Nuclear motion in molecules

Main outcome from the previous lecture was the separation of electronic and nuclear subsystems by using the BOH ansatz for the molecular WF:

$$\Psi(\vec{r},\vec{R},t) = \sum_I \chi_I(R,t)\Phi_I(\vec{r},\vec{R})$$

The electronic WF Φ_I are the solutions of the stationary SE $\hat{H}_e\Phi_I = V_I(\vec{R})\Phi_I$, where

$$\hat{H}_e = \hat{T}_e + U(\vec{r},\vec{R}), \text{ and}$$

the resulting TDSE for $\chi_I(\vec{R},t)$ reads:

$$i\hbar\frac{\partial}{\partial t}\chi_I(\vec{R},t) = \sum_\alpha\left\{\left[-\frac{\hbar^2}{2M_\alpha}\nabla_\alpha^2 + V_I(\vec{R})\right]\chi_I(\vec{R},t) + \sum_J\left(2\vec{F}_{IJ}^{\alpha}(\vec{R})\cdot\nabla_\alpha\chi_J + G_{IJ}^{\alpha}(\vec{R})\chi_J\right)\right\}.$$

Let's consider a simple case when $\vec{F}_{IJ}^{\alpha} = G_{IJ}^{\alpha} = 0$,

then the SE becomes $i\hbar\frac{\partial}{\partial t}\chi_I(\vec{R},t) = \sum_\alpha\left[-\frac{\hbar^2}{2M_\alpha}\nabla_\alpha^2 + V_I(\vec{R})\right]\chi_I$ -

- the motion of wave packet $\chi_I(\vec{R},t)$ in a multidemenseona PES $V_I(\vec{R})$.

To understand this motion, we consider stationary states $\chi_K(\vec{R})$ of the Hamiltonian $\hat{H} = \sum_\alpha\left[-\frac{\hbar^2}{2M_\alpha}\nabla_\alpha^2 + V_I(\vec{R})\right]$

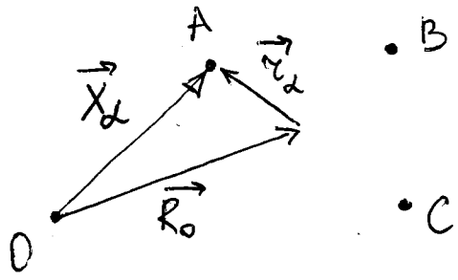
$$\hat{H}\chi_K(\vec{R}) = E_K\chi_K(\vec{R})$$

so E_K are molecular states.

and $\chi(\vec{R},t) = \sum_K C_K(t)\chi_K(\vec{R})$,

Molecular coordinate system. $\underbrace{\quad N \quad}$

A, B, C, ... are atoms



Straightforwardly we solve the SE for the PES where all the atoms move in 3 dimensions, so we have $3N$ coordinates.

A ~~better~~ approach is to introduce center-of-mass internal coordinates shifted from O by $\vec{R}_0$. In this new coordinate system every motion of an atom α can be written as a sum of rotation of the system as a whole and the internal motion.

The change in the position of atom α can be written as

$$d\vec{X}_\alpha = d\vec{R}_0 + d\vec{\varphi} \times \vec{\tau}_\alpha + d\vec{\tau}_\alpha$$

- $d\vec{R}_0$: center of mass motion
- $d\vec{\varphi} \times \vec{\tau}_\alpha$: rotation of the system as a whole
- $d\vec{\tau}_\alpha$: change in the position with respect to other atoms

How to understand the changes in the SE caused by the change of the coordinate system?

We need to change PES and KE operator.

$$\hat{T}_n = -\sum_\alpha{}' \frac{\hbar^2}{2M_\alpha} \nabla_\alpha^2 = +\sum_\alpha{}' \frac{M_\alpha \vec{V}_\alpha^2}{2}$$

$$\vec{V}_\alpha = \frac{d\vec{X}_\alpha}{dt} = \underbrace{\frac{d\vec{R}_0}{dt}}_{\vec{V}_0} + \underbrace{\frac{d\vec{\varphi}}{dt}}_{\vec{\omega}} \times \vec{\tau}_\alpha + \underbrace{\frac{d\vec{\tau}_\alpha}{dt}}_{\vec{V}_\alpha}$$

and we substitute $\vec{V}_\alpha$ to $\hat{T}_n$

$$\hat{T}_n = \sum_\alpha \frac{M_\alpha}{2}\left(\vec{V}_0 + \vec{\omega}\times\vec{r}_\alpha + \vec{V}_\alpha\right)^2 =$$

$$= \sum_\alpha \frac{M_\alpha}{2}\Big[\underbrace{\vec{V}_0^{\,2}}_{\text{I}} + \underbrace{\left[\vec{\omega}\times\vec{r}_\alpha\right]^2}_{\text{II}} + \underbrace{\vec{V}_\alpha^{\,2}}_{\text{III}} +$$

$$+ \underbrace{2\,\vec{V}_0\cdot\left[\vec{\omega}\times\vec{r}_\alpha\right]}_{\text{IV}} + \underbrace{2\,\vec{V}_0\cdot\vec{V}_\alpha}_{\text{V}} + \underbrace{2\left[\vec{\omega}\times\vec{r}_\alpha\right]\cdot\vec{V}_\alpha}_{\text{VI}}\Big]$$

$$M = \sum_\alpha M_\alpha$$

I) $\sum_\alpha \frac{M_\alpha}{2}\vec{V}_0^{\,2} = \frac{M}{2}\vec{V}_0^{\,2}$ is the center of mass motion.

~~We can choose a coordinate system moving with the COM, so that $\vec{V}_0 = 0$!~~

IV) The interaction of translational and rotational D.O.F.

$$\sum_\alpha M_\alpha\,\vec{V}_0\cdot\left[\vec{\omega}\times\vec{r}_\alpha\right] = \sum_\alpha M_\alpha\,\vec{r}_\alpha\cdot\left[\vec{V}_0\times\vec{\omega}\right] =$$

$$= M\,\vec{R}_0\cdot\left[\vec{V}_0\times\vec{\omega}\right].$$

$\vec{R}_0 = \frac{1}{M}\sum_\alpha M_\alpha\vec{r}_\alpha$

Choosing the coordinate system located in the COM ($\vec{R}_0 = 0$), the term IV $\equiv 0$.

Therefore, translations and rotations can be decoupled from each other.

V) The interaction of translational and vibrational D.O.F:

$$\sum_\alpha M_\alpha\,\vec{V}_0\cdot\vec{V}_\alpha = \vec{V}_0\cdot\sum_\alpha M_\alpha\frac{d\vec{r}_\alpha}{dt} = \vec{V}_0\cdot M\frac{d\vec{R}_0}{dt} = M\,\|\vec{V}_0\|^2$$

Therefore, this term gives a number which contributes as a trivial phase to the SE.

II) Rotational motion of the system.

$$\sum_\alpha \frac{M_\alpha}{2}\left[\vec{\omega}\times\vec{r}_\alpha\right]^2 = \qquad (A\times B)\cdot(C\times D) = (A\cdot C)(B\cdot D) + (B\cdot C)(A\cdot D)$$

$$= \sum_\alpha \frac{M_\alpha}{2}\left[(\vec{\omega}\cdot\vec{\omega})(\vec{r}_\alpha\cdot\vec{r}_\alpha) - (\vec{r}_\alpha\cdot\vec{\omega})(\vec{\omega}\cdot\vec{r}_\alpha)\right] =$$

$$= \sum_\alpha \frac{M_\alpha}{2}\left[\vec{\omega}^+|\vec{r}_\alpha|^2\vec{\omega} + \vec{\omega}^+\vec{r}_\alpha\vec{r}_\alpha^+\vec{\omega}\right] =$$

$$= \sum_\alpha \frac{M_\alpha}{2}\left[\vec{\omega}^+\left(|\vec{r}_\alpha|^2\mathbb{1} - \vec{r}_\alpha\vec{r}_\alpha^+\right)\vec{\omega}\right]$$

$$\sum_\alpha M_\alpha\left(|\vec{r}_\alpha|^2\mathbb{1} - \vec{r}_\alpha\vec{r}_\alpha^+\right) = \mathbb{I} \quad \text{- inertia tensor.}$$

Therefore, we have $\frac{1}{2}\vec{\omega}^+\mathbb{I}\vec{\omega}$ - is the energy of the rotating body.

VI) $\sum_\alpha M_\alpha\left[\vec{\omega}\times\vec{r}_\alpha\right]\cdot\vec{v}_\alpha = \vec{\omega}\cdot\left(\sum_\alpha \vec{r}_\alpha\times m_\alpha\vec{v}_\alpha\right) = \vec{\omega}\cdot\sum_\alpha\vec{L}_\alpha = \vec{\omega}\cdot\vec{L}$

This term is responsible for the coupling between rotational and vibrational motion.

In general, it cannot be ignored. But for preliminary consideration we will consider vibrations and rotations independently from each other and consider their coupling later.