

Atoms, many electron theories and the periodic table

Reading:

- ▶ Kasap: 3.7 - 3.8

Hydrogenic atom

- ▶ Single electron with a nucleus of charge $+Ze$, where Z is the atomic number
- ▶ $Z = 1$ is hydrogen, $Z = 2$ is a He^+ ion, $Z = 3$ is Li^{2+} etc.
- ▶ Schrodinger equation

$$-\frac{\hbar^2 \nabla^2 \psi(\vec{r})}{2m} - \frac{Ze^2}{4\pi\epsilon_0 r} \psi(\vec{r}) = E\psi(\vec{r})$$

separable in spherical coordinates resulting in eigenfunctions

$$\psi_{nlm}(\vec{r}) = R_{nl}(r)Y_{lm}(\theta, \phi)$$

and eigen-energies

$$E_{nlm} = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2} \cdot \frac{Z^2}{n^2} = \frac{-Z^2}{2n^2} E_h = \frac{-Z^2}{n^2} \text{Ryd} \approx \frac{-Z^2}{n^2} (13.6 \text{ eV})$$

Atomic quantum numbers

- ▶ For the box, we have n_x , n_y and n_z
- ▶ Now in spherical coordinates, so correspond to r , θ and ϕ
- ▶ Principal quantum number $n = 1, 2, \dots$ is for the radial r direction
- ▶ Angular quantum number $l = 0, 1, 2, \dots, n - 1$ is for the θ direction
- ▶ Azimuthal quantum number $m_l = -l, -l + 1, \dots, +l$ is for the ϕ direction
- ▶ But energy $E_{nlm_l} \propto n^{-2}$ only depends on n
- ▶ States of various l and m_l at same n are 'degenerate' i.e. have same energy

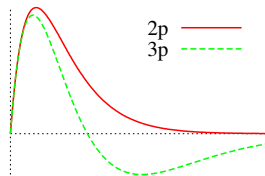
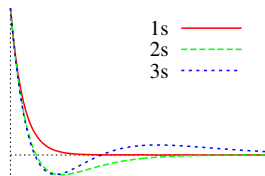
Radial wavefunctions

- ▶ Radial functions of the form

$$R_{nl}(r) \propto \exp\left(\frac{-Zr}{na_0}\right) \cdot r^l \cdot p_{n-l-1}^{(l)}(r)$$

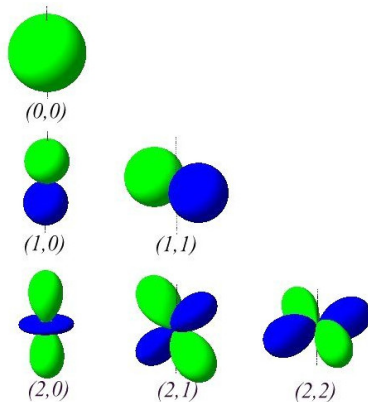
where $a_0 = 4\pi\epsilon_0\hbar^2/(me^2) \approx 0.529 \text{ \AA}$
is the Bohr radius

- ▶ Typical radial extent $\sim na_0/Z$
- ▶ Polynomial degree $n - l - 1$: first n of given l has no nodes, next has one node etc.
- ▶ Remember $l = 0, 1, 2, 3$ denoted by s, p, d, f
- ▶ 1s has no nodes, 2s has 1 node etc.
- ▶ 2p has no nodes, 3p has 1 node etc.



Angular wavefunctions

- ▶ Spherical harmonics $Y_{lm_l}(\theta, \phi) = P_l^{m_l}(\cos \theta)e^{im_l\phi}$
- ▶ Characteristic orbital shapes used in chemistry (typically $\text{Re}Y_{lm}$ and $\text{Im}Y_{lm}$)
- ▶ l controls number of lobes
- ▶ m_l controls number in xy -plane
- ▶ All m_l related by spherical symmetry



Electronic configuration of atoms

- ▶ Pauli exclusion principle: one electron per state (Fermi-Dirac statistics)
- ▶ Spin: $m_s = \pm 1/2$ (2 states)
- ▶ Azimuthal: $m = -l, -l + 1, \dots, +l$ ($2l + 1$ states)
- ▶ Per n and l : $2(2l + 1)$ states
- ▶ Periodic table by orbital being filled (Z range):

1s (1-2)			
2s (3-4)			2p (5-10)
3s (11-12)			3p (13-18)
4s (19-20)		3d (21-30)	4p (31-36)
5s (37-38)		4d (39-48)	5p (49-54)
6s (55-56)	4f (57-70)	5d (71-80)	7p (81-86)
7s (87-88)	5f (89-102)		

The size of atoms

- ▶ Orbital size $\sim na_0/Z$
- ▶ Hydrogen atom $Z = 1, n = 1$: size $\sim a_0 \approx 0.53 \text{ \AA}$
- ▶ Sodium atom $Z = 11, n = 3$: size $\sim 3a_0/11 \approx 0.14 \text{ \AA}$
- ▶ Platinum atom $Z = 78, n = 6$: size $\sim 6a_0/78 \approx 0.04 \text{ \AA}$
- ▶ What's wrong?
- ▶ Hydrogenic orbitals are for one electron systems only!
- ▶ When more than one electron, electron-electron repulsion matters
- ▶ Effective charge seen by outer electrons is approximately that of nucleus + inner electrons

Many-electron Schrodinger equation

- ▶ So far, we discussed wavefunction $\psi(\vec{r})$ satisfying

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + V(\vec{r})\psi = E\psi$$

which is strictly a one-electron theory only.

- ▶ For N electrons, need to keep track of all N electronic coordinates with a wavefunction $\psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$
- ▶ Corresponding Schrodinger equation with e-e interactions:

$$\underbrace{-\frac{\hbar^2}{2m} \sum_i \nabla_{\vec{r}_i}^2 \psi}_{\text{Kinetic}} + \underbrace{\sum_i V(\vec{r}_i)\psi}_{\text{e-nuc}} + \underbrace{\sum_{i \neq j} \frac{e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|} \psi}_{\text{e-e}} = E\psi$$

which is impossible to solve exactly beyond special $N = 2$ cases

Many-electron non-interacting case

- ▶ Without e-e interactions:

$$\underbrace{-\frac{\hbar^2}{2m} \sum_i \nabla_{\vec{r}_i}^2 \psi}_{\text{Kinetic}} + \underbrace{\sum_i V(\vec{r}_i) \psi}_{\text{e-nuc}} = E\psi$$

which is *separable* in each \vec{r}_i .

- ▶ Therefore solution must be consist of products

$$\psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \sim \phi_1(\vec{r}_1) \phi_2(\vec{r}_2) \cdots \phi_N(\vec{r}_N)$$

- ▶ Each 'orbital' ϕ_i : $N = 1$ Schrodinger equation with orbital energy ε_i
- ▶ Total energy $E = \sum_i \varepsilon_i$
- ▶ Strictly, fermionic wavefunctions need to be antisymmetric

$$\Rightarrow \psi = \det[\phi_i(\vec{r}_j)]$$

(Slater determinant)

Kohn-Sham density functional theory (DFT)

- ▶ A single-particle theory

$$-\frac{\hbar^2}{2m} \nabla^2 \phi_i(\vec{r}) + V_{\text{KS}}(\vec{r})\psi = \varepsilon_i \phi_i(\vec{r})$$

in an effective potential $V_{\text{KS}}(\vec{r})$

- ▶ $V_{\text{KS}}(\vec{r}) = V(\vec{r}) +$ contribution from electron density $n(\vec{r})$
- ▶ Total energy $E = \sum_i \varepsilon_i +$ contribution from electron density $n(\vec{r})$
- ▶ Electron density $n(\vec{r}) = \sum_i |\phi_i(\vec{r})|^2$ made self-consistent
- ▶ DFT works surprisingly well even for strongly interacting electrons
- ▶ When DFT does not work, material called 'strongly-correlated'!

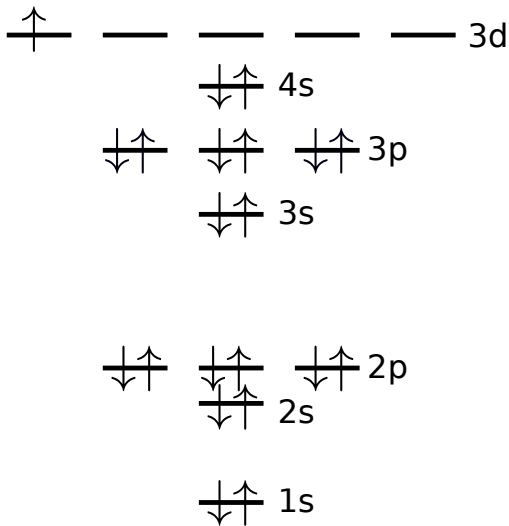
Atoms revisited

- ▶ Orbital energies are those from effective potential (not hydrogenic)
- ▶ For spherical atoms, still degenerate in m and m_s , but not in l
- ▶ At same n , energy increases with l
- ▶ In particular, energy of $(n + 1)s < (n - 1)f < nd < (n + 1)p \Rightarrow$

1s (1-2)			
2s (3-4)			2p (5-10)
3s (11-12)			3p (13-18)
4s (19-20)		3d (21-30)	4p (31-36)
5s (37-38)		4d (39-48)	5p (49-54)
6s (55-56)	4f (57-70)	5d (71-80)	7p (81-86)
7s (87-88)	5f (89-102)		

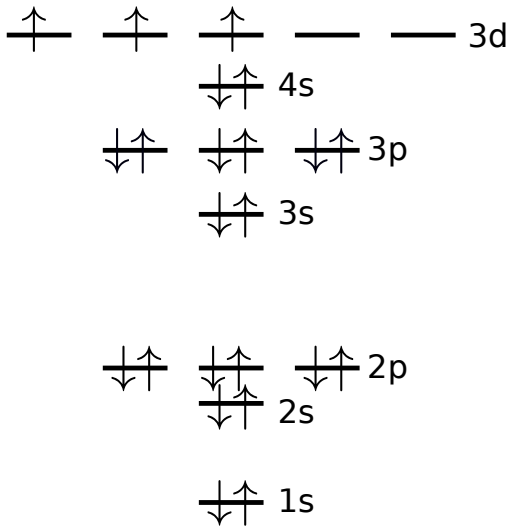
Electronic configuration example: Sc

$Z = 21$, Configuration: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$



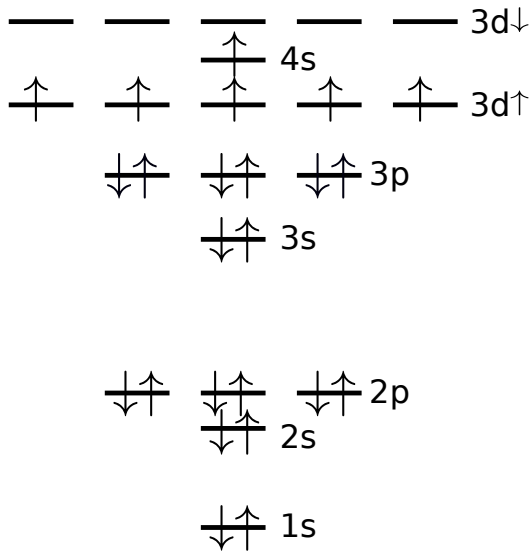
Electronic configuration example: V

$Z = 23$, Configuration: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$



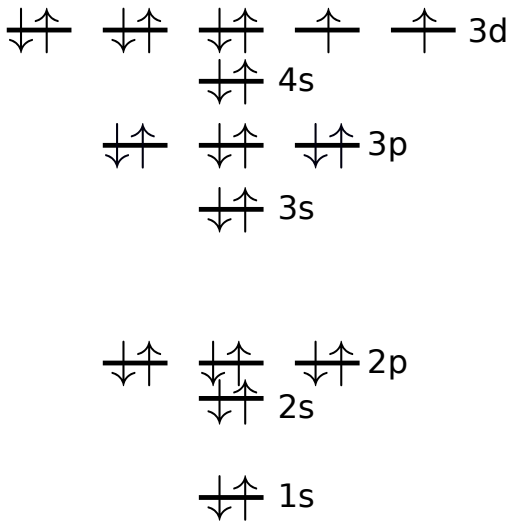
Electronic configuration example: Cr

$Z = 24$, Configuration: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$



Electronic configuration example: Ni

$Z = 28$, Configuration: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$



Electronic configuration example: Cu

$Z = 29$, Configuration: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$

