If atoms and molecules are described by Quantum mechanics, why are we looking at classical problems?

$$\hat{H} = -\sum_{I=1}^{P} \frac{\hbar^2}{2M_I} \nabla_I^2 - \sum_{i=1}^{N} \frac{\hbar^2}{2m} \nabla_i^2 + \frac{e^2}{2} \sum_{I=1}^{P} \sum_{I \neq J}^{P} \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|}$$

$$+ \frac{e^2}{2} \sum_{i=1}^{N} \sum_{i \neq j}^{N} \frac{1}{|\vec{r}_i - \vec{r}_j|} - e^2 \sum_{I=1}^{P} \sum_{i=1}^{P} \frac{Z_I}{|\vec{R}_I - \vec{r}_i|}$$

$$\hat{H} \Psi_n(\vec{R}, \vec{r}) = \mathcal{E}_n \Psi_n(\vec{R}, \vec{r})$$

↳ many body wave function

$$\hat{T}_e = -\sum_{i=1}^{N} \frac{\hbar^2}{2m} \nabla_i^2$$

$$\hat{U}_{ee} = \frac{e^2}{2} \sum_{i=1}^{N} \sum_{i \neq j}^{N} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

$$\hat{V}_{eN} = -e^2 \sum_{I=1}^{P} \sum_{i=1}^{P} \frac{Z_I}{|\vec{R}_I - \vec{r}_i|}$$

$$\hat{T}_N = -\sum_{I=1}^{P} \frac{\hbar^2}{2M_I}$$

$$\hat{U}_{NN} = \frac{e^2}{2} \sum_{I=1}^{P} \sum_{J \neq I}^{P} \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|}$$

If the nuclei were frozen

$$\hat{h}_e \Phi_n(\vec{R}, \vec{r}) = E_n(\vec{R}) \Phi_n(\vec{R}, \vec{r})$$

↳ parameter ≡ configuration of nuclei

$$\hat{h}_e = \hat{T}_e + \hat{U}_{ee} + \hat{V}_{Ne}$$

In general terms

$$\Psi(\vec{R},\vec{r},t) = \sum_n \Theta_n(\vec{R},t)\,\Phi_n(\vec{R},\vec{r})$$

$\Phi_n(\vec{R},\vec{r})$ adiabatic eigenstates

$$\hat{H}\Psi(\vec{R},\vec{r},t) = i\hbar\frac{\partial \Psi(\vec{R},\vec{r},t)}{\partial t}$$

$$\sum_n\left(\hat{T}_e + \hat{T}_N + \hat{U}_{ee} + \hat{V}_{eN} + \hat{U}_{NN}\right)\Theta_n(\vec{R},t)\,\Phi_n(\vec{R},\vec{r}) = i\hbar\frac{\partial}{\partial t}\sum_n \Theta_n(\vec{R},t)\,\Phi_n(\vec{R},\vec{r})$$

$$\sum_n\left[i\hbar\frac{\partial}{\partial t} - \hat{T}_N - \hat{U}_{NN} - E_n(\vec{R})\right]\Theta_n(\vec{R},t)\,\Phi_n(\vec{R},t)$$

defines a potential energy surface
(actually needs to include the NN term)

$$\hat{T}_N\,\Theta_n(\vec{R},t)\,\Phi_n(\vec{R},\vec{r}) = -\sum_{I=1}^{P}\frac{\hbar^2}{2M_I}\nabla_I^2\left[\Theta_n(\vec{R},t)\,\Phi_n(\vec{R},\vec{r})\right]$$

$$= -\sum_{I=1}^{P}\frac{\hbar^2}{2M_I}\nabla_I\left[\left(\nabla_I\Theta_n(\vec{R},t)\right)\Phi_n(\vec{R},\vec{r}) + \Theta_n(\vec{R},t)\,\nabla_I\Phi_n(\vec{R},\vec{r})\right]$$

$$= -\sum_{I=1}^{P}\frac{\hbar^2}{2M_I}\Big[\left(\nabla_I^2\Theta_n(\vec{R},t)\right)\Phi_n(\vec{R},\vec{r}) + \nabla_I\Theta_n(\vec{R},t)\,\nabla_I\Phi_n(\vec{R},\vec{r})$$

$$+ \nabla_I\Theta_n(\vec{R},t)\,\nabla_I\Phi_n(\vec{R},\vec{r}) + \Theta_n(\vec{R},t)\,\nabla_I^2\Phi_n(\vec{R},\vec{r})\Big]$$

$$\sum_n\left[\overbrace{\left(i\hbar\frac{\partial}{\partial t} + \sum_{I=1}^{P}\frac{\hbar^2}{2M_I}\nabla_I^2 - \hat{U}_{NN} - E_n(\vec{R})\right)}^{\hat{H}_{adiabatic}}\Theta_n(\vec{R},t)\right]\Phi_n(\vec{R},\vec{r})$$

$$= -\sum_n\sum_{I=1}^{P}\frac{\hbar^2}{2M_I}\Theta_n(\vec{R},t)\,\nabla_I^2\Phi_n(\vec{R},\vec{r}) - 2\sum_n\sum_{I=1}^{P}\frac{\hbar^2}{2M_I}\nabla_I\Theta_n(\vec{R},t)\,\nabla_I\Phi_n(\vec{R},\vec{r})$$

$\int d\vec{r}\ \Phi_q^*(\vec{R},\vec{r})$ the first term has no dependency on $\vec{r}$

RHS $\sum_n \int d\vec{r}\ \Phi_q^* \hat{H}_{adiabatic} \Theta_n(\vec{R},t)\, \Phi_n(\vec{R},\vec{r}) = \sum_n \hat{H}_{adiabatic}\Theta_n \underbrace{\int d\vec{r}\ \Phi_q^*(\vec{R},\vec{r})\Phi_n(\vec{R},\vec{r})}_{\delta_{qn}}$

$= \hat{H}_{adiabatic}\ \Theta_q(\vec{R},t)$

RHS

$$= -\sum_n \sum_{I=1}^{P} \frac{\hbar^2}{2M_I} \Theta_n(\vec{R},t) \langle \Phi_q | \nabla_I^2 | \Phi_n \rangle$$
$$-2\sum_n \sum_{I=1}^{P} \frac{\hbar^2}{2M_I} \nabla_I \Theta_n(\vec{R},t) \langle \Phi_q | \nabla_I | \Phi_n \rangle$$

couples different electron states

For off-diagonal terms
$q \neq n$

$\int d\vec{R}\ \Phi_q^*(\vec{R},t)$

RHS $\int d\vec{R}\ \Phi_q^*(\vec{R},t)\, \hat{H}_{adiabatic}\ \Phi_q(\vec{R},t)$

RHS

$$= -\sum_n \sum_{I=1}^{P} \frac{\hbar^2}{2M_I} \langle \cancel{\Phi_q | \Theta_n} \rangle \langle \Phi_q | \nabla_I^2 | \Phi_n \rangle$$
$$\underbrace{-2\sum_n \sum_{I=P} \frac{\hbar^2}{2M_I} \langle \Theta_q | \nabla_I | \Theta_n \rangle \langle \Phi_q | \nabla_I | \Phi_n \rangle}_{\text{if } = 0\ \forall n}$$

then $\Theta_{adiabatic}$ is a solution of $\hat{H}_{adiabatic}$

$$\Psi(\vec{R},\vec{r},t) = \Theta_n(\vec{R},t)\, \Phi_n(\vec{R},\vec{r})$$

The necessary condition

$$\left| \sum_{I=1}^{P} \frac{\hbar^2}{M_I} \langle \Theta_q | \nabla_I | \Theta_n \rangle \langle \Phi_q | \nabla | \Phi_n \rangle \right| \ll \left| E_q(\vec{R}) - E_n(\vec{R}) \right|$$

adiabatic approximation!

Furthermore

at $T = 300\,K$ for Hydrogen

$\lambda_T \sim 0.2\,\mathring{A}$

H-H bond in H_2 is $\sim 1\,\mathring{A}$

$\Rightarrow$ movement of nuclei can be treated <u>classically</u>