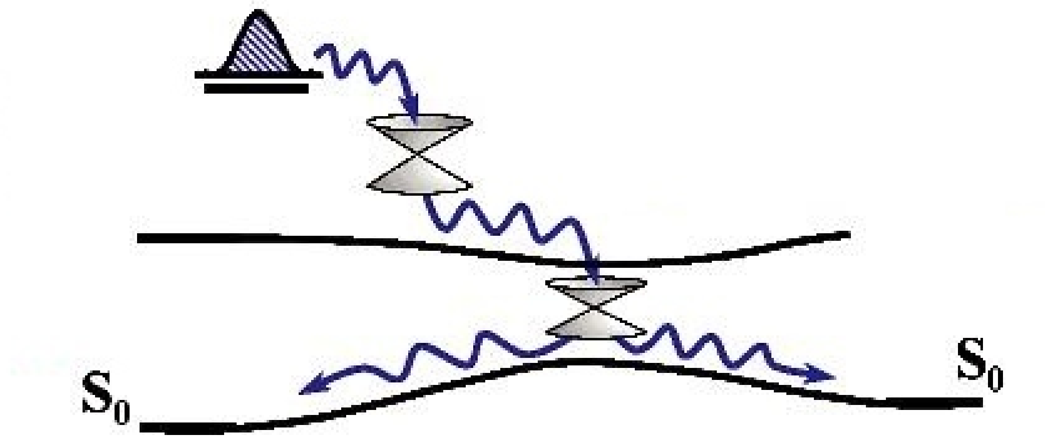
Theoretical Photochemistry WiSe 2017/18

Lecture 3



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

Topics

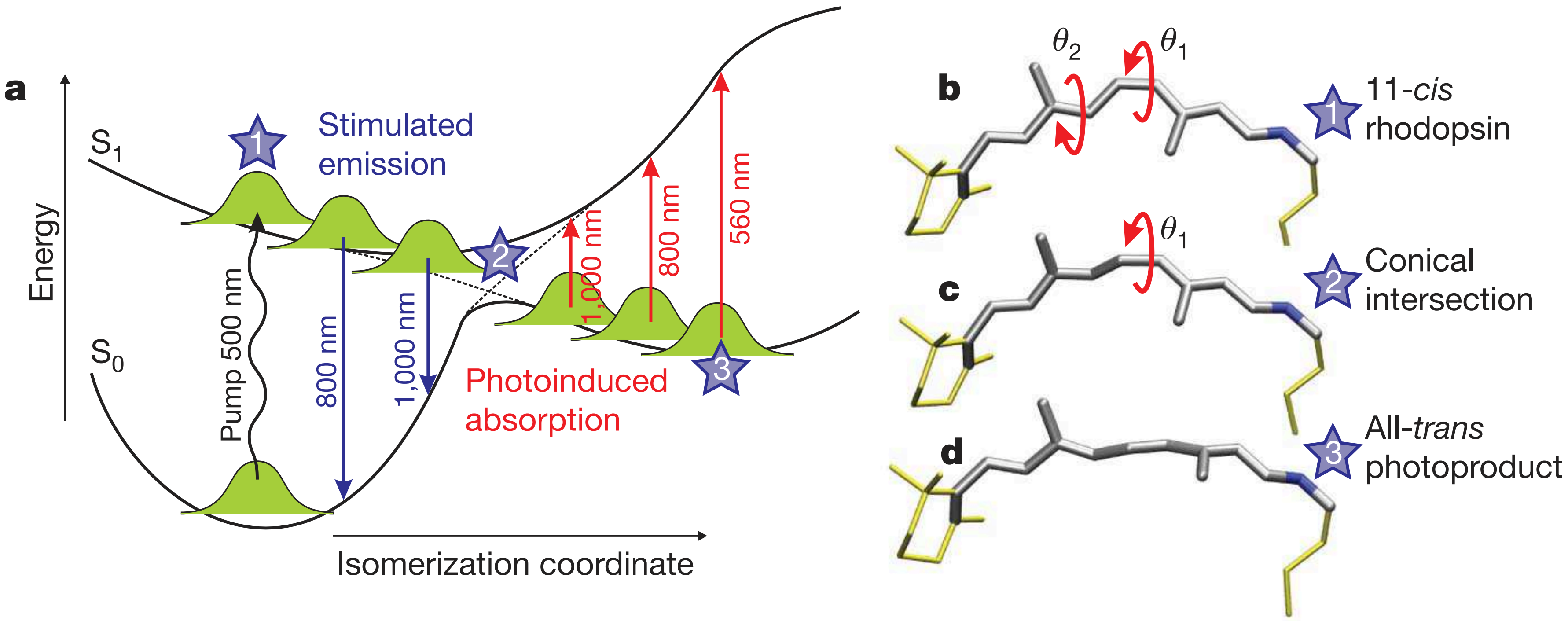
1. Photophysical Processes
3. Wavepackets
5. The Franck-Condon picture of electronic transitions
6. What do we measure experimentally?
2. The Born-Oppenheimer approximation
4. Beyond Born-Oppenheimer – non-adiabatic transitions
7. Conical intersections
8. Examples: Ethene, Protonated Schiff Bases (Retinal), 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).

Non-adiabatic wavepacket motion



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

- **example: isomerisation of retinal**

Coupled BO surfaces: matrix notation

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

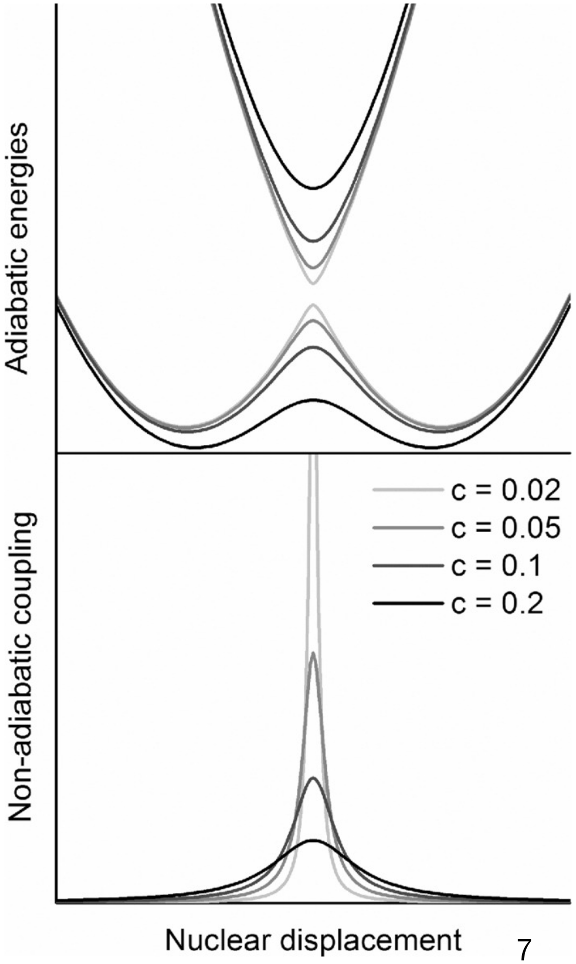
$$=\left[\begin{pmatrix}\hat{T}_N & \hat{\Lambda}_{12}(R)\\ \hat{\Lambda}_{21}(R) & \hat{T}_N\end{pmatrix}+\begin{pmatrix}\epsilon_1(R) & 0\\ 0 & \epsilon_2(R)\end{pmatrix}\right]\begin{pmatrix}\chi_1(R,t)\\ \chi_2(R,t)\end{pmatrix}$$

- non-diagonal representation of the nuclear kinetic energy operator
- diagonal representation of the potential operator (which follows from the fact that the ϵ_n's are eigenvalues of the electronic Schrödinger Equation)

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



“Diabatic” representation

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

$$\Phi^{\mathrm{dia}}(\mathrm{r}_{\mathrm{el}}|\boldsymbol{R}) = \boldsymbol{S}(\boldsymbol{R})\psi^{\mathrm{ad}}(\mathrm{r}_{\mathrm{el}}|\boldsymbol{R})$$

- in turn, a potential type coupling appears:

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

- 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

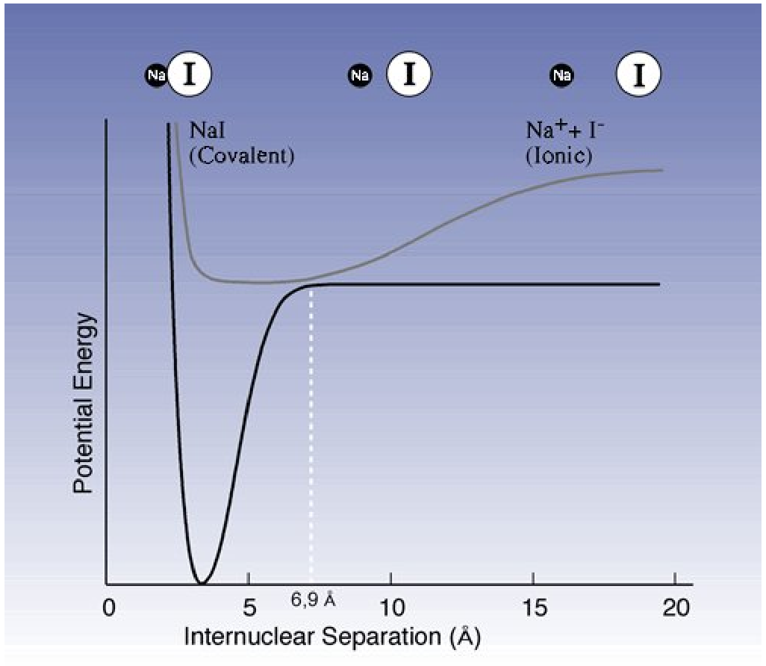
Diabatic representation: matrix notation

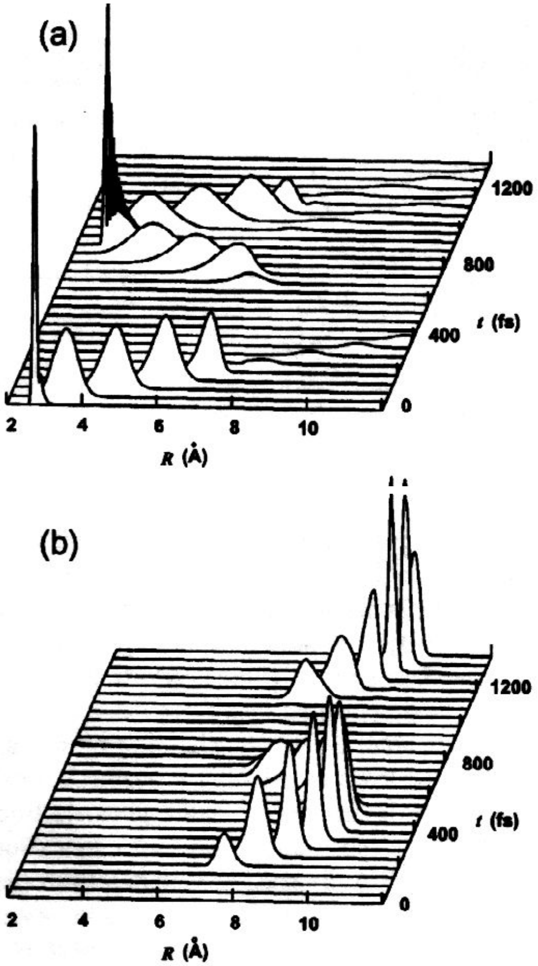
$$i\hbar\frac{\partial}{\partial t}\begin{pmatrix}\tilde{\chi}_1(\boldsymbol{R},t)\\ \tilde{\chi}_2(\boldsymbol{R},t)\end{pmatrix} = \begin{pmatrix}\hat{T}_N + V_1(\boldsymbol{R}) & V_{12}(\boldsymbol{R})\\ V_{21}(\boldsymbol{R}) & \hat{T}_N + V_2(\boldsymbol{R})\end{pmatrix}\begin{pmatrix}\tilde{\chi}_1(\boldsymbol{R},t)\\ \tilde{\chi}_2(\boldsymbol{R},t)\end{pmatrix}$$

$$= \left[\begin{pmatrix}\hat{T}_N & 0\\ 0 & \hat{T}_N\end{pmatrix} + \begin{pmatrix}V_1(\boldsymbol{R}) & V_{12}(\boldsymbol{R})\\ V_{21}(\boldsymbol{R}) & V_2(\boldsymbol{R})\end{pmatrix}\right]\begin{pmatrix}\tilde{\chi}_1(\boldsymbol{R},t)\\ \tilde{\chi}_2(\boldsymbol{R},t)\end{pmatrix}$$

- **diagonal** representation of the nuclear kinetic energy operator
- **non-diagonal** representation of the potential (i.e., diabatic electronic wavefunctions are *not* eigenfunctions of the electronic Hamiltonian!)
- if we diagonalize the diabatic potential matrix, we get the *adiabatic* energies back

Example: dissociation of NaI





(a) = covalent

(b) = ionic

- **in this case, the dynamics is "almost" adiabatic on the upper BO surface**

Diabatic representations – some more detail

- Is it always possible to define the adiabatic-to-diabatic transformation?

$$\boxed{\psi^{\mathrm{dia}}(r_{\mathrm{el}}, R) = S(R)\psi^{\mathrm{ad}}(r_{\mathrm{el}}, R)}$$

in such a way that the non-adiabatic (kinetic-energy) coupling $\hat{\Lambda}_{nm}$ is eliminated. Here,

$$\hat{\Lambda}_{nm} = -\frac{\hbar^2}{2M}\left(F_{nm}\frac{\partial}{\partial R} + G_{nm}\right)$$

$$F_{nm} = \langle\psi_m^{\mathrm{ad}}(r_{\mathrm{el}}, R)|\frac{\partial}{\partial R}\psi_n^{\mathrm{ad}}(r_{\mathrm{el}}, R)\rangle \; ; \; G_{nm} = \langle\psi_m^{\mathrm{ad}}(r_{\mathrm{el}}, R)|\frac{\partial^2}{\partial R^2}\psi_n^{\mathrm{ad}}(r_{\mathrm{el}}, R)\rangle$$

Analysis shows that

- a strictly diabatic basis does not exist, except for special cases (diatomics, “isolated 2-state system” in polyatomics)

Mead & Truhlar, J. Chem. Phys. 77, 6090 (1982)

Quasi-diabatic representations

construct (non-unique) bases which approximately eliminate the $\hat{\Lambda}_{nm}$

- e.g., work with an "isolated two-state system assumption"

– argue that the divergent part of the derivative couplings originates in the direct coupling between the two states

– in addition, only the lowest-order terms in a Taylor expansion around the intersection cause the divergence

$\longrightarrow$ eliminate this dominant contribution

Thiel, Köppel, J. Chem. Phys. 110, 9371 (1999)

- in general: quasi-diabatic bases are smooth w.r.t. molecular properties (e.g., dipole moments)

- for polar solvation problems: define charge-localized ("VB-type") diabatic states