The Nov-velotivistic, spinlese H Atom (or H-like ion)
For an electron in a potential V,

$$H = \left(\frac{p^{*}}{2m} + V\right) \Psi = E \Psi$$

so with $p = -ik \overline{\nabla}$, and for an H
atom of or liptogen-like ion; writing
 $V = -\frac{2Ke^{2}}{r}$ (for infinite rucker mess),
 $\left(-\frac{k^{*}\overline{\nabla}^{*}}{2m} - \frac{2Ke^{2}}{r}\right) \Psi = E \Psi$ ($K = \frac{1}{4\pi E_{0}}$)
Nuclear vection is taken into account by
writing things in terms of relative coerclinates;
for H will get, in the center of mess,
 $K_{*}E_{*} = \left(\frac{1}{m} + \frac{1}{M}\right) \frac{k^{*}\overline{\nabla}^{*}}{r}$
So replace m above with the realisant mass,
 $M = \frac{mM}{m+M}$ (mome; M^{*} maker mose)
 $Then \left(\frac{k^{*}}{2m} \nabla^{*} + \frac{2Ke^{*}}{r} + E\right) \Psi = C$
If we had used atomic units, this would be
 $\left(\frac{\overline{\nabla}^{*}}{2m} + \frac{7}{r} + E\right) \Psi = 0$, where $M = 1$
This isn't always advantageous, we could
easily have overlooked the vedweat mass corrections
if we had used separation in spherical
coordinates; write
 $Y = R(r) Y(r, 0)$

and for convenience define $\Phi(r) \equiv r R(r)$, so $\gamma = \frac{1}{r} \Phi(r) Y(o, \phi)$

Substituting in the Schrödinger equation, $-\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)Y = \lambda Y$ and $\frac{1}{k^2} \frac{d^2 \Phi(r)}{dr^2} + \frac{2}{2} A \left(E + \frac{2ke^2}{r}\right) \Phi(r) = \frac{\lambda}{r^2} \Phi(r)$ Where λ is a sparation constant, the same in Θ and Θ . Angular Solution Equation O can be solved after imposing boundary conditions that Y and its first derivative must be continuous, single-valued and finite. Then $\lambda = \ell(\ell + i) \hbar^2$ $\ell = 0, 1, 2, \cdots$ and Y(0,0) = Yem (0,0) (spherical harmonics) Where m= -l, -l+1, ..., l-1, l The Yem are of course utiquitous creatures, since they are the eigentatures of the operator I?: If we take $\vec{L} = \vec{r} \times \vec{p}$ with $\vec{p} = -i\hbar \vec{\nabla}$, equation \vec{O} is just $\vec{L}^2 Y_{(0,0)} = \lambda Y_{(0,0)}$ $= l(l+i) t^2 Y_{lm}(o, \phi)$ (Note: it's usually obvious when we are using an operator and not a quantum number, so I will normally not distinguish operators with a circumflex or other special notation.)

Properties of the Yem's (many are given in Appendix A.1 of Friedrich's book) The spherical harmonics are given explicitly 64 1 $Y_{em}(\theta, \phi) = (-i)^m \sqrt{\frac{2e+i}{4\pi}(e-m)!} P_{em}(\cos \theta) e^{im\phi}$ 4 This has all of The azimuthal dependence! The phase convention used have is that of Edmonds, and It is not universal! Zare. The Pem's are the associated Legendre functions, $P_{em}(x) = \frac{(1-x^2)^{m/2}}{2^k \ell!} \frac{d^{l+m}}{dx^{l+m}} (x^2-1)^k$ (valid for all integers m) Most standard math tables like Abromowitz & Stegun list countless properties of These things. Get in the habit of using Them -- when doing real physics as opposed to taking a guantum mechanics course, There's no point to continually re-inventing mathematical wheels!

Also, they are predictined in some computer environments, such as Mathematica, Mathematica, Labwindows, ..., Generally Mathematica is the most powerful of these when working with special functions.

That these are also eigenfunctions of
$$L_z$$
 is
 $easily verified ---$
 $L_z Y_{em}(o, \phi) = -i(h) \frac{\partial}{\partial \phi} Y_{em}(o, \phi)$
 $= m(h) Y_{em}(o, \phi)$
So we have,

elgenvalues of
$$L^{2}$$
: $l(l+1) = T^{2}$
elgenvalues of L_{0} : $m = R_{1} = l + j = j$
Note that $H_{1} = L^{2}_{1} = all commutes.$
I is the orbital angular memomentum guantum number
 m is the projection, or "magnetic" guantum number
Appendence of the angular slave functions:
 $\frac{1}{12} \frac{1}{n} = 1$
 $l = 1$ $|m| = 1$
 $l = 1$ $|m| = 1$
 $l = 1$ $|m| = 1$
 $l = 1$ $|m = 0$
 $l = 2$ $|m| = 2$ $|m| = 1$ $m = 0$

$$\frac{Redid wave equation for H'}{1}$$

$$\frac{F}{Putting \lambda = P(P+1) \pi^{2} \quad in \quad @ gives$$

$$\left(-\frac{\pi^{2}}{2fr} \frac{A^{2}}{dr^{2}} + \frac{P(P+1)\pi^{2}}{2fr^{2}} - \frac{2Ke^{2}}{r}\right) D(r) = E D(r)$$

$$\frac{1 - Ain \quad Schrödinger equation with an effective forential having a mation-range Contribugat barrier - V(r) \\ Red = 0$$

$$\frac{V(r)}{R} = 0$$

$$\frac{V(r)}{R} = 0$$

$$\frac{V(r)}{R} = 0 \quad (bov-r)$$

$$\frac{V(r)}{R}$$

Also much used is the Rydberg, $R_y = Rydberg = \pm \frac{M}{m_e}$ howevers $= \frac{MK^2e^4}{2t^2}$ and Ryos = "infinite mass Rydberg constant" $= \frac{m_e K^2 e^4}{2 \pi^2} = 109737, \cdots cm^{-1}$ $50 \overline{E} = -\frac{\overline{z}^2 R_Y}{h^2} (R_Y dberg formula)$ Finally, can write things in terms of the Bohn radius, which for reduced mass u and change Zis, $a = \frac{\pi^2}{\mu Z K e^2} = \frac{Me}{\mu Z} a_0$ $\left(a_{o}=\frac{\hbar^{2}}{m_{e}\kappa e^{2}}\right)$ Then $E = \frac{h^2}{Mg^2} \frac{1}{2h^2} = \frac{Zke^2}{2g} \frac{1}{n^2}$ Note that Friedrich includes a Z² in Ry as well; this is not usual. The energy levels of H are highly <u>degenerate</u>. For a given n, 1) l has n values 2) m has 20+1 values for each l 3 energy When we include electron spin thero's also a degenerate spin doublet in the non-relativistic theory, we will show the Dirac theory removes this, but the l'degeneracy is broken only in OED his the "In a stift" arising from in QED, by the "Lamb shift" arising from Vacuum state interactions. Behavior of bound states They can be written as a multiple of the where $f \equiv \frac{2r}{na}$, and defined above.

Normalization is given by $\int |R|^2 r^2 dr = 1 , so that$ $\int \Phi_{ne}(r) \Phi_{n'e}(r) dr = O_{nn'}$ Explicitly, for the first few levels, $Q_{21} = \frac{r}{a^{3/2}} \frac{1}{2\sqrt{6}} \frac{r}{a} e^{-r/2a}$ $(remember a = \frac{1}{Z} \frac{m_e}{m} a_o)$ These have n-l-1 nodes. In the inner region the shape is nearly independent of n for fixed 2. Solutions for E>0 (continuum) There is total degeneracy here; we still use the Yem's as the angular basis For convenience, but other choices can be made depending on the purpose at hand. The radial solutions are the "regular Coulomb functions" Usually normalized by, $\int \Phi_{E'e} \Phi_{Ee} dr = O(E' - E)$ For low E, just a Bessel function (see Friedrich) and for large r, $\mathcal{R}_{E\ell} \simeq \frac{1}{K} \sqrt{\frac{m}{2\pi}} \left(\frac{8a}{r^2}\right)^{1/4} \sin\left(\sqrt{8r_A} - \ell\pi - \frac{1}{4}\right)$

12-14 On the fottowing pages A several bound and continuum solutions are shown, plotted against VV so the highly excited states are nearly sinuscidal. General properties Many properties of the H atom wave functions are true of highly excited "Rydberg states" in any atom or molecule -at nonpenetrating nearly hydrogenic electron. core Some of these properties are: i) At short range, for fixed l, the where function is independent of m except for a n^{-3/2} scaling due to normalization. This gives vise to many the scaling laws for interactions that depend on the penetration of a Rydberg electron wave function into a non-hydrogenic core. See Bethe PSalpeter for a proof. 2) For fixed no changing & affects only the short-range wave function. (Obvious, since centrifuged correction Vanishes at long vange.)

3) Size $Zr > = Z \Phi / r / 0 >$ = ± (3n² - 2(2+1)) 9 > scales as nº (measures mainly the outer lobe!) 4) Energy spacing $AE = Z^2 R_Y \left(\frac{1}{h^2} - \frac{1}{(n+1)^2}\right)$ $\sim 2 \overline{Z^2 R_Y}$ => scales as /n3, just like core penetration effects. 5) Some other expectation values: $<\frac{1}{r^{2}}>=\frac{1}{a^{2}h^{3}}\frac{1}{l^{2}l^{2}}\propto \frac{1}{h^{3}}$ $\langle \frac{1}{r^3} \rangle = \frac{1}{a^3 n^3} \frac{1}{(2+1)(2+1/2)} \propto \frac{1}{n^3}$ < Fr> is also & 1/n3 for Rec n! Why? Because all stress the shortrange part of the wave function where property 1) tends to dominate the behavior. 6) Dependence on Zi For hydrogenic ions, REX Z² but ad 1/2 So the atomic ions become smaller and move tightly bound, as expected.

have this spectrum: In sum, we -- -> N=2 -----Each flevel has 20+1 values of m For each n, there are In degenerate volues of l For 173, states are named with increasing letters of the alphabet, except "i" is skipped. So R=4 is a g state, etc. The other names are historic: 5 "sharp" p "principal" d "diffuse" f "fine" Degeneracies (2), 3) below unique to H) 1) The m degeneracy is just associated with rotational symmetry, or classically with orbital angular momentum conservation (orbit is in a fixed plane). 2) There's also a symmetry associated with the I degeneracy of the Inems. This is the conservation of the Runge - Lema vector, $\vec{A} = \pm (\vec{L} \times \vec{p} - \vec{p} \times \vec{L}) + e \vec{F}$

Á Classically it's the major axis of the ellipse. [H, A]=0, only For hydrogen (without QED corrections) 3) One can also take advantage of the properties of the R(4) rotation group to solve for the principal quantum number spacing! So it's possible to get everything but the details of the wave functions from group theory. See, for example, Judd, Angular Momentum Theory for Diatomic Molecules The Rydberg Constant There is really only one parameter the non-relativistic theory of H; it. in $R_{70} = \frac{m_e k^2 e^4}{2 t_1^2} = 169737,31568527(73) \text{ cm}$ 15 of all fundamental constants. It This measured measured to si part in 10# by has been i) Zhao & Lichten (Yale) 2) Boshier, Hinds -- (Sussex) 3) Biraben, ---Mansch (Max Planck) This (Saday) The 25 "Balmar A" = 486 mm 1-25 Also Balmar A, Thu two photon transition at 243 nm (to 1.8 parts in 10""!!)







STATES OF HYDROGEN with n = 8 and m = 0 vary in angular momentum from l = 0 to l = 7. Although charge density may seem complex, the nodal lines (where the charge density is zero) are always either circles centered on the nucleus or straight lines passing through the nucleus. In three dimensions the nodal surfaces are spheres or

cones. The charge-density graphs were made with the aid of a computer by William P. Spencer of the Massachusetts Institute of Technology. To make the graphs easier to interpret the charge density was multiplied by r^2 , where r is the distance to the nucleus. The innermost node of the charge density is too close to the nucleus to be seen. 14

Viewing 3-dimensional hydrogen atom wave functions

Much insight about the behavior and scaling of atomic wave functions can be gained simply by looking at them. One approach is to use a mathematical programming environment like Mathematica, and to use its built-in graphics capability.

However, there are some very nice applets available on the web, such as the one illustrated in the snapshot below. It can display 3-d views or slices parallel to any of the coordinate axis planes. It even depicts the time evolution of the wave function as the phase evolves.

The Java applet can be downloaded at <u>http://www.falstad.com/qmatom/</u>. It may also be available in archived .zip form on the Physics 6110 web page, under "Resources."

