# Applications of Quantum Dynamics: Using the Time-Dependent Schrödinger Equation

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## II. Solving the TDSE

To solve the TDSE need

- The Hamiltonian in a set of suitable coordinates
  - Potential surfaces and non-adiabatic couplings
  - Kinetic energy operator
- The form of the initial wavepacket
- An algorithm to integrate the TDSE and evolve wavepacket in time
- A method of extracting the information of interest

# The Standard Method

Have chosen suitable coordinates and obtained **W**, now solve

$$i\frac{\partial}{\partial t}\Psi(\mathbf{q},t) = H\Psi(\mathbf{q},t) \tag{1}$$

Expand the wavefunction in a direct-product basis set

$$\Psi(q_1,\ldots q_f,t) = \sum_{j_1=1}^{N_1}\cdots\sum_{j_p=1}^{N_f} A_{j_1\ldots j_f}(t)\,\chi_{j_1}^{(1)}(q_1)\cdots\chi_{j_f}^{(f)}(q_f) \tag{2}$$

and substituting this into TDSE (or using a variational principle),

$$i\,\dot{A}_{j_1,\ldots j_f} = \sum_{\ell_1,\ldots\ell_f}\langle\chi_{j_1}^{(1)}\cdots\chi_{j_f}^{(f)}|H|\chi_{\ell_1}^{(1)}\cdots\chi_{\ell_f}^{(f)}\rangle\,A_{\ell_1,\ldots\ell_f} \quad . \tag{3}$$

or simply

$$i\dot{\mathbf{A}} = \mathbf{HA} \tag{4}$$





# The Hamiltonian matrix elements

Need to evaluate matrix elements (integrals)

$$\begin{aligned} H_{JL} &= \sum_{\ell_1,\ldots\ell_f}\langle\chi_{j_1}^{(1)}\cdots\chi_{j_f}^{(f)}|H|\chi_{\ell_1}^{(1)}\cdots\chi_{\ell_f}^{(f)}\rangle \\ &= \sum_{\ell_1,\ldots\ell_f}\langle\chi_{j_1}^{(1)}\cdots\chi_{j_f}^{(f)}|T+V|\chi_{\ell_1}^{(1)}\cdots\chi_{\ell_f}^{(f)}\rangle \end{aligned} \tag{5}$$

As written an $N^f \times N^f$ matrix of multi-dimensional integrals!

1. Usually

$$T = \sum_{\kappa} T_\kappa$$

$$T_{JL} = \sum_{\kappa}\langle\chi_{j_\kappa}^{(\kappa)}|T_\kappa|\chi_{\ell_\kappa}^{(\kappa)}\rangle\delta_{J^\kappa L^\kappa} \tag{6}$$

$N \times N$ matrices, which by a suitable choice of basis functions can be solved analytically

2. The potential is a local operator $V(\mathbf{q})$. Thus if basis functions are localised, $\chi_j^{(\kappa)} \approx \delta(q - q_j)$ then

$$\begin{aligned} V_{JL} &= \langle \chi_{j_1}^{(1)} \cdots \chi_{j_f}^{(f)} | V | \chi_{\ell_1}^{(1)} \cdots \chi_{\ell_f}^{(f)} \rangle \\ &= V(q_{j_1} \ldots q_{j_f}) \delta_{JL} \end{aligned} \tag{7}$$

To enable conditions **1** and **2** use a DVR basis set in which

$$\begin{aligned} X_{ij} &= \langle \phi_i | \hat{x} | \phi_j \rangle \\ \mathbf{U}\mathbf{X}\mathbf{U}^T &= \mathbf{x} \end{aligned} \tag{8}$$

where $\phi_i$ are an analytically known FBR. And so

$$\chi_\alpha = \sum_i U_{\alpha i} \phi_i \tag{9}$$

are the DVR, $\chi_\alpha \sim \delta(x - x_\alpha)$. Various DVRs possible.

Beck *et al* Phys. Rep. (2000) **324**: 1





- Problem 3: Expandind TDSE in a basis set results in an $N^f \times N^f$ matrix of multi-dimensional integrals!
- Solution: To solve this use a DVR basis set in which KE integrals known analytically and PE integrals diagonal.
- Result 3: Problem is *discretised* on a grid

Various DVRs possible. Beck *et al* Phys. Rep. (2000) **324**: 1

# Integrating the TDSE

Full solution is

$$\Psi(t) = e^{-\frac{i}{\hbar}\hat{H}t}\Psi(0) \tag{10}$$

**Split-operator method**.

$$e^{-\frac{i}{\hbar}\hat{H}t} \neq e^{-\frac{i}{\hbar}Tt}e^{-\frac{i}{\hbar}Vt} \tag{11}$$

so divide propagation into short steps and approximate

$$\Psi(t+\delta t) = e^{-\frac{i}{2\hbar}V\delta t}e^{-\frac{i}{\hbar}T\delta t}e^{-\frac{i}{2\hbar}\hat{V}\delta t}\Psi(t) \tag{12}$$

**Chebyshev Propagation** Represent propagator by polynomial expansion:

$$e^{-\frac{i}{\hbar}\hat{H}t}\Psi = \sum_n a_n P_n(H)\Psi \tag{13}$$

where $P_n(H)$ are generated by a recurrence relationship





# Larger systems: The MCTDH Method

Standard method nuclear wavefunction expanded in a basis set:

$$\Psi(Q_1,\ldots,Q_f,t) = \sum_{j_1=1}^{N_1}\cdots\sum_{j_f=1}^{N_f} A_{j_1\ldots j_f}(t)\prod_{\kappa=1}^{f}\chi_{j_\kappa}^{(\kappa)}(Q_\kappa) \tag{14}$$

Variational equations of motion for $A$.

$$i\dot{A}_J = \sum_L \langle\Phi_J|H|\Phi_L\rangle A_L \tag{15}$$

Exponential increase in computer resources $\sim N^f$

# Larger systems: The MCTDH Method

The Multiconfiguration Time-Dependent Hartree Method

$$\Psi(Q_1,\ldots,Q_f,t) = \sum_{j_1=1}^{n_1}\cdots\sum_{j_f=1}^{n_f} A_{j_1\ldots j_f}(t)\prod_{\kappa=1}^{f}\varphi_{j_\kappa}^{(\kappa)}(Q_\kappa,t) \tag{16}$$

Variational equations of motion for $A$ and $\varphi$.

$$i\dot{A}_J = \sum_L \langle\Phi_J|H|\Phi_L\rangle A_L \tag{17}$$

$$i\dot{\varphi}^{(\kappa)} = \left(1-P^{(\kappa)}\right)\left(\rho^{(\kappa)}\right)^{-1}\langle\mathbf{H}\rangle^{(\kappa)}\varphi^{(\kappa)} \tag{18}$$

$$\varphi_j^{(\kappa)}(q_\kappa) = \sum_{k=1}^{N_\kappa} a_{kj}^{(\kappa)}(t)\chi_k^{(\kappa)}(q_\kappa) \tag{19}$$

Reduced computer resources $\sim n^f$





$N \sim 50$. $n \sim 10$

| $f$ | $N^f$ | standard (MB) | $n^f$ | MCTDH (MB) |
|---|---|---|---|---|
| 2 | 2,500 | 0.03 | 100 | 0.0015 |
| 3 | 125,000 | 1.9 | 1000 | 0.015 |
| 4 | 6,250,000 | 95.3 | 10000 | 0.15 |
| 5 | 312,500,000 | 4768.4 | 100000 | 1.5 |

Can also “combine modes” to reduce effective dimensionality and thus treat $\sim 20$ DOFs

MCTDH also starting point for more powerful methods and approximations:
ML-MCTDH, GMCTDH, vMCG, DD-vMCG

Reviews:

- Beck *et al* Phys. Rep. (00) 324:1
- Meyer and Worth TCA (03) 109:251
- Meyer, Gatti, andWorth “Multi-Dimensional Quantum Dynamics: MCTDH Theory and Applications (2009) Wiley-VCH

# Summary

To solve the time-dependent by propagating a wavefunction

- Select appropriate coordinates
- Obtain potential energy surface(s) (and couplings)
- Choose a primitive basis set
- Choose integration scheme with controllable error

- Result 4: The TDSE can be solved to provide complete information on the propagating system.
- Problem 4a: Resources grow exponetially. Limits to a few atoms.
- Problem 4b: Production of potential surfaces is huge amount of work. Limits applicability.
- Problem 4c: Potential surfaces need to be in diabatic picture

Next step is to set up, run and analyse simulation





# Initial Wavepacket

The time-dependent Schrödinger Equation is an initial value problem. Start in a single eigenstate then initiate process.

1. Multiply by (transition) dipole operator to model absorption of a photon

$$\Psi(t=0) = \hat{\mu}\psi_i \tag{20}$$

2. For a reaction $AB + C$

$$\Psi(t=0) = \psi_{i,AB}\chi_C(R) \tag{21}$$

where

$$\chi_C(R) = Ne^{-\alpha_0(R-R_0)^2} e^{\frac{i}{\hbar}p(R-R_0)} \tag{22}$$

localises incoming atom with an incoming momentum $p$

# Finding Eigenstate

An elegant way to find the ground-state is to use *energy relaxation*. In this wavepacket propagated in imaginary time. As

$$\Psi(\mathbf{q}, t) = \sum_i c_i \psi_i e^{-\frac{i}{\hbar} E_i t} \tag{23}$$

if $it \rightarrow \tau$ then

$$\Psi(\mathbf{q}, \tau) = \sum_i c_i \psi_i e^{-\frac{1}{\hbar} E_i \tau} \tag{24}$$

and all $c_i \rightarrow 0$ except $c_0$.

Can also use this to obtain excited states.





# Expectation Values

Typical “observables” of interest to the system dynamics are coordinates, momentum and their spread

$$< q_\kappa >, < q_\kappa^2 > \text{ and } < p_\kappa >, < p_\kappa^2 > . \tag{25}$$

Energy flow into modes can be obtained using a “zero-order” Hamiltonian, e.g. if

$$H = \sum_{i=1}^{2} \frac{\omega_i}{2} \left( \frac{\partial^2}{\partial q_i^2} + q_i^2 \right) + q_1 q_2 \tag{26}$$

then evaluate

$$< E_i >= \langle \frac{\omega_i}{2} \left( \frac{\partial^2}{\partial q_i^2} + q_i^2 \right) \rangle \tag{27}$$

# State Populations

Finally, diabatic state populations are obtained from

$$P_\alpha = \langle\Psi(t)|\alpha\rangle\langle\alpha|\Psi(t)\rangle \tag{28}$$

where $|\alpha\rangle$ is a diabatic electronic state.

Adiabatic state populations require transformation. If

$$|\gamma\rangle^{(\mathrm{ad})} = \sum_\alpha S_{\alpha\gamma}|\alpha\rangle \tag{29}$$

then

$$P_\gamma^{(ad)} = \sum_{\alpha\beta}\langle\Psi(t)|\alpha\rangle S_{\alpha\gamma}S^\dagger_{\gamma\beta}\langle\beta|\Psi(t)\rangle \tag{30}$$





If a reaction occurs into different *channels*, e.g.

$$\mathrm{AB} + \mathrm{CD} \begin{array}{l} \longrightarrow AC + BD \\ \longrightarrow AD + BC \end{array}$$

Then probability of a state-to-state reaction is given by *S-Matrix*

$$\Psi_{\beta m}(E) = S_{\beta m,\alpha n}(E)\Psi_{\alpha n}(E) \tag{31}$$

where $\alpha, \beta$ are channels; $m, n$ internal (vibrational) quantum numbers and $E$ total energy. Sum over S-matrix elements at relevent energy to get the *cumulative reaction probability*

$$N(E) = \sum_{\beta m,\alpha n} |S_{\beta m,\alpha n}(E)|^2 \tag{32}$$

which in turn are related to the thermal rate constant

$$k(T) = \frac{1}{hQ}\int_0^\infty N(E)e^{-\frac{E}{kT}}\,dE \tag{33}$$

where $Q$ is the partition function

# Branching ratios and reactivity

Want to now how much goes into different channels. Divide wavefunction

$$\Psi(t) = \Psi_0(t) + \sum_\gamma \Psi_\gamma(t) \tag{34}$$

where

$$\Psi_\gamma(t) = \Theta_\gamma(R - R_c)\Psi(t) \tag{35}$$

Amount in a particular channel $\gamma$ is $\langle\Psi_\gamma(t)|\Psi_\gamma(t)\rangle$
Change is the *flux*

$$\frac{\partial}{\partial t}\langle\Psi_\gamma(t)|\Psi_\gamma(t)\rangle = i\langle\Psi(t)|[H,\Theta_\gamma]|\Psi(t)\rangle = \langle\Psi(t)|\hat{F}|\Psi(t)\rangle \tag{36}$$

And total amount of system that has flowed into $\gamma$ is

$$\sigma_\gamma = \int_{-\infty}^{\infty} dt\langle\hat{F}(t)\rangle \tag{37}$$





# Flux analysis

When a dissociative channel is present, must add a CAP

$$H = H_{sys} - iW_\gamma \tag{38}$$

where $W_\gamma = ax^b\Theta_\gamma$. Can now write

$$\sigma_\gamma = \int_{-\infty}^{\infty} dt\langle\Psi(t)|W_\gamma|\Psi(t)(t)\rangle \tag{39}$$

Can use same formalism to get scattering matrix elements

$$\sum_{\nu'}|S_{\gamma\nu',\alpha\nu}(E)|^2 = \frac{2}{\pi|\Delta(E)|^2}\mathrm{Re}\int_0^T d\tau\, g(\tau)e^{iE\tau} \tag{40}$$

with $g(\tau) = g_w(\tau) + g_\theta(\tau)$ and

$$g_w(\tau) = \int_0^{T-\tau} dt\,\langle\Psi(t)|W_\gamma|\Psi(t+\tau)\rangle \tag{41}$$

$$g_\theta(\tau) = \tfrac{1}{2}\langle\Psi(T-\tau)|\Theta_\gamma|\Psi(T)\rangle \quad , \tag{42}$$

# Spectral Transition Rate

For weak light fields, Fermi's Golden Rule states that the probability for a transition is related to square of the *Transition dipole moment*

$$\mu_{fi} = \int d\tau \, \Psi_f^* \vec{\mu} \Psi_i \qquad = \langle \Psi_f | \vec{\mu} | \Psi_i \rangle$$

by

$$\text{rate} \propto \mu_{fi}^2$$

Using the Born-Oppenheimer Approximation,

$$\Psi(R, r) = \psi(r)\chi(R)$$

we find that

$$\mu_{fi} = \langle \psi_f | \hat{\mu} | \psi_i \rangle \langle \chi_{v'} | \chi_v'' \rangle$$

and

$$I_{fi} \propto |\mu_{fi}^{el}|^2 |\langle \chi_{v'} | \chi_{v''} \rangle|^2$$





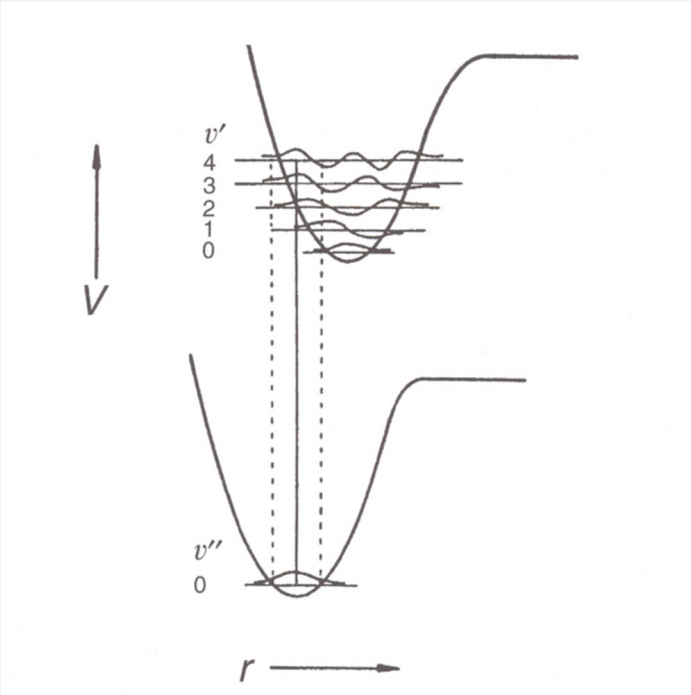
# The Franck-Condon Principle

For a molecule, the intensity of a transition from state $\Psi_i$ to $\Psi_f$ in a light field is proportional to F.C. factors

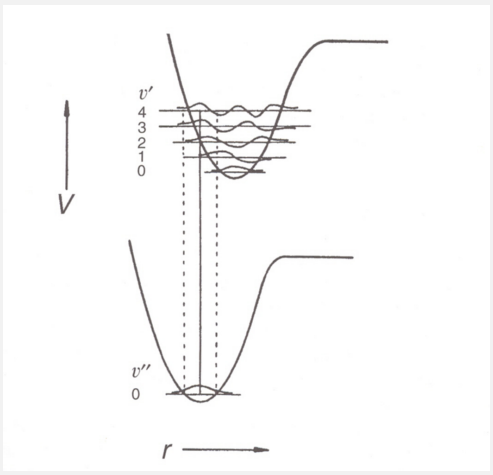
$$\boxed{I_{fi} \propto |\langle \chi_{v'} | \chi_{v''} \rangle|^2}$$

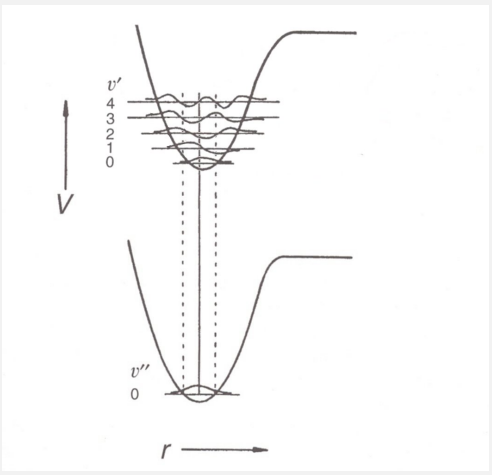
where

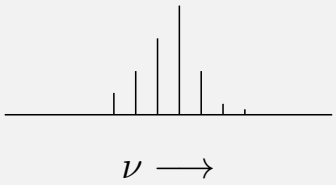
$\chi_{v''}$ lower vibrational level
$\chi_{v'}$ upper vibrational level

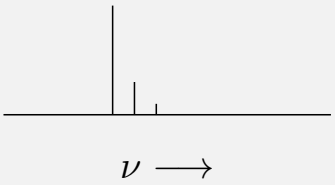


# Types of transitions: Bound-bound



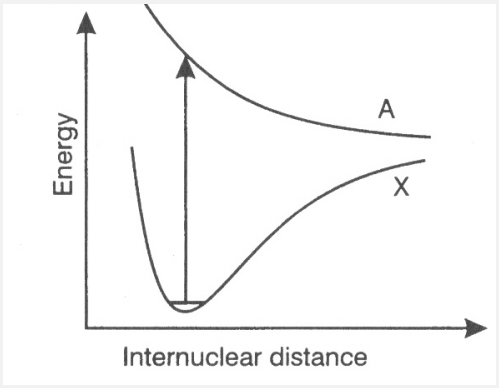



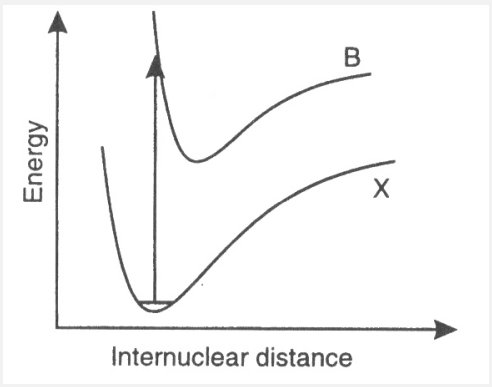



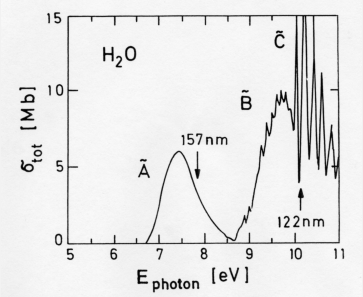





# Types of transitions: Bound-unbound

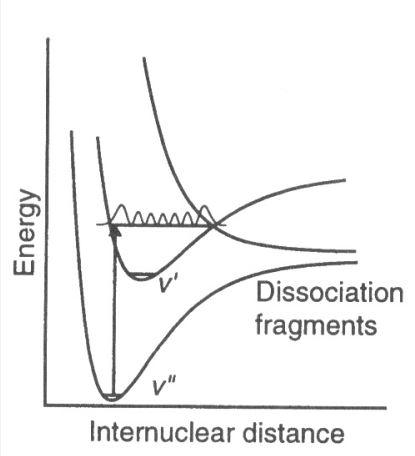


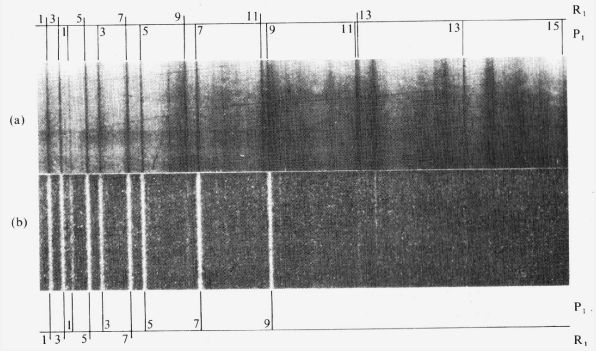




Water band $\tilde{A}$

# Predissociation




$S_2$ absorption (top) and emission (bottom)

Ricks and Barrow *Canad. J. Phys.* **47**: 2423 (1969)





# Golden Rule Spectrum

In the time-dependent picture, the FC absorption spectrum is the Fourier Transform of the autocorrelation function

$$\sigma(\omega) \propto \omega \int_{-\infty}^{\infty} dt\, C(t) e^{i(E_0+\omega)t} \quad , \tag{43}$$

where $E_0$ denotes the ground-state energy and where the autocorrelation function is defined as

$$C(t) = \langle \Psi(0) | \Psi(t) \rangle \qquad = \langle \Psi^*(\tfrac{t}{2}) | \Psi(\tfrac{t}{2}) \rangle \tag{44}$$

Using eigenvalue representation,

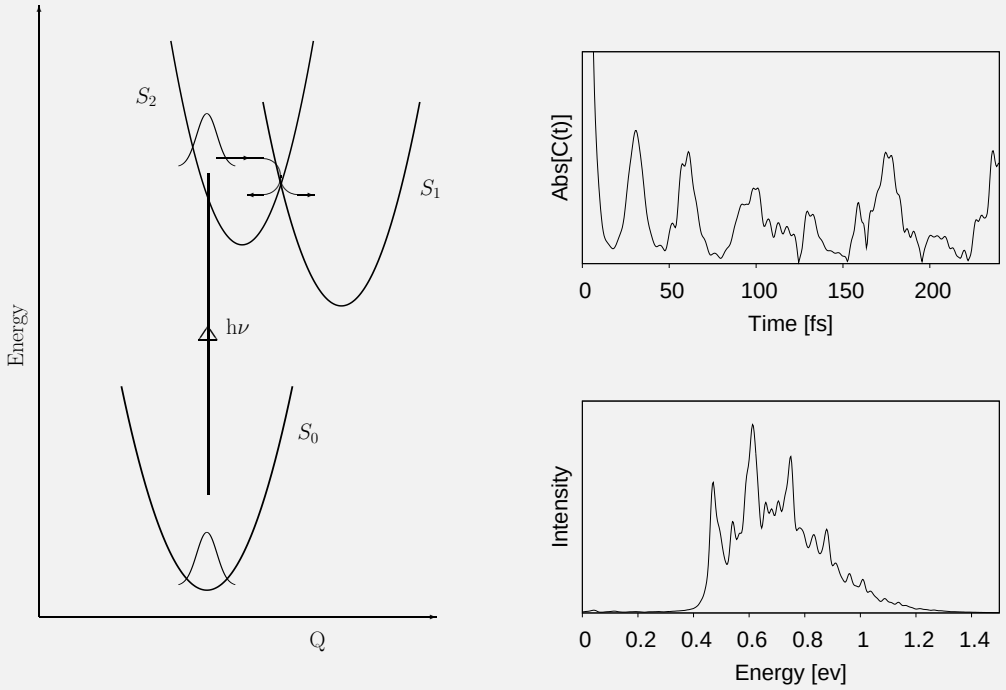
$$C(t) = \sum_i c_i^* c_i e^{i\omega_i t} \tag{45}$$

and

$$\begin{aligned} \int_{-\infty}^{\infty} dt\, C(t) e^{i(E_0+\omega)t} &= \int_{-\infty}^{\infty} dt \sum_i c_i^* c_i e^{-i(E_i-E_0)} e^{i\omega_i t} \\ &= \sum_i c_i^* c_i \delta(E_i - E_0) \end{aligned} \tag{46}$$

# Absorption spectrum

$$\frac{I}{I_0} = e^{-\sigma C l} \tag{47}$$








Golden Rule derived from first-order perturbation theory. Spectrum valid for:

- weak fields
- direct processes

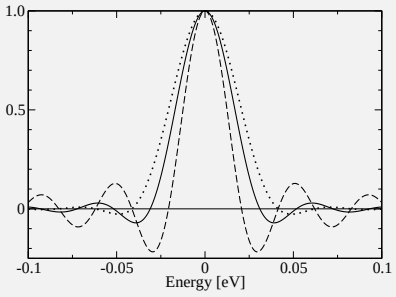
Due to finite propagation multiply C(t) by

$$f(t) = \exp(-t/\tau) \quad . \tag{48}$$

and

$$g_k(t) = \cos^k\left(\frac{\pi t}{2T}\right)\Theta\left(1 - \frac{|t|}{T}\right) \tag{49}$$

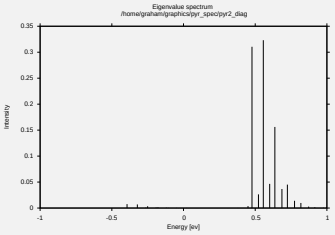
$k = 1$ usually best choice



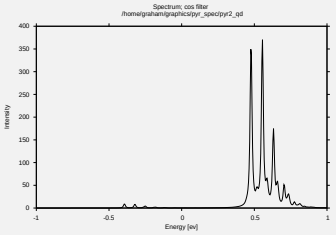

$T$=100 fs.

# Effect of damping

$$H = \sum_{i=1,2} \frac{\omega_i}{2} \left( \frac{\partial^2}{\partial Q_i^2} + Q_i^2 \right) + \begin{pmatrix} E_1 + \kappa^{(1)} Q_1 & \lambda Q_2 \\ \lambda Q_2 & E_2 + \kappa^{(2)} Q_1 \end{pmatrix}$$

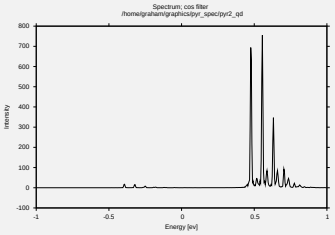



Eigenvalues



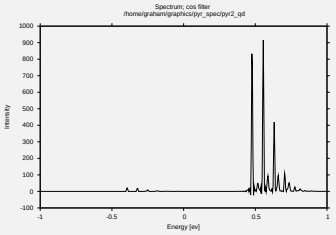

Dynamics

$\tau = 100$ fs




Dynamics

$\tau = 400$ fs




Dynamics

$\tau = 1000$ fs





# Time-resolved spectra

Add light field to Hamiltonian

$$\hat{H} = \hat{H}_M + \hat{H}_{ML} \quad \text{where} \quad \sum_{ij} \mid \psi_i \rangle \mu_{ij} . E(t) \langle \psi_j \mid \tag{50}$$

Time-resolved photo-electron spectrum:
Need to describe free-electron continuum, e.g.

$$\mid \Psi(R,t) \rangle = \mid \tilde{X} \rangle + \mid \tilde{A} \rangle + \sum_{i=1,2} \int_0^\infty dE \mid \tilde{X}_i^I(E) \rangle \tag{51}$$

Spectrum is long-time population of continuum states

$$I(\omega) \propto \sum_{i=1,2} \int_0^\infty dE \mid \langle \Psi(t \to \infty) \mid \tilde{X}_i^I(E) \rangle \mid^2 \tag{52}$$

Domcke and Stock Adv. Chem. Phys. (1997) **100**: 1
Seel and Domcke J. Chem. Phys. (1991) **95**: 7806

# Time-resolved Photo-electron Spectrum: Toluene

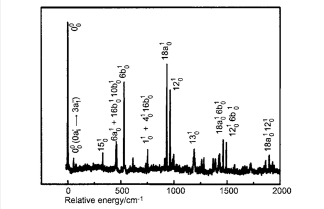



FIG. 1. The $S_0$-$S_1$ excitation spectrum of toluene. Adapted from Hickman *et al.* (Ref. 2), with thanks to W. D. Lawrance.

Create Resonance $\nu_{6a}$ / $\nu_{10b16b}$

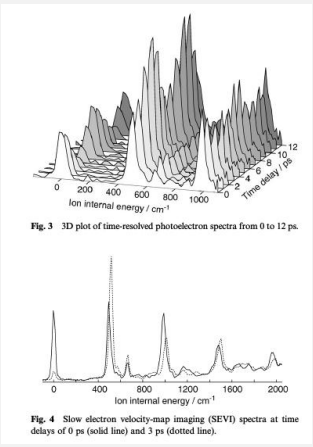
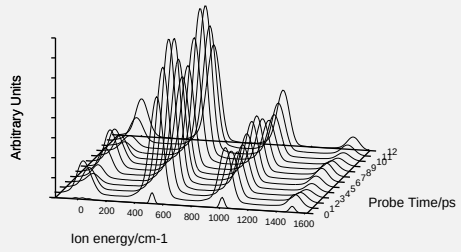


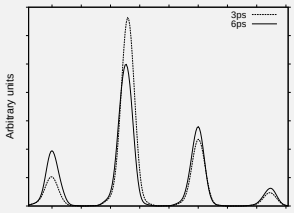

**Fig. 3** 3D plot of time-resolved photoelectron spectra from 0 to 12 ps.

**Fig. 4** Slow electron velocity-map imaging (SEVI) spectra at time delays of 0 ps (solid line) and 3 ps (dotted line).

Davies *et al* PCCP (10) 12: 9872

$$I(\omega) = \lim_{t\to\infty} \sum_{i\in\tilde{X}^+} |C_i^{\tilde{X}^+}(\omega, t)|^2$$




Computationally expensive ....

Richings and Worth JCP (14) 141: 244115





# Summary

- Grid-based quantum dynamics can provide a numerically exact solution to the TDSE
  - Require a primitive basis
  - MCTDH a general algorithm for polyatomic systems

Aim is to simulate a signal that can be related to an experiment

- Initial wavepacket maps onto experimental conditions
- Signal obtained from propagated wavefunction
  - Branching ratios
  - Spectrum

Can then analyse simualation to obtain molecular picture and detailed information: energy flow between modes, state populations, etc. from expectation values.

# Input File

Quantics program driven by an ascii input file. ections reflect the choices to be made:

| | |
|---|---|
| PRIMITIVE-BASIS-SECTION: | the coordinates, no. grid points etc. |
| OPERATOR-SECTION: | file containing the operator |
| INIT_WF-BASIS-SECTION: | the initial wavefuncion |
| SPF-BASIS-SECTION: | the no. of MCTDH basis functions |
| INTEGRATOR-SECTION: | details of the integration scheme |
| RUN-SECTION: | type of calculation to be made |





```
RUN-SECTION
name = hh2
propagation   tfinal = 120.d0   tout = 1.d0   tpsi = 1.d0
psi gridpop steps
end-run-section

OPERATOR-SECTION
opname = h3j0
alter-labels
CAP_rd = CAP [ 6.04  0.002  3 ]   # starting point, strength, order
end-alter-labels
end-operator-section

SPF-BASIS-SECTION
    rd     =  14
    rv     =  10
    theta  =  10
end-spf-basis-section

PRIMITIVE-BASIS-SECTION
#Label     DVR      N       Parameter
    rd     sin      68   1.00d0    9.040d0    #  xi, xf
    rv     sin      48   0.60d0    6.240d0    #  xi, xf
    theta  leg      31     0       even       # l_z, sym (all/even/odd)
end-primitive-basis-section

INTEGRATOR-SECTION
CMF/var =   0.1 , 1.d-5
BS/spf  =    7  , 1.d-6
SIL/A   =   30  , 1.d-5
end-integrator-section

INIT_WF-SECTION
build
    rd    gauss     4.50d0   -8.00d0     0.25d0   # r0,p0, sigma_r
    rv    eigenf      H2     pop=1                 # pop=1 -> ground state
    theta leg         0       0          sym      # l_z, l, sym/no-sym
end-build
end-init_wf-section

end-input
```

# Operator File

```
HAMILTONIAN-SECTION
mode   |   rd   |   rv | theta
```

Defines the operators for the coordinates `rd`, `rv` etc. The coordinate labels are free to be chosen. The Hamiltonian has the form

$$H = \sum_s H_s = \sum_s c_s h_s^{(1)}(x1) h_s^{(2)}(x2) \ldots \tag{53}$$

operators $h_s^{(\kappa)}$ are defined in table. E.g.

```
0.5/mass_rv    |   1     | q^-2 |    j^2
```

is

$$H_2 = \frac{1}{m_{rv}} \frac{1}{(rv)^2} \hat{j}^2 \tag{54}$$

$\hat{j}^2$ is the angular momentum squared operator for `theta`. Note that the potential in this example is a special case, `V`. This is defined separately in the `LABELS-SECTION`.

Any parameters can be given in the `PARAMETERS-SECTION`





```
OP_DEFINE-SECTION
title
H+H2 Reactive Scattering in Jacobian Coordinates. J=0.
Minimum of H_2 curve: 4.74746 eV. Zero point energy of vib.: 0.270 eV
end-title
end-op_define-section

PARAMETER-SECTION
mass_rd = 0.6666666666667, H-mass    # Reduced mass of H--H2 system
mass_rv = 0.50, H-mass               # Reduced mass of H2 molecule
jtot    = 0                          # Total angular momentum
jbf     = 0                          # Projection on BF axis (K, or Omega).
end-parameter-section

HAMILTONIAN-SECTION
-------------------------------------------
  modes       |  rd   |  rv  |  theta
-------------------------------------------
0.5/mass_rd   |  q^-2 |  1   |   j^2
0.5/mass_rv   |  1    | q^-2 |   j^2
1.0           |  KE   |  1   |   1
1.0           |  1    |  KE  |   1
1.0           |  V
-------------------------------------------
end-hamiltonian-section

LABELS-SECTION
V = lsth {jacobian}
end-labels-section

# The following one-dimensional hamiltonian is used to determine the
# eigenstates of H_2. These are then used as initial rv-spf's.

HAMILTONIAN-SECTION_H2
-------------------------------------------
  modes       |  rd   |  rv  |  theta
-------------------------------------------
1.0           |  1    |  KE  |   1
1.0           |  1    | v:H2 |   1
-------------------------------------------
end-hamiltonian-section
```



```
end-operator
```