

## Syllabus PHYS 354 (Intro to Quantum Mechanics)

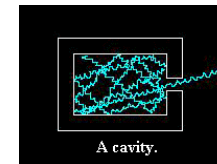
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- Subject of this course:
  - Quantum mechanics
    - Why classical physics fails
    - Schrödinger equation and applications (tunneling)
    - Identical particles & Pauli exclusion principle
    - Entanglement?
- Instructor:
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  - Office hours: Wednesday 10am-11am
- Textbook:
  - A.C. Phillips, Introduction to Quantum Mechanics
- Alternative books at similar level:
  - French and Taylor (more extensive)
  - Hameka (math collected in one chapter)
- Grading:
  - Quiz [Tuesday May 1, 2007]: 10%
  - Midterm [2/3 term Tuesday May 22, 2007]: 20%
  - Homework: 35%
  - Final test: 35%
  - Extra credit for active participation in class: max 4%
- Homework:
  - Due *before class* on Tuesdays (no homework in quiz/exam weeks)
  - Late (< 48 hours) homework will be corrected, but counts only 50%
  - Lowest homework score is dropped

## Old quantum mechanics

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- Around 1900 several physical phenomena could not be properly described with classical physics [Newton's mechanics, Maxwell's electromagnetism, thermodynamics]
- Several hypotheses were proposed that solved those problems
  - But only in an ad hoc manner ("old quantum mechanics")
  - It took 26 years for a coherent formalism to be formulated that incorporated all those adhoceries plus more
    - That formalism is "weird" and quite advanced mathematically
  - We'll take just a few weeks to do the same
  - Let's take a look at some of those problems
- Radiation in thermodynamic equilibrium at temperature T
  - Take a black body, which absorbs all incident radiation, but which generates radiation when heated to T: what spectrum does it radiate??



In order for radiation to reach thermal equilibrium, it must interact with the walls (kept at some fixed temperature T) for some amount of time before escaping

- According to the equi-partition theorem of thermodynamics, every degree of freedom at temperature T has an energy of kT. The number of different em field modes (per volume) in a frequency interval then gives the classical energy density per frequency interval: (Rayleigh-Jeans law)

$$n(\nu)d\nu = 2 \times \frac{4\pi\nu^2}{c^3} d\nu \Rightarrow$$

$$E(\nu)d\nu = \frac{8\pi\nu^2}{c^3} kT d\nu$$

- So at high frequencies the energy per frequency interval blows up, and the total energy is infinite...(and so is the energy needed to heat radiation up by any finite amount). That must be wrong!
- Planck solved this particular problem by hypothesizing that the radiation emitted and absorbed by a black body comes in discrete packets of an energy equal to

$$E = h\nu$$

where h is some constant. So the energy at one particular frequency is always an integer multiple of this quantity.

## Old quantum mechanics

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- Assuming a Boltzmann factor for the probability of having a particular number of such quanta

$$P(n) = \exp(-nh\nu/kT)/Z$$

$$Z = \sum_{n=0}^{\infty} \exp(-nh\nu/kT) = \frac{1}{1 - \exp(-h\nu/kT)}$$

we get an average energy for each frequency

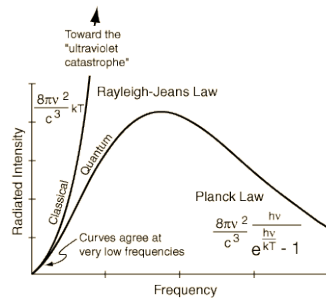
$$\langle E \rangle = \frac{h\nu}{\exp(h\nu/kT) - 1}$$

- This then leads directly to the Planck distribution law for blackbody radiation

$$E(\nu)d\nu = \frac{8\pi h\nu^3}{c^3(\exp(h\nu/kT) - 1)} d\nu$$

- For small frequencies, this agrees with the Rayleigh-Jeans law, but for high frequencies the energy density is much less, thus giving a *finite* total energy.
- Moreover, the form of the spectrum agreed with experiments
- Even better, the constant  $h$  could be determined. It's Planck's constant

$$h = 6.63 \times 10^{-34} \text{ Js}$$



## Old quantum mechanics

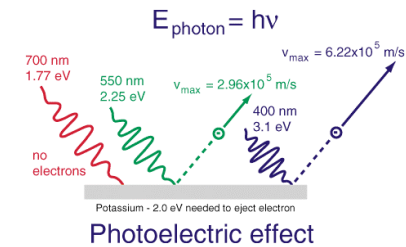
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- Einstein then went one step further in 1905: he assumed all radiation comes in discrete packets of energy  $E=h\nu$ . That allowed him to explain the *photoelectric effect*. The kinetic energy of electrons emitted by a metal illuminated with light of frequency  $\nu$ , is

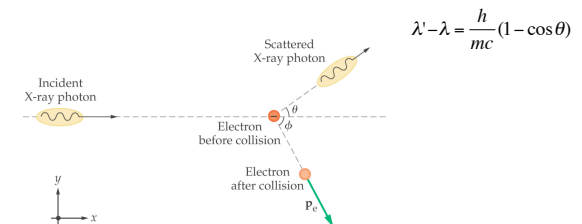
$$E_{\text{kinetic}} = h\nu - W$$

where  $W$  is the "work function" of the metal. The amount of electrons emitted is proportional to the intensity. Classically, it is a mystery as to why the energy of electrons does not depend on the energy (ie intensity) of the light beam. This theory was confirmed accurately only in 1915, by Millikan, who did not believe in quanta (photons)!

$W$  is typically a few eV.



- Einstein's proposal went in fact even further: apart from assigning energy to "photons" he also assigned them momentum  $p=E/c$ , as if photons are really like particles. This assumption was confirmed by the Compton effect in 1923-24: (X-ray) photons scattered off of electrons (that are at rest) change their wavelength depending on the angle of scattering:



## Old quantum mechanics

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- This all makes use of relativistic kinematics (conservation of momentum and energy, see homework!). The quantity

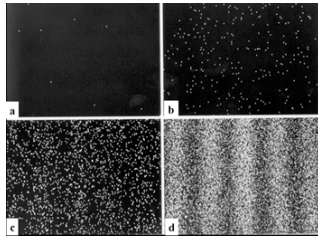
$$\frac{h}{mc} = 2.426 \times 10^{-12} \text{ m}$$

is called the *Compton wavelength* of the electron.

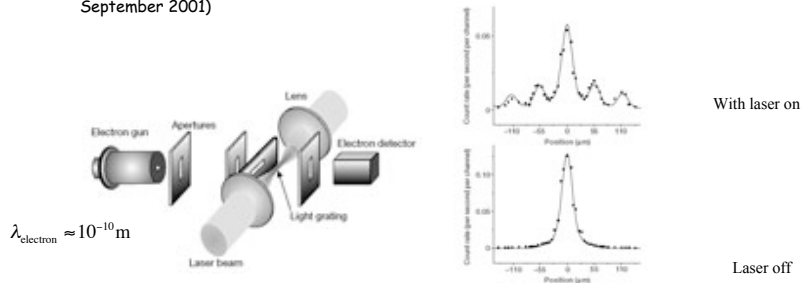
- This should not be confused with the De Broglie wavelength of a particle (for instance an electron) with momentum  $p$ : every particle is a wave with

$$\lambda = \frac{h}{p}$$

- The strange fact that a particle can behave like a wave was verified in double-slit experiments with electrons (and neutrons, and bucky balls (fullerenes)  $C_{60}$ ). This picture shows how an interference pattern is built up over time from single electrons arriving individually on a screen (Tonomura, Hitachi, Am. J. Phys. 57, 117 (1989))



- In the Kapitza-Dirac effect (1933), we go one step further in weirdness: a wave(!) of electrons diffracts from a periodic material (!) consisting of laser light: Figures are from Daniel L. Freimund, Kayvan Aflatooni and Herman Batelaan, Nature 413, 142-143 (13 September 2001)



## Old quantum mechanics

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- The model of an atom used to be that of electrons randomly moving around in a homogeneous "fluid" of positive charge. That changed when Rutherford (1908), after scattering alpha particles off gold foils, inferred the positive charge must be localized within an atom to a small volume: the nucleus. This led to a new model of the atom, the Bohr atom, with three postulates:

1. Atoms can only be in certain discrete energy levels  $E_n$
2. If they "jump" from one level to another, they emit or absorb a photon making up the energy difference, with  $h\nu = E_n - E_m$ .
3. For *circular* orbits (of the electron around the nucleus), angular momentum is quantized:

$$mvr = n\hbar \quad (\hbar = h/(2\pi))$$

- o This last postulate could be understood from the De Broglie wavelength "fitting" on a circular orbit:

$$2\pi r = n\lambda = nh/p = nh/(mv)$$

- Using the balance between Coulomb law and centrifugal force,

$$\frac{Ze^2}{4\pi\epsilon_0 r^2} = \frac{mv^2}{r}$$

and defining the fine-structure constant

$$\alpha = \frac{e^2}{4\pi\epsilon_0 \hbar c} \approx \frac{1}{137}$$

we get:

$$v_n = \frac{\alpha Zc}{n}; \quad r_n = \frac{\hbar n^2}{mcZ}; \quad E_n = -\frac{m(\alpha Zc)^2}{2n^2}$$

- Plugging in numbers gives

$$r_n = \frac{n^2}{Z} 0.53 \times 10^{-10} \text{ m}; \quad E_n = -\frac{Z^2}{n^2} 13.6 \text{ eV}$$

- In spite of its success getting the ionization threshold correctly and getting spectral lines of hydrogen and helium correctly,

$$\hbar\omega_{nm} = \frac{hc}{\lambda_{nm}} = Z^2 \left( \frac{1}{n^2} - \frac{1}{m^2} \right) 13.6 \text{ eV}$$

don't take this model too seriously! 2-electron atoms and finer details of spectra cannot be obtained with this model....

## Old quantum mechanics

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- Anticipating properties of modern quantum mechanics, let's consider *measurements*: think of light going through a polarizing filter. If the polarization of the light is  $\vec{e}$ , and the direction of the polarizer is  $\vec{e}'$ , then the amount of light that goes through is proportional to

$$P \propto |\vec{e} \cdot \vec{e}'|^2$$

- But then think of a single photon: apparently it has a certain *probability*  $P$  to go through the filter: after all, either the full energy  $h\nu$  goes through, or nothing (the frequency does not change!), but the intensity will have to be diminished by the *same* factor  $P$ .
- Probability plays an important role in quantum mechanics. In other parts of physics probabilities arise only from our ignorance about certain properties (like initial conditions of a coin before it is tossed, or in statistical mechanics when we have too many particles to keep track of). In quantum mechanics we need probabilities even if we know everything there is to know!
- Moreover, after the filter, if the photon went through, the polarization of light has changed: it's  $\vec{e}'$  now, not  $\vec{e}$  anymore. Hence
  - You can't measure different properties of the same photon, because the first measurement disturbs the state of the system
  - Even worse, if some properties of a photon are certain, then others (different polarization directions) are uncertain (independent of measurements!)
  - More generally this is known as the Heisenberg uncertainty principle. It applies to pairs of certain observables, like position and momentum, or energy and time, and it's written in the form (we'll be more precise later on)

$$\Delta p \Delta x \sim h \text{ or } \Delta E \Delta t \sim h$$

- Remember the Fourier transform? If one knows the frequency of a wave packet precisely, then the extent of the wave in time is large, and vice versa. That's exactly the same thing, mathematically speaking
- For example, after having measured the position of a particle very accurately, the particle cannot have a well-defined momentum. (For instance, if we used a photon of a sufficiently small wavelength  $\lambda$  to resolve a small length scale, then its momentum is large,  $p=h/\lambda$ , and is (partially) transferred to the particle).
  - Moreover, *even before (and independent of)* the measurement, the particle cannot have had well-defined values for both position and momentum! This point is not always understood in popular accounts of quantum physics.

## Old quantum mechanics

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- Let us consider how the uncertainty principle teaches us something about the wave-particle duality: Suppose we do a double slit experiment with electrons, with momentum  $p$ , and hence a fixed De Broglie wavelength. Suppose we wish to infer from which of the two slits the particle came. We could do that by measuring its transverse momentum on arrival at the screen (by measuring the recoil of the screen)

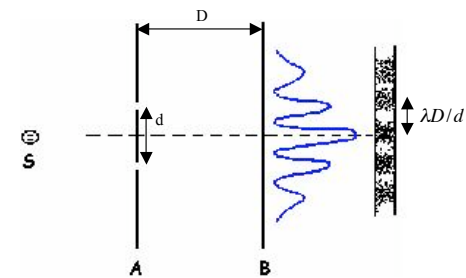


Figure 1 Double-slit experiment

- For example, at the peak in the center of the screen, the momentum should be  $+pd/2D$  if it came from the lower slit, and  $-pd/2D$  if it came from the upper slit. The screen must obey Heisenberg's uncertainty principle. That is, if we determine its momentum better than

$$\Delta p \sim pd/D$$

then the position of the screen is uncertain by an amount

$$\Delta x \sim h/\Delta p = hD/dp = \lambda D/d$$

- But that is just the spacing of the fringes! Thus the interference pattern will be washed out if we try to determine through which slit the electron came. You can't measure both particle and wave properties at the same time. That is what is meant by the "wave-particle duality".

## The Schrödinger equation

- Let's take the fact that everything has a wavelength seriously, and insist on a *wave equation*, even for particles. Consider a plane wave of the form

$$\psi = \exp(ikx - i\omega t)$$

- Then, thinking of the energy of a photon, let us identify

$$\text{energy} \Leftrightarrow \hbar\omega \Leftrightarrow \hbar i \frac{\partial}{\partial t}$$

- Thinking of the De Broglie wavelength of a particle, let us identify

$$\lambda = h / p \Leftrightarrow p = h / \lambda = \hbar k$$

Now that's an abstract way of defining energy and momentum!

$$\text{momentum} \Leftrightarrow \hbar k \Leftrightarrow -\hbar i \frac{\partial}{\partial x}$$

- "So", let us pose that a free particle with mass m (in 1-D) is described by

$$\hbar i \frac{\partial}{\partial t} \psi = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi$$

- This is indeed a wave equation and it obeys the superposition principle.
- Let us make it even more general, by writing

$$\boxed{\begin{aligned} \hbar i \frac{\partial}{\partial t} \psi &= H(x, p) \psi \\ p &= -\hbar i \frac{\partial}{\partial x} \end{aligned}}$$

where H described the energy of the particle (or the Hamiltonian, more generally), expressed in x and p.

This is the (1-D) Schrödinger equation for the wave function of a particle! For example, a 1-D particle in a potential V(x) is described by

$$\hbar i \frac{\partial}{\partial t} \psi = \left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \psi$$

- Of course, the Schrödinger equation cannot be *derived*, it is simply postulated, taking cues from ad hoc assumptions that seemed to work pretty well. The idea is to derive the ad hoc assumptions from this more general formalism, and see where the equation takes us.
- We are going to solve the Schrödinger equation for various forms of the potential. But first, we're going to think about what the wave function actually *means*.

## The Schrödinger equation

- Wave equations describe waves of various sorts: sound waves, water waves, light waves, vibrations of a string, etc. In all those cases the quantity that vibrates or oscillates has a clear meaning: air pressure, water height, electric field, or string amplitude. Those quantities can be measured (more or less) directly, and so can the time derivatives and spatial derivatives that appear in the corresponding wave equations.
- The quantum wave function is different!
  - It can't be measured directly
  - It has no *obvious* physical meaning (we will give it a meaning, of course!)
  - It is complex, and complex numbers do play an important role: "i" appears in the Schrödinger equation, for instance (recall that, even if we use complex notation to describe electromagnetic fields, we really always mean to take the real part of the complex fields)
  - The quantum wave function is meant to describe everything in nature, including particles...
    - The water molecules making up a water wave, are themselves waves according to quantum mechanics.
- The wave function describes *probabilities for physical quantities*. For example,

$$|\psi(x, t)|^2$$

gives the probability to find the particle described by that wave function at position x at time t. More precisely

$$P(x)dx = |\psi(x, t)|^2 dx$$

and so it gives the probability to find the particle in a small interval dx around x.

This prescription is called the Born rule.

- Obviously we have to normalize the wave function such that

$$\int_{-\infty}^{\infty} |\psi(x, t)|^2 dx = 1$$

- Note the wave function cannot be directly measured, as we announced before: you need many measurements on identically prepared particles to estimate the probabilities.
  - Again, probabilities arise even if we know the wave function, and do not necessarily arise from "classical" ignorance

## The Schrödinger equation

- Note we take the absolute value squared: this makes sure we get a real, not complex, number for the probability.
  - o That is not just a random choice, but inspired by two things:
    - The intensity of light can be written as the absolute value squared of the complex electric field amplitude,  $I \sim |E|^2$
    - The probability of a polarized photon to go through a polarizer is also determined by an absolute value squared  $P(\vec{e} \rightarrow \vec{e}') = |\vec{e} \cdot \vec{e}'|^2$
- Back to the Schrödinger equation itself: it can actually be split into two equations in *special* conditions: Suppose we have a (time-independent) function for which

$$H(x, p)\tilde{\psi}(x) = E\tilde{\psi}(x) \quad (*)$$

- o We say that the wave function is an energy eigenstate: it has a well-defined value for the energy, namely E. Note (\*) is a differential equation.
- The Schrödinger equation then tells us that

$$\begin{aligned} i\hbar \partial / \partial t \psi(x, t) = H(x, p)\psi(x, t) = E\psi(x, t) &\Rightarrow \\ \psi(x, t) = \tilde{\psi}(x) \exp(-i\omega(t - t_0)) & \\ \omega = E / \hbar & \end{aligned}$$

- Such a state is called *stationary*: its time dependence is entirely contained in the phase factor, which does not affect the position or momentum probability distributions.
- Eq. (\*) is sometimes called the time-independent Schrödinger equation. But don't think it is *always* valid (only for the stationary states!)
  - o Nevertheless, Eq. (\*) describes perfectly the states required in the Bohr model of an atom, states with a well-defined energy.
  - o Indeed, the type of equation (\*) is called an eigenvalue equation, and it typically has only solutions for certain values of E, thanks to *boundary conditions* that have to be fulfilled (it's a differential equation!): this brings in the discreteness of energy levels automatically.
    - It's similar to vibrations of a *classical* string being determined by the length of the string (boundary conditions on the string), or to the frequency of *classical* light inside a cavity being determined by the length of the cavity (boundary conditions on the mirrors).

## The Schrödinger equation

- Consider a simple example, the free particle. We have the time-independent equation

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \tilde{\psi}(x) = E\tilde{\psi}(x)$$

- The general solution can be written as

$$\begin{aligned} \tilde{\psi}(x) &= A \exp(ipx / \hbar) + B \exp(-ipx / \hbar) \\ p^2 / 2m &= E \end{aligned}$$

- That is, there are two independent solutions, a particle moving to the right or to the left with momentum p; of course both have the same energy. The time-dependent wave function for a particle moving to the right is then

$$\psi(x, t) = \exp(i(px - Et) / \hbar)$$

- Compare this to a plane wave of light

Note: a plane wave is not normalizable!  
It's not a physical solution: instead we should take a *superposition* of waves with different values for E

$$\begin{aligned} \vec{E}(x, t) &= \vec{e} \exp(i(kx - \omega t)) \\ &= \vec{e} \exp(i(px - Et) / \hbar) \end{aligned}$$

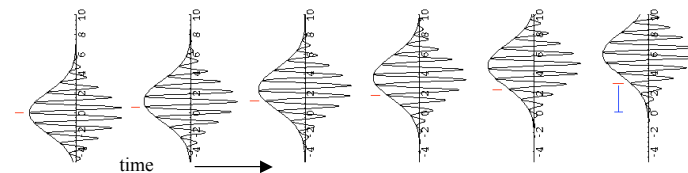
It's the same thing, except for a different relation between momentum and energy:

$$\begin{aligned} \text{particle: } p^2 / 2m &= E \\ \text{photon: } pc &= E \end{aligned}$$

- These relations are equivalent to the dispersion relations in optics. We can distinguish, just as in optics, the group and phase velocities of a particle (in superposition of different E's)

$$\begin{aligned} \text{group velocity: } d\omega / dk &= dE / dp = p / m = v \\ \text{phase velocity: } \omega / k &= E / p = p / 2m = v / 2 \end{aligned}$$

- o So the phase velocity is half the group velocity



Position and momentum

- Quantum mechanics is all about probabilities, obtained from the wave function. Two useful concepts are
  - Expectation values
  - Variances
- If we have a (continuous) probability distribution  $p(x)$ , then the expectation value of any function of  $x$ , say  $f(x)$ , is defined as

$$\langle f(x) \rangle = \int p(x)f(x)dx$$

- The variance of  $f(x)$  is defined as

$$(\Delta f)^2 := \langle (f(x) - \langle f(x) \rangle)^2 \rangle = \int p(x)(f(x) - \langle f(x) \rangle)^2 dx$$

- Note that we can rewrite this as

$$(\Delta f)^2 = \langle f^2(x) \rangle - \langle f(x) \rangle^2$$

- It is this variance that can be used to quantify uncertainty in , e.g., position, as it appears in the Heisenberg uncertainty relations

$$\Delta x = \sqrt{(\Delta x)^2}$$

- For example, what is the average position of a particle? That is, when we average over the probability distribution, what is the expectation value of the position? Answer: by the Born rule it should be:

$$\langle x \rangle = \int | \psi(x,t) |^2 x dx = \int \psi^*(x,t)x\psi(x,t)dx$$

- What is the average momentum of the same particle?? That is more difficult to answer, because we first need a probability distribution over momentum, rather than position. We do that by expanding the wave function in plane waves, which as we already know, have a definite momentum. Thus we take, in fact, the Fourier transform (and its inverse)

$$\psi(x,t) = \frac{1}{\sqrt{2\pi\hbar}} \int \tilde{\Psi}(p,t) \exp(ipx/\hbar) dp$$

$$\tilde{\Psi}(p,t) = \frac{1}{\sqrt{2\pi\hbar}} \int \psi(x,t) \exp(-ipx/\hbar) dx$$

- It can be shown that  $\Psi(p)$  is automatically normalized correctly, if  $\psi(x)$  is.
- The expectation value for the momentum of a particle is then

$$\langle p \rangle = \int | \tilde{\Psi}(p,t) |^2 p dp = \int \tilde{\Psi}^*(p,t)p\tilde{\Psi}(p,t)dp$$

Position and momentum

- But we can also write this as

$$\langle p \rangle = \int \psi^*(x,t)(-i\hbar \partial / \partial x)\psi(x,t)dx$$

- After all, applying  $-i\hbar \partial / \partial x$  to a plane wave simply gives back the plane wave while multiplying it with  $p$ . It is also consistent with what we observed before, that momentum corresponds to  $-i\hbar \partial / \partial x$
- Now suppose we use the Schrödinger equation for a particle: it would be a nice consistency check of all the above relations if we could verify that

$$\langle p \rangle = mv = m d\langle x \rangle / dt$$

- That indeed works out, by using partial integration and assuming the wave function decays to zero when  $x$  goes to infinity (homework!)
- We can generalize the above relation for average momentum to

$$\langle A \rangle = \int \psi^*(x,t)A\psi(x,t)dx \quad (*)$$

where  $A$  could stand for *any operator*, acting on the wave function (a pretty abstract ideal).  $A$  can be a differential operator, like  $d/dx$ , or a simpler multiplicative operator, like ' $x$ ' was. So 'multiplying by  $x$ ' is an operation acting on the wave function, and the expression for  $\langle x \rangle$  is a special case of (\*).

- Note that the order is important!  $\Psi^* A \Psi$  then  $A \Psi$ !
- Let's do something more concrete (although still abstract): "a particle in a box". Let's say we have a potential,  $V(x)=0$  for  $0 < x < a$ , and  $V(x)$  is infinite elsewhere. Then we should solve

$$\hbar i \partial / \partial t \psi(x,t) = (-\hbar^2 \partial^2 / \partial x^2 + V(x))\psi(x,t)$$

$$\psi(x=0) = 0 = \psi(x=a)$$

- The boundary conditions simply express continuity of the wave function, using that the wave function should vanish outside the box, at least for *finite* energy of the particle. The solution inside the box is a superposition of plane waves  $\exp(ikx)$  and  $\exp(-ikx)$ . More precisely, we get for stationary states with a fixed energy (also called eigenstates of energy):

$$\psi_n(x,t) = N \sin(k_n x) \exp(-iE_n t / \hbar) \quad \text{inside box}$$

$$\psi_n(x,t) = 0 \quad \text{outside box}$$

$$k_n = \frac{n\pi}{a} \quad (n \geq 1)$$

$$E_n = \frac{\hbar^2 n^2 \pi^2}{2ma^2} \quad (n \geq 1)$$

$$N = \sqrt{2/a} \quad (\text{normalization})$$

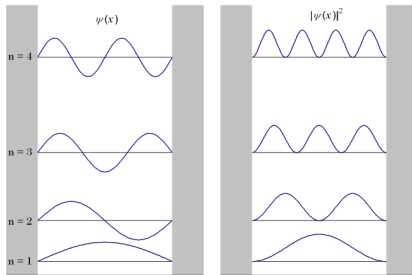
### Position and momentum

- First, note that energies are discrete, not continuous. Bohr's postulate comes out of the formalism
- Second, note these states are neither states with well-defined position for the particle, nor well-defined momentum (see figure with lowest 4 energy states)
- Third, note the lowest-energy state has some positive energy: classically there would be a zero-energy state in which the particle is at rest at some position. But in quantum mechanics you *cannot* have both a well-defined position and a well-defined momentum

- o Indeed, this can be understood quantitatively from the uncertainty principle. The particle's position is clearly determined better than  $\sim a$ , so the momentum can be determined at best up to an uncertainty of  $\sim h/a$ . But that means there is always kinetic energy present of size

$$E = p^2/2m \sim (\Delta p)^2/2m \sim h^2/2ma^2$$

- o Fourth, note from the figure that there are locations where the particle cannot be, if the energy is fixed to some value: classically this would not happen of course. It is due to *destructive* (quantum) interference:
- o the solution of the Schrödinger equation with fixed energy is a *superposition* of two waves, one traveling to the right, the other to the left. Those two waves interfere, constructively or destructively! (And similarly, in the double-slit experiment with electrons, it's two waves emanating from the two slits that interfere on the screen to give rise to an interference pattern)



- In the limit of large n, the energies are still discrete. But the *relative* difference between subsequent energy levels goes to zero: the system becomes more like a classical system with a continuous energy. This is a general postulate (by Bohr), that large n should correspond to the classical limit:

$$\frac{E_{n+1} - E_n}{E_n} \propto \frac{2}{n} \rightarrow 0 \quad (n \rightarrow \infty)$$

### Position and momentum

- What about momentum in this case? You might think that each of the two waves has a well-defined momentum (after all, we have two waves moving to the left and right, respectively), equal to

$$\pm \hbar k_n = \pm \hbar \frac{n\pi}{a}$$

However this is not true because the waves  $\exp(ikx)$  are only finite in length. Thus, even though the energy is well-defined, the momentum is not! The book plots the momentum distribution as well (it's the Fourier transform of the spatial wave function)

- o But in the limit of large n it does become true (again, the particle becomes more classical in that limit)
- What would happen if we would measure position? If we know we have some energy *eigenstate* to start with, then we know the probabilities of finding the particle in some region between x and x+dx. Now recall what apparently happens to the polarization of a photon when we measure it: it changes to the polarization we actually measured. So here too, right after the measurement the wave function describing the particle changes: it will become a wave function localized between x and x+dx!
- This is called the collapse of the wave function. Some people find this mysterious, but it can be most easily understood by interpreting the wave function as nothing more than giving us probabilities: so it is our knowledge that changes after a measurement, hence we ascribe a different wave function after the measurement, consistent with what we have just learned. This new wave function, in turn, gives our best predictions for measurements to follow.
  - o With this interpretation, contrary to what the textbook says, there is no physical mechanism necessary to explain the collapse of the wave function
- In some interpretations of quantum mechanics the wave function is taken much more seriously, as a real property of the particle, much like a classical wave is more than just a description. But this will lead to even more trouble when we consider entanglement (this refers to a strong type of correlation between two different particles)
- Note that for the particle in the box one cannot even measure momentum: that would need a spatially infinitely extended measurement. Indeed, there are no *eigenstates* of momentum in the box.



## Intermezzo

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- Is Quantum Mechanics difficult to understand?
- Feynman once said:
  - "I think it is safe to say that no one understands Quantum Mechanics"
- Bohr said:
  - If quantum mechanics hasn't profoundly shocked you, you haven't understood it yet.
- Why is that? It's because the math is difficult, the connection between the math and the real world is strange, and the resulting description of the real world is counterintuitive:

Math	Math <--> Real world	Real world
Complex numbers	Wave function complex, Cannot be measured directly(*)	Probabilities interfere (e.g. waves from two slits)
Fourier transform	Momentum=Fourier transform of position	Particle does not have well-defined position <i>and</i> momentum
Differential operators Eigenvalue equations	Momentum= $-\hbar i \frac{\partial}{\partial x}$  $\hbar i \frac{\partial}{\partial t} \psi = H(x, \partial / \partial x) \psi$	Particle can be left or right, but not in between Particle can be in superposition of "here" and "there"

- Check for yourself how the statements in the right column arise from the formalism of quantum mechanics *in specific cases!*

(\*) Many measurements of position are necessary to determine  $|\psi(x)|$ , and many measurements are necessary to determine  $|\psi(p)|$ . Together, they determine  $\psi$ , both the absolute value and the complex phase

## Energy and time

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- The Hamiltonian is an operator and it represents the energy. For example

$$H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)$$

- It shows up in the expectation value of energy

$$\langle E \rangle = \int \psi^*(x,t) H \psi(x,t) dx$$

- If we want to calculate the variance of the energy, we would need also

$$\langle E^2 \rangle = \int \psi^*(x,t) H^2 \psi(x,t) dx$$

So we just square the operator, i.e., we apply it twice: watch out for the order in which terms appear!

- We already defined stationary states as states for which  $H\psi(x,t) = E\psi(x,t)$

- In such a state we have, as expected, a zero variance in energy

$$\begin{aligned} \langle E^2 \rangle &= \int \psi^*(x,t) H^2 \psi(x,t) dx = \int \psi^*(x,t) H E \psi(x,t) dx = \\ &= \int \psi^*(x,t) E^2 \psi(x,t) dx = E^2 \Rightarrow (\Delta E)^2 = 0 \end{aligned}$$

- A good reason to call such states stationary is that *any* physical quantity is time-independent: for example, the probability to find a particle in some position is time independent

$$P(x,t) = |\psi(x,t)|^2 = |\psi_E(x) \exp(-iEt/\hbar)|^2 = |\psi_E(x)|^2$$

- For any operator  $A$  that is not explicitly time dependent, we have a time-independent expectation value

$$\langle A(t) \rangle = \int \psi^*(x,t) A \psi(x,t) = \int \psi^*(x) A \psi(x)$$

- But let us look at more general states, for example a superposition of states with different energies, such as

$$\begin{aligned} \psi(x,t) &= a \psi_E(x) \exp(-iEt/\hbar) + b \psi_{E'}(x) \exp(-iE't/\hbar) \\ |a|^2 + |b|^2 &= 1 \end{aligned}$$

- The last line gives the normalization factor. This makes use of the fact that (to be proven in homework!)

$$\int \psi_E^*(x,t) \psi_{E'}(x,t) dx = 0 \text{ if } E' \neq E$$

- We call these states orthogonal

## Time and energy

-18-

- If we use the same relation to calculate the expectation value of the energy, we get

$$\langle E \rangle = \int \psi^*(x,t) H \psi(x,t) dx = |a|^2 E + |b|^2 E'$$

- It looks like we can interpret  $|a|^2$  and  $|b|^2$  as giving the probabilities to find the particle with an energy  $E$  or  $E'$ , respectively. And that's correct! More generally, if we have

$$\psi(x,t) = \sum_n a_n \psi_n(x) \exp(-iE_n t / \hbar)$$

$$\sum_n |a_n|^2 = 1$$

then we can interpret  $|a_n|^2$  as the probability to find the particle with an energy  $E_n$

- Actually, the general solution to the Schrödinger equation can *always* be written in this form, by expanding in energy eigenstates, provided we know *all* eigenvalues for  $E$ !
- The expectation value of energy in this case is

$$\langle E \rangle = \int \psi^*(x,t) H \psi(x,t) dx = \sum_n |a_n|^2 E_n$$

- Probabilities for other quantities typically vary with time now. For instance,

$$|\psi(x,t)|^2 = \sum_m \sum_n a_n a_m^* \psi_n(x) \psi_m^*(x) \exp(-i(E_n - E_m)t / \hbar)$$

- In fact, we can rewrite this as

$$|\psi(x,t)|^2 = \sum_n |a_n|^2 |\psi_n(x)|^2 + \sum_{m \neq n} a_n a_m^* \psi_n(x) \psi_m^*(x) \exp(-i(E_n - E_m)t / \hbar)$$

- The first line gives what you would expect: it just adds up the probabilities to find a particle at position  $x$ , given that the energy is  $E_n$  multiplied by the probability to get that energy. But then the second line gives interference terms. Different probabilities can interfere constructively or destructively, in a time-dependent way.

## Energy and time

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- Let's look at a particle moving in 3-D. If we assume it's in a cubic box, of size  $a \times a \times a$ , then the time-independent Schrödinger equation is

$$\frac{-\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi(x,y,z) = E \psi(x,y,z) \quad \text{inside cube}$$

$$\psi(x,y,z) = 0 \quad \text{outside cube}$$

- The solution is a simple extension of the 1-D solution:

$$\psi_{l,m,n}(x,t) = N \sin(k_l x) \sin(k_m y) \sin(k_n z)$$

$$k_n = n \frac{\pi}{a}$$

$$E_{l,m,n} = (n^2 + m^2 + l^2) \frac{\hbar^2 \pi^2}{2ma^2} := E_1 (n^2 + m^2 + l^2)$$

$$N = \sqrt{8/V}; \quad V = a^3$$

- So the energy levels are discrete. Some values for  $E$  occur multiple times: we call those degenerate energy levels. They arise because of a symmetry in the problem: here the symmetry between  $x,y$  and  $z$ , hence a threefold symmetry. In an atom the same thing happens: certain states can occur multiple times, but others do not. In the end, something similar will explain the periodic system of elements.

	12E <sub>1</sub>
	11E <sub>1</sub> , threefold degenerate
	9E <sub>1</sub> , threefold degenerate
	6E <sub>1</sub> , threefold degenerate
	3E <sub>1</sub>

- Note that here too the lowest energy level has a nonzero energy. In fact, all of three numbers  $l,m,n$  must be nonzero for a valid wave function. So the lowest energy is simply 3 times that of the 1-D particle.
- What if we break the symmetry by a small amount? For instance, what if the sizes of the box are not quite equal? Answer: then the levels that were degenerate will split into three distinct levels, differing by a small amount in energy. That happens in a real atom as well... For instance, a magnetic field in some fixed direction will split initially degenerate energy levels of an atom into multiple levels by breaking rotational symmetry.

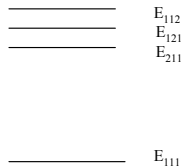
## Time and energy

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- For example, the second level splits into three:

$$E_{l,m,n} = \frac{\hbar^2 \pi^2}{2m} \left( \frac{l^2}{a^2} + \frac{m^2}{b^2} + \frac{n^2}{c^2} \right)$$

- If  $a > b > c$ , then  $E_{112} > E_{121} > E_{211}$  and thus we have levels like this:



- Finally, just as for position and momentum, there is an energy-time uncertainty relation. The meaning is somewhat less clear, because we would not think of measuring the time of a particle as we measure the position of a particle. Instead it refers to, for example, the energy of an unstable particle, or an unstable state of an atom. A stationary state has a perfectly well-defined energy but a decaying particle does not: the uncertainty in energy of an unstable state is

$$\Delta E \sim \frac{\hbar}{\tau} \quad \text{with } \tau \text{ the average lifetime}$$

- Another intermezzo: do we *always* have to use quantum mechanics?

Nope, fortunately not! For instance, take the uncertainty in momentum of an object with weight of  $m=1\text{kg}$ , due to thermal fluctuations at room temperature ( $T=300\text{K}$ ). According to quantum mechanics we cannot know the position perfectly accurately. But, the uncertainty is much smaller than the size of an atom:

$$kT \sim 4 \times 10^{-21} \text{J}$$

$$(\Delta p)^2 \sim 2mkT \Rightarrow \Delta p \sim 10^{-10} \text{kgm/s}$$

$$\Delta x \sim \hbar / \Delta p \sim 10^{-24} \text{m}$$

We are in fact 14 orders of magnitude away from the size of an atom. So we could have an uncertainty in thermal energy that is 28 orders of magnitude larger before we reach that limit.

Note:

$$m \sim 10^{-27} \text{kg for proton}$$

$$m \sim 10^{-31} \text{kg for electron}$$

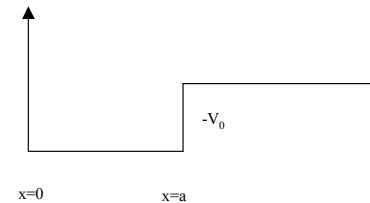
- So the way an atom moves "normally" does not have to be described by quantum mechanics
  - There are cases where you do need quantum mechanics for an atom
- But the way an electron moves inside an atom does need quantum mechanics

## Square wells and barriers

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- Now we get to more realistic and more complicated potentials. Consider this 1-D potential:

$$V(x) = \begin{cases} \infty & \text{for } x < 0 \\ -V_0 & \text{for } 0 < x < a \\ 0 & \text{for } x > a \end{cases}$$



- Classically, we have two types of solutions: if the energy  $E$  of the particle is negative then the particle is trapped inside the well, no matter how small  $V_0$  is. If  $E > 0$  then we could have a particle coming in from the right, gain kinetic energy in the well, bounce off the infinite potential ("mirror") and leave the well again.
- In the quantum case we would like to find all possible eigenvalues for  $E$ , then we can expand the general solution in terms of eigenstates of energy. So we solve

$$\left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right] \psi(x) = E \psi(x)$$

and see for which values of  $E$  we get a correct solution. In particular, we need this:

- The wave function should be continuous at  $x=a$
- The wave function should be differentiable at  $x=a$
- The wave function should be zero at  $x=0$  (because the wave function must be identically zero for all  $x < 0$ )
- We consider two types of solutions (just as in the classical case):
  - Bound states for which  $E < 0$  (those may not exist if the well is shallow! Why not?)
  - Unbound states for which  $E > 0$

### Square wells and barriers

- First the bound states with  $E < 0$ : inside the well we have a positive kinetic energy, and

$$\begin{aligned} [-\frac{\hbar^2 \partial^2}{2m \partial x^2} - V_0] \psi(x) &= E \psi(x) \Rightarrow \\ \psi(x) &= A \sin(k_0 x) + B \cos(k_0 x) \\ k_0 &= \sqrt{\frac{2m(E + V_0)}{\hbar^2}} \end{aligned}$$

- Because of the boundary condition at  $x=0$ , we must have that  $B=0$ , and so

$$\psi(x) = A \sin(k_0 x)$$

- Outside the well, we have a *negative* kinetic energy. Yet there is a solution for that case

$$\begin{aligned} \frac{\hbar^2 \partial^2}{2m \partial x^2} \psi(x) &= -E \psi(x) \Rightarrow \\ \psi(x) &= C \exp(-\alpha x) + D \exp(\alpha x) \\ \alpha &= \sqrt{\frac{-2mE}{\hbar^2}} \end{aligned}$$

- We only get a reasonable solution if  $D=0$ . So we get an exponentially decaying wave function for  $x > a$  (alpha is positive!)

$$\psi(x) = C \exp(-\alpha x) \quad \text{So the particle could be found in a forbidden region of space of size } \sim 1/\alpha$$

- Now we have to match these two solutions at the boundary  $x=a$ . We get two conditions

$$\begin{aligned} \text{continuity:} \quad C \exp(-\alpha a) &= A \sin(k_0 a) \\ \text{differentiability: } -\alpha C \exp(-\alpha a) &= k_0 A \cos(k_0 a) \end{aligned}$$

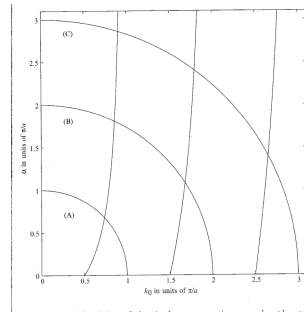
- If we divide these two equations we get rid of the constants  $A$  and  $C$ , and we get

$$\alpha = -k_0 \cot(k_0 a)$$

- This is one equation for two unknowns. But we also have

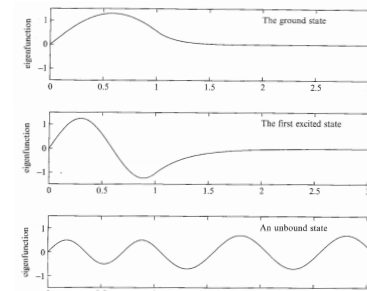
$$\alpha^2 + k_0^2 = \frac{2mV_0}{\hbar^2} =: w^2$$

- We solve these equations graphically by plotting both curves and looking up where they cross (here,  $w = \pi/a$ )



### Square wells and barriers

- We see there are not always solutions. In fact, if  $w < \pi/2a$  there are no bound states (because  $\cot ka > 0$  then). The cotangent keeps changing sign, and we see that we have  $n$  bound states if  $(2n-1)\pi/2a < w < (2n+1)\pi/2a$ . The plot below gives solutions for the case where  $w = 2\pi/a$ , when there should be two solutions.



- Note the wave function is not zero in the "classically forbidden" region. A particle there would have negative kinetic energy! The wave function there decays exponentially.
- Now let's calculate the unbound states with  $E > 0$ : Let's write

$$E = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 k_0^2}{2m} - V_0 \Rightarrow -k^2 + k_0^2 = \frac{2mV_0}{\hbar^2} = w^2$$

- This corresponds to writing the energy outside the well and inside the well, respectively, in terms of wave numbers  $k$  and  $k_0$  for corresponding waves. We write the solutions as

$$\begin{aligned} \psi(x) &= A \sin(k_0 x) \quad \text{inside well} \\ \psi(x) &= B \sin(kx + \delta) \quad \text{outside well } (x > a) \end{aligned}$$

where we already took into account the boundary condition at  $x=0$ . Notice that we have two constants now to choose for the wave function outside the well (for bound states we had only one, because we eliminated the exponentially growing solution). We will have to fit these two solutions at the boundary  $x=a$ .

$$\begin{aligned} \text{continuity:} \quad B \sin(ka + \delta) &= A \sin(k_0 a) \\ \text{differentiability: } Bk \cos(ka + \delta) &= k_0 A \cos(k_0 a) \end{aligned}$$

- Just as we did in the bound case, if we divide these two equations we get rid of  $A, B$ :

$$k \cot(ka + \delta) = k_0 \cot(k_0 a)$$

### Square wells and barriers

- It turns out there are *always* solutions for these equations, we don't have to choose particular values of E. This is thanks to the "extra" parameter delta. That is, one equation (for E) determines both k and k<sub>0</sub> and the remaining equation can be solved for delta (the cotangent varies between -infinity and +infinity, so there is always a solution).

- Outside the well we can rewrite the solution as

$$\begin{aligned} \psi(x) &= B \sin(kx + \delta) = \frac{B}{2i} [\exp(ikx + i\delta) - \exp(-ikx - i\delta)] \\ &= \frac{B \exp(-i\delta)}{2i} [\exp(ikx + 2i\delta) - \exp(-ikx)] \end{aligned}$$

i.e. as a superposition of a wave coming from the right and a wave coming from the left.

Something similar holds inside the well too.

- What if we wish to describe the following process: a wave comes in from the right, enters the well and reflects back? Then we certainly need a nonstationary state, i.e. a superposition of states of different energies. For example, an incoming wave (from +infinity) can be written as

$$\begin{aligned} \Psi_m(x,t) &= \int_0^\infty c(E') \exp(-ik(E')x - iE't/\hbar) dE' \\ k(E) &= \frac{\sqrt{2mE}}{\hbar} \end{aligned}$$

c(E) can be any function: but if we take a function that is nonzero over a range ~h/T, then it describes a wave packet with a duration ~T.

- Suppose we want to describe the same wave packet, but translated in time by some amount tau. That's simple, take:

$$\Psi_m(x,t - \tau) = \int_0^\infty c(E') \exp(-ik(E')x - iE'(t - \tau)/\hbar) dE'$$

and so we get that by replacing

$$c(E') \rightarrow c(E') \exp(iE'\tau/\hbar)$$

- So an energy-dependent phase factor in c(E') corresponds to a time delay. In particular, the phase delta in the reflected wave (see above), also represents a time delay:

$$d\delta(E')/dE' = \text{time delay}$$

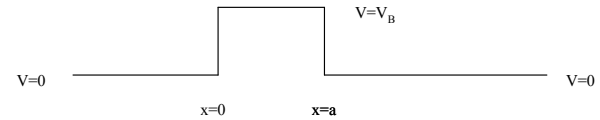
- One gets this by Taylor expanding delta around some central value E:

$$\delta(E') = \delta(E) + d\delta(E')/dE'(E' - E) + \dots$$

- And it's the term linear in E' that gives the time delay.
- So the reflected wave in the square well has a time delay of 2tau: that's the time the particle spends in the well, on average, before leaving it.

### Square wells and barriers

- In general we will see, even for more complicated potentials that
  - Wave functions oscillate in regions where the kinetic energy is positive
  - Wave functions decay exponentially in "classically forbidden" regions where the kinetic energy is negative
  - Potentials that are sufficiently deep can give rise to bound states,
    - the energies of bound states are discrete
  - Particles scattering off of potential wells and escaping to infinity are unbound states
    - The energies of unbound states are continuous (not discrete)
- Now let's look at the opposite of a well, a barrier: a region of space with a higher potential than the outside.



$$V(x) = \begin{cases} 0 & \text{for } x < 0 \\ +V_B & \text{for } 0 < x < a \\ 0 & \text{for } x > a \end{cases}$$

- Classically, two things can happen: if E < V<sub>B</sub> then a particle coming in from, say, the left will reflect (bounce) off the potential. But if E > V<sub>B</sub> then the particle will travel through the potential. Quantum mechanically it's all a bit more complicated and the particle will be both reflected and transmitted.
- As always we solve the time-independent Schrödinger equation, and we can again distinguish two cases E < V<sub>B</sub> and E > V<sub>B</sub>. The former case is the most interesting, and we'll focus on that case. It's easy now to write down the generic form of the solution:

$$\psi_E(x) = \begin{cases} A \exp(ikx) + A' \exp(-ikx) & \text{for } x < 0 \\ B \exp(-\alpha x) + B' \exp(\alpha x) & \text{for } 0 < x < a \\ C \exp(ikx) + C' \exp(-ikx) & \text{for } x > a \end{cases}$$

Note exponential functions in classically forbidden region

where

$$k = \sqrt{\frac{2mE}{\hbar^2}}; \quad \alpha = \sqrt{\frac{2m(V_B - E)}{\hbar^2}}$$

### Square wells and barriers

- Now we have so many free parameters (6) that we can again choose any energy E and find a solution. Moreover, there are *two* types of solutions for each value of E. This degeneracy is related to a symmetry in the problem (which one?).

- o Let's take a particle coming in from the left: we put C=0. We rename some of the coefficients to indicate reflection and transmission coefficients:

$$\psi_E(x) = \begin{cases} A_I \exp(ikx) + A_R \exp(-ikx) & \text{for } x < 0 \\ B \exp(-\alpha x) + B' \exp(\alpha x) & \text{for } 0 < x < a \\ A_T \exp(ikx) & \text{for } x > a \end{cases}$$

- o Then we match the solutions at the two boundaries x=0 and x=a, requiring continuity of both the wave function itself and its first derivative. We get at x=0:

$$\begin{aligned} \text{continuity:} \quad & A_I + A_R = B + B' \\ \text{differentiability:} \quad & ik(A_I - A_R) = \alpha(B' - B) \end{aligned}$$

- o And at x=a we have similarly

$$\begin{aligned} \text{continuity:} \quad & A_T \exp(ika) = B' \exp(ica) + B \exp(-ica) \\ \text{differentiability:} \quad & ikA_T \exp(ika) = \alpha(B' \exp(ica) - B \exp(-ica)) \end{aligned}$$

- o From the equations at x=a we get

$$B' = B \exp(-2ica) \frac{\alpha + ik}{\alpha - ik}$$

- o Instead of looking at the general solution we restrict ourselves to the case of a "wide" barrier, i.e.

$$\exp(-\alpha a) \ll 1$$

- o From the equations at x=0 we get then (neglecting B' compared to B)

$$\begin{aligned} 2ikA_I &= (ik + \alpha)B \\ 2ikA_R &= (ik - \alpha)B \end{aligned}$$

- o For A<sub>T</sub> we get (rewriting B' in terms of B, and then eliminating B in favor of A<sub>T</sub>):

$$A_T = A_I \frac{-4ik\alpha \exp(-\alpha a)}{(\alpha - ik)^2}$$

- o The probability to find the particle in the region to the right goes with the |psi|<sup>2</sup>. So, relative to the incoming wave, the probability of tunneling through the barrier is

$$\left| \frac{A_T}{A_I} \right|^2 = \left| \frac{-4ik\alpha \exp(-\alpha a)}{(\alpha - ik)^2} \right|^2 = \exp(-2\alpha a) \frac{16k^2\alpha^2}{\alpha^2 + k^2}$$

### Square wells and barriers

- The nonzero probability of tunneling is exponentially small in the barrier width a. It also depends on alpha, a parameter with dimensions of 1/length, which in turn depends on how much the barrier is above the energy of the particle.

$$\alpha = \sqrt{\frac{2m(V_B - E)}{\hbar^2}}$$

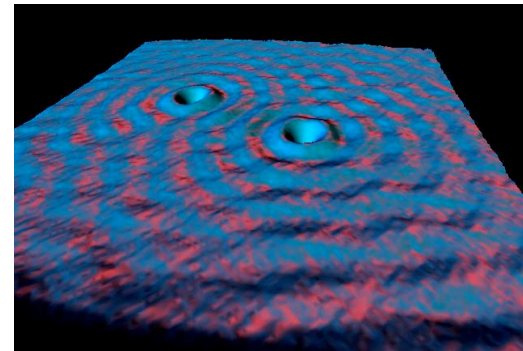
- This exponential dependence can be exploited: a particle is very sensitive to the width of the barrier. For example, take electrons in a metal. From the photoelectric effect you may recall electrons need a few eV of energy to be released from a typical metal. If we have two metals close by, an electron may tunnel from one to the other. We have, roughly,

$$\alpha = \sqrt{\frac{2m(V_B - E)}{\hbar^2}} \approx 10^{10} \text{ m}^{-1}$$

- The change in tunneling probability when the distance a changes, is

$$\frac{\Delta T}{T} \approx -2\alpha \Delta a$$

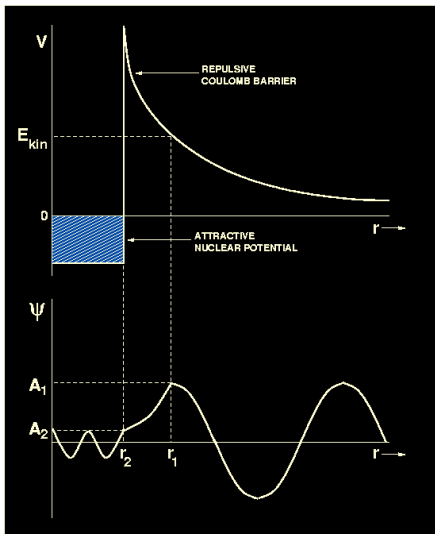
- So if you change the distance between two metals by just 0.01nm, the relative change in T is about 20%! That change can certainly be measured, and the *scanning tunneling microscope* (STM) is based on this effect. It consists of a sharp metal tip (consisting of ~1atom!), that moves over a surface to be investigated. Atomic-size irregularities of the surface can be easily detected that way. Here's an example of an STM image:



Not to be confused with the *scanning electron microscope*, having resolutions of up to a nm!

### Square wells and barriers

- Protons can tunnel too, of course. They do so in the interior of the sun (and other stars). Protons are repelled from each other by the Coulomb force. But when they get really close, they experience the strong force (that holds all nuclei of atoms together!): a strong force with a very short range (~2fm). The could never bridge that distance (given their thermal energy of 1keV only at T=10<sup>7</sup> K) were it were not for the tunneling effect. Protons can tunnel with probability 3x10<sup>-10</sup> and start the fusion process that fuels the sun. Fortunately, it's a small probability and our sun lives quite long.
- This same effect explains why atoms (and the nucleus) actually exist. Tunneling is crucial as it is the first step in the fusion process.
- A rough order of magnitude estimate: with 1keV of energy the protons can approach each other only up to a distance of 10<sup>-12</sup>m (homework!), and the parameter alpha is ~10<sup>15</sup> m<sup>-1</sup>.
- Actually, the (Coulomb) potential is not constant, so alpha is effectively smaller: the proton has to bridge the full energy gap only when it gets close to the 2fm region.
- Here's a picture of the potential barrier and the wave function of the tunneling proton (not to scale!)



### Real observables

- Although we will come back to observables in Section 7, the following is related to homework problems 3-9 and 4-2.
- Recall the expression for the expectation value of momentum:

$$\langle p \rangle = \int \psi^*(x,t)(-\hbar i \partial / \partial x)\psi(x,t)$$

- It may not be clear at all why this would be a *real* number. Let's verify it is real by taking the complex conjugate of this expression:

$$\begin{aligned} \langle p \rangle^* &= \int \psi(x,t)(\hbar i \partial / \partial x)\psi^*(x,t) \\ &= - \int (\hbar i \partial / \partial x)\psi(x,t)\psi^*(x,t) = \langle p \rangle \end{aligned}$$

o So this is a real number, indeed.

- We made use here of integration by parts, and assumed the boundary term vanishes:

$$\begin{aligned} d/dx[f(x)g(x)] &= g(x)df(x)/dx + f(x)dg(x)/dx \Rightarrow \\ \int_a^b f(x)(d/dx)g(x) &= - \int_a^b g(x)(d/dx)f(x) + f(x)g(x)|_a^b \end{aligned}$$

- In quantum mechanics we insist that any observable is represented by an operator *A* that satisfies

$$\int \psi^*(x,t)A\psi(x,t) = \int [A\psi(x,t)]^* \psi(x,t)$$

- Just from this condition we can then show that
  1. The expectation value of *A* is always real
  2. The eigenvalues of *A* are always real
  3. The eigenstates of different eigenvalues are orthogonal

In homework you showed this to be true for energy eigenstates

- That is, we have

1.  $\langle A \rangle^* = \langle A \rangle$
2.  $A\psi_n = \alpha_n\psi_n \Rightarrow \alpha_n^* = \alpha_n$
3.  $\int \psi_n^* \psi_m = 0$  whenever  $\alpha_n \neq \alpha_m$

- This will also imply we can expand an arbitrary wave function as

$$\psi(x) = \sum_n c_n \psi_n(x) \quad \text{with} \quad \sum_n |c_n|^2 = 1$$

The coefficients  $|c_n|^2$  can be interpreted as probabilities to find the value  $\alpha_n$  for the observable *A* in the state described by this wave function

## The harmonic oscillator

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□ The harmonic oscillator is surprisingly important in quantum physics. You might think it just describes a pendulum or a block attached to a string, but the harmonic oscillator is in fact crucial to all kinds of fundamental quantum-mechanical objects

- o Experiments on ions in traps: ions (used for time- and frequency standards or quantum computing) are trapped in a harmonic potential
- o Diatomic molecules are, approximately, described by a harmonic oscillator as far as their vibrational degree of freedom is concerned
- o The electromagnetic field is really a collection of independent harmonic oscillators: each frequency corresponds to one oscillator. We won't be able to treat photons properly yet, but we will recognize certain properties of harmonic oscillators as properties of *photons*
- o Elastic vibrations of solids can be described as harmonic oscillators (these are called *phonons* now, and are very much like photons)
- o On a more complicated level, some of the concepts we encounter in this Section are crucial for quantum field theory

□ The harmonic oscillator is defined by the force  $F(x)=-kx$ , with  $k$  the "spring constant". We will want the potential energy corresponding to that (conservative) force in our Hamiltonian:

$$V(x) = -\int_0^x -kx' dx' = \frac{1}{2}kx^2$$

□ Classically we have

$$\ddot{x} = -\omega^2 x; \quad \omega = \sqrt{k/m} \quad \text{we will use omega rather than k: it has the more obvious physical meaning}$$

$$x(t) = A \cos(\omega t + \delta)$$

□ Classically, we have a strictly periodic motion, with definite position, momentum, and energy:

$$E = \frac{1}{2}m\dot{x}^2 + \frac{1}{2}kx^2 = \frac{1}{2}kA^2 = \frac{1}{2}m\omega^2 A^2$$

□ Quantum-mechanically, we will not have states with well-defined values for all of those quantities. In particular, states with definite energy are stationary (as they always are) and don't oscillate.

□ The Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2}m\omega^2 x^2$$

## The harmonic oscillator

-31-

□ As always we first want to look for states with definite energy  $E$  that evolve as

$$\psi(x,t) = \psi_E(x) \exp(-iEt/\hbar)$$

□ We thus look for states that satisfy

$$\left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2}m\omega^2 x^2\right)\psi_E(x) = E\psi_E(x)$$

□ The potential energy does go to infinity for large  $|x|$ . The wave function must, therefore, go to zero for  $|x|$  large. We expect a *discrete* energy spectrum then, and we denote the allowed energies by  $E_n$ . We number them by  $n=0,1,2,\dots$

□ We first give the solutions and only later derive them:

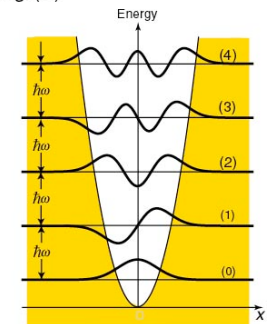
- o The energies turn out to be really simple, and evenly spaced:

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega \quad \text{The term with } 1/2 \text{ gives the } \underline{\text{zero-point energy}}$$

- o Here is a picture of the eigenstates, the wave functions  $\psi_n(x)$

- o Note the number of nodes of excited states!

Fig. (C)



The thick solid curves are the wave functions.  
(0): the ground state  
(1) (2) (3) ...: the excited states

- o Also note the similarity of the energy of the harmonic oscillator and the energy of  $n$  photons: indeed, a photon is an excited state of an oscillator. Not an ordinary oscillator but a more abstract one...

- o These states are stationary and the probability distribution for position does not vary in time

- o The higher-energy wave functions extend farther up the potential hill

- o There are symmetric and anti-symmetric wave functions

- with even and odd parity, respectively.

- Indeed, the Hamiltonian stays the same (is invariant)

under  $x \leftrightarrow -x$ . The negative-parity wave functions change sign,

but that is irrelevant for physical observables. There is no degeneracy here because the mirror image of the eigenstate is the *same* state, unlike in the case of unbound states near a barrier or well (Section 5).



### The harmonic oscillator

- What we don't derive yet is the following: the expectation values for position etc. are

$$\langle x \rangle = 0; \quad \langle x^2 \rangle = (n + \frac{1}{2})a^2 \Rightarrow \Delta x = a\sqrt{n + \frac{1}{2}}$$

$$a = \sqrt{\hbar/m\omega} \quad a \text{ is a length scale}$$

and for momentum we have, very similarly

$$\langle p \rangle = 0; \quad \langle p^2 \rangle = (n + \frac{1}{2})\frac{\hbar^2}{a^2} \Rightarrow \Delta p = \frac{\hbar}{a}\sqrt{n + \frac{1}{2}}$$

- Indeed, note the symmetry of the Hamiltonian under interchanging  $x/a$  and  $ap$

- If we multiply the uncertainties in position and momentum we get

$$\Delta x \Delta p = \hbar(n + \frac{1}{2})$$

- The ground state ( $n=0$ ) actually reaches the *minimum* possible uncertainty
- The expectation values for potential and kinetic energy follow directly from the above:

$$\langle E_{pot} \rangle = \frac{1}{2} m \omega^2 \langle x^2 \rangle = \frac{E_n}{2}$$

$$\langle E_{kin} \rangle = \frac{\langle p^2 \rangle}{2m} = \frac{E_n}{2}$$

- The values of kinetic and potential energy separately fluctuate in the energy eigenstates, but their sum is fixed to be  $E_n$

- What would we need to calculate in order to find the uncertainties in  $E_{kin}$  and  $E_{pot}$ ?

- Let's see if we can guess at least one of the energy eigenstates:

$$\text{If } \varphi(x) = \exp(-(x/b)^2) \text{ then}$$

$$\varphi'(x) = -2x/b^2 \exp(-(x/b)^2)$$

$$\varphi''(x) = (4x^2/b^4 - 2/b^2) \exp(-(x/b)^2)$$

$$\text{choose: } b = \sqrt{2\hbar/m\omega} \text{ then } E = \frac{1}{2}\hbar\omega$$

So we found the ground-state wave function, apparently!

### The harmonic oscillator

- In the stationary states the particle does not seem to oscillate. If we take a superposition of different energy eigenstates then we do get time-dependent position probabilities etc.:

$$\psi(x,t) = \sum_n c_n \psi_n(x) \exp(-iE_n t/\hbar) \Rightarrow$$

$$|\psi(x,t)|^2 = \sum_m \sum_n c_n c_m^* \psi_n(x) \psi_m^*(x) \exp(-i(E_n - E_m)t/\hbar)$$

- The probability distribution thus oscillates at *all* integer multiples of  $\omega$ . The average position, though, oscillates with a frequency  $\omega$ , but not with higher frequencies. This is because integrals like this vanish: (we'll prove this later, maybe)

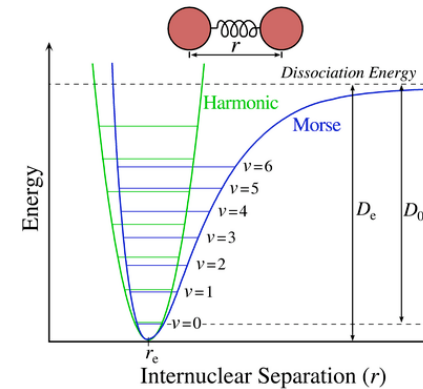
$$\int \psi_m^*(x) x \psi_n(x) dx = 0 \text{ when } |m - n| > 1$$

- Indeed, in arbitrary states we will have the "classical" result

$$\langle x(t) \rangle = A \cos(\omega t + \delta)$$

(In a stationary state we have  $A=0$ )

- Now let's consider a realistic example: Diatomic molecules are approximately described by a harmonic force between the two nuclei. In fact, almost any potential with a minimum is equivalent to a harmonic oscillator near the minimum (Taylor expansion!)



- There is a minimum here because
  - The Coulomb potential forms a barrier when the nuclei are close
  - The electrons no longer bind the two nuclei when they are far apart
  - In between *shared* electrons bind the nuclei ("molecular bond" "covalence bond")

### The harmonic oscillator

- Actually, for large separations between the two nuclei the potential is no longer harmonic, and the energy levels are actually closer to each other than in the exact harmonic oscillator.
- Also note a molecule has more degrees of freedom than the vibrational one, namely rotational and electronic degrees of freedom.
- A molecule absorbs and emits various types of photons depending on which levels the molecule decays from:
  - o Visible light for electronic levels
  - o Infrared light for vibrational levels
  - o Microwave radiation for rotational levels
- The 3-D (isotropic) harmonic oscillator is not much more difficult than the 1-D version: the Hamiltonian is the sum of 3 terms

$$\hat{H}_x = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2} m \omega^2 x^2$$

$$\hat{H} = \hat{H}_x + \hat{H}_y + \hat{H}_z$$

and so the energy eigenstates are products of 3 1-D eigenstates:

$$\hat{H}\psi(x,y,z) = E\psi(x,y,z)$$

$$\psi(x,y,z) = \psi_{n_x}(x)\psi_{n_y}(y)\psi_{n_z}(z)$$

$$E = \hbar\omega(n_x + n_y + n_z + \frac{3}{2})$$

- The 3-D ground state has a zero-point energy of 3 units of the 1-D case
- States with higher energies are more *degenerate*:

	energy	degeneracy
—————	11/2	13
—————	9/2	10
—————	7/2	6
—————	5/2	3
—————	3/2	1

- There is *more* symmetry than for the particle in a cubic box.

### The harmonic oscillator

- The following method to find eigenstates and eigenenergies is quite mathematical, but the technique used will come back in later courses on quantum mechanics:

- First, make the Schrödinger equation dimensionless, by defining

$$x = qa = q\sqrt{\hbar/m\omega}$$

$$E = \epsilon\hbar\omega$$

and writing the wave function as a function of  $q$ , not  $x$

- We get the Schrödinger equation :

$$\left[ -\frac{d^2}{dq^2} + q^2 \right] \psi(q) = 2\epsilon\psi(q)$$

- Now the difference of two squares can be simplified:  $(a-b)(a+b) = a^2 - b^2$ . Here we have to be careful with the order of differentiations, but it is easy to check that

$$\left[ \frac{d}{dq} + q \right] \left[ -\frac{d}{dq} + q \right] f(q) = \left[ -\frac{d^2}{dq^2} + q^2 + 1 \right] f(q)$$

- Similarly we find

$$\left[ -\frac{d}{dq} + q \right] \left[ \frac{d}{dq} + q \right] f(q) = \left[ -\frac{d^2}{dq^2} + q^2 - 1 \right] f(q)$$

- Let's call the two operators appearing here

$$\left[ -\frac{d}{dq} + q \right] := \hat{a}^+; \quad \left[ \frac{d}{dq} + q \right] := \hat{a}^-$$

- Now suppose we have found the  $n$ th eigenfunction. Then we have

$$\hat{a}^- \hat{a}^+ \psi_n(q) = (2\epsilon_n + 1) \psi_n(q) \quad (1)$$

$$\hat{a}^+ \hat{a}^- \psi_n(q) = (2\epsilon_n - 1) \psi_n(q) \quad (2)$$

- Now apply the operator  $\hat{a}^+$  to the first equation

$$\hat{a}^+ (\hat{a}^- \hat{a}^+ \psi_n(q)) = (2\epsilon_n + 1) \hat{a}^+ \psi_n(q)$$

- But, we can also write this as

$$\hat{a}^+ \hat{a}^- (\hat{a}^+ \psi_n(q)) = (2\epsilon_n + 1) (\hat{a}^+ \psi_n(q))$$

- That is, the function  $\hat{a}^+ \psi_n$  is also an eigenstate! In fact, using the second equation (2) we have

$$\hat{a}^+ \hat{a}^- (\hat{a}^+ \psi_n(q)) = (2\epsilon_n + 1) (\hat{a}^+ \psi_n(q)) := (2\epsilon - 1) (\hat{a}^+ \psi_n(q)) \Rightarrow$$

$$\epsilon = \epsilon_n + 1$$

- So by applying the operator  $\hat{a}^+$  we get a new solution where the energy is one unit higher. We call  $\hat{a}^+$  the raising operator. This explains why the energies are evenly spaced.

## The harmonic oscillator

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- Namely, we can first solve this equation

$$\left[ \frac{d}{dq} + q \right] f(q) = 0 \Rightarrow f(q) = C \exp(-q^2)$$

- For this implies:

$$0 = \left[ -\frac{d}{dq} + q \right] \left[ \frac{d}{dq} + q \right] f(q) = \left[ -\frac{d^2}{dq^2} + q^2 - 1 \right] f(q) \Rightarrow$$

$$\left[ -\frac{d^2}{dq^2} + q^2 \right] f(q) = f(q) \Leftrightarrow \epsilon = 1/2 \Leftrightarrow$$

$$f(q) = \psi_0(q)$$

- After that we just keep applying the raising operator to get higher and higher excited states:

$$\left[ -\frac{d}{dq} + q \right] \psi_0(q) = N_1 \psi_1(q) \quad \epsilon_1 = 1 + \epsilon_0 = 3/2 \quad E_1 = (1 + 1/2)\hbar\omega$$

$$\left[ -\frac{d}{dq} + q \right] \psi_1(q) = N_2 \psi_2(q) \quad \epsilon_2 = 1 + \epsilon_1 = 5/2 \quad E_2 = (2 + 1/2)\hbar\omega$$

$$\left[ -\frac{d}{dq} + q \right] \psi_2(q) = N_3 \psi_3(q) \quad \epsilon_3 = 1 + \epsilon_2 = 7/2 \quad E_3 = (3 + 1/2)\hbar\omega$$

etcetera

We do need to normalize the wave functions, but we won't worry about that now

- Since we can write now

$$x = qa = q\sqrt{\hbar/m\omega} = \sqrt{\hbar/m\omega} \frac{\hat{a} + \hat{a}^\dagger}{2}$$

we can use that to calculate integrals like the one we saw before:

$$\int \psi_m^*(x) x \psi_n(x) dx = 0 \quad \text{when } |m - n| > 1$$

Indeed, we can see that the integral is nonzero only for  $|m - n| = 1$ .

- The lowering operator removes one unit of energy: in the context of photons, the operator is also called the *annihilation operator*: it annihilates one photon. We can describe similar operators to described annihilation of particles/antiparticles, such as an electron and positron getting annihilated while creating two gamma photons.
  - o That process is described by two *creation operators* for gamma photons, one annihilation operator for an electron, and one for the positron. We can calculate, e.g., the probabilities for that process, and the result agrees with experiments.

## Commutators

-37-

- We encountered several operators: the Hamiltonian, the momentum operator and the position operator. Unlike when multiplying numbers you have to take into account the order in which you multiply operators. For example, consider the products

$$\hat{x}\hat{p}\psi = -\hbar i x \frac{d}{dx} \psi$$

$$\hat{p}\hat{x}\psi = -\hbar i \frac{d}{dx} [x\psi] = -\hbar i x \frac{d}{dx} \psi - \hbar i \psi$$

- We write the difference between these two expressions as

$$(\hat{x}\hat{p} - \hat{p}\hat{x})\psi = \hbar i \psi \Leftrightarrow \hat{x}\hat{p} - \hat{p}\hat{x} = \hbar i \Leftrightarrow$$

$$[\hat{x}, \hat{p}] = \hbar i$$

- We say, x and p do not commute, and the last line defines the commutator of x and p.
- The commutator is a convenient object because it allows us to see which observables can have well-defined values at the same time. Namely, suppose we have (a complete set of) eigenstates of two observables A and B simultaneously: then A and B must commute:

$$\begin{aligned} \hat{A}\psi &= \alpha\psi \\ \hat{B}\psi &= \beta\psi \\ \hat{A}\hat{B}\psi &= \hat{A}\beta\psi = \alpha\beta\psi = \hat{B}\hat{A}\psi \\ [\hat{A}, \hat{B}] &= 0 \end{aligned}$$

- So a particle cannot have both well-defined position and momentum because x and p do not commute.
- Other examples:
  - o suppose we have a particle in 3-D. Could we have a state with well-defined momenta in the x and y directions, and well-defined position z? Answer: yes, because the three corresponding operators (d/dx, d/dy, z) commute.
  - o Can we have well-defined potential energy and well-defined kinetic energy for a harmonic oscillator? Answer: no, because  $x^2$  and  $p^2$  do not commute.
- There is another nice application of commutators: Consider the time derivative of the expectation value of some operator A:

$$\begin{aligned} \hbar i \frac{d}{dt} \langle A(t) \rangle &= \hbar i \frac{d}{dt} \int \psi^*(x,t) \hat{A} \psi(x,t) \\ &= -\int (\hat{H}\psi)^*(x,t) \hat{A} \psi(x,t) + \int \psi^*(x,t) \hat{A} \hat{H} \psi(x,t) \\ &= -\int \psi^*(x,t) [\hat{H}, \hat{A}] \psi(x,t) \end{aligned}$$

Using that H is Hermitian

## Commutators

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- So a quantity is conserved when it commutes with the Hamiltonian!
  - E.g., energy is conserved because the Hamiltonian commutes with itself...
  - Note we assume here that  $A$  is not *explicitly* time-dependent!
- How could we guess what quantities commute with a given Hamiltonian? Answer: that depends on the *symmetries* of the Hamiltonian: For example:
  - Suppose we have a 3-D particle, and the potential does not depend on  $z$ . Then the momentum in the  $z$ -direction is conserved. This is true classically as well, because there is no force in the  $z$ -direction. Quantum mechanically,  $d/dz$  then commutes with both the kinetic energy and with  $V(x,y)$ . We say, the Hamiltonian is invariant under translations in the  $z$  direction.
  - Similarly, if we have a potential that is invariant under rotations around the  $z$  axis, then the angular momentum in the  $z$  direction is conserved. Let's work that out: Angular momentum in the  $z$  direction is, just as in the classical case:

$$\hat{L}_z = \hat{p}_y \hat{x} - \hat{y} \hat{p}_x \quad \text{Note the order here does not matter, } d/dy \text{ and } x \text{ commute!}$$

If we use cylindrical coordinates

$$\begin{cases} x = \rho \cos \varphi \\ y = \rho \sin \varphi \end{cases} \Rightarrow x^2 + y^2 = \rho^2$$

we can write

$$\begin{aligned} \partial / \partial x &= \cos \varphi \partial / \partial \rho - \rho^{-1} \sin \varphi \partial / \partial \varphi \\ \partial / \partial y &= \sin \varphi \partial / \partial \rho + \rho^{-1} \cos \varphi \partial / \partial \varphi \end{aligned}$$

And so we have

$$\begin{aligned} x \partial / \partial y - y \partial / \partial x &= \\ \rho \sin \varphi \cos \varphi \partial / \partial \rho + \cos^2 \varphi \partial / \partial \varphi - \rho \sin \varphi \cos \varphi \partial / \partial \rho + \sin^2 \varphi \partial / \partial \varphi &= \\ = \partial / \partial \varphi \end{aligned}$$

- So indeed, if the potential does not depend on the angle  $\varphi$  (and hence it's invariant under rotations around the  $z$  axis) then  $d/d\varphi$  will commute with the Hamiltonian.
- For later use we note

$$\hat{L}_z = -\hbar i \partial / \partial \varphi$$

## The structure of quantum mechanics

-39-

- Quantum mechanics uses *two* important concepts:
  - The wave function describes the state of a particle: in fact, it gives a complete description: everything we want to know is "encoded" in the wave function
  - There are operators acting on the wave function: *each* measurable property (i.e. observable) is represented by some operator
- The two concepts come together in the Schrödinger equation (in 1-D)

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

- Thus energy, represented by the Hamiltonian operator, plays a special role, more special than any other observable or operator
- The outcomes for a specific observable are often discrete, rather than continuous. The possible values an observable could have are determined by the eigenvalues of the operators. All operators corresponding to observables have only real eigenvalues.
  - We have seen that eigenvalues of the Hamiltonian determine the possible energies a particle can have in a given potential
  - The corresponding eigenstates of an observable are the unique states in which that observable has a well-defined value. So far we only considered energy eigenstates, but soon we'll include angular momentum eigenstates
- In general, for an arbitrary state, a given observable does not have a well-defined value. Instead, Quantum mechanics gives us *probabilities* for finding certain outcomes of measurements. When expanding the wave function in eigenstates of any observable, the expansion coefficients yield the probabilities to find the corresponding eigenvalues.

$$\begin{aligned} \hat{A} \psi_a(x,t) &= a \psi_a(x,t) \Rightarrow \\ a &\text{ is the eigenvalue} \\ \psi_a &\text{ is the associated eigenstate} \end{aligned}$$

If we expand

$$\begin{aligned} \psi &= \sum_a c_a \psi_a \\ \text{then } \psi(x) &= \sum_n c_n \psi_n(x) \quad \text{with} \quad \sum_n |c_n|^2 = 1 \\ |c_a|^2 &\text{ is the probability to find measurement outcome } a \end{aligned}$$

## The structure of quantum mechanics

-40-

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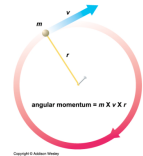
then

$$|c_a|^2 \text{ is the probability to find measurement outcome } a$$

## Angular momentum

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- Classically there is one type of angular momentum, defined by
 
$$\vec{L} = \vec{r} \times \vec{p}$$
 which is a vector with three components (for instance, x,y,z). We call the quantum equivalent the orbital angular momentum.



- Quantum mechanically there is an additional type, spin angular momentum (denoted by S). There is no classical equivalent quantity! It also has three components. We first look at properties of both types of angular momentum without proving or deriving them.
- The sum of the two types of angular momentum is called the total angular momentum, and is denoted by J. So we write

$$\vec{J} = \vec{L} + \vec{S}$$

- In quantum mechanics, we cannot measure all three components of angular momentum at the same time (neither of J, nor L, nor S). And the three components also cannot have a well-defined value (with one exception if all three components are zero). This is because the three components do not commute. So the picture of a vector pointing in a well-defined direction doesn't apply in quantum mechanics.
- Let's consider which quantities do commute. For instance, take the length squared of the orbital angular momentum vector

$$|\vec{L}|^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

- It turns out it commutes with any single one of the three components (we'll get back to this in more detail) of L. (The analogous property holds for S and J)
- What values (i.e. eigenvalues) can  $L^2$  have? Answer:

$$|\vec{L}|^2 \psi_l = \hbar^2 l(l+1) \psi_l$$

$l \geq 0$  an integer

- The number  $l$  is called a quantum number just as  $n$  is used to denote the quantum number for energy. Angular momentum is quantized too, it comes in discrete amounts, just like energy.
- Given states with fixed quantum number  $l$ , what can be the (eigen)values of a given component of angular momentum, say  $L_z$ ? Answer:

$$|\vec{L}|^2 \psi_{l,m} = \hbar^2 l(l+1) \psi_{l,m}$$

$$\hat{L}_z \psi_{l,m} = m \hbar \psi_{l,m}$$

$$-l \leq m \leq l \text{ (integer)}$$

The number  $m$  is yet another quantum number

This scene is described by these equations



### Angular momentum

- For example, let's say we have a particle and know the quantum number  $l=3$ . Then we know the length squared of the L-vector is  $3 \times 4 = 12$  (in units of  $\hbar^2$ ). Now if we measure *any* component of L---the projection of L onto *any* direction---the result can be one of seven different numbers:  $-3, -2, -1, 0, 1, 2, 3$  (in units of  $\hbar$ ).
- Now here we actually have one of those cases where a "realistic" model for quantum mechanics would fail: on the one hand we know that each component squared, whichever one we measure, will have one of four values,  $9, 4, 1, 0$  (in units of  $\hbar^2$ ). And if we add the squares of three orthogonal components, like the  $x, y, z$  components, we must add up to 12. But that can happen only, one would think, if all three terms are equal to 4. But in experiments we certainly do find sometimes 9, sometimes, 1 and sometimes 0. How can the two remaining components ever add up to 3, 11, or 12, respectively??
- The answer is, the other two components simply cannot and do not have well-defined values, once we have measured one component of L. Of course, you could measure another component afterwards, but that will destroy the value you had measured before.
- So again, in quantum mechanics it's not just we don't know certain values of certain observables, but, worse, such values can't even exist.
- It gets even stranger when we consider spin angular momentum. The values of  $S^2$  can take on are

$$|\vec{S}|^2 \psi_s = \hbar^2 s(s+1) \psi_s$$

$s \geq 0$  a "half - integer" (integer multiple of  $1/2$ )

- The components of S take on values

$$|\vec{S}|^2 \psi_{s,m} = \hbar^2 s(s+1) \psi_{s,m}$$

$$\hat{S}_z \psi_{s,m} = \hbar m \psi_{s,m}$$

$m = -s, -s+1, \dots, s-1, s$

- The number m is sometimes given a subscript  $m_s$  to distinguish it from the m quantum number that goes with L (and there's another one going with J, too!)
- Now if we take  $s=3/2$ , then we have

$$|\vec{S}|^2 = S_x^2 + S_y^2 + S_z^2 = \frac{3}{2} \times \frac{5}{2} = \frac{15}{4}$$

$$\{S_x^2, S_y^2, S_z^2\} = \left\{ \frac{9}{4}, \frac{1}{4} \right\}$$

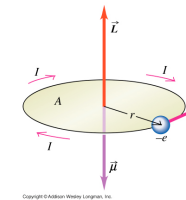
- But you can never add up three values  $9/4$  or  $1/4$ , to add up to  $15/4$ !

### Angular momentum

- How do we measure angular momentum? Usually the particle is charged (with charge q) and then there is a magnetic moment associated with the angular momentum. Classically we have the relation (m is the mass of the particle)

$$\vec{\mu} = \frac{q}{2m} \vec{L}$$

- For instance, for an electron with  $q=-e$  we have this picture:



- The magnetic moment is defined as current times area, with here:

$$\text{current (charge/unit time)} = \frac{qV}{2\pi r}$$

$$\text{area} = \pi r^2$$

$$\text{current} \times \text{area} = \frac{qVr}{2} = \frac{qL}{2m}$$

- Quantum mechanically we have the same relation between orbital angular momentum and magnetic moment. But since L can't be pictured as a vector pointing in a definite direction, nor can the magnetic moment!
- For the relation between spin angular momentum and magnetic moment there is a twist: it depends on what particle we're looking at. For example, for an electron we have

$$\vec{\mu} = g_e \frac{-e}{2m} \vec{S}; \quad g_e \approx -2.0023193043622$$

- The extra factor of almost -2, is called the electron g factor. It can be calculated from (complicated) quantum electrodynamics. It is in fact one of the best known and measured quantities in physics! Theory and experiment agree to one part in  $10^{12}$ .
- Now you might think we're cheating: S is a "half-integer" spin, but then we multiply the magnetic moment by 2!
  - o We can measure that, indeed, there are only 2 values for  $m_s$  for an electron (which has  $s=1/2$ ), namely  $m=-1/2$ ,  $m=+1/2$ . If it were really  $s=1$ , there would be three values,  $m=-1, 0, +1$ .

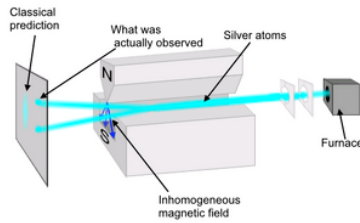
## Angular momentum

- We can measure the magnetic moment by putting the particle in an *inhomogeneous* magnetic field and seeing how it is deflected. In fact, if we want to measure the z-component, we just apply a magnetic field in the z direction. Why is there a force? The magnetic energy is analogous to that of an electric dipole in an electric field:

$$E = -\vec{\mu} \cdot \vec{B}$$

When B depends on position, there is a force,  $F_z = -dE/dz$ .

- Since the magnetic moment is quantized, then so must this force. The force will deflect particles with a magnetic moment in discrete (not continuous) ways. The measurement is done with a Stern-Gerlach device. This measurement (done in 1922) was crucial for discovering half-integer angular momentum.



- Classically, the deflection would be continuous, but in the actual experiment, silver atoms ended up in only two different spots. This corresponds to having a (total) angular momentum of 1/2. Indeed, by measuring the size of the deflection the magnetic moment could be inferred: it agrees with quantum theory
- In quantum mechanics the magnetic moment will always be proportional to the so-called Bohr magneton ( a unit of magnetic moment)

$$\mu_B = \frac{e\hbar}{2m_{electron}}$$

apart from a dimensionless factor. For electrons this factor is of order unity. In general the factor depends on what (charged) particle we have, electron, muon, proton, quark...and on whether the particle has spin angular momentum, orbital angular momentum, or both. Even a neutron has a magnetic moment, because it consists of charged quarks. For neutrons and protons it makes sense to define a similar nuclear magneton, by

$$\mu_N = \frac{e\hbar}{2m_{proton}}$$

## Angular momentum

- In atoms the same effect leads to a shifting of energy levels in a magnetic field. That energy shift can be observed by measuring the wavelength of light emitted by atoms in a magnetic field. It's called the Zeeman effect, and it gives us a different (indirect) way to measure the quantized nature of angular momentum.
- Back to orbital angular momentum: there are three components, given by (classically)

$$\vec{L} = \vec{r} \times \vec{p} \Leftrightarrow \begin{cases} L_x = yp_z - zp_y \\ L_y = zp_x - xp_z \\ L_z = xp_y - yp_x \end{cases}$$

- Quantum mechanically all three components turn into operators, by replacing both position and momentum by their operator equivalents. Those operators act on the same wave function that we have seen many times and that satisfies the Schrödinger equation.
- For example, we can write down expectation values and variances: that in fact shows that an eigenstate of angular momentum has a well-defined value of angular momentum, and zero variance:

$$\hat{L}_x \psi(x) = L_x \psi(x) \Rightarrow \langle \hat{L}_x \rangle = \int \psi(x,t) \hat{L}_x \psi(x,t) = L_x$$

$$\langle \Delta L_x \rangle^2 = \langle \hat{L}_x^2 \rangle - \langle \hat{L}_x \rangle^2 = \int \psi(x,t) \hat{L}_x^2 \psi(x,t) - (L_x)^2 = 0$$

- Now we're going to look at some special functions, that turn out to have "simple" angular momentum properties. First, consider any spherically symmetric wave function

$$\psi(x,y,z) = R(r); \quad R \text{ is any function}$$

- Now it is easy to see that the vector  $r$  is parallel to the gradient of the function. That is, the angular momentum is zero:

$$(\vec{r} \times \vec{\nabla})R(r) = 0 \Rightarrow \hat{L}R = 0$$

$$\vec{\nabla} = \vec{e}_r \frac{\partial}{\partial r} + \dots$$

- So for a spherically symmetric wave function all three components of L are zero! This is an exceptional case where noncommuting operators do have (just one) common eigenstate. Obviously, also  $L^2$  is zero in this case. We have, then, found (a whole set of) eigenstates of zero angular momentum. We denote it by adding two subscript 0's:

$$\psi_{(0,0)}(x,y,z) = R(r)$$

### Angular momentum

- This common eigenstate occurs, in spite of the commutator between, say,  $L_x$  and  $L_y$ , not being zero, because the commutator acting on that special wave function is zero! Namely, we have (homework!)

$$[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z \text{ and cyclic permutations}$$

for the other commutators

- Now consider a slightly more complicated wave function:

$$\psi = R(r) \frac{z}{r} \Rightarrow \hat{L}_z \psi = z \hat{L}_z \frac{R(r)}{r} + \frac{R(r)}{r} \hat{L}_z z$$

- Now the first term is zero, since  $R/r$  is also some function of  $r$  alone; and the second term is easy to calculate: it is zero also, because  $L_z$  contains only derivatives w.r.t.  $y$  and  $x$ . So

$$\hat{L}_z [R(r) \frac{z}{r}] = 0$$

- We can just as easily calculate now:

$$\hat{L}_x [R(r) \frac{z}{r}] = -i\hbar \frac{R(r)}{r} y$$

$$\hat{L}_y [R(r) \frac{z}{r}] = i\hbar \frac{R(r)}{r} x$$

- So the new wave function is an eigenstate of  $L_z$  but not of  $L_x$  or  $L_y$ . But by applying  $L_x$  or  $L_y$  again, we see

$$\psi = R(r) \frac{z}{r} \Rightarrow$$

This does mean  $\psi$  is a superposition of eigenstates of  $L_x$  with eigenvalues  $m_x = +1$  and  $m_x = -1$

$$(\hat{L}_x)^2 \psi = (\hat{L}_y)^2 \psi = \hbar^2 \psi$$

- Since we already know that  $L_z$  gives zero, we get that  $\psi$  is in fact an eigenstate of  $L^2$ , with quantum number  $l=1$  (since then  $l(l+1)=2$ ):

$$\hat{L}^2 \psi = 2\hbar^2 \psi \rightarrow \psi = \psi_{(1,0)}$$

- Obviously, by replacing  $z$  with  $x$  or  $y$ , we can get eigenfunctions of  $L_x$  or  $L_y$  with eigenvalue 0. More interestingly, we can also find the eigenstates of  $L_z$  with different eigenvalues (quantum numbers)  $m=+1$  and  $m=-1$ :

$$\psi_{(1,\pm 1)} = R(r) \frac{x \pm iy}{r} \Rightarrow \hat{L}_z \psi_{(1,\pm 1)} = \pm \hbar \psi_{(1,\pm 1)}$$

- As we announced before, there are no more values for  $m$  allowed, for given  $l=1$ .

### Angular momentum

- We could continue like this and find, by accident, more and more eigenstates of  $L_z$  and  $L^2$ .
- There is also a systematic way, by writing the angular momentum operators in spherical coordinates. You don't need to know the details, but the eigenfunctions are of this form:

$$\psi = R(r) Y_{lm}(\theta, \varphi)$$

$$\hat{L}^2 Y_{lm}(\theta, \varphi) = l(l+1)\hbar^2 Y_{lm}(\theta, \varphi)$$

$$\hat{L}_z Y_{lm}(\theta, \varphi) = m\hbar Y_{lm}(\theta, \varphi)$$

$$l, m \text{ integers, with } |m| \leq l$$

- The  $Y_{lm}$ s are called the spherical harmonics. They are orthogonal in the following sense:

$$\int d\theta \sin\theta \int d\varphi Y_{lm}^*(\theta, \varphi) Y_{l'm'}(\theta, \varphi) = \delta_{ll'} \delta_{mm'}$$

- The  $r$ -dependence of the wave function is not at all determined by angular momentum. This means we can in principle find a third observable, which commutes with both  $L^2$  and  $L_z$ , which determines the function  $r$ . For example, typically this third observable will be the Hamiltonian, provided the potential depends only on  $r$ , not on the angles  $\varphi$  or  $\theta$ .
- The  $\varphi$  dependence of the spherical harmonics is simple:

$$Y_{lm}(\theta, \varphi) = \exp(im\varphi) F(\theta)$$

- The reason for that is as follows. Instead of using spherical coordinates (homework!), let's use cylindrical coordinates to figure this out (the angle  $\varphi$  is the same in both coordinate systems)

- Angular momentum in the  $z$  direction is

$$\hat{L}_z = \hat{p}_y \hat{x} - \hat{y} \hat{p}_x$$

- o If we use cylindrical coordinates

$$\begin{cases} x = \rho \cos \varphi \\ y = \rho \sin \varphi \end{cases} \Rightarrow x^2 + y^2 = \rho^2$$

we can write

$$\partial / \partial x = \cos \varphi \partial / \partial \rho - \rho^{-1} \sin \varphi \partial / \partial \varphi$$

$$\partial / \partial y = \sin \varphi \partial / \partial \rho + \rho^{-1} \cos \varphi \partial / \partial \varphi$$

And so we have

$$x \partial / \partial y - y \partial / \partial x =$$

$$\rho \sin \varphi \cos \varphi \partial / \partial \rho + \cos^2 \varphi \partial / \partial \varphi - \rho \sin \varphi \cos \varphi \partial / \partial \rho + \sin^2 \varphi \partial / \partial \varphi$$

$$= \partial / \partial \varphi$$



### Angular momentum

- The final result for the angular momentum in the z direction is

$$\hat{L}_z = -\hbar i \partial / \partial \varphi$$

- Now we can easily see what the eigenfunctions are of this operator

$$-\hbar i \partial \psi(\varphi) / \partial \varphi = m \hbar \psi(\varphi) \Leftrightarrow \psi(\varphi) \propto \exp(im\varphi)$$

- Now, 'of course', we should have

$$\begin{aligned} \psi(\varphi + 2\pi) &= \psi(\varphi) \Leftrightarrow \\ \exp(im\varphi + 2\pi im) &= \exp(im\varphi) \Leftrightarrow \\ m \text{ an integer} \end{aligned}$$

- But what about spin angular momentum for which m is a half integer??
  - o Answer: the wave function of a half-integer spin particle changes sign when rotated over 360 degrees! Spin is weird.
  - o This sign change can be measured by interference between two beams of, say, neutrons or electrons, one of which is rotated, the other is not.
  - o Particles with half-integer spin are called fermions, as opposed to bosons, which have an integer spin
- Back to symmetry and conserved quantities. In general, if a potential does not depend on the angle phi (and hence it's invariant under rotations around the z axis) then d/dphi will commute with the Hamiltonian. So angular momentum in the z direction is conserved in that case. This is true both classically and quantum mechanically.
- Back to spin angular momentum: it has no equivalent in classical physics. The operator S does not act on the wave function psi that we have used so far (if it did, it would have a classical interpretation!). Instead, we "attach" another type of wave function to each particle that has nonzero spin. For instance, an electron has spin s=1/2, and so there are two states we can distinguish, m=-1/2, and m=+1/2. We write the spin part as a 2-D vector:

$$\Psi = \begin{pmatrix} \psi_{+1/2}(x,t) \\ \psi_{-1/2}(x,t) \end{pmatrix} = \psi_{+1/2}(x,t) \begin{pmatrix} 1 \\ 0 \end{pmatrix} + \psi_{-1/2}(x,t) \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

Spin up                  Spin down

- So it's as if the electron now has two independent wave functions, one for "spin up" and one for "spin down"

### Angular momentum

- Also let's note that every (elementary) particle has one fixed value of the spin quantum number s (electron, proton, neutron, all have s=1/2, photon, W-boson have s=1, graviton s=2).
- So this is unlike orbital ang mom, which could take on any (integer) value, for a given particle.
- Nuclei of atoms also have spin angular momentum, because they consist of protons and neutrons. If we have an odd number of "nucleons", then the nuclear spin is half-integer. So the nuclear spin does depend on which isotope we're looking at. For example, <sup>133</sup>Cs has I=7/2 (denoted by I now!). This, though, does refer to the ground state of the nucleus. The energy needed to excite the nucleus is so large that indeed I=7/2 is the natural value of the nuclear spin.
- Finally, returning to J=L+S. The quantum numbers j,l,s are not completely independent, of course. Thinking about how to add two vectors of given length, we get this: if we fix l and s, then j can take on the values

$$\begin{aligned} j_{\max} &= l + s \\ j_{\min} &= |l - s| \\ j &= j_{\min}, j_{\min} + 1, \dots, j_{\max} - 1, j_{\max} \end{aligned}$$

- The m-values are much easier: we simply have m<sub>j</sub>=m<sub>l</sub>+m<sub>s</sub> ( we usually don't write m<sub>l</sub>!)
- All this is important in order to understand atoms: an electron with spin and fixed orbital angular momentum can combine the two in different ways to make up different states (with slightly different energies).

- The hydrogen atom can be solved completely, in quantum mechanics. So it's an important test for quantum mechanics to compare all results to experiment.
- We first neglect the motion of the proton, and assumed it's fixed in the origin. This is not an approximation: we can separately study the center-of-mass motion, and the relative motion (we'll return to this issue later). The relative motion is what we're interested in, not how the H atom moves as a whole.
- The electron then moves in a spherically symmetric potential,  $V(r)$ , the Coulomb potential.

$$V(r) = \frac{-e^2}{4\pi\epsilon_0 r}$$

- In *any* central potential, angular momentum is conserved. In QM, therefore, all three components of  $L$  commute with the Hamiltonian. So we can try to find states with definite values of energy, the length of  $L$ , and  $L_z$ .

$$\hat{H}\psi = E_n\psi$$

$$\hat{L}^2\psi = l(l+1)\hbar^2\psi$$

$$\hat{L}_z\psi = m\hbar\psi$$

- For the ang mom part, we already gave a name to the eigenfunctions, so we can write (using spherical coordinates, of course)

$$\psi = R(r)Y_{lm}(\theta, \varphi)$$

- Now we "only" need to find the form of the  $r$ -dependent part  $R$ . As always, the more nodes the wave function has, the higher the energy. In fact, let's call the number of nodes in  $R$ ,  $n_r$ . It turns out, the total energy is this:

$$E = -\frac{E_R}{n^2}; \quad \leftarrow \text{just as in the Bohr model!}$$

$$n = n_r + l + 1$$

$$E_R = \frac{\alpha^2 m_e c^2}{2} \approx 13.6\text{eV} = \text{Rydberg energy}$$

$$\alpha = \frac{e^2}{4\pi\epsilon_0 \hbar c} \approx \frac{1}{137} = \text{fine structure constant}$$

- Here,  $n$  is the principal quantum number, and it is simply determined by the sum of  $n_r$  and  $l$ . Indeed, the ang mom contributes, indirectly, to the energy: namely the kinetic energy of the motion perpendicular to  $r$  is proportional to  $L^2$  (also classically).

$$E_{kin} \approx \frac{L^2}{2mr^2} = \frac{l(l+1)\hbar^2}{2mr^2}$$

- This can also be seen as an extra potential energy, the centrifugal energy. If the electron has ang mom, it can't be too close to the origin,  $r=0$ , it's "repelled". See Fig. 9.2 for a plot of the effective potential energy the electron with ang mom  $l$  sees. Thus, all wave functions for  $l>0$  are vanish in the origin (namely like  $\sim r^l$ )
- The function  $R$  decays exponentially with  $r$ . In fact, we have

$$R(r) \sim \exp(-r/na_0)\text{Poly}(r)$$

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{e^2 m} = 0.5 \times 10^{-10} \text{m} \quad (\text{Bohr radius})$$

- Recall the wave function of the harmonic oscillator:  $\exp(-(x/a_0)^2)$  for the HO vs  $\exp(-x/a_0)$  of H. Here  $a$  and  $a_0$  are different! Why does one decay much faster than the other?
- For each energy level  $n$ , there are several possibilities: we only need the number of nodes plus  $l$  equals  $n-1$ . So states with more energy are more degenerate, just as for the harmonic oscillator. We indicate levels by first writing down  $n$ , then a letter indicating with ang mom, where  $s=0$ ,  $p=1$ ,  $d=2$ ,  $f=3$ , etc.
- We can also sketch the wave function belonging to those levels, with all the information we have now. See Table 9.1 and Fig. 9.4.
- The theory so far is non-relativistic. It turns out, taking relativity into account leads to small corrections to the energies (typically, quadratic in the fine structure constant, because the speed of the electron is  $\sim \alpha c$ ).
  - o For example, the 2p state really splits in two different energy states,  $2p_{1/2}$  and  $2p_{3/2}$ , depending on whether the spin of the electron is parallel or anti-parallel to its orbital ang mom, that is, depending on whether the total ang mom quantum number is  $j=1+1/2$ , or  $j=1-1/2$ .
  - o The 2s and 2p states differ in energy, too, as a result of the different way they interact with the vacuum: the Lamb shift is the energy difference between  $2s_{1/2}$  and  $2p_{1/2}$ . due to interaction with the zero-point energy.
  - o These relativistic corrections have been verified to 14 decimal places...
- Another aspect of the H atom: a photon can be emitted when the H atom decays from, say, 2p to 1s. Since the spin of a photon is  $s=1$ , transitions only happen with large probability when the ang mom of the atom,  $l$ , changes by 1 (ang mom conservation!). So indeed a p to s transition works, or d to p, etc.
- Can't a photon have orbital ang mom? Yes it can, but that is transferred to the center-of-mass motion of the atom.

H, He, Li, ...

- Finally, when we separate the center-of-mass motion from the relative motion of the electron and the proton, we actually should define a reduced mass. Namely, we have

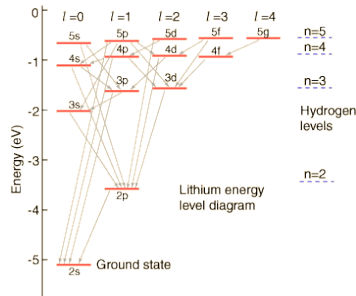
$$\frac{p_p^2}{2m_p} + \frac{p_e^2}{2m_e} = \frac{P^2}{2M} + \frac{p_r^2}{2\mu}$$

$$\mu = \frac{m_p m_e}{M}; M = m_p + m_e$$

- You probably used the same trick in classical mechanics when looking at how the moon orbits around the earth, or how the earth orbits around the sun.
- But it means we should not really use the mass of the electron in the expression for the Rydberg energy and the Bohr radius, but the reduced mass. This just sets a different scale: the formulas for energy etc. still apply, but with a slightly different Rydberg energy and Bohr radius.

$$E' = \frac{\mu}{m_e} E_R; \quad a' = \frac{m_e}{\mu} a_0$$

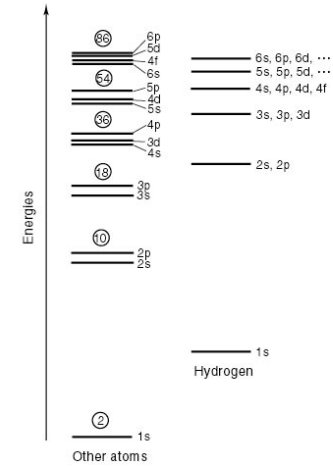
- We can use the information about the H-levels to figure out the periodic system of elements. Namely, chemical properties of atoms are determined by their electronic states. In fact, at room temperature the atom is in its ground state, so we "only" have to figure out the ground states of all atoms in order to understand their chemical behavior.
- Since the electrons do not (or hardly) interact with the neutrons in a nucleus, only the number of protons, Z, is important.
- The spatial states of the H atom translate to other atoms, too. 1s still means a spatial wave function with zero nodes and zero ang mom. But the wave function is more "compressed". That's because each electron "sees" a larger charge than just +e. In fact, at very large distance the electron does see just +e, but close to the nucleus it sees +Ze.
- This also affects the energy levels. They are "stretched out" compared to H. For example, in Li:



H, He, Li, Be, B, C, ...

- In fact, for other atoms with Z>1, we have something like this energy structure:
  - Note, e.g., that 4s tends to be below 3d in atoms with Z>>1!

Fig. (C)



- Now all we have to do is fill up the energy levels with electrons, while using the Pauli exclusion principle.
- Some subtleties:
  - While filling up the 2p levels the electrons first occupy *different* m states [m=-1,0,+1], so they still can avoid each other: this is due to their Coulomb repulsion, not the Pauli effect.
  - When forming molecules the electrons do not have to be completely removed from one atom, but just to a higher excited state.
  - The size of the outer orbit also determines whether an atom likes to donate or accept other atoms' electrons. For example, Li (Z=3) has a "size" 1.59 A, and Ar (a noble gas, with all shells filled) (Z=18) only 0.66 A! Then, K (Z=19) has radius 2.16 A, and is much more reactive, thanks to its outer electron far away from the nucleus.

## Identical particles

-54-

- So far we considered only single particles, now we will look at the quantum description of multiple particles. It's surprising the extension is not quite straightforward. Namely, there is a difference between distinguishable and indistinguishable or identical particles.
- Moreover, entanglement is a typical quantum property that refers to (quantum) correlations between 2 or more systems. Entanglement isn't usually taught in standard quantum mechanics courses, but in the last 10 years or so, entanglement has become much more important, for quantum computing, quantum communication, and quantum cryptography.
- Here we will look at entanglement, the EPR paradox, and Bell inequalities, in addition to what is in Section 10 of the textbook.
- But let's start from the beginning: if we have 1 particle, we know it's described by a wave function (let's consider 1-D for simplicity)

$$\psi(x,t)$$

- What about 2 particles? Let's say we have 2 independent and different particles; e.g. an electron and a proton. Then we have 2 wave functions

$$\begin{aligned} \psi_e(x,t) \\ \psi_p(x,t) \end{aligned}$$

- But how could we combine these into a single wave function that describes both particles? Let's think about probabilities. Suppose we want to write down a joint probability distribution for the positions of both the electron and proton. For independent particles we would simply have a product of two independent probabilities: the probability to find the electron around  $x$  and the proton around  $x'$  is

$$P(x,x',t) = P_e(x,t)P_p(x',t)$$

- Aha! So perhaps we should consider the following the joint wave function describing electron and proton together:

$$\Psi(x,x',t) = \psi_e(x,t)\psi_p(x',t)$$

- The physical meaning of this wave function is fixed by requiring

$$P(x,x',t)dx dx' = |\Psi(x,x',t)|^2 dx dx'$$

- Just as for classical probabilities, we can get the probability distribution for 1 particle by integrating out the other particle:

$$P(x,t)dx = \left[ \int |\Psi(x,x',t)|^2 dx' \right] dx$$

## Identical particles

-55-

- We can apply the superposition principle to 2 particles. This means we can also have joint wave functions of the form (looking here only at a simple example)

$$\Psi(x,x',t) = a\psi_e(x,t)\psi_p(x',t) + b\varphi_e(x,t)\varphi_p(x',t)$$

$\psi, \varphi$  are orthogonal wave functions

$$a, b \text{ are numbers with } |a|^2 + |b|^2 = 1$$

← Normalization!

- Such a state, whenever it *cannot* be written as just 1 product term, is an entangled state. Beware of states like this that look entangled but aren't:

$$\begin{aligned} \Psi(x,x',t) &= \frac{1}{2}[\psi_e(x,t) + \varphi_e(x,t)][\psi_p(x',t) + \varphi_p(x',t)] \\ &= \frac{1}{2}[\psi_e(x,t)\psi_p(x',t) + \varphi_e(x,t)\psi_p(x',t) + \psi_e(x,t)\varphi_p(x',t) + \varphi_e(x,t)\varphi_p(x',t)] \end{aligned}$$

- There is correlation between the two particles in such a state: when you measure the electron and find it in  $\psi$  (psi), then the proton must be in  $\psi$  (psi), too.
  - Because  $\psi$  and  $\varphi$  are orthogonal, they are eigenstates of some observable with different eigenvalues (you knew the converse of this!). This means you can perform a measurement that distinguishes  $\psi$  from  $\varphi$ .
  - One aspect different from classical physics is this: although we have maximum information about the joint system, we do not know everything about each particle! After all, *we do not have a wave function for each particle individually*.
  - There are more consequences...we'll see those later!

- Now consider identical particles, e.g., 2 electrons. In classical physics we could distinguish 2 electrons at all times by just keeping track of where they move. In quantum mechanics we can no longer do that (or even imagine doing that), and identical particles are truly indistinguishable. We require then that

$$\begin{aligned} P(x,x',t) &= P(x',x,t) \Leftrightarrow \\ |\Psi(x,x',t)|^2 &= |\Psi(x',x,t)|^2 \Leftrightarrow \\ \Psi(x,x',t) &= \exp(i\delta)\Psi(x',x,t) \end{aligned}$$

$x, x'$  refer to coordinates of 2 electrons  
However, we can't really distinguish which position is  $x$  and which is  $x'$ .  
So  $x, x'$  are actually not *physical* labels and cannot be measured individually!

- Moreover, because of the symmetry between the two coordinates, we also must have

$$\begin{aligned} \Psi(x,x',t) &= \exp(i\delta)\Psi(x',x,t) \Rightarrow \Psi(x',x,t) = \exp(i\delta)\Psi(x,x',t) \\ \Rightarrow \exp(2i\delta) &= 1 \Leftrightarrow \exp(i\delta) = \pm 1 \end{aligned}$$

## Identical particles

-56-

- Thus there are two possible choices: symmetric (+ sign) wave functions and anti-symmetric (- sign) wave functions.
- This actually corresponds to bosons (integer spin) and fermions (half-integer spin), respectively. This is a very hard theorem to prove...[Pauli]..the spin-statistics theorem
- This symmetry does have consequences. Consider 2 particles (either identical, or distinguishable) in a harmonic oscillator with a Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m} \left[ \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial x'^2} \right] + \frac{1}{2} m \omega^2 (x^2 + x'^2)$$

- o So the particles don't interact with each other
- Suppose we have 2 particles in the ground state (n=0). The wave function would necessarily be symmetric:

$$\Psi(x, x', t) = \psi_{n=0}(x, t) \psi_{n=0}(x', t)$$

So no difference here between distinguishable and indistinguishable particles

- But now suppose we have particles in the states n=0 and n=1: Then we'd have:
  - o For distinguishable particles:

$$\Psi(x, x', t) = \psi_{n=0}(x, t) \psi_{n=1}(x', t) \quad \text{or}$$

$$\Psi(x, x', t) = \psi_{n=1}(x, t) \psi_{n=0}(x', t)$$

- o For "symmetric" indistinguishable particles (bosons):

$$\Psi(x, x', t) = \frac{1}{\sqrt{2}} [\psi_{n=0}(x, t) \psi_{n=1}(x', t) + \psi_{n=1}(x, t) \psi_{n=0}(x', t)]$$

- o For "anti-symmetric" indistinguishable particles (fermions):

$$\Psi(x, x', t) = \frac{1}{\sqrt{2}} [\psi_{n=0}(x, t) \psi_{n=1}(x', t) - \psi_{n=1}(x, t) \psi_{n=0}(x', t)]$$

Energies are the same in the three cases!

These states look entangled but actually are not, in spite of what the book says: The labels x and x' are not physical

- Consider the probability to find both particles in the same position, say X:

$$P = |\psi_{n=0}(X, t) \psi_{n=1}(X, t)|^2 \quad \text{distinguishable particles}$$

$$P = 2 |\psi_{n=0}(X, t) \psi_{n=1}(X, t)|^2 \quad \text{indistinguishable bosons}$$

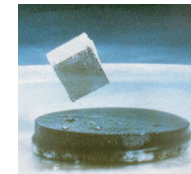
$$P = 0 \quad \text{indistinguishable fermions}$$

- o Bosons huddle together
- o Fermions avoid each other
- o Distinguishable particles don't care

## Identical particles

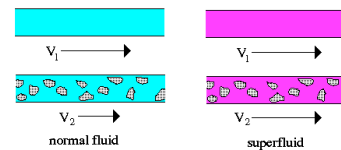
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- Examples of some consequences:
  - o Bose-Einstein condensation (BEC) is an effect relying crucially on this pure quantum effect. It occurs for bosons only, and is the effect that all (non-interacting) bosons end up in the ground state if the temperature is sufficiently low and if the density is sufficiently high.
  - o It used to be one of the holy grails in physics to actually build a BEC, but since the first demonstrations in 1995, many BECs have been produced around the world, including soon(?) here at the UO (Dan Steck).
    - The first BEC consisted of Rb atoms cooled to 170nK; pretty cold.
    - Note the temperature of the universe is T=2.725K (background radiation)
  - o Superconductivity is somewhat similar: it's pairs of electrons with opposite spins ("Cooper pairs") that condense and can move without resistance: note two electrons together have an integer spin and can, under certain conditions, behave like a boson. Superconductivity can be used, e.g. to levitate magnets or trains:



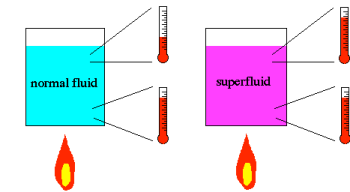
- o Super-fluidity is similar too: liquid He<sup>4</sup> flows without friction: it's BEC but with interacting particles. This effect does not occur for He<sup>3</sup>: why not?

superfluids flow with no resistance



a normal fluid flows with some velocity  $V_1$  – but if resistance is placed in its way it moves with velocity  $V_2$ , where  $V_2 < V_1$  (i.e. slower)

superfluids conduct heat perfectly



with a normal fluid (such as water) it takes time for the heat to travel within the container, thus it is hotter at the bottom of a heating glass

### Identical particles

- The effective repulsion of fermions leads to the Pauli exclusion principle, which just says that 2 electrons can't occupy the same state. This effect will prevent our sun from collapsing further than a white dwarf. Phew.
  - 1 teaspoon of a white dwarf would weigh 5 tons
  - The same effect but for neutrons is the only thing preventing neutron stars from collapsing further under their gravitational interaction (heavier stars still do collapse to a black hole)
- So far we actually left out the spin degree of freedom, which is important in this context. The wave function of 2 electrons must be anti-symmetric. But an electron has spin  $s=1/2$ , so there are 2 independent spin states ( $m=+1/2$  and  $m=-1/2$ ).
  - Also often called "spin up" and "spin down"
- Since the wave function of an electron is the product of the spatial part and the spin part,  $\Psi = \psi(x)\chi$  we can actually have a symmetric spatial part, provided the spin part is anti-symmetric (and vice versa).
  - So 2 fermions can actually be found in the same place, unlike what we said before, provided they are in different spin states.
  - The spin effect actually explains part of the periodic system of elements: 2 electrons "fill" the lowest "shell". That's why He is a noble gas!
- What about more than 2 particles? Fermions still have to be in a state that is anti-symmetric under the exchange of any pair. So, for example, there is no anti-symmetric state for the spins of more than 2 electrons (why not?)
- Multiple bosons still have to be in a state that is completely symmetric.
- Thus there still is a big difference between bosons and fermions: at most 2 electrons can be found in the same location, but N bosons are N! times as likely to be found in the same location as distinguishable particles, because:

$$\Psi(x_1, x_2, \dots, x_N) = \frac{1}{\sqrt{N!}} \sum_{\text{all permutations}} \psi_1 \psi_2 \dots \psi_N \Rightarrow$$

$$\Psi(X, X, \dots, X) = \sqrt{N!} \psi_1(X) \psi_2(X) \dots \psi_N(X) \Rightarrow$$

$$|\Psi(X, X, \dots, X)|^2 = N! |\psi_1(X) \psi_2(X) \dots \psi_N(X)|^2$$

- In fact, a laser can be seen to rely on this effect: photons are bosons, and they like to be in the same state. Thus, once there are a few photons with a certain frequency and polarization, many more will be produced inside a laser cavity. The effect of bosons huddling together is then called stimulate emission. The light from a laser could be viewed as a Bose-Einstein condensate of photons.

### Identical particles

- For 2 electrons there are 4=2x2 different spin states in total. One way to distinguish the 4 states is by total spin ang mom (0 or 1) and the z-components of total spin: there is 1 (anti-symmetric) state with zero spin ang mom

$$\Psi_{0,0} = \frac{1}{\sqrt{2}} [\psi_1 \psi_0 - \psi_0 \psi_1] \quad \text{"singlet" state}$$

and there are three (symmetric) states with total spin ang mom 1

$$\Psi_{1,0} = \frac{1}{\sqrt{2}} [\psi_1 \psi_1 + \psi_0 \psi_0]$$

$$\Psi_{1,-1} = \psi_0 \psi_0 \quad \text{"triplet" states}$$

$$\Psi_{1,1} = \psi_1 \psi_1$$

- It's easy to see which of these 3 states have  $m_s = 0$ ,  $m_s = 1$  or  $m_s = -1$ .
- In a Cooper pair, which of these 4 spin states is occupied by the 2 electrons?
- And in the ground state of He?
- Now onto entanglement (for distinguishable particles for simplicity). Suppose we have 2 particles: question: could we know the sum of their momenta and their relative position?
- Surprisingly, perhaps, yes because those observables commute
 
$$[\hat{p}_1 + \hat{p}_2, \hat{x}_1 - \hat{x}_2] = [\hat{p}_1, \hat{x}_1] - [\hat{p}_2, \hat{x}_2] = -\hbar i + \hbar i = 0$$
  - We used here that observables on different particles commute
  - If that were not the case we would have a problem with special relativity

So we can have a state in which we know precisely the total momentum, say zero, and the distance between the particles, say 1 light year.

- The Einstein-Podolski-Rosen paradox is about such a state. Namely, suppose we measure on particle 1 its position. Then, we also know the position of particle 2 (and we won't know either momentum). On the other hand, if we measure the momentum of particle 1, then we know also the momentum of particle 2. But EPR argued that any manipulation of particle 1 should not change anything about particle 2. So, it means particle 2 should have both a well-defined position and a well-defined momentum (even if we don't know those values beforehand) before the measurements on particle 1. But that means that quantum mechanics is incomplete: QM says one cannot have a state in which both x and p are well defined. See Physical Review 47, 777 (1935).
- When viewing the quantum state as a state of knowledge, the change to particle 2 because of a measurement on particle 1 is nothing paradoxical. In fact, we can mimic the same features with classical probability distributions for (x,p) for each particle. However, this trick does not always work....

## Bell inequalities

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- It turns out one can prove that quantum mechanics does not allow classical probability distributions that can mimic all possible measurements, unless one would allow superluminal communication. The proof of that statement was given by John Bell, by writing down the Bell inequalities that must be satisfied by any local classical model. But quantum mechanics violates those inequalities.
- Consider 2 particles, 1 and 2, and consider 2 different measurements A and B on 1 and C and D on 2.. Assume they have just 2 outcomes, +1 and -1. Denote the outcomes by  $A_1, C_2$  etc
  - E.g., we could be measuring spin ang mom. In 2 different directions, say the z and x directions. +/-1 would correspond to finding +/-hbar/2
- Perhaps the outcomes of the measurements are probabilistic. In any case, if we assume all values are well defined, but we just don't know those values, then we would always have:

$$|(A_1 - B_1)C_2 + (A_1 + B_1)D_2| \leq 2$$

- We write this as the Bell inequality:

$$| \langle A_1 C_2 - B_1 C_2 + A_1 D_2 + B_1 D_2 \rangle | \leq 2$$

- That is, we imagine measuring A or B on particle 1, and, independently, C or D on particle 2, and check for correlations between the two. The inequality does not refer to quantum mechanics at all! QM can violate this inequality, provided the measurements A and B do not commute, and C and D do not commute. Why do we need that condition?
- Consider the singlet state of 2 spins:

$$\Psi_{0,0} = \frac{1}{\sqrt{2}} [\psi_1 \psi_1 - \psi_1 \psi_1]$$

- We can also write this as

$$\Psi_{0,0} = \frac{1}{\sqrt{2}} [(\cos \theta \psi_1 + \sin \theta \psi_1)(\sin \theta \psi_1 - \cos \theta \psi_1) - (\sin \theta \psi_1 - \cos \theta \psi_1)(\cos \theta \psi_1 + \sin \theta \psi_1)]$$

- This just says that no matter in what direction I measure both spins, they will always be opposite. Indeed, this also follows from the fact the singlet state has zero total angular momentum: it's zero in *any* direction.
  - This also means if I measure one spin in some direction n, and find its spin is "up", then the other spin must be "down" along n. The wave function "collapsed".

## Bell inequalities

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- On particle 2, let's measure one of these:

$$\hat{C} := \hat{S}_z = \hat{S} \cdot e_z$$

$$\hat{D} := \hat{S}_x = \hat{S} \cdot e_x$$

In general, we can write the operator for spin in any direction n in the form:  $\hat{S} \cdot n$ .

- Then, if we would measure C or D on particle 1 we would find perfect anti-correlations:

$$\langle \hat{C}_1 \hat{C}_2 \rangle = -1 = \langle \hat{D}_1 \hat{D}_2 \rangle \quad (*)$$

- Now choose A and B such that

$$\hat{A} = \hat{S} \cdot \frac{e_x + e_z}{\sqrt{2}}$$

$$\hat{B} = \hat{S} \cdot \frac{e_x - e_z}{\sqrt{2}}$$

- This actually implies (by inverting these relations) that

$$\hat{C} = \frac{\hat{A} - \hat{B}}{\sqrt{2}}; \hat{D} = \frac{\hat{A} + \hat{B}}{\sqrt{2}}$$

- Rewriting the perfect anti-correlations (\*) in terms of A,B, we get:

$$-2 = \langle \hat{C}_1 \hat{C}_2 + \hat{D}_1 \hat{D}_2 \rangle = \frac{1}{\sqrt{2}} \langle (\hat{A}_1 - \hat{B}_1) \hat{C}_2 + (\hat{A}_1 + \hat{B}_1) \hat{D}_2 \rangle$$

- Now we recognize the terms on the rhs as those appearing in Bell's inequality:

$$\langle (\hat{A}_1 - \hat{B}_1) \hat{C}_2 + (\hat{A}_1 + \hat{B}_1) \hat{D}_2 \rangle = -2\sqrt{2}$$

- But the absolute value of the lhs is supposed to be less than 2! QM violates the Bell inequality!

○  $2\sqrt{2}$  is the maximum violation in QM, in fact.

- What does this mean? Apparently, QM cannot be mimicked by a theory that assumes quantities have values before I measure them...the alternative is to allow a nonlocal theory that incorporates superluminal signaling: that is, if I measure particle 1 and it sends a signal to particle 2 that includes the measurement result, then I can easily violate Bell's inequality, too. In fact, I could get 4 instead of just  $2\sqrt{2}$ .

○ So QM allows a violation less than superluminal signaling would allow.

○ Still, it allows stronger correlations than classical theory does without signaling

○ These correlations can be exploited: E.g. *Quantum cryptography* is secure only when one can prove the existence of (effective) entanglement

○ Note QM does not allow superluminal signaling with entanglement!