That vector with spin

$$\Psi(r,\vartheta,\varphi)=\sum_{\text{all } n}\sum_{\text{all } l}\sum_{m=-l}^{l} A_{nlm}R_{nl}(r)Y_{lm}(\vartheta,\varphi)$$

symbolic ↓ notation

$$|\Psi\rangle=\sum_{\text{all } n}\sum_{\text{all } l}\sum_{m=-l}^{l} A_{nlm}|n\,l\,m\rangle$$

There is an additional parameter that the states have to determine: the spin.

$$|\Psi\rangle=\sum_{\text{all } n}\sum_{\text{all } l}\sum_{m_l=-l}^{l}\sum_{m_s=-\frac{1}{2}}^{\frac{1}{2}} A_{nlm_lm_s}|n\,l\,m_l\,s\,m_s\rangle$$

The basis states are now simultaneous eigenfunctions of:

$$\hat{E}|n\,l\,m_l\,s\,m_s\rangle=E_{nl}|n\,l\,m_l\,s\,m_s\rangle$$

$$\hat{\vec{L}}^2|n\,l\,m_l\,s\,m_s\rangle=\hbar^2 l(l+1)|n\,l\,m_l\,s\,m_s\rangle$$

$$\hat{\vec{S}}^2|n\,l\,m_l\,s\,m_s\rangle=\hbar^2\tfrac{3}{4}|n\,l\,m_l\,s\,m_s\rangle$$

$$\hat{L}_z|n\,l\,m_l\,s\,m_s\rangle=\hbar m_l|n\,l\,m_l\,s\,m_s\rangle$$

$$\hat{S}_z|n\,l\,m_l\,s\,m_s\rangle=\hbar m_s|n\,l\,m_l\,s\,m_s\rangle$$

Note that it was an arbitrary choice to have the basis states have the last 2 properties since L_z and S_z do not change the energy.

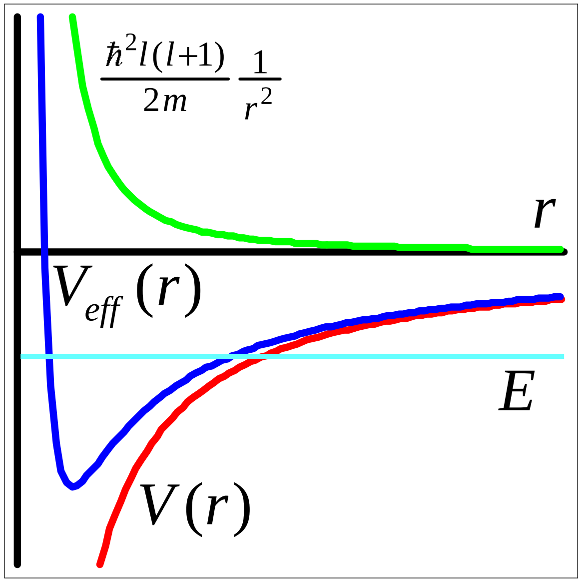
Georg.Hoffstaetter@Cornell.edu

The radial part of the wave function

$$V(r)\Phi(r,\vartheta,\varphi)+\tfrac{1}{2m}\left(\hat{p}_r^2+\tfrac{1}{r^2}\hat{\vec{L}}^2\right)\Phi(r,\vartheta,\varphi)=E\Phi(r,\vartheta,\varphi)$$

$$\Phi(r,\vartheta,\varphi)=R_{nl}(r)\,f(\vartheta,\varphi)\,,\quad \hat{p}_r^2\Phi=-\hbar^2\,\tfrac{1}{r}\tfrac{\partial^2}{\partial r^2}(r\,\Phi)$$

$$-\left[\tfrac{e^2}{4\pi\varepsilon_0}\tfrac{1}{r}-\tfrac{\hbar^2 l(l+1)}{2m}\tfrac{1}{r^2}\right]R_{nl}-\tfrac{\hbar^2}{2m}\tfrac{1}{r}\tfrac{\partial^2}{\partial r^2}(rR_{nl})=E\,R_{nl}$$



The effective radial potential:

$$V_{eff}=-\left[\tfrac{e^2}{4\pi\varepsilon_0 r}-\tfrac{\hbar^2}{2m}\tfrac{l(l+1)}{r^2}\right]=-\tfrac{e^2}{8\pi\varepsilon_0 a_0}\left[\tfrac{2}{r/a_0}-\tfrac{\hbar^2 8\pi\varepsilon_0}{2me^2 a_0}\tfrac{l(l+1)}{(r/a_0)^2}\right]=-E_1\left[\tfrac{2}{\xi}-\tfrac{l(l+1)}{\xi^2}\right]$$

Georg.Hoffstaetter@Cornell.edu

Energy and angular momentum

$$E = \frac{1}{n^2} E_1 \, , \quad E_n = -\frac{1}{n^2}\frac{e^2}{8\pi\varepsilon_0 a_0}$$ turns out to be independent of l.

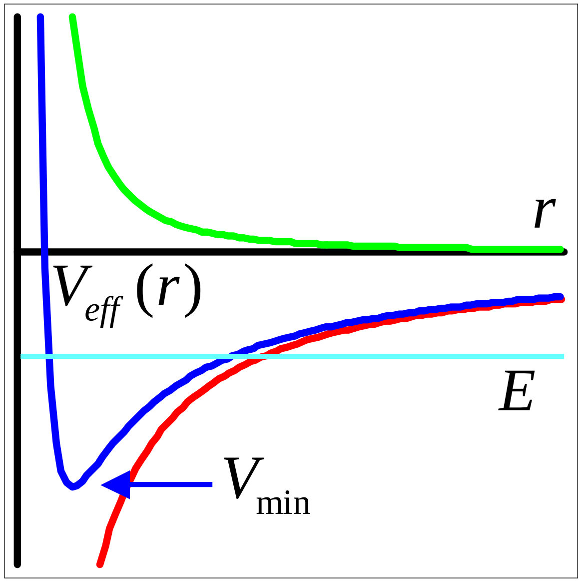
Or, visual reasoning:

E has to be bigger than V_{min}

$$V_{eff} = -\frac{2}{\xi} + \frac{l(l+1)}{\xi^2}$$

$$V'_{eff} = \frac{2}{\xi_{min}{}^2} - 2\frac{l(l+1)}{\xi_{min}{}^3} = 0 \quad \rightarrow \quad \xi_{min} = l(l+1)$$

$$-V_{min} = \frac{1}{l(l+1)} > \frac{E}{E_1} = \frac{1}{n^2} \quad \rightarrow \quad l(l+1) \le n^2$$



$$l \le n-1$$

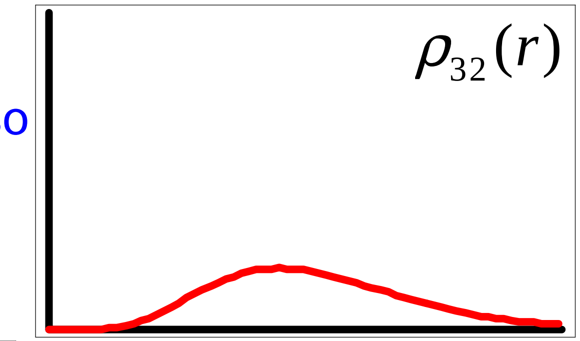
$$l \in \{0, \ldots, n-1\}$$

Georg.Hoffstaetter@Cornell.edu

The complete wave function

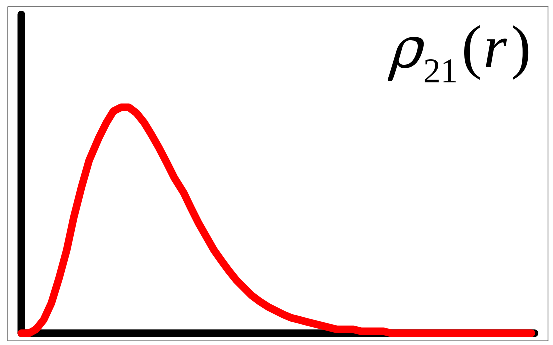
$$\Psi(r,\vartheta,\varphi) = \sum_{\text{all } n} \sum_{\text{all } l} \sum_{m=-l}^{l} A_{nlm} R_{nl}(r) Y_{lm}(\vartheta,\varphi)$$

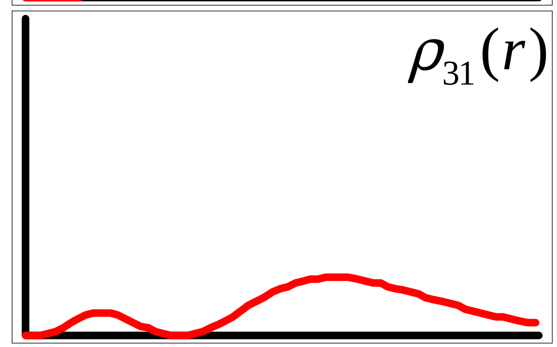
Degeneracy of the Coulomb potential: For all potentials V(r) the energy does not depend on m (and with spin also not on m_s). But in the Coulomb potential it additionally does not depend on *l*.

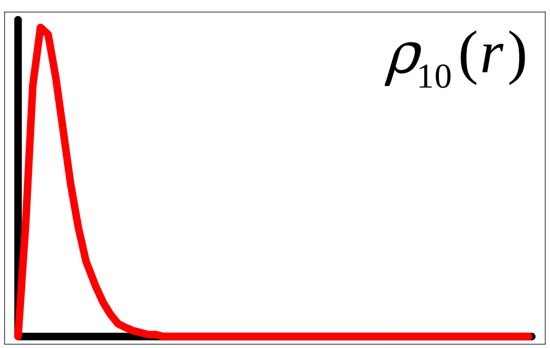


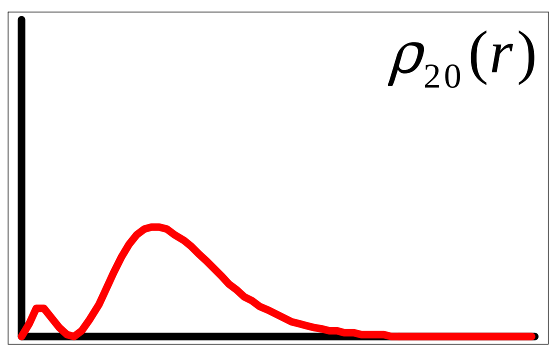
Radial probability distribution:

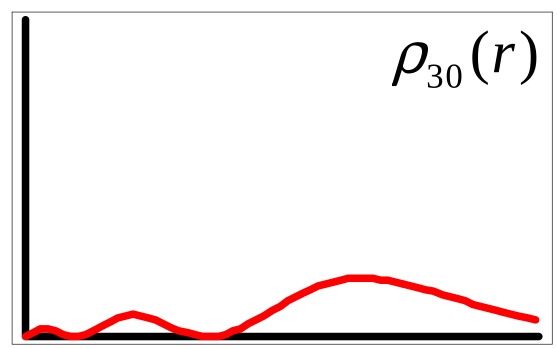
$$\rho_{nl}(r) = 4\pi r^2 \, | R_{nl}(r) |^2$$











Georg.Hoffstaetter@Cornell.edu