Single Electron Atoms

In this section we study the spectrum and wave functions of single electron atoms. These are hydrogen, singly ionized He, doubly ionized Li, etc. We will write the formulae for hydrogen only. To change to one of the other cases, replace e^2 by Ze^2, where Z is the charge on the nucleus. A single electron atom involves two particles, the electron and the nucleus. In all the formulae that follow, the mass m that appears is the *reduced mass* of the electron given by

$$m = \frac{m_e m_Z}{m_e + m_Z},$$

where m_e and m_Z are the actual masses of electron and nucleus. For the case of hydrogen the reduced mass m is $= .98 m_e$.

Writing the Schrödinger equation for an energy eigenstate in hydrogen we have

$$\left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r}\right)\Psi = E\Psi,$$

where the system of electromagnetic units is Gaussian. In these units, the formula for the electric potential is

$$\phi(r) = \frac{q}{r},$$

where as usual

$$\vec{E} = -\vec{\nabla}\phi.$$

Gauss's Law in these units is

$$\vec{\nabla}\cdot\vec{E} = 4\pi\rho(\vec{x}).$$

The Coulomb potential is central, so angular momentum is conserved and we can write the wave function as

$$\Psi = R(r)Y_{lm}(\theta,\phi)$$

The Schrödinger for the radial wave function becomes

$$\left(-\frac{\hbar^2}{2m}(\partial_r^2 + \frac{2}{r}\partial_r) + \frac{\hbar^2}{2mr^2}l(l+1) - \frac{e^2}{r}\right)R = ER.$$

There is a natural length in the problem given by the Bohr radius,

$$a_0 = \frac{\hbar^2}{me^2}.$$

It is convenient to measure quantities in what are called *atomic units*. These are defined by

$$r = r' a_0 \;\; E = E' \frac{e^2}{a_0}.$$

Now dropping the $'$ the radial Schrödinger equation becomes

$$(\partial_r^2 + \frac{2}{r}\partial_r - \frac{l(l+1)}{r^2} + 2(E + \frac{1}{r})R = 0 \tag{1}$$

It is easy to see that R must fall exponentially at large r. Trying this form at all r, we set

$$R = e^{-\beta r}.$$

Substituting in Eq.(1), we obtain

$$(\beta^2 - \frac{2}{r}\beta + 2(E + \frac{1}{r}))e^{-\beta r} = 0$$

Matching powers, we have

$$E = -\frac{\beta^2}{2}, \quad \beta = 1,$$

so this does give a solution. Since this wave function has no zeroes, it must be the ground state. In ordinary units we have (up to a normalization constant),

$$R = \exp(-\frac{r}{a_0}), \quad E = -\frac{e^2}{2a_0}$$

For solutions with $l > 0$, we must supply a power of r as $r \to 0$,

$$l \neq 0, \quad R \to r^l, \quad r \to 0$$

The general form of the radial wave functions is a polynomial in r multiplied by an exponential.

$$P(r)e^{-\beta r}$$

It is a remarkable fact for a Coulomb potential, that the energy depends only on the order of the polynomial $P(r)$. If the order of the polynomial is k, the Bohr formula for the energy involves only $n = k + 1$. Some examples are given in the following table. (The constants β, A, B, are possibly different for different cases.) The fact that say the energy for $n = 2, l = 1$ is the same as for $n = 2, l = 0$ is surprising, because the effective potential in the radial Schrödinger equation is very different for these two cases.

n	l	R
2	1	$r\exp(-\beta r)$
2	0	$(r + A)\exp(-\beta r)$
3	2	$r^2\exp(-\beta r)$
3	1	$r(r + A)\exp(-\beta r)$
3	0	$(r^2 + Ar + B)\exp(-\beta r)$

Assuming that the solutions really are polynomials times exponentials, it is rather easy to show that the energy depends only on the order of the polynomial. Set

$$R = (r^k + Ar^{k-1} + \ldots)e^{-\beta r}$$

Substituting in the radial Schrödinger equation and matching powers of r^k gives

$$\beta^2 + 2E = 0, \quad E = -\frac{\beta^2}{2},$$

so the energy is always determined by the value of β. Matching powers of r^{k-1} gives

$$-2k\beta + \beta^2 A - 2\beta + 2EA + 2 = 0, \;\; 2(k+1)\beta = 2, \;\; \beta = \frac{1}{k+1}$$

which determines β. Note that the coefficient of A automatically vanishes. The energy of a level depends only on k and therefore only on n. We have in atomic units,

$$E = -\frac{1}{2n^2},$$

which is the Bohr formula.

It is possible to keep going and find the polynomials order by order, but to obtain the results in general, we again change units in the radial Schrödinger equation. Writing it once again, we have

$$\left(\partial_r^2 + \frac{2}{r}\partial_r - \frac{l(l+1)}{r^2} + 2(E + \frac{1}{r})\right) R = 0.$$

Now set

$$n = \frac{1}{\sqrt{-2E}}, \;\; \rho = \frac{2r}{n}.$$

At this point, we do not assume that n is an integer. It is real, since we are looking for bound states, and for these $E < 0$. Writing the radial Schrödinger equation in terms of ρ, we have

$$(\partial_\rho^2 + \frac{2}{\rho}\partial_\rho - \frac{l(l+1)}{\rho^2} - \frac{1}{4} + \frac{n}{\rho})R = 0.$$

Now pulling off the small and large ρ behavior we set

$$R = \rho^l w(\rho) \exp(-\frac{\rho}{2}).$$

The radial Schrödinger equation in terms of ρ is now

$$\rho \frac{d^2 w}{d\rho^2} + (2l + 2 - \rho)\frac{dw}{d\rho} + (n - l - 1)w = 0. \tag{2}$$

This is solved by a special function which bears the intimidating name *confluent hypergeometric function*. These are define by the power series,

$$F(\alpha, \gamma, z) = 1 + \frac{\alpha z}{\gamma 1!} + \frac{\alpha(\alpha+1)}{\gamma(\gamma+1)2!}z^2 + \ldots.$$

The solution of Eq.(2) is such a function,

$$w = F(l + 1 - n, 2l + 2, \rho).$$

Now the hypergeometric function will grow in an unacceptable way as $\rho \to \infty$, unless the series terminates. This requires

$$l + 1 - n = -(integer),$$

which finally requires that n be an integer. Use of the series expression for $w(\rho)$ is a fairly efficient way to generate formulae for radial wave functions. A few examples are in the following table.

n	l	α	$w(\rho)$
1	0	0	1
2	0	-1	$1 - \rho/2$
2	1	0	1
3	0	-2	$1 - \rho + \rho^2/6$
3	1	-1	$1 - \rho/4$
3	2	0	1

The Runge-Lenz Vector The reason for the huge degeneracy in the Coulomb problem is that there is another conserved vector in addition to the angular momentum. This is given classically by

$$\vec{U} = \frac{1}{e^2 m}\vec{L} \times \vec{p} + \frac{\vec{r}}{r}.$$

Classical conservation implies that

$$\frac{d\vec{U}}{dt} = \frac{1}{e^2 m}\vec{L} \times \frac{d\vec{p}}{dt} + \frac{d}{dt}(\frac{\vec{r}}{r}) = 0.$$

This can be shown directly using Newton's laws. To find out what the vector $\vec{U}$ is classically first recall that the particle moves classically on an ellipse. Putting the plane of the ellipse in the $x - y$ plane, we have

$$r = \frac{a(1 - \epsilon^2)}{1 + \epsilon \cos\theta},$$

where a is the semi-major axis of the ellipse. Here θ is the angle in plane polar coordinates. Now since $\vec{U}$ is constant, we can evaluate it at any point on the orbit of the particle. A convenient place to do so is when the particle is closest to the origin. This occurs at $\theta = 0$, the so-called perihelion. At this point the velocity is perpendicular to the radius, so $\vec{L} \times \vec{p}$ points inward along $\vec{r}$. This means $\vec{U}$ is either parallel or anti-parallel to $\vec{r}$. We can then get the magnitude of $\vec{U}$ by considering

$$\frac{\vec{U} \cdot \vec{r}}{r} = \frac{1}{e^2 m r}(\vec{L} \times \vec{p}) \cdot \vec{r} + 1.$$

The magnitude of $\vec{L}$ is given by

$$|\vec{L}| = pr.$$

Using this, we have

$$\frac{\vec{U}\cdot\vec{r}}{r} = 1 - \frac{p^2 r}{e^2 m}.$$

Next, we write a formula for the energy of the motion

$$\frac{p^2}{2m} - \frac{e^2}{r} = -\frac{e^2}{2a},$$

where on the right, we used a known formula for the energy. This gives

$$\frac{p^2}{2m} = \frac{e^2(1+\epsilon)}{2a(1-\epsilon)},$$

and at $\theta = 0$ we have

$$r = a(1-\epsilon).$$

We finally obtain

$$\frac{\vec{U}\cdot\vec{r}}{r} = 1 - \frac{e^2(1+\epsilon)}{2a(1-\epsilon)}\frac{2a(1-\epsilon)}{e^2} = -\epsilon,$$

so the vector $\vec{U}$ has magnitude ϵ and points from the origin to the aphelion (farthest point from the origin).

The Quantum Case Quantum mechanically, some care with the order of operators is needed. We have

$$U_i = \frac{1}{me^2}(\epsilon_{ijk}(L_j p_k - p_j L_k)),$$

so for example

$$U_1 = \frac{1}{me^2}(L_2 p_3 - p_2 L_3).$$

The vector $\vec{U}$ is conserved in quantum mechanics as well as classical mechanics,

$$[U_i, H] = 0.$$

NOTE: For more detail on the next few steps, see the lecture notes "Vector Operators."

The degeneracy of the hydrogen spectrum follows easily from the fact the $\vec{U}$ is (i) a rotational vector, (ii) reverses under reflection or parity ($\vec{r} \to -\vec{r}$). Start by considering an energy eigenstate,

$$\Psi_{nlm} = R_{nl}(r)Y_{lm}(\theta,\phi).$$

Now take the matrix element of $\vec{U}$ between this state and a possibly different state,

$$< \Psi_{n',l',m'}|U_i|\Psi_{nlm} >$$

By conservation of $\vec{U}$ the energy cannot change so we have

$$n' = n.$$

Since $\vec{U}$ is a rotational vector we must have $l' = l, l \pm 1$. But parity conservation requires

$$(-1)^{l'} = (-1)^{l+1},$$

so only $l' = l \pm 1$ is allowed. It is easy to show that all the states at a given n can be generated by applying $U_x + iU_y$ to the state $|\Psi_{n00}>$.

To summarize, the operator $\vec{U}$ moves the system around in the manifold of states with different l values for a given n. The conservation of $\vec{U}$ and its vector nature are the crucial facts determining the large degeneracy of the hydrogen spectrum. The existence of an extra conserved vector is unique to a pure Coulomb potential, and therefore this large amount of degeneracy will not occur for other central potentials.

Note The importance of the Runge-Lenz vector was first realized by Pauli, in a beautiful paper which worked out many details of the hydrogen spectrum prior to the discovery of the Schrödinger equation. An English translation of this paper is in "Sources of Quantum Mechanics," edited by Van Der Waerden, Dover Publications. I will loan a copy to anyone interested.