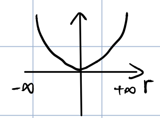
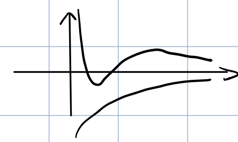
Time independent（独立的） Perturbation（微扰） Theory

$$H = \frac{p^2}{2m} + V(r)$$



Harmonic Oscillator



Hydrogen atom

Morse Potential 莫尔斯势能曲线

$$V(r) = V_{ho}(r) + \underbrace{V(r) - V_{ho}(r)}_{\text{perturbation}}$$

$$H = H_0 + V_1$$

$$H_0 = \frac{p^2}{2m} + \frac{1}{2} m \omega_0^2 x^2$$

$H = H_0 + \lambda H_1$ λ : coeffiential $\lambda \to 0.\ H \to H_0$ $\lambda \to 1.\ H \to H_0 + H_1$

$$H|\varphi_n\rangle = E|\varphi_n\rangle$$

$$|\varphi_n\rangle = |\varphi_n^{(0)}\rangle + \lambda|\varphi_n^{(1)}\rangle + \lambda^2|\varphi_n^{(2)}\rangle + \dots + \lambda^j|\varphi_n^{(j)}\rangle + \dots$$

$$\langle \varphi_n^{(0)} | \varphi_n^{(j)} \rangle = \delta_{j0}$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \lambda^3 E_n^{(3)} + \dots + \lambda^j E_n^{(j)} + \dots$$

$$(H_0 + \lambda H_1)(|\varphi_n^{(0)}\rangle + \lambda|\varphi_n^{(1)}\rangle + \lambda^2|\varphi_n^{(2)}\rangle + \dots) = (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots) \times (|\varphi_n^{(0)}\rangle + \lambda|\varphi_n^{(1)}\rangle + \lambda^2|\varphi_n^{(2)}\rangle + \dots)$$

λ^0 : $H_0|\varphi_n^{(0)}\rangle = E_0^{(0)}|\varphi_n^{(0)}\rangle.$ **(1)**

λ^1 : $H_0|\varphi_n^{(1)}\rangle + H_1|\varphi_n^{(0)}\rangle = E_n^{(0)}|\varphi_n^{(1)}\rangle + E_n^{(1)}|\varphi_n^{(0)}\rangle$ **(2)**

λ^2 : $H_0|\varphi_n^{(2)}\rangle + H_1|\varphi_n^{(1)}\rangle = E_n^{(2)}|\varphi_n^{(0)}\rangle + E_n^{(1)}|\varphi_n^{(1)}\rangle + E_n^{(0)}|\varphi_n^{(2)}\rangle$ **(3)**

λ^1: $\underbrace{\langle \varphi_n^{(0)}|H_0|\varphi_n^{(1)}\rangle}_{E_n^0\langle \varphi_n^{(0)}|\varphi_n^{(1)}\rangle = 0.} + \langle \varphi_n^{(0)}|H_1|\varphi_n^{(0)}\rangle$ 考虑λ^1. 左乘$\langle\varphi_n^{(0)}|$.

$= E_n^{(1)}\langle \varphi_n^{(0)}|\varphi_n^{(0)}\rangle$

$E_n^{(1)} = \langle \varphi_n^{(0)}|H_1|\varphi_n^{(0)}\rangle$ 能量的一次修正.

$\langle \varphi_m^{(0)}|H_1|\varphi_n^{(0)}\rangle + E_m^{(0)}\langle\varphi_m^{(0)}|\varphi_n^{(1)}\rangle$ 左乘 $\langle\varphi_m^{(0)}|$

$= E_n^{(0)}\langle\varphi_m^{(0)}|\varphi_n^{(1)}\rangle + E_n^{(1)}\delta_{mn}$

$m\neq n$ $\delta_{mn}=0$. $(E_n^{(0)}-E_m^{(0)})\langle\varphi_m^{(0)}|\varphi_n^{(1)}\rangle = \langle\varphi_m^{(0)}|H_1|\varphi_n^{(0)}\rangle$

$$\langle\varphi_m^{(0)}|\varphi_n^{(1)}\rangle = \frac{\langle\varphi_m^{(0)}|H_1|\varphi_n^{(0)}\rangle}{E_n^{(0)}-E_m^{(0)}}$$

$$|\varphi_n^{(1)}\rangle = \sum_m |\varphi_m^{(0)}\rangle\langle\varphi_m^{(0)}|\varphi_n^{(1)}\rangle$$

$$= \sum_{m\neq n}\frac{\langle\varphi_m^{(0)}|H_1|\varphi_n^{(0)}\rangle}{E_n^{(0)}-E_m^{(0)}}|\varphi_m^{(0)}\rangle$$

first order correction to wave function. 波函数的一次修正.

non-degenerate case.

λ^2: 左乘 $\langle\varphi_n^{(0)}|$

$$\underbrace{\langle\varphi_n^{(0)}|H_0|\varphi_n^{(2)}\rangle}_{=0} + \langle\varphi_n^{(0)}|H_1|\varphi_n^{(1)}\rangle = E_n^{(2)} + E_n^{(1)}\underbrace{\langle\varphi_n^{(0)}|\varphi_n^{(1)}\rangle}_{=0} + E_n^{(0)}\underbrace{\langle\varphi_n^{0}|\varphi_n^{(2)}\rangle}_{=0}$$

$$E_n^{(2)} = \langle\varphi_n^{(0)}|H_1|\varphi_n^{(1)}\rangle = \sum_{m\neq n}\frac{|\langle\varphi_m^{(0)}|H_1|\varphi_n^{(0)}\rangle|^2}{E_n^{(0)}-E_m^{(0)}}$$

能量的二次修正.

左乘 $\langle\varphi_m^{(0)}|$

$$E_m^{(0)}\langle\varphi_m^{(0)}|\varphi_n^{(2)}\rangle + \langle\varphi_m^{(0)}|H_1|\varphi_n^{(1)}\rangle = E_n^{(1)}\langle\varphi_m^{(0)}|\varphi_n^{(1)}\rangle + E_n^{(0)}\langle\varphi_m^{(0)}|\varphi_n^{(2)}\rangle + E_n^{(2)}\langle\varphi_m^{(0)}|\varphi_n^{(0)}\rangle$$

$m\neq n$. 该项为0.

$$(E_m^{(0)}-E_n^{(0)})\langle\varphi_m^{(0)}|\varphi_n^{(2)}\rangle = E_n^{(1)}\langle\varphi_m^{(0)}|\varphi_n^{(1)}\rangle - \langle\varphi_m^{(0)}|H_1|\varphi_n^{(1)}\rangle$$

$$|\varphi_n^{(2)}\rangle = \sum_{m\neq n}|\varphi_m^{(0)}\rangle\langle\varphi_m^{(0)}|\varphi_n^{(2)}\rangle$$

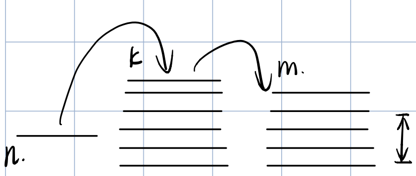
$$= \sum_{m\neq n}\frac{E_n^{(1)}\langle\varphi_m^{(0)}|\varphi_n^{(1)}\rangle}{E_m^{(0)}-E_n^{(0)}}|\varphi_m^{(0)}\rangle - \sum_{m\neq n}\frac{\langle\varphi_m^{(0)}|H_1|\varphi_n^{(1)}\rangle}{E_m^{(0)}-E_n^{(0)}}|\varphi_m^{(0)}\rangle$$

代入 $|\varphi_n^{(1)}\rangle$. $E_n^{(1)}$.

$$|\varphi_n^{(2)}\rangle = \sum_{m\neq n}\frac{\langle\varphi_n^{(0)}|H_1|\varphi_n^{(0)}\rangle}{E_m^{(0)}-E_n^{(0)}}\frac{\langle\varphi_m^{(0)}|H_1|\varphi_n^{(0)}\rangle}{E_n^{(0)}-E_m^{(0)}}|\varphi_m^{(0)}\rangle - \sum_{\substack{m\neq n\\ k\neq n}}\frac{\langle\varphi_m^{(0)}|H_1|\varphi_k^{(0)}\rangle\langle\varphi_k^{(0)}|H_1|\varphi_n^{(0)}\rangle}{(E_m^{(0)}-E_n^{(0)})(E_n^{(0)}-E_k^{(0)})}|\varphi_m^{(0)}\rangle$$

上式已知: $|\varphi_n^{(1)}\rangle = \sum_{m\neq n}\frac{\langle\varphi_m^{(0)}|H_1|\varphi_n^{(0)}\rangle}{E_n^{(0)}-E_m^{(0)}}|\varphi_m^{(0)}\rangle$

$\therefore |\varphi_n^{(1)}\rangle = \sum_{k\neq n}\frac{\langle\varphi_k^{(0)}|H_1|\varphi_n^{(0)}\rangle}{E_n^{(0)}-E_k^{(0)}}|\varphi_k^{(0)}\rangle$.



$$\varphi_n^{(2)} = \sum_{\substack{m\neq n\\ k\neq n}} - \frac{\langle\varphi_m^{(0)}|H_1|\varphi_k^{(0)}\rangle\langle\varphi_k^{(0)}|H_1|\varphi_n^{(0)}\rangle}{(E_n^{(0)}-E_k^{(0)})(E_m^{(0)}-E_n^{(0)})}|\varphi_m^{(0)}\rangle.$$

k和m的取值.

Degenerate perturbation theory 简并微扰理论.

two state model

如何区别简并和非简并.

$H_0|\psi_n^{(0)}\rangle = E_n^{(0)}|\psi_n^{(0)}\rangle$. $n=1,2$.

$$\begin{cases} H_0|\psi_1^{(0)}\rangle = E_1^{(0)}|\psi_1^{(0)}\rangle \\ H_0|\psi_2^{(0)}\rangle = E_2^{(0)}|\psi_2^{(0)}\rangle \end{cases}$$

$$H_0 = \begin{pmatrix} E_1^{(0)} & 0 \\ 0 & E_2^{(0)} \end{pmatrix}$$

$\langle\psi_m^{(0)}|V|\psi_n^{(0)}\rangle$. $V = \begin{pmatrix} V_{11} & V_{12} \\ V_{21} & V_{22} \end{pmatrix}$

$$H = \begin{pmatrix} E_1^{(0)}+V_{11} & V_{12} \\ V_{21} & E_2^{(0)}+V_{22} \end{pmatrix}$$

$H = H_0 + V$.

$E_n^{(1)} = \langle\psi_n^{(0)}|V|\psi_n^{(0)}\rangle = V_{nn}$

$E_1^{(1)} = V_{11}$, $E_2^{(1)} = V_{22}$

$E_1 = E_1^{(0)} + E_1^{(1)} = E_1^{(0)} + V_{11}$ E_1的一次修正

$E_2 = E_2^{(0)} + E_2^{(1)} = E_2^{(0)} + V_{22}$ E_2的一次修正

$E_1^{(1)}$. $E_2^{(1)}$. E_1. E_2 的意义.

$$|H-\lambda I| = \begin{vmatrix} E_1^{(0)}+V_{11}-\lambda & V_{12} \\ V_{21} & E_2^{(0)}+V_{22}-\lambda \end{vmatrix}$$

$$= (E_1^{(0)}+V_{11}-\lambda)(E_2^{(0)}+V_{22}-\lambda) - V_{12}V_{21} = 0.$$

H是厄米算符. $V_{12}=V_{21}=V$.

$$\frac{-b \pm \sqrt{b^2-4ac}}{2a}$$

$$\lambda^2 - (E_1^{(0)}+V_{11}+E_2^{(0)}+V_{22})\lambda + (E_1^{(0)}+V_{11})(E_2^{(0)}+V_{22}) - V^2 = 0.$$

$$\lambda = \frac{1}{2}(E_1^{(0)}+V_{11}+E_2^{(0)}+V_{22}) \pm \frac{1}{2}\sqrt{(E_1^{(0)}+V_{11}+E_2^{(0)}+V_{22})^2 - 4[(E_1^{(0)}+V_{11})(E_2^{(0)}+V_{22}) - V^2]}$$

$$\lambda = \frac{1}{2}(E_1^{(0)}+V_{11}+E_2^{(0)}+V_{22}) \pm \frac{1}{2}\sqrt{(E_1^{(0)}+V_{11}-E_2^{(0)}-V_{22})^2 + 4V^2}$$

比较大小.

if $V \ll |E_1^{(0)}+V_{11}-E_2^{(0)}-V_{22}|$. 则泰勒展开.

$$\lambda = \frac{1}{2}(E_1^{(0)}+V_{11}+E_2^{(0)}+V_{22}) \pm \frac{1}{2}(E_1^{(0)}+V_{11}-E_2^{(0)}-V_{22})\sqrt{1+\frac{4V^2}{(E_1^{(0)}+V_{11}-E_2^{(0)}-V_{22})^2}}$$

$$1 + \frac{V^2}{(E_1^{(0)}+V_{11}-E_2^{(0)}-V_{22})^2}$$

$$\lambda_1 = E_1^{(0)} + V_{11} + \frac{V^2}{E_1^{(0)}+V_{11}-E_2^{(0)}-V_{22}}$$

$$\lambda_2 = E_2^{(0)} + V_{22} + \frac{V^2}{E_2^{(0)}+V_{22}-E_1^{(0)}-V_{11}}$$

$$E_n^{(2)} = \frac{|\langle\psi_m^{(0)}|H_1|\psi_n^{(0)}\rangle|^2}{E_n^{(0)}-E_m^{(0)}}$$

if $V \gg |E_2^{(0)} + V_{22} - E_1^{(0)} - V_{11}|$

$$\lambda = \frac{1}{2}(E_1^{(0)} + V_{11} + E_2^{(0)} + V_{22}) \pm \left[V + \frac{(E_1^{(0)} + V_{11} - E_2^{(0)} - V_{22})^2}{8V}\right]$$

$$\sqrt{V^2 + \frac{(E_1^{(0)} + V_{11} - E_2^{(0)} - V_{22})^2}{4}}$$

$$\Downarrow \qquad \Uparrow$$

$$\boxed{V^2 + \frac{(E_1^{(0)} + V_{11} - E_2^{(0)} - V_{22})^2}{4} + \underbrace{\frac{(E_1^{(0)} + V_{11} - E_2^{(0)} - V_{22})^4}{64V^2}}_{=0.}}$$

$$H = \begin{pmatrix} E_1 & V \\ V & E_2 \end{pmatrix}. \qquad V \ll |E_1 - E_2|.$$

$$\lambda_1 = E_1 + \frac{V^2}{E_1 - E_2}.$$

$$\lambda_2 = E_2 + \frac{V^2}{E_2 - E_1}.$$

$E_1 = E_2 = E.$

$$\begin{pmatrix} E_1 & V \\ V & E_2 \end{pmatrix} \qquad \lambda = E \pm V.$$

简并微扰论 （有限简并）

$$E_n^{(2)} = \sum_{m \neq n} \frac{|\langle \varphi_m^{(0)} | H_1 | \varphi_n^{(0)} \rangle|^2}{E_n^{(0)} - E_m^{(0)}}$$

$$E_n^{(2)} = \sum_{m \neq n} \frac{|\langle \varphi_m^{(0)} | H_1 | \varphi_n^{(0)}(1) \rangle|^2}{E_n^{(0)} - E_m^{(0)}}$$

非简并时，$E_m^{(0)}$、$E_n^{(0)}$ 的态能量均不相同.

但当简并时，存在 $\varphi_n^{(0)}(1)$ 和 $\varphi_n^{(0)}(2)$ 对应相同的能量 $E_n^{(0)}$.

仅要求 $\varphi_m^{(0)} \neq \varphi_n^{(0)}(1)$ 时. 有可能存在 $\varphi_m^{(0)} = \varphi_n^{(0)}(2)$. 使 $E_m^{(0)} = E_n^{(0)}$.

$$\frac{\varphi_n^{(0)}(1) \quad \varphi_n^{(0)}(2)}{E_n^{(0)}}$$

此时分母为0.

$\Rightarrow$ 要求分子为0. 但 $\langle \varphi_m^{(0)} | H_1 | \varphi_n^{(0)}(1) \rangle = \langle \varphi_n^{(0)}(2) | H_1 | \varphi_n^{(0)}(1) \rangle \neq 0$.

∴ 此时不能使用非简并的结论.

$\Rightarrow$ 将 $\varphi_n^{(0)}(1)$. $\varphi_n^{(0)}(2)$ 重新线性组合构造新的基底 $\tilde{\varphi}_n^{(0)}(1)$. $\tilde{\varphi}_n^{(0)}(2)$.

使满足 $\langle \tilde{\varphi}_m^{(0)} | H_1 | \tilde{\varphi}_n^{(0)}(1) \rangle = \langle \tilde{\varphi}_n^{(0)}(2) | H_1 | \tilde{\varphi}_n^{(0)}(1) \rangle = 0$ 恒成立.

$\tilde{\varphi}_n^{(0)}(1) = \quad a\varphi_n^{(0)}(1) + b\varphi_n^{(0)}(2)$

$\tilde{\varphi}_n^{(0)}(2) = \quad c\varphi_n^{(0)}(1) + d\varphi_n^{(0)}(2)$

且 $\langle \tilde{\varphi}_n^{(0)}(i) | \tilde{\varphi}_n^{(0)}(j) \rangle = \delta_{ij}$. ①

$\langle \tilde{\varphi}_n^{(0)}(1) | H_1 | \tilde{\varphi}_n^{(0)}(2) \rangle \equiv 0$. ②

H_1 是厄米算符. 所有本征态正交归一. ① 成立.

$$\begin{cases} H_1 | \tilde{\varphi}_n^{(0)}(1) \rangle = E_n^{(0)} \tilde{\varphi}_n^{(0)}(1). \\ H_1 | \tilde{\varphi}_n^{(0)}(2) \rangle = E_n'^{(0)} \tilde{\varphi}_n^{(0)}(2). \end{cases} \longrightarrow \begin{aligned} \langle \tilde{\varphi}_n^{(0)}(2) | H_1 | \tilde{\varphi}_n^{(0)}(1) \rangle &= \langle \tilde{\varphi}_n^{(0)}(2) | E_n^{(0)} | \tilde{\varphi}_n^{(0)}(1) \rangle \\ &= E_n^{(0)} \cdot 0 \\ &= 0 \end{aligned}$$

② 成立.

求 $\hat{H}'$ 的本征态.

$\because \hat{H}' | \varphi_n^{(0)}(1) \rangle = \hat{H}'_{11} | \varphi_n^{(0)}(1) \rangle + \hat{H}'_{21} | \varphi_n^{(0)}(2) \rangle +$ 其余.

$\hat{H}'$