Physics 200-04

Periodic Table

One of the successes of the old quantum theory was an explanation of the periodic table.

Bohr, in his original deriviation of the energy levels of the H atom used just the circular orbits in deriving the energy levels

$$E = \frac{mZ^2e^4}{8\epsilon_0^2 h^2} \frac{1}{n^2} \tag{1}$$

but it was clear that the classical system had more degrees of freedom than that. In particular the classical system could have a variety of angular momenta for each energy. The electron could circle the central atom in circular and in elliptic orbits. (Just as with the planets, the electron would circle the central nucleus with the nucleus at one of the foci of the ellipse.) Sommerfeld thus postulated that there was a separate quantization condition for each degree of freedom, which he took to be the radial motion and the angular motion.

Thus we can write the three conditions as

$$n_1 h = \int p_r \dot{r} dt$$
$$n_2 h = \int p_\theta r \dot{\theta} dt$$
$$n_3 h = \int p_\phi r \sin(\theta) \dot{\phi} dt \tag{2}$$

where p_r, p_θ, and p_ϕ are the components of the ordinary momentum $m\vec{v}$ in the directions r, θ, ϕ. The terms $\dot{r}$, $r\dot{\theta}$, and $r\sin(\theta)\dot{\phi}$ the velocity of the particle in those directions.(The dot over an expression means the time derivative of that expression).

Now,

$$\int p_\theta r\dot{\theta} + p_\phi r \sin(\theta)\dot{\phi} dt = \int m v_\theta^2 + m v_\phi^2 dt. \tag{3}$$

But the term on the right hand side is invariant under a rotation of the whole system. Thus, in order to find the energy, we can always rotate the whole system, so that the orbit lies entirely in the x-y plane, and such that $\dot{\tilde{\theta}}$ is zero.

Ie, we can solve the equations for the orbit in the x-y plane, and then afterwards rotate back into the frame in which the orbit is inclined to the x-y plane.

For an orbit in the x-y plane only we then have the single quantization condition

$$(n_2 + n_3)h = \int p_\phi r \dot{\tilde{\phi}} dt \tag{4}$$

where $\tilde{\phi}$ is the angle ϕ in the new rotated coordinates.

We can thus assume that we are looking at the orbit lying in the x-y plane. We can now write two quantization conditions– one refering to motion in the angular direction, and one in the radial direction.

$$n_1 h = \int p_r \dot{r} dt$$
$$(n_2 + n_3)h = \int p_{\tilde{\phi}} r \dot{\tilde{\phi}} dt \tag{5}$$

In this case n_1 can go from 0 (if the orbit is circular, and there is no radial motion). However $n_2 + n_3$ can only go from 1, since it makes no sense to think about an orbit with zero angular momentum– it would go right through the central nucleus.

There exists a so called Virial theorem for any power law central potential. The simplest way to see this is to write Newton's law second law as

$$m \frac{d^2 \vec{r}}{dt^2} = -\vec{\nabla} V(r) \tag{6}$$

where $\vec{\nabla}$ is the gradient of the central force potential which depends only on the distance r from the center. Take the dot product of both sides with $\vec{r}$ and average over an orbit, remembering that

$$\vec{\nabla} V(r) = \frac{dV(r)}{dr} \frac{\vec{r}}{r} \tag{7}$$

(ie the force only has a component in the r direction) Thus we have

$$\int m \frac{d^2 \vec{r}}{dt^2} \cdot \vec{r} dt = -\int \frac{dV(r)}{dr} \frac{\vec{r}}{r} \cdot \vec{r} dt \tag{8}$$

Now,

$$\frac{d^2\vec{r}}{dt^2} \cdot \vec{r} = \frac{d}{dt}\left(\frac{d\vec{r}}{dt} \cdot \vec{r}\right) - \frac{d\vec{r}}{dt} \cdot \frac{d\vec{r}}{dt} \tag{9}$$

and thus the left hand side becomes

$$\frac{d\vec{r}}{dt} \cdot \vec{r}\Big|_0^T - \int_0^T mv^2 dt = -\int r\frac{dV(r)}{dr}dt \tag{10}$$

If we take T to be one period, then the first term is zero since in the periodic orbit all the terms repeat themselves after time T. Thus the average value of twice the kinetic energy equals the average value of $r\frac{dV}{dr}$. If V is a power law potential, $V = Ar^\alpha$ then $r\frac{dV}{dr} = \alpha V(r)$. Thus for any power law potential the average kinetic energy is $\frac{\alpha}{2}$ times the average potential energy. For the charge or the gravitational case, $\alpha = -1$, so the average potential energy is minus twice the kinetic energy. Ie, the total energy (potential plus kinetic energy) is the average of minus the kinetic energy.

The total energy is

$$E = KE + PE \tag{11}$$

so for the Coulomb problem,

$$E = KE + PE = KE - 2KE = -KE = -\frac{1}{2}(m\dot{r}^2 + mr^2\dot{\theta}^2) = -\frac{1}{2}(p_r\dot{r} + p_\theta\dot{\theta})(12)$$

Integrating over one period, we have

$$ET = \frac{1}{2}(n_1 + n_2 + n_3)h \tag{13}$$

where T is one period, since the terms on the right are just the sum of the two actions.

We now need to figure out what T is in terms of the properties of the orbit. It turns out that T depends only on the energy$E$.

To find T takes a bit more work. The angular momentum $r^2\frac{d\tilde{\phi}}{dt}$ is just twice the rate of change of the area of the orbit times the mass. (see fig 1). (The area of the small triangle is $\frac{1}{2}base\ x\ height = \frac{1}{2}r\frac{d\theta}{dt}\delta t\ r$ This means that the area of the ellipse , which is $\frac{\pi ab}{4}$ where a is the length of the major axis

and b is the minor axis, is twice the integral of the angular momentum over the period. However the equation of motion of the particle so that

$$\frac{d}{dt}(r^2\frac{d\tilde{\phi}}{dt} = 0 \tag{14}$$

Since the angular momentum is conserved, it is the same over time, so we have

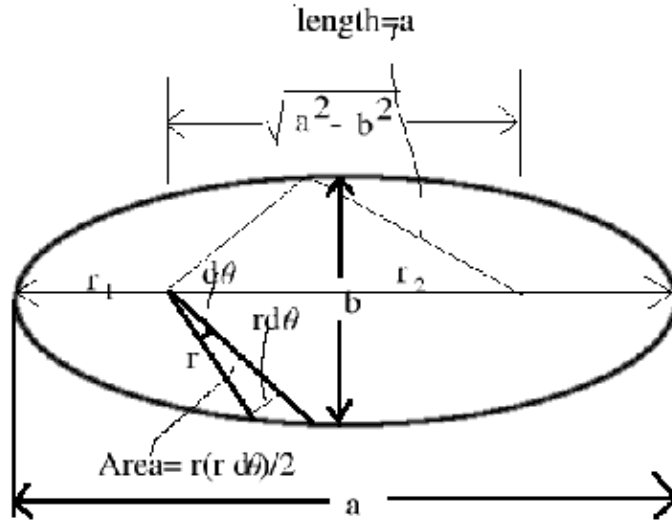$$p_\theta T = m\pi\frac{ab}{2} \tag{15}$$

Figure 1: The definition of various quantities for an ellipse. The nucleus of the atom is assumed to be at the left focus of the ellipse.

Finally, we can use the fact that the nucleus is at the focus of the ellipse, and we can use that, at the closest approach and furthest approach to the

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center, the radial velocity is zero. Since the angular momentum is $mr^2\dot{\theta} = p_\theta$, we have that $\dot{\theta} = \frac{p_\theta}{r^2}$. At the closest approach to the sun, we have

$$
\begin{aligned}
E &= \frac{1}{2}(p_\theta\dot{\theta} - \frac{Ze^2}{4\pi\epsilon_0 r} \\
&= \frac{1}{2}\frac{p_\theta^2}{mr^2} - \frac{Ze^2}{4\pi\epsilon_0 r}
\end{aligned}
\tag{16}
$$

Solving this equation for the two values of r (closest and most distant approach), r_1 and r_2, and adding them to get the semi-major axis, we have

$$
a = \frac{Ze^2}{4\pi\epsilon_0 E}
\tag{17}
$$

or

$$
E = \frac{Ze^2}{4\pi\epsilon_0 a}
\tag{18}
$$

Ie, the total energy depends only on a the major axis of the ellipse.

Finally using the fact that for an ellipse, the length of the string from one focus to the ellipse and then to the other focus is always constant, and is thus equal to a, we find that the difference between the two solutions for r, which is just the distance between the two foci, is equal to $\sqrt{a^2 + b^2}$.

$$
r1 - r2 = \sqrt{\left(\frac{Ze^2}{4\epsilon_0 E}\right)^2 + 4\frac{p_\theta^2}{2m^2 E}}
\tag{19}
$$

from which we immediately read off that

$$
b = \frac{p_\theta}{m\sqrt{E/2}}
\tag{20}
$$

Thus

$$
T = \pi\frac{ab}{p_\theta} = \pi\frac{Ze^2}{4\pi\epsilon_0 E}\frac{1}{\sqrt{E/2}}
\tag{21}
$$

and

$$
ET = \frac{Ze^2}{4\epsilon_0\sqrt{E/2}} = (n_1 + n_2 + n3)h
\tag{22}
$$

Thus the energy depends only on $n = n_1 + n_2 + n_3$ and this is the n in Bohr's formula. Usually $n_2 + n_3$ is called $l + 1$ so that l goes from 0 to n-1.

Since the major axis is the same for a given n, for large n but low l, the radial quantum number n_1 is large. which means that the orbit has a large change in r during the orbit. Ie, the orbit is elliptical and the electron spends more time near the central charge. Because the central charge is screened by the other electrons when the electron under consideration is far away, the energy of the high l states for a given n is higher than for low l. (the greater positive charge seen by the electron which comes nearer the nucleus binds it more tightly making the energy lower.)

It was found experimentally by putting the atom into a magnetic field (Zeeman effect) that each of the states with quanum number l had 2(2l+1) substates. This could be understood if we assume that n_3 has values from 0 to $n_2 - 1 = l$ only, and that for each value except $n_3 = 0$, the electron could orbit in two directions– clockwise or counterclockwise as seen from above. Ie, for each non-zero value there were 2 states and for zero only 1. However, there seemed to be two extra states for each of the above values. of n_1, n_2 and $m = \pm n_3$

This "explains" the periodic table. Using the Pauli exclusion principle, one would expect to fill the lower n befor higher, and the lower l before the higher. Thus, first n=1 l=0, then n=2 l=0, then n=2 l=1, then n=3 l=0, n=3 l=1. However, because of their plunging closer to the nucleus the n=3 l=2 have a higher energy than the n=4 l=0 and n=4 l=1. Thus the order essentially is

$$
\begin{array}{cc}
n & l \\
1 & 0 \\
2 & 0 \\
2 & 1 \\
3 & 0 \\
3 & 1 \\
4 & 0 \\
4 & 1 \\
3 & 2 \\
5 & 0 \\
4 & 2
\end{array}
\tag{23}
$$

5	1
6	0
4	3
5	2
6	1
7	1
5	3
6	2
7	2

Actually one of the l=2 electrons sneaks in befor the l=3 shell fills up for the higher n states.

Suddenly one could see reason in the periodic table– reasons why various of the elements had such similar chemical properties. (eg, C and Si are very similar, and this is because they occur at the same filling of an l=2 shell, only in one case with n=2 and the other with n=3.)

In the periodic table accompanying this, the small numbers under the element name refer to the principle quantum number (the first number) the l quantum number (with s meaning l=0, p meaning l=1, d meaning l=2 and f meaning l=3. These have historical significance s=sharp, p=principle, d=diffuse)