371(6): Wavefunctions of Atoms from a Lagrange Method

First consider non-relativistic quantum mechanics in which the classical hamiltonian is:

$$H = \frac{1}{2}mv^2 + U \quad -(1)$$

and the classical lagrangian is:

$$\mathcal{L} = \frac{1}{2}mv^2 - U \quad -(2)$$

In order to simplify the problem use plane polar coordinates (r, ϕ) and consider the attraction of an electron to a proton in a plane. The Coulomb potential is:

$$U = -\frac{e^2}{4\pi\epsilon_0 r} \quad -(3)$$

and

$$v^2 = \dot{r}^2 + r^2\dot{\phi}^2 \quad -(4)$$

The proper Lagrange variables are r and ϕ, and the Euler Lagrange equations are:

$$\frac{\partial\mathcal{L}}{\partial r} = \frac{d}{dt}\left(\frac{\partial\mathcal{L}}{\partial\dot{r}}\right) \quad -(5)$$

and

$$\frac{\partial\mathcal{L}}{\partial\phi} = \frac{d}{dt}\left(\frac{\partial\mathcal{L}}{\partial\dot{\phi}}\right) \quad -(6)$$

i.e

$$m\left(\ddot{r} - r\dot{\phi}^2\right) = -\frac{\partial U}{\partial r} = -\frac{e^2}{4\pi\epsilon_0 r^2} \quad -(7)$$

and

$$\dot{\phi} = \frac{L}{mr^2} \quad -(8)$$

where the angular momentum L is a constant of motion.

The ~~s~~ two equations (7) and (8) give the differential equation:

$$m\left(\ddot{r} - \frac{L^2}{m^2 r^3}\right) = -\frac{e^2}{4\pi\epsilon_0 r^2} \quad - (9)$$

i.e.

$$m\ddot{r} = \frac{L^2}{mr^3} - \frac{e^2}{4\pi\epsilon_0 r^2} \quad - (10)$$

This can be solved for $\dot{r}(t)$ and $r(t)$ using Maxima. In orbital theory in a plane, eq. (10) is the Leibniz equation:

$$m\ddot{r} = \frac{L^2}{mr^3} - \frac{mMG}{r^2} \quad - (11)$$

Here:

$$F_c = \frac{L^2}{mr^3} \quad - (12)$$

is the centrifugal force.

In both cases the orbit is a conic section:

$$r = \frac{\alpha}{1 + \epsilon\cos\phi} \quad - (13)$$

The square of the momentum is:

$$p^2 = m^2\dot{r}^2 + \frac{L^2}{r^2} \quad - (14)$$

where $\dot{r}$ and r are known from eq. (10). The quantization of the classical orbit (13) to a quantum orbital takes place through:

$$-i\hbar^2\nabla^2\phi = p^2\phi \quad - (15)$$

) In plane polar coordinates:

$$\nabla^2 \phi = \frac{\partial^2 \phi}{\partial r^2} + \frac{1}{r}\frac{\partial \phi}{\partial r} + \frac{1}{r^2}\frac{\partial^2 \phi}{\partial \phi^2} \quad -(16)$$

So the orbital wavefunctions ϕ of this idealized atom are given by:

$$\frac{\partial^2 \phi}{\partial r^2} + \frac{1}{r}\frac{\partial \phi}{\partial r} + \frac{1}{r^2}\frac{\partial^2 \phi}{\partial \phi^2} = \left(m^2 \frac{\partial r}{\partial t} + \frac{L^2}{r^2} \right) \phi \quad -(17)$$

in which:

$$r = \frac{\alpha}{1 + \epsilon \cos \phi} \quad -(18)$$

Eqs. (17) and (18) can be solved simultaneously for $\phi(r)$ and $\phi(\phi)$.

The advantage of this method is that it can be extended to three dimensions, and the wavefunctions of the H atom found. It can also be used to solve the Dirac equation in a new way. This will be the subject of future notes.
