Chapter 3.

Many-Electron Atoms

Reading: Bransden & Joachain, Chapter 8

Central Field Approximation

Assumption: each of the atomic electrons moves in an effective spherically symmetric potential $V(r)$ created by the nucleus and all the other electrons.

Hamiltonian of the N-electron atom

$$H = \sum_{i=1}^{N}\left(-\frac{\hbar^2}{2m}\nabla_{\vec{r}_i}^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_i}\right) + \sum_{i>j}^{N}\sum_{j=1}^{N}\frac{e^2}{4\pi\varepsilon_0 r_{ij}}$$

$$= \sum_{i=1}^{N}\left(-\frac{1}{2}\nabla_{\vec{r}_i}^2 - \frac{Z}{r_i}\right) + \sum_{i>j}^{N}\sum_{j=1}^{N}\frac{1}{r_{ij}} \qquad \text{in a.u.}$$

No spin-orbit interactions, spin-spin interactions, relativistic effects, nuclear corrections etc.

Schrödinger equation

$$\left[\sum_{i=1}^{N}\left(-\frac{1}{2}\nabla_{\vec{r}_i}^2 - \frac{Z}{r_i}\right) + \sum_{i>j}^{N}\sum_{j=1}^{N}\frac{1}{r_{ij}}\right]\Psi(q_1, q_2, ..., q_N) = E\Psi(q_1, q_2, ..., q_N), \quad q_i = (\vec{r}_i, s_i)$$

Total wave function: antisymmetric

$$P_{ij}\Psi(..., q_i, ..., q_j, ..) = \Psi(..., q_j, ..., q_i, ..) = -\Psi(..., q_i, ..., q_j, ..)$$

Schrödinger equation for spatial wave function

$$\left[\sum_{i=1}^{N}\left(-\frac{1}{2}\nabla_{\vec{r}_i}^2-\frac{Z}{r_i}\right)+\sum_{i>j}^{N}\sum_{j=1}^{N}\frac{1}{r_{ij}}\right]\psi(\vec{r}_1,\vec{r}_2,...,\vec{r}_N)=E\,\psi(\vec{r}_1,\vec{r}_2,...,\vec{r}_N)$$

Central field approximation (independent particle model):
Each electron moves in an effective spherically symmetric potential $V(r)$ created by the nucleus and all the other electrons.

$$V(r)=-\frac{Z}{r}+S(r),\quad \sum_{i=1}^{N}S(r_i)\approx\sum_{i>j}^{N}\sum_{j=1}^{N}\frac{1}{r_{ij}}$$

Screening

$$V(r)\to-\frac{Z}{r},\qquad r\to 0$$

$$V(r)\to-\frac{Z-(N-1)}{r},\qquad r\to\infty$$

$$V(r)\to ?$$ at intermediate distance

Thomas-Fermi and Hartree-Fock methods

Unperturbed Hamiltonian

$$H = H_c + H_1$$

$$H_c = \sum_{i=1}^{N}\left(-\frac{1}{2}\nabla_{\vec{r}_i}^2 + V(r_i)\right) = \sum_{i=1}^{N} h_i, \qquad h_i = -\frac{1}{2}\nabla_{\vec{r}_i}^2 + V(r_i)$$

$$H_1 = \sum_{i>j}^{N}\sum_{j=1}^{N}\frac{1}{r_{ij}} - \sum_{i=1}^{N}\left(\frac{Z}{r_i} + V(r_i)\right) = \sum_{i>j}^{N}\sum_{j=1}^{N}\frac{1}{r_{ij}} - \sum_{i=1}^{N} S(r_i) \quad << \quad \sum_{i>j}^{N}\sum_{j=1}^{N}\frac{1}{r_{ij}}$$

Schrödinger equation for central field wave function

$$H_c\psi_c = \sum_{i=1}^{N}\left[-\frac{1}{2}\nabla_{\vec{r}_i}^2 + V(r_i)\right]\psi_c = E_c\psi_c$$

separable into N equations

$$\psi_c = u_{a_1}(r_1)u_{a_2}(r_2)...u_{a_N}(r_N)$$

$$\left[-\frac{1}{2}\nabla_{\vec{r}}^2 + V(r)\right]u_{nlm_l}(\vec{r}) = E_{nl}\,u_{nlm_l}(\vec{r})$$

one-electron or central field orbitals

$$u_{nlm_l}(\vec{r}) = R_{nl}(r)Y_{lm_l}(\theta,\phi)$$

$\neq \psi_{nlm}(\vec{r})$: hydrogen wave function

- $V(r)$ spherically symmetric $\rightarrow$ E_{nl} are independent of m_l
- E_{nl} depend on both n and l.

Spin-Orbitals and Slater Determinants

Spin-orbitals: $u_{nlm_l m_s}(q) = u_{nlm_l}(\vec{r})\chi_{1/2,m_s} = R_{nl}(r)Y_{lm_l}(\theta,\phi)\chi_{1/2,m_s}$

$$\left[-\frac{1}{2}\nabla_{\vec{r}}^2 + V(r)\right]u_{nlm_l m_s} = E_{nl}\,u_{nlm_l m_s}$$

Slater determinants

Total N-electron (central field) wave function $\Psi_c(q_1, q_2, ..., q_N)$
: antisymmetric (Pauli exclusion principle).

$$\Psi_c(q_1, q_2, ..., q_N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} u_\alpha(q_1) & u_\beta(q_1) & \cdots & u_\nu(q_1) \\ u_\alpha(q_2) & u_\beta(q_2) & \cdots & u_\nu(q_2) \\ \vdots & \vdots & \ddots & \vdots \\ u_\alpha(q_N) & u_\beta(q_N) & \cdots & u_\nu(q_N) \end{vmatrix}$$

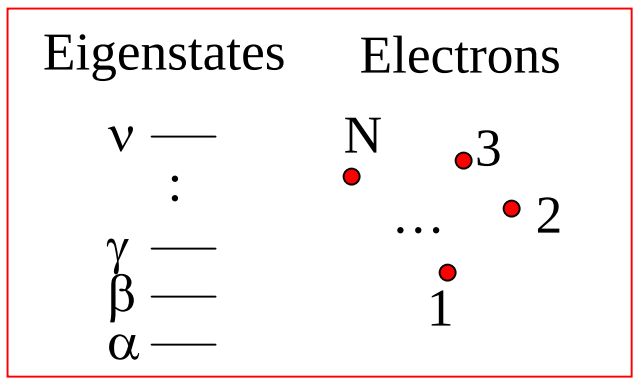
Quantum numbers
$\alpha, \beta, ..., \nu$
$\rightarrow \quad (n, l, m_l, m_s)$

describing an atom in which one electron is in sate α, another in state β, and so on.

Eigenvalue: $E_c = E_\alpha + E_\beta + \cdots + E_\nu$

$$\Psi(..., q_j, ..., q_i, ..) = -\Psi(..., q_i, ..., q_j, ..)$$

$\alpha = \beta \quad \rightarrow \quad \Psi = 0$ Pauli exclusion principle



The Slater determinant will vanish if two electrons have the same values of the four quantum numbers n, l, m_l and m_s (two columns are equal in the determinant).

→ Pauli exclusion principle: no two electrons in an atom can have the same set of the four quantum numbers n, l, m_l and m_s.

The Slater determinant includes $N!$ permutations of $q_1, q_2, \ldots, q_N$.

+1: even permutation, –1: odd permutation

$$\Psi_c(q_1, q_2, ..., q_N) = \frac{1}{\sqrt{N!}} \sum_P (-1)^P P u_\alpha(q_1) u_\beta(q_2) \ldots u_\nu(q_N)$$

Permutation of the electron coordinates

Sum over all permutations

e.g. He ground state $(1s)^2\ {}^1S$: $u_{100,1/2} = u_{100}(r)\chi_\uparrow, \quad u_{100,-1/2} = u_{100}(r)\chi_\downarrow$

$$\Psi_c(q_1, q_2) = \frac{1}{\sqrt{2!}} \begin{vmatrix} u_\alpha(q_1) & u_\beta(q_1) \\ u_\alpha(q_2) & u_\beta(q_2) \end{vmatrix} = \frac{1}{\sqrt{2}} \begin{vmatrix} u_{100}(r_1)\chi_\uparrow(1) & u_{100}(r_1)\chi_\downarrow(1) \\ u_{100}(r_2)\chi_\uparrow(2) & u_{100}(r_2)\chi_\downarrow(2) \end{vmatrix}$$

$$= u_{100}(r_1)u_{100}(r_2)\frac{1}{\sqrt{2}}\left[\chi_\uparrow(1)\chi_\downarrow(2) - \chi_\uparrow(2)\chi_\downarrow(1)\right] = u_{100}(r_1)u_{100}(r_2)\frac{1}{\sqrt{2}}\left[\left|\uparrow\downarrow\right\rangle - \left|\downarrow\uparrow\right\rangle\right]$$

Electron States in a Central Field

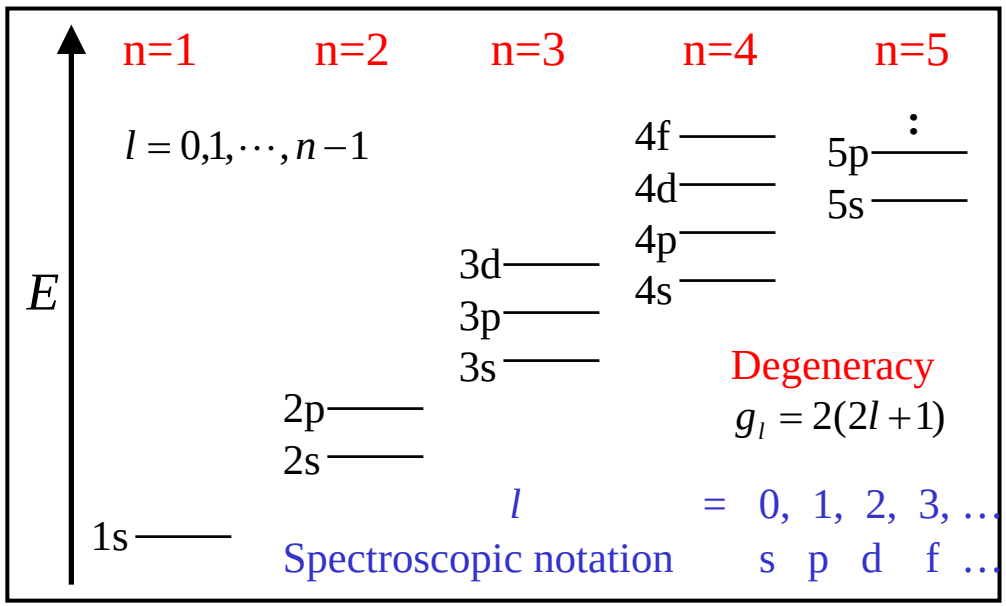
Eigenstate $$\Psi_c(q_1, q_2, \ldots, q_N) = \frac{1}{\sqrt{N!}} \sum_P (-1)^P P u_\alpha(q_1) u_\beta(q_2) \ldots u_\nu(q_N)$$

Eigenvalue $$E_c = E_\alpha + E_\beta + \cdots + E_\nu$$

$$\Rightarrow \quad u_{nlm_l m_s}(q) = R_{nl}(r) Y_{lm_l}(\theta, \phi) \chi_{1/2, m_s}, \quad E = E_{nl}$$

$$-\frac{1}{2}\left[\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{l(l+1)}{r^2}\right] R_{nl}(r) + V(r) R_{nl}(r) = E_{nl} R_{nl}(r)$$

Ordering of individual energy levels E_{nl}



$E_{nl} \uparrow \leftarrow n \uparrow$ for given l

$E_{nl} \uparrow \leftarrow l \uparrow$ for given n

more screening because of the larger angular momentum

$E_{nl} \uparrow \leftarrow (n+l) \uparrow$

$E_{4s} < E_{3d}$ different from H atom

$(E_{n+1} > E_n)$

Shells and subshells

Average radius of electron orbit in a hydrogenic atom $\langle r \rangle_{nlm} \sim \frac{n^2}{Z} a_0$

Electrons which have the same value of the principal quantum number *n* are said to belong to the same *shell*.
- Maximum number of electrons in a shell = $2n^2$ (closed or filled shell)

Electrons having the same value of *n* and *l* are said to belong to the same *subshell*.
- Maximum number of electrons in a subshell, degeneracy = $2(2l+1)$
- Closed (or filled) subshell: an assembly of $2(2l+1)$ equivalent electrons

Degeneracy

$$d = \frac{\delta!}{\nu!(\delta-\nu)!}$$

ν : number of electrons occupying a E_{nl} level
δ= $2(2l+1)$: degeneracy of the level
c.f. d=1 for a closed subshell.

e.g. Ground state of the carbon atom ($1s^2\ 2s^2 2p^2$)

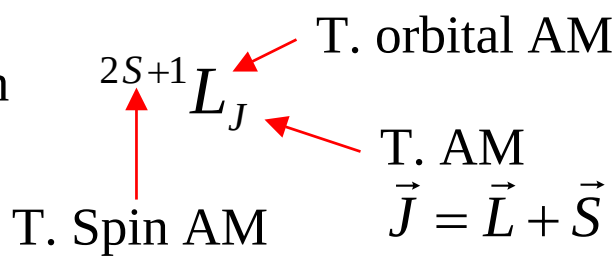
$1s: \quad \nu = 2, \quad \delta = 2, \quad d = 1$
$2s: \quad \nu = 2, \quad \delta = 2, \quad d = 1$ ⇒ $g = 15$
$2p: \quad \nu = 2, \quad \delta = 6, \quad d = 15$

Periodic System of the Elements

Ground state of neutral atoms (Pauli exclusion principle):
Z electrons (Z: atomic number, nuclear charge) occupy the lowest individual energy levels.

Valence electrons: electrons are in the the subshell of highest energy
- least tightly bound electrons
- in insufficient numbers to form another closed subshell

Russell-Saunders notation



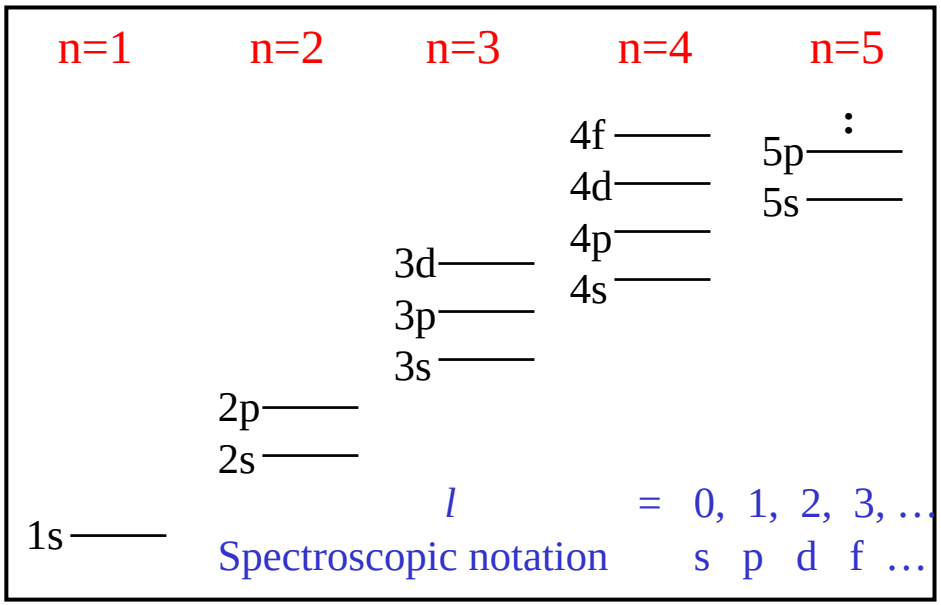
e.g. H $^2S_{1/2}$

He $^1S_0$

Electron configuration: filling up shell and subshell structure

n =1 (K-Shell)

Z	Element	El. Config.
1	H	1s
2	He	$1s^2$



n =2 (L-Shell)

Z	Element	El. Config.
3	Li	[He]2s
4	Be	[He] $2s^2$
5	B	[He] $2s^2 2p$
…	…	…
10	Ne	[He] $2s^2 2p^6$

n =3 (M-Shell)

Z	Element	El. Config.
11	Na	[Ne] 3s
…	…	…
18	Ar	[Ne] $3s^2 3p^6$

Since $E_{4s} < E_{3d}$ (screening by [Ar]), the added electrons in K (Z=19) and Ca (Z=20) go into the 4s rather than the 3d subshell.

n =4 (N-Shell)

Z	Element	El. Config.
19	K	[Ar]4s
20	Ca	[Ar] $4s^2$
21	Sc	[Ar] $4s^2 3d$
…	…	…
24	Cr	[Ar] $4s 3d^5$
25	Mn	[Ar] $4s^2 3d^5$
…	…	…
29	Cu	[Ar] $4s 3d^{10}$
30	Zn	[Ar] $4s^2 3d^{10}$
31	Ga	[Ar] $4s^2 3d^{10} 4p$
…	…	…
36	Kr	[Ar] $4s^2 3d^{10} 4p^6$

$E_{4s} \sim E_{3d}$

First transition (iron) group, 3d

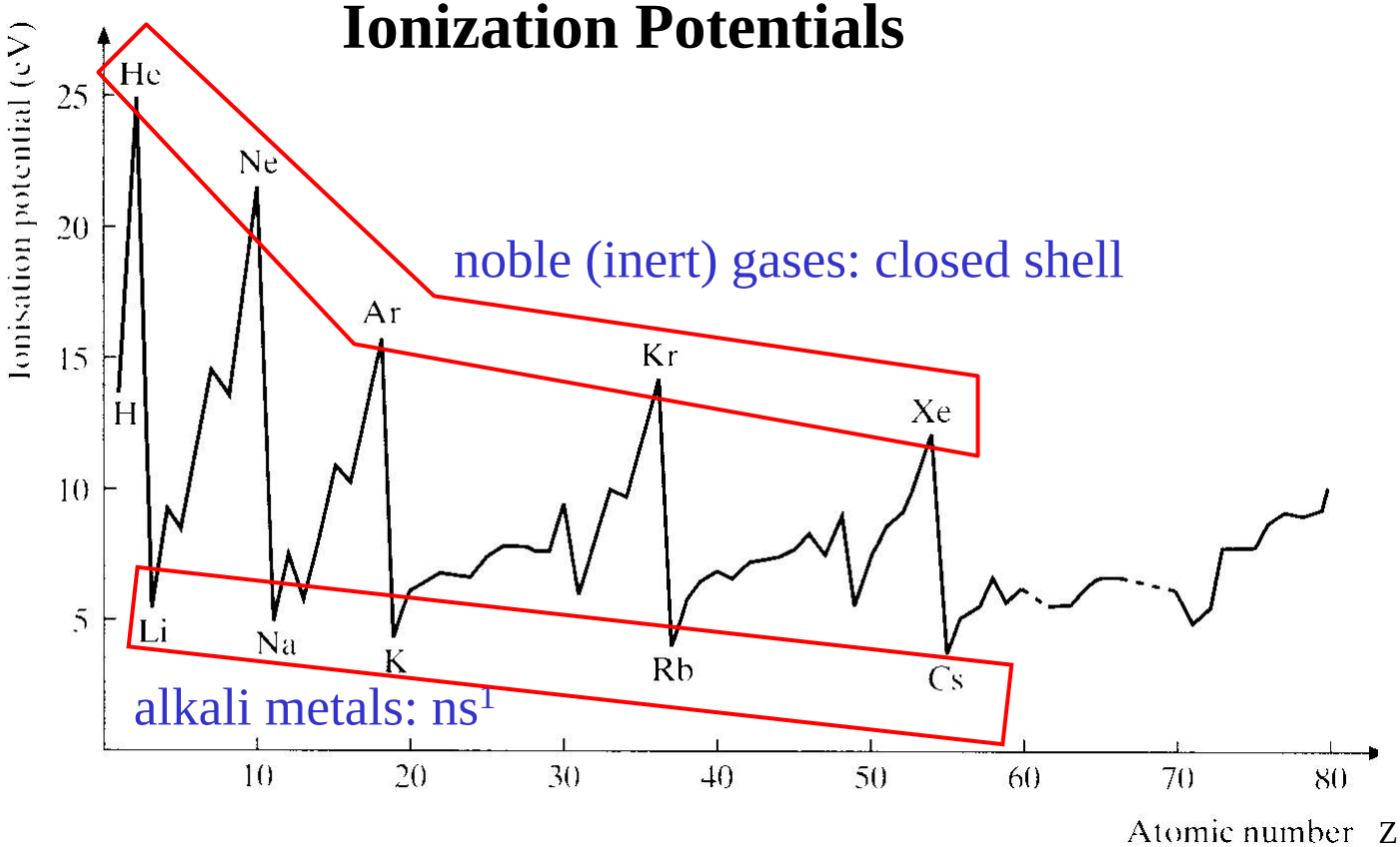
Second transition (palladium) group, 4d
(from Z=39 to Z=48)
Third transition (platinum) group, 5d
(from Z=71 to Z=80)

Rare-earth elements (lanthanides), 4f ~ 5d
from Z=57 to Z=70

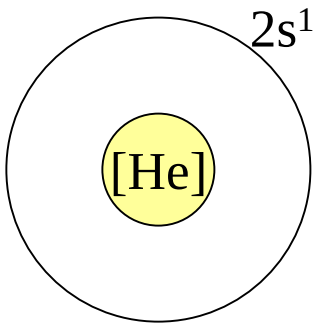
Actinides, 5f ~ 6d
from Z=89 to Z=102

For large Z, relativistic effects (e.g., spin-orbit coupling) become important and prevent the simple decoupling of the space and spin parts of the wave functions.

Ionization Potentials



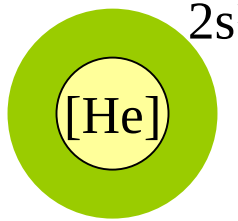
Li (Z=3)



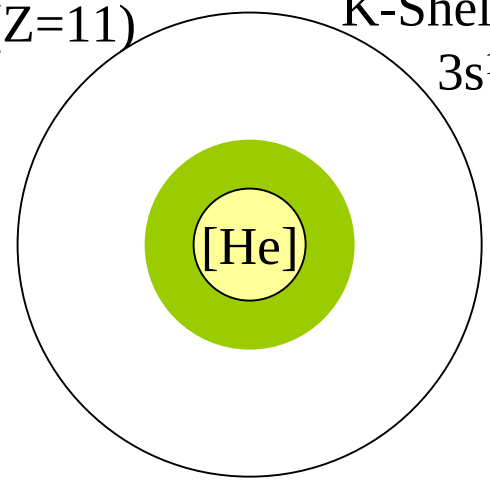
L-Shell

$$\langle r \rangle_{nlm} \sim \frac{n^2}{Z} a_0$$

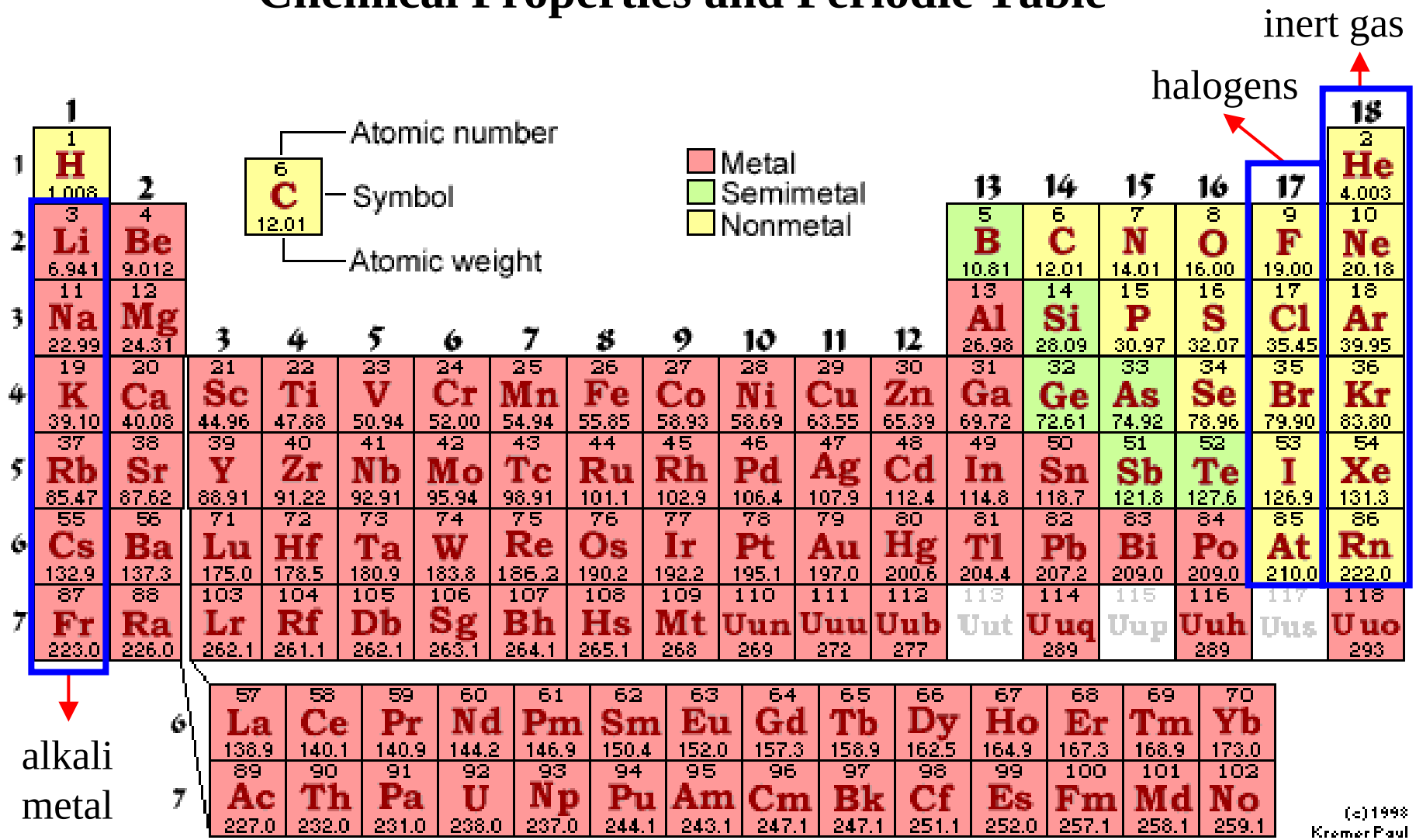
Ne (Z=10)



Na (Z=11)



Chemical Properties and Periodic Table



Pauli's exclusion principle → diversity of chemical and material properties

Models for Central Field Approximation

Central field approximation (independent particle model):
Each electron moves in an effective spherically symmetric potential $V(r)$ created by the nucleus and all the other electrons.

$$V(r) = -\frac{Z}{r} + S(r), \quad \sum_{i=1}^{N} S(r_i) \approx \sum_{i>j}^{N} \sum_{j=1}^{N} \frac{1}{r_{ij}}$$

Screening

$$V(r) \to -\frac{Z}{r}, \qquad r \to 0$$

$$V(r) \to -\frac{Z-(N-1)}{r}, \qquad r \to \infty$$

$$V(r) \to ?$$ at intermediate distance

Thomas-Fermi and Hartree-Fock methods

Fermi Electron Gas

Fermi electron gas:
A system consisting of a large number *N* of free electrons confined to a certain region of space (large cube of side *L*: 3D infinite potential well).

Free particle Schrödinger equation: $$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi(\vec{r})=E\psi(\vec{r})$$

Spatial Eigenfunctions $$\psi_{n_x n_y n_z}(\vec{r})=\left(\frac{8}{L^3}\right)^{\frac{1}{2}}\sin\left(\frac{n_x\pi}{L}x\right)\sin\left(\frac{n_y\pi}{L}y\right)\sin\left(\frac{n_z\pi}{L}z\right)$$

vanishing at the boundary $\quad n_x, n_y, n_z = 1,2,3,\cdots$

Energy eigenvalues $$E_{n_x n_y n_z}=\frac{\pi^2\hbar^2}{2mL^2}\left(n_x^2+n_y^2+n_z^2\right)=\frac{\pi^2\hbar^2}{2mL^2}n^2$$

(i) degenerated

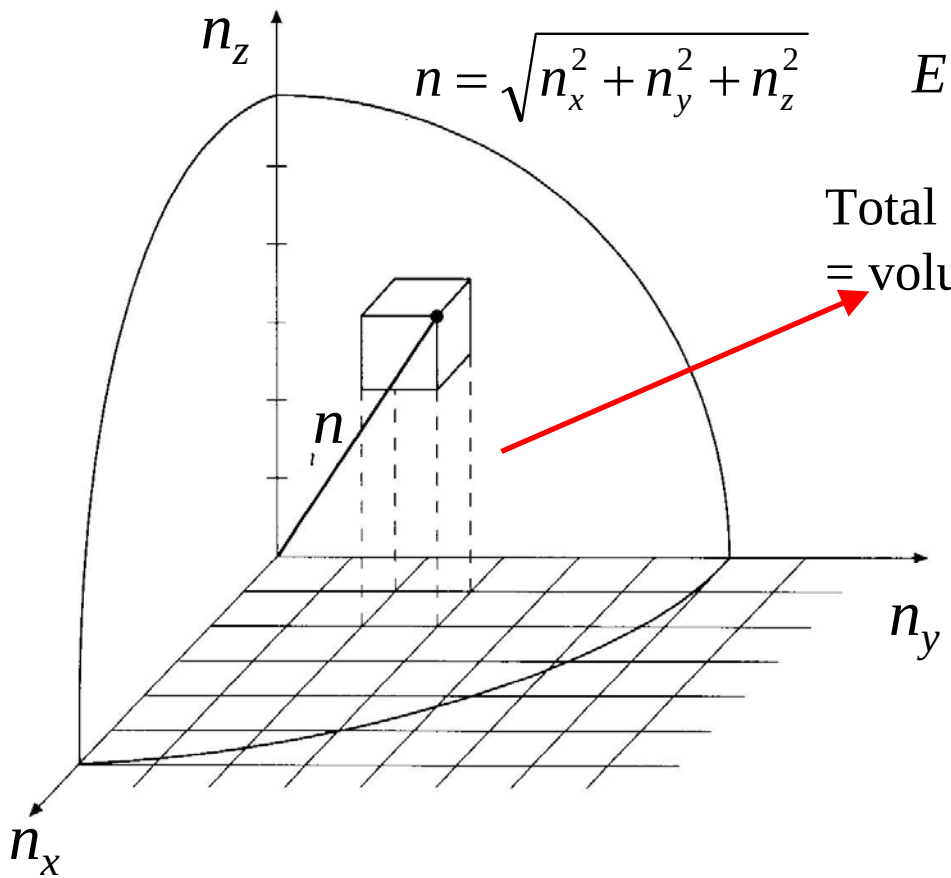
(ii) $\Delta E \propto \frac{1}{L^2}$

Total wave functions $$\psi_{n_x n_y n_z m_s}(q)=\psi_{n_x n_y n_z}(\vec{r})\chi_{1/2,m_s}$$

Density of states $D(E)$:

Number of electron quantum states (spin-orbitals) per unit energy range

$D(E)dE$ - Number of electron states between E and $E+dE$



$$n = \sqrt{n_x^2 + n_y^2 + n_z^2} \qquad E = \frac{\pi^2 \hbar^2}{2mL^2} n^2 \quad \rightarrow \quad n = \frac{L}{\pi}\sqrt{\frac{2mE}{\hbar^2}}$$

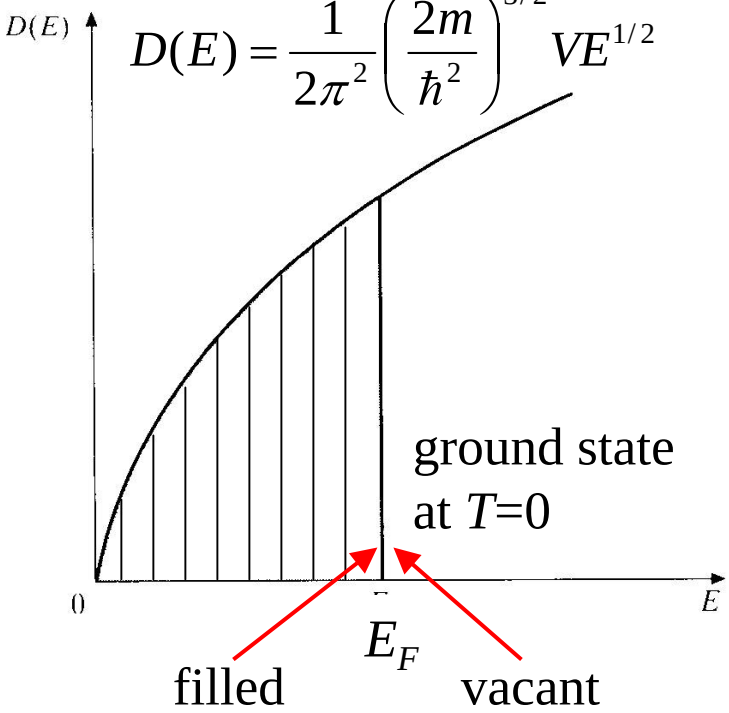
Total number of states for energies up to E = volume of the piece of the sphere × 2

$$N_s = 2\frac{1}{8}\frac{4}{3}\pi n^3 = \frac{1}{3}\pi n^3$$

$$= \frac{1}{3}\pi\left(\frac{L}{\pi}\right)^3\left(\frac{2mE}{\hbar^2}\right)^{3/2}$$

$$= \frac{1}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} VE^{3/2}$$

$$\rightarrow \quad dN_s = D(E)dE = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} VE^{1/2}dE \quad \rightarrow \quad D(E) = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} VE^{1/2}$$



$$D(E) = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} VE^{1/2}$$

Fermi energy E_F

$$N = \int_0^{E_F} D(E)dE = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} V\int_0^{E_F} E^{1/2}dE$$

$$= \frac{1}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} VE_F^{3/2}$$

$$\Rightarrow \quad E_F = \frac{\hbar^2}{2m}\left(3\pi^2\rho\right)^{2/3}, \quad \rho = \frac{N}{V}$$

$$= \frac{\hbar^2 k_F^2}{2m}, \quad \boxed{k_F = \left(3\pi^2\rho\right)^{1/3}}$$

⇒ Thomas-Fermi theory

$$E_{tot} = \int_0^{E_F} ED(E)dE = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} V\int_0^{E_F} E^{3/2}dE = \frac{1}{5\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} VE_F^{5/2} = \frac{3}{5}NE_F$$

$$\overline{E} = \frac{E_{tot}}{N} = \frac{3}{5}E_F$$

Thomas-Fermi Theory

N-electron atom: Fermi electron gas in the ground state, confined to a region of space by a central potential $V(r)$ ($V \to 0$, $r \to \infty$). $V(r) = ?, \quad \rho(r) = ?$

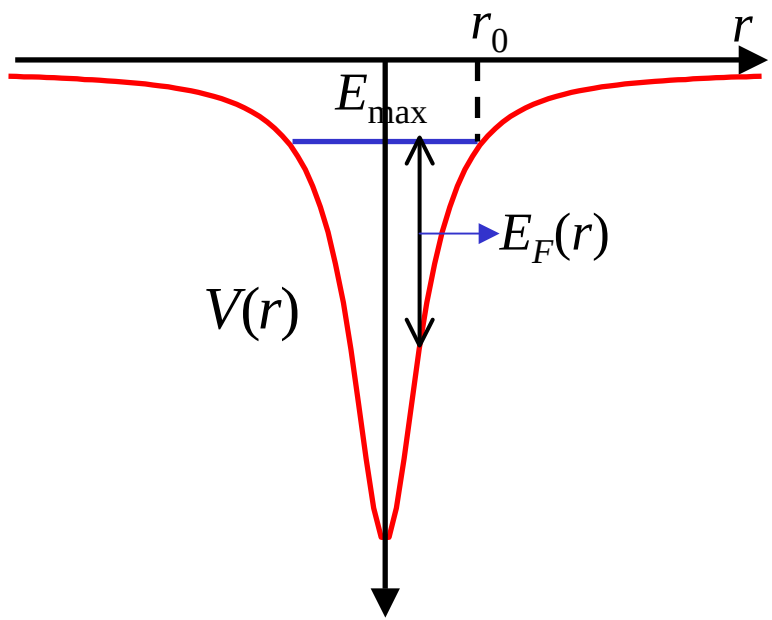
Total energy of an electron $E = \dfrac{p^2}{2m} + V(r) < 0, \quad E_{\max} = E_F + V(r)$

independent of r

$$E_{\max} = \frac{\hbar^2 k_F^2}{2m} + V(r) \quad \to \quad k_F^2(r) = \frac{2m}{\hbar^2}\left[E_{\max} - V(r)\right], \quad k_F = \left(3\pi^2\rho\right)^{1/3}$$

$$\rho(r) = \frac{k_F^3}{3\pi^2} = \frac{1}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\left[E_{\max} - V(r)\right]^{3/2}$$

$$= 0 \quad (V > E_{\max})$$



$E_{\max} = V(r_0)$ at r=r_0 : boundary

Electrostatic potential $\phi(r) = -\frac{1}{e}V(r)$

$$\Phi(r) = \phi(r) - \phi_0$$

$$\phi_0 = -\frac{E_{\max}}{e}$$

$$\rightarrow \quad \rho(r) = \begin{cases} \frac{1}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\left[e\Phi(r)\right]^{3/2}, & \Phi \geq 0 \\ 0, & \Phi < 0 \end{cases}$$

Poisson's equation $\nabla^2\Phi(r) = \frac{1}{r}\frac{d^2}{dr^2}\left[r\Phi(r)\right] = \frac{e}{\varepsilon_0}\rho(r)$

$$\Rightarrow \quad \frac{1}{r}\frac{d^2}{dr^2}\left[r\Phi(r)\right] = \begin{cases} \frac{e}{3\pi^2\varepsilon_0}\left(\frac{2m}{\hbar^2}\right)^{3/2}\left[e\Phi(r)\right]^{3/2}, & \Phi \geq 0 \\ 0, & \Phi < 0 \end{cases}$$

Boundary condition $\lim_{r\to 0} r\Phi(r) = \frac{Ze}{4\pi\varepsilon_0}$

Normalization $4\pi\int_0^{r_0}\rho(r)r^2dr = N$

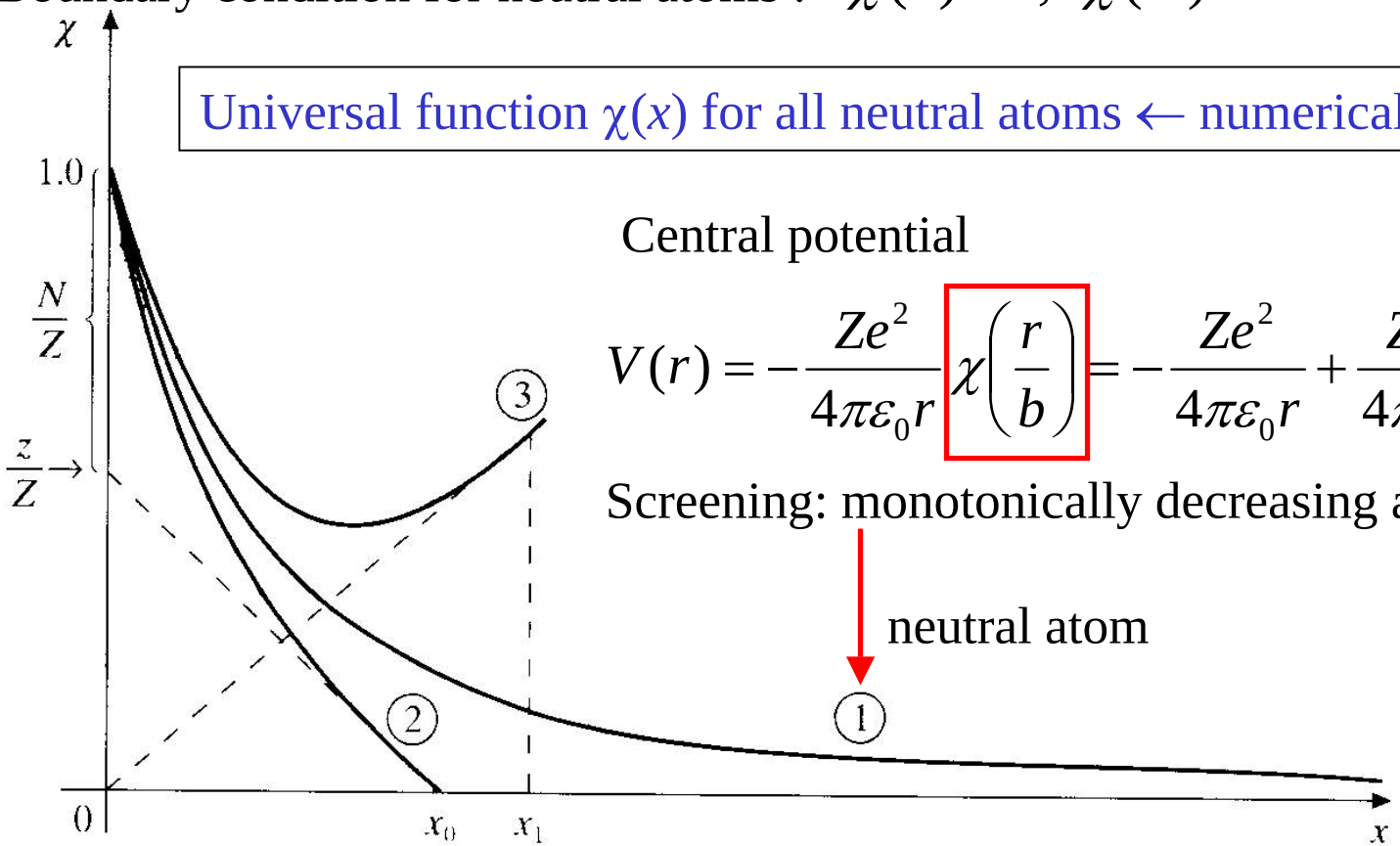
Dimensionless variable x and function χ

$$r = bx, \quad r\Phi(r) = \frac{Ze}{4\pi\varepsilon_0}\chi(x) \quad \text{where} \quad b = \frac{(3\pi)^{2/3}}{2^{7/3}} a_0 Z^{-1/3}$$

$$\frac{d^2\chi(x)}{dx^2} = \begin{cases} x^{-1/2}\chi^{3/2}(x), & \chi \geq 0 \\ 0, & \chi < 0 \end{cases}$$

Thomas-Fermi equation

Boundary condition for neutral atoms : $\chi(0) = 1, \ \chi(\infty) = 0$



Universal function $\chi(x)$ for all neutral atoms ← numerical integration

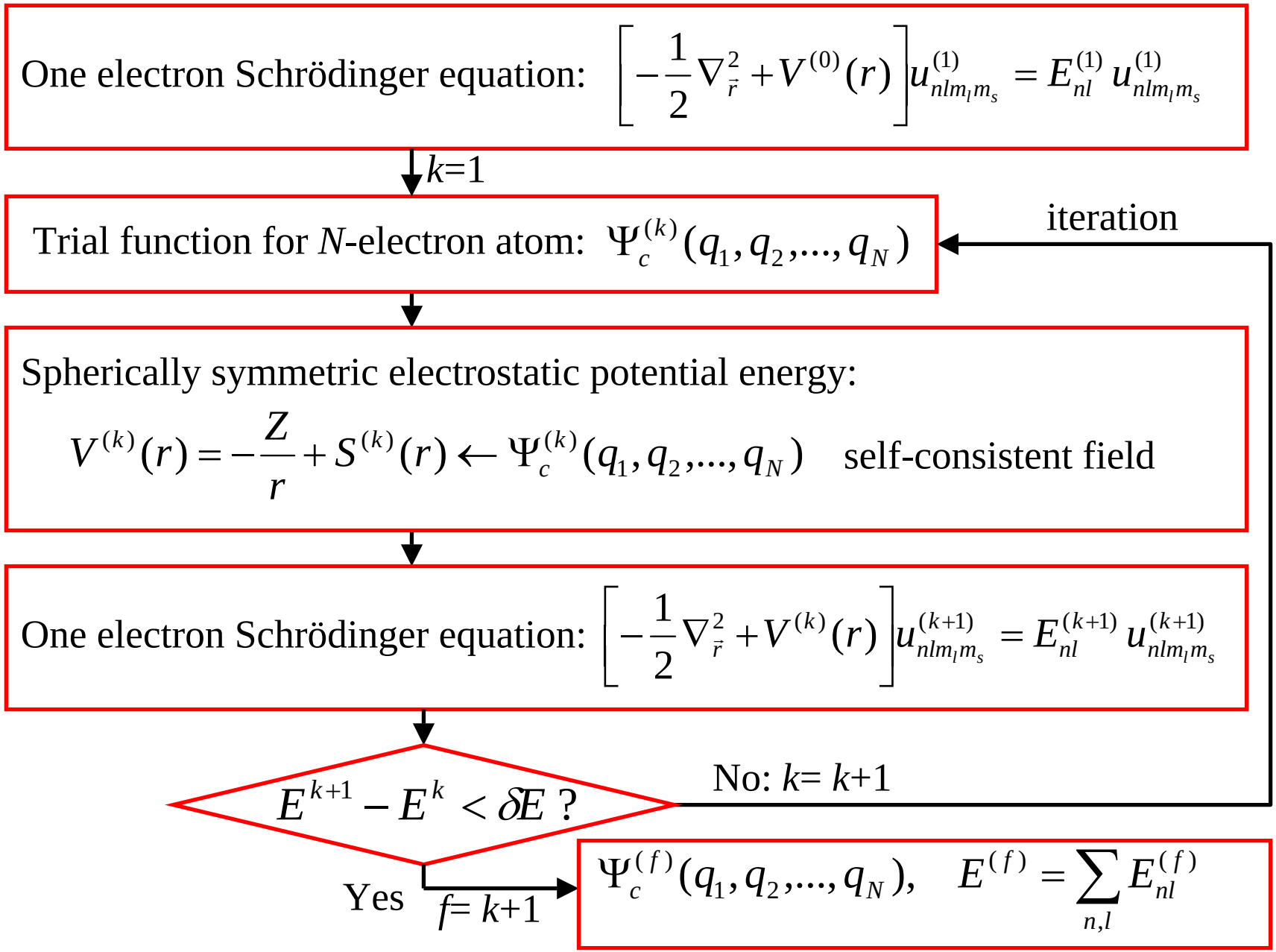
Central potential

$$V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r}\chi\left(\frac{r}{b}\right) = -\frac{Ze^2}{4\pi\varepsilon_0 r} + \frac{Ze^2}{4\pi\varepsilon_0 r}\left[1 - \chi\left(\frac{r}{b}\right)\right]$$

Screening: monotonically decreasing as r increases

neutral atom

Hartree-Fock Method: Self-Consistent Field



Non-relativistic Hamiltonian for N-electron atom $H = H_1 + H_2$

$$H_1 = \sum_{i=1}^{N}\left(-\frac{1}{2}\nabla_{\vec{r}_i}^2 - \frac{Z}{r_i}\right) = \sum_{i=1}^{N} h_i, \qquad h_i = -\frac{1}{2}\nabla_{\vec{r}_i}^2 - \frac{Z}{r_i}$$

$$H_2 = \sum_{i>j}^{N}\sum_{j=1}^{N}\frac{1}{r_{ij}}$$

Variational method: trial function for *N*-electron atom = Slater determinant

Expectation value of Hamiltonian (energy) for a trial wave function, ϕ

$$E_0 \le E[\Phi] = \langle \Phi | H | \Phi \rangle, \quad \langle \Phi | \Phi \rangle = 1$$

$$\Phi(q_1, q_2, ..., q_N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} u_\alpha(q_1) & u_\beta(q_1) & \cdots & u_\nu(q_1) \\ u_\alpha(q_2) & u_\beta(q_2) & \cdots & u_\nu(q_2) \\ \vdots & \vdots & \ddots & \vdots \\ u_\alpha(q_N) & u_\beta(q_N) & \cdots & u_\nu(q_N) \end{vmatrix}$$

Quantum numbers

$\alpha, \beta, ..., \nu$

$\rightarrow \quad (n, l, m_l, m_s)$

Orthonormal spin-orbitals $\langle u_\mu | u_\lambda \rangle = \int u_\mu^*(q) u_\lambda(q) dq = \delta_{\mu\lambda}$

$$\Phi(q_1, q_2, \ldots, q_N) = \frac{1}{\sqrt{N!}} \sum_P (-1)^P P \, u_\alpha(q_1) u_\beta(q_2) \ldots u_\nu(q_N) = \sqrt{N!} A \Phi_H$$

where $A = \frac{1}{N!} \sum_P (-1)^P P$ and $\Phi_H(q_1, q_2, \ldots, q_N) = u_\alpha(q_1) u_\beta(q_2) \ldots u_\nu(q_N)$

Hermitian and projection operator $\left(A^2 = A\right)$

H_1 and H_2 are invariant under permutations of the electron coordinates

$$H_1 = \sum_{i=1}^{N} \left(-\frac{1}{2} \nabla_{\vec{r}_i}^2 - \frac{Z}{r_i} \right) = \sum_{i=1}^{N} h_i, \quad H_2 = \sum_{i>j}^{N} \sum_{j=1}^{N} \frac{1}{r_{ij}} \Rightarrow \quad [H_1, A] = [H_2, A] = 0$$

Energy expectation value for the trial wave function, Φ

$$E[\Phi] = \langle \Phi | H | \Phi \rangle = \langle \Phi | H_1 | \Phi \rangle + \langle \Phi | H_2 | \Phi \rangle$$

$$\langle \Phi | H_1 | \Phi \rangle = N! \langle \Phi_H | A H_1 A | \Phi_H \rangle = N! \langle \Phi_H | H_1 A^2 | \Phi_H \rangle = N! \langle \Phi_H | H_1 A | \Phi_H \rangle$$

$$= \sum_{i=1}^{N} \sum_P (-1)^P \langle \Phi_H | h_i P | \Phi_H \rangle = \sum_{i=1}^{N} \langle \Phi_H | h_i | \Phi_H \rangle \quad \Leftarrow \quad \langle u_\mu | u_\lambda \rangle = \delta_{\mu\lambda}$$

$$= \sum_\lambda \langle u_\lambda(q_i) | h_i | u_\lambda(q_i) \rangle = \sum_\lambda I_\lambda, \quad I_\lambda = \langle u_\lambda(q_i) | h_i | u_\lambda(q_i) \rangle$$

$$\langle \Phi | H_2 | \Phi \rangle = N! \langle \Phi_H | A H_2 A | \Phi_H \rangle = N! \langle \Phi_H | H_2 A^2 | \Phi_H \rangle = N! \langle \Phi_H | H_2 A | \Phi_H \rangle$$

$$= \sum_{i>j}^{N} \sum_{j=1}^{N} \sum_{P} (-1)^P \langle \Phi_H | \frac{1}{r_{ij}} P | \Phi_H \rangle = \sum_{i>j}^{N} \sum_{j=1}^{N} \langle \Phi_H | \frac{1}{r_{ij}} (1 - P_{ij}) | \Phi_H \rangle$$

$$= \sum_{(\lambda,\mu)} \left[\langle u_\lambda(q_i) u_\mu(q_j) | \frac{1}{r_{ij}} | u_\lambda(q_i) u_\mu(q_j) \rangle - \langle u_\lambda(q_i) u_\mu(q_j) | \frac{1}{r_{ij}} | u_\mu(q_i) u_\lambda(q_j) \rangle \right]$$

$$= \frac{1}{2} \sum_{\lambda \neq \mu} \sum_{\mu} \left[\langle u_\lambda(q_i) u_\mu(q_j) | \frac{1}{r_{ij}} | u_\lambda(q_i) u_\mu(q_j) \rangle \right.$$

$$\left. - \langle u_\lambda(q_i) u_\mu(q_j) | \frac{1}{r_{ij}} | u_\mu(q_i) u_\lambda(q_j) \rangle \right]$$

$$= \frac{1}{2} \sum_{\lambda \neq \mu} \sum_{\mu} \left[J_{\lambda\mu} - K_{\lambda\mu} \right]$$

$$\lambda, \mu = \alpha, \beta, \ldots, \nu$$

$$J_{\lambda\mu} = \langle u_\lambda(q_i) u_\mu(q_j) | \frac{1}{r_{ij}} | u_\lambda(q_i) u_\mu(q_j) \rangle$$ Direct term

$$K_{\lambda\mu} = \langle u_\lambda(q_i) u_\mu(q_j) | \frac{1}{r_{ij}} | u_\mu(q_i) u_\lambda(q_j) \rangle$$ Exchange term

Energy expectation value for a trial wave function, Φ

$$E[\Phi] = \langle \Phi | H_1 | \Phi \rangle + \langle \Phi | H_2 | \Phi \rangle = \sum_{\lambda} I_{\lambda} + \frac{1}{2} \sum_{\lambda} \sum_{\mu} [J_{\lambda\mu} - K_{\lambda\mu}]$$

$E[\Phi]$ is stationary with respect to variations of the spin-orbitals u_λ ($\lambda=\alpha,\beta,\ldots,\nu$).

Variational equation (p130-136):

$$\delta E - \sum_{\lambda} \sum_{\mu} \varepsilon_{\lambda\mu} \delta \langle u_\mu | u_\lambda \rangle = 0 \quad \rightarrow \quad \delta E - \sum_{\lambda} \varepsilon_{\lambda} \delta \langle u_\lambda | u_\lambda \rangle = 0$$

Lagrange multipliers

diagonalization

Hartree-Fock equations

$$\left(-\frac{1}{2} \nabla^2_{\vec{r}_i} - \frac{Z}{r_i} \right) u_\lambda(q_i) + \left[\sum_{\mu} \int u^*_\mu(q_j) \frac{1}{r_{ij}} u_\mu(q_j) dq_j \right] u_\lambda(q_i)$$

$$- \sum_{\mu} \left[\int u^*_\mu(q_j) \frac{1}{r_{ij}} u_\lambda(q_j) dq_j \right] u_\mu(q_i) = E_\lambda u_\lambda(q_i), \quad \lambda, \mu = \alpha, \beta, \ldots, \nu$$

Spin-orbitals: $u_\lambda(q_i) = u_\lambda(\vec{r}_i)\chi_{1/2,m_s^\lambda}$

$= V_\mu^d(\vec{r}_i)$: direct operator

$$\left(-\frac{1}{2}\nabla_{\vec{r}_i}^2 - \frac{Z}{r_i}\right)u_\lambda(\vec{r}_i) + \left[\sum_\mu \int u_\mu^*(\vec{r}_j)\frac{1}{r_{ij}}u_\mu(\vec{r}_j)d\vec{r}_j\right]u_\lambda(\vec{r}_i)$$

$$-\sum_\mu \delta_{m_s^\lambda, m_s^\mu}\left[\int u_\mu^*(\vec{r}_j)\frac{1}{r_{ij}}u_\lambda(\vec{r}_j)d\vec{r}_j\right]u_\mu(\vec{r}_i) = E_\lambda u_\lambda(\vec{r}_i), \quad \lambda,\mu = \alpha,\beta,\ldots,\nu$$

$= V_\mu^{ex}(\vec{r}_i)u_\lambda(\vec{r}_i)$

: exchange operator

$$\rightarrow \left\{\left(-\frac{1}{2}\nabla_{\vec{r}_i}^2 - \frac{Z}{r_i}\right) + \sum_\mu \left[V_\mu^d(\vec{r}_i) - \delta_{m_s^\lambda, m_s^\mu}V_\mu^{ex}(\vec{r}_i)\right]\right\}u_\lambda^{(k+1)}(\vec{r}_i) = E_\lambda u_\lambda^{(k+1)}(\vec{r}_i)$$

$u_\mu^{(k)}(\vec{r}_i)$

$$\rightarrow \left\{\left(-\frac{1}{2}\nabla_{\vec{r}_i}^2 - \frac{Z}{r_i}\right) + V^d(r_i) - V^{ex}(r_i)\right\}u_\lambda(\vec{r}_i) = E_\lambda u_\lambda(\vec{r}_i)$$

Corrections to the Central Field Approximation

Correlation effects

$$H = H_{HF} + H_1, \quad H_{HF} = \sum_{i=1}^{N} h_{HF}(i) \qquad E_{corr} = E_{exact} - E_{HF} < 0$$

because $E_0 \le E_{HF} = E[\Phi] = \langle \Phi | H | \Phi \rangle$

Spin-orbit interactions

$$H_2 = \sum_i \xi(r_i) \vec{L}_i \cdot \vec{S}_i, \quad \xi(r_i) = \frac{1}{2m^2c^2} \frac{1}{r_i} \frac{dV(r_i)}{dr_i}$$

relativistic correction

Total Hamiltonian

$$H = H_{HF} + H_1 + H_2$$

(i) $|H_1| >> |H_2|$ L-S (or Russell-Saunders) coupling case: small and intermediate Z

(ii) $|H_1| << |H_2|$ *j-j* coupling case: large Z

L-S Coupling

Unperturbed Hamiltonian $H = H_{HF} + H_1$ where $|H_1| >> |H_2|$

Energy eigenstate of H_{HF}, $|\gamma\rangle$ (γ : level configuration of H_c) is degenerated.

e.g. carbon atom, C, $1s^2\ 2s^2 2p^2$, g=15

H_1 lifts part of the degeneracy, but not completely: 3 states. $^1S,\ ^1D,\ ^3P$

Since $\left[H, \vec{L}\right] = \left[H, \vec{S}\right] = 0$ where $\vec{L} = \sum_i \vec{L}_i, \quad \vec{S} = \sum_i \vec{S}_i,$

$\rightarrow$ energy eigenstates can be written as $|\gamma\, LSM_L M_S\rangle$

$\rightarrow$ Energy eigenvalues are independent of M_L and M_S . $|\gamma\, LS\rangle$

Terms: energy levels corresponding to definite values of L and S, ^{2S+1}L

Multiplicity: $2S+1$ = 1(singlet), 2(doublet), 3(triplet), 4, …

$$L = 0,\ 1,\ 2,\ 3, \cdots$$
$$S, P, D, F, \cdots$$

Closed subshell: L=0, S=0, ^1S

Incomplete subshells: optically active electrons

1. Non-equivalent electrons: electrons belonging to different subshells

Pauli exclusion principle is automatically satisfied.

Addition of angular momentum $\vec{L} = \vec{L}_1 + \vec{L}_2$ and $\vec{S} = \vec{S}_1 + \vec{S}_2$

$$L = |l_1 - l_2|, |l_1 - l_2| + 1, \cdots, l_1 + l_2$$

$$S = |s_1 - s_2|, |s_1 - s_2| + 1, \cdots, s_1 + s_2$$

(i) Configuration *n*p *n*'p

$$l_1 = l_2 = 1, \quad s_1 = s_2 = 1/2 \quad \Rightarrow \quad L = 0, 1, 2, \quad S = 0, 1$$

Terms: ${}^1S,\ {}^1P,\ {}^1D,\ {}^3S,\ {}^3P,\ {}^3D$

(ii) Configuration *n*p *n*'d

$$l_1 = 1, l_2 = 2, \quad s_1 = s_2 = 1/2 \quad \Rightarrow \quad L = 1, 2, 3, \quad S = 0, 1$$

Terms: ${}^1P,\ {}^1D,\ {}^1F,\ {}^3P,\ {}^3D,\ {}^3F$

(iii) Configuration *n*p *n*'p *n*"d

configuration *n*p *n*'p $l_1 = 0, 1, 2, \quad s_1 = 0, 1$

+ configuration *n*"d $l_2 = 2, \quad s_2 = 1/2$

$^1S\ (l_1 = 0, s_1 = 0) \rightarrow L = 2, S = 1/2, \quad ^2D$

$^1P\ (l_1 = 1, s_1 = 0) \rightarrow L = 1, 2, 3, S = 1/2, \quad ^2P,\ ^2D,\ ^2F$

$^1D\ (l_1 = 2, s_1 = 0) \rightarrow L = 0, 1, 2, 3, 4, S = 1/2, \quad ^2S,\ ^2P,\ ^2D,\ ^2F,\ ^2G$

$^3S\ (l_1 = 0, s_1 = 1) \rightarrow L = 2, S = 1/2, 3/2, \quad ^2D,\ ^4D$

$^3P\ (l_1 = 1, s_1 = 1) \rightarrow L = 1, 2, 3, S = 1/2, 3/2, \quad ^2P,\ ^2D,\ ^2F,\ ^4P,\ ^4D,\ ^4F$

$^3D\ (l_1 = 2, s_1 = 1) \rightarrow L = 1, 2, 3, 4, S = 1/2, 3/2, \quad ^2S,\ ^2P,\ ^2D,\ ^2F,\ ^2G,$

$^4S,\ ^4P,\ ^4D,\ ^4F,\ ^4G$

Terms: $^2S,\ ^2P,\ ^2D,\ ^2F,\ ^2G,\ ^4S,\ ^4P,\ ^4D,\ ^4F,\ ^4G$

Number of identical terms: 2 4 6 4 2 2 3 2

2. Equivalent electrons: electrons belonging to same subshells

Pauli exclusion principle rules out certain values of L and S.

(i) Configuration ns^2

Closed subshell: M_L , $M_S = 0 \rightarrow L=0$, $S=0$, term ^1S

$$l_1 = l_2 = 0, \quad s_1 = s_2 = 1/2 \quad \Rightarrow \quad L = 0, \quad S = 0, 1$$

Terms: ^1S, ^3S → Not allowed because of the Pauli exclusion principle

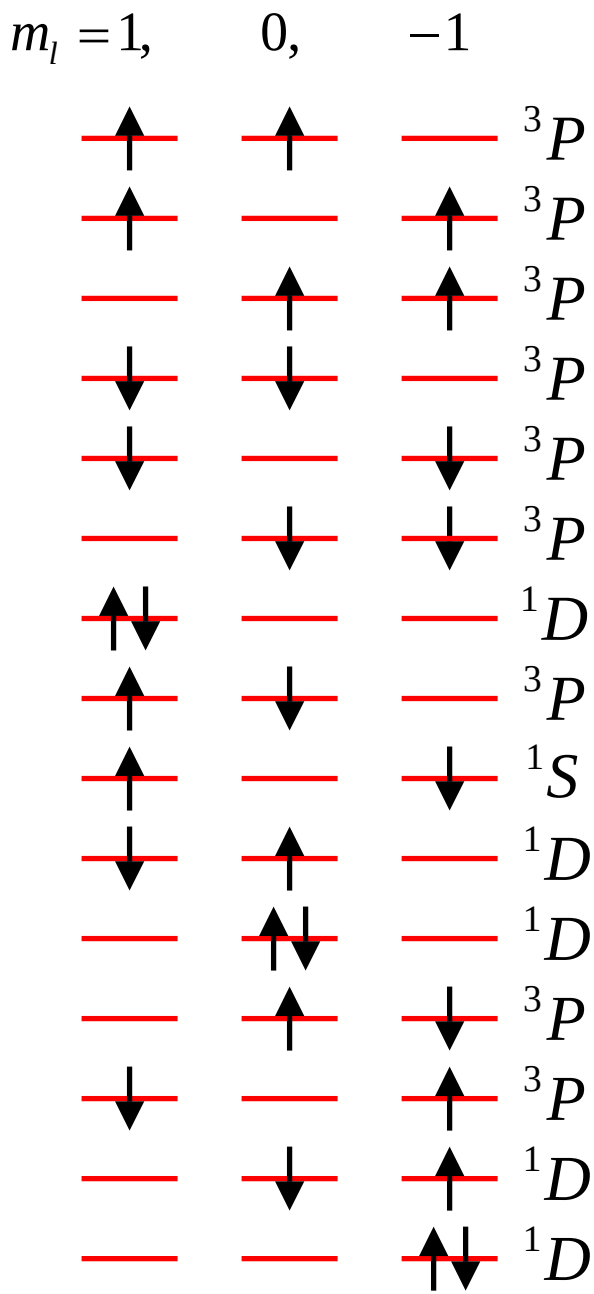
(ii) Configuration np^2, $g = 15$

$$l_1 = l_2 = 1, \quad s_1 = s_2 = 1/2 \quad \Rightarrow \quad L = 0, 1, 2, \quad S = 0, 1$$

Terms: ^1S, ^1P, ^1D, ^3S, ^3P, ^3D

Not allowed because of the Pauli exclusion principle

Number	m_{l1}	m_{s1}	m_{l2}	m_{s2}	$M_L = m_{l1} + m_{l2}$	$M_S = m_{s1} + m_{s2}$
1	1	½	0	½	1	1
2	1	½	-1	½	0	1
3	0	½	-1	½	-1	1
4	1	-½	0	-½	1	-1
5	1	-½	-1	-½	0	-1
6	0	-½	-1	-½	-1	-1
7	1	½	1	-½	2	0
8	1	½	0	-½	1	0
9	1	½	-1	-½	0	0
10	0	½	1	-½	1	0
11	0	½	0	-½	0	0
12	0	½	-1	-½	-1	0
13	-1	½	1	-½	0	0
14	-1	½	0	-½	-1	0
15	-1	½	-1	-½	-2	0



Terms: ^1S, ^1P, ^1D, ^3S, ^3P, ^3D

$(M_L = 2, M_S = 1)$ is missing : no ^3D, $(L = 2, S = 1)$

$(M_L = 2, M_S = 0)$ $(M_L = -2, M_S = 0)$: term with L=2 must exist.

$\rightarrow$ ^1D, $(L = 2, S = 0)$

degeneracy = 5

$(M_L = 1, M_S = 1)$ $(M_L = -1, M_S = -1)$ ... : term with L=1, S=1 must exist.

$\rightarrow$ ^3P, $(L = 1, S = 1)$

degeneracy = 9

5+9=14 : eliminate ^1P and ^3S

$(M_L = 0, M_S = 0)$

^1D

^3P

^1S degeneracy = 1

Fine Structure of terms in L-S coupling

Total Hamiltonian

$H = H_{HF} + H_1 + H_2$ $\quad H_1$ Correlation effects

^{2S+1}L

Energy eigenstates

$$H_2 = \sum_i \xi(r_i)\vec{L}_i \cdot \vec{S}_i, \quad \xi(r_i) = \frac{1}{2m^2c^2}\frac{1}{r_i}\frac{dV(r_i)}{dr_i}$$

Spin-orbit interactions

$|H_1| >> |H_2|$ L-S (or Russell-Saunders) coupling case

$\left[H_2, \vec{L}\right] \neq 0, \quad \left[H_2, \vec{S}\right] \neq 0$ but $\left[H_2, \vec{J}\right] = 0$ where $\vec{J} = \vec{L} + \vec{S}$

$$H_2 = \overline{A}\,\vec{L}\cdot\vec{S} = \frac{1}{2}\overline{A}\left(J^2 - L^2 - S^2\right)$$

H_2 lifts part of the degeneracy of a state represented by a term $^{2S+1}L \rightarrow {}^{2S+1}L_J$

$$J = |L - S|, |L - S| + 1, \ldots, L + S$$

Degeneracy $^{2S+1}L \rightarrow {}^{2S+1}L_J$

$$g = (2L+1)(2S+1) \qquad g = \sum_{J=|L-S|}^{L+S}(2J+1) = (2L+1)(2S+1)$$

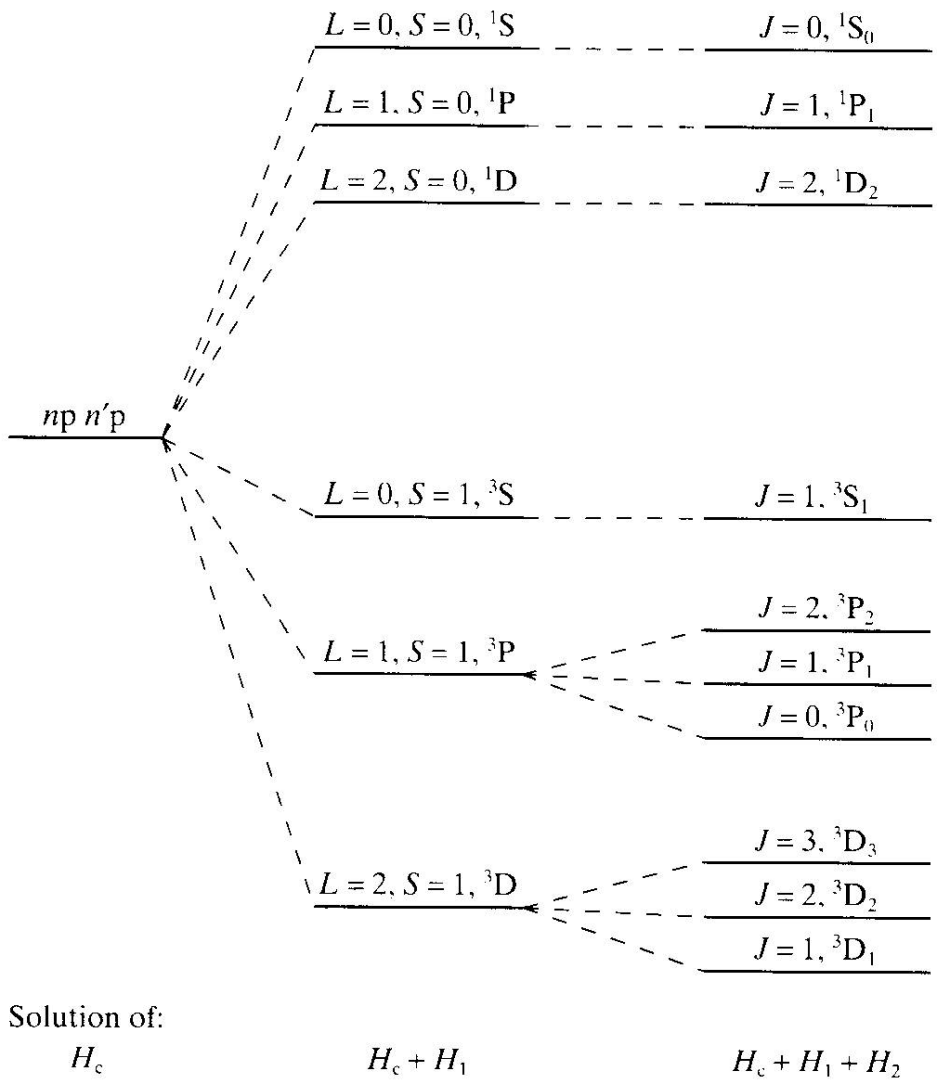
Configuration *n*p *n'*p

$$l_1 = l_2 = 1, \quad s_1 = s_2 = 1/2$$
$$\Rightarrow \quad L = 0, 1, 2, \quad S = 0, 1$$

Terms: $^1S,\ ^1P,\ ^1D,\ ^3S,\ ^3P,\ ^3D$

Hund's rules

1. For given term,
   largest $S \rightarrow$ lowest energy
2. For given S,
   largest $L \rightarrow$ lowest energy



j-j Coupling

$$|H_1| << |H_2| \qquad H_2 = \sum_i \xi(r_i)\vec{L}_i \cdot \vec{S}_i, \quad \xi(r_i) = \frac{1}{2m^2c^2}\frac{1}{r_i}\frac{dV(r_i)}{dr_i}$$

Hamiltonian $\tilde{H} = H_{HF} + H_2 = \sum_{i=1}^{N} \tilde{h}_i = \sum_{i=1}^{N} \left(h_i + \xi(r_i)\vec{L}_i \cdot \vec{S}_i\right)$

$$\tilde{h}_i = h_i + \frac{1}{2}\xi(r_i)\left(J_i^2 - L_i^2 - S_i^2\right) \qquad \left[h_i, \vec{J}_i\right] \rightarrow \left|n_i l_i j_i\right\rangle$$

Energy $\tilde{E} = \sum_{i=1}^{N} E_{n_i l_i j_i}$