

II-atom Radial Wavefns. Bound States & Continuum. Need for Spin.

The hydrogen-atom radial wavefn of Eq. (19) can now be written (w/o norm) as:

$$R(\rho) \propto \rho^{l+1} e^{-\kappa \rho} F(-N; 2l+2; 2\kappa \rho) \begin{cases} N = n - (l+1) = 0, 1, 2, \dots & \begin{matrix} \int n=1, 2, 3, \dots \\ l=0, 1, \dots, n-1 \end{matrix} \\ \kappa = Z/n, \quad \rho = r/a_0; \end{cases}$$

or

$$\rightarrow R(\rho) \propto \rho^{l+1} e^{-\kappa \rho} L_N^{2l+1}(2\kappa \rho) \rightarrow \rho^n e^{-\kappa \rho}, \text{ as } \rho \rightarrow \infty. \quad (21n)$$

The quantization condition $\kappa = Z/n$ renders $R(\rho)$ finite at all ρ .

Integrals over Laguerre polynomials \times powers \times exponentials are tabulated [see e.g. Gradshteyn & Ryzhik, Secs. 7.41-7.42]. From these we can generate a norm...

$$\left[\int_0^\infty [R(\rho)]^2 d\rho = 1, \text{ if } R_{nl}(\rho) = A_{nl} \left(\frac{2Z\rho}{n} \right)^{l+1} e^{-\frac{Z\rho}{n}} F(-n+l+1; 2l+2; \frac{2Z\rho}{n}) \right],$$

where: $A_{nl} = \frac{1}{(2l+1)!} \sqrt{\frac{Z}{n^2} (n+l)! / (n-l-1)!}$ \leftarrow after Davydov Eq. (38.16). (21o)

Other integrals for expectation values (e.g. $\langle \frac{1}{\rho} \rangle = Z/n^2$) can be handled similarly.

* other def^{ns}: $L_N^b(z) = \left\{ \frac{\Gamma(b+1+N)}{N! \Gamma(b+1)} \right\} F(-N; b+1; z) \int \begin{matrix} \text{Morse \& Feshbach, p. 785;} \\ \text{Merzbacher "QM" Eq. (10.89a);} \end{matrix}$

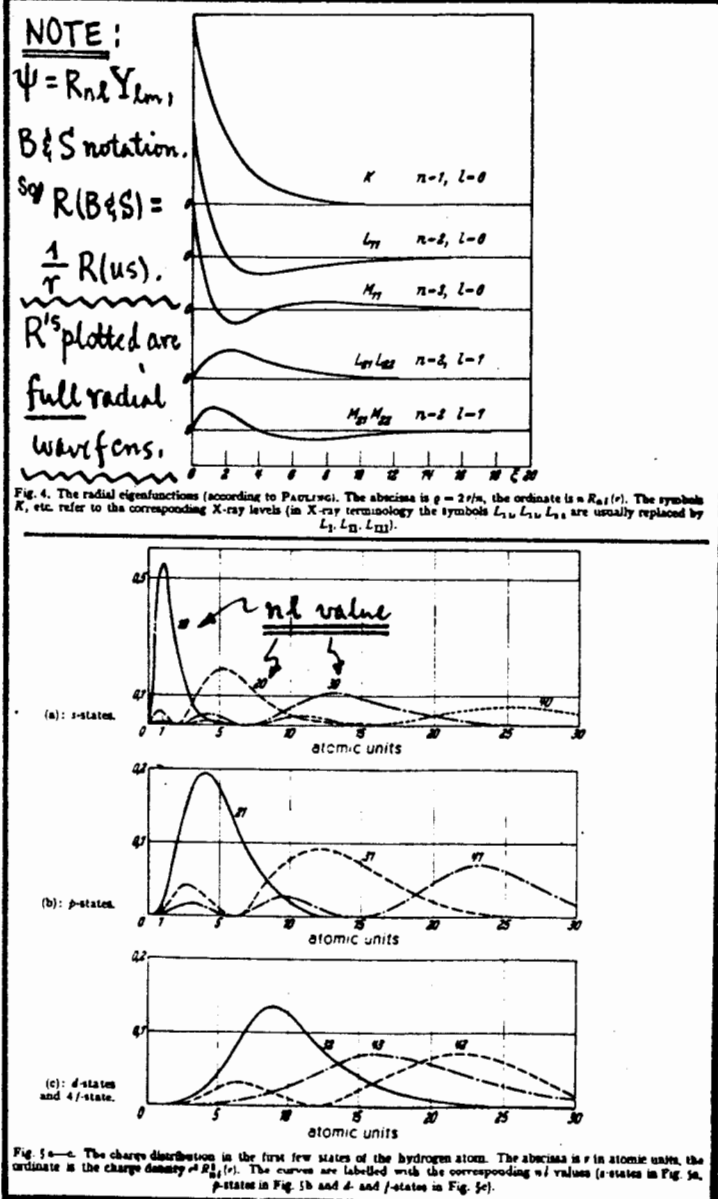
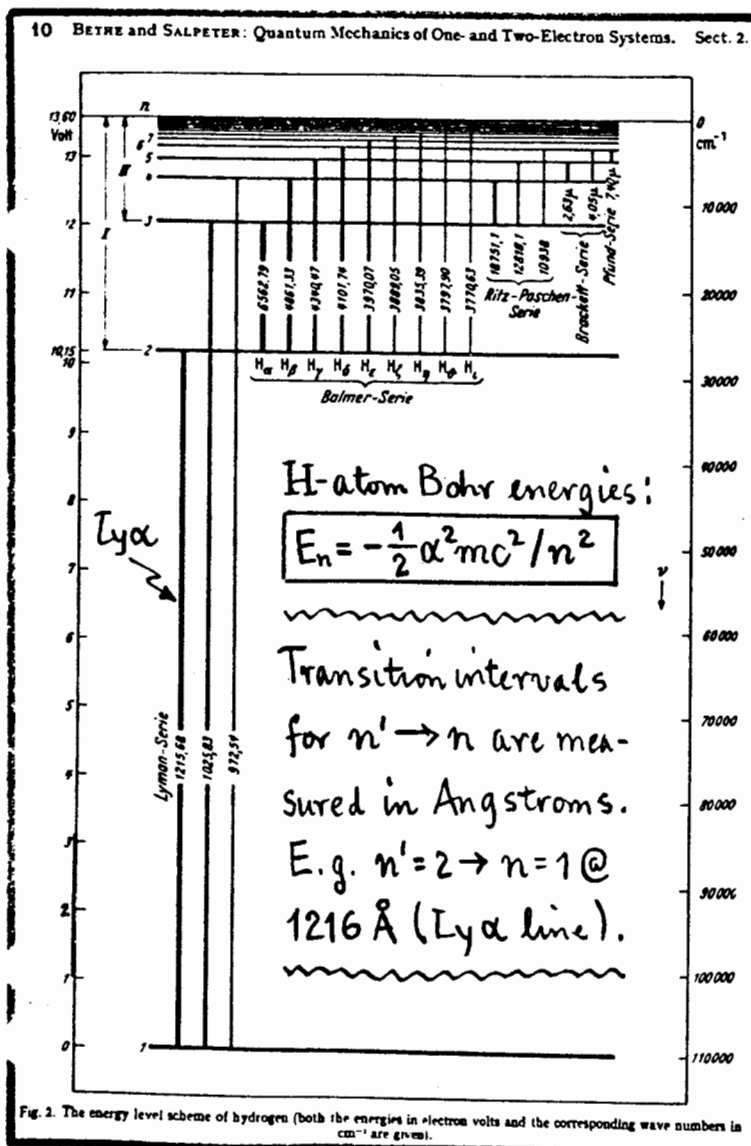
$$L_N^b(z) = \left\{ \frac{\Gamma(b+1+N)}{N! \Gamma(b+1)} \right\} F(-N; b+1; z) \int \begin{matrix} \text{NBS Handbook \# (13.6.9);} \\ \text{Gradshteyn \& Ryzhik \# (8.972.1).} \end{matrix}$$

5) All this "Confluent Lore" makes the H-atom problem ~ easy, and it will be useful in many other QM applications. But now, back to details of the H-atom.

It is helpful to draw pictures of what we've calculated so far. Below are figures taken from H.A. Bethe & E.E. Salpeter "QM of One- and Two-Electron Atoms" (Academic Press, 1957). They show the Bohr energies for the hydrogen atom ($Z=1$): $E_n = -\frac{1}{2} \alpha^2 mc^2 / n^2$ [Eq. (20), above], and -- in the second figure -- plots of the radial wavefun vs r [$R(B\&S) = \frac{1}{r} R(us)$, in Eq. (210)]. In Figs. 5a-c below, note the ~ strong localizations of the density $|R(us)|^2$ at specific r 's; these are the "orbits".

BOHR ENERGIES

RADIAL DISTRIBUTIONS



It is worth noting that the Bohr energies $E_n = -\frac{1}{2}(Z\alpha)^2 mc^2/n^2$ are highly degenerate. The overall H-atom system is described by the quantum #'s n , l , & m which specify the state $\Psi_{n\ell m}(r) = \frac{1}{r} R_{n\ell}(r) Y_{\ell m}(\theta, \varphi)$, with ranges:

QUANTUM #	ALLOWED VALUES	TOTAL # VALUES
principal (Bohr) : n	$1, 2, 3, \dots, \infty$	∞
ℓ momentum : ℓ	$0, 1, \dots, n-1$	n , given n
ℓ mom. projection : m	$-\ell, -\ell+1, \dots, +\ell$	$2\ell+1$, given ℓ

(22)

The total # different states $|n\ell m\rangle$ for given n is : $\sum_{\ell=0}^{n-1} (2\ell+1) = n^2$, and all these states have the same value of energy, E_n . This fact is semi-remarkable, and in fact isn't true in the "real" H-atom ($^{1/2}$ electron & proton spin, etc.), as we shall show later. Nevertheless, a few remarks are in order.

REMARKS

1. The m-degeneracy is easy to understand... in any central force problem, there is by definition no preferred (internal) axis on which the ℓ momentum can project, so any m -value is equivalent to any other, and cannot affect the energy of a state. The radial eqn [Eq. (1)] doesn't contain m , in fact. The m -degeneracy can be removed by supplying an external field axis [e.g. magnetic field B (Zeeman effect)].
2. The ℓ -degeneracy is "accidental", and peculiar to the $1/r$ potential. In fact the radial eqn [Eq. (1)] does contain ℓ , and for general central potentials $V(r)$ the bound state energies $E_{N\ell}$ will depend on ℓ as well as some radial quantum # N . It just happens for $1/r$ that the combination $n = N + \ell + 1$ appears, and there is no explicit ℓ -dependence. The ℓ -degeneracy is lifted by any departure from $V \sim 1/r$, or by external electric fields E (Stark Effect).
3. Spectroscopic Notation: states with $\ell=0$ are called s-states, $\ell=1 \leftrightarrow$ p-states, $\ell=2 \leftrightarrow$ d, $\ell=3 \leftrightarrow$ f, $\ell=4 \leftrightarrow$ g, etc. (from ancient spectroscopy: S=sharp, p=principal, d=diffuse, f=fundamental, etc (line shapes))

6) The H-atom bound-state problem is solved [in first approxn] by the energies E_n of Eq. (20) and radial wavefns $R_n(\rho)$ of Eq. (21a). There is more to do on the bound-state problem, e.g. adding electron & proton spin, etc., but -- before we look into that -- we can consider the continuum states of the H-atom ... i.e. the situation where the electron is free, and "orbits" the proton at energies $E > 0$. This is useful for (A) an ionization process, where the atom receives an energy increment ΔE which frees the electron [$E(\text{bound}) + \Delta E = E(\text{free}) > 0$], (B) a process of scattering, where an otherwise free electron collides with a proton at $E > 0$.

When $E(\text{bound}) < 0 \rightarrow E(\text{free}) > 0$ in the radial eqn [Eq. (15) above], all that happens is the energy parameter E changes sign. We have...

$$\rightarrow \left\{ \frac{d^2}{d\rho^2} + \left[2E + \frac{2Z}{\rho} - \frac{l(l+1)}{\rho^2} \right] \right\} R(\rho) = 0 \quad \checkmark \quad K^2 = -2E = -2E(\text{free})/E_0 < 0; \quad (23)$$

so $K = ik$, $k = \sqrt{2E(\text{free})/E_0}$.

Asymptotics are...

$$\left\{ \begin{array}{l} \rho \rightarrow 0 : R(\rho) \sim \rho^{l+1}, \text{ finite as } \rho \rightarrow 0; \\ \rho \rightarrow \infty : R(\rho) \sim e^{\pm ik\rho}, \text{ both signs OK;} \end{array} \right\} \quad R(\rho) = C_{kl} \overset{\text{norm const}}{\rho^{l+1}} e^{\pm ik\rho} f(\rho); \quad (24)$$

and $\rightarrow f(\rho) = F\left(\underbrace{l+1 + \frac{iZ}{k}}_a; \underbrace{2l+2}_b; 2ik\rho\right) \leftarrow K = ik \text{ in Eq. (19).} \quad (25)$

There is now no reason that $R(\infty)$ vanish [as for a bound state], so the parameter $a = l+1 + i(Z/k)$ need not be quantized. In fact the energy $E(\text{free}) = \frac{1}{2} E_0 k^2$ can be anything, so $0 \leq k < \infty$ continuously. The continuum wavefn is:

$$\left\{ \begin{array}{l} R(\rho) = C_{kl} \rho^{l+1} e^{\pm ik\rho} F\left(l+1 \mp \frac{iZ}{k}; 2l+2; \mp 2ik\rho\right) \\ \approx \sqrt{\frac{2}{\pi}} \sin\left[k\rho + \frac{Z}{k} \ln 2k\rho - \frac{1}{2} l\pi + \delta_l(k)\right] \end{array} \right. \quad \int \text{phase shift: } \delta_l(k) = \arg \Gamma\left(l+1 - \frac{iZ}{k}\right). \quad (26)$$

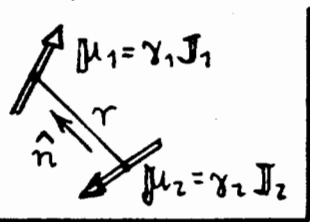
Last result from Landau & Lifshitz "QM" (1965), § 36. As $\rho \rightarrow \infty$, $\frac{1}{\rho} R(\rho)$ behaves like a spherical wave. The relative sign of the charge changes when $Z \rightarrow (-)Z$.

7) At this point, we have pretty well nailed down the Coulomb interaction between a spinless electron & spinless proton, for both bound & free states. But $V(r) = -Ze^2/r$ is not the only way these particles interact... when they are properly invested with their spin & momenta, they acquire magnetic moments, and then they interact via magnetic fields as well electric fields. The magnetic interaction energies are typically very much smaller than the electronic binding energies [viz $E_{\text{mag}} \sim \alpha^2 E_{\text{binding}}$], but they generate easily measured and "interesting" energy splittings in atoms. We will study this.

Any charged particle with some attendant & momentum \mathbf{J} (could be an intrinsic spin \mathbf{S} , or orbital & mom. \mathbf{L}) has an associated magnetic moment, written as

→ $\boldsymbol{\mu}_J = \gamma \mathbf{J}$, $\gamma = \text{const}$, called the gyromagnetic ratio [Jackson, Eq. (5.59)]. (27)

If \mathbf{J} is measured in units of \hbar (i.e. \mathbf{J} is dimensionless), then for (e, m) typically: $\gamma = g \mu_B$, where $\mu_B = e\hbar/2mc$ is the Bohr magneton, and the g -factor is a number [$g(\text{electron}) \approx 2$, $g(\text{proton}) \approx 2 \times 2.79/1836$, etc.]. In any case, if two such particles are at distance r from one another [as the e & p in an H-atom], they will interact -- at the very least -- by the classical dipole-dipole interaction [note Jackson Eq. (5.73)]...



$$E = -\boldsymbol{\mu}_1 \cdot \mathbf{B}_2 = -\frac{1}{r^3} \boldsymbol{\mu}_1 \cdot [3\hat{n}(\hat{n} \cdot \boldsymbol{\mu}_2) - \boldsymbol{\mu}_2],$$

$$\text{or } E_{\text{mag}} = \frac{\gamma_1 \gamma_2}{r^3} [\mathbf{J}_1 \cdot \mathbf{J}_2 - 3(\hat{n} \cdot \mathbf{J}_1)(\hat{n} \cdot \mathbf{J}_2)]. \quad (28)$$

This is one form of magnetic energy (there are others)... the point is that E_{mag} involves the "coupling" of & momenta \mathbf{J}_1 & \mathbf{J}_2 . In QM, the \mathbf{J} 's are operators which generate distinct quantum states all by themselves. This notion is not fully incorporated in the above H-atom treatment (we've only included $\mathbf{J} = \mathbf{L}$ (orbital)).

→ So, to add magnetic energies to the H-atom, we must study & momentum coupling.