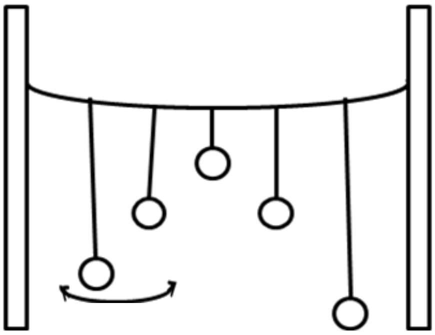
2. Light/matter interaction（光和物質的相互作用）

Light/matter interaction
- Light absorption (光吸収)
- Light emission （發光）
- Light scattering （光零乱）

2.1 Resonance energy transfer（共振能量転移）

Coupled Pendulums

２.

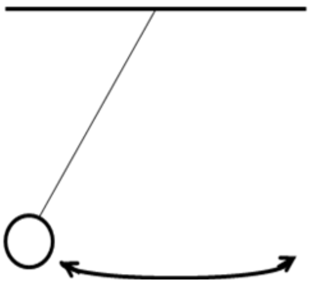


Pendulum frequency in *classical mechanics* ν

$$\nu = \frac{1}{2\pi}\sqrt{\frac{g}{l}}$$

g : gravitational acceleration

l : string length



Pendulum frequency in *quantum mechanics*:
Eigen frequency of an electron in a steady state

$$\frac{ih}{2\pi}\frac{\partial\psi}{\partial t} = H\psi$$: Time-dependent Schrödinger equation

time-independent H

$$H\psi_0 = E\psi_0$$

$$\psi = \psi_0 e^{-\frac{iE}{\hbar}t} \qquad \nu = \frac{E}{h}$$

Electron in the ground state	$E = 0$, $\nu = 0$	$\rightarrow$	still pendulum
Electron in the excited state with energy E	$E = E$, $\nu = \dfrac{E}{h}$	$\rightarrow$	pendulum oscillating with frequency ν

Energy transfer occurs only between two pendulums with the same frequency
能量転移可能在共振的時候

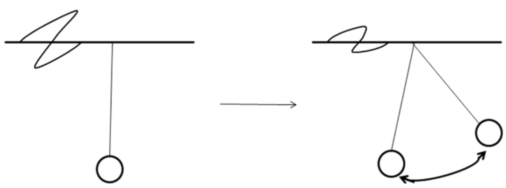
$$\Downarrow$$

Light absorption/emission occurs only between two electrons with the same frequency

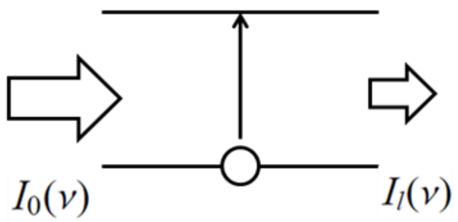
2.2 Light absorption (induced absorption)

Light having the frequency same as the eigen frequency of an electron is absorbed.

Pendulum mpdel



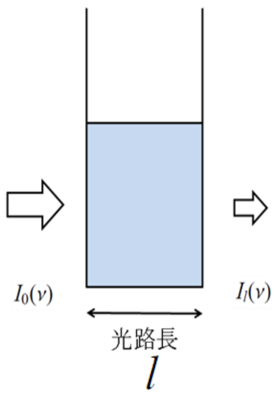
Two-level model



Lambert-Beer's law

$$\frac{I_l(\nu)}{I_0(\nu)} = 10^{-\epsilon c l} \qquad A = \log_{10}\frac{I_0(\nu)}{I_l(\nu)} = \epsilon c l$$

$\epsilon(\nu)$	: molar absorbity	$\mathrm{mol^{-1}dm^{3}cm^{-1}}$
c	: molar concentration	$\mathrm{mol\ dm^{-3}}$
l	: optical path length	cm
A	: absorbance	



$$\epsilon(\nu) = \frac{\sigma(\nu) N_A}{10^3 \ln 10} = 2.6 \times 10^{20} \sigma(\nu)$$

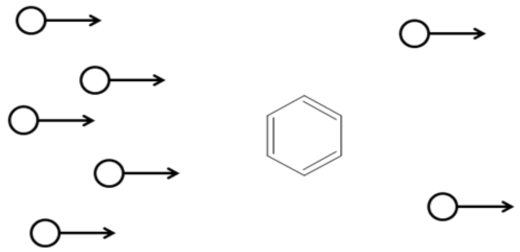
N_A: Abogadoro number

$\sigma(\nu)$: absorption cross section cm^2

Absorption cross section （吸収截面積）

Strongly absorbing molecule

$\sigma \sim 10^{-16}\mathrm{cm}^2 = 1\text{Å}^2 \qquad \epsilon \sim 10^4$

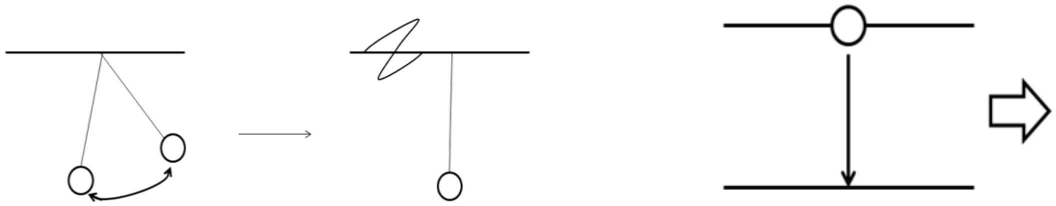


2.3 Light emission

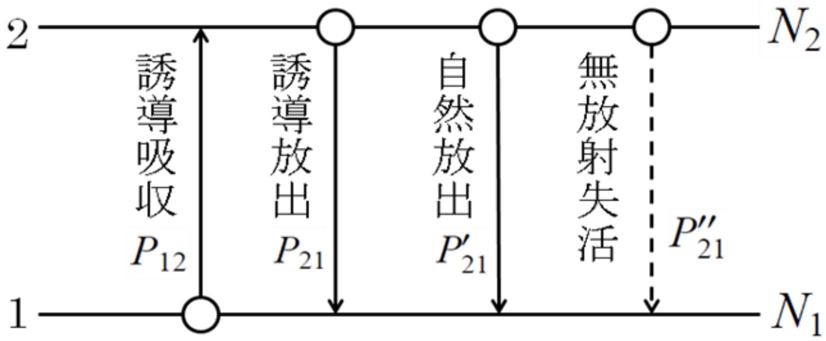
$\left\{ \begin{array}{l} \text{Induced emission（受激發射）} \\ \text{Spontaneous emission（自發輻射）} \end{array} \right.$

Induced emission

Spontaneous emission



Dynamics of a two-level system interacting with light



P : probability per second

P_{12}: induced absorption（受激吸収）
P_{21}: induced emission（受激發射）
P'_{21}: spontaneous emission（自發輻射）
P''_{21}: non-radiative de-activation（無輻射失活）

$$P_{12} = P_{21} = B\rho(\nu_0)$$ B : Einstein B coefficient

$$B = \frac{2\pi^2}{3\epsilon_0 h^2}|\langle 2 \mid \mu \mid 1 \rangle|^2$$

$\langle 2 \mid \mu \mid 1 \rangle$: transition dipole moment

$\rho(\nu_0)$: radiation energy density $\mathrm{J\,m^{-3}(s^{-1})^{-1}}$

$\propto \ I$: incident light intensity

$$I = c\int \rho(\nu)d\nu \quad \mathrm{J\,m^{-2}s^{-1}}$$

$$P'_{21} = A = \frac{1}{\tau_r}$$ A : Einstein A coefficient, τ_r : radiative lifetime

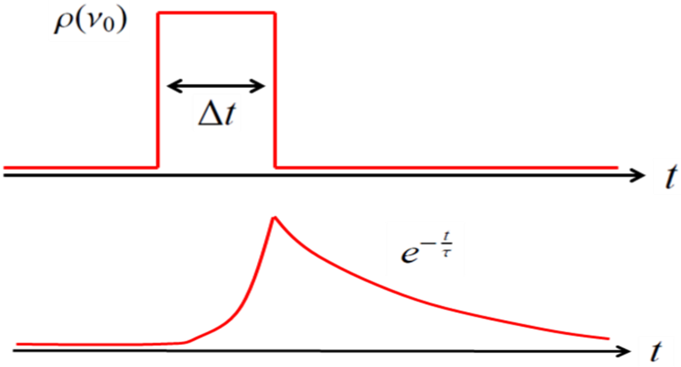
$$A = \frac{16\pi^3\nu_0^3}{3\epsilon c_0 h}|\langle 2 \mid \mu \mid 1 \rangle|^2 \qquad \frac{A}{B} = \frac{8\pi h\nu_0^3}{c_0^3}$$

$$P''_{21} = \frac{1}{\tau_{nr}}$$ τ_{nr} **:** non-radiative lifetime (reaction, energy transfer, etc.)

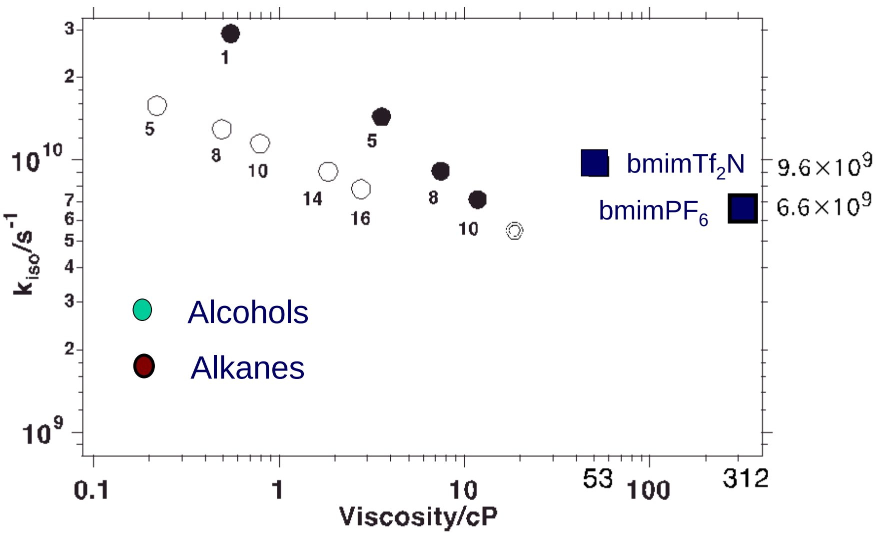
Time-dependent population changes with interaction with light

$$\frac{dN_2}{dt} = P_{12}N_1 - P_{21}N_2 - P'_{21}N_2 - P''_{21}N_2$$
$$= B\rho(\nu_0)(N_1 - N_2) - \frac{1}{\tau}N_2$$

τ : lifetime of level 2 $$\frac{1}{\tau} = \frac{1}{\tau_r} + \frac{1}{\tau_{nr}}$$

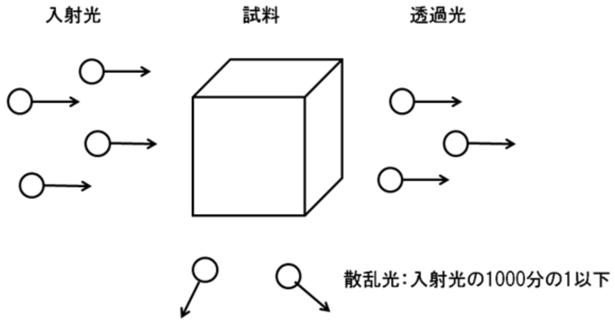


Isomerization rates of S1 trans-stilbene in different solvents



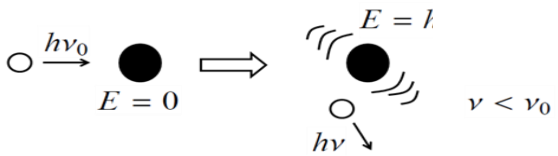
Light scattering

Absorption and emission occur simultaneously.

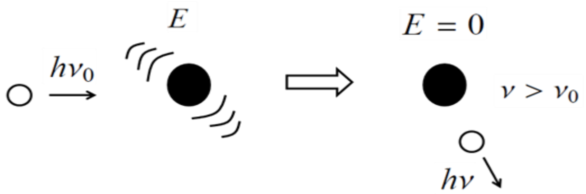


Light scattering
- Elastic scattering: Rayleigh scattering → blue sky, red sun
- Inelastic scattering: Raman scattering → spectroscopy

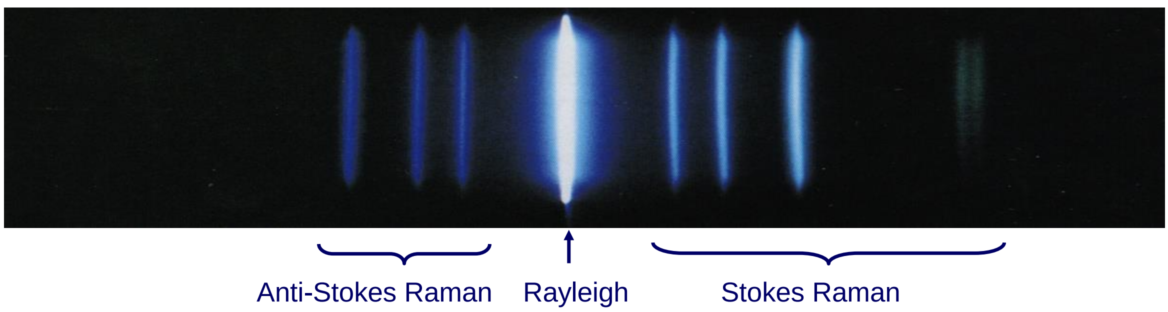
Stokes Raman scattering



Anti-Stokes Raman scattering

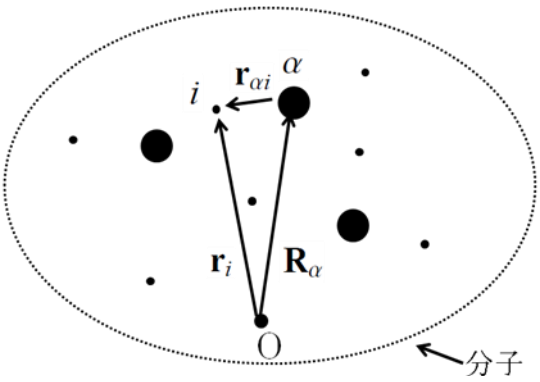


Raman shift $\nu - \nu_0 = \pm\dfrac{E}{h}$ - : Stokes + : Anti-Stokes



3. Born-Oppenheimer Approximation

3.1 Separation of electronic and nuclear motions （電子的運動和核的運動的分離）



Electron: $m_e = 9.1 \times 10^{-31}\mathrm{kg}$

Proton: $m_p = 1.67 \times 10^{-27}\mathrm{kg}$

$$\frac{m_p}{m_e} = 1.8 \times 10^3$$

Molecular Hamiltonian

$$H = \underbrace{-\sum_{\alpha} \frac{\hbar^2}{2M_\alpha}\nabla^2_{\mathbf{R}_\alpha}}_{\text{Nucleus kinetic energy}} \underbrace{-\sum_{i} \frac{\hbar^2}{2m_e}\nabla^2_{\mathbf{r}_i}}_{\text{Electro kinetic ene}} \underbrace{-\sum_{\alpha}\sum_{i} \frac{Z_\alpha e^2}{r_{\alpha i}}}_{\text{Attraction between nucleus and electron}} \underbrace{+\sum_{i<i} \frac{e^2}{r_{ij}}}_{\text{Repulsior among electrons}} \underbrace{+\sum_{\alpha<\beta} \frac{Z_\alpha Z_\beta e^2}{R_{\alpha\beta}}}_{\text{Repulsion among nuclei}}$$

M_α : Mass of nucleus α

$\nabla_{\mathbf{R}_\alpha}$: Differentiation with respect to the coordinate of nucleus α

m_e : Mass of electron

$\nabla_{\mathbf{r}_i}$: Differentiation with respect to the coordinate of electron i

e : Charge of electron

Z_α : Atomic number of nucleus α

$r_{\alpha i}$: Distance between nucleus α and electron i

r_{ij} : Distance between electron i and electron j

$R_{\alpha\beta}$: Distance between nucleus α and nucleus β

cf. $H = p^2/2\mathrm{m} + V$, $p=-i\hbar d/dq$ ($qp-pq=i\hbar$)

$$H\psi = E\psi$$

NOT solvable! (不能解！)

Adiabatic approximation（絕熱近似）

$$H(\nabla_{\mathbf{R}_\alpha}, \nabla_{\mathbf{r}_i}, \mathbf{R}_\alpha, \mathbf{r}_i)\psi(\mathbf{R}_\alpha, \mathbf{r}_i) = E\psi(\mathbf{R}_\alpha, \mathbf{r}_i)$$

Differential equation with respect to $\mathbf{R}_\alpha$ and $\mathbf{r}_i$

Adiabatic approximation $\nabla_{\mathbf{R}_\alpha} = 0$ $\mathbf{R}_\alpha$ fixed

$$H_e(\nabla_{\mathbf{r}_i}, \mathbf{R}_\alpha, \mathbf{r}_i)\psi_e(\mathbf{R}_\alpha, \mathbf{r}_i) = E_e(\mathbf{R}_\alpha)\psi_e(\mathbf{R}_\alpha, \mathbf{r}_i)$$

$$H_e = H + \sum_\alpha \frac{\hbar^2}{2M_\alpha}\nabla^2_{\mathbf{R}_\alpha}$$

Differential equation with respect to $\mathbf{r}_i$

Fixed parameter $\mathbf{R}_\alpha$

Obtain an adiabatic solution

1) Assume that $H_e\psi_e = E_e\psi_e$ is solved.

Energy $E^l_e(\mathbf{R}_\alpha)$

Eigen function $\psi^l_e(\mathbf{R}_\alpha, \mathbf{r}_i)$

$$H_e\psi^l_e(\mathbf{R}_\alpha, \mathbf{r}_i) = E^l_e(\mathbf{R}_\alpha)\psi^l_e(\mathbf{R}_\alpha, \mathbf{r}_i)$$

l : quantum number

2) Expand $\psi(\mathbf{R}_\alpha, \mathbf{r}_i)$ into a power series of $\psi^l_e(\mathbf{R}_\alpha, \mathbf{r}_i)$

$$\psi(\mathbf{R}_\alpha, \mathbf{r}_i) = \sum_l \psi^l_e(\mathbf{R}_\alpha, \mathbf{r}_i)\phi^l_n(\mathbf{R}_\alpha)$$

$\phi^l_n(\mathbf{R}_\alpha)$: expansion coefficient

3) Introducing into Schrödinger equation

$$H = H_e - \sum_\alpha \frac{\hbar^2}{2M_\alpha}\nabla^2_{\mathbf{R}_\alpha}$$

$$H\psi = E\psi$$

$$\left(-\sum_{\alpha}\frac{\hbar^2}{2M_\alpha}\nabla^2_{\mathbf{R}_\alpha} + H_e\right)\sum_{l}\psi^l_e(\mathbf{R}_\alpha, \mathbf{r}_i)\phi^l_n(\mathbf{R}_\alpha) = E\sum_{l}\psi^l_e(\mathbf{R}_\alpha, \mathbf{r}_i)\phi^l_n(\mathbf{R}_\alpha)$$

$$\Big\downarrow \quad H_e\psi_e = E_e\psi_e$$

$$\sum_{l}\left(-\sum_{\alpha}\frac{\hbar^2}{2M_\alpha}\nabla^2_{\mathbf{R}_\alpha} + E^l_e(\mathbf{R}_\alpha)\right)\psi^l_e(\mathbf{R}_\alpha, \mathbf{r}_i)\phi^l_n(\mathbf{R}_\alpha) = E\sum_{l}\psi^l_e(\mathbf{R}_\alpha, \mathbf{r}_i)\phi^l_n(\mathbf{R}_\alpha)$$

4) Multiply $\psi^{l'}_e(\mathbf{R}_\alpha, \mathbf{r}_i)^*$ from the left-hand side and integrate over $\boldsymbol{r}$

$$\int \psi^{l'}_e(\mathbf{R}_\alpha, \mathbf{r}_i)^*\psi^l_e(\mathbf{R}_\alpha, \mathbf{r}_i)d\mathbf{r}_i = \delta_{ll'}$$

$$\sum_{l}\int \psi^{l'}_e\left(-\sum_{\alpha}\frac{\hbar^2}{2M_\alpha}\nabla^2_{\mathbf{R}_\alpha}\right)\psi^l_e\phi^l_n d\mathbf{r} + \sum_{l}E^l_e\int \psi^{l'*}_e\psi^l_e\phi^l_n d\mathbf{r}$$
$$= E\sum_{l}\int \psi^{l'*}_e\psi^l_e\phi^e_n d\mathbf{r}$$

$$\sum_{l}\int \psi^{l'}_e\left(-\sum_{\alpha}\frac{\hbar^2}{2M_\alpha}\nabla^2_{\mathbf{R}_\alpha}\right)\psi^l_e\phi^l_n d\mathbf{r} + E^{l'}_e\phi^{l'}_n = E\phi^{l'}_n$$

5) Born-Oppenheimer approximation

「 $\nabla_{\mathbf{R}_\alpha}\psi^l_e(\mathbf{R}_\alpha, \mathbf{r}_i) = 0$ 」

ψ^l_e does not change with a small change of $\mathbf{R}_\alpha$

$$\nabla^2_{\mathbf{R}_\alpha}\psi^l_e\phi^l_n = \nabla_{\mathbf{R}_\alpha}\{\cancel{(\nabla_{\mathbf{R}_\alpha}\psi^l_e)}\phi^l_n + \psi^l_e\nabla_{\mathbf{R}_\alpha}\phi^l_n\}$$
$$= \psi^l_e\nabla^2_{\mathbf{R}_\alpha}\phi^l_n$$

$$-\sum_{l} \underbrace{\int \psi_e^{l'*}\psi_e^{l} d\mathbf{r}}_{\delta_{ll'}} \sum_{\alpha} \frac{\hbar^2}{2M_\alpha}\nabla^2_{\mathbf{R}_\alpha}\phi_n^{l} + E_e^{l'}\phi_n^{l'} = E\phi_n^{l'}$$

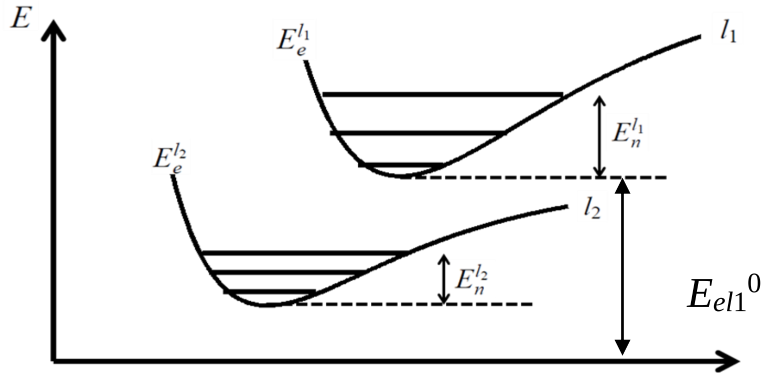
$$\underbrace{-\sum_{\alpha} \frac{\hbar^2}{2M_\alpha}\nabla^2_{\mathbf{R}_\alpha}\phi_n^{l'}(\mathbf{R}_\alpha)}_{\text{Nuclear kinetic energy}} + \underbrace{E_e^{l'}(\mathbf{R}_\alpha)\phi_n^{l'}(\mathbf{R}_\alpha)}_{\text{potential energy}} = \underbrace{E\phi_n^{l'}(\mathbf{R}_\alpha)}_{\text{total energy}}$$

$l' \to l$

$$\begin{cases} H_n^{l}(\nabla_{\mathbf{R}_\alpha}, \mathbf{R}_\alpha)\phi_n^{l}(\mathbf{R}_\alpha) = E_n^{l}\phi_n^{l}(\mathbf{R}_\alpha) \\ H_n^{l} = -\sum_{\alpha} \frac{\hbar^2}{2M_\alpha}\nabla^2_{\mathbf{R}_\alpha} + E_e^{l'}(\mathbf{R}_\alpha) \end{cases}$$

$E_n{}^{l} = E - E_{el}{}^{0}$

$E_e{}^{l'} = E_e{}^{l} - E_{el}{}^{0}$



$$H(\nabla_{\mathbf{R}_\alpha}, \nabla_{\mathbf{r}_i}, \mathbf{R}_\alpha, \mathbf{r}_i)\psi(\mathbf{R}_\alpha, \mathbf{r}_i) = E\psi(\mathbf{R}_\alpha, \mathbf{r}_i)$$

$$\begin{cases} H_e(\nabla_{\mathbf{r}_i}, \mathbf{R}_\alpha, \mathbf{r}_i)\psi_e(\mathbf{R}_\alpha, \mathbf{r}_i) = E_e(\mathbf{R}_\alpha)\psi_e(\mathbf{R}_\alpha, \mathbf{r}_i) \\ H_n(\nabla_{\mathbf{R}_\alpha}, \mathbf{R}_\alpha)\psi_n^{l}(\mathbf{R}_\alpha) = E_n^{l}\psi_n^{l}(\mathbf{R}_\alpha) \end{cases}$$

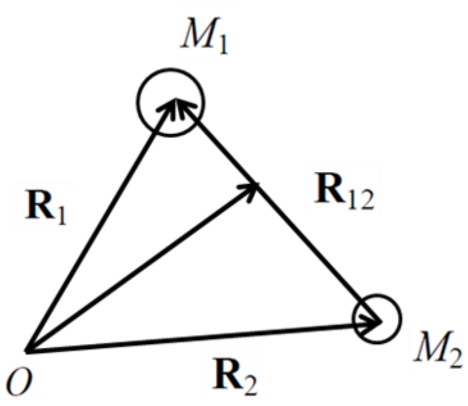
$\mathbf{R}_\alpha$ is parameter (constant)

$\mathbf{R}_\alpha$ is variable

Electronic and nuclear motions are separated!（電子的運動和核的運動分離！）

3. 2 Separation of vibrational, rotational and translational motions

A diatomic molecule



Hamiltonian H_n

$$H_n = -\frac{\hbar^2}{2M_1}\nabla^2_{\mathbf{R}_1} - \frac{\hbar^2}{2M_2}\nabla^2_{\mathbf{R}_2} + E_e(\mathbf{R}_1, \mathbf{R}_2)$$

$$= -\frac{\hbar^2}{2M_1}\nabla^2_{\mathbf{R}_1} - \frac{\hbar^2}{2M_2}\nabla^2_{\mathbf{R}_2} + E_e(R_{12}) \qquad R_{12} = |\mathbf{R}_{12}|$$

$$\left.\begin{matrix}\mathbf{R}_1 \\ \mathbf{R}_2\end{matrix}\right\} \longrightarrow \begin{matrix}\mathbf{R}_{12} = \mathbf{R}_1 - \mathbf{R}_2 \\ \mathbf{R} = \dfrac{M_1\mathbf{R}_1 + M_2\mathbf{R}_2}{M_1 + M_2}\end{matrix}$$

$$H_n = \underbrace{-\frac{\hbar^2}{2(M_1 + M_2)}\nabla^2_R}_{H_t\text{ (translation)}} \underbrace{- \frac{(M_1 + M_2)\hbar^2}{2M_1M_2}\nabla^2_{\mathbf{R}_{12}} + E_e(R_{12})}_{\text{vibration and rotation}}$$

$$\frac{M_1 + M_2}{M_1M_2} = \frac{1}{\mu} \quad \mu$$

Schrödinger equation for vibration and rotation

$$\left(-\frac{1}{2\mu}\nabla^2_{\mathbf{R}_{12}} + E_e(R_{12})\right)\psi_{rv}(\mathbf{R}_{12}) = E_{rv}\psi_{rv}(\mathbf{R}_{12})$$

ψ_{rv} : vibration rotation eigen function

$$\mathbf{R}(x, y, z)$$
$$\downarrow$$
$$\mathbf{R}(r, \theta, \phi)$$
$$r_{12} = r$$

$$H_{rv} = -\frac{\hbar^2}{2\mu}\left\{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right\} + E_e(r)$$

$$= -\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + E_e(r) + \frac{\tilde{L}^2}{2\mu r^2}$$

$$\tilde{L}^2 = -\hbar^2\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right\}$$

$$\tilde{L}^2 Y_l^m(\theta, \phi) = l(l+1)\hbar^2 Y_l^m(\theta, \phi)$$

$Y_l^m(\theta, \phi)$: spherical harmonics

$$\tilde{L}_z Y_l^m(\theta, \phi) = m\hbar Y_l^m(\theta, \phi)$$

Rigid body approximation (neglecting vibration-rotation interaction)

$$\frac{\tilde{L}^2}{2\mu r^2} = \frac{\tilde{L}^2}{2\mu r_0^2}$$

r_0: interatomic distance at the potential minimum

$$H_{rv} = \underbrace{-\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + E_e(r)}_{\text{vibration}} + \underbrace{\frac{\tilde{L}^2}{2\mu r_0^2}}_{\text{rotation}}$$

$$H_{rv}\phi(r,\theta,\phi) = E_{rv}\phi(r,\theta,\phi)$$

$$\Downarrow \quad \phi(r,\theta,\phi) = \phi_v(r)Y_l^m(\theta,\phi)$$

$$\begin{cases} \dfrac{\tilde{L}^2}{2\mu r_0^2}Y_l^m(\theta,\phi) = \dfrac{1}{2\mu r_0^2}l(l+1)\hbar^2 Y_l^m(\theta,\phi) \\ \left\{-\dfrac{\hbar^2}{2\mu}\dfrac{1}{r^2}\left(r^2\dfrac{\partial}{\partial r}\right) + E_e(r) + \dfrac{l(l+1)\hbar^2}{2\mu r_0}\right\}\psi_v^l(r) = E_{rv}^l\psi_v^l(r) \end{cases}$$

$$\boxed{\begin{gathered} H(\nabla_{\mathbf{R}_\alpha}, \nabla_{\mathbf{r}_i}, \mathbf{R}_\alpha, \mathbf{r}_i)\psi(\mathbf{R}_\alpha, \mathbf{r}_i) = E\psi(\mathbf{R}_\alpha, \mathbf{r}_i) \\ \Downarrow \\ \begin{cases} H_e(\nabla_{\mathbf{r}_i}, \mathbf{R}_\alpha, \mathbf{r}_i)\psi_e(\mathbf{R}_\alpha, \mathbf{r}_i) = E_e(\mathbf{R}_\alpha)\psi_e(\mathbf{R}_\alpha, \mathbf{r}_i) \\ \left\{-\dfrac{\hbar^2}{2\mu}\dfrac{1}{r^2}\left(r^2\dfrac{\partial}{\partial r}\right) + E_e(r) + \dfrac{l(l+1)\hbar^2}{2\mu r_0}\right\}\psi_v^l(r) = E_{rv}^l\psi_v^l(r) \\ \dfrac{\tilde{L}^2}{2\mu r_0^2}Y_l^m(\theta,\phi) = \dfrac{1}{2\mu r_0^2}l(l+1)\hbar^2 Y_l^m(\theta,\phi) \end{cases} \end{gathered}}$$