Identical Particles

- We would like to move from the quantum theory of hydrogen to that for the rest of the periodic table
  - One electron atom to multielectron atoms
- This is complicated by the interaction of the electrons with each other and by the fact that the electrons are identical
  - The Schrodinger equation for the two electron atom can only be solved by using approximation methods

Identical Particles

- In classical mechanics, identical particles can be identified by their positions
- In quantum mechanics, because of the uncertainty principle, identical particles are indistinguishable
  - This effect is connected with the Pauli exclusion principle and is of major importance in determining the properties of atoms, nuclei, and bulk matter

Identical Particles

Consider two particles, then $\Psi(x,t) \to \Psi(x_1,x_2,t)$

The time dependent Schrodinger equation is

$$i\hbar \frac{\partial \Psi(x_1,x_2,t)}{\partial t} = \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x_1^2} - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial x_2^2} + V(x_1,x_2) \right] \Psi(x_1,x_2,t)$$

The time independent Schrodinger equation is

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x_1^2} - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial x_2^2} + V(x_1,x_2) \right] \psi(x_1,x_2) = E\,\psi(x_1,x_2)$$

And note here we have used labels that identify particles 1 and 2

Identical Particles

- An important case is when the particles do not interact with each other
  - This is called the independent particle model
  - It's the starting point for the He atom e.g.

Then $V(x_1, x_2) = V_1(x_1) + V_2(x_2)$

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x_1^2} + V_1(x_1) - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial x_2^2} + V_2(x_2)\right]\psi(x_1, x_2) = E\psi(x_1, x_2)$$

This suggests we can write $\psi(x_1, x_2) = \psi(x_1)\psi(x_2)$ and $E = E_1 + E_2$

Which leads to

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx_1^2} + V_1(x_1)\right]\psi(x_1) = E_1\psi(x_1)$$

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx_2^2} + V_2(x_2)\right]\psi(x_2) = E_2\psi(x_2)$$

Identical Particles

- Let's say particle 1 is in quantum state m and particle 2 is in quantum state n

$$\psi(x_1, x_2) = \psi_m(x_1)\psi_n(x_2)$$

- If we interchange the two particles then

$$\psi(x_1, x_2) = \psi_m(x_2)\psi_n(x_1)$$

- We get different wave functions (and probability densities) so the two particles are distinguishable
  - Two particles are indistinguishable if we can exchange their labels without changing a measurable quantity
  - Thus neither of the solutions above is satisfactory

Identical Particles

- In fact there are two ways to construct indistinguishable wave functions

$$\psi_s = \frac{1}{\sqrt{2}}\left(\psi_m(x_1)\psi_n(x_2) + \psi_m(x_2)\psi_n(x_1)\right)$$

$$\psi_a = \frac{1}{\sqrt{2}}\left(\psi_m(x_1)\psi_n(x_2) - \psi_m(x_2)\psi_n(x_1)\right)$$

- Ψ_s is a symmetric wave function under particle interchange of $1 \leftrightarrow 2$
  - $\Psi_s \rightarrow \Psi_s$
- Ψ_a is a antisymmetric wave function under particle interchange of $1 \leftrightarrow 2$
  - $\Psi_a \rightarrow -\Psi_a$
- The probability density remains unchanged under particle interchange of $1 \leftrightarrow 2$

Identical Particles

- All particles with integer spin are called bosons
  - Spin 0,1,2,…
  - Photon, pions, Z-boson, Higgs
- All particles with half integer spin are called fermions
  - Spin 1/2, 3/2, …
  - Electron, proton, neutron, quarks, …
- For the next few lectures we'll focus on the fermions (electrons)

Identical Particles

- The wave function of a multi-particle system
  - of identical fermions is antisymmetric under interchange of any two fermions
  - of identical bosons is symmetric under interchange of any two bosons
- The Pauli exclusion principle follows from these principles
  - No two identical electrons (fermions) can occupy the same quantum state

$$\psi_a = \frac{1}{\sqrt{2}}\left(\psi_m(x_1)\psi_n(x_2) - \psi_m(x_2)\psi_n(x_1)\right)$$

for $m = n$ (same quantum state)

$$\psi_a = \frac{1}{\sqrt{2}}\left(\psi_m(x_1)\psi_m(x_2) - \psi_m(x_2)\psi_m(x_1)\right) = 0$$

Identical Particles

- What about 3 particles?
- Symmetric

$$\psi_s = \left(\psi_m(x_1)\psi_n(x_2)\psi_o(x_3) + \psi_o(x_1)\psi_m(x_2)\psi_n(x_3) + \psi_n(x_1)\psi_o(x_2)\psi_m(x_3)\right)$$

$$\psi_s = \left(\psi_m(x_1)\psi_n(x_2)\psi_o(x_3) + permutations\right)$$

- Antisymmetric
  - Use the Slater determinant

$$\psi_a = \frac{1}{\sqrt{3!}}\det\begin{vmatrix}\psi_m(1) & \psi_m(2) & \psi_m(3)\\ \psi_n(1) & \psi_n(2) & \psi_n(3)\\ \psi_o(1) & \psi_o(2) & \psi_o(3)\end{vmatrix}$$

$$\psi_a = \frac{1}{\sqrt{6}}\left(\psi_m(1)\psi_n(2)\psi_o(3) - \psi_m(1)\psi_n(3)\psi_o(2)\right.$$
$$+ \psi_m(2)\psi_n(3)\psi_o(1) - \psi_m(2)\psi_n(1)\psi_o(3)$$
$$\left. + \psi_m(3)\psi_n(1)\psi_o(2) - \psi_m(3)\psi_n(2)\psi_o(1)\right)$$

Identical Particles

- Just a reminder, we are presently only working with the space wave functions
  - We'll get to spin in a little bit
- A consequence of identical particles is called exchange "forces"
  - Symmetric space wave functions behave as if the particles attract one another
  - Antisymmetric wave functions behave as if the particles repel one another

Infinite Square Well

- Quick review. For an infinite well at x=0 and x=L

$$\text{Solutions are } \psi_n(\mathrm{x}) = \sqrt{\frac{2}{\mathrm{L}}}\sin\frac{\mathrm{n}\pi\mathrm{x}}{\mathrm{L}}$$

$$E = n^2 \frac{\pi^2\hbar^2}{2mL^2}$$

Identical Particles

- Let's return to the infinite well problem only now with two particles
  - Case 1 distinguishable particles

$$\psi(x_1, x_2) = \psi_m(x_1)\psi_n(x_2)$$

  - Case 2 identical particles (symmetric)

$$\psi(x_1, x_2) = \frac{1}{\sqrt{2}}\left(\psi_m(x_1)\psi_n(x_2) + \psi_m(x_2)\psi_n(x_1)\right)$$

  - Case 3 identical particles (antisymmetric)

$$\psi(x_1, x_2) = \frac{1}{\sqrt{2}}\left(\psi_m(x_1)\psi_n(x_2) - \psi_m(x_2)\psi_n(x_1)\right)$$

Identical Particles

- What is the probability that both particles will be on the left side of the well?

$$P = \int_0^{L/2} \int_0^{L/2} \left|\psi(x_1, x_2)\right|^2 dx_1 dx_2$$

- Case 1

$$P = \int_0^{L/2} \left|\psi_m(x_1)\right|^2 dx_1 \int_0^{L/2} \left|\psi_n(x_2)\right|^2 dx_2$$

$$P = \frac{2}{L}\frac{2}{L} \int_0^{L/2} \frac{\sin^2 m\pi x}{L} dx \int_0^{L/2} \frac{\sin^2 n\pi x}{L} dx$$

$$P = \frac{4}{L^2}\frac{L}{4}\frac{L}{4} = \frac{1}{4}$$

Identical Particles

- Case 2 and 3

$$P = \frac{1}{2}\int_0^{L/2}\left[\psi_m^2(x_1)\psi_n^2(x_2) + \psi_m^2(x_2)\psi_n^2(x_1) \pm 2\psi_m(x_1)\psi_n(x_2)\psi_m(x_2)\psi_n(x_1)\right]dx_1 dx_2$$

$$P = \frac{1}{2}\left[\frac{1}{4} + \frac{1}{4} \pm \int_0^{L/2}\psi_m(x_1)\psi_n(x_1)dx_1 \int_0^{L/2}\psi_m(x_2)\psi_n(x_2)dx_2\right]$$

$$P = \frac{1}{4} \pm \left(\int_0^{L/2}\psi_m(x_2)\psi_n(x_2)dx_2\right)^2$$

$$P = \frac{1}{4} \pm K \text{ where } K > 0$$

- For a symmetric wave function (+) the particles are more likely on the same side (attracted)
- For the antisymmetric wave function (-) the particles are more likely on opposite sides (repel)

Identical Particles

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$$\psi_a = \frac{1}{\sqrt{2}}\left(\psi_m(x_1)\psi_n(x_2) - \psi_m(x_2)\psi_n(x_1)\right)$$

for $m = n$ (same quantum state)

$$\psi_a = \frac{1}{\sqrt{2}}\left(\psi_m(x_1)\psi_m(x_2) - \psi_m(x_2)\psi_m(x_1)\right) = 0$$

Periodic Table

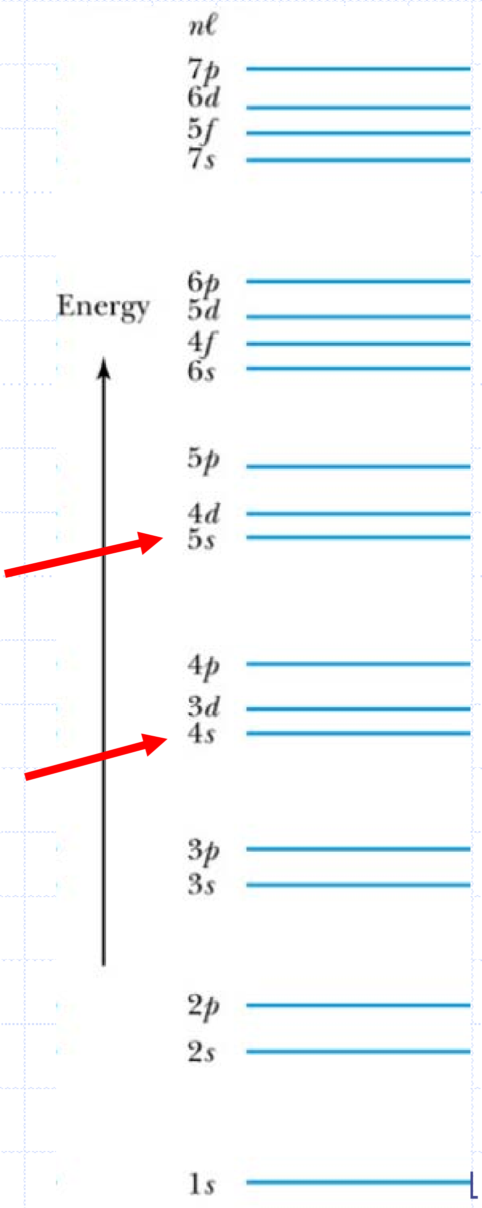
- The Pauli exclusion principle is the basis of the periodic table
  - This is why all the electron's don't simply fall into the ground state – because they are fermions
  - Recall there were 4 quantum numbers that specified the complete hydrogen wave function: n, l, m_l, and m_s
  - No two electrons in the same atom can have these same quantum numbers

Periodic Table

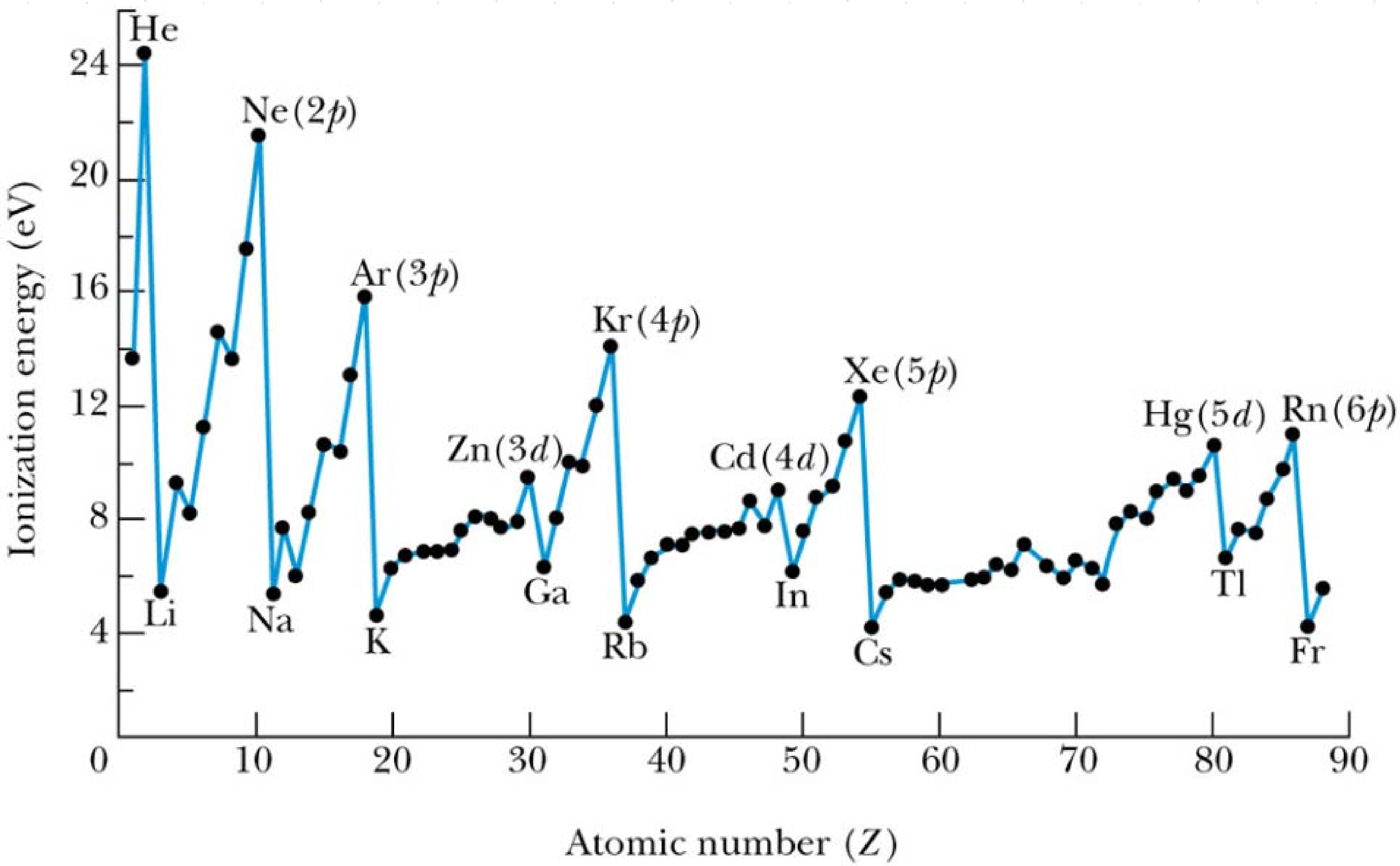
- Building the periodic table
  - Principle quantum number n forms shells
  - Orbital angular momentum quantum number l forms subshells
    - l=0,1,2,3,... are called s,p,d,f,...
  - Each m_l can hold two electrons, one spin up (m_s=1/2) and one spin down (m_s=-1/2)
  - The electrons tend to occupy the lowest energy level possible
  - Electrons obey the Pauli exclusion principle

Periodic Table

- Energy levels
  - Note for multielectron atoms, states of the same n and different l are no longer degenerate
  - This is because of screening effects
  - Referring back to the radial probability distributions, because the s states have non-zero probability of being close to the nucleus, their Coulomb potential energy is lower



Ionization Potential



Periodic Table

- Hydrogen (H)
  - $1s^1$
- Helium (He)
  - $1s^2$ – closed shell and chemically inert
- Lithium (Li)
  - $1s^2 2s$ – valence +1, low I, partially screened, chemically very active
- Beryllium (Be)
  - $1s^2 2s^2$ – Closed subshell but the 2s electrons can extend far from the nucleus

Periodic Table

- Boron (B)
  - $1s^22s^22p^1$ – Smaller I than Be because of screening
- Carbon (C)
  - $1s^22s^22p^2$ – I actually increases because the electrons can spread out in 2/3 l state lobes
  - The valence is +4 since an energetically favorable configuration is $1s^22s^12p^3$
- Nitrogen (N)
  - $1s^22s^22p^3$ – See comments for C. Electrons spread out in 3/3 l state lobes
- Oxygen (O)
  - $1s^22s^22p^4$ – Two of the l state electrons are "paired"
  - Electron-electron repulsion lowers I

Periodic Table

- Fluorine (F)
  - $1s^2 2s^2 2p^5$ – Very chemically active because it can accept an electron to become a closed shell
- Neon (Ne)
  - $1s^2 2s^2 2p^6$ – Like He

Transition elements (groups 3–12)

shells	Alkalis	earths															Halogens	gases
Groups:	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	1 H																	2 He
$1s^2$	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
$2s^22p^6$	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
$3s^23p^6$	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
$3d^{10}4s^24p^6$	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
$4d^{10}5s^25p^6$	55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
$4f^{14}5d^{10}6s^26p^6$	87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112						

Lanthanides	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinides	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Periodic Table

- Periodic table is arranged into groups and periods
- Groups
  - Have similar shell structure hence have similar chemical and physical properties
  - Examples are alkalis, alkali earths, halogens, inert gases
- Periods
  - Correspond to filling d and f subshells
  - Examples are transition metals (3d,4d,5d), lanthanide (4f), and actinide (5f) series
  - Because there are many unpaired electrons, spin is important for these elements and there are large magnetic effects