Lecture 9 - Wave packet and ultra-fast phenomena

1. Time-dependent representation
2. The concept of wave packets
3. Comparison with classical trajectories
4. Representation (grids, basis functions)
5. Numerical techniques for propagation of wave packets.
6. Multidimensional wave packets

Quantum Character of Nuclear Motion

Situations when the quantum character of the nuclear motion has to be considered:

1. Potential barriers and tunneling effects.
2. Properties strongly dependent on nuclear coordinates.
3. Ultra-fast electronic transitions.
4. Violations of Born-Oppenheimer approximation (potential curve crossings).

Schrödinger Equation and BO Approximation

The molecular Hamiltonian

$$H = T_n + T_e + V_{ee} + V_{en} + V_{nn}$$

Molecular Schrödinger equation

$$H|k^n, i^e\rangle = E_{k(i)}|k^n, i^e\rangle$$

The heart of the Born-Oppenheimer approximation: separation of the state $|k^n, i^e\rangle$ to electronic and nuclear parts.

BO Approximation

The electronic wave function changes *slowly* with the nuclear geometry.

$$|k^n, i^e\rangle = |k_i^n\rangle|i^e\rangle$$

The electronic Hamiltonian includes static nuclear repulsion

$$H_e = H - T_n = T_e + V_{ee} + V_{en} + V_{nn}$$

Electronic Schrödinger equation (nuclear geometry fixed)

$$H_e|i^e\rangle = E_i^e|i^e\rangle$$

Time-dependent Representation

Solve time-dependent Schrödinger equation:

$$H\Psi(R,t) = i\hbar\frac{\partial}{\partial t}\Psi(R,t)$$

Possible approaches:

1. Solve in the frequency domain by diagonalizing the Hamiltonian.
2. Propagate in the time domain.

For modelling of short laser pulses etc., the latter is preferable.

Ehrenfest Theorem

A – operator related to an observable

$$\langle A \rangle = \frac{1}{i\hbar}\langle [A, H] \rangle + \left\langle \frac{\partial A}{\partial t} \right\rangle$$

Example:

$$H(x, p, t) = \frac{p^2}{2m} + V(x, t)$$

The derivative of the expectation value of momentum operator:

$$\frac{d}{dt}\langle p \rangle = \langle -\nabla V(x, t) \rangle = \langle F \rangle$$

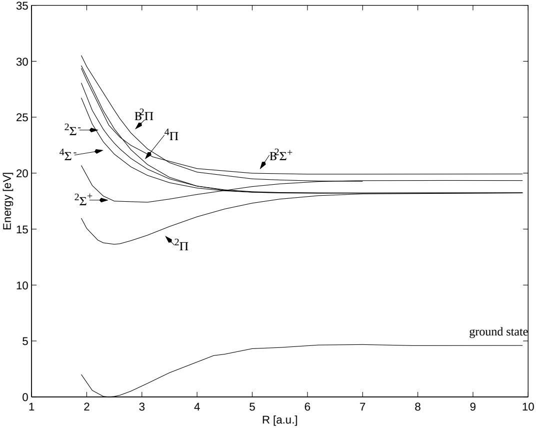
Correspondence to Newton's second law.

Potentials And Basis Sets

- The potentials can be obtained from *ab initio* calculation.
- Empirical parameters used as well (harmonic or Morse potentials most common).
- Numerical grids simple to implement.
- Multidimensional cases may require more sophisticated basis functions to reduce the calculation time (but make the implementation more complex).

Vibrational Schrödinger Equation

$$T_n|k_i^n\rangle + E_i^e(R)|k_i^n\rangle = E|k_i^n\rangle$$



Potential surfaces of HCl and HCl$^+$.

Typical Calculation

1. Find the initial wave packet $\varphi_0(x)$ (compute lowest eigenvector of ground state Hamiltonian?).
2. Add the perturbation/excite the wave packet.
3. Compute correlation functions

$$C(t) = \langle \varphi(x,0) | \varphi(x,t) \rangle$$

Absorption Calculations

The time evolution of the nuclear state determined by time-dependent Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}|k_i^n(t)\rangle = H_n|k_i^n(t)\rangle$$

$$H_n = T_n + E_i^e(R)$$

The autocorrelation function: an overlap between the initial state $|i(t=0)\rangle$ and the state $|i(t)\rangle$

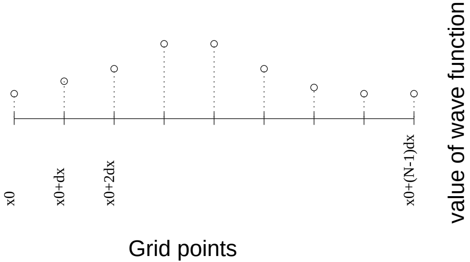
$$C(t) = \langle i|i(t)\rangle = \langle i|e^{-iHt/\hbar}|i\rangle \ ,$$

The absorption cross section

$$\sigma(\omega) \propto C(\omega) = \int_{-\infty}^{\infty} C(t)e^{-i\omega t}\mathrm{d}t$$

Evaluation Method

Simplest grid:



Time-independent part:

$$\boxed{\begin{aligned} &H_n|0\rangle = E_0|0\rangle \\ &\qquad \Rightarrow |i(t=0)\rangle = |0\rangle \end{aligned}}$$

$$\boxed{\begin{aligned} &\mathbf{H}\cdot\mathbf{F}_0 = E_0\mathbf{F}_0 \\ &\qquad \Rightarrow \mathbf{F}^{n=0} = \mathbf{F}_0 \end{aligned}}$$

Evaluation Method, cont

Time-dependent part:

$$H'_n|i(t)\rangle = i\hbar\frac{\partial}{\partial t}|i(t)\rangle$$

$$|i(t+\mathrm{d}t)\rangle = U^{\mathrm{d}t}|i(t)\rangle$$

$$\Rightarrow C(t) = \langle i(0)|i(t)\rangle$$

$$\mathbf{F}^{n+1} = \mathbf{U}\cdot\mathbf{F}^{n}$$

$$\Rightarrow C_n = \left(\mathbf{F}^0\right)^* \cdot \mathbf{F}^n$$

Wave packet propagation method must preserve the norm and correctly propagate the phase.

Evaluation Method, cont

1. At each time step, evaluate $C(t)$.
2. After finished calculation, perform Fourier transform $C(t) \rightarrow C(\omega)$:

$$\boxed{C(\omega) = \int_{-\infty}^{\infty} C(t) e^{-i\omega t} \mathrm{d}t}$$

$$\boxed{C_k = \sum_{n=0}^{N-1} C_n e^{-ikn/2\pi}}$$

Finding Initial State

Simplest Approach:

$$\begin{aligned} \psi_j^n &= \Psi(x_j, t_n), & \psi_{j+1}^n &= \Psi(x_{j+1}, t_n), \\ \psi_j^{n+1} &= \Psi(x_j, t_{n+1}), & V_j &= V(x_j)\,. \end{aligned}$$

Gives:

$$\begin{aligned} -\frac{1}{2M}\frac{-2\psi_j + \psi_{j-1} + \psi_{j+1}}{\Delta x^2} + V_j\psi_j &= E_{(k)}\psi_j \\ &\Updownarrow \\ \mathbf{H}\cdot\mathbf{F}_{(k)} &= E_{(k)}\mathbf{F}_{(k)} \end{aligned}$$

Better approximations to the ∇^2 operator exist.

Explicit Propagation (Euler)

$$\psi_j^{n+1} = \psi_j^n - i\Delta t\frac{2\psi_j^n - \psi_{j-1}^n - \psi_{j+1}^n}{2M\Delta x^2} - i\Delta t V_j\psi_j^n$$

$$\mathbf{F}^{n+1} = \mathbf{U}\cdot\mathbf{F}^n; \qquad \mathbf{U} = \mathbf{I} - i\Delta t\,\mathbf{H}'$$

The propagation operator is not unitary: wave packet norm not preserved.

Explicit Unitary Propagation

Three-step explicit method.

A stable and unitary discretization is obtained by applying a centered time difference

$$i\frac{\Psi(x,t+\Delta t)-\Psi(x,t-\Delta t)}{2\Delta t} = \frac{2\Psi(x,t)-\Psi(x-\Delta x,t)-\Psi}{2M\Delta x^2} + V(x)\Psi(x,t)\ ,$$

which leads to a three-step explicit method

$$\psi_j^{n+1} = \psi_j^{n-1} - 2i\Delta t\left(\frac{2\psi_j^n - \psi_{j+1}^n - \psi_{j-1}^n}{2M\,\Delta x^2} + V_j\psi_j^n\right)$$

- fast method: involves only matrix-vector multiplication and vector addition.
- Problems with eg. absorbing boundary conditions.

Semi-Implicit Propagation

Cayley Method

The Schrödinger equation is then approximated by following finite-difference equation

$$i\frac{\mathbf{F}^{n+1}-\mathbf{F}^{n}}{\Delta t}=\frac{1}{2}[\mathbf{H}'\cdot\mathbf{F}^{n+1}+\mathbf{H}'\cdot\mathbf{F}^{n}]=\frac{1}{2}\mathbf{H}'\cdot[\mathbf{F}^{n+1}+\mathbf{F}^{n}]$$

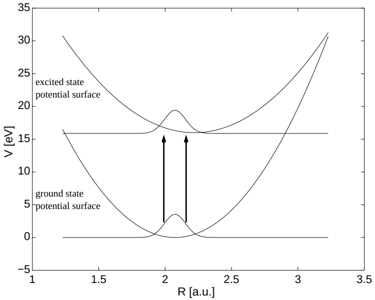
where the Hamiltonian H' is approximated as follows

$$(\mathbf{H}'\cdot\mathbf{F}^{n})_j=-\frac{1}{2m}\frac{\psi_{j-1}^{n}-2\psi_{j}^{n}+\psi_{j+1}^{n}}{\Delta x^2}+V_j\psi_j^n$$

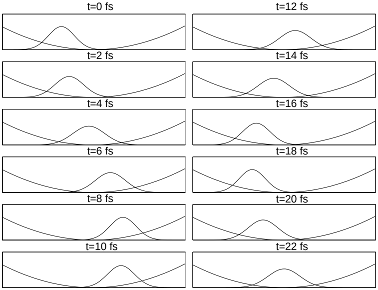
Recommendation: use FFT to implement the momentum operator

Vibrations in Bound Potentials

The harmonic potential approximation: The excitation from N_2 $X^1\Sigma_g^+$ to N_2^+ $A^2\Pi_u$ state.

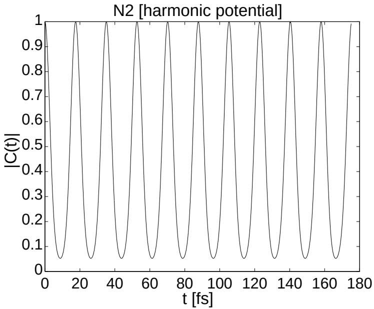


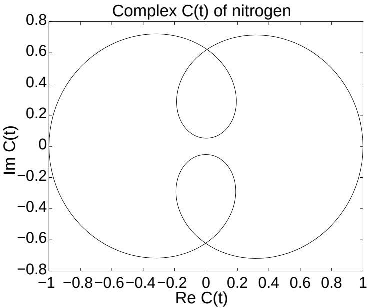
The wave packet evolution on N_2^+ $A^2\Pi_u$ surface.



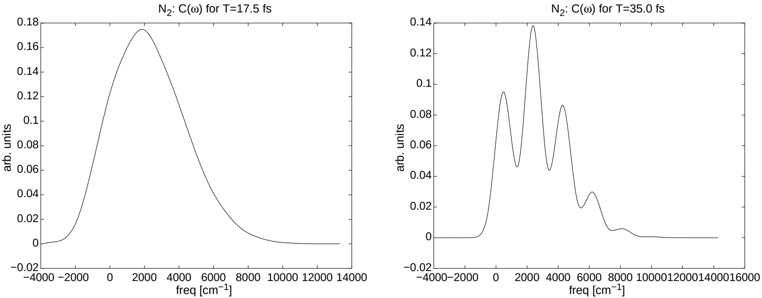
Autocorrelation Function in Time Domain

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



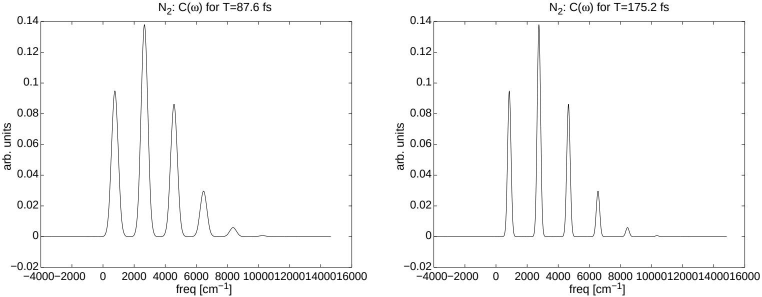


Autocorrelation Function in Frequency Domain



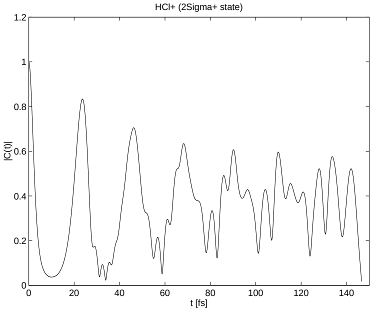
Short life-time destroys the structure of the spectrum.

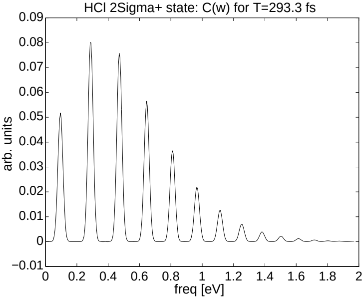
Autocorrelation Function $C(\omega)$, cont.



Long life time makes the features sharp.

Autocorrelation Function in Anharmonic Potential

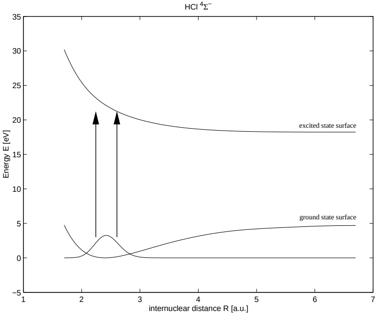




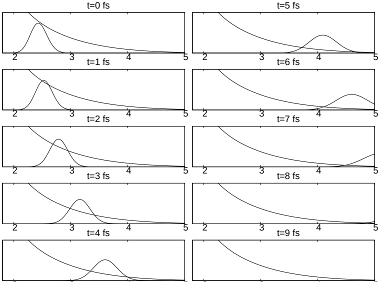
Anharmonicity destroys the perfect periodicity of the vibrations.

Evolution in Dissociative Potentials

. . . from excitation to separation. . .

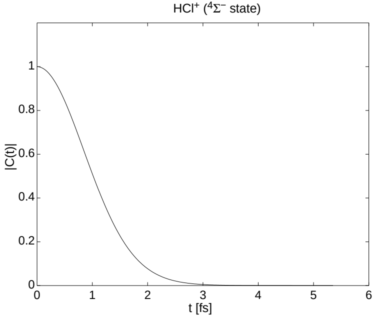


The potential surfaces relevant to excitation from ground state of HCl to the $B^2\Pi$ state of HCl^+

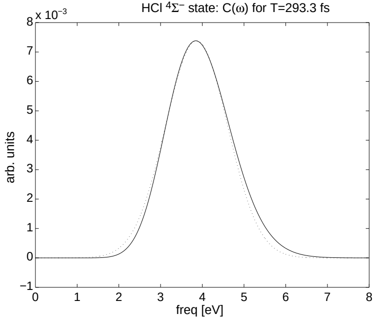


The evolution of the wave packet on the excited state potential surface of HCl^+ $(^4\Sigma^-)$

$C(t)$ and $C(\omega)$ in Dissociative Potentials



The autocorrelation function $C(t)$ for the HCl^+ molecule in the ${}^4\Sigma^-$ state.



The autocorrelation function $C(\omega)$ for the HCl^+ molecule in the ${}^4\Sigma^-$ state.

Multidimensional Propagation

Outlook 1D case: representation on 256 points.
3D case: representation on $256 \times 256 \times 256 = 16777216$ points. Mission Impossible
Issues:

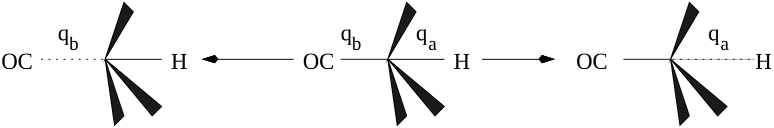
- How to decrease the dimension?
  - reaction coordinates
  - decoupled vibrations
- How to cope with nonseparable motion modes?

Decreasing the Dimension

Photodissociation of $\mathrm{HCo(CO)_4}$:

$$\begin{aligned}\mathrm{HCo(CO)_4} &\xrightarrow{h\nu} \mathrm{H} + \mathrm{Co(CO)_4}\,, \\ \mathrm{HCo(CO)_4} &\xrightarrow{h\nu} \mathrm{CO} + \mathrm{HCo(CO)_3}\,.\end{aligned}$$

Two reaction coordinates: q_a and q_b



Managing the Multidimensional Problem

- initial state: the evolution in imaginary time or Standard direct methods for eigenvalue calculation.
- The evolution – tough, time-consuming task.
    - Sometimes assumption about weak coupling modes allows to simplify the calculation.