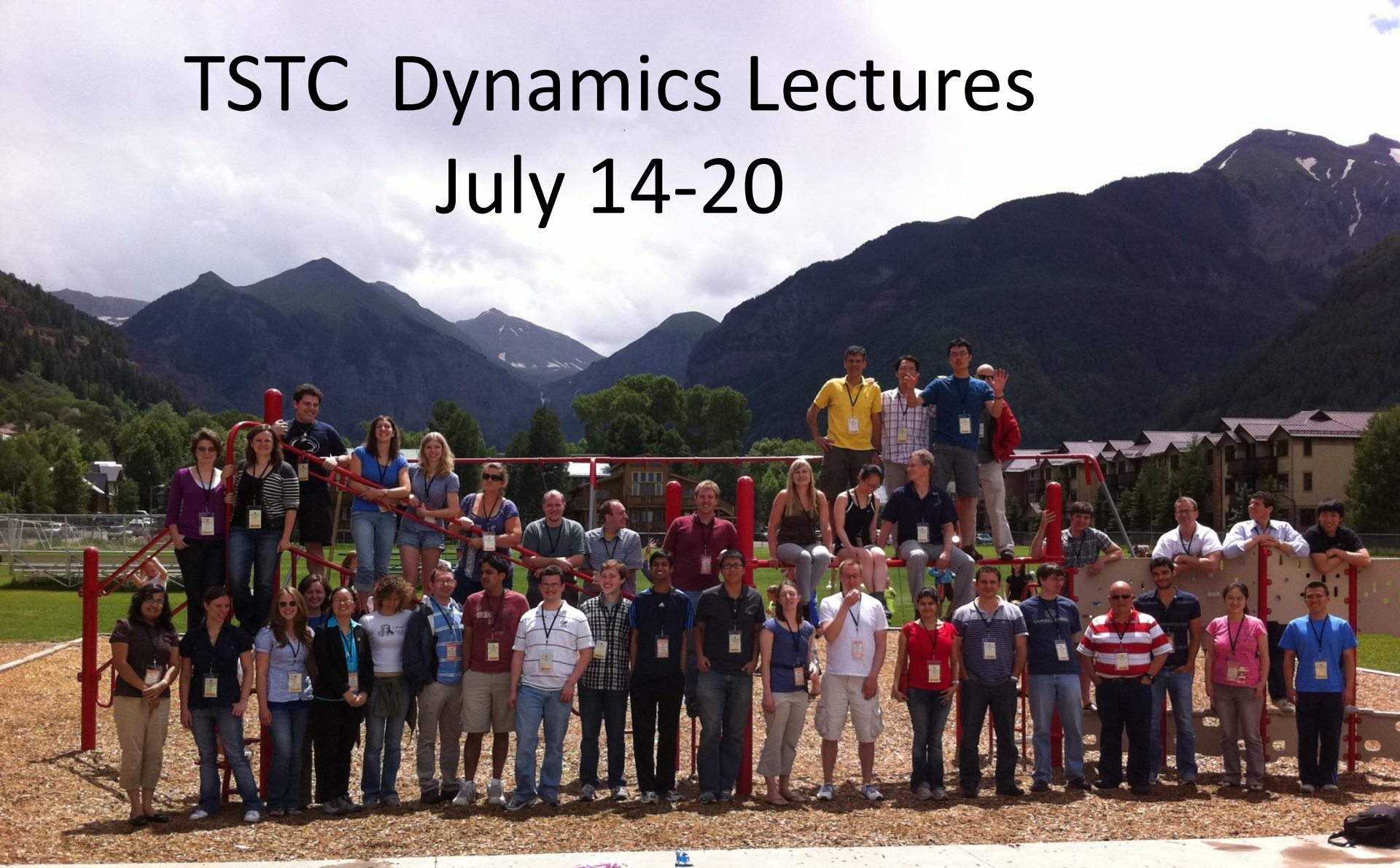
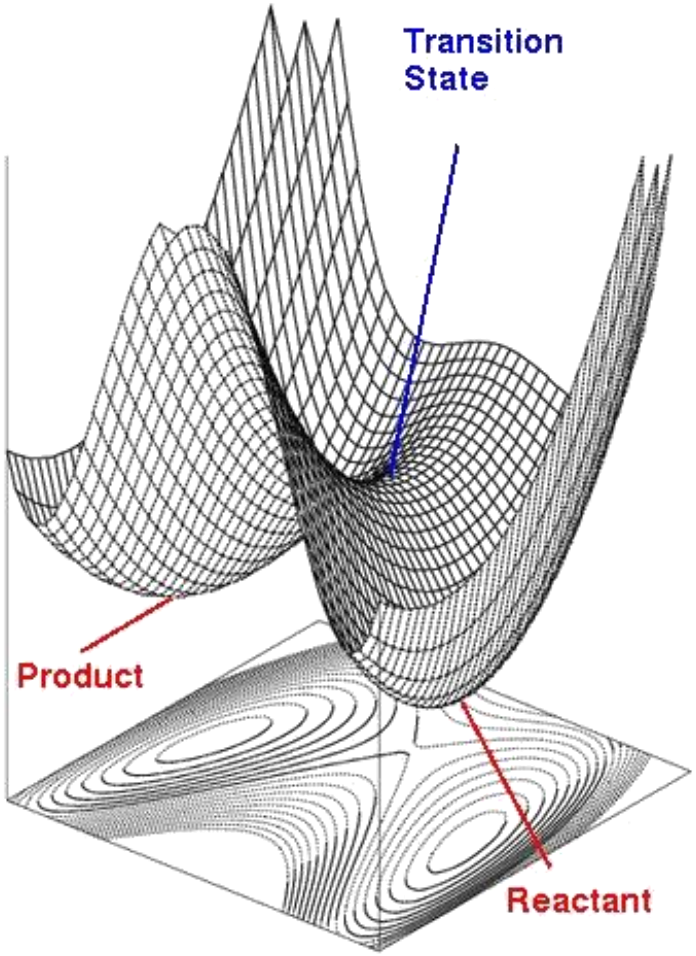
TSTC Dynamics Lectures
July 14-20



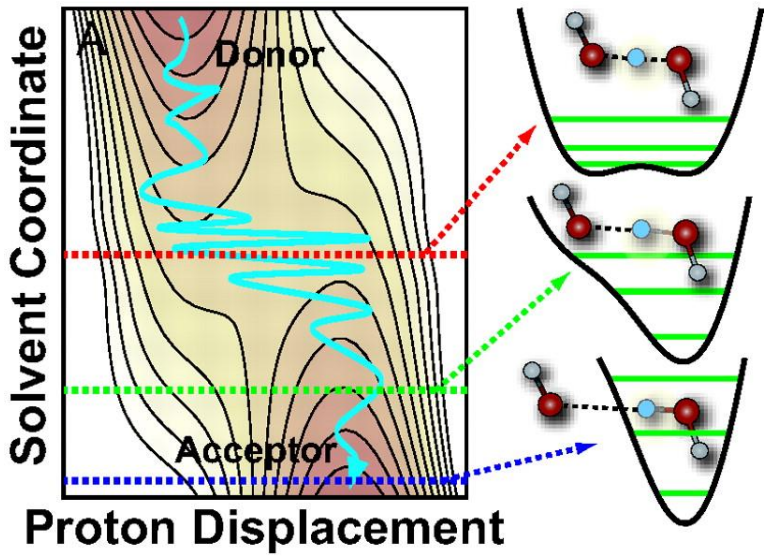
Ned Sibert
University of Wisconsin

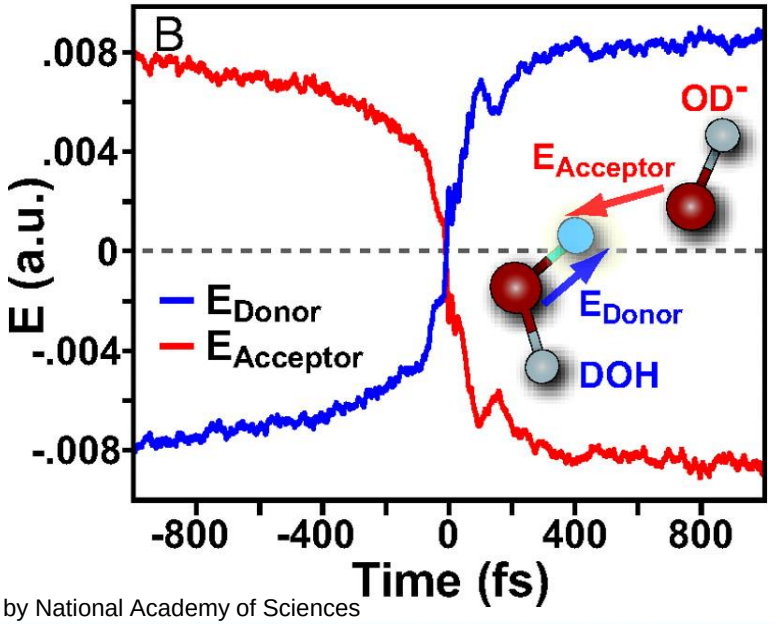
Transition State Theory and Beyond



$$k(T) = \frac{kT}{h}\frac{Q^{\ddagger}(T)}{Q_r(T)}$$

Collective reaction coordinate for proton transfer.

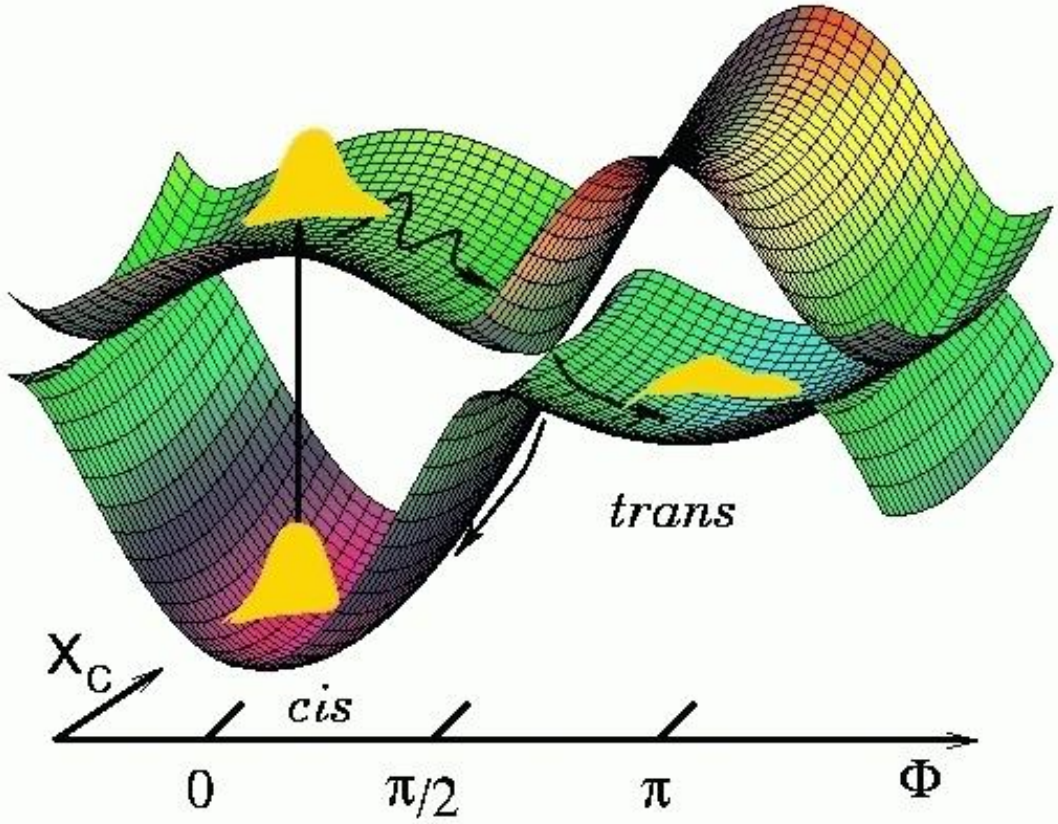




It is generally accepted that the anomalous diffusion of the aqueous hydroxide ion results from its ability to accept a proton from a neighboring water molecule; yet, many questions exist concerning the mechanism for this process. What is the solvation structure of the hydroxide ion? In what way do water hydrogen bond dynamics influence the transfer of a proton to the ion?

Roberts S T et al. PNAS 2009;106:15154-15159

Conical Intersections

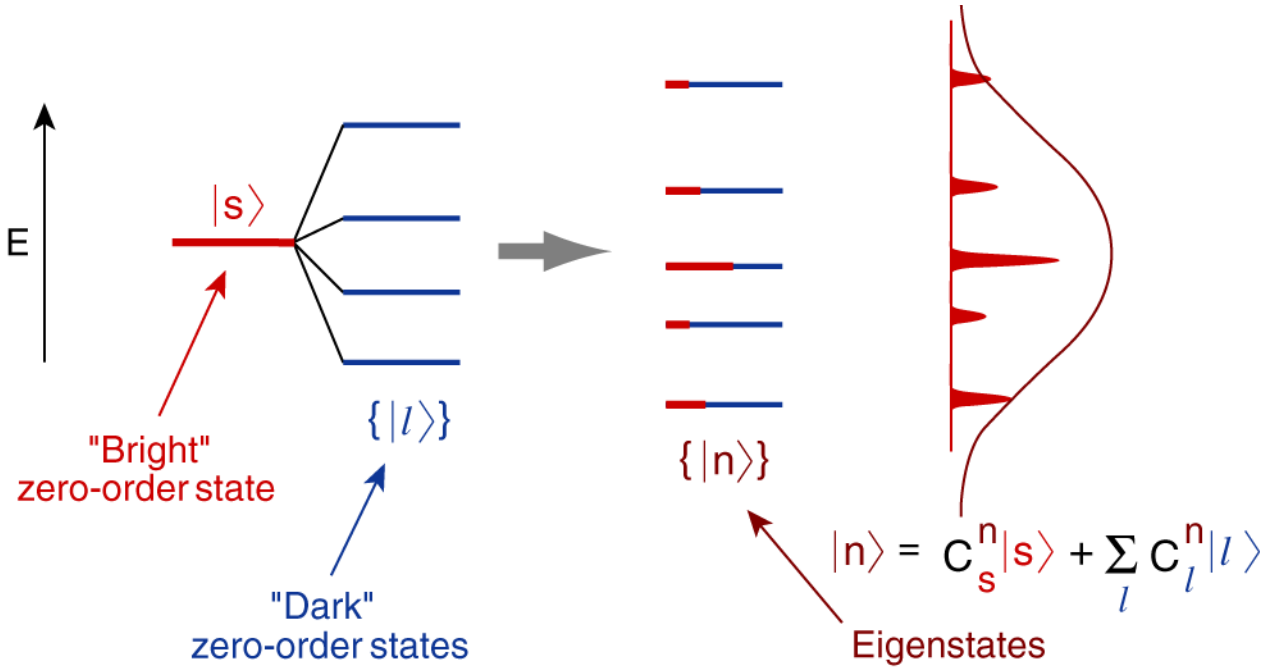


A recently proposed model of the photoinduced *cis-trans*isomerization of retinal in rhodopsin, representing the first step in vision. Shown are two-dimensional potential-energy surfaces of the ground and excited electronic states. The photoreaction is initiated via vertical excitation by a pump laser pulse, which prepares a vibrational wave packet on the excited electronic state. The wave packet is seen to bifurcate at a *conical intersection* of the adiabatic surfaces, whereby the *photoproduct* is formed with high efficiency and within only 200 fs such as the making and breaking of chemical bonds in real time, that is, on a femtosecond time scale.

Femtosecond time-resolved spectroscopy of the dynamics at conical intersections, G. Stock and W. Domcke, *in: Conical Intersections, eds: W. Domcke, D. R. Yarkony, and H. Koppel, (World Scientific, Singapore, 2003)*

Intramolecular Dynamics Background

Sparse Multiple States



Slide borrowed from F. Crim

Think-Pair-Share

How fast ($\Delta E\, \Delta t \geq \hbar$) would your laser pulse need to be to get electronic dynamics?

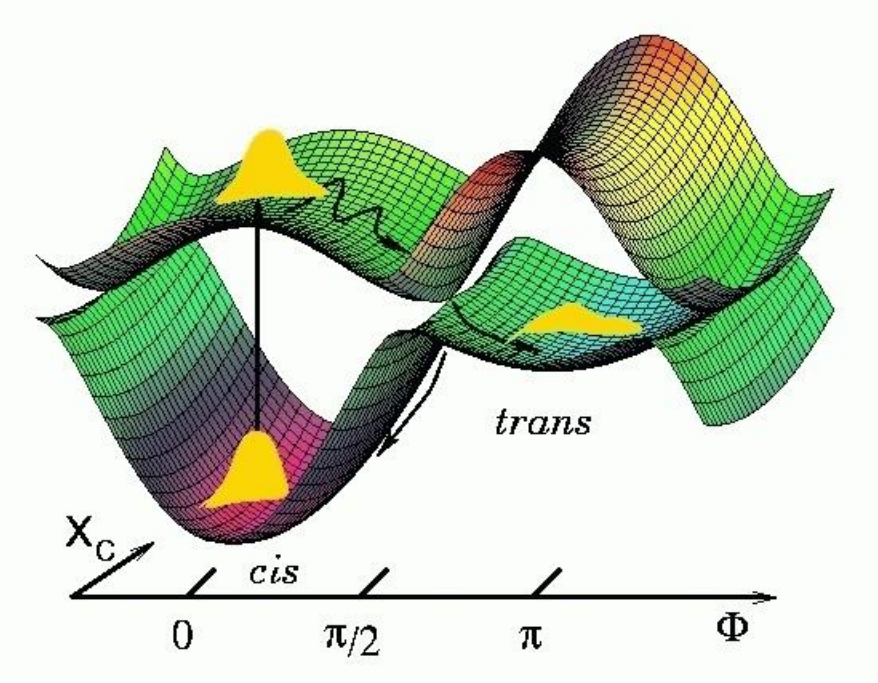
A. 10^{-21} s

B. 10^{-18} s

C. 10^{-15} s

D. 10^{-12} s

Dynamics



One needs to solve

$$i\hbar\frac{\partial\psi(x,t)}{\partial t} = \hat{H}\psi$$

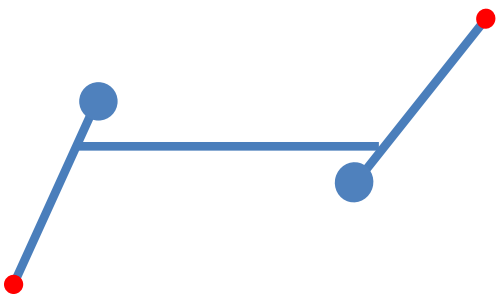
directly or solve $H\Psi_n(x) = E_n\Psi_n(x)$ and calculate

$$\psi(x,t) = \sum_n c_n\Psi_n(x)e^{-iE_nt/\hbar}$$

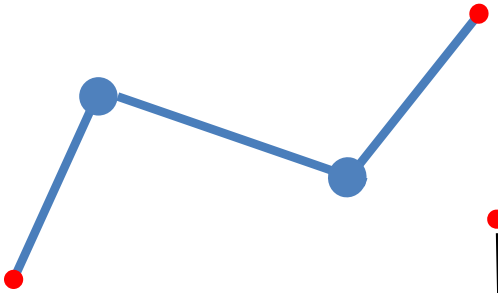
Here we review a few select tools of the trade.

Coordinates
Acetylene Example

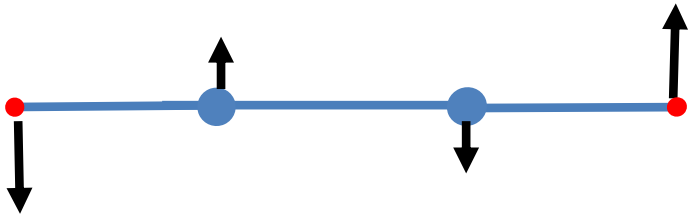
Jacobi Coordinates



Internal Coordinates



Normal Coordinates



JOURNAL OF CHEMICAL PHYSICS VOLUME 112, NUMBER 3 15 JANUARY 2000

Rovibrational Hamiltonians for general polyatomic molecules in spherical polar parametrization. I. Orthogonal representations

Mirjana Mladenović
Institut für Physikalische Chemie, Universität Göttingen, Tammannstr. 6, D-37077 Göttingen, Germany

Think-Pair-Share

Which coordinate system is well suited for describing the acetylene/vinylidene isomerization?

A. Jacobi
B. Normal
C. Internal
D. None of the above

A matrix representation of your Hamiltonian

A useful way to represent H this is to divide it into 2 parts $H=H^0+V$, where V is hopefully small and H^0 has known solutions

$$H^0|n\rangle = E_n|n\rangle$$

that enable one to define a basis set. One must then evaluate

$$\langle m|H|n\rangle = E_n\delta_{mn} + \langle m|V|n\rangle$$

This integration is over multiple degrees of freedom. If V is a polynomial, then the integration can be broken down into a sum of separable terms. Otherwise integration is painful. Think back to Gaussian based electronic structure calculations.

Gaussian Quadrature (see Tannor page 286)

Consider approximating the integral of a function $f(x)$ by a finite sum:

$$\int_a^b dx\ w(x)f(x) \approx \sum_{i=1}^{N} W_i f(x_i),$$

where $w(x)$ is a positive weight function and the N values of $\{W_i\}$ are the weights to be given to the N function values $f(x_i)$.

In Gaussian Quadrature the x_i and W_i are chosen to give exact results if $f(x)$ is a polynomial of degree $2N-1$ or less.

Discrete Variable Representation (DVR)

Consider the example of the sinc DVR

$$\chi_n(x) = \frac{\sin[(x - x_n)\pi/\delta]}{[(x - x_n)\pi/\sqrt{\delta}]}$$

where $x_n = x_0 + n\delta$. The key feature of the DVR is

$$\chi_n(x_j) = \delta^{-1/2}\delta_{nj}$$

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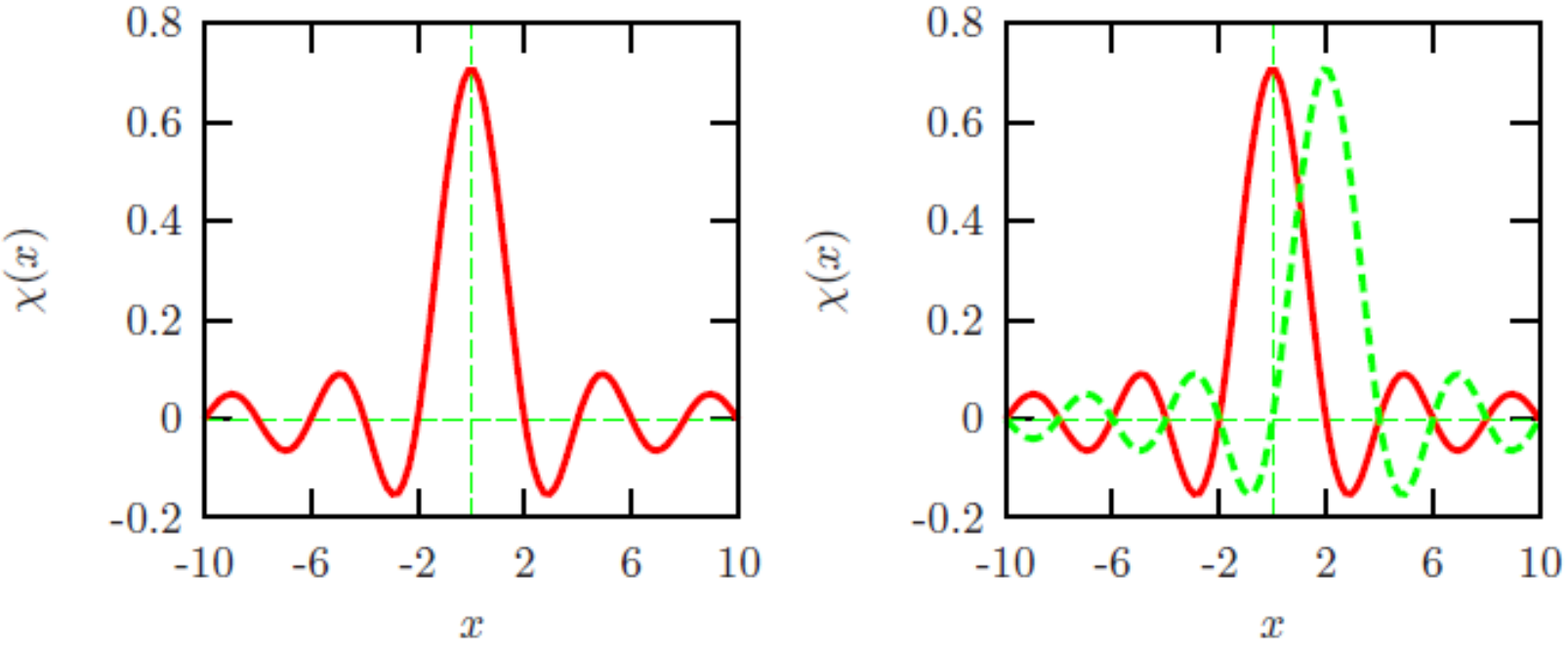


Discrete Variable Representation (DVR)

The potential matrix elements are evaluated implicitly by quadrature

$$\int dx\ \chi_n(x)^* V(x) \chi_m(x) \approx \sum_j w_j \chi_n(x_j)^* V(x_j) \chi_m(x_j)$$

$$= V(x_m)\delta_{mn}.$$

♠ Potential matrix elements are diagonal. ♠

For Gauss-Hermite DVR one diagonalizes the position matrix in a harmonic oscillator basis set.

Set up the position matrix **x**

Diagonalize **x** to obtain $\mathbf{X} = \mathbf{U}^t\mathbf{x}\mathbf{U}$

$$\chi_i = \sum_{j=1}^{N} U_{ji} \psi_j$$

The Kinetic Energy Matrix Elements are easy to evaluate.

Set up the position matrix kinetic energy matrix **t**

Diagonalize **x** to obtain $\mathbf{X} = \mathbf{U}^{t}\mathbf{x}\mathbf{U}$

Transform **T** to obtain $\mathbf{T} = \mathbf{U}^{t}\mathbf{t}\mathbf{U}$

The Kinetic Energy Matrix Elements are easy to evaluate.

A novel discrete variable representation for quantum mechanical reactive scattering via the *S*-matrix Kohn method

Daniel T. Colbert and William H. Miller J. Chem. Phys. **96** (3), 1 February 1992

1. $(-\infty, \infty)$ interval

In this case, $a \to -\infty$, $b \to \infty$, so a finite grid spacing $\Delta x = (b-a)/N$ requires that $N \to \infty$ also. With $\{x_i\}$ defined as in Eq. (A2), one also has $i + i' \to \infty$, but $i - i'$ is finite. Equation (A6) thus becomes

$$T_{ii'} = \frac{\hbar^2}{2m\Delta x^2}(-1)^{i-i'}\begin{cases} \pi^2/3, & i = i' \\ \dfrac{2}{(i-i')^2}, & i \neq i' \end{cases}, \qquad \text{(A7)}$$

and the grid is now specified more conveniently as $x_i = i\Delta x$, $i = 0, \pm 1, \pm 2, \ldots$.

Think-Pair-Share

The biggest drawback of the DVR representation is that

A. The variational principle no longer holds.
B. While the potential is sparse, KE is not.
C. The matrix elements are difficult to calculate.
D. Basis sets are large.

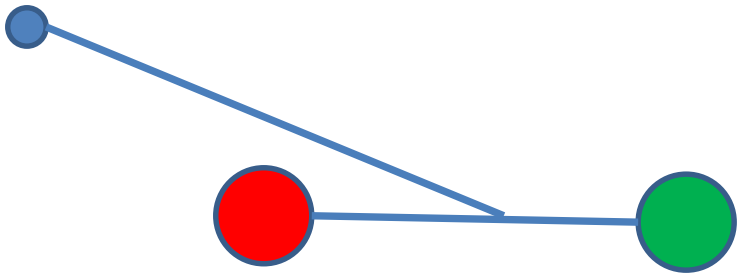
Adiabatic approximation and nonadiabatic corrections in the discrete variable representation: Highly excited vibrational states of triatomic molecules

J. C. Light and Z. Bačić[a)]
The Department of Chemistry and the James Franck Institute, The University of Chicago, Chicago, Illinois 60637

(Received 2 June 1987; accepted 26 June 1987)

An adiabatic approximation for the calculation of excited vibrational ($J = 0$) levels of triatomic molecules is developed using the discrete variable representation (DVR). The DVR

HCN isomerization reaction



Adiabaticity and the DVR

Consider a 2-D Hamiltonian with a fast r and a slow R DOF.

$$H = T_R + T_r + V(R, r).$$

In Born-Oppenheimer we solve fast r DOF at each value of R as

$$[T_r + V(R, r)]\psi_k(r; R) = E_k(R)\psi_k(r; R)$$

Adiabaticity and the DVR

Consider a 2-D Hamiltonian with a fast r and a slow R DOF.

$$H = T_R + T_r + V(R, r).$$

In Born-Oppenheimer we solve fast r DOF at each value of R as

$$[T_r + V(R, r)]\psi_k(r; R) = E_k(R)\psi_k(r; R)$$

In DVR our basis is

$$\psi_{k_m}(r)\chi_m(R),$$

where

$$[T_r + V(R_m, r)]\psi_{k_m}(r) = E_{km}\psi_{k_m}(r).$$

This leads to the following *sparse* matrix representation

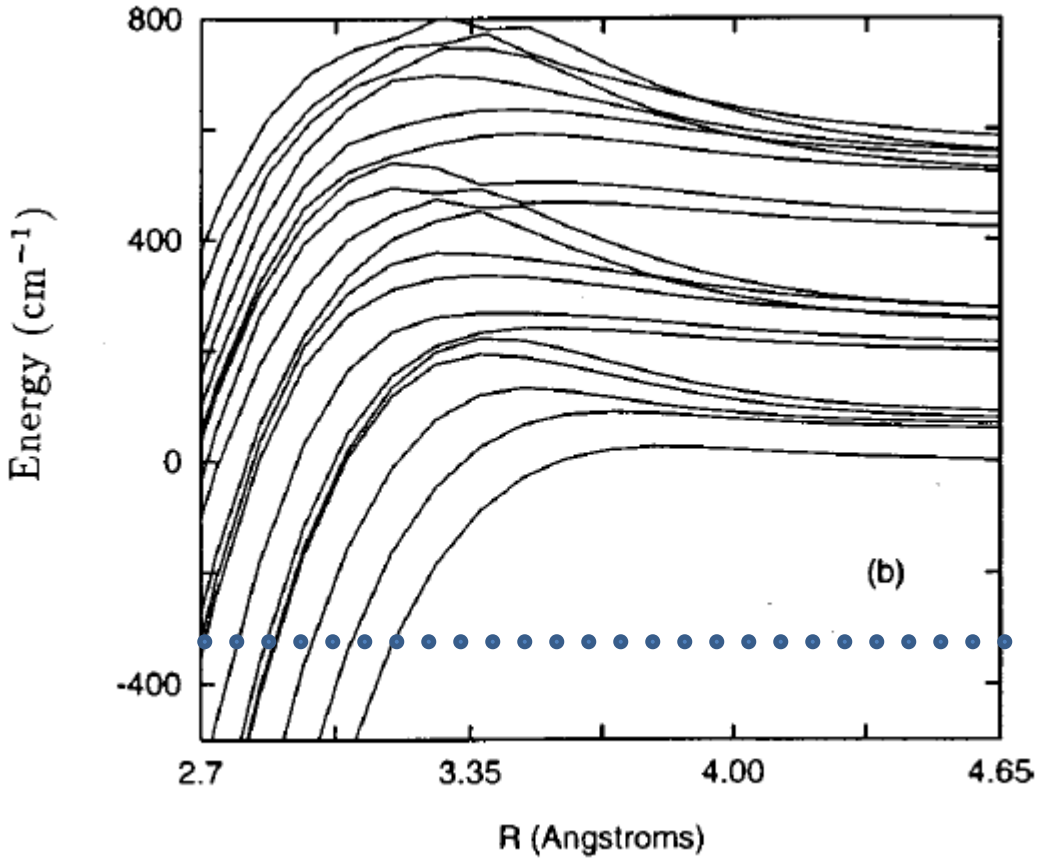
$$\langle k_m, m|H|k'_{m'}, m'\rangle = E_{km}\delta_{kk'}\delta_{mm'} + \langle m|T_R|m'\rangle\langle k_m|k'_{m'}\rangle.$$

PROVE THIS

Overlap Integral

$$CH_3 + H \rightarrow CH_4$$

Plot of transitional modes as a function of R.



SACM
and
Variational RRKM

$$k(E,J) = \frac{N(E,J)}{h\rho^R(E,J)}.$$

Think-Pair-Share

A simple HF electronic structure code might be 10,000 lines. A simple MD code might be 1000 lines of code. A simple DVR code for coupling 2 electronic states and 1 vibrational DOF might be

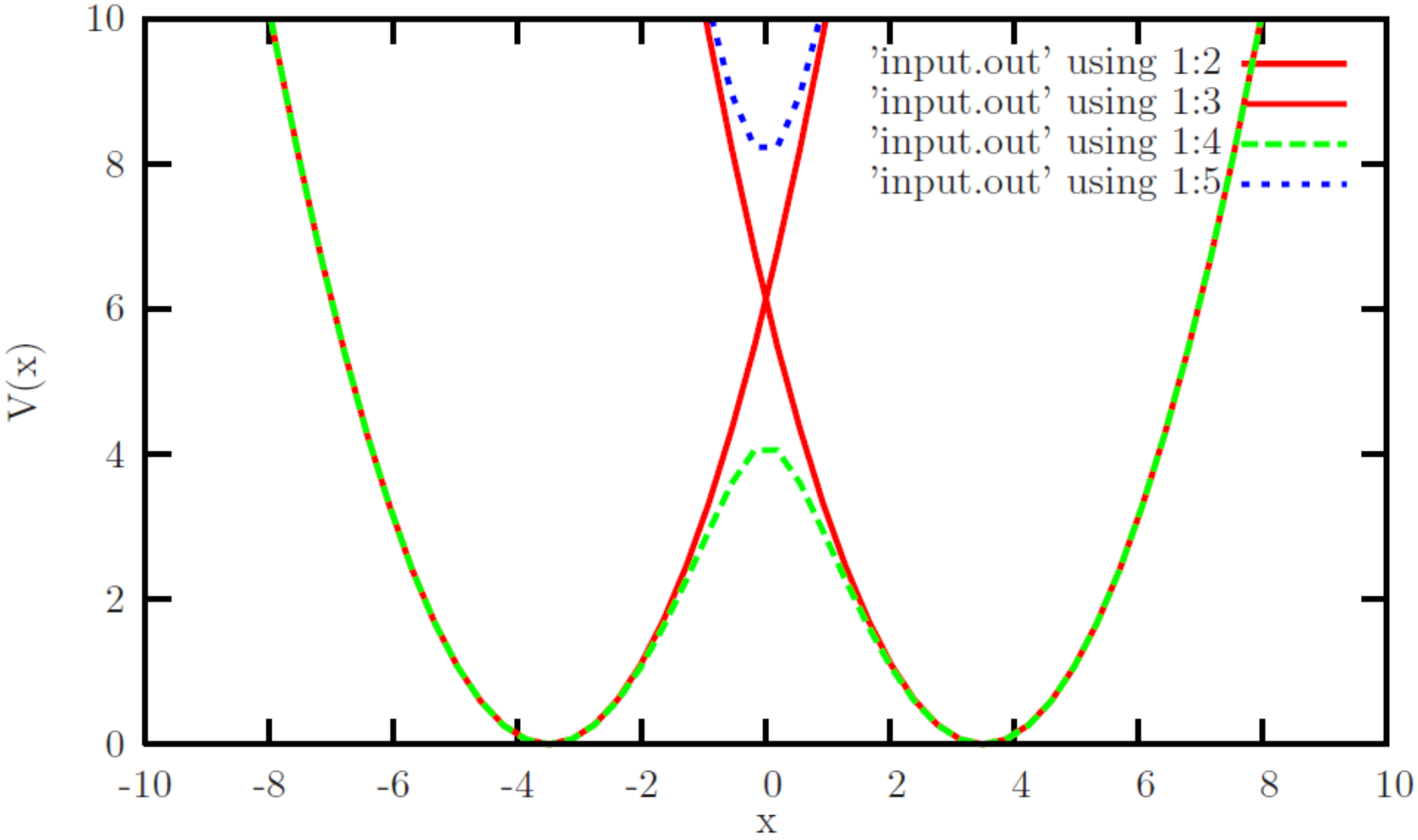
A. 10,000 lines.

B. 1,000 lines.

C. 100 lines.

D. 10 lines.

Home Work Calculation



```
 delx = (xmax-xmin)/dfloat(npoints-1)  !grid spacing
!    ------------------------------------------------------------------------
!    set up the kinetic energy operator
     con = 0.5d0/delx**2
     t(0) = con*pi**2/3.d0
     sone = -1.d0
     do i = 1,npoints
       t(i) = con*sone*2.d0/dfloat(i)**2
       sone = -sone
     enddo
     write(*,*)t

     do i = 1,npoints
      do ip = 1,i
        h(i,ip) = t(iabs(i-ip))
        h(ip,i) = h(i,ip)
        h(i+npoints,ip+npoints) = h(i,ip)
        h(ip+npoints,i+npoints) = h(ip,i)
      enddo
     enddo
```

$$T_{ii'} = \frac{\hbar^2}{2m\Delta x^2}(-1)^{i-i'}\begin{cases}\pi^2/3, & i = i' \\ \dfrac{2}{(i-i')^2}, & i \neq i'\end{cases},$$

Diabat 1

Diabat 2

```
!    ------------------------------------------------------------
!    add on the potential contribution
     xx = xmin-delx
     do i = 1,npoints
      xx = xx + delx
      v11 = 0.5d0*(xx+xe)**2
      v22 = 0.5d0*(xx-xe)**2
      v12 = v120*dexp(-(xx/alp)**2)
      h(i,i)                 = v11 + h(i,i)
      h(i+npoints,i+npoints) = v22 + h(i+npoints,i+npoints)
      h(i+npoints,i)         = v12
      vadl = (v11+v22)/2.d0-0.5d0*dsqrt((v11-v22)**2+4.d0*v12**2)
      vadu = (v11+v22)/2.d0-0.5d0*dsqrt((v11-v22)**2+4.d0*v12**2)
      write(17,'(4f10.5)')xx,v11,vadl,vadu
     enddo
```

Diagonal-Diabat Potentials

Off-Diagonal Diabat Potentials

The DVR provides a matrix representation of the Hamiltonian. What next?

One needs to solve

$$i\hbar\frac{\partial\psi(x,t)}{\partial t} = \hat{H}\psi$$

directly or solve $H\Psi_n(x) = E_n\Psi_n(x)$ and calculate

$$\psi(x,t) = \sum_n c_n\Psi_n(x)e^{-iE_nt/\hbar}$$

One goal is to calculate a spectrum or short time dynamics.

$$\Sigma(\omega) = \int_{-\infty}^{+\infty} dt\langle\phi|\phi(t)\rangle e^{i\omega t} = \sum_n \left|\langle\phi|\Psi_n\rangle\right|^2 \delta(E_n/\hbar - \omega)$$

The Lanczos Method

$$T_m = \begin{bmatrix} \alpha_1 & \beta_1 & & & \\ \beta_1 & \alpha_2 & \beta_2 & & \\ & \ddots & \ddots & \ddots & \\ & & \beta_{m-2} & \alpha_{m-1} & \beta_{m-1} \\ & & & \beta_{m-1} & \alpha_m \end{bmatrix}$$

Create a tridiagonal matrix.

The Lanczos Method

Start with an initial vector $|\psi_1\rangle = |\phi\rangle$.

- Calculate $H|\psi_1\rangle = |\chi\rangle$
- Orthogonalize vector $|\chi\rangle \rightarrow |\chi\rangle - |\psi_1\rangle\langle\psi_1|\chi\rangle$
- Normalize to obtain $|\psi_2\rangle = \langle\chi|\chi\rangle^{-1/2}|\chi\rangle$

We construct matrix elements.

- Calculate $\alpha_1 = \langle\psi_1|H|\psi_1\rangle$
- Calculate $\beta_1 = \langle\psi_1|H|\psi_2\rangle$
- Calculate $\alpha_2 = \langle\psi_2|H|\psi_2\rangle$

Continue the process.

- Calculate $H|\psi_2\rangle = |\chi\rangle$
- Orthogonalize $|\chi\rangle \rightarrow |\chi\rangle - \sum_{i=1}^{2} |\psi_i\rangle\langle\psi_i|\chi\rangle$
- Normalize to obtain $|\psi_3\rangle = \langle\chi|\chi\rangle^{-1/2}|\chi\rangle$

Lanczos with DVR's

The previous equations were written in braket notation as

$$\left|\chi\right\rangle = H\left|\psi\right\rangle$$

To implement this in a basis you multiply both sides by $\left\langle i\right|$ to give

$$\left\langle i\middle|\chi\right\rangle = \left\langle i\middle|H\middle|\psi\right\rangle$$

Now insert the identity, $\sum_j \left|j\right\rangle\left\langle j\right| = 1$, to obtain

$$\left\langle i\middle|\chi\right\rangle = \sum_j \left\langle i\middle|H\middle|j\right\rangle\left\langle j\middle|\psi\right\rangle$$

This is just matrix multiplication. Use sparse matrix methods.

The Lanczos Method

First we construct the tridiagonal matrix

$$T_m = \begin{bmatrix} \alpha_1 & \beta_1 & & & \\ \beta_1 & \alpha_2 & \beta_2 & & \\ & \ddots & \ddots & \ddots & \\ & & \beta_{m-2} & \alpha_{m-1} & \beta_{m-1} \\ & & & \beta_{m-1} & \alpha_m \end{bmatrix}$$

Next we diagonalize it. Note we only retain three vectors at any time.

Since our $|\phi\rangle$ is part of the tridiagonal matrix we can calculate the spectrum in the Krylov space.

$$\Sigma(\omega) = \int_{-\infty}^{+\infty} dt \langle \phi | \phi(t) \rangle e^{i\omega t} = \sum_n \left| \langle \phi | \Psi_n \rangle \right|^2 \delta(E_n / \hbar - \omega)$$

Solutions to TDSE

For $H = H^0 + V$ with small coupling solve

- $i\hbar\dot{c}_j = \sum_k c_k V_{kj} \exp[i(E_j - E_k)t/\hbar]$.

For small dispersion use Askar and Cakmak [JCP **68**, 2794 (1978).]

- $\psi(t + \Delta t) \approx \psi(t - \Delta t) - 2i\Delta t \hat{H}\psi(t)$,

where error is $O[(\Delta t)^3 \sigma_E^3]$.
To combine with FFT use the split-operator

- $e^{-iH\Delta t/\hbar} \approx e^{-iT\Delta t/\hbar} e^{-iV\Delta t/\hbar}$.

For high accuracy use polynomial expansion

- $e^{-iH\Delta t/\hbar} \approx \sum_n a_n P_n(H)$.

A Fourier Method Solution for the Time Dependent Schrödinger Equation as a Tool in Molecular Dynamics

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AND

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JOURNAL OF COMPUTATIONAL PHYSICS **52**, 35–53 (1983)

KK combined FFT with the split-operator

$$e^{-iH\Delta t/\hbar} \approx e^{-iT\Delta t/\hbar} e^{-iV\Delta t/\hbar}$$

as follows: step 1

$$\left[e^{-iV\Delta t/\hbar}\psi(x,t)\right].$$

step 2

$$FT\left[e^{-iV\Delta t/\hbar}\psi(x,t)\right]$$

step 3

$$\left\{e^{-ik^2t/\hbar} FT\left[e^{-iV\Delta t/\hbar}\psi(x,t)\right]\right\}$$

step 5

$$e^{-iH\Delta t/\hbar}\psi(x,t) \approx FT^{-1}\left\{e^{-ik^2t/\hbar} FT\left[e^{-iV\Delta t/\hbar}\psi(x,t)\right]\right\}$$

The split-operator applied to a conical intersection

THE JOURNAL OF CHEMICAL PHYSICS **122**, 224315 (2005)

Time-dependent quantum wave-packet description of the $^1\pi\sigma^*$ photochemistry of phenol

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(Received 14 January 2005; accepted 21 March 2005; published online 15 June 2005)

CHEMPHYSCHEM
MINIREVIEWS

ChemPubSoc Europe

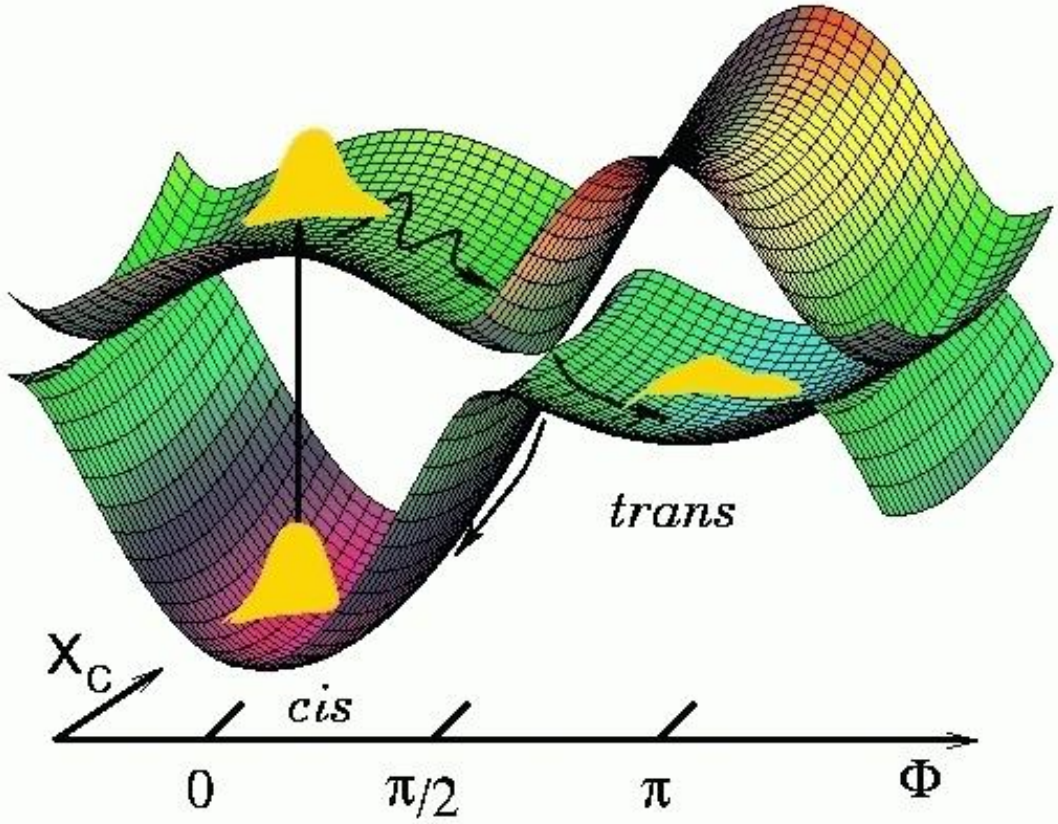
DOI: 10.1002/cphc.201201096

Theoretical Methods for Ultrafast Spectroscopy

Roberto Marquardt*[a]

Time-resolved spectroscopy in the femtosecond and attosecond time domain is a tool to unravel the dynamics of nuclear and electronic motion in molecular systems. Theoretical insight into the underlying physical processes is ideally gained by solving the time-dependent Schrödinger equation. In this work, methods currently used to solve this equation are reviewed in a compact presentation. These methods involve numerical representations of wavefunctions and operators, the calculation of time evolution operators, the setting up of the Hamiltonian operators and the types of coordinates to be used hereto. The advantages and disadvantages of some methods are discussed.

Ultrafast nonadiabatic photoreactions



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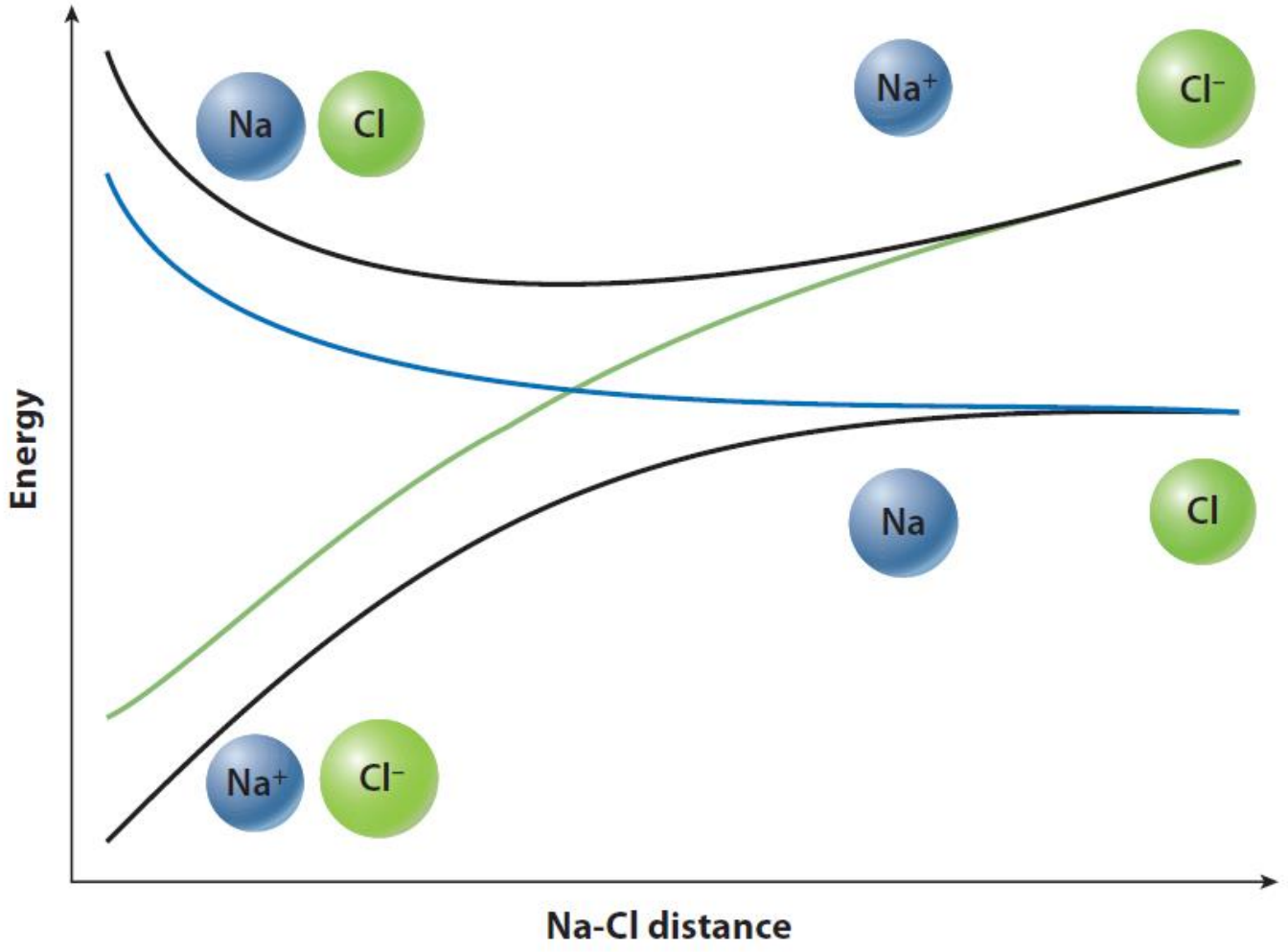
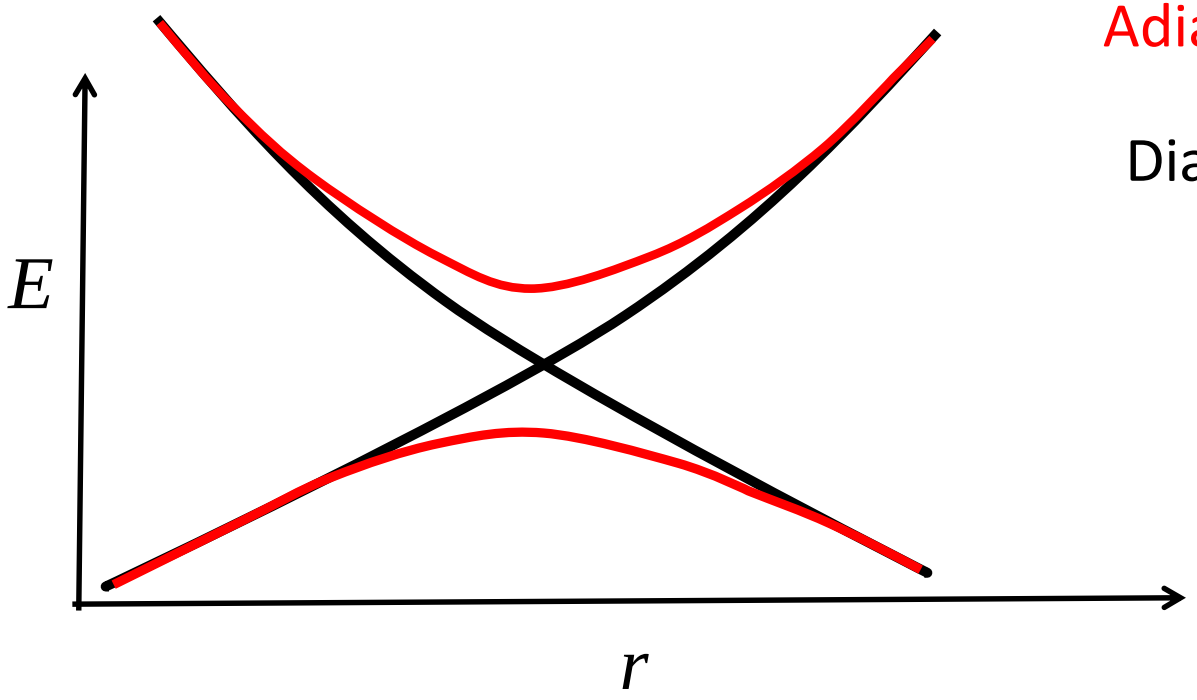
Femtosecond time-resolved spectroscopy of the dynamics at conical intersections, G. Stock and W. Domcke, *in: Conical Intersections, eds: W. Domcke, D. R. Yarkony, and H. Koppel, (World Scientific, Singapore, 2003)*

Background/Basics for Conical Intersections

The Diabatic Picture of Electron Transfer, Reaction Barriers, and Molecular Dynamics, T. Voorhis *et al.* Annu. Rev. Phys. Chem. **61,** 149 (2009).



Avoided Crossing of Two Potential Energy Curves



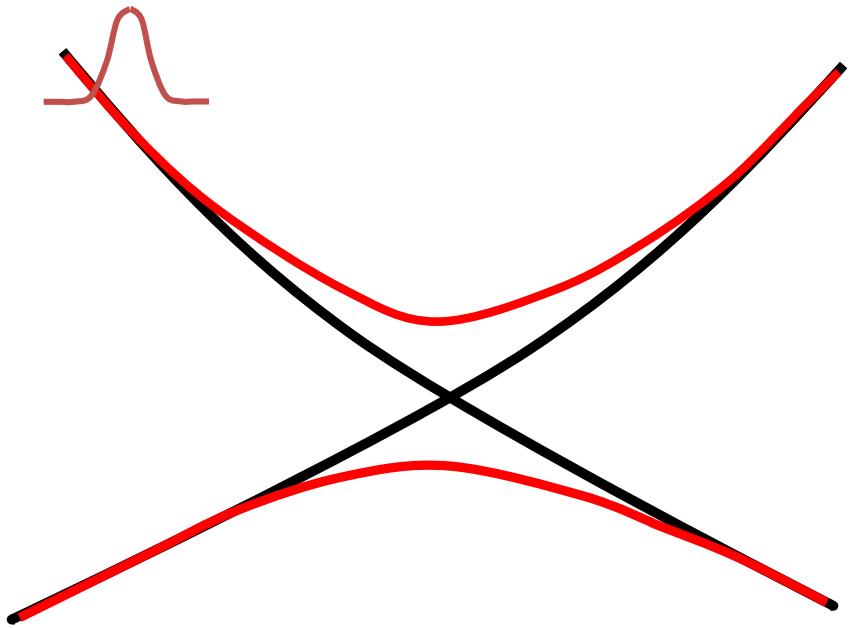
Adiabatic Potentials

Diabatic Potentials

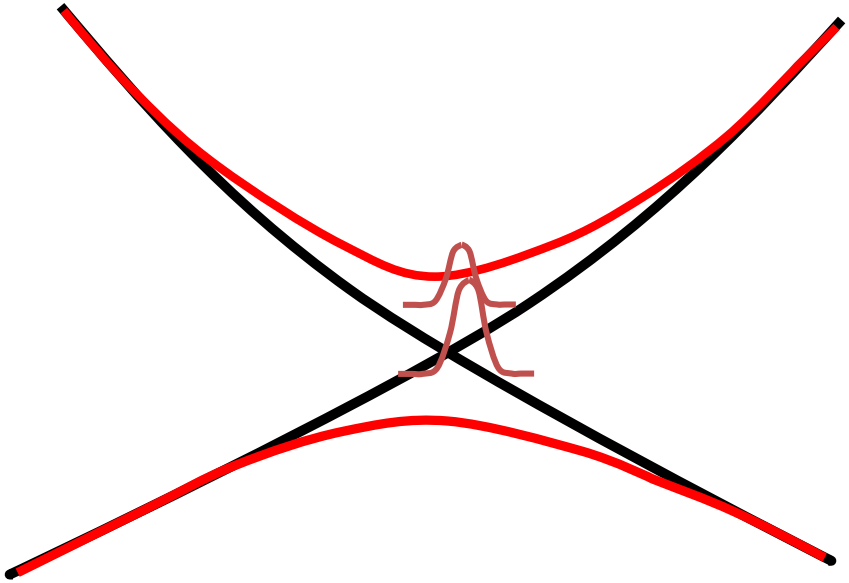
$$\begin{vmatrix} V_{11}(r)-E & V_{12}(r) \\ V_{12}(r) & V_{22}(r)-E \end{vmatrix} = 0$$

V_{ii} are diabatic surfaces

E are adiabatic surfaces



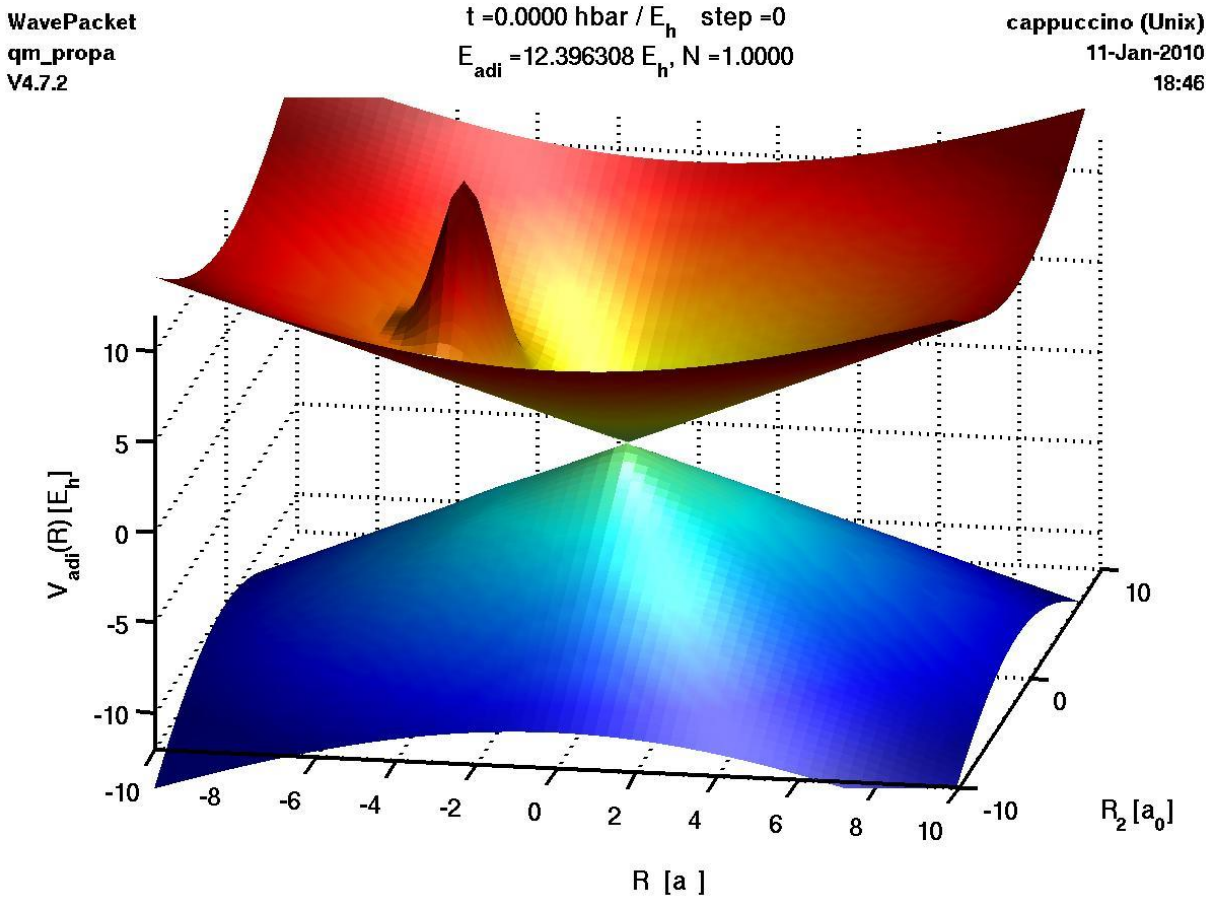
Hopping probability depends on size of V_{12}.
If $V_{12}=0$, red and black curves are same.



$$\begin{vmatrix} V_{11}(r)-E & V_{12}(r) \\ V_{12}(r) & V_{22}(r)-E \end{vmatrix} = 0$$

In higher dimensions this is more complicated.

$$\begin{vmatrix} V_{11}(r,s)-E & V_{12}(r,s) \\ V_{12}(r,s) & V_{22}(r,s)-E \end{vmatrix} = 0$$



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The Challenges of Open Shell Systems

T. A. Barckholtz and T. A. Miller, Int. Rev. Phys. Chem. **17, 435 (1998).**

Hoper, Botschwina,and Koppel. *Theoretical study of the Jahn-Teller effect in the X^2 E CH_3O* JCP **112, 4132 (2000).**

John F. Stanton and Mitchio Okumura, *On the vibronic level structure in the NO_3 radical: Part III. Observation of intensity borrowing via ground state mixing, PCCP*, 2009, 11, 4742 – 4744.

A model spin-vibronic Hamiltonian for twofold degenerate electron systems: A variational *ab initio* study of $\tilde{X}^2E\,CH_3O^{\bullet}$

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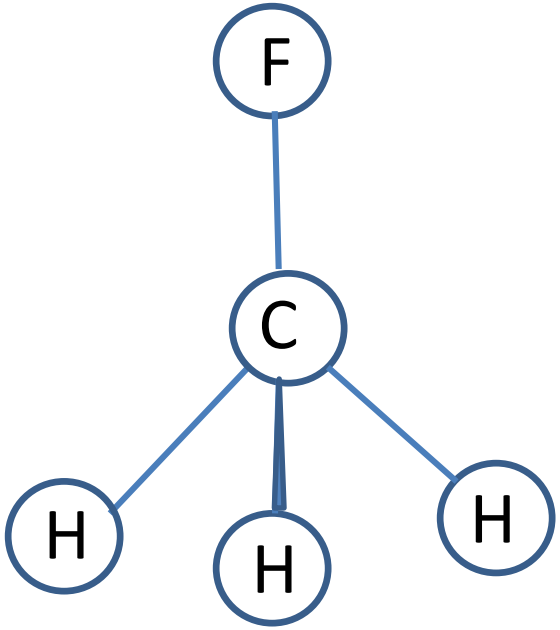
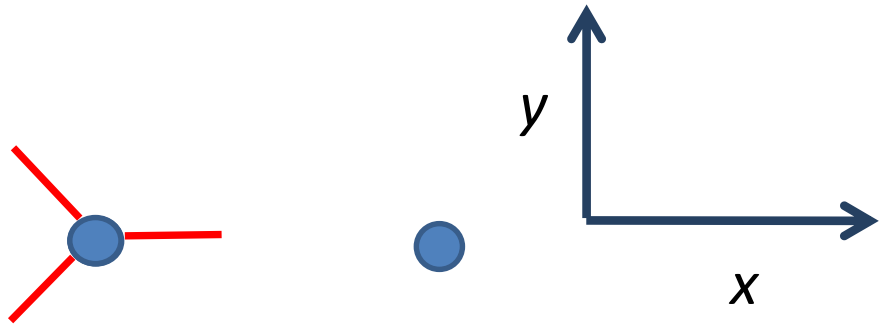
Motivation for Studying Methoxy

There is long standing interest in open shell systems due to their relevance to combustion and atmospheric chemistry.

Given their reactivity, there are inherent experimental difficulties in their spectroscopic characterization. Therefore, theoretical descriptions of the spectroscopy and dynamics can contribute to the characterization of these molecules.

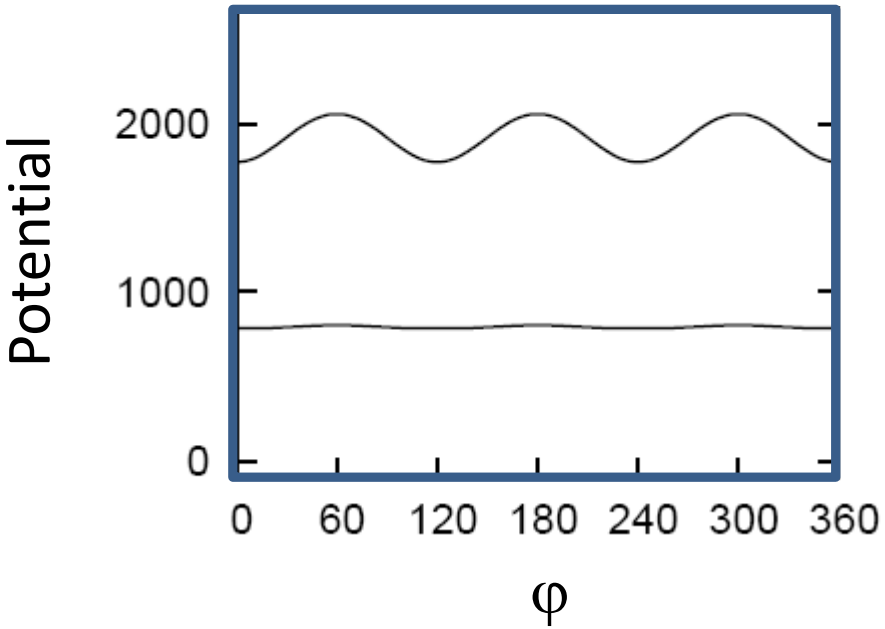

F
C
H
H
H

The potential for CHF_3 bending mode.



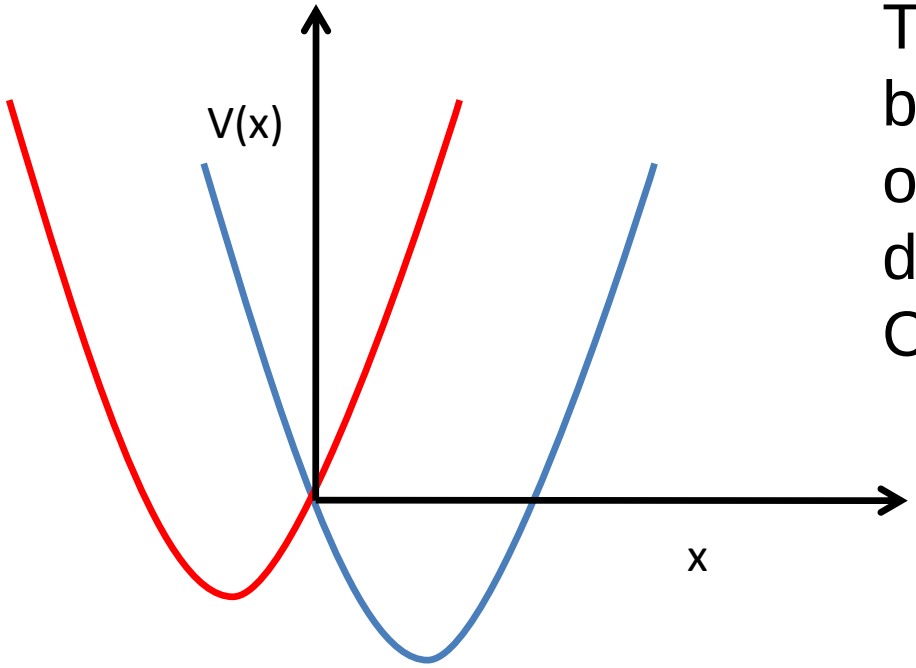
$$x = r\cos\varphi$$

$$y = r\sin\varphi$$



$$V = \frac{k}{2}(x^2 + y^2) + \lambda(3xy^2 - x^3)$$

Form of the potential



The odd electron can be in the p_x or the p_y orbital of O. We get 2 degenerate states at C_{3v} geometry.

What can we learn about the shape of this potential based on symmetry?

Why isn't the minimum at the origin?

The adiabatic potential must have 3-fold symmetry.

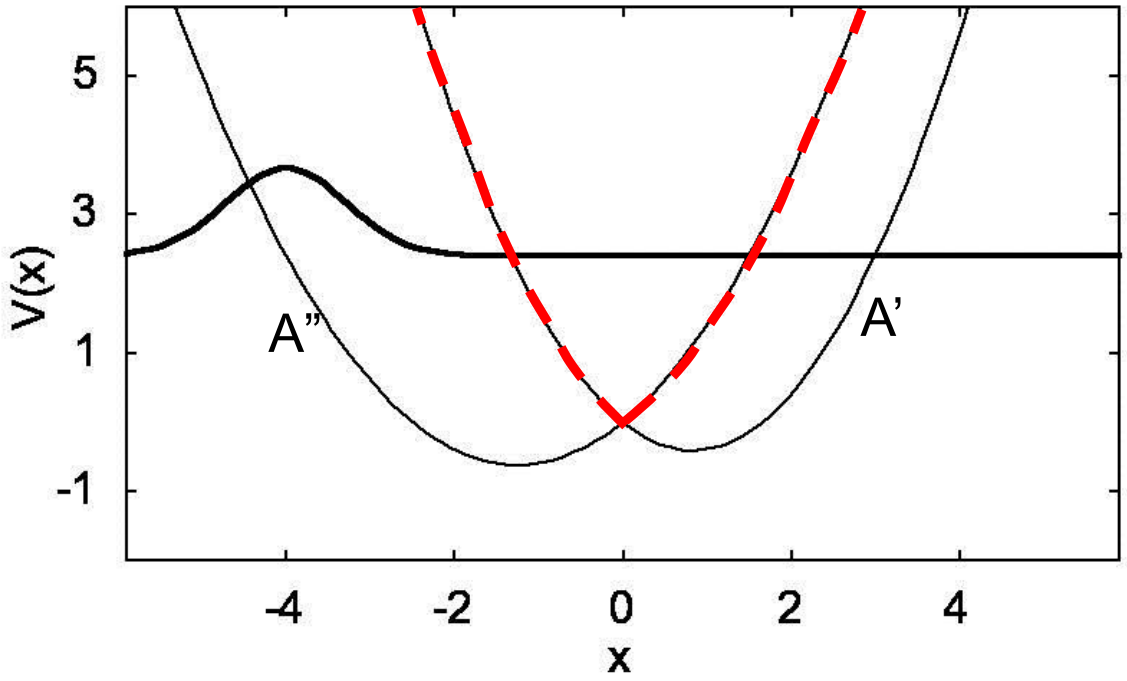
$$|\mathbf{V} - W\mathbf{I}| = 0$$

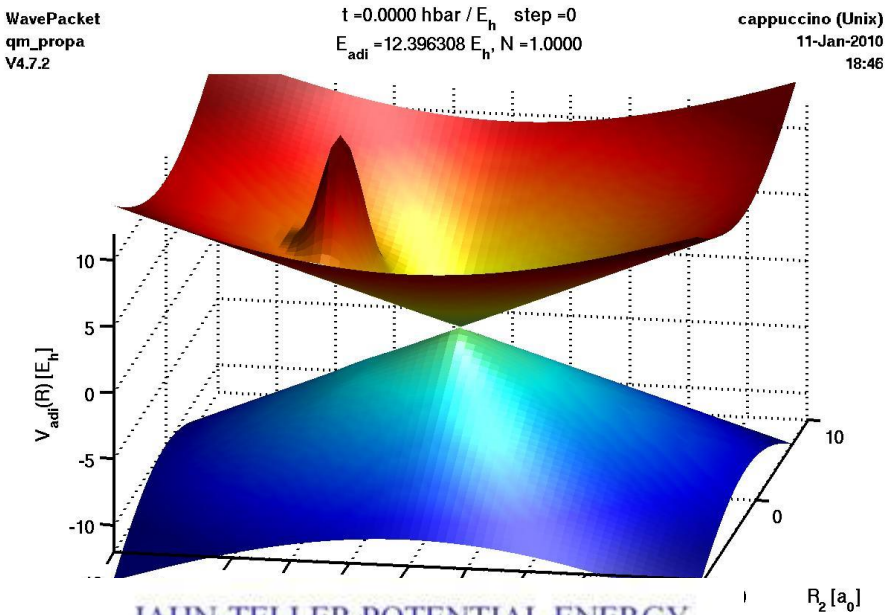
$$\begin{vmatrix} a^{11}\cos(\phi) - W & b^{21}\sin(\phi) \\ b^{12}\sin(\phi) & a^{22}\cos(\phi) - W \end{vmatrix} = 0$$

$$a^{11}a^{22}\cos^2(\phi) - b^{12}b^{21}\sin^2(\phi) - W(a^{11}+a^{22})\cos(\phi) + W^2 = 0$$

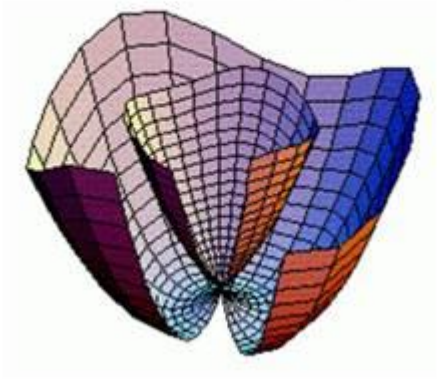
$$W = \pm a^{11}\rho = \pm\alpha\rho$$

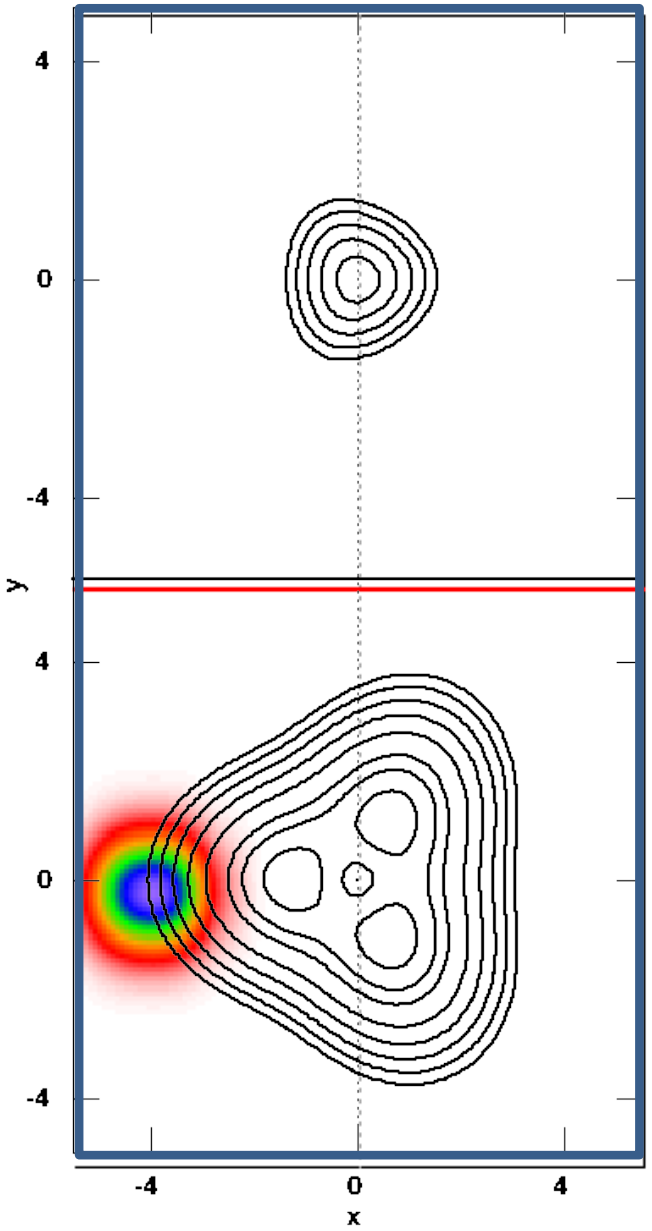
$$V_{11} = \quad f_{11}x + f_{20}(x^2 + y^2) + f_{22}(x^2 - y^2)$$
$$V_{22} = -f_{11}x + f_{20}(x^2 + y^2) - f_{22}(x^2 - y^2)$$
$$V_{12} = -f_{11}y + f_{22}(2xy)$$





JAHN-TELLER POTENTIAL ENERGY SURFACE (PES)





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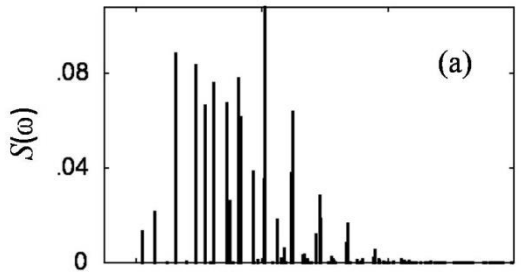
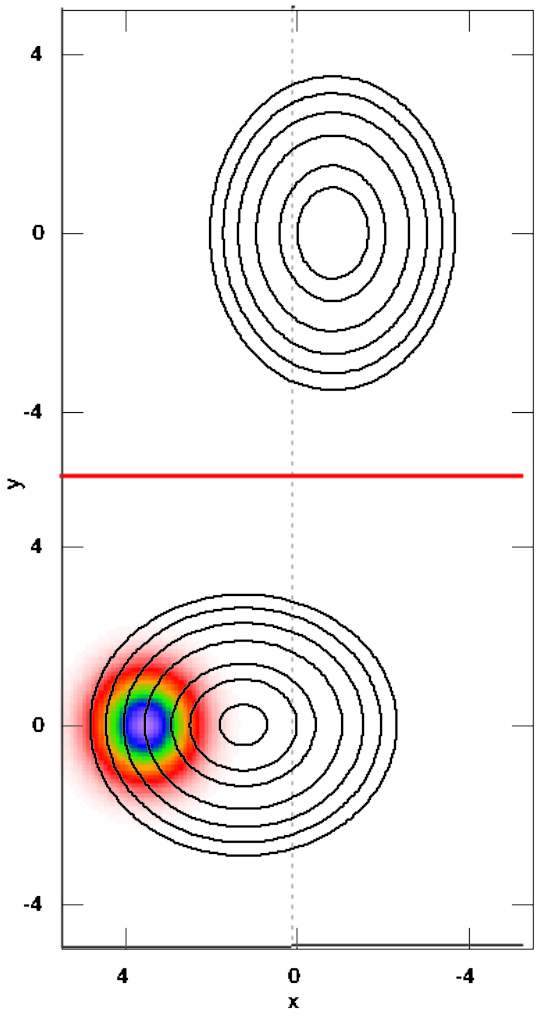
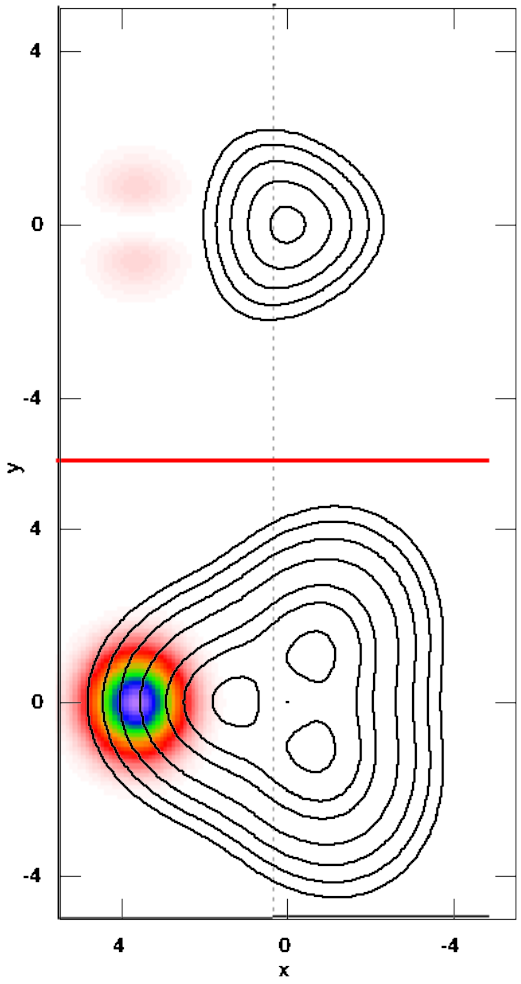
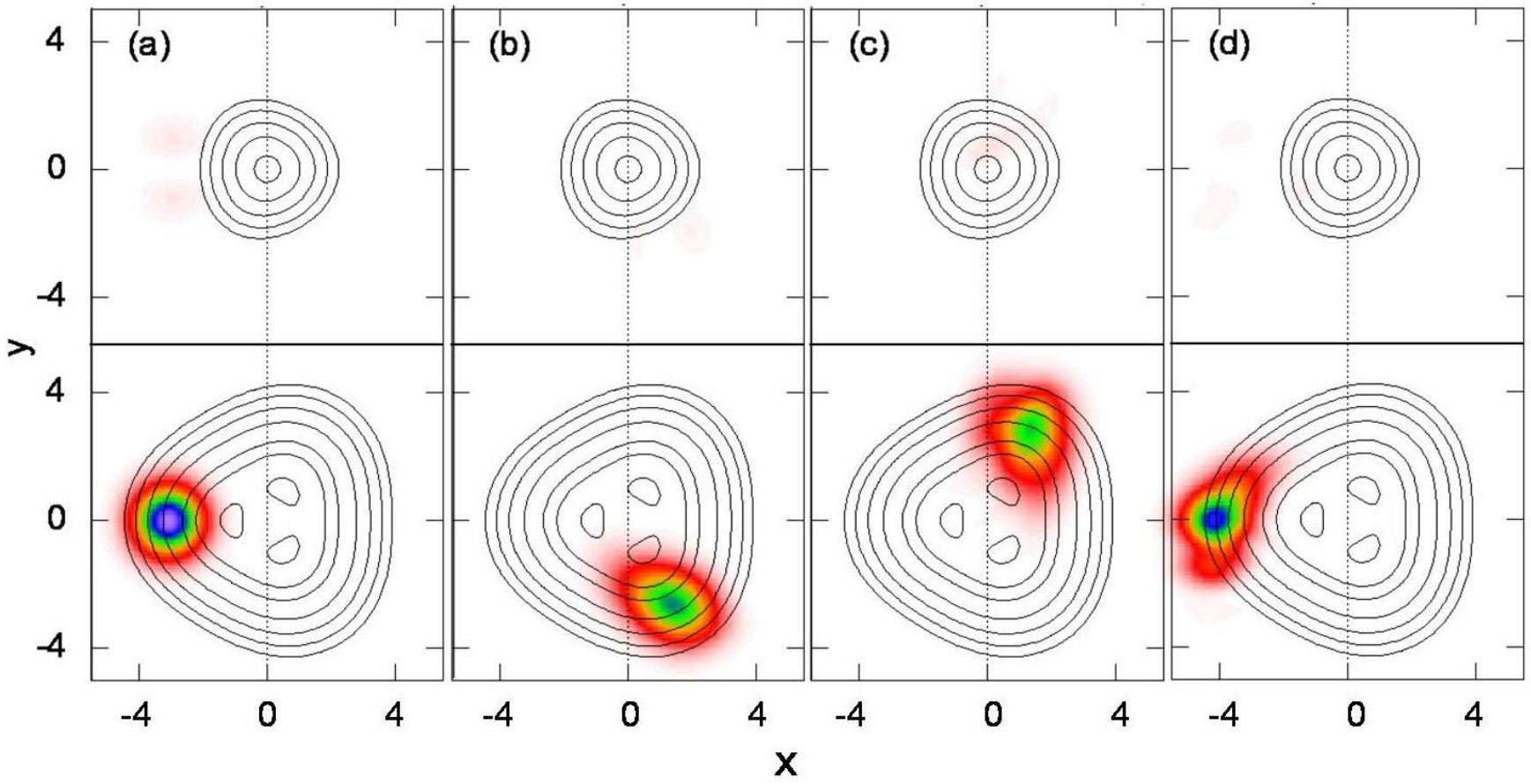
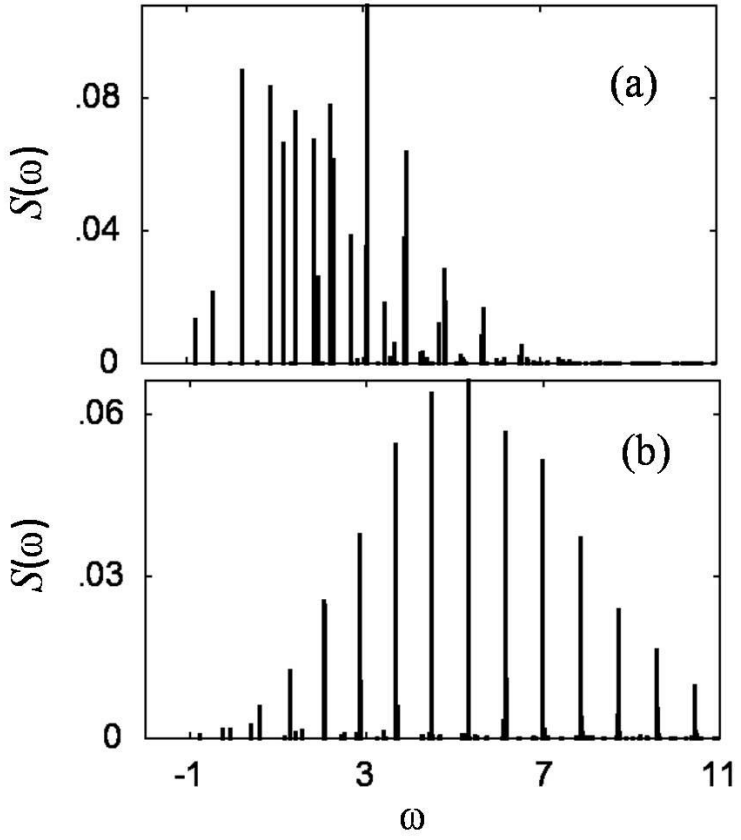

(a)
S(ω)
.08
.04
0
ω


4
0
-4
y
x

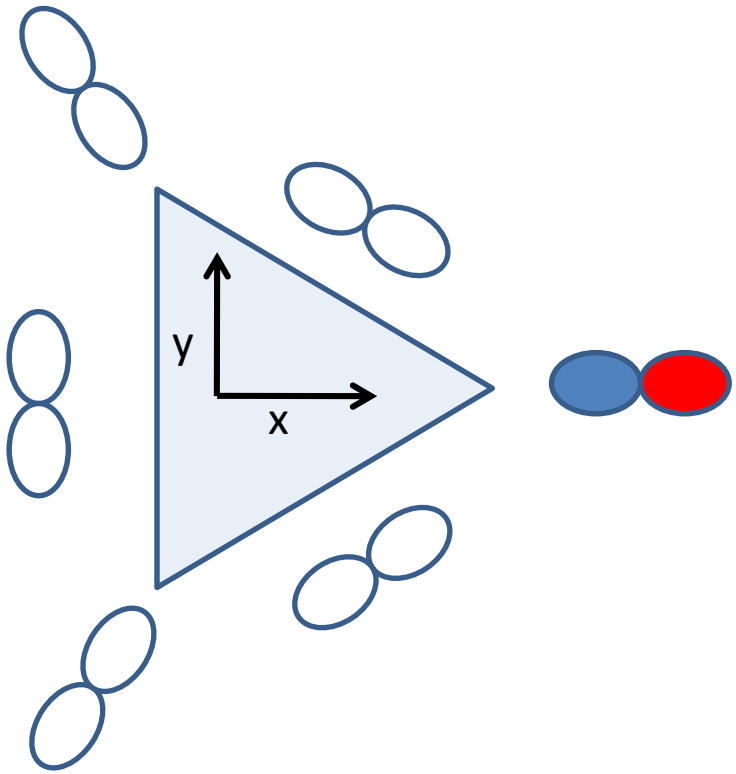

4
0
-4
y
x


(a)
(b)
(c)
(d)
4
0
-4
y
x

Spectra Associated w Gaussians



The Berry Phase



Symmetry wrt to the y axis tells us the potential must have the form

$$V = \begin{pmatrix} \alpha x & \gamma y \\ \gamma y & \beta x \end{pmatrix}$$

Symmetry wrt to the 3 fold rotation tells us the potential must have the form

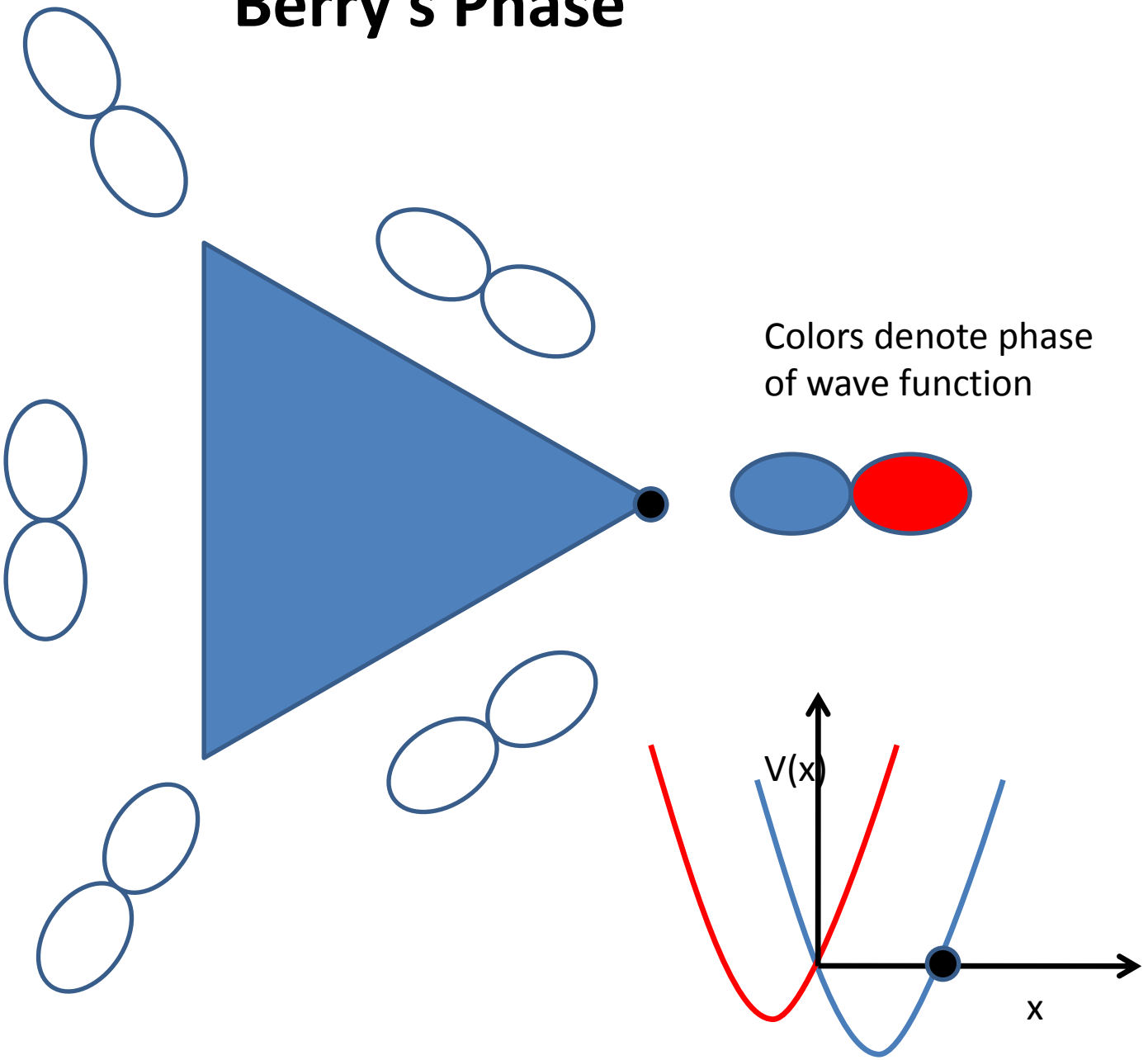
$$\alpha = -\beta = -\gamma$$

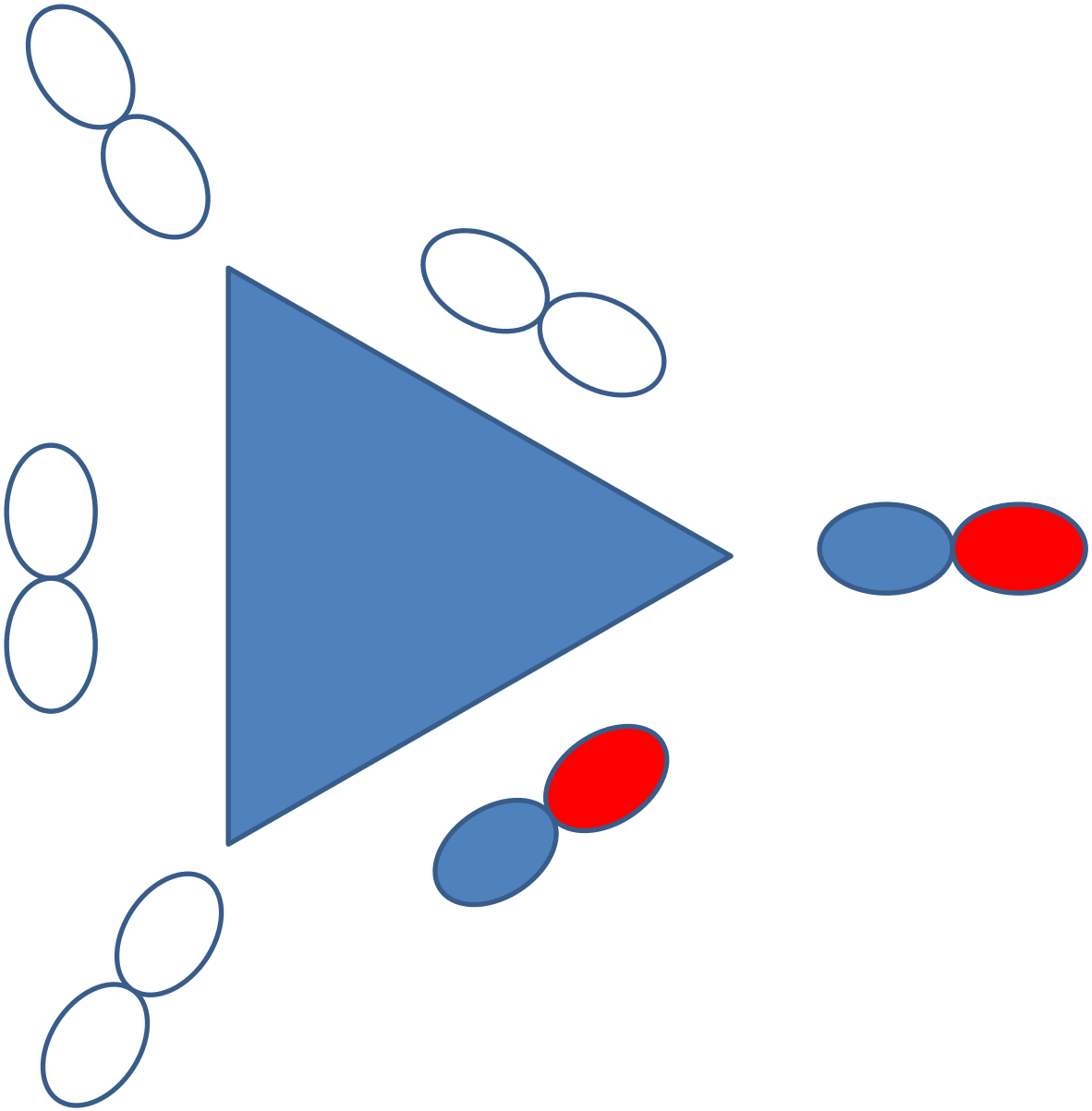
The transformation to the adiabatic representation is given by $W=U^{T}VU$

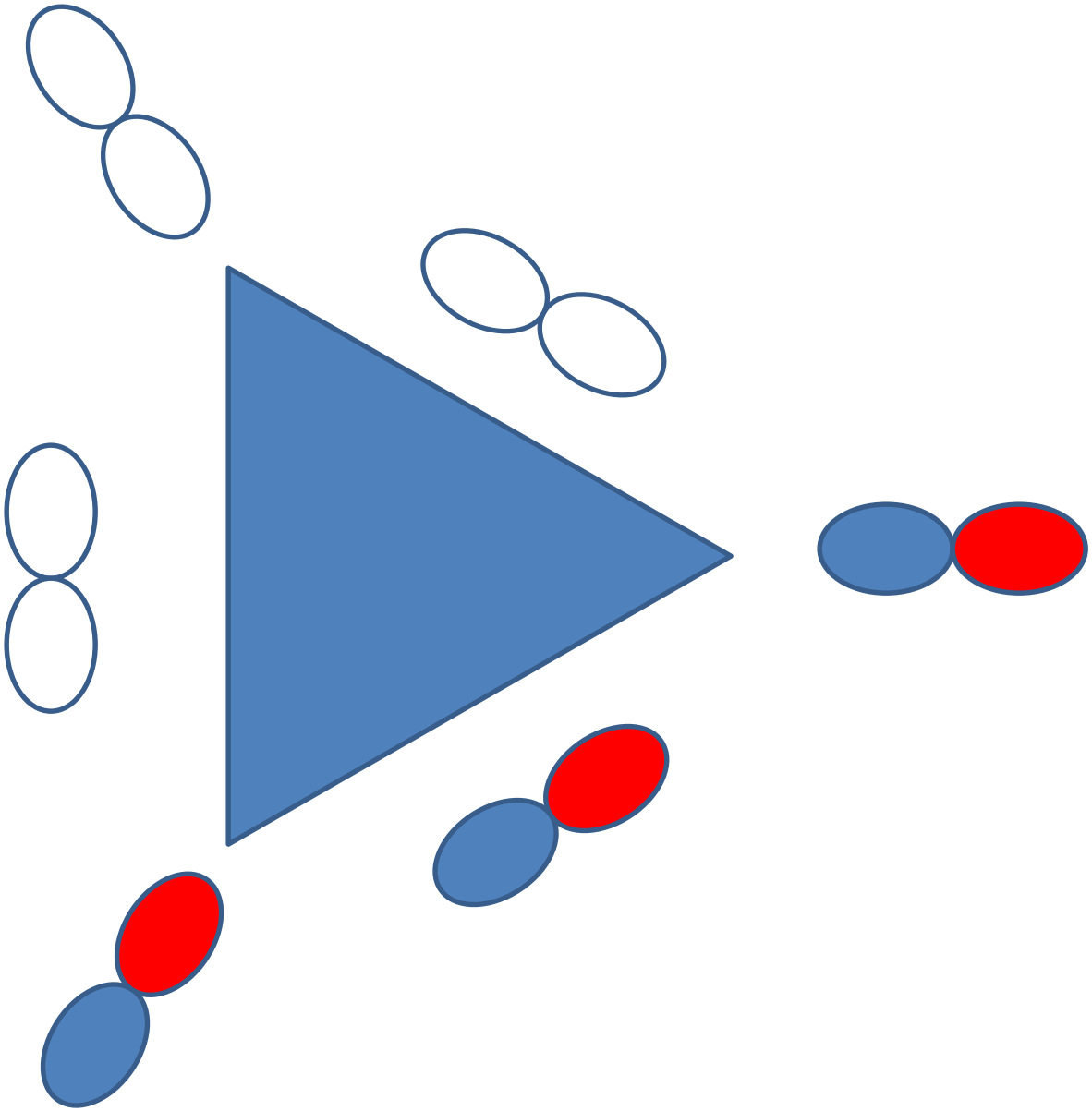
$$U = \begin{pmatrix} \cos(\phi/2) & \sin(\phi/2) \\ -\sin(\phi/2) & \cos(\phi/2) \end{pmatrix}$$

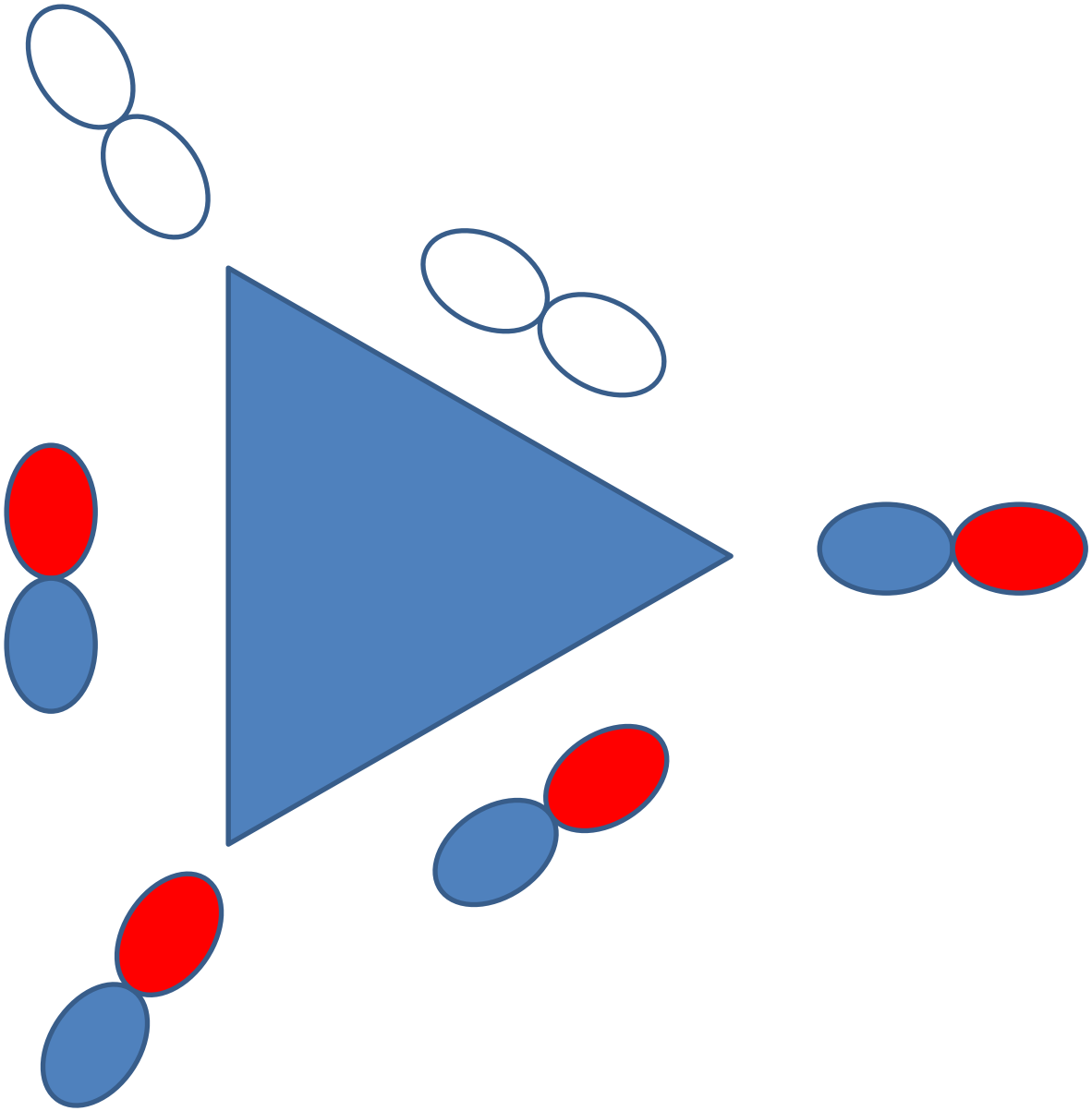
$$W = \begin{pmatrix} \alpha\rho & 0 \\ 0 & -\alpha\rho \end{pmatrix}$$

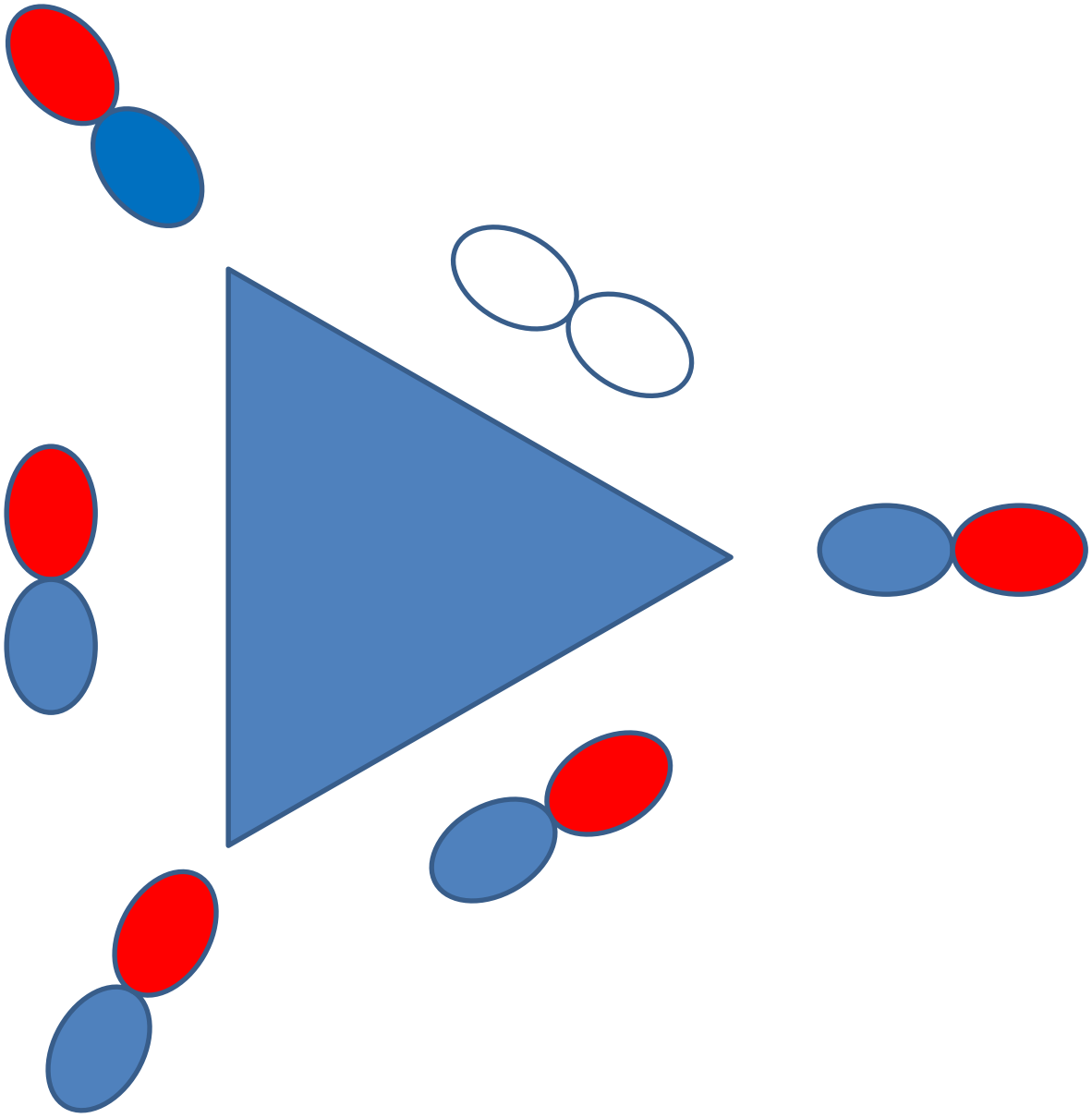
Berry's Phase

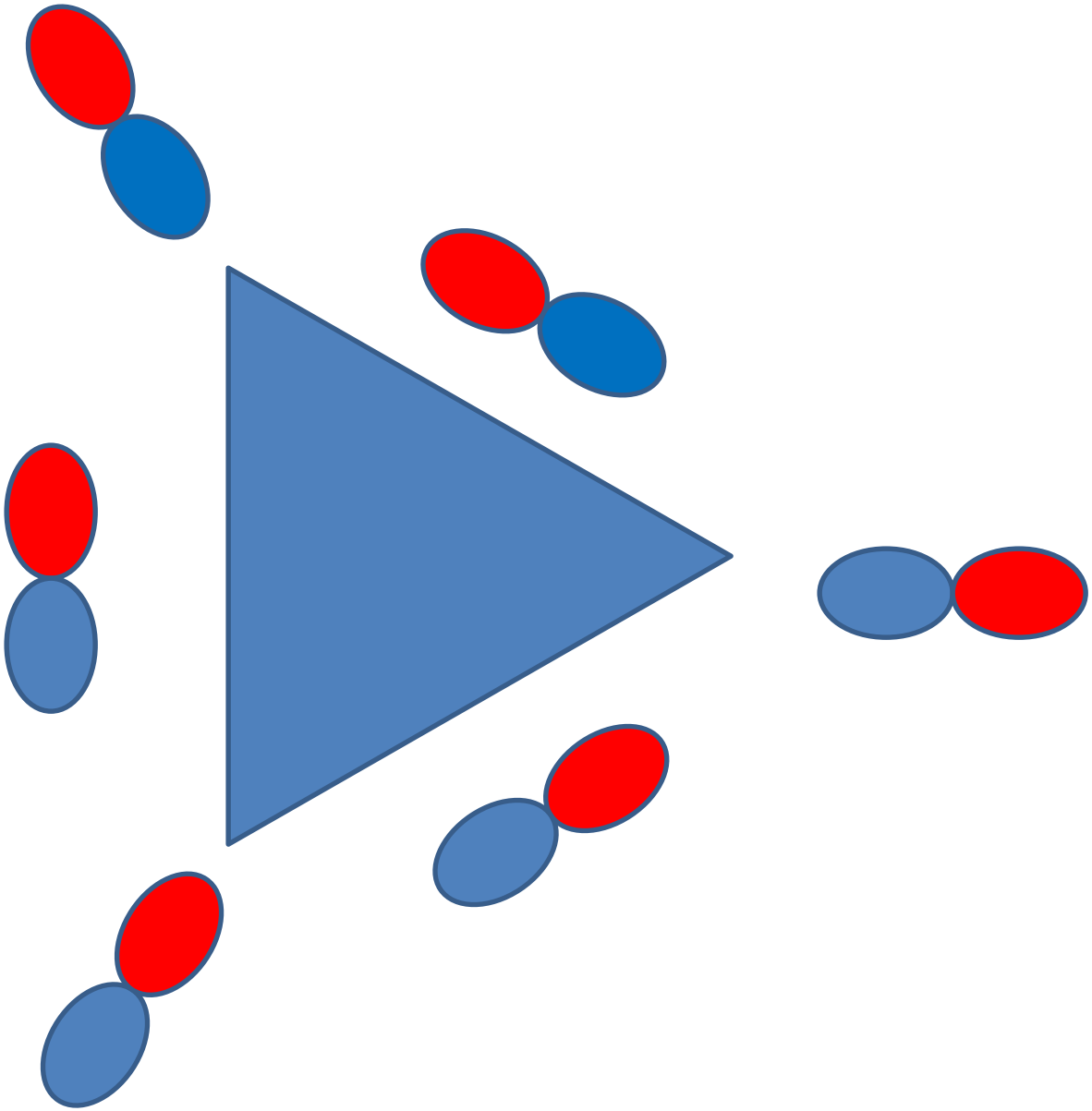


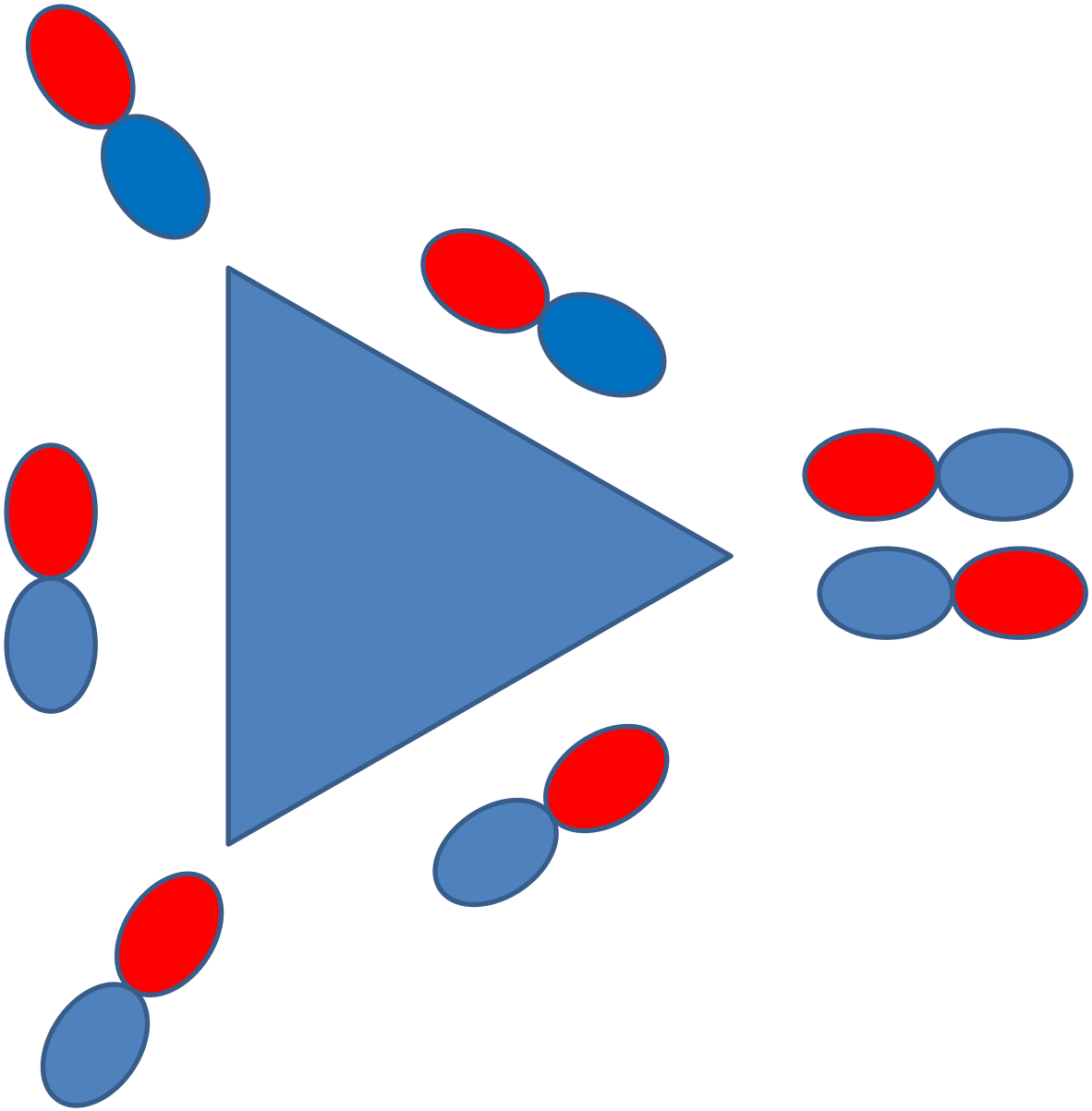












Vibrational dynamics around the conical intersection: a study of methoxy vibrations on the $\tilde{X}^2E$ surface

Jayashree Nagesh and Edwin L. Sibert* ***Phys. Chem. Chem. Phys.***, 2010, **12**, 8250-8259

THE JOURNAL OF CHEMICAL PHYSICS **134**, 044101 (2011)

On the construction of quasidiabatic state representations of bound adiabatic state potential energy surfaces coupled by accidental conical intersections: Incorporation of higher order terms

Joseph Dillon,[1,a)] David R. Yarkony,[1,b)] and Michael S. Schuurman[2,c)]
[1]*Department of Chemistry, Johns Hopkins University, Baltimore, Maryland 21218, USA*
[2]*Steacie Institute for Molecular Sciences, National Research Council, Ottawa K1N 6C1, Canada*

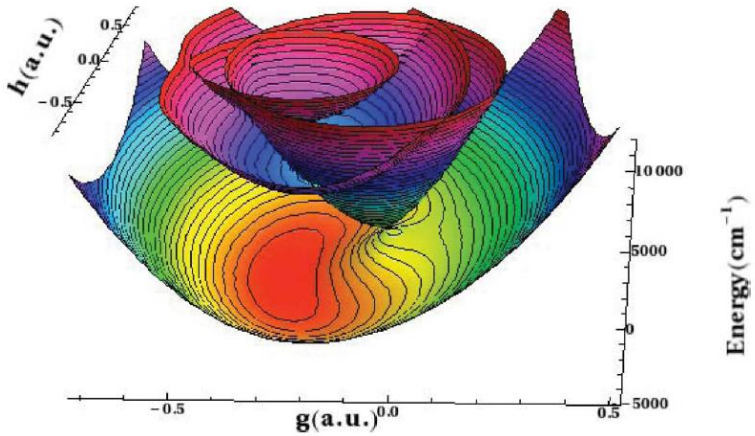


FIG. 2. Plot of energy of $^2B_1$, $^2A_1$, $^2A_2$, and $^2B_2$ states in the g–h plane.

Some concluding comments.

Nonadiabatic reactive scattering in atom+triatom systems: Nascent rovibronic distributions in $F+H_2O \rightarrow HF+OH$

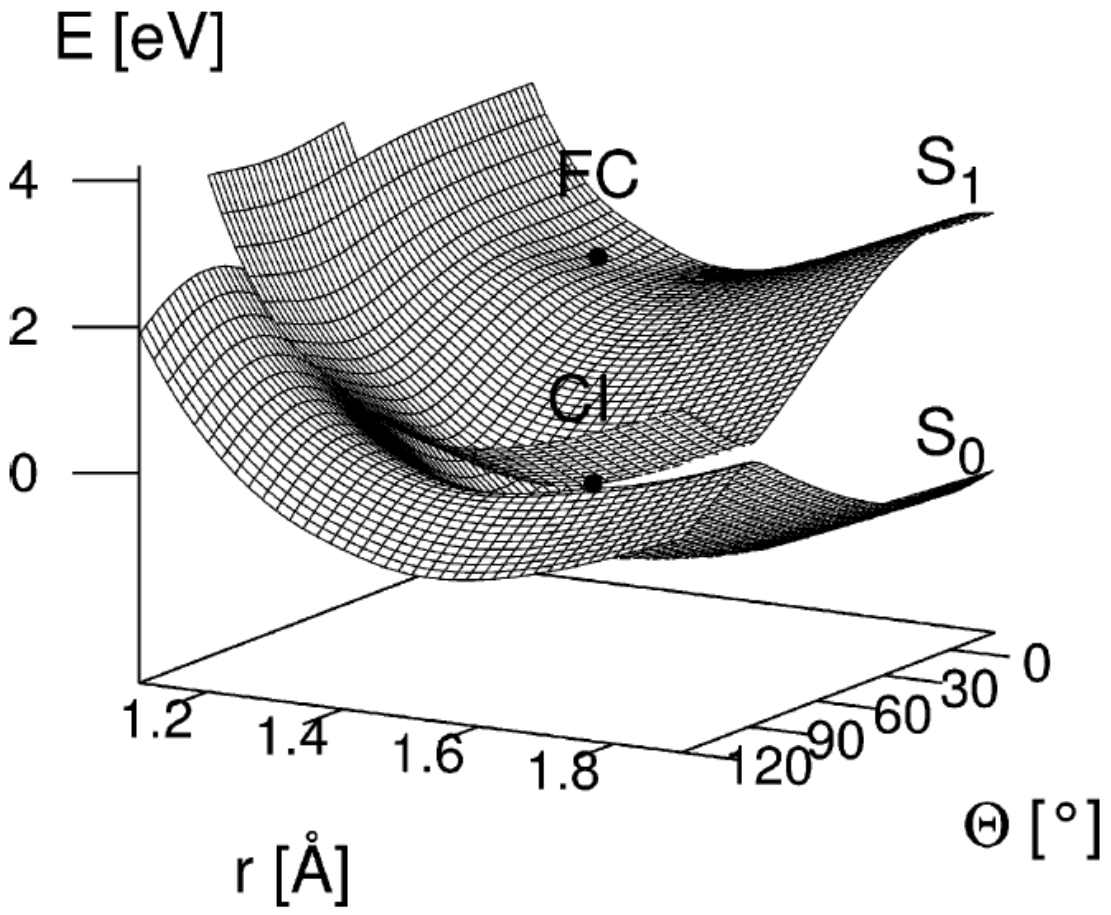
This is due in part to the greatly increased complexity of polyatomic systems, the subsequent computational cost of theoretically treating multisurface dynamics, and the growing importance of conical intersections in such problems.

The notion that a reaction occurs on a single electronic surface remains the dominant zeroth order paradigm in chemical physics. However, this situation has been slowly changing, as nonadiabatic reaction dynamics in benchmark triatomic systems have recently received considerable experimental and theoretical attention.

Michael Ziemkiewicz and David J. Nesbitt[a)]

THE JOURNAL OF CHEMICAL PHYSICS 131, 054309 (2009)

Excited-State Charge Transfer at a Conical Intersection: Effects of an Environment



Irene Burghardt*,† and James T. Hynes*,†,‡

J. Phys. Chem. A **2006,** *110,* 11411−11423