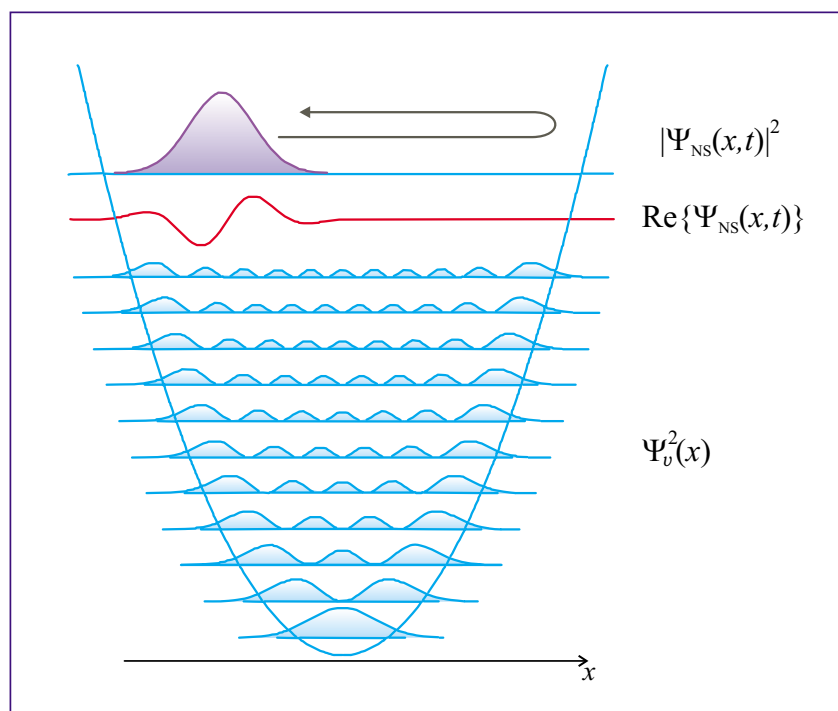


Femtosecond Reaction Dynamics

Time dependent formalism of quantum mechanics, with applications,
for undergraduate students of chemistry.



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Sommersemester 2000

<http://www-chem.unifr.ch/ma>

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Preface

Description of time-dependent processes is one of the most beautiful chapters of quantum mechanics. It has been useful in many areas of chemistry, for example photochemistry and understanding the properties of short-lived negative ions. It has become very popular with the invent of femtosecond laser experiments, and even more popular because of the award of the Nobel Prize to professor Zewail.

My interest in the properties of wave packets was awakened many years ago because of its usefulness in rationalizing the motion of nuclei in short negative ions, encountered in electron-molecule scattering. But I am fascinated by the more recent applications in femtosecond chemistry which are, of course, even more exciting because they permit explicit observation of the time dependence. I have therefore included them in this course although my own research is concerned with electron-molecule collisions and not with femtosecond laser chemistry.

The course emphasizes graphical illustrations of the concepts, and not complex mathematics. It is designed for undergraduate students of chemistry, who know the time-independent Schrödinger equation, are familiar with the concepts of atomic and molecular orbitals, molecular vibration and rotation, but who have not been exposed to the time-dependent formalism of quantum mechanics.

1. Objectives

- Description of motion in classical mechanics involves the position of an object expressed as a function of time. For example, a pendulum moves from left to right and back again.
- Description of motion in quantum mechanics, as far as it is generally taught in undergraduate chemistry courses, involves a wave function which does not depend on time. The probability $P(x) = \Psi^2(x)$ to find the particle in various places thus also does not depend on time, the particle “does not move”.

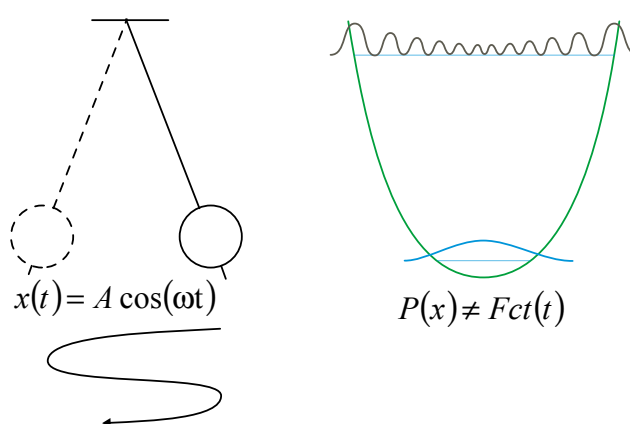


Figure 1-1. Description of motion in classical physics and in quantum mechanics.

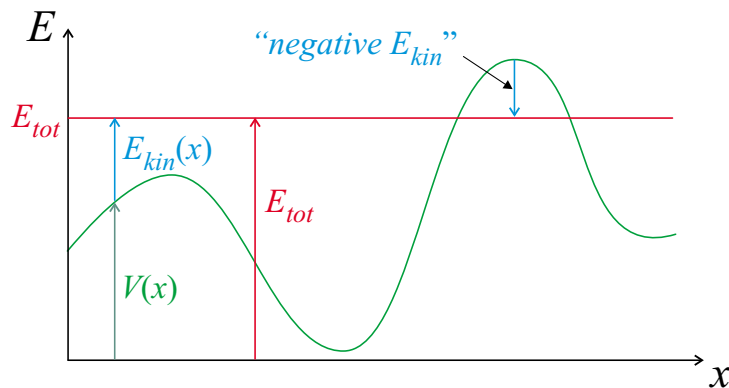
- In this lecture you will learn how to describe motion in quantum mechanics in the sense that the probability to find a particle is in one place at a given time, and at a different place some time later.
- You will learn about the time-dependent Schrödinger equation, and the properties of its solutions for various model potentials.
- We will then discuss about applications in electron-molecule scattering and in femtosecond laser experiments.

2. Time independent Schrödinger equation

- As an introduction, we will consider the solutions of the time independent Schrödinger equation which you already know, but from a slightly different point of view, which will permit extension into the time dependent formalism.
- In particular, you will learn how to construct qualitative wave functions for various potentials and understand how does their shape depend on the shape of the potential.

2.1. Properties of the wave functions.

- we are looking for the solutions of the Schrödinger equation in a one-dimensional potential:



- The time-independent Schrödinger equation is then:

$$\begin{aligned} (\hat{T} + V(x))\Psi(x) &= E_{tot} \cdot \Psi(x) \\ -\frac{\hbar}{2m} \frac{d^2}{dx^2} \Psi(x) + V(x) \cdot \Psi(x) &= E_{tot} \cdot \Psi(x) \end{aligned} \quad (1)$$

let's reformulate it a little:

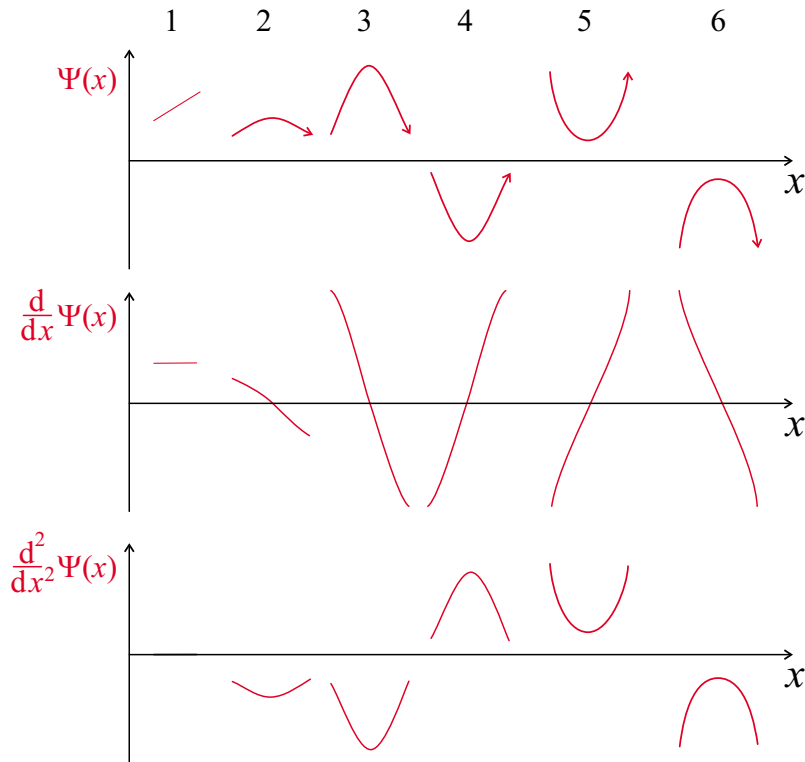
$$\begin{aligned} -\frac{\hbar}{2m} \frac{d^2}{dx^2} \Psi(x) &= [E_{tot} - V(x)] \cdot \Psi(x) \\ \frac{d^2}{dx^2} \Psi(x) &= -\frac{2m}{\hbar} [E_{tot} - V(x)] \cdot \Psi(x) \\ \frac{d^2}{dx^2} \Psi(x) &= -\frac{2m}{\hbar} \cdot E_{kin} \cdot \Psi(x) \end{aligned} \quad (2)$$

- Equation (2) tells us that a 'good' wavefunction is one whose second derivative is proportional to the kinetic energy and to the value of the wave function (at any given x).

- Let's see what is the graphical meaning of the second derivative.

Remember that a derivative is just the slope of the curve. The first derivative is a curve showing the slope of the original function; the second derivative is obtained by drawing the slope of the first derivative.

Let's draw the second derivatives of a few trial functions and see what we learn:



- Looking at the functions 1, 2, and 3 we see that the second derivative has something to do with the curvature of the original function. The function 1 is a straight line, is not curved, and the second derivative is zero. The function 2 is slightly curved and the second derivative (in the absolute value) is small. Finally the function 3 is more curved and its second derivative is (in the absolute value) large.

Observation I: Second derivative expresses the curvature of a function. The second derivative (the absolute value) is large when the original function is strongly curved.

- There is another interesting observation: The sign of the second derivative is opposite to the sign of the original function in the cases 2, 3, and 4. The sign is the same in the cases 5 and 6.

Observation II: Functions curved back towards the axis have 2nd derivative with the opposite sign.

Functions curved away from the axis have 2nd derivative with the same sign.

- Finally the curves 2 – 6 show that curved functions can be formed whose second derivatives have the same shape as the original function — as required by the Schrödinger equation.

The Schrödinger equation thus places the following requirements on the wave function:

- $E_{kin} > 0$ \longrightarrow wave function bends towards the axis
- $E_{kin} < 0$ \longrightarrow wave function bends away from the axis
- the curvature is proportional to
 - the mass m
 - the absolute value of E_{kin}
 - the absolute value of wave function $\Psi(x)$

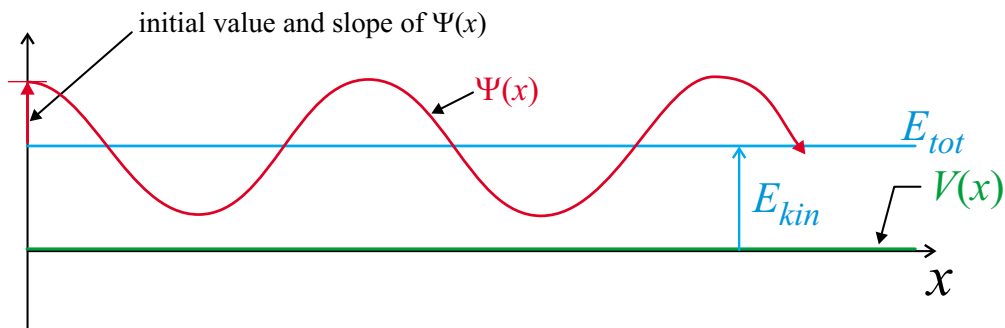
In the following section we will construct and understand the wave functions in several model potentials.

2.2. Wave functions in several model potentials.

A very pretty simulation allowing you to draw your own potentials is given by Cemal Yalabik of the Bilkent University at his web page:

<http://www.fen.bilkent.edu.tr/~yalabik/applets/1d.html>

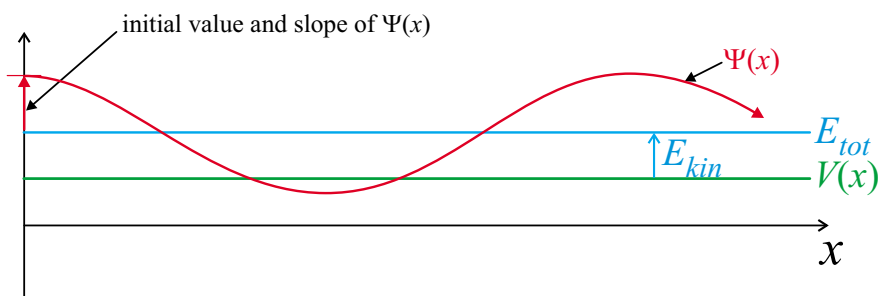
2.2.1. Free particle



- Suitable initial values of $\Psi(x)$ and its slope are chosen on the left.
- The kinetic energy is positive, $\Psi(x)$ curves towards the axis.

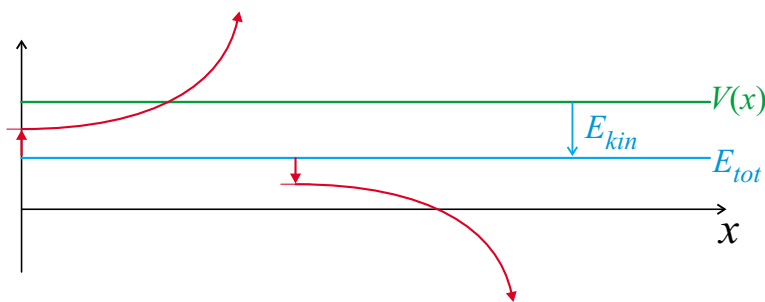
- The value of $\Psi(x)$ decreases, therefore its curvature also decreases. $\Psi(x)$ becomes zero as it crosses the axis and it becomes a straight line at this point.
- $\Psi(x)$ curves back up after crossing the zero line. Its (absolute) value increases initially after crossing the zero line, and it consequently becomes more and more curved (as if being afraid of departing too far from the base line).
- If you continue to draw the red line according to these rules, you obtain a cosine wave! You see why $\Psi(x)$ is called the wave function.

Now try the same thing with less kinetic energy:



- $\Psi(x)$ is now less curved — the wavelength becomes longer. Our rules contain the de Broglie relation $\Lambda = \frac{h}{p}$!

What happens when the kinetic energy becomes negative?

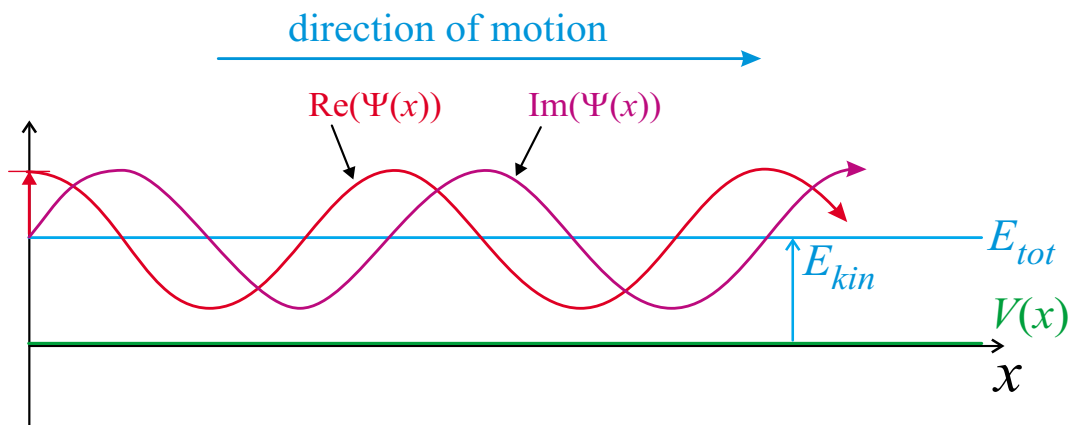


- $\Psi(x)$ curves away from the baseline. The farther it gets, the more it curves. It departs from the baseline exponentially.

A more precise description of a free particle.

- The cosine function has one problem: The probability density $P(x) = \Psi^2(x)$ oscillates with x , which is not physically reasonable. We need a wave function which oscillates, but gives probability density which does not oscillate.
- These requirements are fulfilled by a complex wave function

$$\Psi(x) = A e^{i\frac{p}{\hbar}x} = A \left(\cos \frac{p}{\hbar}x + i \sin \frac{p}{\hbar}x \right) \quad (3)$$



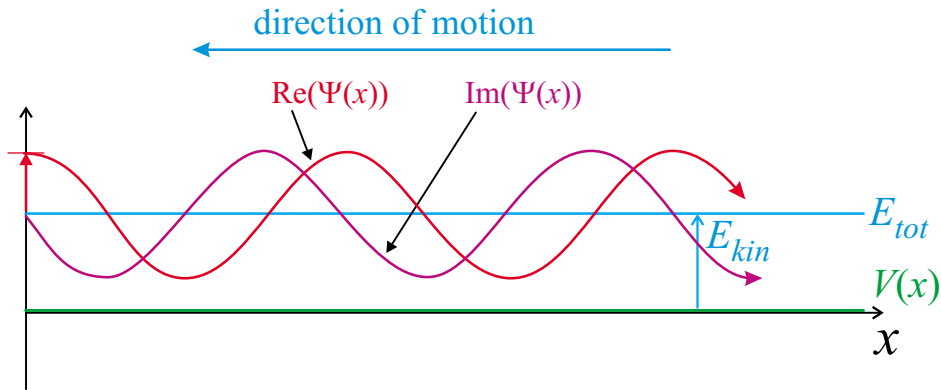
The real part of the wave function, $\text{Re}(\Psi(x))$, is shown in red.

The imaginary part of the wave function, $\text{Im}(\Psi(x))$, is shown in purple.

- Note that if the particle moves in the opposite direction, with an impulse $-p$ (where p is the absolute value of the negative impulse), then the wave function is

$$\Psi(x) = A e^{i\frac{p}{\hbar}x} = A \left(\cos \frac{-p}{\hbar}x + i \sin \frac{-p}{\hbar}x \right) = A \left(\cos \frac{p}{\hbar}x - i \sin \frac{p}{\hbar}x \right)$$

that is, the imaginary part is shifted by 180° . It is the phase relation of the real and the imaginary parts which determine whether the particle moves left or right!



- The probability density is now a constant, as it should be:

$$P(x) = |\Psi(x)|^2 = \Psi(x) \cdot \Psi^*(x) = A^2 \left(\cos^2 \frac{p}{\hbar} x + \sin^2 \frac{p}{\hbar} x \right) = A^2 = \text{const.}$$

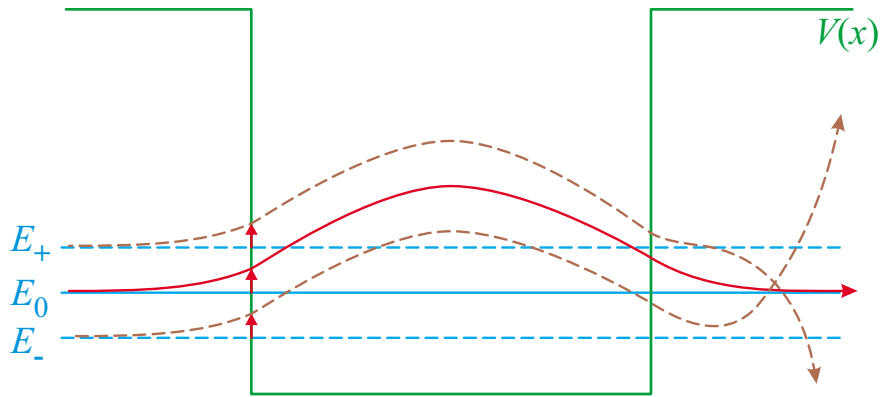
- The impulse p becomes imaginary when the “kinetic energy” is negative, and the wave function becomes a true exponential:

$$\Psi(x) = A e^{\beta x}, \quad \text{where } \beta = \sqrt{-2mE_{kin}}$$

where E_{kin} is negative, making the argument of the square root positive.

2.2.2. Particle in a potential well

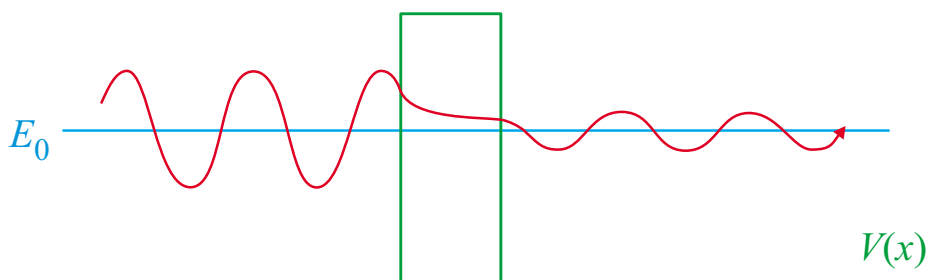
- Consider the energy E in the diagram below. The kinetic energy is negative outside the well — the wave function is curved away from the axis. One can prevent that it “runs away” towards infinite values by a suitable choice of the initial values of the wave function at the left edge of the potential well. The wave function is chosen to slope towards the axis to the left. Since it curves away from the axis, its slope is less and less as we move further left. But the curvature diminishes, since the value of the wave function drops. With proper choice of the initial slope and value, the wave function is “captured” by the axis, it approaches it closer and closer, until it is nearly zero, but then it no longer curves, and remains zero.
- The wave function is curved towards the axis within the well. For E it reaches the right edge of the well too high, outside the well it curves away from the axes and “runs away”. Such function can not be normalized and is not physically meaningful. There is no meaningful wave function for the energy E !
- There is no meaningful wave function for the energy E_+ either, this time it is curved too much within the well and “runs away” downward.



- But there is an energy, E_0 , when the curvature within the well is just right, and the function remains finite on both sides.
- The boundary conditions and the wavy nature of Ψ leads to *discrete energy levels* for a potential well.

2.2.3. Potential barrier

- Imagine the particle coming from the left. The wave function curves towards the axis as long as the potential energy is positive. It starts to curve away from the axis when it enters the “forbidden” region, just as if it would leave the potential well in the previous example. But the barrier stops before the wave function completely “dies off” to zero. Small remaining amplitude “survives” and continues oscillating after the end of the barrier. There is a (small) probability for the particle to *tunnel through the barrier*.



- Consider the role of the height and the width of the barrier and the mass of the particle!
- Applications:
 - Scanning tunneling microscopy.
 - Certain chemical reactions (in particular proton transfer) proceed even at 0 K.

An example from the book of V. A. Benderskii *et al.* “Chemical Dynamics at Low Temperatures” (Phys. Chem. library S.8.91) is given below.

Note that the reaction rate no longer depends on temperature at the right side of the graph, that is at very low temperatures. Thermal energy is not needed to overcome an activation barrier — the proton tunnels through.

Note further that the tunneling rate is much less for D^+ than for H^+ .

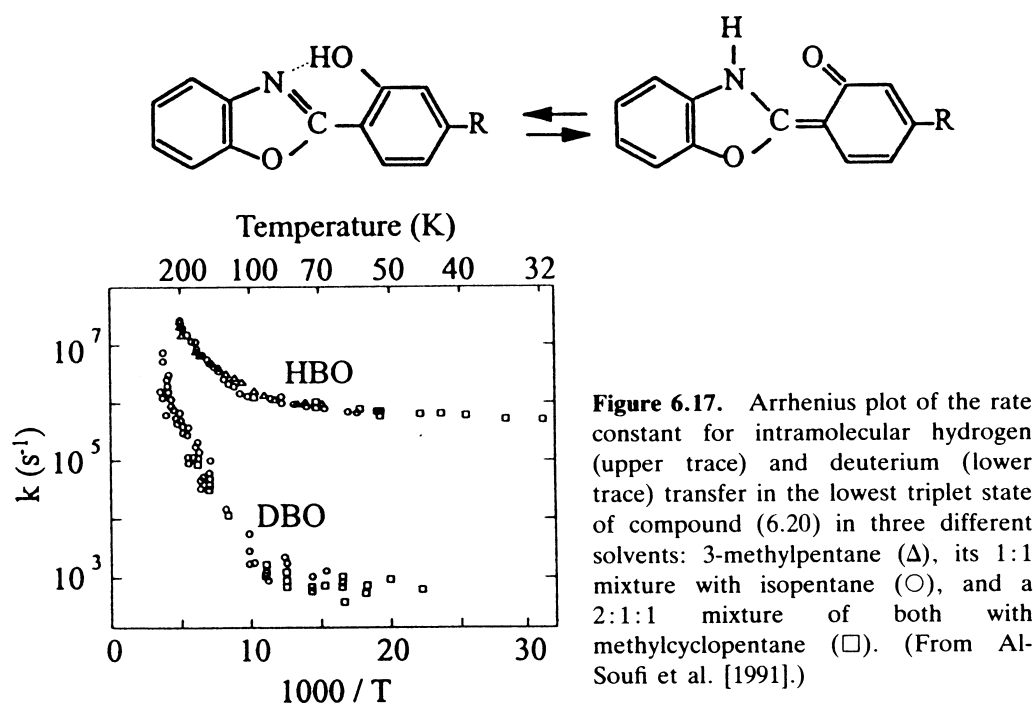
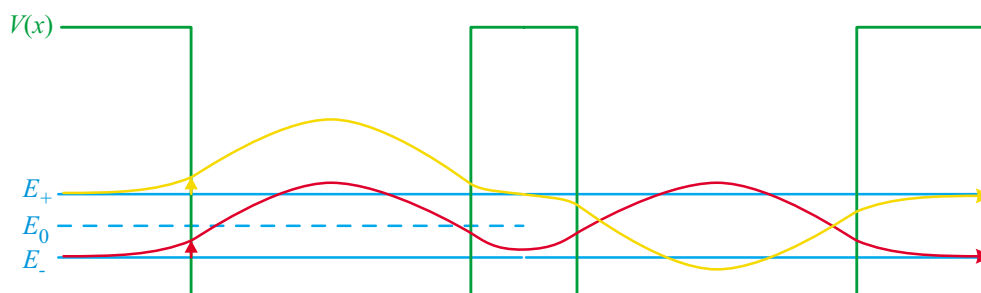


Figure 6.17. Arrhenius plot of the rate constant for intramolecular hydrogen (upper trace) and deuterium (lower trace) transfer in the lowest triplet state of compound (6.20) in three different solvents: 3-methylpentane (Δ), its 1:1 mixture with isopentane (\circ), and a 2:1:1 mixture of both with methylcyclopentane (\square). (From Al-Soufi *et al.* [1991].)

2.2.4. Double potential well

- The dashed blue line is the energy of the discrete state of a single well.
- Double well has two solutions, one slightly below, the other slightly above the solution of a single well.



- Consider the role of the width and the height of the barrier between the two wells.
- Can you see how the two solutions can be approximated as the in-phase and the out-of-phase superpositions of the wave functions of a single well?
- Do you see the relation to the LCAO-MO approximation?

Applications

- The umbrella vibration of NH_3 and PH_3

2.2.5. Potential well with thin walls: resonances

- There is a solution for each energy, but the amplitude inside is generally small: There is a continuum of states located mainly outside of the well.

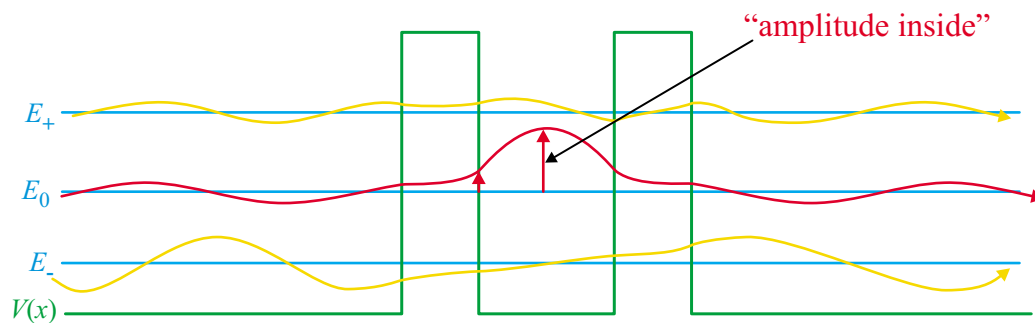


Figure 2-1. Wave functions in a potential well with thin walls.

- Now consider the wave function at the energy E_0 , the same energy where a well with infinitely thick walls (as in the figure above) would have its discrete solution. Here the wave function accumulates inside the well, and starts to “die out” exponentially in the “forbidden region” within the walls, just as in the “normal” potential well. But the wall is now not infinitely thick, and some of the wave function survives, gets outside, to become a free particle.
- If the spectrum, that is the “amplitude inside” is plotted schematically against energy, one obtains accumulation of the wave function inside the well over a certain range of energies. The center of the peak is around the energy at which the same potential well, but with infinitely thick walls, would have its discrete state.

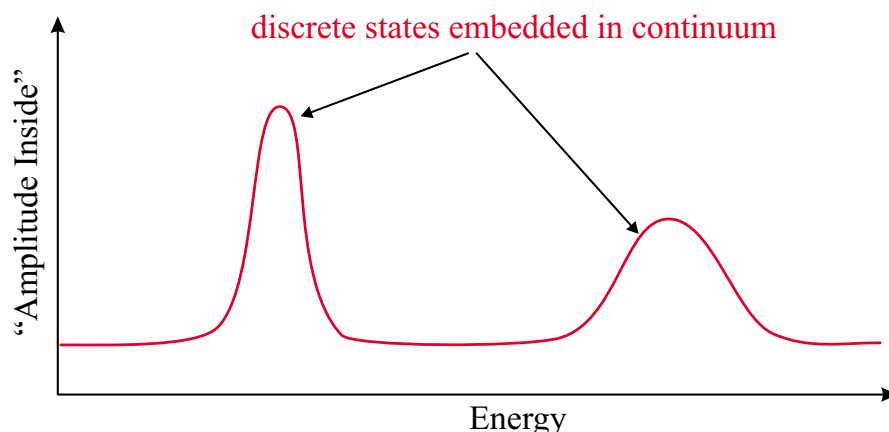


Figure 2-2. Spectrum of states in a potential well with thin walls.

- This “build-up” of wave function is called a “quasidiscrete state”, a “discrete state embedded in (or coupled to) a continuum”, or a “resonance”.

Questions: 1. Consider the role of the wall thickness and height. (including infinitely thick and infinitely thin walls)

2. Why is the second band in figure 2-2 drawn wider than the first band?

Applications

- Negative ions: resonances in the collisions of free electrons with molecules. For example, the outermost electron of the negative ion of nitrogen, N_2^- , is coupled to the continuum of free electrons: $N_2^- \rightarrow N_2 + e^-$
- Autoionizing states of atoms and molecules. Example is helium with two electrons in a $2s$ orbital, $2s^2$, coupled to a continuum of an ion and a free electron $He(2s^2) \rightarrow He^+(1s) + e^-$.
- α decay of radioactive nuclei.

2.3. Rotation.

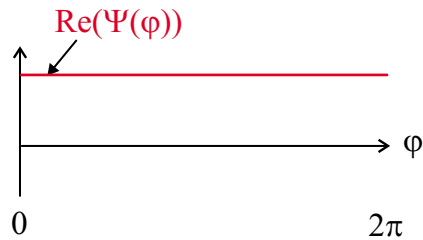
Rotation closely resembles the motion of a free particle, except that the particle moves in a circle. The fact that the wave function has to repeat itself after each 2π leads to quantization of energy and angular momentum.

You already learned (in course of physical chemistry I and II) the wave functions for the rotator with a fixed axis:

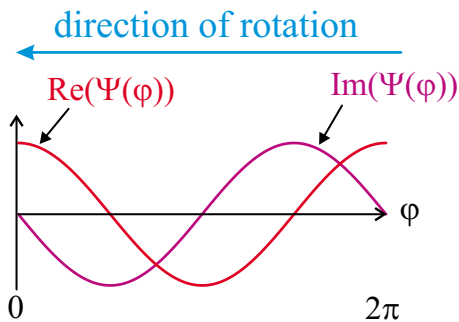
$$\Psi(\varphi) = \sqrt{\frac{1}{2\pi}} e^{ik\varphi}, \quad k = 0, \pm 1, \pm 2, \dots$$

Graphically:

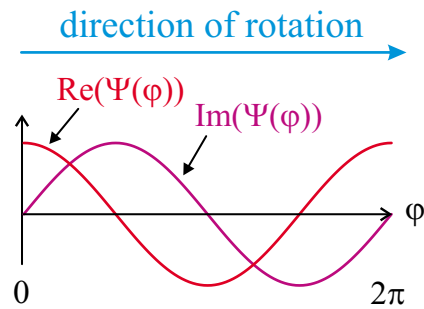
$$k = 0$$



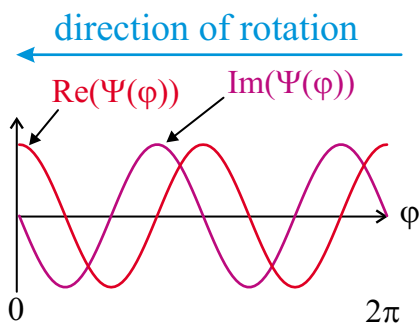
$$k = -1$$



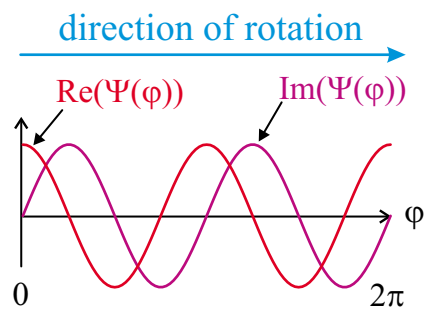
$$k = +1$$



$$k = -2$$



$$k = +2$$



etc.

- The dependence on φ is similar to what you just learned about a free particle, the phase difference between the real and the imaginary parts determines whether the particle rotates left or right.
- The probability density does not depend on φ , for any k !

$$W = |\Psi(\varphi)|^2 = \left| \sqrt{\frac{1}{2\pi}} e^{ik\varphi} \right|^2 = \frac{1}{2\pi}$$

- Consider the wave functions for the 2p electrons of the hydrogen atom.

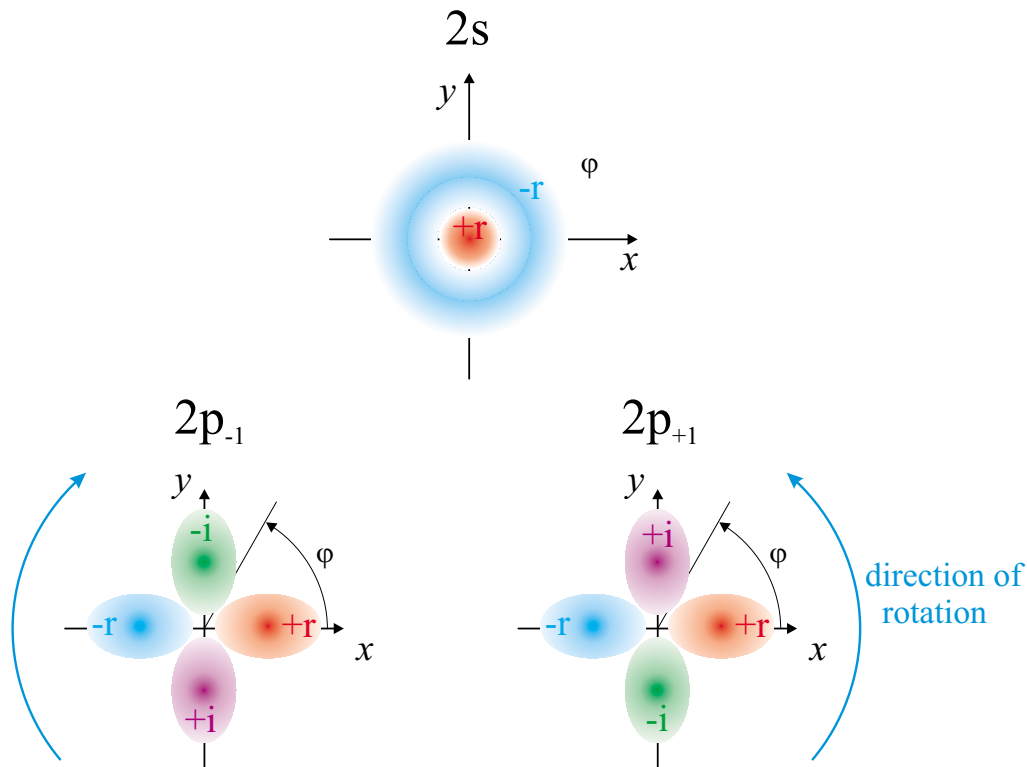
$n = 2, l = 1, m = 1$ — the $2p_{+1}$ orbital:

$$\Psi_{211} = N \rho e^{\frac{p}{2}} \sin \theta e^{i\varphi}$$

and $n = 2, l = 1, m = -1$ — the $2p_{-1}$ orbital:

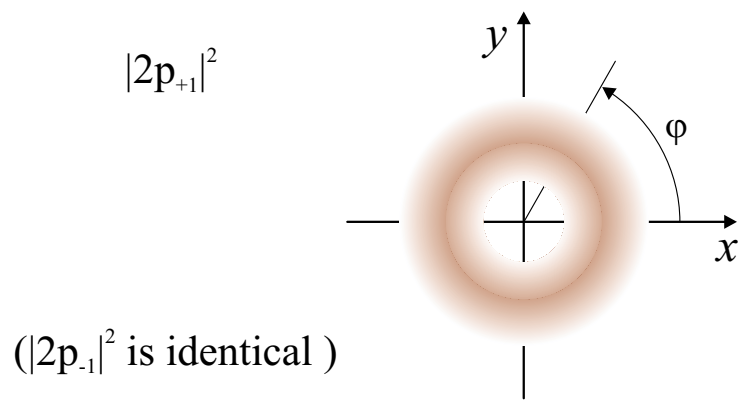
$$\Psi_{21-1} = N \rho e^{\frac{p}{2}} \sin \theta e^{-i\varphi}$$

The part dependent on φ has the same form as the wave function for the rotator above. Diagrams of the $2p_{-1}$ the $2p_{+1}$ orbitals could thus be drawn as follows (the 2s orbital is included for comparison):



(four colors are needed to draw complex orbitals — red and blue stand for positive and negative real numbers, violet and green for positive and negative imaginary numbers)

But remember that the probability density for both of them does not depend on φ .



3. The Stern-Gerlach experiment: the basic concepts of quantum mechanics

In your study of chemistry you have probably learned so far that “good wave functions” (i.e., describing properly the nature) are those which satisfy the (time-independent) Schrödinger equation. Wave functions not satisfying the Schrödinger equation are “bad”.

It is necessary to learn more concepts of quantum mechanics, “to widen the horizon”, in order to understand the subtleties of the time-dependent phenomena. We have to extend the notion of what are “good” and “bad” wave functions. The behavior of the orientation of angular momentum is particularly suitable to illustrate the new concepts.

The presentation given here is based on the beautiful book **Feynman Lectures on Physics** (volume III)

3.1. Measurement of the “z-component” of angular momentum.

Imagine a particle with an angular momentum of 1. The angular momentum could be due to nuclear spin or to orbital angular momentum of an electron in a p-atomic orbital, we do not care.

The axis of rotation can have different orientations. Can we measure the orientation?

We can measure the component of the angular momentum in some direction (let’s call it z-direction) — this gives us a hint on the orientation. (Actually, in the quantum world we can not measure the other two components separately — part of the information about the exact orientation of the angular momentum vector remains hidden to us. The “z-component” is *all* we can hope to know about the orientation.)

If the rotating particle is charged, the angular momentum is associated with a magnetic moment, the particle behaves as a little magnet. We shall measure the orientation of this tiny magnet.

- Imagine a tiny magnet immersed in an outside magnetic field — there is no net force. At first you may think that the outside field will turn the tiny magnet around until its north pole points towards south pole of the big magnet (the orientation of the least energy). But do not forget that the tiny magnet is spinning — spinning objects are hard to tilt, they will precess.
- A tiny magnet immersed in an inhomogeneous field, like on the right side of the picture, will experience a small force, because the field at the upper end of the magnet is stronger. The force is a measure of the z-component of the angular momentum — it is zero for a horizontal orientation of the tiny magnet (the field is

equally strong on both ends), it points downwards for a magnet oriented south down.

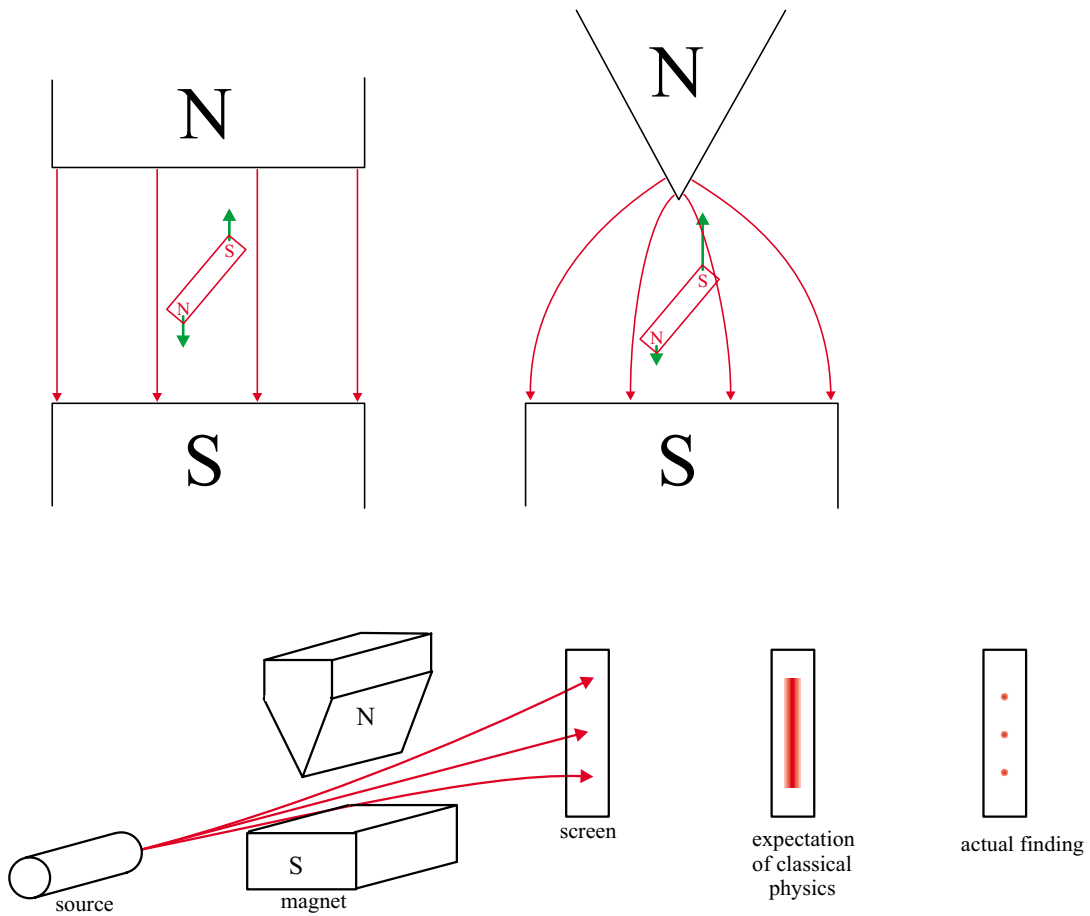


Figure 3-1. Forces acting on a tiny magnet in a homogeneous (left) and inhomogeneous (right) magnetic field.

- This force will cause deflection of particles in the set-up shown above. A fluorescent screen at the end will tell us how much was a particle deflected, that is, how large was its z -component of the angular momentum.

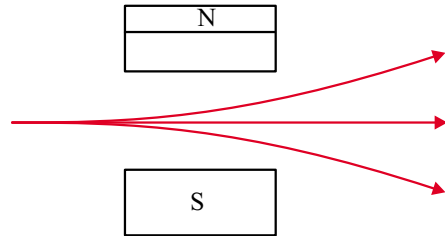
3.2. Quantization of P_z

- The orientations of the particles from the source are entirely statistically distributed — we would expect to find all values of P_z from $-P$ to $+P$ (where P is the total angular momentum). But this is not at all what happens!!

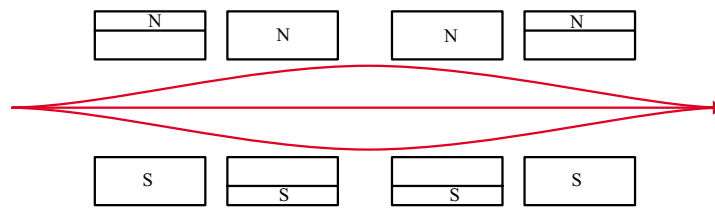
In reality, the experiment finds only three discrete values of P_z : $-\hbar$, 0 , and \hbar .

- We say that P_z is quantized. Of course you already know that, but it is good to recall how perturbing and contraintuitive this property of small particles is.
- We shall express the quantization with a quantum number l_z , with possible values -1, 0, ans 1.

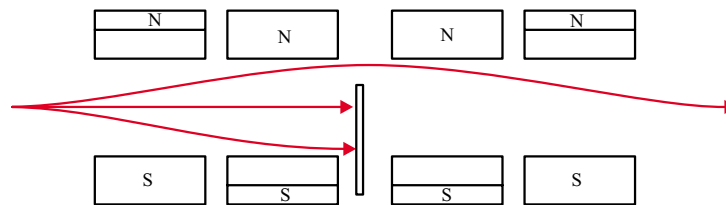
Let's look at the experiment from the side to make the drawing simpler:



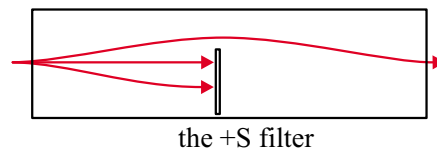
Now let's put four such filters in series, the second and third upside down, so that the particle trajectories are pushed back into one line:



Now let's stop the particles with $l_z = -1$ and $l_z = 0$ with a piece of metal, so that only particles with $l_z = 1$ will leave the apparatus:

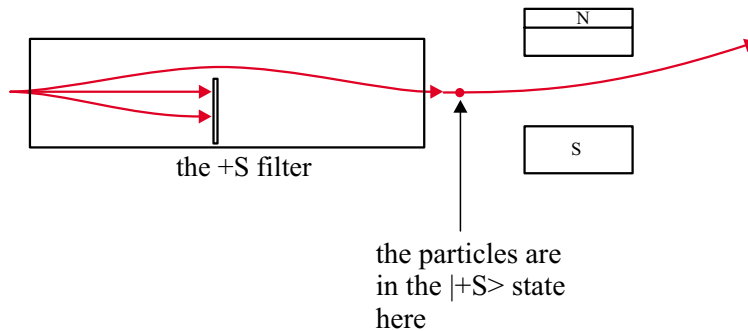


Let's call this a filter (with respect to l_z) and make a simplified drawing of it. Let's say that this filter is upright ("senkrecht") and therefore call it the S-filter. Since only particles with $l_z = +1$ pass, lets call it the +S-filter.



3.3. Eigenstates

Now let's make a "Gedankenexperiment". Let's take a mixture of particles from a source, pass them through the +S filter and measure their z-component of angular momentum P_z .



The result is what you may have expected: The particles which had $l_z = +1$ in the first deflector, will have it also in the second deflector. Nothing flipped the axis of rotation, so it stayed the same.

We shall say that the particles after passing the +S filter are in a *pure state*. We shall write this state as $|+S\rangle$. The "half bracket" is called a "ket" (the second half of the word bra-ket).

The $|+S\rangle$ state is an **Eigenstate** of the z-component of the angular momentum with the eigenvalue $P_z = +\hbar$.

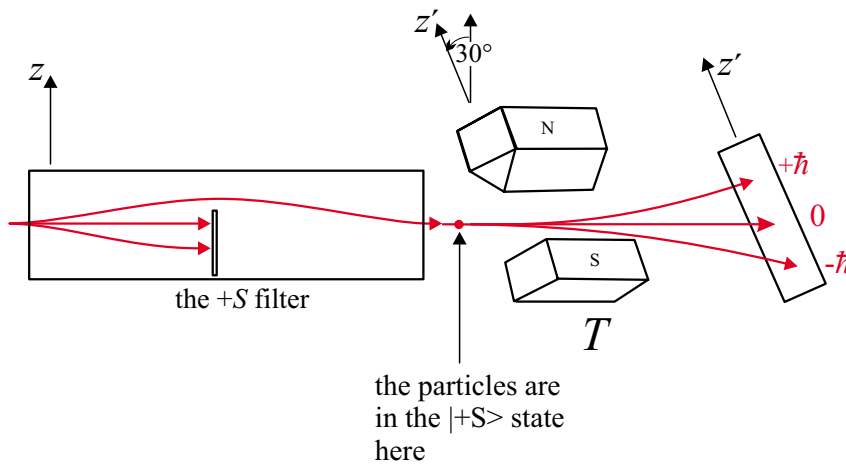
Note that this is a physical, not a mathematical definition of an eigenstate!

Now we have a source of particles in a pure quantum state and we can do more experiments with them.

3.4. Rotation of the frame of reference

We shall try to better understand the deeply perturbing fact of quantization, the fact that the experiment always finds the particle with angular momentum upright or horizontal, but never tilted at an intermediate angle.

It appears impossible. If we prepare the particle on the pure "upright" state $|+S\rangle$, and then look at them with a second magnet which is tilted with respect to S, let's call it T (for tilted). S measures the component P_z along the axis z, T the component $P_{z'}$ along the rotated axis z' . The angle between z and z' is 30° . We must then find the particle tilted with respect to z' , right? In fact we expect the result of the measurement to be $\hbar \cdot \cos 30^\circ = 0,87 \cdot \hbar$.



This is not at all what happens! We obtain the result $+\hbar$ for some particles, 0 for others, and $-\hbar$ for the rest. The component of the angular momentum is quantized, not with respect to the original axis z , but with respect to the new measurement z' !

Let's make a simplified drawing before continuing. The skewed rectangle indicates tilted magnets.

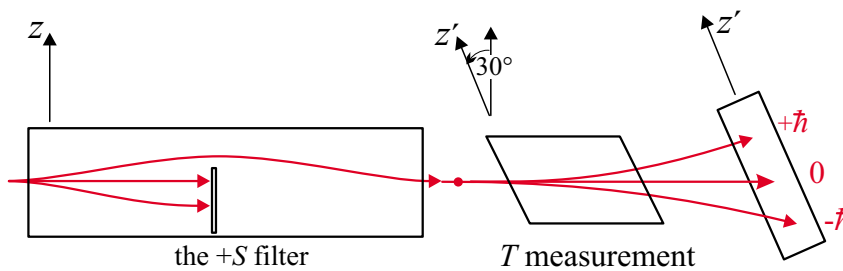
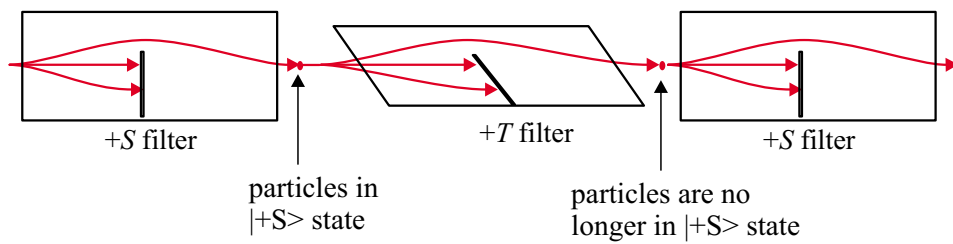


Figure 3-1.

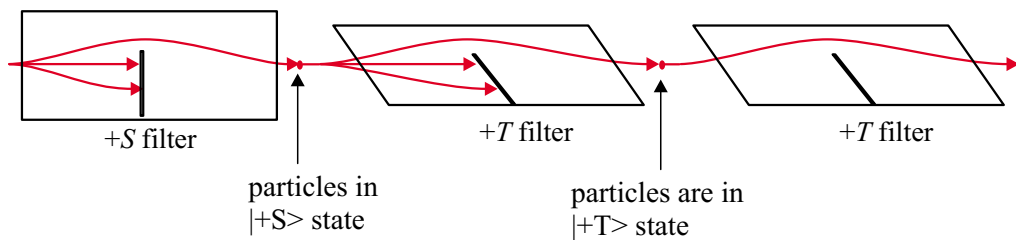
3.5. Collapse of states (wave functions)

We can now study the properties of the particles which passed the second magnet. We shall turn the measuring magnet into a filter, say $+T$, and pose the question in which state are the particles after they left the $+T$ filter. One may expect that they will be in the $|+S\rangle$ state, because we prepared them in the $|+S\rangle$ state originally, and the T filter does not try to change the orientation of the angular momentum, it does not apply any torque, it only measures the component along z' and selects some particles.

But a second S filter tells us that the particle “have forgotten” that they were in the $|+S\rangle$ state.



A second T filter shows that they are now in eigenstates with respect to the z' axis, they are in the $|+T\rangle$ state.



The mere fact of observing the particles in the $|+T\rangle$ state changed their state from $|+S\rangle$ to $|+T\rangle$.

This is again very perturbing. Measurement plays a very important role in quantum mechanics: it can change the state things are in. The old state “collapses” into a new state.

This property of nature has remarkable consequences, exemplified by the famous “Schrödinger cat”. The mere fact that someone opens the box with the cat (i.e., makes a “measurement”) changes its state (“from half alive, half dead” to either “alive” or “dead”). You’ll find many pages on this in the internet. The keywords to look for are Schrödinger cat, Einstein Podolsky Rosen (EPR) paradox, collapse of wave function, entanglement, dephasing, quantum computing.

There is another important message in the above pictures: States which are not eigenstates of something may be perfectly physically meaningful (in the sense that they can be prepared experimentally). Thus the $|+S\rangle$ state is well defined and meaningful, despite the fact that it is not an eigenstate of the T filter. This message will be important later, when we shall be talking of states which are not eigenstates of the Hamiltonian operator, that is are not solutions of the Schrödinger equation. This may be perturbing for chemists who grew up in the belief (at least I did) that only wave functions which are solutions of the Schrödinger equation are “good” wave functions.

3.6. Amplitudes and probabilities

A way to look at the above picture is: A particle is prepared in the $|+S\rangle$ state and the T filter asks “is the particle in the $|+T\rangle$ state?” In certain percentage of the cases the answer is “yes” otherwise “no”. We would like to know the probability W of “yes” and “no”.

It turns out that the probability is not the primary variable, there is something more fundamental behind it, we shall call it the **amplitude** A . The amplitude may be negative or even complex. The probability is calculated as the square of the absolute value of A

$$W = |A|^2$$

We shall write the amplitude to find a particle, originally prepared in the state $|+S\rangle$, in the state $|+T\rangle$ in a later measurement as

$$A = \langle +T | +S \rangle$$

The right part of the expression, $|+S\rangle$, is called ket (you already know this), the left part, $\langle +T |$, is called bra. Note that the expression is read from right to left.

The amplitudes for all the combinations of preparing a particle in an eigenstate in one frame of reference and finding it in an eigenstate of a frame of reference rotated by an angle α can be expressed in a form of a matrix.

	$ -S \rangle$	$ 0S \rangle$	$ +S \rangle$
$ -T \rangle$	$\frac{1}{2}(1 + \cos \alpha)$	$-\frac{1}{\sqrt{2}} \sin \alpha$	$\frac{1}{2}(1 - \cos \alpha)$
$ 0T \rangle$	$\frac{1}{\sqrt{2}} \sin \alpha$	$\cos \alpha$	$-\frac{1}{\sqrt{2}} \sin \alpha$
$ +T \rangle$	$-\frac{1}{2}(1 - \cos \alpha)$	$\frac{1}{\sqrt{2}} \sin \alpha$	$\frac{1}{2}(1 + \cos \alpha)$

You can now calculate the outcome of the experiment in figure 3-1!

$$\langle +T | +S \rangle = \frac{1}{2}(1 + \cos(30^\circ)) = 0,933; \quad W = \langle +T | +S \rangle^2 = 0,871$$

$$\langle 0T | +S \rangle = -\frac{1}{\sqrt{2}} \sin(30^\circ) = -0,354; \quad W = \langle 0T | +S \rangle^2 = 0,125$$

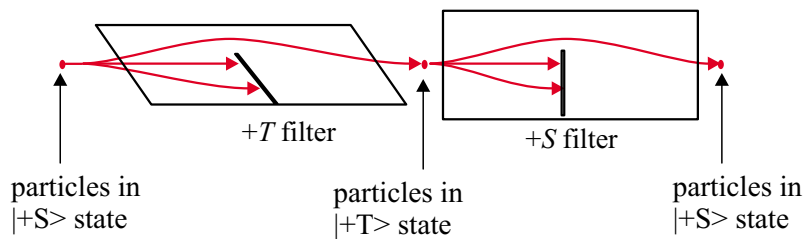
$$\langle -T | +S \rangle = \frac{1}{2}(1 - \cos(30^\circ)) = 0,067; \quad W = \langle -T | +S \rangle^2 = 0,004$$

The sum of the probabilities is 1, as it should.

Note that the *average* value of P_z is $\hbar \cdot \cos 30^\circ = 0,87 \cdot \hbar$, that is, our expectation above is true for the average value, but not for the individual results of the measurements.

$$\overline{P_z} = 0,871 \cdot \hbar + 0,125 \cdot 0 + 0,004 \cdot (-\hbar) = 0.87\hbar$$

The amplitude for two filters in series is equal to the product of the amplitudes of the individual filters. As an example, the amplitude that a particle originally in the $|+S\rangle$ state (prepared by a $+S$ filter not shown in the figure) passes a $+T$ filter and then a $+S$ filter

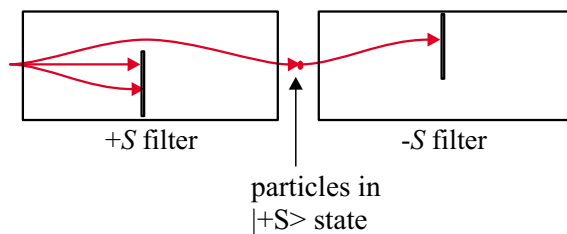


is

$$A = \langle +S | +T \rangle \langle +T | +S \rangle$$

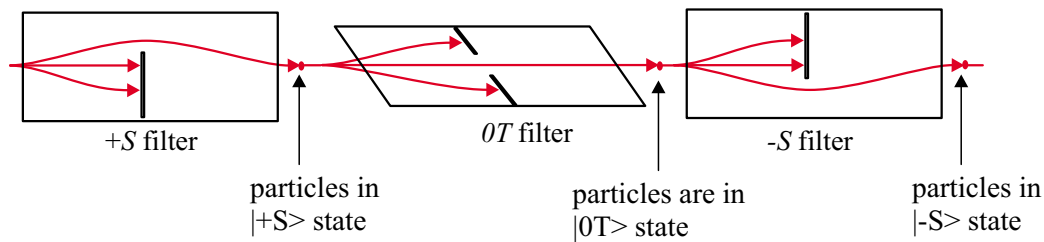
Exercise: calculate the value and the corresponding probability for $\alpha=30^\circ$

All this can have incredible consequences. The amplitude that a particle originally in the $|+S\rangle$ state is found in the $| -S \rangle$ state in a second filter is, of course, zero: the pure $|+S\rangle$ will be found to be a pure $|+S\rangle$ in the second filter.



Exercise: calculate this amplitude using the above matrix

Now put a $0T$ filter between the $+S$ and the $-S$ filter:



Is it not incredible? We introduced an additional filter into the way of the particles, taking some of the particles *away*, and the result is that *more* particles come out at the end! This shows that amplitudes undergo interference!

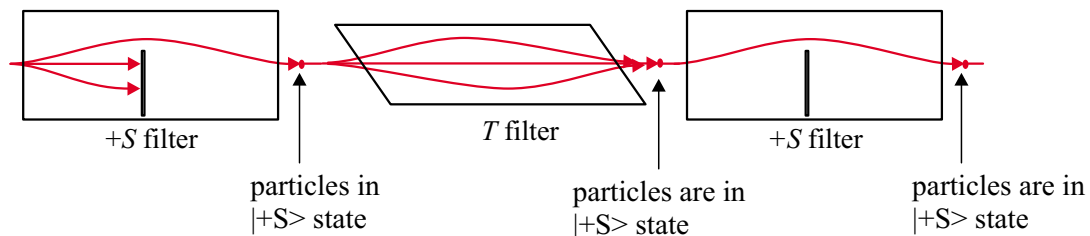
The amplitude for particles coming out at the end is

$$A = \langle -S | 0T \rangle \langle 0T | +S \rangle$$

Exercise: calculate the amplitude and probability with T at $\alpha = 30^\circ$ and verify that they are not zero

3.7. Superposition and base sets

Now consider this arrangement:



Particles initially in the $|+S\rangle$ state are introduced into the T filter and separated into the $| -T \rangle$, $| 0T \rangle$, and $| +T \rangle$ states, but their paths are not perturbed, we **do not observe**, we **do not know** which way they took. Their paths are led together after the T filter in a coherent way. The state is not changed by the T filter in such a case, the particles remain in the $|+S\rangle$ state.

The amplitude for a particle to pass where several unperturbed paths are available is the **sum** of the amplitudes of the individual paths. In the above situation we have:

$$A = \langle +S | -T \rangle \langle -T | +S \rangle + \langle +S | 0T \rangle \langle 0T | +S \rangle + \langle +S | +T \rangle \langle +T | +S \rangle = 1$$

Exercise: verify that the expressions in the matrix above satisfy this relation

Now let's make a little abstraction. We write the above expression as

$$A = \langle +S | \{ | -T \rangle \langle -T | + S \rangle + | 0T \rangle \langle 0T | + S \rangle + | +T \rangle \langle +T | + S \rangle \} = 1$$

Remember that $\langle +S | +S \rangle = 1$. This means that the expression in the curly bracket above is nothing but $| +S \rangle$. We thus write:

$$| +S \rangle = | -T \rangle \langle -T | + S \rangle + | 0T \rangle \langle 0T | + S \rangle + | +T \rangle \langle +T | + S \rangle$$

Remember that $\langle -T | +S \rangle, \langle 0T | +S \rangle$ are amplitudes, that is just numbers (positive, negative, sometimes complex), $| -T \rangle, | 0T \rangle$, and $| +T \rangle$ are states. The above expression thus means that the $| +S \rangle$ state can be expressed as a **linear superposition** of the states $| -T \rangle, | 0T \rangle$, and $| +T \rangle$, with the coefficients $\langle -T | +S \rangle, \langle 0T | +S \rangle$, etc. If we call these coefficients c_1, c_2 , and c_3 , we can write:

$$| +S \rangle = c_1 \cdot | -T \rangle + c_2 \cdot | 0T \rangle + c_3 \cdot | +T \rangle$$

The states $| -T \rangle, | 0T \rangle$, and $| +T \rangle$ are called the **base set** used to express $| +S \rangle$. The basis set should be **complete**, that is, it should include all the eigenstates of a given measurement (in mathematical terms: of an operator), in our case of the T filter.

In general we can write for some state $| Q \rangle$

$$| Q \rangle = \sum_i c_i \cdot | i \rangle$$

3.8. The wave function

All this is very different from the quantum mechanics which you learned so far, centered around the wave function. You may ask: where is the wave function in all this?

Remember that wave function is a number (may be complex), depending on some coordinate (x, y, z , or ϕ for molecular rotation). Wave function is thus not a ket.

Remember further that the square (of the absolute value) of the wave function is equal to the probability (density) of finding the particle in a given location. This means that the wave function corresponds to an amplitude in the above terminology. The wave function of some state $| Q \rangle$ is

$$\Psi(x, y, z) = \langle i_{x,y,z} | Q \rangle$$

where $\langle i_{x,y,z} |$ are the eigenfunctions of position. Imagine them to be delta functions around the positions x, y, z . The state $| Q \rangle$ is expressed as a superposition of the base

states $\langle i_{x,y,z} |$, and the wave function are the coefficients. The probability to find the particle at this position is thus

$$W = \left| \langle i_{x,y,z} | Q \rangle \right|^2 = |\Psi(x, y, z)|^2$$

as you would expect.

Of course, the eigenfunction of position are not very useful, except as a base set in the above expressions. If you want to think of an experiment (i.e., a measurement) which would prepare a particle (an electron) in such a state, imagine a very fast particle (say a fast α particle) hitting an atom. The α particle has a very short DeBroglie wavelength and is thus capable of localizing the position of the electron in the atom (at the moment of the collision) to a precision much better than the dimension of the atom. This “measurement” thus converts the original state of the electron into one which is close to our eigenstate of position. (If you forgot how a measurement converts one state into another, see above) The price for this is, of course, that the new state is no longer an eigenstate of energy, the electron gained an unknown large amount of energy in the collision and races away at high speed. You will learn about the properties of states which are not eigenstates of energy in the next section: they form wave packets.

3.9. Summary

In this chapter we learned to understand a number of important concepts of quantum mechanics:

- quantization
- eigenstates
- collapse of a state (wave function) upon measurements
- amplitudes and probabilities
- superposition principle
- base sets
- wave function

We also learned that “good” states (i.e., wave functions) are not only those which are solutions of the Schrödinger equation (that is, eigenstates of the energy (Hamiltonian) operator). The determining factor for whether a state (wave function) are “good” or useless is whether it can be prepared in some kind of experiment.

Further reading:

- R. P. Feynman, R. B. Leighton, M. Sands: The Feynman Lectures on Physics, Adison-Wesley (1963), Vol. III.
- Alastair I. M. Rae; Quantum Mechanics, Institute of Physics Publishing (1992).

4. The time dependent formalism

4.1. The time dependent Schrödinger equation

The equation which appears to describe correctly this world (except relativistic effects) is

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + V \cdot \Psi \quad (4)$$

where $\Psi = \Psi(x, y, z, t)$ is the time dependent wave function, $V = V(x, y, z)$ is the potential energy (we shall only discuss potentials which do not depend on time) and the “upside-down delta” is a shorthand notation: $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$.

As in chapter 2, we shall consider only one dimension for simplicity. The time dependent Schrödinger equation for one dimension is

$$i\hbar \frac{\partial}{\partial t} \Psi(x, t) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \Psi(x, t) + V(x) \cdot \Psi(x, t) \quad (5)$$

This looks fairly frightening, but the solution is surprisingly simple:

$$\Psi(x, t) = \Psi(x) \cdot e^{-i\frac{E}{\hbar}t} \quad (6)$$

where $\Psi(x)$ is the time independent wave function, that is the solution of the time independent Schrödinger equation which you already know from chapter 2.

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \Psi(x) + V(x) \cdot \Psi(x) = E_{tot} \cdot \Psi(x) \quad (1)$$

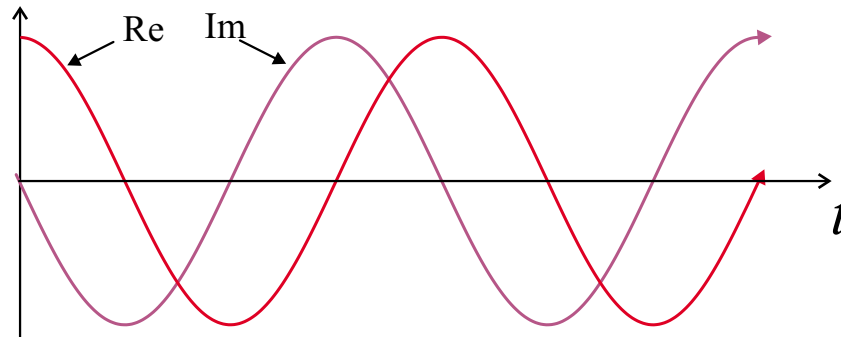
Exercise: Prove that the wave function (6) is a solution of the equation (5).

So far it was simple: The hard part is solving the time independent Schrödinger equation (1) (we discussed this in some length in chapter 2). Once this is done, just

multiply with the trivial factor $e^{-i\frac{E}{\hbar}t}$ and, voilà, the time dependent wave function is done.

Let's plot the magic factor $e^{-i\frac{E}{\hbar}t}$ to become familiar with it.

We have $e^{-i\frac{E}{\hbar}t} = \cos\left(\frac{E}{\hbar}t\right) - i\sin\left(\frac{E}{\hbar}t\right)$. The diagram below shows the real part in red, the imaginary part in violet.



The factor $e^{-i\frac{E}{\hbar}t}$ with which the function is multiplied is thus first real, then negative imaginary, then negative real, then positive imaginary, ... The factor makes the function blink like a firefly! The frequency of the blinking is proportional to the total energy.

4.2. Stationary and nonstationary states

What is the consequence on the probability density?

$$W = |\Psi(x,t)|^2 = |\Psi(x)|^2 \cdot \left| e^{-i\frac{E}{\hbar}t} \right|^2 = |\Psi(x)|^2 \cdot \left\{ \cos^2\left(\frac{E}{\hbar}t\right) + \sin^2\left(\frac{E}{\hbar}t\right) \right\} = |\Psi(x)|^2$$

The probability density is the same as for the time-independent Schrödinger equation! It does not depend on time, does not move in space. We still do not have a wave function describing a particle which is in one place at some time, and in a different place at a later time. We have not achieved our goal.

Such a wave function, whose probability density does not depend on time, is called a **stationary wave function**, the state which it describes is called a **stationary state**.

Our goal is a wave function with probability density moving around — a **nonstationary wave function**, describing a **nonstationary state**.

Such a wave function can be constructed as a **superposition of stationary wave functions** having different energies.

This may seem disturbing at first. A superposition of stationary wave functions having different energies is no longer a solution of the Schrödinger equation. Is it a “good” wave function then?

You have familiarized yourselves with this type of questions in chapter 3. It is perfectly feasible in nature to prepare a particle, a molecule or something else in a state which is not an eigenstate of some measurement, even in a state which is not an eigenstate of energy. As long as you find circumstances, “crazy” fields and forces etc., which prepare your system in such a state, it is a “good” state and the wave function describing it is a “good” wave function.

Most spectroscopies prepare molecules in stationary states, you learned about microwave spectroscopy which prepared the molecule in the $J=1$, $J=2$, etc. states, about IR spectroscopy which prepared the molecules in the $\nu=1$, $\nu=2$, etc. states. These states had definite energies, they were eigenstates of energy, they were stationary states. Their wave functions were solutions of the Schrödinger equation.

Strictly speaking, even these states were not 100% stationary, if you leave, for example HCl in the $\nu=1$ state alone for some time, it will emit an IR photon and change its state to $\nu=0$. The probability density thus does depend on time a little. But the nonstationary character is very weak, and we neglected it in the lecture at that time.

We shall learn later what fields and forces are required to prepare molecules in states which are not eigenstates of energy, that is, in nonstationary states. (You guess, it is femtosecond laser pulses.)

What you learned about Schrödinger equation is not lost, however, even when we now deal with wave functions which are not solutions of the Schrödinger equation. The solutions of the Schrödinger equation are very useful as a base set. We shall express the nonstationary states as superpositions of stationary states (you learned about the superposition principle in chapter 3.7). The first step in solving the problem will be solving the Schrödinger equation.

To summarize, we have the following procedure to deal with quantum chemical problems:

Step 1: Solve the time independent Schrödinger equation \rightarrow time independent wave function $\Psi(x)$.

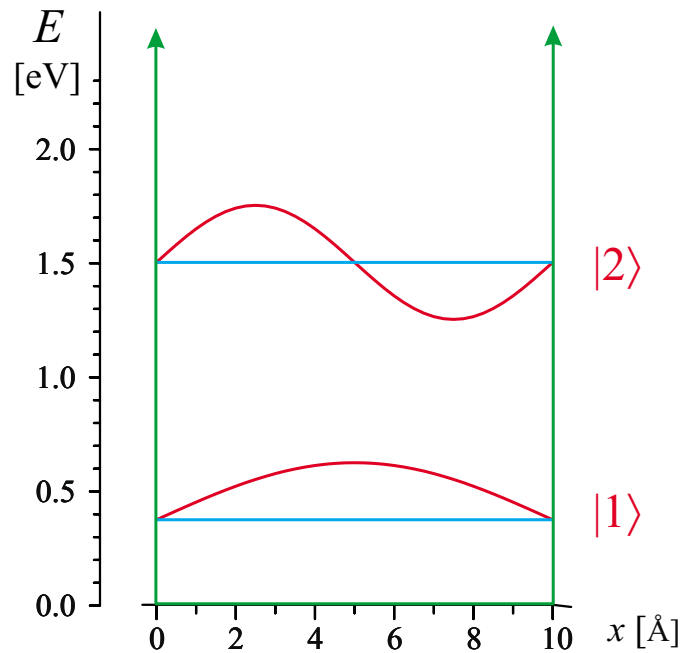
Step 2: Add the $e^{-i\frac{E}{\hbar}t}$ factor \rightarrow time dependent, but stationary wave function $\Psi(x,t)$.

Step 3: Use the wave functions from Step 2 as a base set to form time dependent non stationary wave function $\Psi_{NS}(x,t)$.

Note that the wave functions in Step 3 no longer describe eigenstates of energy. Energy measurements will give statistically distributed results. But this had to be expected. One formulation of the Heisenberg's uncertainty principle is $\Delta E \cdot \Delta t \approx \hbar$. This means that exact knowledge of energy ($\Delta E = 0$) is only possible with a complete lack of knowledge about the temporal development of the particle's position.

4.3. Electron in a box

Let's first see what are the properties of superpositions of stationary wave functions. The simplest example is a particle in a potential well. Take, as an example, an electron in a potential well with a width $L = 10 \text{ \AA}$, the walls infinitely high.



The solutions of the Schrödinger equation have energies

$$E_n = \frac{h^2}{8mL^2} n^2$$

The time-independent wave functions are

$$\Psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L} x\right)$$

The time-dependent wave functions are

$$\Psi_n(x, t) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L} x\right) e^{-i\frac{E_n}{\hbar} t}$$

Now we can build our first nonstationary wave function $\Psi_{\text{NS}}(x, t)$, as a superposition of the two lowest stationary wave function.

$$\Psi_{\text{NS}}(x, t) = \frac{1}{\sqrt{2}} \{\Psi_1(x, t) + \Psi_2(x, t)\} = \sqrt{\frac{1}{L}} \left\{ \sin\left(\frac{\pi}{L} x\right) e^{-i\frac{E_1}{\hbar} t} + \sin\left(\frac{2\pi}{L} x\right) e^{-i\frac{E_2}{\hbar} t} \right\}$$

What is the proper origin of the energy scale? Can we choose a different origin of the energy scale, lying let's say 1 eV higher or lower? If we do, the time-dependent wave functions change, the factors $e^{-i\frac{E}{\hbar}t}$ oscillate with different frequencies! The answer is yes, any origin of the energy scale is allowed. The physically observable results, like a speed of a moving particle, depend only on the differences of the frequencies, not on the absolute frequencies.

This means that, to make the mathematics simple, we can choose a new origin of the energy scale at the energy of the lowest state, $|1\rangle$. The oscillating factor of the lowest state then becomes $e^0 = 1$, and the expression for the wave function simplifies:

$$\Psi_{\text{NS}}(x, t) = \sqrt{\frac{1}{L}} \left\{ \sin\left(\frac{\pi}{L}x\right) + \sin\left(\frac{2\pi}{L}x\right) e^{-i\frac{E_2-E_1}{\hbar}t} \right\}$$

We can easily figure out qualitatively what does this function look like at two distinct points in time, namely then when imaginary component of the oscillating factor becomes zero. The factor is then 1 and -1 :

$$t_0 = 0 \quad \therefore \quad e^{-i\frac{E_2-E_1}{\hbar}t} = 1$$

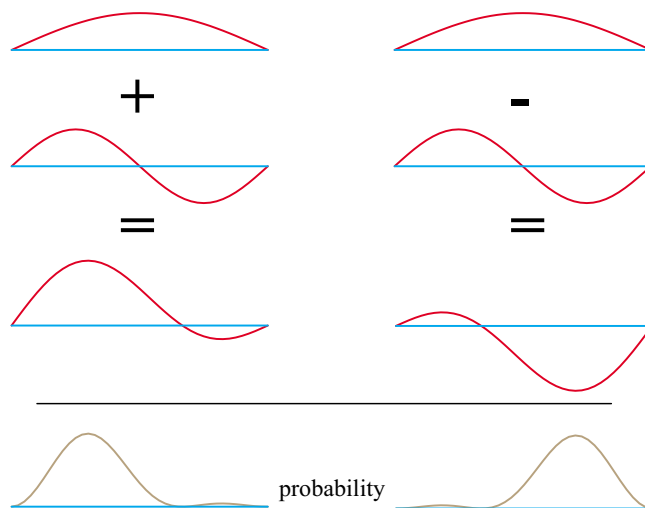
$$\text{and} \quad t_{\frac{1}{2}} = \frac{\pi\hbar}{E_2 - E_1} \quad \therefore \quad e^{-i\frac{E_2-E_1}{\hbar}t} = e^{-i\pi} = -1$$

$$t = t_0 \quad \therefore \quad \Psi_{\text{NS}}(x) = \frac{1}{\sqrt{2}} \{\Psi_1(x) + \Psi_2(x)\}$$

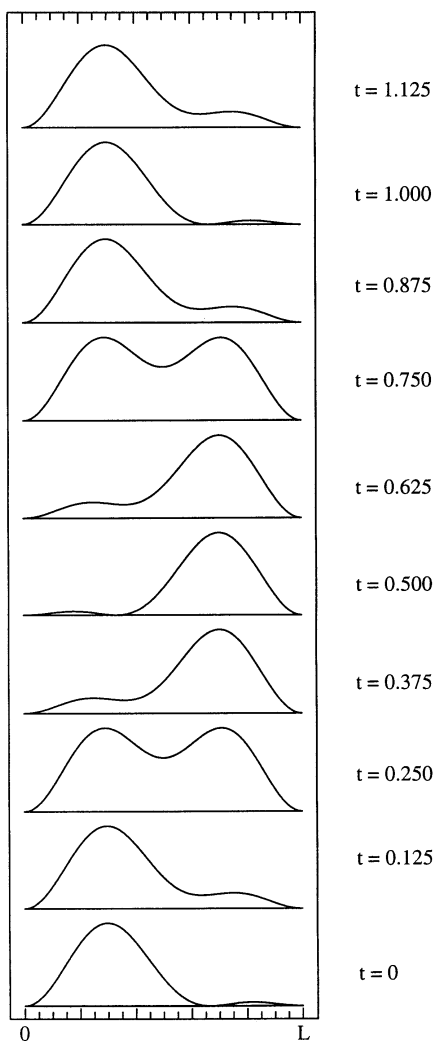
$$t = t_{\frac{1}{2}} \quad \therefore \quad \Psi_{\text{NS}}(x) = \frac{1}{\sqrt{2}} \{\Psi_1(x) - \Psi_2(x)\}$$

The nonstationary wave function is the sum of the stationary wave functions at $t = 0$, then it becomes complex, but a while later, at $t_{1/2}$, it becomes real again, and equal to the difference of the stationary wave functions. Then the wave function becomes complex again, and after $t = 2 t_{1/2}$ it becomes identical to what it was at $t = 0$, and the whole cycle repeats periodically.

Let's estimate graphically what the wave function looks like at $t = 0$ and at $t_{1/2}$:



The probability densities shown at the bottom of the picture show that the particle was more on the left side of the box at $t = 0$, more on the right side of the box at $t_{1/2}$. We reached our goal! The time $t_{1/2}$ is, for our example, 1.8 ps. Electrons move fast.



The picture on the left shows the probability $|\Psi_{NS}(x,t)|^2$ to find the electron in the box for various intermediate times.

The price is that the nonstationary state is no longer an eigenstate of energy. If you measured the energy of the particle in this state, you would obtain, statistically distributed, the values E_1 and E_2 . This is analogous to the situation which we encountered in section 3.4.

4.4. Free particle

You already know the wave function from section 2.2.1:

$$\Psi(x) = A e^{i\frac{p}{\hbar}x} = A \left(\cos \frac{p}{\hbar}x + i \sin \frac{p}{\hbar}x \right) \quad (3)$$

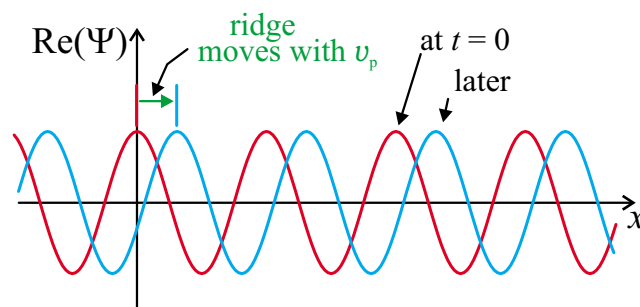
Now you know that writing down the time dependent wave function is easy:

$$\Psi(x,t) = A e^{i\frac{p}{\hbar}x} e^{-i\frac{E}{\hbar}t} = A e^{i\left(\frac{p}{\hbar}x - \frac{E}{\hbar}t\right)} \quad (7)$$

What does this function mean? Let's look only at the real part of this function for simplicity:

$$\text{Re}\{\Psi(x,t)\} = \text{Re}\left\{ A e^{i\left(\frac{p}{\hbar}x - \frac{E}{\hbar}t\right)} \right\} = A \cos\left(\frac{p}{\hbar}x - \frac{E}{\hbar}t\right)$$

At time $t = 0$ it is $\cos \frac{p}{\hbar}x$, a cosine wave with the DeBroglie wavelength. Later, it is the same cosine wave, but shifted along x .



Let's look with what speed does the wave move. Look at the position of the first ridge, that is at the place where the argument of the cosine is equal to zero.

$$\frac{p}{\hbar}x - \frac{E}{\hbar}t = 0$$

The position of this ridge is at $x = \frac{E}{p}t$

The speed with which the wave moves is called the **phase velocity** v_p .

$$v_p = \frac{x}{t} = \frac{E}{p}$$

What does the probability density?

$$W = |\Psi(x,t)| = A^2 \left| e^{i\left(\frac{p}{\hbar}x - \frac{E}{\hbar}t\right)} \right|^2 = A^2$$

The probability density is a constant, it does not change with time.

We did not have to calculate that. So far we talk about a state with a unique, definite energy E , such a state is stationary, and the probability distribution of stationary states do not change with time.

The phase velocity is thus not very helpful, it does not have physical meaning.

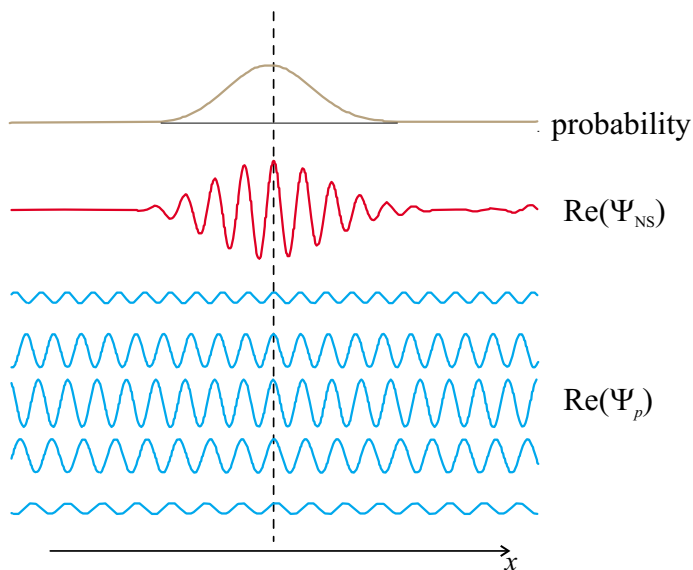
There is another problem with v_p — it depends on the choice of the origin of the energy scale, physically meaningful variables should not do that. The phase velocity may even exceed the speed of light.

As with the particle in the box above, we have to construct nonstationary wave functions as superpositions of the stationary ones to get explicitly moving particles.

A particularly meaningful way to do this is to take many stationary waves with various impulses p centered around some impulse p_0 , and have the coefficients c_p follow a Gaussian distribution. (The sum can actually be replaced with an integral because p is continuous.)

$$\Psi_{\text{NS}}(x,t) = \sum_p c_p \cdot \Psi_p(x,t)$$

The picture below shows the real part of the wave functions: the stationary wave functions are in blue, their sum in red, and the probability density in brown.



All the constituent stationary waves add constructively at the position indicated by the dashed line. The waves get more and more out of phase to the left and right of this position, they add more and more destructively, and their sum becomes zero after a few oscillations. We obtain a **wave packet**. The wave has also an imaginary part, and the two give the probability a simple Gaussian shape.

The wave packet moves, but not with the phase velocity v_p .

We shall consider the sum of only two stationary waves to find out the velocity of the wave packet. First, we shall derive a useful formula for the sum of two exponentials with imaginary exponents $e^{i\alpha}$ and $e^{i\beta}$.

First note that α can be written as

$$\alpha = \frac{\alpha + \beta}{2} + \frac{\alpha - \beta}{2}$$

and similarly for β :

$$\beta = \frac{\alpha + \beta}{2} - \frac{\alpha - \beta}{2}$$

We then have

$$e^{i\alpha} = e^{i\frac{\alpha+\beta}{2}} \cdot e^{i\frac{\alpha-\beta}{2}}$$

and

$$e^{i\beta} = e^{i\frac{\alpha+\beta}{2}} \cdot e^{-i\frac{\alpha-\beta}{2}}$$

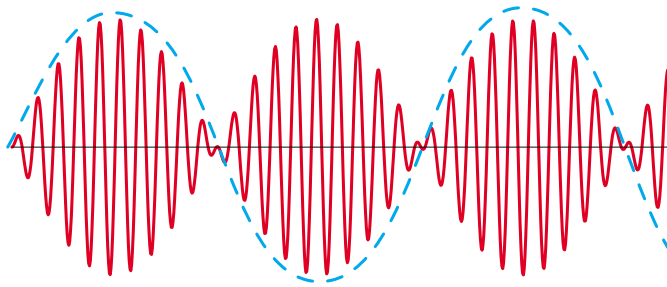
For the sum of the two exponentials we can write

$$\begin{aligned} e^{i\alpha} + e^{i\beta} &= e^{i\frac{\alpha+\beta}{2}} \cdot \left\{ e^{i\frac{\alpha-\beta}{2}} + e^{-i\frac{\alpha-\beta}{2}} \right\} = \\ &= e^{i\frac{\alpha+\beta}{2}} \cdot \left\{ \cos\frac{\alpha-\beta}{2} + i \sin\frac{\alpha-\beta}{2} + \cos\frac{\alpha-\beta}{2} - i \sin\frac{\alpha-\beta}{2} \right\} = \\ &= e^{i\frac{\alpha+\beta}{2}} \cdot 2 \cos\frac{\alpha-\beta}{2} \end{aligned}$$

Now we shall apply this formula to a simple nonstationary wave function, made up of two stationary waves

$$\begin{aligned} \Psi_{NS}(x, t) &= A \left\{ e^{i\left(\frac{p_1}{\hbar}x - \frac{E_1}{\hbar}t\right)} + e^{i\left(\frac{p_2}{\hbar}x - \frac{E_2}{\hbar}t\right)} \right\} = \\ &= 2A e^{i\left(\frac{p_1+p_2}{2\hbar}x - \frac{E_1+E_2}{2\hbar}t\right)} \cdot \cos\left(\frac{p_1-p_2}{2\hbar}x - \frac{E_1-E_2}{2\hbar}t\right) \end{aligned}$$

The picture below shows the fast oscillating exponential in red, the slowly oscillating cosine in blue. ($\frac{p_0}{\hbar} = \frac{p_1 + p_2}{2\hbar} = 2$, $\frac{p_1 - p_2}{2\hbar} = 0.1$)



The probability density is

$$W = |\Psi_{\text{NS}}(x, t)|^2 = 4A^2 \left| e^{i\left(\frac{p_1 + p_2}{2\hbar}x - \frac{E_1 + E_2}{2\hbar}t\right)} \right|^2 \cdot \cos^2\left(\frac{p_1 - p_2}{2\hbar}x - \frac{E_1 - E_2}{2\hbar}t\right) =$$

$$= 4A^2 \cdot \cos^2\left(\frac{p_1 - p_2}{2\hbar}x - \frac{E_1 - E_2}{2\hbar}t\right)$$

This describes a train of wave packets. To find the velocity with which the wave packets move, consider at which position is a spot for which the argument under the cosine is constant, e.g., equal to zero.

$$\frac{p_1 - p_2}{2\hbar}x - \frac{E_1 - E_2}{2\hbar}t = 0$$

$$x = \frac{E_1 - E_2}{p_1 - p_2}t$$

The wave packet thus moves — we shall call its velocity the **group velocity** v_g .

$$v_g = \frac{x}{t} = \frac{E_1 - E_2}{p_1 - p_2} = \frac{dE}{dp}$$

Is this something familiar? The total energy of a *classical* particle with the velocity v is the potential energy V plus the kinetic energy

$$E = V + \frac{m}{2}v^2 = V + \frac{p^2}{2m}$$

The group velocity is

$$v_g = \frac{dE}{dp} = \frac{d}{dp}\left(V + \frac{p^2}{2m}\right) = \frac{2p}{2m} = \frac{mv}{m} = v$$

The wave packet moves with the same velocity as a classical particle!

What a miracle. The obscure complex oscillating factor $e^{-i\frac{E}{\hbar}t}$ somehow leads to the same velocity as classical physics!

The wave packets constructed in this way also obey the Heisenberg's uncertainty (some people argue that the term indeterminacy would be more appropriate) principle.

The wave packets widen as they move along! A classical picture helps you to understand why: The particle described by the wave packet does not have a definite energy, so there are components which are faster and move ahead, and components which are slower, and lag behind. We shall return to this later, in section 6.9.

The program "Superwave" shows a moving picture of a train of wave packets. It lets you experiment with E_1 and E_2 and thus change the width of the wave packets, and the phase and group velocities. You can even have the phases going backward and the wave packet going forward!

(http://www-chem.unifr.ch/pc/dir_allan/SuperWave.html)

4.5. Nonstationary wave functions in various potentials

A very pretty real-time simulation allowing you to exercise the subject of this section is given by Cemal Yalabik of the Bilkent University at his web page. You can draw your potential there.

http://www.fen.bilkent.edu.tr/~yalabik/applets/t_d_quant.html

4.5.1. Harmonic potential

- A suitable superposition of the time-independent wave functions $\psi_v(x)$ gives a wave packet whose shape is identical to the shape of the $v = 1$ wave function. (with thanks to Dr. Duška Popović for teaching me these formulas)

$$\Psi_{NS}(x, t) = \sum_{v=0}^{\infty} c_v e^{-i\frac{E}{\hbar}t} \psi_v(x)$$

where the optimum coefficients are given by

$$c_v = \frac{\alpha^n}{\sqrt{n!}} e^{-\frac{|\alpha|^2}{2}}$$

α is a measure of the mean energy of the oscillator according to the relation $E = \hbar\omega|\alpha|^2$, with ω being the classical angular frequency of the oscillator.

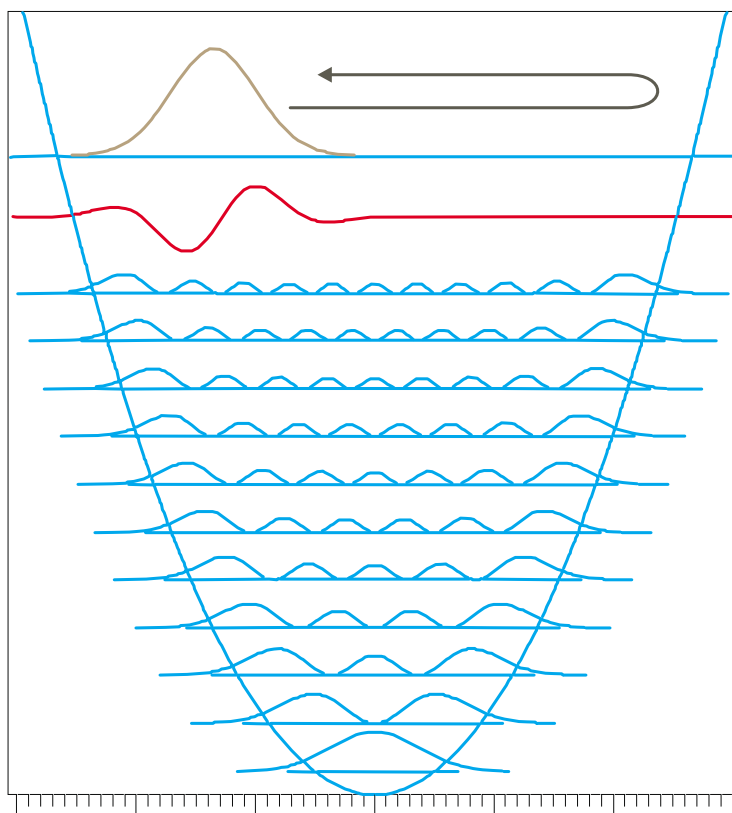
- This wave packet oscillates with the frequency of the classical oscillator!
- Increasing mean energy increases the amplitude, but not the frequency of the oscillations of the wave packet.

The program “Superwave” shows a moving picture of the wave packet, with real time feedback. (http://www-chem.unifr.ch/pc/dir_allan/SuperWave.html)

This program allows you to choose the right superposition to make a nice wave packet oscillating with varying amplitude. But it also allows you to choose the individual coefficients manually. This generally results in irregular waves wildly splashing around. There is something interesting about the apparently irregular motion of these waves — it repeats itself with a certain period. This phenomenon is called the **recurrence**, the period the **recurrence time**.

This phenomenon is general. If you have a certain number of factors $e^{-i\frac{E}{\hbar}t}$ oscillating with different frequencies, you can always calculate a time after which all the phases have the same relation as in the beginning. The behaviour of any quantum system is repetitive.

This may seem to have serious philosophical consequences. Does it mean that historical events recur in regular intervals? — They don't. The recurrence time becomes longer dramatically with the complexity of the system. Small molecules may have recurrence time of picoseconds or microseconds, but larger systems have *very* long recurrence times. Many years ago, professor Martin Quack gave us an exercise: calculate the recurrence time of a bottle of whisky. I do not remember the exact answer, but it is *much* longer than the known age of the universe. So there is little chance that Napoleon will come again...



4.5.2. Potential barrier: tunnelling

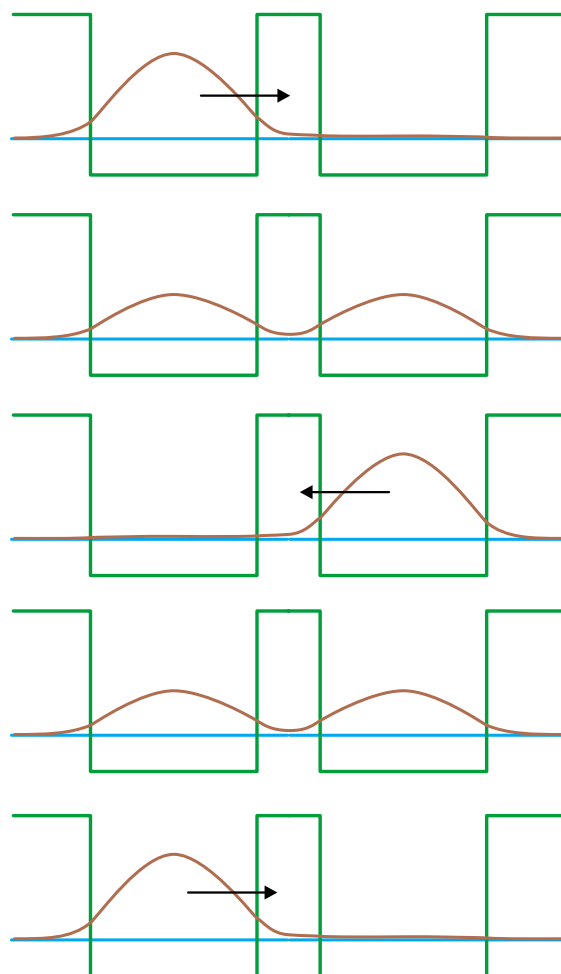
This is a qualitative picture of what happens when a wave packet is sent towards a potential barrier:

A beautiful animated view in two dimensions is shown by Géza Márk of the Technical University of Budapest at the web page

http://newton.phy.bme.hu/education/schrd/2d_tun/2d_tun.html

4.5.3. Double potential well: isomerization

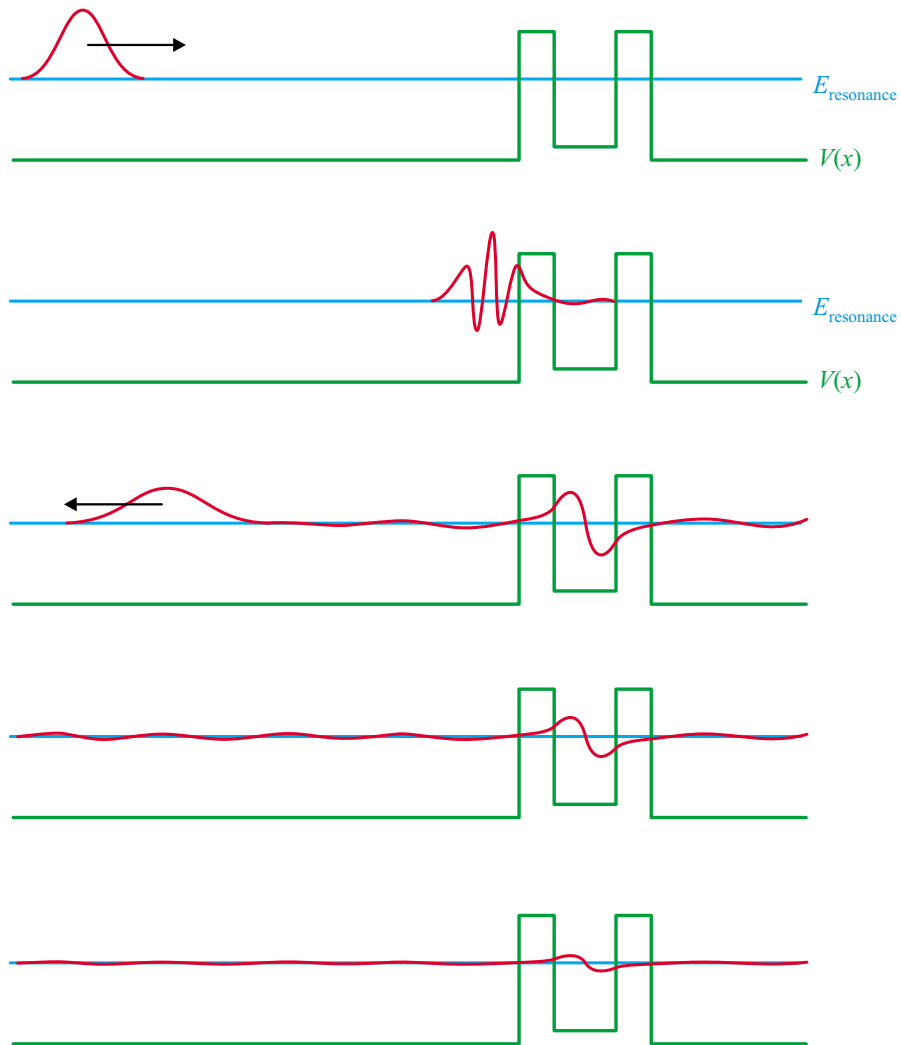
A nonstationary wave function made of the two lowest stationary solutions (see section 2.2.4) results in a wave packet slowly “sneaking” from one well to the other. (This picture shows the probability, that is the square of the wave function)



The oscillations become faster when the barrier is more transparent (narrower, lower).

4.5.4. Potential well with thin walls: resonances

This is a qualitative picture of what happens when a wave packet is sent towards a potential well with thin walls:



When the mean energy of the wave packet is near the energy of the resonance (see section 2.2.5), part of it is trapped. It then slowly leaks out. This explains the temporary negative ions in electron scattering.

4.6. Rotation

The stationary wave functions have been discussed in section 2.3.

Nonstationary wave functions can be formed as superpositions of the stationary wave functions with different energies.

The simplest example is a superposition of the wavefunctions with $k = 0$ and $k = +1$.

$$\begin{aligned}\Psi_{\text{NS}} &= \sqrt{\frac{1}{2}} \left(\Psi_{k=0}(\varphi) + \Psi_{k=+1}(\varphi) \cdot e^{-i\frac{E}{\hbar}t} \right) = \sqrt{\frac{1}{4\pi}} \left(1 + e^{i\varphi} \cdot e^{-i\frac{E}{\hbar}t} \right) = \\ &= \sqrt{\frac{1}{4\pi}} \left(1 + e^{i\left(\varphi - \frac{E}{\hbar}t\right)} \right) = \sqrt{\frac{1}{4\pi}} (1 + e^{i\alpha})\end{aligned}$$

where α is a shorthand for $\varphi - \frac{E}{\hbar}t$.

We want to know what does the probability density do:

$$\begin{aligned}W &= |\Psi_{\text{NS}}|^2 = \frac{1}{4\pi} \left| 1 + e^{i\alpha} \right|^2 = \frac{1}{4\pi} \left\{ (1 + \cos \alpha + i \sin \alpha) \cdot (1 + \cos \alpha - i \sin \alpha) \right\} = \\ &= \frac{1}{4\pi} \left\{ (1 + \cos \alpha)^2 + \sin^2 \alpha \right\} = \frac{1}{4\pi} \left\{ 1 + \cos^2 \alpha + 2 \cos \alpha + \sin^2 \alpha \right\} = \frac{1}{2\pi} (1 + \cos \alpha)\end{aligned}$$

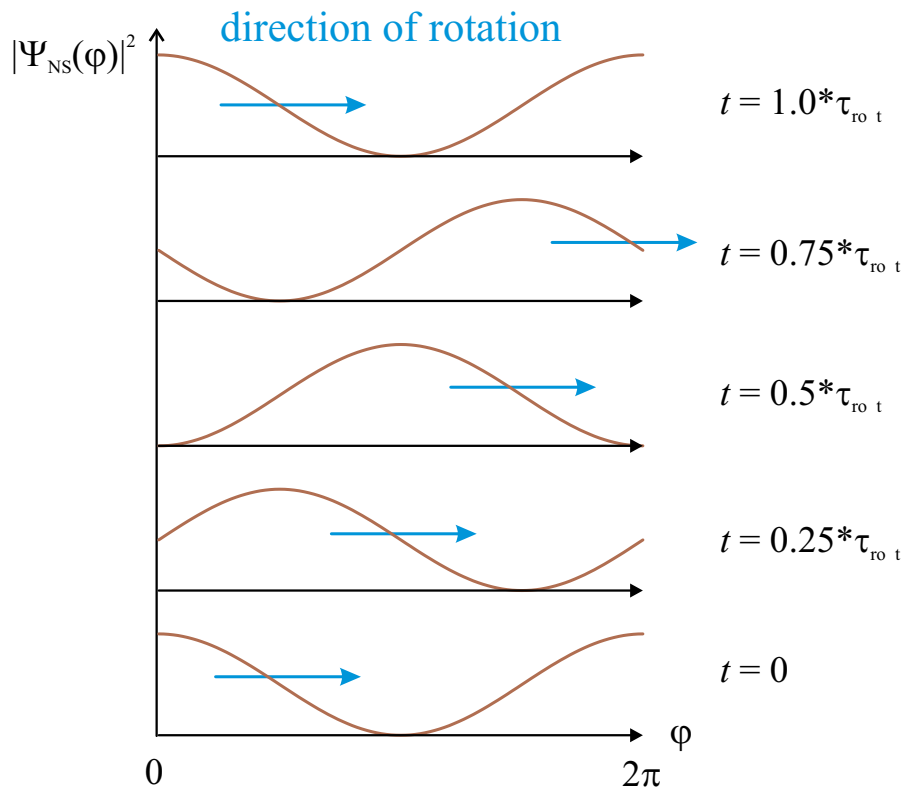
and after replacing α with the full argument

$$W = \frac{1}{2\pi} \left\{ 1 + \cos \left(\varphi - \frac{E}{\hbar}t \right) \right\}$$

What does this function look like? First note that it is repetitive, it repeats itself after the time τ_{rot}

$$\begin{aligned}\frac{E}{\hbar} \tau_{\text{rot}} &= 2\pi \\ \tau_{\text{rot}} &= 2\pi \frac{\hbar}{E} = \frac{h}{E}\end{aligned}$$

We can now draw what does the function look like at $t = 0$, $t = \tau_{\text{rot}}/4$, $t = \tau_{\text{rot}}/2$, etc.



We have a wave packet rotating around!

We can also make a three-dimensional nonstationary wave function by superposing, for example, the 3s and the 3p₊₁ orbitals in an atom such as Na. The result is a wave packet of an electron orbiting around a positive ion core. Such states have actually been prepared!

4.7. Conclusions

The somewhat obscure complex oscillating factor $e^{-i\frac{E}{\hbar}t}$ have appeared useless in the beginning. But accomplishes wonders! It is capable of correctly describing all time dependent phenomena:

- motion of a free particle
- harmonic oscillator
- tunneling
- the flip-flop inversion of ammonia
- the time delay in electron collisions caused by resonances

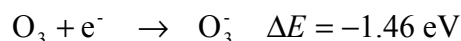
5. Applications in electron scattering

The wave packet picture is very useful for the description of certain negative ions.

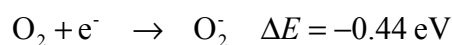
Negative ions are intermediates in most chemical reactions induced by electron impact. Electron impact induced chemistry is normally not part of chemical curriculum, but is widely used in industry. Ozone is synthesized using electron impact in discharges. Ozone is used for certain industrial synthesis, for chlorine-free bleaching of paper, and disinfecting drinking water. Electron impact (electrical discharges) in various gases are used in the majority of production steps of integrated circuits for electronics, for treatment of surfaces, etc. In terms of industrial sales, electron impact induced chemistry is very important.

5.1. Trapping of electrons

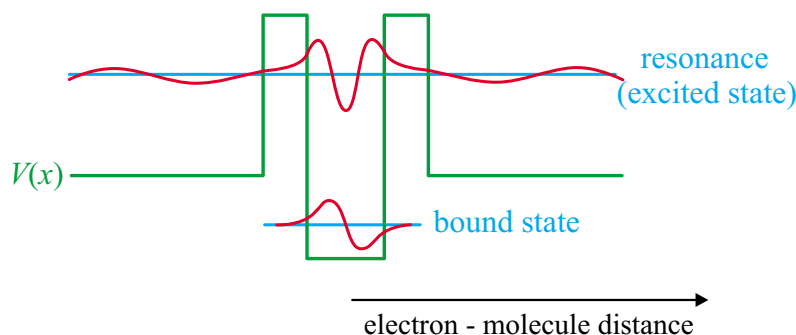
There are two fundamental types of negative ions. The first are **bound negative ions**, where the electron attachment is exothermic:



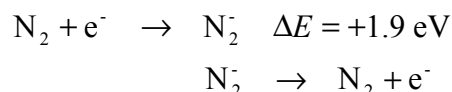
or



A very schematic diagram in terms of what you learned in chapter 2 would look like this: (the upper red curve is normally not occupied by an electron — it is an excited state of the negative ion)

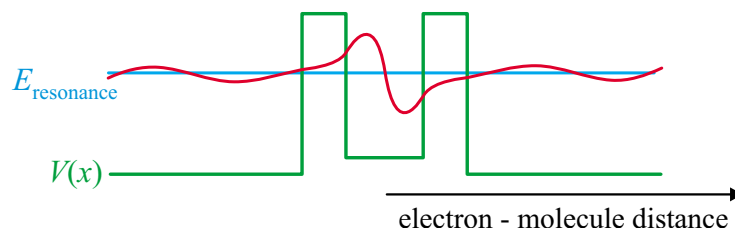


The electron attachment is endothermic in the second kind of the negative ions:



The second process is called **autodetachment**, the electron departs spontaneously. This negative ion is thus of the type “**resonance**” or “discrete state embedded in the continuum” in the nomenclature of section 2.2.5.

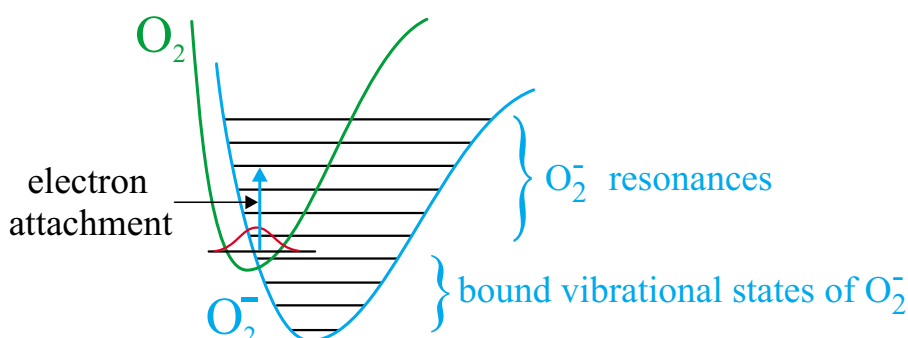
A very schematic diagram in terms of what you learned in chapter 2 would look like this:



5.2. Nuclear motion in temporary negative ions

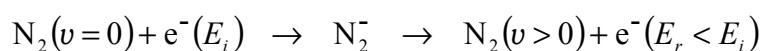
We shall now be concerned with the vibrational structure of the negative ions of the second type. It can be studied in electron attachment experiments, whereby an electron is attached to a neutral molecule in its vibrational ground state to produce the negative ion in various vibrational levels as illustrated in the figure below.

(note that the horizontal scale in the two pictures above was the electron – molecule distance, in the pictures below the distance between the nuclei)

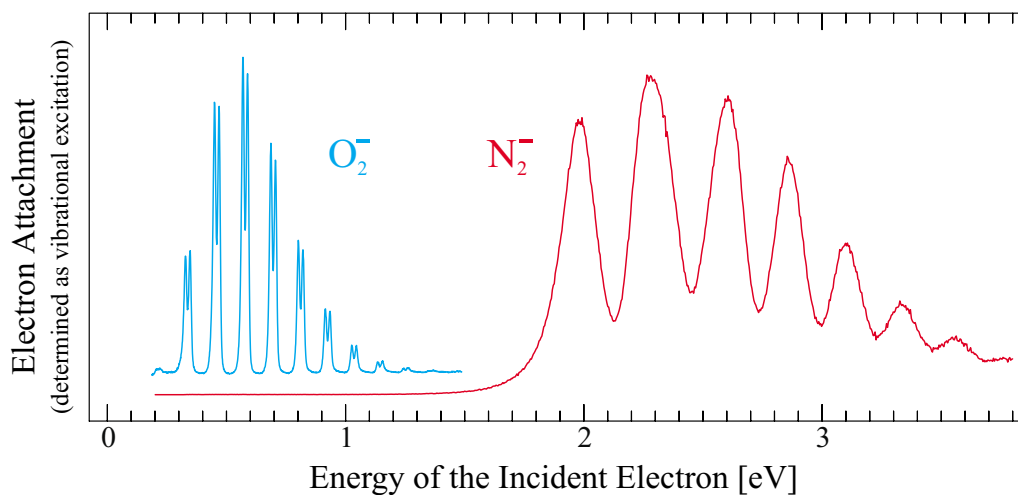


The situation is slightly complicated in O_2^- by the fact that that the lowest four vibrational levels are bound anions, the higher levels are resonances since the electron can autodeattach. But it should not be too confusing, we are concerned only with the higher levels here, the resonances.

How does one measure the attachment spectra? The resulting “resonance” N_2^- (or O_2^- in a high vibrational state) can not be detected directly in a mass spectrometer because they decay by autodeattachment long before they reach the detector. But the resonance can be detected indirectly, because it causes vibrational excitation of the molecule. The vibrational excitation causes the ejected electron to have less energy than the incident electron, and this **energy loss** serves to detect the vibrational excitation, which in turn evidences an attachment of the electron to form a temporary negative ion, the resonance:



The figure below shows the observed spectra of O_2^- and N_2^- . Both spectra were recorded with the same instrumental resolution.

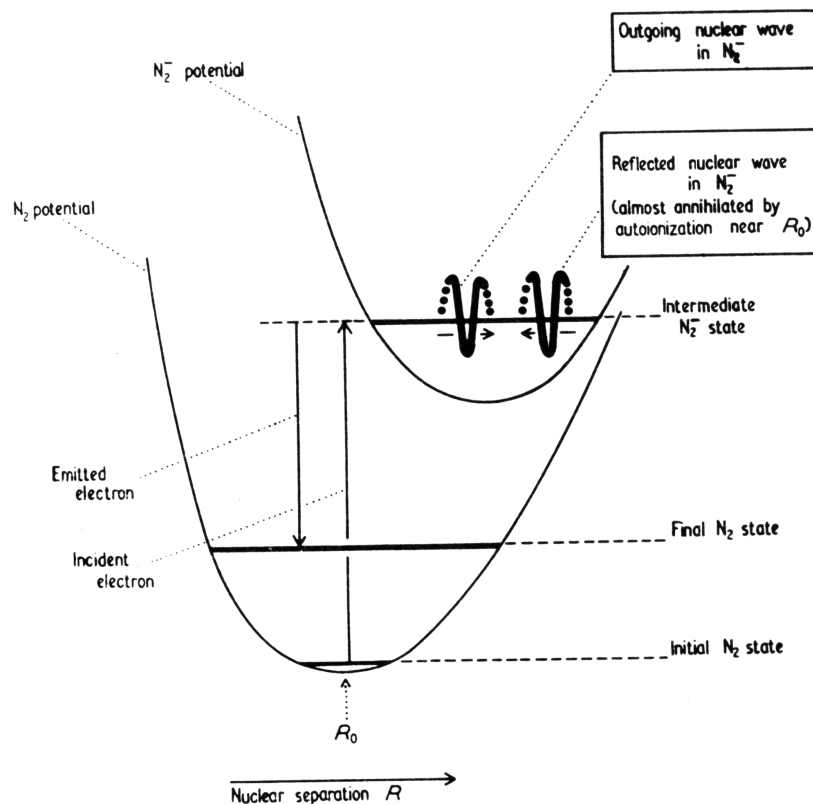


The spectrum of O_2^- consists of sharp equidistant peaks, as expected for vibrational structure.

The doubling of the peaks is caused by spin-orbit coupling and is not important for this discussion. (there are two electronic states of O_2^- lying close to each other, one with the spin and orbital angular momenta parallel, the other antiparallel to each other, i.e. ${}^2\Pi_{g,\frac{3}{2}}$ and ${}^2\Pi_{g,\frac{1}{2}}$)

In contrast, the spectrum of N_2^- shows broad bands, which are obviously not the sharp, discrete, stationary vibrational states which you know from courses about vibrational spectroscopy.

The structure has been rationalized in terms of wave packets of the moving nuclei:



The consequence of the fast autodetachment and the resulting very short lifetime of N_2^- is that its potential curve does not have a definite energy, it has a certain energy width Γ of the order of 0.1 eV. The nuclear motion is thus best viewed not as a stationary vibrational wave function with a discrete energy, but as a single “forth-and-back” (that’s why the theory is called a “boomerang” model) of a wave packet.

(figure from: D. T. Birtwistle and A. Herzenberg, “Vibrational Excitation of N_2 by Resonance Scattering of Electrons”, *J. Phys. B* **4** (1971) 53.)

6. Applications with femtosecond lasers

6.1. Preparation of vibrational wave packets

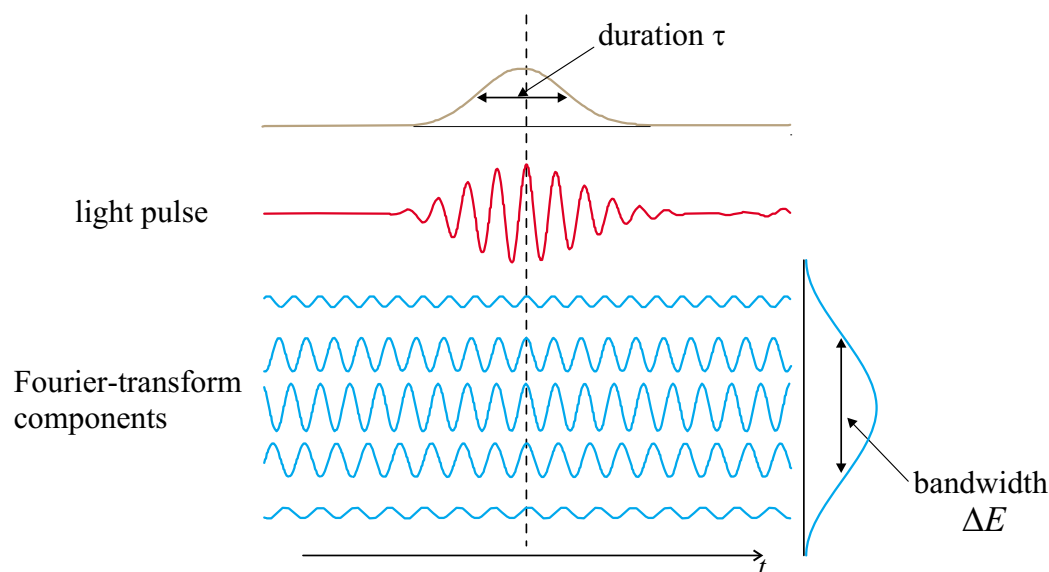
We have seen that the wave packets do not have a unique energy. Their preparation thus requires non-monochromatic light.

This appears to be an easy requirement — simply take a white lamp. But each photon of this white light was prepared through an electronic transition in the hot tungsten wire of the bulb, each is monochromatic by itself. White light from an incandescent bulb is just a mixture of monochromatic photons.

We need light source where each photon is non-monochromatic. Fourier transform tells us that the corresponding light pulse must be very short.

A very short light pulse will excite a superposition of several vibrational levels simultaneously, with the same phase, giving a vibrational wave packet.

The short light pulse can be represented as a superposition of many continuous electromagnetic waves with different frequencies.



The pulse **duration** τ and the **bandwidth** ΔE have the relation

$$\Delta E \cdot \tau = \hbar$$

A good quality light pulse will satisfy this relation. Such light pulse is said to be “**transform-limited**”. Real pulses may have longer τ or larger ΔE (it is easy to make non-monochromatic light — just take a bad monochromator).

This means that a 50 ns long transform limited pulse has a bandwidth of

$$\Delta E = \frac{6.6 \times 10^{-34} \text{ Js}}{2\pi \times 50 \times 10^{-15} \text{ s}} \approx 2 \times 10^{-21} \text{ J} \quad (1.3 \text{ kJ/mol}, 13 \text{ meV}, 100 \text{ cm}^{-1})$$

For comparison, the B excited state of I₂ has a vibrational wavenumber $\tilde{\nu}_e = 125 \text{ cm}^{-1}$. A 50 ns pulse is just right to excite a nonstationary state superimposed from several vibrational levels.

For comparison, the period of oscillation of the electric field of light with $\lambda = 600 \text{ nm}$ is

$$\tau_E = \frac{1}{\nu} = \frac{\lambda}{c} = \frac{600 \times 10^{-9} \text{ m}}{3 \times 10^8 \text{ m/s}} = 2 \times 10^{-15} \text{ s} = 2 \text{ fs}$$

This means that a 50 ns long light pulse consists of only about 25 oscillations of the electric field! The length of this pulse is around 15 μm !

6.2. The Franck-Condon principle

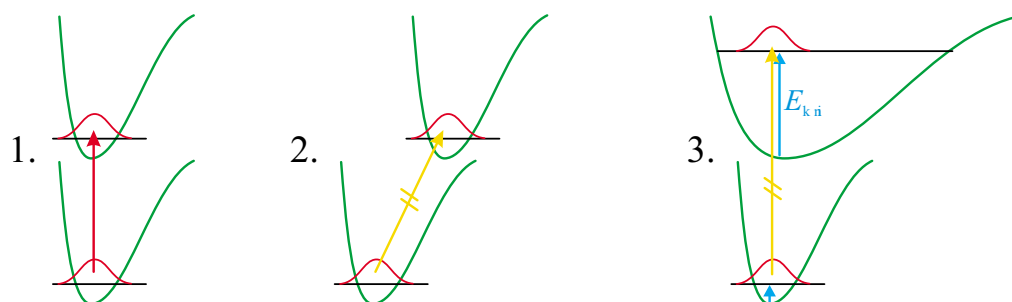
Franck-Condon (FC) principle is needed for direct observation of the motion of wave packets.

It is useful to recall the FC principle here with emphasis on wave packets.

The FC principle is based on the fact that electrons move much faster than nuclei. An electron transition (change of electronic motion) is fast on the time scale of the motion of the nuclei. (we shall later discuss exceptions to this rule)

This means that the state of motion (position and impulse) of the nuclei does not change during the electronic transition.

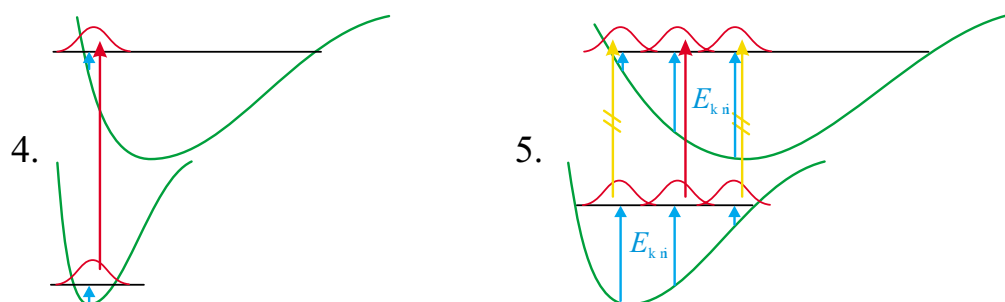
Examples:



Case 1. is FC allowed, both the position and the momentum are the same. (The momentum is small in the vibrational ground state.)

Case 2. is FC forbidden. The momentum of the nuclei small in both the upper and lower states, but the position is different.

Case 3. is also FC forbidden. The position is the same, but the nuclei are nearly standing still on the lower surface, but moving fast on the upper surface.

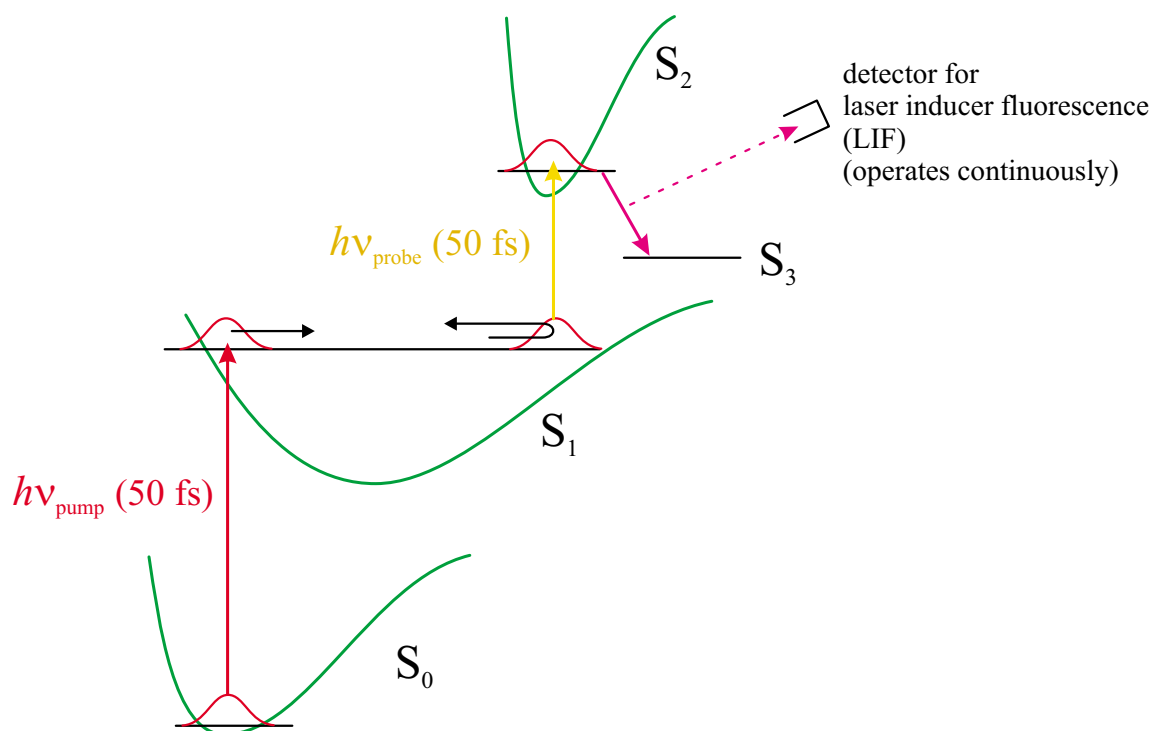


Case 4. is FC allowed, position is the same, and nuclei are nearly standing still at the turning point on the upper surface.

Case 5. Only one of the three transitions shown is FC allowed. The position is O.K. in all three cases, but only in one case do the nuclei have the same momentum on both the lower and the upper surfaces. (The wave packets must move in the same direction in this case for the transition to be allowed.)

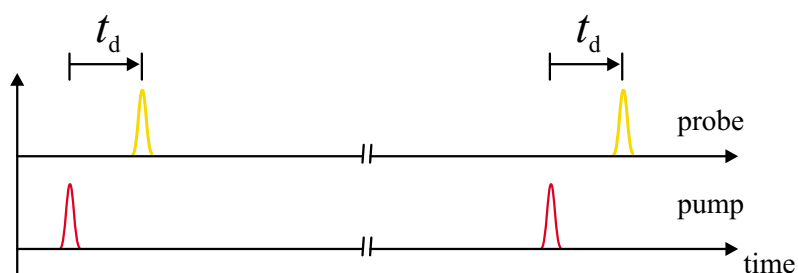
6.3. Observation of wave packets

Motion of wave packets can be observed directly in molecules with suitably arranged potential surfaces, like in the example below:

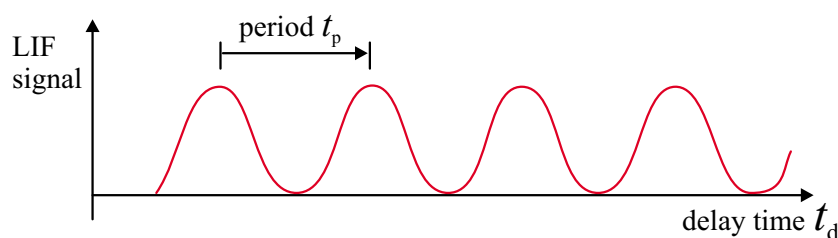


A pump pulse excites the molecule to the S_1 state, forming a nonstationary vibrational state (a superposition of several stationary states). After a variable delay time, during which the wave packet is allowed to move, a second laser pulse attempts to excite the molecule from S_1 to S_2 . The excitation succeeds only if the wave packet is in a position making the transition Franck-Condon allowed, otherwise it fails. The S_2 state is detected by its luminescence.

Timing diagram:



The experiment consists of repetitive pump and probe pulses with slowly increasing delay time. The luminescence signal is plotted against the delay time:



A specific example is I_2 .

The two figures below are from the classical papers M. Gruebele and A. H. Zewail, *J. Chem. Phys.* **98** (1993) 883, and Bowman, Dantus, and Zewail, *Chem. Phys. Lett.* **161** (1989) 297.

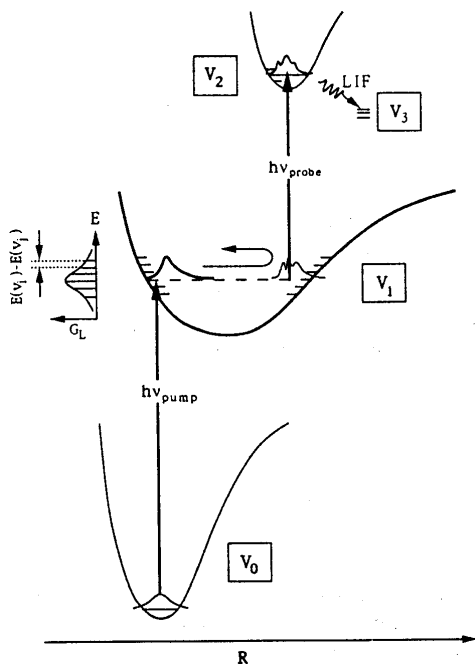


FIG. 1. Schematic of the femtosecond pump-probe experiment for a bound potential; the wave packet formed on the intermediate surface (V_1) consists of a number of eigenstates covered by the laser bandwidth G_L and with characteristic frequencies $E(v_i) - E(v_j)$; these frequencies are preserved in the coherence of the transient obtained by probing the packet to a final surface (V_2), from where it can be detected by LIF to V_3 (or through mass spectrometry or other means).

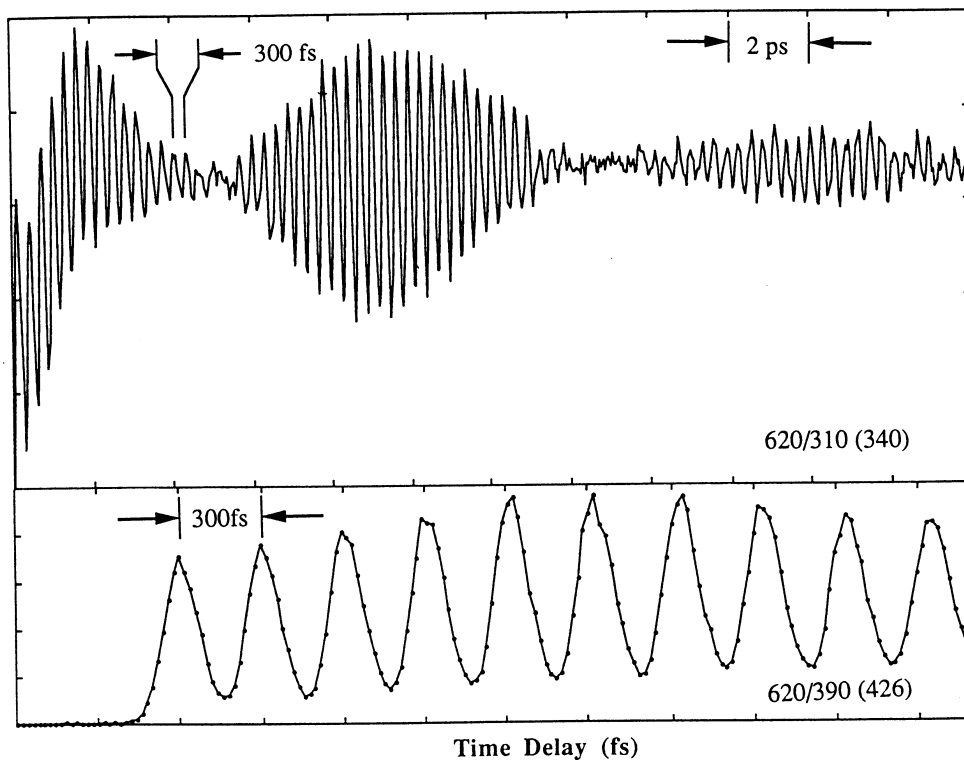


Fig. 2. Top: Typical FTS transient obtained for 620/310 (340) showing the wave packet dynamics in the strongly bound B state. Bottom: Typical FTS transient, 620/390 (426), showing the period of oscillation to be invariant with the probe wavelength. Note that the time scales are different for the two transients.

The measured period is $t_p = 300$ fs.

The spectroscopically measured vibrational spacing of the B state of I_2 is $\tilde{\nu}_e^B = 125 \text{ cm}^{-1}$ (see the book of Herzberg and Huber).

This corresponds to a classical vibrational period of

$$\tau = \frac{1}{\nu} = \frac{\lambda}{c} = \frac{1}{c\tilde{\nu}_e} = \frac{1}{3 \times 10^8 \times 1.25 \times 10^4} = 2.7 \times 10^{-13} \text{ s} = 270 \text{ fs}$$

The same number has been measured in two entirely different experiments: once in the **time domain** in the modern femtosecond experiment, once in the **energy domain** in the classical experiment!

On a more sophisticated level, both methods can be used to obtain not only the vibrational frequency, but also finer details of the shape of the potential curve.

6.4. Molecular dissociation

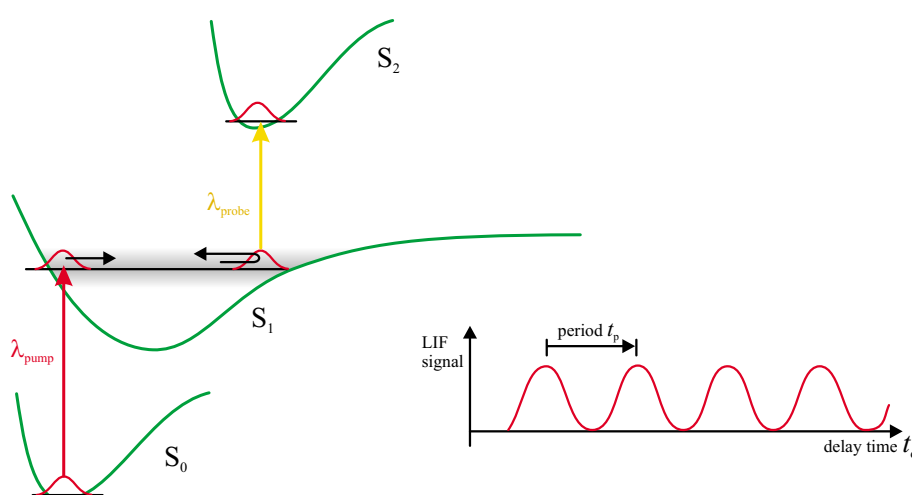
Changing the wavelength of the pump radiation can vary the mean energy of the wave packet.

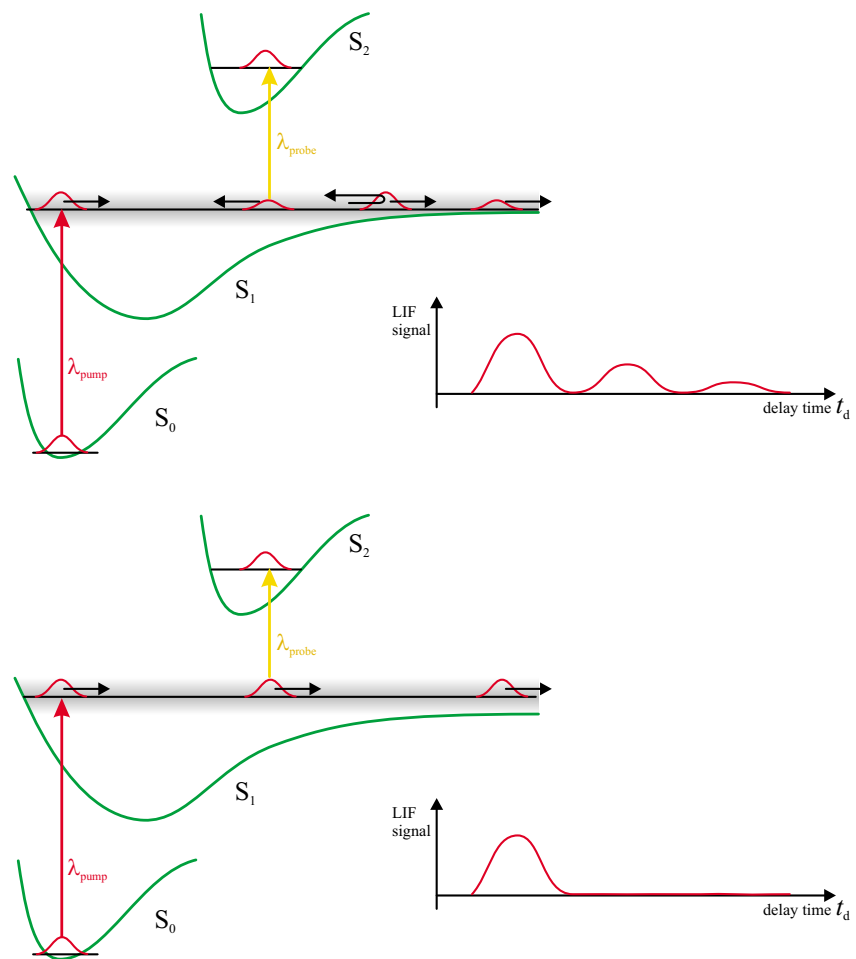
Remember that wave packets do not have sharp energy — a fading gray band in the picture below schematically indicates this.

The lowest energy pump pulse (top of the picture) prepares a wave packet entirely below the dissociation limit. It oscillates within the potential well for a long time.

The intermediate energy pump pulse prepares the wave packet with energies, which span the dissociation limit. It splits at the outer flank of the well, part of it escapes and the molecule dissociates, part of it oscillates within the potential well with progressively diminishing amplitude.

The highest energy pump pulse prepares the wave packet above the dissociation limit. It escapes and the molecule dissociates.





Shown below are two figures from the original work of A. H. Zewail.

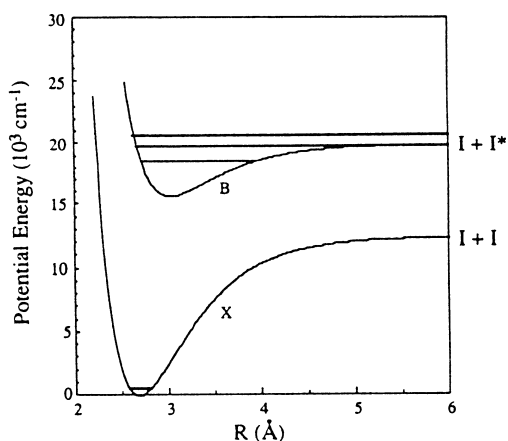
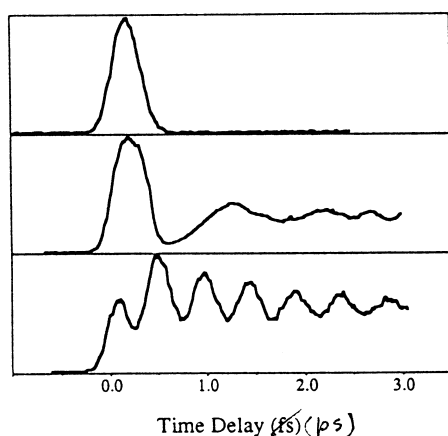


Fig. 10. Wave packet dynamics (bottom) of iodine at three energies (top); below, at, and above dissociation to $I + I^*$.



From A. H. Zewail, "Femtosecond Reaction Dynamics", ed. D. A. Wiersma, North Holland, Amsterdam 1994 (ETH library P 81 617a:42)

6.5. Solvent effect

The above experiment has also been performed with 100 bars of argon as a buffer gas, acting as a dilute solvent.

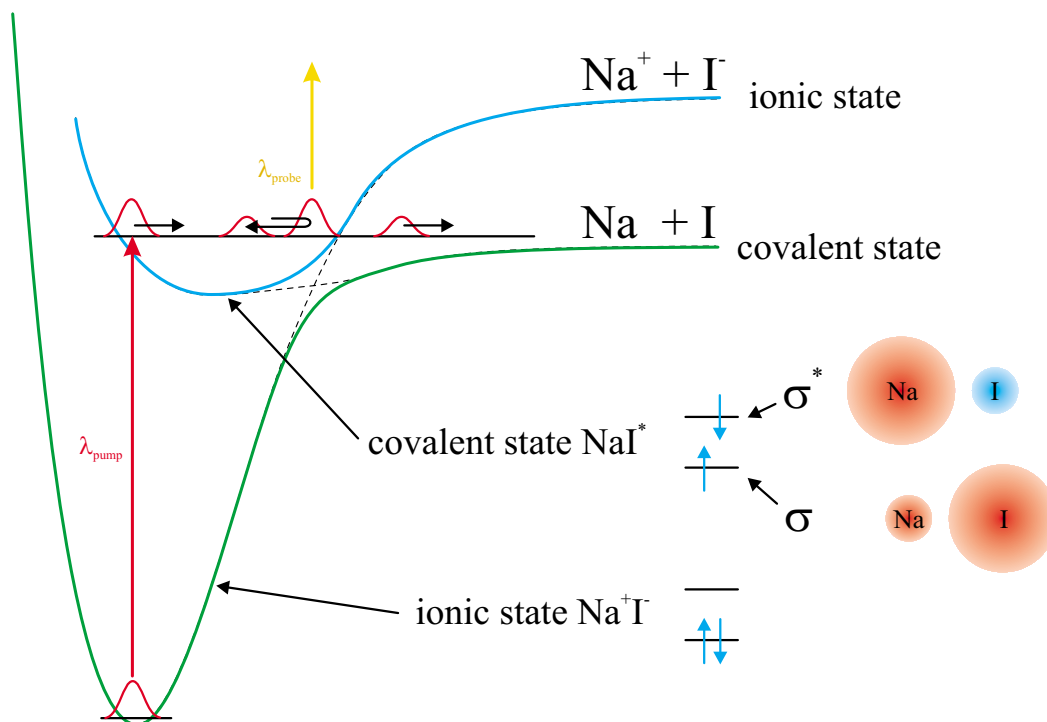
Argon atoms collide with the iodine molecules in irregular intervals, each time reflecting part of the wave packet.

The collisions quickly wash out the oscillations when the pump pulse is below the dissociation limit.

The cage effect (a partly "hindered" dissociation) is observed with the pump pulse above the dissociation limit.

6.6. Predissociation: A potential well with a leak

The picture below shows a schematic diagram of the potential surfaces of NaI.



The ground electronic state is, as you know, ionic. The doubly occupied σ orbital has a much larger coefficient on the more electronegative iodine.

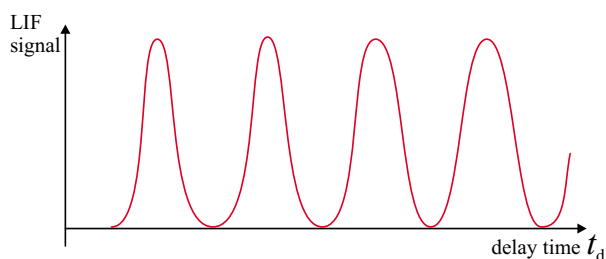
The dissociation energy of this state is, however, high.

The electronically excited state has a much more even charge distribution because the σ^* orbital has a larger coefficient on Na — hence the “covalent state”.

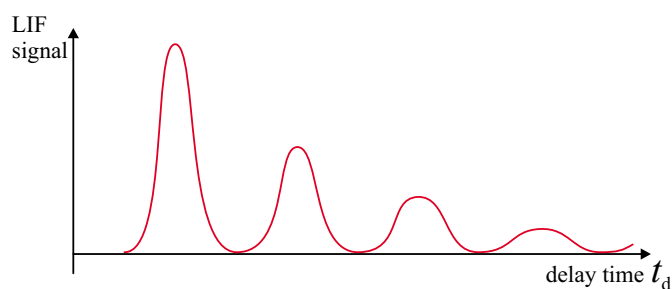
The dissociation energy of the covalent state is lower, and the two potential curves thus cross.

The complete Hamiltonian mixes the two states a little, however. This mixing has little effect when the two states are far apart in energy, but becomes important near the crossing, when the ionic and covalent states are very close to each other. It leads to an “avoided crossing”; the true, adiabatic potential curves (shown in color in the figure) do not cross. (The original ionic and covalent states are called the diabatic states — they are shown dashed in the figure.)

If the nuclei moved strictly on the adiabatic potential curves, then we would expect them to oscillate on the excited state potential curve just as we saw in I_2 .



But the true signal decreases exponentially:

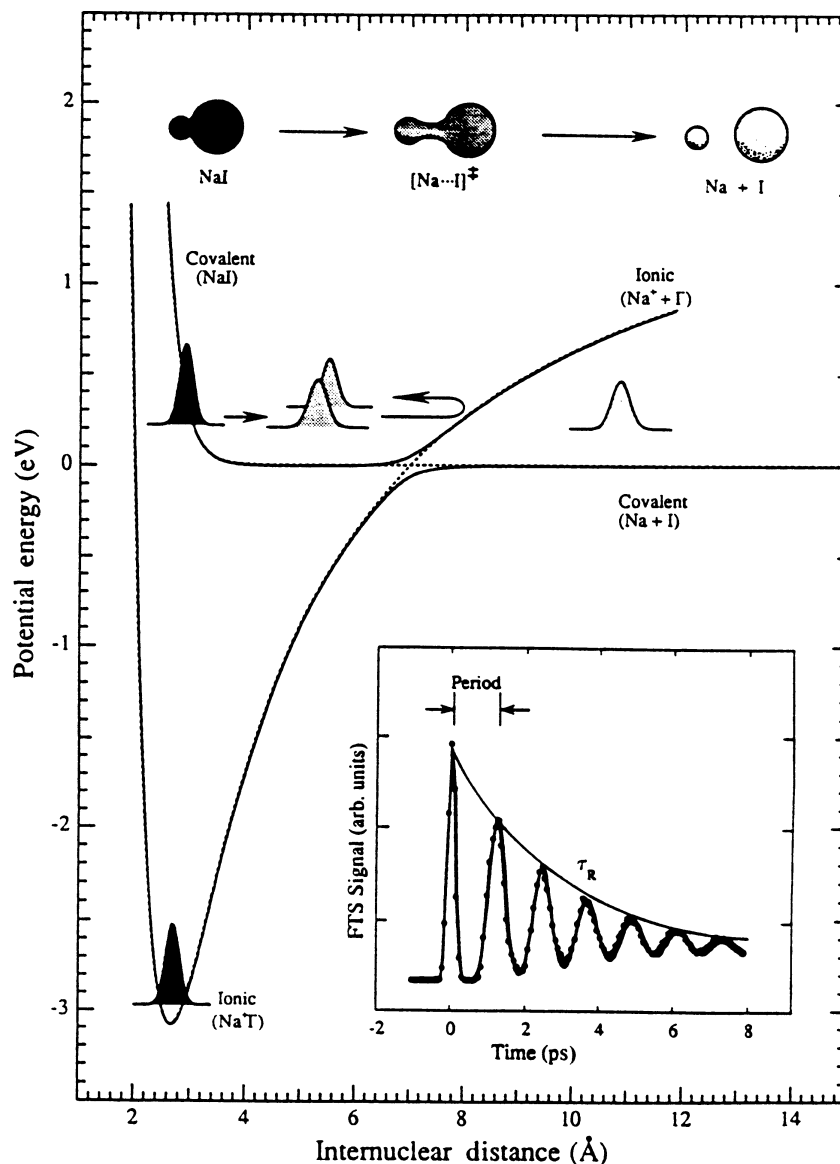


What is the cause? The break down of Born-Oppenheimer approximation. At places where the nature of the electron configuration changes very rapidly with R over a short section of the adiabatic potential curve, the potential curves partly lose their meaning. This means that the nuclei no longer move strictly on the potential curves, there is a certain probability that they “jump” from one potential curve to another.

The consequence in our case is that the wave packet is split near the avoided crossing; one part is reflected back and performs one mode oscillation, the other part moves out (this is called predissociation). The reflected portion of the wave packet returns and is split again, etc.

The femtosecond experiment shows this phenomenon with a beautiful clarity!

Shown below is a figure from the original work of Mokhtari, Cong, Herek, and Zewail, *Nature* **348** (1990) 225.



6.7. Recurrence

You have seen in section 4.5.1 that a suitably prepared wave packet in a harmonic potential does not get broader (in contrast to most other wave packets, for example the wave packet of a free particle, section 4.4).

Real potential curves are anharmonic, however, and the wave packets may be slightly non-ideal. The consequence is that the wave packets broaden and broaden, and oscillations in the experiment become shallower and shallower, until they disappear entirely.

Recurrence (a phenomenon which you already know from section 4.5.1) occurs quite quickly in this simple system, however, and the original wave packet re-emerges from the chaos, the oscillations in the experiment reappear after some time, become deeper and deeper, then the packet broadens again, the oscillations disappear, etc.

The recurrence time bears information on the anharmonicity and may thus be used to obtain the shape of the potential curve.

6.8. Molecular rotation

The effect of rotation becomes apparent in the experiment with I_2 when longer time periods are observed

The role of rotation may be understood in a more classical context. Initial orientation of the rotating molecules in the electronically excited state is obtained by use of linearly polarized light. Molecules whose transition dipole moment (oriented along the bond) is oriented along the direction of the electric field of the pump laser pulse are excited most efficiently, molecules oriented perpendicularly are not excited.

The wavelength of the probe radiation is chosen such as to observe in the same Franck Condon region in which they were excited.

Vibration is much faster than rotation — the vibrational oscillations are superimposed on the slower changes due to rotation.

When the probe radiation is polarized parallel to the pump pulse (denoted \parallel in the figure) then the signal is strong initially, before rotational motion reorients the transition dipoles away from the optimal direction. Signal then decreases as molecules turn away from this direction because of their thermal rotation.

When the probe radiation is polarized perpendicularly to the pump pulse (denoted \perp in the figure) then the signal is weak initially, but then increases as molecules turn away from the perpendicular direction.

Consider the molecules to be rotators with a fixed axis of rotation. What would be the classical period of rotation? You learned that the angular momentum of the quantum mechanical (QM) rotator is

$$P = k \cdot \hbar$$

The angular momentum of a classical object rotating with the angular velocity ω is

$$P = I \cdot \omega$$

The classical object having the same angular momentum as the QM rotator would thus spin with the angular velocity

$$\omega = \frac{k \cdot \hbar}{I} \quad (\text{radians/second})$$

The classical rotational period is thus

$$\tau_{\text{rot}} = \frac{2\pi}{\omega} = \frac{2\pi I}{k\hbar} = \frac{2\pi}{4\pi cB} = \frac{1}{2cB}$$

where $B = \frac{\hbar}{4\pi cI}$ is the rotational constant.

In I_2 we have $B_e = 0.02904 \text{ cm}^{-1} = 2.904 \text{ m}^{-1}$ (see the book of Herzberg and Huber: Constants of Diatomic Molecules), $\tau_{\text{rot}} = 570 \text{ ps}$.

The experimental result shows rotational recurrences after 610 ps, a very similar value.

The difference is due primarily to rotational stretching (J values around 20 are excited in I_2 at room temperature).

Rotational recurrences are actually observed after $\frac{1}{2}, 1, \frac{3}{2}$, etc. classical rotational periods.

A whole group of recurrences is observed because I and therefore the classical rotational period depend on the vibrational quantum number in the upper electronic state.

Shown below is a figures from the original work of Dantus, Bowman, and Zewail, *Nature* **343** (1990) 737.

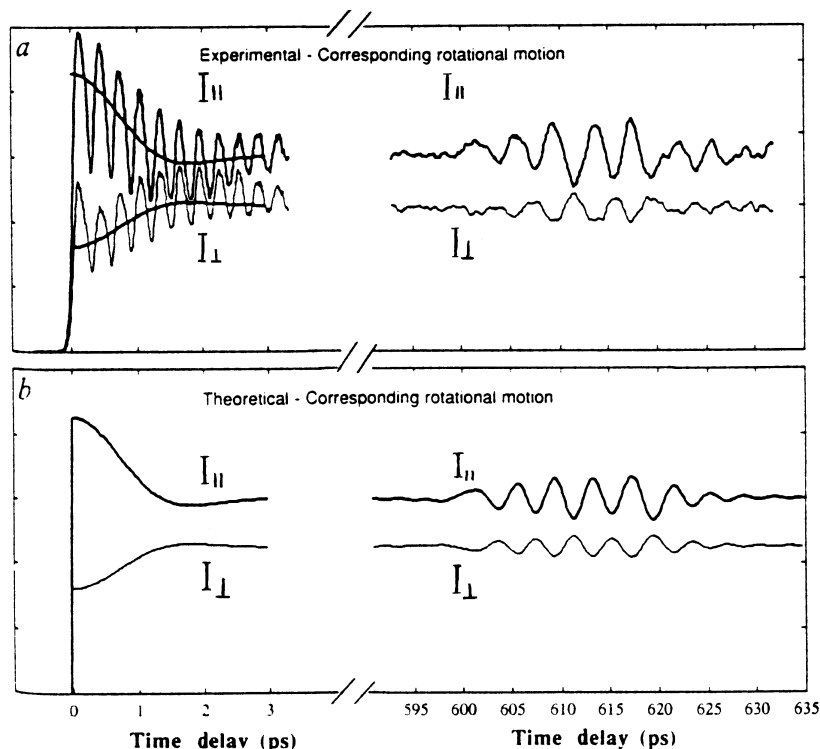


FIG. 3 Polarized FTS of molecular iodine. *a*, Transients showing the initial dephasing owing to molecular rotation (left) and the appearance of full recurrences at a later time (right). Parallel and perpendicular probe orientations are shown (see text), and are 180° out of phase, as expected. The rapid oscillations are due to vibrational excitation; six levels are accessed (the solid line through these on the left is a guide to the eye). Half recurrences were observed experimentally, but are not shown here. Note that the time scale is discontinuous. *b*, Calculated results for rotational dephasing (left) and rephasing (right), assuming excitation of vibrational levels 7 to 12 and taking into account vibrational and rotational coupling and centrifugal distortion.

6.9. Chirped pulses: focussing the wave packets

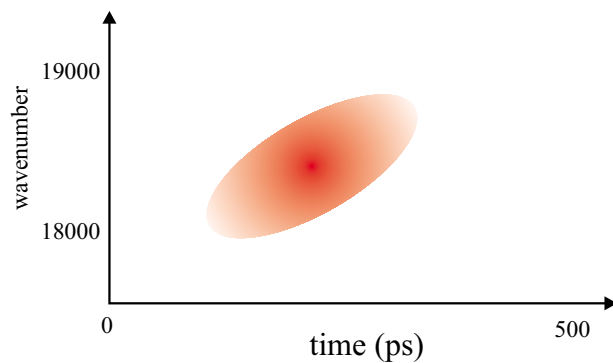
Remember that wave packets generally broaden as they move along. This is because the “faster components” in the superposition “run ahead”, the slower “lag behind”.

Wave packets on a harmonic potential are, as you have seen, an exception. Real potential curves are anharmonic, however, and the wave packets on them do broaden.

This means that it should be possible to make a wave packet which is not very narrow initially, but where the “slow components” in the front, the “fast components” are in the back. Such a wave packet would become *narrower* as it moves, reaching its narrowest width, and then broaden as all wave packets do.

Such self-focussing wave packet can be prepared by a “chirped” light pulse, that is a pulse where mean wavelength increases during the pulse duration.

Mean photon energy – time relationship of such a pulse with “positive” chirp is shown schematically below.



Chirped pulses are easier to make than one may guess. In fact short laser pulses become chirped as they move through some medium, for example air or glass. This is because index of refraction of the medium, and thus the speed with which light propagates, generally depend on wavelength. The index of refraction increases as one approaches an absorption band, which means that red light propagates faster in air than blue or ultraviolet light (leading to a negative chirp).

Reference: B. Kohler, J. L. Krause, F. Raksi, K. R. Wilson, V. V. Yakovlev, R. M. Whitnell, Y. Yan, *Acc. Chem. Res.* **28** (1995) 133.