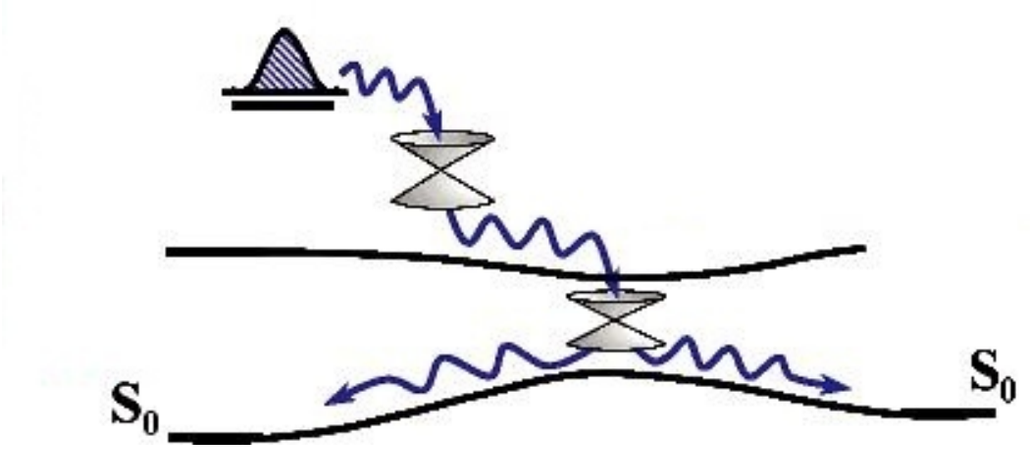
Theoretical Photochemistry SoSe 2014

Lecture 9



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http://www.theochem.uni-frankfurt.de/teaching/ $\longrightarrow$ 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. Dynamics: trajectories or wavefunctions?
10. Some electronic structure aspects
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**

How to 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 many molecular applications Newton's equations work fine . . .
. . . but photochemistry requires wavepacket dynamics!

When is quantum dynamics needed?

- depending on the nuclear mass, the classical limit (action $S \gg \hbar$) may not be reached
- tunneling effects
- correct description of zero-point energy
- resolution of vibrational fine structure
- wavepacket motion
- nonadiabatic dynamics: nuclear-electronic ("vibronic") coupling effects

Quantum dynamics – recap

• 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

Exercise

(1) Use the particular solution

$$\boxed{\Psi(x,t) = \psi_n(x)\exp(-iE_nt/\hbar)}$$

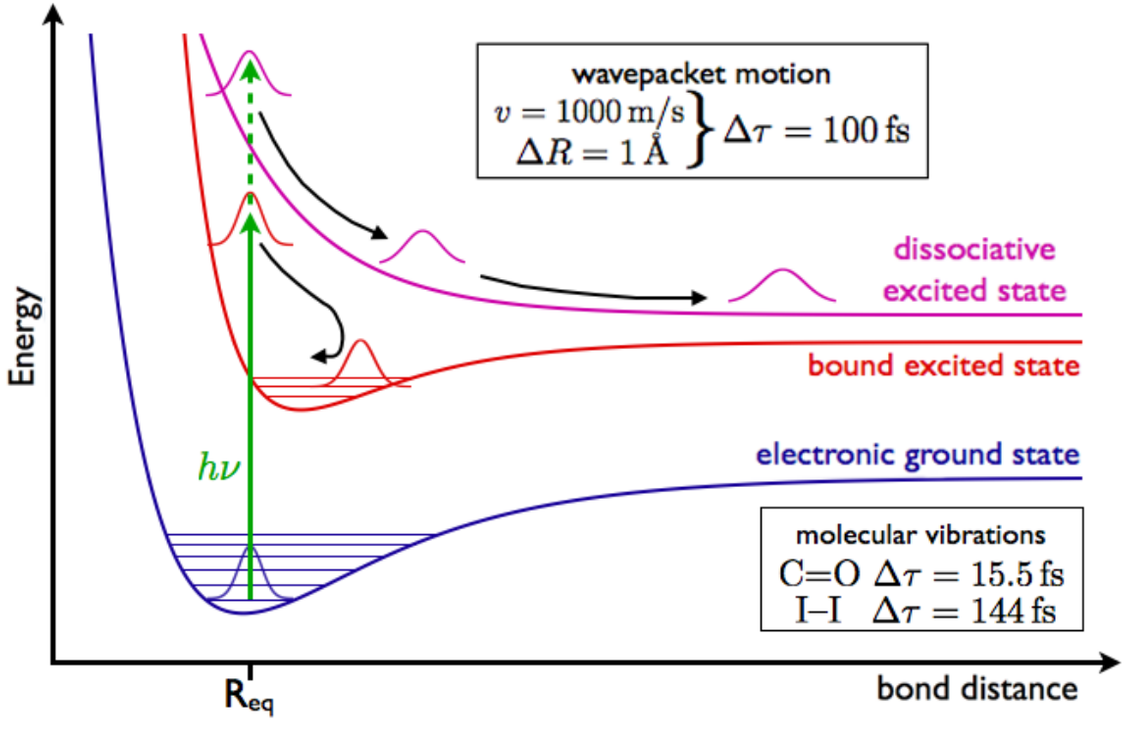
of the time-dependent Schrödinger equation, where $\psi_n(x)$ is assumed to be an eigenfunction of the Hamiltonian, to calculate the expectation value of an observable $\hat{O}$ (i.e., any observable is allowed!). Is the expectation value $\langle\hat{O}\rangle$ time-dependent?

(2) Next, try a linear combination (i.e., a minimal wavepacket):

$$\boxed{\Psi(x,t) = c_n\,\psi_n(x)\exp(-iE_nt/\hbar) + c_{n'}\,\psi_{n'}(x)\exp(-iE_{n'}t/\hbar)}$$

and verify whether the expectation value $\langle\hat{O}\rangle$ is time-dependent. Interpret the difference between the results of (1) and (2).

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, $\psi(x, t = 0) = \sum_n c_n \varphi_n(x)$.**

Wavepackets – recap

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

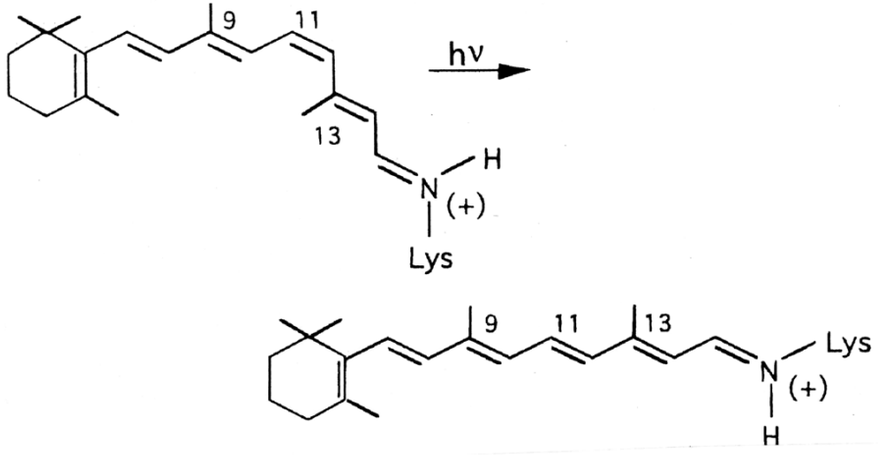
$$\chi_0(x,t)|G\rangle \quad \xrightarrow{h\nu} \quad \chi_0(x,t)|E\rangle = \sum_n c_n \, \varphi_n^E(x) \exp(-\frac{iE_n t}{\hbar})|E\rangle$$

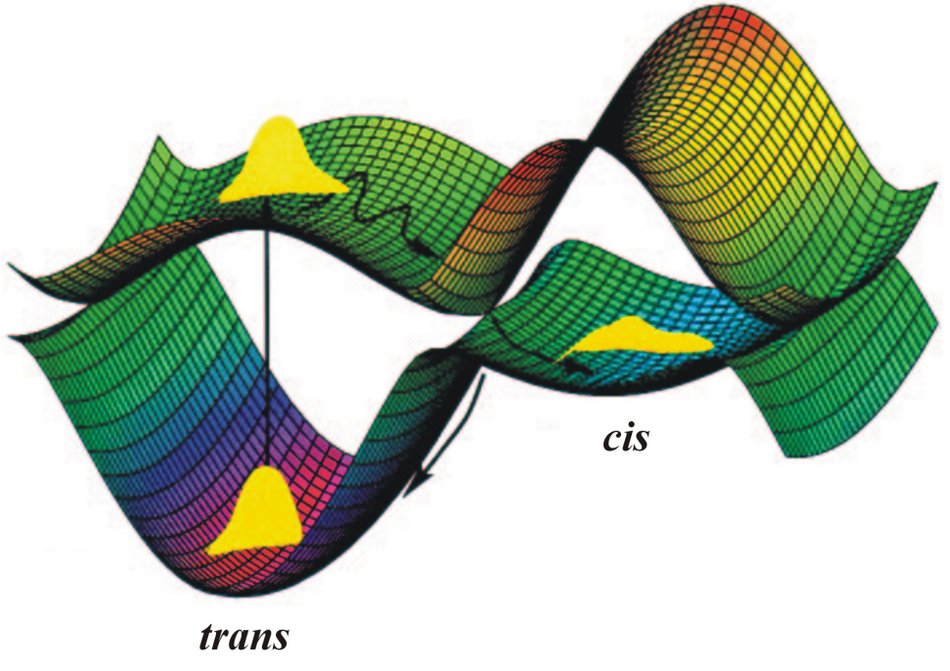
  where $\varphi_n^E(x)$ are the vibrational eigenstates of the excited-state BO-surface

- 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"):

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

Nonadiabatic wavepacket dynamics





S. Hahn and G. Stock, J. Phys. Chem. B 104, 1146 (2000).

- here, retinal isomerisation: primary process of vision
- relevant coordinates: twist + skeletal stretch + . . .
- excited-state decay in the protein: $\sim$ 200 fs / in solution phase: $\sim$ 5 ps

Gaussian Wavepackets (GWP's) = phase-space points + quantum uncertainty

- **casting quantum dynamics in terms of point-like trajectories is generally difficult**

- **describing quantum dynamics in terms of "semi-localized" objects is preferable ⟶ Gaussian wavepackets**

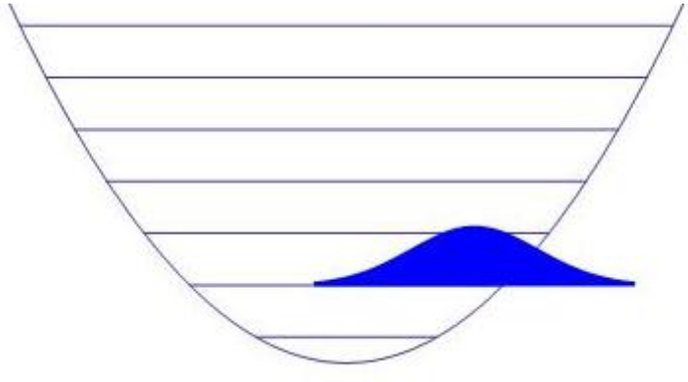
$$\psi(x|qp) \quad = \quad \exp\Big(-\alpha(x-q)^2 + \frac{i}{\hbar}p(x-q) + \frac{i}{\hbar}\gamma\Big)$$

such that $\langle\psi|\hat{x}|\psi\rangle = q$ **and** $\langle\psi|\hat{p}|\psi\rangle = p$**.**

Special case: "coherent state" (CS)

$$\psi(x|qp) \;=\; \exp\Big(-\alpha_{\rm CS}(x-q)^2 + \frac{i}{\hbar}p(x-q) + \frac{i}{\hbar}\gamma\Big) \quad ; \quad \alpha_{\rm CS} = m\omega/2\hbar$$

- displaced HO ground state – constant width!
- alternative notation: "$|z\rangle$" states:



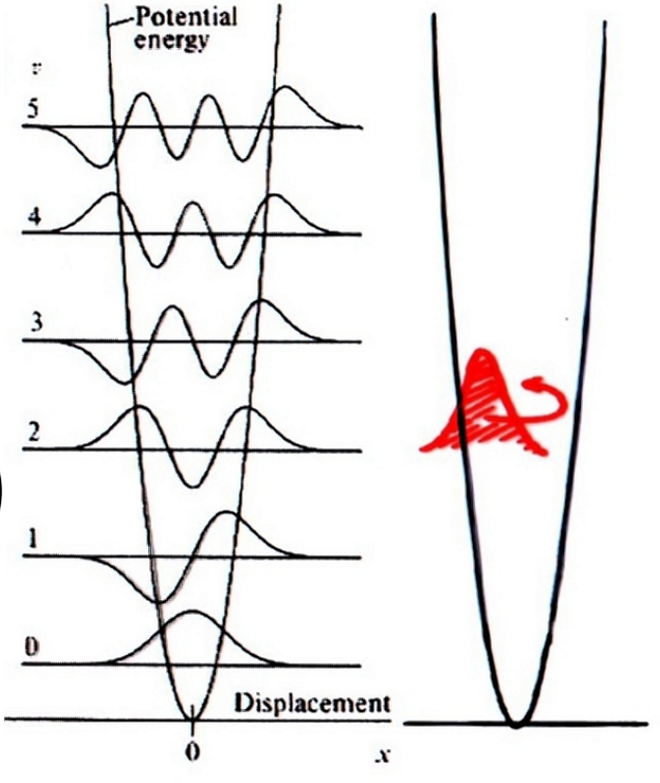
$$z \;=\; \frac{1}{\sqrt{2}}\Big(\zeta^{1/2}q + i\frac{1}{\hbar^{1/2}\zeta^{1/2}}p\Big)$$

$$\langle x|z\rangle \;=\; \Big(\frac{\zeta}{\pi}\Big)\exp\Big(-\frac{\zeta}{2}(x-q)^2 + \frac{i}{\hbar}p(x-q) + \frac{i}{2\hbar}\Big)$$

- "generalized phase-space points" which occupy an "irreducible" phase space area given by the uncertainty product $\Delta x\Delta p = \hbar/2$

How do GWP's move?

- $\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}kx^2 \qquad k = m\omega^2$



- **time-evolving wavepacket:**

$$\Psi(x,t) = \sum_n a_n \varphi_n(x) \exp\Big(-\frac{i}{\hbar}\hbar\omega(n+1/2)t\Big)$$

- **wavepacket at time $t = mT$**
where $T = 2\pi/\omega$ is the classical period:

$$\begin{aligned}\Psi(x, t = mT) &= \sum_n a_n \varphi_n(x) \exp\Big(-\frac{i}{\hbar}\hbar\omega(n+1/2)mT\Big) \\ &= \exp(-i2\pi m(n+1/2))\Psi(x,0) = (-1)^m \Psi(x,0)\end{aligned}$$

- **the wavepacket oscillates with the classical period T**

GWP's follow a classical path

(Heller 1975)

$$\psi(x,t) = \exp\left(-\alpha_t (x-q_t)^2 + \frac{i}{\hbar} p_t (x-q_t) + \frac{i}{\hbar}\gamma_t\right)$$

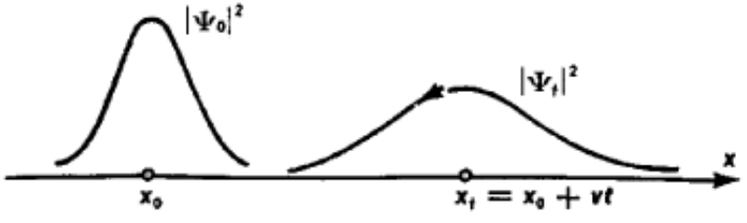
$$\Lambda(t) = \{q_t, p_t, \alpha_t, \gamma_t\}$$

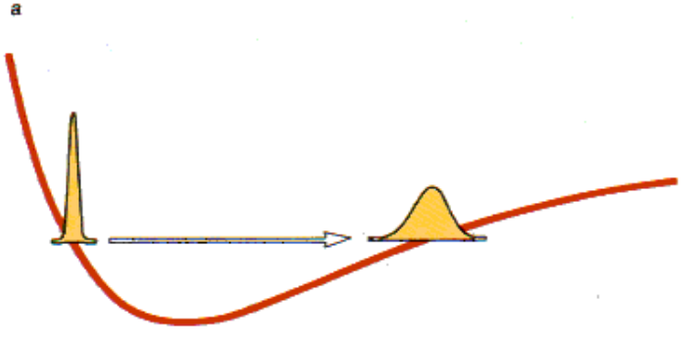
time-dependent parameters

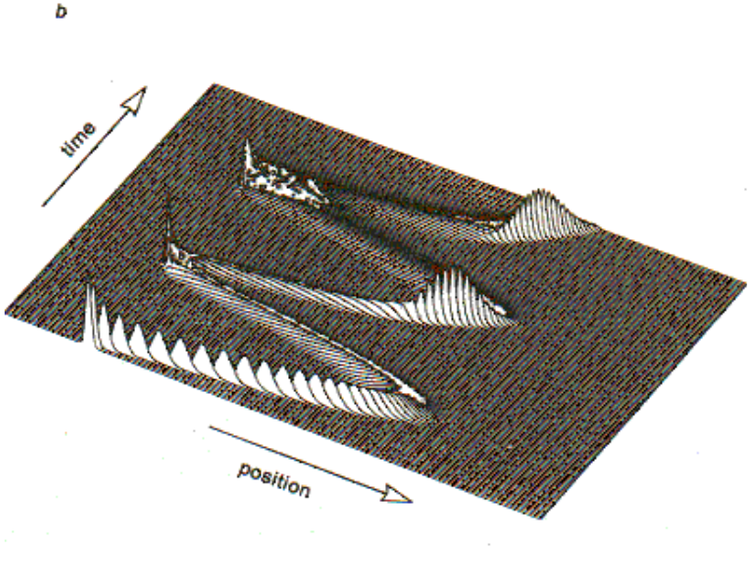
$$\begin{aligned}
\dot{q}_t &= p_t/m \\
\dot{p}_t &= -\left(\frac{\partial V(x)}{\partial x}\right)_{x=q_t} \\
\dot{\alpha}_t &= -\frac{2i\hbar}{m}{\alpha_t}^2 - \frac{i}{2\hbar}\left(\frac{\partial^2 V(x)}{\partial x^2}\right)_{x=q_t} \\
\dot{\gamma}_t &= -\frac{\hbar^2 \alpha_t}{m} + \frac{p_t^2}{2m} - V \equiv -\frac{\hbar^2 \alpha_t}{m} + L
\end{aligned}$$

- center position and momentum evolve classically: Ehrenfest's theorem
- width parameter: relates to wavepacket spreading (linear stability)
- phase parameter: relates to the classical action $S = \int dt\ L_{\rm cl}$
- equations are exact for a harmonic potential; for a general potential, they follow from a variational principle + local harmonic approximation

Wavepackets spread with time



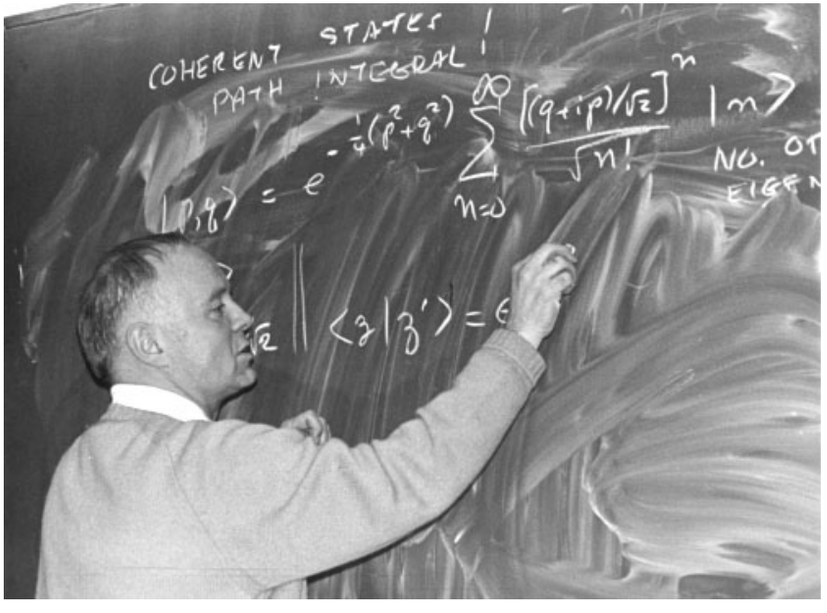




- **free particle:**
  $\Delta x(t) = 1/2\sqrt{(1 + \hbar^2\alpha_0^2 t^2/m^2)/\alpha_0}$

- **(an)harmonic oscillator:**
  width spreads and contracts periodically

Except for coherent states, which don't spread!



CS's = displaced ground state GWP's with minimum uncertainty

photograph: John Klauder

$$\langle x|z\rangle = \left(\frac{\zeta}{\pi}\right)\exp\left(-\frac{\zeta}{2}(x-q)^2+\frac{i}{\hbar}p(x-q)+\frac{ipq}{2\hbar}\right) \qquad \zeta = m\omega/\hbar$$

$$= e^{-|z|^2/2}\sum_{n=0}^{\infty}\frac{1}{\sqrt{n!}}z^n|\psi_n\rangle \qquad z=\frac{1}{\sqrt{2}}\left(\zeta^{1/2}q+i\frac{1}{\hbar^{1/2}\zeta^{1/2}}p\right)$$

Some analytical results

- **free particle GWP: explicit time dependence**
- **GWP in a harmonic potential**
- **CS's are minimum uncertainty wavepackets**

Free particle GWP: explicit time dependence

- initial condition: $\psi(x,0) = Ae^{-\alpha_0 x^2}$ $\qquad A = (2\mathrm{Re}(\alpha_0)/\pi)^{1/4}$
- expand in free-particle states and obtain time dependence:

$$\psi(x,0) = \int_{-\infty}^{\infty} dk\, a(k) e^{ikx} \qquad \psi(x,t) = \int_{-\infty}^{\infty} dk\, a(k) e^{ikx - i\frac{\hbar k^2}{2m}t}$$

- coefficients are given as

$$a(k) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dx \psi(x,0) e^{-ikx} = \frac{A}{2\pi}\sqrt{\frac{\pi}{\alpha_0}} e^{-k^2/4\alpha_0}$$

- integrate to obtain

$$\psi(x,t) = \frac{A}{\sqrt{1 + \frac{2i\hbar\alpha_0 t}{m}}} e^{-x^2/(\frac{1}{\alpha_0} + \frac{2i\hbar t}{m})}$$

again a Gaussian state!

Another way of obtaining the free-particle solution

- **assume** that the state remains Gaussian and use the *ansatz*:

$$\psi(x,t) = \exp\left(-\alpha_t(x-q_t)^2 + \frac{i}{\hbar}p_t(x-q_t) + \frac{i}{\hbar}\gamma_t\right)$$

- insert into the time-dependent Schrödinger equation

- obtain equations of motion for the parameters:

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} \longrightarrow \begin{aligned} \dot{q}_t &= \frac{p_t}{m} \\ \dot{p}_t &= 0 \\ \dot{\alpha}_t &= -\frac{2i\hbar}{m}\alpha_t^2 \\ \dot{\gamma}_t &= -\frac{p_t^2}{2m} + p_t\dot{q}_t - \frac{\hbar^2\alpha_t}{m} \end{aligned}$$

- integrate equations of motion, to obtain the same result as before

GWP's & CS's in a harmonic potential

- follow the same procedure as before, i.e., Gaussian $ansatz$
- obtain equations of motion for the parameters:

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + \frac{1}{2}m\omega^2 x^2 \longrightarrow \begin{aligned} \dot{q}_t &= \frac{p_t}{m} \\ \dot{p}_t &= -m\omega^2 q_t^2 \\ \dot{\alpha}_t &= -\frac{2i\hbar}{m}\alpha_t^2 + \frac{i}{2\hbar}m\omega^2 \\ \dot{\gamma}_t &= \frac{p_t^2}{2m} - \frac{1}{2}m\omega^2 q_t^2 - \frac{\hbar^2\alpha_t}{m} \equiv L_{\rm cl} - \frac{\hbar^2\alpha_t}{m} \end{aligned}$$

- identify special condition for which the width matrix does not change:

if $\alpha_t = \frac{m\omega}{2\hbar}$ then $\dot{\alpha}_t = 0$ coherent state

CS's are minimum uncertainty wavepackets

- **calculate uncertainty product $\Delta x \Delta p$ for a general Gaussian:**

$$\begin{aligned}
\Delta x &= \sqrt{\langle \hat{x}^2 \rangle - \langle \hat{x} \rangle^2} = \sqrt{\frac{1}{4\mathrm{Re}\alpha}} \\
\Delta p &= \sqrt{\langle \hat{p}^2 \rangle - \langle \hat{p} \rangle^2} = \left(2\hbar^2 \alpha - \frac{\hbar^2 \alpha^2}{\mathrm{Re}\alpha} \right)^{1/2} = \frac{\hbar |\alpha|}{\sqrt{\mathrm{Re}\alpha}} \\
\Delta x \Delta p &= \frac{\hbar}{2} \frac{|\alpha|}{\mathrm{Re}\alpha}
\end{aligned}$$

- **for real and positive α: minimum uncertainty product:**

$$\Delta x \Delta p = \frac{\hbar}{2}$$

- **for the free particle wavepacket:**

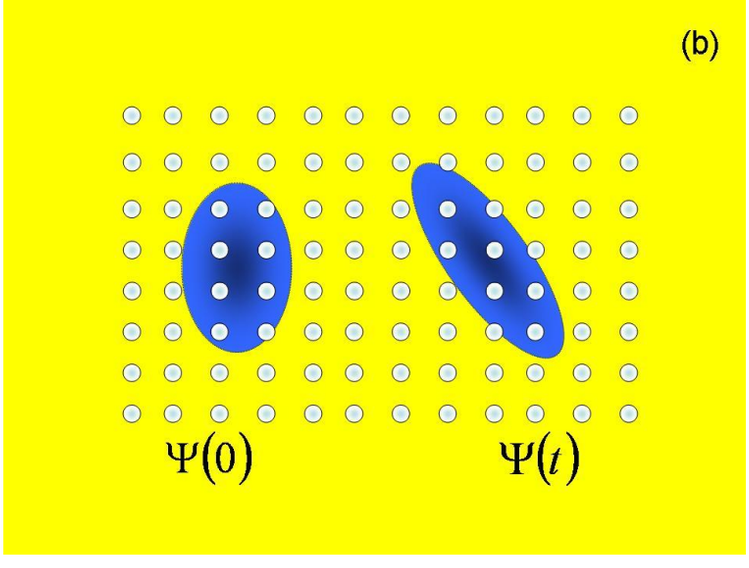
$$\Delta x(t) \Delta p(t) = \frac{\hbar}{2} \sqrt{1 + \frac{4\hbar^2 \alpha_0^2 t^2}{m^2}} \geq \frac{\hbar}{2}$$

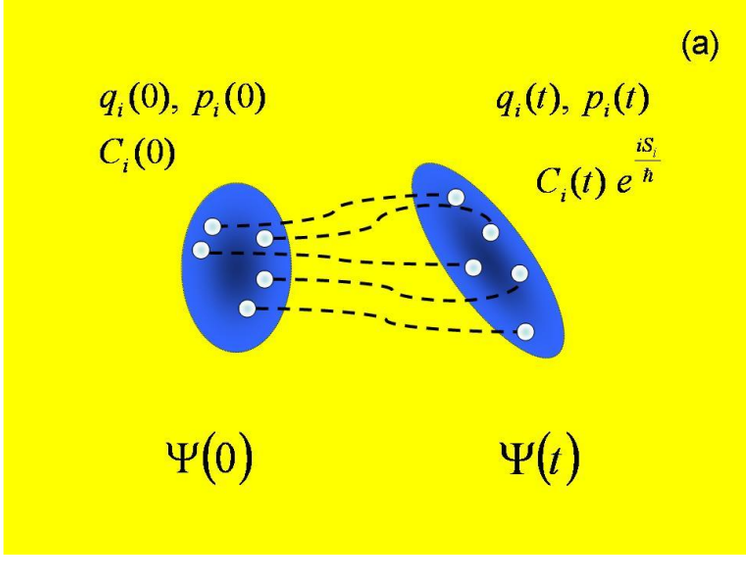
Numerical solution of the TDSE

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

concept: expand Ψ in a basis set

Basis Sets – Static or Time-Dependent





(illustration by D. Shalashilin)

High-dimensional quantum simulations

- **standard wavepacket propagation:** not beyond $\sim$5 degrees of freedom
- **mean-field methods:** very efficient but not accurate enough
- **multiconfigurational mean-field methods:** significant improvement – accurate quantum dynamics for $\sim$100 degrees of freedom (and up to $\sim$1000 degrees of freedom or more for "multi-layer" approaches!)

Standard wavepacket propagation methods

$$\begin{aligned} \Psi(r_1, \ldots, r_f; t) &= \sum_{j_1=1}^{N_1} \cdots \sum_{j_f=1}^{N_f} C_{j_1 \ldots j_f}(t) \prod_{\kappa=1}^{f} \theta_{j_\kappa}^{(\kappa)}(r_\kappa) \\ &= \sum_J C_J(t) \Theta_J \end{aligned}$$

where the $\theta_{j_\kappa}^{(\kappa)}$ are time-independent basis functions, e.g., localized DVR (discrete variable representation) functions, with $\langle \theta_j | \hat{x}_j | \theta_l \rangle = x_j \delta_{jl}$

$$i\dot{C}_J = \sum_L H_{JL} C_L \qquad \text{with} \qquad H_{JL} = \langle \Theta_J | H | \Theta_L \rangle$$

⟶ solve via split-operator, Chebyshev, Lanczos etc. integrators

exponential scaling of numerical effort $\sim f N^{f+1}$

⟶ Hence, up to 5–6 degrees of freedom feasible

Mean-field approximation: time-dependent Hartree

$$\Psi(r_1, \ldots, r_f; t) \quad = \quad c(t) \prod_{\kappa=1}^{f} \phi_\kappa(r_\kappa, t)$$

i.e., separable form use constraint: $\langle \phi_\kappa | \dot{\phi}_\kappa \rangle = 0$

$$\begin{aligned} i\dot{c} &= \langle H \rangle \, c \\ i\dot{\phi}_\kappa &= \left(\hat{H}^{(\kappa)} - \langle H \rangle \right) \phi_\kappa \end{aligned}$$

evolution in the κth subspace

with $\langle H \rangle = \langle \phi_1 \ldots \phi_f | H | \phi_1 \ldots \phi_f \rangle$

and $\hat{H}^{(\kappa)} = \langle \phi_1 \ldots \phi_{\kappa-1} \phi_{\kappa+1} \ldots \phi_f | H | \phi_1 \ldots \phi_{\kappa-1} \phi_{\kappa+1} \ldots \phi_f \rangle$

time-dependent mean-field Hamiltonian

Linear scaling of numerical effort $\longrightarrow$ many degrees of freedom!

Multi-Configuration Time-Dependent Hartree (MCTDH)

Meyer, Manthe, Cederbaum, Chem. Phys. Lett. 165, 73 (1990), Beck et al., Phys. Rep. 324, 1 (2000)

- multiconfigurational expansion of the wavefunction

$$\Psi(\mathrm{r},t) = \sum_J A_J(t)\Phi_J(\mathrm{r},t) = \sum_{j_1} \dots \sum_{j_N} A_{j_1 \dots j_N}(t) \prod_{\kappa=1}^{N} \varphi_{j_\kappa}^{(\kappa)}(\mathrm{r}_\kappa,t)$$

- time-dependent configurations Φ_J / single-particle functions (spf) φ_{j_κ}
- use the Dirac-Frenkel variational principle $\langle \delta\Psi | H - i\partial_t | \Psi \rangle = 0$:

coefficients:

$$i\dot{A}_J = \sum_L \langle \Phi_J | H | \Phi_L \rangle A_L$$

spf's :

$$i\dot{\varphi}^{(\kappa)} = \left(\hat{1} - \hat{P}^{(\kappa)}\right) \left[\rho^{(\kappa)}\right]^{-1} \hat{H}^{(\kappa)} \varphi^{(\kappa)}$$

- for large systems, use combined modes, i.e., multidimensional $\varphi^{(\kappa)}$'s

"Mixed quantum-classical" approaches

- **Mean-field (Ehrenfest) approach**
- **Surface Hopping approach**
- **Many variants of these two approaches**

Mean-field (Ehrenfest) approach

- **the classical subsystem moves on an average potential due to the quantum subsystem:**

$$M\ddot{\boldsymbol{R}} = \boldsymbol{F}_{\mathrm{cl}} + \boldsymbol{F}_{\mathrm{MF}}$$

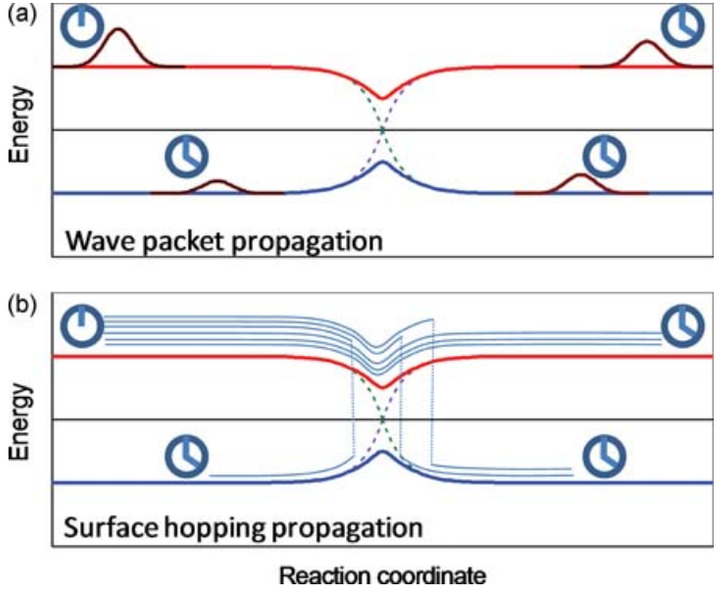
$$\boldsymbol{F}_{\mathrm{MF}} = -\boldsymbol{\nabla}_{\boldsymbol{R}}\langle\psi|\boldsymbol{H}(r,\boldsymbol{R})|\psi\rangle$$

- **the quantum subsystem evolves under the time-dependent Hamiltonian $\boldsymbol{H}(r,\boldsymbol{R}(t))$:**

$$i\hbar\dot{\psi} = (\boldsymbol{H}_0 + \boldsymbol{H}(r,\boldsymbol{R}(t)))\psi$$

- **state-specific evolution of the classical subsystem, and quantum-classical correlations, are not correctly accounted for**

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):

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

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

- 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 $\Pi_k(t) = N_k(t)/N_T$

(De-)coherence problem

- **both in the mean-field (Ehrenfest) and surface hopping scheme, the evolution of the quantum subsystem is "too coherent", since the quantum mechanical (wavepacket) nature of the nuclei is not accounted for**

- **in the case of surface hopping, introduce corrections which make the wavefunction collapse onto one or the other state – so-called decoherence corrections**

- **other problems: zero-point energy, tunneling . . .**

What exactly is coherence?

- **wavefunction picture: coherent superposition states, say for TLS**

$$|\Psi(t)\rangle = c_1|\phi_1\rangle \exp\left(-\frac{i}{\hbar}E_1 t\right) + c_2|\phi_2\rangle \exp\left(-\frac{i}{\hbar}E_2 t\right)$$

- **this translates as follows to the density operator picture:**

$$\begin{aligned}\hat{\rho}(t) &= |\Psi(t)\rangle\langle\Psi(t)| = \sum_{i,j=1,2} c_i c_j^* \exp\left(-\frac{i}{\hbar}(E_i - E_j)t\right)|\phi_i\rangle\langle\phi_j| \\ &\equiv \sum_{i,j=1,2} \rho_{ij}(t)|\phi_i\rangle\langle\phi_j|\end{aligned}$$

$i = j$: **populations,** $i \neq j$: **coherences**

- **now include vibrations and/or ensemble average:**
  $\hat{\rho} = \sum_n p_n |\Psi_n(t)\rangle\langle\Psi_n(t)| \longrightarrow$ **dephasing (“**T_2**”, “decoherence”)**

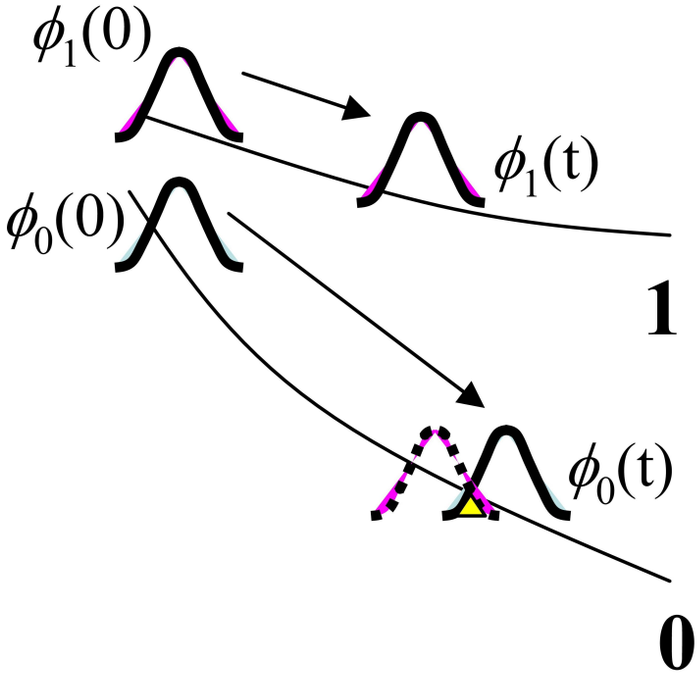
How coherence gets lost

$$|\psi(t)\rangle = c_0|0\rangle|\phi_0(t)\rangle + c_1|1\rangle|\phi_1(t)\rangle$$

$$\hat{\rho}(t) = |\psi(t)\rangle\langle\psi(t)|$$

time-evolving coherence:

$$\begin{aligned}\rho_{01}(t) &= \mathrm{Tr}\{|0\rangle\langle 1|\hat{\rho}(t)\} \\ &= \langle 1|\hat{\rho}(t)|0\rangle \\ &= c_1^* c_0 \langle\phi_1(t)|\phi_0(t)\rangle\end{aligned}$$



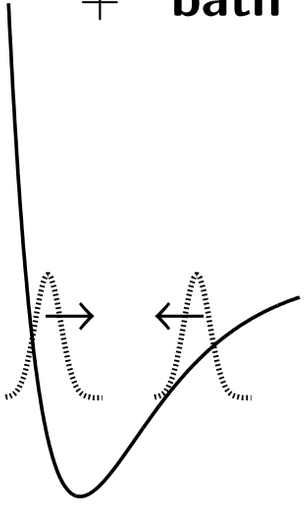
picture: P. Rossky et al.

- **coherence $\propto$ overlap of nuclear wavefunctions**
- **loss of coherence cannot be captured by a classical trajectory picture**

“Cat states” and decoherence

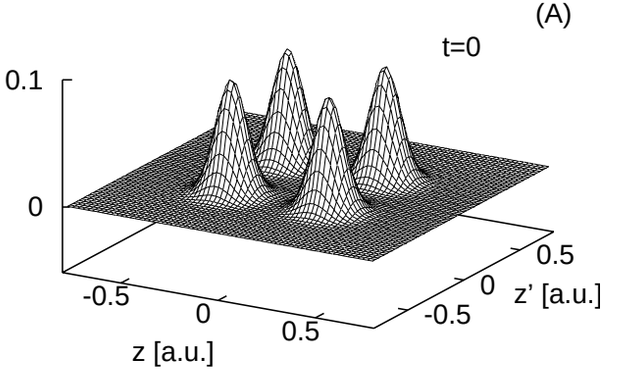
superposition of two wavepackets

+ “bath” of (60) harmonic oscillators

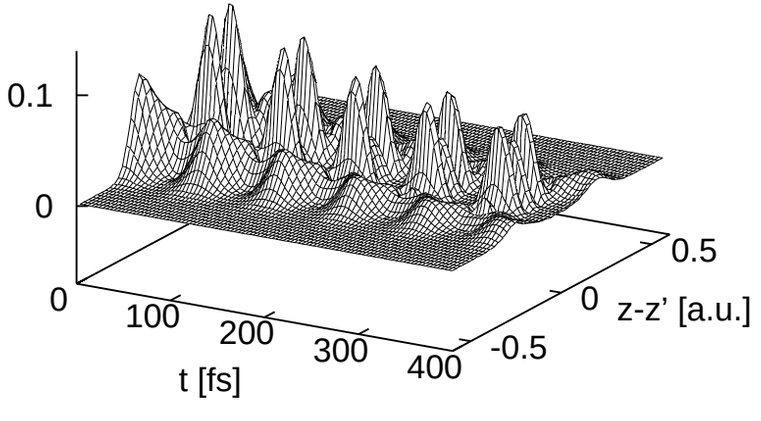


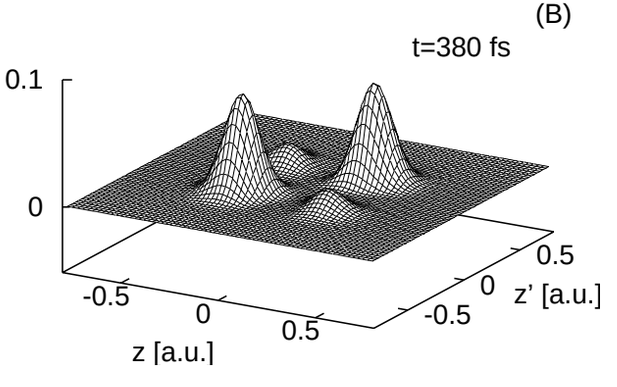
Burghardt, Nest, Worth,

J. Chem. Phys. 119, 5364 (2003)



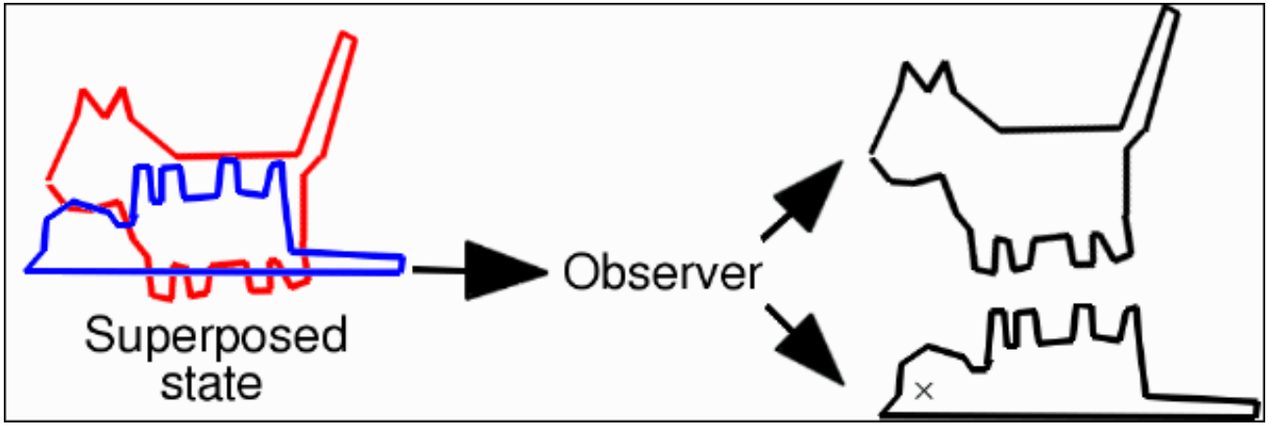
off-diagonal : coherence





Coherent superpositions & measurement process

$$|\Psi_{\mathrm{cat}}\rangle = 1/\sqrt{2}\left(|\mathrm{alive}\rangle + |\mathrm{dead}\rangle\right)$$



- the measurement picks up one or the other eigenstate, $|\mathrm{alive}\rangle$ *or* $|\mathrm{dead}\rangle$
- the measurement changes the system: projection onto the corresponding eigenstate – "wavefunction collapse", "reduction of the wavepacket"