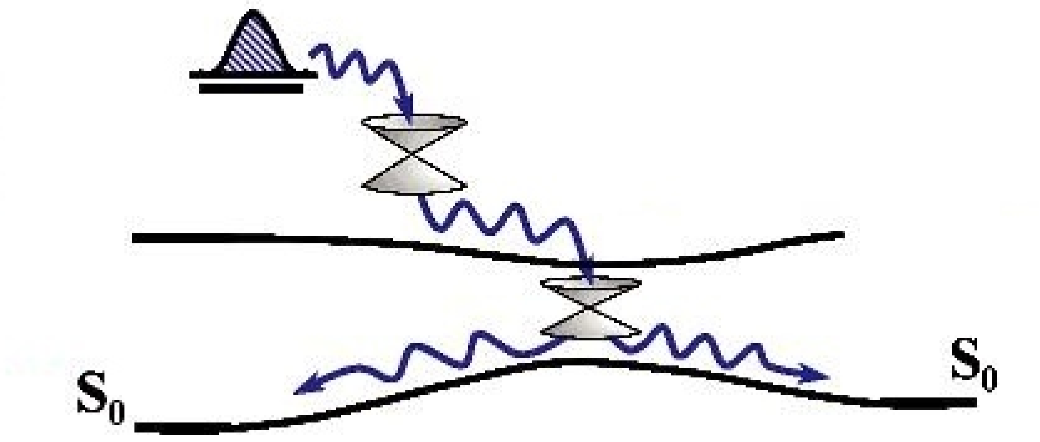
Theoretical Photochemistry WiSe 2017/18

Lecture 2



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http://www.theochem.uni-frankfurt.de/teaching/ ⟶ Theoretical Photochemistry

Topics

1. Photophysical Processes
3. Wavepackets
5. The Franck-Condon picture of electronic transitions
6. What do we measure experimentally?
2. The Born-Oppenheimer approximation
4. Beyond Born-Oppenheimer – non-adiabatic transitions
7. Conical intersections
8. Examples: Ethene, Protonated Schiff Bases (Retinal), Azobenzene
9. Some electronic structure aspects
10. Dynamics: trajectories or wavefunctions?
11. Wavefunction propagation techniques

12. **Trajectory surface hopping techniques**
13. **Non-linear optical spectroscopy: calculation of spectroscopic signals**
14. **Extended systems: Excitons, light-harvesting, etc.**
15. **Solvent/environmental effects**

Literature

1. P. W. Atkins and R. Friedman, Molecular Quantum Mechanics, 5th Edition, Oxford University Press (2011).
2. D. Tannor, Introduction to Quantum Mechanics: A Time-Dependent Perspective, University Science Books (2006).
3. M. Klessinger, J. Michl, Excited States and Photochemistry of Organic Molecules, VCH-Wiley (1995).
4. I. N. Levine, Quantum Chemistry, 6th Edition, Pearson International Edition (2009).
5. F. Jensen, Introduction to Computational Chemistry, 2nd Edition, Wiley (2007).
6. C. J. Cramer, Essentials of Computational Chemistry – Theories and Models, 2nd Edition, Wiley (2004).

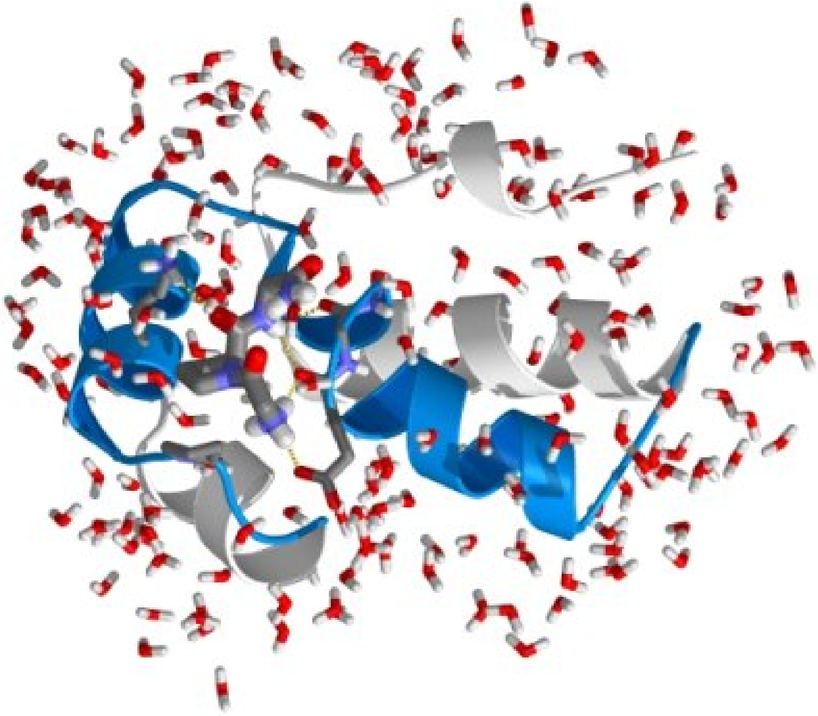
Starting point: the molecular Hamiltonian

all electrons and nuclei

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

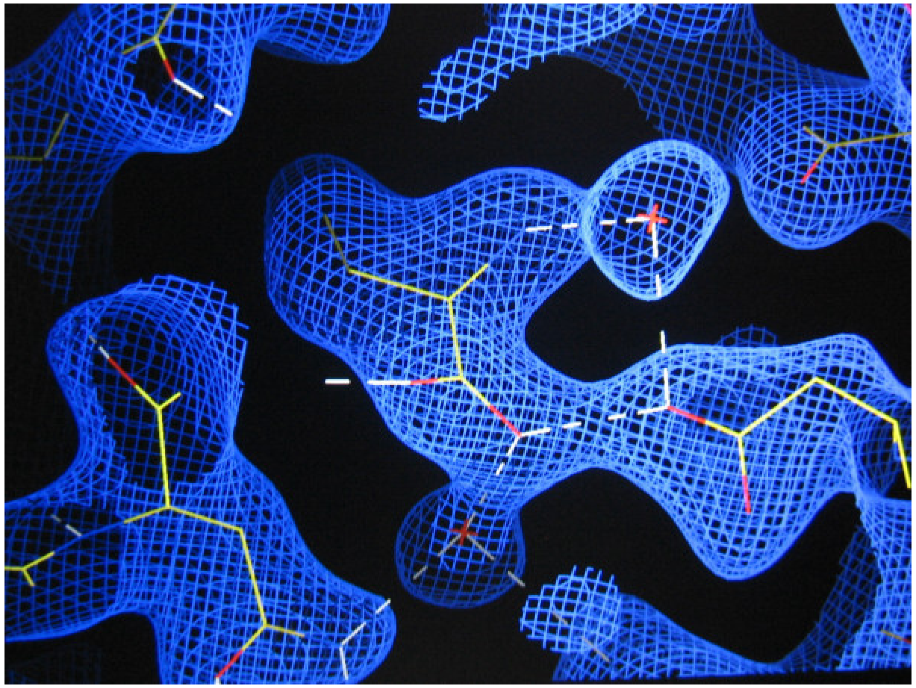
$$\boxed{i\hbar\frac{\partial}{\partial t}\psi = \hat{H}\psi \qquad\qquad \hat{H}\psi = E\psi}$$

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



- Quantum ⟶ 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

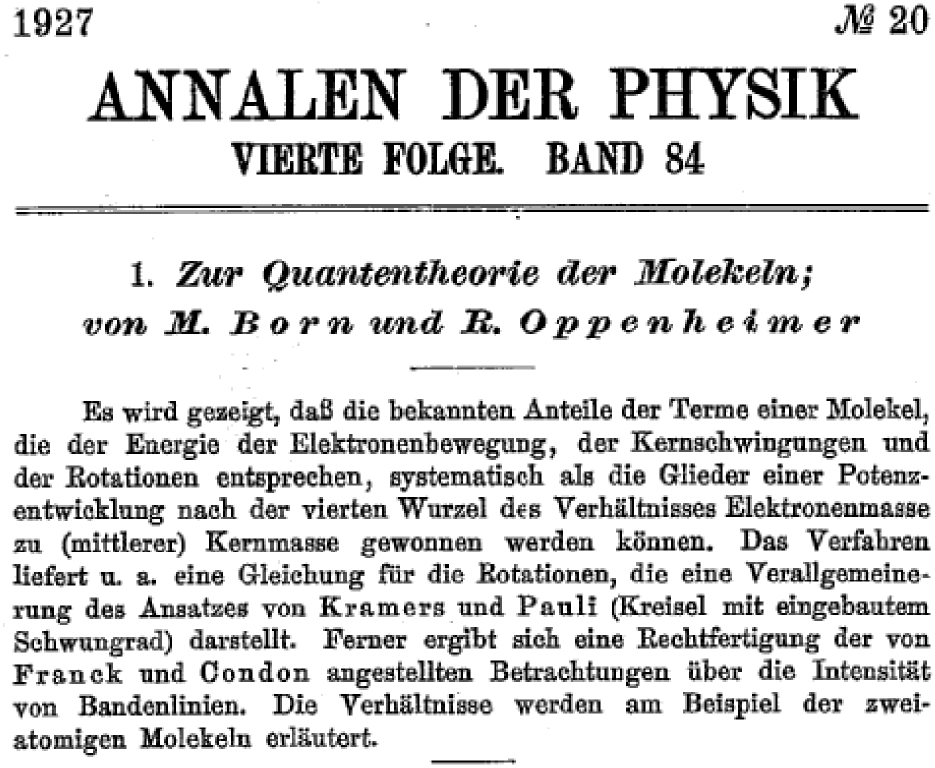
1 – **Born-Oppenheimer approximation**: separate the electronic and nuclear motions and generate effective potentials for the nuclear motion

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**



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ANNALEN DER PHYSIK

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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

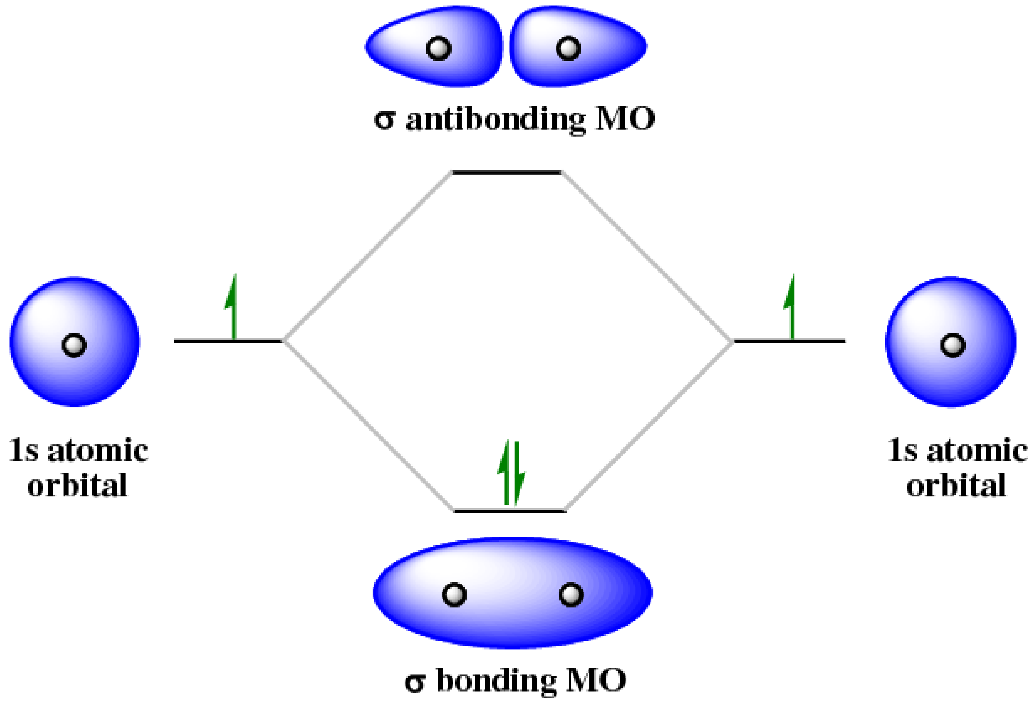
$$i\hbar\frac{\partial\Psi}{\partial t} = (\hat{T} + \hat{V})\Psi$$

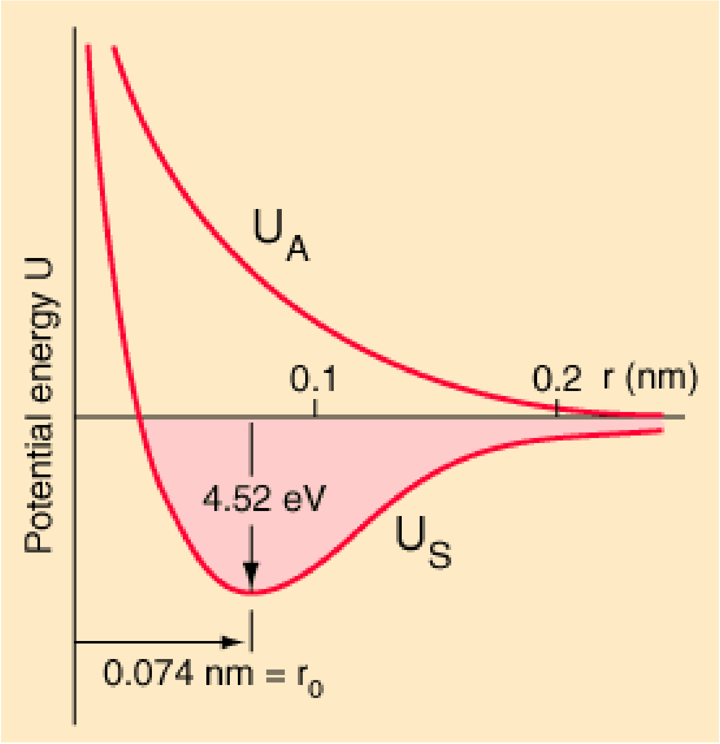
or

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

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

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

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

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

- **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

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

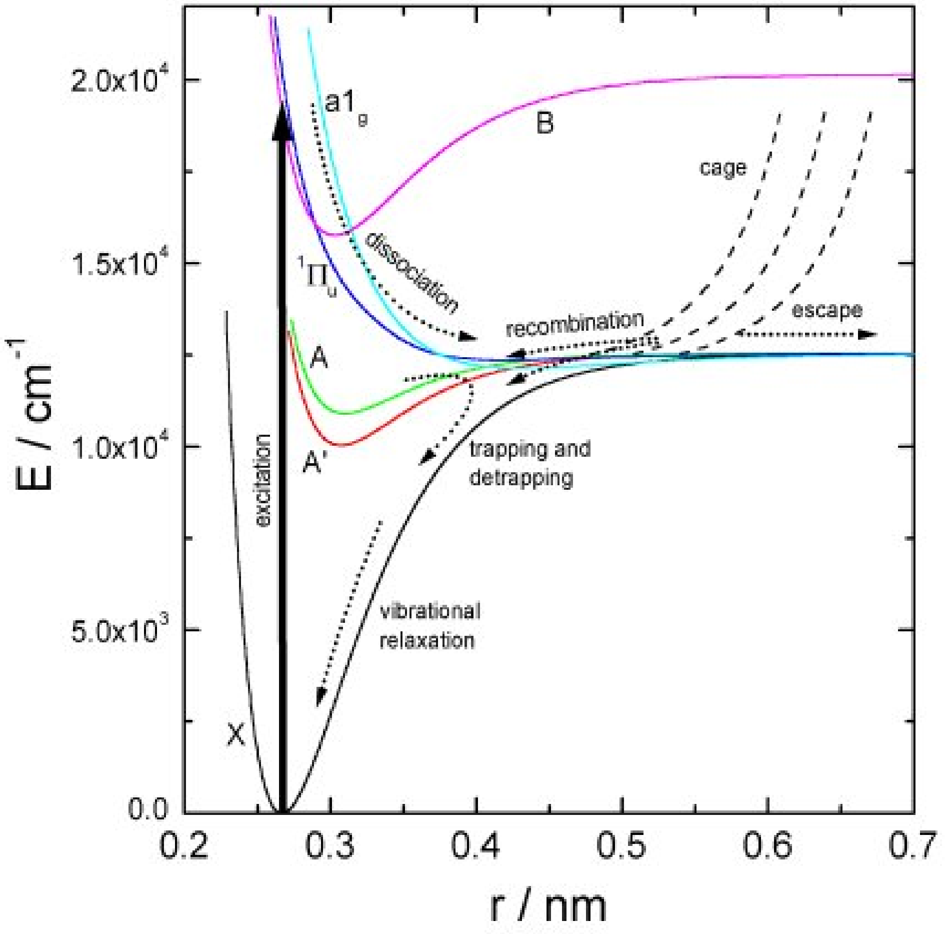
we obtain nuclear motion in terms of the SE (or TDSE) for the nuclear wavefunction $\chi_n(R,t)$ on the nth Born-Oppenheimer surface:

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

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

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

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):

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

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:

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

The Group Born-Oppenheimer Approximation

- **use the improved** *ansatz*
  $\Psi_T(r_{\mathrm{el}}, R) = \sum_n \psi_n(r_{\mathrm{el}}|R)\chi_n(R)$
- **where** $\psi_n(r_{\mathrm{el}}|R)$ **= solutions of the electronic Schrödinger Equation:**
  $\hat{H}_{\mathrm{el}}\psi_n(r_{\mathrm{el}}|R) = \epsilon_n(R)\psi_n(r_{\mathrm{el}}|R)$
- **now integrate over the electronic coordinates and find that the nuclear wavefunctions** $\{\chi_n(R)\}$ **are coupled to each other:**
  $$\Big(-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial R^2} + \epsilon_n(R)\Big)\chi_n + \sum_m \hat{\Lambda}_{mn}\chi_m = E\chi_n$$
- **where the non-adiabatic couplings are given as**
  $$\hat{\Lambda}_{mn} = -\frac{\hbar^2}{M}\langle\psi_m|\frac{\partial}{\partial R}|\psi_n\rangle\frac{\partial}{\partial R} + \langle\psi_m|\hat{T}_N|\psi_n\rangle$$

Non-adiabatic couplings

The non-adiabatic couplings are often re-written as follows:

$$\begin{aligned}\hat{\Lambda}_{mn} &= -\frac{\hbar^2}{M}\langle\psi_m|\frac{\partial}{\partial R}|\psi_n\rangle\frac{\partial}{\partial R} + \langle\psi_m|\hat{T}_N|\psi_n\rangle \\ &= -\frac{\hbar^2}{2M}\Big(2F_{mn}\frac{\partial}{\partial R} + G_{mn}\Big)\end{aligned}$$

where F_{mn} = non-adiabatic derivative couplings

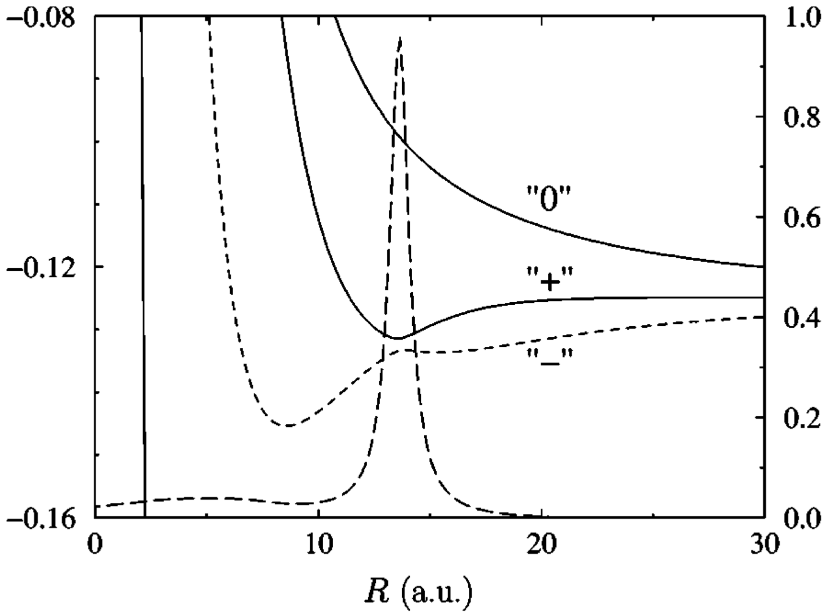
where G_{mn} = non-adiabatic scalar couplings

Coupled BO surfaces: matrix notation

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

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

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

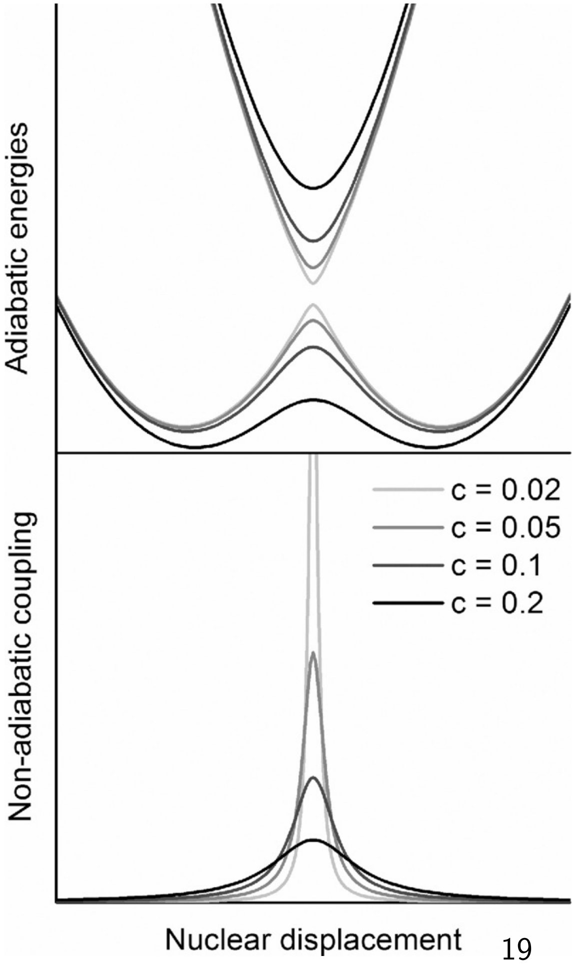


coupling through nuclear kinetic energy!

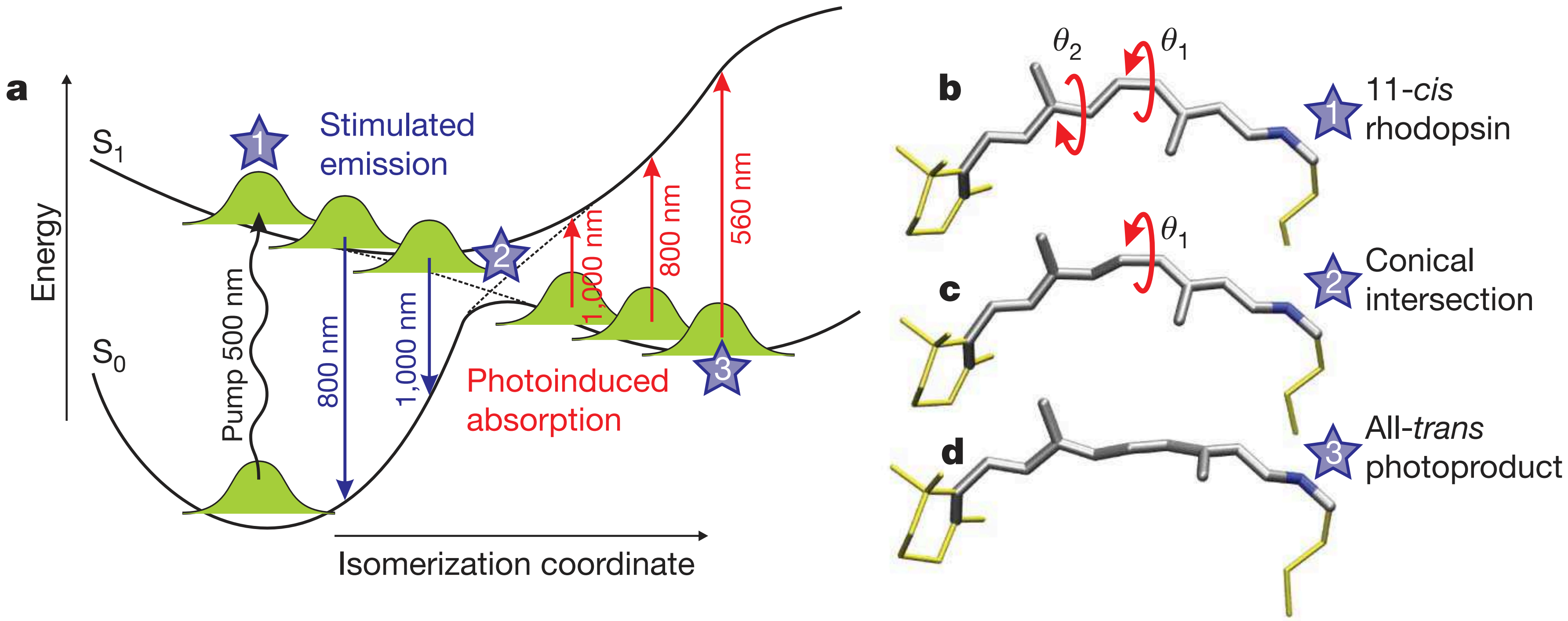
Non-adiabatic coupling at an “avoided crossing”

The non-adiabatic coupling becomes very large at a so-called avoided crossing

This is because the character of the electronic wavefunction changes very rapidly



Wavepacket motion through an avoided crossing



Polli et al., Nature 467, 440 (2010)

- **example: isomerisation of retinal**