

Quantum molecular dynamics

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When does classical mechanics fail?

A measure of a quantum character of an object with mass m and kinetic energy E is its de Broglie wavelength:

$$\lambda = h / \sqrt{2mE}$$

If d is a characteristic size of a system, then:

$\lambda \ll d \longrightarrow$ classical mechanics,

$\lambda \gtrsim d \longrightarrow$ quantum mechanics.

1 of selected objects

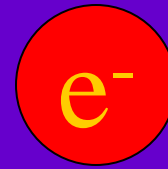


1. A student running
not to miss a class:

classical

$$m = 70 \text{ kg}, v = 5 \text{ m/s} \longrightarrow \lambda \sim 10^{-36} \text{ m}$$

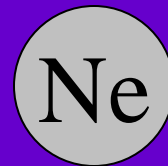
2. A valence electron:



quantal

$$m = 9 \times 10^{-31} \text{ kg}, E = 1 \text{ eV} \longrightarrow \lambda \sim 10^{-9} \text{ m}$$

2. A vibrating neon atom:

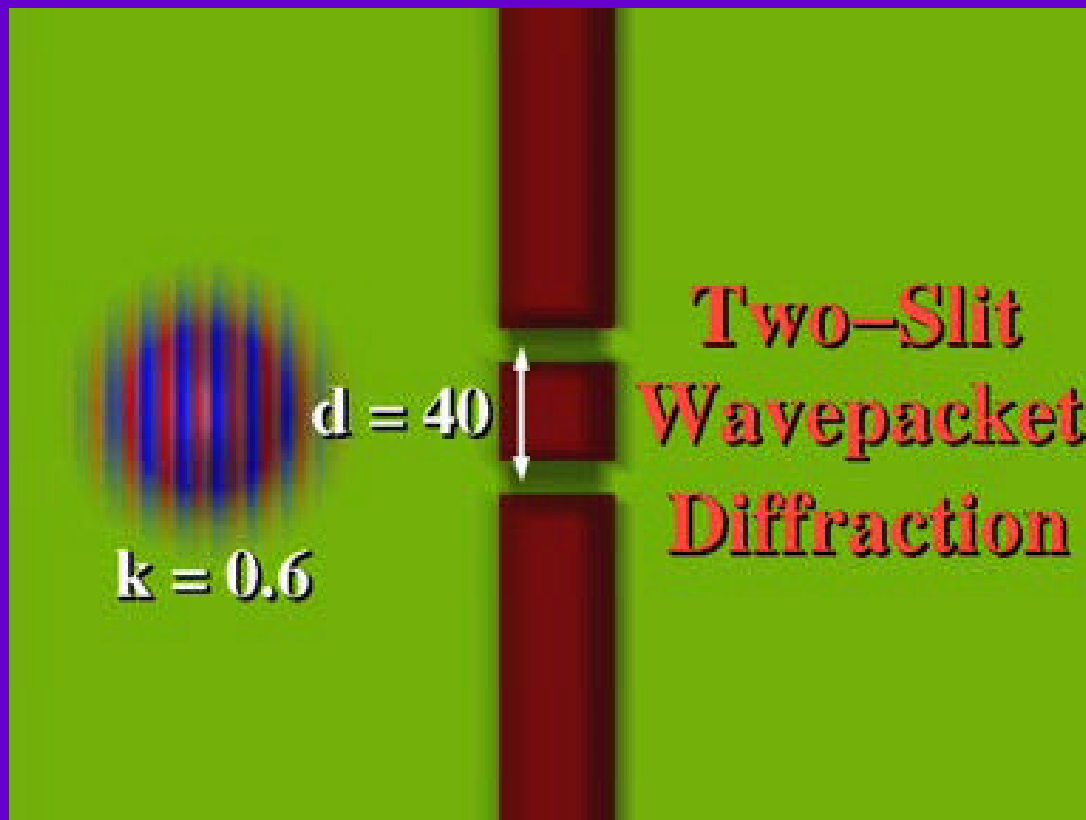


semi-quantal

$$m = 2 \times 10^{-26} \text{ kg}, E = 0.01 \text{ eV} \longrightarrow \lambda \sim 10^{-10} \text{ m}$$

Particle-wave dualism

Demonstration of a wave character of quantum objects:



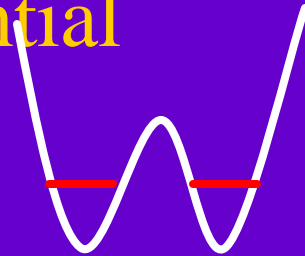
R. Kosloff et al., HU Jerusalem

Quantum motions of atoms

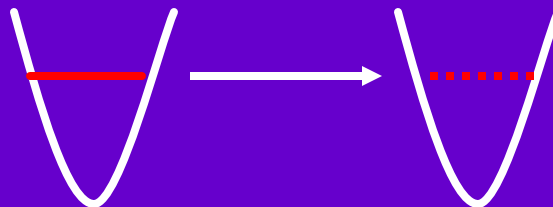
1. Zero point vibrations - energy can not drop below $\hbar\omega/2$



2. Tunneling - passing under the barrier of a double well potential

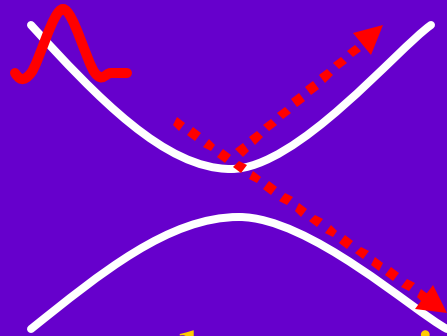


3. Quantum resonant energy transfer, interferences

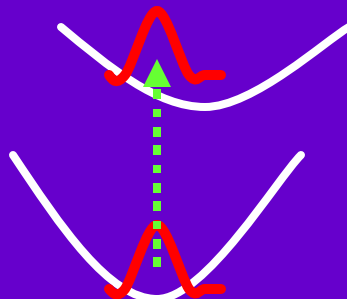


Quantum interactions

1. With electrons: Non-adiabatic interactions - avoided crossings, conical intersections

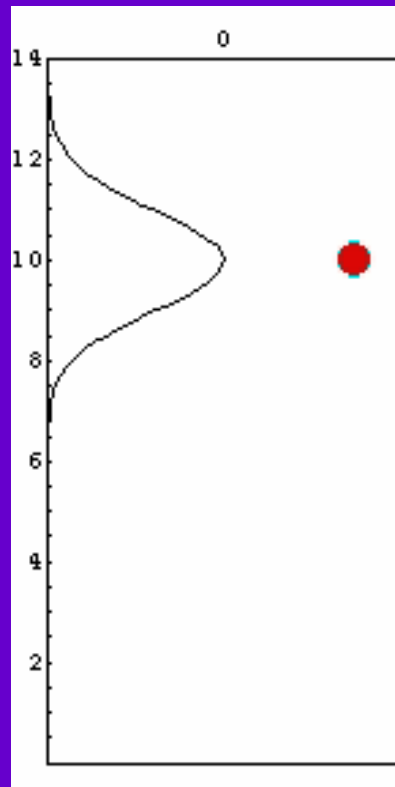


2. With photons: electronic/vibrational/rotational photoexcitations - spectroscopy, reaction control by optical pulses



Quantum vs. classical mechanics

Comparison between a classical and quantum
“tennis ball”: *elastic bouncing from the ground*



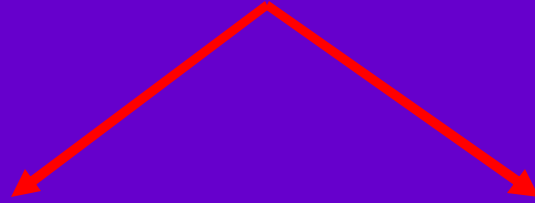
M. Reed, Yale University

Time dependent/independent mechanics

Classical mechanics:

time-dependent (dynamical Newton's equations)

Quantum mechanics:



time independent: $H\Psi = E\Psi$ dependent: $i\hbar\partial\Psi/\partial t = H\Psi$

stationary bound and scattering states Ψ_j, E_j ; time-independent Hamiltonians

dynamical evolution, non-stationary $\Psi(t)$; also for time-dependent Hamiltonians

Hamiltonians

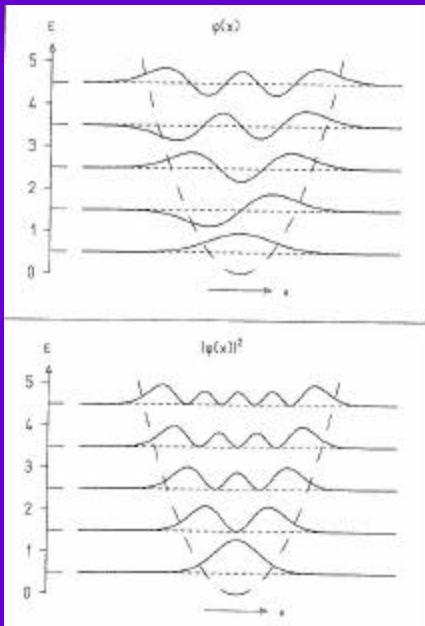
For a time-independent Hamiltonian - equivalent:

$$\Psi(t) = \sum_j \Psi_j \exp[(-i/\hbar)E_j t]$$

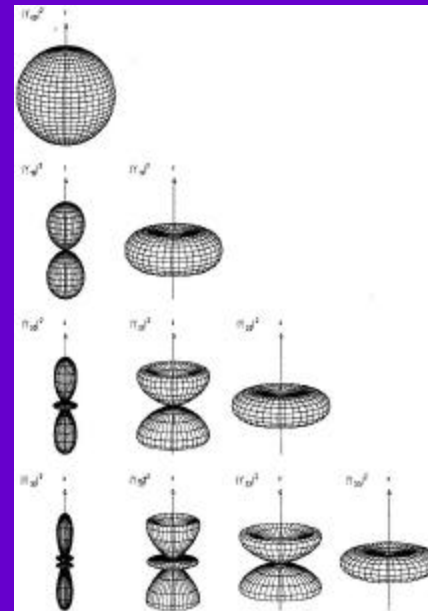
Time-dependent Schrödinger equation: a numerically exact solution

1. Wave function discretization:

- basis set expansion (orthogonal polynomials)



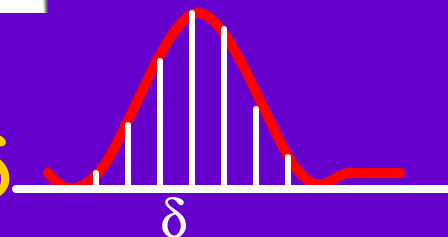
*vibrations:
harmonic
oscillator
eigenfunctions*



*rotations:
spherical
harmonics*

- expansion on a grid (ekvidistant or

non-ekvidistant), n points, $k_{\max} = \pi h / \delta$



2. Expansion of the evolution operator U :

$$i\hbar\partial\Psi(t)/\partial t = H\Psi(t) \longrightarrow \Psi(t+\Delta t) = U \Psi(t) = e^{-iH \Delta t/\hbar} \Psi(t)$$

i) Second order differences (SOD): Taylor expansion of

~~$$U = 1 - iH\Delta t/\hbar + \dots \longrightarrow \Psi(t+\Delta t) = \Psi(t) - i\Delta t H \Psi(t)/\hbar$$~~

numerically unstable - necessary symmetrization (+/- Dt)

$$\Psi(t+\Delta t) = \Psi(t-\Delta t) - 2i\Delta t H \Psi(t)/\hbar$$

conditionally stable: for $Dt < \hbar/E_{max}$

error of the SOD method: $O(Dt^3)$

SOD: Local (small Dt), simple, not very accurate method, OK also for time-dependent Hamiltonians.

ii) *Split operator method (S-O):*

~~$U \approx e^{-i\mathbf{T} \Delta t / \hbar} \cdot e^{-i\mathbf{V} \Delta t / \hbar}$...operators T and V do not commute!~~

$U \approx e^{-i\mathbf{T} \Delta t / (2\hbar)} \cdot e^{-i\mathbf{V} \Delta t / (2\hbar)} \cdot e^{-i\mathbf{V} \Delta t / (2\hbar)} \cdot e^{-i\mathbf{T} \Delta t / (2\hbar)}$ or

$U \approx e^{-i\mathbf{V} \Delta t / (2\hbar)} \cdot e^{-i\mathbf{T} \Delta t / (2\hbar)} \cdot e^{-i\mathbf{T} \Delta t / (2\hbar)} \cdot e^{-i\mathbf{V} \Delta t / (2\hbar)}$ (ekviv.)

error of the S-O method: $O(Dt^3)$, smaller prefactor than SO

S-O: Local (small $D t$), more accurate than the SO method, OK also for time-dependent Hamiltonians.

iii) *Chebyshev method:*

$U = \sum a_n P_n(-iH_{\text{norm}})$...orthogonal polynomials expansion

$P_n = \cos [n \arccos(x)]$... n -th Chebyshev polynomial

$a_n = 2 J_n[(E_{\text{max}} - E_{\text{min}})t/(2?)]$...Bessel functions

Error of the Chebyshev method $\sim e^{-N}$

Chebyshev: Global method (large time step), exact (exponentially converging, OK only for time-independent Hamiltonians.

iv) *Other global methods:*

Lanzos method orthogonal polynomials constructed by a repeated action of the Hamiltonian on the wave function

t ' method employs an auxiliary time variable t' , also for $H(t)$

3. Action of Hamiltonian H on wave function Ψ :

$H = T + V$...kinetic and potential energy operators

In coordinate representation: $\Psi = \Psi(\mathbf{x}, t)$, $V = V(\mathbf{x})$

$V(\mathbf{x})\Psi(\mathbf{x}, t)$...local point-by-point multiplication on a grid

$T = (-\hbar^2/2m)\Delta$...non-local Laplacean differential operator

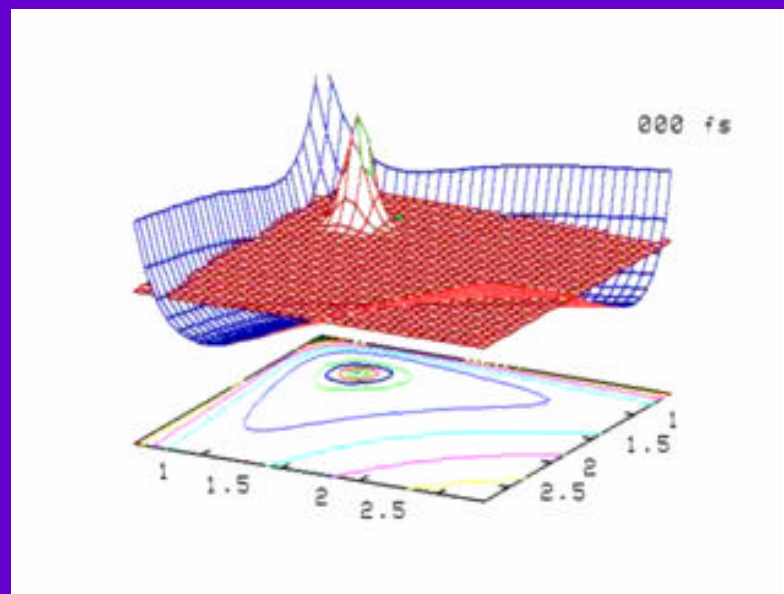
~~$$\Delta \Psi(\mathbf{x}_i, t) = (\Psi(\mathbf{x}_{i+1}, t) + \Psi(\mathbf{x}_{i-1}, t) - 2\Psi(\mathbf{x}_i, t))/\delta x^2$$~~

semilocal approximation-violates uncertainty relations

Fourier transform $\Psi(\mathbf{x}, t) \longrightarrow \Phi(\mathbf{k}, t)$, multiplication by k^2 , back Fourier transform, fast - FFT

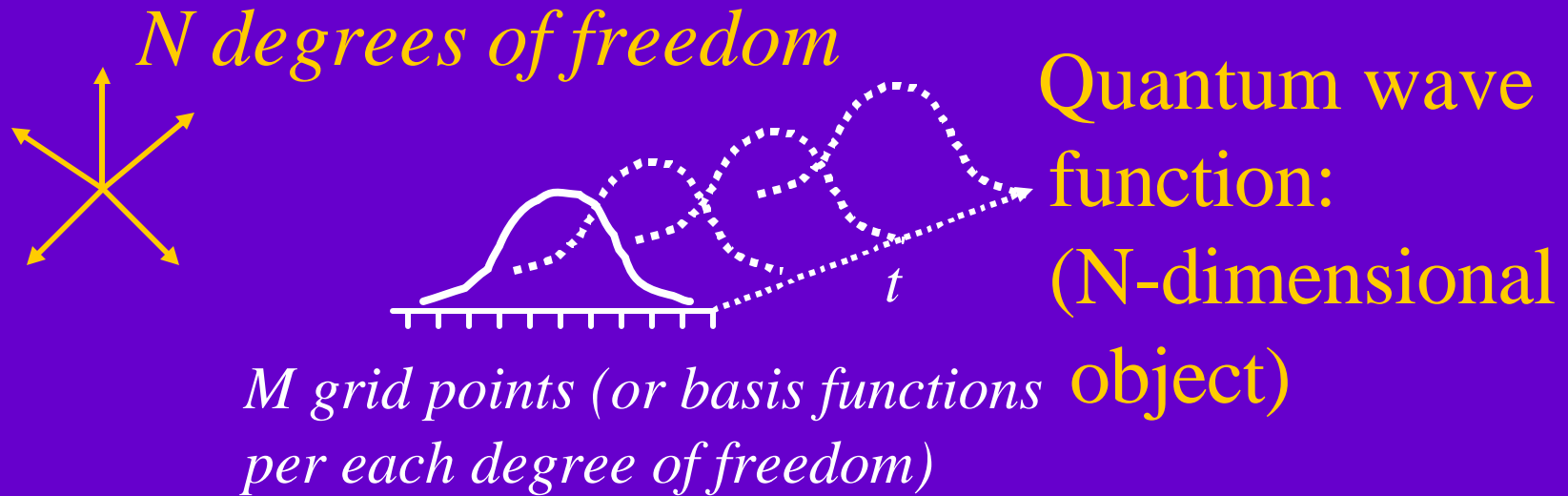
Wavepacket propagation in 2D

C-H bond dissociation in acetylene by a sequence of ultrafast IR pulses:



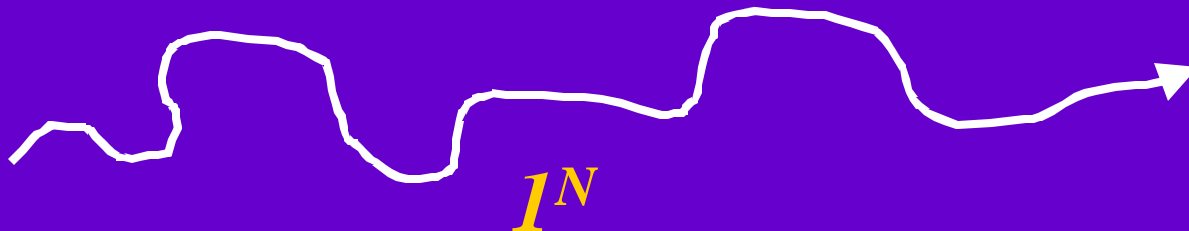
J. T. Muckerman, Brookhaven National Laboratory

Scaling of computational effort



M^N (exponential) scaling

Compare...



Classical trajectory (1-dimensional object)

Time-dependent Schrödinger equation: approximate solution

*Numerically exact <4 atoms
(< 6 degrees of freedom)*

Larger systems: APPROXIMATE METHODS

- self-consistent field methods,
- semi-classical and quasi-classical methods

Self-consistent field method

Separable (Hartree) approximation:

$$\Psi(q_1, \dots, q_N, t) = e^{i\gamma(t)} \prod_i \psi_i(q_i, t)$$

\longrightarrow $i\hbar \partial \psi_i(q_i, t) / \partial t = h_i(t) \psi_i(q_i, t)$

“separate” Schrödinger equation for each mode

$$h_i(t) = T_i + V_i(q_i, t)$$

$$V_i(q_i, t) = \langle \psi_1 \dots \psi_{i-1} \psi_{i+1} \dots \psi_N | V(q_1, \dots, q_N) | \psi_1 \dots \psi_{i-1} \psi_{i+1} \dots \psi_N \rangle$$

*inter-mode coupling in the self-consistent field approximation:
time-dependence of effective single mode Hamiltonians*

variationally best single mode approximation

Classical separable potentials

instead of:

$$V_i(q_i, t) = \langle \Psi_{1\dots i-1} \Psi_{i+1\dots N} | V(q_1, \dots, q_N) | \Psi_{1\dots i-1} \Psi_{i+1\dots N} \rangle$$

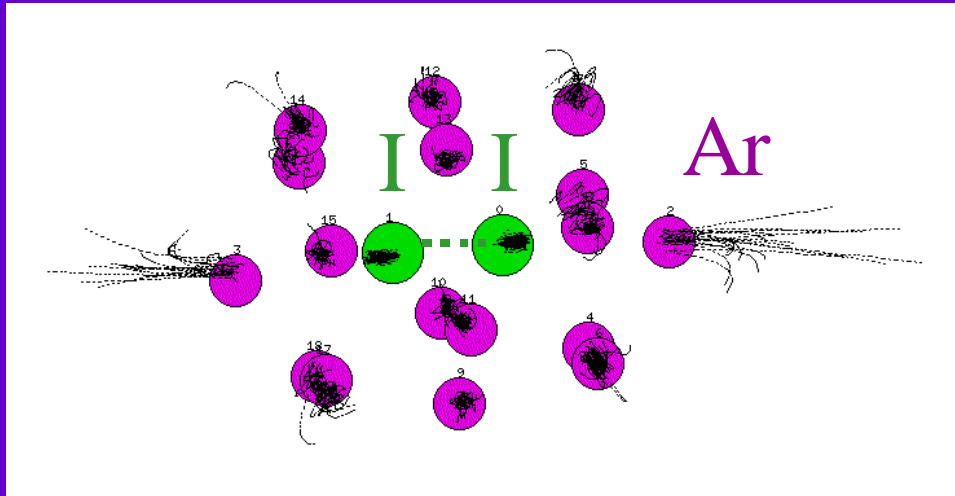
averaging over auxiliary classical trajectories:

$$V_i^{\text{CSP}}(q_i, t) = \sum_j V(q_1^j, \dots, q_{i-1}^j, q_i, q_{i+1}^j, \dots, q_N^j) \omega^j$$

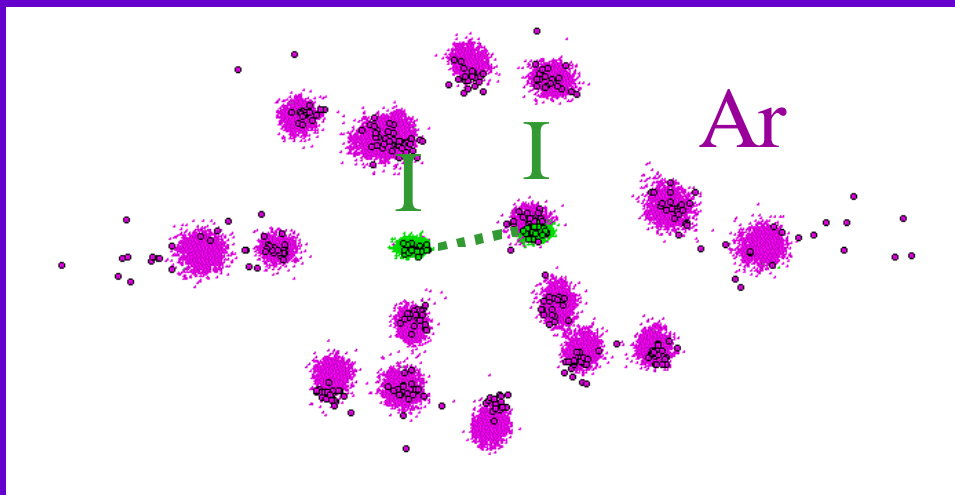
Replacing (N-1) dimensional quadratures by a summation over a set of 100-1000 trajectories - computationally immensely more efficient:

instead of ~10 up to ~1000 atoms

Picosecond dynamics after photoexcitation of I_2 in argon



classical dynamics



quantum (CSP) dynamics

Configuration interaction and multiconfiguration methods

Wave function as a sum of Hartree products:

$$\Psi(q_1, \dots, q_N, t) = \sum_j c_j(t) \prod_i \psi_{ji}(q_i, t)$$

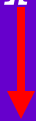
*Application of the time-dependent
variational principle:*

Configuration interaction: variation of coefficients $c_j(t)$

*Multiconfiguration methods: variation of $c_j(t)$
and $\psi_{ji}(q_i, t)$*

Semiclassical methods

Expansion of the evolution operator $U=e^{-i\mathbf{H}\Delta t/\hbar}$ in \hbar
first “quantum” term (containing the Planck constant)
proportional to $\left\| \frac{\partial^3 V}{\partial x^3} \right\| x^3$



Dynamics on a constant, linear, or quadratic potential is “classical”

Quadratic potential: harmonic oscillator

Solution - a generalized Gaussian:

$$\Psi(x,t) = \exp\left\{ (i/\hbar)[a_t(x-x_t)^2 + p_t(x-x_t) + c_t] \right\}$$

Equations of motion for a generalized Gaussian

$$dx_t/dt = p_t/m$$

$$dp_t/dt = -dV(x_t)/dx$$

Classical Newton equations of motion for the time evolution of the mean position and mean momentum of the generalized Gaussian

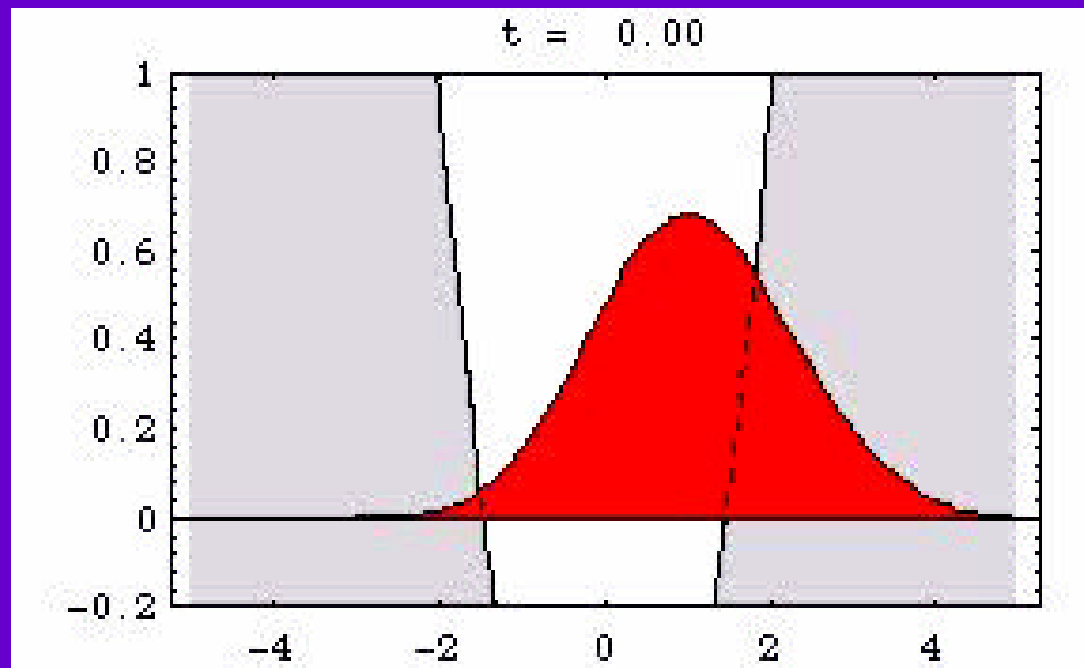
$$da_t/dt = -2a_t^2/m - d^2V(x_t)/dx^2/2$$

$$dc_t/dt = i\hbar a_t/m + p_t^2/2m - V(x_t)$$

“Non-classical” equations of motion for the time evolution of the width and phase of the generalized Gaussian

In a quadratic potential Gaussian remains a Gaussian

Position, momentum, width, and phase of the Gaussian evolves in time:



B. Thaller, University of Graz

Quasi-classical methods

Wigner transformation:

$$F(q,p,t) = (1/\pi\hbar) \int dx e^{-2ipx/\hbar} \Psi^*(q-x,t) \Psi(q+x,t)$$

Classical phase variables q, p

Equation of motion:

$$\partial F/\partial t = -p/m \cdot \partial F/\partial q + \partial V/\partial q \cdot \partial F/\partial p + O[\hbar^2 \partial^3 V/\partial q^3 \cdot \partial^3 F/\partial p^3]$$

Classical equation of motion

1. Wigner mapping of the initial wave function onto a distribution of classical initial conditions q_i, p_i .
2. Propagation of a set of classical trajectories.

Wavepacket analysis

-“*Eye-based analysis*” - amplitude and phase.

-*Autocorrelation function:*

$$C(t) = \langle \Psi(0) | \Psi(t) \rangle$$

Direct connection with spectroscopy, e.g.:

$$I(\omega) \sim \omega \cdot 2\text{Re} \int_0^{\infty} C(t) e^{i(E + \hbar\omega)t} dt$$

Absorption spectrum as a Fourier transform of the autocorrelation function.

Quantum dynamics: Conclusions

When?

- quantum effects not only for electrons but also in the dynamics of atoms and molecules
- low temperatures, light atoms (H, He, ...)

What?

- zero point vibrations, tunneling, resonant energy transfer
- non-adiabatic interactions with electrons
- spectroscopy

How?

- time-dependent vs. time-independent approaches to the Schrödinger equation
- numerically exact solution for small systems
- approximate methods for large systems

Further study material:

www.molecular.cz

in construction....



....operating from Sept. 2002