



Laser Seminar
NCCR MUST Seminar
1st to 4th October, 2012



Time & Location:	1 st October	16:00 – 18:30	HPV G 5	
	2 nd October	16:00 – 18:30	HPV G 4	
	3 rd October	15:00 – 17:00	HPH G 2	
	4 th October	17:00 – 19:30	HPV G 4	16:30 Apéro Invitation

ETH Zurich, Hönggerberg Campus

Host: Ursula Keller, Ultrafast Laser Physics, D-PHYS, Direction Committee of ETH-FAST
Hans Jakob Wörner, Ultrafast Spectroscopy+Attosecond Science, D-CHAB

More Info: www.opteth.ethz.ch/news/laser_seminar
www.nccr-must.ch/fast_centers/eth-fast/eth-fast_fellows.html

Albert Stolow
University of Ottawa
&
National Research Council Canada

2012 FAST Lectures

**Molecular Dynamics,
Wavepacket Dynamics**

Lecture 1

**Albert Stolow
University of Ottawa
&
National Research Council Canada**

What is a Molecule?

A molecule is “composed” of atoms, or, more generally as a collection of charged particles, positive nuclei and negative electrons.

The kinetic and potential energies of the charged particles is given by:

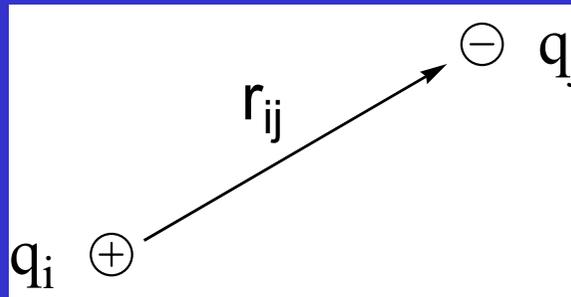
$$V_{ij} = V(r_{ij}) = \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} = \frac{q_i q_j}{r_{ij}}$$

Potential Energy

$$\hat{T} = \frac{m_i v_i^2}{2} + \frac{m_j v_j^2}{2}$$

Kinetic Energy

Electric interactions between charged particles is the only force required to describe molecular phenomena, including chemical reaction.



Time Dependent Schrödinger Equation

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

Separation of variables $\Psi(\vec{r}, t) = \Phi(t) \psi(\vec{r})$

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

Time-independent Schrödinger Eq'n

$$\hat{H}\Psi = E\Psi$$

$$i\hbar \frac{\partial \Phi(t)}{\partial t} = E \Phi(t)$$


$$\Phi(t) = e^{-iEt/\hbar}$$

Full wavefunction:

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

Hamiltonian for a N-particle system

$$\hat{H} = \hat{T} + \hat{V}$$

Sum of kinetic (T) and potential (V) energy

$$\hat{T} = \sum_{i=1}^N \hat{T}_i = -\sum_{i=1}^N \frac{\hbar^2}{2m_i} \nabla_i^2$$

Kinetic energy

$$\hat{V} = \sum_{i=1}^N \sum_{j>1}^N V_{ij} = \sum_{i=1}^N \sum_{j>1}^N \frac{q_i q_j}{r_{ij}}$$

Potential energy

Complete Hamiltonian: dynamics of all electrons and nuclei within a molecule or atom are described.

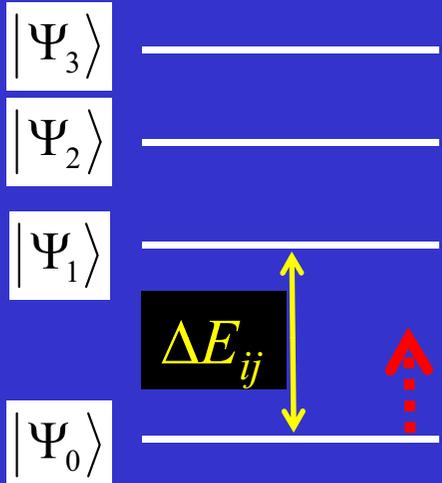
Anything else involves approximations....

The Adiabatic Approximation

A. Messiah "Quantum Mechanics" Vol.2. (p.744 and following)

Eigensolutions to the time-independent Schrödinger equation:

$$\hat{H}\Psi_i = E_i\Psi_i$$



Apply a time-dependent interaction potential $\hat{A}(t)$ which evolves the state vector (potentially leading to transitions between states).

Evolution operator: $\hat{U}(t) = e^{i\hat{A}(t)/\hbar}$

Transition probability:

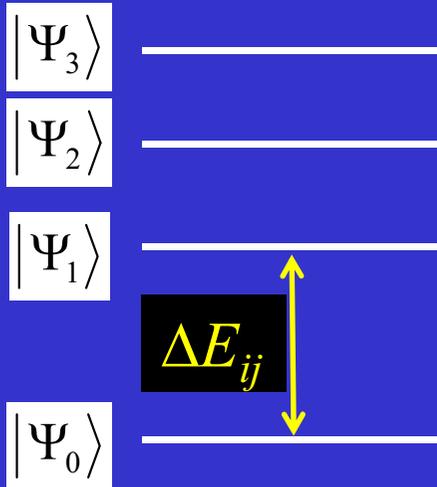
$$p_{i \rightarrow j} = \left| \langle \Psi_j | \hat{U}(t_0, t_1) | \Psi_i \rangle \right|^2$$

In the adiabatic approximation, the state vector evolves such that there is no change in eigenvalue (i.e. no transition):

$$p_{i \rightarrow j} \ll 1$$

The Adiabatic Approximation

A. Messiah "Quantum Mechanics" Vol.2. (p.744 and following)



In the adiabatic approximation, the state vector evolves such that there is no change in eigenvalue (i.e. no transition), only a change in phase.

$$\hat{U}(t_1, t_0) |\Psi_i\rangle_0 \approx e^{i/\hbar \int_{t_0}^{t_1} d\tau E_i(\tau)} |\Psi_i\rangle_0$$

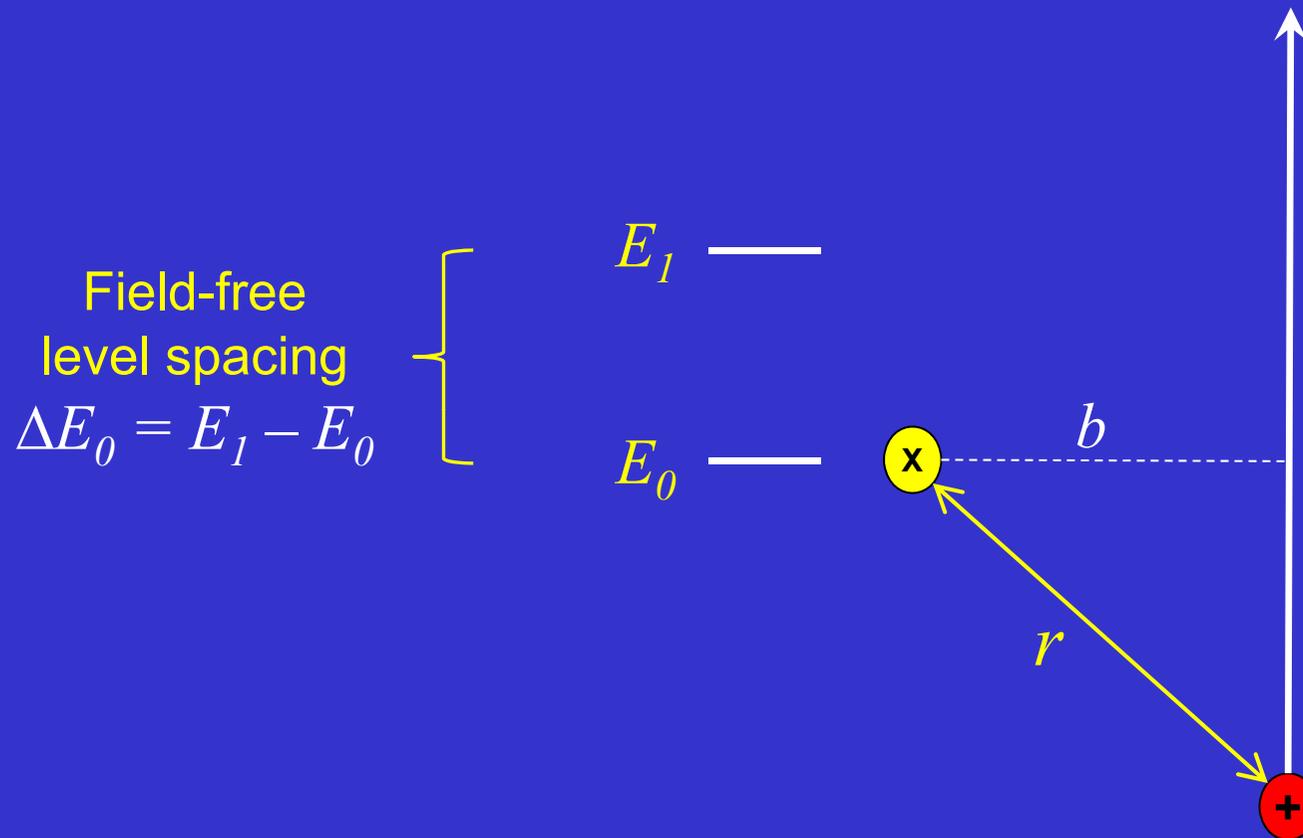
The condition for the validity of the adiabatic approximation is:

Rate of change of state vector $|i\rangle \ll \Delta E_{ij} / \hbar$ Bohr frequency

The Adiabatic Approximation: Heuristics

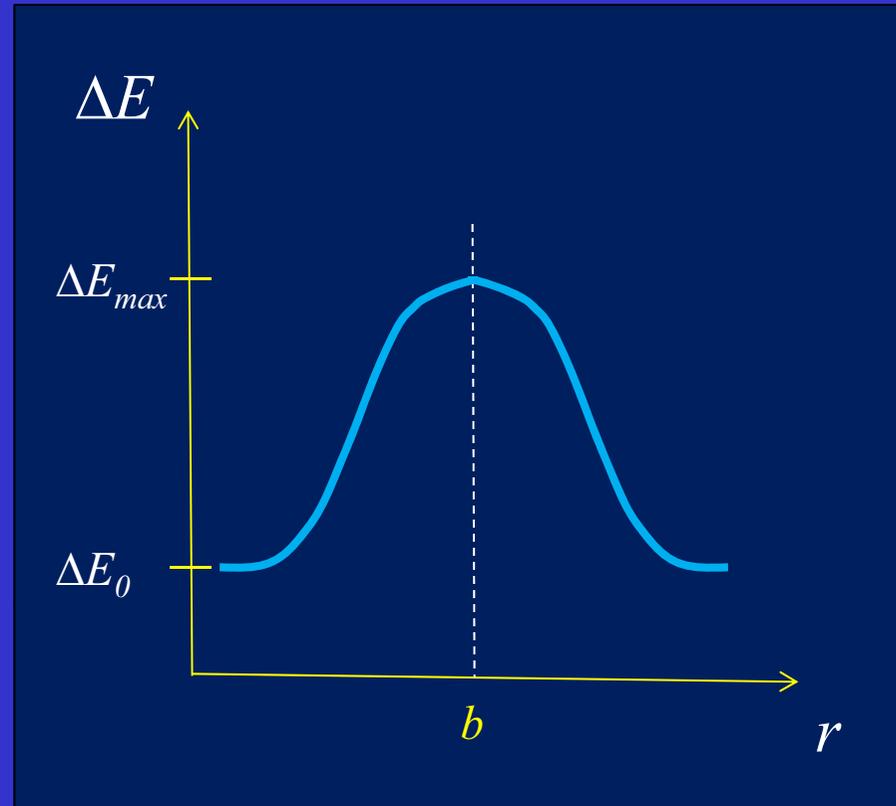
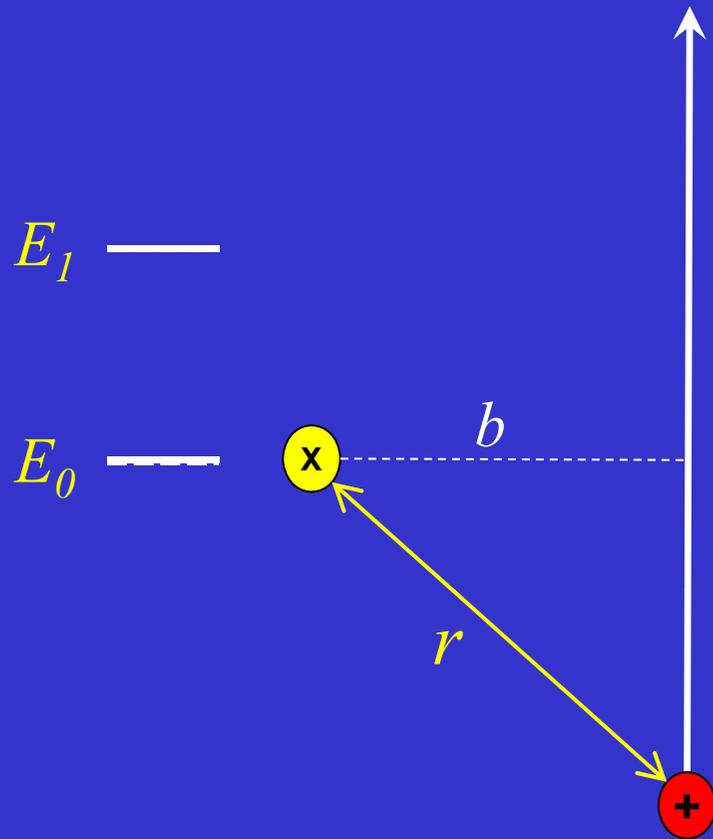
Stationary atom **X** with electronic eigenenergies E_i interacting with a massive charged particle (monopole).

The Stark effect on the atom depends only on their separation r .



At $r = \pm \infty$, the field-free level spacing ΔE_0 obtains.

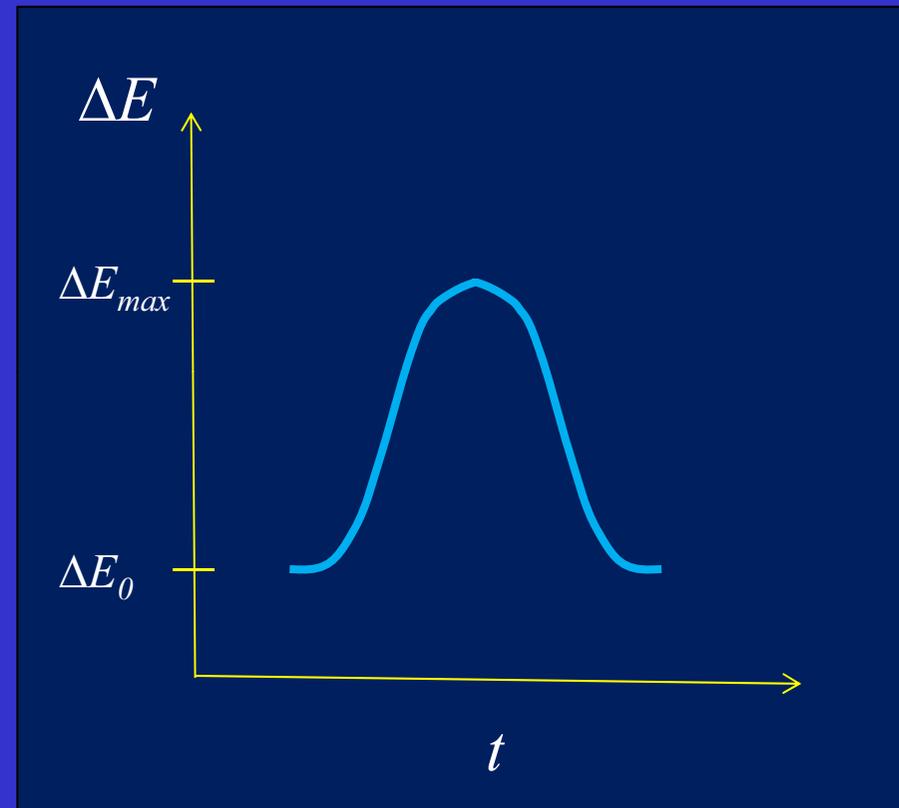
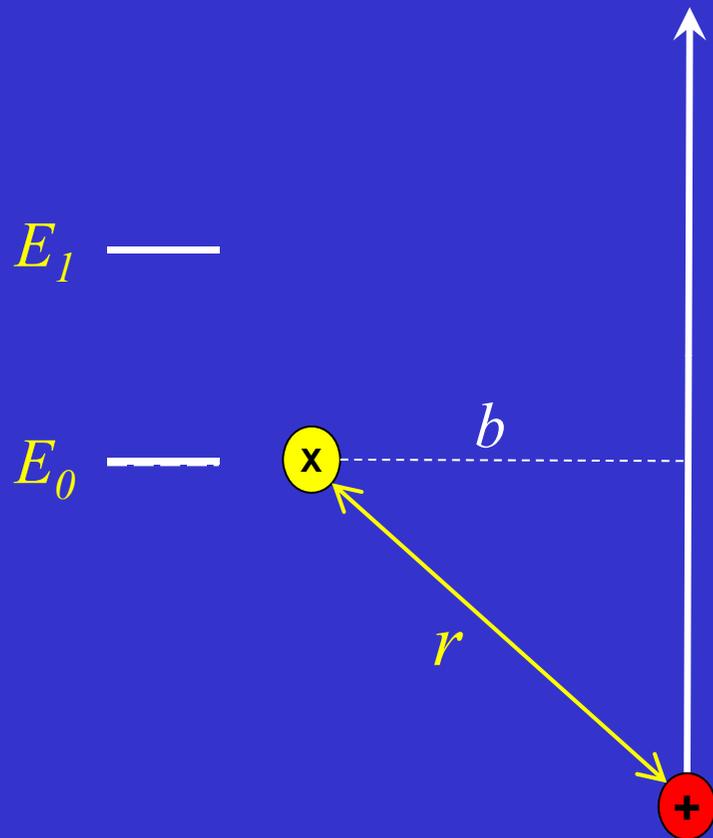
The Adiabatic Approximation: Heuristics



If we slowly move the charge, the Stark shift evolves slowly from zero, maximizing at b and then returning to the field-free value.

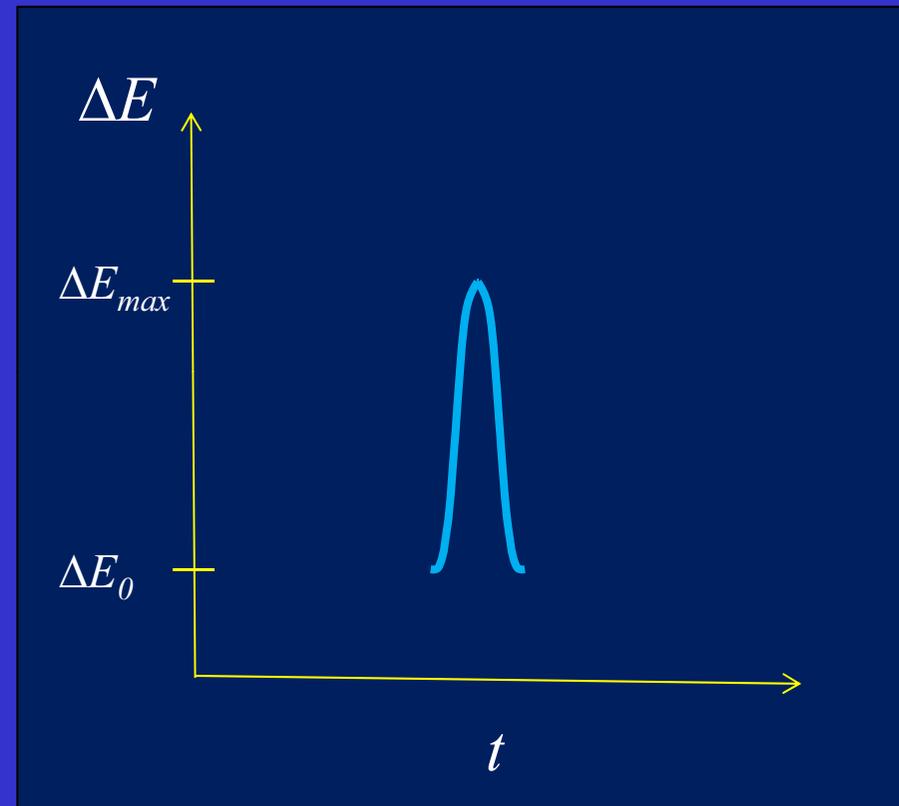
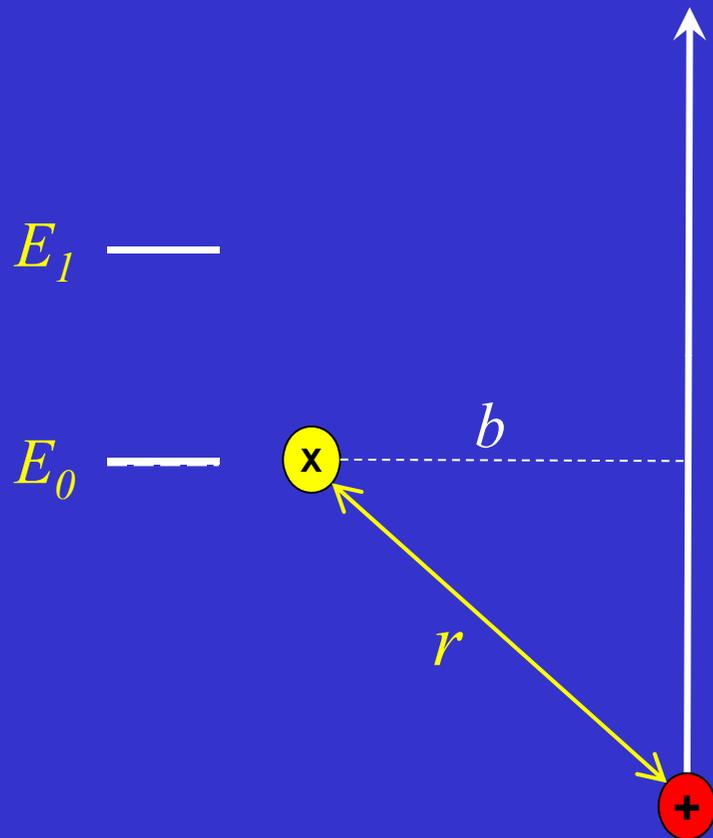
The Adiabatic Approximation: Heuristics

What if we roll the charged particle past the atom, faster and faster?
The atom feels a time-dependent electric field: a pulse!



The Adiabatic Approximation: Heuristics

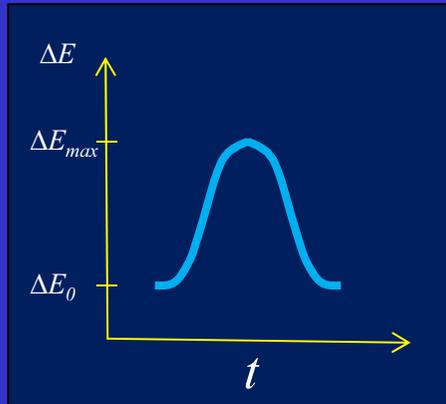
What if we roll the charged particle past the atom, faster and faster?
The atom feels a time-dependent electric field: a pulse!



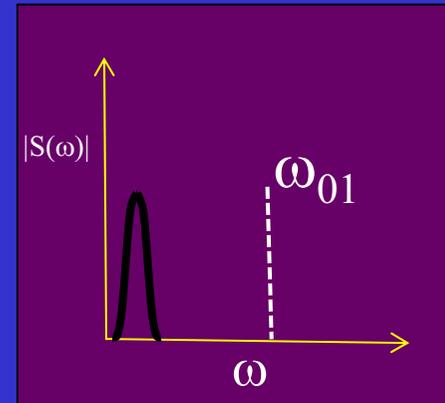
The Adiabatic Approximation: Heuristics

What are the Fourier components of this time-dependent electric field pulse?

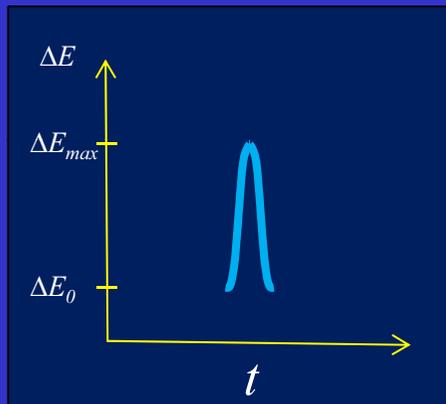
SLOW



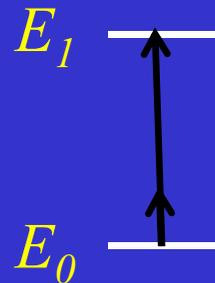
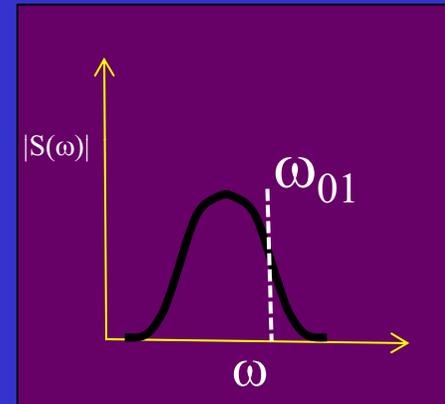
F.T. →



FAST



F.T. →



~~FAST~~ = adiabatic (transition)

The Adiabatic Approximation

So what does this mean?

- In Quantum Mechanics, time scales are measured by inverse level spacings. For the atom, $2\pi/\omega_{01}$ is the time scale of electronic motion. The 'speed' of the 'collision' is measured by the Fourier components of the interaction.
- When the time scale of the atomic motion is slow compared to electronic time scales, **ADIABATIC** behaviour obtains. The electron easily follows the time-dependent field. The atom remains in the same state after the 'collision'.
- When the time scale of the atomic motion is comparable to electronic time scales, **NONADIABATIC** behaviour obtains. The electron cannot keep up with the time-dependent field – a transition occurs – and the atom is in a different state after the 'collision'.

In molecules and solids, this adiabatic separation of electronic from atomic motions is called the Born-Oppenheimer approximation

Born-Oppenheimer Adiabatic Approximation

- Separation of electronic and nuclear coordinates is the central approximation of molecular physics. The idea of 'structure of matter' depends on it.

The nuclei (\mathbf{R}) move on a potential defined by the electronic (\mathbf{r}) energy

$$H\Psi(\mathbf{R}, \mathbf{r}) = E\Psi(\mathbf{R}, \mathbf{r})$$

electronic Hamiltonian

$$H = T_N + (T_e + V_{ee} + V_{eN} + V_{NN}) = T_N + H_e$$

- Since the nuclei are so much heavier (slower) than the electrons, assume T_N is a perturbation on H_e and start by find 'frozen core' solutions of the electronic Schrödinger equation:

$$H_e \Psi_i^e(\mathbf{r}, \mathbf{R}) = V_i(\mathbf{R}) \Psi_i^e(\mathbf{r}, \mathbf{R})$$

These are the electronic energies and wavefunctions from *ab initio* computations

\mathbf{r} = electronic coordinates, \mathbf{R} = nuclear coordinates

**Assuming the atoms are 'frozen' $T_N = 0$ is (very crudely)
the Born-Oppenheimer Approximation**

The Born-Oppenheimer Approx'n

Potential Energy Surfaces

Electronic Schrödinger equation depends parametrically on the nuclear coordinate \mathbf{R} .

$$H_e \Psi_i^e(\mathbf{r}, \mathbf{R}) = V_i(\mathbf{R}) \Psi_i^e(\mathbf{r}, \mathbf{R})$$

For each nuclear geometry \mathbf{R} there is an electronic energy $V_i(\mathbf{R})$.

If the atoms are moving (e.g. vibrating), then $V_i(\mathbf{R})$ evolves adiabatically with \mathbf{R} .

$V_i(\mathbf{R})$ is a $(3N-6)$ dimensional potential energy surface.

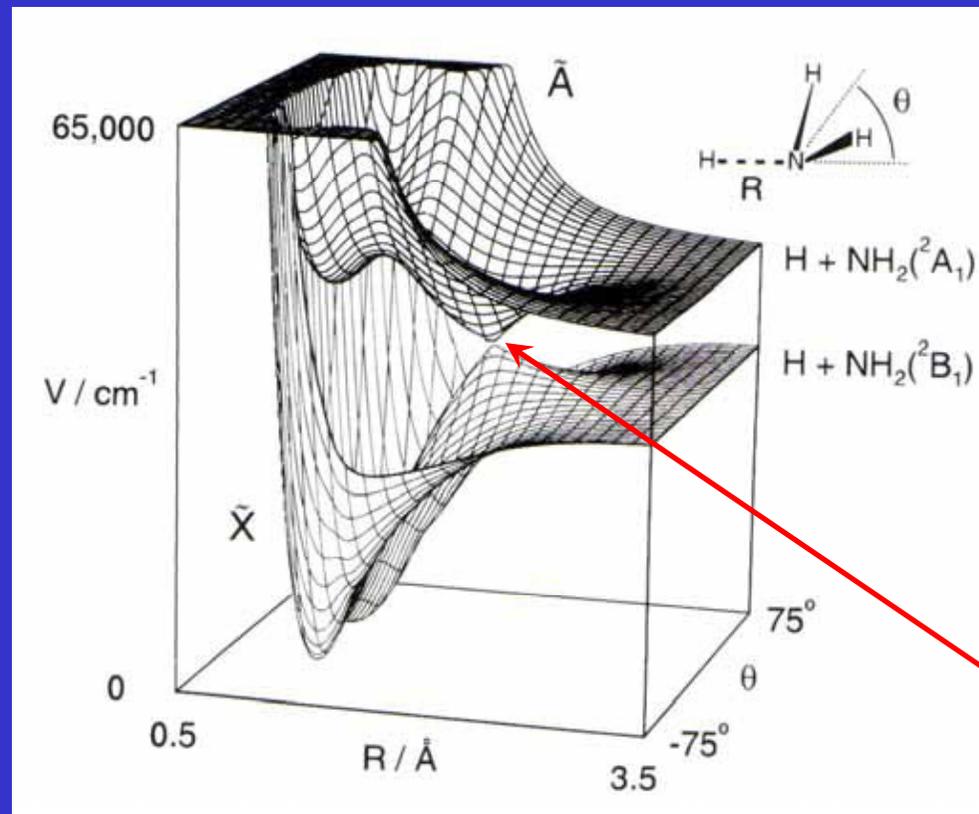
The BOA allows solution of the nuclear Schrödinger equation which yields the vibrational wavefunctions $\chi(\mathbf{R})$ for each electronic state

$$\hat{H}_N \chi_N(\mathbf{R}) = T_N + \underline{V_i(\mathbf{R})} = E \chi_N(\mathbf{R})$$

Potential Energy Surfaces

Defines both molecular structure & vibrational dynamics

Example:
Ammonia NH_3



But
what
happens
when
P.E.S.
cross?

Failure of the Born-Oppenheimer Approx'n

- The BOA is exact if the atoms are frozen. It's breakdown is uniquely due to the motions of the atoms. The nuclear kinetic energy operator:

$$T_N = \frac{\hbar^2}{2m_N} \nabla \cdot \nabla$$

- The coupling of electronic states by motions of the atoms. The faster the atoms move, the stronger is the coupling. This is a derivative coupling:

$$\mathbf{F}_{ji}(\mathbf{R}) = \left\langle \Psi_j^e(\mathbf{R}) \left| \nabla \Psi_i^e(\mathbf{R}) \right. \right\rangle$$

Non-local,
Depends on velocities

Equivalently

$$\mathbf{F}_{ji}(\mathbf{R}) = \frac{\left\langle \Psi_j^e(\mathbf{R}) \left| \nabla H_e \right| \Psi_i^e(\mathbf{R}) \right\rangle}{V_i(\mathbf{R}) - V_j(\mathbf{R})}$$

Denominator depends on the level spacings ...

- When electronic states are well separated in energy, the BOA is a good one.
- When states come close in energy, the time-dependent electric field due to the motion of the charged atoms can itself induce an electronic transition.
The BOA fails and electronic & vibrational motions become strongly coupled.

Failure of the Born-Oppenheimer Approx'n

- What happens when electronic state potentials cross?

$$\mathbf{F}_{ji}(\mathbf{R}) = \lim_{\Delta E_{ij} \rightarrow 0} \frac{\langle \Psi_j^e(\mathbf{R}) | \nabla H_e | \Psi_i^e(\mathbf{R}) \rangle}{\Delta E_{ij}} = \infty$$

- Recall that $\mathbf{F}_{ii}(\mathbf{R}) \sim$ zero in the Born-Oppenheimer approximation, therefore

When two (or more states) get close in energy, the Born-Oppenheimer approximation fails.

The nuclear and electronic degrees of freedom are *coupled*.

Equivalently, the strength of the derivative coupling serves as an indicator of the validity of the Born-Oppenheimer approximation.

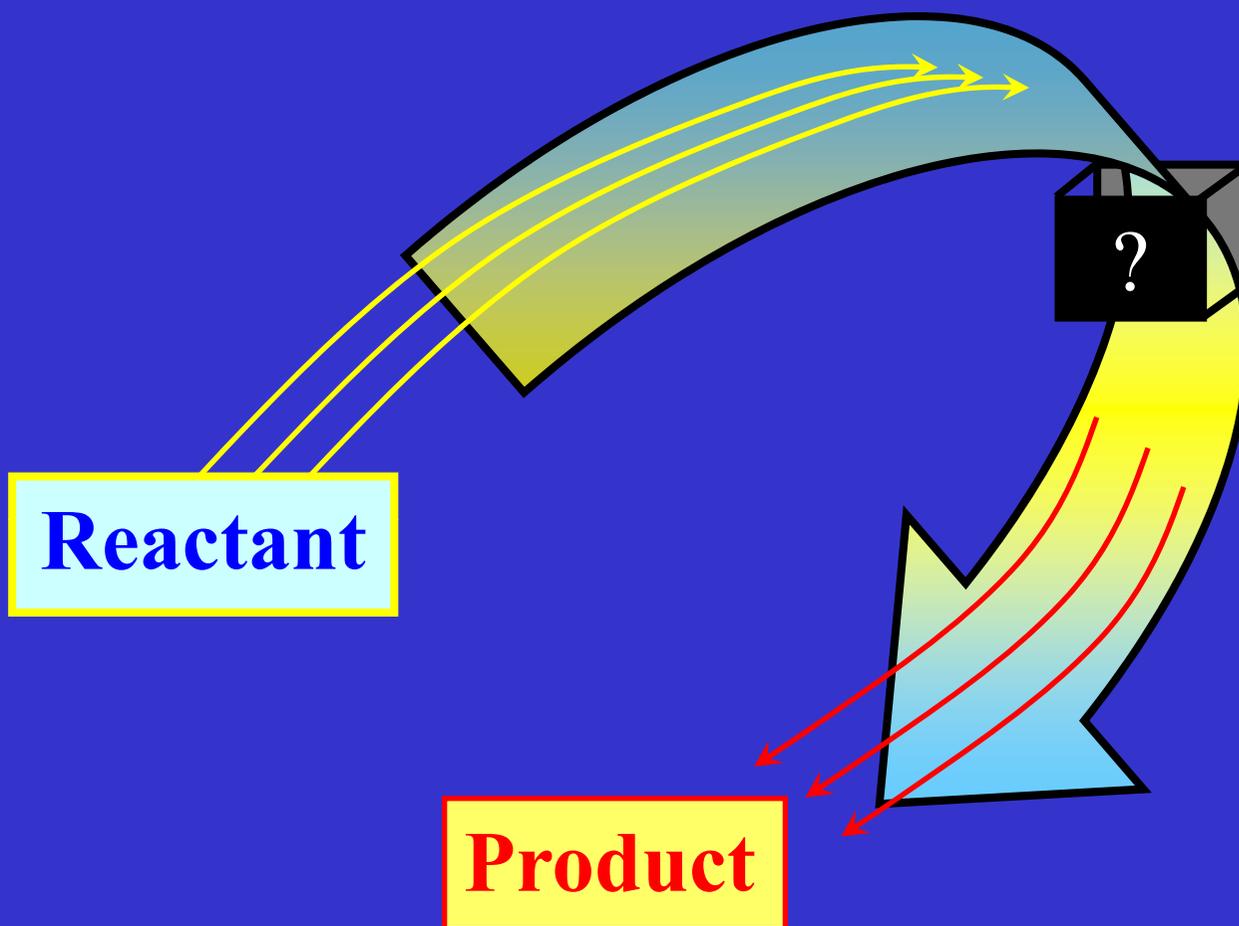
Statement: Chemistry is Not Possible

- Typical bond energy $\sim 3\text{-}4\text{ eV}$
- Typical collision energy at $kT \sim 25\text{ meV}$
- Therefore chemistry is impossible.

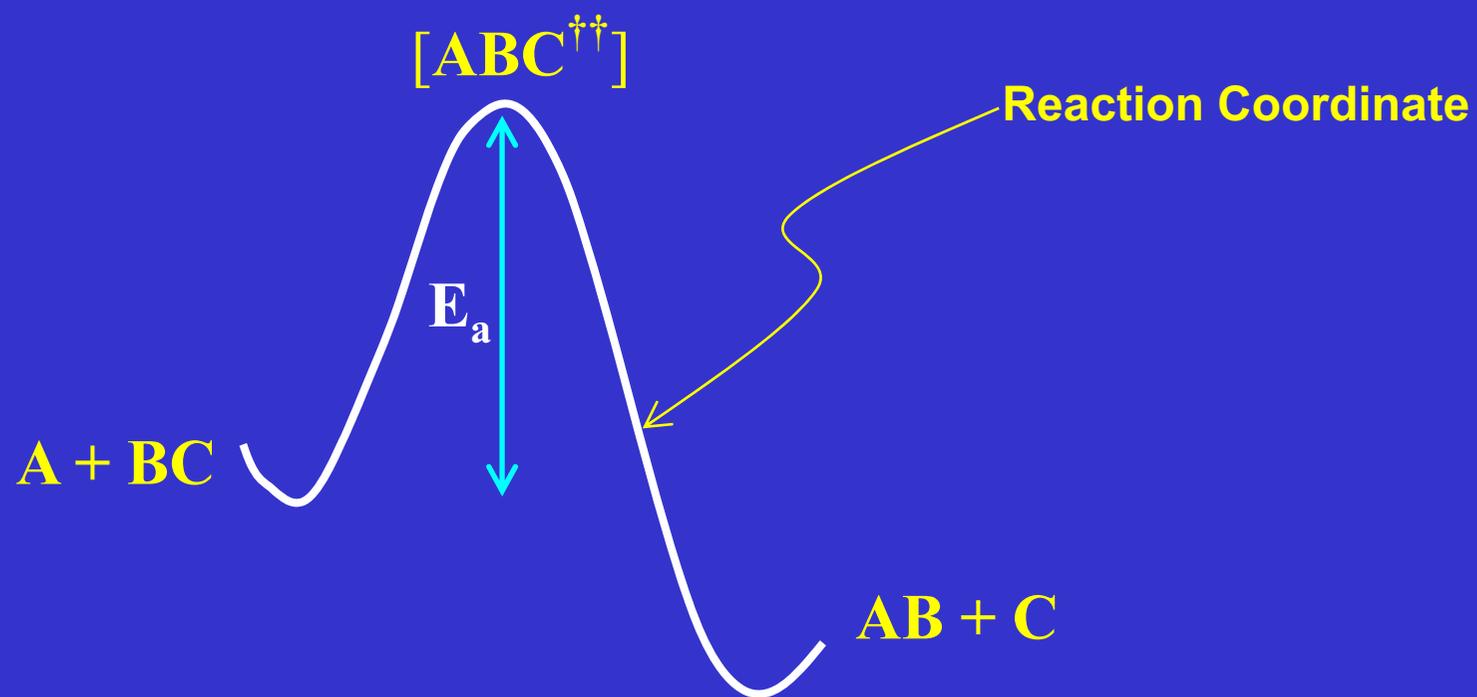
What is wrong with this statement?

- The old bonds do NOT need to be broken before the new bonds form. It happens simultaneously, concertedly.
- It is this complex, coupled dance of both atoms and valence electrons that we call **CHEMISTRY**.

The Arrow of Chemistry



Chemical Reaction Kinetics

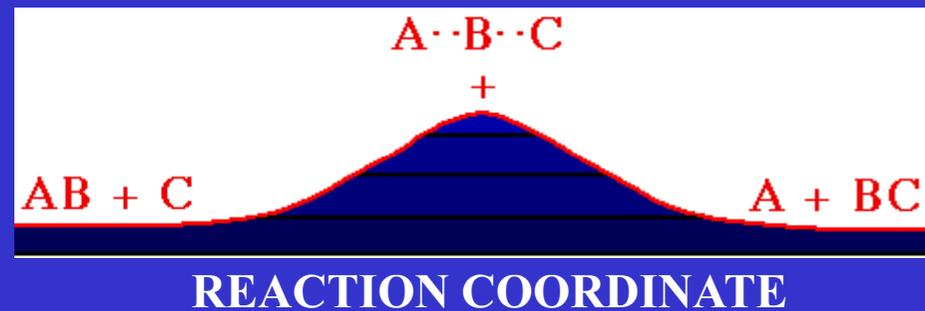
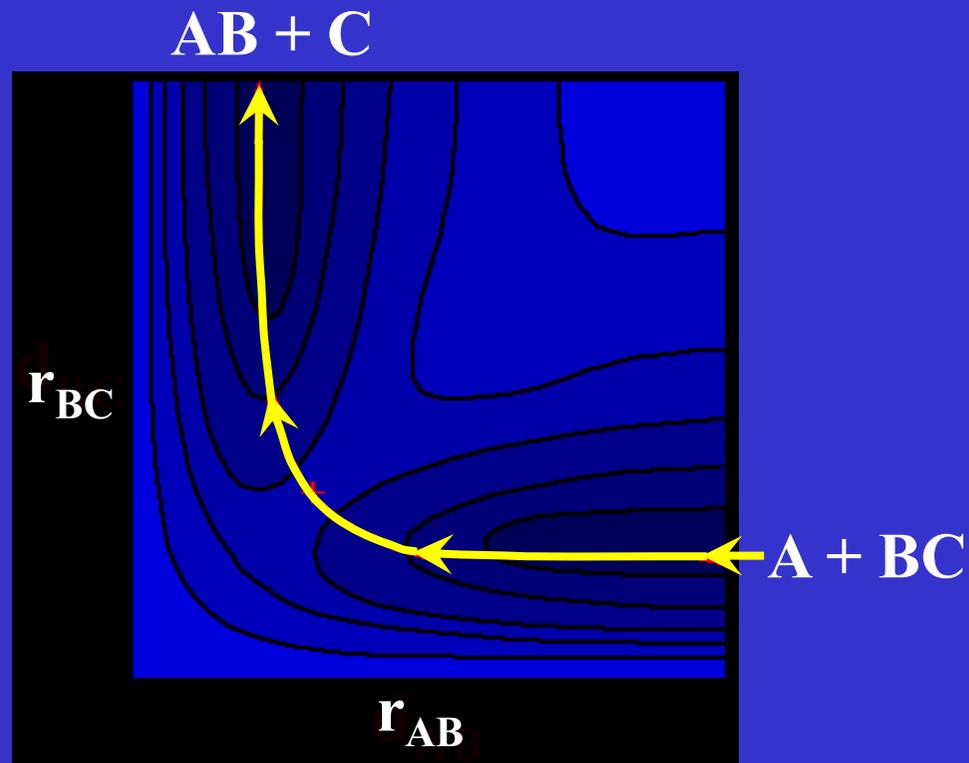


$$-\frac{\partial[BC]}{\partial t} = \frac{\partial[AB]}{\partial t} = k[A][BC]$$

$$k \propto A(T) e^{-E_a/RT}$$

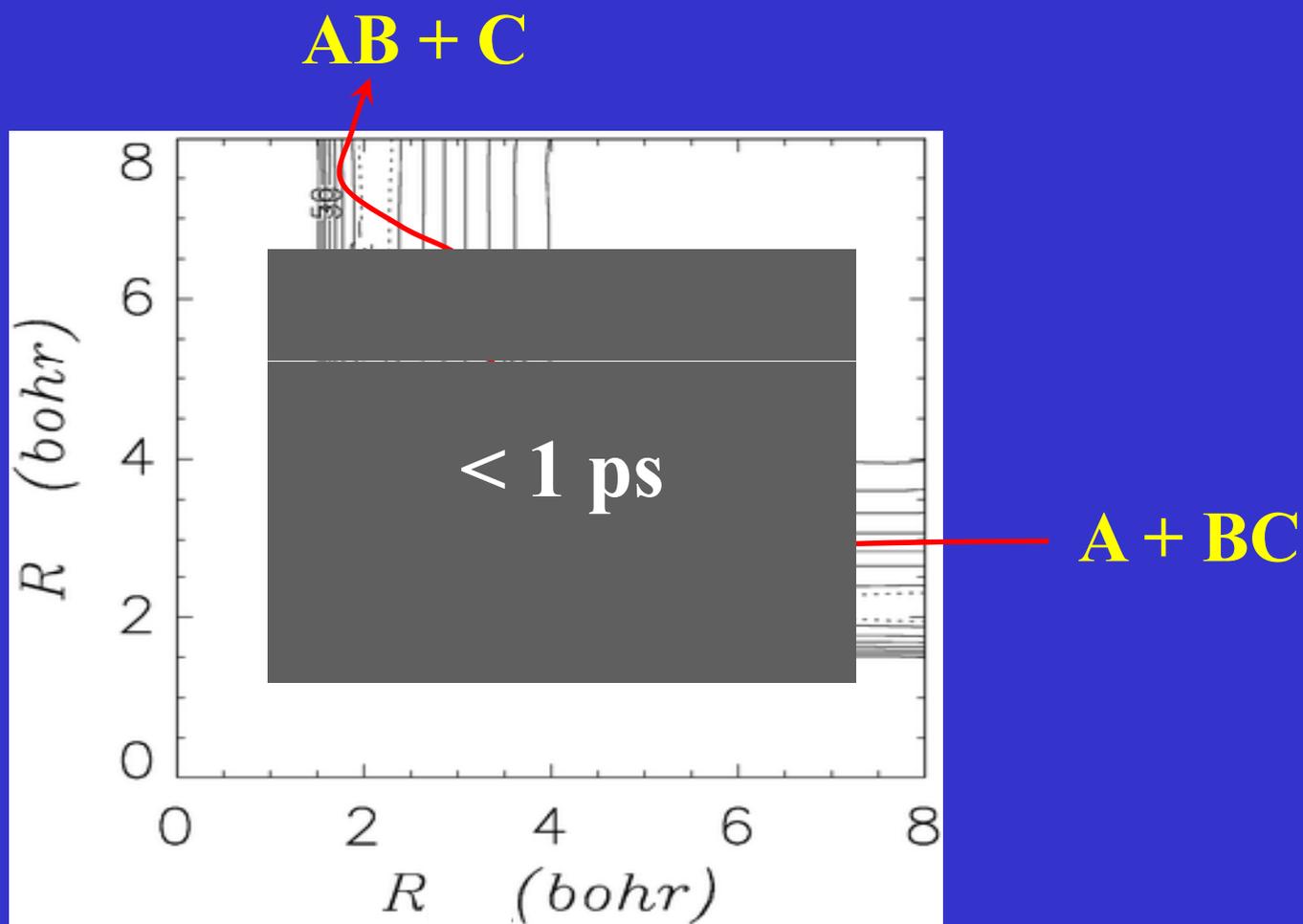
Chemical Reaction Dynamics

POTENTIAL
ENERGY
SURFACE



Chemical Reaction Dynamics

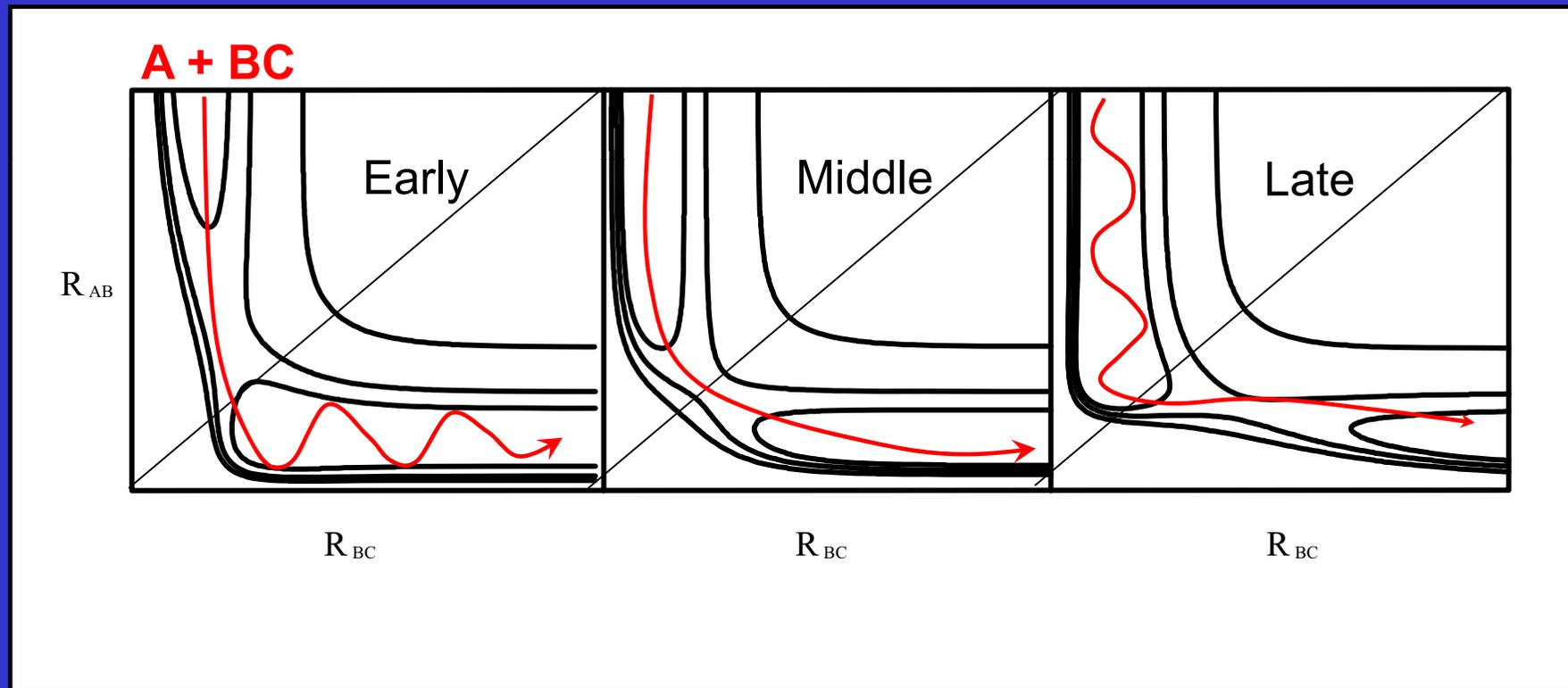
A concerted rearrangement of both the atoms and the **valence** electrons



Polanyi Rules

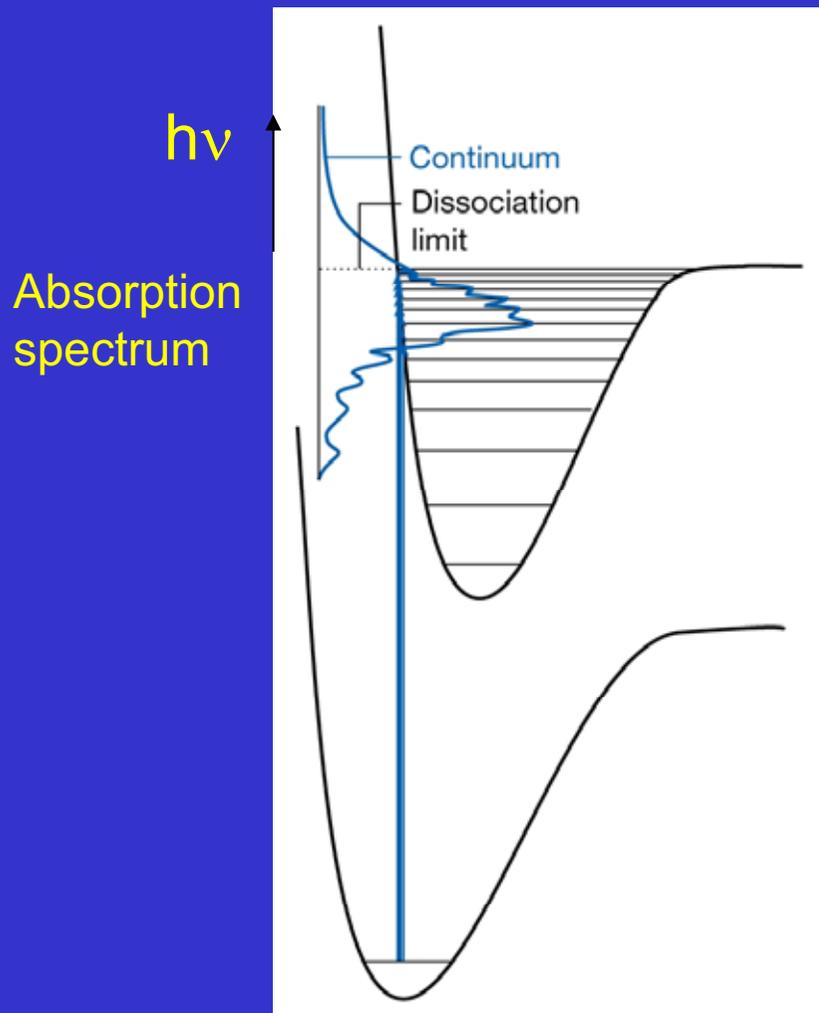


- Topography of the Transition State region
- Role of translational vs. vibrational energy



Photodissociation Dynamics: A 'half' collision

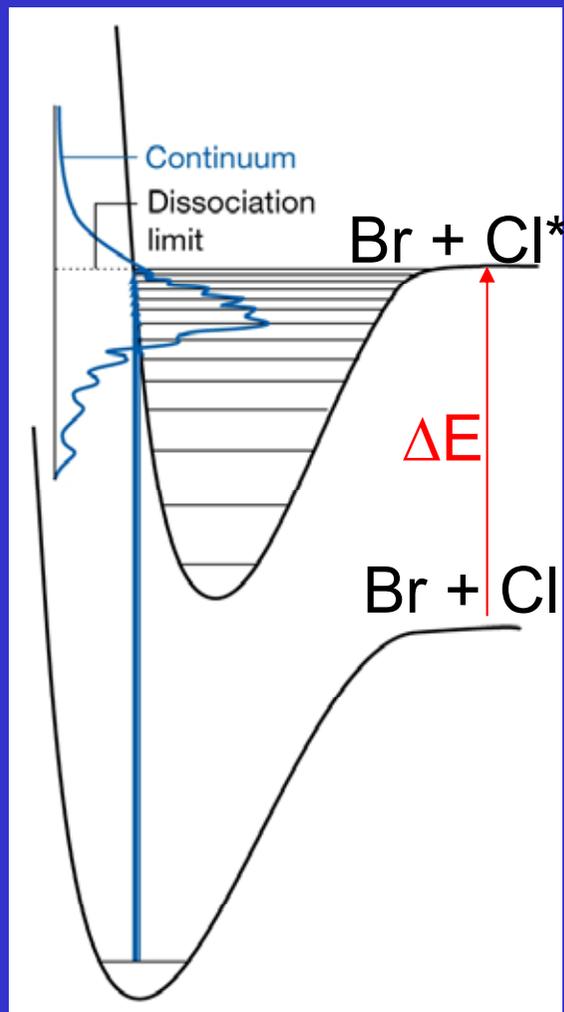
Direct dissociation: photoexcitation into a continuum



Absorption spectrum becomes continuous at sufficiently short wavelengths as $h\nu$ crosses a dissociation threshold

Photodissociation Dynamics

The excited state may correlate to different dissociation products than does the ground state



e.g., for BrCl, the first excited state correlates with Br + Cl*

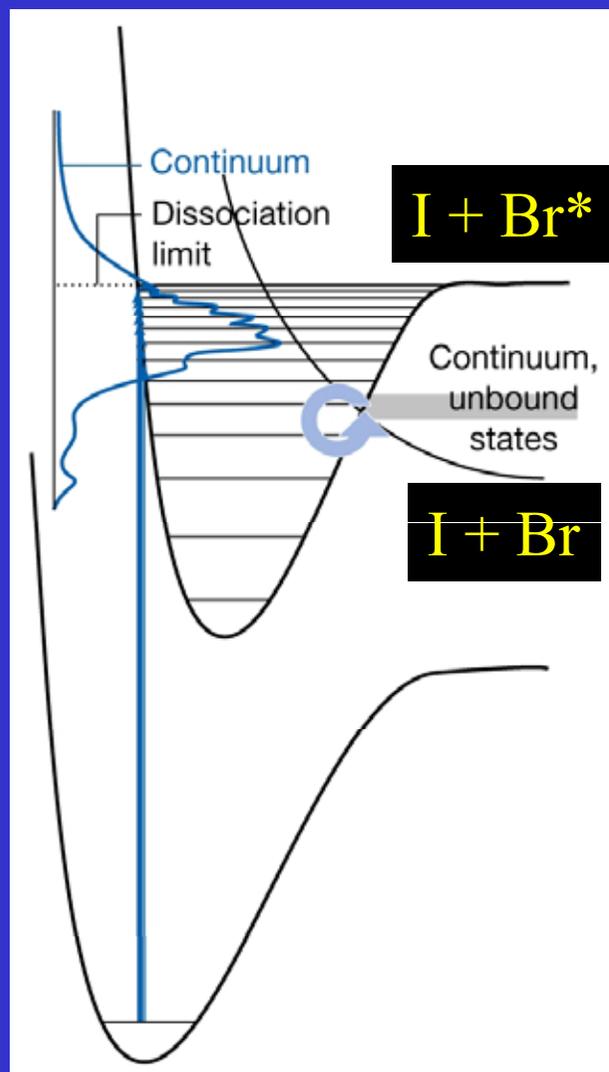
Cl* \equiv $^2P_{1/2}$ state

Cl \equiv $^2P_{3/2}$ state

(energy difference = ΔE , spin-orbit splitting)

Non-adiabatic Photodissociation Dynamics

Predissociation: non-adiabatic coupling



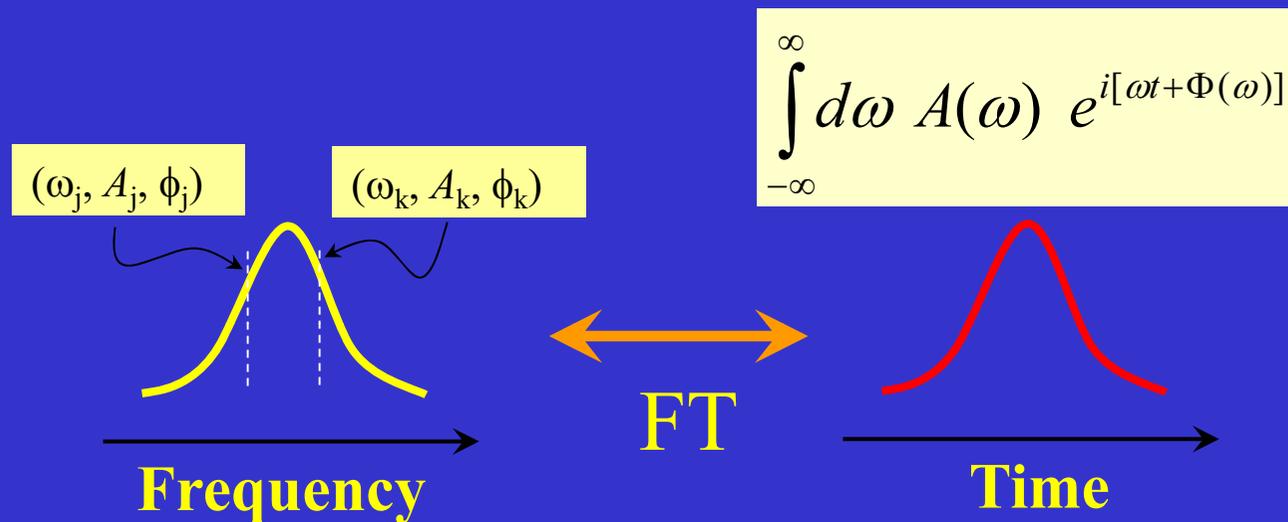
Molecule excited to bound state – vibrates for perhaps a few periods then undergoes non-adiabatic curve crossing and dissociates on repulsive PE curve.



Connection with Optics

Ultrashort Laser Pulses

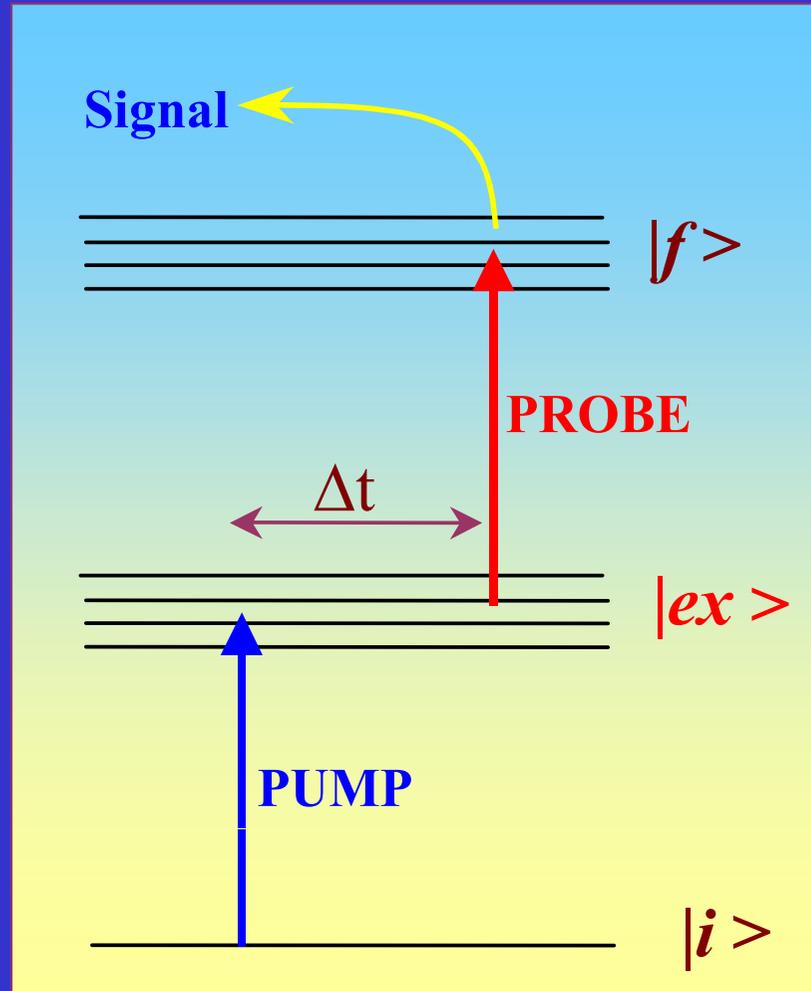
A broad superposition of optical frequencies with *well defined* amplitudes $A(\omega)$ and phases $\Phi(\omega)$.



It is this exquisite control over amplitude and optical phase that we transfer to material systems, in order to measure their response.

Pump-probe spectroscopy.

ULTRAFAST PUMP-PROBE SPECTROSCOPY



- ⇒ Prepare an excited state with a **PUMP** pulse
- ⇒ Let it evolve for a time Δt
- ⇒ Project it with a **PROBE** pulse onto a final state
- ⇒ Detect a signal (particle or photon) related to the probability of being in that final state

I have made no comment about pulse durations.
The following arguments apply for ANY pulse duration.

Time Dependent Schrödinger Equation

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

Separation of variables $\Psi(\vec{r}, t) = \Phi(t) \psi(\vec{r})$

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

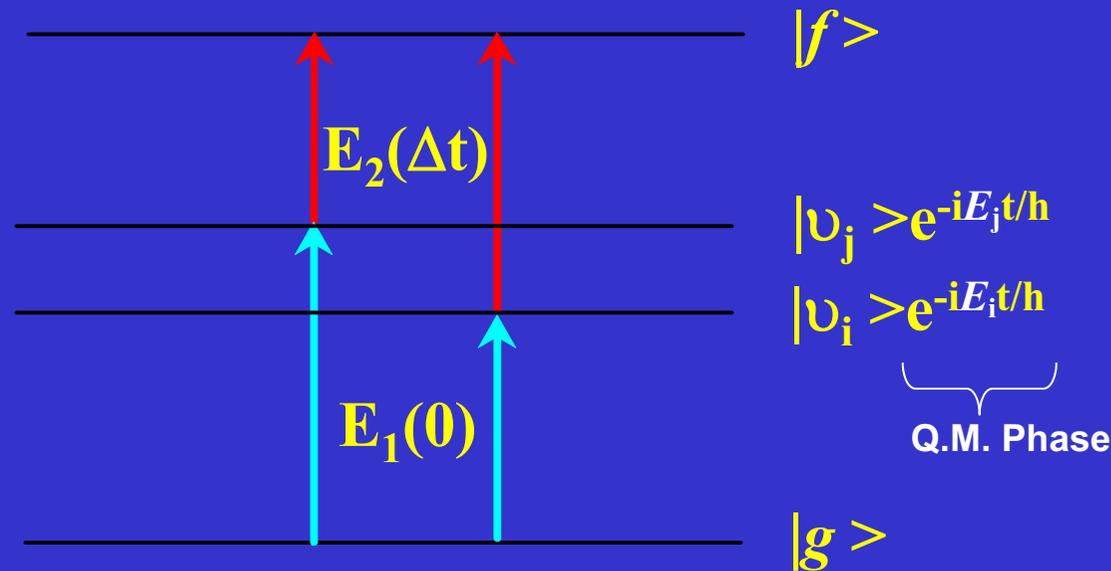
$$i\hbar \frac{\partial \Phi(t)}{\partial t} = E \Phi(t)$$


$$\Phi(t) = e^{-iEt/\hbar}$$

Full wavefunction:

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

Interference between Coherent Two-Photon Transitions



$$P_{g-f}(\Delta t) = \left| \langle f | \mu \cdot \mathbf{E}_2 | v_i e^{-iE_i t/\hbar} \rangle \langle v_i | \mu \cdot \mathbf{E}_1 | g \rangle + \langle f | \mu \cdot \mathbf{E}_2 | v_j e^{-iE_j t/\hbar} \rangle \langle v_j | \mu \cdot \mathbf{E}_1 | g \rangle \right|^2$$

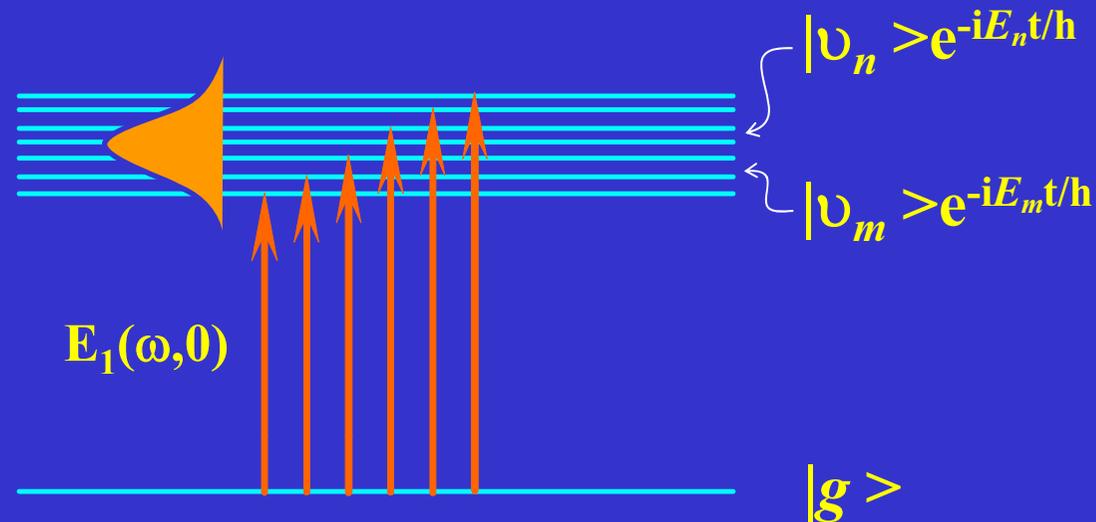
$$\propto b_1^2 + b_2^2 + 2b_1 b_2 \cos\{(E_j - E_i)\Delta t/\hbar\}$$

Quantum Beat

A time-domain two slit interference pattern

Creation of a Wavepacket

Using very short coherent pulses, we can span *many* intermediate states. We therefore prepare a multi-level coherent superposition: a “wavepacket”.

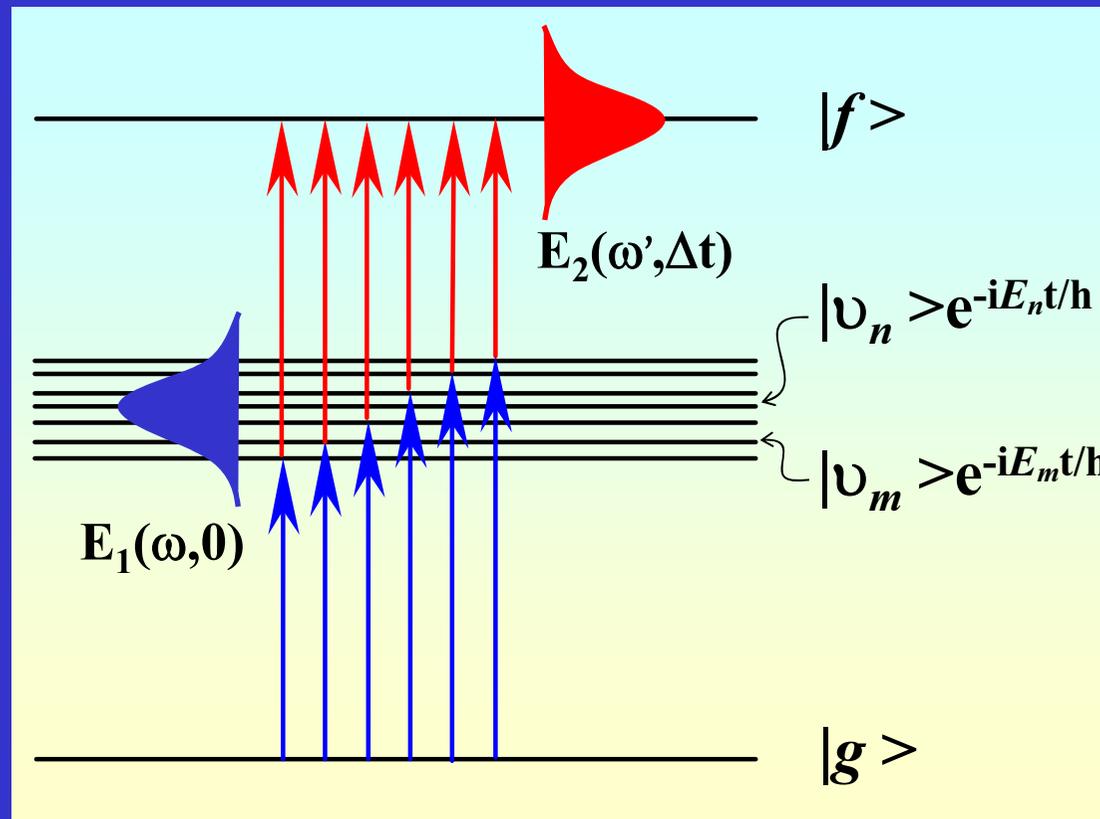


$$|\chi(\Delta t)\rangle = \sum_n a_n |v_n\rangle e^{-i2\pi c E_n(v_n)\Delta t}$$

where $a_n = \langle v_n | \mu \cdot \mathbf{E}_1 | g \rangle$

Wavepackets often behave like zeroth order states and can exhibit classical localization.

Probing Wavepacket Dynamics: Multiple Coherent Two-Photon Transitions



Multiple Coherent Two-Photon Transitions

Wavepacket

$$|\chi(\Delta t)\rangle = \sum_n a_n |v_n\rangle e^{-i2\pi c E_n(v_n)\Delta t}$$

Project onto final state

$$P_{g-f} = \left| \langle f | \mu \cdot \mathbf{E}_2 | \chi(\Delta t) \rangle \right|^2$$

$$P_{g-f} = \sum_n \sum_m b_n b_m \cos \{ (E_n - E_m) 2\pi c \Delta t + \phi_{nm} \}$$

where $b_n = a_n \langle f | \mu \cdot \mathbf{E}_2 | v_n \rangle$

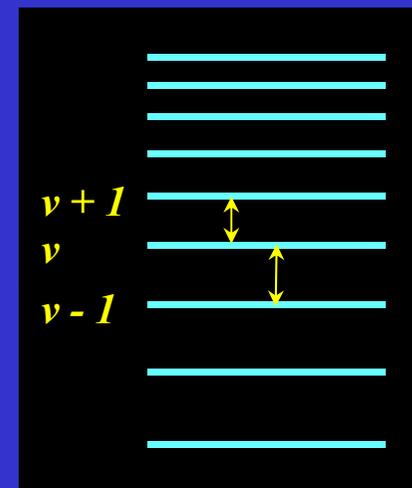
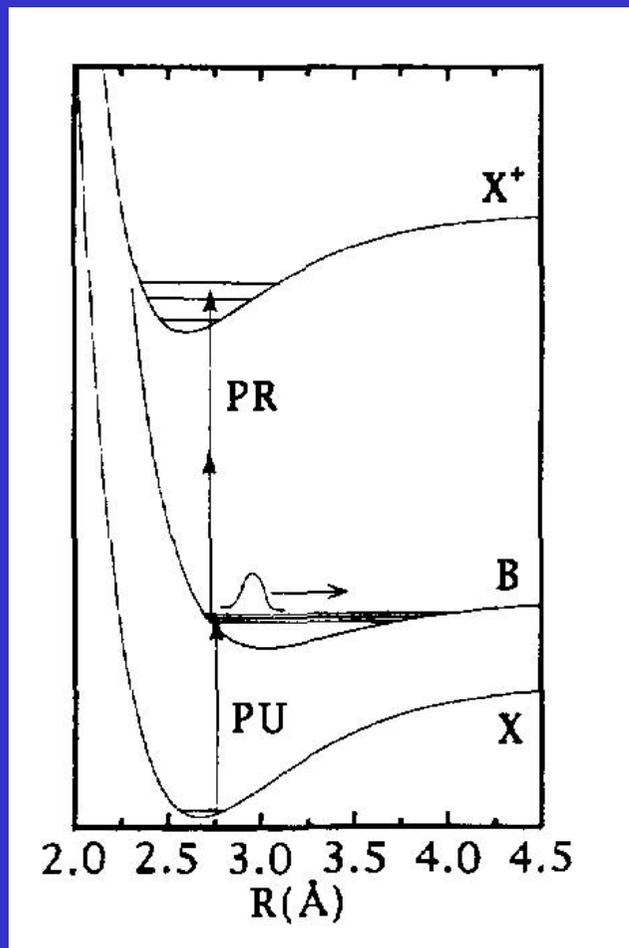
The modulation frequencies are given by the set of level spacings $\{E_n - E_m\}$ in the problem.

Wavepacket detection yields a time-domain multiple slit interference pattern

Example: Diatomic wavepacket dynamics

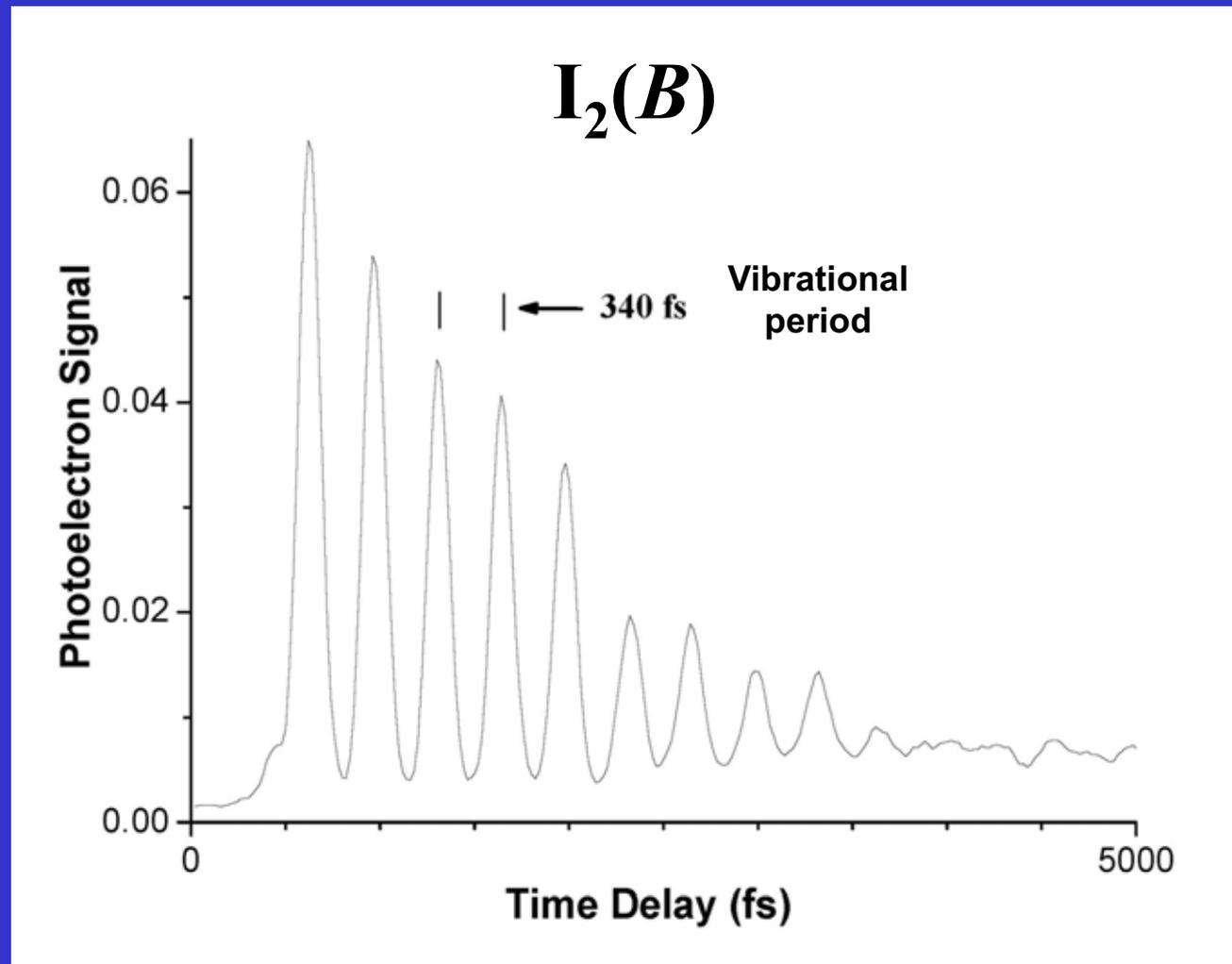
I_2 B-state probed by time-resolved photoelectron spectroscopy

- Excite I_2 to the B-state, making a vibrational wavepacket.
- Detect the wavepacket dynamics via two-photon ionization to the cation ground state.

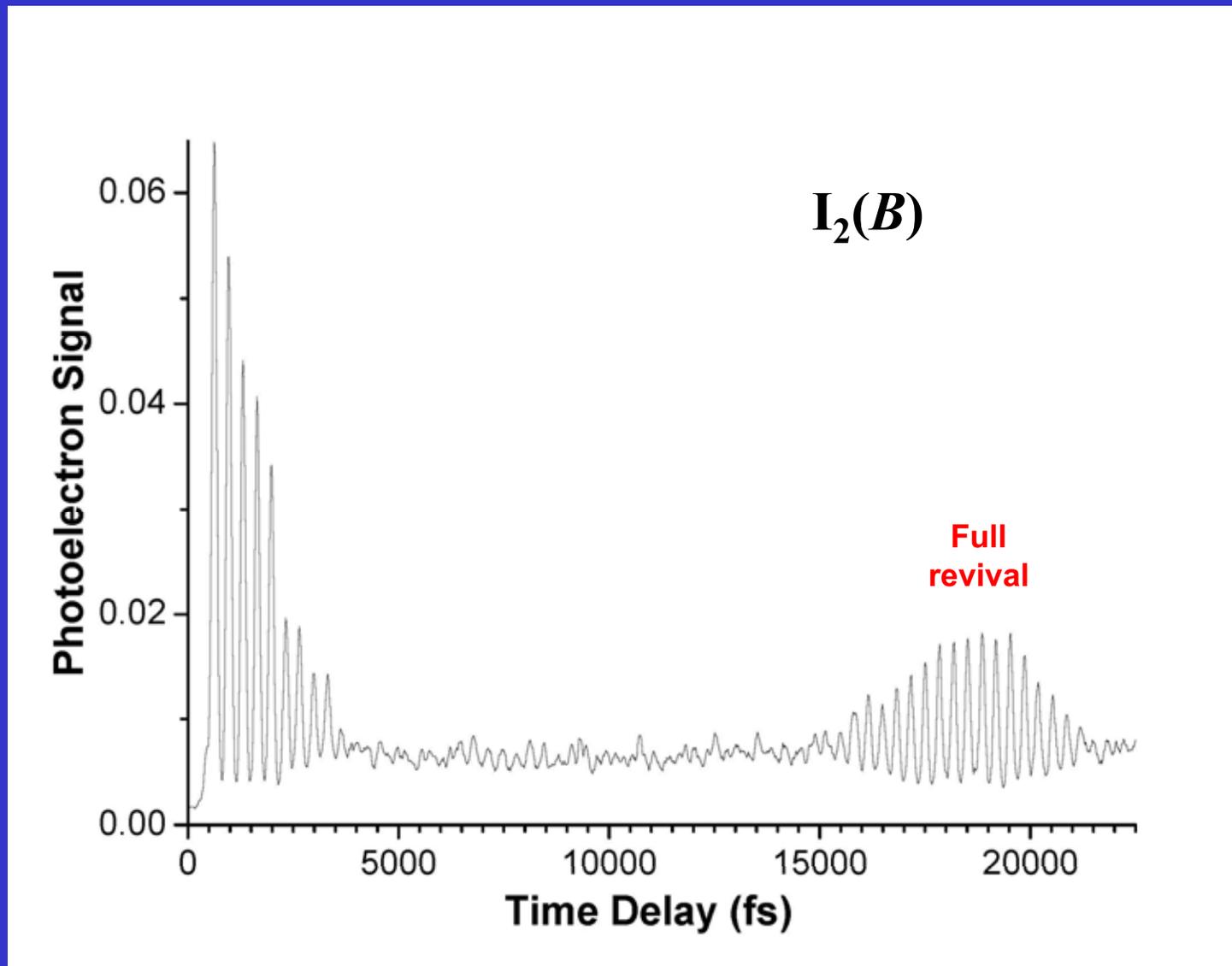


Example: Diatomic wavepacket dynamics

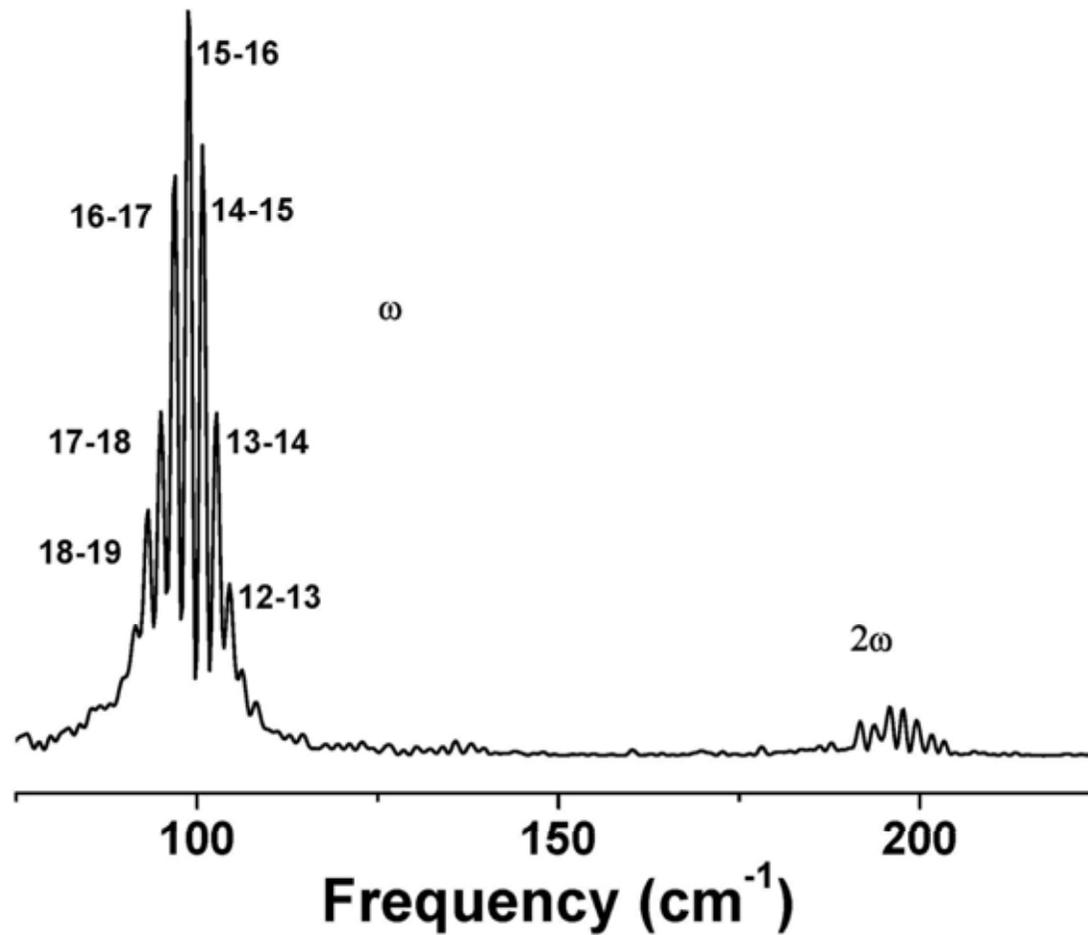
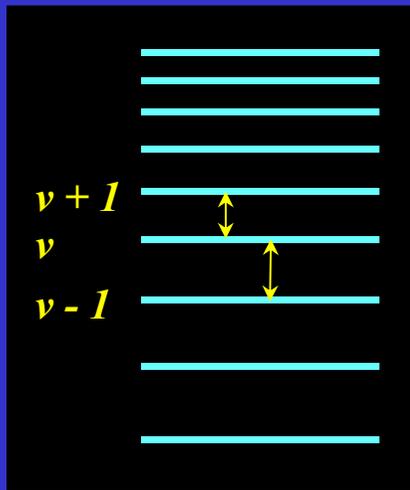
I. Fischer, D.M. Villeneuve, M.J.J. Vrakking & A. Stolow
Journal of Chemical Physics 102, 5566 (1995)



Wavepacket Dephasing and Revival



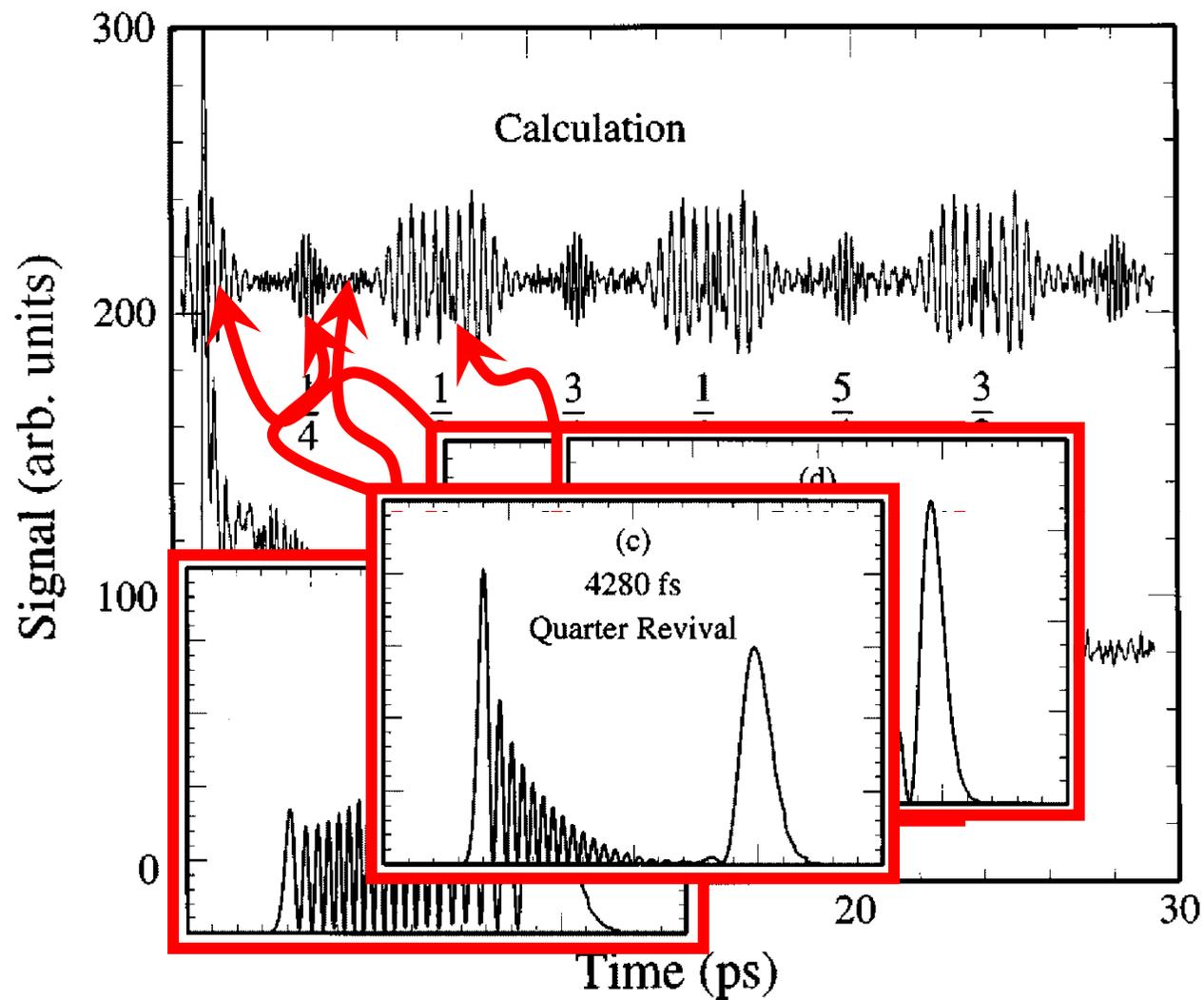
Diatomic wavepacket dynamics



Non-classical States: Fractional Revivals

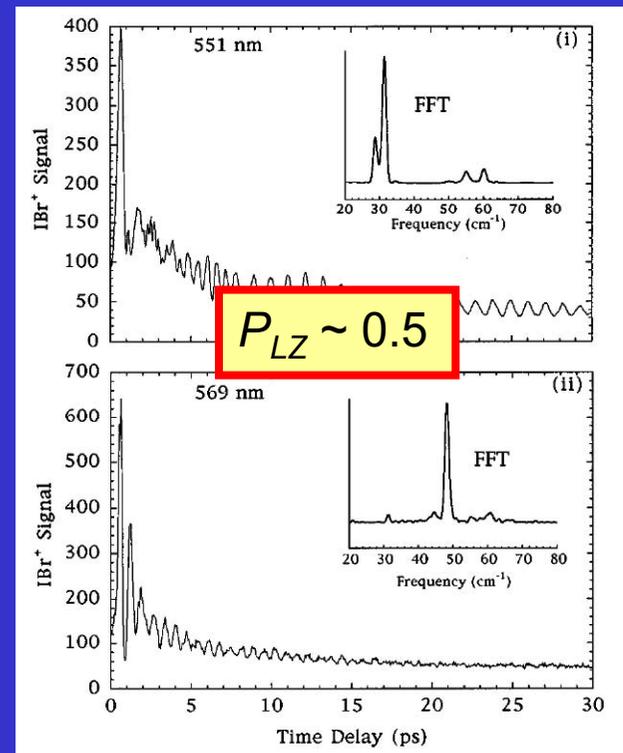
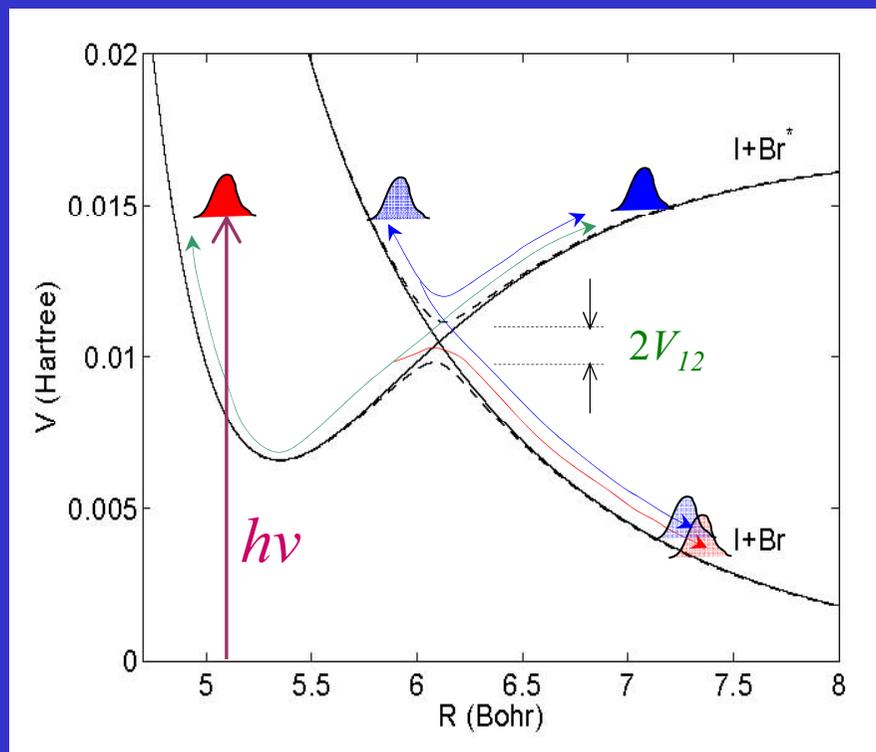
M.J.J. Vrakking, D.M. Villeneuve & A. Stolow
Physical Review A 54, 37R (1996)

$\text{Br}_2(B)$



Photodissociation Dynamics of IBr

Electronic Branching at an Avoided Crossing



Intermediate case coupling: $V_{12} \sim 100 \text{ cm}^{-1}$
Bound diabat $B \ ^3\Pi_{0+} \rightarrow \text{I} + \text{Br}^*$
Dissociative diabat $Y(0^+) \rightarrow \text{I} + \text{Br}$

Interference between diabatic and adiabatic wavepackets

MJJ Vrakking, DM Villeneuve, A Stolow. *J.Chem.Phys.* 105, 5647 (1996)
 M Shapiro, MJJ Vrakking, A Stolow. *J.Chem.Phys.* 110, 2465 (1999)

Multiple Coherent Two-Photon Transitions

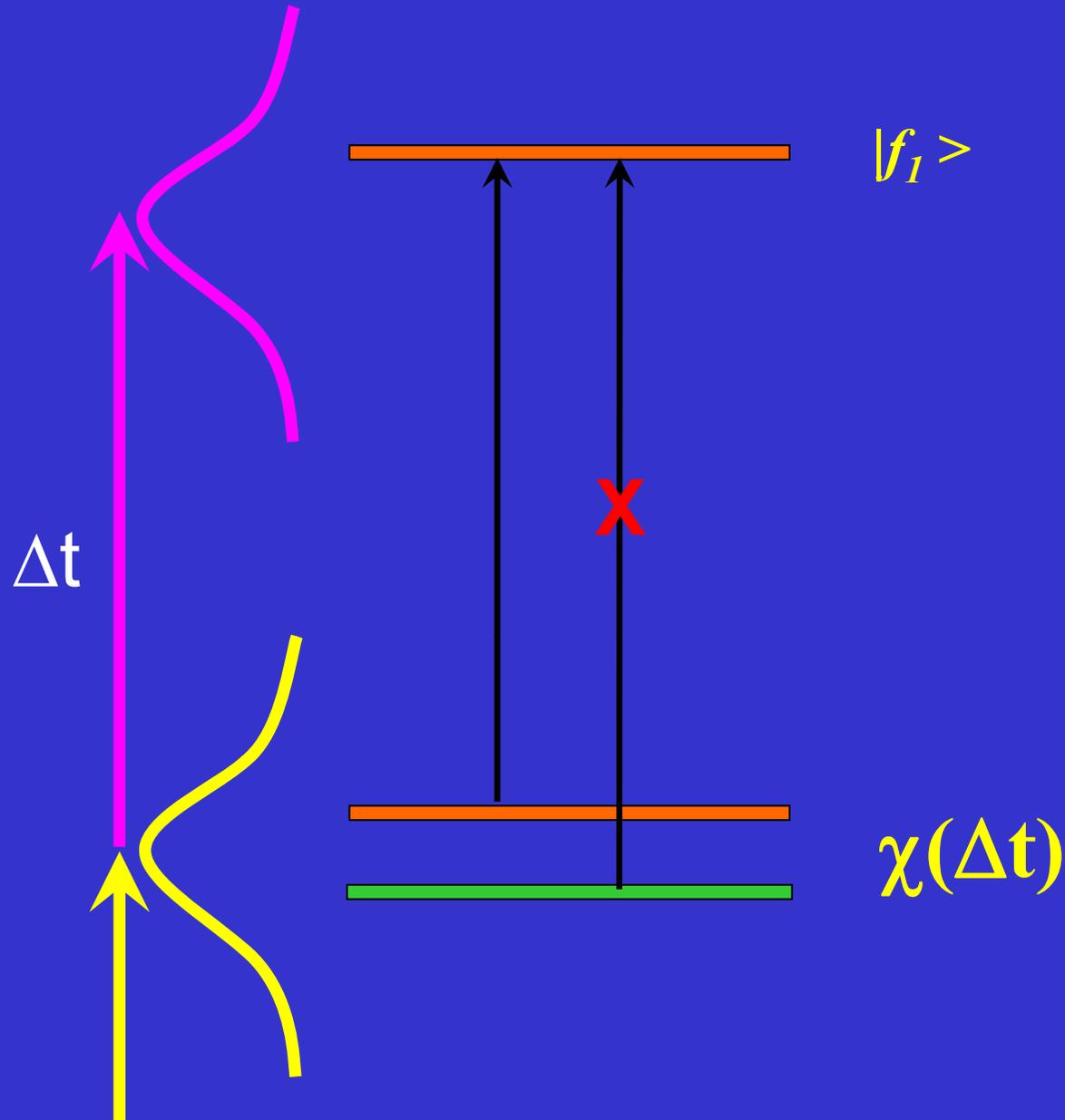
The modulation amplitude at a given frequency depends on the relative transition probabilities $|f\rangle \leftarrow |v_n\rangle$ vs. $|f\rangle \leftarrow |v_m\rangle$

The choice of the final state $|f\rangle$, which acts as a *template* for the wavepacket projection, is critically important.

We might expect that different final states should exhibit differing sensitivities to components of the Wavepacket Dynamics.

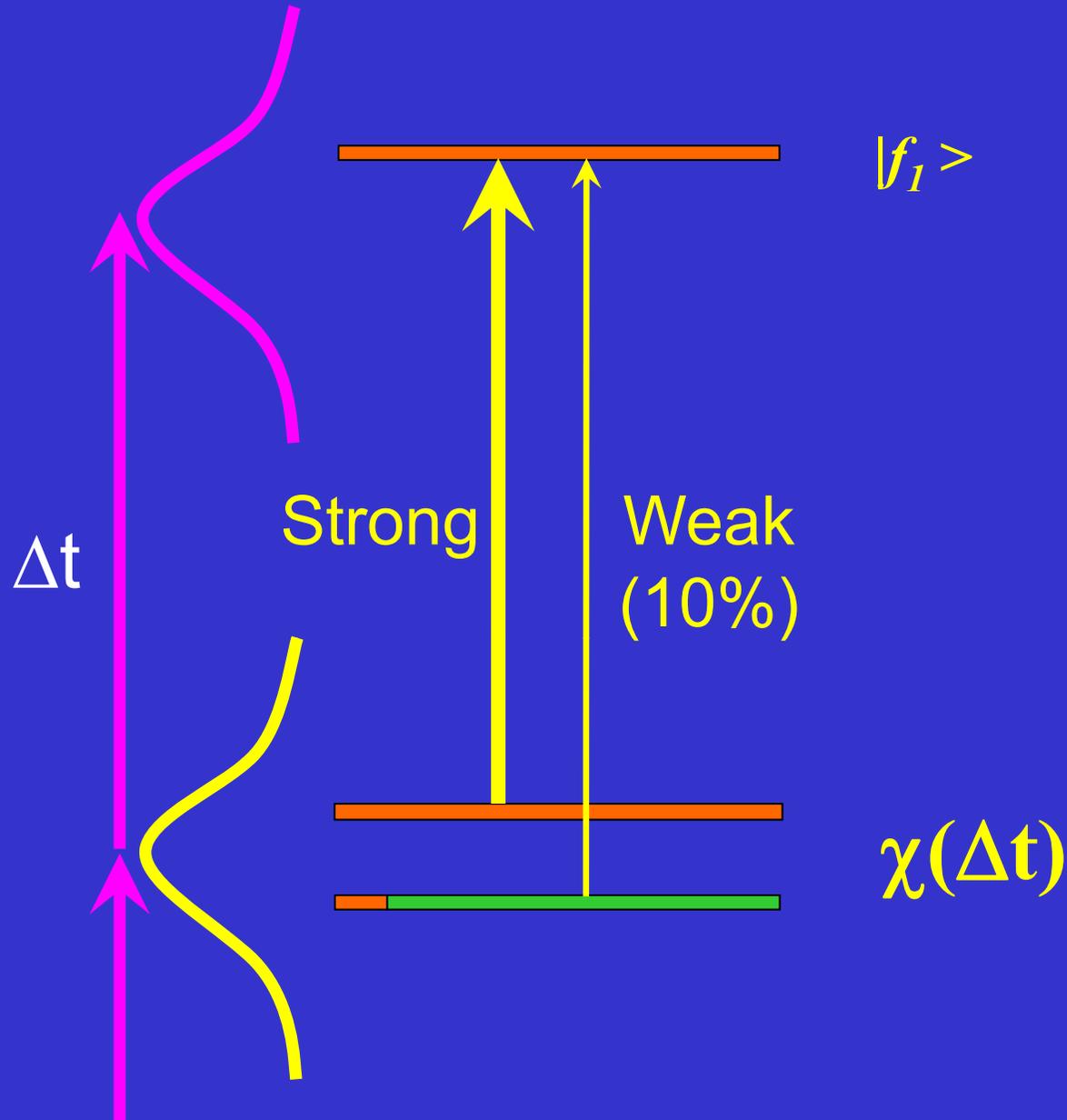
The choice of final state also determines what is detected: Scattered or absorbed X-ray photon, scattered electron, ion, high harmonic light, photofragment, UV-Vis photon, *whatever....*

Role of the Final State



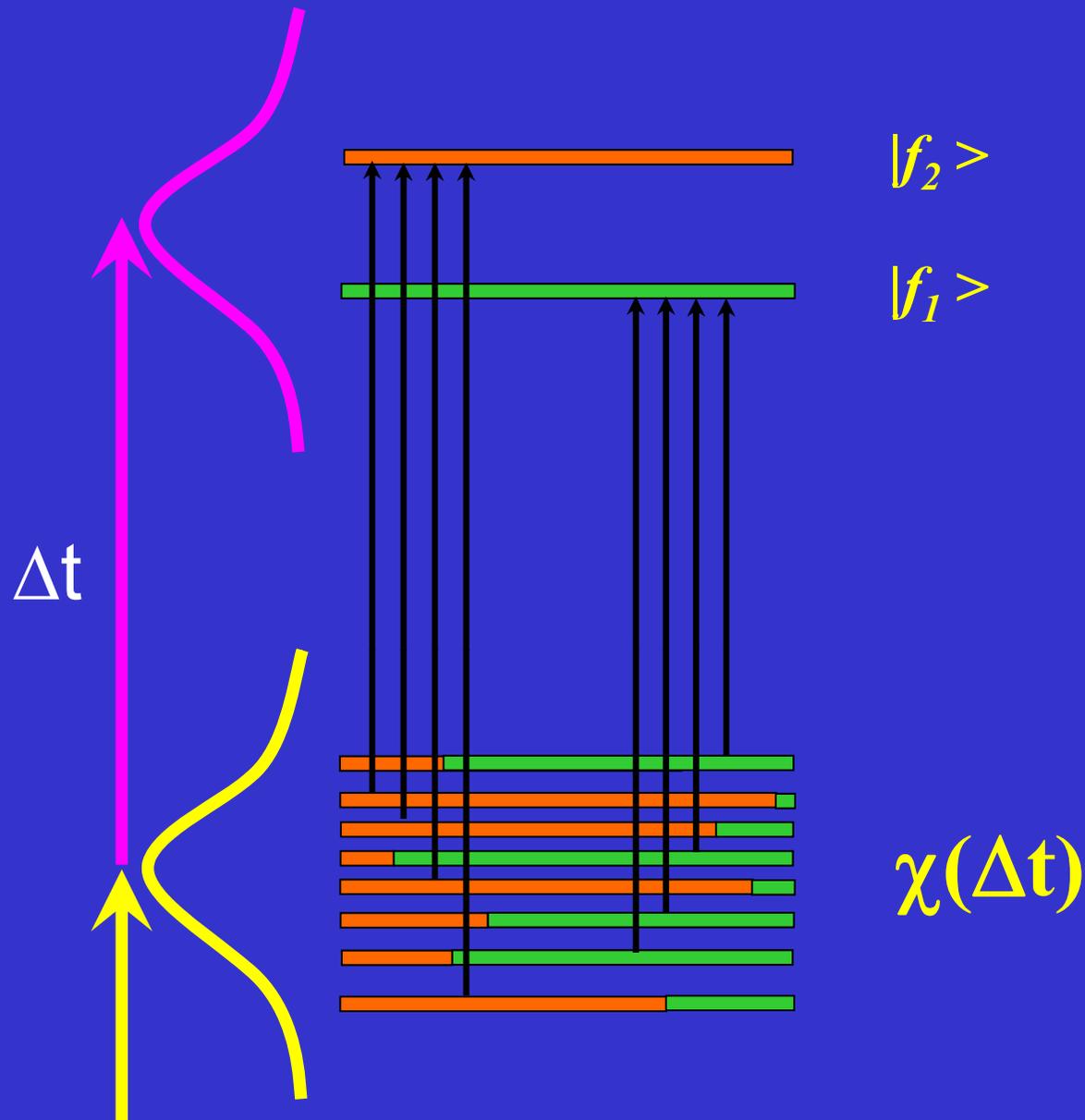
A pump-probe signal will be measured but will not change with time.

Role of the Final State



The 'less orange' state can only add or subtract 10% to the pump-probe signal

Role of the Final State: Complex Wavepackets



The detected signal should be *dispersed* with respect to the final states $|f_i\rangle$

Role of the Final State in Wavepacket Dynamics

Notice

Nothing was mentioned about the degree of freedom involved.

Electronic, vibrational, rotational, spin....

Nothing was mentioned about the time scale.

Attosecond, femtosecond, nanosecond....

These arguments apply to ANY degree of freedom in a complex wavepacket.

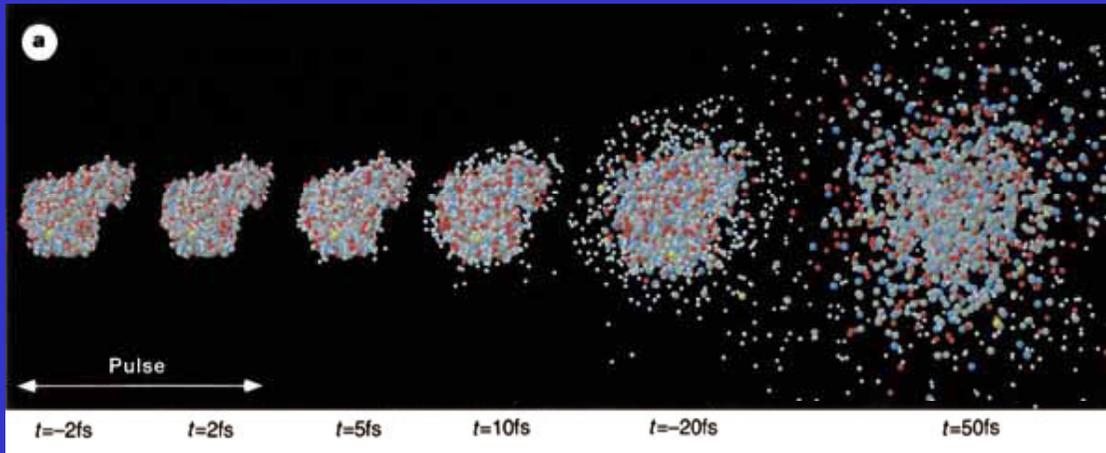
Other Probes of Molecular Wavepacket Dynamics?

Spectroscopy can be sometimes annoying....
So what about other probes of wavepacket dynamics?

e.g. Time-resolved Electron or X-ray Diffraction

This promises to give directly the positions of the atoms as a function of time.

- X-Ray diffraction: Free Electron Lasers



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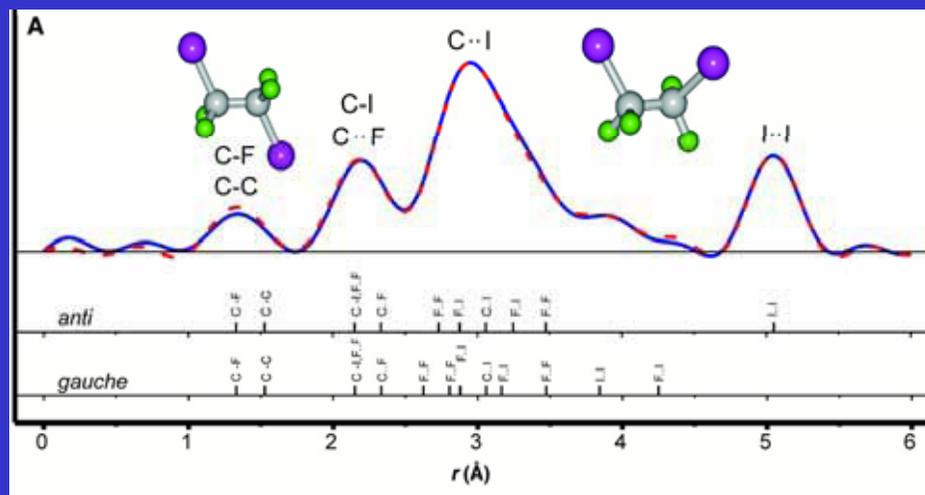
Potential for biomolecular imaging with femtosecond X-ray pulses

Richard Neutze*, Remco Wouts*, David van der Spoel*, Edgar Weckert†† & Janos Hajdu*

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- Ultrafast electron diffraction



19 JANUARY 2001 VOL 291 SCIENCE www.sciencemag.org

Direct Imaging of Transient Molecular Structures with Ultrafast Diffraction

Hyocheol Ihee, Vladimir A. Lobastov, Udo M. Gomez, Boyd M. Goodson, Ramesh Srinivasan, Chong-Yu Ruan, Ahmed H. Zewail*

But wait!

Does this mean that if we use time-resolved diffraction that molecules will now behave classically?

What happened to Quantum Mechanics?

Diffraction Probes of Wavepacket Dynamics

Relevance to Chemistry

Time-resolved Electron or X-ray Diffraction

- Diffraction-based methods probe the spatial distribution of the **total electron density**, which tends to be localized (**inner shell**) around the atomic cores.
- Molecular vibrations behave **quantum mechanically**, independent of the probe method.
- Diffraction methods will not be very sensitive to the more diffuse **valence electron distributions**, the ones that are relevant to chemical reactions.

FIN
de
Lecture 1