Chapter 5: Rotation And Vibration of Molecules

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1 Introduction

系统中包含 M 个原子核和 N 个电子，薛定谔方程写为

$$H(\vec{R}_1.\cdots,\vec{R}_M;\vec{r_1},\cdots,\vec{r}_N)\psi(\vec{R}_1.\cdots,\vec{R}_M;\vec{r_1},\cdots,\vec{r}_N)=E\psi(\vec{R}_1.\cdots,\vec{R}_M;\vec{r_1},\cdots,\vec{r}_N) \tag{1}$$

进行符号简化

$$\vec{R}=\vec{R}_1.\cdots,\vec{R}_M \tag{2}$$

$$\vec{r}=\vec{r_1},\cdots,\vec{r}_N \tag{3}$$

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

将哈密顿量写成

$$H(\vec{R},\vec{r})=H_{\mathrm{N}}(\vec{R})+H_{\mathrm{el}}(\vec{r})+V(\vec{R},r) \tag{5}$$

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

将波函数近似写成

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

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

$$\left[H_{\mathrm{N}}(\vec{R})+H_{\mathrm{el}}(\vec{r})+V(\vec{R},r)\right]A(\vec{R})n(\vec{R},\vec{r})=EA(\vec{R})n(\vec{R},\vec{r}) \tag{7}$$

电子波函数满足薛定谔方程

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

于是

$$\left[H_{\mathrm{N}}(\vec{R})+U_n(\vec{R})\right]A(\vec{R})n(\vec{R},\vec{r})=EA(\vec{R})n(\vec{R},\vec{r}) \tag{9}$$

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

$$\left[H_{\mathrm{N}}(\vec{R})+U_n(\vec{R})\right]A(\vec{R})=EA(\vec{R}) \tag{10}$$

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 $\int \mathrm{d}\vec{r}n^\dagger(\vec{R},\vec{r})$ 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

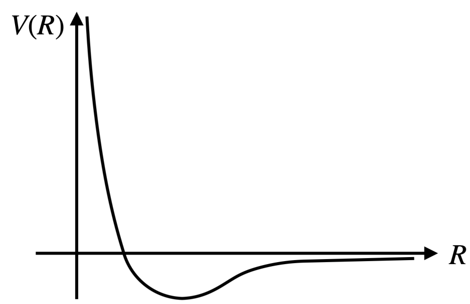
$$A(\vec{R}) = \psi(\vec{R}_1, \vec{R}_2) \tag{11}$$

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

$$\left[H_{\mathrm{N}}(\vec{R}) + V(\vec{R}_1 - \vec{R}_2)\right]\psi(\vec{R}_1, \vec{R}_2) = E_{\mathrm{total}}\psi(\vec{R}_1, \vec{R}_2) \tag{13}$$

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

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 $V(0) \to \infty, V(\infty) \to 0^-$，当 $x \to \infty$ 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

$$\vec{R}_c = \frac{M_1\vec{R}_1 + M_2\vec{R}_2}{M_1 + M_2} \qquad \vec{R} = \vec{R}_1 - \vec{R}_2 \tag{15}$$

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

其中

$$M = M_1 + M_2 \qquad \mu = \frac{M_1 M_2}{M_1 + M_2} \tag{17}$$

薛定谔方程改写为

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

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

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

质心坐标部分薛定谔方程

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

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

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

$$E_{\mathrm{total}} = E_c + E \tag{22}$$

进一步分离变量

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

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

$$\nabla^2_{\vec{R}} = \frac{1}{R^2}\frac{\partial}{\partial R}R^2\frac{\partial}{\partial R} - \frac{\vec{L}^2}{\hbar^2 R^2} = \frac{1}{R}\frac{\mathrm{d}^2}{\mathrm{d}R^2}R - \frac{\vec{L}^2}{\hbar^2 R^2} \tag{24}$$

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

于是

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

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

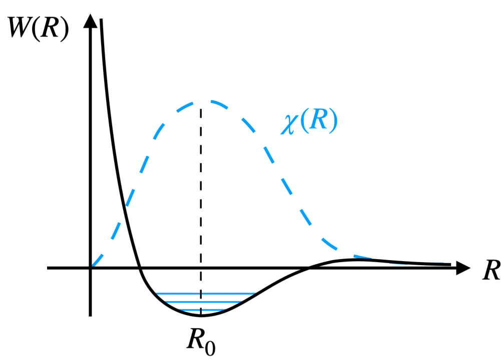
边界条件

$$\chi(\infty) = 0 \qquad \chi(0) = 0 \tag{28}$$

定义

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

由于当 $R \to \infty$ 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

$$\left.\frac{\mathrm{d}W}{\mathrm{d}R}\right|_{R_0} = 0 \tag{30}$$

$$\left.\frac{\mathrm{d}V}{\mathrm{d}R}\right|_{R_0} = \frac{L(L+1)\hbar^2}{\mu R_0^3} \tag{31}$$

将 $W(R)$ 在 R_0 处泰勒展开，并略去高阶项

$$\begin{aligned} W(R) =& W(R_0) + \left.\frac{\mathrm{d}W}{\mathrm{d}R}\right|_{R_0}(R-R_0) + \frac{1}{2}W''(R_0)(R-R_0)^2 + \frac{1}{3!}W'''(R)(R-R_0)^3 + \cdots \\ =& W(R_0) + \frac{1}{2}W''(R_0)(R-R_0)^2 \end{aligned} \tag{32}$$

定义

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

则

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

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

其中

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

令 $\xi = R - R_0$，进行符号简化

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

边界条件

$$\chi(R=0) = \chi(\xi=-R_0) = 0 \qquad \chi(\xi=\infty) = 0 \tag{38}$$

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

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

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

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

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

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

其中 $\left(\nu + \frac{1}{2}\right)\hbar\omega_0$ 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 H_2

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

$\chi(S_{1z}, S_{2z})$ 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。

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

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。

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

$\chi(S_{1z}, S_{2z})$ 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

$$\vec{R}_c = \frac{\vec{R}_1 + \vec{R}_2}{2} \to \vec{R}_c \qquad \vec{R} = \vec{R}_1 - \vec{R}_2 \to -\vec{R} \tag{45}$$

$$R \to R \qquad \theta \to \pi - \theta \qquad \phi \to \pi + \phi \tag{46}$$

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

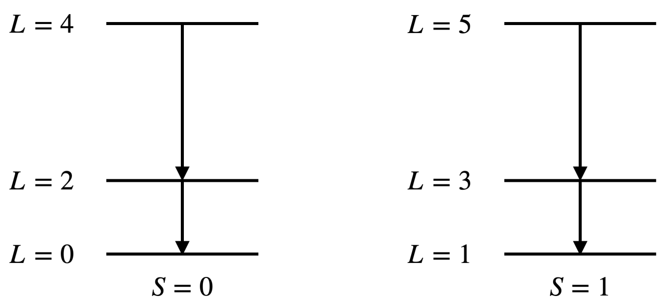
- 当 L 是偶数时
$$\Psi(\vec{R}_1, \vec{R}_2) = \frac{\chi_{\nu,L}(R)}{R} Y_{L,M}(\theta,\phi)\chi_0(S_{1z}, S_{2z}) \tag{48}$$
$Y_{L,M}(\theta,\phi)$ 不变号，则 $\chi_0(S_{1z}, S_{2z})$ 变号，对应自旋单态。

- 当 L 是奇数时
$$\Psi(\vec{R}_1, \vec{R}_2) = \frac{\chi_{\nu,L}(R)}{R} Y_{L,M}(\theta,\phi)\chi_1(S_{1z}, S_{2z}) \tag{49}$$
$Y_{L,M}(\theta,\phi)$ 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

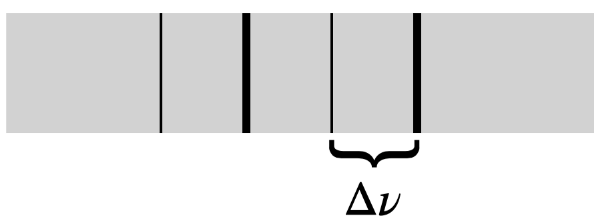
$$(S = 1) : (S = 0) = 3 : 1 \tag{50}$$

三重态氢分子 $(S = 1)$ 我们也叫正氢 (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 $L \to L - 2$。光谱能量

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



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

Example: Order Estimate of $E_{\rm e}$, $E_{\rm vib}$, $E_{\rm rot}$

从基态到第一激发态
$$E_{\rm e} \sim \frac{\hbar^2}{ma^2} \tag{53}$$
a 约为两原子核之间的距离，m 是电子质量。

$$E_{\rm vib} \sim \hbar\omega_0 \sim \hbar\frac{\hbar\alpha^2}{\mu} = \frac{\hbar^2\alpha^2}{\mu} \tag{54}$$

$$E_{\mathrm{rot}} \sim \frac{\hbar^2}{J} = \frac{\hbar^2}{\mu R_0^2} \tag{55}$$

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

$$E_{\mathrm{vib}} \sim x^2 \frac{\hbar^2}{\mu R_0^2} \tag{56}$$

比较 E_{e} 和 E_{vib}

$$E_{\mathrm{e}} \gg E_{\mathrm{vib}} \tag{57}$$

比较 E_{vib} 和 E_{rot}

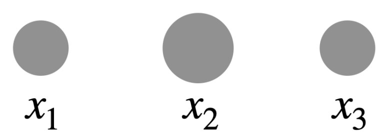
$$E_{\mathrm{vib}} \gg E_{\mathrm{rot}} \tag{58}$$

故

$$E_{\mathrm{e}} \gg E_{\mathrm{vib}} \gg E_{\mathrm{rot}} \tag{59}$$

3 Vibrations of A Linear Triatomic Molecule

排成一条线的三原子分子，如 CO_2



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

令

$$x_1 - x_2 = \tilde{x}_1 \qquad x_3 - x_2 = \tilde{x}_3 \tag{61}$$

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

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

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

则

$$\begin{aligned} V(x_1, x_2, x_2) =& V(\tilde{x}_1, x_2, \tilde{x}_3) \doteq V(\tilde{x}_1, \tilde{x}_3) \\ =& V(\tilde{x}_1^{(0)}, \tilde{x}_3^{(0)}) + \left.\frac{\partial V}{\partial \tilde{x}_1}\right|_{\tilde{x}_1^{(0)}} (\tilde{x}_1 - \tilde{x}_1^{(0)}) + \left.\frac{\partial V}{\partial \tilde{x}_3}\right|_{\tilde{x}_3^{(0)}} (\tilde{x}_3 - \tilde{x}_3^{(0)}) \\ &+ \frac{1}{2} \left.\frac{\partial^2 V}{\partial \tilde{x}_1^2}\right|_{\tilde{x}_1^{(0)}} (\tilde{x}_1 - \tilde{x}_1^{(0)})^2 + \frac{1}{2} \left.\frac{\partial^2 V}{\partial \tilde{x}_3^2}\right|_{\tilde{x}_3^{(0)}} (\tilde{x}_3 - \tilde{x}_3^{(0)})^2 + \cdots \\ =& V(\tilde{x}_1^{(0)}, \tilde{x}_3^{(0)}) + \frac{1}{2} \left.\frac{\partial^2 V}{\partial \tilde{x}_1^2}\right|_{\tilde{x}_1^{(0)}} (\tilde{x}_1 - \tilde{x}_1^{(0)})^2 + \frac{1}{2} \left.\frac{\partial^2 V}{\partial \tilde{x}_3^2}\right|_{\tilde{x}_3^{(0)}} (\tilde{x}_3 - \tilde{x}_3^{(0)})^2 \\ =& V(\tilde{x}_1^{(0)}, \tilde{x}_3^{(0)}) + \frac{1}{2} k_1^2 (x_1 - x_2 - a_1)^2 + \frac{1}{2} k_2^2 (x_3 - x_2 - a_2)^2 \end{aligned} \tag{65}$$

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

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

$$H\Psi(x_1, x_2, x_3) = E\Psi(x_1, x_2, x_3) \tag{67}$$

引入质心坐标

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

$$\xi = x_2 - x_1 - a \qquad \eta = x_3 - x_2 - a \tag{69}$$

进行微分变换

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

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

$$\frac{\partial}{\partial x_3} = \frac{m_3}{M}\frac{\partial}{\partial X} + \frac{\partial}{\partial \eta} \tag{72}$$

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

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

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

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

薛定谔方程

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

分离变量

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

质心部分是 trivial 的，我们对此不感兴趣

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

相对坐标部分

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

$$E = E_c + \tilde{E} \tag{81}$$

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

$$\xi' = \xi\cos\alpha + \eta\sin\alpha \tag{82}$$

$$\eta' = -\xi\sin\alpha + \eta\cos\alpha \tag{83}$$

代入相对坐标部分薛定谔方程

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

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

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

解得

$$\tan 2\alpha=\frac{2m_1m_3}{m_2(m_1-m_3)}\tag{86}$$

Eq.(84) 整理得

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

令

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

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

则

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

分离变量

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

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

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

$$\tilde{E}=E_A+E_B\tag{94}$$

两个方程都是谐振子。定义

$$\omega_A=\sqrt{\frac{k}{A}}\qquad\qquad\omega_B=\sqrt{\frac{k}{B}}\tag{95}$$

得到能谱

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

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

Example: CO_2 (O=C=O)

对于二氧化碳分子

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

$$A = m_1 \qquad\qquad B = \frac{m_1 + m_2}{2m_1 + m_2} \tag{99}$$

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

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