Introduction to Quantum Dynamics: Solving the Time-Dependent Schrödinger Equation

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Dynamical phenomena are described by the **Time-Dependent Schrödinger Equation**

$$\boxed{i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{R},\mathbf{r},t) = \hat{H}\Psi(\mathbf{R},\mathbf{r},t)} \quad (1)$$

A **wavepacket** evolves in time driven by the Hamiltonian

$$\Psi(\mathbf{q},t) = \sum_i c_i\psi_i e^{-\frac{i}{\hbar}E_i t} \quad (2)$$

where ψ_i are the eigenfunctions of the Hamiltonian

- D.J. Tannor “Introduction to Quantum Mechanics: A Time-Dependent Perspective” (2007) University Science Books http://www.weizmann.ac.il/chemphys/tannor/Book/
- G. C. Schatz and M.A. Ratner “Quantum mechanics in chemistry” (2002) Dover
- P.W. Atkins and R.S. Friedman “Molecular Quantum Mechanics” (2004) Oxford
- K.C. Kulander “Time-dependent methods for quantum dynamics” (1991) Elsevier

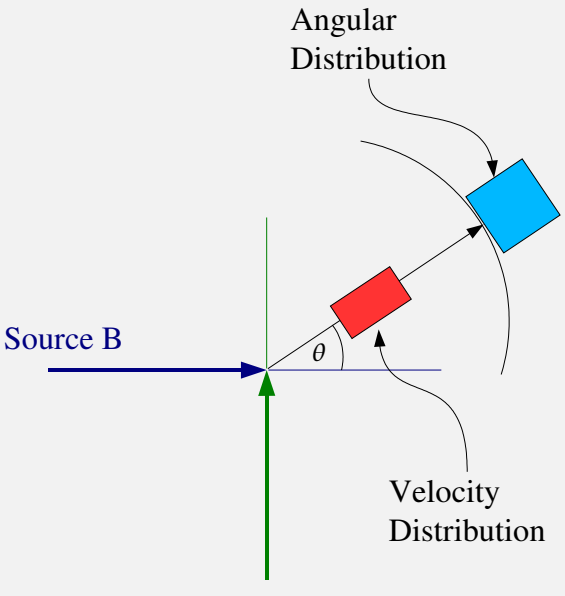
Aim of lectures:

- Introduce Chemical Dynamics
  - Molecular Beams (scattering)
  - Time-resolved spectroscopy (femtochemistry)
- The Time-dependent Schr"odinger Equation (TDSE)
  - Born-Oppenheimer Approximation.
  - Adiabatic and Diabatic Pictures
- Techniques used to solve TDSE numerically
- What is possible (bottlenecks / restrictions)

Molecular Beams and Scattering

Collimated beams of reactants intersect at right angles in high vacuum ($> 10^{-7}$ Torr)

Crossed Molecular Beams



Single collision (if any) occurs in crossing zone.

Collisions may result in 3 types of scattering:

- **Elastic** – Translational ΔE

$$A + BC(\nu, J) \longrightarrow A + BC(\nu, J)$$

- **Inelastic** – Rotational / vibrational ΔE

$$A + BC(\nu, J) \longrightarrow A + BC(\nu', J')$$

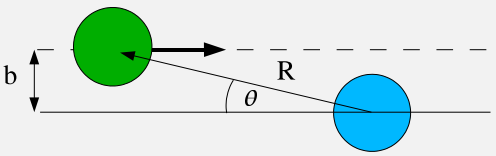
- **Reactive** – New chemical products

$$A + BC(\nu, J) \longrightarrow AB(\nu', J') + C$$

Must be able to distinguish new products from the background of elastic / inelastic scattered reactants. Implies sensitive and selective detector

- Time-of-flight mass spectrometer (TOF)
  - "universal detector"
  - velocity and product identification
- specific rotational / vibrational states probed by laser

The Cross-section



Differential cross-section, $\frac{d\sigma_c}{d\omega}$, is effective target size as a function of scattering angle.

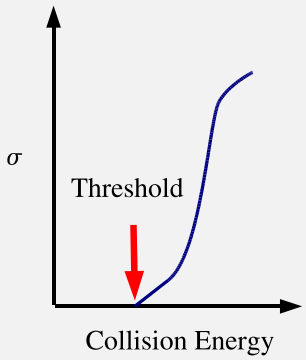
$$\sigma_c = \int_0^{2\pi} d\theta \int_0^{\pi} d\phi \frac{d\sigma_c}{d\omega}$$

Not every collision results in reaction **Reaction cross-section**

$$\sigma_r < \sigma_c$$

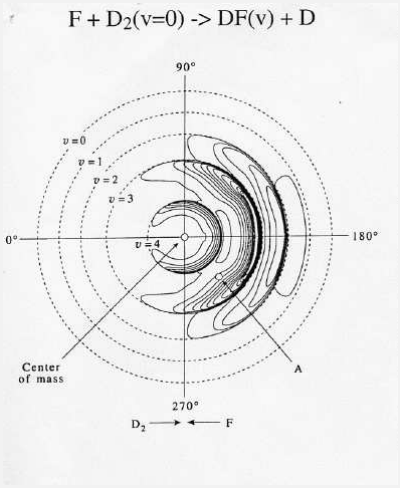
b – impact parameter
R, θ – coordinates
Collision cross-section, σ_c, is effective target size.

Expect a minimum translation energy for reaction



Example: $F + D_2 \longrightarrow DF + D$

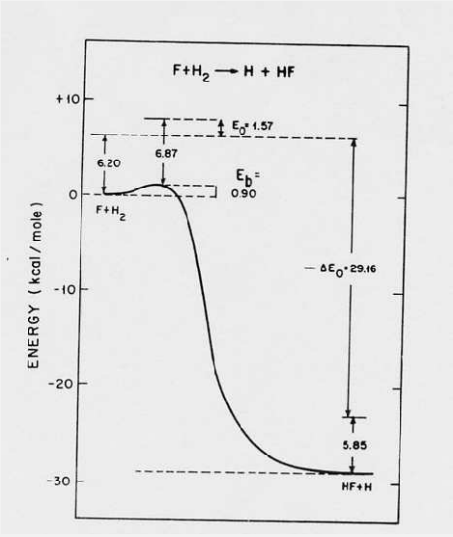
Differential cross section at a relative energy of 1.82 kcal mol^{-1} shows probability of DF appearing at angle Θ and velocities (distance from scattering centre).

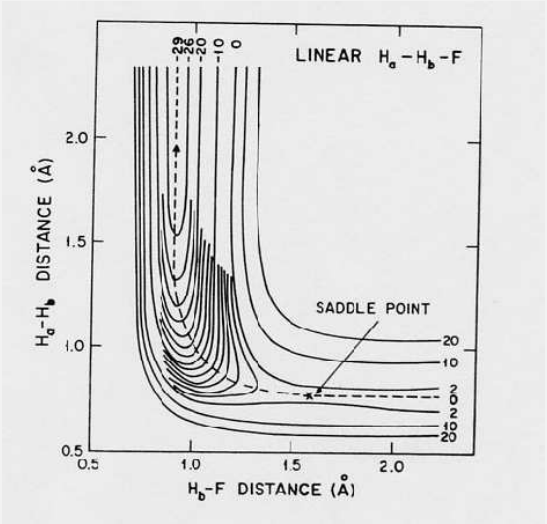


- Contour map inhomogenous: Preferential orientations.
  - Mostly back scattered $\Rightarrow$ head-on.
- All collisions have same relative velocities (kinetic energies). Each reaction releases same energy, distributed between translational and internal (vib-rot)
  - Higher vibration $\Rightarrow$ slower recoil

$\Theta = 180°$ initial direction of F beam

$F + H_2$ Potential Surfaces

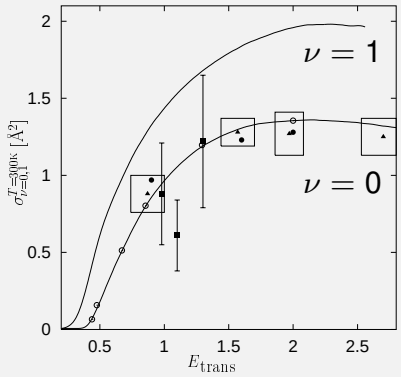




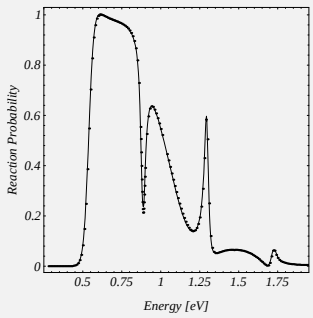
Product is **hot** with populated high vibrational states.
Infrared *chemiluminescence* results – emission due to excited states generated in chemical reaction

$H + H_2 \longrightarrow H_2 + H$

Simplest “Reaction”

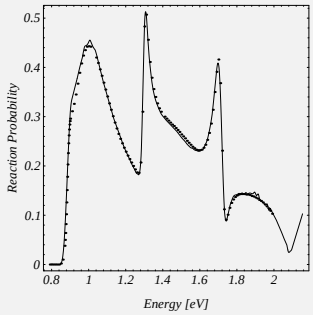


Reaction Cross-section (probability) for H + D_2



$\nu = 0 \rightarrow \nu = 0$

$\hbar\omega = 0.27eV$

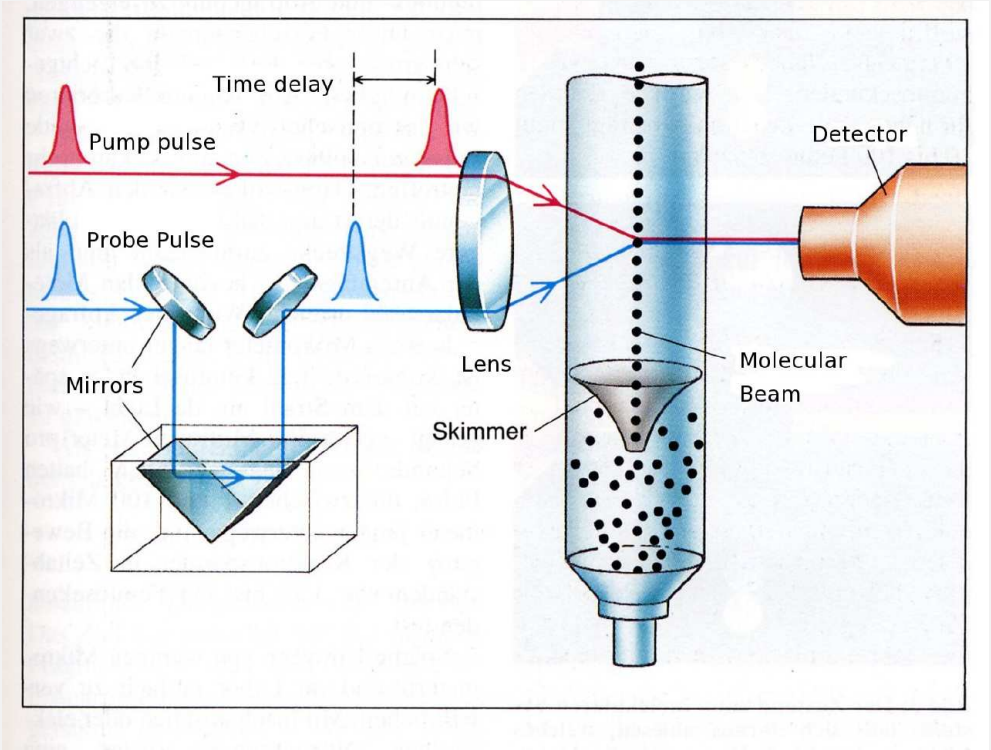


$\nu = 1 \rightarrow \nu = 1$

$\hbar\omega = 0.79eV$

State-to-state cross-sections H + H_2

Pump-Probe Experiments: Femtochemistry



Ultrafast molecular vibrations are the fundamental motions that characterize chemical bonding and determine molecular dynamics at the molecular level.

Typical periods of motion: Vibrational $\sim$ 100 fs (1 fs = 10^{-15} s)
Rotational $\sim$ 100 ps (1 ps = 10^{-12} s)

Short (femtosecond) laser pulses allow us to “watch” the molecular motion

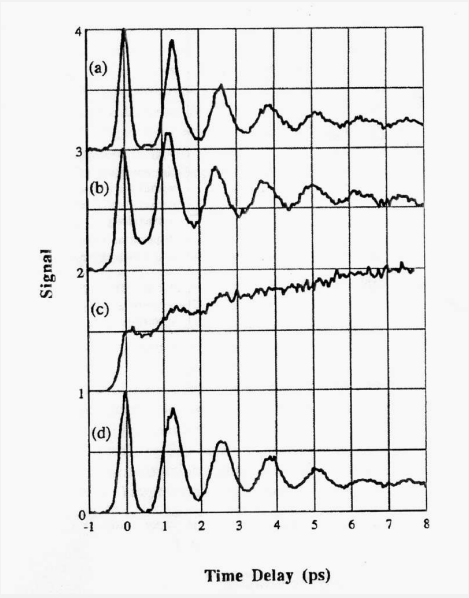
Basic scheme:

1. **pump** laser pulse starts reaction
2. **probe** laser pulse probes molecules as reaction proceeds
3. Detection of probe signal

Transient Spectra for NaI dissociation

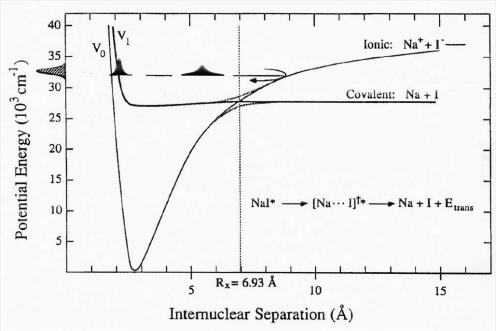
$$\mathrm{NaI}^* \longrightarrow [\mathrm{Na}\cdots\mathrm{I}]^{\ddagger *} \longrightarrow \mathrm{Na} + \mathrm{I}$$

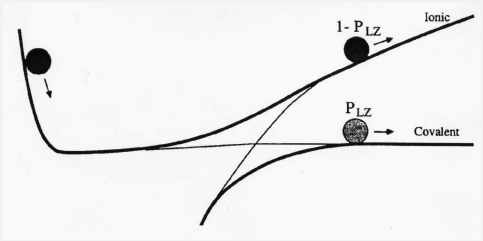
Pump constant, change probe



- (c) is resonant with Na D-lines
  - step-wise escape of Na
- non-resonant same frequency
  - trapped portion of wavepacket
  - T = 1.2 ps

Energetics described by the covalent (NaI) and ionic (Na^+I^-) potential energy curves which cross at an internuclear distance R_C



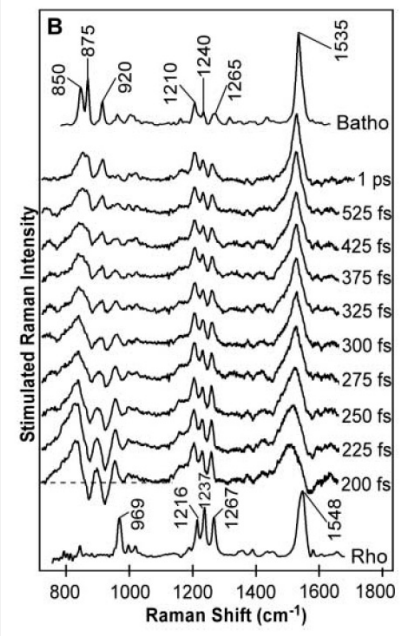


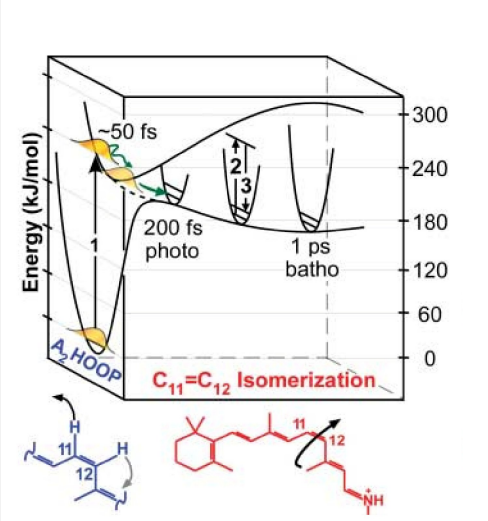
Non-adiabatic (2 interacting states).

- In adiabatic picture curves do not cross
  - If system is adiabatic, bound-state
- In diabatic picture curves cross
  - If system is diabatic, dissociation

Which it is depends on coupling between states.

Time-resolved study - Rhodopsin





- Initial excitation - HOOP mode
- after 50 fs $S_1 \longrightarrow S_2$
- energy $\longrightarrow$ HT

Kukura *et al* Science 310: 1006 (2005)

The Time-Dependent Schrödinger Equation

$$\boxed{i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{R},\mathbf{r},t) = \hat{H}\Psi(\mathbf{R},\mathbf{r},t)} \tag{3}$$

If the Hamiltonian is time-independent, formal solution

$$\Psi(t) = \exp\left(-i\hat{H}t\right)\Psi(0) \tag{4}$$

Further, if we can write

$$\Psi(x,t) = \Psi_i(x)e^{-i\omega_i t} \tag{5}$$

Phase factor

then

$$i\hbar\frac{\partial}{\partial t}\Psi(x,t) = \hbar\omega_i\Psi_i(x)e^{-i\omega_i t} \tag{6}$$

by comparison with the TDSE, Ψ_i are solutions to the time-independent Schrödinger equation

$$\hat{H}\Psi_i = E_i\Psi_i = \hbar\omega_i\Psi_i \tag{7}$$

Ψ_i is a Stationary State as expectation values (properties) are time-independent

$$\langle\hat{O}\rangle = \langle\Psi_i|\hat{O}|\Psi_i\rangle e^{i\omega_i t}e^{-i\omega_i t} = \langle\Psi_i|\hat{O}|\Psi_i\rangle \tag{8}$$

If wavefunction is a superposition of stationary states,

$$\chi(x,t) = \sum_i c_i\Psi_i(x)e^{-i\omega_i t} \tag{9}$$

now,

$$\langle\hat{O}\rangle(t) = -i\hbar\sum_i\sum_j c_i^* c_j\langle\Psi_i|O|\Psi_j\rangle e^{i(\omega_i-\omega_j)t} \tag{10}$$

An expectation value changes with time and depends on the initial function (c_i coefficients).

A non-stationary wavefunction is called a WAVEPACKET.

Free Particle

The functions

$$\Psi_k = e^{ikx} e^{-i\frac{E}{\hbar}t}$$

represent a particle with an exact momentum

$$\hat{p}\Psi_k = -i\hbar\frac{d}{dx}\Psi_k = k\hbar\Psi_k$$

But, particle is not localised. Take a superposition

$$\chi(x,t) = \int_{-\infty}^{\infty} dk\, C(k)\Psi_k(x,t)$$

where $C(k)$ is a suitable function

E.g. Form a Gaussian wavepacket

$$C(k) = N\exp\left[\frac{-a^2(k-k_0)^2}{2}\right]$$

$$\chi(x,t) = N_0 e^{i\gamma}\exp\left[-\frac{x - x_0(t)x_0(t)}{2a^2\delta} + ik_0x\right]$$

where

$$x_0(t) = \frac{\hbar k_0 t}{m}$$

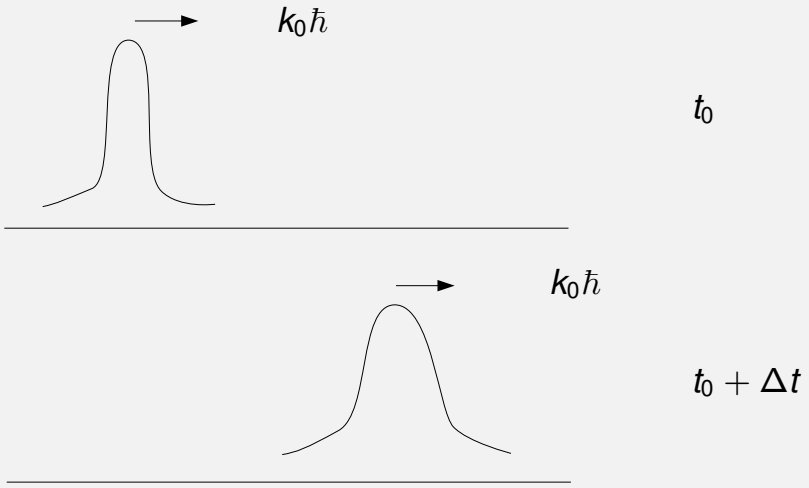
so wavepacket moves to right with velocity $\frac{\hbar k_0}{m}$.

The functions Ψ_k form a basis sutiable to describe free motion.

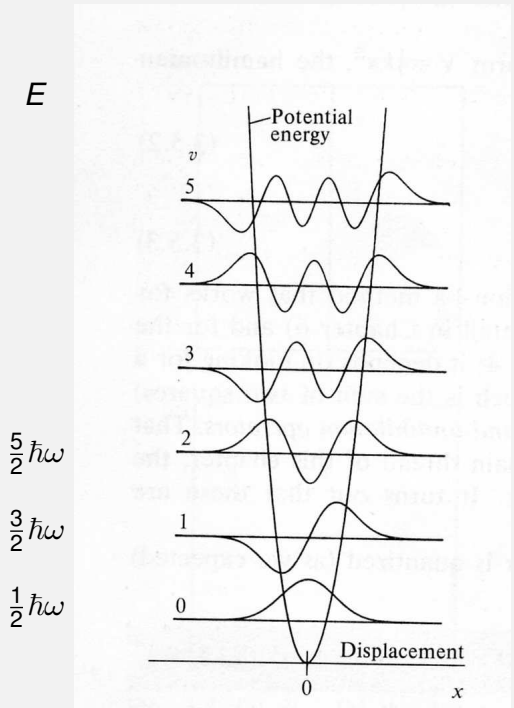
Further, width of density, $< x^2 > - < x >^2$, is

$$\Delta(t) = a\left[(\ln 2)\left(1 + \frac{\hbar^2 t^2}{m^2 a^4}\right)\right]^{\frac{1}{2}}$$

and as time increases. packet spreads out.



Bound Motion



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

$$\begin{aligned}
\Psi_0 &= N_0 e^{-\frac{1}{2}\frac{m\omega^2}{\hbar}x^2} \\
\Psi_1 &= N_1\sqrt{\frac{m\omega^2}{\hbar}}\,x\,e^{-\frac{1}{2}\frac{m\omega^2}{\hbar}x^2} \\
\Psi_2 &= N_2\left(4\frac{m\omega^2}{\hbar}x^2 - 2\right)e^{-\frac{1}{2}\frac{m\omega^2}{\hbar}x^2}
\end{aligned}$$

The functions Ψ_k form a basis suitable to describe bound motion.

$$\chi(x,t) = \sum_i c_i(t)\Psi_i(x,t)$$

The Born-Oppenheimer Approximation

Start using Born representation

$$\Psi(\mathbf{q},\mathbf{r}) = \sum_i \chi_i(\mathbf{q})\Phi_i(\mathbf{r};\mathbf{q}) \quad , \tag{11}$$

where electronic functions are solutions to *clamped nucleus Hamiltonian*

$$\hat{H}_{\mathrm{el}}\Phi_i(\mathbf{r};\mathbf{q}) = V_i(\mathbf{R})\Phi_i(\mathbf{r};\mathbf{q}) \quad . \tag{12}$$

The full Hamiltonian is

$$\hat{H}(\mathbf{q},\mathbf{r}) = \hat{T}_n(\mathbf{q}) + \hat{H}_{\mathrm{el}}(\mathbf{q},\mathbf{r}) \quad , \tag{13}$$

Integrate out electronic degrees of freedom to obtain

$$\left[-\frac{1}{2M}(\nabla\mathbf{1} + \mathbf{F})^2 + \mathbf{V}\right]\chi = i\hbar\frac{\partial\chi}{\partial t} \quad , \tag{14}$$

The Adiabatic Picture

where

$$\mathbf{F}_{ij} = \langle\Phi_i \mid \nabla\Phi_j\rangle \tag{15}$$

is the *derivative coupling* vector

Assuming $\frac{\mathbf{F}}{M} \approx 0$

$$\left[\hat{T}_n + V\right]\chi = i\hbar\frac{\partial\chi}{\partial t} \tag{16}$$

and nuclei move over a single *adiabatic* potential energy surface, V, which can be obtained from quantum chemistry calculations.

Unfortunately,

$$\mathbf{F}_{ij} = \frac{\langle\Phi_i \mid \left(\nabla\hat{H}_{\mathrm{el}}\right) \mid \Phi_j\rangle}{V_j - V_i} \quad \text{for } i \neq j \quad . \tag{17}$$

The Diabatic Picture

First we separate out a group of coupled states from the rest

$$\left[(\hat{T}_n \mathbf{1}^{(g)} + \mathbf{F}^{(g)})^2 + \mathbf{V}^{(g)}\right] \boldsymbol{\chi}^{(g)} = i\hbar \frac{\partial \boldsymbol{\chi}^{(g)}}{\partial t} \quad , \tag{18}$$

To remove singularities, find a suitable unitary transformation

$$\tilde{\mathbf{\Phi}} = \mathbf{S}(\mathbf{q})\mathbf{\Phi} \tag{19}$$

such that the Hamiltonian can be written

$$[T_N \mathbf{1} + \mathbf{W}]\, \boldsymbol{\chi} = i\hbar \frac{\partial \boldsymbol{\chi}}{\partial t} \quad , \tag{20}$$

where all elements of **W** are potential-like terms

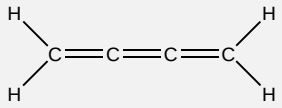
Worth and Cederbaum Ann. Rev. Phys. Chem. (2004) **55**: 127

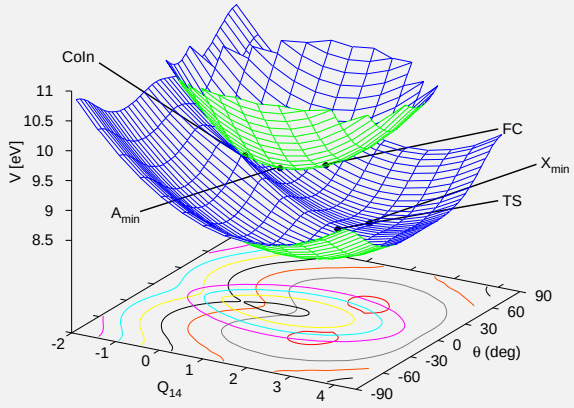
- Result 1: Electronic motion contained in potential energy surfaces which can be calculated using quantum chemistry
- Problem 1: Potential surfaces are calculated in the adiabatic picture. Dynamics run in the diabatic picture

Solution is to *diabatise* adiabatic surfaces for the dynamics. Non-trivial.

Conical Intersections

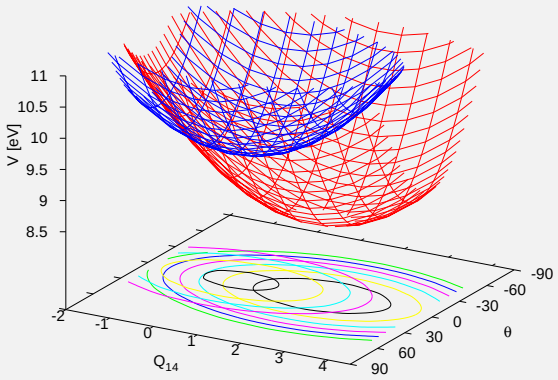
Butatriene Radical Cation





Adiabatic

Diabatic

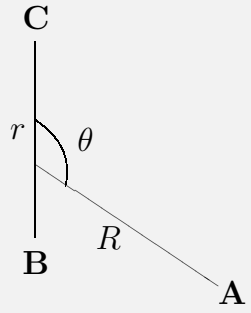


Coordinates: The Kinetic Energy Operator

In Cartesian coordinates,

$$T = \sum_{i=1}^{N} -\frac{1}{2m_i} \sum_{\alpha=1}^{3} \frac{\partial^2}{\partial x_{i\alpha}^2} \tag{21}$$

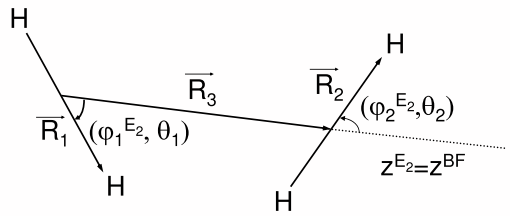
This includes COM and ROT - continua. To remove these contributions use, e.g. Jacobi coordinates



$$\begin{aligned} T \;=\; & -\frac{1}{2\mu_R R^2}\frac{\partial^2}{\partial R^2} - \frac{1}{2\mu_r r^2}\frac{\partial^2}{\partial r^2} \\ & +\left(\frac{1}{2\mu_R R^2} + \frac{1}{2\mu_r r^2}\right) j^2 \\ & -\frac{1}{2\mu_R R^2}\left(J(J+1) - 2K^2\right) \\ & -\frac{1}{2\mu_R R^2}\sqrt{\left(J(J+1) - K(K\pm 1)\right)} j_{\pm} \end{aligned} \tag{22}$$

Sukiasyan and Meyer JCP (02) : 116

6 Dimensional Jacobi Coordinates



$$
\begin{aligned}
2\hat{\mathbf{T}} \;=\; & -\sum_{i=1}^{3} \frac{1}{\mu_i R_i} \frac{\partial^2}{\partial R_i^2} R_i + \left(\frac{1}{\mu_1 R_1^2} + \frac{1}{\mu_3 R_3^2}\right)(\vec{L}_1^{\dagger}\vec{L}_1)_{BF} \\
& + \left(\frac{1}{\mu_2 R_2^2} + \frac{1}{\mu_3 R_3^2}\right)(\vec{L}_2^{\dagger}\vec{L}_2)_{BF} \\
& + \frac{(\vec{J}^2 - 2\vec{J}(\vec{L}_1 + \vec{L}_2) + 2\vec{L}_1\vec{L}_2)_{BF}}{\mu_3 R_3^2} \quad . \qquad (23)
\end{aligned}
$$

Gatti *et al* JCP (05) **123**: 174311

Other coordinates: Hyperspherical, Radau, ...

Normal modes

Final example, choose rectilinear coordinates so that force constant matrix (Hessian) is diagonal,

$$W_{ij} = \frac{\partial^2 V}{\partial x_i \partial x_j} \qquad (24)$$

then expanding around the minimum on the potential surface

$$V = \sum_{i=1}^{3N-6} \frac{\omega_i}{2} Q_i^2 + O(3) \qquad (25)$$

COM and ROT removed and

$$T = \sum_{i=1}^{3N-6} -\frac{\omega_i}{2} \frac{\partial^2}{\partial Q_i^2} \qquad (26)$$

Very simple, but PES only suitable for small displacements.

Wilson, Cross and Decius “Molecular Vibrations” (1980) Dover

- Result 2: Can select coordinates so that COM (and some ROT) motion removed and KEO has a simple form.
- Problem 2: In general, simple KEO coordinates are not optimal for PES representation.

In general, simple KEO coordinates are not optimal for PES representation and vice versa

Summary

- Chemical physics is study of molecular interactions and resulting dynamics
- Molecular beam scattering experiments provide details of interactions on ground-state
  - Cross-section relates to probability of process, e.g. reaction, occuring
- Femtochemistry experiments probe dynamics on excited surface
  - pump-probe experiments create and watch wavepacket
- Initialisation of a reaction creates a wavepacket, a solution of the TDSE
- Starting point to solving the TDSE is the Born-Oppenheimer Approximation
  - Nuclear / electronic coupling leads to breakdown of BO
  - Adiabatic and Diabatic Pictures
- To solve TDSE need $\hat{H}$: PES + KEO