When are electrons fast and are Born and Oppenheimer correct?

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Han-Sur-Lesse, Winter 2003

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1d. What is the limit of spectral structure: intra molecular energy relaxation?

2a. Schrödinger Equation and the Born-Oppenheimer Separation

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2c. Non-adiabatic interactions

2d. Diabatic and adiabatic states

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Four hours of Lectures

3a. Collisions with 0 eV electrons: fast or slow

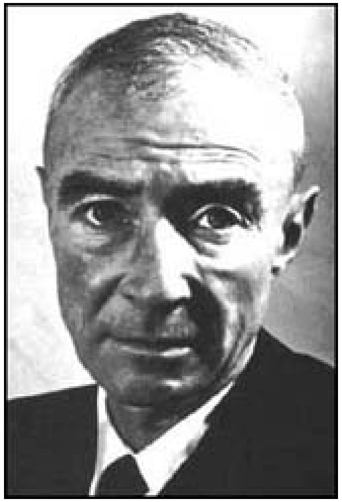
3b. Continua in molecular physics

3c. Dissociative recombination: radiation, dissociation and autoionization

3d. A mystery for theoretical chemists

Lecture 1 --- 1

- A short history:
- **Robert Oppenheimer**
- **Julius Robert Oppenheimer** was born in on 22nd April, 1904. He studied at Harvard University before working with Ernest Rutherford at Cambridge University and later with Max Born in Gottingen, Germany.



Lecture 1 --- 2

- A short history:
- **Max Born** was born in Breslau, Germany, on 11th December, 1882. He studied physics at the University of Gottingen and obtained his doctorate in 1907 .

Grandfather of Olivia Newton-John

Lecture 1 --- 3

One-particle Schrödinger Wave- Equation:

$$i\hbar\frac{\partial\psi(\mathbf{r},t)}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r},t) + V(\mathbf{r})\psi(\mathbf{r},t)$$

Wave function

Kinetic energy

Potential energy

Erwin Schrödinger

Born: 12 Aug 1887 in Erdberg, Vienna, Austria
Died: 4 Jan 1961 in Vienna, Austria

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One-particle Schrödinger Wave- Equation: time dependent

$$i\hbar\frac{\partial\psi(\mathbf{r},t)}{\partial t}=-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r},t)+V(\mathbf{r})\psi(\mathbf{r},t)$$

Potential energy: if time independent, then

phase factor:

the magic of QM

$$\psi(\mathbf{r},t)=\psi(\mathbf{r})e^{-iEt/\hbar}$$

The observable!!

Another is transition strength

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r})+V(\mathbf{r})\psi(\mathbf{r})=E\psi(\mathbf{r})$$

One-particle Schrödinger Wave-Equation: time independent

The Molecular Schrödinger Wave- Equation: all interactions of known electrostatic nature

$$\hat{T} = -\frac{\hbar^2}{2}\sum_i \frac{1}{m_i}\nabla^2$$

Total kinetic energy

$$\hat{V}(\mathbf{r}) = \sum_{i>j} \frac{Z_i Z_j e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

Total potential energy, i , j nuclei/electrons

$$\hat{H} = -\sum_A \frac{1}{2M_A}\nabla_A^2 - \sum_i \frac{1}{2}\nabla_i^2 + \sum_{A>B} \frac{Z_A Z_B}{R_{AB}} - \sum_{Ai} \frac{Z_A}{r_{Ai}} + \sum_{i>j} \frac{1}{r_{ij}}$$

The Hamiltonian in the case of a molecule, A,B: nuclei; ‘i’ electrons (in atomic units)

Lecture 1 --- 5b

Atomic Units:

m_e (mass electron)= 1 a.u. (9.1 10^{-31} kg)
r_e(radius first Bohr orbit)) = 1 a.u. (0.529 10^{-10} meter)
t = 1 a.u. (time of 1 rad of the round trip of 13.6 eV electron) (2.417 10^{-17} sec)
q_e(charge electron) = 1 a.u. (1.60 10^{-19} C)

Derived:
v = 1 a.u ($c/\alpha = 3\ 10^8/137$ m/s)
E= 1.a.u. (27.21 eV, 4.4 10^{-18} J = 1 Rydberg)
$h/(2\pi)$ = 1 (a.u.of energy)*1 a.u. of time) =1 (1.05 10^{-34} Js)
c= 137 a.u. of velocity

The Equation Providing: Potential Energy Surface

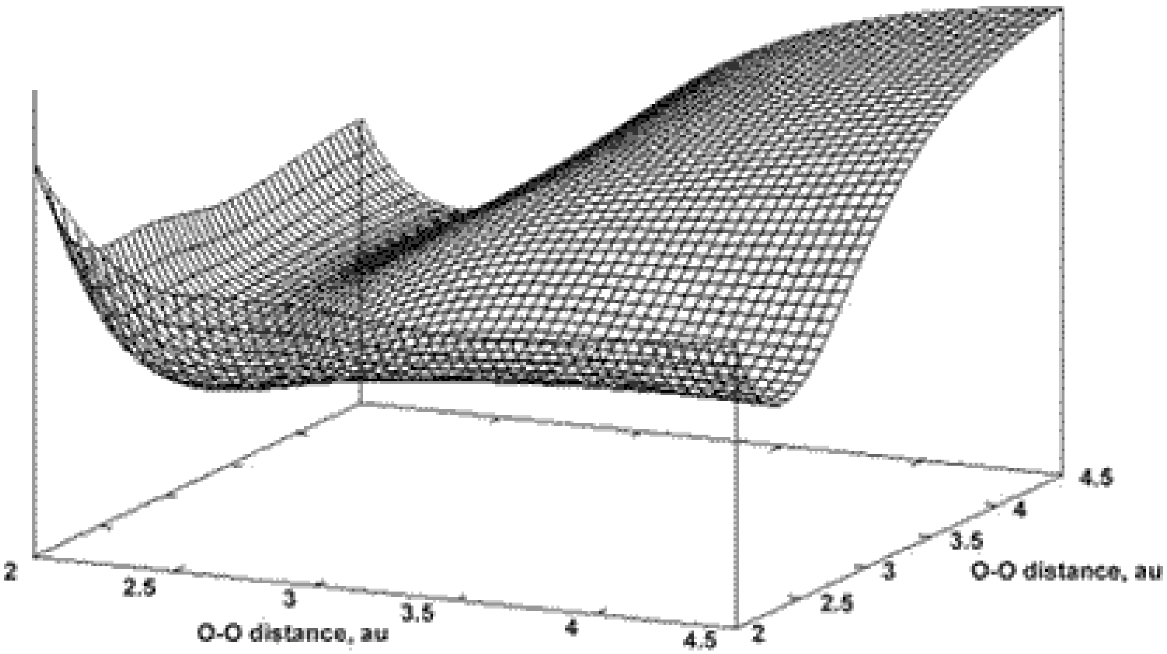
$$\left[-\frac{1}{2}\sum_{i}\nabla_i^2-\sum_{iA}\frac{Z_A}{r_{iA}}+\sum_{i>j}\frac{1}{r_{ij}}\right]\psi_e(\mathbf{r};\mathbf{R})=E_e\psi_e(\mathbf{r};\mathbf{R})$$

$E_e(\mathbf{R})$: multidimensional potential energy surface:

Electrons Calculated Away:

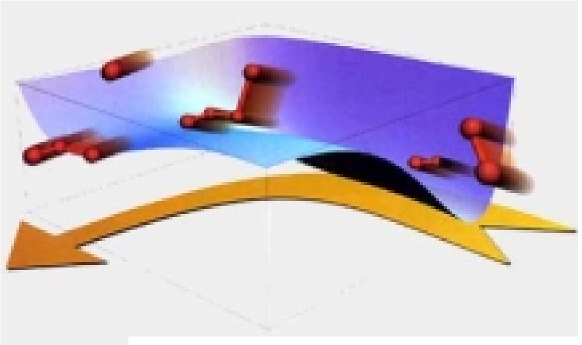
Is this an observable?

Lecture 1 --- 7

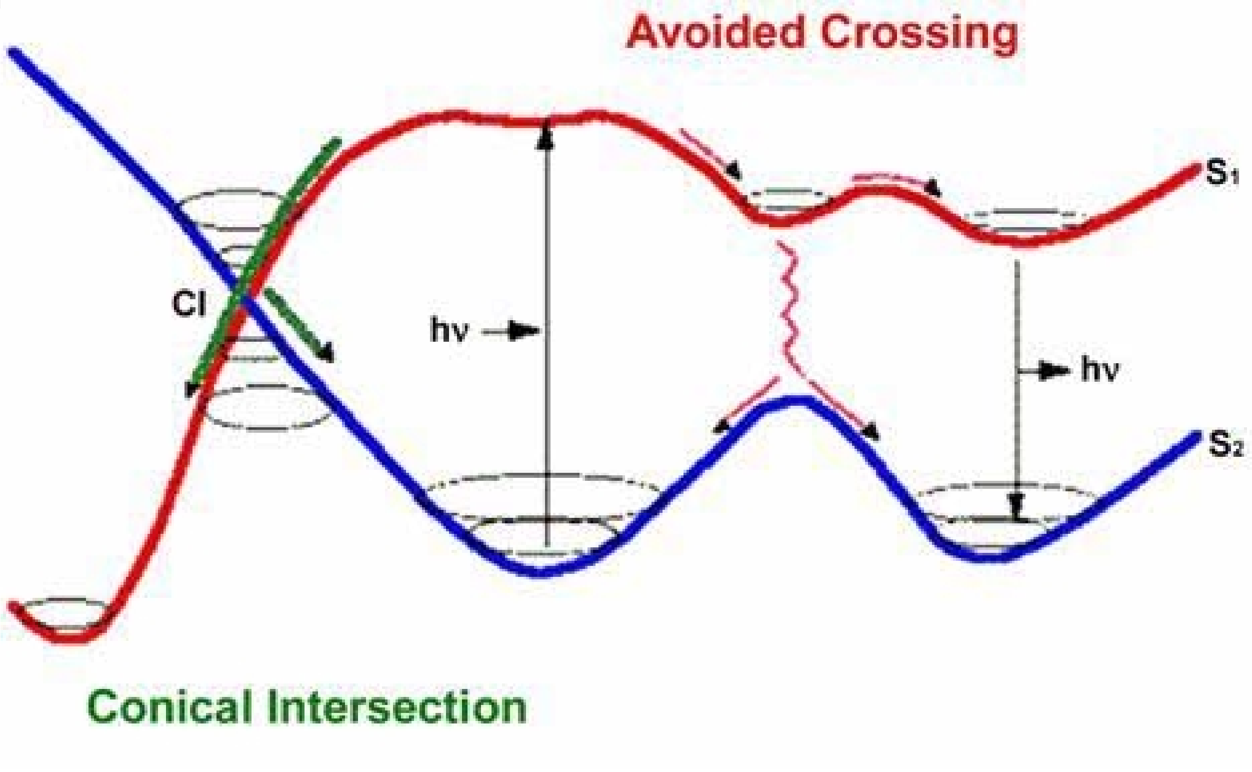


This figure shows O_3, where the bond angle of ozone is constrained at 117°, and the two bond lengths form the *x*- and *y*-axes of the graph:

Lecture 1 --- 8



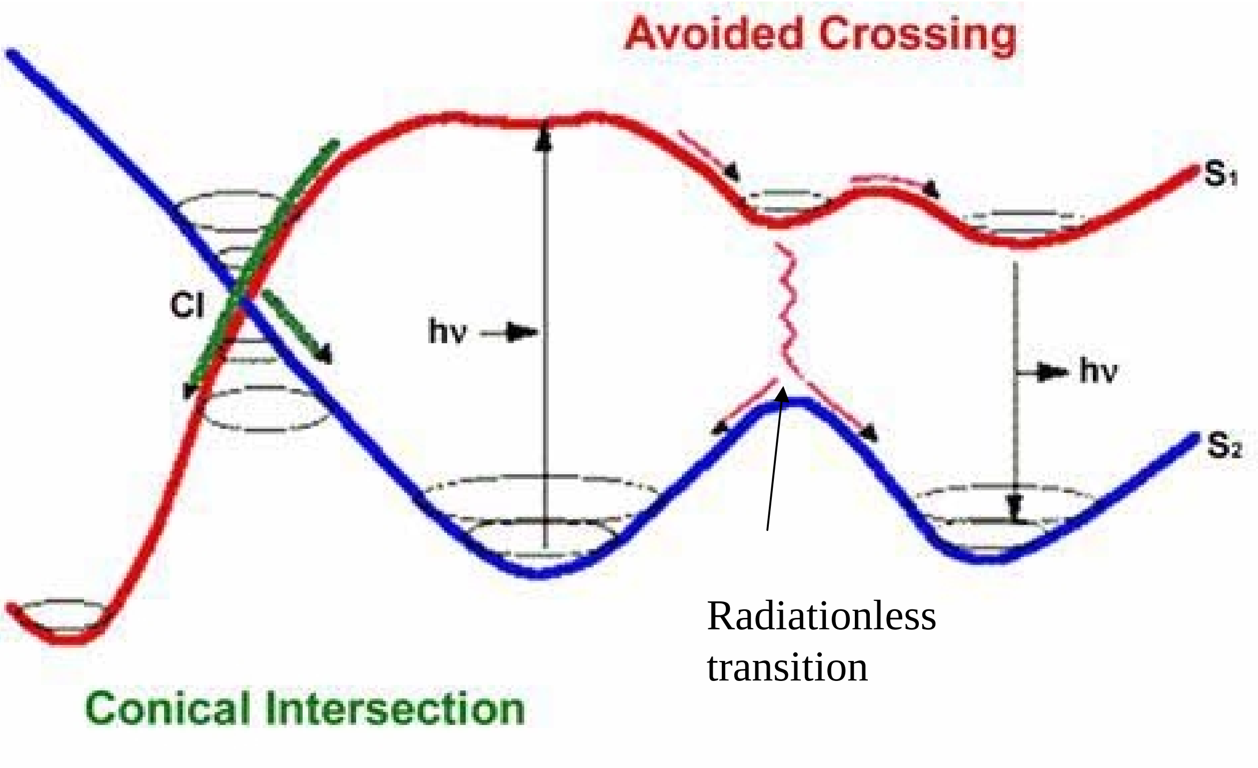
Complex PES and PES complexities



Complex PES and PES complexities

Eugene Paul Wigner
Born: 17 Nov 1902 in Budapest, Hungary
Died: 1 Jan 1995 in Princeton, New Jersey, USA

Next lecture!



Radiationless transition

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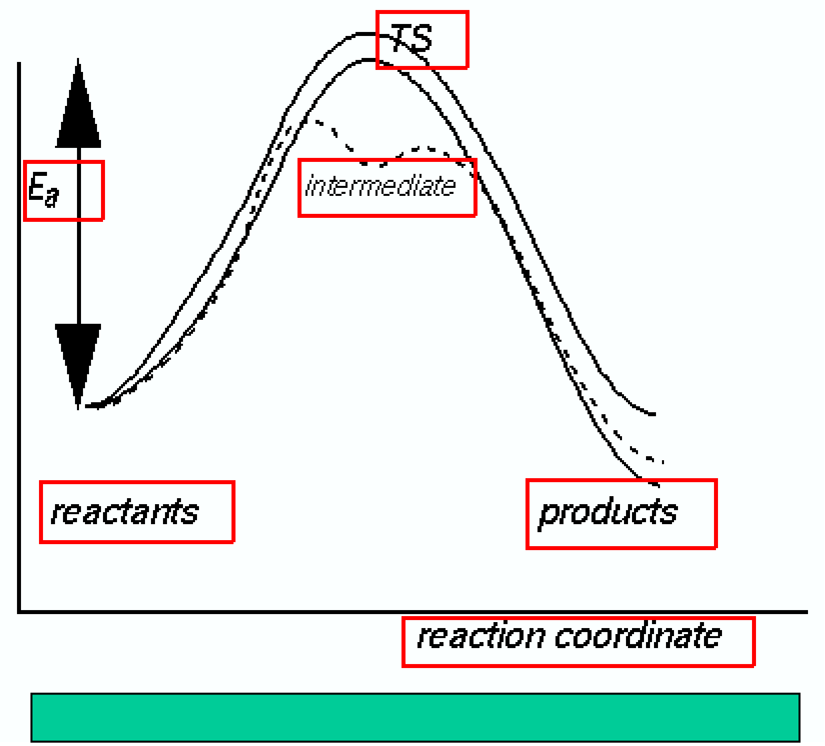


Discussion Points:

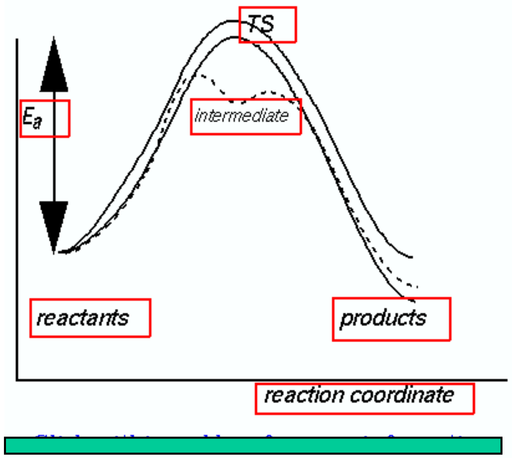
(1) Does nature want to go to minimum in PES?

(2) How does nature go from reactants to products?

(3) Single versus very many collisions

(4) Internal degrees of freedom as local energy bath (entropy)

Lecture 1 --- 10b



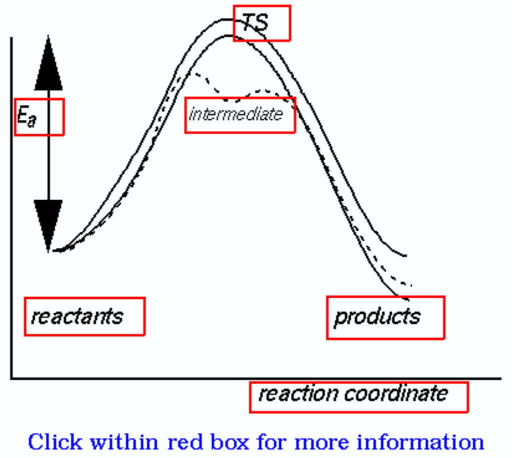
Discussion Points:

(1) Does nature want to go to a minimum in PES?

Answer:

NO, no such a law exists. Only conservation of energy in a closed system. Hence preference is observed in case of dissipation possibilities (multiple collisions, radiation) or the practical situation that the density of states in degrees of freedom not shown in the PES effectively generate continuum allowing ‘dissipation’.

Lecture 1 --- 10c



Discussion Points:

(1) How does nature go from reactants to products?

Answer:

- Start at proper energy (total energy above TS)
- Embed reactants in collisions such that thermal fluctuations help the way up and over the TS
- Remove products

Lecture 1 --- 11

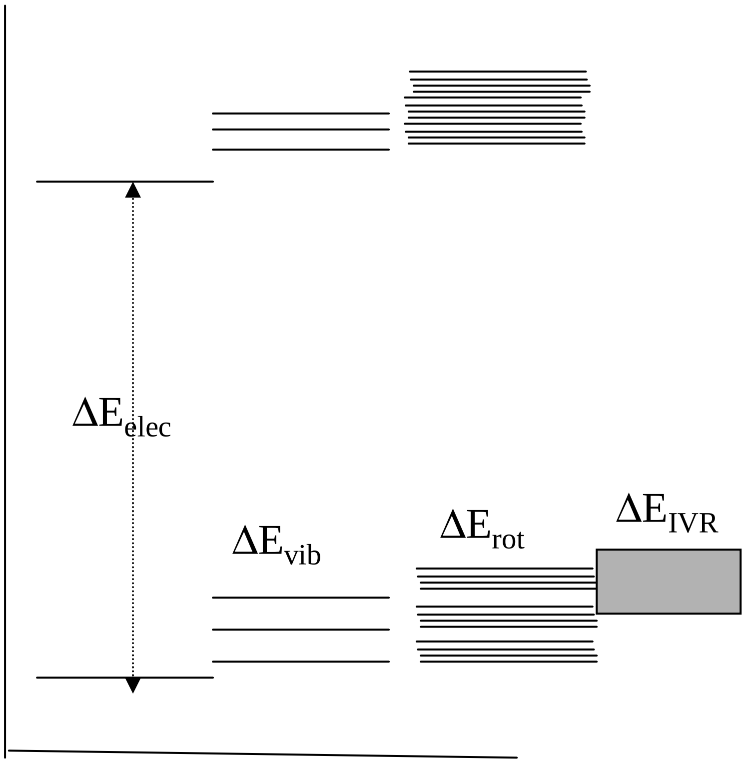
Eigenvalue Problems and Time Scales of Associated Classical Motion.

The solution of the SE:
eigen-energies
excitation strengths

$\Delta E . \Delta\tau > h$

Classical period

Energy spacing



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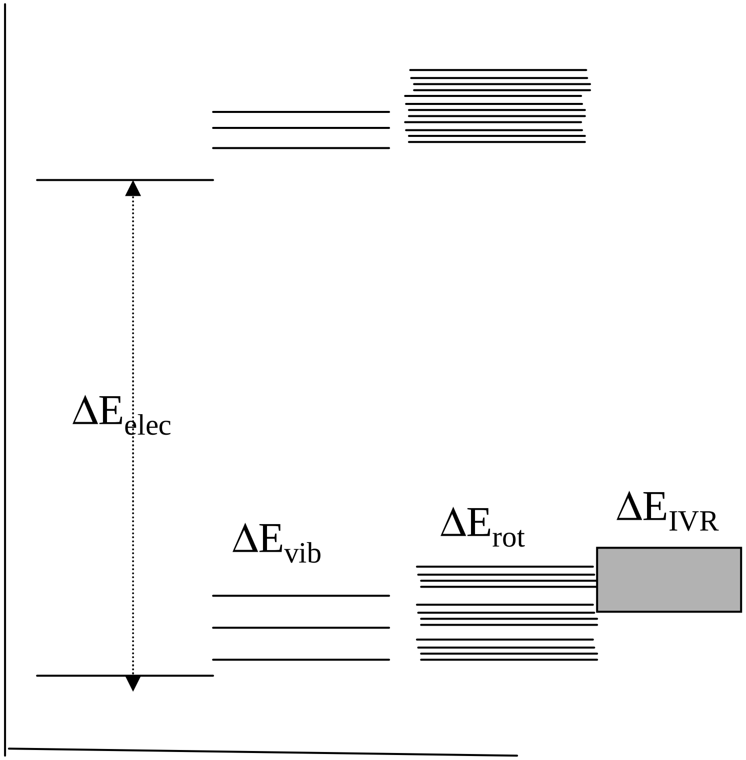
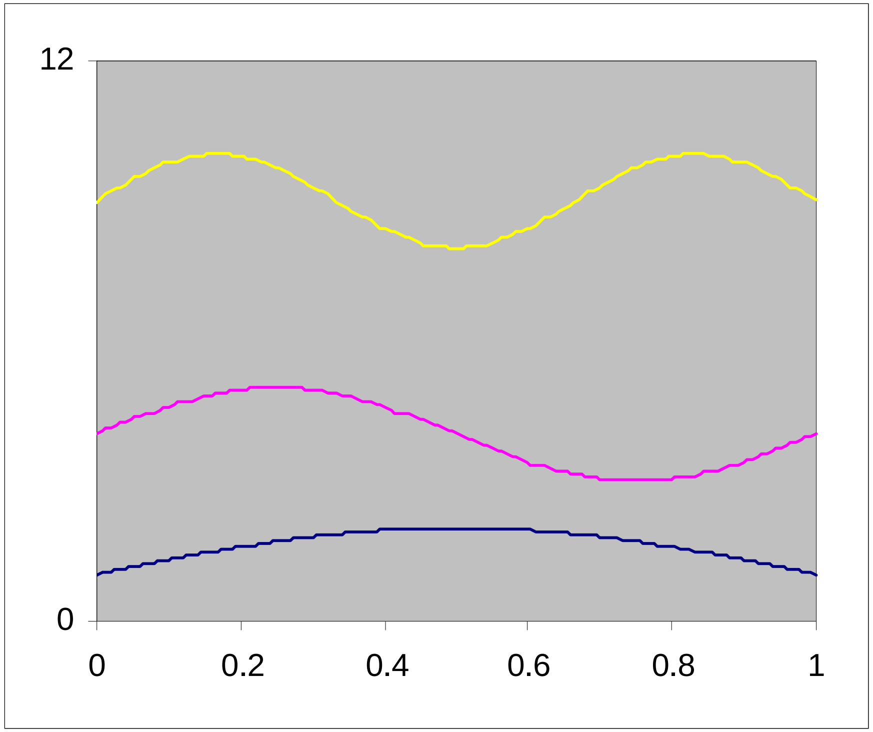
tau (sec)	E (eV)	E(cm-1)	Label
1.52E-16	27.2	219382.4	electronic
3.04E-16	13.6	109691.2	
1.03E-15	4	32262.12	
#DIV/0!	0	0	
1.38E-14	0.3	2419.659	vibration
4.13E-14	0.1	806.553	
#DIV/0!	0	0	
4.13E-13	0.01	80.6553	rotation
2.07E-13	0.02	161.3106	H2
#DIV/0!	0	0	
4.13E-12	0.001	8.06553	rotation
2.07E-12	0.002	16.13106	heavy
#DIV/0!	0	0	
4.13E-10	**0.00001**	**0.080655**	**pi-sigma**
2.07E-10	**0.00002**	**0.161311**	**symmetry**



$$\Delta E.\ \Delta\tau > h$$

Lecture 1 --- 13

$\Delta E.\ \Delta\tau > h$: energy spacing and classical periods



Particle in box

$E_n = n^2h^2/(8mL^2)$

$\Delta E_{n+1.n} = (2n+1)h^2/(8mL^2)$

$v = \sqrt{}(2E/m) = nh/(2mL)$

$t = (2L/v) = 4mL^2/(nh)$

Dus:

$\mathbf{t = h/\Delta E_{n+1.n}}$

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$\Delta E.\ \Delta\tau > h$

$$V(x) = kx^2/2$$

$$f = (k/m)^{1/2}/(2\pi)$$

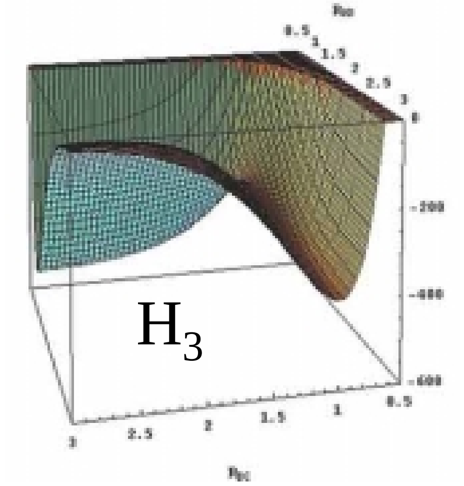
$$E_n = (n + 1/2)hf$$

Harmonic Oscillator

$\Delta E = hf$

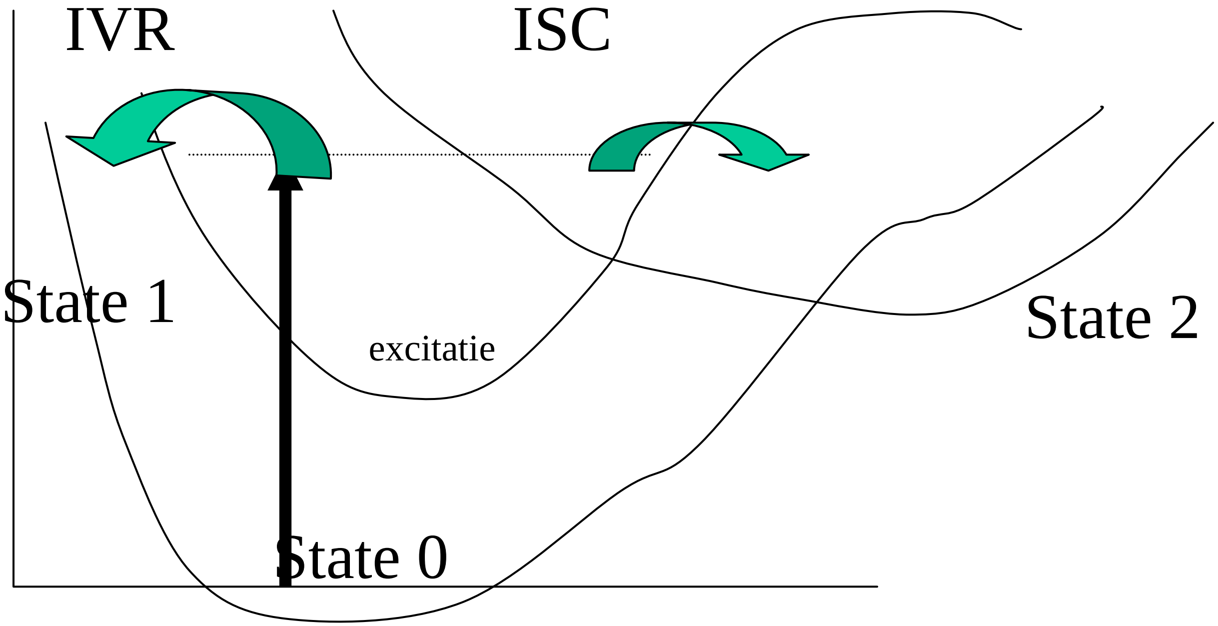
$t = f^{-1} = h/\Delta E$

Intra-molecular processes and discrete spectral structures.



Discussions.

- When does spectral structure disappear in IVR/ISC
- Where does the energy go in IVR/ISC
- What determines the visibility of the structure

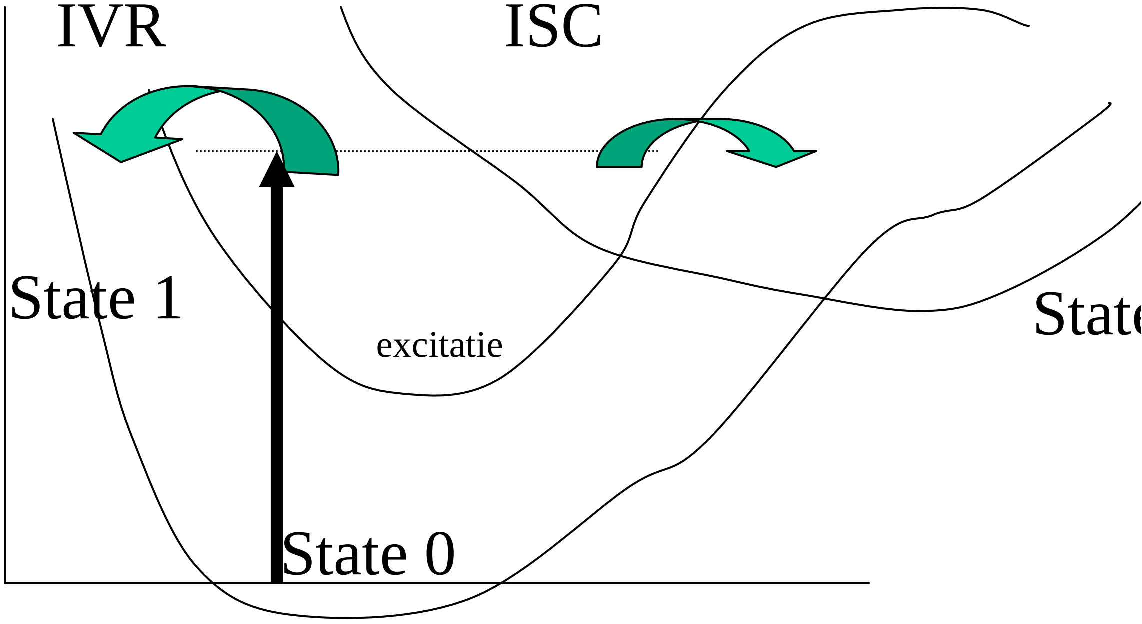


Lecture 1 --- 15b

Discussions.

- Where does the energy go in IVR/ISC
- Answer:
  nowhere, total energy is a conserved quantity, IVR requires such a high density of state that even a (super) high resolution laser excites a coherent (initially) wavepacket (bright state)

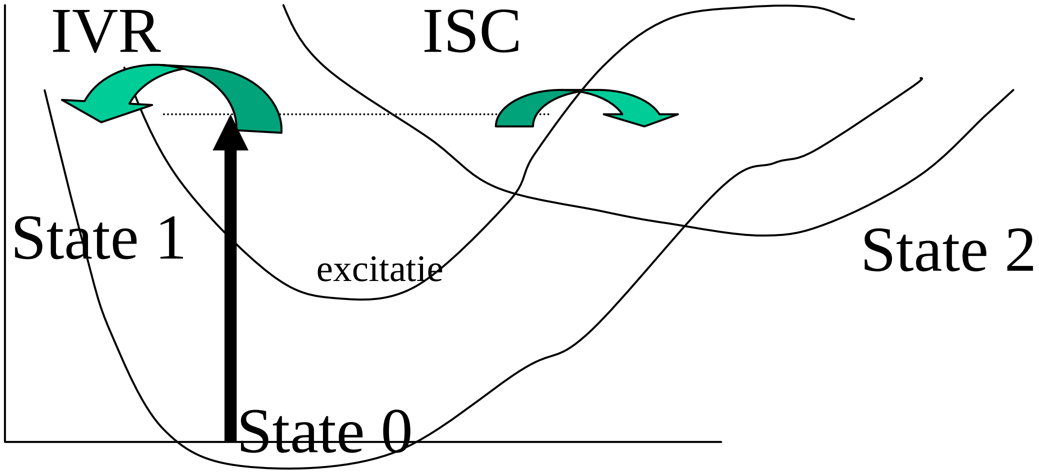
Intra-molecular processes and discrete spectral structures.



Intra-molecular processes and discrete spectral structures.

Discussions.

- When does spectral structure disappear in IVR/ISC
- Answer:
  (a) this question depends on the resolution of the person who asks the question
  (b) when radiation causes line broadening more than level spacing
  (the dark states become a statistical bath)
  (c) then the line becomes homogeneously broadened



Born-Oppenheimer Separation

$$\hat{H} = -\sum_{A} \frac{1}{2M_A}\nabla_A^2 - \sum_{i} \frac{1}{2}\nabla_i^2 + \sum_{A>B} \frac{Z_A Z_B}{R_{AB}} - \sum_{Ai} \frac{Z_A}{r_{Ai}} + \sum_{i>j} \frac{1}{r_{ij}}$$

$$\hat{H}\psi(q_1, q_2) = E\psi(q_1, q_2)$$

To be solved q_1 *nuclei,* q_2 *electrons*

$$\psi(q_1, q_2) = \psi_1(q_1)\psi_2(q_2)$$

$$\hat{H} = \hat{H}_1(q_1) + \hat{H}_2(q_2)$$

Ansatz/ Wisdom

and

Requirement: can we separate H?

Consequence:

$$\hat{H}\psi(q_1,q_2) = E\psi(q_1,q_2)$$

$$(\hat{H}_1+\hat{H}_2)\psi_1(q_1)\psi_2(q_2) = E_1\psi_1(q_1)\psi_2(q_2)+E_2\psi_1(q_1)\psi_2(q_2)$$

$$\hat{H}_1\psi_1(q_1)\psi_2(q_2)+\hat{H}_2\psi_1(q_1)\psi_2(q_2) = (E_1+E_2)\psi_1(q_1)\psi_2(q_2)$$

The Hamiltonian

$$\hat{H} = -\sum_{A} \frac{1}{2M_A}\nabla_A^2 - \sum_{i} \frac{1}{2}\nabla_i^2 + \sum_{A>B} \frac{Z_A Z_B}{R_{AB}} - \sum_{Ai} \frac{Z_A}{r_{Ai}} + \sum_{i>j} \frac{1}{r_{ij}}$$

$$\hat{H} = \hat{T}_N(\mathbf{R}) + \hat{T}_e(\mathbf{r}) + \hat{V}_{NN}(\mathbf{R}) + \hat{V}_{eN}(\mathbf{r},\mathbf{R}) + \hat{V}_{ee}(\mathbf{r})$$

The term giving problems for separation:

$$\sum_{Ai} \frac{Z_A}{r_{Ai}}$$

Step 1 write:

$$\psi(\mathbf{r},\mathbf{R}) = \psi_e(\mathbf{r})\psi_N(\mathbf{R})$$

And substitute

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$$\{\hat{T}_N(\mathbf{R})+\hat{T}_e(\mathbf{r})+\hat{V}_{eN}(\mathbf{r},\mathbf{R})+\hat{V}_{NN}(\mathbf{R})+\hat{V}_{ee}(\mathbf{r})\}\phi_e(\mathbf{r};\mathbf{R})\phi_N(\mathbf{R}) = E_{tot}\phi_e(\mathbf{r};\mathbf{R})\phi_N(\mathbf{R})$$

Remove kinetic operator of the nuclei: define electronic Hamiltonian

$$\hat{H}_{el} = \hat{T}_e(\mathbf{r}) + \hat{V}_{eN}(\mathbf{r};\mathbf{R}) + \hat{V}_{NN}(\mathbf{R}) + \hat{V}_{ee}(\mathbf{r})$$

Because: $$\hat{T}_e\phi_e(\mathbf{r};\mathbf{R})\phi_N(\mathbf{R}) = \phi_N(\mathbf{R})\hat{T}_e\phi_e(\mathbf{r};\mathbf{R})$$

Substitution gives: $$\hat{H}_{el}\phi_e(\mathbf{r};\mathbf{R}) = E_{el}\phi_e(\mathbf{r};\mathbf{R})$$

If the following would hold $$\hat{T}_N\phi_e(\mathbf{r};\mathbf{R})\phi_N(\mathbf{R}) = \phi_e(\mathbf{r};\mathbf{R})\hat{T}_N\phi_N(\mathbf{R})$$

Then: $$\phi_e\cancel{(}\mathbf{r};\mathbf{R})\hat{T}_N\phi_N(\mathbf{R}) + \phi_N(\mathbf{R})\phi_e(\mathbf{r}\cancel{;}\mathbf{R})(E_e + \hat{V}_{NN}) = E_{tot}\phi_e(\cancel{\mathbf{r}};\mathbf{R})\phi_N(\mathbf{R})$$

Lecture 1 --- 19b

$$\{\hat{T}_N(\mathbf{R})+\hat{T}_e(\mathbf{r})+\hat{V}_{eN}(\mathbf{r},\mathbf{R})+\hat{V}_{NN}(\mathbf{R})+\hat{V}_{ee}(\mathbf{r})\}\phi_e(\mathbf{r};\mathbf{R})\phi_N(\mathbf{R}) = E_{tot}\phi_e(\mathbf{r};\mathbf{R})\phi_N(\mathbf{R})$$

$$\boxed{\begin{gathered}\hat{H}_{el}\phi_e(\mathbf{r};\mathbf{R}) = E_{el}\phi_e(\mathbf{r};\mathbf{R}) \\ \{\hat{T}_N + E_e + \hat{V}_{NN}\}\phi_N(\mathbf{R}) = E_{tot}\phi_N(\mathbf{R})\end{gathered}}$$

$$\{\hat{T}_N(\mathbf{R})+\hat{T}_e(\mathbf{r})+\hat{V}_{eN}(\mathbf{r},\mathbf{R})+\hat{V}_{NN}(\mathbf{R})+\hat{V}_{ee}(\mathbf{r})\}\phi_e(\mathbf{r};\mathbf{R})\phi_N(\mathbf{R}) = E_{tot}\phi_e(\mathbf{r};\mathbf{R})\phi_N(\mathbf{R})$$

In reality we get:

$$\begin{aligned}&\phi_e(\mathbf{r};\mathbf{R})\hat{T}_N\phi_N(\mathbf{R}) + \phi_N(\mathbf{R})\phi_e(\mathbf{r};\mathbf{R})(E_e + \hat{V}_{NN})\\ &-\left\{\sum_A \frac{1}{2M_A}(2\nabla_A\phi_e(\mathbf{r};\mathbf{R})\nabla_A\phi_N(\mathbf{R}) + \phi_N(\mathbf{R})\nabla_A^2\phi_e(\mathbf{r};\mathbf{R}))\right\} = E_{tot}\phi_e(\mathbf{r};\mathbf{R})\phi_N(\mathbf{R})\end{aligned}$$

Next step: multiply with $\phi_e(\mathbf{r};\mathbf{R})$ and integrate over electronic coordinates:

$<\phi_e(\mathbf{r};\mathbf{R})|\phi_e(\mathbf{r};\mathbf{R})>=0$. This gives:

$$\boxed{T_N\phi_N(\mathbf{R}) + (E_e+V_{NN}-E_{tot})\phi_N(\mathbf{R}) = \sum_A(1/(2M_A))\{<\phi_e(\mathbf{r};\mathbf{R})|\nabla|\phi_e(\mathbf{r};\mathbf{R})>\nabla\phi_N(\mathbf{R}) + <\phi_e(\mathbf{r};\mathbf{R})\nabla^2\phi_e(\mathbf{r};\mathbf{R})>\phi_N(\mathbf{R})\}}$$

Nuclear SE

Non- BO terms

$$-\left\{\sum_A \frac{\hbar^2}{2M_A}\left(2\nabla_A\phi_e(\mathbf{r};\mathbf{R})\nabla_A\phi_N(\mathbf{R})+\phi_N(\mathbf{R})\nabla_A^2\phi_e(\mathbf{r};\mathbf{R})\right)\right\}$$

These terms cause non-adiabatic interaction terms or: when non-zero the concept of potential curves breaks down

Gives rise to Adiabatic Correction as it behaves as a potential (Born-Huang)

$<\phi_e(\mathbf{r};\mathbf{R})\nabla^2\phi_e(\mathbf{r};\mathbf{R})>$

$E_e(\mathbf{R})+V_{NN}+<\phi_e(\mathbf{r};\mathbf{R})\nabla^2\phi_e(\mathbf{r};\mathbf{R})>$

The Adiabatic potential

Now we have a more complete description but a hard to solve problem.

If $\{\phi_{e,i}(\mathbf{r};\mathbf{R})\}$ forms a complete set of Eigenfunctions of H_{el} then:
The solution of the any problem can be written as:

$$\Psi(\mathbf{r};\,\mathbf{R}) = \sum \phi_{e,i}(\mathbf{r};\mathbf{R})\,\phi_{N,i}(\mathbf{R})$$

and the Equation to solve becomes:

$$T_N\,\phi_{Ni}(\mathbf{R}) + (E_{ei}+V_{NN}-E_{tot})\,\phi_{Ni}(\mathbf{R}) =$$

$$(^1/_{2M})\{\underset{=0}{\cancel{\langle\phi_{ei}(\mathbf{r};\mathbf{R})|\nabla|\phi_{ei}(\mathbf{r};\mathbf{R})\rangle}}\,\nabla\phi_{Ni}(\mathbf{R}) + \langle\phi_{ei}(\mathbf{r};\mathbf{R})|\nabla^2|\phi_{ei}(\mathbf{r};\mathbf{R})\rangle\,\phi_{Ni}(\mathbf{R})\}$$

$$+$$

$$\sum_j(^1/_{2M})\{\langle\phi_{ei}(\mathbf{r};\mathbf{R})|\nabla|\phi_{ej}(\mathbf{r};\mathbf{R})\rangle\,\nabla\phi_{Nj}(\mathbf{R}) + \langle\phi_{ei}(\mathbf{r};\mathbf{R})|\nabla^2|\phi_{ej}(\mathbf{r};\mathbf{R})\rangle\,\phi_{Nj}(R)\,\}$$

Coupling terms (coupled equations needed for solution)

The equation below implies that the physics of a system may take place on multiple potential energy surfaces simultaneously (hence the coupled equations):

$$
\begin{aligned}
&T_N\,\phi_{Ni}(\mathbf{R}) + (E_{ei}+V_{NN}-E_{tot})\,\phi_{Ni}(\mathbf{R}) = \\
&(^1/_{2M})\{<\phi_{ei}(\mathbf{r;R})|\nabla^2|\phi_{ei}(\mathbf{r;R})>\,\phi_{Ni}(\mathbf{R})\} + \\
&\sum_j(^1/_{2M})\{<\phi_{ei}(\mathbf{r;R})|\nabla|\phi_{ej}(\mathbf{r;R})>\,\nabla\phi_{Nj}(\mathbf{R}) + <\phi_{ei}(\mathbf{r;R})|\nabla^2|\phi_{ej}(\mathbf{r;R})>\,\phi_{Nj}(R)\,\}
\end{aligned}
$$

Note: couplings are in some sense always the result of a primitively chosen basis set. For all problems a basis of eigenfunctions exist. Couplings is often not a physical interaction between physical entities.

Non-adiabatic interaction terms, some properties?

Complete set: $<\phi_i| \phi_j> = 0, i \neq j$

(I) $<\phi_i| d/dR|\phi_j> \neq 0, \quad i \neq j$ (note: $\nabla = d/dR$ in one dimension)

(II) $<\phi_i| d/dR|\phi_i> = 0,$

because: $d<\phi_i| \phi_i>/dR = 0 = 2 <\phi_i| d/dR|\phi_i>$

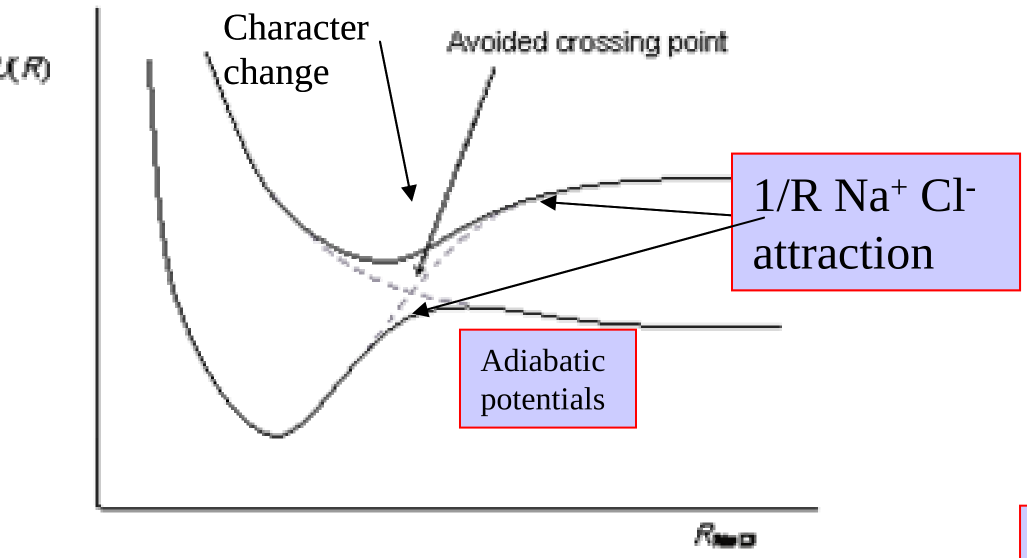
$d<\phi_i| \phi_j>/dR = 0 = <\phi_i| d/dR|\phi_j> + <\phi_j| d/dR|\phi_i>$

(operator antisymmetric)

(II) $<\phi_i| d^2/dR^2|\phi_j> \neq 0, \quad$ all i,j

hence: d^2/dR^2 term gives both diagonal adiabatic correction, and interaction between states

Two –state diatomic system.
Diabatic States?



1/R Na^+ Cl^- attraction

Adiabatic potentials

Suspicion: $<\phi_1| d/dR|\phi_2> \neq 0$

The pragmatic solution:
Diabatic states: recipe in general subjective
sacrifice: $<\phi_1| H_{el} |\phi_2> = 0$
demand: $<\phi_1| d/dR|\phi_2> = 0$

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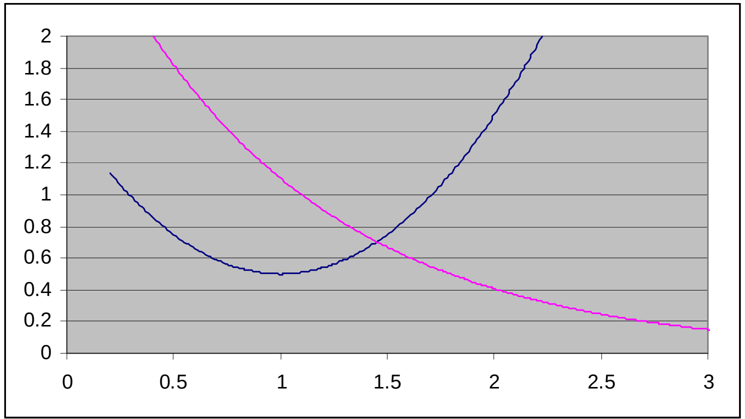
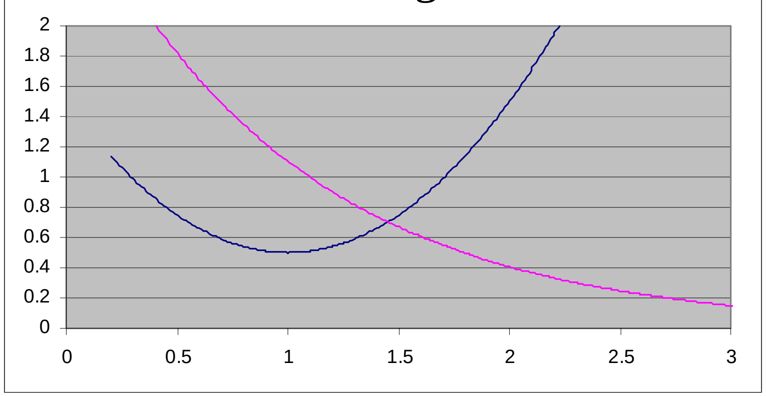
H_{el}-coupling

Small Large

crossing

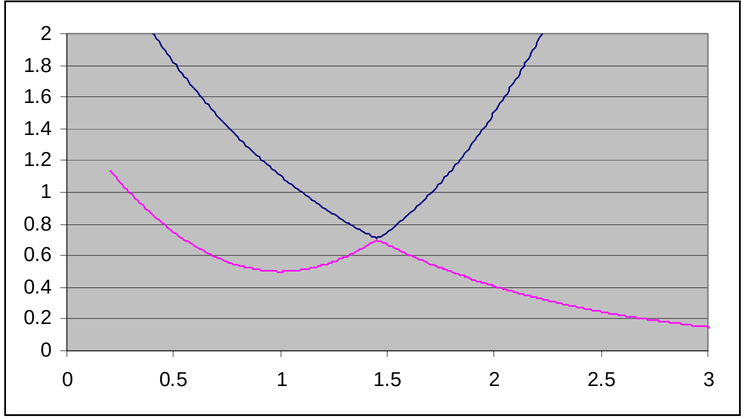


crossing

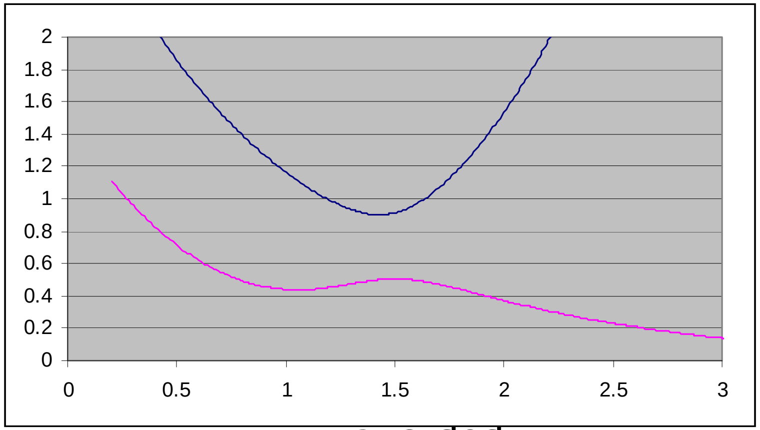


Diabatic
states

Adiabatic
states



avoided
crossing



avoided
crossing

d/dR-coupling

Sharp, high Broad, low

Consequences and some aspects in words:

- for adiabatic states a procedure exists!
- for diabatic states no universal procedure exist!
- possibilities:

retain all CI coefficients determined for R_e for all R . . .

use derived quantities as a dipole moment to keep character constant

use adiabatic states and generate locally diabatic states

- Couplings due d^2/dR^2 not taken into account.

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Two –state diatomic system:

$\phi_{d1}(\mathbf{r}; \mathbf{R})= \cos(\theta(R))\, \phi_{a1}(\mathbf{r}\, ; \mathbf{R}) + \sin(\theta(R))\, \phi_{a2}\, (\mathbf{r}\, ; \mathbf{R})$

$\phi_{d2}= -\sin(\theta)\, \phi_{a1} + \cos(\theta)\, \phi_{a2}$

$< \phi_{d1}|\, \phi_{d2}> =0$

define two state rotation, $\theta= \theta(R)$ such that:

$< \phi_{d1}|d/dR|\, \phi_{d2}> = 0$

Consequences

(1): $< \phi_{a1}|d/dR|\, \phi_{a2}> = ½\, (V_{ad1}-V_{ad2})$

at distance of closest approach

(2): $\int< \phi_{a1}|d/dR|\, \phi_{a2}>\, dR= \pi/2$ (!)

(3): $V_{d1}= \cos^2(\theta)\, V_{ad1}+\sin^2(\theta)\, V_{ad2}$

$V_{d2}= \cos^2(\theta)\, V_{ad2}+\sin^2(\theta)\, V_{ad1}$

(3): $V_{a1,2}= 0.5\{(V_{d1}+V_{d2})^2 \pm ((V_{d1}-V_{d2})^2 + 4H_{12}{}^2)^{1/2}\}$

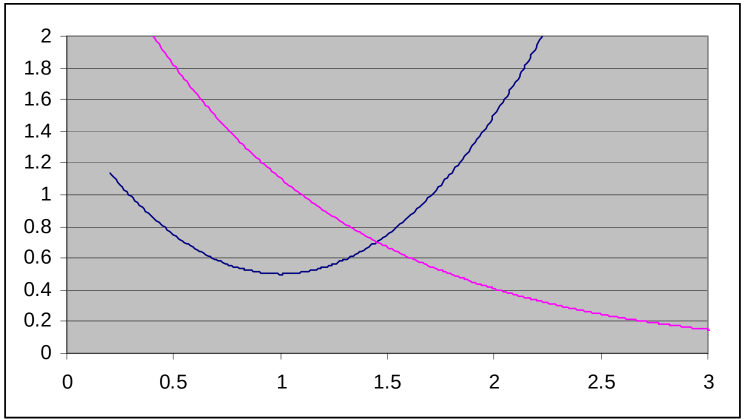
Lecture 1 --- 27b

H_{el}-coupling

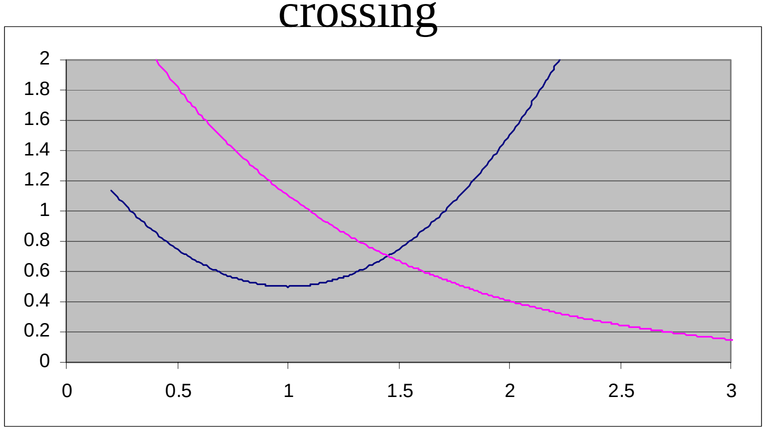
Small Large

Diabatic states

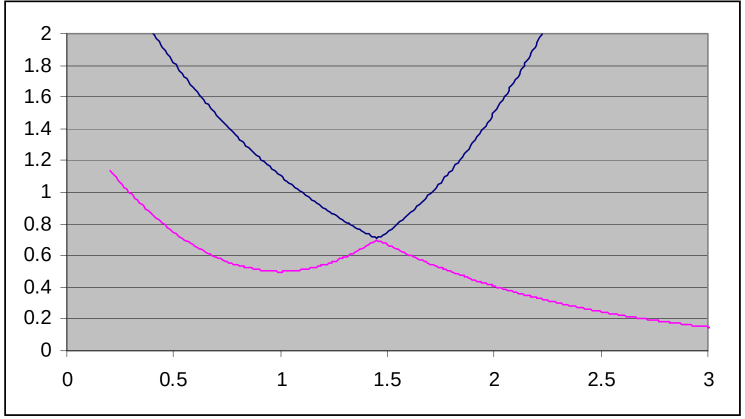
crossing



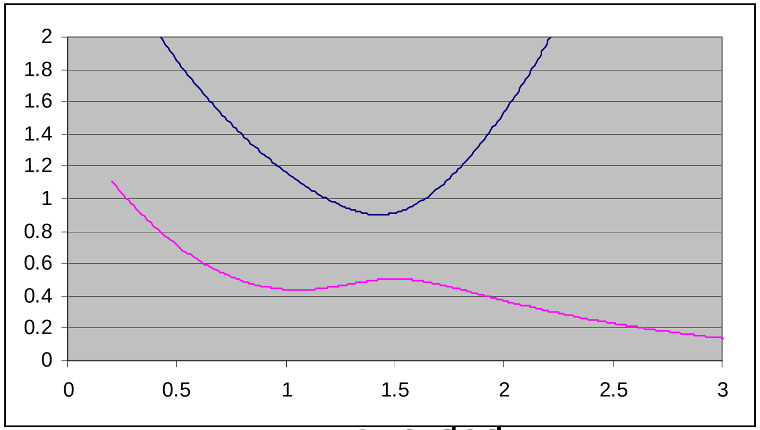
crossing



Adiabatic states



avoided crossing



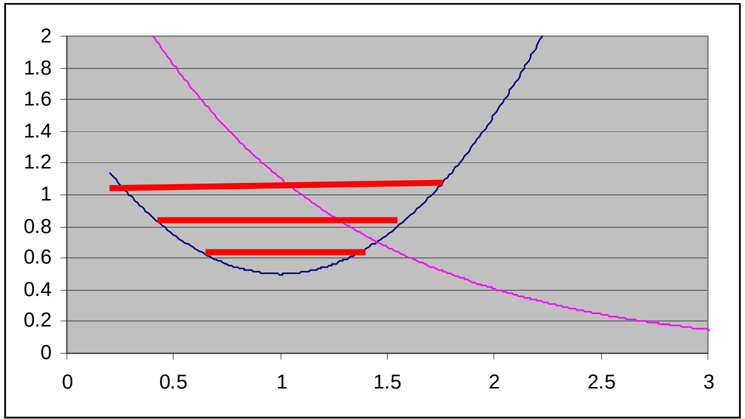
avoided crossing

d/dR-coupling

Sharp, high Broad, low

Lecture 1 --- 27c

crossing

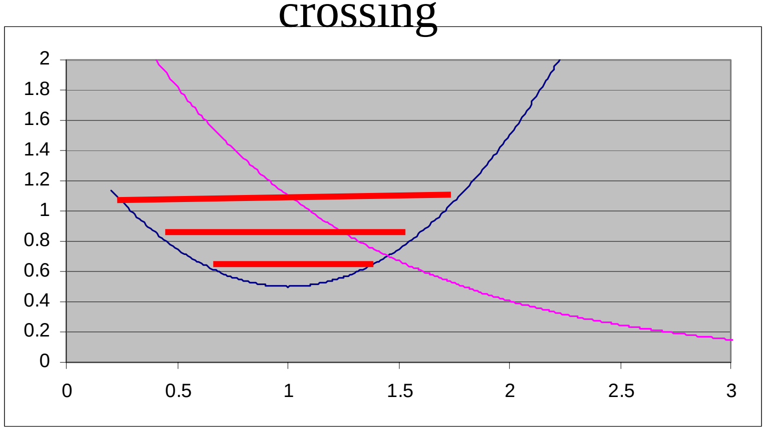


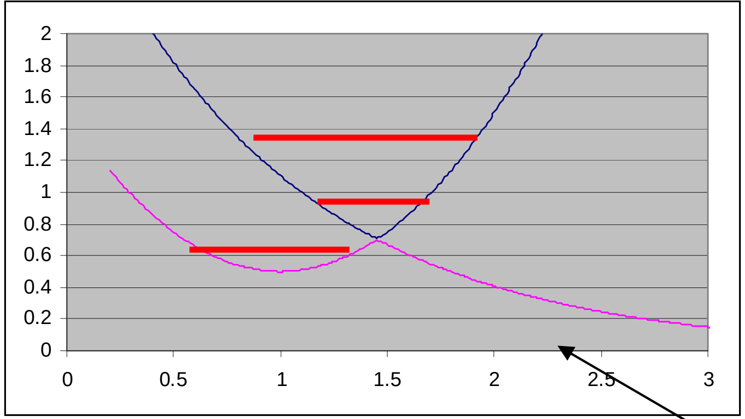
H_{el}-coupling

Small Large

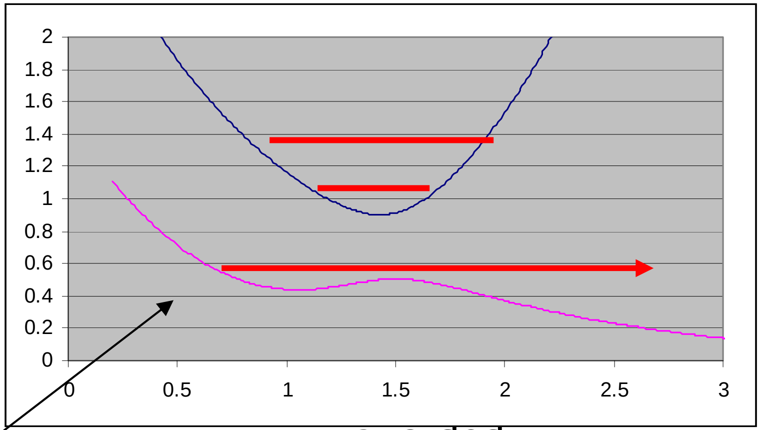
Diabatic
states

crossing





Adiabatic
states



avoided
crossing

d/dR-coupling

Sharp, high Broad, low

avoided
crossing

Diabatic to Adiabatic

- $T_N\, \phi_{\mathrm{Nd1}}(\mathbf{R}) \;+ (E_{d1} - E_{tot})\, \phi_{\mathrm{Nd1}}(\mathbf{R}) = H_{el}\, \phi_{\mathrm{Nd2}}(\mathbf{R})$
  $T_N\, \phi_{\mathrm{Nd2}}(\mathbf{R}) \;+ (E_{d2} - E_{tot})\, \phi_{\mathrm{Nd1}}(\mathbf{R}) = H_{el}\, \phi_{\mathrm{Nd2}}(\mathbf{R})$

(numerical more simple, no derivative)

- Should be equivalent to:

- $T_N\, \phi_{\mathrm{Na1}}(\mathbf{R}) \;+ (E_{a1} - E_{tot})\, \phi_{\mathrm{Na1}}(\mathbf{R}) = < \phi_{\mathrm{ea1}}|\mathrm{d/dR}|\, \phi_{\mathrm{ea2}}> \mathrm{d}\phi_{\mathrm{Nd2}}(\mathbf{R})/\mathrm{dR}$
  $T_N\, \phi_{\mathrm{Na2}}(\mathbf{R}) \;+ (E_{a2} - E_{tot})\, \phi_{\mathrm{Na2}}(\mathbf{R}) = < \phi_{\mathrm{ea2}}|\mathrm{d/dR}|\, \phi_{\mathrm{ea1}}> \mathrm{d}\phi_{\mathrm{Nd1}}(\mathbf{R})/\mathrm{dR}$

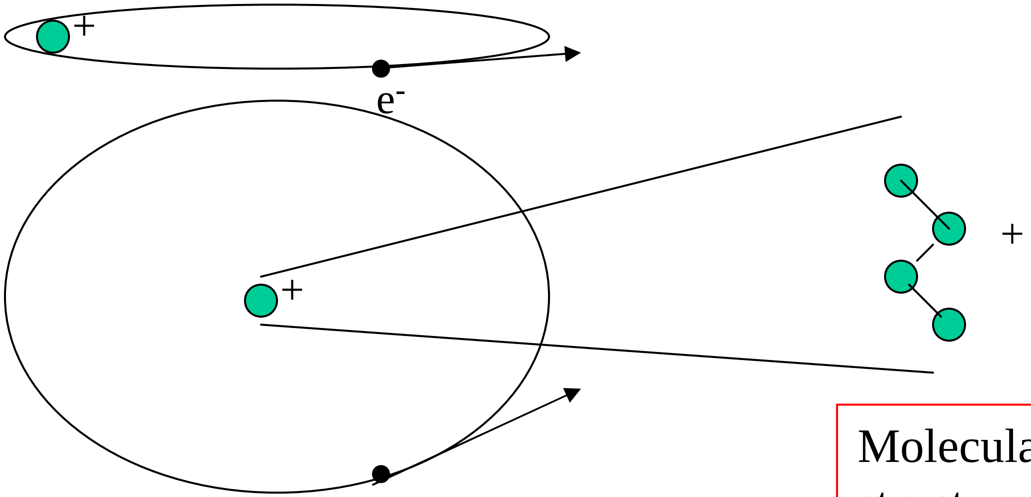
- Special: if $\mathrm{H}_{\mathrm{el}} \cong 0$ than nature is perfectly diabatic and

$< \phi_{\mathrm{ea1}}|\mathrm{d/dR}|\, \phi_{\mathrm{ea2}}> \cong \pi/2.\delta(\mathrm{R}-\mathrm{R}_c)$ $(\theta(\mathrm{R})= \pi/2$ Heavyside$(\mathrm{R}_c))$

The world of large series of *electronically* highly excited states: Rydberg States.

$n, l(\cong 1, << n)$

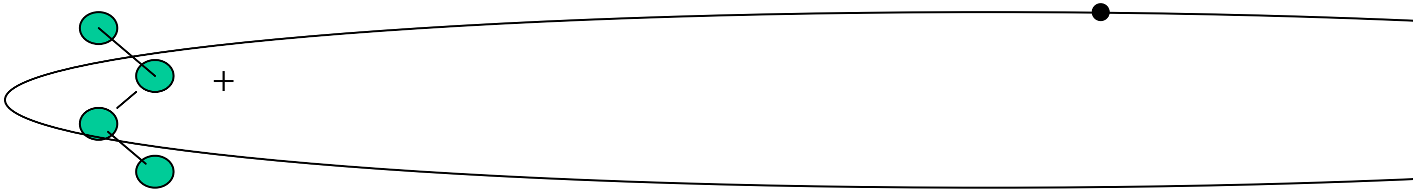
$n, l(\cong n\text{-}1)$



Molecular structure: probed at small **r** (small *l*)

The world of large series of *electronically* highly excited states: Rydberg States.

Outside area: analytical (H-like)



n,l($\cong$1, <<*n*)

Electron core scattering: deceleration/ acceleration (phase shift → quantum defect → energy shift:

All Rydberg states get their particular character at the core only!

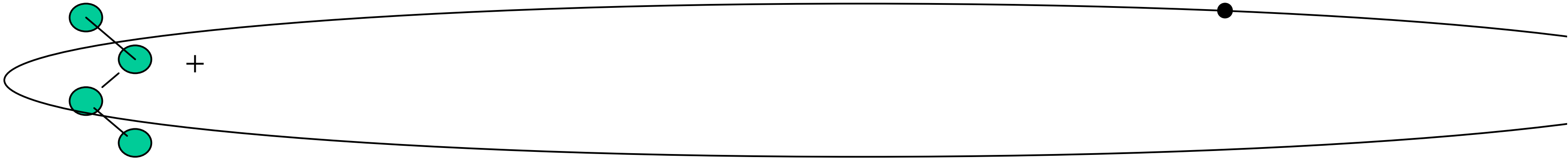
For molecules:

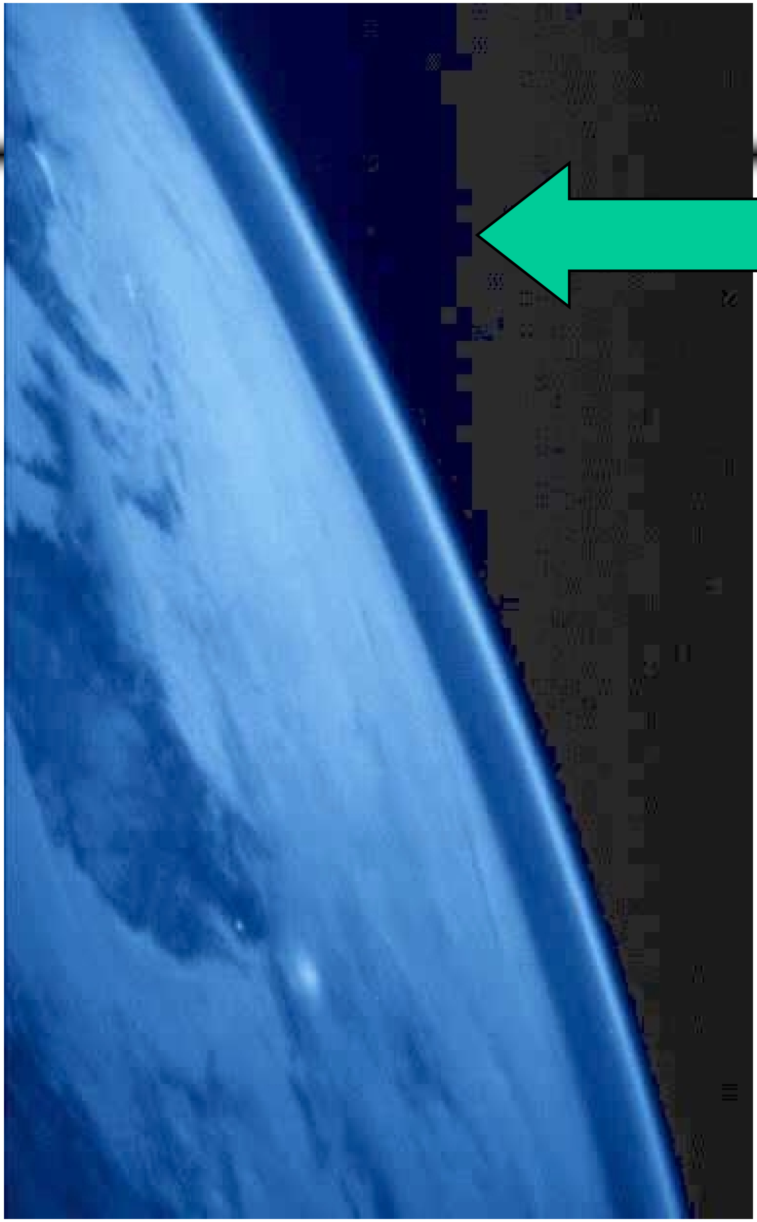
*quantum defect = QD(**R**)*

Lecture 1 --- 30

Difference between the Ion and the Rydberg States is:
scattering of the electrons on the core, which affects the description of other electrons etc.
Potential curve of Ion State is slightly different: the quantum defect: $\delta(R) \neq$ constant but a function of R.

→ $\langle d/dR \rangle$ coupling and $\langle d^2/dR^2 \rangle$ adiabatic correction follow directly from $\delta(R)$ and do no longer require a separate non-BO calculation (Child, Stolyarov: Phys. RevA,2001)





$O+O+O \rightarrow O_2 + O(^1S)$

WHY??

Aurorae, $O(^1S)$

Dissociative Recombination

The reaction in the case of:

O_2^+ (v=0) + e^- (at 0 eV)

$\rightarrow O(^3P) + O(^3P) + 6.95\ \text{eV}$

$\rightarrow O(^1D) + O(^3P) + 4.99\ \text{eV}$

$\rightarrow O(^1D) + O(^1D) + 3.02\ \text{eV}$

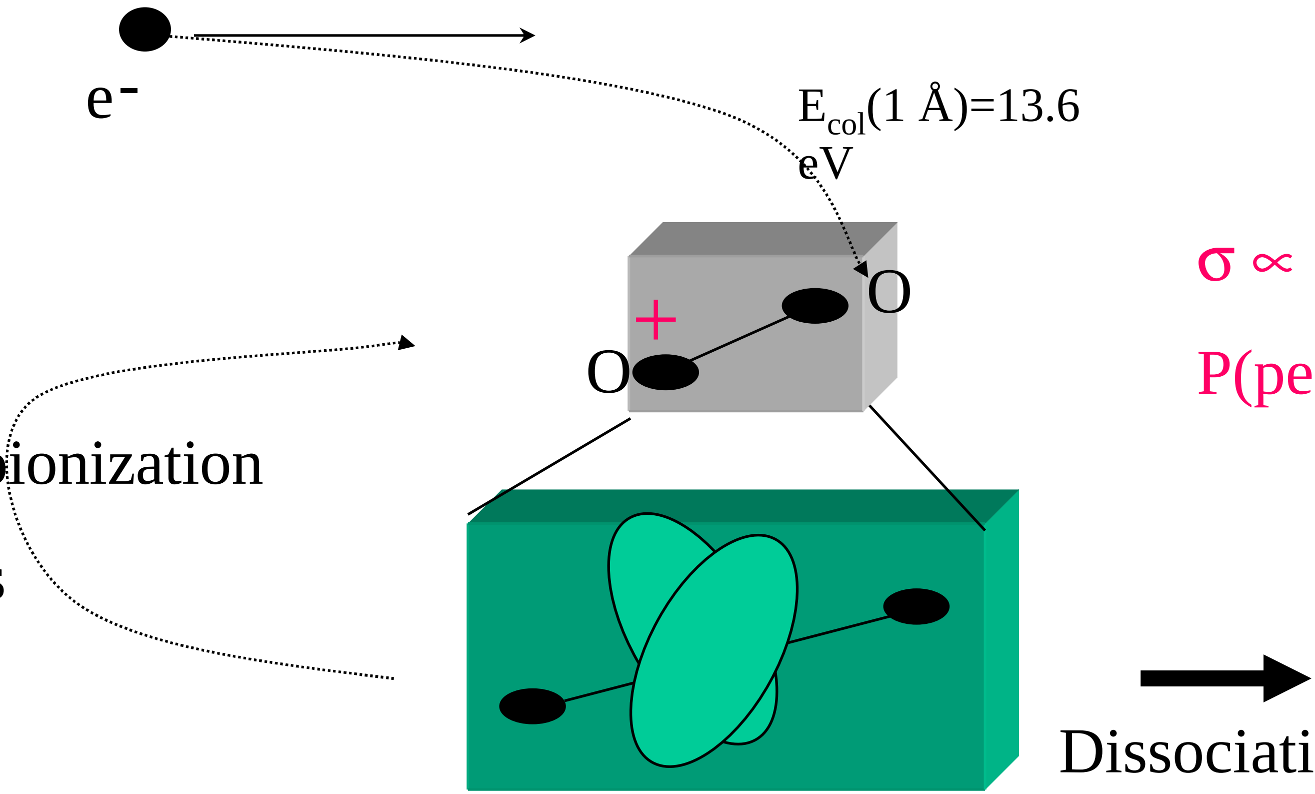
$\rightarrow O(^3P) + O(^1S) + 2.77\ \text{eV}$

$\rightarrow O(^1D) + O(^1S) + 0.8\ \text{eV}$

630.0 nm

557.7 nm

When electrons meet an ion…..



E near 0 eV

e⁻

E_{col}(1 Å)=13.6 eV

$\sigma \propto 1/E$,

P(per hit)= 0.05

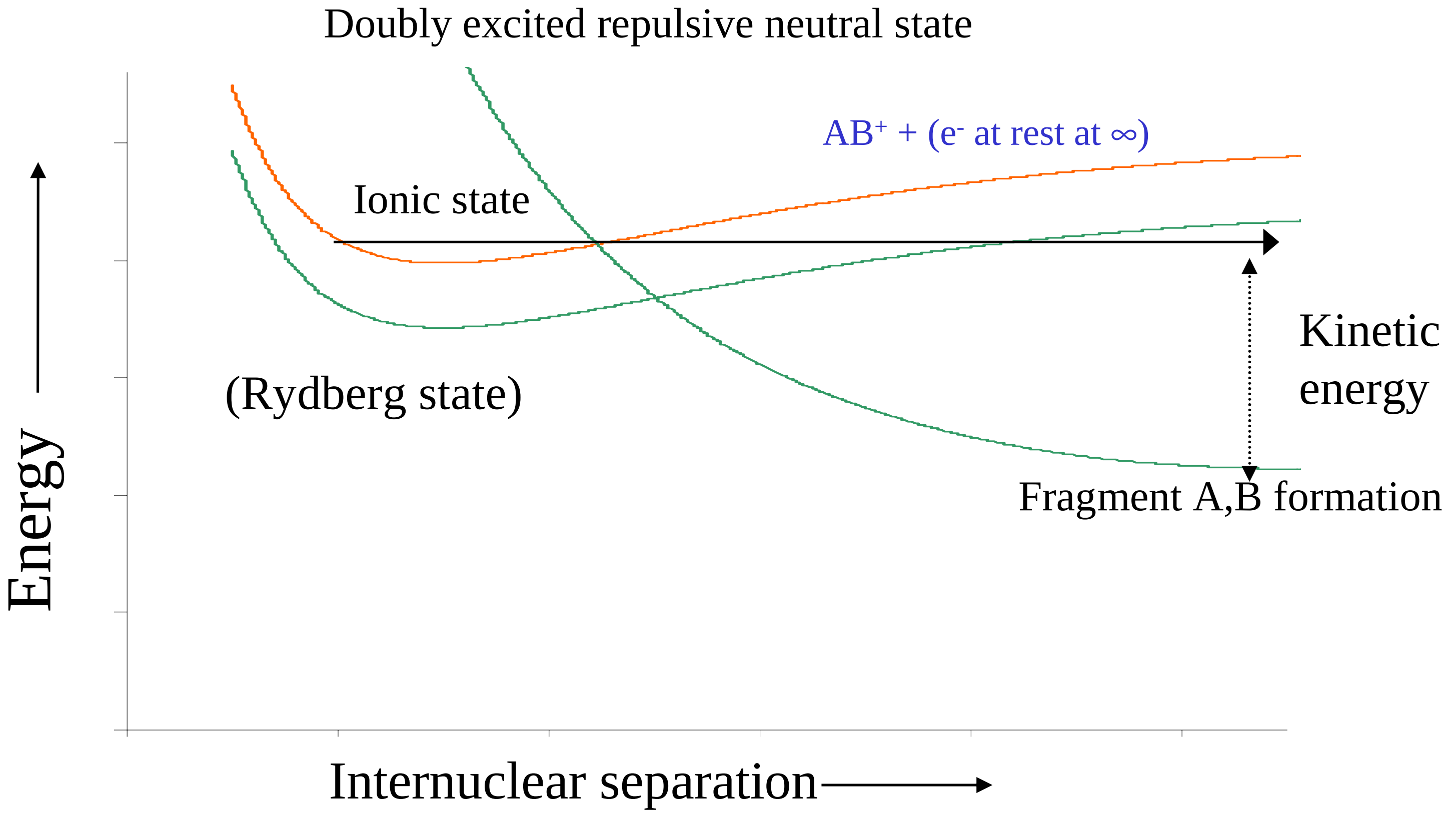
Autoionization

10 fs

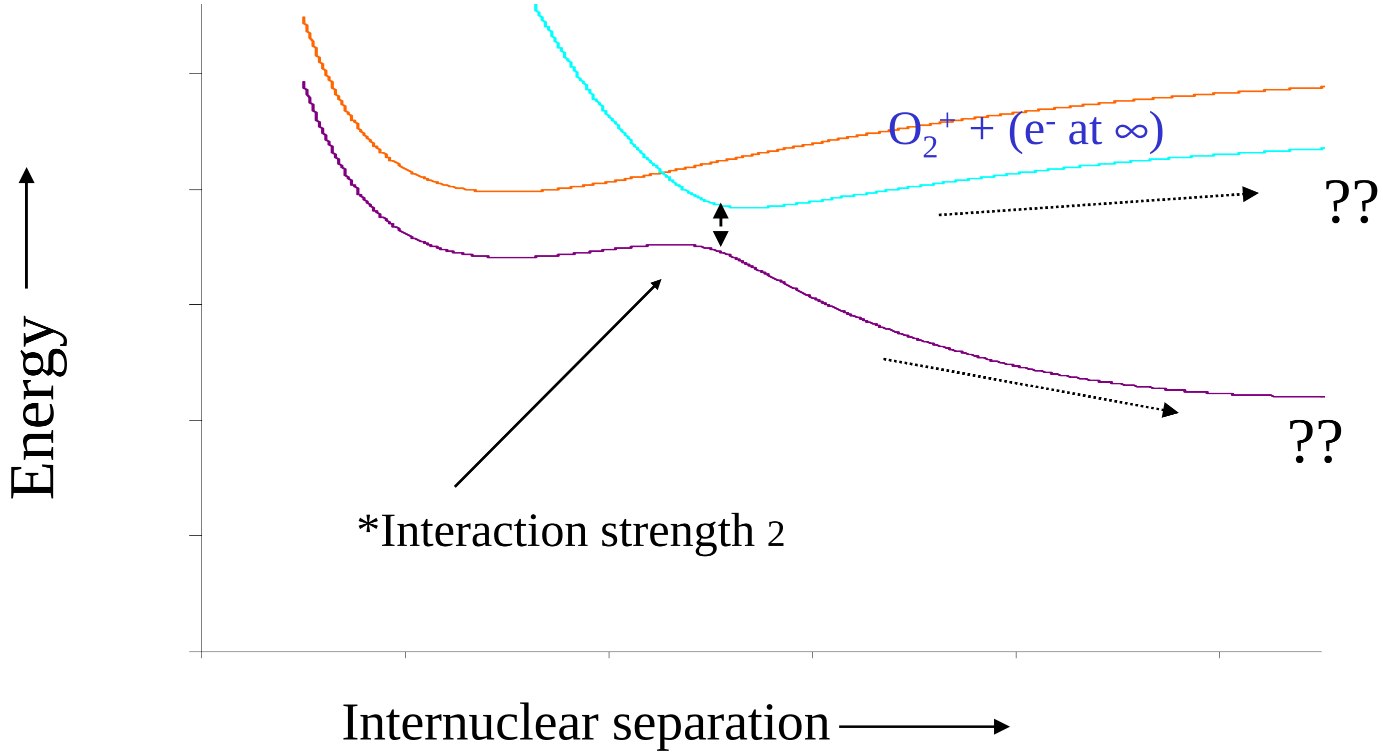
Dissociation (10 fs)

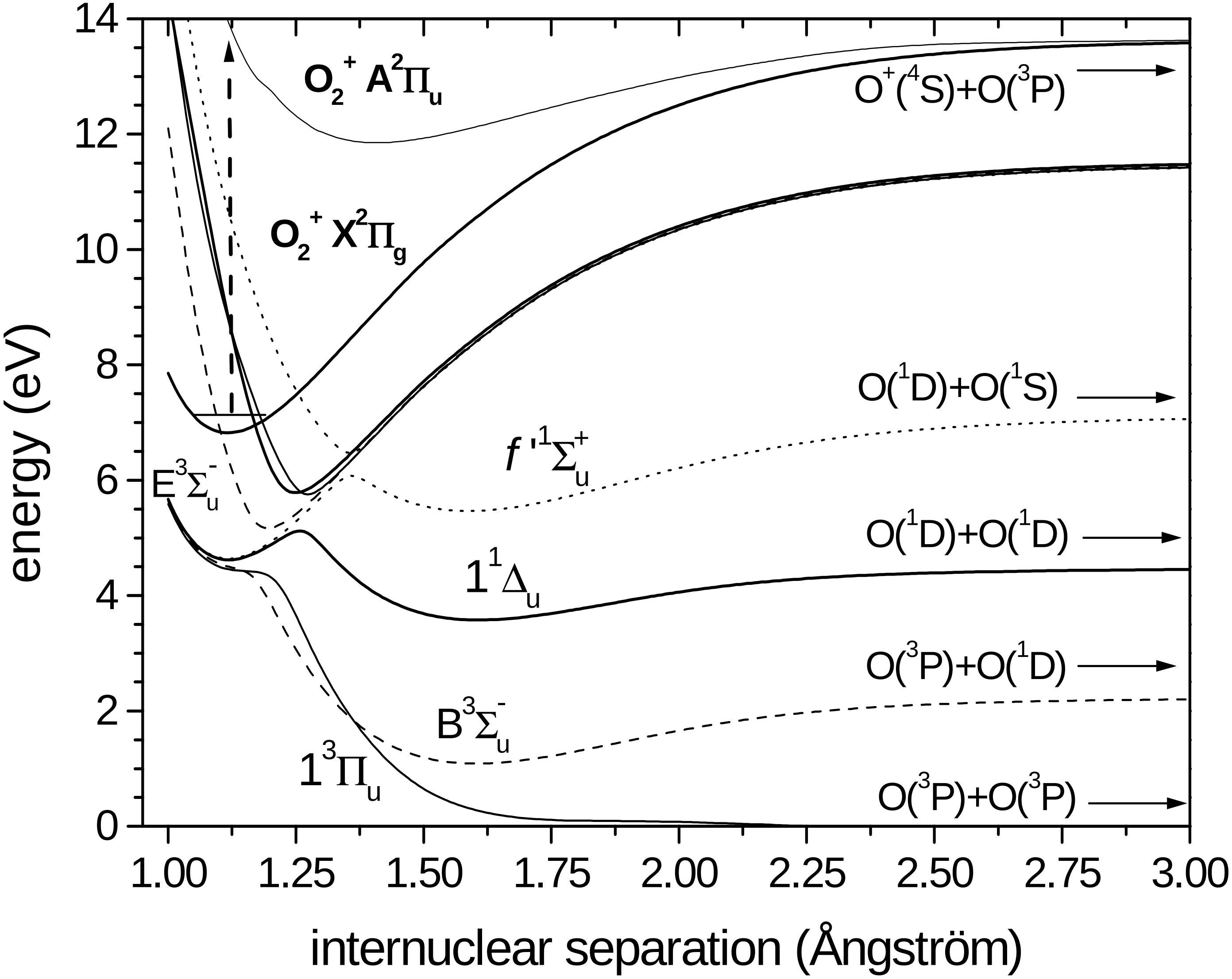
Radiation (ns)

Dissociative Recombination
a simplified potential energy diagram

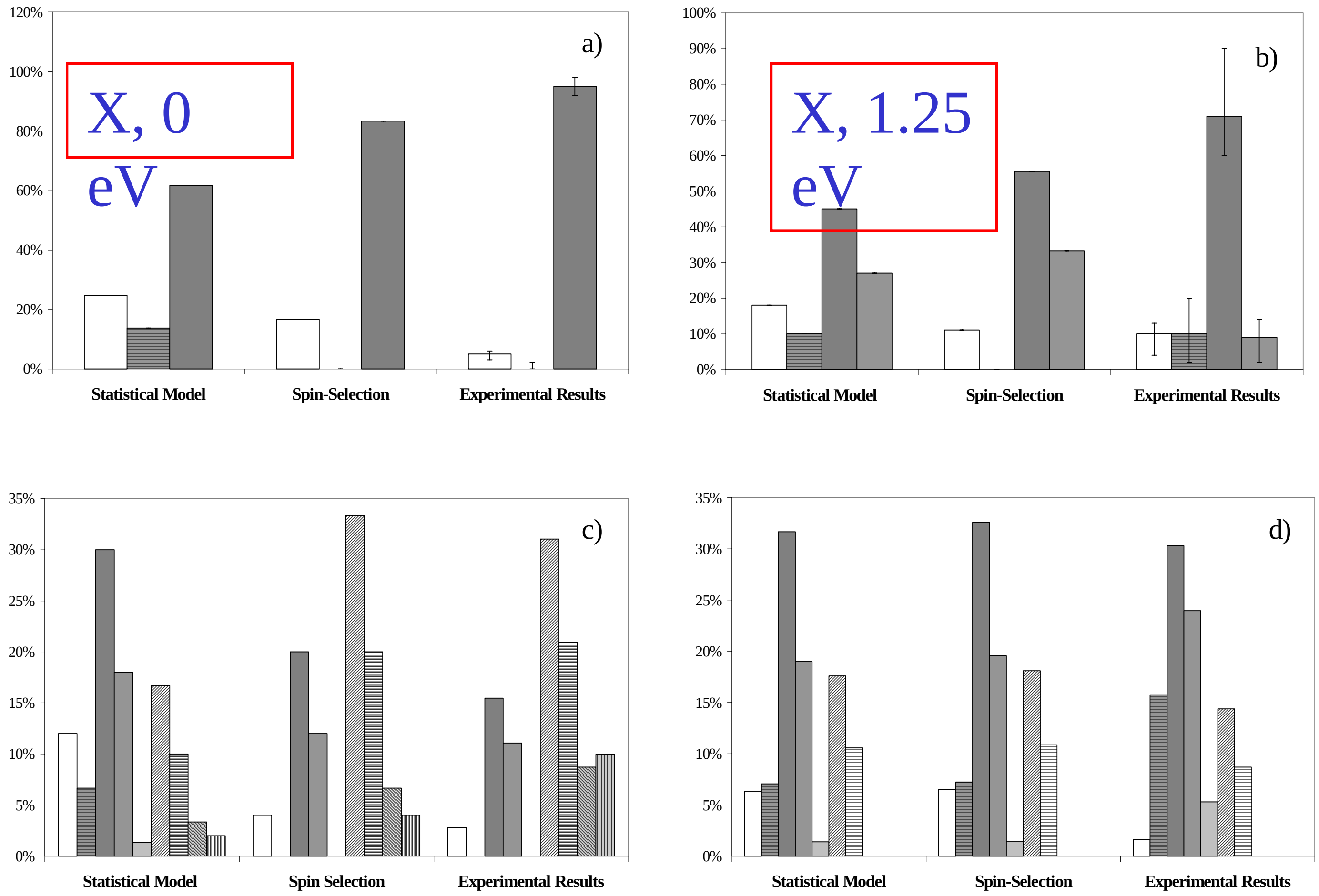


Dissociative Recombination what determines its efficiency?




14
12
10
8
6
4
2
0
energy (eV)
1.00
1.25
1.50
1.75
2.00
2.25
2.50
2.75
3.00
internuclear separation (Ångström)
O_2^+ $A^2\Pi_u$
O_2^+ $X^2\Pi_g$
$O^+(^4S)+O(^3P)$
$O(^1D)+O(^1S)$
$f\ '^1\Sigma_u^+$
$E^3\Sigma_u^-$
$O(^1D)+O(^1D)$
$1^1\Delta_u$
$O(^3P)+O(^1D)$
$B^3\Sigma_u^-$
$1^3\Pi_u$
$O(^3P)+O(^3P)$

NO$^+$: confrontation with statistical model with spinconservation



X, 0 eV

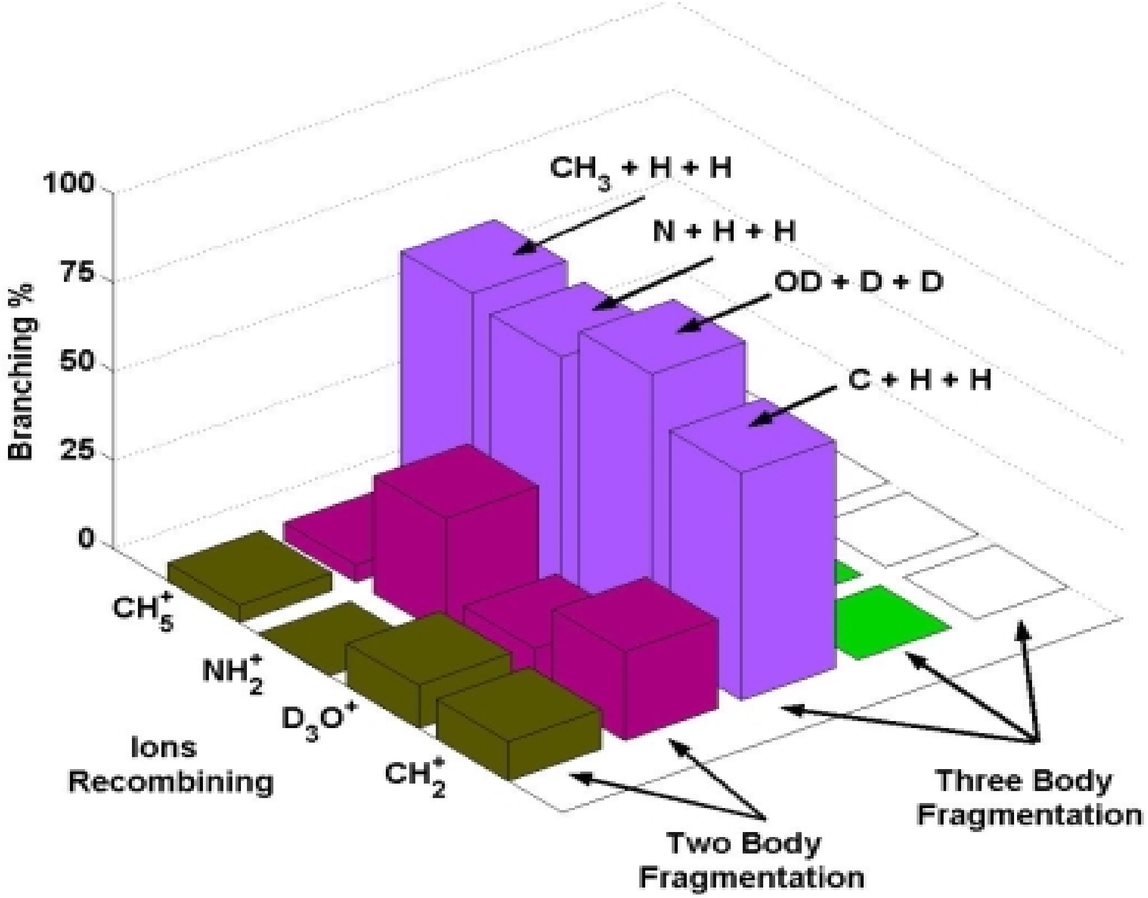
X, 1.25 eV

X, 5 eV = a$^3\Sigma$+, 0 eV

From 2 to 3 atoms: also 3 fragments?

The neutral product branching ratios in DR of

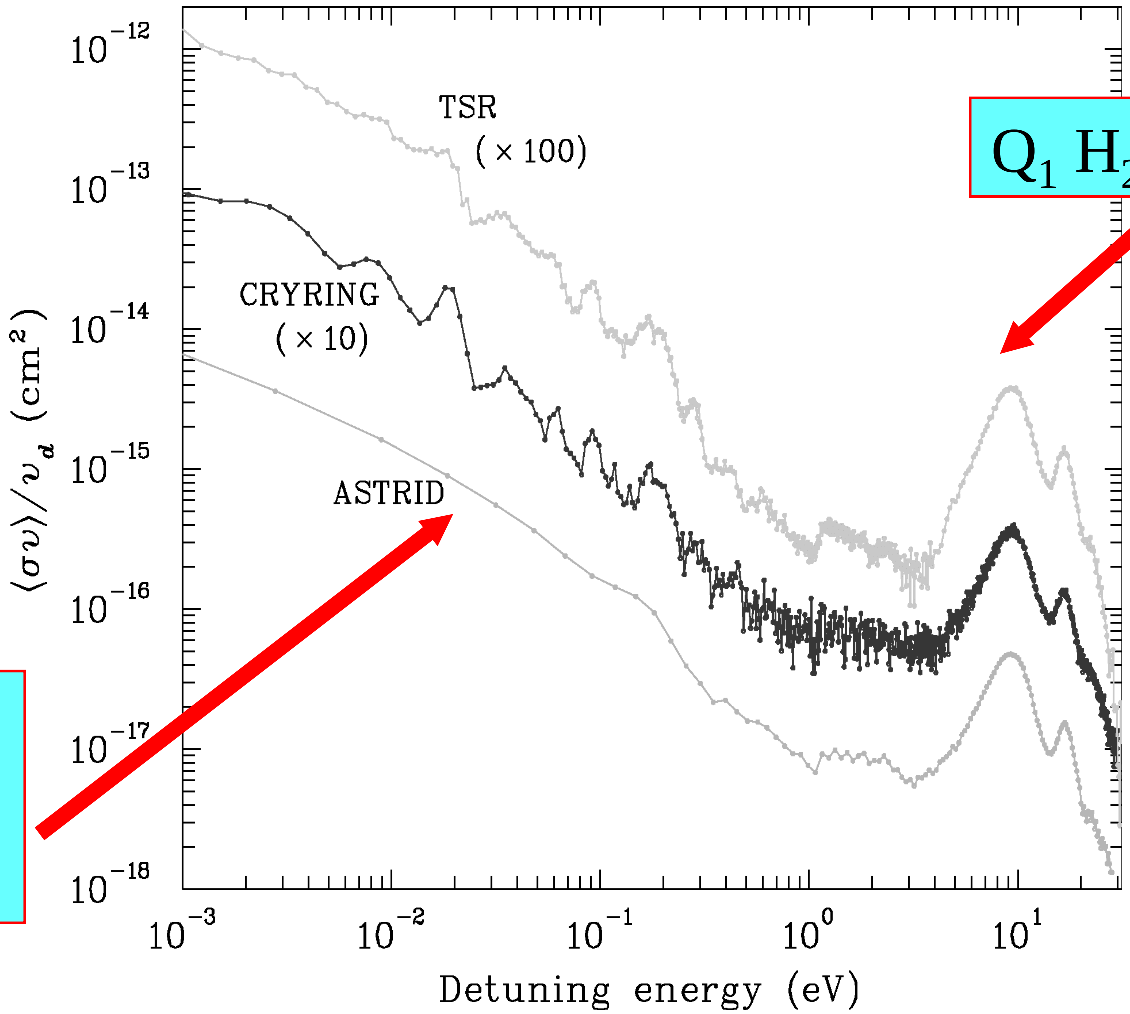
H_3^+, NH_2^+, H_2O^+, D_3O^+, CH_2^+, and CH_5^+



Mysteries in DR

- *The quantum chemistry suggests great specificity: however rates/cross sections are nearly system independent*
- *The quantum chemistry suggests selective dissociations: however a statistical model provides predictive power, WHY? (note: nature does not goes to lowest state!)*
- *Would quantum chemistry predict three body fragmentation in DR of polyatomic ions*
- *Is the essential difference that the world of many excited states is very different from ground state intuition?*

Dissociative recombination of HD^+



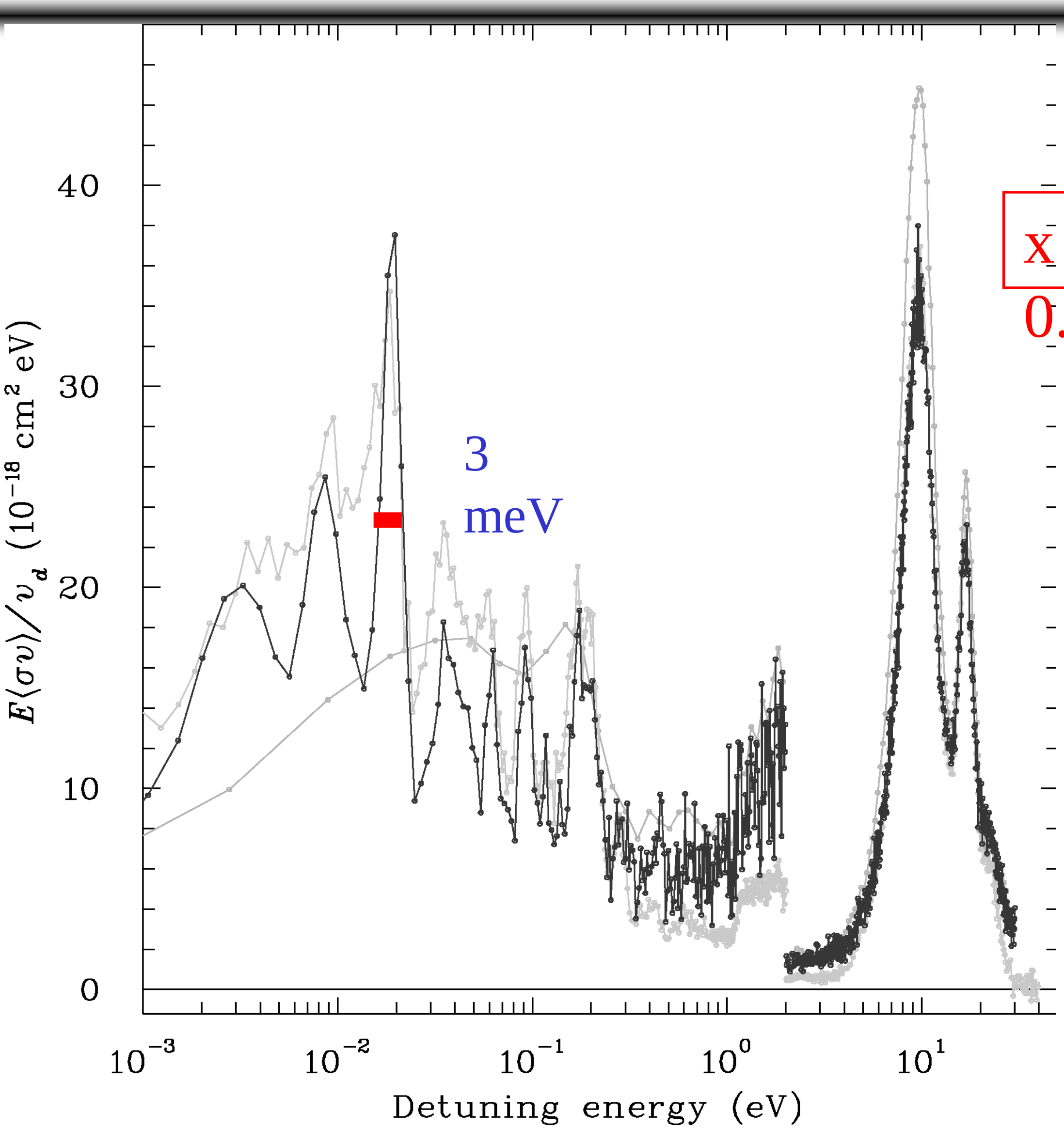
Q_1 H_2^{**} $({}^1\Sigma_g^+)$

1/E and Rydberg resonances

Dissociative recombination of HD^+ (J=0,1,,4)

Cross section times energy:

close to 1/E



3 meV

x 0.1