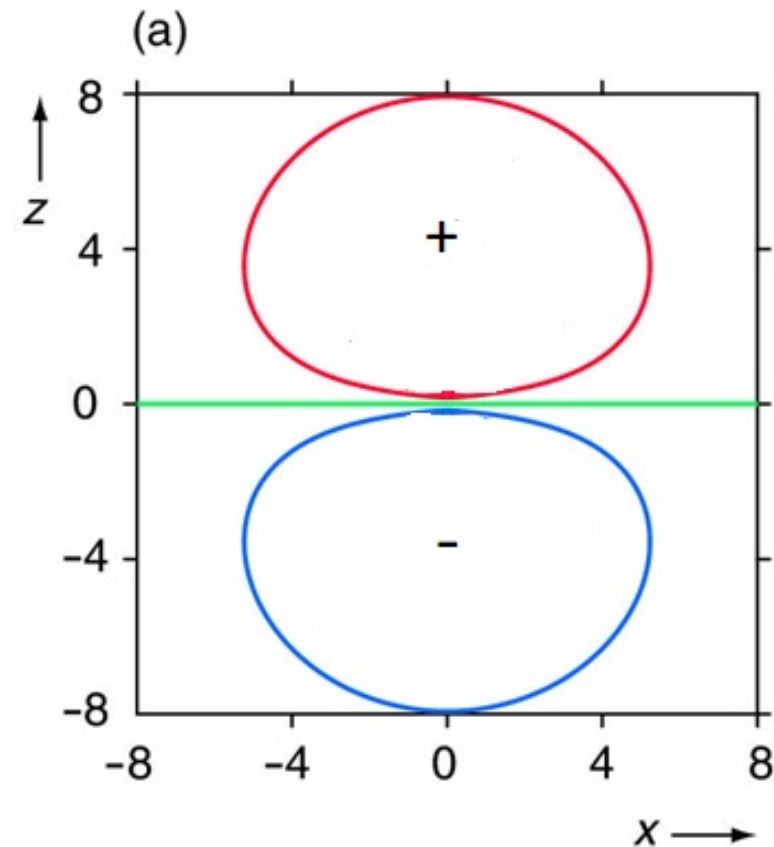
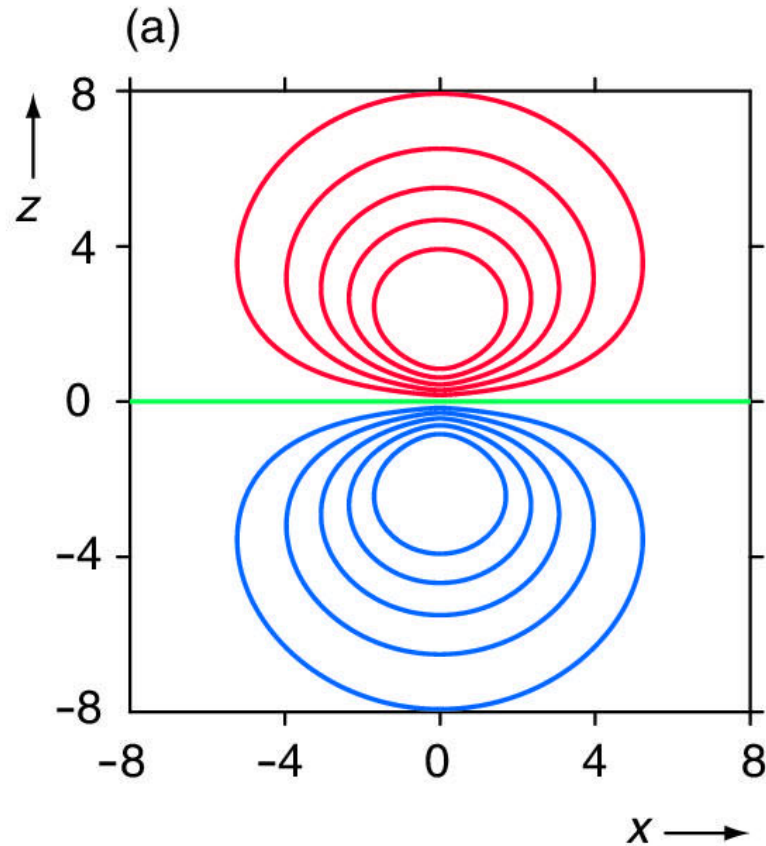
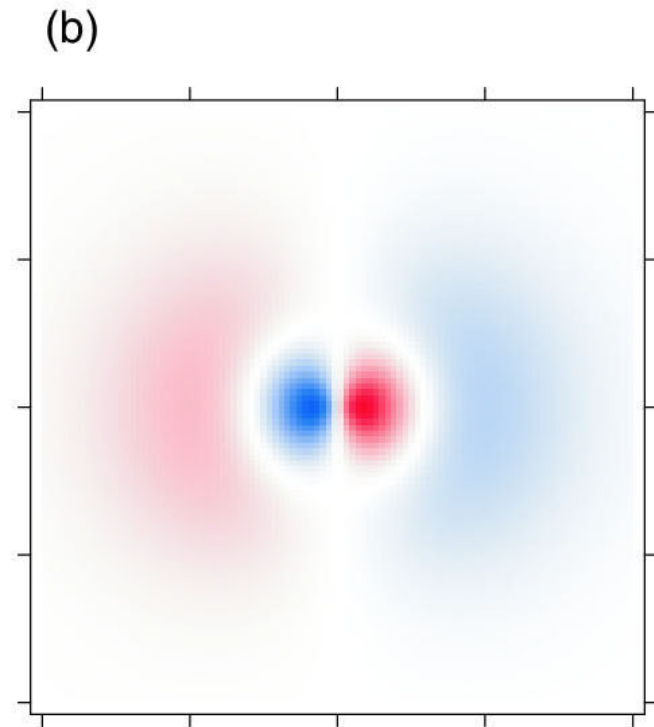
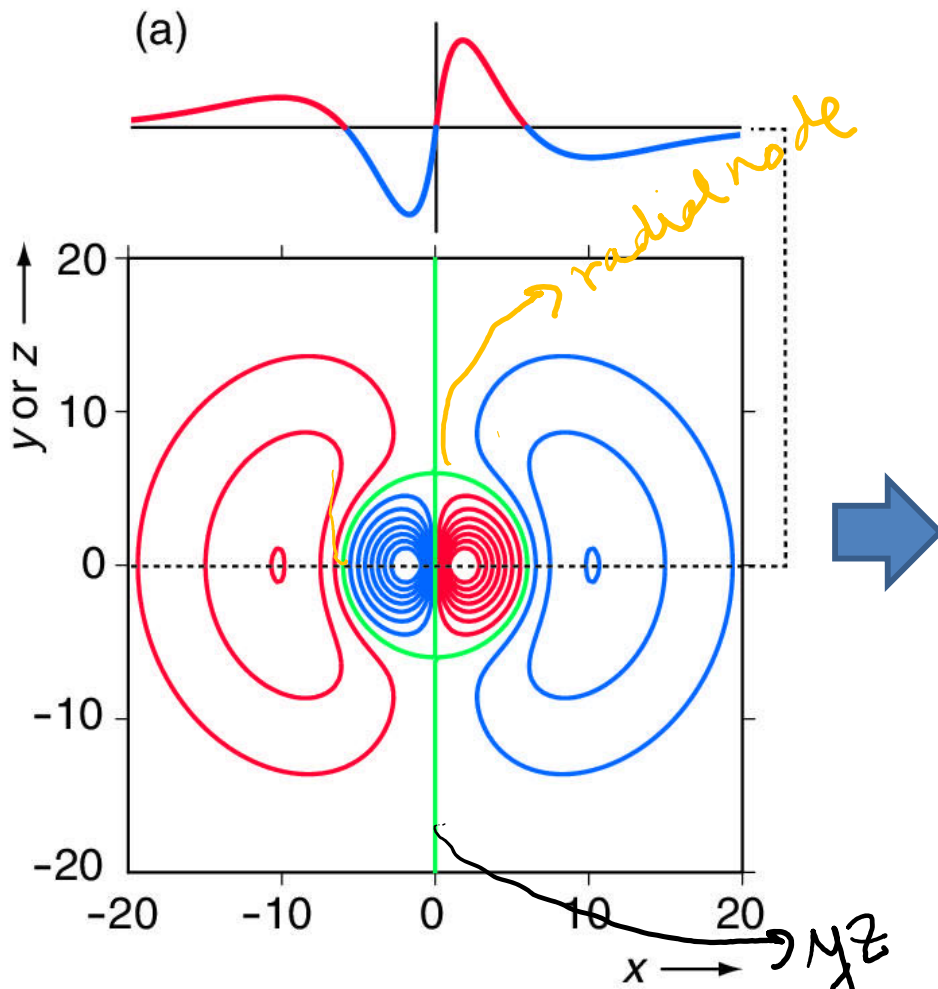


Wavefunction/ Probability-density contours for $2p_z$



Wavefunction/Probability-density contours for $3p_x$

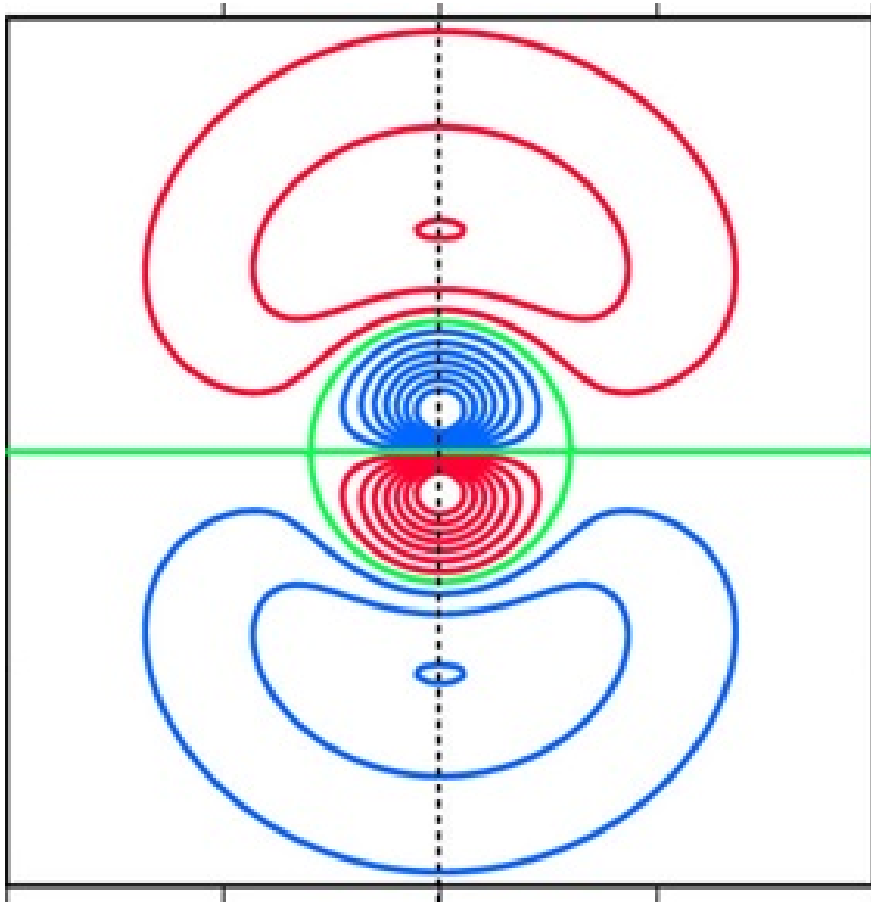
$3p$
 $3 - 1 - 1 = 1$
 $\downarrow \downarrow$
 no. of radial nodes
 \downarrow
 $n - l - 1$
 angular node = 1



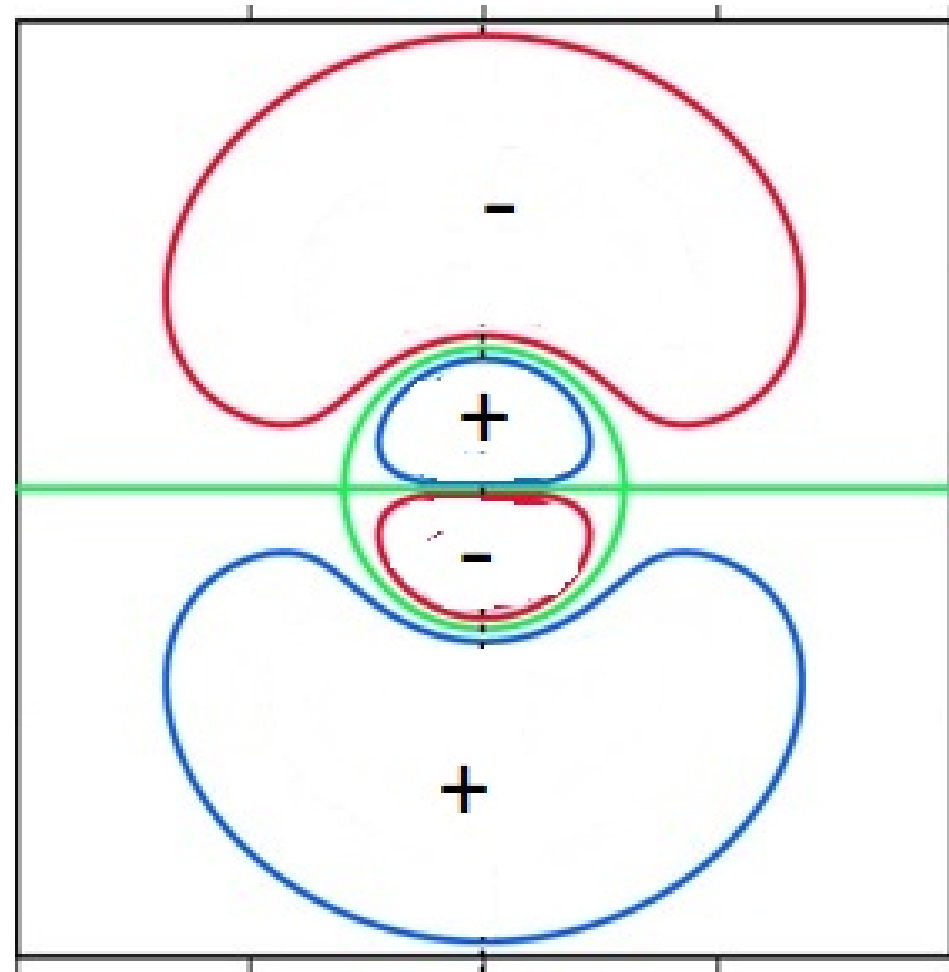
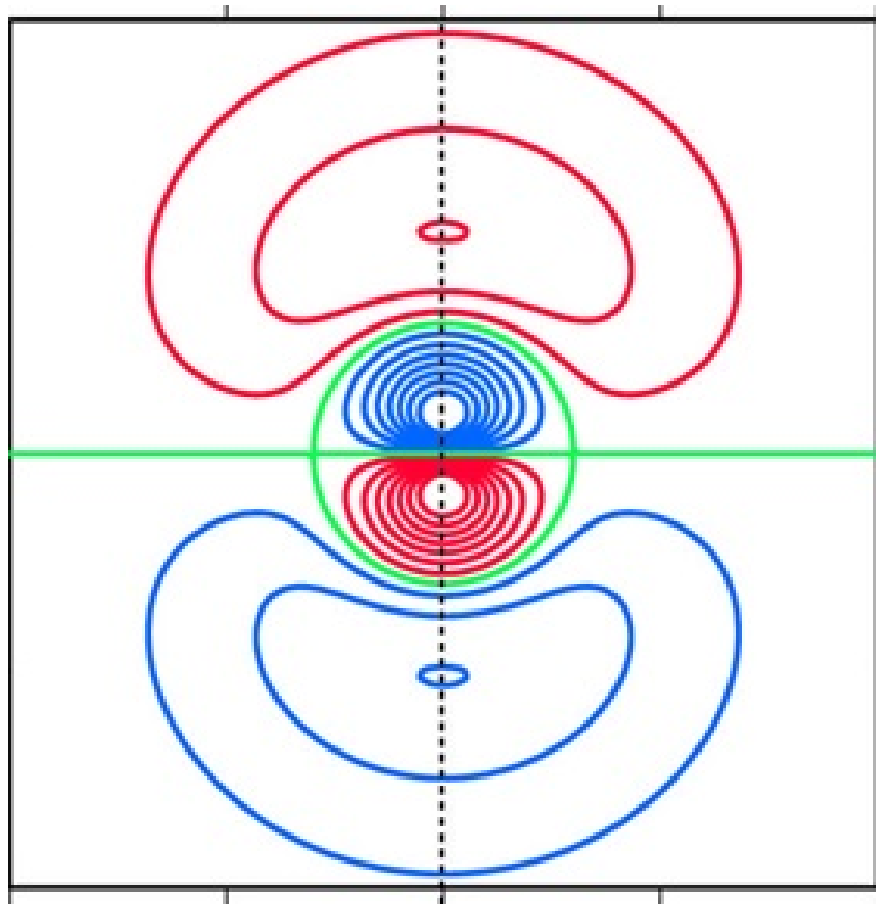
yz plane is the angular node

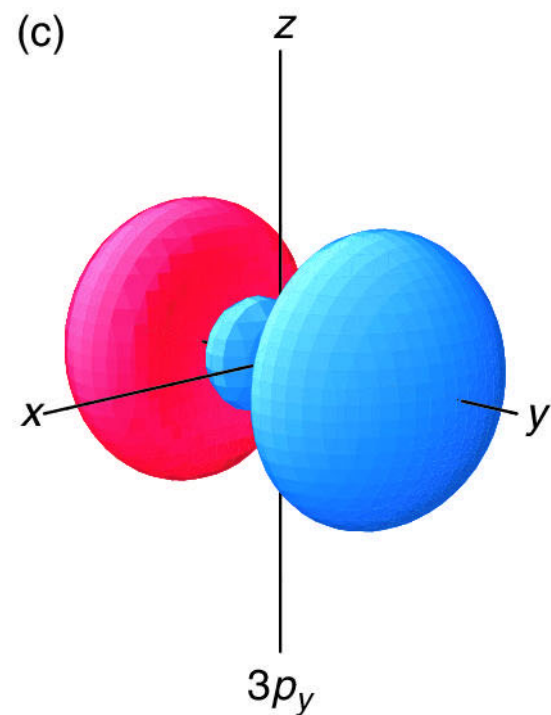
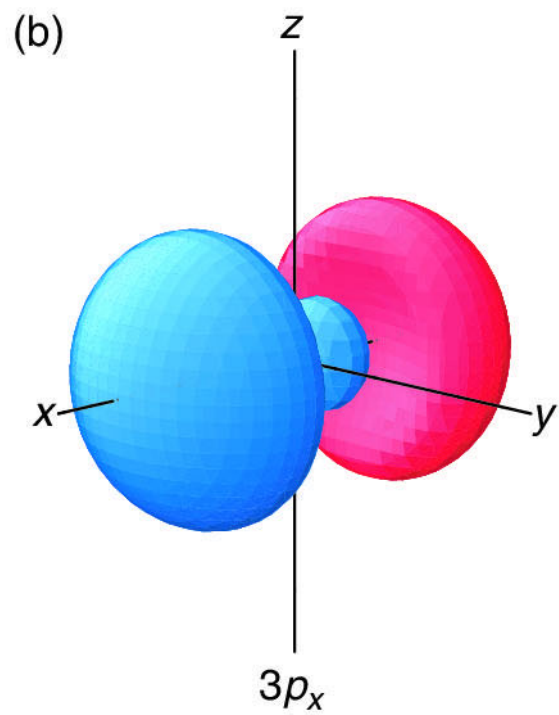
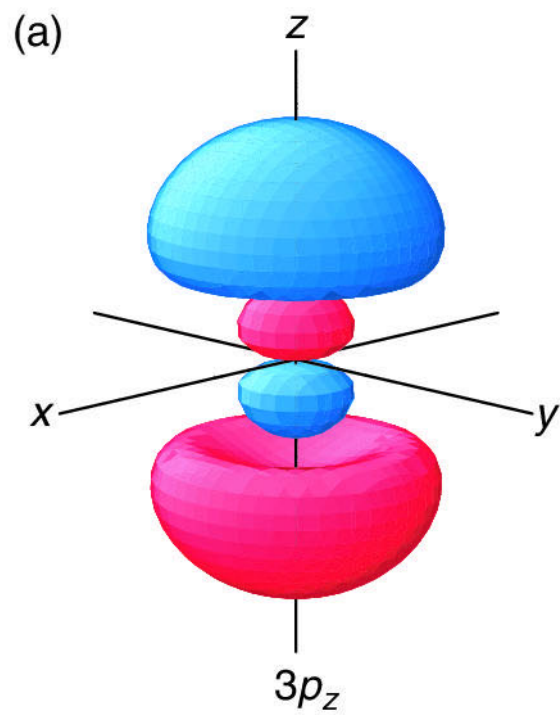
Probability-density contours for

$3p_x$



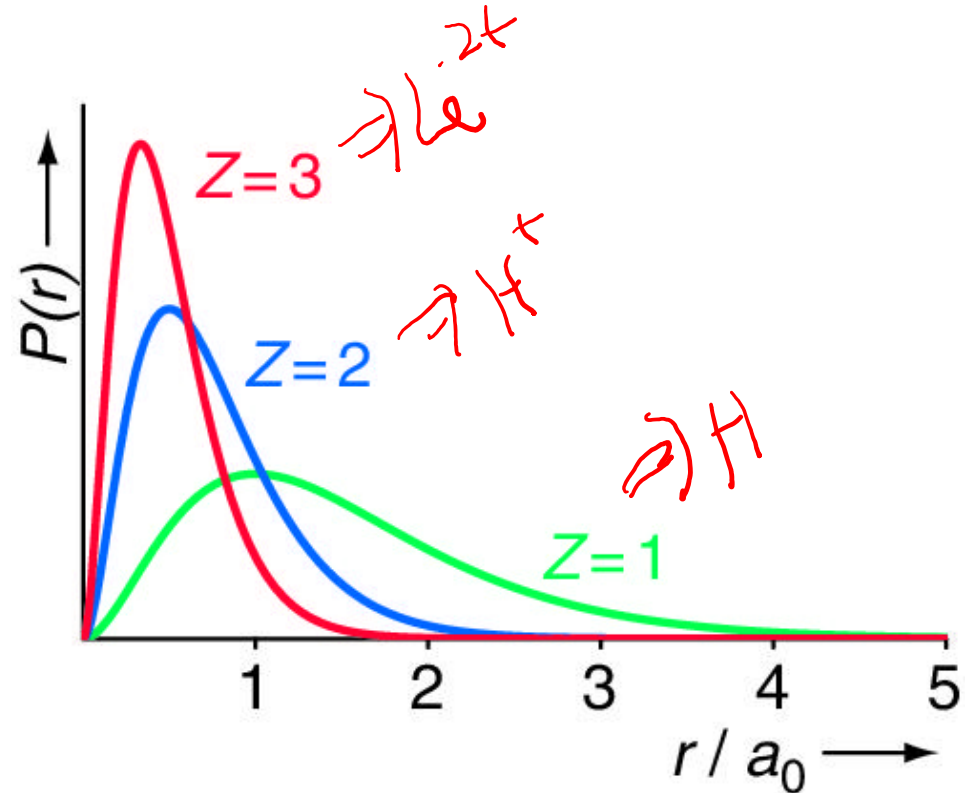
Probability-density contours for $3p_x$





Hydrogen-like atoms

Plot of RDFs of 1s electron
with increasing Z

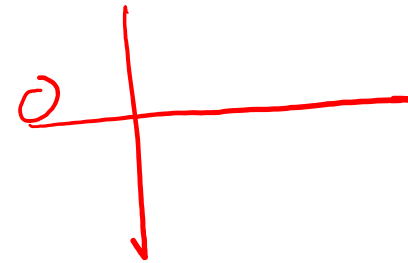


$$E_n = -\frac{Z^2 R_H}{n^2}.$$

$$1s: R_{1,0}(r) = N_{1,0} \exp\left(-\frac{Zr}{a_0}\right)$$

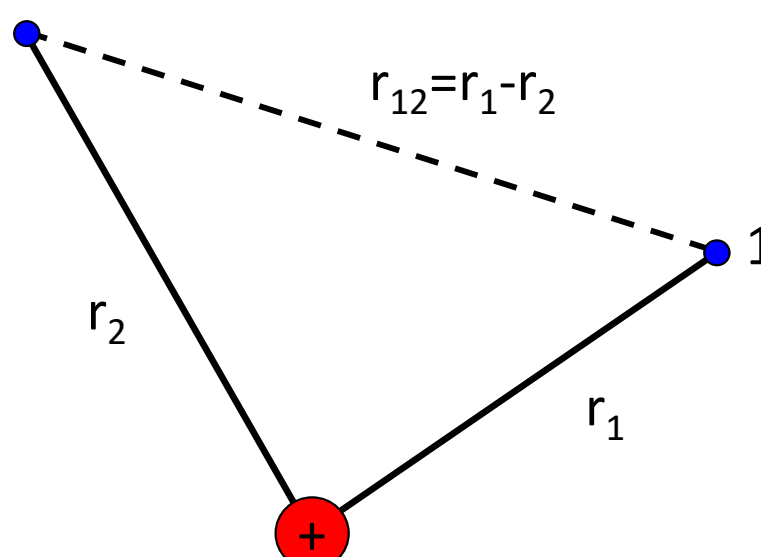
$$2s: R_{2,0}(r) = N_{2,0} \left(2 - \frac{Zr}{a_0}\right) \exp\left(-\frac{Zr}{2a_0}\right).$$

Binding energy
Higher $Z \rightarrow$
more tightly bound



He-atom (2e): 3-particle system!

Diagram illustrating the Hamiltonian for the He-atom (2e) system, showing the kinetic energy of electrons and the potential energy terms (Nucleus-Electron attraction and Electron-Electron repulsion).

$$\hat{H} = \underbrace{\frac{\hat{\mathbf{p}}_1^2}{2m_e}}_{\text{Kinetic Energy Of Electron 1}} + \underbrace{\frac{\hat{\mathbf{p}}_2^2}{2m_e}}_{\text{Kinetic Energy Of Electron 2}} + \underbrace{\frac{Ze^2}{4\pi\epsilon_0} \frac{1}{\hat{r}_1}}_{\text{Nucleus-Electron 1 Attraction}} - \underbrace{\frac{Ze^2}{4\pi\epsilon_0} \frac{1}{\hat{r}_2}}_{\text{Nucleus-Electron 2 Attraction}} + \underbrace{\frac{e^2}{4\pi\epsilon_0} \frac{1}{|\hat{\mathbf{r}}_1 - \hat{\mathbf{r}}_2|}}_{\text{Electron-Electron Repulsion}}$$


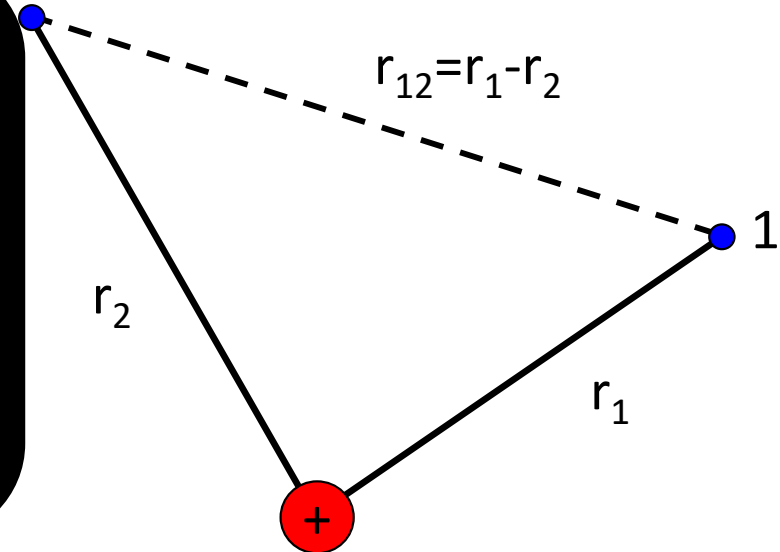
$$\hat{H}_{He} = \hat{H}_1^{1e}(r_1, \theta_1, \phi_1) + \hat{H}_2^{1e}(r_2, \theta_2, \phi_2) + \frac{1}{r_{12}}$$

$$\Psi_{He}(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2)$$

$$\hat{H}_{He} \Psi_{He}(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2) = E \Psi_{He}(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2)$$

- Consequence: Binding energies is not in nice analytical forms- numerical solutions
- For atoms more than 3 electrons, SE can not be solved even numerically

He-atom (2e): 3-particle system!



$$\Psi_{He}(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2)$$

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- Consequence: Binding energies is not in nice analytical forms- numerical solutions
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Orbital Approximation for N electrons

One electron orbital approximation used

SE for He atom: 2 electron system

$$\Psi_{He}(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2) \approx \Psi_1(r_1, \theta_1, \phi_1) \Psi_2(r_2, \theta_2, \phi_2) \rightarrow \Psi_1(\vec{r}_1) \Psi_2(\vec{r}_2)$$

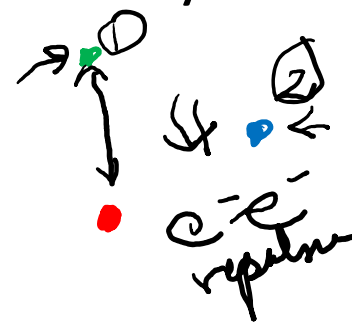
$$\Psi_{He}(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2, r_3, \theta_3, \phi_3) \approx \Psi_1(r_1, \theta_1, \phi_1) \cdot \Psi_2(r_2, \theta_2, \phi_2) \cdot \Psi_3(r_3, \theta_3, \phi_3)$$

- ψ of He which is strictly a wave function with 6 variables
- Electron 1 have its own wave function and electron 2 have its own wave function
- Wave function for electron 1 have a hydrogen like wave function: ψ_{100} of the electron in He will be ψ_{100} of the H-atom.

Orbital Approximation

- We assume that each electron experiences the nuclear charge and an average repulsion from all the other electrons in the atoms
- This allows us to generate a set of a set of orbitals that closely relate to the AO's of hydrogen

$$\Psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_{lm}(\theta, \phi)$$



- The angular part remains the same but the radial parts differ- however the radial parts are quite similar in form
- The electronic structure of the multi electron atom can be described in terms of occupation of these orbitals

→ Ψ_{200Li}

When we write $Li\ 2s^1$ the orbitals are not the same as hydrogen- but it is sufficiently close in form to be used the same label

Electronic Configurations

- $\psi_{\text{He}} = \psi_{\text{H}1s} \times \psi_{\text{H}1s}$, or generally, what we write as $1s^2$
- $\psi_{\text{He}}(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2) = \psi_{100}(r_1, \theta_1, \phi_1) \psi_{100}(r_2, \theta_2, \phi_2)$
- $\psi_{\text{Li}}(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2, r_3, \theta_3, \phi_3) = \psi_{100}(r_1, \theta_1, \phi_1) \psi_{100}(r_2, \theta_2, \phi_2) \psi_{200}(r_3, \theta_3, \phi_3)$, we write as $1s^2, 2s^1$

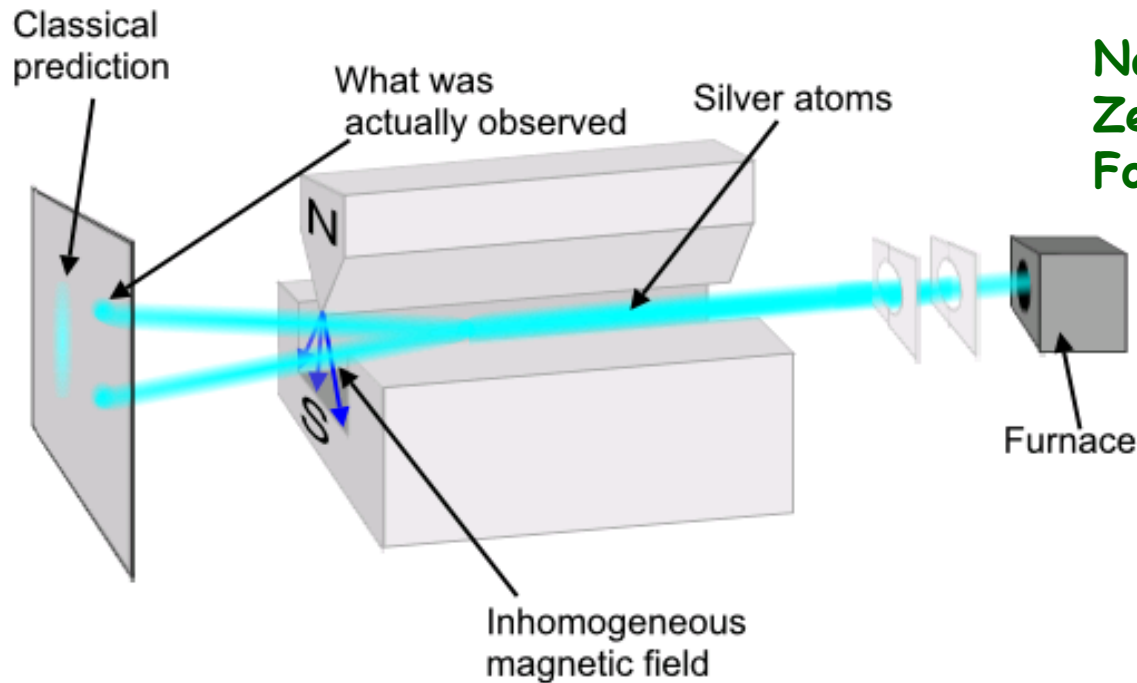
$$\begin{array}{l} \text{He} \Rightarrow 1s^2 \\ \psi_{\text{He}} \approx \psi_{100} \times \psi_{100} \end{array}$$

Electronic configurations (ns^x, np^y, \dots) which you know are nothing but short hand notations for the electron wave functions within this one electron approximation.

Why is Li $1s^2 2s^1$ and NOT $1s^3$ or $1s^2 2p^1$?

Intrinsic Angular Momentum: "Spin"

Uhlenbeck and Goudsmit (1925) showed that these were two angular momentum states - the electron has intrinsic angular momentum - "SPIN" angular momentum



Na/Ag atoms: ns^1 : $l=0$:
Zero Orbital Momentum
For 1S electrons

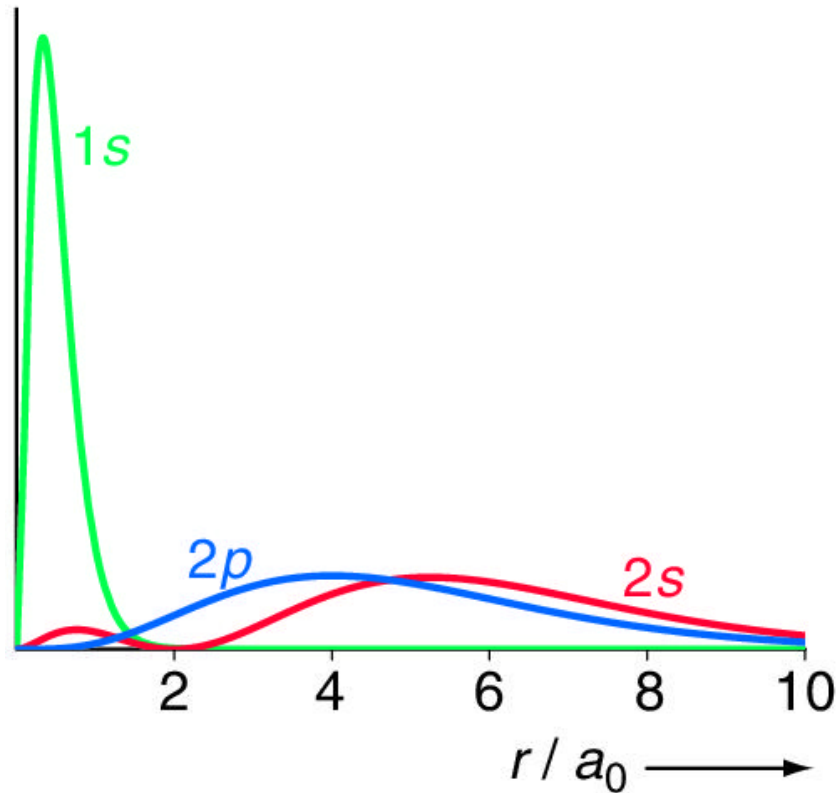


Dirac subsequently solves the relativistic Schrodinger equation to arrive at the fourth quantum number m_s

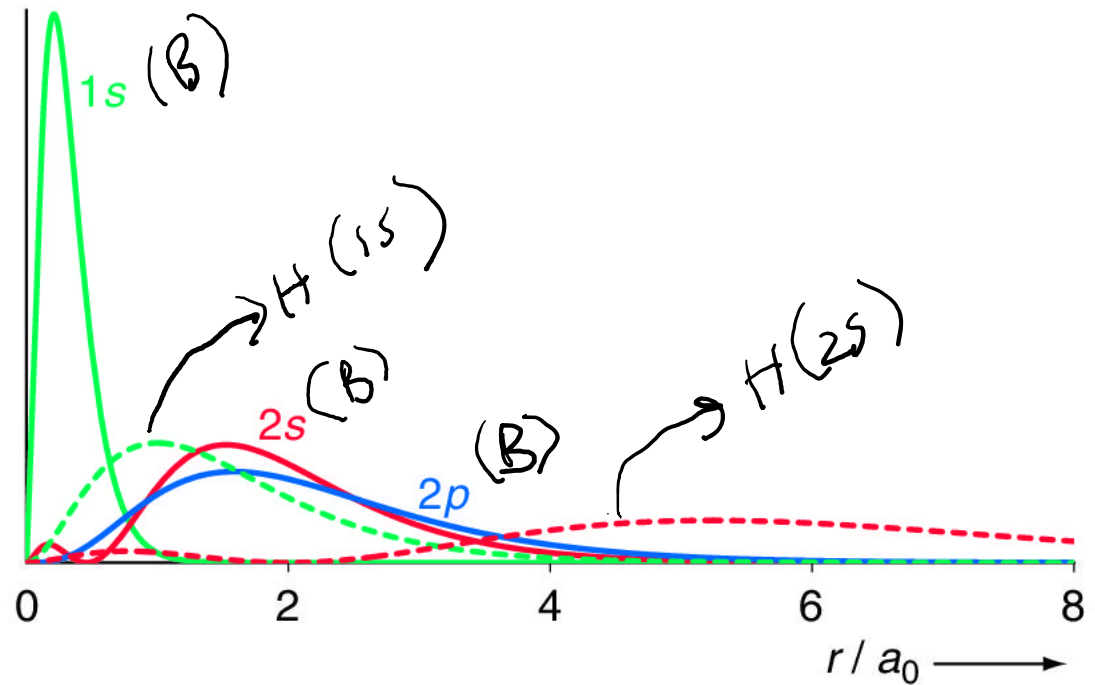
Spin

- Spin is entirely a quantum mechanical phenomenon- there is no classical analogy Spin is intrinsic angular momentum- it is an intrinsic part of a particle such as the electron
 - The spin quantum number comes from solving the relativistic Schrodinger equation
 - When you solve this equation, it drops the fourth quantum number which is called m_s
 - This m_s has two values, one is $+1/2$ and the other is $-1/2$
- **Pauli Exclusion Principle: “No two electrons in the same atom can have the same set of four quantum numbers”**
 - **For He the two sets: $1,0,0,+1/2$ and $1,0,0,-1/2$**

Wave-function of an Multi-electron Atom: Li



RDP of occupied orbitals of Li

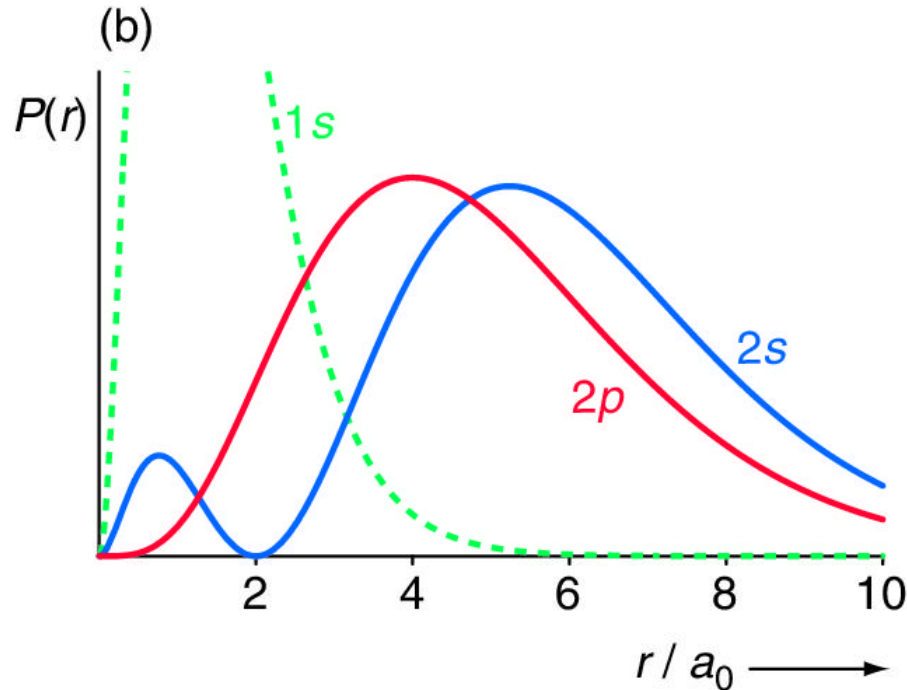


RDP of occupied orbitals of B and comparison with H (dashed lines)

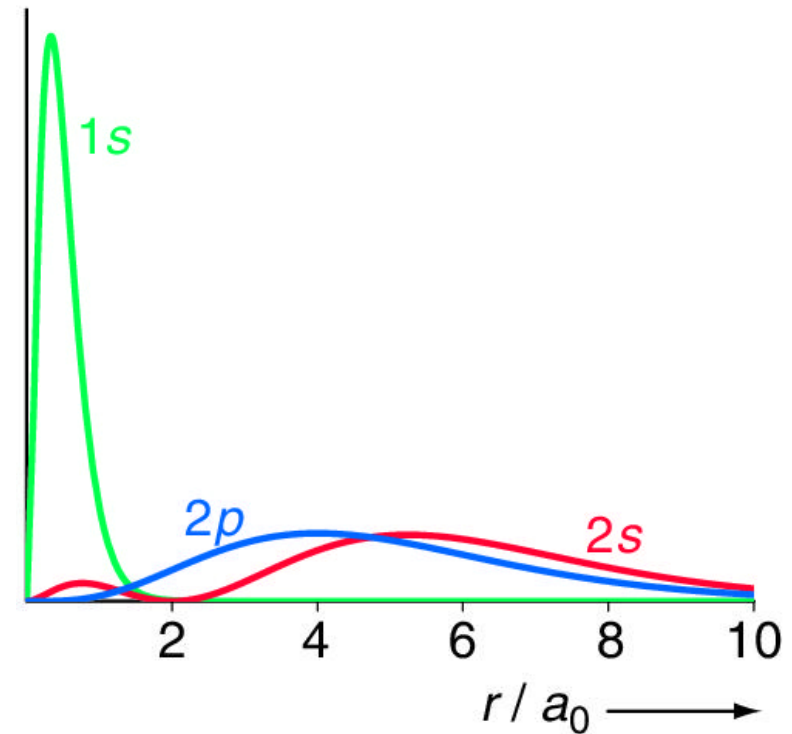
- The shapes of RPD for H and Li look similar
- The maxima of the RPD for B is much closer to the nucleus than H: more positive charge of the nucleus
- Example: the most probable value for 1s in Ar is $0.1 a_0$ while that of H-atom is a_0

Wavefunction of multi-electron

RPD of H-atom



RPD of Li-atom



- The RPD of $n=1$ in Li is much closer to the nucleus than $n=2$: spatially separated
- Brings back the idea of “shells” you have learnt in +2