

\* Hamiltonian for an atom with  $Z$  protons (and electrons)

$$\mathcal{H} = \sum_{j=1}^Z \left\{ \underbrace{-\frac{\hbar^2}{2m} \nabla_j^2 - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_j}}_{\mathcal{H}_j \text{ (single electron)}} \right\} + \underbrace{\frac{1}{2} \frac{1}{4\pi\epsilon_0} \sum_{j \neq k}^Z \frac{e^2}{|\vec{r}_j - \vec{r}_k|}}_{\text{electron repulsion.}}$$

- will use perturbation and variational methods to deal with the electron repulsion.

- the single-particle terms are separable:

$$\text{if } \mathcal{H}_j \psi_j = E_j \psi_j \quad \text{then} \quad \mathcal{H}[\psi_1 \psi_2 \dots \psi_Z] = (E_1 + E_2 + \dots + E_Z) [\psi_1 \psi_2 \dots \psi_Z]$$

- must still antisymmetrize whole wave function.

$$\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_Z, \vec{s}_1, \vec{s}_2, \dots, \vec{s}_Z) = \psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_Z) \chi(\vec{s}_1, \vec{s}_2, \dots, \vec{s}_Z) \quad \left. \begin{array}{l} \vec{r}_i = \text{position} \\ \vec{s}_i = \text{spin} \end{array} \right\} \text{ of } i^{\text{th}} \text{ electron}$$

$$P_{ij} \Psi = P_{ij} \psi \cdot P_{ij} \chi = \pm \psi \cdot \mp \chi = -\Psi \quad \text{for fermions}$$

• thus two valid combinations:  $\psi_S \chi_A$  &  $\psi_A \chi_S$  (other possibilities too!)

(different states, for example consider 2 electrons.

in states  $\psi_a, \psi_b$ , either with spin  $\uparrow$  or  $\downarrow$

$$\left. \begin{array}{l} \psi_a(\vec{r}_1) \chi_{\uparrow}(\vec{s}_1) \cdot \psi_b(\vec{r}_2) \chi_{\uparrow}(\vec{s}_2) \\ \psi_a(\vec{r}_1) \chi_{\uparrow}(\vec{s}_1) \cdot \psi_b(\vec{r}_2) \chi_{\downarrow}(\vec{s}_2) \\ \psi_a(\vec{r}_1) \chi_{\downarrow}(\vec{s}_1) \cdot \psi_b(\vec{r}_2) \chi_{\uparrow}(\vec{s}_2) \\ \psi_a(\vec{r}_1) \chi_{\downarrow}(\vec{s}_1) \cdot \psi_b(\vec{r}_2) \chi_{\downarrow}(\vec{s}_2) \end{array} \right\} \Rightarrow \begin{array}{l} \psi_A \left\{ \begin{array}{l} [\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) - \psi_b(\vec{r}_1)\psi_a(\vec{r}_2)] [\chi_{\uparrow}(\vec{s}_1)\chi_{\uparrow}(\vec{s}_2)] \\ [\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) - \psi_b(\vec{r}_1)\psi_a(\vec{r}_2)] [\chi_{\uparrow}(\vec{s}_1)\chi_{\downarrow}(\vec{s}_2) + \chi_{\downarrow}(\vec{s}_1)\chi_{\uparrow}(\vec{s}_2)] \\ [\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) - \psi_b(\vec{r}_1)\psi_a(\vec{r}_2)] [\chi_{\downarrow}(\vec{s}_1)\chi_{\downarrow}(\vec{s}_2)] \end{array} \right\} \begin{array}{l} S=1 \\ \text{triplet} \end{array} \chi_S \\ \psi_S \left\{ [\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) + \psi_b(\vec{r}_1)\psi_a(\vec{r}_2)] [\chi_{\uparrow}(\vec{s}_1)\chi_{\downarrow}(\vec{s}_2) - \chi_{\downarrow}(\vec{s}_1)\chi_{\uparrow}(\vec{s}_2)] \right\} \begin{array}{l} S=0 \\ \text{singlet} \end{array} \chi_A \end{array}$$

• note that 4 states of the form  $\psi(\vec{r}_1) \chi(\vec{s}_1) \psi(\vec{r}_2) \chi(\vec{s}_2)$  disappeared due to antisymmetry.

• there is only one state with  $a=b$  since  $\psi_a \psi_a$  symmetric:  
 $\psi_a(\vec{r}_1) \psi_a(\vec{r}_2) (\uparrow\downarrow - \downarrow\uparrow)$

\* Helium atom:  $\Psi(\vec{r}_1, \vec{r}_2) = \Psi_{nlm}(\vec{r}_1) \Psi_{n'l'm'}(\vec{r}_2)$   $\chi(\vec{s}_1, \vec{s}_2) = \begin{cases} |1, m\rangle \text{ triplet} \\ |0, 0\rangle \text{ singlet} \end{cases}$

•  $E \propto \frac{Z}{r} \propto Z^2$  since  $r \propto \frac{1}{Z}$  so  $E = 4(E_n + E_{n'})$

$\Psi_0 = \Psi_{100}(\vec{r}_1) \Psi_{100}(\vec{r}_2) = \frac{8}{\pi a^3} e^{-2(r_1+r_2)/a}$   $\chi_0 = |0, 0\rangle = (\uparrow\downarrow - \downarrow\uparrow)$

$\Psi_0$  symmetric  $\rightarrow \chi_0$  antisymmetric (singlet) : **PARAHELIUM**

$E_0 = -8 \cdot 13.6 \text{ eV} = -109 \text{ eV}$  singlet vs.  $-79 \text{ eV}$  singlet observed.  
(interaction energy = 30 eV)


• excited states may be either be:

$[\Psi_{nlm}(\vec{r}_1) \Psi_{100}(\vec{r}_2) + \Psi_{100}(\vec{r}_1) \Psi_{nlm}(\vec{r}_2)] |0, 0\rangle$  **PARAHELIUM**

$[\Psi_{nlm}(\vec{r}_1) \Psi_{100}(\vec{r}_2) - \Psi_{100}(\vec{r}_1) \Psi_{nlm}(\vec{r}_2)] |1, \pm 1\rangle$  **ORTHOHELIUM**

para helium: 1S, 2S, 3S, 4S, ...  
2P, 3P, 4P, ...  
3D, 4D, ...  
4F, ...

- capital letters: TOTAL N, L, M
- same as single excited electron n, l, m

ortho helium:  2S, 3S, 4S, ...  
2P, 3P, 4P, ...  
3D, 4D, ...  
4F, ...

\* Atoms

	K	L	M	N	O	P	Q
n=1	1s						
n=2	2s	2p					
n=3	3s	3p	3d				
n=4	4s	4p	4d	4f			
n=5	5s	5p	5d	5f	5g, 5h, 5i, 5k, ...		
n=6	6s	6p	6d	6f			
n=7	7s	7p	7d				

Labels: sharp (1s), principle (2s, 2p), diffuse (3d), fundamental (4f, 5f, ...)

spectroscopic term

$2S+1 L_J$

\* capital letters for multiparticle state

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Alk  
1s  
2s  
3s

Halogen  
1s  
2p  
3p  
Trans. Metals

2s			2p
3s		Trans. Metals	3p
4s		3d	4p
5s	Ls/Ac	4d	5p
6s	4f	5d	6p
7s	5f	6d	7p

19	20	Transition Metals										Main Group Elements					
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
55	56	* 57-70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85
Cs	Ba	*	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	
87	88	89-102	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117
Fr	Ra	**	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuq	Uub	Unlabeled					

\* Lanthanide series

57	58	59	60	61	62	63	64	65	66	67	68	69	70
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb

\*\* Actinide series

89	90	91	92	93	94	95	96	97	98	99	100	101	102
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No

\* Hund's Rules: (remember antisymmetrization always)

1) the state with largest S comes first. (lowest energy)

2) for given spin, the highest L comes first

3) if a subshell is less than half full then  $J = |L - S|$  comes first  
otherwise  $J = |L + S|$  comes first

see Problem 5.13 for examples.