Multi-Electron Atoms

- Start with Helium: He\(^+\) - same as H but with \(Z=2\)
- He - 2 electrons. No exact solution of S.E. but can use H wave functions and energy levels as starting point. We’ll use some aspects of perturbation theory but skip Ritz variational technique (which sets bounds on what the energy can be)
- nucleus screened and so \(Z(\text{effective})\) is < 2
- “screening” is ~same as e-e repulsion (for He, we’ll look at e-e repulsion. For higher \(Z\), we’ll call it screening)
- electrons are identical particles. Will therefore obey Pauli exclusion rule (can’t have the same quantum numbers). This turns out to be due to the symmetry of the total wave function
Schrod. Eq. For He

• have kinetic energy term for both electrons (1+2)

\[- \frac{\hbar^2}{2m} \nabla^2_1 \psi_T - \frac{\hbar^2}{2m} \nabla^2_2 \psi_T + V_T \psi_T = E_T \psi_T\]

\[V_T = V(\vec{r}_1) + V(\vec{r}_2) + V_{12}(\vec{r}_1 - \vec{r}_2)\]

• $V_{12}$ is the e-e interaction. Let it be 0 for the first approximation, that is for the base wavefunctions and then treat it as a (large) perturbation

• for the unperturbed potential, the solutions are in the form of separate wavefunctions

\[\psi_T(\vec{r}_1, \vec{r}_2) = \psi(\vec{r}_1)\psi(\vec{r}_2)\]

\[E_T = E_1 + E_2\]
Apply symmetry to He

• The total wave function must be antisymmetric
• but have both space and spin components and so 2 choices:

\[
\psi_{He} = \psi_{space}\psi_{spin} \implies \text{either}
\]

\[
\psi_{space} = \text{symmetric} \quad \oplus \quad \psi_{spin} = \text{antisym}
\]

\[
\text{OR} \quad \psi_{space} = \text{antisym} \quad \oplus \quad \psi_{spin} = \text{sym}
\]

• have 2 spin 1/2 particles. The total S is 0 or 1

\[
\psi_{spin} \quad \quad S \quad m_s \quad m_{s1} \quad m_{s2}
\]

\[
\begin{array}{c|cccc}
\uparrow_1 \uparrow_2 & 1 & 1 & \frac{1}{2} & \frac{1}{2} \\
\frac{1}{\sqrt{2}} (\downarrow_1 \uparrow_2 + \uparrow_1 \downarrow_2) & 1 & 0 & \pm \frac{1}{2} & \mp \frac{1}{2} \\
\downarrow_1 \downarrow_2 & 1 & -1 & -\frac{1}{2} & -\frac{1}{2} \\
\frac{1}{\sqrt{2}} (\downarrow_1 \uparrow_2 - \uparrow_1 \downarrow_2) & 0 & 0 & \mp \frac{1}{2} & \pm \frac{1}{2}
\end{array}
\]

• S=1 is spin-symmetric \quad S=0 is spin-antisymmetric
He spatial wave function

• There are symmetric and antisymmetric spatial wavefunctions which go with the anti and sym spin functions. Note \(a,b\) are the spatial quantum numbers \(n,l,m\) but not spin

\[
\psi_{\text{space (sym)}} = \frac{1}{\sqrt{2}} (\psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1))
\]
\[
\psi_{\text{space (asym)}} = \frac{1}{\sqrt{2}} (\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1))
\]

• when two electrons are close, the antisymmetric state is suppressed (goes to 0 if exactly the same point). symmetric state is enhanced

• “Exchange Force” \(S=1\) has the electrons (on average) further apart (as antisymmetric space). So smaller repulsive potential and so lower energy

• if \(a=b\), same space state, must have symmetric space and antisymmetric spin \(S=0\) (“prove” Pauli exclusion)
He Energy Levels

• V terms in Schrod. Eq.:

\[ V = -\frac{2e^2}{4\pi\varepsilon_0 r_1} - \frac{2e^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_1 - \vec{r}_2|} \]

• Oth approximation. Ignore e-e term.

\[ E_T = E_1 + E_2 = -\frac{4 \cdot 13.6 eV}{n_1^2} - \frac{4 \cdot 13.6 eV}{n_2^2} \]

\begin{align*}
&n_1 = n_2 = 1 \quad \Rightarrow \quad -109 \text{ eV} \\
&n_1 = 1(2), \, n_2 = 2(1) \quad \Rightarrow \quad -68 \text{ eV} \\
&n_1 = n_2 = 2 \quad \Rightarrow \quad -27 \text{ eV}
\end{align*}

• 0.5th approximation: Guess e-e term. Treat electrons as point objects with average radius (for both n=1) \( a_0/Z \) (Z=2). electrons on average are \(~0.7a_0\) apart with repulsive energy:

\[ \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_1 - \vec{r}_2|} = \frac{e^2}{4\pi\varepsilon_0 a_0} \times 1.4 = 13.6 eV \times 1.4 = 19 eV \]
He Energy Levels II

• V terms in Schrod. Eq.:

\[ V = -\frac{2e^2}{4\pi\varepsilon_0 r_1} - \frac{2e^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_1 - \vec{r}_2|} \]

• First approximation: look at expectation value of e-e term which will depend on the quantum states (i,j) of the 2 electrons and if S=0 or 1

\[ E'_{ij} = E_{ij} + \langle V_{ij} \rangle \quad \text{with} \quad \langle V_{ij} \rangle = \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_1 - \vec{r}_2|} \]

• Assume first order wavefunction for ground state has both electrons in 1S \( \phi_{100} \) (spin S=0)

\[ u_o(\vec{r}_1, \vec{r}_2) = \phi_{100}(\vec{r}_1)\phi_{100}(\vec{r}_2) \]

• expectation value

\[ \langle V_{11} \rangle = \iiint u^*(1,2) \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_1 - \vec{r}_2|} u(1,2) d^3\vec{r}_1 d^3\vec{r}_2 \]

\[ \text{with} \quad u^*(1,2)u(1,2) = |\phi_{100}(\vec{r}_1)|^2 |\phi_{100}(\vec{r}_2)|^2 \]

\[ \text{and} \quad \frac{1}{|\vec{r}_1 - \vec{r}_2|} = \frac{1}{(r_1^2 + r_2^2 - 2r_1r_2 \cos \theta_{12})^{1/2}} \]
He Energy Levels III

• do integral. Gets 34 eV. The \( \langle V_{11} \rangle \) is measured to be 30 eV \( \rightarrow \) 
  \( E(\text{ground}) = -109 + 30 = -79 \) eV

• For \( n_1=1, \ n_2=2 \). Can have \( L_2=0,1 \). Either \( S=0 \) or \( S=1 \). The space symmetrical states \( (S=0) \) have the electrons closer \( \rightarrow \) larger \( \langle V_{12} \rangle \) and larger \( E \)

• formally
  \[
  \langle V_{12} \rangle = \langle \psi_{12} \mid \frac{e^2}{4\pi\varepsilon_0} \mid \vec{r}_1 - \vec{r}_2 \mid \psi_{12} \rangle 
  \]
  \[
  \psi_{12} = \phi_{100}(1)\phi_{2l0}(2) \pm \phi_{100}(2)\phi_{2l0}(1) 
  \]
  \[
  |\psi_{12}|^2 = |\phi_{100}(1)|^2|\phi_{2l0}(2)|^2 + |\phi_{100}(2)|^2|\phi_{2l0}(1)|^2 
  \pm \phi_{100}^*(2)\phi_{2l0}^*(1)\phi_{100}(1)\phi_{2l0}(2) \pm \phi_{100}^*(1)\phi_{2l0}^*(2)\phi_{100}(2)\phi_{2l0}(1) 
  \]

• first two terms are identical \( \rightarrow \) ”\( J_{nl} \)” as are the second two “\( K_{nl} \)”. Both positive definite. Gives

  \[
  \langle V_{12} \rangle \equiv \Delta E^{(S=0,1)}_{2,l} = J_{2,l} \pm K_{2,l} \quad \text{1 e in n}=1 \text{ state} 
  \]
  \[
  \Rightarrow \Delta E^{(S=0,1)}_{n,l} = J_{n,l} \pm K_{n,l} 
  \]
He Energy Levels III

- $L=0$ and $L=1$ have different radial wavefunctions. The $n=2$, $L=1$ has more “overlap” with the $n=1$, $L=0$ state $\Rightarrow$ electrons are closer $\Rightarrow$ larger $\langle V_{12} \rangle$ and larger $E$

- usually larger effect than two spin states. Leads to Hund’s rules (holds also in other atoms)
Multi-Electron Atoms

- can’t solve S.E. exactly → use approximations
- Hartree theory (central field model) for n-electron atoms. Need an antisymmetric wave function (1,2,3 are positions; i,j,k…are quantum states)

\[ \psi(1,2,3\ldots\text{n}) = \sum_{\text{all terms}} \psi_i(1)\psi_j(2)\psi_k(3)\ldots \]

\[ \sum \Rightarrow \text{n! terms / antisymmetrical} \]

\[ n = 3 \Rightarrow \frac{1}{\sqrt{6}} \begin{vmatrix} \psi_a(1) & \psi_a(2) & \psi_a(3) \\ \psi_b(1) & \psi_b(2) & \psi_b(3) \\ \psi_c(1) & \psi_c(2) & \psi_c(3) \end{vmatrix} \]

- while it is properly antisymmetric for any 1 ↔ j practically only need to worry about valence effects
Schrod. Eq. For multi-electron

- have kinetic energy term for all electrons
  \[- \frac{\hbar^2}{2m} \nabla^2_1 \psi_T - \frac{\hbar^2}{2m} \nabla^2_2 \psi_T + \ldots - \frac{\hbar^2}{2m} \nabla^2_n \psi_T\]
- and (nominally) a complete potential energy:
  \[V_T = \sum_i \frac{-Ze^2}{4\pi\varepsilon_0 r_i} + \sum_n \sum_{n'} \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_n - \vec{r}_{n'}|}\]
- Simplify if look at 1 electron and sum over all the others
- \(\Rightarrow\) ~spherically symmetric potential as filled subshells have no (theta,phi) dependence. Central-Field Model. Assume:

\[V(r) = - \frac{Z_e(r)e^2}{4\pi\varepsilon_0 r} \text{ with } Z_e(0) = Z, Z_e(\infty) = 1\]

\[Y_{lm}(\theta,\phi) \Rightarrow "\text{good" eigenfunctions}\]
\[l, m_l \Rightarrow "\text{good" eigenvalues}\]
Multi-electron Prescription

• “ignore” e-e potential..that is include this in a guess at the effective Z
• energy levels can depend on both n and L
• wavefunctions are essentially hydrogen-like

1. guess at effective Z: $Z_e(r)$
2. solve (numerically) wave equation
3. fill energy levels using Pauli principle
4. use wavefunctions to calculate electrons’ average radii (radial distribution)
5. redetermine $Z_e(r)$
6. go back to step 2
First guess

- electron probability $P(r)$. Electrons will fill up “shells” (Bohr-like)

Assume all electrons for given $n$ are at the same $r$ with a $V_n$ for each $n$. Know number of electrons for each $n$. One can then smooth out this distribution to give a continuous $Z(r)$

$$V_n(r) = -\frac{Z_n e^2}{r}$$
Argon  $Z=18$

- First shell  $n=1$  1S  $Z_1 \sim 18-2 = 16$
- Second shell  $n=2$  2S,2P  $Z_2 \sim 18-2-8 = 8$
- Third shell  $n=3$  3S,3P  $Z_3 \sim 18-10-8/4 = 4$

- for the outermost shell…good first guess is to assume half the electrons are “screening”. Will depend on where you are in the Periodic Table

- guess energy levels.

$$E_n = -\left(\frac{Z_n}{n}\right)^2 \cdot 13.6eV$$

$$E_1 \approx -(16)^2 13.6 = -3500eV$$

$$E_2 \approx -(\frac{8}{2})^2 13.6 = -220eV$$

$$E_3 \approx -(\frac{4}{3})^2 13.6 = -24eV$$
Atomic Energy Levels

After some iterations, get generalizations

A for the innermost shell: \( Z_1 \approx Z - 2 \implies \)
\[
\begin{align*}
    r_1 & \approx \frac{1}{Z - 2} a_0 \\
    E_1 & \approx (Z - 2)^2 E_1(H)
\end{align*}
\]

B Outermost shell \( Z_n \approx n \implies \)
\[
\begin{align*}
    r_n & \approx \frac{n^2}{Z_n} a_0 \approx n a_0 \\
    E_n & \approx \frac{Z_n^2}{n^2} E_1(H) \approx E_1(H)
\end{align*}
\]

• atoms grow very slowly in size. The energy levels of the outer/valence electrons are all in the eV range
Comment on X-ray Spectra

- If one removes an electron from an inner orbit of a high Z material, many transitions occur as other electrons “fall”

- as photon emitted, obey

\[ \Delta m = 0, \pm 1 \quad \Delta l = \pm 1 \]

- “large” energies so emit x-ray photons. Or need x-ray photons (or large temperature or scotch tape) to knock one of the electrons out

\[ E_{1s} = (Z - 2)^2 \times 13.6eV \approx 90\,keV (Z = 82) \]

\[ T \approx \frac{90\,keV}{k} \approx 10^9 \,^0K \]

- study of photon energy gives effective Z for inner shells
Spectroscopic States in Atoms

- Only valence electrons need to be considered (inner “shield” nucleus)
- Filled subshells have $L=0$ and $S=0$ states (like noble gases).
- Partially filled subshells: need to combine electrons, make antisymmetric wavefunctions, and determine $L$ and $S$. Energy then depends on $J/L/S$
- If $>1/2$ filled subshell then ~same as treating “missing” electrons like “holes”. Example: 2P no. states=6
  1 electron $\leftrightarrow$ 5 electrons
  2 electrons $\leftrightarrow$ 4 electrons
  3 electrons
  6 electrons (filled)
  (can prove by making totally antisymmetric wavefunctions)
Periodic Table

• Follow “rules”

• for a given $n$, outer subshell with the lowest $L$ has lowest $E$ ($S<P<D$). Reason: lower $L \rightarrow$ smaller $\langle r \rangle \rightarrow$ larger effective $Z$

• For a given $L$, lowest $n$ has lowest energy (smaller $n$ and smaller $\langle r \rangle$)

• no rule if both $n, L$ are different. Use Hartree or exp. Observation. Will vary for different atoms

• the highest energy electron (the next state being filled) is not necessarily the one at the largest radius (especially $L=4$ f-shells)

\[ <r_{2p}> < <r_{2s}> \text{ for H but “bump” in 2S at low } r \text{ gives smaller } <r> \text{ for higher } Z \text{ (need to weight by effective } Z) \]
Alkalis

- Filled shell plus 1 electron. Effective Z 1-2 and energy levels similar to Hydrogen

$$E = \frac{Z_{\text{eff}}^2}{n^2} E_H \quad \text{with} \quad Z_{\text{eff}} (n, l)$$

- have spin-orbit coupling like H

\[ \Delta j = 0, \pm 1 \quad \Delta l = \pm 1 \]

<table>
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<tr>
<th>E(eV)</th>
<th>-6</th>
<th>-5</th>
<th>-4</th>
<th>-3</th>
<th>-2</th>
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<td>13.6</td>
<td>(1.2)^2</td>
<td>(1.7)^2</td>
<td>2S</td>
<td>3P</td>
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<tr>
<td></td>
<td>(\approx )</td>
<td>13.6</td>
<td>13.6</td>
<td>4S</td>
<td>3D</td>
</tr>
<tr>
<td></td>
<td>(\approx )</td>
<td>(-\frac{13.6}{n^2})</td>
<td>(-\frac{(1.2)^2}{n^2})</td>
<td>(-\frac{(1.7)^2}{n^2})</td>
<td>4P</td>
</tr>
</tbody>
</table>

H | Li | Na
Helium Excited States

- Helium: 1s\(^2\) ground state. 1s2s 1s2p first two excited states. Then 1s3s 1s3p and 1s3d as one electron moves to a higher energy state.

- combine the L and S for the two electrons to get the total L,S,J for a particular quantum state. Label with a spectroscopic notation

- Atoms “LS” coupling: (1) combine \( L_i \) give total L (2) combine \( S_i \) to give total S; (3) combine L and S to give J

- (nuclei use JJ: first get \( J_i \) and then combine Js to get total J)

- as wavefunctions are different, average radius and ee separation will be different \( \rightarrow \) 2s vs 2p will have different energy (P further away, more shielding, higher energy)

- S=0 vs S=1 S=1 have larger ee separation and so lower energy

- LS coupling similar to H \( \rightarrow \) Lower J, lower E
Helium Spectroscopic States

- $D=$ degeneracy = number of states with different quantum numbers (like $S_z$ or $L_z$) in this multiplet

$$l_1 = 0,1,2 \otimes l_2 = 0 \implies L = 0,1,2 \quad (d = 1,3,5)$$

$$s_1 = \frac{1}{2} \otimes s_2 = \frac{1}{2} \implies S = 0 \oplus S = 1 \quad (d = 1,3)$$

$$2s+1 \ L_j \implies level \begin{array}{c|c|c|c}
L & S & states \\
\hline
1s1s & 0 & 0 & ^1S_0 \quad (d = 1) \\
1s2p & 1 & 0 & ^1P_1 \quad (d = 3) \\
1s2p & 1 & 1 & ^3P_0, ^3P_1, ^3P_2 \quad (d = 1,3,5) \\
1s2s & 0 & 0 & ^1S_0, ^3S_1 \quad (d = 1,3) \\
\hline
1s3s \iff 1s2s & 1s3p \iff 1s2p \quad (higher \ E) \\
1s3d & 2 & 0 & ^1D_2 \quad (d = 5) \\
1s3d & 2 & 1 & ^3D_1, ^3D_2, ^3D_3 \quad (d = 3,5,7) \\
\end{array}$$
Helium: States, Energies and Transitions

- Transitions - First Order Selection Rules (time dep. Pert. Theory)
  \[ \Delta s = 0 \Rightarrow no \ spin \ flip \]
  \[ \Delta l = \pm 1 \Rightarrow as \ photon \ S = 1 \]
  \[ \Delta j = 0, \pm 1 \quad no \ 0 \rightarrow 0 \ (^3S_1 \rightarrow ^3P_1 \ OK) \]

- Metastable 2S with S=1 state - long lifetime

\[ E \]
\[ \begin{array}{ccc}
1 & \text{Singlet } S=0 \\
2 & \\\n3 & \\
\end{array} \]
\[ ^1S_0 \quad ^1P_1 \quad ^1D_2 \]
\[ \]
\[ ^3S_1 \quad ^3P_{0,1,2} \quad ^3D_{3,2,1} \]

Triplet S=1
Spectroscopic States if >1 Valence Electron

- Look at both allowed states (which obey Pauli Exclusion) and shifts in energy
- Carbon: 1s^22s^22p^2 ground state. Look at the two 2p highest energy electrons. Both electrons have S=1/2

<table>
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<th>&quot; #2&quot;</th>
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<td>3  0</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>3  1</td>
</tr>
</tbody>
</table>

- combine the L and S for the two electrons to get the total L,S,J for a particular quantum state
States for Carbon II

- $2p^13s^1$ different quantum numbers $\Rightarrow$ no Pauli Ex.
- 12 states = 6 (L=1, S=1/2) times 2 (L=0, S=1/2)

$$
\begin{align*}
L_1 = 1 \otimes l_2 &= 0 \implies L = 1 \quad (d = 3) \\
S_1 = \frac{1}{2} \otimes s_2 &= \frac{1}{2} \implies S = 0 \oplus S = 1 \quad (d = 1,3) \\
J &= L + S \implies 1 \otimes 0 = 1;1 \otimes 1 = 2 \oplus 1 \oplus 0
\end{align*}
$$

$$
\begin{array}{c|c|c}
L \quad & S \quad & states \\
\hline
1 \quad 0 & 1P_1 & (d = 3) \\
1 \quad 1 & 3P_0 \quad 3P_1 \quad 3P_2 & (d = 1,3,5)
\end{array}
$$

- where $d$=degeneracy = the number of separate quantum states in that multiplet
- $2p^13p^1$ different quantum numbers $\rightarrow$ no Pauli Ex.

36 states = 6 ($L=1$, $S=1/2$) times 6 ($L=01$ $S=1/2$)

\[ l_1 = 1 \otimes l_2 = 1 \Rightarrow L = 0,1,2 \quad (d = 1,3,5) \]

\[ s_1 = \frac{1}{2} \otimes s_2 = \frac{1}{2} \Rightarrow S = 0 \oplus S = 1 \quad (d = 1,3) \]

\[ J = L + S \Rightarrow 0 \otimes 0 = 0; 1 \otimes 0 = 1; 2 \otimes 0 = 2 \]

\[ 0 \otimes 1 = 1; 1 \otimes 1 = 2 \oplus 1 \oplus 0; 2 \otimes 1 = 3 \oplus 2 \oplus 1; \]

\[ 2s+1 \quad L_j \quad \Rightarrow \quad L \quad | \quad S \quad | \quad states \quad (degeneracy) \]

<table>
<thead>
<tr>
<th></th>
<th>0</th>
<th>0</th>
<th>$^1S_0$</th>
<th>($d = 1$)</th>
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<td>0</td>
<td>$^1P_1$</td>
<td>($d = 3$)</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>0</td>
<td>$^1D_2$</td>
<td>($d = 5$)</td>
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<tr>
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<td>1</td>
<td>$^3S_1$</td>
<td>($d = 3$)</td>
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<tr>
<td>1</td>
<td>1</td>
<td>$^3P_0$ $^3P_1$ $^3P_2$</td>
<td>($d = 1,3,5$)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>$^3D_1$ $^3D_2$ $^3D_3$</td>
<td>($d = 3,5,7$)</td>
<td></td>
</tr>
</tbody>
</table>

- where $d$=degeneracy = $2j+1$
• 2p\(^2\) state: same L+S+J combinations as the 2p\(^1\)3p\(^1\) but as both n=2 need to use Pauli Exclusion reject states which have the same

\[ ^3D_3 \quad m_j = 3 \implies \]
\[ m_{l_1} = m_{l_2} = 1 \otimes m_{s_1} = m_{s_2} = \frac{1}{2} \]

• not allowed. Once one member of a family is disallowed, all rejected

\[ \implies no \quad ^3D_{1,2,3} \quad states \]

• But many states are mixtures. Let:

\[ |S, S_z\rangle = A(S_1, S_{1z}) + B(S_2, S_{2z}) \]
\[ |0, 0\rangle = \frac{1}{\sqrt{2}} (\frac{1}{2}, \frac{1}{2}) - \frac{1}{\sqrt{2}} (\frac{1}{2}, -\frac{1}{2}) \]
\[ |1, 0\rangle = \frac{1}{\sqrt{2}} (\frac{1}{2}, \frac{1}{2}) + \frac{1}{\sqrt{2}} (\frac{1}{2}, -\frac{1}{2}) \]
• Need a stronger statement of Pauli Exclusion principle (which tells us its source)

• Total wavefunction of n electrons (or n Fermions) must be antisymmetric under the exchange of any two electron indices

• 2 electrons spin part of wavefunction: \( S = 0 \) or \( S = 1 \)

\[
S = 1 \quad + \text{symmetry} \quad 1 \leftrightarrow 2
\]

\[
S = 0 \quad - \text{symmetry} \quad 1 \leftrightarrow 2
\]

• So need the spatial part of the wavefunction to have

\[
S = 1, \text{need } "L" \text{ have} \quad - \text{symmetry} \quad 1 \leftrightarrow 2
\]

\[
S = 0, \text{need } "L" \text{ have} \quad + \text{symmetry} \quad 1 \leftrightarrow 2
\]

\[
D \text{ states} \quad L = 2 \quad \Rightarrow \quad + \quad \Rightarrow \quad ^1D_2 \quad (S = 0, \text{deg} = 5)
\]

\[
P \text{ states} \quad L = 1 \quad \Rightarrow \quad - \quad \Rightarrow \quad ^3P_{2,1,0} \quad (S = 1, \text{deg} = 5,3,1)
\]

\[
S \text{ states} \quad L = 0 \quad \Rightarrow \quad + \quad \Rightarrow \quad ^1S_0 \quad (S = 0, \text{deg} = 1)
\]

• other states not allowed (but are in in 2p3p)
Building Wave Functions

- Use $2p^2$ how to build up more complicated wave functions.
- All members of the same multiplet have the same symmetry.
- Redo adding two spin $1/2 \rightarrow S=0,1$. Start with state of maximal $S_z$. Always symmetric (all in same state)

$$\begin{align*}
|S = 1, S_z = 1\rangle &= |S_{z1} = \frac{1}{2}, S_{z2} = \frac{1}{2}\rangle \\
\text{use stepdown } S_- &\Rightarrow |1,0\rangle = \frac{1}{\sqrt{2}} (|\frac{1}{2}, -\frac{1}{2}\rangle + |\frac{-1}{2}, \frac{1}{2}\rangle) \\
\text{must be symmetric. repeat } &\Rightarrow |1,-1\rangle = |\frac{-1}{2}, -\frac{1}{2}\rangle
\end{align*}$$

- Other states must be orthogonal (different $S_{zi}$ are orthogonal to each other. But some states are combinations, like a rotation, in this case of 45 degrees)

$$|S = 0, S_z = 0\rangle = \frac{1}{\sqrt{2}} (|\frac{1}{2}, -\frac{1}{2}\rangle - |\frac{-1}{2}, \frac{1}{2}\rangle)$$

- $S=0$ is antisymmetric by inspection
Building Wave Functions

• Adding 2 \( L=1 \) is less trivial  \( \Rightarrow 2,1,0 \)

• \( L=2 \). Values in front of each term are Clebsch-Gordon coeff. Given by “eigenvalues” of stepdown operator

\[
|L = 2, S_z = 2\rangle = |L_{z1} = 1, L_{z2} = 1\rangle
\]

use stepdown \( L_- \)  \( \Rightarrow |2,1\rangle = \frac{1}{\sqrt{2}} (|1,0\rangle + |0,1\rangle) \) \( \Rightarrow \frac{1}{\sqrt{6}} (|1,-1\rangle + 2|0,0\rangle + |-1,1\rangle) \)

• other states are orthogonal. Given by CG coefficients/inspection

\[
|L = 1, L_z = 1\rangle = \frac{1}{\sqrt{2}} (|1,O\rangle - |O,1\rangle) \\
|1,O\rangle = \frac{1}{2} (|1,-1\rangle - |-1,1\rangle)
\]

• \( L=1 \) is antisymmetric by inspection. Do stepdown from \( L=1 \) to \( L=0 \)

\[
|L = 0, L_z = O\rangle = \frac{1}{\sqrt{3}} (|1,-1\rangle - |O,O\rangle + |-1,1\rangle)
\]

• \( L=0 \) symmetric by inspection. Also note orthogonality: \( A*C=1-2+1 \) and \( B*C=1-1 \)
More Energy Levels in Atoms

- If all (both) electrons are at the same \( n \). Use Hund’s Rules (in order of importance)
- minimize \( ee \) repulsion by maximizing \( ee \) separation \( \rightarrow \) “exchange force” where antisymmetric spatial wavefunction has largest spatial separation
- \( \rightarrow \) maximum \( S \) has minimum \( E \)
- different \( L \) \( \rightarrow \) different wavefunctions \( \rightarrow \) different effective \( Z \) (radial distributions) \( \rightarrow \) maximum \( L \) has minimum \( E \)
- \( \rightarrow \) minimum \( J \) has minimum \( E \) unless subshell >1/2 filled and then
  - \( \rightarrow \) minimum \( J \) has maximum \( E \)

\[
\vec{L} \cdot \vec{S} \text{ coupling (} S \neq 0 \text{)} \approx \text{Hydrogen} \\
\langle \Delta E \rangle = K\left( j(j + 1) - l(l + 1) - s(s + 1) \right)
\]
**3d4p  S=0,1  L=1,2,3**

**J splitting**

\[
\Delta E(j) = K \left( j(j+1) - l(l+1) - s(s+1) \right)
\]

\[
\Delta E(j + 1) = K \left( (j+1)(j+2) - l(l+1) - s(s+1) \right)
\]

\[
\Delta E(j + 1) - \Delta E(j) = K \left( (j+1)(j+2-j) \right) = 2K(j + 1)
\]

**Lande interval rule**

P460 - Helium