LECTURE #11

CLASSICALLY, A RIGID OBJECT CAN HAVE TWO KINDS OF ANGULAR MOMENTUM:

(a) ORBITAL : $\vec{L} = \vec{r} \times \vec{p}$

(b) SPIN : $\vec{S} = I\omega$ ← ANGULAR FREQUENCY

↑ MOMENT OF INERTIA

→ DUE TO MOTION ABOUT THE CENTER OF MASS

QUANTUM MECHANICALLY, A POINT PARTICLE CAN ALSO HAVE ANOTHER FORM OF ANGULAR MOMENTUM, WHICH IS ALSO CALLED "SPIN" WITH QUANTUM NUMBERS s, m_s

NOTE: THE ANALOGY TO CLASSICAL PHYSICS IS SUSPECT SINCE A POINT PARTICLE (e.g., AN ELECTRON) CANNOT HAVE ITS SPIN ANGULAR MOMENTUM DECOMPOSED INTO ORBITAL ANGULAR MOMENTUM OF ITS CONSTITUENT PARTS.

HOWEVER, POINT PARTICLES DO HAVE AN INTRINSIC ANGULAR MOMENTUM THAT IS INDEPENDENT OF SPACE AND DESCRIBED BY THE FOLLOWING COMMUTATION RELATIONS:

$$[S_x, S_y] = i\hbar S_z, \quad [S_y, S_z] = i\hbar S_x, \quad [S_z, S_x] = i\hbar S_y$$

$$\Rightarrow S^2 |s\, m_s\rangle = \hbar^2 s(s+1) |s\, m_s\rangle ; \quad S_z |s\, m_s\rangle = \hbar m |s\, m_s\rangle$$

THIS TIME THE EIGENFUNCTIONS ARE NOT SPHERICAL HARMONICS (SINCE THEY ARE INDEPENDENT OF SPACE). THUS, THE HALF-INTEGER VALUES OF s AND m_s ARE ALLOWED:

$S = 0, \frac{1}{2}, 1, \frac{3}{2}, \ldots \;;\; m_S = -S, -S+1, \ldots, S-1, S$

EVERY ELEMENTARY PARTICLE HAS A <u>SPECIFIC</u> AND <u>IMMUTABLE</u> VALUE OF S:

PI MESONS: SPIN ZERO
ELECTRONS: SPIN $\frac{1}{2}$
PHOTONS: SPIN 1
DELTAS: SPIN $\frac{3}{2}$
GRAVITONS: SPIN 2
⋮

THUS, WE CAN CATEGORIZE <u>TWO CLASSES OF PARTICLES</u>:

(1) <u>BOSONS</u>: PARTICLES WITH INTEGER SPIN
(e.g., PHOTONS, PHONONS, MESONS, ...)

IF YOU HAVE TWO IDENTICAL BOSONS IN STATES a AND b, THE TOTAL WAVEFUNCTION IS:

$$\psi(\vec{r}_1, \vec{r}_2) = A\left[\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) + \psi_b(\vec{r}_1)\psi_a(\vec{r}_2)\right]$$

<u>NOTE</u>: IF BOTH PARTICLES ARE IN STATE a,

$$\psi(\vec{r}_1, \vec{r}_2) = 2A\,\psi_a(\vec{r}_1)\psi_a(\vec{r}_2)$$

$\Rightarrow$ THERE CAN BE MANY BOSONS IN THE SAME STATE

(2) FERMIONS: PARTICLES WITH HALF-INTEGER SPIN (e.g., PROTONS, ELECTRONS, ...)

$$\begin{cases} s = \frac{1}{2} \\ m_s = -\frac{1}{2}, \frac{1}{2} \end{cases}$$

SPIN DOWN

SPIN UP

IF YOU HAVE TWO IDENTICAL FERMIONS IN STATES a AND b, THE TOTAL WAVEFUNCTION IS:

$$\psi(\vec{r}_1, \vec{r}_2) = A\left[\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) - \psi_b(\vec{r}_1)\psi_a(\vec{r}_2)\right]$$

NOTE: IF BOTH PARTICLES ARE IN STATE a,

$$\psi(\vec{r}_1, \vec{r}_2) = 0 \rightarrow \text{THERE IS NO WAVEFUNCTION}$$

$\Rightarrow$ THERE CANNOT BE MORE THAN ONE FERMION IN THE SAME STATE

$\hookrightarrow$ PAULI EXCLUSION PRINCIPLE

NOTE: $\psi(\vec{r}_1, \vec{r}_2) = \pm\psi(\vec{r}_2, \vec{r}_1)$

+ FOR BOSONS $\downarrow$ SYMMETRIC, − FOR FERMIONS $\downarrow$ ANTI-SYMMETRIC

NOTE: THE ANTISYMMETRY CONDITION FOR FERMIONS IS A CONDITION FOR THE ENTIRE WAVEFUNCTION (SPACE + SPIN)

IN SUMMARY, FOUR QUANTUM NUMBERS UNIQUELY DESCRIBE ELECTRONS IN A SPHERICALLY SYMMETRIC COULOMB POTENTIAL:

$$\left.\begin{array}{l} n = 1, 2, \ldots \\ 0 \le \ell \le n-1 \\ |m_\ell| \le \ell \\ m_s = \pm \frac{1}{2} \end{array}\right\} \text{NO TWO ELECTRONS CAN BE IN THE SAME STATE (PAULI)}$$

WHAT ABOUT THE REST OF THE PERIODIC TABLE?

HOW ABOUT HELIUM? 2 PROTONS, 2 NEUTRONS, 2 ELECTRONS

ELECTRICALLY NEUTRAL $\Rightarrow$ NO INFLUENCE ON e^-

2 ELECTRONS $\Rightarrow$ SCH. EQ. BECOMES:

$$-\frac{\hbar^2}{2m}\left(\nabla_1^2\psi + \nabla_2^2\psi\right) + \frac{1}{4\pi\epsilon_0}\Big(\underbrace{-\frac{2e^2}{r_1} - \frac{2e^2}{r_2}}_{\text{FACTOR OF TWO RESULTS FROM 2 PROTONS}} + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}\Big)\psi = E\psi$$

$e^- - e^-$ REPULSION

IN GENERAL, FOR A NEUTRAL ATOM OF ATOMIC NUMBER Z,

$$H = \sum_{j=1}^{Z}\left[-\frac{\hbar^2}{2m}\nabla_j^2 - \left(\frac{1}{4\pi\epsilon_0}\right)\frac{Ze^2}{r_j}\right] + \frac{1}{2}\,\frac{1}{4\pi\epsilon_0}\sum_{j\ne k}^{Z}\frac{e^2}{|\vec{r}_j - \vec{r}_k|}$$

TAKES CARE OF DOUBLE COUNTING IN THE SUM

<u>NOTE</u>: EVEN FOR HELIUM, THE SCH. EQ. CANNOT BE SOLVED EXACTLY. CONSEQUENTLY, QUANTUM CHEMISTRY IS AN EXERCISE IN APPROXIMATING THE HAMILTONIAN.

IF WE DECIDE TO NEGLECT $e^- - e^-$ INTERACTIONS,

$$E_n = (-13.6\,eV)\frac{Z^2}{n^2} \quad \text{(FOR EACH ELECTRON)}$$

$\Rightarrow$ GROUND STATE OF HELIUM : $E = (2)(2^2)(-13.6\,eV) \approx -109\,eV$

BUT THE MEASURED VALUE IS: $-79\,eV$

$\Rightarrow$ $e^- - e^-$ INTERACTIONS ARE IMPORTANT AND WILL COMPLICATE THE PERIODIC TABLE

* HOW MANY DEGENERATE STATES FOR EACH PRINCIPAL QUANTUM NUMBER?

<u>RECALL</u>: $\ell \le n-1$, $|m_\ell| \le \ell$, $m_s = \pm\frac{1}{2}$

$$\therefore \underbrace{2}_{\text{SPIN}} \sum_{\ell=0}^{n-1} (2\ell+1) = 2\left[2\,\tfrac{1}{2}n(n-1) + n\right] = 2n^2$$

* PAULI EXCLUSION SAYS THAT NO $2e^-$ CAN BE IN THE SAME STATE

$\Downarrow$

WE WOULD EXPECT EACH SHELL TO FILL UP AS WE INCREASE Z

$\Rightarrow$ PERIODIC TABLE SHOULD HAVE ROWS OF

$n=1$ (2)
$n=2$ (8)
$n=3$ (18)
$n=4$ (32)
$n=5$ (50)
⋮

BUT, THE PERIODIC TABLE HAS ROWS OF 2, 8, 8, 18, 18, ...

(e^- - e^- REPULSION SPLITS THE DEGENERACY OF n AND THUS THROWS OFF THE COUNTING)

$\boxed{\text{SEE TABLE 4.1}}$

Table 4.1 *The electronic configurations of the elements*

Atomic number	Element symbol	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f
		Number of electrons									
1	H	1									
2	He	2									
3	Li	2	1								
4	Be	2	2								
5	B	2	2	1							
6	C	2	2	2							
7	N	2	2	3							
8	O	2	2	4							
9	F	2	2	5							
10	Ne	2	2	6							
11	Na	2	2	6	1						
12	Mg	2	2	6	2						
13	Al	2	2	6	2	1					
14	Si	2	2	6	2	2					
15	P	2	2	6	2	3					
16	S	2	2	6	2	4					
17	Cl	2	2	6	2	5					
18	A	2	2	6	2	6					
19	K	2	2	6	2	6	—	1			
20	Ca	2	2	6	2	6	—	2			
21	Sc	2	2	6	2	6	1	2			
22	Ti	2	2	6	2	6	2	2			
23	V	2	2	6	2	6	3	2			
24	Cr	2	2	6	2	6	5	1			
25	Mn	2	2	6	2	6	5	2			
26	Fe	2	2	6	2	6	6	2			
27	Co	2	2	6	2	6	7	2			
28	Ni	2	2	6	2	6	8	2			
29	Cu	2	2	6	2	6	10	1			
30	Zn	2	2	6	2	6	10	2			
31	Ga	2	2	6	2	6	10	2	1		
32	Ge	2	2	6	2	6	10	2	2		
33	As	2	2	6	2	6	10	2	3		
34	Se	2	2	6	2	6	10	2	4		
35	Br	2	2	6	2	6	10	2	5		
36	Kr	2	2	6	2	6	10	2	6	—	—

Atomic number	Element symbol	4s	4p	4d	4f	5s	5p	5d	5f	5g	6s
		Number of electrons									
37	Rb	2	6	—	—	1	—	—	—	—	—
38	Sr	2	6	—	—	2	—	—	—	—	—
39	Y	2	6	1	—	2					
40	Zr	2	6	2	—	2					
41	Nb	2	6	4	—	1					
42	Mo	2	6	5	—	1					
43	Tc	2	6	6	—	1					
44	Ru	2	6	7	—	1					
45	Rh	2	6	8	—	1					
46	Pd	2	6	10	—	—					
47	Ag	2	6	10	—	1					
48	Cd	2	6	10	—	2					
49	In	2	6	10	—	2	1				
50	Sn	2	6	10	—	2	2				
51	Sb	2	6	10	—	2	3				
52	Te	2	6	10	—	2	4				
53	I	2	6	10	—	2	5				
54	Xe	2	6	10	—	2	6				
55	Cs	2	6	10	—	2	6				1
56	Ba	2	6	10	—	2	6				2
57	La	2	6	10	—	2	6	1			2
58	Ce	2	6	10	2	2	6	—			2
59	Pr	2	6	10	3	2	6	—			2
60	Nd	2	6	10	4	2	6	—			2
61	Pm	2	6	10	5	2	6	—			2
62	Sm	2	6	10	6	2	6	—			2
63	Eu	2	6	10	7	2	6	—			2
64	Gd	2	6	10	7	2	6	1			2
65	Tb	2	6	10	8	2	6	1			2
66	Dy	2	6	10	9	2	6	1			2
67	Ho	2	6	10	10	2	6	1			2
68	Er	2	6	10	11	2	6	1			2
69	Tm	2	6	10	12	2	6	1			2
70	Yb	2	6	10	13	2	6	1			2
71	Lu	2	6	10	14	2	6	1			2
72	Hf	2	6	10	14	2	6	2	—	—	2

Atomic number	Element symbol	5p	5d	5f	5g	6s	6p	6d	6f	7s	7p
		Number of electrons									
73	Ta	6	3	—	—	2	—	—	—	—	—
74	W	6	4			2					
75	Re	6	5			2					
76	Os	6	6			2					
77	Ir	6	9			0					
78	Pt	6	9			1					
79	Au	6	10			1					
80	Hg	6	10			2					
81	Tl	6	10			2	1				
82	Pb	6	10			2	2				
83	Bi	6	10			2	3				
84	Po	6	10			2	4				
85	At	6	10			2	5				
86	Rn	6	10			2	6				
87	Fr	6	10			2	6			1	
88	Ra	6	10			2	6			2	
89	Ac	6	10			2	6	1		2	
90	Th	6	10			2	6	2		2	
91	Pa	6	10			2	6	3		2	
92	U	6	10			2	6	4		2	
93	Np	6	10	5		2	6	—		2	
94	Pu	6	10	5		2	6	1		2	
95	Am	6	10	6		2	6	1		2	
96	Cm	6	10	7		2	6	1		2	
97	Bk	6	10	8		2	6	1		2	
98	Cf	6	10	9		2	6	1		2	
99	—	6	10	10		2	6	1		2	
100	—	6	10	11		2	6	1		2	