Quantum Mechanics Notes
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Lecture 1 part 1
Introduction to the Schrödinger equation

1 The Schrödinger equation.

We begin with the Schrödinger equation. Most properties of matter under ordinary conditions are determined by solutions of this equation. Most of this class is exploring what we can derive or guess about these solutions, whether exact, approximate, computed, or surmised.

Continuing common practice, I explain the Schrödinger equation through "historical fiction", the way it might have gone, but did not actually. Only the names have not been changed. My favorite factual account of the origin of quantum mechanics is *Twenty Years That Shook Physics* by George Gamov. It is commonly said (see below) that quantum mechanics arose because small particles, electrons in particular, were observed to act in ways counter to classical mechanics. In fact, it arose because classical ideas of chaos and statistical mechanical mechanics are insonsistent with a system with infinitely many degrees of freedom (or "modes") such as electro-magnetic waves, even without observation. This fact was overlooked by theorists (Maxwell, Boltzmann, Jeans, etc.) until it was brought to their attention by experimentalists. I am planning some material on "black body" radiation for later.

We start with the discovery that elementary particles (electrons and neutrons at first) have a "wave like quality". Actually, wave/particle uncertainty and debate has a long history. Newton argued that light was a particle, a view that was temporarily put to rest by Maxwell 150 years later. Modern applied mathematicians often say that wave packet solutions of wave equations behave much like particles if the wavelength is small enough (compared to something). The wavelength of light is so small that Newton had trouble telling the difference between particle like solutions and particles. Today, you can observe diffraction patterns in light for just a few dollars. The only reasonable way to explain diffraction patterns is through interference of waves. The diffraction patterns of particles are too small to be seen without more expensive equipment.

Electrons were discovered in 1895. Soon after, beams of electrons were passed through crystals to produce diffraction patterns like light passing through diffraction gratings. In 1915 Count De Broglie proposed that a moving electron has a wave associated to it with wave number proportional to its momentum,

$$p = \hbar k \; . \tag{1}$$

Here $p = mv$ is the momentum of the electron of mass m and velocity v, $\hbar$ is a small constant, Planck's constant, and k is the wave number of the electron. A wave with wave number k has the form $e^{ik\cdot x}$. The value of Planck's constant is $\hbar \approx 6.6 \cdot 10^{-16}$ev $\cdot$ sec. Accelerating an electron through 100 volts gives a wavelength of about[1] $3\mathring{A}$, which is a typical crystal lattice spacing.[2]

Erwin Schrödinger formulated a partial differential equation (PDE) around the DeBroglie relation (1). The relation $p = mv$, $v = p/m = \hbar k/m$ may be viewed as a relation between the speed of a wave and its wave number. If you know the relation between the speed of a wave and it's wave number, you can guess the PDE through the concept of "group velocity", which I now explain. Suppose we have some medium in which a wave with wave number k oscillates in time with frequency ω. That means that there are solutions of the form

$$\psi(x,t) = e^{-i\omega t} e^{ik\cdot x} \; .$$

Here ω may be more or less any function of k. The minus sign in front of ωt makes most of the other signs come out plus. The group velocity is given by

$$v_g = \nabla_k \omega \; .$$

What moves with speed k is a "wave packet", see below. Note that k and x and v may be vectors. Schrödinger found part of his equation by asking what dispersion relation would give (1) and then what PDE would give that dispersion relation. First, (1) gives

$$\nabla_k \omega = \hbar k \; ,$$

which leads to

$$\omega = \frac{\hbar}{2m} k^2 \; . \tag{2}$$

We often write k^2 in place of $|k|^2$. The PDE with this dispersion relation is:

$$\partial_t \psi = \frac{-\hbar}{2m} \triangle \psi \; . \tag{3}$$

This is the Schrödinger equation for a "free" particle, a particle that does not feel any forces. According to classical mechanics, such a free particle would move in a straight line at constant speed. The quantum anologue is that k, ω, and the group velocity do not change with tine. The PDE (3) allows one to calculate several physical effects not immediately apparent in the dispersion relation (1) such as wave packet spreading, diffration, and interference.

Schrödinger guessed the general equation for a particle that feels forces using reasoning that I explain in slightly more modern language. We start an idea that became central in quantum mechanics, the relationship between "observable" quantities (position, momentum energy, ...) and operators having those quantities as eigenvalues. The function with pure wave number k is $e^{ik\cdot x}$. We want the operator, $\widehat{p}$, that produces the momentum as an eigenvalue:

$$\widehat{p} e^{ik\cdot x} = p e^{ik\cdot x} = \hbar k e^{ik\cdot x} \; .$$

[1] Å is for the Swedish physicist Ångsrtöm, pronounced Oh-ngstrom

[2] See the appendix to this lecture for information on units and orders of magnitude.

Here $\widehat{p}$ is an operator (or vector of operators) and p is a number (or vector). The natural choice (and probably the only truly possible choice) is

$$\widehat{p} = \frac{\hbar}{i} \bigtriangledown_x \ . \tag{4}$$

The energy of a free particle in classical mechanics is $mv^2/2 = \frac{p^2}{2m}$. Then we can guess that for a quantum free particle, the energy operator is

$$\widehat{H} = \frac{\widehat{p}^2}{2m} = -\frac{\hbar^2}{2m} \triangle \ .$$

Note that the free particle Schrödinger equation (3) may be written

$$i\hbar\partial_t\psi = \widehat{H}\psi \ . \tag{5}$$

In (5), $i\hbar\partial_t$ seems to play the role of energy in much the way $\frac{\hbar}{i}\partial_x = -i\hbar\partial_x$ plays the role of momentum. Note, however, the change of sign. This suggests the relation between the energy, e, of a particle and it's "frequency", ω:

$$e = \hbar\omega \ . \tag{6}$$

You should check that the right side has units ML^2/T^2 of energy. This relation was proposed by Max Planck in a somewhat different context. The e was a "quantum" (i.e. an amount) of energy and ω was the frequency of a classical harmonic oscillator. In (6), e is kinetic energy of a particle and ω is a quantum oscillation frequency that has no classical counterpart.

The relation (6) is so ingrained in physicists' thinking that energies are frequently reported as frequencies, for example in megaHertz. Often a quantum system such as an atom will go from one energy state to another by emmiting electromagnetic radiation. The frequency of the radiation, in terms of the energy difference, is given by $\hbar\omega = \Delta e$. For electromagnetic radiation there is a relation between frequency and wavelength, λ, given by the fact that such waves move at the speed of light, $c \approx 3 \times 10^8 m/sec$ (You can think of this as another group velocity.): $\lambda = 2\pi c/\omega$. In this way, energies or energy differences can be specified as wavelengths. For example, the Feynman Lectures (vol 3, page 9-2) discusses a Δe of $10^{-4} ev$ which corresponds to 2.4×10^{10} Hertz (cycles per second) and a wavelength of 1.25cm.

Schrödinger continued the anology with classical mechanics to guess a term to add to (5) when forces are acting on a particle. In classical mechanics, if the force on a particle at location x is the vector function $F(x)$, then the potential energy is the scalar function $V(x)$ with $F = -\bigtriangledown V$. The forces we study in elementary quantum mechanics have a potential energy function. The total energy is the sum of the kinetic and potential energies $H = \frac{p^2}{2m} + V(x)$. Conservation of energy in this case says that if $(x(t), p(t))$ is the position and momentum of the classical particle at time t, then $H(x(t), p(t))$ is independent of

t. The simplest classical conservation laws, conservation of energy, momentum, and angular momentum, have quantum anologues. The more exotic ones, such as the conserved quantities for the Toda lattice, do not seem to. H is for Hamilton, who developed the "Hamiltonian" formalism of classical mechanics, not to be confused with the hamiltonian operator of quantum mechanics.

So, we want to build an operator that represents $H = p^2/2m + V$. We have the kinetic energy part, $p^2/2m$. If we suppose the operator corresponding to $V(x)$ is multiplication by $V(x)$, we get

$$i\hbar\partial_t\psi = \frac{1}{2m}\widehat{p}^2\psi + V\psi = -\frac{\hbar^2}{2m}\triangle\psi + V\psi \; . \tag{7}$$

This is the equation Schrödinger proposed. It seems to be right!

2 The correspondence principle.

The correspondence principle refers to the relationship between quantum mechanics and classical mechanics. Historically, this has taken several forms. Today, the correspondence principle usually means that solutions of the Schrödinger equation behave like classical particles if the mass is large and we don't look too closely. I now sketch the "WKB" construction that does this. For most of the rest of the course, we will focus on ways classical and quantum mechanics are different. Solutions of the Schrödinger equation can a immitate classical particle by forming a *wave packet*, a function (or "state") that is reasonably localized in space and has a reasonably specific wave number (momentum). For the $100ev$ electron, if we have 100 wavelengths in the packet, then the size of the packet is about $3 \cdot 10^{-6}cm$, still much smaller than the components of a vacuum tube and hard to detect in a lab.

To say this mathematically, suppose we choose a length scale in which $k = O(1)$. Then we take initial initial data

$$\psi(x,0) = A(\epsilon x, 0)e^{ik\cdot x} \; .$$

We seek a solution approximately in the form

$$\psi(x,t) = A(\epsilon x, \epsilon t)e^{i(k\cdot x - \omega t)} \; .$$

If we insert this into the free Schrödinger equation (3) and calculate using the dispersion relation (2) we get

$$A_t + \frac{\hbar}{m}k\cdot\nabla A = O(\epsilon) \; .$$

If we ignore the small term on the right side the solution is

$$A(x,t) = A_0\left(x - \frac{\hbar k t}{m}\right) = A_0(x - vt) \quad \text{where } v = \frac{p}{m} = \text{classical particle velocity.}$$

The conclusion is that if there is no force ($V \equiv 0$), wave packets approximately move in a straight line with constant speed. The shape of the wave packet does not change.

This argument seems very simple. When we study electrons in crystals we will see dispersion relations more interesting than $v \sim k$ that lead to pretty exotic behavior.

Even when the force is not zero classical mechanics can come out of the evolution of wave packet solutions of the Schr"odinger equation. We can construct wave packet solutions if the crest to crest variation in the potential is small. We also need the crest to crest variation in the amplitude to be small as in the free particle case. These requirements are easier to fullfill for massive particles, since, for a given speed, the wavelength is inversely proportional to the mass. This construction is called *geometric optics* or the *WKB* approximation (Wentzel, Kramers, Br??, who adapted the geometric optics construction to quantum mechanics).

There are several other ways to under what is called "semiclassical" analysis – semiclassical because it gives classical mechanics and corrections to it. One is using the Wigner transform and is very recent. Another method uses the "Feynman integral". While the Feynman integral is not an integral in the formal mathematical sense, it does allow us to derive approximate solutions of the form (8) without guessing that ansatz. It also gives a physical meaning to the action function, S, see below.

We can let a presumed correspondence principle guide our construction of an approximate solution of the Schrödinger equation. For this general discussion we will take a different point of view in the scaling. Before we thought of the wavelength as $O(1)$ and the amplitude as slowly varying. Now we will think of the amplitude variation scale as $O(1)$ and the wavelength as very small. It turns out that a simple way to do this is to imagining $\hbar$ as a small parameter that goes to zero. The correspondence principle then says that "quantum mechanics goes to classical mechanics as $\hbar \to 0$. This is a bit unphysical since the actual value of $\hbar$ does not change.

Since we expect the momentum to change, quantum mechanics tells us that the wave number also must change. The first problem (and, as it turns out, the hardest), then, is to find a function that has a local wave number that varies from place to place. The WKB answer to this is

$$\psi(x) = e^{iS(x)/\hbar} .$$

This is seen by expanding $S(x)$ in a Taylor series about a point x_0:

$$S(x) = S(x_0) + \bigtriangledown S(x_0) \cdot (x - x_0) + O(|x - x_0|^2) .$$

Close to x_0, but not too close, $\bigtriangledown S(x_0) \cdot (x - x_0)/\hbar$ may be large while $O(|x - x_0|^2)/i\hbar$ is small. For example, if[3] $|x - x_0| = \hbar^{2/3}$ then $|(x - x_0)/\hbar| = \hbar^{-1/3}$, which goes

[3]This does not make dimensional sense because x and $\hbar^{2/3}$ have different units. It does make the mathematical point, however.

to infinity as $\hbar \to 0$, but the remainder term is $|x - x_0|^2 / \hbar = \hbar^{1/3}$ which goes to zero with $\hbar$. In this region, we have the approximation

$$\psi(x) \approx e^{S(x_0)/i\hbar} \cdot e^{ik\cdot(x-x_0)} ,$$

where $k = -\bigtriangledown S(x_0)/\hbar$. The approximation here is dropping the term $\exp(O(x - x_0)/\hbar))$, which is close to one. The conclusion is that, near x_0 but over many wave crests, the function ψ looks more or less like a simple plane wave with wave vector k. Using the basic relation $p = \hbar k$, the wave function ψ has momentum approximately $\bigtriangledown S(x_0)$ at x_0.

We need a wave function whose amplitude and momentum varies as a function of x and t. A natural ansatz for this is

$$\psi(x,t) = A(x,t) e^{iS(x,t)/\hbar} . \tag{8}$$

We calculate

$$\frac{\hbar}{i} \bigtriangledown \psi = \left(\bigtriangledown S \cdot A + \frac{\hbar}{i} \bigtriangledown A \right) e^{iS(x,t)/\hbar} , \tag{9}$$

which gives the approximate relation $p = \bigtriangledown S$ if $|\hbar \bigtriangledown A| << |A \bigtriangledown S|$. Putting (9) into (7) and calculating gives

$$\begin{aligned} -S_t A + i\hbar A_t &= \frac{|\bigtriangledown S|^2}{2m} A - \frac{i\hbar}{m} \bigtriangledown S \cdot \bigtriangledown A - \frac{i\hbar}{2m} \triangle S \cdot A \\ &- \frac{\hbar^2}{2m} \triangle A + VA . \end{aligned}$$

We can construct an approximate solution by collecting terms with a common power of $\hbar$. The largest terms are

$$-S_t = \frac{|\bigtriangledown S|^2}{2m} + V , \tag{10}$$

which is the *eikonal* equation. The terms proportional to $\hbar$ give

$$A_t + \frac{1}{m} \bigtriangledown S \cdot \bigtriangledown A + \frac{1}{2m} \triangle S \cdot A = 0 . \tag{11}$$

which is the *transport* equation.

We can construct solutions of (10) using classical mechanics (up to a point). This is called *Hamilton Jacobi* theory. The solution of (11) also uses classical mechanics and gives information on the physical meaning of ψ.

The classical equations of motion, Newton's law, $-\bigtriangledown V = F = ma = m\ddot{x}$ may be written as a pair of first order equations for x and $p = m\dot{x}$ as

$$\dot{x} = \frac{1}{m} p \tag{12}$$

and

$$\dot{p} = -\bigtriangledown V(x) . \tag{13}$$

We will worry about initial conditions soon, but first we show that with the formal association $p = \bigtriangledown S$, (10) is equivalent to (12) and (13). If we take (12) as the definition of $\dot{x}$, then we need to see whether $\dot{p} = \bigtriangledown V$ is consistent with (10). Differentiate (10) to get the evolution equation for $\bigtriangledown S$:

$$\begin{aligned}
-\partial_t S &= \frac{1}{2m}\sum_j \partial_{x_j} S \partial_{x_j} S + V \\
-\partial_t \partial_{x_k} &= \frac{1}{m}\sum_j \partial_{x_j} S \cdot \partial_{x_j} \partial_{x_k} S + \partial_{x_j} V
\end{aligned}$$

Now collect all terms involving S on the left and rewrite this in vector notation:

$$\partial_t \bigtriangledown S + \frac{1}{m} (\bigtriangledown S \cdot \bigtriangledown) \bigtriangledown S = - \bigtriangledown V \ .$$

The left side of this is exactly

$$\frac{d}{dt} \bigtriangledown S(x(t), t) \ ,$$

when $\dot{x} = \frac{1}{m} \bigtriangledown S$. With this, we construct S itself using

$$\begin{aligned}
\frac{d}{dt} S(x(t), t) &= \partial_t S + \dot{x} \cdot \bigtriangledown S \\
&= \partial_t S + \frac{1}{m} \left| \bigtriangledown S \right|^2 \ .
\end{aligned}$$

Substituting (10) then gives

$$\frac{d}{dt} S = \frac{1}{2m} \left| \bigtriangledown S \right|^2 + V(x) \ . \tag{14}$$

All these bits of algebra may be turned into a cookbook recipe for constructing S satisfying (10) with suitable initial conditions.

1. With initial data $S(x, 0)$, compute $p_0(x) = \bigtriangledown S(x, 0)$.

2. For each x_0, compute $x(x_0, t)$ by solving (12) and (13) from ODE initial data $x(0) = x_0$, $p(0) = p_0(x_0) = \bigtriangledown S(x_0, 0)$. These trajectories $(x(t), p(t))$ are called *rays*[4] in geometric optics.

3. For each ray, compute the values of S along $x(t)$ using (14).

4. For each (x, t), find x_0 with $x(x_0, t) = x$. This is possible for small enough t but probably will not be possible if t is too large.

[4]This is a bit of a misnomer. Normally, a ray would be the path of a beam of light in a possibly inhomogeneous medium. That would be a curve in three dimensional space. The object called a ray in WKB/geometric optics is a path in six dimensional space. Sometimes these paths are called "bicharacteristics" to remind us that we have doubled the dimension.

5. (As desired) Check that the $S(x,t)$ constructed this way satisfies the evolution equation (10) and the initial conditions.

We can solve the transport equation also with the help of rays. If we multiply (11) by A, we get

$$\frac{1}{2}\partial_t A^2 + \frac{1}{2m} \bigtriangledown S \cdot \bigtriangledown A^2 + \frac{1}{2m} \bigtriangleup S \cdot A^2 = 0 \ ,$$

or

$$\partial_t A^2 + \frac{1}{m} \bigtriangledown \cdot \left(\bigtriangledown S \cdot A^2 \right) = 0 \ . \tag{15}$$

Note that $|\psi|^2 = A^2$ (we supposed implicitly above that A is real.). Equation (15) is an equation for conservation of $|\psi|^2$, not ψ. This suggests that $|\psi|^2$ represents mass or probability density, which is conserved along particle trajectories. Note, the value of A^2 is not constant along trajectories. Rather, mass is carried along trajectories and also conserved. This forces the mass density, A^2, to increase if the rays compress space, for example.

3 Intpretation and Quantum interference

Implicit in the wave packet construction is the supposition that the size of ψ has to do with where the particle is. There are two ways (at least) to understand this relationship

1. The wave packet is the particle. Packets only look like particles because we don't look closely enough.

2. Particles are particles. $\psi(x,t)$ tells us how likely it is for the particle to be at x at time t. Actually, ψ is not real, let alone positive, but $\int |\psi(x,t)|^2 \, dx$ is independent of t and $|\psi(x,t)|^2$ is positive. This suggests (the Born interpretation) that $|\psi(x,t)|^2$ is the probability density for the electron to be at x at time t.

I believe 1 but almost everybody else chooses 2. This is discussed at some length in Feynmann. The two slit experiment (a gedanken, or thought, experiment since it is technically hard to actually do this) seems to support 2.

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4 Interacting particles and statistics

The term "statistics" refers to symmetries of the solution of the multibody Schrödinger equation under exchange of "identical" particles. The kinds of symmetry are called kinds of statistics because the distinction first came up in quantum statistical mechanics. This has nothing to do with statistics as in data collection and analysis.

First, what is the multibody Schrödinger equation? If we have two electrons whose positions might be $x \in R^3$ and $y \in R^3$ then $|\psi(x,y,t)|^2$ is the joint probability density for one to be at x and the other to be at y at time t. The potential energy, $V(x,y)$, may depend on the relative positions of the two particles. Classicly, the force on the x particle would be $\bigtriangledown_x V$ and the force on the y particle would be $\bigtriangledown_x V$. The particles interact if, for example, the force on the x particle depends on y. The total energy, or Hamiltonian, is the sum of the kinetic energies of the two particles and the potential energy:

$$H = \frac{1}{2m_x} p_x^2 + \frac{1}{2m_y} p_y^2 + V(x,y) \ .$$

For example, for two electrons about a fixed nucleus with charge +2 we have

$$V(x,y) = \frac{1}{|x-y|} - \frac{2}{|x|} - \frac{2}{|y|} \ ;$$

as the two electrons repel each other but are attracted to the nucleus. The Schrödinger operator corresponding to this has a kinetic energy part (assuming the masses are equal)

$$\frac{1}{2m}\widehat{p}_x^2 + \frac{1}{2m}\widehat{p}_y^2 = \frac{\hbar^2}{2m}\left(\triangle_x + \triangle_y\right) = \frac{\hbar^2}{2m} \triangle \ .$$

Therefore, the evolution equation is

$$i\hbar \partial_t \psi = -\frac{\hbar^2}{2m} \triangle_x \psi - \frac{\hbar^2}{2m} \triangle_y \psi + \left(\frac{1}{|x-y|} - \frac{2}{|x|} - \frac{2}{|y|} \right) \psi \ . \qquad (16)$$

What makes the physics of electrons hard is that there are many particles interacting. (elaborate) While solving (16) is not a challenge in the 21^{st} century, an accurate first principles method for 10 interacting electrons has yet to be found.

A mathematician might think that with the formulation of the Schrödinger equation and its interpretation the physics is over and only the solution (math) remains. On the contrary, the formulation is not complete: we need to introduce electron spin, the theory of observation, and, right now, *statistics*. As we will see later, much of the "solution" of the Schrödinger equation is really physically or experimentally motivated heuristics. We can not, for example, explain superconductivity starting with the n body Schrödinger equation even though we have a reasonable heuristic picture, the BCS theory, of how it works.

"Statistics", or exchange symmetry, arises from the symmetry of multi body Schrödinger equations such as (16) with respect to exchange of x and y variables. Physically, this represents the hypothesis that electrons are indistinguishable, that is makes no sense to say "electron A is at x and electron B is at y". It is impossible to attach labels to electrons. If two electrons to in to an interaction and two come out, there is no way to say which of the outcoming electrons was which of the ingoing electrons. Mathematically, that says that not only the equation is invariant under particle exchange, but also the probability density is:

$$|\psi(x,y,t)|^2 = |\psi(y,x,t)|^2 \; .$$

The most obvious way to make this happen is to require that

$$\psi(x,y,t) = \psi(y,x,t) \; . \tag{17}$$

Another way is

$$\psi(x,y,t) = -\psi(y,x,t) \; . \tag{18}$$

If the wave function satisfies (17) then the particles are called bosons and are said to satisfy Bose Einstein statistics. If the wave function is skew symmetric (18) then the particles are fermions and satisfy Fermi Dirac statistics. It is a deep rule of physics (that I don't understand and can't explain) that particles with integer spin (photons being the most important for us) are bosons while particles with half integer spin (electrons, protons, etc.) are fermions. The mathematicians' definition of indistinguishable probably should be that the evolution equation preserves the potential symmetries of the wave function. By this definition, particles with different masses or different electrical charge (or spin) would not be indistinguishable, duh!

This discussion goes over to systems of n indistinguishable particles. The wave function will be $\psi(x_1,\ldots,x_n)$, where $x_j \in R^3$ is the location of the j^{th} particle. will be either symmetric or skew symmetric under exchange of coordintes.

5 Appendix: units and orders of magnitude

A hydrogen atom as about 1Å= 10^{-10}meters across. The distance between atoms in a molecule is also on the order of 1 or 2 Å. A molecule with several atoms might be $10\AA = 10^{-9}$meters = 1 nm (nanometer). Machines built of individual atoms are called "nanoscale". The wave length of visible light is at least 1000nm $= 1\mu = 10^{-6}M$. An atom or small molecule is tiny by comparison.

The electron volt, ev, is a natural energy scale for atomic physics. Another unit is the Rydberg: $1 \; Rd \approx 27 \; ev$. An ev is the amount of energy gotten by moving an electron (or proton) through one volt of electric potential. Start withthe work formula

$$\text{Work} = \text{Force} \times \text{distance} \; .$$

In an electric field, the force is proportional to the electric field strength (measured, say, in volts/meter) and the charge of the particle

$$\text{force} = \text{field strength} \times \text{charge} \; .$$

The charge of an electron or proton is called e. Actually, the electron charge is -1 since it is negative by convention. A field pushes an electron and a proton in opposite directions. The charge e was first measured by Milliken in the famous oil drop experiment. A 100 volt potential difference between two electric plates one cm apart out produce a 10^4 volts/meter electric field between the plates. Moving an electron through one volt (i.e. $10^{-4}M = 100\mu$) corresponds to one ev of work, or energy.

The "ground state" energy needed to remove the electron from a hydrogen atom is (almost) exactly half a Rydberg (this is the definition of the Ry), which is about 13 ev. The ground state energy for a carbon atom (C), which has 6 electrons, is about 1000 ev. The energy required to remove a single electron from C (go from 6 to 5) is about 11 ev. The "electron affinity" of C (the energy gained by adding a seventh electron) is about 1 ev. Thus, if we calculate the electron affinity of C by computing the energy of the 6 and 7 electron system and subtracting, we need the ground state energy accurate to one part in 1000 at least. The chemical properties of atoms are determined by energy differences this size or smaller. In computational quantum mechanics, achieving "chemical accuracy" is an outstanding challenge.

Planck's constant, $\hbar$, has units of action, which is energy $\times$ time. We use the notation $[x]$ to mean "the units of x". We also use L, T, M, to represent length, time, and mass respectively. The units operation commutes with multiplication: $[xy] = [x][y]$, and $[ax] = [x]$ if a is a "pure" number. For example, for momentum, p, we have $[p] = [mv] = [m][v] = ML/T$. From the deBroglie relation we find $[p] = [\hbar][k]$. We know that $[k] = 1/L$ because xk is dimensionless, which is because of the expression e^{ikx}, which would not make sense unless the exponent were dimensionless. This gives

$$[\hbar] = ML^2/T = ML^2/T^2 \cdot T = ET ,$$

where $E = ML^2/T^2$ is the unit of energy (recall energy $= mv^2/2$). It happens that the units of action are the same as those of angular momentum, $\omega = p \times r$ (This is the angular momentum of a single particle moving with momentum p and displacement r from some point. ω us the angular momentum of the particle about that point. Both p and r are vectors, so ω is also. To find the angular momentum of an extended body, you have to integrate. The units of angular momentum are

$$[\omega] = [p]L = ML^2/T = [\hbar] .$$

It is common that angular momentum is quantized in multiples of $\hbar$.

6 Problems

1. What energy, in electron volts, corresponds to visible light with a wavelength of 1μ? If a carbon atom gives off light of that wavelength through a transition with that Δe, what fraction of the ground state energy was that?

2. In sepcial relativity, the energy of a particle with mass (often called "rest mass") m and momentum p is given by

$$e^2 = c^2p^2 + m^2c^4 .$$

This reduces to $e = mc^2$ for a particle at rest. From this and the basic Planck and DeBroglie relations $e = \hbar\omega$ and $p = \hbar k$, find a PDE involving $\partial_t \psi$ and $\triangle \psi$ for a particle with no force on it. This is the Klein Gordon equation.

3. What fraction of the speed of light is a 1000 ev electron traveling? The (rest) mass of an electron is $9.1 \cdot 10^{-26}$ grams. Although this has nothing to so with quantum mechanics, it is good to keep in mind for atomic physics later.

4. Suppose $\widehat{H}$ is any self adjoint operator:

$$\left\langle \widehat{H}\psi \mid \psi \right\rangle = \left\langle \psi \mid \widehat{H}\psi \right\rangle = \left\langle \psi \mid \widehat{H} \mid \psi \right\rangle \quad \text{Def'n of last term.}),$$

and that $i\hbar\partial_t \psi = \widehat{H}\psi$.

i. Show that $\partial_t \langle \psi \mid \psi \rangle = 0$. This is called "conservation of mass" in QM because . . .

ii. Show that $\partial_t \left\langle \psi \mid \widehat{H} \mid \psi \right\rangle = 0$. This is conservation of energy.

5. If $x \in R^3$ and $y \in R^3$ are locations of two particles, and the potential depends only on the distance between the particles, show that $\partial_t \langle \psi \mid \widehat{p}_{\text{tot}}\psi \rangle = 0$. Here $\widehat{p}_{\text{tot}} = \widehat{p}_x + \widehat{p}_y$ is the total momentum operator. This is true even when the masses of the particles are different. This is conservation of momentum in QM.

6. For this problem, suppose particles move in one dimension. Take $V(x) = -\frac{1}{2}x^2$ and work through the WKB approximation with initial data $\psi(x,0) = e^{ikx/\hbar}$. Find the rays and use them to construct S and A. After the fact, you can check directly that a quadratic function of x for each t, $S(x,t) = a(t)x^2 + b(t)x + c(t)$ works. Is this an exact solution? If not, can you find the exact solution with a similar ansatz?

7. For a function $f(x)$ we have the Fourier transform given by

$$\widehat{f}(k) = \mathcal{F}[f(x)](k) = \frac{1}{(2\pi)^{d/2}} \int e^{-ik\cdot x} f(x)dx \ .$$

If the function f is not in L^1, we may attempt to define

$$\widehat{f}(k) = \lim_{\epsilon \to 0} \mathcal{F}[f(x)e^{-\epsilon x^2/2}](k) \ . \tag{19}$$

i. Show that if f and $\widehat{f}$ are both bounded, then $\widehat{f}$ may be defined by a formula almost identical to (19). You may need to review the properties of the ordinary Fourier transform to do this, but take these properties for granted.

ii. Work in one dimension. Compute $\widehat{f}$ when $f(x) = e^{i\alpha x^2/2}$ for a real α. Be careful to identify $\sqrt{i} = e^{i\pi/4}$ or $\sqrt{i} = -e^{i\pi/4}$ depending on the sign of α.

iii. If ψ satisfies the free Schrödinger equation (3) with $\psi(x, 0) = \delta(x)$, find $\widehat{\psi}(k, t)$ by taking the Fourier transform of (3) and using part ii above. This is $G(x, t)$, the free Schrödinger Green's function (or "propagator", or "fundamental solution").

iv. If we solve (3) with initial data $\psi(x, 0) = f(x)$ having compact support and being smooth, show taht $\psi(x, t) = \int G(x - y, t) f(y) dy$.

v. Show that if fx) has compact support, even though it may not be smooth, $\psi(x, t)$ is an analytic function of x for any $t \neq 0$. Note that positive and negative t are both possible. Mathematicians call this dispersive regularization, and it is very useful in mathematical studies of nonlinear Schrödinger equations.