Wave packet dynamics
and
Simulation of Pump-probe spectra

Wave packet dynamics :

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time-dependent view of quantum mechanics
Fundamental description of collision processes
link with classical mechanics
intuitive

two aspects :
wave packet dynamics as 'numerical tool'
for time-independent observables
photoabsorption spectrum (first lecture)
experimental realisation of wave packets:
femtosecond spectroscopy (third lecture)

Outline

Lecture 1

Wave packet dynamics:
General aspects
Gaussian wave packets
Wave packets as a link to classical mechanics

Field-matter interaction:
Time-dependent perturbation theory
Photoabsorption spectra from a time-dependent view

Lecture 2

Numerical methods of wave packet propagation
Representation of wavefucntions
Propagation methods
A critical comparison

Lecture 3

Femtosecond spectroscopy:
Simulation of pump-probe spectra

Lecture 1

Part 1

General aspects

Gaussian wave packets

connection with classical mechanics: Ehrenfest's theorem

Part 2

Field-matter interaction

Time-dependent perturbation theory

Photoabsorption spectra from a time-dependent view

The 1-D Gaussian wave packet: V=0

- the time evolution of a free Gaussian wave packet is given by:

$$\begin{aligned} x_t &= x_0 + \frac{p_0}{m} t \\ p_t &= p_0 \\ \alpha_t &= \frac{\alpha_0}{1 + \frac{2i\hbar\alpha_0 t}{m}} \end{aligned}$$

- expectation values $\langle x \rangle, \langle p \rangle$ move classically !

$$\begin{aligned} \langle x \rangle(t) &= \langle x \rangle(t=0) + \frac{\langle p \rangle(t=0)}{m} t \\ \langle p \rangle &= \langle p \rangle(t=0) \end{aligned}$$

- wave packet shows $dispersion$

$$\Delta x = \Delta x_0 \sqrt{1 + \frac{4\hbar^2 \alpha_0^2}{m} t^2}$$

The 1-D Gaussian wave packet: $V = \frac{1}{2}m\omega^2 x^2$

- the time evolution of a Gaussian wave packet is given by:

$$\begin{aligned} x_t &= x_0 \cos(\omega t) + \frac{p_0}{m\omega} \sin(\omega t) \\ p_t &= p_0 \cos(\omega t) + m\omega x_0 \sin(\omega t) \end{aligned}$$

$$\alpha_t = a \left(\frac{\alpha_0 \cos(\omega t) + ia \sin(\omega t)}{i\alpha_0 \sin(\omega t) + a \cos(\omega t)} \right)$$

here: $a = \frac{m\omega}{2\hbar}$

- expectation values $\langle x \rangle, \langle p \rangle$ move classically !
- width of wave packet changes periodically, except for $\alpha_0 = a$!
  corresponds to the width of the ground state wavefunction
  $\Longrightarrow$ coherent state

- this is an extremely good (fast) test for any numerical propagation scheme !

Quantum-classical correspondence: Ehrenfest's theorem

- Q: do the expectation values always move according to classical mechanics ?:

$$i\hbar\frac{\partial\chi(x,t)}{\partial t} = \left(\frac{p^2}{2m}+V(x)\right)\chi(x,t)$$

consider a time-independent observable A and a wavefunction χ:

$$\begin{aligned}\langle A\rangle &= \langle\chi|A|\chi\rangle\\ \frac{d\langle A\rangle}{dt} &= \langle\dot\chi|A|\chi\rangle+\langle\chi|A|\dot\chi\rangle\\ &= \frac{1}{i\hbar}\langle\chi|[A,H]|\chi\rangle\end{aligned}$$

- specifically, for $A=x$ and $A=p$ we find:

$$\frac{d}{dt}\langle x\rangle = \frac{\langle p\rangle}{m} \tag{1}$$

$$\frac{d}{dt}\langle p\rangle = -\langle\frac{\partial V}{\partial x}\rangle \tag{2}$$

if

$$\langle\frac{\partial V}{\partial x}\rangle \stackrel{?}{=} \left.\frac{\partial V}{\partial x}\right|_{x=\langle x\rangle}$$

holds, eq. (1,2) form a closed set of differential equations
corresponding to Hamiltons equations in classical mechanics
check: true for constant, linear, harmonic potential
not true in general
approximately true for a well-localized wavepacket:
(hint: expand potential around center of wave packet,
if harmonic approximation to potential holds
across the width of wave packet $\Longrightarrow$: OK

- wave packet dynamics with Gaussians (E. Heller)

Lecture 1

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Part 2

Field-matter interaction

Time-dependent perturbation theory

Photoabsorption spectra from a time-dependent view

Maxwell's equations and Electromagnetic Potentials

electric and magnetic fields:

$$\nabla \times \mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{B}}{\partial t} \qquad \nabla \cdot \mathbf{E} = 0$$
$$\nabla \times \mathbf{B} = \frac{1}{c}\frac{\partial \mathbf{E}}{\partial t} \qquad \nabla \cdot \mathbf{B} = 0$$

scalar and vector potential:

$$\begin{aligned} \mathbf{E} &= -\nabla\phi - \frac{1}{c}\frac{\partial \mathbf{A}}{\partial t} \\ \mathbf{B} &= \nabla \times \mathbf{A} \end{aligned}$$

$\mathbf{A}$ and ϕ obey:

$$\begin{aligned} \nabla^2\phi &= 0 \\ \nabla^2\mathbf{A} &= \frac{1}{c^2}\frac{d^2\mathbf{A}}{dt^2} \end{aligned}$$

hence a free-space solution is:

$$\mathbf{A}(\mathbf{r},t) = \mathbf{A}_0 \sin(\mathbf{k}\cdot\mathbf{r} - \omega t)$$

which implies

$$\mathbf{E}(\mathbf{r},t) = \frac{\omega}{c}\mathbf{A}_0 \cos((\mathbf{k}\cdot\mathbf{r} - \omega t) \equiv \boldsymbol{\varepsilon}\mathrm{E}_0 \cos((\mathbf{k}\cdot\mathbf{r} - \omega t) \tag{3}$$
$$\mathbf{B}(\mathbf{r},t) = \mathbf{A}_0(\mathbf{k}\times\boldsymbol{\varepsilon}) \cos((\mathbf{k}\cdot\mathbf{r} - \omega t) \tag{4}$$

electromeagnetic energy in volume V:

$$E = \frac{1}{8\pi}\int_V d^3r \left(\mathbf{E}^2 + \mathbf{B}^2\right)$$

Energy density, photon flux and absorption spectrum

electromagnetic energy in volume V:

$$E \;=\; \frac{1}{8\pi}\int_V d^3r\left(\mathbf{E}^2+\mathbf{B}^2\right)$$

using eq.(3,4) with $\mathbf{E},\mathbf{B}$ constant in volume V we obtain:

$$E \;=\; V\frac{\mathrm{E}_0^2}{8\pi}$$

Einstein relation: energy of a single photon is quantized: $\hbar\omega$, hence

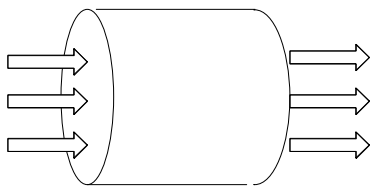
$$E \;=\; N\hbar\omega$$

relation between photon density $\frac{N}{V}$ and classical electrical field amplitude E_0:

$$\left(\frac{N}{V}\right) \;=\; \frac{\mathrm{E}_0^2}{8\pi\hbar\omega}$$

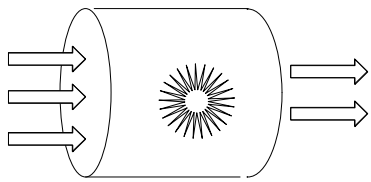
photon flux:
number of photons per unit area per unit time passing a particluar location:

$$\text{photon flux} \;=\; \left(\frac{N}{V}\right)\,c = \frac{\mathrm{E}_0^2 c}{8\pi\hbar\omega}$$



absorption spectrum:

$$\sigma(\omega) \;=\; \frac{\text{transition rate}}{\text{incident photon flux}}$$



Field-Matter interaction

- Dipole approximation:
  typical values for molecular spectroscopy in the optical range:
  laser wavelength: $\lambda = 600nm$
  dimensions of atom/molecule: 10 Å
  $\Longrightarrow$ fields are spacially constant at atomic level
  $\Longrightarrow$ neglect $\mathbf{k} \cdot \mathbf{r}$ electric and magnetic fields:

$$\begin{aligned} \mathbf{A}(\mathbf{r}, t) &\equiv \mathbf{A}(t) \\ \mathbf{E}(\mathbf{r}, t) &\equiv \mathbf{E}(t) \\ \mathbf{B}(\mathbf{r}, t) &\equiv \mathbf{B}(t) \end{aligned}$$

- Molecular field-free Hamiltonian with masses m_j and charges q_j:

$$H_0 = \frac{1}{2} \sum_j m_j \mathbf{p}_j^2 + V(\mathbf{r}_1, \cdots)$$

- Molecule-field interaction: minimal coupling,
  $\mathbf{p}_j \longrightarrow \mathbf{p}_j - \frac{q_j}{c}\mathbf{A}$, identical to Lorenz force:

$$H_C(t) = \frac{1}{2} \sum_j m_j \left(\mathbf{p}_j - \frac{q_j}{c} \mathbf{A}(t) \right)^2 + V(\mathbf{r}_1, \cdots)$$

  Hamiltonian has become $time\text{-}dependent$ by virtue of $\mathbf{A}(t)$

Field-Matter interaction 2

- field-free Hamiltonian:

$$H_0 \;=\; \frac{1}{2}\sum_j m_j \mathbf{p}_j^2 + V(\mathbf{r}_1, \cdots)$$

- minimal coupling Hamiltonian H_C:

$$H_C(t) \;=\; \frac{1}{2}\sum_j m_j \left(\mathbf{p}_j - \frac{q_j}{c}\mathbf{A}(t)\right)^2 + V(\mathbf{r}_1, \cdots)$$

- time-dependent Schrödinger equation:

$$i\hbar\frac{\partial\psi_C(t)}{\partial t} \;=\; H_C(t)\psi_C(t)$$

change gauge by unitary transformantion:

$$\psi(t) \;=\; e^{-\frac{i}{\hbar}\sum_j \frac{q_j}{c}\mathbf{r}_j\cdot\mathbf{A}(t)}\;\psi_C(t)$$

leads to

$$i\hbar\frac{\partial\psi(t)}{\partial t} \;=\; \left(H_0(t) - \boldsymbol{\mu}\cdot\mathbf{E}(t)\right)\;\psi(t)$$

with $\boldsymbol{\mu}$ being the *dipole moment*:

$$\boldsymbol{\mu} \;=\; \sum_j q_j \mathbf{r}_j$$

- note: no weak field assumption, only *dipole* approximation

Time-dependent perturbation theory

- for weak electric fields, the interaction energy $W(t) = -\boldsymbol{\mu} \cdot \mathbf{E}(t)$ can be viewed as time-dependent perturbation:

$$i\hbar \frac{\partial \Psi}{\partial t} \;=\; (H_0 + W(t))\, \Psi(t)$$

- change to interaction representation:

$$\widetilde{\Psi}(t) = e^{iH_0 t}\Psi(t) \qquad \widetilde{W}(t) = e^{iH_0 t} W(t) e^{-iH_0 t}$$

Schrödinger equation in interaction representation:

$$i\hbar \frac{\partial \widetilde{\Psi}(t)}{\partial t} \;=\; \widetilde{W}(t)\widetilde{\Psi}(t)$$

interaction starts at t_0, one can integrate from t_0 to t:

$$\widetilde{\Psi}(t) \;=\; \widetilde{\Psi}(t_0) - \frac{i}{\hbar}\int_{t_0}^{t} dt'\; \widetilde{W}(t')\widetilde{\Psi}(t')$$

iteration yields perturbative expansion:

$$\widetilde{\Psi}(t) \;=\; \underbrace{\widetilde{\Psi}(t_0)}_{zero} - \underbrace{\frac{i}{\hbar}\int_{t_0}^{t} dt'\; \widetilde{W}(t')\widetilde{\Psi}(t_0)}_{first} - \underbrace{\frac{1}{\hbar^2}\int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' \widetilde{W}(t')\widetilde{W}(t'')\widetilde{\Psi}(t_0)}_{second} + \cdots$$

First order expression in Schrödinger representation:

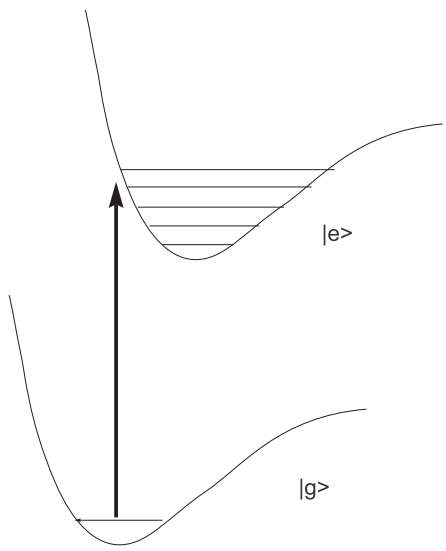
$$\Psi(t) \;=\; e^{-\frac{i}{\hbar}H_0(t-t_0)}\Psi(t_0) - \frac{i}{\hbar}\int_{t_0}^{t} dt'\; e^{-\frac{i}{\hbar}H_0(t-t')} W(t') e^{-\frac{i}{\hbar}H_0(t'-t_0)}\; \Psi(t_0)$$

Electronic excitation by time-dependent perturbation theory

- First order expression in Schrödinger representation ($t_0 = 0$):

$$\Psi(t) \;=\; e^{-\frac{i}{\hbar}H_0 t}\Psi(0) - \frac{i}{\hbar}\int_0^t dt'\; e^{-\frac{i}{\hbar}H_0(t-t')}W(t')e^{-\frac{i}{\hbar}H_0 t'}\;\Psi(0)$$

- suppose that the field induces a transition from an electronic ground state $|g\rangle$ to an electronic excited state $|e\rangle$:



- Born-Oppenheimer separation:

$$\Psi(t) \;=\; \underbrace{\psi_g(r,t)}_{\text{nuclear wf}}\,|g> + \underbrace{\psi_e(r,t)}_{\text{nuclear wf}}\,|e>$$

if initially the molecule is in its electronic ground state $|g>$
the light interaction leads to excitation
$\Longrightarrow$ transfer of population to the excited state $|e>$.

Electronic excitation by time-dependent perturbation theory

- To calculate the excited state wavefunction, we project onto $|e\rangle$:

$$\psi_e(r,t) \;=\; -\frac{i}{\hbar}\int_0^t dt'\; e^{-\frac{i}{\hbar}H_e(t-t')}\boldsymbol{\mu}_{eg}\mathbf{E}(t')e^{-\frac{i}{\hbar}H_g t'}\;\psi_g(r,0)$$

with

$$\begin{aligned} H_g(r) &= \langle g|H_0|g\rangle = T_r + V_g(r) \\ H_e(r) &= \langle e|H_0|e\rangle = T_r + V_e(r) \\ \boldsymbol{\mu}_{eg} &= \langle e|\boldsymbol{\mu}|g\rangle(r) \end{aligned}$$

- this general expression is valid for arbitrary field shape:
  $\Longrightarrow$ cw-absorption spectroscopy
  $\Longrightarrow$ femtosecond spectroscopy
  $\Longrightarrow$ control through pulse shaping

Absorption cross section from wave packet dynamics

- central relationship between absorption and dynamics

$$\sigma(\omega) \;=\; \frac{2\pi\omega}{3\hbar c} \int\limits_{-\infty}^{\infty} dt \; \underbrace{\langle \phi_e(0) | \phi_e(t) \rangle}_{C(t)} \, e^{-\frac{i}{\hbar}\left(E_g - \hbar\omega\right)t}$$

- properties of the correlation function:

$$C(t) \;=\; C^*(-t)$$

($\Longrightarrow \sigma(\omega)$ is real)

- practical calculation:
  1. calculate ground state ψ_g ($\longleftarrow$ wave packet dynamics)
  2. multiply ψ_g with transition dipole moment μ_{eg}: $promoted\ state\ \phi_e$
  3. propagate ϕ_e on excited state surface ($\longleftarrow$ wave packet dynamics)
  4. calculate $C(t)$
  5. take Fourier transform of $C(t)$

- key quantity:

$$C(t) \;=\; \langle \phi_e(0) | \phi_e(t) \rangle$$

- $\phi_e(t)$ is a $wave\ packet$ on the excited state surface
  $\Longrightarrow$ exhibits time dependence
- How to calculate $\phi_e(t)$?

- wave packet propagation:

$$\phi_e(t) \;=\; e^{-\frac{i}{\hbar}H_e t} \, \phi_e(0)$$

Summary

Part 1

General aspects
Gaussian wave packets
connection with classical mechanics: Ehrenfest's theorem

Part 2

Field-matter interaction
Time-dependent perturbation theory
Photoabsorption spectra from a time-dependent view

Key references

- wave packets: general aspects, Gaussian wave packets:
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  Quantum mechanics, Vol 1 (Wiley, NY, 1977)
  E. J. Heller, *J. Chem. Phys.* **62**, 1544 (1975), ibid. **65**, 4979 (1976)

- spectra from correlation functions:
  E. J. Heller, *Acc. Chem. Res.* **14**, 368 (1981)
  E. J. Heller, S. Tomsovic, Physics Today, July 1993
  R. Schinke, Photodissociation Dynamics, Cambridge University Press (1993)

Lecture 2

- Numerical methods of wave packet propagation
- Representation of wavefunctions
  grids
  basis
  pseudospectral methods
  DVR

- Propagation methods
  Second Order Differencing
  Cayley's method (Crank-Nicholson)
  Split-Operator
  A critical comparison

  (Chebyshev, Lanczos)

  Time-dependent self consistent field (TDSCF)
  Multi-Configuration Time-Dependent Hartree (MCTDH)

Numerical methods for exact time propagation

- time-dependent Schrödinger equation:

$$i\hbar\frac{\partial}{\partial t}\chi(t) \;=\; H\chi(t)$$

$$\chi(t) \;=\; \underbrace{e^{-\frac{i}{\hbar}Ht}}_{\text{propagator}}\,\chi(0)$$

problems:

- represent $\chi(0), \chi(t)$ on computer
  ($\Longrightarrow$: approximation through truncation)
- calculate/approximate propagator
- apply propagator (or approx. prop.) to wavefunction representation

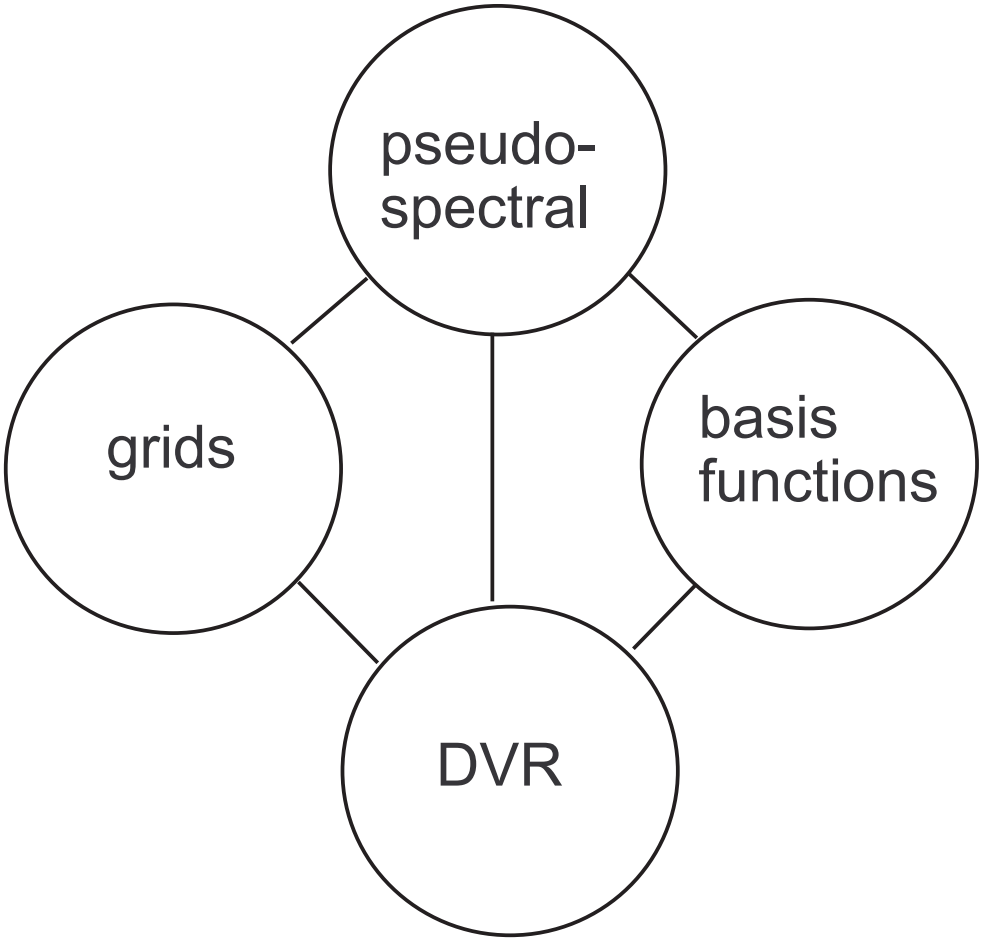
Numerical methods for time-independent Schrödinger equation

$$H\chi \;=\; E\chi$$

problems:

- represent χ on computer
  ($\Longrightarrow$: approximation through truncation)
- calculate/approximate Hamiltonian
- apply Hamiltonian to wavefunction representation

Representation of wavefucntions on a computer



- how to represent $\chi(r)$?
- how to calculate $H\chi(r)$?

Represenatation of wavefunctions on a grid

- choose grid of N points: r_n
- wavefunction is represented by a vector of length N

$$\chi_n^{(g)} \;=\; \chi(r_n)$$

- potential operator by multiplication with potential at grid points:

$$V(r)\chi(r) \;\approx\; V(r_n)\chi_n^{(g)}$$

- kinetic operator by finite differences:

$$T\chi(r) \;=\; -\frac{\hbar^2}{2m}\left(\frac{\chi_{n+1}^{(g)} - \chi_n^{(g)}}{r_{n+1} - r_n} - \frac{\chi_n^{(g)} - \chi_{n-1}^{(g)}}{r_n - r_{n-1}}\right)$$

  or higher order finite differnces
- advantages: conceptually simple
- disadvantages: only precise with large number N of points

Represenatation of wavefunctions in a set of basis functions

- choose basis set $|\phi_j\rangle$ of N orthgonal functions:

$$\chi(r) \;\approx\; \chi^{(s)}(r) \;=\; \sum_{j=0}^{N} c_j \phi_j(r)$$

$\Longrightarrow$: Schrödinger equation becomes a matrix equation

- potential operator by matrix multiplication
  with potential matrix $V_{jj'} = \langle \phi_j | V | \phi_{j'} \rangle$

$$\sum_{j'=0}^{N} V_{jj'} c_{j'}$$

- kinetic operator by matrix multiplication
  with kinetic matrix $T_{jj'} = \langle \phi_j | T | \phi_{j'} \rangle$

$$\sum_{j'=0}^{N} T_{jj'} c_{j'}$$

- or in general: multiplication with Hamiltonian matrix
  with kinetic matrix $H_{jj'} = \langle \phi_j | H | \phi_{j'} \rangle$

$$\sum_{j'=0}^{N} H_{jj'} c_{j'}$$

- disadvantage:
  for high dimensions calculation of matrix elements expensive
  time-dependent Hamiltonians: redo every timestep !
  $H_{jj'}$ might be large

Pseudospectral methods

- choose basis set $|\phi_j\rangle$ of N orthonormal functions
- choose set of N grid points r_n

$$\chi(r) \;\approx\; \chi^{(s)}(r) \;=\; \sum_{j=0}^{N} c_j \phi_j(r)$$

- we *impose*:

$$\chi(r_n) \;=\; \chi^{(s)}(r_n)$$

from which we can define the function values on the grid points:

$$\chi_n^{(g)} \;=\; \sum_{j=0}^{N} c_j \phi_j(r_n)$$

- define the *collocation matrix* R_{jn}

$$R_{nj} \;=\; \phi_j(r_n)$$

if R_{nj} can be inverted, one can switch between representations:

$$c_j \;=\; \sum_{n=0}^{N} R_{jn}^{-1} \chi_n^{(g)}$$

- application of potential energy operator: grid representation

$$V(r_n)\chi_n^{(g)}$$

- application of kinetic energy operator: spectral representation:

$$\begin{aligned}
T\chi_n^{(g)} \;=\; \sum_{j=0}^{N} \left(T\phi_j(r)\right)_{r=r_n} c_j \;&=\; \sum_{j=0}^{N-1} \underbrace{\left(T\phi_j(r)\right)_{r=r_n}}_{\text{analytic}} \left(\sum_{n'=0}^{N-1} R_{jn'}^{-1} \chi_{n'}^{(g)}\right) \\
&=\; \sum_{n'=0}^{N-1} \underbrace{\left[\sum_{j=0}^{N-1} \left(T\phi_j(r)\right)_{r=r_n} R_{jn'}^{-1}\right]}_{\text{constant}} \chi_{n'}^{(g)} \\
&=\; \sum_{n'=0}^{N-1} \underbrace{M_{nn'}}_{\text{T-matrix}} \; \chi_{n'}^{(g)}
\end{aligned}$$

DVR: discrete variable representation

- aim:
  use basis: kinetic energy (derivatives) can be calculated exactly
  use grid: potential is diagonal (multiplication with potential at grid points)

- choose basis set $|\phi_j\rangle$ of N orthgonal functions:

$$\chi(r) \;\approx\; \chi^{(s)}(r) \;=\; \sum_{j=0}^{N-1} c_j \phi_j(r)$$

- construct position matrix:

$$M_{jj'} \;=\; \langle \phi_j | r | \phi_{j'} \rangle$$

- diagonalize postition matrix $M_{jj'}$

$$\mathbf{U}^\dagger \mathbf{M} \mathbf{U} \;=\; \mathbf{D}$$

  the transformation matrix defines a second orthogonal basis set: $\delta_n(r)$
  (the eigenvectros of a hermitian operator are orthogonal)
  'DVR basis'

$$\chi(r) \;\approx\; \chi^{(s)}(r) \;=\; \sum_{j=0}^{N-1} \chi_n^{(g)} \delta_n(r)$$

  choose as grid points the eigenvalues of $\mathbf{M}$

- hence by construction we have:

$$\langle \delta_n | r | \delta_{n'} \rangle \;=\; r_n \delta_{nn'}$$

  due to truncation of the initial basis $|\phi_j\rangle$ the
  $|\delta_n\rangle$ are also only approximately complete:

$$\sum_{n=0}^{N-1} |\delta_n\rangle\langle\delta_n| \;\approx\; 1 \quad (= 1 \text{ for} N \to \infty)$$

DVR: discrete variable representation

- potential matrix elements in the $\delta_n\rangle$-basis are well-approximated by:

$$\langle\delta_n|V(r)|\delta_{n'}\rangle \;=\; V(r_n)\delta_{nn'}$$

  proof: expand $V(r)$ in a Taylor series

- application of potential energy operator: grid representation

$$V(r_n)\chi_n^{(g)}$$

- application of kinetic energy operator: spectral representation:

$$T\chi_n^{(g)} \;=\; \underbrace{\sum_{j=0}^{N-1} U_{nj} \sum_{j'=0}^{N-1} T_{jj'} \sum_{n'=0}^{N-1} U^*_{j'n'}}_{K_{nn'}} \chi_{n'}^{(g)}$$

Propagators

- aim:
  approximate the quantum mechanical propagator:

$$e^{-iHt}$$

- 2 classes:
  global: approximate e^{-iHt}
  iterative: $e^{-iHt} = e^{-iH\Delta t} \cdots e^{-iH\Delta t} \quad t = N\Delta t$, approximate $e^{-iH\Delta t}$

- global only for time-independent Hamiltonians
- for femtosecond pulse interaction: iterative procedure

$$\chi(t+\Delta t) \;=\; e^{-\frac{i}{\hbar}\Delta t H}\chi(t)$$

- Taylor expansion: not stable upon iteration !

$$\chi(t+\Delta t) \;=\; \left(1 - \frac{i}{\hbar}H - \frac{1}{\hbar^2}H^2 + \cdots\right)\chi(t)$$

- in general: stability upon iteration if also the
  $approximate$ short time propagator in unitary:

$$\begin{aligned} \chi(t+\Delta t) &= \mathbf{U}^{app}\chi(t) \\ (\mathbf{U}^{app})^\dagger\,\mathbf{U}^{app} &= 1 \quad \text{exactly!} \end{aligned}$$

- why ? norm is $strictly$ conserved also upon $approximate$ propagation

$$\begin{aligned} \langle\chi(t+\Delta t)|\chi(t+\Delta t)\rangle &= \langle\chi(t)|\,(\mathbf{U}^{app})^\dagger\,\mathbf{U}^{app}|\chi(t)\rangle \\ &= \langle\chi(t)|\chi(t)\rangle \end{aligned}$$

- this does not mean that the propagation is exact !

  watch out for effects of finite Δt
  $always$ converge final results (observables) with respect to Δt

Short-time propagators

- Second order differencing
- (implicit) Cayley's method
- Split-Operator method
- short iterative Lanczos

- (time-dependent self consistent field)
- (Multi-Configuration Time-Dependent Hartree) (MCTDH)

Global propagators

- Chebyshev
- Lanczos

Second-order differencing

use backward/forward first order expression:

$$\chi(t+\Delta t) = \left(1 - \frac{i}{\hbar}\Delta t H\right)\chi(t)$$
$$\chi(t-\Delta t) = \left(1 + \frac{i}{\hbar}\Delta t H\right)\chi(t)$$

combine:

$$\chi(t+\Delta t) - \chi(t-\Delta t) = -\frac{2i}{\hbar}\Delta t H \chi(t)$$
$$\chi(t+\Delta t) = \chi(t-\Delta t) - \frac{2i}{\hbar}\Delta t H \chi(t)$$

- storage requirements: $\chi(t), \chi(t-\Delta t)$
- operations: $H\chi(t)$
  can be done with any representation

- characteristics:
  stable for sufficiently small Δt: at least: $\Delta t < \frac{\hbar}{E_{max}}$
  conservation of Re$\langle\chi(t)|\chi(t+\Delta t)\rangle$
- requires Hermitian Hamiltonian

Implicit Cayley's method

- use backward/forward expression for intermediate time $t + \frac{\Delta t}{2}$:

$$\chi(t + \frac{\Delta t}{2}) \;=\; e^{\frac{i}{\hbar}\frac{\Delta t}{2}H}\chi(t + \Delta t) \;\;=\;\; e^{-\frac{i}{\hbar}\frac{\Delta t}{2}H}\chi(t)$$

- first order expressions for the short-time propagators

$$\left(1 + \frac{i}{\hbar}\frac{\Delta t}{2}H\right)\chi(t + \Delta t) \;=\; \left(1 - \frac{i}{\hbar}\frac{\Delta t}{2}H\right)\chi(t)$$

$$\chi(t + \Delta t) - \chi(t) \;=\; -\frac{i}{\hbar}\frac{\Delta t}{2}H\left(\chi(t + \Delta t) + \chi(t)\right)$$

define an *increment* function $\delta(t) = \chi(t + \Delta t) - \chi(t)$

$$\delta(t) \;=\; -\frac{i}{\hbar}\frac{\Delta t}{2}H\left(\delta(t) + 2\chi(t)\right)$$

iteration to fixpoint:

- algorithm:
  $\chi(t)$ known
  take $\delta^{(0)}(t) = 0$
  calculate:

$$\delta^{(n+1)}(t) \;=\; -\frac{i}{\hbar}\frac{\Delta t}{2}H\left(\delta^{(n)}(t) + 2\chi(t)\right)$$

  until convergence $\bar{\delta}(t)$
  update $\chi(t + \Delta t) = \chi(t) + \bar{\delta}(t)$

- storage requirements: $\chi(t), \delta(t)$ (iteration can be done in place)
- operations: $H\chi(t)$
  can be done with any representation

- characteristics:
  at *each* timestep iteration required
  however: with Δt small (required in any case) fast convergence

FFT-Split-Operator method

- works only for Hamiltonians of the form $H = T(\text{momenta}) + V(\text{position})$
- approximate short time propagator as:

$$\chi(t+\Delta t) \;=\; e^{-\frac{i}{\hbar}\Delta t H}\chi(t) \;\;=\;\; e^{-\frac{i}{\hbar}\frac{\Delta t}{2}V}\; e^{-\frac{i}{\hbar}\Delta t T}\; e^{-\frac{i}{\hbar}\frac{\Delta t}{2}V}$$

- extremely efficient with
  Fourier pseudo-spectral representation of wavefunctions

$$\chi_n^{(g)}(t+\Delta t) =$$

$$\underbrace{e^{-\frac{i}{\hbar}\frac{\Delta t}{2}V(r_n)}}_{e^{-\frac{i}{\hbar}\frac{\Delta t}{2}V}}\;\underbrace{\sum_{j=0}^{N-1}\frac{1}{\sqrt{N}}e^{i\frac{2\pi jn}{N}}}_{FFT^{-1}}\;\underbrace{e^{-\frac{i}{\hbar}\Delta t\left(\frac{\hbar^2}{2m}k_j^2\right)}}_{e^{-\frac{i}{\hbar}\Delta t T}}\;\Big[\underbrace{\sum_{n'=0}^{N-1}\frac{1}{\sqrt{N}}e^{-\frac{2\pi jn'}{N}}}_{FFT}\;\underbrace{e^{-\frac{i}{\hbar}\frac{\Delta t}{2}V(r_{n'})}}_{e^{-\frac{i}{\hbar}\frac{\Delta t}{2}V}}\;\chi_{n'}^{(g)}(t)\Big]$$

- algorithm:

$$\chi_n^{(g)}(t+\Delta t) = \;\; e^{-\frac{i}{\hbar}\frac{\Delta t}{2}V} \;\; \xleftarrow{\text{FFT}^{-1}} \;\; e^{-\frac{i}{\hbar}\Delta t T} \;\; \xleftarrow{\text{FFT}} \;\; e^{-\frac{i}{\hbar}\frac{\Delta t}{2}V} \;\; \chi_n^{(g)}(t)$$

- storage requirements: $\chi_n^{(g)}(t)$
- advantage:
  $e^{-\frac{i}{\hbar}\frac{\Delta t}{2}V}$ is local in grid representation
  $e^{-\frac{i}{\hbar}\Delta t T}$ is local in momentum representation

- characteristics:
  time-reversal symmetry: replace $\Delta t \longrightarrow -\Delta t$
  $(\mathbf{U}^{app})^\dagger\,\mathbf{U}^{app} = 1$:
  conserves norm even for *finite* Δt

- efficient algorithm: calculate discrete Fourier transform by FFT:
  scaling $\sim NlogN \Longrightarrow$: fast
- works also for *time-dependent* Hamiltonian

Comparison

	Hamiltonian time-dep. (fs-pulses)	Hamiltonian non-herm. (abs. pot)	Hamiltonian w/ cross-terms (spher. coo.)	repr.	grid
SOD	+	-	+	any	any
Imp. Cayley	+	+	+	any	any
FFT-SO	+	+	-	FFT	equidist.

	posivive	negative
SOD	• flexible: any representation • time-dep. Hamiltonian	• no absorbing potentials • for large spectral radius: $\Longrightarrow$ small Δt
Implicit Cayley	• flexible: any representation • unitary • time-dep. Hamiltonian	• iteration for each timestep
FFT-SO	• fast + efficient • unitary • time-dep. Hamiltonian	• equidistant grid • no cross terms in Hamiltonian

Chebyshev scheme

- global propagator or
  iterative propagation with long timesteps

- idea: polynomial approximation to the propagator

$$e^{-\frac{i}{\hbar}Ht}\chi(0) \;\approx\; \sum_{n=0}^{N} a_n P_n\left(-\frac{i}{\hbar}Ht\right)\chi(0)$$

  for a given order, Chebyshev yields the polynomial approximation
  with the smallest maximal error in the interval $[-1,1]$
  in comlex plane: convergence in unit circle ([-i,i]) on imaginary axis
  $\Longrightarrow$: spectral range shifting of H necessary

  hint: consider $\chi(0)$ as eigenfunction of H with eigenenergy E

- disdvantage: outside $[-1,1]$ polynomial expansion does not converge:
  $\Longrightarrow$: spectral range shifting of H $important$

- advantage: big timesteps (one)
- not unitary
- disadvantage:
  works only for time-independent Hamiltonians

Lanczos scheme

- global or iterative (short iterative Lanczos SIL)
- idea: express propagator in an optimal basis that is different at each timestep and for each initial wavefunction

$$e^{-\frac{i}{\hbar}Ht}\chi(0) \approx \underbrace{\chi(0)}_{q_0} - \frac{i}{\hbar}\underbrace{H\chi(0)}_{q_1} - \frac{1}{\hbar^2}\underbrace{H^2\chi(0)}_{q_2} - \frac{i}{\hbar^3}\underbrace{H^3\chi(0)}_{q_3} + \cdots$$

use $q_n = H^n\chi(0)$ as a basis set in which the propagator is developed

- advantage: flexible
  high order $\longrightarrow$ big timestep
  low order $\longrightarrow$ small timestep (SIL)

- disdvantage: time-independent Hamiltonian
  for SIL H can be time-dependent, but less efficient

Time dependent self consistent field (TD-SCF)

- for many degrees of freedom (~ 4) quantum mechanics becomes hard
- approximation: TD-SCF

- suppose two degrees of freedom x, y
- TD-SCF: express 2-dimensional wavefunction as product at all times

$$\chi(x,y,t) \;=\; a(t)\;\phi^{(x)}(x,t)\;\phi^{(y)}(y,t)$$

note: this decomposion is $not\ unique$
phases and real valued factors can be shifted between factors
constraints:

$$\langle\phi^{(x)}|\dot{\phi}^{(x)}\rangle \;=\; \langle\phi^{(y)}|\dot{\phi}^{(y)}\rangle \;=\; 0$$

fixes phases and imposes normalization of the $\phi^{(x)}, \phi^{(y)}$
into Schrödinger's equation:

$$i\hbar\dot{a}(t) \;=\; \bar{H}a(t)$$

$$\begin{aligned} i\hbar\dot{\phi}^{(x)}(t) &= \left(H^{(x)} - \bar{H}\right)\phi^{(x)}(t) \\ i\hbar\dot{\phi}^{(y)}(t) &= \left(H^{(y)} - \bar{H}\right)\phi^{(y)}(t) \end{aligned}$$

$$\begin{aligned} \bar{H} &= \langle\phi^{(x)}|\langle\phi^{(y)}|H|\phi^{(y)}\rangle\phi^{(x)}\rangle \\ H^{(x)} &= \langle\phi^{(y)}|H|\phi^{(y)}\rangle \\ H^{(y)} &= \langle\phi^{(x)}|H|\phi^{(x)}\rangle \end{aligned}$$

2-dim Schrödinger equation is replaced by
two 1-dim Schrödinger equations
x-DOF experiences a mean potential averaged over y-DOF
and vice versa

- note: even with H time independent, $H^{(x)}$ and $H^{(y)}$ are time dependent
  $\longrightarrow$ need propagators that allow time-dependent Hamiltonians

- allows quantum propagations for $many$ DOF
- disadvantage: approximate, quality of approximation hard to estimate

Multi-Configuration time-dependent Hartree (MCTDH)

(Meyer, Manthe, Cederbaum)

- for many degrees of freedom (~ 4) quantum mechanics becomes hard
- method: MCTDH

- approximate, but converges to exact
- suppose two degrees of freedom x, y
- MCTDH: express 2-dimensional wavefunction as sum over product

$$\chi(x,y,t) \;=\; \sum_{n=1}^{N} \sum_{m=1}^{M} a_{nm}(t)\; \phi_n^{(x)}(x,t)\; \phi_m^{(y)}(y,t)$$

  for $N, M \longrightarrow \infty$ this is exact
  note: this decomposion is $not\ unique$
  phases and real valued factors can be shifted between factors
  constraints:

$$\langle \phi_n^{(x)} | \dot{\phi}_{n'}^{(x)} \rangle \;=\; \delta_{nn'} \qquad \langle \phi_m^{(y)} | \dot{\phi}_{m'}^{(y)} \rangle \;=\; \delta_{mm'}$$

  fixes phases and imposes normalization and orthogonality of the $\phi_n^{(x)}, \phi_m^{(y)}$

- into Schrödinger's equation yields:
  coupled equations of motion for the functions $|\phi_n^{(x)}\rangle,\ |\phi_m^{(y)}\rangle$
- for $N \longrightarrow \infty, M \longrightarrow \infty$ the $|\phi_n^{(x)}\rangle,\ |\phi_m^{(y)}\rangle$ are complete:
  $\Longrightarrow$ MCTDH becomes exact
  $|\phi_n^{(x)}\rangle,\ |\phi_m^{(y)}\rangle$ become time independent
- advantages: storage of wavefunction possible
- can be combined with any representation: DVR, Fourier grid, basis sets individually for each degree of freedom
  if N_b and M_b basis vectors (DVR points, grid points) are required for the x and y DOF respectively, storage is:
  $N * N_b + M * M_b$ as compared to $N_b * M_b$
  in general: $N_b >> N, M_b >> M$
- gain even more drastic for more degrees of freedom

Multi-Configuration time-dependent Hartree (MCTDH)

(Meyer, Manthe, Cederbaum)

$$\chi(x,y,t) \;=\; \sum_{n=1}^{N}\sum_{m=1}^{M} a_{nm}(t)\;\phi_n^{(x)}(x,t)\;\phi_m^{(y)}(y,t)$$

constraints (other constrains possible):

$$\langle\phi_n^{(x)}|\dot{\phi}_{n'}^{(x)}\rangle \;=\; \langle\phi_m^{(y)}|\dot{\phi}_{m'}^{(y)}\rangle \;=\; 0$$

fixes phases and imposes normalization and orthogonality of the $\phi_n^{(x)}, \phi_m^{(y)}$ into Schrödinger's equation:

$$i\hbar\dot{a}_{nm}(t) \;=\; \bar{H}_{nn'mm'}a_{n'm'}(t)$$

$$i\hbar\sum_{n=1}^{N}\rho_{n'n}^{(x)}|\dot{\phi}_n^{(x)}\rangle \;=\; \left(1-P^{(x)}\right)\sum_{n=1}^{N}H_{n'n}^{(x)}|\phi_n^{(x)}\rangle$$

$$i\hbar\sum_{m=1}^{M}\rho_{m'm}^{(y)}|\dot{\phi}_m^{(y)}\rangle \;=\; \left(1-P^{(y)}\right)\sum_{m=1}^{M}H_{m'm}^{(y)}|\phi_m^{(y)}\rangle$$

$$\begin{aligned}
\bar{H}_{nn'mm'} &= \langle\phi_n^{(x)}|\langle\phi_m^{(y)}|H|\phi_{m'}^{(y)}\rangle|\phi_{n'}^{(x)}\rangle\\
H_{nn'}^{(x)} &= \sum_{m=1}^{M}\sum_{m'=1}^{M} a_{n'm'}^{*}a_{nm}\langle\phi_{m'}^{(y)}|H|\phi_m^{(y)}\rangle\\
H_{mm'}^{(y)} &= \sum_{n=1}^{N}\sum_{n'=1}^{N} a_{n'm'}^{*}a_{nm}\langle\phi_{n'}^{(x)}|H|\phi_n^{(x)}\rangle
\end{aligned}$$

$$P^{(x)} \;=\; \sum_{n=1}^{N}|\phi_n^{(x)}\rangle\langle\phi_n^{(x)}| \qquad P^{(y)} \;=\; \sum_{m=1}^{M}|\phi_m^{(y)}\rangle\langle\phi_m^{(y)}|$$

$$\rho_{nn'}^{(x)} \;=\; \sum_{m=1}^{M}a_{n'm}^{*}a_{nm} \qquad \rho_{mm''}^{(y)} \;=\; \sum_{n=1}^{N}a_{nm}^{*}a_{nm'}$$

- coupled equations of motion for the functions $|\phi_n^{(x)}\rangle,\ |\phi_m^{(y)}\rangle$
- for $N \longrightarrow \infty, M \longrightarrow \infty$ the $|\phi_n^{(x)}\rangle,\ |\phi_m^{(y)}\rangle$ are complete:
  $\Longrightarrow P^{(x)} = P^{(y)} = 1 \quad |\phi_n^{(x)}\rangle,\ |\phi_m^{(y)}\rangle$ become time independent,
  eq. for a_{nm} becomes normal spectral representation
  of Hamiltonian in a time *independent* basis

Summary

- Numerical methods of wave packet propagation
- Representation of wavefucntions
  grid, basis, pseudospectral methods, DVR

- Propagation methods
  Second Order Differencing
  Cayley's method (Crank-Nicholson)
  Split-Operator
  A critical comparison

  (Chebyshev, Lanczos)

  Time-dependent self consistent field (TDSCF)
  Multi-Configuration Time-Dependent Hartree (MCTDH)

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Lecture 3

- Simulation of Pump-Probe spectra
  realisation of wave packets: femtosecond pulse excitation
  time dependent perturabtion theory with arbitrary pulse shapes
  wave packet dynamics induced by femtosecond pulse excitation

  detection of moving wave packets: the pump-probe scheme
  examples of pump-probe spectra in small molecules

- Classical simulations of pump-probe spectra

Molecular spectroscopy

- excitation of internal degrees of freedom with electric fields

$$
\begin{aligned}
(ABC)_i &\xrightarrow{\hbar\omega} (ABC)_f \\
&\xrightarrow{\hbar\omega} (ABC)_f^+ + e^- \\
&\xrightarrow{\hbar\omega} (AB)_f + C_{f'} \\
&\xrightarrow{\hbar\omega} \text{combinations of the above}
\end{aligned}
$$

Excitation of internal degrees of freedom

- rotation (microwave)
- vibration (infrared)
- electronic (visible, UV)

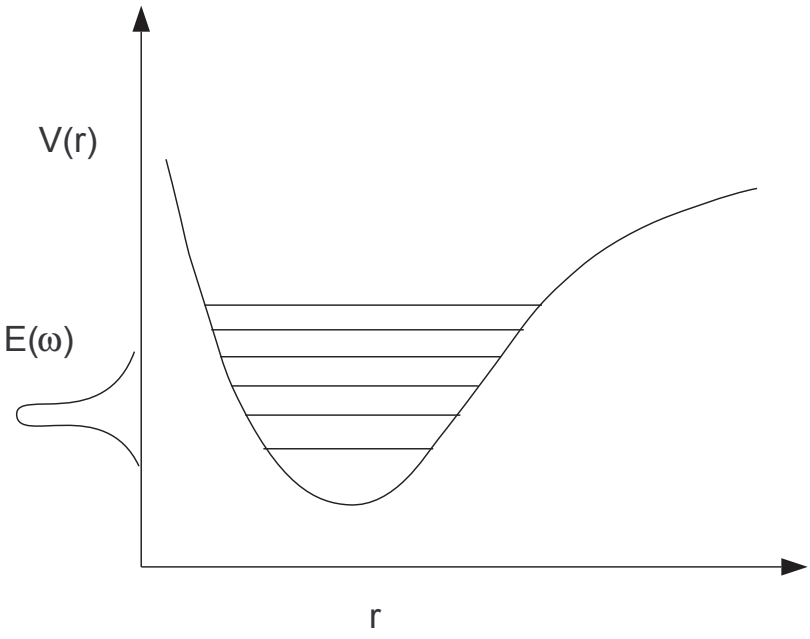
here:
electronic and vibrational excitation
ionization

Molecular spectroscopy with cw-pulses:

- pulse duration: $\tau(pulse) \sim$ nanoseconds
- molecular timescales (example: Na_2(X))
  electronic $\sim$ 2 femtoseconds
  vibrations $\sim$ 200 femtoseconds
  rotations: $\sim$ 10 picoseconds

$$\tau(pulse) >> \tau(el), \tau(vib), \tau(rot)$$

- in energy domain: excitation of stationary states

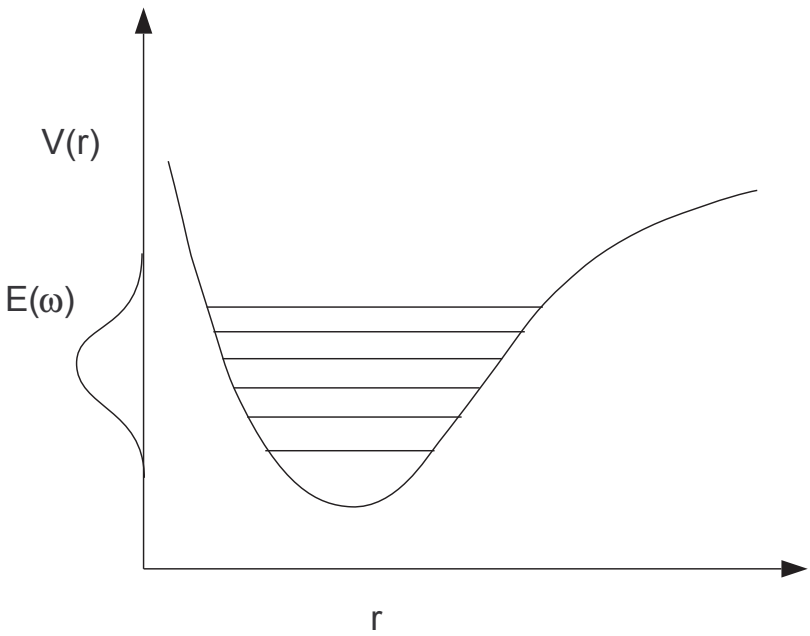


Molecular spectroscopy with short pulses:

- pulse duration: $\tau(pulse) \sim$ 100 fs
- molecular timescales (example: Na_2(X))
  electronic $\sim$ 2 femtoseconds
  vibrations $\sim$ 200 femtoseconds
  rotations: $\sim$ 10 picoseconds

$$\tau(pulse) < \tau(vib), \tau(rot)$$

- in energy domain: excitation of vibrational/rotational wave packets



Calculation of short-pulse excitation:

- how to calculate short pulse excitation with realistic pulse shapes
- suppose weak pulses $\Longrightarrow$ time-dependent perturbation theory

$$\psi_e(r,t) \;=\; -\frac{i}{\hbar}\int_0^t e^{-\frac{i}{\hbar}H_e(t-t')}\boldsymbol{\mu}_{eg}\mathbf{E}(t)e^{-\frac{i}{\hbar}H_g t'}\;\psi_g(r,0)$$

with

$$\begin{aligned} H_g(r) &= \langle g|H_0|g\rangle = T_r + V_g(r) \\ H_e(r) &= \langle e|H_0|e\rangle = T_r + V_e(r) \\ \boldsymbol{\mu}_{eg} &= \langle e|\boldsymbol{\mu}|g\rangle(r) \end{aligned}$$

this expression is valid for arbitrary fields

- suppose short pulse starting at $t = 0$

$$\begin{aligned} \mathbf{E}(t) &= \boldsymbol{\varepsilon}\mathrm{E}_0 f(t)\cos(\omega t) = \boldsymbol{\varepsilon} f(t)\frac{\mathrm{E}_0}{2}\left(e^{-i\omega t} + e^{-i\omega t}\right) \\ f(t) &= \text{plulse shape} \end{aligned}$$

yields:

$$\begin{aligned} \psi_e(t) \;=\; & -\frac{i}{\hbar}\frac{\mathrm{E}_0}{2}\int_0^t e^{-\frac{i}{\hbar}H_e(t-t')}\left(\boldsymbol{\mu}_{eg}\boldsymbol{\varepsilon}\right) f(t)\; e^{-i\omega t'}e^{-\frac{i}{\hbar}H_g t'}\;\psi_g(0) \quad \text{resonant} \\ & -\frac{i}{\hbar}\frac{\mathrm{E}_0}{2}\int_0^t e^{-\frac{i}{\hbar}H_e(t-t')}\left(\boldsymbol{\mu}_{eg}\boldsymbol{\varepsilon}\right) f(t)\; e^{i\omega t'}e^{-\frac{i}{\hbar}H_g t'}\;\psi_g(0) \quad \text{non}-\text{resonant} \end{aligned}$$

if $\hbar\omega \approx V_e - V_g$ in the Franck-Condon region,
the *resonant* term dominates

$$\psi_e(t) \;=\; -\frac{i}{\hbar}\frac{\mathrm{E}_0}{2}\int_0^t e^{-\frac{i}{\hbar}H_e(t-t')}\left(\boldsymbol{\mu}_{eg}\boldsymbol{\varepsilon}\right) f(t)\; e^{-i\omega t'}e^{-\frac{i}{\hbar}H_g t'}\;\psi_g(0)$$

Numerical calculation by wave packet propagation

- discretize time integral:

$$\psi_e(t) \;=\; -\frac{i}{\hbar}\frac{\mathrm{E}_0}{2}\Delta t \sum_{n=0}^{N} e^{-\frac{i}{\hbar}H_e(N-n)\Delta t}\left(\boldsymbol{\mu}_{eg}\boldsymbol{\varepsilon}\right) f(n\Delta t)\; e^{-i\omega t'} e^{-\frac{i}{\hbar}H_g n\Delta t}\;\psi_g(0)$$
$$t' = n\Delta t, t = N\Delta t$$

- this can be written in an iterative way:

$$\psi_e(t+\Delta t) \;=\; e^{-\frac{i}{\hbar}H_e\Delta t}\psi_e(t) - \underbrace{\Delta t\frac{i}{\hbar}\frac{\mathrm{E}_0}{2}}_{C}\left(\boldsymbol{\mu}_{eg}\boldsymbol{\varepsilon}\right) f(t+\Delta t)\; e^{-i\omega(t+\Delta t)} e^{-\frac{i}{\hbar}H_g\Delta t}\;\psi_g(t)$$

- further simplifications if the system is initially in an eigenstate of energy E_g:

$$\psi_e(t+\Delta t) \;=\; e^{-\frac{i}{\hbar}H_e\Delta t}\psi_e(t) - C\left(\boldsymbol{\mu}_{eg}\boldsymbol{\varepsilon}\right) f(t+\Delta t)\; e^{-\frac{i}{\hbar}\left(E_g+\hbar\omega\right)(t+\Delta t)}\;\psi_g(0)$$

- $\Longrightarrow$ first order short pulse excitation can easily be performed within any $iterative$ propagation scheme

- algorithm:

  1. start at $t = 0$ with $\psi_e(r, t = 0) \equiv 0$
  2. propagate $\psi_e(r,t) \longrightarrow \psi_e(r, t+\Delta t)$
  3. add:

$$\psi_e(r, t+\Delta t) := \psi_e(r, t+\Delta t) - C\left(\boldsymbol{\mu}_{eg}\boldsymbol{\varepsilon}\right) f(t+\Delta t)\; e^{-\frac{i}{\hbar}\left(E_g+\hbar\omega\right)(t+\Delta t)}\;\psi_g(0)$$

  4. loop over 2.+3.

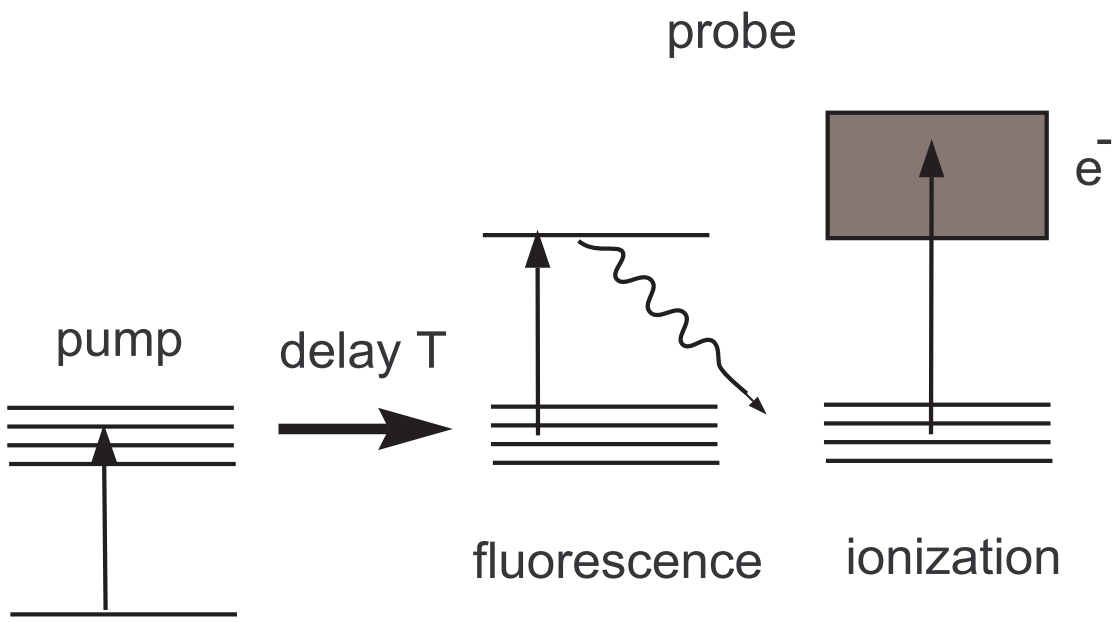
  after the pulse has finished, $f(t)$ is zero and

  2. propagate $\psi_e(r,t) \longrightarrow \psi_e(r, t+\Delta t)$

The pump-probe scheme

- fs-pulse excitation leads to wave packet creation
- wavepackets=non stationary states: dynamics
- how to detect wp-dynamics experimentally ?
  $\Longrightarrow$ pump-probe scheme:
  1. use a first femtosecond laserpulse to create a wave packet
  2. use a second, *time-delayed* laserpulse for detection:

  detection:
  excitation to higher electronic state $\longrightarrow$ fluorescence
  ionisation $\longrightarrow$ electron or ion signal
- recorded signal as function of pump-probe delay
  $\Longrightarrow$ detection of molecuar dynamics in real time



Calculation of probe step: electronic excitation + fluorescence

- probe pulse starts interacting with the molecular sample at T
- probe pulse excites molecule to higher electronic state $|s\rangle$
  experimental detection: fluorescence
  $\Longrightarrow$ signal $\sim$ total population in state $|s\rangle$
  consider weak pulses: time-dependent perturbation theory
  equivalent expression for the probe step:

$$\psi_s(t) \;=\; -\frac{i}{\hbar}\frac{\mathrm{E}_0}{2}\int_T^t e^{-\frac{i}{\hbar}H_s(t-(t'-T))}\,(\boldsymbol{\mu}_{se}\boldsymbol{\varepsilon})\,f(t-T)\;e^{-i\omega(t'-T)}e^{-\frac{i}{\hbar}H_e(t'-T)}\;\psi_e(T)$$

- note difference between pump-pulse:
  'initial' state $\psi_e(T)$ is *not stationary*

- total population in electronics state $|s\rangle$ after the end of the pulse:

$$P_s(T) \;=\; \lim_{t\longrightarrow\infty}\langle\psi_s(t)|\psi_s(t)\rangle$$

- experimental possibilities: detect $P_s(T)$

Numerical calculation of probe excitation

- discretize time integral:

$$\psi_s(t) \;=\; -\frac{i}{\hbar}\frac{\mathrm{E}_0}{2}\Delta t \sum_{n=0}^{N} e^{-\frac{i}{\hbar}H_s(N-n)\Delta t}\,(\boldsymbol{\mu}_{se}\boldsymbol{\varepsilon})\,f(n\Delta t)\;e^{-i\omega t'}e^{-\frac{i}{\hbar}H_e n\Delta t}\;\psi_e(T)$$
$$t' = n\Delta t, t = N\Delta t$$

- this can be written in an iterative way:

$$\psi_s(t+\Delta t) \;=\; \underbrace{e^{-\frac{i}{\hbar}H_s\Delta t}\psi_s(t)}_{\text{propagation}} - \underbrace{\Delta t\frac{i}{\hbar}\frac{\mathrm{E}_0}{2}}_{C}\,(\boldsymbol{\mu}_{se}\boldsymbol{\varepsilon})\,f(t+\Delta t)\;e^{-i\omega(t+\Delta t)}\,\underbrace{e^{-\frac{i}{\hbar}H_e\Delta t}\;\psi_e(T)}_{\text{propagation}}$$

- propagation on surface $|e\rangle$ and $|s\rangle$ in parallel:
- algorithm:

1. start at $t = T$ with $\psi_e(r, t = T)$ and $\psi_s(r, t = T) \equiv 0$
2. propagate $\psi_e(r,t) \longrightarrow \psi_e(r, t+\Delta t)$
3. propagate $\psi_s(r,t) \longrightarrow \psi_s(r, t+\Delta t)$
4. add:

$$\psi_s(r, t+\Delta t) := \psi_s(r, t+\Delta t) - C\left(\boldsymbol{\mu}_{eg}\boldsymbol{\varepsilon}\right) f(t+\Delta t)e^{-i\omega(t+\Delta t)}\;\psi_e(t+\Delta t)$$

4. loop over 2.-4.

after the pulse has finished, f(t) is zero and

3. propagate $\psi_s(r,t) \longrightarrow \psi_s(r, t+\Delta t)$

but P_s remains constant

Summary

- Simulation of Pump-Probe spectra
  realisation of wave packets: femtosecond pulse excitation
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  wave packet dynamics induced by femtosecond pulse excitation

  detection of moving wave packets: the pump-probe scheme
  examples of pump-probe spectra in small molecules

- Classical simulations of pump-probe spectra

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