Exact QM solution in one-electron atoms.

McMurry Ch 7.1 and 7.2. SP Ch 2.1, Foot Ch 2.
Exercises: 12 - 15. (H4 and H5)

SE: $(-\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r})\Psi = E\Psi$

$$E_n = -R_M \cdot \frac{Z^2}{n^2}$$

$$\Psi_{n,\ell,m}(r,\theta,\varphi) = R_{n,\ell}(r)\cdot Y_{\ell,m}(\theta,\varphi)$$

$$\int_0^{\infty}\int_0^{\pi}\int_0^{2\pi} \left|R_{n,\ell}(r)\cdot Y_{\ell,m}(\theta,\varphi)\right|^2 r^2 \sin\theta dr d\theta d\varphi = 1$$

$$R(\rho) = \rho^{\ell}\cdot e^{-\rho}\cdot c_0\cdot(1+\sum_{k=0}^{n-\ell-1}\frac{c_k}{c_0}\cdot\rho^k), \quad \rho = \frac{Z}{na_0}\cdot r$$

$c_0 \neq 0$ determined from the normalization condition.

$$c_{k+1} = -2c_k\frac{n-(\ell+k+1)}{(\ell+k+2)(\ell+k+1)-\ell(\ell+1)},\ k = 0,1,\ldots,n-\ell-1$$

$$< r_{n\ell} > = \int R^*(r)\cdot r\cdot R(r)\cdot r^2 dr = \frac{1}{2Z}[3n^2 - \ell(\ell+1)]$$

One-electron atoms in spherical coordinates

$$\mathbf{L}_x = i\hbar(\sin\varphi\frac{\partial}{\partial\theta} + \frac{\cos\varphi}{\tan\theta}\frac{\partial}{\partial\varphi}),$$

$$\mathbf{L}_y = i\hbar(-\cos\varphi\frac{\partial}{\partial\theta} + \frac{\sin\varphi}{\tan\theta}\frac{\partial}{\partial\varphi}),$$

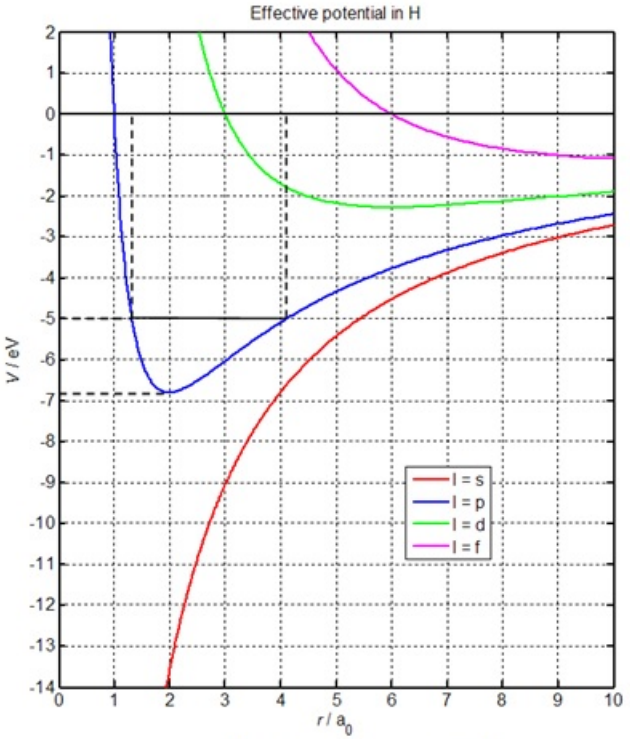
$$\mathbf{L}_z = -i\hbar\frac{\partial}{\partial\varphi}$$

$$\mathbf{L}^2 = -\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \frac{1}{\tan\theta}\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right)$$

$$H = -\frac{\hbar^2}{2\mu}\cdot(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}) - \frac{Ze^2}{4\pi\varepsilon_0\cdot r}$$

$$= -\frac{\hbar^2}{2\mu}\cdot\left[\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{r^2}\left(\frac{\partial^2}{\partial\theta^2}+\frac{1}{\tan\theta}\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right)\right] - \frac{Ze^2}{4\pi\varepsilon_0\cdot r}$$

$$= -\frac{\hbar^2}{2\mu}\cdot\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{L^2}{2\mu\cdot r^2} - \frac{Ze^2}{4\pi\varepsilon_0\cdot r}$$



$$V_{eff} = \frac{\hbar^2 \ell \cdot (\ell + 1)}{2\mu \cdot r^2} - \frac{Ze^2}{4\pi\varepsilon_0 \cdot r}$$

In atomic physics the value of ℓ is always given as a letter: $\ell = 0 \rightarrow$ s, $1 \rightarrow$ p, $2 \rightarrow$ d, $3 \rightarrow$ f, $4 \rightarrow$ g, h, i, (j), k, l, ...

A p electron with an energy of -5 eV is classically constrained to oscillate between $1.4 < r < 4\ a_0$ whereas with an energy of about -6.8 eV it can only move in a circular orbit with a radius of $2a_0$.

Note, only s-electrons can move close to the nucleus. Very important later on!!

Series solution of the radial differential equation.

$$f''-2f'-(\frac{\ell(\ell+1)}{\rho^2}-\frac{2Z}{a_0\kappa\rho})f=0 \quad (8)$$

Ansatz:

$$f(\rho)=\rho^s\cdot\sum_{k=0}^{\infty}c_k\rho^k \quad c_0\neq 0.$$

Calculate the derivatives and collect terms with similar powers in (8)

$$\sum_{k=0}^{\infty}c_k[(s+k)(s+k-1)-\ell(\ell+1)]\rho^{s+k-2}+\sum_{k=0}^{\infty}c_k[\frac{2Z}{a_0\kappa}-2(s+k)]\rho^{s+k-1}=0$$

The lowest order term arise from the first sum with $k = 0$. If we write that term separately the first sum will start with $k = 1$ and both sums will be in powers of $s + k – 1$. If we change summation index in the first sum from k to $k + 1$ we can write everything as a single summation:

$$c_0\cdot[s(s-1)-\ell(\ell+1)]\rho^{s-2}+$$

$$\sum_{k=0}^{\infty}\{c_{k+1}\cdot[(s+k+1)(s+k)-\ell(\ell+1)]+2c_k\cdot[\frac{Z}{a_0\kappa}-(s+k)]\}\rho^{s+k-1}=0$$

If the polynomial is zero for all values of ρ then each coefficient must be zero individually. Since we assumed $c_0\neq 0$ the first term gives $s=\ell+1$ or $s=-\ell$. The last possibility must be ignored since it leads to a non-normalizable function $P(\rho)$ when $\rho\to 0$.

To make everything within the curly brackets equal to zero in the remaining summation the c - coefficients must satisfy the recursion relation (using $s=\ell+1$)

$$c_{k+1}=-2c_k\frac{(Z/a_0\kappa)-(\ell+k+1)}{(\ell+k+2)(\ell+k+1)-\ell(\ell+1)}$$

For large k the ratio of the coefficients will be $c_{k+1}/c_k=2k/k^2=2/k$. This ratio is the same as that between successive terms in the expansion of

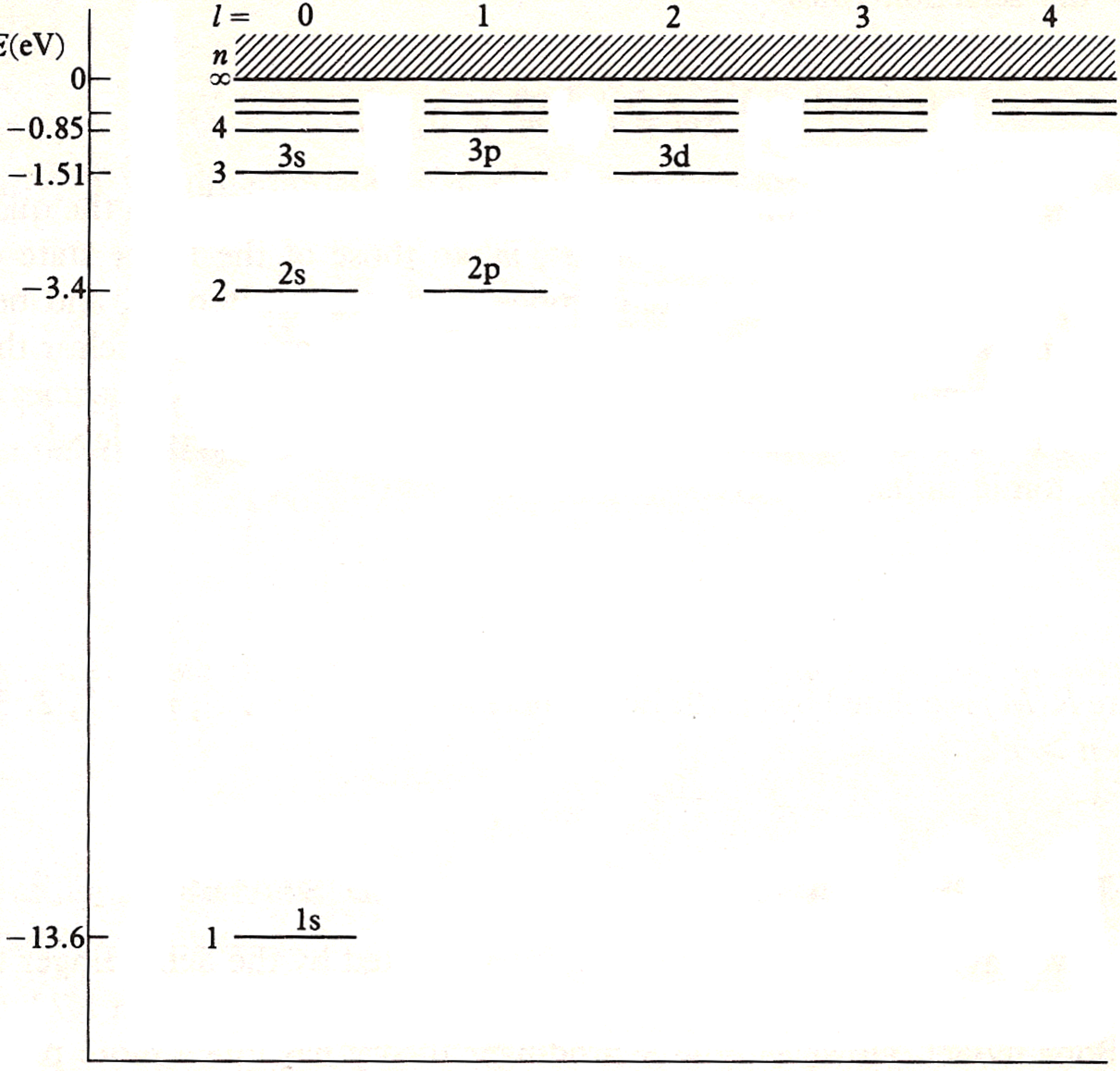
$$e^{2\rho}=1+\frac{2\rho}{1!}+\frac{2^2}{2!}\rho^2+....+\frac{2^{k-1}}{(k-1)!}\rho^{k-1}+\frac{2^k}{k!}\rho^k+...$$

Hence, for large ρ the two functions behave similar and $P(\rho)\approx e^{-\rho}\cdot e^{2\rho}\to\infty$ when $\rho\to\infty$. Thus it is not normalizable and the series must be truncated, i.e. for some $k=N=0,1,2...$ $(Z/a_0\kappa)-(\ell+N+1)=0$.

Introducing the main quantum number $n=\ell+N+1=1,2,3,...$ we obtain finally $\kappa=Z/a_0n$ and hence a quantized energy:

$$E_n=-\frac{\hbar^2}{2\mu a_0^2}\cdot\frac{Z^2}{n^2}.$$

Thus the reasonable demand that the wavefunction is normalizable leads to a quantized energy!!



3.2 Energy-level diagram for atomic hydrogen.

Table 2.2 Radial hydrogenic wavefunctions $R_{n,l}$ in terms of the variable $\rho = Zr/(na_0)$, which gives a scaling that varies with n. The Bohr radius a_0 is defined in eqn 1.40.

$$R_{1,0} = \left(\frac{Z}{a_0}\right)^{3/2} 2\,\mathrm{e}^{-\rho}$$

$$R_{2,0} = \left(\frac{Z}{2a_0}\right)^{3/2} 2\,(1-\rho)\,\mathrm{e}^{-\rho}$$

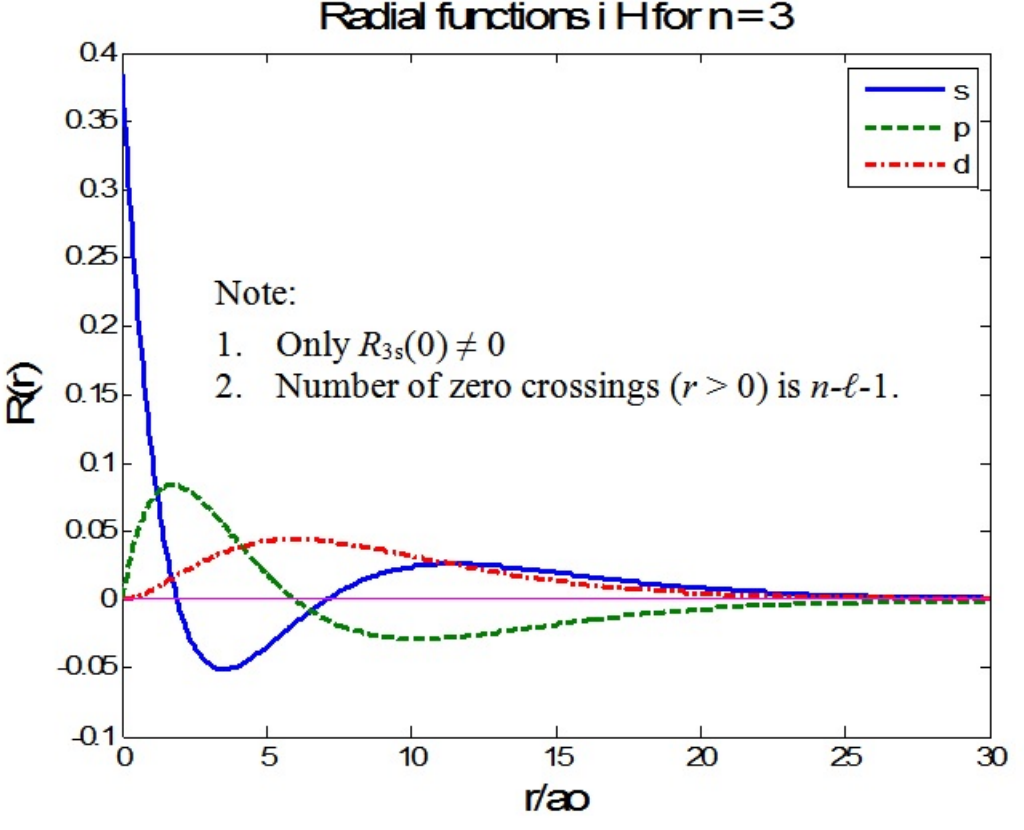
$$R_{2,1} = \left(\frac{Z}{2a_0}\right)^{3/2} \frac{2}{\sqrt{3}}\,\rho\,\mathrm{e}^{-\rho}$$

$$R_{3,0} = \left(\frac{Z}{3a_0}\right)^{3/2} 2\left(1-2\rho+\frac{2}{3}\rho^2\right)\mathrm{e}^{-\rho}$$

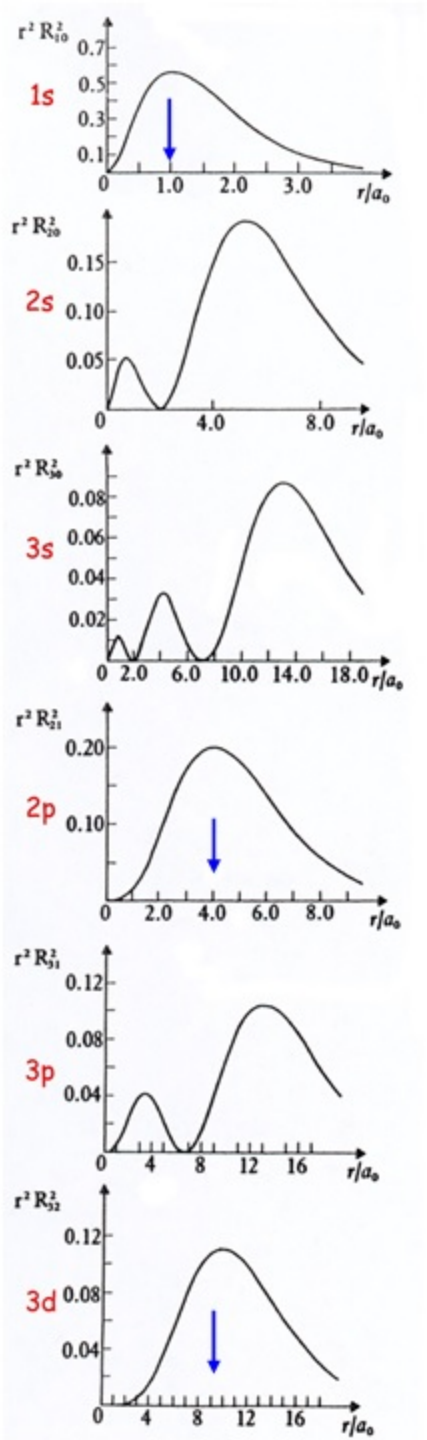
$$R_{3,1} = \left(\frac{Z}{3a_0}\right)^{3/2} \frac{4\sqrt{2}}{3}\,\rho\left(1-\frac{1}{2}\rho\right)\mathrm{e}^{-\rho}$$

$$R_{3,2} = \left(\frac{Z}{3a_0}\right)^{3/2} \frac{2\sqrt{2}}{3\sqrt{5}}\,\rho^2\,\mathrm{e}^{-\rho}$$

Normalisation: $\displaystyle\int_0^\infty R_{n,l}^2\, r^2\,\mathrm{d}r = 1$


Radial functions i Hfor n = 3
s
p
d
Note:
1. Only $R_{3s}(0) \neq 0$
2. Number of zero crossings ($r > 0$) is n-ℓ-1.
R(r)
r/ao
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
-0.05
-0.1
0
5
10
15
20
25
30

Radial probability distribution in H.



For 1s, 2p, 3d,... i.e.

$n, \ell = n - 1$

the most probable distance r_n is given by:

$$r_n = a_0 \frac{n^2}{Z}$$

i.e. the same result as in the Bohr model!

Number of minima:

$N = n - \ell - 1$

Summary one-electron atoms.

Bohr:

$$r_n = a_0 \cdot \frac{n^2}{Z}, \qquad a_0 = 0.529 \text{ Å}.$$

$$v_n = \alpha \cdot c \cdot \frac{Z}{n}, \qquad \alpha = \frac{1}{137}$$

$$E_n = -R_M \cdot \frac{Z^2}{n^2}, \quad R_M = \frac{m}{M+m} \cdot 109737 \text{ cm}^{-1}$$

Quantum mechanics

$$(-\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r})\Psi = E\Psi$$

$$E_n = -R_M \cdot \frac{Z^2}{n^2} \quad (E \text{ in cm}^{-1})$$

Only for the Coulomb potential is E independent of ℓ.

$n = 1, 2, 3..... \quad \ell = 0, 1, 2, ...(n-1) \quad m = -\ell, -\ell+1, ...\ell$

$$\Psi_{n,\ell,m}(r,\theta,\varphi) = R_{n,\ell}(r) Y_{\ell,m}(\theta,\varphi)$$

$$R(\rho) = \rho^{\ell} \cdot e^{-\rho} \cdot c_0 \cdot (1 + \sum_{k=1}^{n-\ell-1} \frac{c_k}{c_0} \cdot \rho^k), \quad \rho = \frac{Z}{a_0 n} \cdot r$$

$c_0 \neq 0$ determined from the normalization condition.

$R(\rho)$ has $n - \ell - 1$ zeros for $r > 0$

$$\int_0^{\infty}\int_0^{\pi}\int_0^{2\pi} \left| R_{n,\ell}(r) \cdot Y_{\ell,m}(\theta,\varphi) \right|^2 r^2 \sin\theta dr d\theta d\varphi = 1$$

$$< r_{n\ell} > = \int R^*(r) \cdot r \cdot R(r) \cdot r^2 dr = \frac{1}{2Z}[3n^2 - \ell(\ell+1)]$$