Chemistry 3830

Electron Configuration

Solving Schröderinger's Equation

$$\hat{H}\Psi = E\Psi$$

$$\Psi = R(r)\Theta(\theta)\Phi(\varphi) = R(r)Y(\theta,\varphi)$$

radial wavefunction angular wavefunction

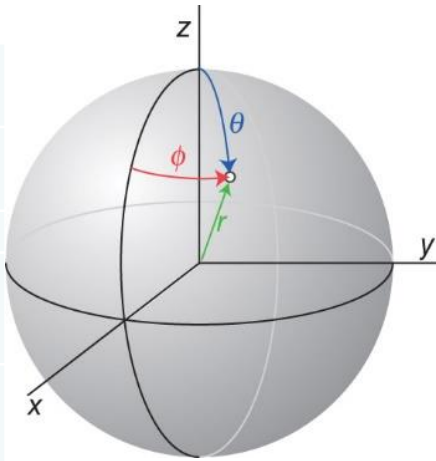
"solving Schrödinger's equation"

$$\Psi = R_{n,l}(r)Y_{l,m_l}(\theta,\varphi)$$

Only certain wavefunctions are allowed!
Only certain quantum numbers are allowed!

Electronic Wavefunctions – Mathematical Description

$$\Psi_{n,l,m_l} = R_{n,l}(r)Y_{l,m_l}(\theta,\varphi)$$



Some complete Hydrogenic wavefunctions (products of Radial and Angular components)

Quantum numbers			Spherical-polar solutions to the Schrödinger equation	Cartesian angular functions
n	l	m_l		
1	0	0	$\Psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} \cdot e^{-r/a_0}$	None
2	1	0	$\Psi_{210} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2} \cdot \frac{1}{a_0} e^{-r/2a_0} \cdot r \cdot cos\theta$	$r \cdot cos\theta = z$
2	1	1	$\Psi_{211} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2} \cdot \frac{1}{a_0} e^{-r/2a_0} \cdot r \cdot sin\theta \cdot e^{2i\varphi}$	No easy conversion
2	1	1/-1	$\Psi_{221} - \Psi_{21-1} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2} \cdot \frac{1}{a_0} e^{-r/3a_0} \cdot r \cdot sin\theta cos\varphi$	$r \cdot sin\theta cos\varphi = x$
3	2	-1	$\Psi_{32-1} = \frac{1}{81}\sqrt{\frac{2}{\pi}}\left(\frac{1}{a_0}\right)^{3/2} \cdot \left(\frac{1}{a_0}\right)^{2} e^{-r/3a_0} \cdot r^2 \cdot sin\theta cos\theta e^{-i\varphi}$	No easy conversion
3	2	1/-1	$\Psi_{321} - \Psi_{32-1} = \frac{1}{81}\sqrt{\frac{2}{\pi}}\left(\frac{1}{a_0}\right)^{3/2} \cdot \left(\frac{1}{a_0}\right)^{2} e^{-r/3a_0} \cdot r^2 \cdot sin\theta cos\theta sin\varphi$	$r \cdot sin\theta cos\theta sin\varphi = yz$

Euler equations: $e^{i\varphi} = cos\varphi + i\, sin\varphi$ $e^{-i\varphi} = cos\varphi - i\, sin\varphi$

Electronic Wavefunctions – Mathematical Description

Complex wavefunctions $\Psi_{n,l,m_l} = R_{n,l}(r)Y_{l,m_l}(\theta,\varphi)$

Information about angular momentum

Use in computations

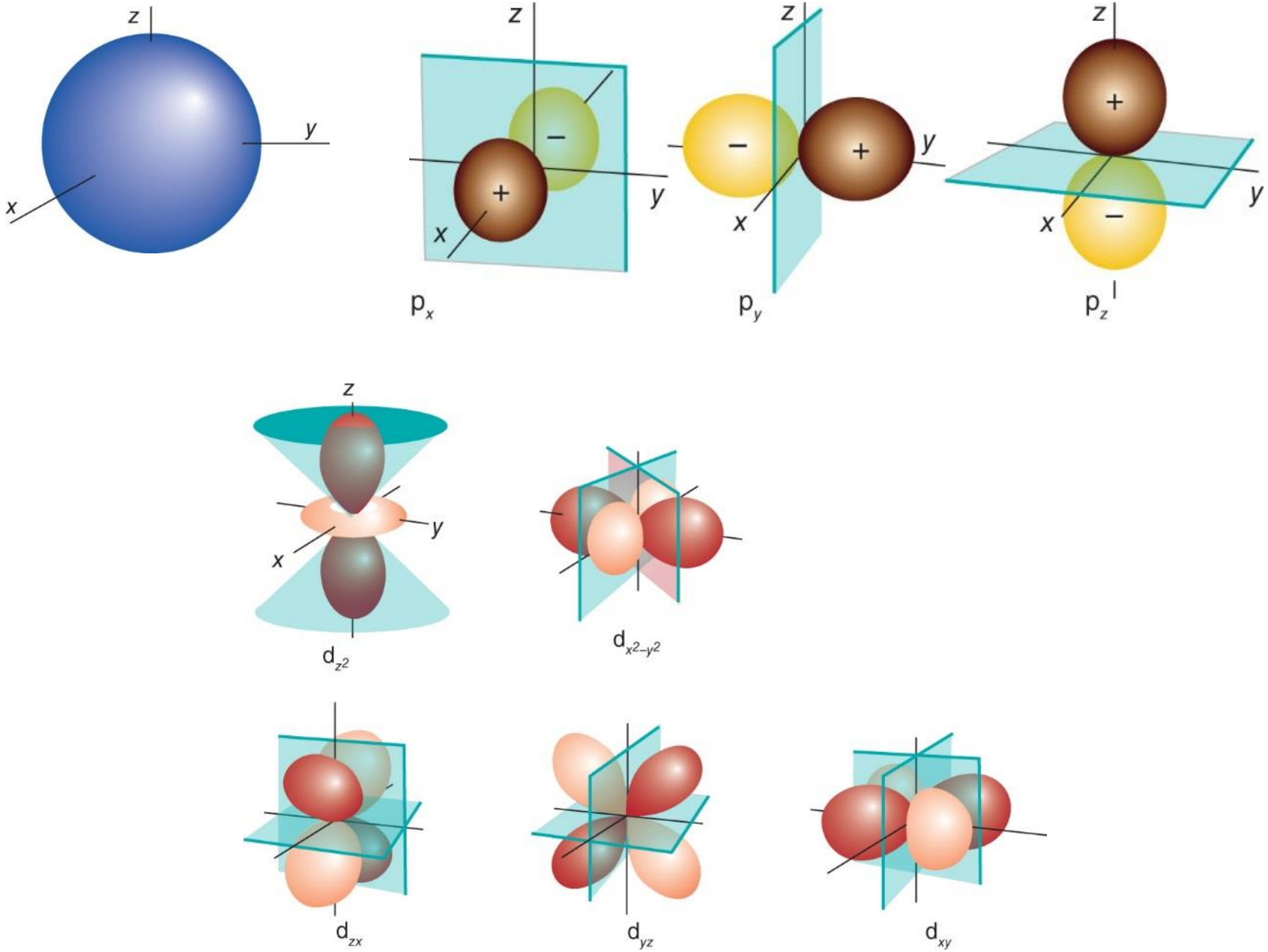
Real wavefunctions (linear combinations of complex wavefunctions)

p_x, p_y, d_{xy}, etc.

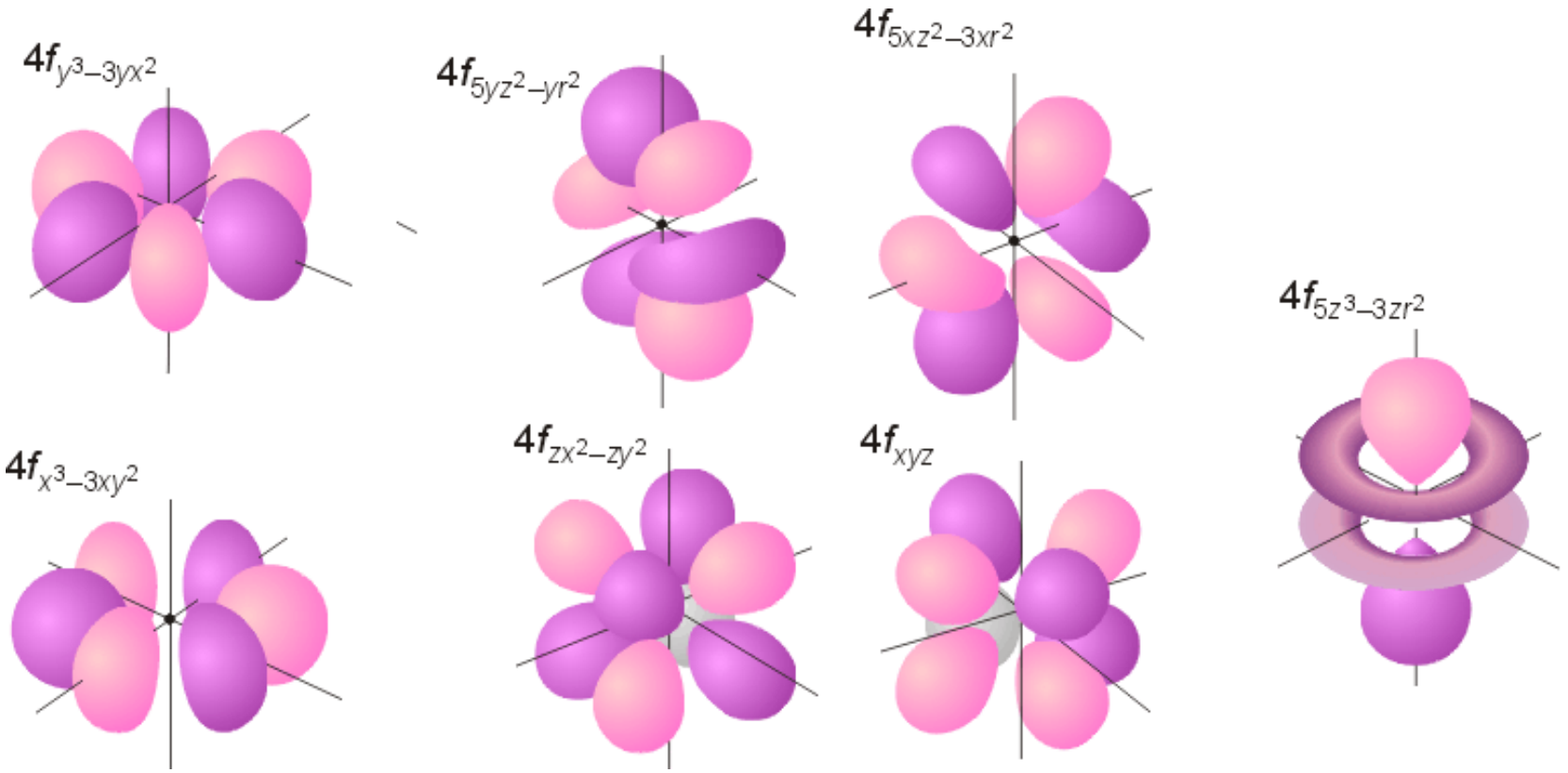
Information about shape

Use for visualization in chemistry

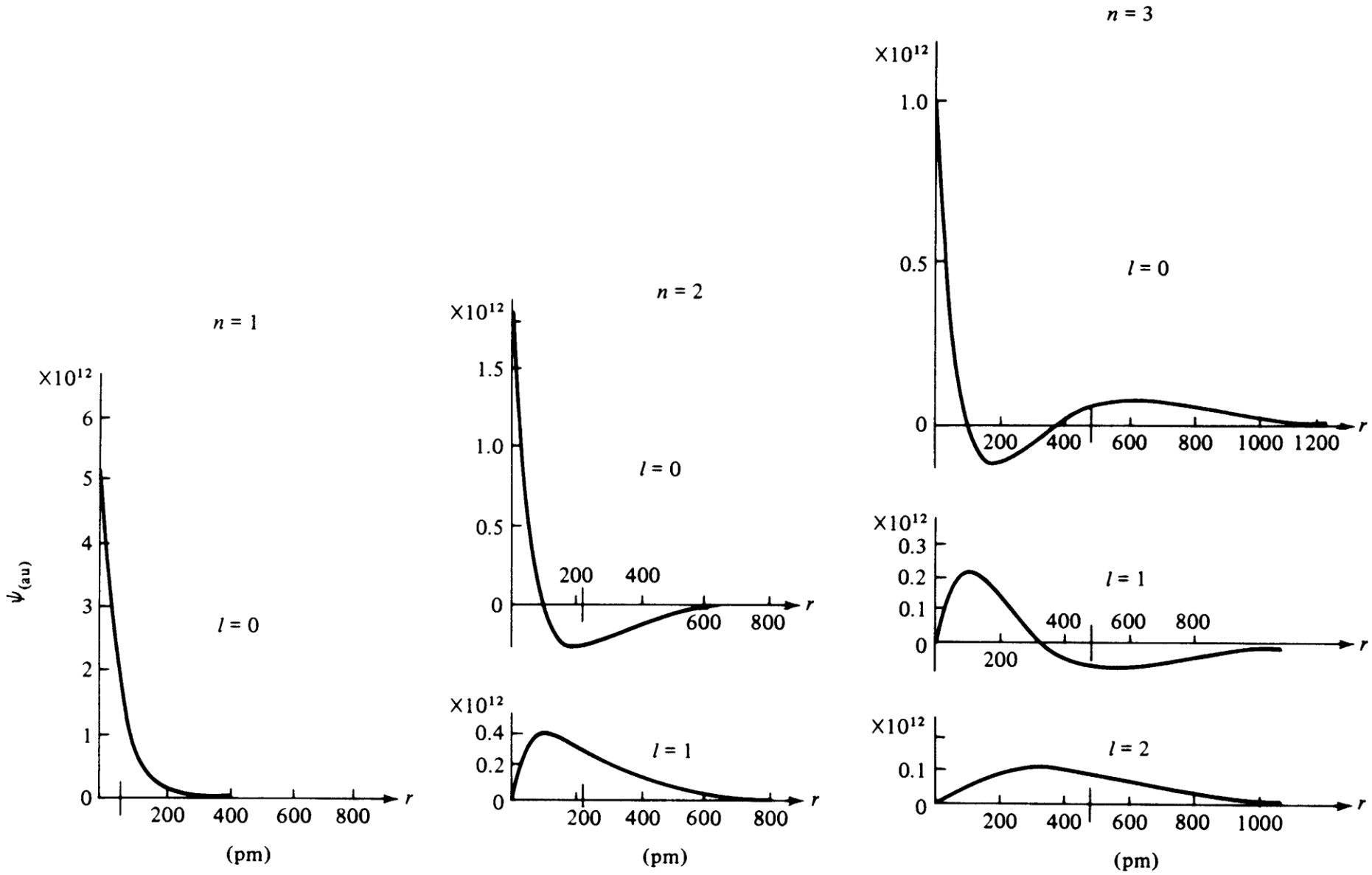
s, *p*, and *d* Orbitals



f Orbitals


$4f_{y^3-3yx^2}$
$4f_{5yz^2-yr^2}$
$4f_{5xz^2-3xr^2}$
$4f_{5z^3-3zr^2}$
$4f_{x^3-3xy^2}$
$4f_{zx^2-zy^2}$
$4f_{xyz}$

Electronic Wavefunctions – Radial Function

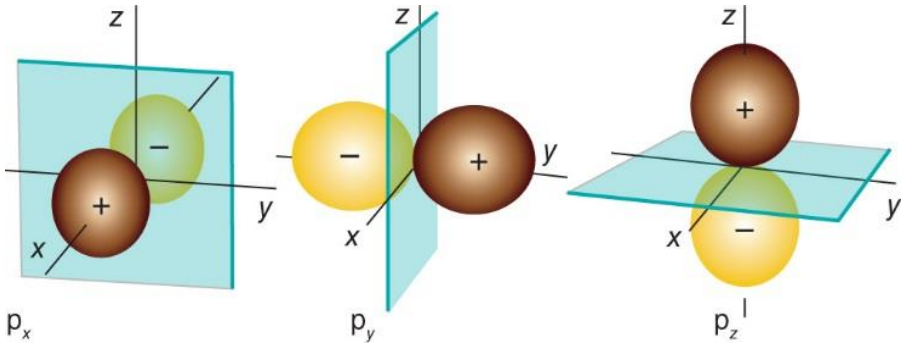


Orbitals, Ψ, and Ψ^2

Orbitals = electronic wavefunction Ψ

Orbitals are mathematical functions and they have signs (phases)!!!

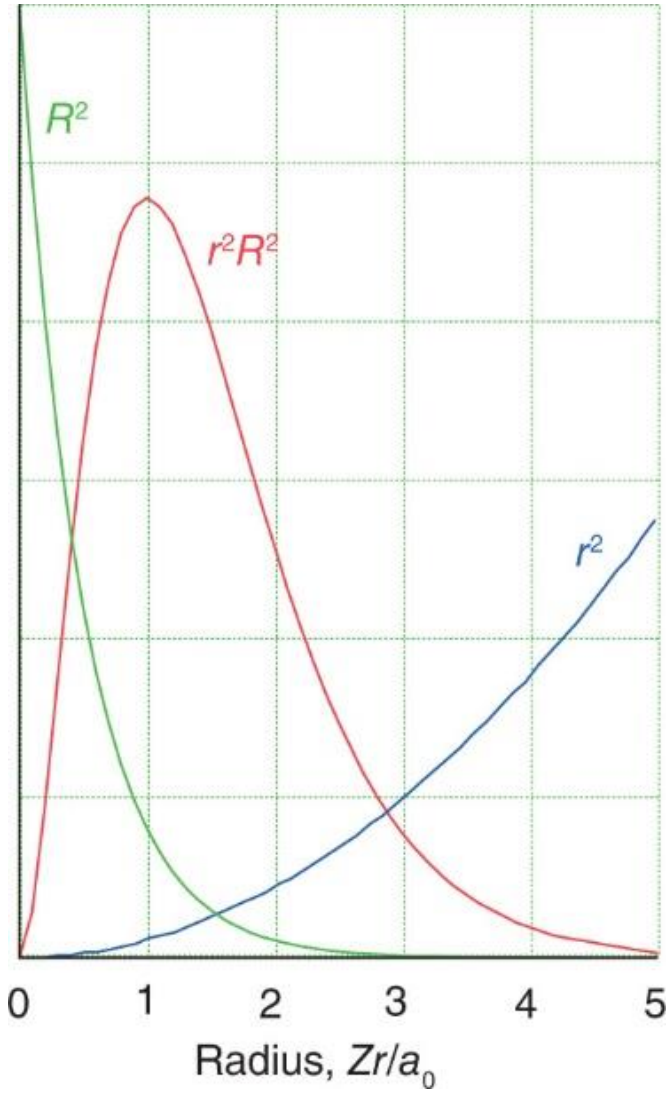
The phases of orbitals cannot be directly observed.



The electron density (probability of finding electrons in a space), i.e., Ψ^2 can be observed.

Ψ^2 and the Radial Distribution Function $4\pi r^2\Psi^2$

Radial distribution function = radial probability function
= function of finding the electron at a certain distance from the nucleus



Radial distribution function is a projection of electron density onto a single radial axis.

$4\pi r^2$ = surface area of the sphere

Small r values:

small surface area of the sphere (small surface area to 'collect' the electron density).

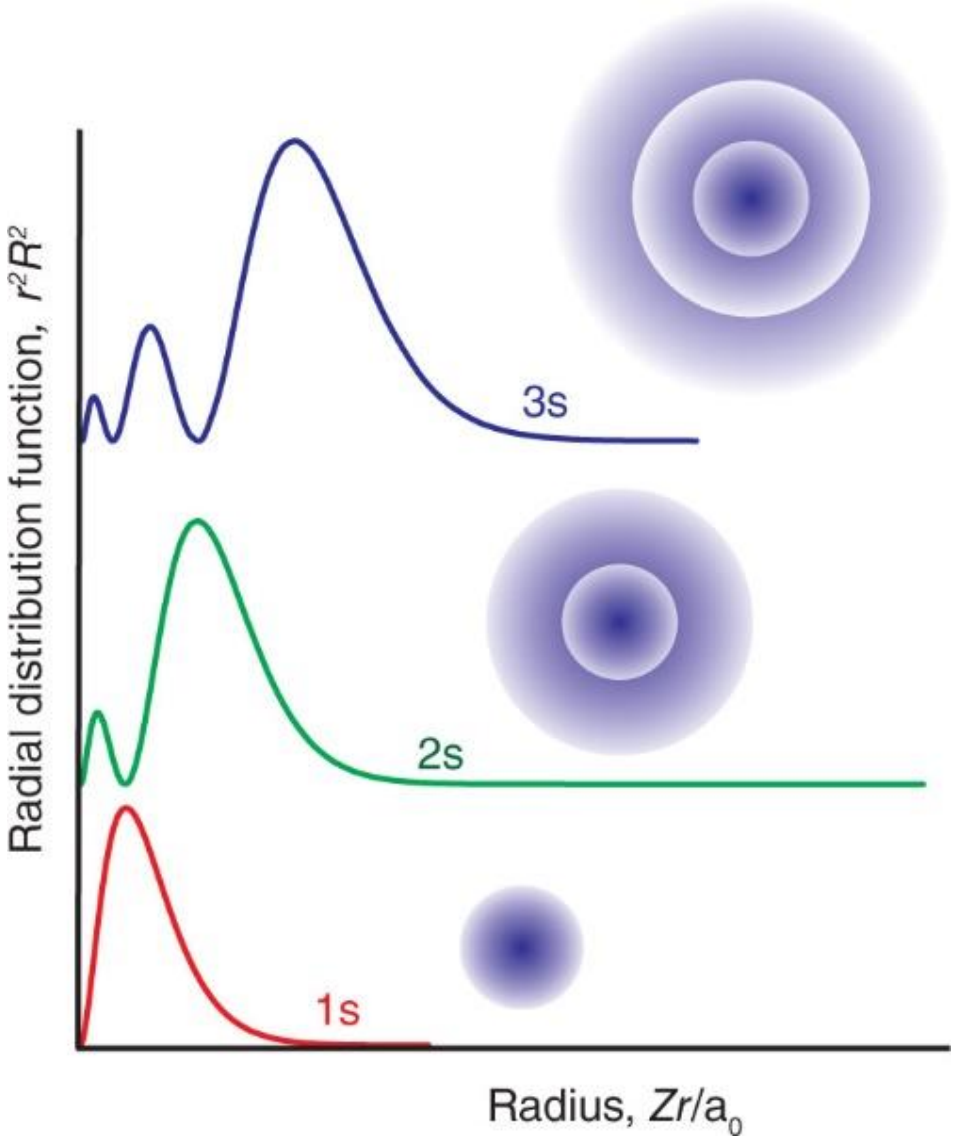
Large r values:

large surface area of the sphere (large surface area to 'collect' the electron density), but electron density, Ψ^2, is small.

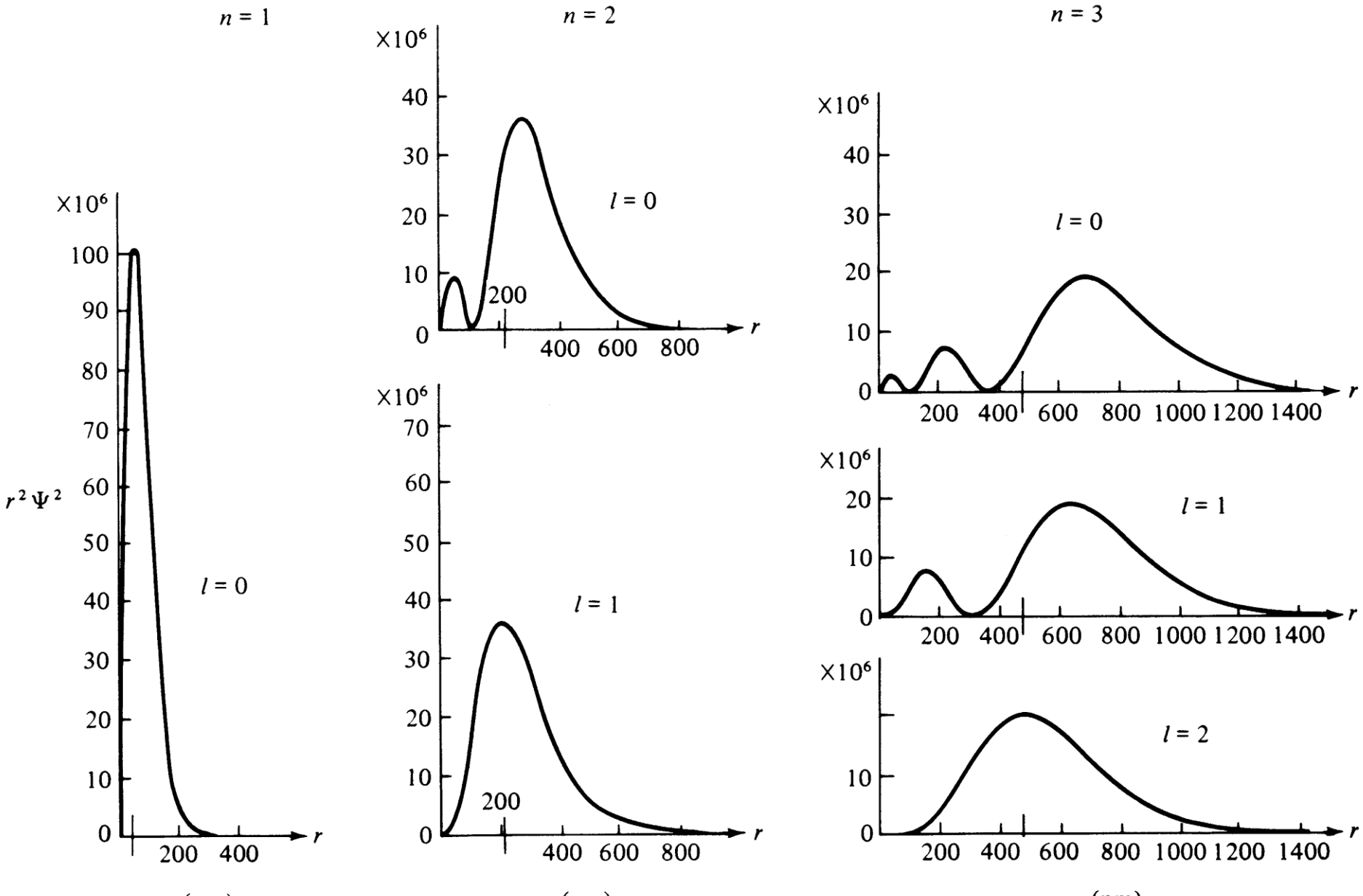
Intermediate r values:

Optimal combination of surface area and electron density, Ψ^2.

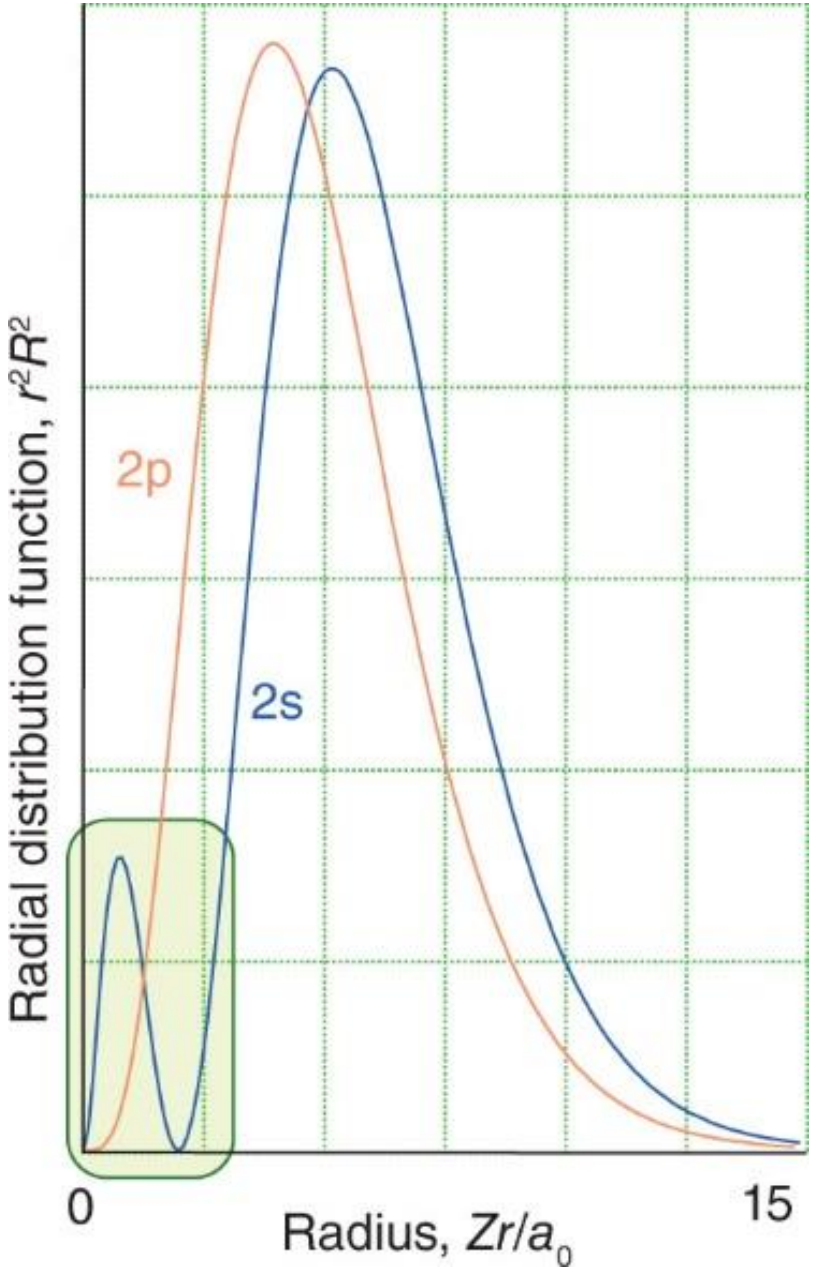
Ψ^2 and the Radial Distribution Function $4\pi r^2\Psi^2$



Electronic Wavefunctions – Radial Distribution Function



Shielding of Nuclear Charge and Penetration Effect



For the H atom, the 2p and 2s orbitals are degenerate.

In the presence of a second electron, the 2p and 2s orbitals are NOT degenerate.

If the 1s orbital is filled with one or two electrons, there is a difference between a 2s and a 2p electron.

A 2s electron has electron density closer to the nucleus than a 2p electron (the local maximum of the radial distribution function).

Therefore, the 2s electron experiences a larger nuclear charge than the 2p electron.

The nuclear charge is more **shielded** for the 2p than for the 2s electron.

The 2s electron is better in **penetrating** the 1s electron cloud.

Orbitals in a Multi-Electron System

$$\hat{H}\Psi = E\Psi$$

Kinetic energy of nucleus

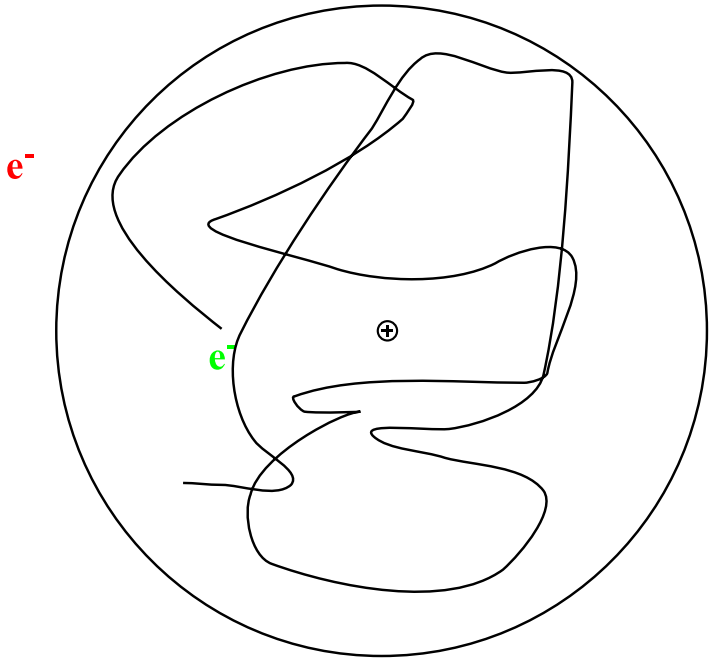
Kinetic energy of electron 1

Kinetic energy of electron 2

Potential energy:
Electron 1-nucleus attraction

Potential energy:
Electron 2-nucleus attraction

Potential energy:
Electron 1 electron 2 repulsion



No analytical solution to Schrödinger's equation possible!

Approximation needed!

Hartree-Fock Self-Consistent Field Method

HF SCF Method

1. Assume reasonable Ψs for all electrons, except electron i.

2. Calculate the effect of the average, combinded field of the nucleus and all other electrons on electron i. Generate a Hamiltonian for electron i: h_i

3. Obtain Ψ_i from $h_i \Psi_i = E_i \Psi_i$

4. Use Ψ_i to calculate average field of electron i.
   Generate Hamiltonian for electron j: h_j

5. Calculate Ψ_j

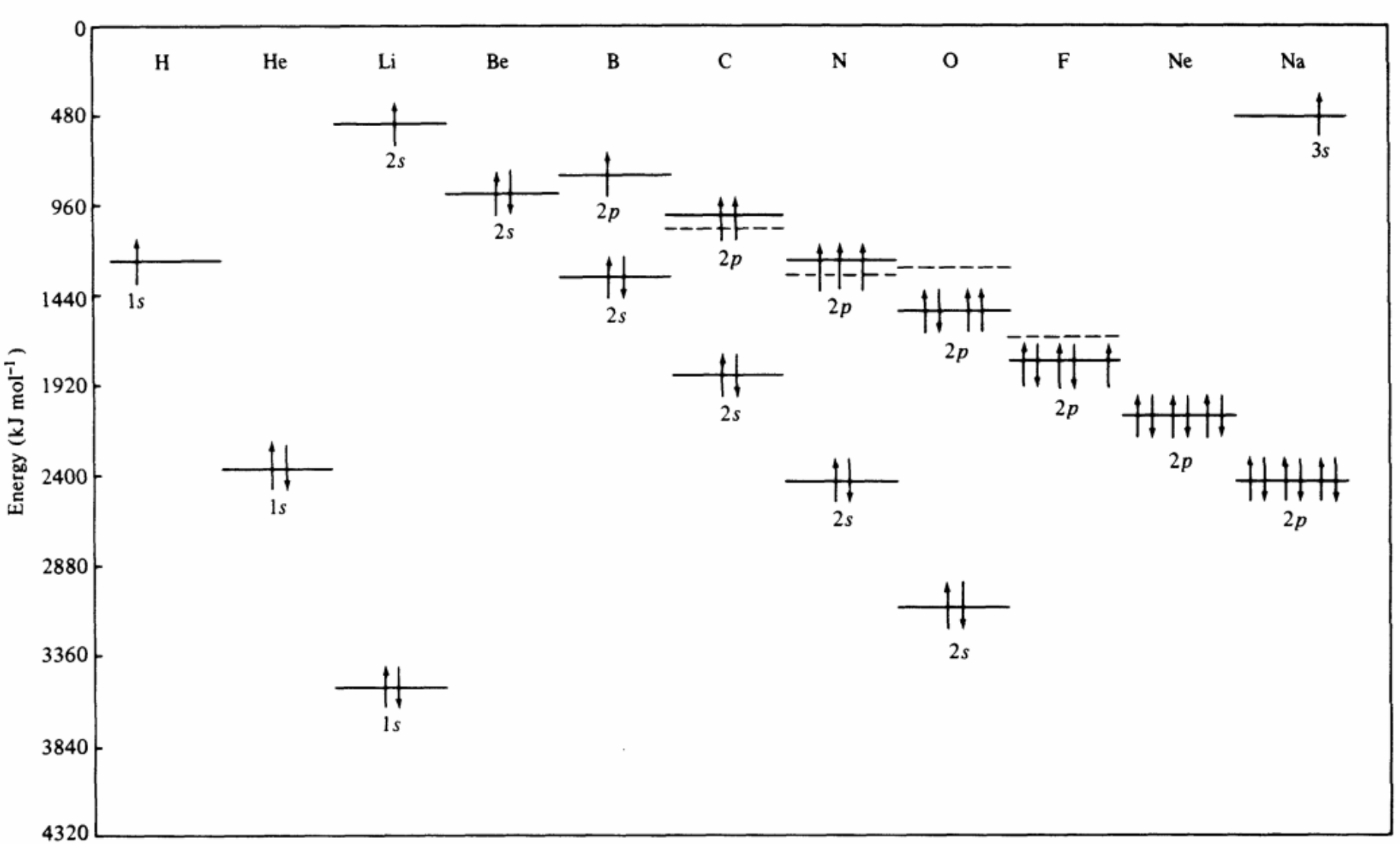
6. Do this for all electrons

7. Then go through all electron again
   with improved wavefunctions.

8. Repeat the cycle until the overall energy
   does not change anymore (self consistent field).

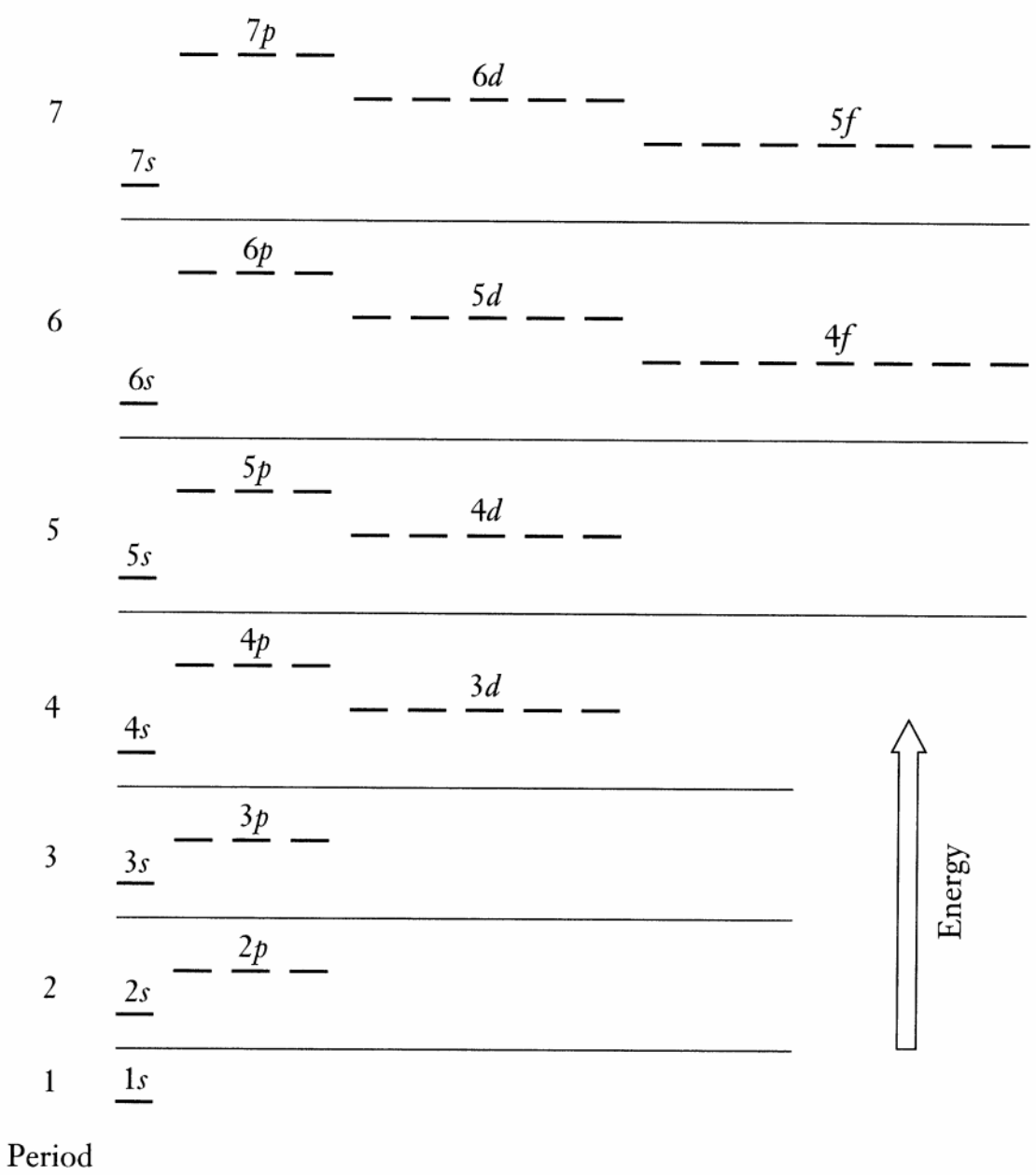
PROBLEM: Electron correlation is not accounted for!

Multi-Electron Atoms



Valence orbitals: Ionization energy of orbitals are between 480 and 2400 kJ/mol

Multi-Electron Atoms



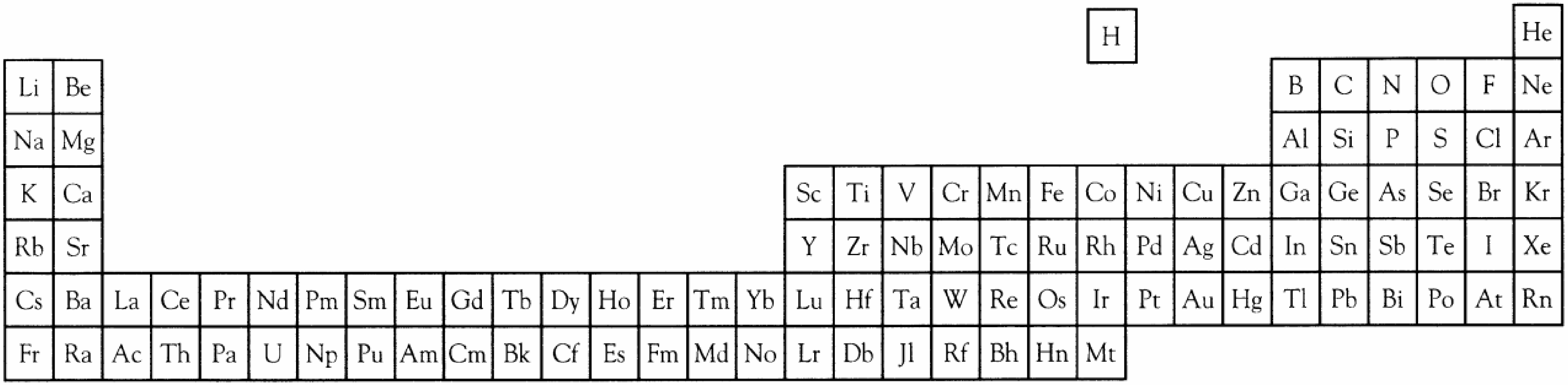
Electron Configuration of the Elements

Aufbau Principle

Pauli Exclusion Principle

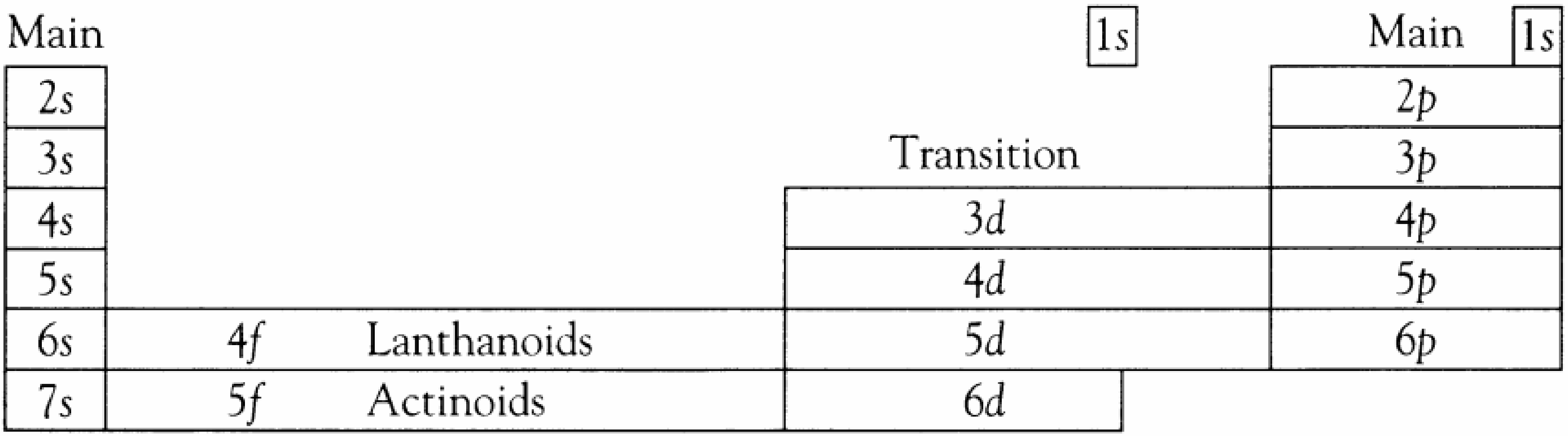
Hund’s Rule(s)

Aufbau (Building-up) Principle



Na $[Ne]3s^1$ Cl $[Ne]3s^2 3p^5$

As $[Ar]4s^2 3d^{10} 4p^3$ Cl^- $[Ne]3s^2 3p^6$ (≡ [Ar])



Exceptions to the Aufbau Principle

Element Electron Configurations
(only the last subshell is shown unless the Aufbau order is non-standard for a given atom)

1												13	14	15	16	17	18
$1s^1$ 1	2											$2p^1$ 5	$2p^2$ 6	$2p^3$ 7	$2p^4$ 8	$2p^5$ 9	$1s^2$ 2
$2s^1$ 3	$2s^2$ 4											$2p^1$ 5	$2p^2$ 6	$2p^3$ 7	$2p^4$ 8	$2p^5$ 9	$2p^6$ 10
$3s^1$ 11	$3s^2$ 12	3	4	5	6	7	8	9	10	11	12	$3p^1$ 13	$3p^2$ 14	$3p^3$ 15	$3p^4$ 16	$3p^5$ 17	$3p^6$ 18
$4s^1$ 19	$4s^2$ 20	$3d^1$ 21	$3d^2$ 22	$3d^3$ 23	$4s^13d^5$ 24	$3d^5$ 25	$3d^6$ 26	$3d^7$ 27	$3d^8$ 28	$4s^13d^{10}$ 29	$3d^{10}$ 30	$4p^1$ 31	$4p^2$ 32	$4p^3$ 33	$4p^4$ 34	$4p^5$ 35	$4p^6$ 36
$5s^1$ 37	$5s^2$ 38	$4d^1$ 39	$4d^2$ 40	$5s^14d^4$ 41	$5s^14d^5$ 42	$4d^5$ 43	$5s^14d^7$ 44	$5s^14d^8$ 45	$5s^04d^{10}$ 46	$5s^14d^{10}$ 47	$4d^{10}$ 48	$5p^1$ 49	$5p^2$ 50	$5p^3$ 51	$5p^4$ 52	$5p^5$ 53	$5p^6$ 54
$6s^1$ 55	$6s^2$ 56	La-Lu	$5d^2$ 72	$5d^3$ 73	$5d^4$ 74	$5d^5$ 75	$5d^6$ 76	$5d^7$ 77	$6s^15d^9$ 78	$6s^15d^{10}$ 79	$5d^{10}$ 80	$6p^1$ 81	$6p^2$ 82	$6p^3$ 83	$6p^4$ 84	$6p^5$ 85	$6p^6$ 86
$7s^1$ 87	$7s^2$ 88	Ac-Lr	$6d^2$ 104	$6d^3$ 105	$6d^4$ 106	$6d^5$ 107	$6d^6$ 108	$6d^7$ 109	110	111							

Developed by Prof. R. T. Boeré (updated January, 1999)

↓

$4f^05d^1$ 57	$4f^15d^1$ 58	$4f^3$ 59	$4f^4$ 60	$4f^5$ 61	$4f^6$ 62	$4f^7$ 63	$4f^75d^1$ 64	$4f^9$ 65	$4f^{10}$ 66	$4f^{11}$ 67	$4f^{12}$ 68	$4f^{13}$ 69	$4f^{14}$ 70	$5d^1$ 71
$5f^06d^1$ 89	$5f^06d^2$ 90	$5f^26d^1$ 91	$5f^36d^1$ 92	$5f^46d^1$ 93	$5f^6$ 94	$5f^7$ 95	$5f^76d^1$ 96	$5f^9$ 97	$5f^{10}$ 98	$5f^{11}$ 99	$5f^{12}$ 100	$5f^{13}$ 101	$5f^{14}$ 102	$6d^1$ 103

Electron Configuration of Ions

Cl $[Ne]3s^2 3p^5$

V $[Ar]4s^2 3d^3$

V^{2+} $[Ar]3d^3$ (NOT $[Ar]4s^2 3d^1$!!!!)