Phys 492
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Lecture #15: Identical Particles Continued

I. First excited state of Helium (Z=2)

$$E^0_{n_1 n_2} = -\frac{mc^2 (Z\alpha)^2}{2}\left(\frac{1}{n_1^2}+\frac{1}{n_2^2}\right)$$

$$E^0_{11} = -\frac{4mc^2\alpha^2}{2}(2) = -\frac{8mc^2\alpha^2}{2} = -108.8 \text{ eV}$$

$$E^0_{12} = -\frac{4mc^2\alpha^2}{2}\left(1+\frac{1}{4}\right) = -\frac{5}{2}mc^2\alpha^2 = -68.0 \text{ eV}$$

$$\hat{H}' = \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$$ rotationally invariant, does not depend on spin

total spin $\vec{S} = \vec{S}_1 + \vec{S}_2$

$|\vec{S}|^2$ eigenvalue $0 \le S \le 1$ $S = 0, 1$

$$[\hat{H}', \hat{S}^2] = 0 \quad \text{and} \quad [\hat{H}', \hat{L}^2] = 0 = [\hat{H}', \hat{L}_z]$$

Without spin-orbit interaction, L and S are separately conserved.

So $\hat{H}'$ is diagonal in basis l, m_l, s, m_s

$|l_1 - l_2| \le l \le l_1 + l_2$ $l = 0, 1$

$\psi = (\text{space}) \times (\text{spin})$

$(\text{spin}) = \chi_{00}$ (antisymmetric) singlet

or $\chi_{1 m_s}$ (symmetric) triplet

$(\text{space}) = \psi_{1s} \otimes (\psi_{2s} \text{ or } \psi_{2p})$

where –

$\psi_{2s} = \psi_{200}$ singlet

$\psi_{2p} = \psi_{21m_l}$ triplet

total of 4 space × 4 spin = 16 states

totally antisymmetric wave function

$$\psi_+(\text{space})\,\chi_{00} \quad ; \quad \psi_-(\text{space})\,\chi_{1m_s}$$

$$\psi_\pm(1s,2s) = \frac{1}{\sqrt{2}}\left[\psi_{1s}(1)\psi_{2s}(2) \pm \psi_{1s}(2)\psi_{2s}(1)\right]$$

$$\psi_\pm(1s,2p) = \frac{1}{\sqrt{2}}\left[\psi_{1s}(1)\psi_{2p}(2) \pm \psi_{1s}(2)\psi_{2p}(1)\right]$$

Because $\hat{H}'$ is rotationally invariant

$\langle\psi|\hat{H}'|\psi\rangle$ does not depend on m_ℓ, m_s.
the s quantum number goes with the opposite symmetry of the spatial wave function: $s=0$ is antisymmetric, $s=1$ is symmetric

correction	ℓ	s	mult.	ψ
$E_+'(s,s)$	0	0	1	$\psi_+(1s,1s)\,\chi_{00}$
$E_-'(s,s)$	0	1	3	$\psi_-(1s,1s)\,\chi_{1m_s}$
$E_+'(s,p)$	1	0	3	$\psi_+(1s,2p)\,\chi_{00}$ $m_\ell=-1,0,1$
$E_-'(s,p)$	1	1	9	$\psi_-(1s,2p)\,\chi_{1m_s}$ $m_\ell=-1,0,1$ $m_s=-1,0,1$
			16	

Consider $E_\pm(1s, 2p)$:

$$E^1_\pm(1s,2p) = \int d^3r_1\, d^3r_2\ \psi^*_\pm(\vec{r}_1,\vec{r}_2)\,\frac{e^2}{|\vec{r}_1-\vec{r}_2|}\,\psi_\pm(\vec{r}_1,\vec{r}_2)$$

$$= \frac{1}{2}\int d^3r_1\, d^3r_2 \Big\{ \left(\psi^*_{1s}(1)\psi^*_{2p}(2) \pm \psi^*_{1s}(2)\psi^*_{2p}(1)\right)$$

$$\frac{e^2}{|\vec{r}_1-\vec{r}_2|}\left(\psi_{1s}(1)\psi_{2p}(2) \pm \psi_{1s}(2)\psi_{2p}(1)\right)\Big\}$$

$$= \frac{1}{2}\int d^3r_1\, d^3r_2 \left[|\psi_{1s}(1)|^2|\psi_{2p}(2)|^2 + |\psi_{1s}(2)||\psi_{2p}(1)|^2\right]\frac{e^2}{|\vec{r}_1-\vec{r}_2|}$$

$$\pm \frac{1}{2}\int d^3r_1\, r_2 \Big[\psi^*_{1s}(1)\psi^*_{2p}(2)\psi_{1s}(2)\psi_{2p}(1)$$

$$+ \psi^*_{1s}(2)\psi^*_{2p}(1)\psi_{1s}(1)\psi_{2p}(2)\Big]\frac{e^2}{|\vec{r}_1-\vec{r}_2|}$$

then we can exchange dummies $\vec{r}_1, \vec{r}_2$

$$= \int d^3r_1\, d^3r_2\, |\psi_{1s}(1)|^2|\psi_{2p}(2)|^2\frac{e^2}{|\vec{r}_1-\vec{r}_2|}$$

$$\pm \int d^3r_1\, d^3r_2\ \psi^*_{2p}(2)\psi_{1s}(2)\frac{e^2}{|\vec{r}_1-\vec{r}_2|}\psi_{2p}(1)\psi^*_{1s}(1)$$

$\equiv J \pm K$ $\quad$ J, K both manifestly positive and all ψ_{21m_ℓ} will give same number.

$J = 13.2\,eV$, $K = 0.9\,eV$

$$E_\pm = \underbrace{E^0_{12}}_{=-13.6*2^2(1+1/4)=-68.0} + J \pm K = (-54.8 \pm 0.9)\,eV$$

Similarly $E'_{\pm}(1s,2s) = J' \pm K' = (11.4 \pm 1.2)\,eV$

$$E_{\pm}(1s,2s) = -56.6\,eV \pm 0.9\,eV$$

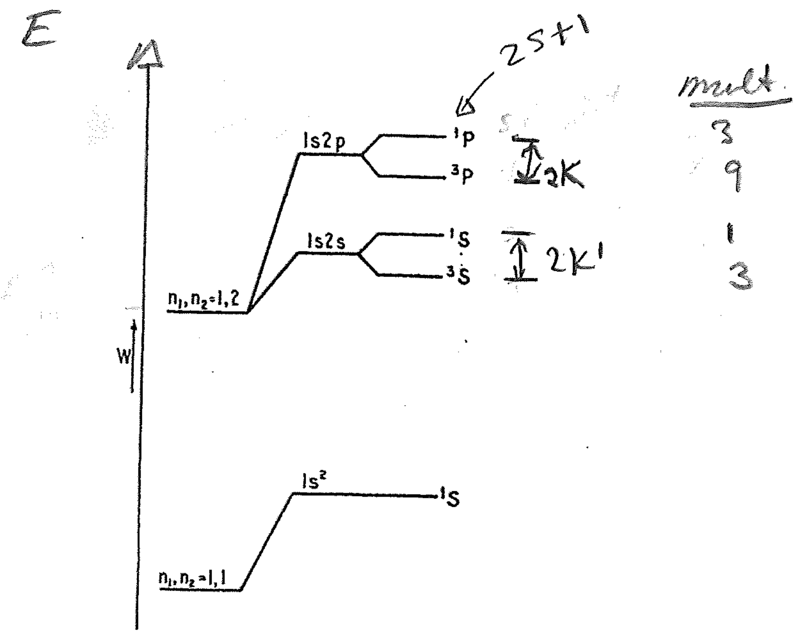


FIG. 29-1.—The splitting of energy levels for the helium atom.

From Pauling & Wilson

example of Hund's rule 1:
1. states with highest S have lower energy

A bit about multielectron atoms

$$\hat{H} = \sum_{i=1}^{Z} \left(\frac{\hat{p}_i^2}{2m} - \frac{Ze^2}{r_i} \right) + \hat{V}_C + \hat{V}_{SO} + \hat{V}_{SS}$$

Coulomb, spin-orbit, spin-spin

$$\hat{V}_C = \sum_{\text{pairs } i,j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

Anti-symmetrized zeroth order wave function by Slater-Determinant:

$$\psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_a(1) & \psi_a(2) & \cdots & \psi_a(N) \\ \psi_b(1) & \psi_b(2) & \cdots & \psi_b(N) \\ \vdots & & & \\ \psi_n(1) & \psi_n(2) & \cdots & \psi_n(N) \end{vmatrix} \quad \downarrow \text{state label}$$

$\xrightarrow{\hspace{3em}}$ particle label

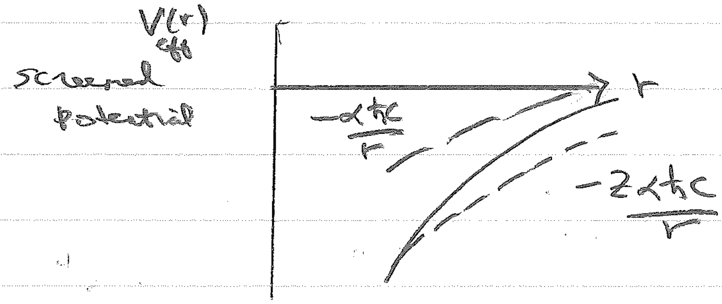
<u>for example</u> He ground state (trivial example)

state $\longrightarrow$

$$\psi = \frac{1}{\sqrt{2!}} \begin{vmatrix} \psi_1(1s)\uparrow_1 & \psi_1(1s)\downarrow_1 \\ \psi_2(1s)\uparrow_2 & \psi_2(1s)\downarrow_2 \end{vmatrix} \quad \begin{array}{c} \text{particle} \\ \downarrow \end{array}$$

$$= \psi_1(1s)\,\psi_2(1s)\,\frac{1}{\sqrt{2}}\left(\uparrow_1\downarrow_2 - \downarrow_1\uparrow_2\right)$$

Independent particle Model: each electron moves in effective screened potential



$$V(r) \cong \frac{e^2}{r}\left[Z - \int_0^r d^3r'\, \rho(r')\right]$$

all other electrons

Some computational schemes: statistical model, Hartree's self-consistent field

$$V_i(r_i) = -\frac{Ze^2}{r_i} + \sum_{j\neq i} \int d^3r_j \left|\psi_j(\vec{r}_j)\right|^2 \frac{e^2}{r_{ij}}$$

$V_c(r)$ does not go like $1/r$, so states of given n with different l are no longer degenerate.

Closed subshell (l) is spherically symmetric

$$\sum_{m=-l}^{+l} |Y_{lm}|^2 = \frac{2l+1}{4\pi}$$

Electron shells

closed sub-shell=
Nobel gases

n	shell (n)	# states $= 2n^2$	Configuration
1	K	2	$1S^2$
2	L	8	$2S^2 2p^6$
3	M	18	$3S^2 3p^6 3D^{10}$
4	N	32	$4S^2 4p^6 4D^{10} 4F^{14}$

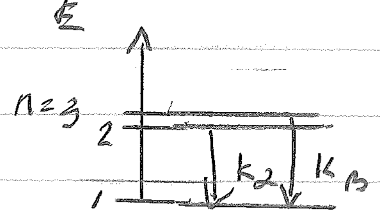
K-shell electrons see screened nuclear charge

$$E_{1s} \cong (Z-1)^2(-13.6\,eV)$$

Moseley (1913) determined Z of element Al(13) – Ag(47) by mono-energetic e^- scattering:

$$e^- + A_A^Z = (A_A^Z)^{+*} + 2e^-$$

$$\hookrightarrow (A_A^Z)^{+} + \gamma_K$$



observed $\sqrt{F} \sim (Z-1)$

$$\Delta E = h f_N = (-13.6)(Z-1)^2\left(1 - \frac{1}{n^2}\right)$$

Order in periodic table by chemical property explained by nuclear charge Z!

Valence ≡ # extra/missing e^- in outer shell

Nobel (inert) gases have filled outer shells

recall $R_{nl} \xrightarrow[r \to 0]{} r^l$

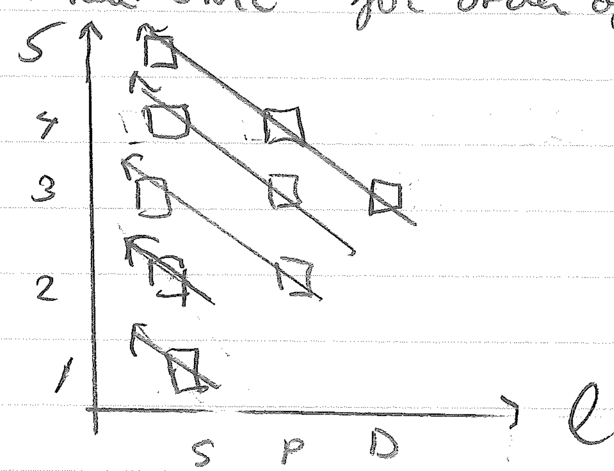
So lower l states provide more screening leading to

$$E_{n,s} < E_{n,p} < E_{n,D}$$

$Ar\ (Z=18)$: $1s^2 2s^2 2p^6 3s^2 3p^6$

1^{st} break $K\ (Z=19) = [Ar]\,4s$

Useful mnemonic for order of electron



Nobel gases appear in large peaks in plot of ionization energy vs Z

$\underline{He}$ $1s^2$ closed K

Li $[He]2s$

⋮

$\underline{Ne}$ $[He]2s^2 2p^6$ closed L

Na $[Ne]\,3s$

⋮

closed M

$\underline{Ar}$ $[Ne]\,3s^2\,3p^6$

K $[Ar]\,4s$

⋮

filled first

$\underline{Kr}$ $[Ar]\,4s^2\,3d^{10}\,4p^6$ closed N

Rb $[Kr]\,5s$

Ground state wave function open subshell ("optically active") electrons

Two common approximation schemes:

Spin-spin > orbit-orbit > S-orbit
L-S (Russel Saunders)
for $Z \gtrsim 30$, spin-orbit > orbit-orbit
jj coupling

L-S: $\vec{L} = \sum_{\text{valence}} \vec{L}_i$, $\vec{S} = \sum_{\text{valence}} \vec{S}_i$; $\vec{J} = \vec{L} + \vec{S}$

e.g. $i=2$ $|l_1 - l_2| \le L \le l_1 + l_2$; $S = 0, 1$; $|L-S| < J < L+S$

$\hat{J}^2$, $\hat{J}_z$, $\hat{L}^2$, $\hat{S}^2$ all commute

$|n \, j \, m_j \, l \, s\rangle \sim {}_n^{2S+1}L_j$ notation

nobel gases all are ${}^1S_0$ states
Converse not true, e.g. Mg: [Ne] $(3s)^2$ ${}^1S_0$

Hund's Rules (Gasiorowicz)

① State with largest s lies lowest

② for given s, state with max ℓ lowest

③ for given ℓ, s

sub shell < ½ full $\quad j = |\ell - s|$ lowest

sub shell > ½ full $\quad j = \ell + s$ lowest

① largest spin state is symmetric
spatial state anti-symmetric reduces overlaps

② higher ℓ wave function has more lobes, reducing overlaps

③ reduces spin-orbit coupling

Spin-Orbit for 1 extra electron in ℓ=1 orbital

$$\hat{H}_{so} = -\vec{\mu}\cdot\vec{B}' = \frac{eg}{2mc}\vec{S}\cdot\vec{B}' \qquad \vec{\mathcal{E}} = -\vec{\nabla}\phi \qquad V = -e\phi$$

$$\vec{B}' = -\frac{1}{c}\vec{v}\times\vec{\mathcal{E}}$$

$$\vec{\nabla}V = \frac{\hat{r}}{r}\frac{dV}{dr} \qquad = \frac{-1}{ec}\vec{v}\times\vec{\nabla}V$$

Thomas precession

$$\hat{H}_{so} = \frac{1}{2}\frac{e}{mc}\vec{S}\cdot\left[\frac{-1}{ec}\vec{v}\times\left(\frac{\vec{r}}{r}\frac{dV}{dr}\right)\right]$$

g=2

$$= -\frac{1}{2}\frac{1}{m^2c^2}\vec{S}\cdot\vec{p}\times\frac{\vec{r}}{r}\frac{dV}{dr} = +\frac{1}{2m^2c^2}\vec{S}\cdot\vec{L}\,\frac{1}{r}\frac{dV}{dr}$$

$$\langle\hat{H}_{so}\rangle = +\frac{1}{2m^2c^2}\langle\vec{L}\cdot\vec{S}\rangle\left\langle\frac{1}{r}\frac{dV}{dr}\right\rangle$$

$$= +\frac{1}{4m^2c^2}\left[j(j+1) - \ell(\ell+1) - s(s+1)\right]\left\langle\frac{1}{r}\frac{dV}{dr}\right\rangle$$

Since $\left\langle\frac{1}{r}\frac{dV}{dr}\right\rangle > 0$ lowest j has lowest energy
for shell > ½ filled, absence of electron is
+ charge hole which reverses sign of $\langle\hat{H}_{so}\rangle$.