Notes for Lecture 3

Atoms, Molecules

3.1 Hydrogen Atom, continued

By solving

$$m\frac{v^2}{r} = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r^2} \tag{3.1}$$

and

$$mvr = n\hbar, \quad n = 1, 2, 3, \cdots \tag{3.2}$$

together, we can get "orbit quantization" and energy quantization, the latter of which is exact even in the full-blown quantum mechanics. First, we multiply the first equation by r and get

$$mv^2 = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r} \tag{3.3}$$

This is an important result, actually. It says

$$2T = -V \tag{3.4}$$

where $T = \frac{mv^2}{2}$ is the kinetic energy, and $V = -\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}$ is the potential energy.

Multiplying Eq. 3.3 by r^2, we get

$$\begin{aligned} mv^2r^2 &= \frac{1}{4\pi\varepsilon_0}e^2 r \\ (mvr)^2 &= \frac{me^2}{4\pi\varepsilon_0} r \\ n^2\hbar^2 &= \frac{me^2}{4\pi\varepsilon_0} r && \text{Use Eq. 3.2} \\ r &= \frac{4\pi\varepsilon_0\hbar^2}{me^2} n^2 \\ &= \frac{\hbar}{mc}\frac{4\pi\varepsilon_0\hbar c}{e^2} n^2 = \frac{\hbar}{mc}\frac{1}{\alpha} n^2 \end{aligned}$$

This means that the radius is quantized in the Bohr picture!

$$r_n = a_B n^2 \tag{3.5}$$

In the last step, the "Bohr radius" a_B is defined as

$$a_B = \frac{\hbar}{mc}\frac{1}{\alpha} = 0.529\text{Å} \tag{3.6}$$

where $\frac{\hbar}{mc}$ is the Compton wavelength of the electron and

$$\alpha = \frac{e^2}{4\pi\varepsilon_0\hbar c} = \frac{1}{137.0} \tag{3.7}$$

is the so-called "fine structure constant," which is a very important dimensionless number in all quantum mechanics.

Eq. 3.5 leads to the energy quantization. Note that, from Eq. 3.4, the total energy $E = T + V = -V/2 + V = V/2$. Thus,

$$\begin{aligned} E_n &= -\frac{1}{2}\cdot\frac{e^2}{4\pi\varepsilon_0}\cdot\frac{1}{r_n} \\ &= -\frac{1}{2}\cdot\frac{e^2}{4\pi\varepsilon_0}\cdot\frac{mc}{\hbar}\alpha\frac{1}{n^2} \\ &= -\frac{mc^2}{2}\alpha^2\frac{1}{n^2} \end{aligned}$$

which leads to

$$E_n = -\frac{R}{n^2} \tag{3.8}$$

where the Rydberg constant $R \equiv \frac{mc^2}{2}\alpha^2 = 13.6$ eV.

This is the grand result of Bohr's atomic theory!

3.2 Hydrogen Molecule

Let us consider the simplest case of the hydrogen molecule, a classic example of a covalently bonded molecule. It is the case of a sharing of two electrons between two protons, thereby lowering the total energy.

Before we attack the molecule problem, we first consider H_2^+, i.e. the problem of two protons and one electron.

It is helpful to think of this from the elementary "tunneling" point of view. Suppose there is an electron in a potential well. Suppose there is another potential well, identical in shape, but centered at a different position, and unoccupied by any electron. When these two wells are far from each other, these two wells are separate, and that is that. The electron in well simply stays there, and the other remains empty. However, if these two potential wells are brought together close to each other, things change in quantum mechanics. The electron will be able to tunnel to the other well, through the potential barrier. This is a quantum effect. Now, if you wait long (compared to the atomic time scale – which is very short!), then the electron will have tunneled through the barrier many many times. Eventually it will settle down to the new ground state (by emitting extra energy by light), and that ground state will be a symmetric state. See the activity slides ("A" is the symmetric state, while "B" is the anti-symmetric state).

We wish to do some math to see this clearly in the case of H_2^+. Before doing that, some mathematical review of quantum mechanics seems helpful.

3.2.1 Schrödinger equation and wave function

For simplicity, we will consider a one dimensional problem only. To go from one dimension to three dimensions use this substitution table: $dx \to dV$ and $\partial/\partial x \to \vec{\nabla}$.

In this note, we also consider a fixed time only. However, I will use the notation $\partial/\partial x$ in preference to d/dx, in anticipation of a generalization to the time dependent case. This is my habit. If you like, you can mentally change all $\partial/\partial x$ to d/dx, and you'll be OK.

$\psi(x)$ is the notation that we use for the wave function at a fixed time. The (time-independent) Schrödinger equation reads

$$H\psi(x) = E\psi(x) \tag{3.9}$$

$$(T+V)\psi(x) = E\psi(x) \tag{3.10}$$

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\psi(x) = E\psi(x) \tag{3.11}$$

Here, H, T, and V are the Hamiltonian operator, the kinetic energy operator, and the potential energy operator. In QM, these things are called operators, since they act on a wave function, e.g. ψ. The above equation is called an *eigenvalue equation* in the mathematical language. The eigenvalue of the Hamiltonian operator is E. The eigenfunction (or the "eigenvector") corresponds to $\psi(x)$. Much of QM is to solve for E and its corresponding eigenfunction $\psi(x)$.

The meaning of the wave function, e.g. ψ, is the probability amplitude. What this means is that

$$P(x) = \psi(x)^*\psi(x) = |\psi(x)|^2$$

gives the probability distribution function. This means that

$$P(x)dx$$

gives the probability that the particle will be found between x and $x + dx$. For a stable particle (like an electron with not too high an energy), the particle should not just disappear or appear suddenly. This means that the total probability that an existing particle will be found somewhere must be 1. This gives the so-called **wave function normalization** condition.

$$\int_{-\infty}^{\infty} dx\psi(x)^*\psi(x) = 1 \tag{3.12}$$

This is a condition that should be satisfied by any physical wave function at any time!

Another physically plausible condition is that

$$\psi(x \to \pm\infty) = 0 \tag{3.13}$$

This means that the particle is confined in a finite space. This is a very reasonable condition, but it can be relaxed for some special eigenfunctions, for the mathematical convenience, as you will learn in QM. However, the physics is quite clear, and so, in this note, we will assume the above condition.

The concept of the **expectation value** is important. If you measure the kinetic energy of a particle many times, then the average of those measurement will converge to the expectation value of the kinetic energy

$$\langle T \rangle = \int_{-\infty}^{\infty} dx \psi^* T \psi$$
$$= \int_{-\infty}^{\infty} dx \psi^* \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \right) \psi$$

Integrating by parts, and using Eq. 3.13, we get

$$\langle T \rangle = \frac{\hbar^2}{2m} \int_{-\infty}^{\infty} dx \left| \frac{\partial \psi}{\partial x} \right|^2 \tag{3.14}$$

So, the greater the magnitude of the slope of the wave function is, the greater the kinetic energy will be.

The expectation value of the potential energy is given by

$$\langle V \rangle = \int_{-\infty}^{\infty} dx \psi^* V(x) \psi \tag{3.15}$$

In general, for *any* operator, O, its expectation value is given by $\int_{-\infty}^{\infty} dx \psi^* O \psi$.

Finally, note, from Eqs. 3.9, 3.10,3.12,

$$E = \langle H \rangle \tag{3.16}$$
$$= \langle T \rangle + \langle V \rangle \tag{3.17}$$

Please review the activity slides, with these last four equations in mind.