Born - Oppenheimer approximation and beyond

Molecular Hamiltonian:

$$\hat{H} = -\sum_\alpha \frac{\hbar^2}{2M_\alpha} \nabla_\alpha^2 \underbrace{}_{\hat{T}_n} - \frac{\hbar^2}{2m} \sum_i \nabla_i^2 \underbrace{}_{\hat{T}_e} + \frac{1}{2} \sum_{\alpha \neq \beta} \frac{Z_\alpha Z_\beta e^2}{|\vec{R}_\alpha - \vec{R}_\beta|} +$$

$$\left. + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} - \sum_{\alpha, i} \frac{Z_\alpha e^2}{|\vec{R}_\alpha - \vec{r}_i|} \right\} u(\vec{r}, \vec{R})$$

We are interested to solve the molecular Schrödinger equation:

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

This is too complicated problem to solve directly.
We need to find more efficient way to do it.

Let's expand the full molecular WF in a basis:

$$\Psi(\vec{r}, \vec{R}, t) = \sum_i \chi_i(\vec{R}, t) \, \Phi_i(\vec{r}, \vec{R})$$

$$\hat{H} \Psi = \left(\hat{T}_n + \hat{H}_e\right) \sum_i \chi_i \Phi_i = \left(-\sum_\alpha \frac{\hbar^2}{2M_\alpha} \nabla_\alpha^2 + H_e\right) \sum_i \chi_i \Phi_i =$$

$$= \sum_\alpha \sum_i \left(-\frac{\hbar^2}{2M_\alpha} \left(\nabla_\alpha^2 \chi_i \, \Phi_i + 2 \nabla_\alpha \chi_i \cdot \nabla_\alpha \Phi_i + \chi_i \nabla_\alpha^2 \Phi_i\right) + \chi_i \hat{H}_e \Phi_i\right)$$

We also have

$$i\hbar \frac{\partial}{\partial t} \Psi = i\hbar \frac{\partial}{\partial t} \sum_i \chi_i(\vec{R}, t) \, \Phi_i(\vec{r}, \vec{R}) = i\hbar \sum_i \frac{\partial}{\partial t} \chi_i \, \Phi_i$$

We project on ϕ_j, thus we have:
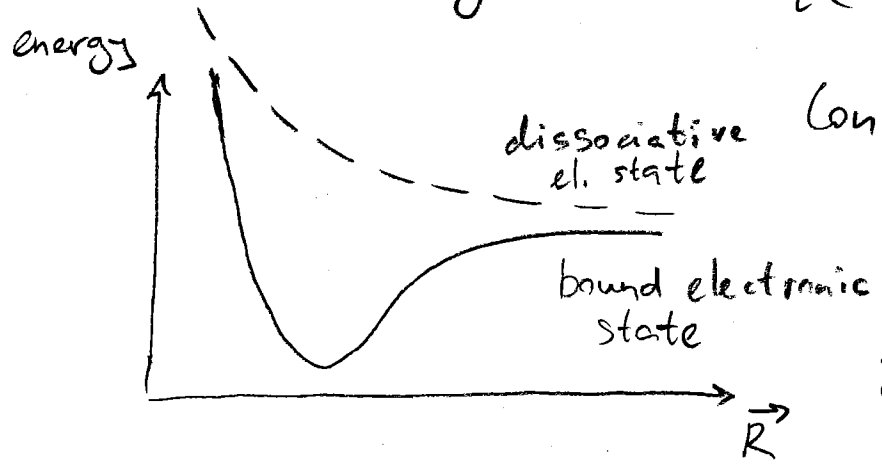
$$i\hbar\frac{\partial}{\partial t}\chi_j = \sum_\alpha \left[-\frac{\hbar^2}{2M_\alpha}\nabla_\alpha^2 \chi_j + \sum_i \langle \phi_j | \hat{H}_e | \phi_i \rangle \chi_i \right.$$

$$\left. + \sum_i \left(2\langle \phi_j | \nabla_\alpha | \phi_i \rangle \cdot \nabla_\alpha \chi_i + \langle \phi_j | \nabla_\alpha^2 | \phi_i \rangle \right) \right]$$
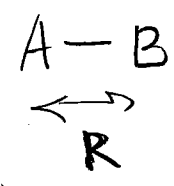
We have two options to simplify the above equation.

I) We can choose the basis $\{\phi_i\}$ such that

$$\hat{H}_e \, \phi_i(\vec{z}, \vec{R}) = V_i(\vec{R}) \phi_i(\vec{z}, \vec{R}).$$

$\hat{H}_e$ is electronic operator which depends on $\vec{R}$ as parameters. Therefore for every $\vec{R}$ we will have a set of eigenvalues $V_i(\vec{R})$ which are then functions of $\vec{R}$.

energy

dissociative el. state

bound electronic state

Consider diatomic molecule

$$A - B$$

$\overleftrightarrow{R}$

if $R \to \infty$ the terms in Hamiltonian $\hat{H}_e$ can be splited in A and B subsystems leading thus to two atoms A and B

Non-adiabatic couplings:

$$\vec{F}_{ji} = \langle \varphi_j | \vec{\nabla}_\alpha | \varphi_i \rangle \quad \text{and} \quad \langle \varphi_j | \nabla_\alpha^2 | \varphi_i \rangle = G_{ji}$$

Acting by ∇_α on $\vec{F}_{ji}$ we get:

$$\nabla \cdot F_{ji} = \langle \nabla \varphi_j | \nabla \varphi_i \rangle + \underbrace{\langle \varphi_j | \nabla^2 | \varphi_i \rangle}_{G_{ji}}$$

$$\uparrow$$

$$\sum_K |\varphi_k\rangle\langle\varphi_k|$$

$$G_{ji} = \nabla \cdot F_{ji} - \langle \nabla \varphi_j | \sum_K |\varphi_k\rangle\langle\varphi_k | \nabla \varphi_i \rangle =$$

$$= \nabla \cdot F_{ji} - \sum_K \langle \nabla \varphi_j | \varphi_k \rangle\langle\varphi_k | \nabla | \varphi_i \rangle$$