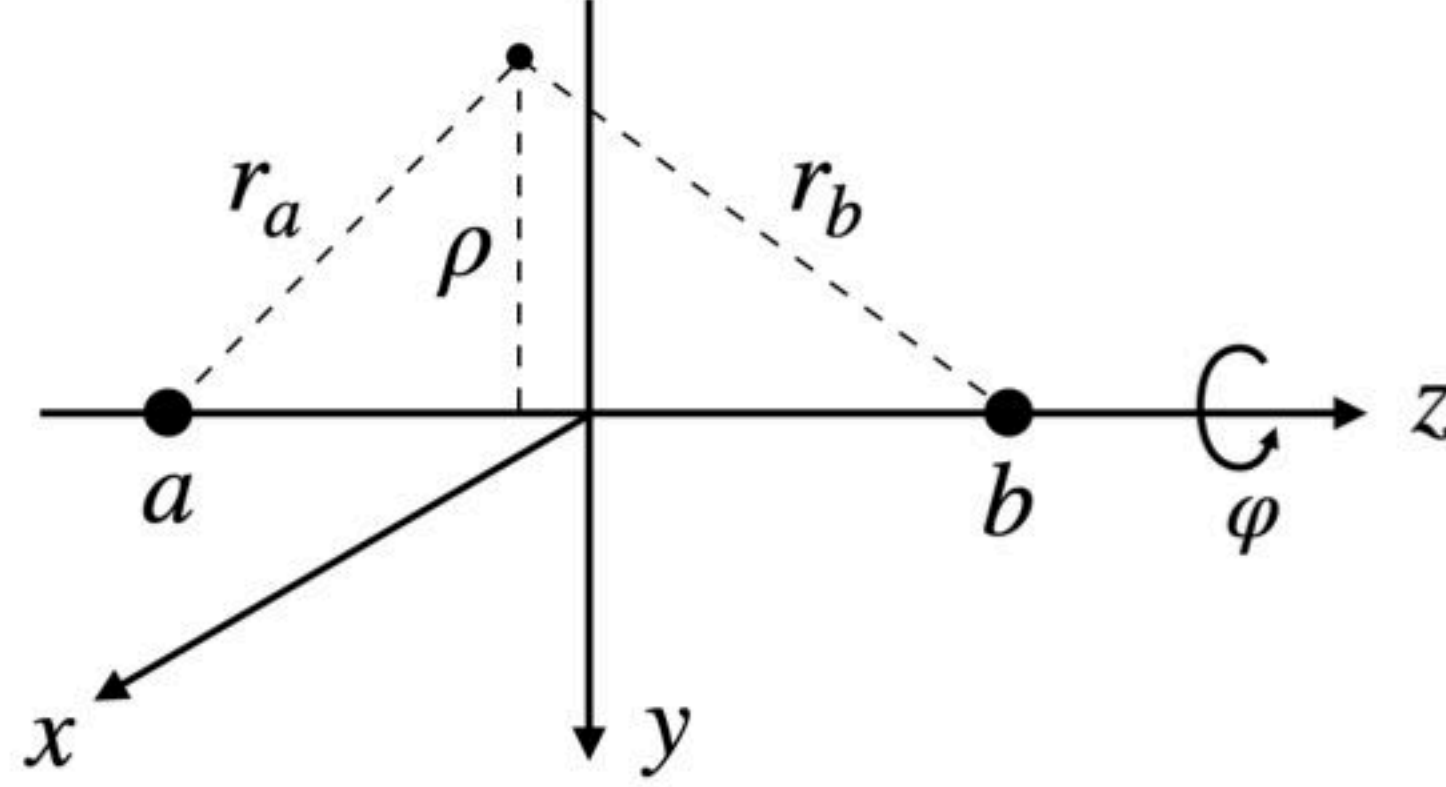
$$\begin{aligned} \langle b | H_{\text{el}} | a \rangle &= \langle b | \left(-\frac{\lambda^2}{2} - \frac{1-\lambda}{r_a} - \frac{1}{r_b} \right) |a\rangle \\ &= -\frac{\lambda^2}{2} J - (1-\lambda) \langle b | \frac{1}{r_a} |a\rangle - \langle b | \frac{1}{r_b} |a\rangle \\ &= -\frac{\lambda^2}{2} J - (2-\lambda)\varsigma \end{aligned} \quad (137)$$

其中

$$\kappa = \langle a | \frac{1}{r_b} |a\rangle \quad \varsigma = \langle b | \frac{1}{r_a} |a\rangle \quad (138)$$

故

$$\begin{aligned}
 E_{\pm} &= \frac{1}{R} + \bar{H} \\
 &= \frac{1}{R} + \frac{1}{1 \pm J} \left\{ \left[-\frac{\lambda^2}{2} - \lambda(1 - \lambda) - \kappa \right] \pm \left[-\frac{\lambda^2}{2} J - (2 - \lambda)\varsigma \right] \right\} \\
 &= \frac{1}{R} - \frac{\lambda^2}{2} + \frac{\lambda(\lambda - 1) - \kappa \pm (\lambda - 2)\varsigma}{1 \pm J}
 \end{aligned} \tag{139}$$



在椭球坐标系中能够最好地体现对称性，引入旋转椭球坐标系 (ξ, η, φ) ，令

$$\begin{cases} \xi = \frac{1}{R}(r_a + r_b) \\ \eta = \frac{1}{R}(r_a - r_b) \\ \varphi \end{cases} \quad \text{且} \quad \begin{cases} 1 \leq \xi \leq \infty \\ -1 \leq \eta \leq 1 \\ 0 \leq \varphi \leq 2\pi \end{cases} \tag{140}$$

根据上图

$$\begin{cases} \sqrt{r_a^2 - \rho^2} - \frac{R}{2} = z \\ \frac{R}{2} - \sqrt{r_b^2 - \rho^2} = z \end{cases} \tag{141}$$

解得

$$\rho = \frac{R}{2} \sqrt{(\xi^2 - 1)(1 - \eta^2)} \tag{142}$$

$$x = \frac{R}{2} \sqrt{(\xi^2 - 1)(1 - \eta^2)} \cos \varphi \tag{143}$$

$$y = \frac{R}{2} \sqrt{(\xi^2 - 1)(1 - \eta^2)} \sin \varphi \tag{144}$$

$$z = \frac{r_a^2 - r_b^2}{2R} = \frac{R\xi\eta}{2} \tag{145}$$

则

$$\begin{aligned}
 d\vec{r} &= dx dy dz \\
 &= \begin{vmatrix} \frac{\partial x}{\partial \eta} & \frac{\partial x}{\partial \xi} & \frac{\partial x}{\partial \varphi} \\ \frac{\partial y}{\partial \eta} & \frac{\partial y}{\partial \xi} & \frac{\partial y}{\partial \varphi} \\ \frac{\partial z}{\partial \eta} & \frac{\partial z}{\partial \xi} & \frac{\partial z}{\partial \varphi} \end{vmatrix} d\xi d\eta d\varphi \\
 &= \begin{vmatrix} -\frac{R\eta}{2} \sqrt{\frac{\xi^2 - 1}{1 - \eta^2}} \cos \varphi & \frac{R\xi}{2} \sqrt{\frac{1 - \eta^2}{\xi^2 - 1}} \cos \varphi & -\frac{R}{2} \sqrt{(\xi^2 - 1)(1 - \eta^2)} \sin \varphi \\ -\frac{R\eta}{2} \sqrt{\frac{\xi^2 - 1}{1 - \eta^2}} \sin \varphi & \frac{R\xi}{2} \sqrt{\frac{1 - \eta^2}{\xi^2 - 1}} \sin \varphi & \frac{R}{2} \sqrt{(\xi^2 - 1)(1 - \eta^2)} \cos \varphi \\ \frac{R}{2} \xi & \frac{R}{2} \eta & 0 \end{vmatrix} d\xi d\eta d\varphi \\
 &= \frac{R^3}{8} (\xi^2 - \eta^2) d\xi d\eta d\varphi
 \end{aligned} \tag{146}$$

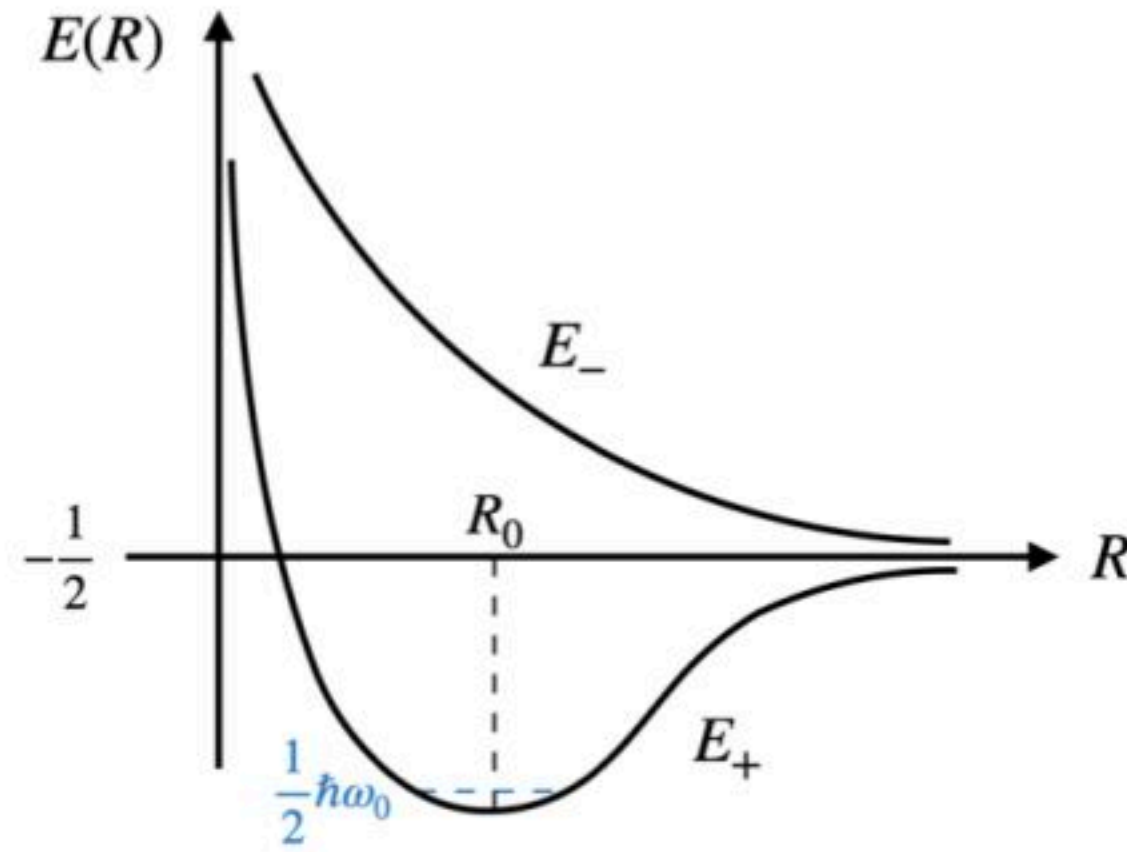
$$\begin{aligned}
J &= \frac{\lambda^3}{\pi} \int d\vec{r} e^{-\lambda(r_a+r_b)} = \frac{\lambda^3}{\pi} \int \frac{R^3}{8} (\xi^2 - \eta^2) e^{-\lambda R \xi} d\xi d\eta d\varphi \\
&= \frac{\lambda^3}{\pi} \int_1^\infty d\xi \int_{-1}^1 d\eta \int_0^{2\pi} d\varphi \frac{R^3}{8} (\xi^2 - \eta^2) e^{-\lambda R \xi} = \frac{R^3 \lambda^3}{4} \int_1^\infty d\xi \int_{-1}^1 d\eta (\xi^2 - \eta^2) e^{-\lambda R \xi} \\
&= \frac{R^3 \lambda^3}{4} \int_1^\infty d\xi \left(2\xi^2 - \frac{2}{3} \right) e^{-\lambda R \xi} = \left(1 + \lambda R + \frac{1}{3} \lambda^2 R^2 \right) e^{-\lambda R}
\end{aligned} \tag{147}$$

$$\begin{aligned}
\kappa &= \langle a | \frac{1}{r_b} | a \rangle = \frac{\lambda^3}{\pi} \int d\vec{r} \frac{e^{-2\lambda r_a}}{r_b} \\
&= \frac{\lambda^3}{\pi} \int_1^\infty d\xi \int_{-1}^1 d\eta \int_0^{2\pi} d\varphi \frac{R^3}{8} (\xi^2 - \eta^2) \frac{e^{-\lambda R(\xi+\eta)}}{R(\xi-\eta)} \\
&= \frac{1}{R} [1 - (1 + \lambda R) e^{-2\lambda R}]
\end{aligned} \tag{148}$$

$$\varsigma = \langle b | \frac{1}{r_a} | a \rangle = \int \frac{\psi_a \psi_b}{r_a} d\vec{r} = \frac{\lambda^3}{\pi} \int d\vec{r} \frac{e^{-\lambda(r_a+r_b)}}{r_b} = \lambda(1 + \lambda R) e^{-\lambda R} \tag{149}$$

代回 Eq.(139) 得

$$\begin{aligned}
E_{\pm} &= \frac{1}{R} - \frac{\lambda^2}{2} + \frac{\lambda(\lambda-1) - \kappa \pm (\lambda-2)\varsigma}{1 \pm J} \\
&= \frac{1}{R} - \frac{\lambda^2}{2} + \frac{\lambda(\lambda-1) - \frac{1}{R} [1 - (1 + \lambda R) e^{-2\lambda R}] \pm (\lambda-2)\lambda(1 + \lambda R) e^{-\lambda R}}{1 \pm (1 + \lambda R + \frac{1}{3} \lambda^2 R^2) e^{-\lambda R}}
\end{aligned} \tag{150}$$



显然 E_+ 是我们的解, 由 $\frac{\partial E_{\pm}}{\partial \lambda} = 0$ 解出

$$R_0 = 2.08 \text{ a.u.} = 1.10 \text{ \AA} \tag{151}$$

在实验中我们得到的值是

$$R_{0\text{exp}} = 1.06 \text{ \AA} \tag{152}$$

$$E_+(R_0) = -0.587 \text{ a.u.} \tag{153}$$

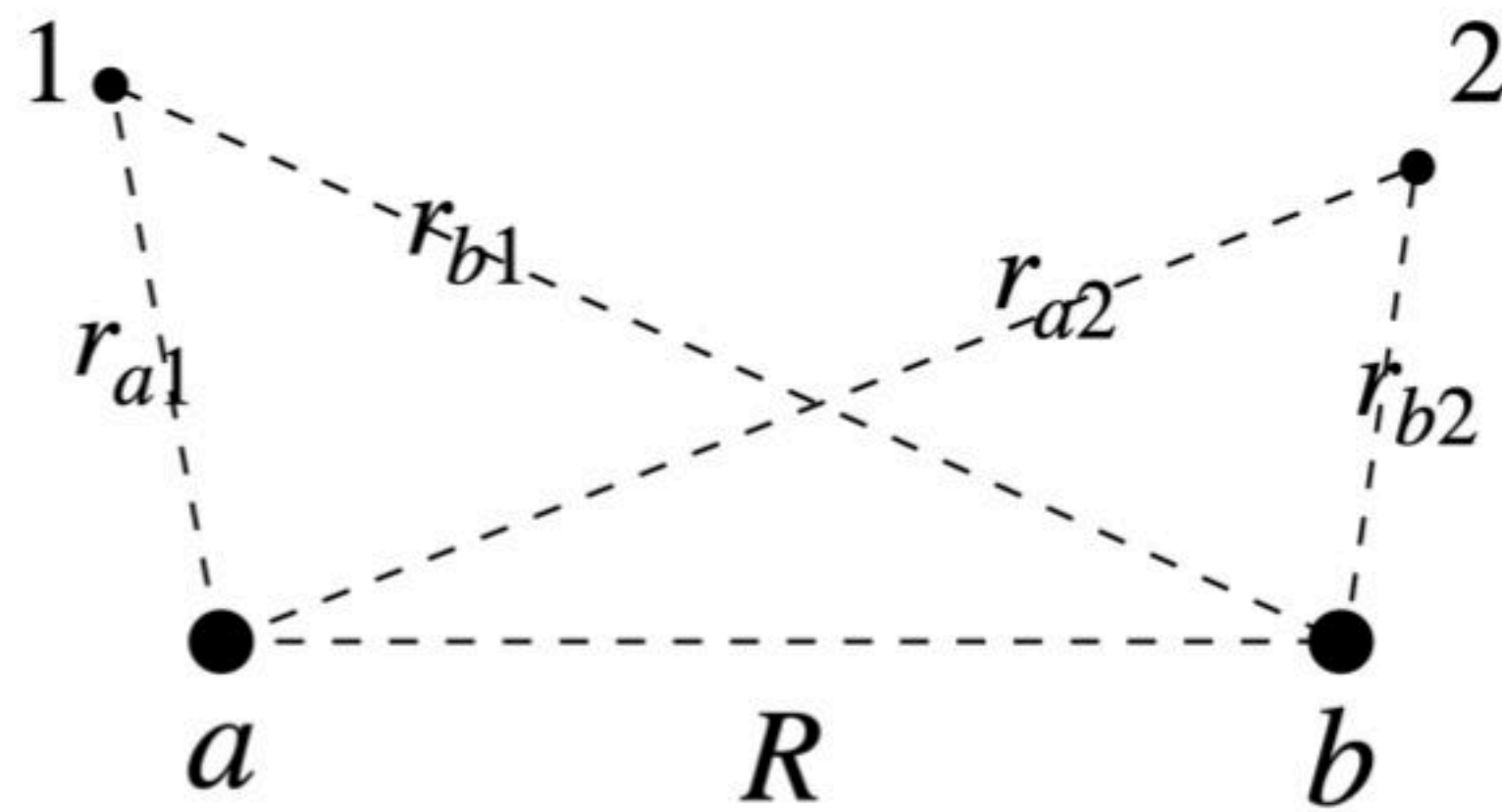
电离能

$$D = -E_+(R_0) - \frac{1}{2} \hbar \omega_0 - \frac{1}{2} = 0.082 \text{ a.u.} = 2.24 \text{ eV} \tag{154}$$

实验结果

$$D_{\text{exp}} = 2.65 \text{ eV} \tag{155}$$

6 H_2



$$H = H_{\text{el}} + \frac{1}{R} \quad (156)$$

$$H_{\text{el}} = -\frac{1}{2} (\nabla_1^2 + \nabla_2^2) + \frac{1}{r_{12}} - \left(\frac{1}{r_{a1}} + \frac{1}{r_{a2}} + \frac{1}{r_{b1}} + \frac{1}{r_{b2}} \right) \quad (157)$$

我们要做的事依旧是解薛定谔方程

$$H\Psi(1, 2) = E\Psi(1, 2) \quad (158)$$

氢分子体系无法严格解，我们用轨道线性组合 (LCAO) 的方式求解。设电子轨道波函数

$$\psi(r) = \frac{\lambda}{\sqrt{\pi}} e^{-\lambda r} \quad (159)$$

氢分子有两个电子，需要考虑全同性原理，空间部分波函数 $\Psi(1, 2)$

- 对称

$$\begin{aligned} \Psi_+(1, 2) &= [\psi(r_{a1}) + \psi(r_{b1})][\psi(r_{a2}) + \psi(r_{b2})] \\ &= \psi(r_{a1})\psi(r_{a2}) + \psi(r_{b1})\psi(r_{b2}) + \psi(r_{a1})\psi(r_{b2}) + \psi(r_{b1})\psi(r_{a2}) \end{aligned} \quad (160)$$

当电子 1, 2 都离某个原子核很近时，前两项会把能量抬得非常高，于是丢掉前两项，仍然满足对称性。(heiler-london approximation)

$$\Psi_+(1, 2) = \psi(r_{a1})\psi(r_{b2}) + \psi(r_{b1})\psi(r_{a2}) \quad (161)$$

对应自旋波函数反对称，对应自旋单态 $\chi_0(s_{1z}, s_{2z})$ 。

- 反对称

$$\Psi_-(1, 2) = \psi(r_{a1})\psi(r_{b2}) - \psi(r_{b1})\psi(r_{a2}) \quad (162)$$

对应自旋波函数对称，对应自旋三重态 $\chi_1(s_{1z}, s_{2z})$ 。

故空间部分

$$\Psi_{\pm}(1, 2) = \psi(r_{a1})\psi(r_{b2}) \pm \psi(r_{b1})\psi(r_{a2}) \quad (163)$$

接下来计算 H_{el} 的期待值 \bar{H}_{el}

$$\begin{aligned} \bar{H}_{\text{el}} &= \langle \Psi_{\pm} | H_{\text{el}} | \Psi_{\pm} \rangle \\ &= \langle \psi(r_{a1})\psi(r_{b2}) \pm \psi(r_{b1})\psi(r_{a2}) | H_{\text{el}} | \psi(r_{a1})\psi(r_{b2}) \pm \psi(r_{b1})\psi(r_{a2}) \rangle \\ &= \langle \psi(r_{a1})\psi(r_{b2}) | H_{\text{el}} | \psi(r_{a1})\psi(r_{b2}) \rangle + \langle \psi(r_{b1})\psi(r_{a2}) | H_{\text{el}} | \psi(r_{b1})\psi(r_{a2}) \rangle \\ &\quad \pm \langle \psi(r_{a1})\psi(r_{b2}) | H_{\text{el}} | \psi(r_{b1})\psi(r_{a2}) \rangle \pm \langle \psi(r_{b1})\psi(r_{a2}) | H_{\text{el}} | \psi(r_{a1})\psi(r_{b2}) \rangle \\ &= 2 [\langle \psi(r_{a1})\psi(r_{b2}) | H_{\text{el}} | \psi(r_{a1})\psi(r_{b2}) \rangle \pm \langle \psi(r_{b1})\psi(r_{a2}) | H_{\text{el}} | \psi(r_{a1})\psi(r_{b2}) \rangle] \end{aligned} \quad (164)$$

计算 $H_{\text{el}} |\psi(r_{a1})\psi(r_{b2})\rangle$

$$\begin{aligned} H_{\text{el}} |\psi(r_{a1})\psi(r_{b2})\rangle &= \left(-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 + \frac{1}{r_{12}} - \frac{1}{r_{a1}} - \frac{1}{r_{a2}} - \frac{1}{r_{b1}} - \frac{1}{r_{b2}} \right) |\psi(r_{a1})\psi(r_{b2})\rangle \\ &= \left(-\frac{1}{2}\nabla_1^2 - \frac{\lambda}{r_{a1}} - \frac{1}{2}\nabla_2^2 - \frac{\lambda}{r_{b2}} - \frac{1-\lambda}{r_{a1}} - \frac{1-\lambda}{r_{b2}} + \frac{1}{r_{12}} - \frac{1}{r_{a2}} - \frac{1}{r_{b1}} \right) |\psi(r_{a1})\psi(r_{b2})\rangle \quad (165) \\ &= \left(-\frac{\lambda^2}{2} - \frac{1-\lambda}{r_{a1}} - \frac{\lambda^2}{2} - \frac{1-\lambda}{r_{b2}} + \frac{1}{r_{12}} - \frac{1}{r_{a2}} - \frac{1}{r_{b1}} \right) |\psi(r_{a1})\psi(r_{b2})\rangle \end{aligned}$$

故

$$\begin{aligned} &\langle \Psi_{\pm} | H_{\text{el}} | \Psi_{\pm} \rangle \\ &= 2 [\langle \psi(r_{a1})\psi(r_{b2}) | H_{\text{el}} | \psi(r_{a1})\psi(r_{b2}) \rangle \pm \langle \psi(r_{b1})\psi(r_{a2}) | H_{\text{el}} | \psi(r_{a1})\psi(r_{b2}) \rangle] \\ &= 2 \left[\langle \psi(r_{a1})\psi(r_{b2}) | -\frac{\lambda^2}{2} - \frac{1-\lambda}{r_{a1}} | \psi(r_{a1})\psi(r_{b2}) \rangle + \langle \psi(r_{a1})\psi(r_{b2}) | -\frac{\lambda^2}{2} - \frac{1-\lambda}{r_{b2}} | \psi(r_{a1})\psi(r_{b2}) \rangle \right. \\ &\quad - \langle \psi(r_{a1})\psi(r_{b2}) | \frac{1}{r_{a2}} | \psi(r_{a1})\psi(r_{b2}) \rangle - \langle \psi(r_{a1})\psi(r_{b2}) | \frac{1}{r_{b1}} | \psi(r_{a1})\psi(r_{b2}) \rangle \\ &\quad \left. + \langle \psi(r_{a1})\psi(r_{b2}) | \frac{1}{r_{12}} | \psi(r_{a1})\psi(r_{b2}) \rangle \right] + 2 \left[\langle \psi(r_{a2})\psi(r_{b1}) | -\frac{\lambda^2}{2} - \frac{1-\lambda}{r_{a1}} | \psi(r_{a1})\psi(r_{b2}) \rangle \right. \\ &\quad + \langle \psi(r_{a2})\psi(r_{b1}) | -\frac{\lambda^2}{2} - \frac{1-\lambda}{r_{b2}} | \psi(r_{a1})\psi(r_{b2}) \rangle - \langle \psi(r_{a2})\psi(r_{b1}) | \frac{1}{r_{a2}} | \psi(r_{a1})\psi(r_{b2}) \rangle \\ &\quad \left. - \langle \psi(r_{a2})\psi(r_{b1}) | \frac{1}{r_{b1}} | \psi(r_{a1})\psi(r_{b2}) \rangle + \langle \psi(r_{a2})\psi(r_{b1}) | \frac{1}{r_{12}} | \psi(r_{a1})\psi(r_{b2}) \rangle \right] \\ &= 2 \left[\langle \psi(r_{a1}) | -\frac{\lambda^2}{2} - \frac{1-\lambda}{r_{a1}} | \psi(r_{a1}) \rangle + \langle \psi(r_{b2}) | -\frac{\lambda^2}{2} - \frac{1-\lambda}{r_{b2}} | \psi(r_{b2}) \rangle \right. \\ &\quad \left. - \langle \psi(r_{b2}) | \frac{1}{r_{a2}} | \psi(r_{b2}) \rangle - \langle \psi(r_{a1}) | \frac{1}{r_{b1}} | \psi(r_{a1}) \rangle + \langle \psi(r_{a1})\psi(r_{b2}) | \frac{1}{r_{12}} | \psi(r_{a1})\psi(r_{b2}) \rangle \right] \\ &\quad + 2 \left[\langle \psi(r_{b1}) | -\frac{\lambda^2}{2} - \frac{1-\lambda}{r_{a1}} | \psi(r_{a1}) \rangle J + \langle \psi(r_{a2}) | -\frac{\lambda^2}{2} - \frac{1-\lambda}{r_{b2}} | \psi(r_{b2}) \rangle J \right. \\ &\quad \left. - \langle \psi(r_{a2}) | \frac{1}{r_{a2}} | \psi(r_{b2}) \rangle J - \langle \psi(r_{b1}) | \frac{1}{r_{b1}} | \psi(r_{a1}) \rangle J + \langle \psi(r_{a2})\psi(r_{b1}) | \frac{1}{r_{12}} | \psi(r_{a1})\psi(r_{b2}) \rangle \right] \\ &= 2 \left[2 \langle \psi(r_{a1}) | -\frac{\lambda^2}{2} - \frac{1-\lambda}{r_{a1}} | \psi(r_{a1}) \rangle - 2 \langle \psi(r_{b2}) | \frac{1}{r_{a2}} | \psi(r_{b2}) \rangle + \langle \psi(r_{a1})\psi(r_{b2}) | \frac{1}{r_{12}} | \psi(r_{a1})\psi(r_{b2}) \rangle \right] + \\ &\quad 2 \left[2 \langle \psi(r_{b1}) | -\frac{\lambda^2}{2} - \frac{1-\lambda}{r_{a1}} | \psi(r_{a1}) \rangle J - 2 \langle \psi(r_{a2}) | \frac{1}{r_{a2}} | \psi(r_{b2}) \rangle J + \langle \psi(r_{a2})\psi(r_{b1}) | \frac{1}{r_{12}} | \psi(r_{a1})\psi(r_{b2}) \rangle \right] \\ &= 2(2\mathcal{A} - 2\mathcal{K} + \mathcal{K}') \pm 2(2\mathcal{A}'J - 2\mathcal{E}J + \mathcal{E}') \\ &= 2[2(\mathcal{A} \pm \mathcal{A}'J) - 2(\mathcal{K} + \mathcal{E}J) + \mathcal{K}' \pm \mathcal{E}'] \end{aligned} \quad (166)$$

令 $\rho = \lambda R$, 上式中

$$\mathcal{A} = \langle \psi(r_{a1}) | -\frac{\lambda^2}{2} - \frac{1-\lambda}{r_{a1}} | \psi(r_{a1}) \rangle = -\frac{\lambda^2}{2} - (1-\lambda)\lambda = \frac{\lambda^2}{2} - \lambda \quad (167)$$

$$\mathcal{A}' = \langle \psi(r_{b1}) | -\frac{\lambda^2}{2} - \frac{1-\lambda}{r_{a1}} | \psi(r_{a1}) \rangle = -\frac{\lambda^2}{2}J + (\lambda-1)\mathcal{E} \quad (168)$$

$$\mathcal{K} = \langle \psi(r_{b2}) | \frac{1}{r_{a2}} | \psi(r_{b2}) \rangle = \frac{1}{R} [1 - (1+\lambda R)e^{-2\lambda R}] = \frac{\lambda}{\rho} [1 - (1+\rho)e^{-2\rho}] \quad (169)$$

$$\begin{aligned} \mathcal{K}' &= \langle \psi(r_{a1})\psi(r_{b2}) | \frac{1}{r_{12}} | \psi(r_{a1})\psi(r_{b2}) \rangle = \frac{\lambda^4}{\pi} \int d\vec{r}_1 d\vec{r}_2 \frac{\exp[-2\lambda(r_{a1} + r_{b2})]}{r_{12}} \\ &= \frac{\lambda}{\rho} \left[1 - \left(1 + \frac{11}{8}\rho + \frac{3}{4}\rho^2 + \frac{1}{4}\rho^3 \right) e^{-2\rho} \right] \end{aligned} \quad (170)$$

$$\mathcal{E} = \langle \psi(r_{a2}) | \frac{1}{r_{a2}} | \psi(r_{b2}) \rangle = \lambda(1 + \lambda R)e^{-\lambda R} = \lambda(1 + \rho)e^{-\rho} \quad (171)$$

$$\begin{aligned} \mathcal{E}' &= \langle \psi(r_{a2})\psi(r_{b1}) | \frac{1}{r_{12}} | \psi(r_{a1})\psi(r_{b2}) \rangle = \frac{\lambda^4}{\pi} \int d\vec{r}_1 d\vec{r}_2 \frac{\exp[-2\lambda(r_{a1} + r_{a2} + r_{b1} + r_{b2})]}{r_{12}} \\ &= \lambda \left[\left(\frac{5}{8} - \frac{23}{20}\rho - \frac{3}{5}\rho^2 - \frac{1}{15}\rho^3 \right) e^{-2\rho} + \frac{6}{5} \frac{\varphi(\rho)}{\rho} \right] \end{aligned} \quad (172)$$

其中

$$\varphi(\rho) = J^2(\rho) (\ln \rho + c) - J^2(-\rho)E_1(4\rho) + 2J(\rho)J(-\rho)E_1(2\rho) \quad (173)$$

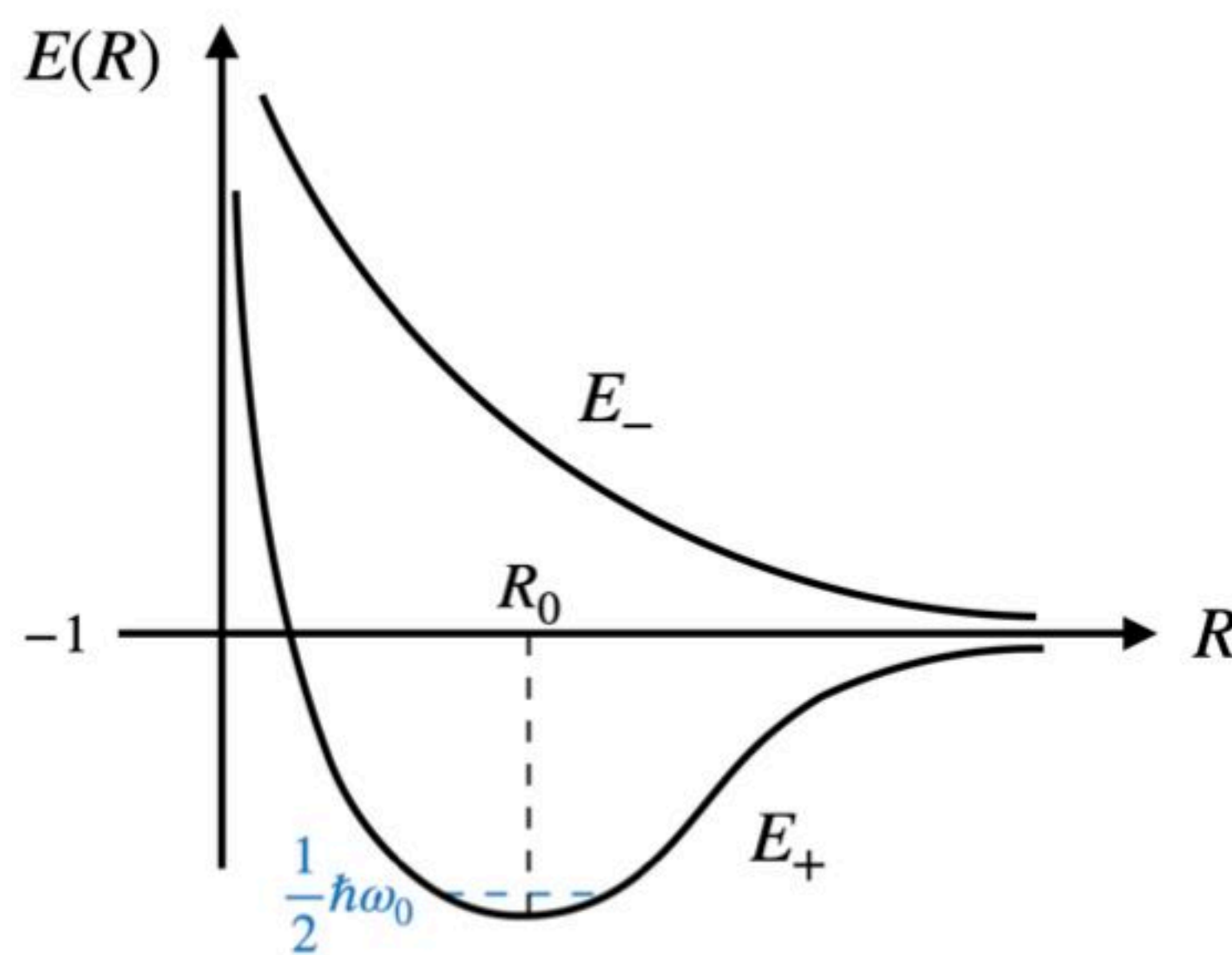
$$E_1(x) = \int_x^\infty \frac{1}{t} e^{-t} dt \quad (174)$$

$$J = \langle \psi(r_{a1}) | \psi(r_{b1}) \rangle = \langle \psi(r_{a2}) | \psi(r_{b2}) \rangle = \left(1 + \lambda R + \frac{1}{3}\lambda^2 R^2 \right) e^{-\lambda R} = \left(1 + \rho + \frac{1}{2}\rho^2 \right) e^{-\rho} \quad (175)$$

归一化因子

$$\langle \Psi_\pm | \Psi_\pm \rangle = \langle \psi(r_{a1})\psi(r_{b2}) \pm \psi(r_{a2})\psi(r_{b1}) | \psi(r_{a1})\psi(r_{b2}) \pm \psi(r_{a2})\psi(r_{b1}) \rangle = 2 \pm 2J^2 \quad (176)$$

$$E_\pm = \frac{1}{R} + \frac{\langle \Psi_\pm | H_{\text{el}} | \Psi_\pm \rangle}{\langle \Psi_\pm | \Psi_\pm \rangle} = \frac{1}{R} + \frac{1}{1 \pm J^2} [2(\mathcal{A} \pm \mathcal{A}'J) - 2(\mathcal{K} + \mathcal{E}J) + \mathcal{K}' \pm \mathcal{E}'] \quad (177)$$



基态体系处于能量最低状态， E_- 不稳定， E_+ 稳定，因此空间部分波函数对称。数值结果

$$E_+(R_0) = -1.139 \text{ a.u.} \quad (178)$$

由 $\frac{\partial E_+}{\partial \lambda} = 0$ 解出

$$\lambda = 1.166 \quad (179)$$

$$R_0 = 1.458 \text{ a.u.} = 0.77 \text{ \AA} \quad (180)$$

电离能

$$D = -1 - (E_+ + \frac{1}{2}\hbar\omega_0) = 0.129 \text{ a.u.} = 3.54 \text{ eV} \quad (181)$$

实验结果

$$D_{\text{exp}} = 4.45 \text{ eV} \quad (182)$$

我们可以通过添加变分参数使结果更精确，例如一个参数时

$$\psi(r) = \frac{\lambda}{\sqrt{\pi}} e^{-\lambda r} \quad (183)$$

两个参数

$$\psi(r) = \frac{\lambda_1^{\frac{3}{2}}}{\sqrt{\pi}}(1 + \lambda_2 r)e^{-\lambda_1 r} \quad (184)$$

为什么反对称波函数比对称波函数能量高呢?这其中蕴涵着很深刻的物理意义——化学键 (chemical bond)。接下来我们来讨论这个问题

$$\bar{H} = \frac{\langle \Psi_{\pm}(1, 2) | H | \Psi_{\pm}(1, 2) \rangle}{\langle \Psi_{\pm}(1, 2) | \Psi_{\pm}(1, 2) \rangle} = \frac{\langle \psi(r_{a1})\psi(r_{b2}) | H | \psi(r_{a1})\psi(r_{b2}) \rangle \pm \langle \psi(r_{b1})\psi(r_{a2}) | H | \psi(r_{a1})\psi(r_{b2}) \rangle}{1 \pm J^2} \quad (185)$$

$$H = \frac{1}{R} - \frac{1}{2}(\nabla_1^2 + \nabla_2^2) + \frac{1}{r_{12}} - \left(\frac{1}{r_{a1}} + \frac{1}{r_{a2}} + \frac{1}{r_{b1}} + \frac{1}{r_{b2}} \right) \quad (186)$$

$$\Psi_{\pm}(1, 2) = [\psi(r_{a1})\psi(r_{b2}) \pm \psi(r_{b1})\psi(r_{a2})] \chi_{0,1}(s_{1z}, s_{2z}) \quad (187)$$

前面我们得出 $\lambda = 1.166$ ，由于我们要讨论的是 $E_+ < E_-$ 的物理内涵，因此取 $\lambda = 1$ 对结果影响不大。简单起见，我们直接取 $\lambda = 1$ ，即 $\psi(r)$ 为氢原子的波函数，重复之前的步骤。

$$\psi(r) = \frac{1}{\sqrt{\pi}}e^{-r} \quad (188)$$

$$H |\psi(r_{a1})\psi(r_{b2})\rangle = \left[\frac{1}{R} + 2E_0^{\text{H-atom}} + \left(\frac{1}{r_{12}} - \frac{1}{r_{a2}} - \frac{1}{r_{b1}} \right) \right] |\psi(r_{a1})\psi(r_{b2})\rangle \quad (189)$$

$$\begin{aligned} \bar{H}(1 \pm J^2) = & \frac{1}{R} + 2E_0^{\text{H-atom}} + \langle \psi(r_{a1})\psi(r_{b2}) | \frac{1}{r_{12}} - \frac{1}{r_{a2}} - \frac{1}{r_{b1}} | \psi(r_{a1})\psi(r_{b2}) \rangle \\ & \pm \left[J^2 \left(\frac{1}{R} + 2E_0^{\text{H-atom}} \right) + \langle \psi(r_{b1})\psi(r_{a2}) | \frac{1}{r_{12}} - \frac{1}{r_{a2}} - \frac{1}{r_{b1}} | \psi(r_{a1})\psi(r_{b2}) \rangle \right] \end{aligned} \quad (190)$$

最终得到

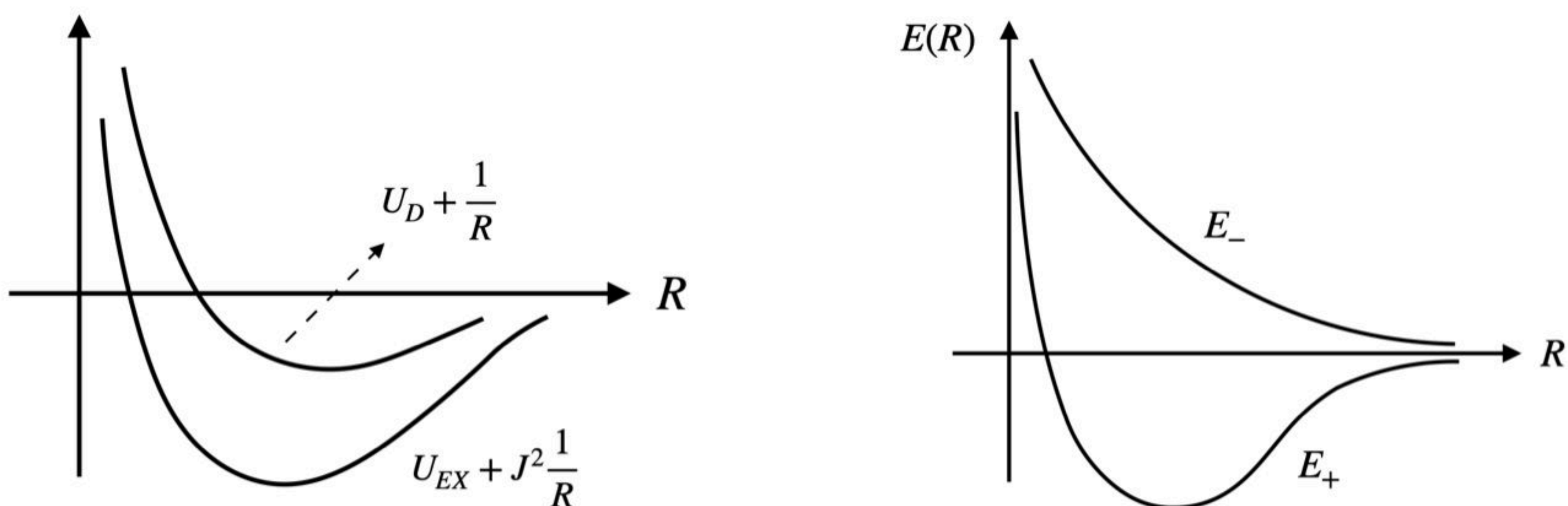
$$E_{\pm} = \frac{1}{R} + 2E_0^{\text{H-atom}} + \frac{U_D \pm U_{\text{EX}}}{1 \pm J^2} = 2E_0^{\text{H-atom}} + \frac{(U_D + \frac{1}{R}) \pm (U_{\text{EX}} + J^2 \frac{1}{R})}{1 \pm J^2} \quad (191)$$

D 代表 direct, EX 代表 exchange

$$U_D = -2K + K' \quad (192)$$

$$U_{\text{EX}} = -2J\mathcal{E} + \mathcal{E}' \propto J \quad (193)$$

计算 U_D 和 U_{EX} 的数值结果



$$\langle \psi(r_{a1})\psi(r_{b2}) | H | \psi(r_{a1})\psi(r_{b2}) \rangle \pm \langle \psi(r_{b1})\psi(r_{a2}) | H | \psi(r_{a1})\psi(r_{b2}) \rangle \quad (194)$$

第一项由直接相互作用引起，第二项由交换相互作用引起。

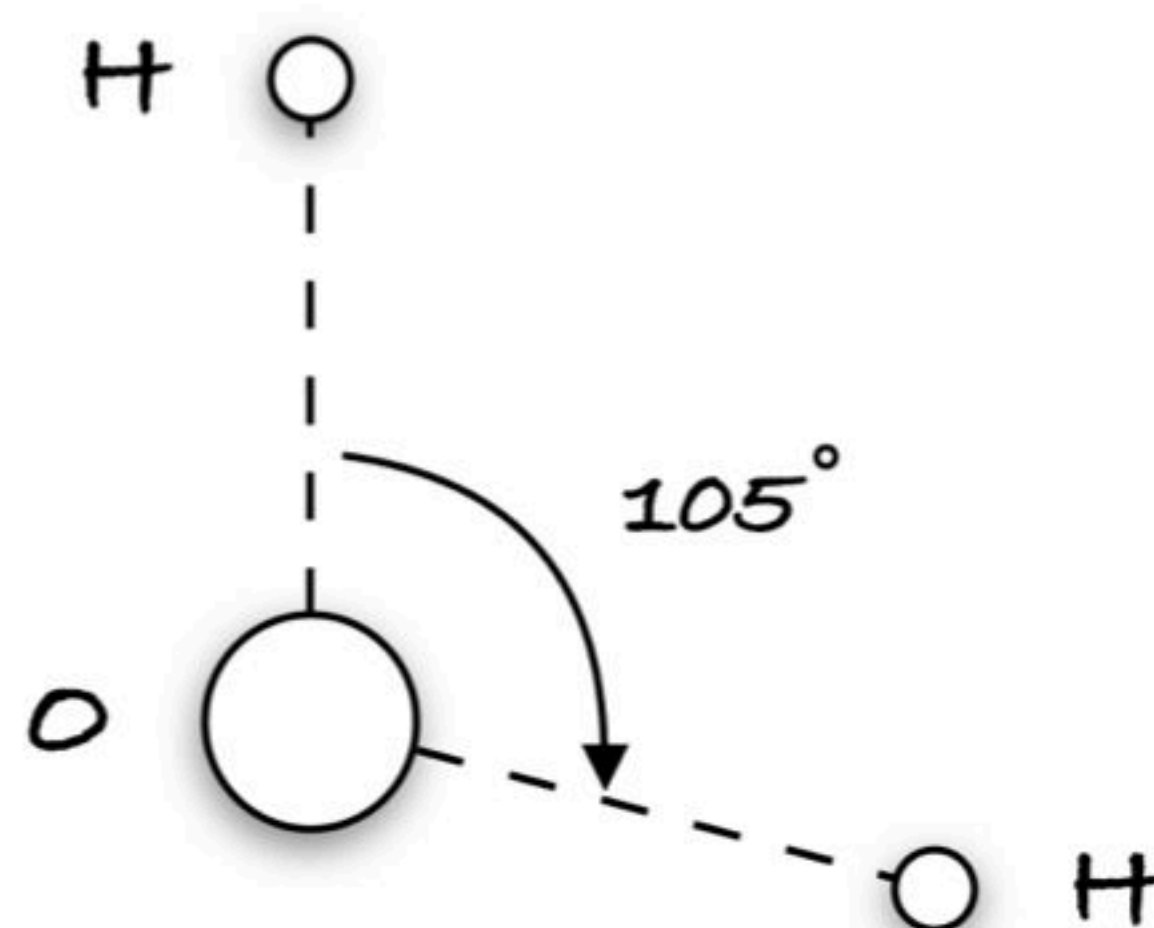
$U_{\text{EX}} \sim J$ ， J 是交叠积分，因此 J 越大， $|U_{\text{EX}}|$ 越大，势阱越深，体系越稳定。而两个氢原子的波函数重合部分越多， J 越大， E_+ 越小，体系越稳定；而 E_- 反而变大，体系不稳定。

这也正是我们中学时所学的电子云重叠，引起化学键。

7 Theory of Chemical Bonds

该理论由 Pauli 提出，又名 Pauli chemical bonds theory。

Example: H₂O



为什么 H₂O 具有这样的结构？首先讨论 H 和 O 的原子结构 (括号中数字是电子的编号)

$$\text{H: } 1s^1(5) \quad \text{H: } 1s^1(6) \quad \text{O: } 1s^2 2s^2 2p^4$$

p 有 3 个轨道，可以填充 6 个电子

$$\begin{array}{ccc} 2p_x & 2p_y & 2p_z \\ \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow \end{array}$$

根据 Hund's rule，要使能量最低，三个电子自旋方向相同，任意一个 $2p$ 轨道中填充第 4 个电子

$$\begin{array}{ccc} 2p_x & 2p_y & 2p_z \\ \uparrow(1) & \uparrow(2) & \uparrow(3)\downarrow(4) \end{array}$$

未填满的 p_x 和 p_y 轨道分别与 H 原子电子配对形成化学键。

$$[\psi_{2p_x}(1)\psi_H(5) + \psi_{2p_x}(5)\psi_H(1)]\chi_0(s_{1z}, s_{2z}) \quad (195)$$

$$[\psi_{2p_x}(2)\psi_H(6) + \psi_{2p_x}(6)\psi_H(2)]\chi_0(s_{1z}, s_{2z}) \quad (196)$$

p_x, p_y, p_z 互相垂直，但由于有 H 原子排斥势的影响，两个化学键之间角度增大。Pauli 理论大致上解释了 H₂O 的结构。

Example: NH₃

N 原子结构 $1s^2 2s^2 2p^3$

$$\begin{array}{ccc} 2p_x & 2p_y & 2p_z \\ \uparrow & \uparrow & \uparrow \end{array}$$

则三个氢原子电子自旋方向向下，分别与 p_x, p_y, p_z 轨道电子配对。 p_x, p_y, p_z 轨道正交，但由于有 H 原子的影响，成键角度约为 107°

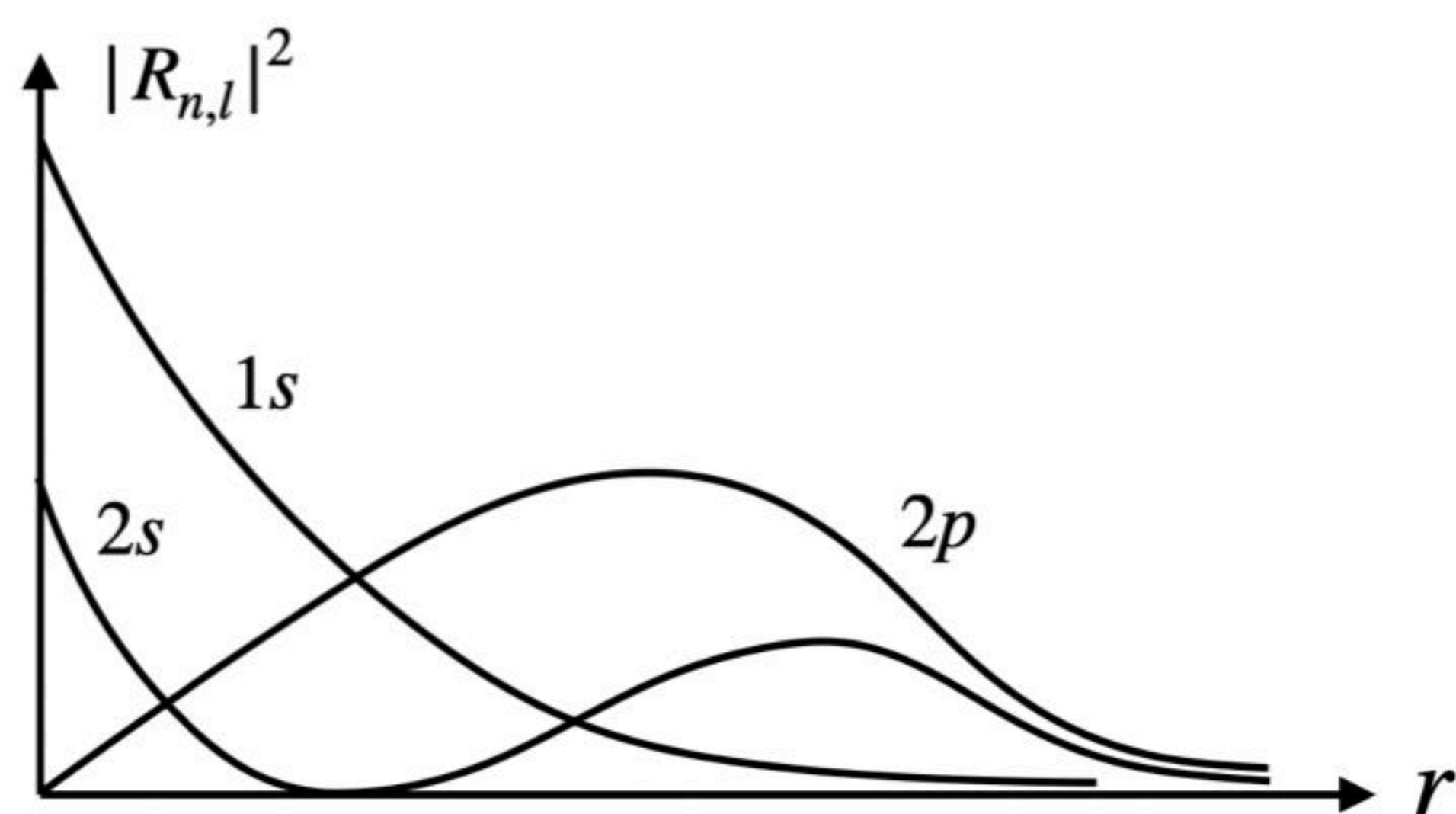
Example: CH₄

Pauli 理论能解释所有分子结构吗? 我们来看看 CH₄。N 原子结构 $1s^2 2s^2 2p^2$

$$\begin{array}{ccc} 2p_x & 2p_y & 2p_z \\ \uparrow & \uparrow & \end{array}$$

根据刚刚的 Pauli 理论无法解释 CH₄ 如何成键, 由此 Pauli 提出 Pauli 杂化轨道理论。

- 1s 轨道: $R_{1,0}(r) \sim e^{-r}$
- 2s 轨道: $R_{2,0}(r) \sim (1-r)e^{-r}$
- 2p 轨道: $R_{2,1}(r) \sim re^{-r}$



2s 轨道和 2p 轨道径向波函数在末端相近, 2s 电子可以认为是外壳层电子, 2s 轨道可以和 2p 轨道重新杂化。轨道波函数

$$\psi_{2s} = R_{2s}(r) \quad (197)$$

$$\psi_{2px} = \frac{\sqrt{3}}{4\pi} R_{2p}(r) \sin \theta \cos \varphi \quad (198)$$

$$\psi_{2py} = \frac{\sqrt{3}}{4\pi} R_{2p}(r) \sin \theta \sin \varphi \quad (199)$$

$$\psi_{2pz} = \frac{\sqrt{3}}{4\pi} R_{2p}(r) \cos \theta \quad (200)$$

为了讨论方便, 我们认为 $R_{2s}(r) \doteq R_{2p}(r)$

$$\psi_{2s} = 1 \quad (201)$$

$$\psi_{2px} = \sqrt{3} \sin \theta \cos \varphi \quad (202)$$

$$\psi_{2py} = \sqrt{3} \sin \theta \sin \varphi \quad (203)$$

$$\psi_{2pz} = \sqrt{3} \cos \theta \quad (204)$$

使用 LCAO 法, 令

$$\psi_i(\vec{r}) = a\psi_{2s} + b_i\psi_{2px} + c_i\psi_{2py} + d_i\psi_{2pz} \quad (i = 1, 2, 3, 4) \quad (205)$$

由对称性得到

$$|b_i| = |c_i| = |d_i| \quad (206)$$

四个轨道正交且分别归一

$$\int |\psi_i(\vec{r})|^2 d\vec{r} = a^2 + 3b_i^2 = 1 \quad (207)$$

$$\psi_i(\vec{r}) = a\psi_{2s} + b_i(\psi_{2px} + \psi_{2py} + \psi_{2pz}) \quad (i = 1, 2, 3, 4) \quad (208)$$

选择第一象限中与 x, y, z 轴夹角都相同的方向

$$\sin \varphi = \cos \varphi = \frac{1}{\sqrt{2}} \quad \cos \theta = \frac{1}{\sqrt{3}} \quad \sin \theta = \frac{\sqrt{2}}{\sqrt{3}} \quad (209)$$

则

$$\psi_{2s} = \psi_{2px} = \psi_{2py} = \psi_{2pz} = 1 \quad (210)$$

$$\psi_1(\vec{r}) = a + 3b_1 = a + \sqrt{3(1-a^2)} \quad (211)$$

当 ψ_1 最大时

$$\frac{d}{da} [a + \sqrt{3(1-a^2)}] = 0 \quad (212)$$

解得

$$a = \frac{1}{2} \quad b = \frac{1}{2} \quad (213)$$

$$\psi_1(\vec{r}) = \frac{1}{2}(\psi_{2s} + \psi_{2px} + \psi_{2py} + \psi_{2pz}) \quad (214)$$

ψ_2, ψ_3, ψ_4 与 ψ_1 正交

$$\psi_2(\vec{r}) = \frac{1}{2}(\psi_{2s} - \psi_{2px} + \psi_{2py} + \psi_{2pz}) \quad (215)$$

$$\psi_3(\vec{r}) = \frac{1}{2}(\psi_{2s} + \psi_{2px} - \psi_{2py} + \psi_{2pz}) \quad (216)$$

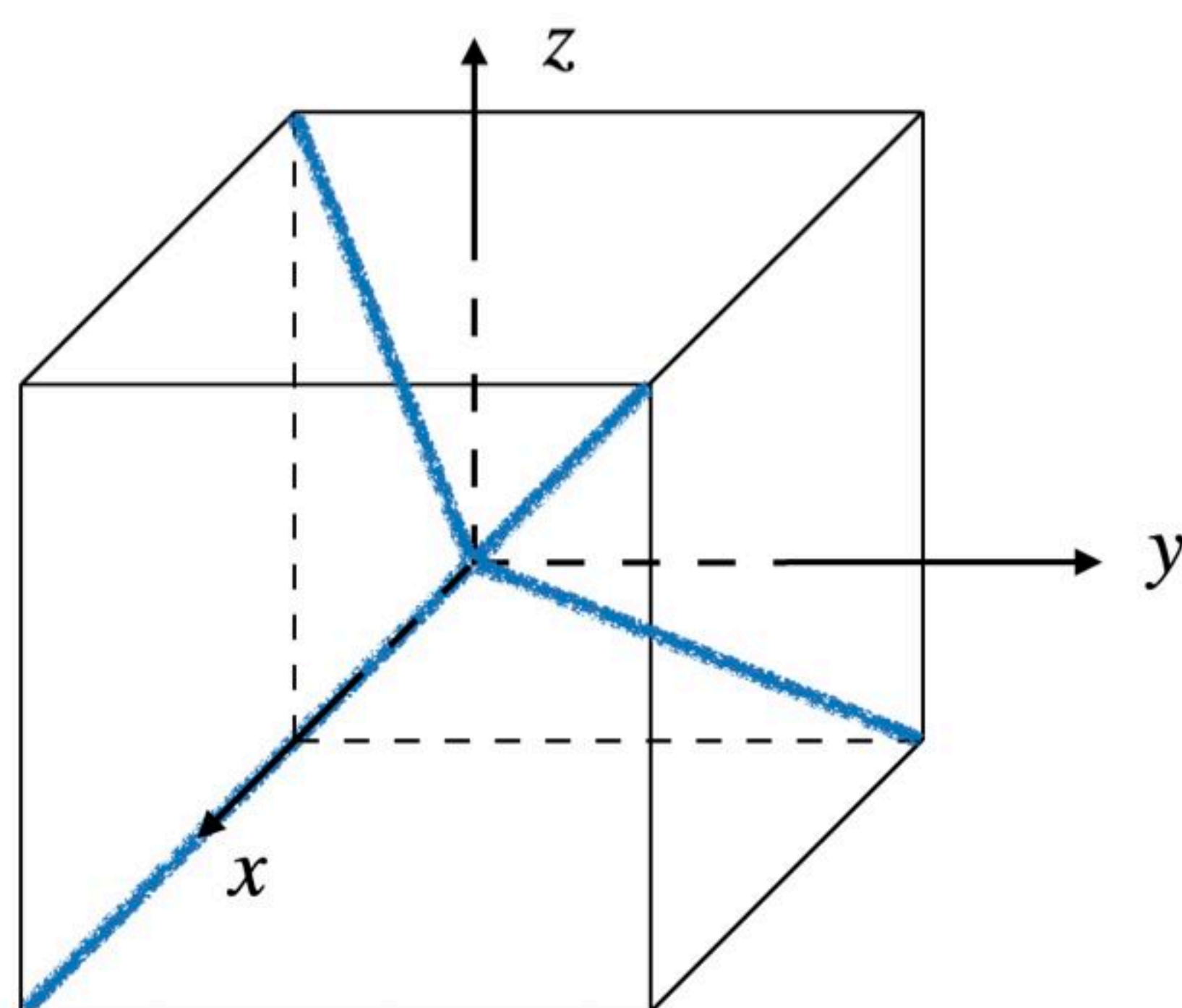
$$\psi_4(\vec{r}) = \frac{1}{2}(\psi_{2s} + \psi_{2px} + \psi_{2py} - \psi_{2pz}) \quad (217)$$

这 4 个轨道显然满足

$$\langle \psi_i | \psi_j \rangle = \delta_{i,j} \quad (218)$$

CH_4 的 4 个 H 原子的电子分别与这 4 个轨道配对。化学键

$$[\psi_i(a)\psi_H(b) + \psi_i(b)\psi_H(a)] \chi_0(s_{az}, s_{bz}) \quad (219)$$



在化学上使用 LCAO 方法，取完备积系数作变分参数，从而得到轨道波函数；而在固体物理中，LCAO 发展为 TB 近似 (Tight-Binding approximation)，即

$$\psi_{n\vec{k}}(\vec{r}) = \sum_{\vec{R}} e^{i\vec{k} \cdot \vec{R}} \psi_n(\vec{r} - \vec{R}) \quad (220)$$

Chapter 7: Introduction to Many-body Theory

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1 Introduction

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

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

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

若粒子间存在相互作用 $V(\vec{r}_i, \vec{r}_j)$

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

Example: N -Electrons Atom (N 个电子的原子)

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

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

猜测多体的薛定谔方程为

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

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

$$H\Psi_n(x_1, \dots, x_N) = E_n \Psi_n(x_1, \dots, x_N) \quad (7)$$

根据全同性原理，交换两粒子位置，波函数对称或反对称。

- 对于费米子，波函数反对称

$$\Psi_n(x_1, \dots, x_i, \dots, x_j, \dots, x_N) = -\Psi_n(x_1, \dots, x_j, \dots, x_i, \dots, x_N) \quad (8)$$

- 对于玻色子，波函数对称

$$\Psi_n(x_1, \dots, x_i, \dots, x_j, \dots, x_N) = \Psi_n(x_1, \dots, x_j, \dots, x_i, \dots, x_N) \quad (9)$$

体系能量

$$E = \langle \Psi | H | \Psi \rangle \quad (10)$$

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

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

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

密度算符

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

体系密度

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

根据全同性原理，交换两个电子波函数不变

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

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

对于无相互作用的系统

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

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

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

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

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

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

显而易见 $\psi_n(x)$ 满足

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

则

$$E = \sum_{i=1}^N \varepsilon_{n_i} \quad (23)$$

轨道

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

交换两个粒子，Eq.(21) 不满足对称性，因此我们需要将 Ψ 对称化

- 对于费米子

$$\Psi(x_1, \dots, x_N) = \frac{1}{\sqrt{N!}} \sum_P (-1)^P P[\psi_{n_1}(x_1) \cdots \psi_{n_N}(x_N)] \quad (25)$$

P 是交换次数，总交换数是 $N!$ 。

- 对于玻色子

$$\Psi(x_1, \dots, x_N) = \frac{1}{\sqrt{N!}} \sum_P P[\psi_{n_1}(x_1) \cdots \psi_{n_N}(x_N)] \quad (26)$$

接下来先讨论费米子

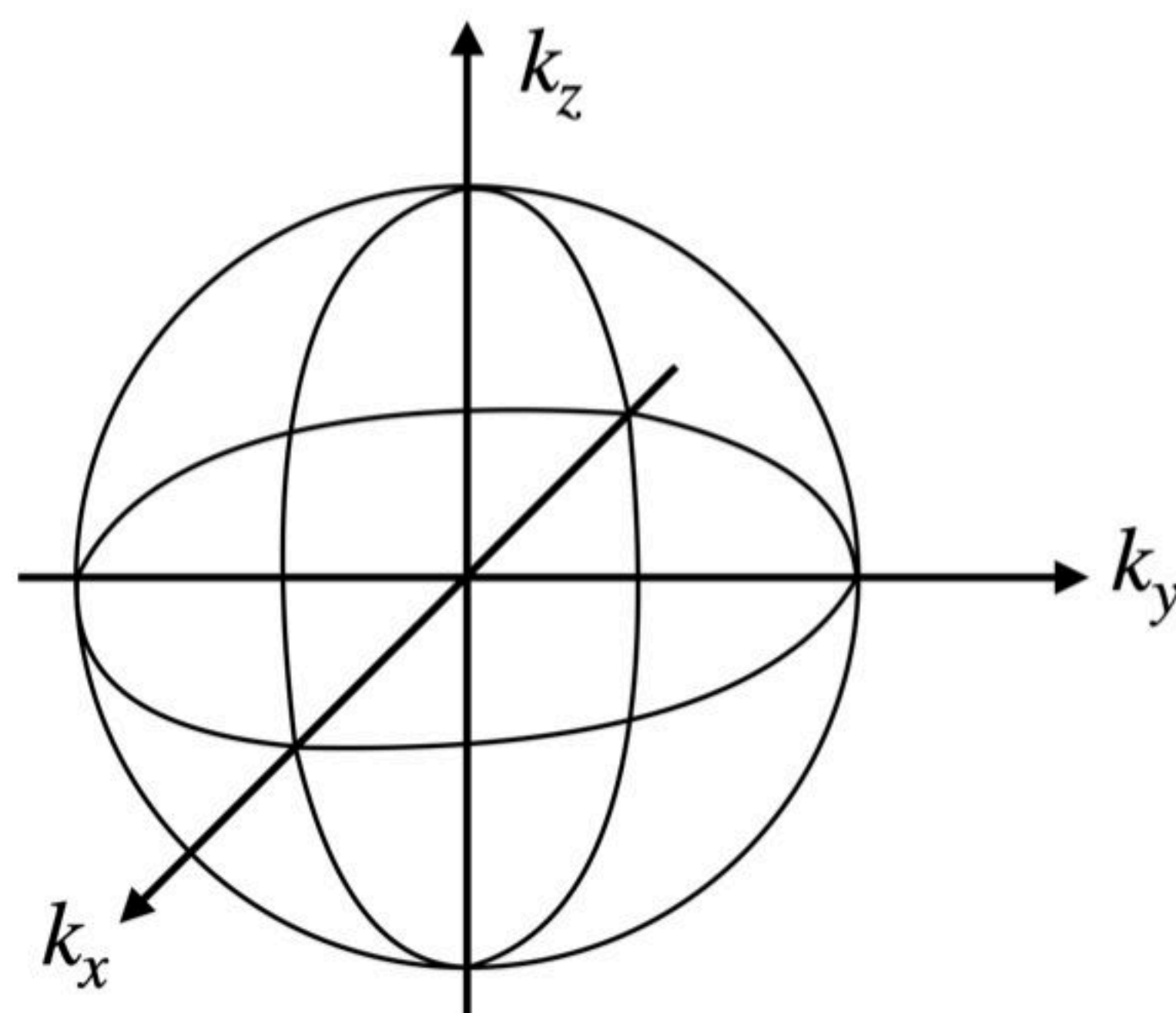
$$\begin{aligned} \Psi(x_1, \dots, x_N) &= \frac{1}{\sqrt{N!}} \sum_P (-1)^P P[\psi_{n_1}(x_1) \cdots \psi_{n_N}(x_N)] \\ &= \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{n_1}(x_1) & \psi_{n_1}(x_2) & \cdots & \psi_{n_1}(x_N) \\ \psi_{n_2}(x_1) & \psi_{n_2}(x_2) & \cdots & \psi_{n_2}(x_N) \\ \cdots & \cdots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

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

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

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

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



k_F 由密度 n 决定，接下来推导 n 与 k_F 的关系。粒子数

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

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

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

当体积 $V \rightarrow \infty$ 时, 和化为积分的形式

$$\sum_{\vec{k}} \rightarrow \frac{V}{(2\pi)^3} \int d\vec{k} \quad (32)$$

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

体系密度

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

由于粒子从内层开始填充, 故体系处于基态。体系能量 (设无粒子相互作用)

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

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

$$P = - \left. \frac{dE}{dV} \right|_N = - \frac{3}{5} N \left. \frac{d\varepsilon_F}{dV} \right|_N = - \frac{3}{5} N \frac{d}{dV} \left(\frac{\hbar^2 k_F^2}{2m} \right) \quad (36)$$

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

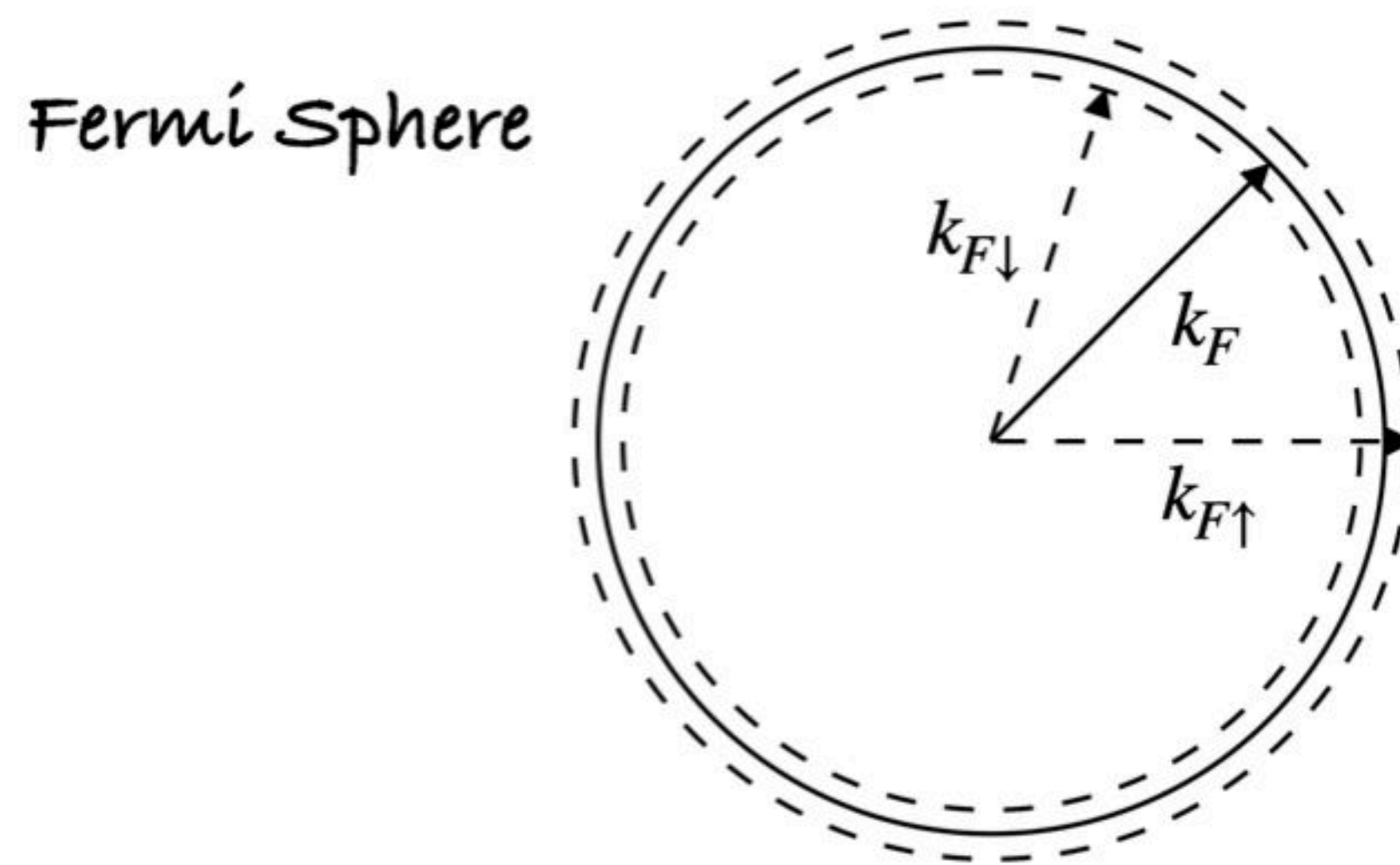
$$P = - \frac{3}{5} N \frac{d}{dV} \left(\frac{\hbar^2 k_F^2}{2m} \right) = \frac{1}{5} \frac{\hbar^2}{m} (3\pi^2)^{\frac{2}{3}} n^{\frac{5}{3}} \quad (38)$$

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

$$\Psi(x_1, \dots, x_N) = \psi_0(x_1) \cdots \psi_0(x_N) \quad (39)$$

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

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



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

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

设加一个很小的磁场，使两个费米球分开很小的距离，讨论磁化率

$$\varepsilon_{F\uparrow} - \mu_B B = \varepsilon_{F\downarrow} + \mu_B B \quad (40)$$

得到

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

又

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

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

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

磁化强度

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

磁化率

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

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

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

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

4 Fermi Gas Model for Nuclei

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

在前面对自由电子气体的讨论中我们得到 (这里的 N 是电子数)

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

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

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

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

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

另一种写法

$$B(Z, A) = a_v A - a_s A^{\frac{2}{3}} - a_c \frac{Z^2}{A^{\frac{1}{3}}} - a_{sy} \frac{(N - Z)^2}{A} + B_p \tag{51}$$

接下来解释各项。假设 $n = \frac{A}{V}$ 为一定值

1. Volume energy $\sim V \sim A \quad \Rightarrow \quad a_v A$
2. Surface energy $\sim S \sim V^{\frac{2}{3}} \sim A^{\frac{2}{3}} \quad \Rightarrow \quad a_s A^{\frac{2}{3}}$

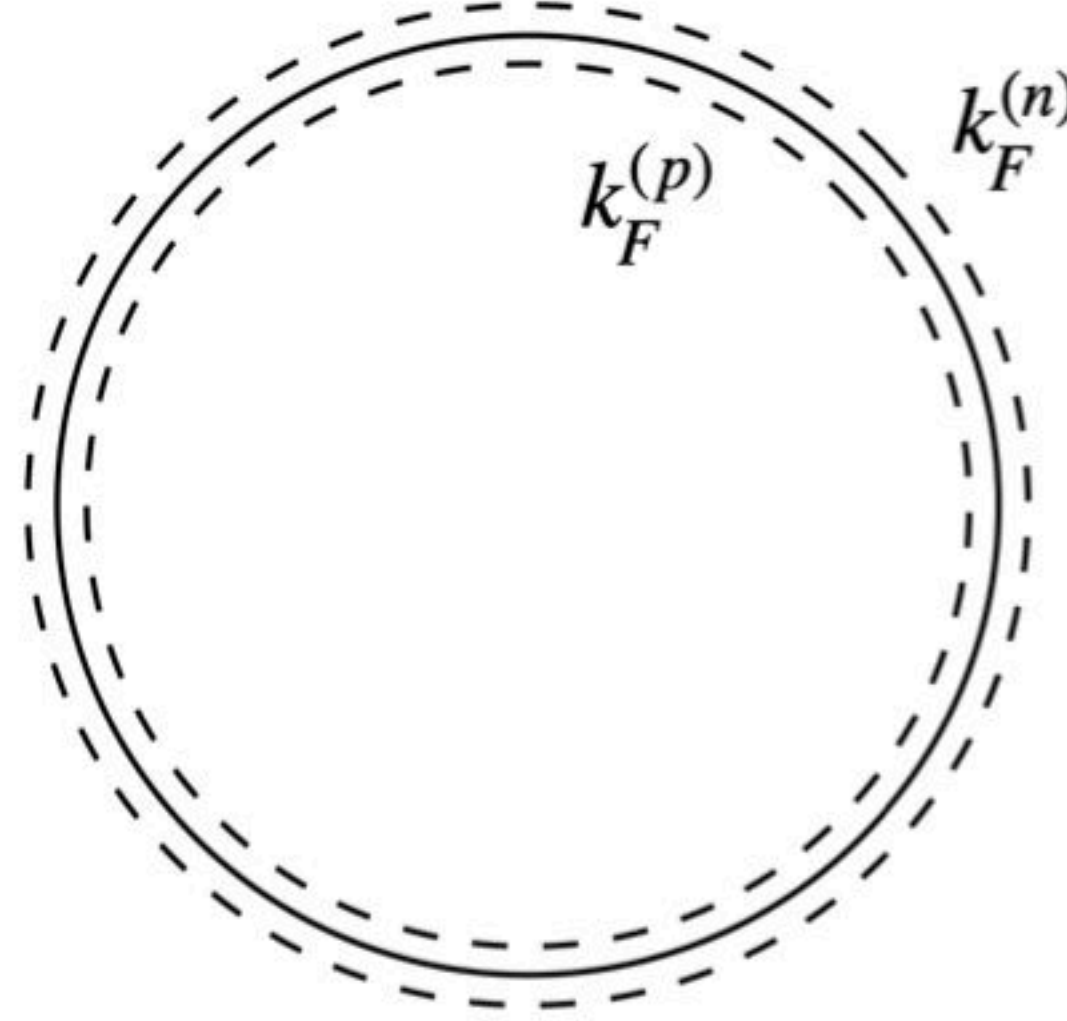
3. Coulomb energy

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

4. Symmetry energy

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

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



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

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

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

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

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

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

6. 核势对中子和质子的影响一样，不考虑。

5 Thomas-Fermi Theory

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

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

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

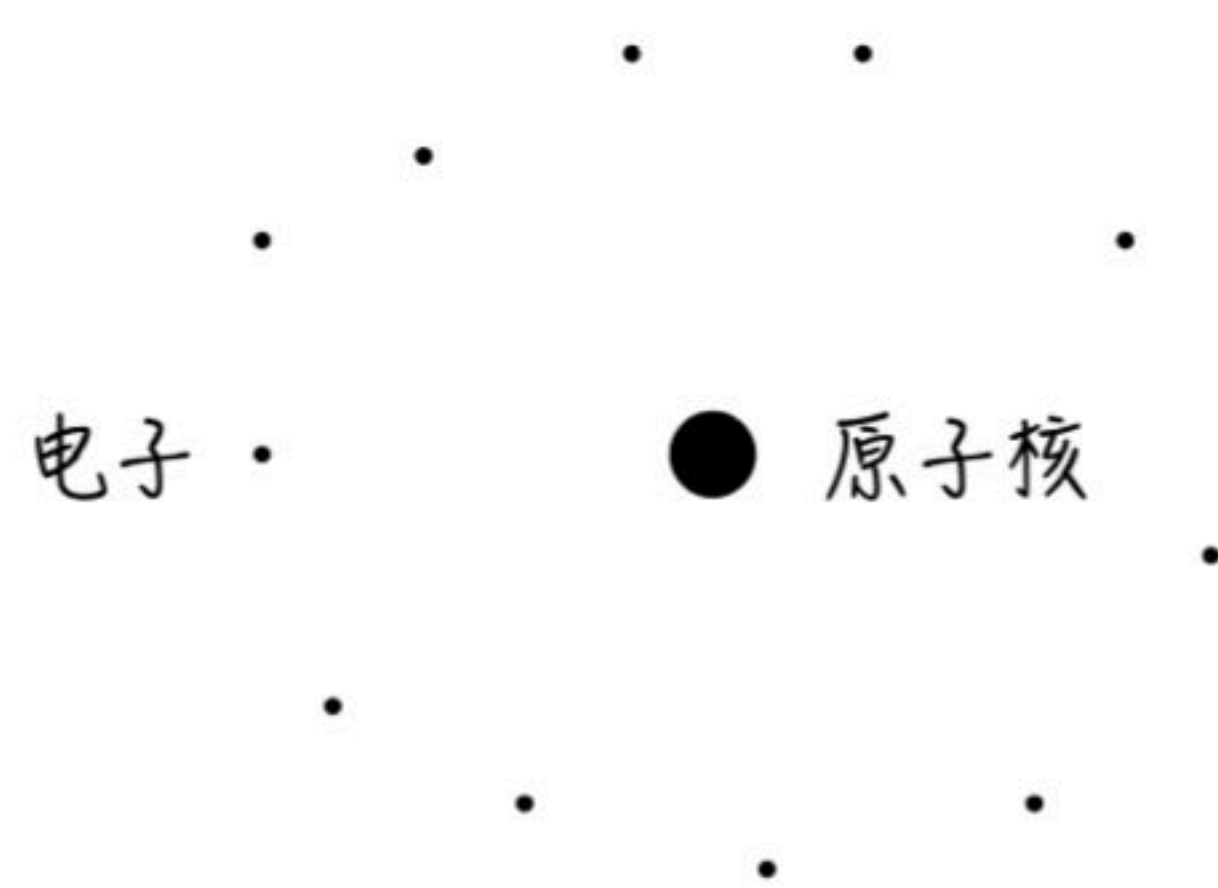
电子的相互作用势

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

求解薛定谔方程的本征态和本征能

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

目前唯一能严格解的是氢原子，但我们可以用近似的方法解钠原子。



电子密度分布

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

核密度分布

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

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

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

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

$$\rho = \frac{1}{3\pi^2} k_F^3 \quad (65)$$

类似地，对于近似均匀体系

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

体系能量守恒

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

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

有效势

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

其中 v_H 是 Hartree potential

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

满足 Poisson equation。故

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

先考察 $v_{\text{ext}}(\vec{r})$

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

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

接下来看 $v_H(\vec{r})$

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

即

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

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

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

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

故

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

即

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

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

设体系处于球对称

$$\nabla^2 = \frac{1}{r} \frac{d^2}{dr^2} r \quad (81)$$

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

这是非线性常微分方程，无严格解。

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

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

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

$$\varphi(r=0) = 1 \quad \varphi(r \rightarrow \infty) = 0 \Rightarrow v_H(r \rightarrow \infty) = \frac{Z}{r} \quad (85)$$

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

令 $x = \alpha r$,

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

则

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

边界条件

$$\varphi(x=0) = 1 \quad \varphi(x \rightarrow \infty) = 0 \quad (89)$$

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

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

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

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

当 $r \rightarrow \infty$ 时

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

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

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

当 $x \rightarrow 0$ 时, 令 $\varphi(x) = 1 + cx$

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

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

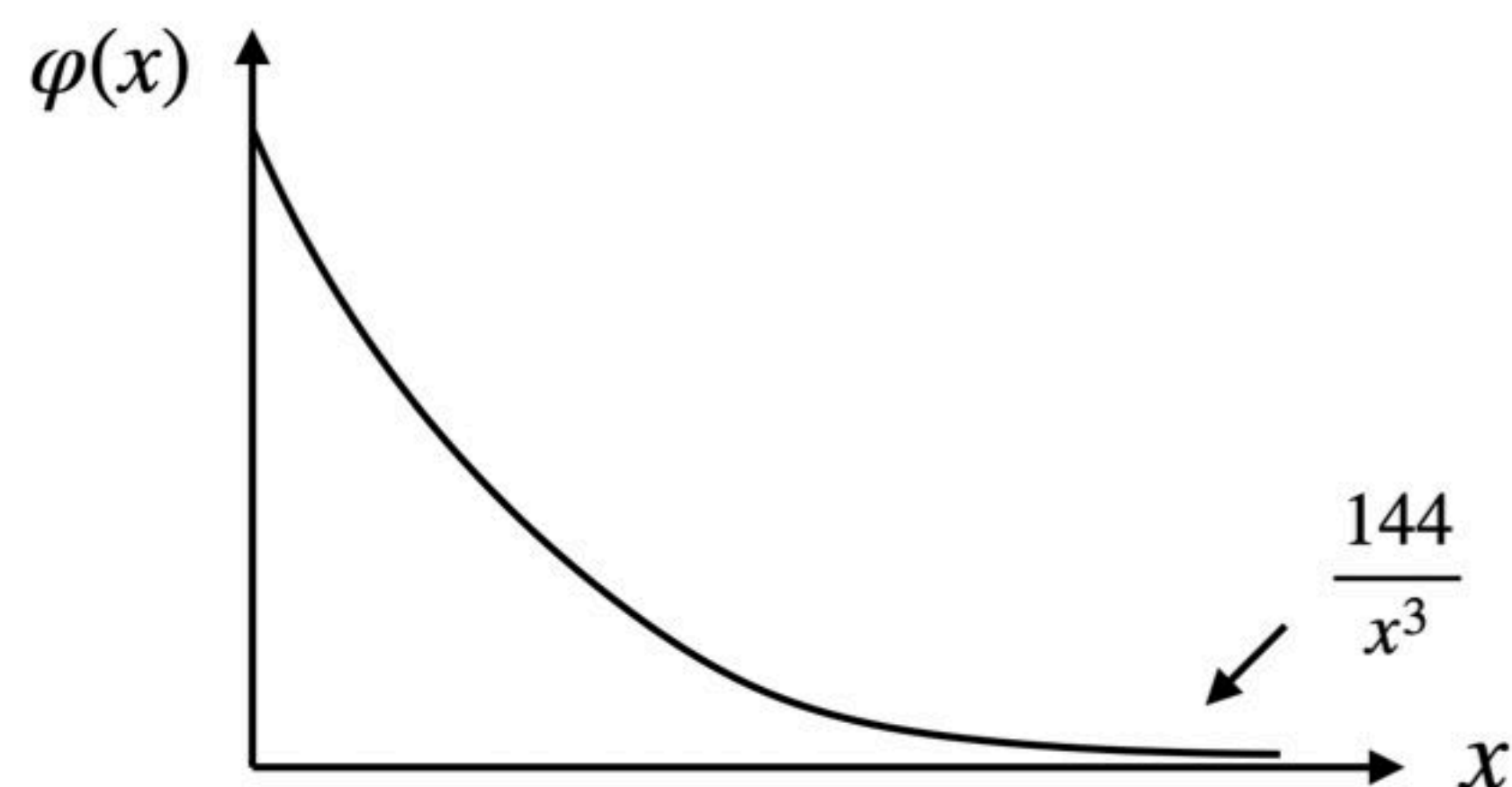
$$v_H(r=0) + v_{\text{ext}}(r \rightarrow 0) = (1 + c\alpha r)v_{\text{ext}}(r \rightarrow 0) \quad (97)$$

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

得到

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

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



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

6 Hartree Theory

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

$$H\Psi_n = E_n \Psi_n \quad (102)$$

符号简化, 令

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

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

则

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

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

$$\Psi_H(x_1, \dots, x_N) = \psi_1(x_1) \cdots \psi_N(x_N) \quad (106)$$

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

$$\int \Psi_H^\dagger(x_1, \dots, x_N) \Psi_H(x_1, \dots, x_N) dx_1 \cdots dx_N = 1 \quad (107)$$

假设自旋部分自动求和

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

体系密度

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

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

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

计算 \bar{H}

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

计算 $\delta\bar{H}$

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

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

即

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

令

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

v_H 是 orbital-dependent Hartree potential。

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

我们得到 orbital-dependent Hartree equation

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

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

Hartree 理论可以再做进一步简化。将求和号拿入积分号中

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

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

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

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

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

7 Hartree-Fock Theory

Hartree 中波函数

$$\Psi_H(x_1, \dots, x_N) = \psi_1(x_1) \cdots \psi_N(x_N) \quad (121)$$

不满足对称性, 将它对称化

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

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

波函数归一化, 自旋部分自动求和

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

假设有 2 个粒子

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

这是我们最熟悉的波函数, 波函数空间部分对称, 自旋部分反对称。

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

满足归一化条件。

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

计算 \bar{H}

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

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

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

故

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

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

计算 $\delta\bar{H}_{\text{exchange}}$

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

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

则

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

我们前面已经定义过 $v_H^i(\vec{r})$

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

令

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

则

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

我们来分析 Eq.(138)

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

则

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

Orbital-dependent Hartree equation

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

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