

⑧
11/18/05

Now we consider hydrogen and hydrogen-like (one-electron) atoms, including

$$\text{H}, \text{He}^+, \text{Be}^{++}, \dots, \text{U}^{91+}, \dots$$

We will use a spinless, electrostatic, nonrelativistic model with potential $V(r) = -Ze^2/r$, what we will call the Bohr-Schrödinger model.

We begin with atomic units. These are units such that $\boxed{m = e = \hbar = 1}$, commonly used in atomic physics. In A.U., the quantities a_0 etc. introduced above all become unity:

$$a_0 = \frac{\hbar^2}{me^2} = 0.5 \text{ \AA} = \text{Bohr radius}$$

$$K_0 = \frac{me^4}{\hbar^2} = 27 \text{ eV} = 2 \times \text{binding energy of H.}$$

$$v_0 = \frac{e^2}{\hbar} = \alpha c = \frac{1}{137} c = \text{velocity of electron in gnd state of H.}$$

$$T_0 = \frac{\hbar^3}{me^4} = 2 \times 10^{-17} \text{ sec} = \frac{\text{period of orbital motion}}{2\pi} \text{ of electron in gnd state of H.}$$

Notice in particular v_0 . The electron is fast but still mostly nonrelativistic. Notice, in A.U. $c = \frac{1}{\alpha} = 137$ (speed of light).

The radial Sch. eqn. for H-like atom is

$$-\frac{\hbar^2}{2\mu} \frac{d^2 f}{dr^2} + \left[\frac{l(l+1)\hbar^2}{2\mu r^2} - \frac{Ze^2}{r} \right] f = E f,$$

(9)

11/18/05

where $\mu =$ reduced (electron-nucleus) mass. To put this eqn into dim' less form, we introduce modified atomic units, for which

$$\sqrt{Ze^2} = \cancel{m} \mu = \hbar = 1.$$

Since $\mu \approx m$, the main change is $e^2 \rightarrow Ze^2$. In modified A.U. the units are

$$\text{length} = a = \frac{\hbar^2}{\mu Ze^2} \approx \frac{a_0}{Z}$$

$$\text{energy} = K = \frac{\mu Z^2 e^4}{\hbar^2} \approx Z^2 K_0$$

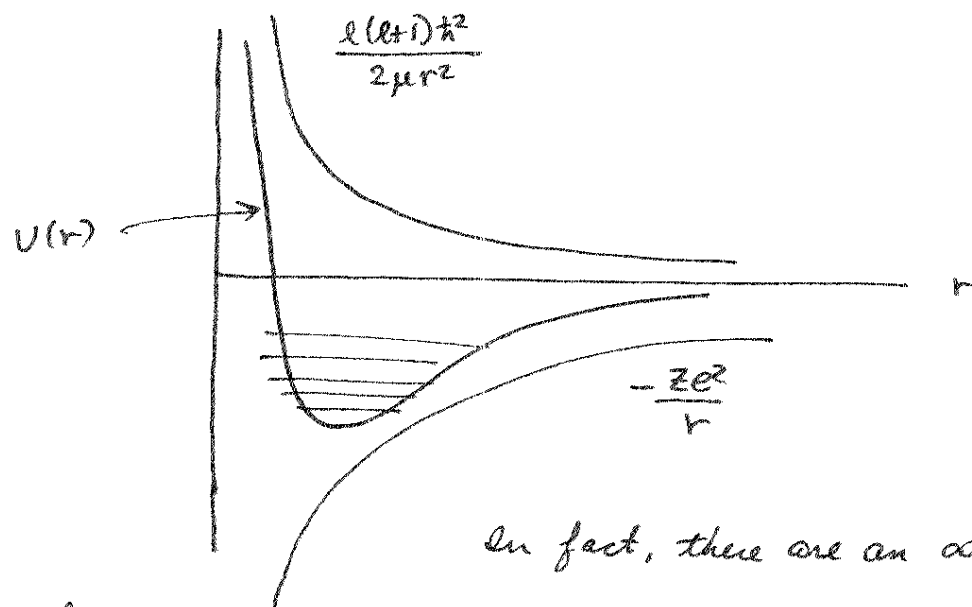
$$\text{velocity } v = \frac{Ze^2}{\hbar} = (Z\alpha)c = Zv_0.$$

etc. Notice the unit of velocity, $\frac{v}{c} = Z\alpha$. For H this is small ($1/137$) but for U it is $92/137 \approx 0.6$. For heavy atoms, the nonrelativistic Sch. eqn is not a good appx.

In modified A.U., the Sch. eqn. becomes

$$\frac{d^2 f}{dr^2} + \left[-\frac{\ell(\ell+1)}{r^2} + \frac{2}{r} + 2E \right] f = 0.$$

Before analyzing, look at the potentials. The true Coulomb potential dominates at large r , the centrif at small r , creating a well for bound states:



(10)

11/18/05.

In fact, there are an ∞ # of bound states.

There are also continuum states (for any $E \geq 0$).

Let's look for bound states, $E < 0$. We set

$$\nu = \frac{1}{\sqrt{-2E}}, \quad \rho = \frac{2r}{\nu}, \quad \text{modified radial var.}$$

Sch. eqn. becomes

$$\frac{d^2 f}{d\rho^2} + \left[-\frac{l(l+1)}{\rho^2} + \frac{\nu}{\rho} - \frac{1}{4} \right] f = 0. \quad (\text{RSE})$$

Standard techniques show that you only get a square-integrable solution when $\nu = n =$ an integer in the range,

$$n = l+1, l+2, \dots, \infty$$

where we are thinking of l as given since it's a parameter of the RSE.

n is the principal qu. #. The wave fns are

$$f_{nl}(\rho) = \rho^{l+1} e^{-\rho/2} L_{n-l-1}^{2l+1}(\rho)$$

$\uparrow$ assoc. Laguerre polynomial.

Note that they are polynomials times exponentials $e^{-r/n}$.

11/18/05

The energies are

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

indep. of l . The fact that E_n is indep. of l is due to the extra symmetry possessed by Coulomb potential. Any non-Coulomb radial potential introduced as a perturbation will restore the l -dependence.

Thinking of n as given first, then the allowed ranges on quantum numbers are

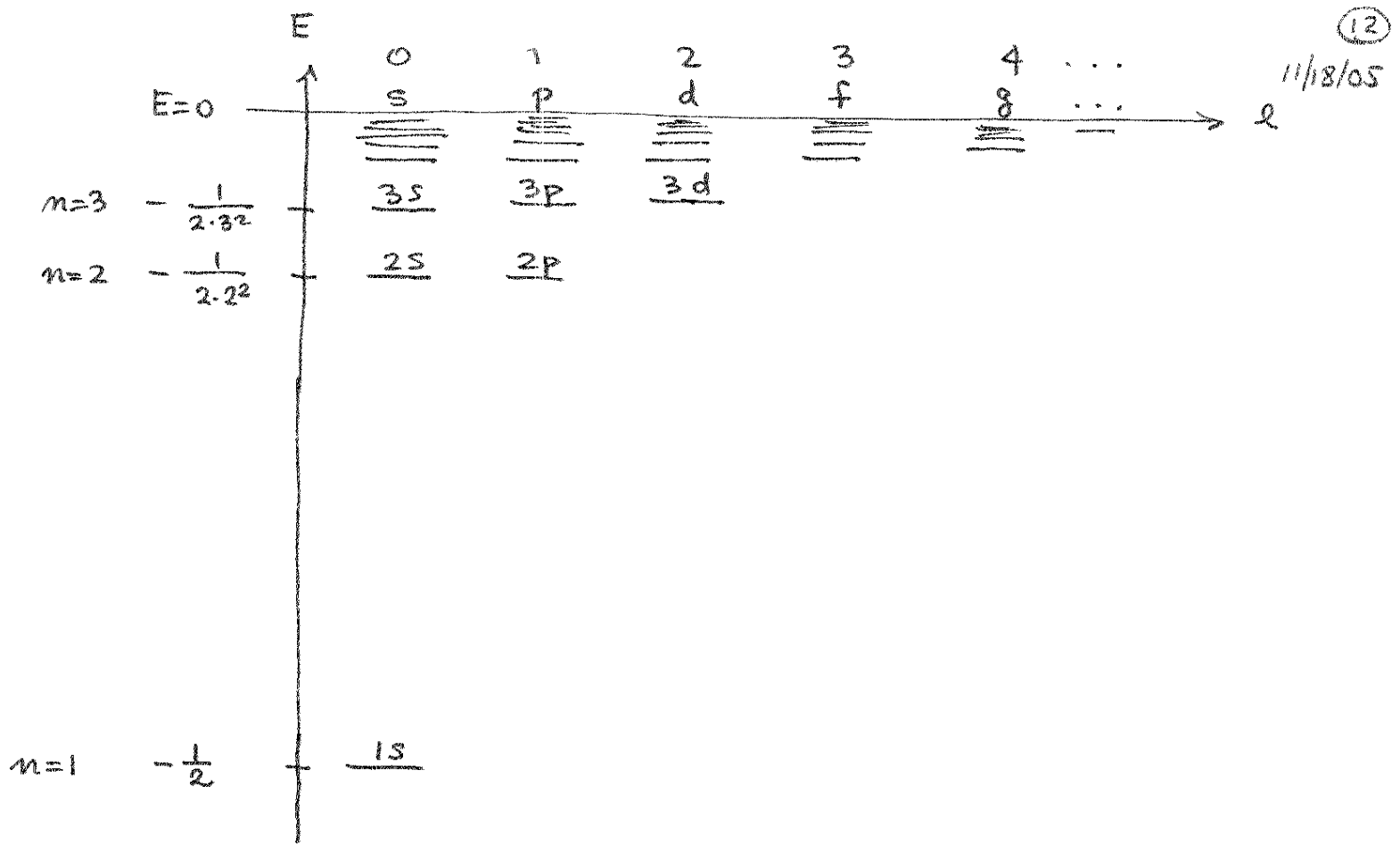
$$n = 1, 2, 3, \dots \quad \infty$$

$$l = 0, 1, \dots, n-1.$$

The degeneracy is

$$\text{degen}(E_n) = \sum_{l=0}^{n-1} (2l+1) = n^2.$$

The energy levels are traditionally arranged in a Brother diagram, basically one for which the horizontal axis is ang. mom. and the vertical energy. $E=0$ is at the top since we're interested in bound states with $E < 0$. The angular momentum values are traditionally indicated by their letter codes s, p, d, f, etc.



An ∞ # of levels accumulate near $E=0$ in each column.

The symbols $2s, 3p$ etc. label an n and l value, hence a set of $2l+1$ states. The levels across each row are equal in energy, because of the extra degen. in H.

Interesting ways of breaking the l -degeneracy include the following. First, the volume effect modifies the $1/r$ potential by taking account of the fact that the charge in the nucleus is not a point, but spread out over the volume of the nucleus. This causes the Coulomb singularity to be smoothed out. The volume effect mainly affects the s -states, raising their

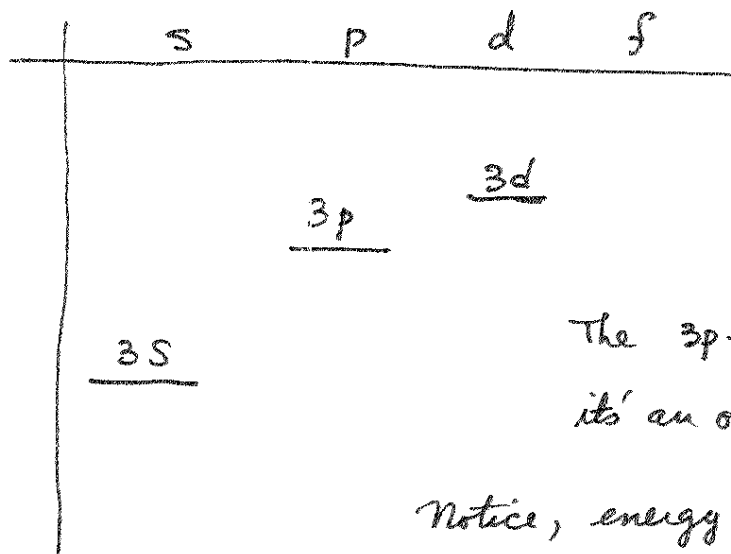
energy, since only s-waves are $\neq 0$ at $r=0$. But it does introduce an l -dependence to the energy levels.

11/18/05

Another way is to look at alkali atoms. ~~the~~ Li, Na, K, Rb, Cs, Fr which have a single electron outside closed shells. A model for alkalis treats them as single electron systems, moving in a screened potential,

$$V(r) \sim \begin{cases} -\frac{Ze^2}{r}, & r \rightarrow 0 \\ -\frac{e^2}{r}, & r \rightarrow \infty \end{cases}$$

since for small r there is no screening and for large r the electron sees a nucleus + core w. charge -1 . This potential is not even close to a single Coulomb potential since Z_{eff} is a rapid fn. of r inside the core. For example, in Na you have the diagram,



There are no $n=1,2$ levels for Na, because the core states are filled.

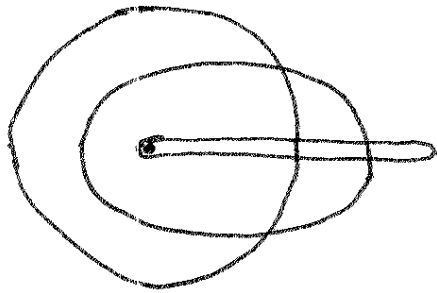
The 3p-3s splitting is not small, it's an optical transition.

Notice, energy levels are E_{nl} (the generic form).

(14)

11/18/05

The rule $l=0, \dots, n-1$ in H-like atoms has a classical rationale. Consider classical motion in the force center $F = -\frac{k}{r^2}$, $k = Ze^2$ for our problem. Three classical orbits of the same energy might look like this:



These are 3 ellipses with same semi-major axis a . For the circle, $r=a$. The classical energy is a fn. only of the semi-major axis:

$$E = -\frac{k}{2a}.$$

The 3 ellipses differ however in their angular momentum. The thin orbit (eccentricity $e=1$) has $L=0$, while the circular one has $L = L_{\max}$, the maximum value L can have for the given E . In fact, it's easy to show that

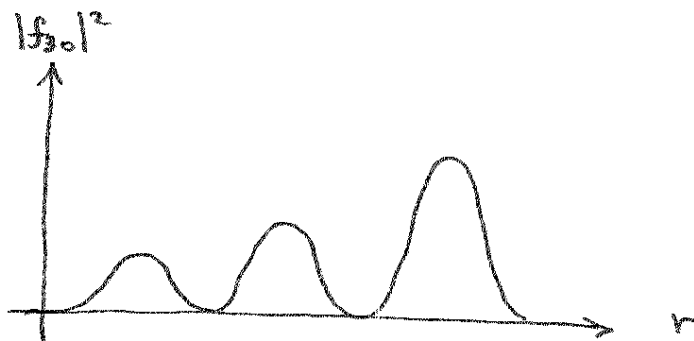
$$L_{\max} = \sqrt{mk a^2} = \sqrt{\frac{mk^2}{(-2E)}}.$$

This classical relation $0 \leq L \leq L_{\max}(E)$ is exactly the analog

(15)

11/18/05

of $l=0, \dots, n-1$ in QM. Thus the states $l=n-1$ correspond to circular orbits, while those for $l=0$ correspond to the needle orbits. The needle orbits extend out twice as far as the circular orbits, and also extend in to the nucleus. You can see all of this in the plots of some radial wave functions, e.g. for $n=3$, $l=0, 1, 2$:



class. orbit.

