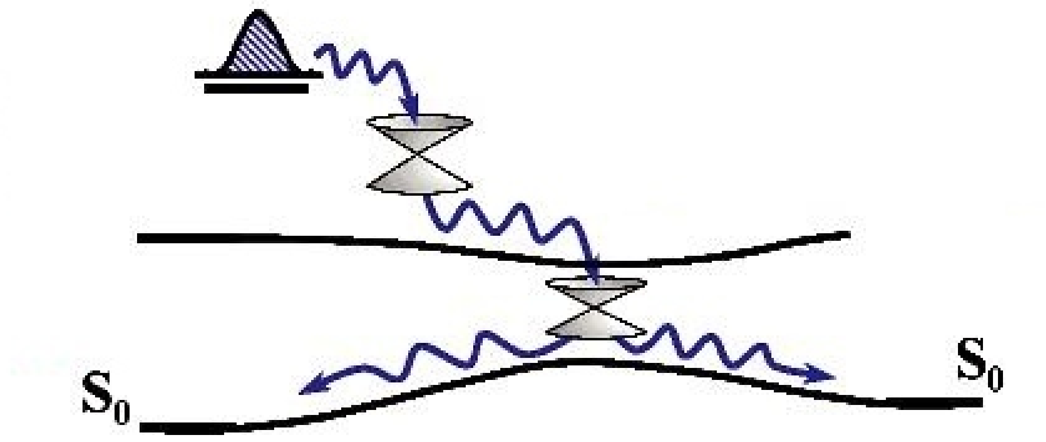
Theoretical Photochemistry WiSe 2016/17

Lecture 6



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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 & dynamics aspects
10. More on 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).

Some Comments: Electronic Structure & Dynamics Methods

(1) **Potential Energy Surfaces (PES): From QM to QM/MM to MM**

(2) **Dynamics: From Quantum to Classical**

(3) **"Direct Dynamics" ("on-the-fly" Electronic Structure)**

Electronic structure for excited states: Post-Hartree-Fock approaches needed!

- **Hartree-Fock method:** Slater determinant ("antisymmetrized product")
- yields ground-state electronic wavefunction
- single-configurational approach
- correlations not treated adequately

for electronically excited states:

- correlated wavefunctions
- multi-configurational approaches needed

Hartree-Fock method

Starting point: e.g., Schrödinger equation for N electrons, 1 nucleus:

$$\boxed{H\Psi = E\Psi}$$

$$\begin{aligned} H &= -\sum_{i=1}^{N}\frac{\hbar^2}{2m_e}\nabla_i^2 - \frac{e^2}{4\pi\epsilon_0}\left\{\sum_{i=1}^{N}\frac{Z}{r_{iR}} - \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{r_{ij}}\right\} \\ &= \sum_i h_i^{(1)} + \frac{e^2}{4\pi\epsilon_0}\sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{r_{ij}} \end{aligned}$$

Ψ is given as a Slater determinant ($this\ is\ an\ assumption!$):

$$\Psi(1,2,\ldots N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \phi_a(1) & \phi_b(1) & \ldots & \phi_z(1) \\ \phi_a(2) & \phi_b(2) & \ldots & \phi_z(2) \\ \vdots & \vdots & \ldots & \vdots \\ \phi_a(N) & \phi_b(N) & \ldots & \phi_z(N) \end{vmatrix} \equiv \frac{1}{\sqrt{N!}}\left| \phi_a(1) \quad \phi_b(2) \quad \ldots \quad \phi\right.$$

Hartree-Fock equations

The Hartree-Fock equation is an effective 1-particle Schrödinger equation for the "optimal" spin orbitals $\phi_s(1)$:

$$\left\{h^{(1)}(1) + v^{\text{eff}}(1)\right\}\phi_s(1) = \epsilon_s \phi_s(1)$$

$$v^{\text{eff}}(1) = \sum_{r=1}^{N} J_r(1) - K_r(1)$$

- due to the structure of the operators J_r and K_r, the HF equation for ϕ_s depends on *all* spin orbitals ϕ_r ($r = 1, \ldots, N$)!
- $F = h^{(1)} + v^{\text{eff}}$ is denoted **Fock operator**

Coulomb and exchange operators

Mean-field operators J_r und K_r:

$$J_r(1)\phi_s(1) = \frac{e^2}{4\pi\epsilon_0}\left\{\int d\tau_2\, \phi_r^*(2)(\frac{1}{r_{12}})\phi_r(2)\right\}\phi_s(1)$$ **Coulomb operator**

$$\begin{aligned} K_r(1)\phi_s(1) &= \frac{e^2}{4\pi\epsilon_0}\left\{\int d\tau_2\, \phi_r^*(2)(\frac{1}{r_{12}})\hat{P}_{12}\phi_r(2)\right\}\phi_s(1) \\ &= \frac{e^2}{4\pi\epsilon_0}\left\{\int d\tau_2\, \phi_r^*(2)(\frac{1}{r_{12}})\phi_s(2)\right\}\phi_r(1) \end{aligned}$$ **Exchange operator**

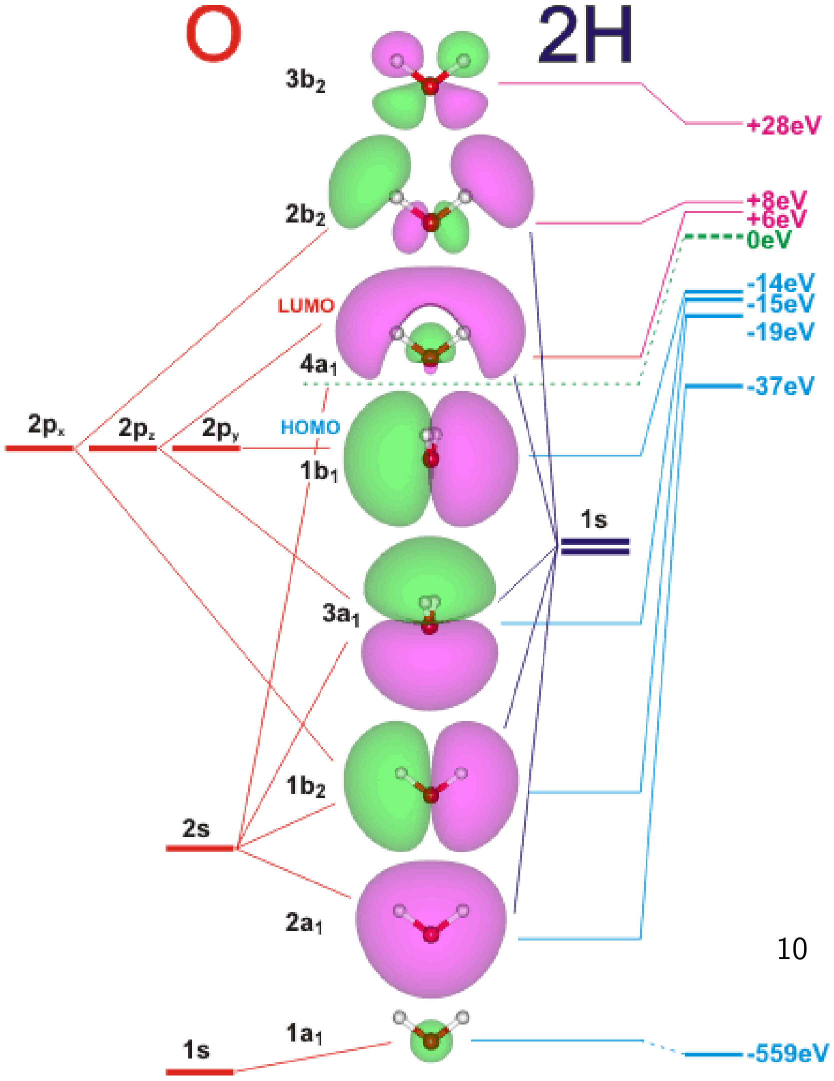
$$(J_r - K_r)\phi_s(1) = \frac{e^2}{4\pi\epsilon_0}\left\{\int d\tau_2\, \phi_r^*(2)(\frac{1}{r_{12}})(1-\hat{P}_{12})\phi_r(2)\right\}\phi_s(1)$$

Eigenvalues and eigenfunctions of the Hartree-Fock equation: occupied vs. virtual orbitals

$$\left\{h^{(1)}(1) + v^{\text{eff}}(1)\right\}\phi_n(1) = \epsilon_n \phi_n(1)$$

$\epsilon_n\{n = 1, \ldots, N\}$
= occupied spin orbitals
(N = number of electrons)

$\epsilon_n\{n = N, \ldots\}$
= unoccupied ("virtual") spin orbitals



Excited States: Post-Hartree-Fock Methods – expensive!

- **variational methods**
  - Configuration Interaction = CI
  - Multiconfigurational methods: Multiconfiguration Self-Consistent Field (MCSCF), Complete-Active-Space Self-Consistent Field (CASSCF)
  - Multi-reference methods (e.g., MRCI)

- **Coupled-Cluster Approaches**
  - e.g., CC2 = 2nd-order CC
  - EOM-CCSD = Equation of Motion-CC-Singles-Doubles

- **Time-Dependent Density Functional Theory (TD-DFT)**
  - very popular . . . but handle with care!

TD-DFT – Some remarks

Time dependent Kohn-Sham Equations:

$$\left(-\frac{1}{2}\nabla^2 + v_s(\mathrm{r},t)\right)\phi_i(\mathrm{r},t) = i\frac{\partial}{\partial t}\phi_i(\mathrm{r},t)$$

with the effective potential

$$v_s(\mathrm{r},t) = v_{\mathrm{ext}}(\mathrm{r},t) + v_J(\mathrm{r},t) + v_{\mathrm{xc}}(\mathrm{r},t)$$

where $v_{\mathrm{xc}}(\mathrm{r},t) = v_{\mathrm{xc}}[\rho(\mathrm{r},t)]$ **= exchange correlation functional**

time-dependent density: $\rho(\mathrm{r},t) = \sum_{i=1}^{N} |\phi_i(\mathrm{r},t)|^2$

- **however, TD-DFT uses a perturbative Linear Response (LR) version of the above equations!**
- **problems: many approximate functionals, charge transfer described incorrectly (⟶ long-range corrections . . .)**

Configuration Interaction (CI)

$$|\Psi\rangle = |\Psi_0\rangle + \sum_J C_J\, |\Psi_J\rangle$$

- $|\Psi_0\rangle = (N!)^{-1/2}|\psi_i(1)\psi_j(2)\ldots\psi_n(N)|$ = HF Slater determinant

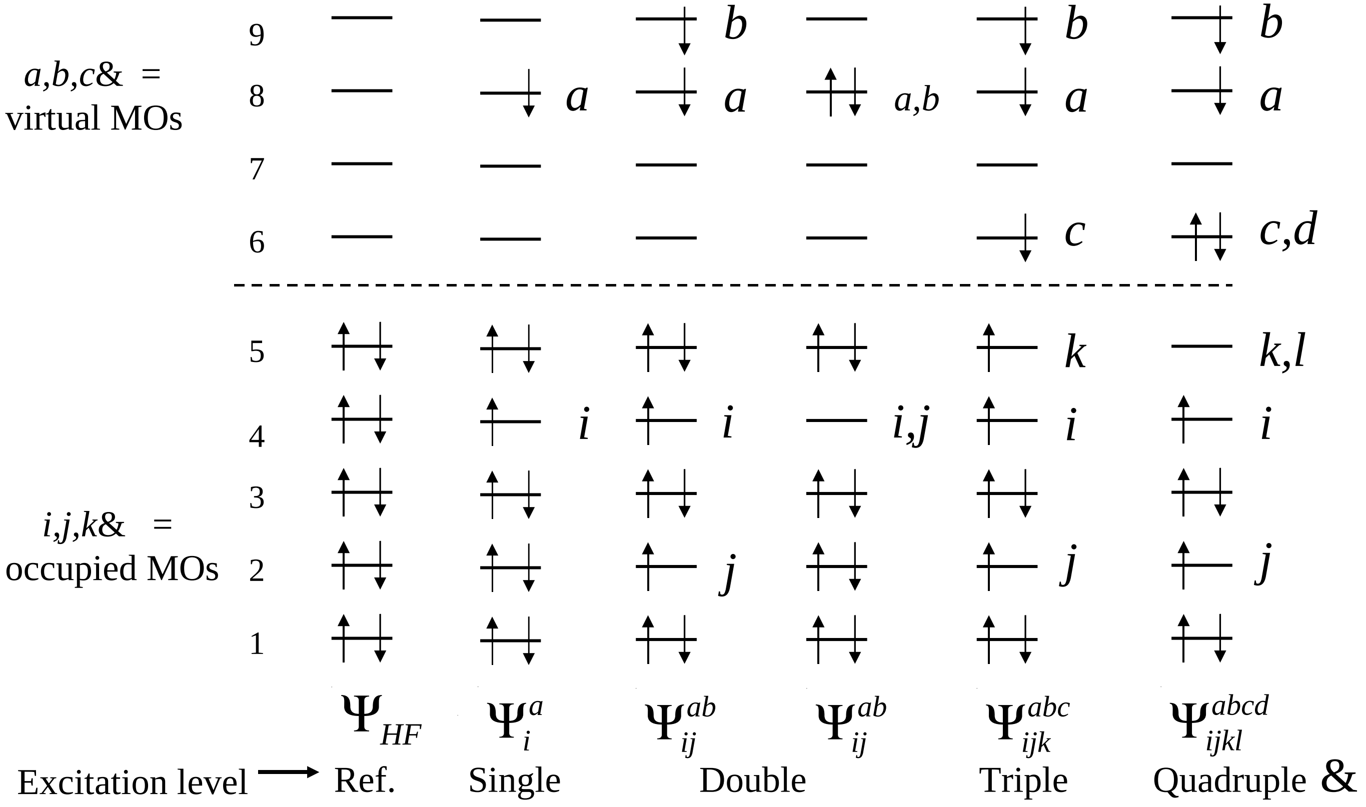
- $|\Psi_J\rangle$ = excited Slater determinants (i.e., with excitations to virtual orbitals)

- calculate coefficients C_J variationally ($\longrightarrow$ secular equation)

- here, each determinant contains MO's whose AO coefficients are fixed: $\psi_i(1) = \sum_n c_{in}\phi_n(1)$

Configuration Interaction (CI)

Generate excited Slater determinants by promoting up to N electrons from the N/2 occupied to M-N/2 virtuals:



CISD

E.g., CISD = Configuration Interaction (CI) with Singles and Doubles

NB. Single excitations (“singles”) do not mix with the Hartree-Fock ground state: Brillouin’s Theorem

This is why a substantial improvement will result from double excitations (“doubles”)

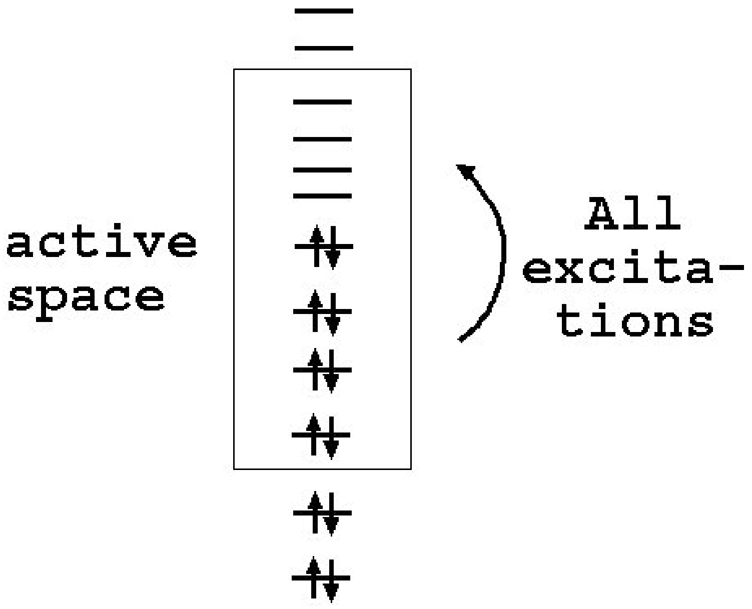
Multiconfiguration Self-Consistent Field (MCSCF)

$$|\Psi\rangle = |\Psi_0\rangle + \sum_J C_J\,|\Psi_J\rangle$$

- formally the same wavefunction *ansatz* as in the CI approach
- $|\Psi_J\rangle = (N!)^{-1/2}|\psi_i(1)\psi_j(2)\ldots\psi_n(N)|$ = Slater determinant
- But differently from CI: AO coefficients of MO's, $\psi_i(1) = \sum_n c_{in}\phi_n(1)$, are now also optimized!
- i.e., both the C_J's and the c_{in}'s are re-calculated

Complete Active Space Self-Consistent Field (CASSCF)

- excitations within an "active space"
- generally highest occupied and lowest unoccupied orbitals
- within the CAS space: full CI



Coupled Cluster (CC) Approach

Development of the wavefunction in terms of a "Cluster Operator":

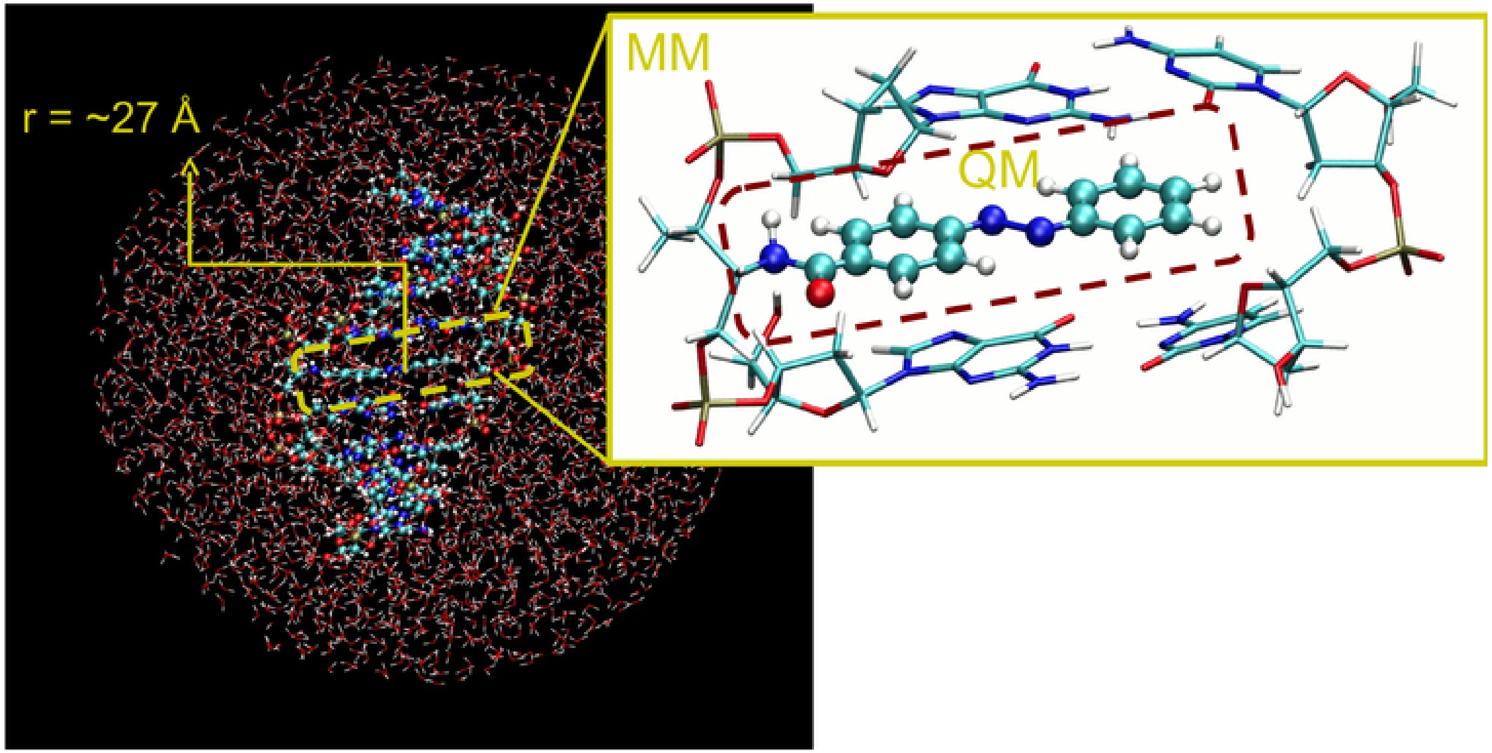
$$\begin{aligned}\Psi &= e^{C}\Psi_0 \\ &= \left(1 + C + \frac{1}{2}C^2 + \frac{1}{3!}C^3 + \ldots\right)\Psi_0\end{aligned}$$

Here, C is the sum of k-electron excitation operators:

$$C = C_1 + C_2 + C_3 + \ldots$$

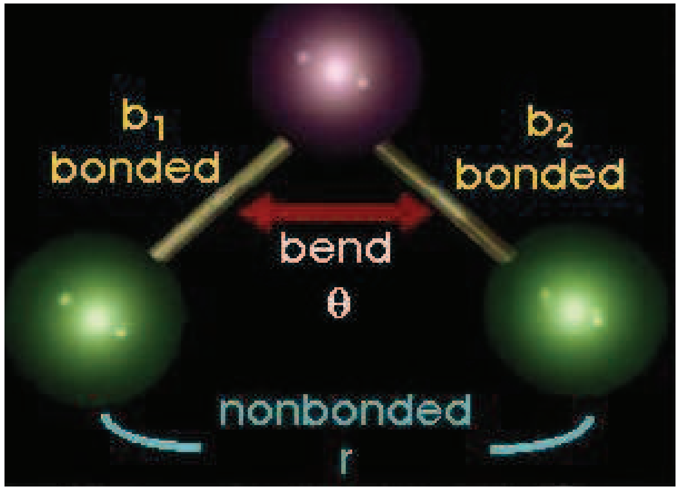
- C generates k-th order excited determinants
- $C \simeq C_1 + C_2$: CCSD (Coupled Cluster Singles Doubles)
- $C \simeq C_1 + C_2 + C_3$: CCSDT (Coupled Cluster Singles Doubles Triples)

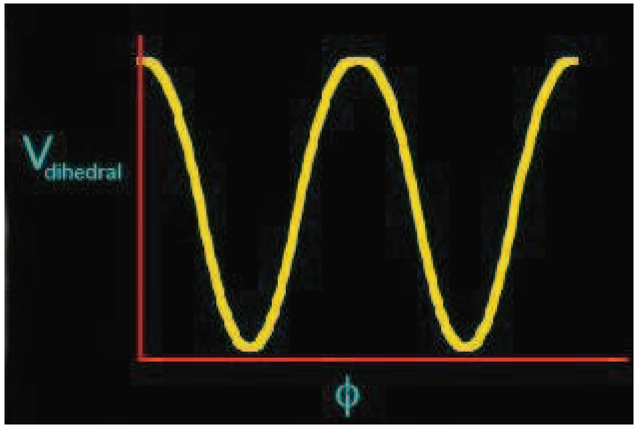
QM/MM: Quantum Mechanics/Molecular Mechanics hybrid approach



- **2013 Nobel Prize for Martin Karplus/Michael Levitt/Arieh Warshel**

MM: Force Fields

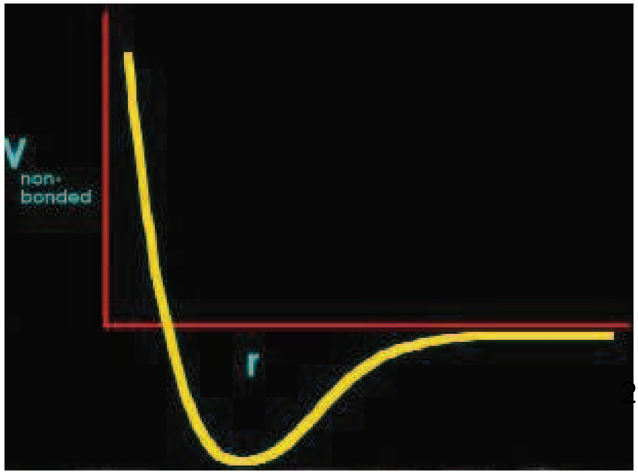




dihedral angle

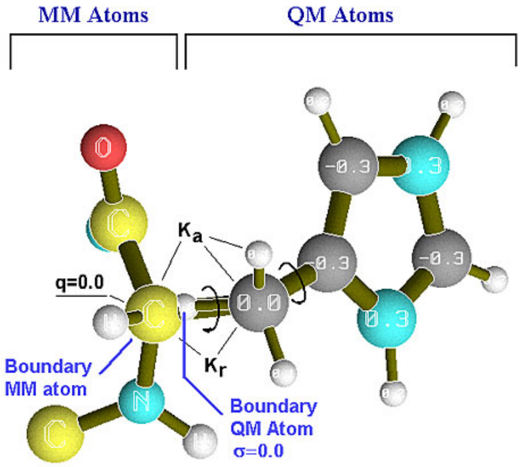
typical force fields:

$$
\begin{aligned}
V_{\text{bond}}(r) &= \frac{1}{2}k(r-r_0)^2 \\
V_{\text{angular}}(\phi) &= \frac{1}{2}(1+\cos(m\phi-\delta))^2 \\
V_{\text{vdW}}(r_{ij}) &= \frac{C_{12}}{r_{ij}^{12}} - \frac{C_6}{r_{ij}^{6}}
\end{aligned}
$$



nonbonded interaction

QM/MM, cont'd



$$
\begin{aligned}
\hat{H} &= \hat{H}_{\mathrm{QM}} + \hat{H}_{\mathrm{QM/MM}} + \hat{H}_{\mathrm{MM}} \\
\hat{H}_{\mathrm{QM/MM}} &= -\sum_{i}^{\text{electrons}} \sum_{j}^{\text{MM atoms}} \frac{Q_j}{r_{ij}} + \sum_{i}^{\text{nuclei}} \sum_{j}^{\text{MM atoms}} \left(\frac{Z_i Q_j}{R_{ij}} + \left\{ \frac{A_{ij}}{R_{ij}^{12}} - \frac{B_{ij}}{R_{ij}^{6}} \right\} \right) \\
\hat{H}_{\mathrm{MM}} &= \sum_{\text{nonbonded}} \left[\frac{A_{ij}}{R_{ij}^{12}} - \frac{B_{ij}}{R_{ij}^{6}} + \frac{q_i q_j}{R_{ij}} \right] + \sum_{\text{bonds}} K_b (R - R_0)^2 + \ldots
\end{aligned}
$$

Some Comments: Electronic Structure & Dynamics Methods

(1) Potential Energy Surfaces (PES): From QM to QM/MM to MM

(2) Dynamics: From Quantum to Classical

(3) “Direct Dynamics” (“on-the-fly” Electronic Structure)

Hierarchy of approaches

- **quantum dynamics** (that's the only accurate approach!)
- **mean-field (Ehrenfest)** approach
- **surface hopping** approach
- **Landau-Zener transitions**: simple semiclassical picture ("back of the envelope" approach)

Quantum dynamics – basics

- The time evolution of a non-stationary state (wavepacket) $\Psi(x,t)$ is given in terms of the time-dependent Schrödinger equation (TDSE):

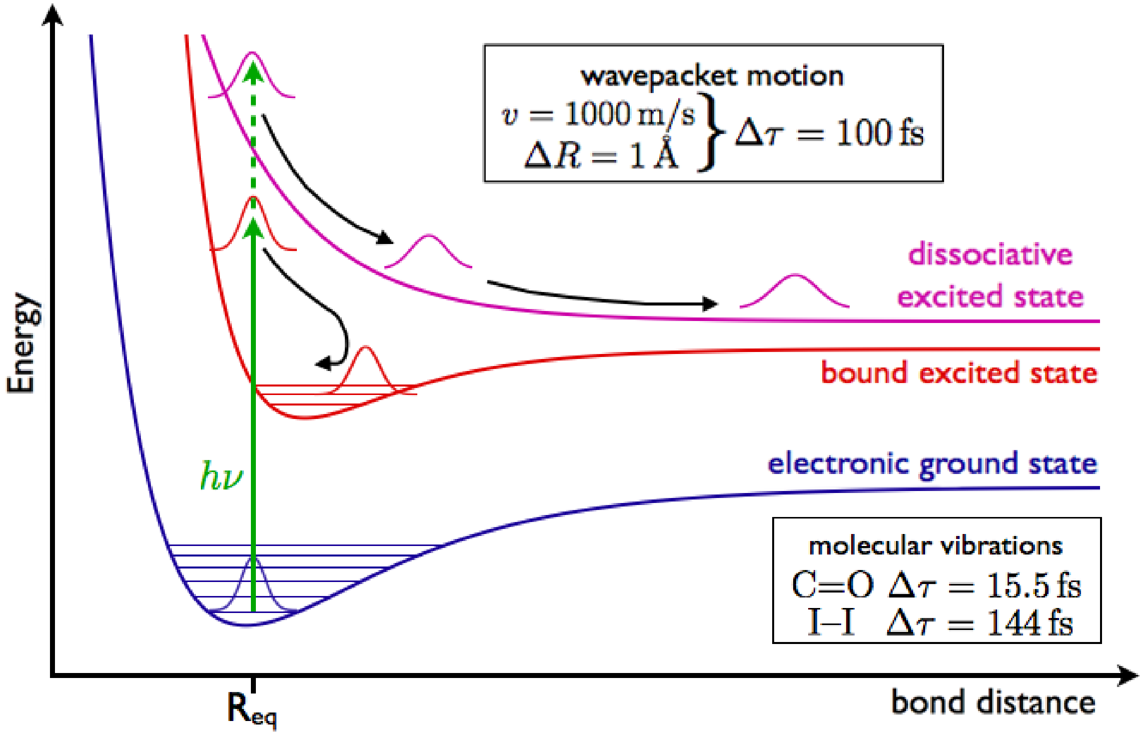
$$i\hbar\frac{\partial\Psi}{\partial t} = \hat{H}\Psi = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right)\Psi$$

- Particular solution, for eigenstates:

$$\Psi_n(x,t) = \varphi_n(x)\exp\left(-\frac{i}{\hbar}E_n t\right)$$

- wavepackets are coherent superpositions of such eigenstate solutions
- Examples which allow for analytical solutions: particle-in-a-box, free particle wavepacket, Gaussian wavepackets
- In general, we need to integrate the TDSE numerically

Light-induced wavepacket dynamics



- laser excitation leads to a "vertical" transition (i.e., nuclear geometry unchanged)
- thus, a wavepacket is created that is a coherent superposition of vibrational eigenstates, $\psi(x, t = 0) = \sum_n c_n \varphi_n(x)$.

Vibronic wavepackets

- In a femtosecond optical experiment, vibrational wavepackets are created in the electronically excited state $|E\rangle$,

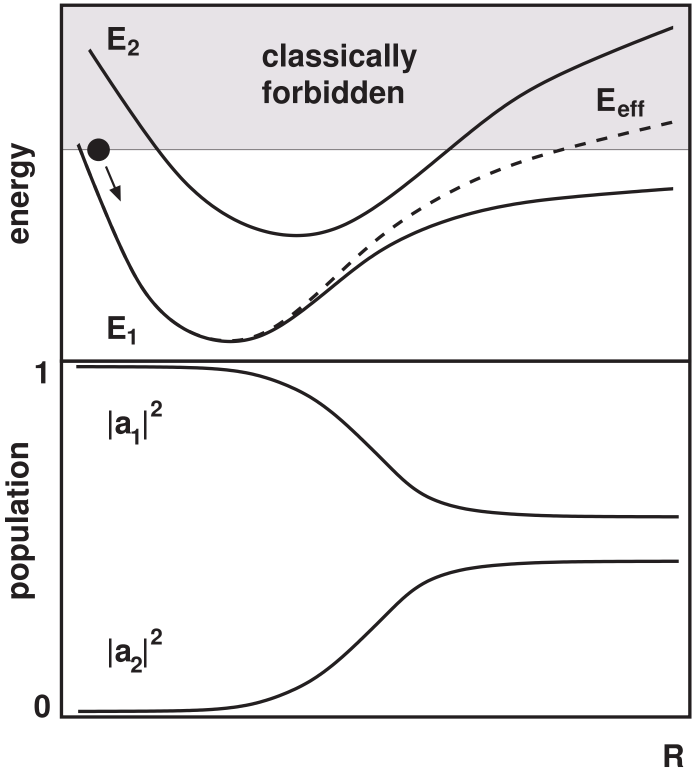
  $$\chi_0(x,t)|G\rangle \quad \xrightarrow{h\nu} \quad \chi_0(x,t)|E\rangle = \sum_n c_n\, \varphi_n^E(x)\exp(-\frac{iE_n t}{\hbar})|E\rangle$$

  where $\varphi_n^E(x)$ are the vibrational eigenstates of the excited-state BO-surface

- Due to the non-adiabatic ("non-Born-Oppenheimer") coupling between $|E\rangle$ and $|G\rangle$, these wavepackets can evolve into coherent superpositions involving $both$ electronic states ("vibronic wavepackets"):

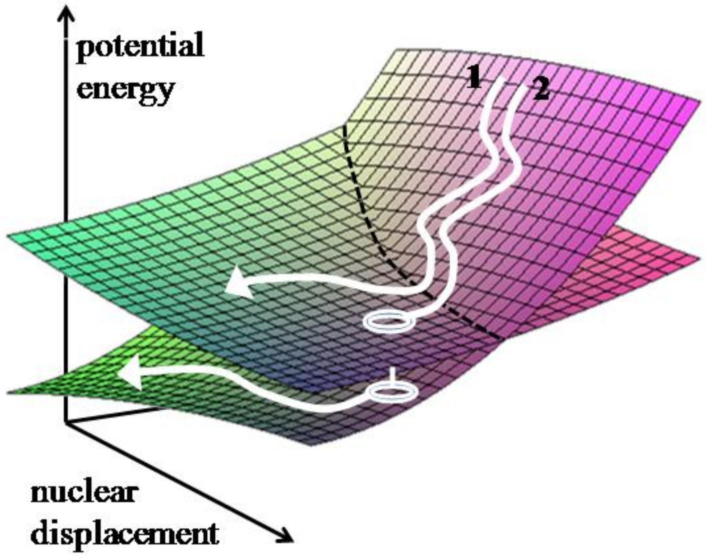
  $$|\psi(x,t)\rangle = \sum_n c_n\, \varphi_n^E(x)\exp(-\frac{iE_n^E t}{\hbar})|E\rangle + \sum_n d_n\, \varphi_n^G(x)\exp(-\frac{iE_n^G t}{\hbar})|G\rangle$$

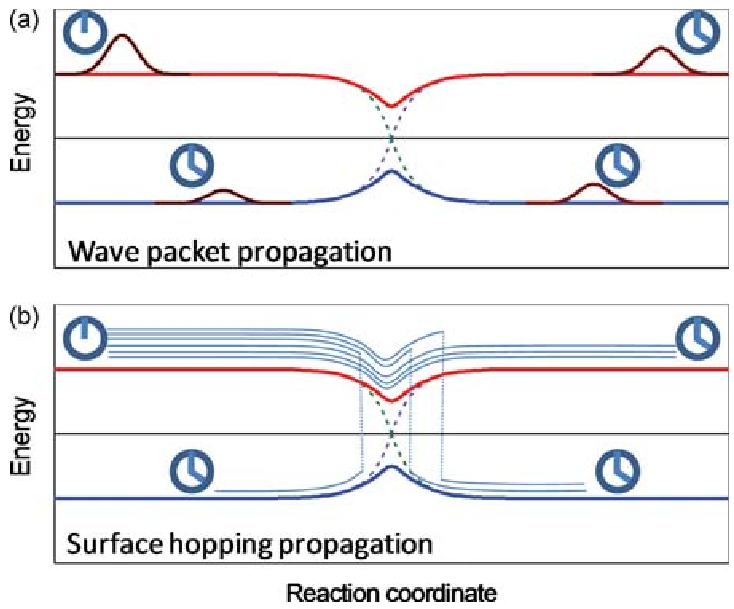
Mean-Field (Ehrenfest) Approach



- **classical trajectory motion on a mean (averaged) potential surface** $E_{\text{eff}}(R) = |a_1(R)|^2 E_1 + |a_2(R)|^2 E_2$

Surface hopping approach





picture: M. Barbatti

- **the electronic wavefunction is propagated coherently:**

$$i\hbar\dot{\psi} = (H_0 + H(r, R_j(t)))\psi$$

- **the trajectories $R_j(t)$ move classically on the kth surface until they perform a stochastic "hop" to another surface ℓ, with probability $T_{k\to\ell}$**

Surface hopping – some more details

- propagation of the quantum (electronic) wavefunction coefficients in the adiabatic representation, for the jth trajectory:

  $$\dot{C}_k^{(j)} = -iC_k^{(j)}\omega_k^{(j)} - \sum_\ell C_\ell^{(j)} \dot{Q}^{(j)} G_{k\ell}^{(j)}$$

  where $G_{k\ell}^{(j)}$ is the nonadiabatic coupling vector, $G_{k\ell} = \langle\psi_k|\partial/\partial Q|\psi_\ell\rangle$

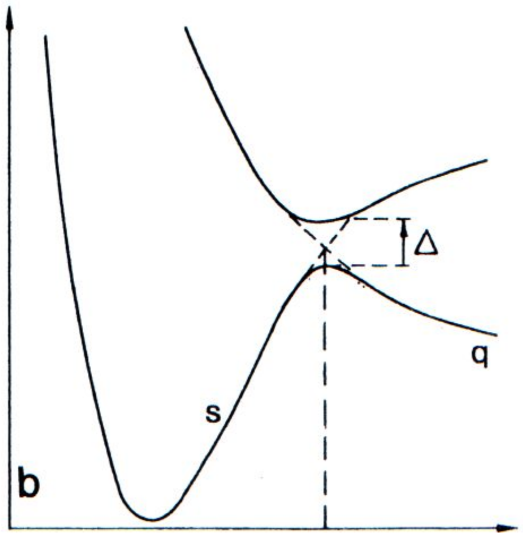
- the hopping probability is evaluated as follows ("fewest switches" algorithm by Tully):

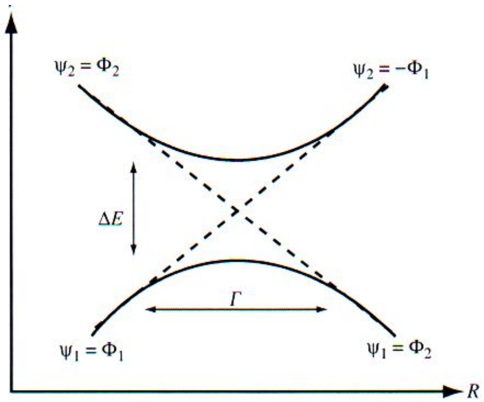
  $$T_{k\ell}^{(j)} = \text{max}\Big\{0, \frac{B_{kl}^{(j)}}{p_k^{(j)}}\Delta t\Big\}$$

  where $B_{kl}^{(j)} = 2\text{Re}(\rho_{\ell k}^{(j)} G_{k\ell}^{(j)})\dot{Q}^{(j)}$, $\rho_{\ell k}^{(j)} = C_k^{(j)} C_\ell^{*(j)}$, $p_k = C_k^{(j)} C_k^{*(j)}$

- consistency problem: one should have $\bar{p}_k(t) = \Pi_k(t)$, where $\bar{p}_k = (1/N_T)\sum_j p_k^{(j)}$ and $\Pi_k(t) = N_k(t)/N_T$

Landau-Zener transition probabilities



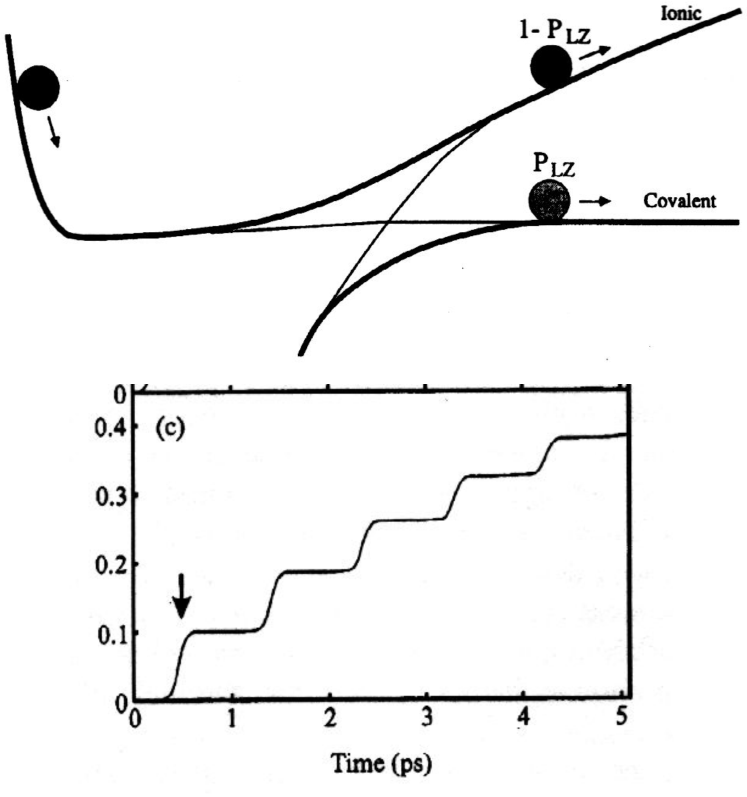


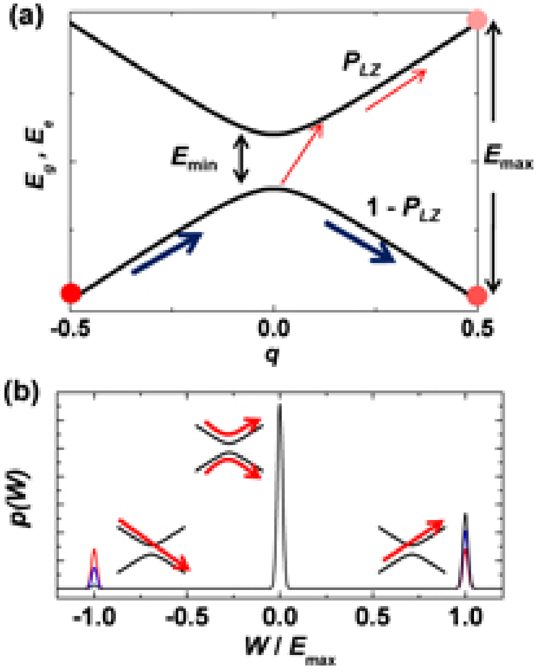
$$P = \exp\left(-\frac{\pi \gamma_{LZ}}{2}\right) \qquad \gamma_{LZ} = \frac{\Delta^2}{\hbar v |F_2 - F_1|}$$

v = particle velocity ; F_i = potential slope ; Δ = energy gap

P = transition probability between adiabatic states

Interpretation via repeated Landau-Zener crossings





- "almost" classical picture
- the curve crossing event is treated semiclassically

Wavepackets on coupled potential surfaces: NaI

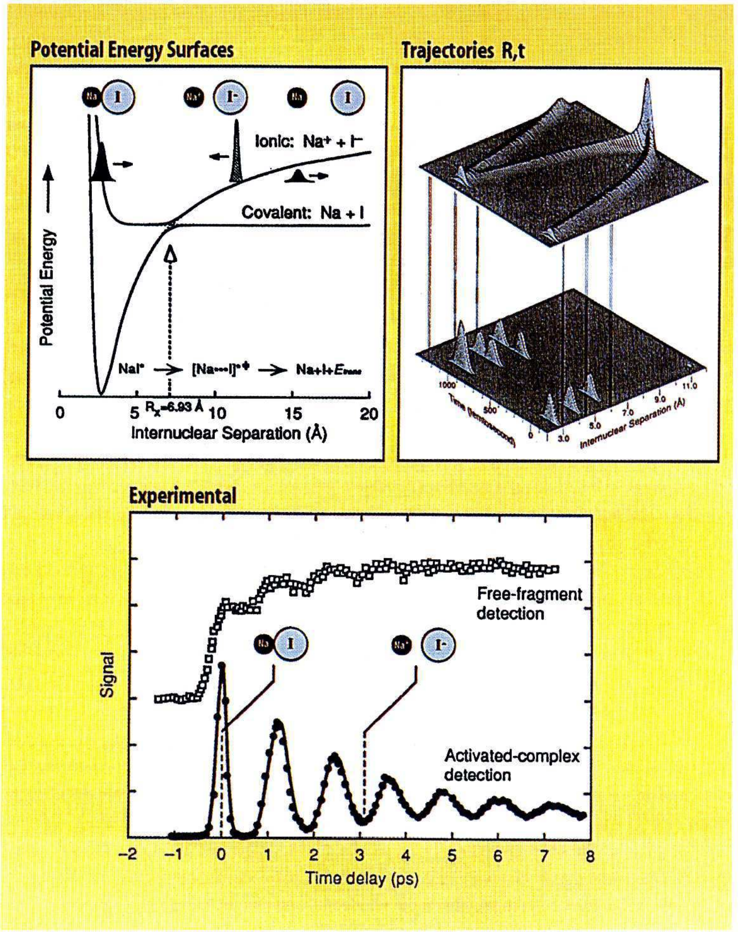


Figure 15. Femtochemistry of the NaI reaction, the paradigm case. The experimental results show the resonance motion between the covalent and ionic structures of the bond, and the time scales for the reaction and for the spreading of the wave packet. Two transients are shown for the activated complexes in transition states and for final fragments. Note the "quantized" behavior of the signal, not simply an exponential rise or decay of the ensemble. The classical motion is simulated as trajectories in space and time (top). [Ref. B1, B4, B12, B14, B17, B19, B28, 56]

$\text{NaI}^* \longrightarrow \text{Na} + \text{I}$

(Zewail & co (1989))

- **many oscillations between covalent and ionic states**

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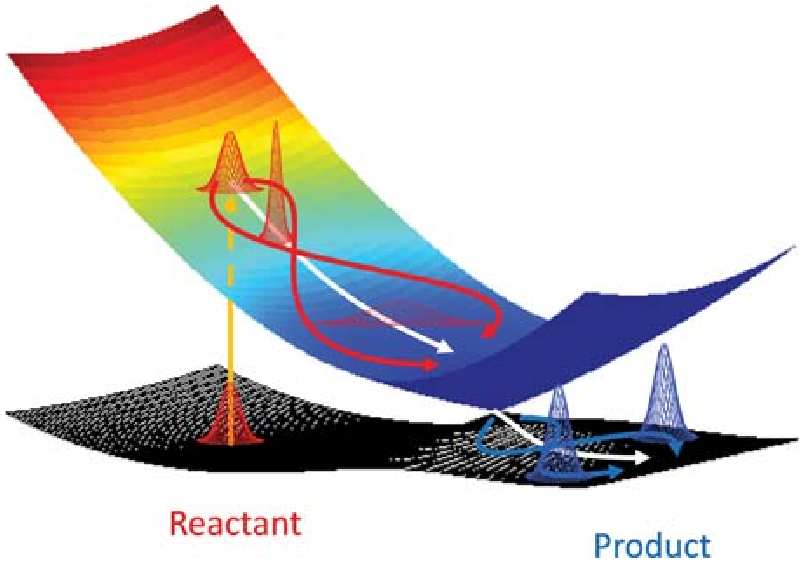
"On-the-fly" calculations



- "on-the-fly" electronic structure calculations, moving with a trajectory
- rectilinear coordinates
- calculate Gradients & Hessian
- on-the-fly adiabatic PES – but possibly diabatic dynamics

Lasorne, Robb, Worth, PCCP 9, 3210 (2007), Worth, Robb, Burghardt, Faraday Discuss. 127, 307 (2004)