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

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

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

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

$$\int \psi^\dagger \psi \mathrm{d}\tau = 1 \tag{2}$$

做虚变化

$$\psi \to \psi + \delta\psi \tag{3}$$

$$\psi^\dagger \to \psi^\dagger + \delta\psi^\dagger \tag{4}$$

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

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

$$\delta\bar{H} = \delta \int \psi^\dagger H\psi \mathrm{d}\tau = 0 \tag{6}$$

由于约束条件

$$\int \psi^\dagger \psi \mathrm{d}\tau = 1 \tag{7}$$

引入 Lagrange 乘子

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

故

$$H\psi = \lambda\psi \qquad\qquad H^\dagger\psi^\dagger = \lambda\psi^\dagger \tag{9}$$

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

假设

$$H\psi_\lambda = E_\lambda\psi_\lambda \tag{10}$$

则

$$E_\lambda = \int \psi_\lambda^\dagger H\psi_\lambda \mathrm{d}\tau \tag{11}$$

ψ_λ 满足

$$\int \psi_\lambda^\dagger \psi_\lambda \mathrm{d}\tau = 1 \tag{12}$$

做虚变化

$$\psi_\lambda \to \psi_\lambda + \delta\psi_\lambda \tag{13}$$

$$\psi_\lambda^\dagger \to \psi_\lambda^\dagger + \delta\psi_\lambda^\dagger \tag{14}$$

由于虚变化前后都要满足 Eq.(12)

$$\int (\psi_\lambda^\dagger + \delta\psi_\lambda^\dagger)(\psi_\lambda + \delta\psi_\lambda)\mathrm{d}\tau = \int \mathrm{d}\tau[\psi_\lambda^\dagger\psi_\lambda + \psi^\dagger(\delta\psi) + (\delta\psi_\lambda^\dagger)\psi_\lambda + (\delta\psi_\lambda^\dagger)(\delta\psi_\lambda)] = 1 \tag{15}$$

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

接下来看 E_λ

$$E_\lambda \to E_\lambda + \delta E_\lambda = \int \mathrm{d}\tau(\psi_\lambda^\dagger + \delta\psi_\lambda^\dagger)H(\psi_\lambda + \delta\psi_\lambda) \tag{17}$$

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

$$H\psi_\nu = E_\nu\psi_\nu \tag{19}$$

ψ_ν 构成完备积，用它来展开 ψ_λ

$$\delta\psi_\lambda = \sum_\nu \delta a_\nu\psi_\nu \tag{20}$$

将 $\delta\psi$ 代入 Eq.(18)

$$\delta E_\lambda = -E_\lambda\sum_\nu |\delta a_\nu|^2 + \sum_\nu E_\nu|\delta a_\nu|^2 = 0 \tag{21}$$

当 $\delta a_\nu \neq 0$ 时

$$\frac{\delta E_\lambda}{\delta a_\nu} = 0 \tag{22}$$

对于基态 $E_\lambda = E_0$

$$\delta E_\lambda = -E_0\sum_\nu |\delta a_\nu|^2 + \sum_\nu E_\nu|\delta a_\nu|^2 \geq -E_0\sum_\nu |\delta a_\nu|^2 + E_0\sum_\nu |\delta a_\nu|^2 = 0 \tag{23}$$

$$\frac{\delta^2 E_\lambda}{\delta a_\nu^2} \geq 0 \tag{24}$$

基态中 E_λ 即严格解对应极小值。在 Hilbert 空间中 $\int \mathrm{d}\tau|\psi|^2 = 1$ 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

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

同样我们也有

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

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

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

对应

$$J(y) = \int_a^b \left[P(x)y'^2 + Q(x)y^2\right] \mathrm{d}x \tag{28}$$

变分条件是 $\int_a^b y^2\mathrm{d}x = 1,\ y(a) = 0,\ y(b) = 0$。

2 Ritz Variational Theory

从另一个角度看

$$\int \psi^\dagger H\psi\mathrm{d}\tau \geq E_0 \tag{29}$$

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

$$\psi = \sum_{n=0}^{\infty} c_n\varphi_n \tag{30}$$

$$H\varphi_0 = E_0\varphi_0 \tag{31}$$

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

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

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

$$\int |\psi|^2\mathrm{d}q = 1 \tag{33}$$

计算 $\bar{H}$

$$\bar{H}(c_1, \cdots, c_N) = \frac{\int \mathrm{d}q\psi^\dagger(q, c_1, \cdots, c_N)H\psi(q, c_1, \cdots, c_N)}{\int |\psi|^2\mathrm{d}q} \tag{34}$$

$$\delta\bar{H}(c_1, \cdots, c_N) = \sum_{i=1}^{N} \frac{\partial\bar{H}}{\partial c_i}\delta c_i = 0 \tag{35}$$

故

$$\frac{\partial\bar{H}}{\partial c_i} = 0 \qquad \text{for} \qquad i = 1, 2, 3, \cdots \tag{36}$$

Example

$$H=-\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}x^2}+\frac{k}{2}x^2 \tag{37}$$

用变分原理解 $H\psi(x)=E\psi(x)$，取试探波函数

$$\psi(x)=ce^{-\lambda x^2}=\left(\frac{2\lambda}{\pi}\right)^{\frac{1}{4}}e^{-\lambda x^2} \tag{38}$$

计算 $\bar{H}$

$$\begin{aligned}\bar{H}&=\int\psi^\dagger H\psi\mathrm{d}x\\&=\int\psi^\dagger\left(-\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}x^2}+\frac{k}{2}x^2\right)ce^{-\lambda x^2}\mathrm{d}x\\&=\int\left(\frac{2\lambda}{\pi}\right)^{\frac{1}{2}}\left[\left(\frac{k}{2}-2\lambda^2\right)x^2+\lambda\right]e^{-2\lambda x^2}\mathrm{d}x\\&=\frac{\lambda}{2}+\frac{k}{8\lambda}\end{aligned} \tag{39}$$

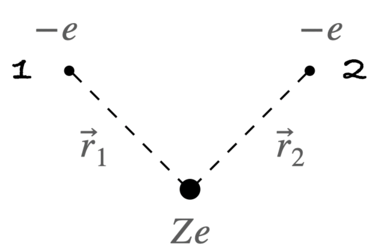
$$\frac{\partial\bar{H}}{\partial\lambda}=\frac{1}{2}-\frac{k}{8\lambda^2}=0 \tag{40}$$

得到 $\lambda=\frac{1}{2}\sqrt{k}$，代回 Eq.(39) 和 Eq.(38)，得

$$\bar{H}=\frac{1}{2}\sqrt{k} \tag{41}$$

$$\psi=\left(\frac{\sqrt{k}}{\pi}\right)^{\frac{1}{4}}e^{-\frac{1}{2}\sqrt{k}x^2} \tag{42}$$

3 He Atom



$$H=-\frac{\hbar^2}{2m}\left(\nabla_1^2+\nabla_2^2\right)-\frac{Ze^2}{r_1}-\frac{Ze^2}{r_2}+V\left(|\vec{r}_1-\vec{r}_2|\right) \tag{43}$$

取自然单位制 (natural unit)，令 $e^2=1,m=1,\hbar=1$

$$H=-\frac{1}{2}\left(\nabla_1^2+\nabla_2^2\right)-\frac{Z}{r_1}-\frac{Z}{r_2}+V\left(|\vec{r}_1-\vec{r}_2|\right) \tag{44}$$

薛定谔方程

$$H(\vec{r}_1,\vec{r}_2)\Psi(\vec{r}_1,\sigma_1;\vec{r}_2,\sigma_2)=E\Psi(\vec{r}_1,\sigma_1;\vec{r}_2,\sigma_2) \tag{45}$$

波函数分为空间部分和自旋部分

$$\Psi(\vec{r}_1,\sigma_1;\vec{r}_2,\sigma_2)=\Psi(\vec{r}_1,\vec{r}_2)\chi(\sigma_1,\sigma_2)=\begin{cases}\Psi(\vec{r}_1,\vec{r}_2)\chi_s(\sigma_1,\sigma_2) & (\text{singlet 单态})\\\Psi(\vec{r}_1,\vec{r}_2)\chi_t(\sigma_1,\sigma_2) & (\text{triplet 三重态})\end{cases} \tag{46}$$

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

$$H_0 = -\frac{1}{2}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{Z}{r_1} - \frac{Z}{r_2} \tag{47}$$

$$H = H_0 + V\left(|\vec{r}_1 - \vec{r}_2|\right) = H_0 + H' \tag{48}$$

First Method: Perturbation Theory

$$H_0\Psi^{(0)}(\vec{r}_1, \vec{r}_2) = E_0\Psi^{(0)}(\vec{r}_1, \vec{r}_2) \tag{49}$$

$$\Psi^{(0)}(\vec{r}_1, \vec{r}_2) = \psi_{100}(\vec{r}_1)\psi_{100}(\vec{r}_2) \tag{50}$$

ψ_{100} 是基态 $(n = 1, l = 0, m = 0)$ 氢原子薛定谔方程的解，满足

$$\left(-\frac{1}{2}\nabla^2 - \frac{Z}{r}\right)\psi_{100}(\vec{r}) = \varepsilon_0^{(0)}\psi_{100}(\vec{r}) \tag{51}$$

$$\varepsilon_0^{(0)} = -\left.\frac{Z^2}{2n^2}\right|_{n=1} = -\frac{1}{2}Z^2 \tag{52}$$

$$\psi_{100}(\vec{r}) = \frac{Z^{\frac{3}{2}}}{\sqrt{\pi}}e^{-Zr} \tag{53}$$

在微扰论中，基态 He 原子

$$E_0 = E_0^{(0)} + E_0^{(1)} + E_0^{(2)} + \cdots \tag{54}$$

根据之前我们计算的结果

$$E_0^{(0)} = 2\varepsilon_0^{(0)} = -Z^2 \tag{55}$$

接下来计算一级微扰 $E_0^{(1)}$

$$\begin{aligned} E_0^{(1)} &= \left\langle \Psi^{(0)}\right| H' \left|\Psi^{(0)}\right\rangle \\ &= \int \mathrm{d}\vec{r}_1\mathrm{d}\vec{r}_2\Psi^{(0)\dagger}(\vec{r}_1, \vec{r}_2)H'\Psi^{(0)}(\vec{r}_1, \vec{r}_2) \\ &= \int \mathrm{d}\vec{r}_1\mathrm{d}\vec{r}_2\Psi^{(0)\dagger}(\vec{r}_1, \vec{r}_2)V(|\vec{r}_1 - \vec{r}_2|)\Psi^{(0)}(\vec{r}_1, \vec{r}_2) \\ &= \int \mathrm{d}\vec{r}_1\mathrm{d}\vec{r}_2|\psi_{100}(r_1)|^2|\psi_{100}(r_2)|^2V(|\vec{r}_1 - \vec{r}_2|) \\ &= \int \mathrm{d}\vec{r}_1\mathrm{d}\vec{r}_2\left(\frac{z^3}{\pi}\right)^2e^{-2Z(r_1+r_2)}V(|\vec{r}_1 - \vec{r}_2|) \end{aligned} \tag{56}$$

令

$$V(|\vec{r}_1 - \vec{r}_2|) = \frac{1}{|\vec{r}_1 - \vec{r}_2|} = \frac{1}{r_{12}} \tag{57}$$

$$E_0^{(1)} = \int \mathrm{d}\vec{r}_1\mathrm{d}\vec{r}_2\left(\frac{z^3}{\pi}\right)^2e^{-2Z(r_1+r_2)}\frac{1}{r_{12}} = \left(\frac{z^3}{\pi}\right)^2I(Z) \tag{58}$$

其中

$$I(Z) = \int \mathrm{d}\vec{r}_1\mathrm{d}\vec{r}_2e^{-2Z(r_1+r_2)}\frac{1}{r_{12}} = \frac{5\pi^2}{8\lambda^5} \tag{59}$$

代入 Eq.(58) 得到

$$E_0^{(1)} = \frac{5}{8}Z \tag{60}$$

$$E_0 = E_0^{(0)} + E_0^{(1)} = -Z^2 + \frac{5}{8}Z \tag{61}$$

二级微扰

$$E_0^{(2)} = \sum_n{}' \frac{|\langle 0| H' |n\rangle|^2}{E_0^{(0)} - E_n^{(0)}} \tag{62}$$

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

$$\Psi(\vec{r}_1, \vec{r}_2) = \frac{Z^3}{\pi} \exp[-Z(r_1 + r_2)] \tag{63}$$

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

$$\Phi(\vec{r}_1, \vec{r}_2, \lambda) = \frac{\lambda^3}{\pi} \exp[-\lambda(r_1 + r_2)] \tag{64}$$

将试探波函数写成以下形式

$$\Phi(\vec{r}_1, \vec{r}_2) = U(r_1)U(r_2) \tag{65}$$

$$U(r) = \sqrt{\frac{\lambda^3}{\pi}} \exp(-\lambda r) \tag{66}$$

计算 $\bar{H}$

$$\begin{aligned} \bar{H} &= \int \mathrm{d}\vec{r}_1 \mathrm{d}\vec{r}_2 \Phi^\dagger \left(-\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1} - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_2} + \frac{1}{r_{12}}\right)\Phi \\ &= \int \mathrm{d}\vec{r}_1 \mathrm{d}\vec{r}_2 U(r_1)U(r_2) \left(-\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1} - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_2} + \frac{1}{r_{12}}\right) U(r_1)U(r_2) \end{aligned} \tag{67}$$

$U(r)$ 是类氢离子的波函数，满足以下微分方程

$$\left(-\frac{1}{2}\nabla^2 - \frac{\lambda}{r}\right) U(r) = -\frac{\lambda^2}{2}U(r) \tag{68}$$

$$\begin{aligned} \bar{H} &= \int \mathrm{d}\vec{r}_1 \mathrm{d}\vec{r}_2 U(r_1)U(r_2) \left(-\frac{1}{2}\nabla_1^2 - \frac{\lambda}{r_1} - \frac{Z-\lambda}{r_1} - \frac{1}{2}\nabla_2^2 - \frac{\lambda}{r_1} - \frac{Z-\lambda}{r_1} + \frac{1}{r_{12}}\right) U(r_1)U(r_2) \\ &= \int \mathrm{d}\vec{r}_1 \mathrm{d}\vec{r}_2 \left(-\lambda^2 - \frac{Z-\lambda}{r_1} - \frac{Z-\lambda}{r_2} + \frac{1}{r_{12}}\right)\left(\frac{\lambda^3}{\pi}\right)^2 \exp[-2\lambda(r_1 + r_2)] \end{aligned} \tag{69}$$

类氢原子 $\frac{1}{r}$ 的平均值

$$\int U^2(r)\frac{1}{r}\mathrm{d}\vec{r} = \frac{\lambda}{a_0} \tag{70}$$

a_0 是玻尔原子半径，取自然单位制 $a_0 = 1$

$$\int U^2(r)\frac{1}{r}\mathrm{d}\vec{r} = \lambda \tag{71}$$

故

$$\bar{H} = -\lambda^2 - 2(Z-\lambda)\lambda + \frac{5}{8}\lambda = \lambda^2 - \left(2Z - \frac{5}{8}\right)\lambda \tag{72}$$

$$\frac{\partial \bar{H}}{\partial \lambda} = 2\lambda - 2Z + \frac{5}{8} = 0 \qquad \Rightarrow \qquad \lambda = Z - \frac{5}{16} \tag{73}$$

代回 Eq.(72)

$$\bar{H} = \left(Z - \frac{5}{16}\right)^2 - 2\left(Z - \frac{5}{16}\right)^2 = -\left(Z - \frac{5}{16}\right)^2 \tag{74}$$

$$E \le -\left(Z-\frac{5}{16}\right)^2 = -Z^2+\frac{5}{8}Z-\frac{25}{256} \tag{75}$$

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

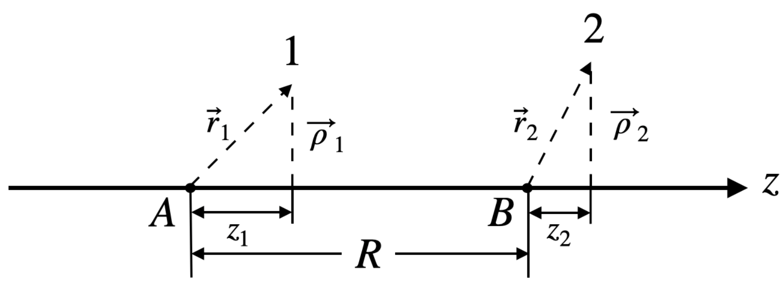
$$\Phi(\vec{r}_1,\vec{r}_2,\lambda)=\frac{\lambda^3}{\pi}\exp[-\lambda(r_1+r_2)] \tag{76}$$

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

$$\Phi(\vec{r}_1,\vec{r}_2,\lambda)=\frac{\lambda^3}{\pi}\exp[-\lambda(r_1+r_2)](1+cr_{12}) \tag{77}$$

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)



$$\vec{r}=(\vec{\rho},z) \qquad r^2=\rho^2+z^2 \tag{78}$$

$$H=H_0+H' \tag{79}$$

$$H_0=-\frac{1}{2}\left(\nabla_1^2+\nabla_2^2\right)-\frac{1}{r_1}-\frac{1}{r_2} \tag{80}$$

$$H'=-\frac{1}{r_{1B}}-\frac{1}{r_{2A}}+\frac{1}{r_{12}}+\frac{1}{R} \tag{81}$$

讨论两个基态氢原子

$$\Phi_0(\vec{r}_1,\vec{r}_2)=\varphi_{100}(\vec{r}_1)\varphi_{100}(\vec{r}_2) \tag{82}$$

令 $R\to\infty$，展开 H'

$$\begin{aligned}\frac{1}{r_{12}}&=\frac{1}{|\vec{r}_1-\vec{r}_2|}=\frac{1}{\sqrt{(R+z_2-z_1)^2+(\vec{\rho}_1-\vec{\rho}_2)^2}}\\&=\frac{1}{R}\left[1+\frac{2(z_2-z_1)}{R}+\frac{(z_2-z_1)^2+(\vec{\rho}_1-\vec{\rho}_2)^2}{R^2}\right]^{-\frac{1}{2}}\end{aligned} \tag{83}$$

当 $x\to0$ 时，$(1+x)^{-\frac{1}{2}}=1-\frac{1}{2}x+\frac{3}{8}x^2-\frac{5}{16}x^3+\cdots$，利用这个关系式展开上式 $(R\to\infty)$

$$\begin{aligned}\frac{1}{r_{12}}&=\frac{1}{R}\left[1-\frac{(z_2-z_1)}{R}-\frac{(z_2-z_1)^2+(\vec{\rho}_1-\vec{\rho}_2)^2}{2R^2}+\frac{3(z_2-z_1)^2}{2R^2}\right]\\&=\frac{1}{R}\left[1-\frac{(z_2-z_1)}{R}+\frac{2(z_2-z_1)^2-(\vec{\rho}_1-\vec{\rho}_2)^2}{2R^2}\right]\end{aligned} \tag{84}$$

$$\frac{1}{r_{1B}}=\frac{1}{\sqrt{(R-z_1)^2+\rho_1^2}}=\frac{1}{R}\left[1-\frac{2z_1}{R}+\frac{r_1^2}{R^2}\right]^{-\frac{1}{2}}=\frac{1}{R}\left(1+\frac{z_1}{R}-\frac{r_1^2}{2R^2}+\frac{3z_1^2}{2R^2}\right) \tag{85}$$

$$\frac{1}{r_{2A}} = \frac{1}{\sqrt{(R+z_2)^2+\rho_2^2}} = \frac{1}{R}\left[1+\frac{2z_2}{R}+\frac{r_2^2}{R^2}\right]^{-\frac{1}{2}} = \frac{1}{R}\left(1-\frac{z_2}{R}-\frac{r_2^2}{2R^2}+\frac{3z_2^2}{2R^2}\right) \tag{86}$$

故

$$\begin{aligned}
H' =& -\frac{1}{r_{1B}}-\frac{1}{r_{2A}}+\frac{1}{r_{12}}+\frac{1}{R}\\
=&\frac{1}{R}\left\{-\left(1+\frac{z_1}{R}-\frac{r_1^2}{2R^2}+\frac{3z_1^2}{2R^2}\right)-\left(1-\frac{z_2}{R}-\frac{r_2^2}{2R^2}+\frac{3z_2^2}{2R^2}\right)\right.\\
&\left.+\left[1-\frac{(z_2-z_1)}{R}+\frac{2(z_2-z_1)^2-(\vec{\rho}_1-\vec{\rho}_2)^2}{2R^2}\right]+1\right\}\\
=&\frac{1}{R}\left[\frac{2(z_2-z_1)^2-(\vec{\rho}_1-\vec{\rho}_2)^2}{2R^2}+\frac{r_1^2+r_2^2}{2R^2}-\frac{3(z_1^2+z_2^2)}{2R^2}\right]\\
=&\frac{1}{R^3}\left(\vec{\rho}_1\cdot\vec{\rho}_2-2z_1z_2\right)=\frac{1}{R^3}\left(\vec{r}_1\cdot\vec{r}_2-3z_1z_2\right)
\end{aligned} \tag{87}$$

First Method: Perturbation Theory

一级微扰

$$E^{(1)} = \langle 0|\, H'\, |0\rangle = \int \mathrm{d}\vec{r}_1\mathrm{d}\vec{r}_2\varphi_{100}^\dagger(r_1)\varphi_{100}^\dagger(r_2)\frac{1}{R^3}\left(\vec{r}_1\cdot\vec{r}_2-3z_1z_2\right)\varphi_{100}(r_1)\varphi_{100}(r_2)=0 \tag{88}$$

二级微扰

$$E^{(2)} = {\sum_n}' \frac{|\langle 0|\, H'\, |n\rangle|^2}{E_0-E_n} \tag{89}$$

二级微扰很难计算，需要先做近似

$$E_0 = -\frac{1}{2}\frac{1}{n^2}\bigg|_{n=1}\cdot 2 = -1 \tag{90}$$

$$E_1 = -\frac{1}{2}\frac{1}{n^2}\bigg|_{n=2}\cdot 2 = -\frac{1}{4} \tag{91}$$

因此

$$\begin{aligned}
E^{(2)} \geq& {\sum_n}'\frac{|\langle 0|\, H'\, |n\rangle|^2}{E_0-E_1} = \frac{1}{E_0-E_1}{\sum_n}'|\langle 0|\, H'\, |n\rangle|^2\\
=&\frac{1}{E_0-E_1}{\sum_n}'\langle 0|\, H'\, |n\rangle\langle n|\, H'\, |0\rangle\\
=&\frac{1}{E_0-E_1}\left(\sum_n\langle 0|\, H'\, |n\rangle\langle n|\, H'\, |0\rangle-\langle 0|\, H'\, |0\rangle\langle 0|\, H'\, |0\rangle\right)\\
=&\frac{1}{E_0-E_1}\left[\langle 0|\, H'^2\, |0\rangle-(\langle 0|\, H'\, |0\rangle)^2\right]=\frac{1}{E_0-E_1}\langle 0|\, H'^2\, |0\rangle\\
=&\frac{1}{E_0-E_1}\int\mathrm{d}\vec{r}_1\mathrm{d}\vec{r}_2\frac{1}{R^6}\left(\vec{r}_1\cdot\vec{r}_2-3z_1z_2\right)^2\Phi_0^\dagger(\vec{r}_1,\vec{r}_2)\Phi_0(\vec{r}_1,\vec{r}_2)\\
=&\frac{1}{E_0-E_1}\frac{1}{R^6}\int\mathrm{d}\vec{r}_1\mathrm{d}\vec{r}_2\left[(\vec{r}_1\cdot\vec{r}_2)^2-6\vec{r}_1\cdot\vec{r}_2z_1z_2+9z_1^2z_2^2\right]|\varphi_{100}(r_1)|^2|\varphi_{100}(r_2)|^2\\
=&\frac{1}{E_0-E_1}\frac{1}{R^6}\int\mathrm{d}\vec{r}_1\mathrm{d}\vec{r}_2(x_1^2x_2^2+y_1^2y_2^2+4z_1^2z_2^2+2x_1x_2y_1y_2-4x_1x_2z_1z_2-4y_1y_2z_1z_2)|\Phi_0(\vec{r}_1,\vec{r}_2)|^2\\
=&\frac{1}{E_0-E_1}\frac{6}{R^6}\left(\int\mathrm{d}\vec{r}_1|\varphi_{100}(r_1)|^2\frac{r_1^2}{3}\right)^2=\frac{1}{E_0-E_1}\frac{6}{R^6}=-\frac{8}{R^6}
\end{aligned} \tag{92}$$

$$\Delta E = E^{(1)}+E^{(2)} \geq -\frac{8}{R^6} \tag{93}$$

Second Method: Variational Principle

假设

$$\psi(\vec{r}_1,\vec{r}_2)=\varphi_{100}(r_1)\varphi_{100}(r_2)(1+\lambda H')=\Phi_0(\vec{r}_1,\vec{r}_2)(1+\lambda H') \tag{94}$$

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

$$\bar{H}=\frac{\iint \mathrm{d}\vec{r}_1\mathrm{d}\vec{r}_2\psi^\dagger(\vec{r}_1,\vec{r}_2)(H_0+H')\psi(\vec{r}_1,\vec{r}_2)}{\iint \mathrm{d}\vec{r}_1\mathrm{d}\vec{r}_2|\psi(\vec{r}_1,\vec{r}_2)|^2} \tag{95}$$

令分子为 N，分母为 D

$$D=\iint \mathrm{d}\vec{r}_1\mathrm{d}\vec{r}_2|\psi(\vec{r}_1,\vec{r}_2)|^2=\iint \mathrm{d}\vec{r}_1\mathrm{d}\vec{r}_2|\Phi_0(\vec{r}_1,\vec{r}_2)|^2(1+\lambda H')^2=1+\lambda^2\langle 0|H'^2|0\rangle \tag{96}$$

$$\begin{aligned}
N&=\iint \mathrm{d}\vec{r}_1\mathrm{d}\vec{r}_2\psi^\dagger(\vec{r}_1,\vec{r}_2)(H_0+H')\psi(\vec{r}_1,\vec{r}_2)\\
&=\iint \mathrm{d}\vec{r}_1\mathrm{d}\vec{r}_2\Phi_0^\dagger(\vec{r}_1,\vec{r}_2)(1+\lambda H')(H_0+H')(1+\lambda H')\Phi_0(\vec{r}_1,\vec{r}_2)\\
&=\langle 0|H_0+\lambda H_0H'+H'+\lambda H'^2+\lambda H'H_0+\lambda^2H'H_0H'+\lambda H'^2+\lambda^2H'^3|0\rangle\\
&=E_0+(2\lambda E_0+1)\langle 0|H'|0\rangle+2\lambda\langle 0|H'^2|0\rangle+\lambda^2\langle 0|H'H_0H'|0\rangle+\lambda^2\langle 0|H'^3|0\rangle\\
&=E_0+2\lambda\langle 0|H'^2|0\rangle+\lambda^2\langle 0|H'H_0H'|0\rangle
\end{aligned} \tag{97}$$

接下来证明 $\langle 0|H'H_0H'|0\rangle=0$

$$\begin{aligned}
\langle 0|H'H_0H'|0\rangle&=\langle 0|\frac{1}{R^3}(x_1x_2+y_1y_2-2z_1z_2)H_0\frac{1}{R^3}(x_1x_2+y_1y_2-2z_1z_2)|0\rangle\\
&=\frac{1}{R^6}\int \mathrm{d}\vec{r}_1\mathrm{d}\vec{r}_2\Phi_0^\dagger(\vec{r}_1,\vec{r}_2)(x_1x_2H_0x_1x_2+x_1x_2H_0y_1y_2-2x_1x_2H_0z_1z_2+y_1y_2H_0x_1x_2+\\
&\quad y_1y_2H_0y_1y_2-2y_1y_2H_0z_1z_2-2z_1z_2H_0x_1x_2-2z_1z_2H_0y_1y_2+4z_1z_2H_0z_1z_2)\Phi_0(\vec{r}_1,\vec{r}_2)\\
&=\frac{1}{R^6}\int \mathrm{d}\vec{r}_1\mathrm{d}\vec{r}_2\Phi_0^\dagger(\vec{r}_1,\vec{r}_2)(x_1x_2H_0x_1x_2+y_1y_2H_0y_1y_2+4z_1z_2H_0z_1z_2)\Phi_0(\vec{r}_1,\vec{r}_2)\\
&=\frac{6}{R^6}\int \mathrm{d}\vec{r}_1\mathrm{d}\vec{r}_2\Phi_0^\dagger(\vec{r}_1,\vec{r}_2)x_1x_2[h_0(\vec{r}_1)+h_0(\vec{r}_2)]x_1x_2\Phi_0(\vec{r}_1,\vec{r}_2)\\
&=\frac{12}{R^6}\int \mathrm{d}\vec{r}_1\mathrm{d}\vec{r}_2\Phi_0^\dagger(\vec{r}_1,\vec{r}_2)x_1x_2h_0(\vec{r}_1)x_1x_2\Phi_0(\vec{r}_1,\vec{r}_2)\\
&=\frac{12}{R^6}\int \varphi_{100}^\dagger(r_1)x_1h_0(\vec{r}_1)x_1\varphi_{100}(r_1)\mathrm{d}\vec{r}_1\int \varphi_{100}^\dagger(r_2)x_2^2\varphi_{100}(r_2)\mathrm{d}\vec{r}_2\\
&=\frac{12}{R^6}A\int \varphi_{100}^\dagger(r_2)x_2^2\varphi_{100}(r_2)\mathrm{d}\vec{r}_2
\end{aligned} \tag{98}$$

其中

$$h_0(\vec{r})=-\frac{1}{2}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+V(r) \tag{99}$$

$$h_0(\vec{r})\varphi_{100}(\vec{r})=\varepsilon_0\varphi_{100}(\vec{r}) \tag{100}$$

$$\varepsilon_0=\frac{1}{2}E_0=-\frac{1}{2}\frac{1}{n^2}\bigg|_{n=1}=-\frac{1}{2} \tag{101}$$

$$\langle r\rangle=\int r|\varphi(r)|^2\mathrm{d}\vec{r}=4\pi\int r^3|\varphi(r)|^2\mathrm{d}r=4\int_0^\infty r^3e^{-2r}\mathrm{d}r=4\cdot\frac{3}{8}=\frac{3}{2} \tag{102}$$

$$\langle r^2\rangle=\int r^2|\varphi(r)|^2\mathrm{d}\vec{r}=4\pi\int r^4|\varphi(r)|^2\mathrm{d}r=4\int_0^\infty r^4e^{-2r}\mathrm{d}r=4\cdot\frac{3}{4}=3 \tag{103}$$

$$\begin{aligned}
A &= \int \varphi^{\dagger}_{100}(r_1) x_1 h_0(\vec{r}_1) x_1 \varphi_{100}(r_1) \mathrm{d}\vec{r}_1 \\
&= \int \varphi^{\dagger}_{100}(r) x \left[-\frac{1}{2} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V(r) \right] x \varphi_{100}(r) \mathrm{d}\vec{r} \\
&= \int \varphi^{\dagger}_{100}(r) \left[-\frac{1}{2} x \frac{\partial^2}{\partial x^2} x - \frac{1}{2} x^2 \left(\frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + x^2 V(r) \right] \varphi_{100}(r) \mathrm{d}\vec{r} \\
&= \int \varphi^{\dagger}_{100}(r) \left[-x \frac{\partial}{\partial x} - \frac{1}{2} x^2 \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + x^2 V(r) \right] \varphi_{100}(r) \mathrm{d}\vec{r} \\
&= \int \varphi^{\dagger}_{100}(r) x^2 h_0(\vec{r}) \varphi_{100}(r) \mathrm{d}\vec{r} - \int \varphi^{\dagger}_{100}(r) x \frac{\partial}{\partial x} \varphi_{100}(r) \mathrm{d}\vec{r}
\end{aligned} \tag{104}$$

$$\int \varphi^{\dagger}_{100}(r) x \frac{\partial}{\partial x} \varphi_{100}(r) \mathrm{d}\vec{r} = -\int \varphi^{\dagger}_{100}(r) \frac{r}{3} \varphi_{100}(r) \mathrm{d}\vec{r} = -\frac{1}{3} \langle r \rangle \tag{105}$$

$$\begin{aligned}
A = &\int \varphi^{\dagger}_{100}(r) x^2 h_0(\vec{r}) \varphi_{100}(r) \mathrm{d}\vec{r} + \frac{1}{3} \langle r \rangle = \frac{1}{3} \varepsilon_0 \int \varphi^{\dagger}_{100}(r) r^2 \varphi_{100}(r) \mathrm{d}\vec{r} + \frac{1}{3} \langle r \rangle \\
= &\frac{1}{3} \varepsilon_0 \langle r^2 \rangle + \frac{1}{3} \langle r \rangle = \frac{1}{3} \left(-\frac{1}{2} \langle r^2 \rangle + \langle r \rangle \right) = \frac{1}{3} \left(-\frac{1}{2} \cdot 3 + \frac{3}{2} \right) = 0
\end{aligned} \tag{106}$$

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

$$q = \langle 0 | H'^2 | 0 \rangle = \frac{6}{R^6} \tag{109}$$

$$\bar{H} = \frac{E_0 + 2\lambda q}{1 + \lambda^2 q} \tag{110}$$

$$\frac{\partial \bar{H}}{\partial \lambda} = \frac{2q \left(1 + \lambda^2 q\right) - \left(E_0 + 2\lambda q\right) 2\lambda q}{\left(1 + \lambda^2 q\right)^2} = 0 \tag{111}$$

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 $x \to 0$ 时，$\frac{1}{1+x} = 1 - x$，由于 q 是小量，$\bar{H}$ 化为

$$\bar{H} = \frac{E_0 + 2\lambda q}{1 + \lambda^2 q} \doteq (E_0 + 2\lambda q)(1 - \lambda^2 q) \doteq E_0 + (2\lambda - \lambda^2 E_0) q \tag{114}$$

$$\frac{\partial \bar{H}}{\partial \lambda} = (2 - 2\lambda E_0) q = 0 \quad \Rightarrow \quad \lambda = \frac{1}{E_0} \tag{115}$$

$$\bar{H} = E_0 + \frac{1}{E_0} q \tag{116}$$

因此

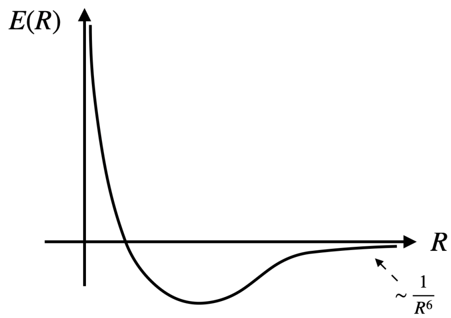
$$\Delta E \le \frac{1}{E_0} q = \frac{1}{E_0} \langle 0 | H'^2 | 0 \rangle = \frac{1}{E_0} \frac{6}{R^6} = -\frac{6}{R^6} \tag{117}$$

前面我们通过微扰论已经给出结果

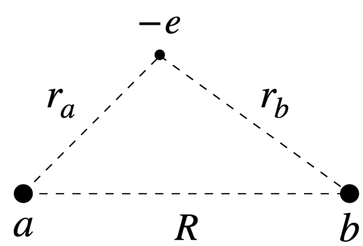
$$\Delta E \geq -\frac{8}{R^6} \tag{118}$$

因此，在自然单位制下

$$-\frac{8}{R^6} \leq \Delta E \leq -\frac{6}{R^6} \tag{119}$$



5 Hydrogen Molecule Ion 氢分子离子



$$H = \frac{1}{R} + H_{\rm el} \tag{120}$$

电子部分哈密顿量

$$H_{\rm el} = -\frac{1}{2}\nabla^2 - \frac{1}{r_a} - \frac{1}{r_b} \tag{121}$$

我们的目的是解薛定谔方程

$$H\psi = E\psi \tag{122}$$

或写成

$$H_{\rm el}\psi = \left(-\frac{1}{2}\nabla^2 - \frac{1}{r_a} - \frac{1}{r_b}\right)\psi = \left(E - \frac{1}{R}\right)\psi \tag{123}$$

根据经验引入变分波函数，用线性组合的方式

$$\psi = c_a \frac{\lambda^{\frac{3}{2}}}{\sqrt{\pi}} e^{-\lambda r_a} + c_b \frac{\lambda^{\frac{3}{2}}}{\sqrt{\pi}} e^{-\lambda r_b} \tag{124}$$

$$\int |\psi|^2 \mathrm{d}\vec{r} = 1 \tag{125}$$

根据波函数的对称性

$$c_a = \pm c_b \tag{126}$$

$$\psi_\pm = c_a \left(\frac{\lambda^{\frac{3}{2}}}{\sqrt{\pi}} e^{-\lambda r_a} \pm \frac{\lambda^{\frac{3}{2}}}{\sqrt{\pi}} e^{-\lambda r_b} \right) = c_a(\psi_a \pm \psi_b) \tag{127}$$

接下来通过波函数归一化来定参数 c_a

$$\langle\psi_\pm|\psi_\pm\rangle = c_a^2\langle\psi_a\pm\psi_b|\psi_a\pm\psi_b\rangle = c_a^2\left(\langle\psi_a|\psi_a\rangle+\langle\psi_b|\psi_b\rangle\pm 2\langle\psi_a|\psi_b\rangle\right) = c_a^2(2\pm 2\langle\psi_a|\psi_b\rangle) = 1 \tag{128}$$

令

$$J = \langle\psi_a|\psi_b\rangle = \langle\psi_b|\psi_a\rangle = \frac{\lambda^3}{\pi}\int \mathrm{d}\vec{r}e^{-\lambda(r_a+r_b)} \tag{129}$$

则

$$c_a = (2\pm 2J)^{-\frac{1}{2}} \tag{130}$$

$$\psi_\pm = (2\pm 2J)^{-\frac{1}{2}}(\psi_a\pm\psi_b) \tag{131}$$

接下来计算 $\bar{H}$

$$H = \frac{1}{R} + H_{\mathrm{el}} \tag{132}$$

第一项 $\frac{1}{R}$trivial，我们来关注第二项

$$\bar{H}_{\mathrm{el}} = \langle\psi_\pm|H_{\mathrm{el}}|\psi_\pm\rangle = \frac{1}{2\pm 2J}\langle\psi_a\pm\psi_b|H_{\mathrm{el}}|\psi_a\pm\psi_b\rangle \tag{133}$$

符号简化，令 $|a\rangle = |\psi_a\rangle, |b\rangle = |\psi_b\rangle$

$$\begin{aligned}\bar{H}_{\mathrm{el}} =& \frac{1}{2\pm 2J}\langle a\pm b|H_{\mathrm{el}}|a\pm b\rangle \\ =& \frac{1}{2\pm 2J}\left(\langle a|H_{\mathrm{el}}|a\rangle + \langle b|H_{\mathrm{el}}|b\rangle \pm \langle a|H_{\mathrm{el}}|b\rangle \pm \langle b|H_{\mathrm{el}}|a\rangle\right) \\ =& \frac{1}{1\pm J}(\langle a|H_{\mathrm{el}}|a\rangle \pm \langle b|H_{\mathrm{el}}|a\rangle)\end{aligned} \tag{134}$$

计算 $H_{\mathrm{el}}|a\rangle$

$$\begin{aligned}H_{\mathrm{el}}|a\rangle &= \left(-\frac{1}{2}\nabla^2 - \frac{1}{r_a} - \frac{1}{r_b}\right)|a\rangle = \left(-\frac{1}{2}\nabla^2 - \frac{1}{r_a} - \frac{1}{r_b}\right)|a\rangle \\ &= \left(-\frac{1}{2}\nabla^2 - \frac{\lambda}{r_a} - \frac{1-\lambda}{r_a} - \frac{1}{r_b}\right)|a\rangle \\ &= \left(-\frac{\lambda^2}{2} - \frac{1-\lambda}{r_a} - \frac{1}{r_b}\right)|a\rangle\end{aligned} \tag{135}$$

则

$$\begin{aligned}\langle a|H_{\mathrm{el}}|a\rangle =& \langle a|\left(-\frac{\lambda^2}{2} - \frac{1-\lambda}{r_a} - \frac{1}{r_b}\right)|a\rangle \\ =& -\frac{\lambda^2}{2} - (1-\lambda)\langle a|\frac{1}{r_a}|a\rangle - \langle a|\frac{1}{r_b}|a\rangle \\ =& -\frac{\lambda^2}{2} - \lambda(1-\lambda) - \kappa\end{aligned} \tag{136}$$

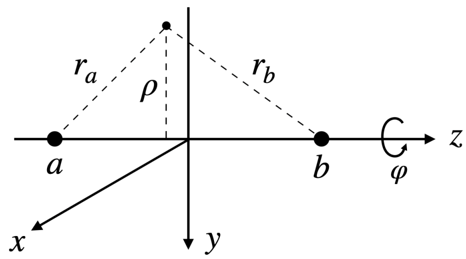
$$\begin{aligned}\langle b|H_{\mathrm{el}}|a\rangle =& \langle b|\left(-\frac{\lambda^2}{2} - \frac{1-\lambda}{r_a} - \frac{1}{r_b}\right)|a\rangle \\ =& -\frac{\lambda^2}{2}J - (1-\lambda)\langle b|\frac{1}{r_a}|a\rangle - \langle b|\frac{1}{r_b}|a\rangle \\ =& -\frac{\lambda^2}{2}J - (2-\lambda)\varsigma\end{aligned} \tag{137}$$

其中

$$\kappa = \langle a|\frac{1}{r_b}|a\rangle \qquad \varsigma = \langle b|\frac{1}{r_a}|a\rangle \tag{138}$$

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

$$\begin{cases}\xi=\frac{1}{R}(r_a+r_b)\\ \eta=\frac{1}{R}(r_a-r_b)\\ \varphi\end{cases}\qquad \text{且} \qquad \begin{cases}1\le\xi\le\infty\\ -1\le\eta\le 1\\ 0\le\varphi\le 2\pi\end{cases} \tag{140}$$

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

$$\begin{aligned}\mathrm{d}\vec{r}=&\mathrm{d}x\mathrm{d}y\mathrm{d}z\\ =&\begin{vmatrix}\frac{\partial x}{\partial\eta} & \frac{\partial x}{\partial\xi} & \frac{\partial x}{\partial\varphi}\\ \frac{\partial y}{\partial\eta} & \frac{\partial y}{\partial\xi} & \frac{\partial y}{\partial\varphi}\\ \frac{\partial z}{\partial\eta} & \frac{\partial z}{\partial\xi} & \frac{\partial z}{\partial\varphi}\end{vmatrix}\mathrm{d}\xi\mathrm{d}\eta\mathrm{d}\varphi\\ =&\begin{vmatrix}-\frac{R\eta}{2}\sqrt{\frac{\xi^2-1}{1-\eta^2}}\cos\varphi & \frac{R\xi}{2}\sqrt{\frac{1-\eta^2}{\xi^2-1}}\cos\varphi & -\frac{R}{2}\sqrt{(\xi^2-1)(1-\eta^2)}\sin\varphi\\ -\frac{R\eta}{2}\sqrt{\frac{\xi^2-1}{1-\eta^2}}\sin\varphi & \frac{R\xi}{2}\sqrt{\frac{1-\eta^2}{\xi^2-1}}\sin\varphi & \frac{R}{2}\sqrt{(\xi^2-1)(1-\eta^2)}\cos\varphi\\ \frac{R}{2}\xi & \frac{R}{2}\eta & 0\end{vmatrix}\mathrm{d}\xi\mathrm{d}\eta\mathrm{d}\varphi\\ =&\frac{R^3}{8}(\xi^2-\eta^2)\mathrm{d}\xi\mathrm{d}\eta\mathrm{d}\varphi\end{aligned} \tag{146}$$

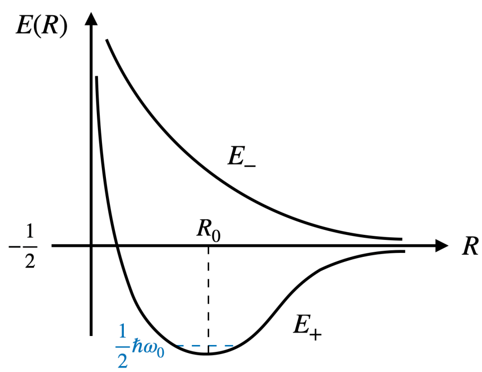
$$\begin{aligned}J =&\frac{\lambda^3}{\pi}\int \mathrm{d}\vec{r}e^{-\lambda(r_a+r_b)} = \frac{\lambda^3}{\pi}\int \frac{R^3}{8}(\xi^2-\eta^2)e^{-\lambda R\xi}\mathrm{d}\xi\mathrm{d}\eta\mathrm{d}\varphi \\ =&\frac{\lambda^3}{\pi}\int_1^\infty \mathrm{d}\xi\int_{-1}^1\mathrm{d}\eta\int_0^{2\pi}\mathrm{d}\varphi\frac{R^3}{8}(\xi^2-\eta^2)e^{-\lambda R\xi} = \frac{R^3\lambda^3}{4}\int_1^\infty\mathrm{d}\xi\int_{-1}^1\mathrm{d}\eta(\xi^2-\eta^2)e^{-\lambda R\xi} \\ =&\frac{R^3\lambda^3}{4}\int_1^\infty\mathrm{d}\xi\left(2\xi^2-\frac{2}{3}\right)e^{-\lambda R\xi} = \left(1+\lambda R+\frac{1}{3}\lambda^2R^2\right)e^{-\lambda R}\end{aligned} \tag{147}$$

$$\begin{aligned}\kappa = \langle a|\frac{1}{r_b}|a\rangle =& \frac{\lambda^3}{\pi}\int\mathrm{d}\vec{r}\frac{e^{-2\lambda r_a}}{r_b} \\ =&\frac{\lambda^3}{\pi}\int_1^\infty\mathrm{d}\xi\int_{-1}^1\mathrm{d}\eta\int_0^{2\pi}\mathrm{d}\varphi\frac{R^3}{8}(\xi^2-\eta^2)\frac{e^{-\lambda R(\xi+\eta)}}{R(\xi-\eta)} \\ =&\frac{1}{R}\left[1-(1+\lambda R)e^{-2\lambda R}\right]\end{aligned} \tag{148}$$

$$\varsigma = \langle b|\frac{1}{r_a}|a\rangle = \int\frac{\psi_a\psi_b}{r_a}\mathrm{d}\vec{r} = \frac{\lambda^3}{\pi}\int\mathrm{d}\vec{r}\frac{e^{-\lambda(r_a+r_b)}}{r_b} = \lambda(1+\lambda R)e^{-\lambda R} \tag{149}$$

代回 Eq.(139) 得

$$\begin{aligned}E_\pm =&\frac{1}{R}-\frac{\lambda^2}{2}+\frac{\lambda(\lambda-1)-\kappa\pm(\lambda-2)\varsigma}{1\pm J} \\ =&\frac{1}{R}-\frac{\lambda^2}{2}+\frac{\lambda(\lambda-1)-\frac{1}{R}\left[1-(1+\lambda R)e^{-2\lambda R}\right]\pm(\lambda-2)\lambda(1+\lambda R)e^{-\lambda R}}{1\pm\left(1+\lambda R+\frac{1}{3}\lambda^2R^2\right)e^{-\lambda R}}\end{aligned} \tag{150}$$



显然 E_+ 是我们的解，由 $\frac{\partial E_+}{\partial\lambda}=0$ 解出

$$R_0 = 2.08\text{ a.u.} = 1.10\text{ Å} \tag{151}$$

在实验中我们得到的值是

$$R_{0\exp} = 1.06\text{ Å} \tag{152}$$

$$E_+(R_0) = -0.587\text{ a.u.} \tag{153}$$

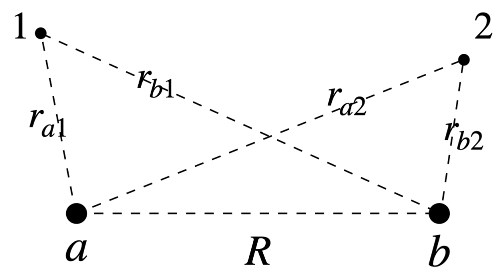
电离能

$$D = -E_+(R_0)-\frac{1}{2}\hbar\omega_0-\frac{1}{2} = 0.082\text{ a.u.} = 2.24eV \tag{154}$$

实验结果

$$D_{\exp} = 2.65eV \tag{155}$$

6 $\mathbf{H}_2$



$$H = H_{\text{el}} + \frac{1}{R} \tag{156}$$

$$H_{\text{el}} = -\frac{1}{2}\left(\nabla_1^2 + \nabla_2^2\right) + \frac{1}{r_{12}} - \left(\frac{1}{r_{a1}} + \frac{1}{r_{a2}} + \frac{1}{r_{b1}} + \frac{1}{r_{b2}}\right) \tag{157}$$

我们要做的事依旧是解薛定谔方程

$$H\Psi(1,2) = E\Psi(1,2) \tag{158}$$

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

$$\psi(r) = \frac{\lambda}{\sqrt{\pi}} e^{-\lambda r} \tag{159}$$

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

$$\begin{aligned}\Psi_+(1,2) =& [\psi(r_{a1}) + \psi(r_{b1})][\psi(r_{a2}) + \psi(r_{b2})] \\ =& \psi(r_{a1})\psi(r_{a2}) + \psi(r_{b1})\psi(r_{b2}) + \psi(r_{a1})\psi(r_{b2}) + \psi(r_{b1})\psi(r_{a2})\end{aligned} \tag{160}$$

  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。(heilter-london approximation)

$$\Psi_+(1,2) = \psi(r_{a1})\psi(r_{b2}) + \psi(r_{b1})\psi(r_{a2}) \tag{161}$$

  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

$$\Psi_-(1,2) = \psi(r_{a1})\psi(r_{b2}) - \psi(r_{b1})\psi(r_{a2}) \tag{162}$$

  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

$$\Psi_\pm(1,2) = \psi(r_{a1})\psi(r_{b2}) \pm \psi(r_{b1})\psi(r_{a2}) \tag{163}$$

接下来计算 H_{el} 的期待值 $\bar{H}_{\text{el}}$

$$\begin{aligned}\bar{H}_{\text{el}} &= \langle\Psi_\pm| H_{\text{el}} |\Psi_\pm\rangle \\ &= \langle\psi(r_{a1})\psi(r_{b2}) \pm \psi(r_{b1})\psi(r_{a2})| H_{\text{el}} |\psi(r_{a1})\psi(r_{b2}) \pm \psi(r_{b1})\psi(r_{a2})\rangle \\ &= \langle\psi(r_{a1})\psi(r_{b2})| H_{\text{el}} |\psi(r_{a1})\psi(r_{b2})\rangle + \langle\psi(r_{b1})\psi(r_{a2})| H_{\text{el}} |\psi(r_{b1})\psi(r_{a2})\rangle \\ &\quad \pm \langle\psi(r_{a1})\psi(r_{b2})| H_{\text{el}} |\psi(r_{b1})\psi(r_{a2})\rangle \pm \langle\psi(r_{b1})\psi(r_{a2})| H_{\text{el}} |\psi(r_{a1})\psi(r_{b2})\rangle \\ &= 2\left[\langle\psi(r_{a1})\psi(r_{b2})| H_{\text{el}} |\psi(r_{a1})\psi(r_{b2})\rangle \pm \langle\psi(r_{b1})\psi(r_{a2})| H_{\text{el}} |\psi(r_{a1})\psi(r_{b2})\rangle\right]\end{aligned} \tag{164}$$

计算 $H_{\text{el}}\left|\psi(r_{a1})\psi(r_{b2})\right\rangle$

$$\begin{aligned}
H_{\text{el}}\left|\psi(r_{a1})\psi(r_{b2})\right\rangle &= \left(-\frac{1}{2}\nabla_1^2-\frac{1}{2}\nabla_2^2+\frac{1}{r_{12}}-\frac{1}{r_{a1}}-\frac{1}{r_{a2}}-\frac{1}{r_{b1}}-\frac{1}{r_{b2}}\right)\left|\psi(r_{a1})\psi(r_{b2})\right\rangle \\
&= \left(-\frac{1}{2}\nabla_1^2-\frac{\lambda}{r_{a1}}-\frac{1}{2}\nabla_2^2-\frac{\lambda}{r_{b2}}-\frac{1-\lambda}{r_{a1}}-\frac{1-\lambda}{r_{b2}}+\frac{1}{r_{12}}-\frac{1}{r_{a2}}-\frac{1}{r_{b1}}\right)\left|\psi(r_{a1})\psi(r_{b2})\right\rangle \\
&= \left(-\frac{\lambda^2}{2}-\frac{1-\lambda}{r_{a1}}-\frac{\lambda^2}{2}-\frac{1-\lambda}{r_{b2}}+\frac{1}{r_{12}}-\frac{1}{r_{a2}}-\frac{1}{r_{b1}}\right)\left|\psi(r_{a1})\psi(r_{b2})\right\rangle
\end{aligned} \tag{165}$$

故

$$\begin{aligned}
&\left\langle\Psi_\pm\right| H_{\text{el}}\left|\Psi_\pm\right\rangle \\
=&2\left[\left\langle\psi(r_{a1})\psi(r_{b2})\right| H_{\text{el}}\left|\psi(r_{a1})\psi(r_{b2})\right\rangle \pm \left\langle\psi(r_{b1})\psi(r_{a2})\right| H_{\text{el}}\left|\psi(r_{a1})\psi(r_{b2})\right\rangle\right] \\
=&2\Bigg[\left\langle\psi(r_{a1})\psi(r_{b2})\right|-\frac{\lambda^2}{2}-\frac{1-\lambda}{r_{a1}}\left|\psi(r_{a1})\psi(r_{b2})\right\rangle+\left\langle\psi(r_{a1})\psi(r_{b2})\right|-\frac{\lambda^2}{2}-\frac{1-\lambda}{r_{b2}}\left|\psi(r_{a1})\psi(r_{b2})\right\rangle \\
&-\left\langle\psi(r_{a1})\psi(r_{b2})\right|\frac{1}{r_{a2}}\left|\psi(r_{a1})\psi(r_{b2})\right\rangle-\left\langle\psi(r_{a1})\psi(r_{b2})\right|\frac{1}{r_{b1}}\left|\psi(r_{a1})\psi(r_{b2})\right\rangle \\
&+\left\langle\psi(r_{a1})\psi(r_{b2})\right|\frac{1}{r_{12}}\left|\psi(r_{a1})\psi(r_{b2})\right\rangle\Bigg]+2\Bigg[\left\langle\psi(r_{a2})\psi(r_{b1})\right|-\frac{\lambda^2}{2}-\frac{1-\lambda}{r_{a1}}\left|\psi(r_{a1})\psi(r_{b2})\right\rangle \\
&+\left\langle\psi(r_{a2})\psi(r_{b1})\right|-\frac{\lambda^2}{2}-\frac{1-\lambda}{r_{b2}}\left|\psi(r_{a1})\psi(r_{b2})\right\rangle-\left\langle\psi(r_{a2})\psi(r_{b1})\right|\frac{1}{r_{a2}}\left|\psi(r_{a1})\psi(r_{b2})\right\rangle \\
&-\left\langle\psi(r_{a2})\psi(r_{b1})\right|\frac{1}{r_{b1}}\left|\psi(r_{a1})\psi(r_{b2})\right\rangle+\left\langle\psi(r_{a2})\psi(r_{b1})\right|\frac{1}{r_{12}}\left|\psi(r_{a1})\psi(r_{b2})\right\rangle\Bigg] \\
=&2\Bigg[\left\langle\psi(r_{a1})\right|-\frac{\lambda^2}{2}-\frac{1-\lambda}{r_{a1}}\left|\psi(r_{a1})\right\rangle+\left\langle\psi(r_{b2})\right|-\frac{\lambda^2}{2}-\frac{1-\lambda}{r_{b2}}\left|\psi(r_{b2})\right\rangle \\
&-\left\langle\psi(r_{b2})\right|\frac{1}{r_{a2}}\left|\psi(r_{b2})\right\rangle-\left\langle\psi(r_{a1})\right|\frac{1}{r_{b1}}\left|\psi(r_{a1})\right\rangle+\left\langle\psi(r_{a1})\psi(r_{b2})\right|\frac{1}{r_{12}}\left|\psi(r_{a1})\psi(r_{b2})\right\rangle\Bigg] \\
&+2\Bigg[\left\langle\psi(r_{b1})\right|-\frac{\lambda^2}{2}-\frac{1-\lambda}{r_{a1}}\left|\psi(r_{a1})\right\rangle J+\left\langle\psi(r_{a2})\right|-\frac{\lambda^2}{2}-\frac{1-\lambda}{r_{b2}}\left|\psi(r_{b2})\right\rangle J \\
&-\left\langle\psi(r_{a2})\right|\frac{1}{r_{a2}}\left|\psi(r_{b2})\right\rangle J-\left\langle\psi(r_{b1})\right|\frac{1}{r_{b1}}\left|\psi(r_{a1})\right\rangle J+\left\langle\psi(r_{a2})\psi(r_{b1})\right|\frac{1}{r_{12}}\left|\psi(r_{a1})\psi(r_{b2})\right\rangle\Bigg] \\
=&2\Bigg[2\left\langle\psi(r_{a1})\right|-\frac{\lambda^2}{2}-\frac{1-\lambda}{r_{a1}}\left|\psi(r_{a1})\right\rangle-2\left\langle\psi(r_{b2})\right|\frac{1}{r_{a2}}\left|\psi(r_{b2})\right\rangle+\left\langle\psi(r_{a1})\psi(r_{b2})\right|\frac{1}{r_{12}}\left|\psi(r_{a1})\psi(r_{b2})\right\rangle\Bigg]+ \\
&2\Bigg[2\left\langle\psi(r_{b1})\right|-\frac{\lambda^2}{2}-\frac{1-\lambda}{r_{a1}}\left|\psi(r_{a1})\right\rangle J-2\left\langle\psi(r_{a2})\right|\frac{1}{r_{a2}}\left|\psi(r_{b2})\right\rangle J+\left\langle\psi(r_{a2})\psi(r_{b1})\right|\frac{1}{r_{12}}\left|\psi(r_{a1})\psi(r_{b2})\right\rangle\Bigg] \\
=&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} \tag{166}$$

令 $\rho=\lambda R$，上式中

$$\mathcal{A}=\left\langle\psi(r_{a1})\right|-\frac{\lambda^2}{2}-\frac{1-\lambda}{r_{a1}}\left|\psi(r_{a1})\right\rangle=-\frac{\lambda^2}{2}-(1-\lambda)\lambda=\frac{\lambda^2}{2}-\lambda \tag{167}$$

$$\mathcal{A}'=\left\langle\psi(r_{b1})\right|-\frac{\lambda^2}{2}-\frac{1-\lambda}{r_{a1}}\left|\psi(r_{a1})\right\rangle=-\frac{\lambda^2}{2}J+(\lambda-1)\mathcal{E} \tag{168}$$

$$\mathcal{K}=\left\langle\psi(r_{b2})\right|\frac{1}{r_{a2}}\left|\psi(r_{b2})\right\rangle=\frac{1}{R}\left[1-(1+\lambda R)e^{-2\lambda R}\right]=\frac{\lambda}{\rho}\left[1-(1+\rho)e^{-2\rho}\right] \tag{169}$$

$$\begin{aligned}
\mathcal{K}'=\left\langle\psi(r_{a1})\psi(r_{b2})\right|\frac{1}{r_{12}}\left|\psi(r_{a1})\psi(r_{b2})\right\rangle&=\frac{\lambda^4}{\pi}\int \mathrm{d}\vec{r}_1\mathrm{d}\vec{r}_2\frac{\exp[-2\lambda(r_{a1}+r_{b2})]}{r_{12}} \\
=&\frac{\lambda}{\rho}\left[1-\left(1+\frac{11}{8}\rho+\frac{3}{4}\rho^2+\frac{1}{4}\rho^3\right)e^{-2\rho}\right]
\end{aligned} \tag{170}$$

$$\mathcal{E} = \langle\psi(r_{a2})|\,\frac{1}{r_{a2}}\,|\psi(r_{b2})\rangle = \lambda(1+\lambda R)e^{-\lambda R} = \lambda(1+\rho)e^{-\rho} \tag{171}$$

$$\begin{aligned}\mathcal{E}' &= \langle\psi(r_{a2})\psi(r_{b1})|\,\frac{1}{r_{12}}\,|\psi(r_{a1})\psi(r_{b2})\rangle = \frac{\lambda^4}{\pi}\int \mathrm{d}\vec{r}_1\mathrm{d}\vec{r}_2\frac{\exp[-2\lambda(r_{a1}+r_{a2}+r_{b1}+r_{b2})]}{r_{12}} \\ &=\lambda\left[\left(\frac{5}{8}-\frac{23}{20}\rho-\frac{3}{5}\rho^2-\frac{1}{15}\rho^3\right)e^{-2\rho}+\frac{6}{5}\frac{\varphi(\rho)}{\rho}\right]\end{aligned} \tag{172}$$

其中

$$\varphi(\rho) = J^2(\rho)\left(\ln\rho + c\right) - J^2(-\rho)E_1(4\rho) + 2J(\rho)J(-\rho)E_1(2\rho) \tag{173}$$

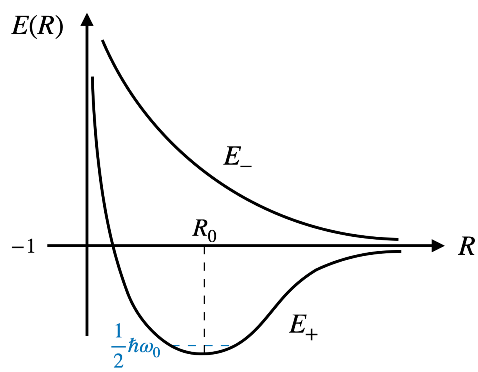
$$E_1(x) = \int_x^\infty \frac{1}{t}e^{-t}\mathrm{d}t \tag{174}$$

$$J = \langle\psi(r_{a1})|\psi(r_{b1})\rangle = \langle\psi(r_{a2})|\psi(r_{b2})\rangle = \left(1+\lambda R+\frac{1}{3}\lambda^2R^2\right)e^{-\lambda R} = \left(1+\rho+\frac{1}{2}\rho^2\right)e^{-\rho} \tag{175}$$

归一化因子

$$\langle\Psi_\pm|\Psi_\pm\rangle = \langle\psi(r_{a1})\psi(r_{b2})\pm\psi(r_{a2})\psi(r_{b1})|\psi(r_{a1})\psi(r_{b2})\pm\psi(r_{a2})\psi(r_{b1})\rangle = 2\pm 2J^2 \tag{176}$$

$$E_\pm = \frac{1}{R}+\frac{\langle\Psi_\pm|\,H_{\mathrm{el}}\,|\Psi_\pm\rangle}{\langle\Psi_\pm|\Psi_\pm\rangle} = \frac{1}{R}+\frac{1}{1\pm J^2}[2(\mathcal{A}\pm\mathcal{A}'J)-2(\mathcal{K}+\mathcal{E}J)+\mathcal{K}'\pm\mathcal{E}'] \tag{177}$$



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

$$E_+(R_0) = -1.139 \text{ a.u.} \tag{178}$$

由 $\frac{\partial E_+}{\partial\lambda} = 0$ 解出

$$\lambda = 1.166 \tag{179}$$

$$R_0 = 1.458 \text{ a.u.} = 0.77\mathring{\mathrm{A}} \tag{180}$$

电离能

$$D = -1-(E_+ + \frac{1}{2}\hbar\omega_0) = 0.129 \text{ a.u.} = 3.54eV \tag{181}$$

实验结果

$$D_{\exp} = 4.45eV \tag{182}$$

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

$$\psi(r) = \frac{\lambda}{\sqrt{\pi}}e^{-\lambda r} \tag{183}$$

两个参数

$$\psi(r)=\frac{\lambda_1^{\frac{3}{2}}}{\sqrt{\pi}}(1+\lambda_2 r)e^{-\lambda_1 r} \tag{184}$$

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

$$\bar{H}=\frac{\langle\Psi_\pm(1,2)|\,H\,|\Psi_\pm(1,2)\rangle}{\langle\Psi_\pm(1,2)|\Psi_\pm(1,2)\rangle}=\frac{\langle\psi(r_{a1})\psi(r_{b2})|\,H\,|\psi(r_{a1})\psi(r_{b2})\rangle\pm\langle\psi(r_{b1})\psi(r_{a2})|\,H\,|\psi(r_{a1})\psi(r_{b2})\rangle}{1\pm J^2} \tag{185}$$

$$H=\frac{1}{R}-\frac{1}{2}\left(\nabla_1^2+\nabla_2^2\right)+\frac{1}{r_{12}}-\left(\frac{1}{r_{a1}}+\frac{1}{r_{a2}}+\frac{1}{r_{b1}}+\frac{1}{r_{b2}}\right) \tag{186}$$

$$\Psi_\pm(1,2)=\left[\psi(r_{a1})\psi(r_{b2})\pm\psi(r_{b1})\psi(r_{a2})\right]\chi_{0,1}(s_{1z},s_{2z}) \tag{187}$$

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。

$$\psi(r)=\frac{1}{\sqrt{\pi}}e^{-r} \tag{188}$$

$$H\,|\psi(r_{a1})\psi(r_{b2})\rangle=\left[\frac{1}{R}+2E_0^{\text{H-atom}}+\left(\frac{1}{r_{12}}-\frac{1}{r_{a2}}-\frac{1}{r_{b1}}\right)\right]|\psi(r_{a1})\psi(r_{b2})\rangle \tag{189}$$

$$\begin{aligned}\bar{H}(1\pm J^2)=&\frac{1}{R}+2E_0^{\text{H-atom}}+\langle\psi(r_{a1})\psi(r_{b2})|\,\frac{1}{r_{12}}-\frac{1}{r_{a2}}-\frac{1}{r_{b1}}\,|\psi(r_{a1})\psi(r_{b2})\rangle\\&\pm\left[J^2\left(\frac{1}{R}+2E_0^{\text{H-atom}}\right)+\langle\psi(r_{b1})\psi(r_{a2})|\,\frac{1}{r_{12}}-\frac{1}{r_{a2}}-\frac{1}{r_{b1}}\,|\psi(r_{a1})\psi(r_{b2})\rangle\right]\end{aligned} \tag{190}$$

最终得到

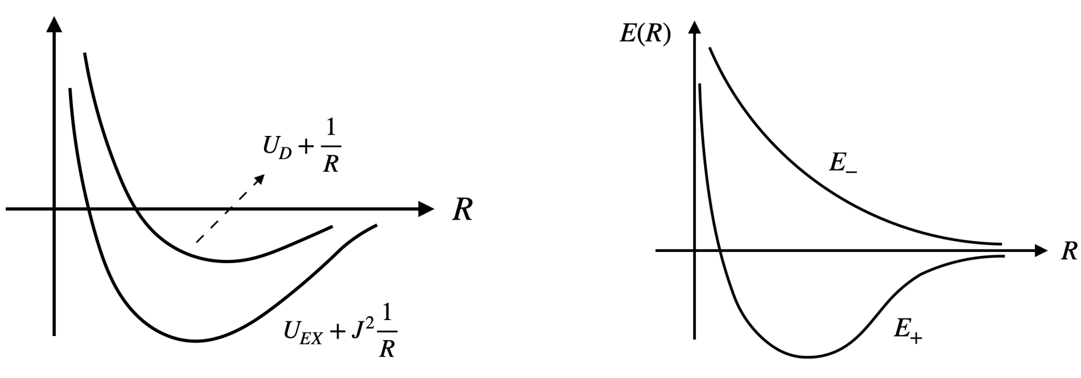
$$E_\pm=\frac{1}{R}+2E_0^{\text{H-atom}}+\frac{U_{\mathrm{D}}\pm U_{\mathrm{EX}}}{1\pm J^2}=2E_0^{\text{H-atom}}+\frac{\left(U_{\mathrm{D}}+\frac{1}{R}\right)\pm\left(U_{\mathrm{EX}}+J^2\frac{1}{R}\right)}{1\pm J^2} \tag{191}$$

D 代表 direct，EX 代表 exchange

$$U_{\mathrm{D}}=-2\mathcal{K}+\mathcal{K}' \tag{192}$$

$$U_{\mathrm{EX}}=-2J\mathcal{E}+\mathcal{E}'\propto J \tag{193}$$

计算 U_{D} 和 U_{EX} 的数值结果



$$\langle\psi(r_{a1})\psi(r_{b2})|\,H\,|\psi(r_{a1})\psi(r_{b2})\rangle\pm\langle\psi(r_{b1})\psi(r_{a2})|\,H\,|\psi(r_{a1})\psi(r_{b2})\rangle \tag{194}$$

第一项由直接相互作用引起，第二项由交换相互作用引起。

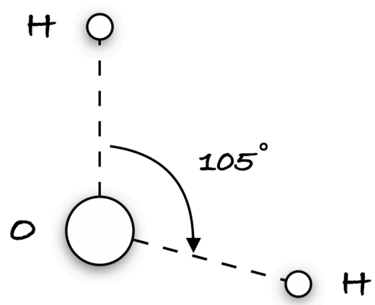
$U_{\mathrm{EX}}\sim J$，J 是交叠积分，因此 J 越大，$|U_{\mathrm{EX}}|$ 越大，势阱越深，体系越稳定。而两个氢原子的波函数重合部分越多，J 越大，E_+ 越小，体系越稳定；而 E_- 反而变大，体系不稳定。

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: H_2O



为什么 H_2O 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)

$$\text{H: } 1s^1(5) \qquad \text{H: } 1s^1(6) \qquad \text{O: } 1s^2 2s^2 2p^4$$

p 有 3 个轨道，可以填充 6 个电子

$$\begin{matrix} 2p_x & 2p_y & 2p_z \\ \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow \end{matrix}$$

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

$$\begin{matrix} 2p_x & 2p_y & 2p_z \\ \uparrow(1) & \uparrow(2) & \uparrow(3)\downarrow(4) \end{matrix}$$

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。

$$[\psi_{2px}(1)\psi_H(5) + \psi_{2px}(5)\psi_H(1)]\,\chi_0(s_{1z}, s_{2z}) \tag{195}$$

$$[\psi_{2px}(2)\psi_H(6) + \psi_{2px}(6)\psi_H(2)]\,\chi_0(s_{1z}, s_{2z}) \tag{196}$$

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 H_2O 的结构。

Example: NH_3

N 原子结构 $1s^2 2s^2 2p^3$

$$\begin{matrix} 2p_x & 2p_y & 2p_z \\ \uparrow & \uparrow & \uparrow \end{matrix}$$

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°

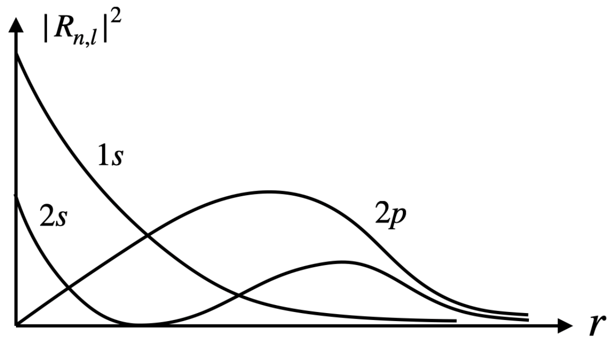
Example: CH_4

Pauli 理论能解释所有分子结构吗？我们来看看 CH_4。N 原子结构 $1s^2 2s^2 2p^2$

$2p_x$	$2p_y$	$2p_z$
↑	↑	

根据刚刚的 Pauli 理论无法解释 CH_4 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

$$\psi_{2s} = R_{2s}(r) \tag{197}$$

$$\psi_{2px} = \frac{\sqrt{3}}{4\pi} R_{2p}(r) \sin\theta \cos\varphi \tag{198}$$

$$\psi_{2py} = \frac{\sqrt{3}}{4\pi} R_{2p}(r) \sin\theta \sin\varphi \tag{199}$$

$$\psi_{2pz} = \frac{\sqrt{3}}{4\pi} R_{2p}(r) \cos\theta \tag{200}$$

为了讨论方便，我们认为 $R_{2s}(r) \doteq R_{2p}(r)$

$$\psi_{2s} = 1 \tag{201}$$

$$\psi_{2px} = \sqrt{3} \sin\theta \cos\varphi \tag{202}$$

$$\psi_{2py} = \sqrt{3} \sin\theta \sin\varphi \tag{203}$$

$$\psi_{2pz} = \sqrt{3} \cos\theta \tag{204}$$

使用 LCAO 法，令

$$\psi_i(\vec{r}) = a\psi_{2s} + b_i\psi_{2px} + c_i\psi_{2py} + d_i\psi_{2pz} \qquad (i = 1, 2, 3, 4) \tag{205}$$

由对称性得到

$$|b_i| = |c_i| = |d_i| \tag{206}$$

四个轨道正交且分别归一

$$\int |\psi_i(\vec{r})|^2 \mathrm{d}\vec{r} = a^2 + 3b_i^2 = 1 \tag{207}$$

$$\psi_i(\vec{r}) = a\psi_{2s} + b_i \left(\psi_{2px} + \psi_{2py} + \psi_{2pz}\right) \qquad (i = 1, 2, 3, 4) \tag{208}$$

选择第一象限中与 x, y, z 轴夹角都相同的方向

$$\sin\varphi = \cos\varphi = \frac{1}{\sqrt{2}} \qquad \cos\theta = \frac{1}{\sqrt{3}} \qquad \sin\theta = \frac{\sqrt{2}}{\sqrt{3}} \tag{209}$$

则

$$\psi_{2s} = \psi_{2px} = \psi_{2py} = \psi_{2pz} = 1 \tag{210}$$

$$\psi_1(\vec{r}) = a + 3b_1 = a + \sqrt{3(1-a^2)} \tag{211}$$

当 ψ_1 最大时

$$\frac{\mathrm{d}}{\mathrm{d}a}\left[a + \sqrt{3(1-a^2)}\right] = 0 \tag{212}$$

解得

$$a = \frac{1}{2} \qquad\qquad b = \frac{1}{2} \tag{213}$$

$$\psi_1(\vec{r}) = \frac{1}{2}\left(\psi_{2s} + \psi_{2px} + \psi_{2py} + \psi_{2pz}\right) \tag{214}$$

ψ_2, ψ_3, ψ_4 与 ψ_1 正交

$$\psi_2(\vec{r}) = \frac{1}{2}\left(\psi_{2s} - \psi_{2px} + \psi_{2py} + \psi_{2pz}\right) \tag{215}$$

$$\psi_3(\vec{r}) = \frac{1}{2}\left(\psi_{2s} + \psi_{2px} - \psi_{2py} + \psi_{2pz}\right) \tag{216}$$

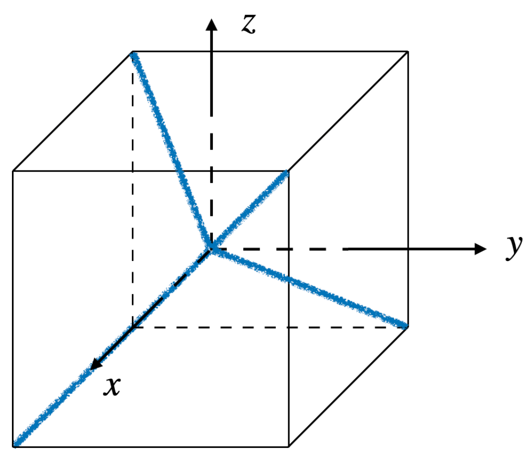
$$\psi_4(\vec{r}) = \frac{1}{2}\left(\psi_{2s} + \psi_{2px} + \psi_{2py} - \psi_{2pz}\right) \tag{217}$$

这 4 个轨道显然满足

$$\langle\psi_i|\psi_j\rangle = \delta_{i,j} \tag{218}$$

CH_4 的 4 个 H 原子的电子分别与这 4 个轨道配对。化学键

$$\left[\psi_i(a)\psi_H(b) + \psi_i(b)\psi_H(a)\right]\chi_0(s_{az}, s_{bz}) \tag{219}$$



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

$$\psi_{n\vec{k}}(\vec{r}) = \sum_{\vec{k}} e^{i\vec{k}\cdot\vec{R}}\psi_n(\vec{r} - \vec{R}) \tag{220}$$