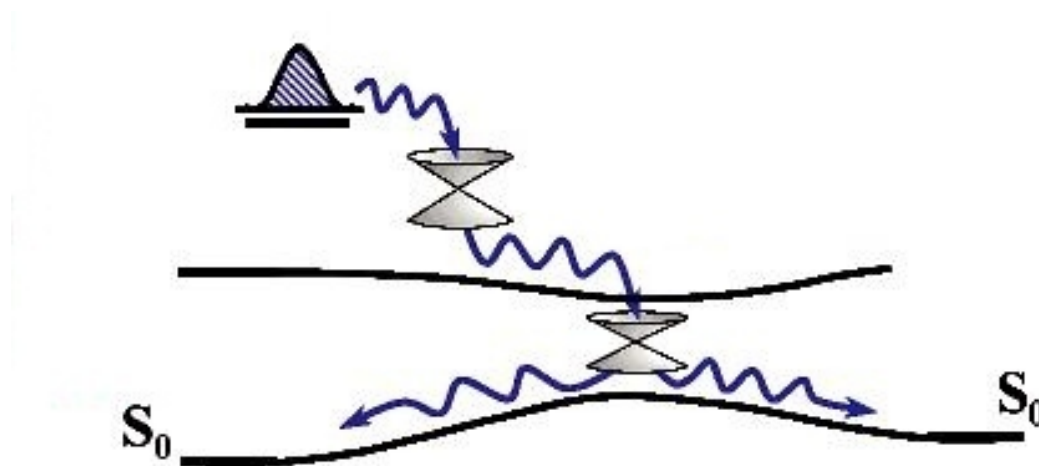


Ringvorlesung Biophysik 2017

Born-Oppenheimer Approximation & Beyond



Irene Burghardt (burghardt@chemie.uni-frankfurt.de)

<http://www.theochem.uni-frankfurt.de/teaching/>

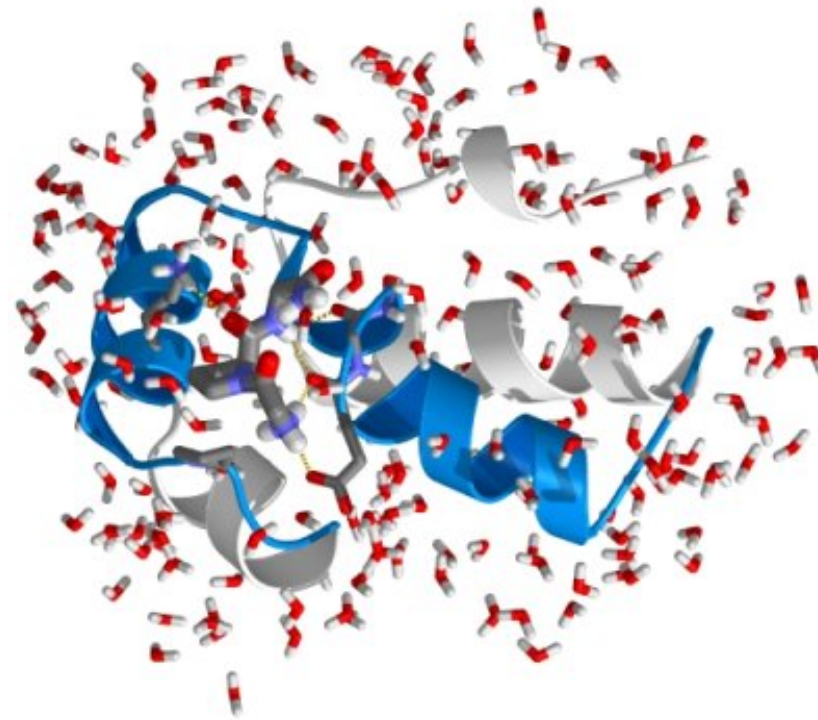
Starting point: the molecular Hamiltonian

all electrons and nuclei

$$\begin{aligned}\hat{H} &= \hat{T}_e + \hat{T}_N + \hat{V}_e + \hat{V}_N + \hat{V}_{eN} \\ &= - \sum_{i=1}^{N_e} \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{a=1}^{N_N} \frac{\hbar^2}{2M_a} \nabla_a^2 \\ &\quad + \frac{e^2}{4\pi\epsilon_0} \left\{ \sum_{i=1}^{N_e} \sum_{j>i}^{N_e} \frac{1}{r_{ij}} + \sum_{a=1}^{N_N} \sum_{b>a}^{N_N} \frac{Z_a Z_b}{r_{ab}} - \sum_{i=1}^{N_e} \sum_{a=1}^{N_N} \frac{Z_a}{r_{ia}} \right\}\end{aligned}$$

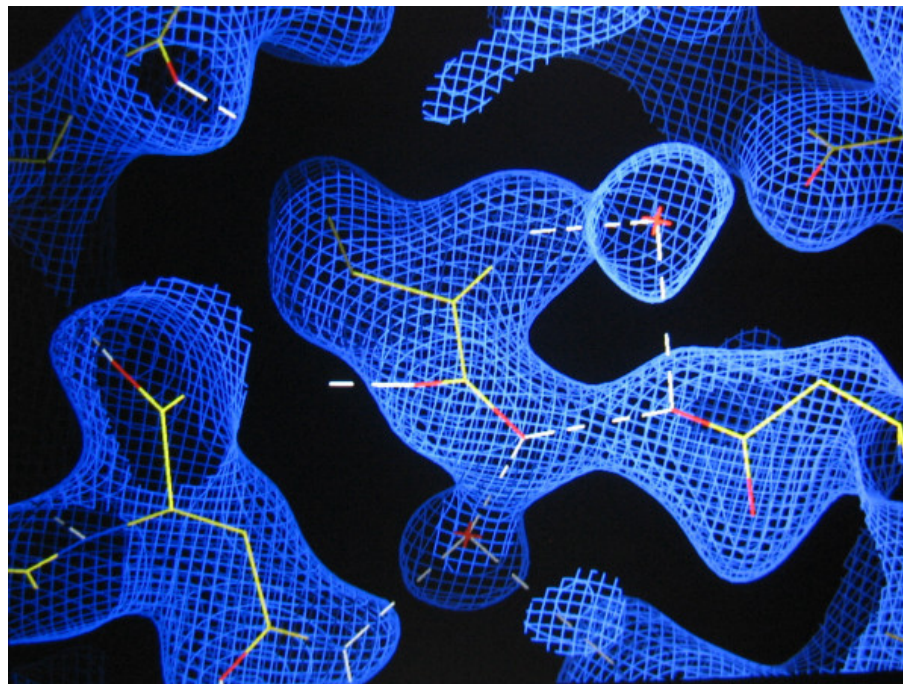
$$i\hbar \frac{\partial}{\partial t} \psi = \hat{H} \psi \qquad \hat{H} \psi = E \psi$$

But we might eventually do classical molecular dynamics (MD) simulations, e.g., for proteins



- Quantum \longrightarrow classical transition due to decoherence
- Do any quantum effects survive?

Of course the electrons always need a quantum mechanical treatment. . .



. . . but they are usually integrated out so as to yield effective potentials for the nuclear motion (Born-Oppenheimer approach)

Two Steps

- 1 – **Born-Oppenheimer approximation**: separate the electronic and nuclear motions and generate effective potentials for the nuclear motion
- 2 – **follow the dynamics of the nuclei**, either using quantum dynamics (time-dependent Schrödinger equation) or else using classical dynamics (Newton's equations)(*)

(*) . . . or else using a variety of semiclassical and “mixed” quantum-classical approaches

Step 1. The Born-Oppenheimer Approximation



Max Born Robert Oppenheimer

1927

№ 20

ANNALEN DER PHYSIK VIERTE FOLGE. BAND 84

1. *Zur Quantentheorie der Molekeln;* *von M. Born und R. Oppenheimer*

Es wird gezeigt, daß die bekannten Anteile der Terme einer Molekel, die der Energie der Elektronenbewegung, der Kernschwingungen und der Rotationen entsprechen, systematisch als die Glieder einer Potenzentwicklung nach der vierten Wurzel des Verhältnisses Elektronenmasse zu (mittlerer) Kernmasse gewonnen werden können. Das Verfahren liefert u. a. eine Gleichung für die Rotationen, die eine Verallgemeinerung des Ansatzes von Kramers und Pauli (Kreisel mit eingebautem Schwungrad) darstellt. Ferner ergibt sich eine Rechtfertigung der von Franck und Condon angestellten Betrachtungen über die Intensität von Bandenlinien. Die Verhältnisse werden am Beispiel der zweiatomigen Molekeln erläutert.

- Expansion in orders of the mass ratio $m/M \sim 1/1836$

Step 2: calculate the dynamics of the nuclei

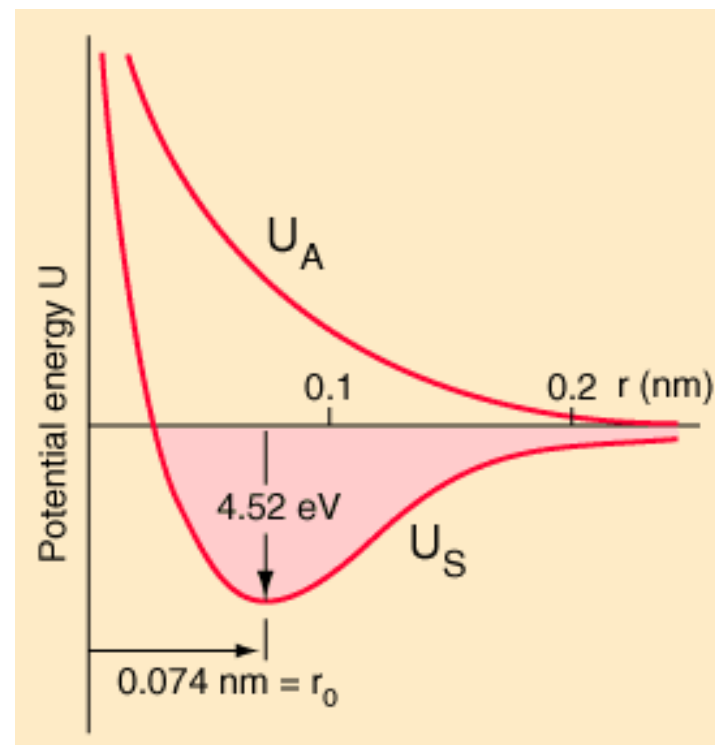
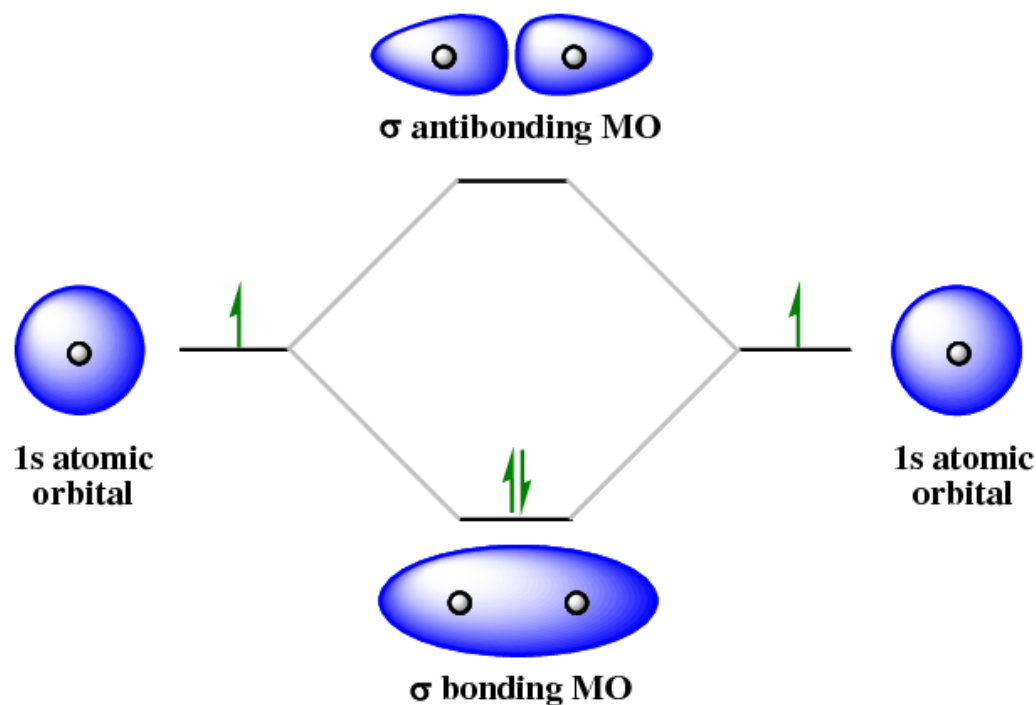
$$i\hbar \frac{\partial \Psi}{\partial t} = (\hat{T} + \hat{V}) \Psi$$

or

$$\dot{q} = \frac{p}{m} \quad \dot{p} = -\nabla V$$

In most biological applications, Newton's equations are used!

Molecular Potential Energy Surfaces (PES's)



- simplest picture: bonding/non-bonding combinations of atomic orbitals
- account for the overall symmetry of the wavefunction

Born-Oppenheimer – basics

Using the idea of an **adiabatic separability of the time scales for electronic vs. nuclear motion**, separate the total Hamiltonian

$$\begin{aligned}\hat{H}_T &= \hat{T}_e + \hat{V}_e + \hat{T}_N + \hat{V}_N + \hat{V}_{eN} \\ &= \hat{T}_N + \hat{H}_{el}\end{aligned}$$

and solve the electronic Schrödinger equation first – disregarding \hat{T}_N :

$$\hat{H}_{el}\psi_n(r_{el}|R) = \epsilon_n(R)\psi_n(r_{el}|R)$$

- The eigenvalues $\epsilon_n(R)$ depend parametrically on the nuclear coordinate(s) and constitute the Born-Oppenheimer surfaces

Born-Oppenheimer, cont'd

If we assume that the overall wavefunction (electronic + nuclear) can be written as

$$\Psi_T(r_{\text{el}}, R) = \psi_n(r_{\text{el}}|R)\chi_n(R)$$

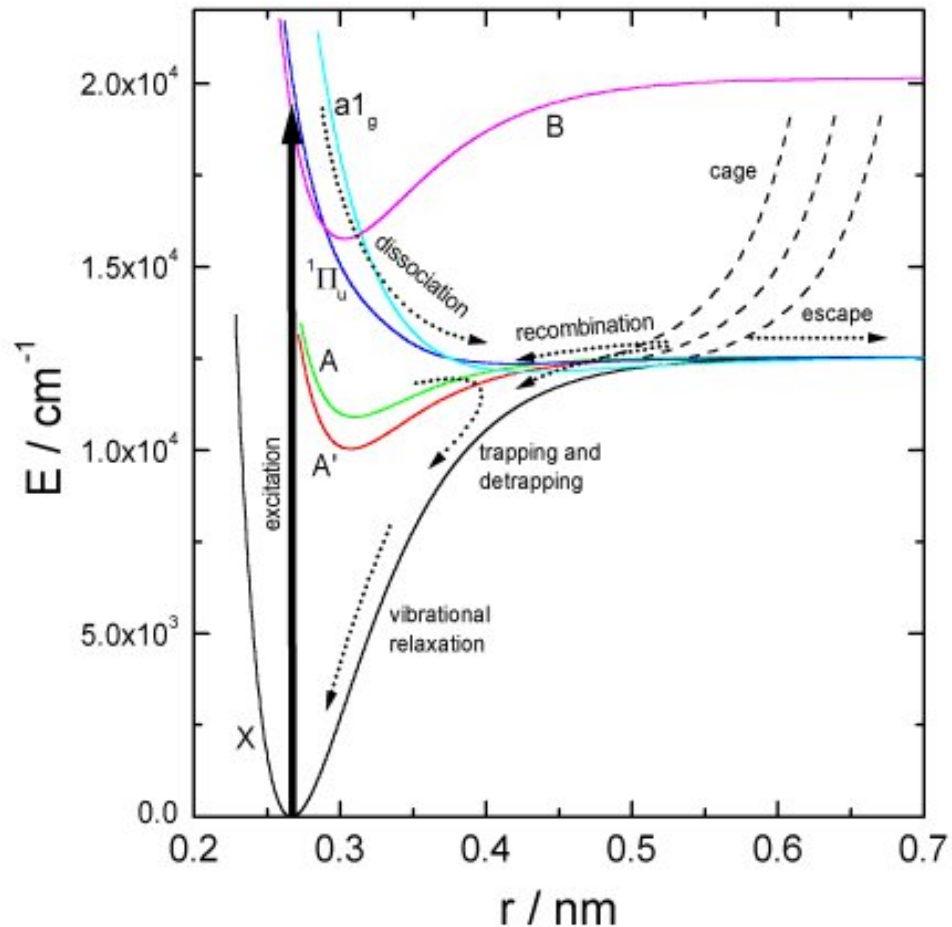
we obtain nuclear motion in terms of the SE (or TDSE) for the nuclear wavefunction $\chi_n(R, t)$ on the n th Born-Oppenheimer surface:

$$\left(-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial R^2} + \epsilon_n(R)\right)\chi_n = E\chi_n \quad i\hbar\frac{\partial\chi_n}{\partial t} = \left(-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial R^2} + \epsilon_n(R)\right)\chi_n$$

- Thus we have separated the electronic-nuclear problem into two parts:

$$\hat{H}_{\text{el}}\psi_n(r_{\text{el}}|R) = \epsilon_n(R)\psi_n(r_{\text{el}}|R) \quad ; \quad i\hbar\dot{\chi}_n = \left(\hat{T}_N + \epsilon_n(R)\right)\chi_n$$

But something isn't quite right...



- Born-Oppenheimer surfaces for the I_2 molecule
- note that in the BO picture, **the nuclei move only on a given BO surface at a time**
- thus, the **multiple crossings of the I_2 potentials are indicative of a breakdown of the BO approximation**

What was wrong about our Born-Oppenheimer derivation?

We have neglected that the **nuclear kinetic energy operator** can have non-zero matrix elements between different **electronic** wavefunctions (since these depend parametrically upon the nuclear coordinates):

$$\langle \psi_1(\mathbf{r}_{\text{el}}|\mathbf{R}) | \hat{T}_N | \psi_2(\mathbf{r}_{\text{el}}|\mathbf{R}) \rangle \chi_2(\mathbf{R}) \neq 0$$

This generates a coupling between different electronic states, and we obtain **“non-adiabatic” transitions** if the states come energetically close to each other. A more general wave function *ansatz* is therefore needed:

$$\Psi_T(\mathbf{r}_{\text{el}}, \mathbf{R}) = \sum_n \psi_n(\mathbf{r}_{\text{el}}|\mathbf{R}) \chi_n(\mathbf{R})$$

The Group Born-Oppenheimer Approximation

- use the improved *ansatz*

$$\Psi_T(r_{\text{el}}, R) = \sum_n \psi_n(r_{\text{el}}|R) \chi_n(R)$$

- where $\psi_n(r_{\text{el}}|R)$ = solutions of the electronic Schrödinger Equation:
 $\hat{H}_{\text{el}} \psi_n(r_{\text{el}}|R) = \epsilon_n(R) \psi_n(r_{\text{el}}|R)$

- now integrate over the electronic coordinates and find that **the nuclear wavefunctions $\{\chi_n(R)\}$ are coupled to each other:**

$$\left(-\frac{\hbar^2}{2M} \frac{\partial^2}{\partial R^2} + \epsilon_n(R) \right) \chi_n + \sum_{m \neq n} \hat{\Lambda}_{mn} \chi_m = E \chi_n$$

- where the **non-adiabatic couplings** are given as

$$\hat{\Lambda}_{mn} = -\frac{\hbar^2}{M} \langle \psi_m | \frac{\partial}{\partial R} | \psi_n \rangle \frac{\partial}{\partial R} + \langle \psi_m | \hat{T}_N | \psi_n \rangle$$

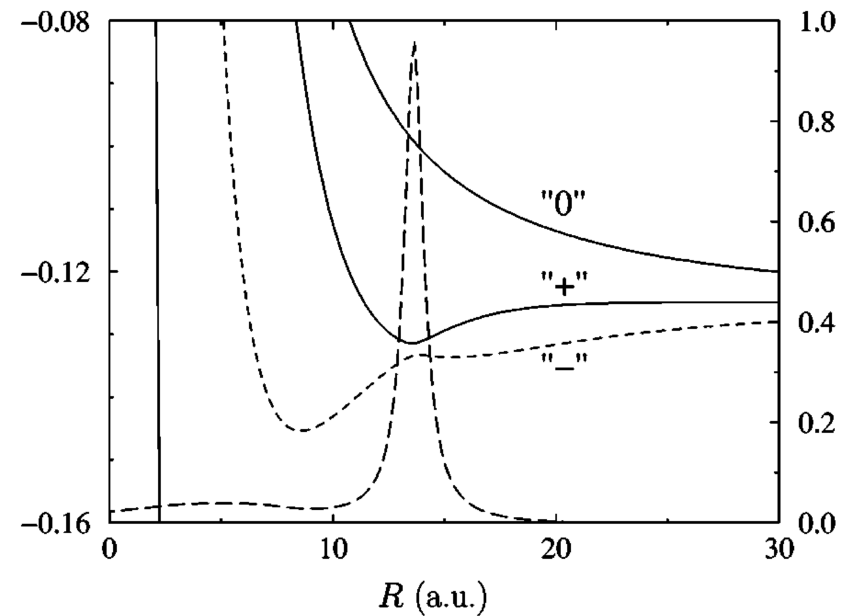
Coupled BO surfaces: non-adiabatic effects

$$i\hbar \frac{\partial}{\partial t} \begin{pmatrix} \chi_1(\mathbf{R}, t) \\ \chi_2(\mathbf{R}, t) \end{pmatrix} = \begin{pmatrix} \hat{T}_N + \epsilon_1(\mathbf{R}) & \hat{\Lambda}_{12}(\mathbf{R}) \\ \hat{\Lambda}_{21}(\mathbf{R}) & \hat{T}_N + \epsilon_2(\mathbf{R}) \end{pmatrix} \begin{pmatrix} \chi_1(\mathbf{R}, t) \\ \chi_2(\mathbf{R}, t) \end{pmatrix}$$

$$\hat{T}_N = -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial R^2}$$

$$\hat{\Lambda}_{12}(\mathbf{R}) = -\frac{\hbar^2}{M} \langle \psi_1 | \frac{\partial}{\partial \mathbf{R}} | \psi_2 \rangle \frac{\partial}{\partial \mathbf{R}} + \langle \psi_1 | \hat{T}_N | \psi_2 \rangle$$

coupling through nuclear kinetic energy!



“Diabatic” representation

- unitary transformation of electronic wavefunctions such that the kinetic energy couplings (almost) vanish,

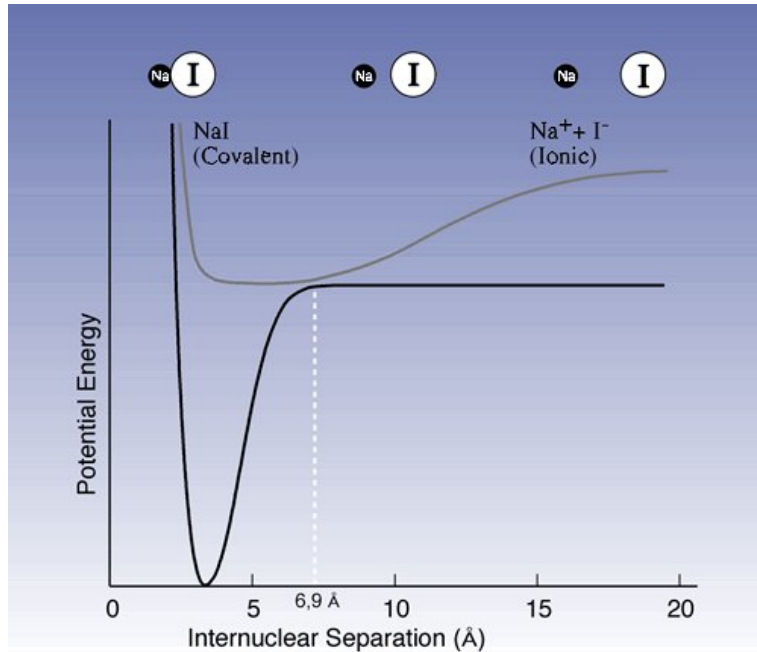
$$\Phi^{\text{dia}}(\mathbf{r}_{\text{el}}; \mathbf{R}) = S(\mathbf{R})\psi^{\text{ad}}(\mathbf{r}_{\text{el}}; \mathbf{R})$$

- in turn, a potential type coupling appears:

$$i\hbar \frac{\partial}{\partial t} \begin{pmatrix} \tilde{\chi}_1(\mathbf{R}, t) \\ \tilde{\chi}_2(\mathbf{R}, t) \end{pmatrix} = \begin{pmatrix} \hat{T}_N + V_1^{\text{dia}}(\mathbf{R}) & \mathbf{V}_{12}(\mathbf{R}) \\ \mathbf{V}_{21}(\mathbf{R}) & \hat{T}_N + V_2^{\text{dia}}(\mathbf{R}) \end{pmatrix} \begin{pmatrix} \tilde{\chi}_1(\mathbf{R}, t) \\ \tilde{\chi}_2(\mathbf{R}, t) \end{pmatrix}$$

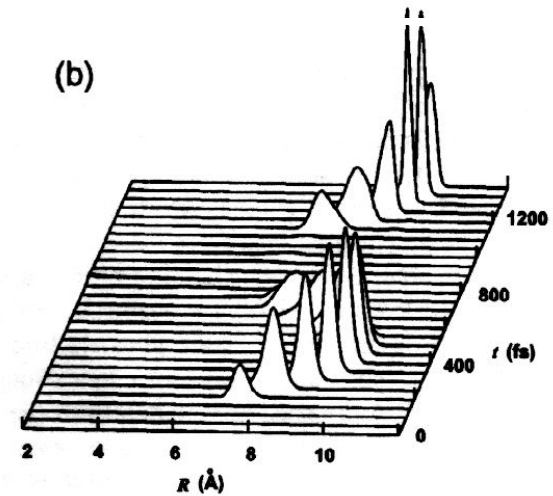
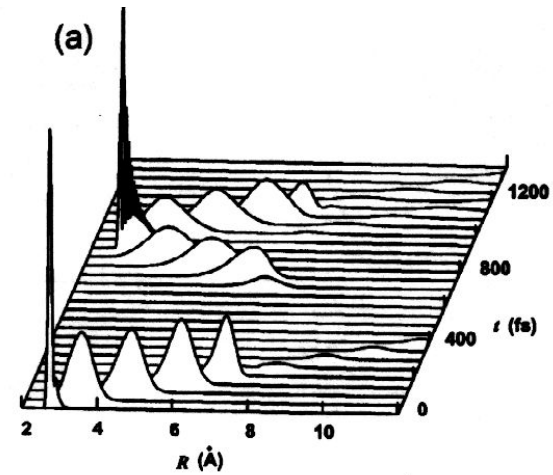
- in practice, one often prefers to work with a diabatic representation, since the diabatic states have a well-defined electronic character, and the calculation of derivative couplings is avoided

Example: dissociation of NaI



(a) = covalent

(b) = ionic



- in this case, the dynamics is “almost” adiabatic on the upper BO surface