

Chapter 5. Atomic structure

I. Hydrogenic atoms

H, He⁺, Li²⁺ (nucleus + single e⁻)

Spectra of hydrogen atom

Wavenumber:

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} \quad (\text{cm}^{-1})$$

ν : frequency (s⁻¹, Hz)

λ : wavelength (nm)

c : speed of light (3.0 × 10⁸ m/s)

Rydberg's formula:

$$\tilde{\nu} = R_{\text{H}} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad R_{\text{H}} = 109677 \text{ cm}^{-1} \text{ (Rydberg's constant)}$$

$$n_1 = 1, n_2 > n_1$$

$$n_1 = 2, \quad ..$$

$$n_1 = 3, \quad ..$$

Lyman series (UV)

Balmer series (VIS)

Paschen series (IR)

Example: Origin of the Balmer series

$$\tilde{\nu} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = 109677 \text{ cm}^{-1} \left(\frac{1}{2^2} - \frac{1}{3^2} \right) = 15232.9 \text{ cm}^{-1}$$
$$\lambda = \frac{1}{\tilde{\nu}} = \frac{1}{15232.9 \text{ cm}^{-1}} = 6.565 \times 10^{-5} \text{ cm} = 656.5 \text{ nm}$$

Bohr's atom model

$$h\nu = E_2 - E_1$$

$$\tilde{\nu} = \frac{\nu}{c} = E_2 / ch - E_1 / ch = T_2 - T_1$$

Ritz combination principle: wavenumber of a spectral line is the difference of two terms.

Quantum mechanical description:

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

where the total Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{\hbar^2}{2m_n} \nabla_n^2 + V$$

where the potential is :

$$V(r) = \frac{1}{4\pi\epsilon_0} \left(\frac{-Ze^2}{r} \right) \quad (\text{Coulomb attraction})$$

After removal of center of mass, the reduced Hamiltonian:

$$\begin{aligned}\hat{H} &= -\frac{\hbar^2}{2\mu} \nabla_r^2 + V \\ &= -\frac{\hbar^2}{2\mu} \frac{1}{r} \frac{\partial^2}{\partial r^2} r + \frac{\hat{l}^2}{2\mu r^2} - \frac{Ze^2}{4\pi\epsilon_0 r}\end{aligned}$$

where reduced mass is $\mu = m_e m_n / (m_e + m_n)$.

Separation of motion

$$\Psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$$

Schrödinger eqn is reduced to two eqns:

i. Angular eqn

$$\hat{l}^2 Y_{l,m_l}(\theta, \phi) = l(l+1)\hbar^2 Y_{l,m_l}(\theta, \phi)$$

with spherical harmonics $Y_{l,m_l}(\theta, \phi)$ as the solution.

ii. Radial eqn

$$\left[-\frac{\hbar^2}{2\mu r} \frac{d^2}{dr^2} r - \frac{Ze^2}{4\pi\epsilon_0 r} + \frac{l(l+1)\hbar^2}{2\mu r^2} \right] R(r) = ER(r)$$

(Coulomb + centrifugal potential)

Solution:

$$R_{n,l}(r) = \rho^l L_{n,l}(\rho) e^{-\rho/2}$$

where $L_{n,l}$ the associated Laguerre polynomial and

$$\rho = \frac{2Z\mu r}{n m_e a_0}$$

$a_0 = 52.9$ pm: Bohr radius

Atomic orbital:

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

Quantum numbers:

Principal: $n = 1, 2, 3, \dots$

Angular momentum: $l = 0, 1, 2, \dots, n-1$

Magnetic: $m_l = 0, \pm 1, \pm 2, \dots, \pm l$

For each n , there are n different l .

For each n and l , there are $2l+1$ different m_l .

For each n , there are $\Sigma(2l+1) = n^2$ degeneracy.

n, l, m_l uniquely specify an atomic orbital.

Classification of orbitals

Shell: orbitals with the same n .

$$\begin{array}{cccccc} n = & 1, & 2, & 3, & 4, & \dots \\ & \text{K} & \text{L} & \text{M} & \text{N} & \dots \end{array} \quad n^2 \text{ orbitals in a shell}$$

Subshell, orbitals with the same n but different l .

$$\begin{array}{cccccc} l = & 0, & 1, & 2, & 3, & 4, & \dots \\ & s & p & d & f & g & \dots \end{array} \quad 2l + 1 \text{ orbitals a subshell}$$

Energy quantization

$$E_n = \frac{-Z^2 \mu e^4}{32\pi^2 \epsilon_0^2 \hbar^2} \frac{1}{n^2} = -\frac{hcR_H}{n^2} \quad (\text{independent of } l \text{ and } m_l)$$

Transition wavenumber:

$$\tilde{\nu} = \frac{E_{n_2} - E_{n_1}}{\hbar c} = -\frac{R_H}{n_2^2} - \left(-\frac{R_H}{n_1^2} \right) = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

which is the Rydberg's formula.

Ionization energy: E_{\min} to remove e^- from its ground state.

For H ($n=1$),

$$I = -hcR_H = 2.179 \times 10^{-18} \text{ J} = 13.6 \text{ eV}$$

Atomic orbitals:

s orbitals ($l=0$)

$$\Psi_{1s} = \sqrt{\frac{1}{\pi a_0^3}} e^{-r/a_0} \quad (\text{spherical})$$

Probability to find e^- at a point (r, θ, ϕ):

$$P = \Psi_{1s}^2 d\tau = \left(\frac{1}{\pi a_0^3} \right) e^{-2r/a_0} r^2 \sin \theta dr d\theta d\phi$$

Probability to find e^- on a spherical shell

$$P dr = \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi \Psi^* \Psi r^2 dr = 4\pi r^2 \left(\frac{1}{\pi a_0^3} \right) e^{-2r/a_0} dr$$

Radial distribution function

$$P_r = \Psi^2 4\pi r^2$$

Most probable radius:

$$\begin{aligned} \frac{dP_r}{dr} &= 4\pi \left(1/\pi a_0^3 \right) \frac{d}{dr} (e^{-2r/a_0} r^2) \\ &= C \left[\frac{d}{dr} (e^{-2r/a_0}) r^2 + e^{-2r/a_0} \frac{d}{dr} r^2 \right] \end{aligned}$$

$$\begin{aligned}
&= C \left[-\frac{2r^2}{a_0} e^{-2r/a_0} + 2re^{-2r/a_0} \right] \\
&= C \left[-\frac{2r^2}{a_0} + 2r \right] e^{-2r/a_0}
\end{aligned}$$

at maximum when

$$-2r^2/a_0 + 2r = 0, \quad \text{or} \quad r = a_0$$

ns wavefunction has $n-1$ nodes.

$$\Psi_{2s} = \left(\frac{1}{8\pi a_0^3} \right)^{1/2} \left(2 - \frac{r}{a_0} \right) e^{-r/2a_0} = 0$$

It has 1 node at $r = 2a_0$

p orbitals ($l = 1$)

Zero at $r=0$ and non-spherical.

Three degenerate p orbitals ($m_l = 0, \pm 1$):

For $m_l = 0, p_z$

$$\Psi_0 \propto f(r) \cos \theta = r \cos \theta f'(r) = z f'(r)$$

For $m_l = \pm 1$,

$$p_{+1}: \quad \Psi_{+1} \propto f(r) \sin \theta e^{i\phi}$$

$$p_{-1}: \quad \Psi_{-1} \propto f(r) \sin \theta e^{-i\phi}$$

Linear combinations:

$$\begin{aligned} p_x: \quad \Psi_x &\propto \Psi_{+1} + \Psi_{-1} = f(r) \sin \theta (e^{i\phi} + e^{-i\phi}) \\ &= f'(r) \sin \theta \cos \phi \\ &= r \sin \theta \cos \phi f''(r) = x f''(r) \end{aligned}$$

$$\begin{aligned} p_y: \quad \Psi_y &\propto \Psi_{+1} - \Psi_{-1} = f(r) \sin \theta (e^{i\phi} - e^{-i\phi}) \\ &= y f''(r) \end{aligned}$$

Each p orbital has a nodal plane where $\Psi = 0$.

d orbitals ($l = 2$)

There are five d orbitals ($m_l = 0, \pm 1, \pm 2$).

Spectral transition and selection rules

Spectrum: recording of transitions between states.

$$h\nu = |E_2 - E_1|$$

Not all transitions are allowed

Selection rules for hydrogenic atoms:

$$\Delta l = \pm 1, \quad \Delta m_l = 0, \pm 1$$

Angular momentum conservation law ($J_{\text{photon}} = 1 \hbar$)

Example:	$1s \rightarrow 2s,$	$\Delta l = 0,$ forbidden
	$1s \rightarrow 2p_z,$	$\Delta l = 1, \Delta m_l = 0,$ allowed
	$3d \rightarrow 5s,$	$\Delta l = -2,$ forbidden
	$5s \rightarrow 2p,$	$\Delta l = 1,$ allowed

II. Atomic units

Action: $\hbar = 1$

Mass: $m_e = 1$

Charge: $q_e = \frac{e}{\sqrt{4\pi\epsilon_0}} = 1$

Length: $a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = 1 \text{ bohr}$

Energy: $-2E_{1s}(\text{H}) = 27.211 \text{ eV} = 1 \text{ hartree } (E_h)$

Time: $2.42 \times 10^{-17} \text{ s} = 0.0242 \text{ fs} = 1 \text{ atu}$

H-atom Hamiltonian:

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{Z}{r}$$

III. Structure of many-electron atoms

Helium atom

Hamiltonian ($\hbar = 1$)

$$\hat{H} = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \quad (Z=2)$$

No analytical solution for $\hat{H}\Psi = E\Psi$.

0th order approximation:

$$\hat{H}_0 = \hat{h}_1 + \hat{h}_2$$

$$|\psi^0\rangle = |n_1 l_1 m_1\rangle |n_2 l_2 m_2\rangle$$

$$E^0 = -\frac{Z^2}{2n_1^2} - \frac{Z^2}{2n_2^2} \quad (\hbar = 1)$$

For the ground state, $E^0 = -4$ hartree. Bad approximation of the exact result of -2.904 hartree, due to ignoring $1/r_{12}$.

Including 1st order perturbation:

$$E = -4 + \left\langle \psi^0 \left| \frac{1}{r_{12}} \right| \psi^0 \right\rangle = -4 + \frac{5}{8} 2 = -2.75 \text{ hartree}$$

Variational treatment:

Trial wavefunction (ground state):

$$|\psi\rangle = \sqrt{\frac{\lambda^3}{\pi}} e^{-\lambda r_1} \sqrt{\frac{\lambda^3}{\pi}} e^{-\lambda r_2}$$

where $\lambda = Z - \sigma$ is effective charge with σ as shielding factor.

$$E = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} = -\lambda^2 - 2(Z - \lambda)\lambda + \frac{5\lambda}{8}$$

Varying λ :

$$\frac{dE}{d\lambda} = -2\lambda - 2Z + 4\lambda + \frac{5}{8} = 0$$

that is

$$\lambda = Z - \frac{5}{16}$$

and

$$E = -\left(Z - \frac{5}{16}\right)^2 = -2.85 \text{ hartree} \quad (Z=2)$$

In multi-electron atoms, the nuclear Coulomb field exerted on an electron is shielded by other electrons.

Pauli exclusion principle

Electrons are indistinguishable Fermions that carry spins ($s = 1/2$). There are two types of spins corresponding to $m_s = \pm 1/2$:

$$|\alpha\rangle = |s, m_s\rangle = \left| \frac{1}{2}, \frac{1}{2} \right\rangle$$
$$|\beta\rangle = |s, m_s\rangle = \left| \frac{1}{2}, -\frac{1}{2} \right\rangle$$

with

$$\hat{S}^2 |s, m_s\rangle = s(s+1)\hbar^2 |s, m_s\rangle = \frac{3}{4}\hbar^2 |s, m_s\rangle$$
$$\hat{S}_z |s, m_s\rangle = m_s \hbar |s, m_s\rangle = \pm \frac{1}{2} \hbar |s, m_s\rangle$$

Pauli principle:

For Fermions, the wavefunction is antisymmetric under exchange.

Exchange operator:

$$\hat{X}_{12} |\phi(x_1, x_2)\rangle = |\phi(x_2, x_1)\rangle$$

Antisymmetry:

$$\hat{X}_{12} |\phi(x_1, x_2)\rangle = |\phi(x_2, x_1)\rangle = -|\phi(x_1, x_2)\rangle$$

Possible He ground state wavefunctions:

$$\begin{aligned}
 |\psi_1\rangle &= |1s(1)\rangle|1s(2)\rangle|\alpha(1)\rangle|\alpha(2)\rangle = |1s1s\rangle|\alpha\alpha\rangle \\
 |\psi_2\rangle &= |1s(1)\rangle|1s(2)\rangle|\alpha(1)\rangle|\beta(2)\rangle = |1s1s\rangle|\alpha\beta\rangle \\
 |\psi_3\rangle &= |1s(1)\rangle|1s(2)\rangle|\beta(1)\rangle|\alpha(2)\rangle = |1s1s\rangle|\beta\alpha\rangle \\
 |\psi_4\rangle &= |1s(1)\rangle|1s(2)\rangle|\beta(1)\rangle|\beta(2)\rangle = |1s1s\rangle|\beta\beta\rangle
 \end{aligned}$$

We note that

$$\hat{X}_{12}|\psi_1\rangle = |\psi_1\rangle, \quad \hat{X}_{12}|\psi_4\rangle = |\psi_4\rangle$$

so they violate Pauli principle and are not allowed.

To construct allowed wavefunctions, we use the projection operator $(1 - \hat{X}_{12})/\sqrt{2}$ to antisymmetrize:

$$|\psi'_1\rangle = \frac{1}{\sqrt{2}}(1 - \hat{X}_{12})|\psi_1\rangle = 0$$

$$\begin{aligned}
 |\psi'_2\rangle &= \frac{1}{\sqrt{2}}(1 - \hat{X}_{12})|\psi_2\rangle = \frac{1}{\sqrt{2}}(|\psi_2\rangle - |\psi_3\rangle) \\
 &= \frac{1}{\sqrt{2}}|1s1s\rangle(|\alpha\beta\rangle - |\beta\alpha\rangle)
 \end{aligned}$$

$$|\psi'_3\rangle = \frac{1}{\sqrt{2}}|1s1s\rangle(|\beta\alpha\rangle - |\alpha\beta\rangle) = -|\psi'_2\rangle$$

$$|\psi'_4\rangle = 0$$

Indeed, the antisymmetrized wavefunctions satisfy the Pauli principle:

$$\begin{aligned}
 \hat{X}_{12} \frac{1}{\sqrt{2}} |1s1s\rangle (|\alpha\beta\rangle - |\beta\alpha\rangle) \\
 &= \frac{1}{\sqrt{2}} |1s1s\rangle (|\beta\alpha\rangle - |\alpha\beta\rangle) \\
 &= -\frac{1}{\sqrt{2}} |1s1s\rangle (|\alpha\beta\rangle - |\beta\alpha\rangle)
 \end{aligned}$$

There are two electrons in the 1s orbital with opposite spins!

Total spin:

$$\begin{aligned}
 \hat{S}^2 |\psi\rangle &= (\hat{S}_1 + \hat{S}_2)^2 |\psi\rangle \\
 &= [\hat{S}_1^2 + \hat{S}_2^2 + 2(\hat{S}_{1z}\hat{S}_{2z} + \hat{S}_{1y}\hat{S}_{2y} + \hat{S}_{1x}\hat{S}_{2x})] |\psi\rangle \\
 &= [\hat{S}_1^2 + \hat{S}_2^2 + 2\hat{S}_{1z}\hat{S}_{2z} + \hat{S}_{1+}\hat{S}_{2-} + \hat{S}_{1-}\hat{S}_{2+}] |\psi\rangle \\
 &= \left[\frac{1}{2} \left(\frac{1}{2} + 1 \right) + \frac{1}{2} \left(\frac{1}{2} + 1 \right) - 2 \frac{1}{2} \frac{1}{2} - 1 \right] \hbar^2 |\psi\rangle \\
 &= S(S+1)\hbar^2 |\psi\rangle = 0
 \end{aligned}$$

$$\hat{S}_z |\psi\rangle = (\hat{S}_{1z} + \hat{S}_{2z}) |\psi\rangle = M_s \hbar |\psi\rangle = 0$$

which corresponds to $S=M_s=0$, or a singlet state. In deriving the above results, we have used

$$\begin{aligned}
& 2(\hat{S}_{1y}\hat{S}_{2y} + \hat{S}_{1x}\hat{S}_{2x}) \\
&= (\hat{S}_{1x} + i\hat{S}_{1y})(\hat{S}_{2x} - i\hat{S}_{2y}) + (\hat{S}_{1x} - i\hat{S}_{1y})(\hat{S}_{2x} + i\hat{S}_{2y}) \\
&= \hat{S}_{1+}\hat{S}_{2-} + \hat{S}_{1-}\hat{S}_{2+} \\
&(\hat{S}_{1+}\hat{S}_{2-} + \hat{S}_{1-}\hat{S}_{2+})(|\alpha\beta\rangle - |\beta\alpha\rangle) \\
&= -\hbar(|\alpha\beta\rangle - |\beta\alpha\rangle)
\end{aligned}$$

Excited state He:

Antisymmetrization of possible wavefunctions:

$$\begin{aligned}
|\psi_1\rangle &= |1s2s\rangle|\alpha\alpha\rangle \\
|\psi_2\rangle &= |1s2s\rangle|\alpha\beta\rangle \\
|\psi_3\rangle &= |1s2s\rangle|\beta\alpha\rangle \\
|\psi_4\rangle &= |1s2s\rangle|\beta\beta\rangle
\end{aligned}$$

yields:

$$|\psi'_1\rangle = \frac{1}{\sqrt{2}}(|\alpha\alpha\rangle(|1s2s\rangle - |2s1s\rangle))$$

$$|\psi'_2\rangle = \frac{1}{\sqrt{2}}(|1s2s\rangle|\alpha\beta\rangle - |2s1s\rangle|\beta\alpha\rangle)$$

$$|\psi'_3\rangle = \frac{1}{\sqrt{2}}(|1s2s\rangle|\beta\alpha\rangle - |2s1s\rangle|\alpha\beta\rangle)$$

$$|\psi'_4\rangle = \frac{1}{\sqrt{2}}(|\beta\beta\rangle(|1s2s\rangle - |2s1s\rangle))$$

The total spin:

$$\hat{S}^2|\alpha\alpha\rangle = 2\hbar^2|\alpha\alpha\rangle \quad (S=1)$$

$$\hat{S}_z|\alpha\alpha\rangle = \hbar|\alpha\alpha\rangle \quad (M_s=1)$$

$$\hat{S}^2|\beta\beta\rangle = 2\hbar^2|\beta\beta\rangle \quad (S=1)$$

$$\hat{S}_z|\beta\beta\rangle = -\hbar|\beta\beta\rangle \quad (M_s=-1)$$

but $|\psi'_2\rangle$ and $|\psi'_3\rangle$ are not eigenfunctions of \hat{S}^2 .

Linear combination of the two yields:

$$|\psi''_2\rangle = \frac{1}{2}(|1s2s\rangle + |2s1s\rangle)(|\alpha\beta\rangle - |\beta\alpha\rangle)$$

$$|\psi''_3\rangle = \frac{1}{2}(|1s2s\rangle - |2s1s\rangle)(|\alpha\beta\rangle + |\beta\alpha\rangle)$$

and

$$\hat{S}^2(|\alpha\beta\rangle - |\beta\alpha\rangle) = 2\hbar^2(|\alpha\beta\rangle - |\beta\alpha\rangle) \quad (S=1)$$

$$\hat{S}_z(|\alpha\beta\rangle - |\beta\alpha\rangle) = 0 \quad (M_s=0)$$

$$\hat{S}^2(|\alpha\beta\rangle + |\beta\alpha\rangle) = 0 \quad (S=0)$$

$$\hat{S}_z(|\alpha\beta\rangle + |\beta\alpha\rangle) = 0 \quad (M_s=0)$$

So, excited He has two configurations:

Singlet excited state ($S=0, M_s=0$):

$$\frac{1}{2}(|1s2s\rangle + |2s1s\rangle)(|\alpha\beta\rangle - |\beta\alpha\rangle)$$

Triplet excited state ($S=1, M_s=0, \pm 1$):

$$\frac{1}{\sqrt{2}}(|1s2s\rangle - |2s1s\rangle) \begin{cases} |\alpha\alpha\rangle \\ |\beta\beta\rangle \\ \frac{1}{\sqrt{2}}(|\alpha\beta\rangle + |\beta\alpha\rangle) \end{cases}$$

Energy of triplet:

$$\begin{aligned} E &= \frac{1}{2} \langle \alpha\alpha | (\langle 1s2s | - \langle 2s1s |) \hat{H} (|1s2s\rangle - |2s1s\rangle) | \alpha\alpha \rangle \\ &= \frac{1}{2} (\langle 1s2s | \hat{H} | 1s2s \rangle + \langle 2s1s | \hat{H} | 2s1s \rangle \\ &\quad - \langle 1s2s | \hat{H} | 2s1s \rangle - \langle 2s1s | \hat{H} | 1s2s \rangle) \\ &= \langle 1s2s | \hat{H} | 1s2s \rangle - \langle 1s2s | \hat{H} | 2s1s \rangle \end{aligned}$$

Note $\hat{H} = \hat{h}_1 + \hat{h}_2 + 1/r_{12}$,

$$\begin{aligned} E &= \langle 1s2s | \hat{h}_1 + \hat{h}_2 + \frac{1}{r_{12}} | 1s2s \rangle - \langle 1s2s | \hat{h}_1 + \hat{h}_2 + \frac{1}{r_{12}} | 2s1s \rangle \\ &= E_{1s} + E_{2s} + J_{1s2s} - K_{1s2s} \end{aligned}$$

because

$$\langle 1s2s | \hat{h}_1 + \hat{h}_2 | 1s2s \rangle = E_{1s} + E_{2s}$$

$$\langle 1s2s | \hat{h}_1 + \hat{h}_2 | 2s1s \rangle = 0$$

The coulomb integral:

$$J_{1s2s} = \langle 1s2s | \frac{1}{r_{12}} | 1s2s \rangle$$

which is repulsion between 1s and 2s electrons, always positive.

The exchange integral:

$$K_{1s2s} = \langle 1s2s | \frac{1}{r_{12}} | 2s1s \rangle$$

which is due to exchange antisymmetry, mostly positive.

For singlet excited state:

$$E_S = E_{1s} + E_{2s} + J_{1s2s} + K_{1s2s}$$

Singlet excited state has higher energy than triplet, as spatial wave function of triplet is antisymmetric. (Hund's rule)

Many-electron atoms

$$\hat{H} = -\frac{1}{2} \sum_i \nabla_i^2 - \sum_i \frac{Z}{r_i} + \sum_i \sum_{j>i} \frac{1}{r_{ij}}$$

Hartree approximation: express total spatial wave function as product of orbitals:

$$|\Psi(1,2,\dots,N)\rangle = |\psi(1)\rangle |\psi(2)\rangle \dots |\psi(N)\rangle$$

It ignores the spins and correlations between electrons.

Hartree-Fock approximation: Hartree+antisymmetrization

Slater determinants always satisfy Pauli principle.

$$\begin{aligned} |\Psi\rangle &= \frac{1}{\sqrt{N!}} \begin{vmatrix} |\chi_1(1)\rangle & |\chi_2(1)\rangle & \dots & |\chi_N(1)\rangle \\ |\chi_1(2)\rangle & & & \\ \dots & & & \\ |\chi_1(N)\rangle & & & |\chi_N(N)\rangle \end{vmatrix} \\ &= |\chi_1 \chi_2 \dots \chi_N| \end{aligned}$$

where $|\chi\rangle$ contain both spin and orbital parts and is called a spin-orbital.

Pauli principle: no two electrons can occupy the same spin-orbital.

Slater determinants may not be eigenfunction of \hat{S} .

He triplet ($M_s=1$):

$$\begin{aligned}
 |\Psi\rangle &= \frac{1}{\sqrt{2}} \begin{vmatrix} |1s(1)\rangle|\alpha(1)\rangle & |2s(1)\rangle|\alpha(1)\rangle \\ |1s(2)\rangle|\alpha(2)\rangle & |2s(2)\rangle|\alpha(2)\rangle \end{vmatrix} \\
 &= \frac{1}{\sqrt{2}} [|1s(1)\rangle|\alpha(1)\rangle|2s(2)\rangle|\alpha(2)\rangle - |2s(1)\rangle|\alpha(1)\rangle|1s(2)\rangle|\alpha(2)\rangle] \\
 &= \frac{1}{\sqrt{2}} |\alpha(1)\rangle|\alpha(2)\rangle [|1s(1)\rangle|2s(2)\rangle - |2s(1)\rangle|1s(2)\rangle]
 \end{aligned}$$

Abbreviations:

$$|\Psi\rangle = |1s \ 2s|$$

Be ground state ($1s^2 2s^2$):

$$|\Psi\rangle = |1s \ \overline{1s} \ 2s \ \overline{2s}|$$

where the bar stands for a β electron.

Hartree-Fock equations (close-shell singlet):

$$\hat{F}_i |\chi_i\rangle = \varepsilon_i |\chi_i\rangle$$

which are single electron equations for the spin-orbitals. The Fock operator is an effective Hamiltonian:

$$\hat{F}_i = -\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} + \sum_{j=1}^N [2\hat{J}_j(i) - \hat{K}_j(i)]$$

averaged over all other electrons. The Coulomb and exchange operators are defined in terms of the corresponding integrals:

$$\hat{J}_j |\chi_i(1)\rangle = \left\{ \left\langle \chi_j(2) \left| \frac{1}{r_{12}} \right| \chi_j(2) \right\rangle \right\} |\chi_i(1)\rangle$$

$$\hat{K}_j |\chi_i(1)\rangle = \left\{ \left\langle \chi_j(2) \left| \frac{1}{r_{12}} \right| \chi_i(2) \right\rangle \right\} |\chi_j(1)\rangle$$

The solution must be solved iteratively using the self-consistent field (SCF) approach, because the Fock operator depends on the spin-orbitals.

H-F energy:

$$E = 2 \sum_{i=1}^N \varepsilon_i - \sum_{i,j=1}^N (2J_{ij} - K_{ij})$$

Koopmans' theorem:

- Ionization energy is approximately the energy of the highest occupied orbital: $I \approx -\varepsilon_H$
- Electron affinity is approximately the energy of the lowest unoccupied orbital: $EA \approx -\varepsilon_L$

It is only an approximation because of electrons relaxation.

Electron correlation:

H-F approximation assumes single electron motion in a mean field generated by other electrons. It thus ignores the correlation between electrons.

Correlation energy:

$$E_{corr} = E_{exact} - E_{HF}$$

Usually small, but can be very important, can be taken into account using variational or perturbative methods.

Relativistic contributions

- spin is a relativistic effect, its contribution comes in the form of spin-orbit coupling
- often large in heavy atoms as electrons moves very fast, approaching the speed of light.

Building-up (Aufbau) principle:

Electronic configuration of an atom can be determined by the following rules:

i. Orbital ordering: Because of shielding ($Z_{eff} = Z - \sigma$), the atomic orbitals are not degenerate and have the following energy order:

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, ...

σ is the shielding constant, $s < p < d$.

ii. Pauli exclusion principle

2 e⁻ may occupy one orbital with opposite spins (α and β).

iii. Double occupancy rule

Electrons occupy different orbitals of a given subshell before doubly occupying any one of them.

Carbon atom (6 e⁻): [He]2s² 2p¹ 2p¹ (an open shell atom).

Valence electrons: outmost shell e⁻, 2s, 2p for C

Core electrons: inner shell e⁻.

iv. Hund's rule (spin)

Unpaired electrons tend to have parallel spins. (spin correlation)

The 2 p e⁻ in C have parallel spin $\alpha\alpha$ ($\beta\beta$).

Oxygen atom (8 e⁻)



III Atomic spectra

An electronic configuration may give several states. Each state is represented by a term symbol:

$${}^{2S+1}L_J$$

Total orbital angular momentum L of an atom

$$L = l_1 + l_2 + \dots \quad (\text{vector sum})$$

For a two-electron atom

$$L = |l_1 - l_2|, |l_1 - l_2| + 1, \dots, l_1 + l_2 \quad (\text{Clebsch-Gordan series})$$

Code of L :

$L:$	0	1	2	3	4	...
	S	P	D	F	G	...

Example: L for $3p^1 3d^1$.

$$l_1 = 1 \text{ and } l_2 = 2.$$

so $L = 1, 2, 3$ or three terms P, D, F

Total spin angular momentum S of an atom

$$S = s_1 + s_2 + \dots$$

For a two-electron atom

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

The multiplicity is $2S + 1$

Example: S for a two e^- atom.

$$s_1 = 1/2, s_2 = 1/2,$$

so $S = 0, 1$, or multiplicity = 1 (singlet), 3 (triplet).

Total angular momentum (Russell-Saunders coupling)

$$\mathbf{J} = \mathbf{L} + \mathbf{S}$$

or

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

Examples: Ground and excited state Na, $[\text{Ne}]3s^1$, $[\text{Ne}]3p^1$.

Single electron (ignore inner e^-), $l = 0, s = 1/2$,

$$L = 0, \quad S = 1/2 \quad (2S+1 = 2), \quad J = 1/2$$

So the ground state term is $^2S_{1/2}$

$$L = 1, \quad S = 1/2 \quad (2S+1 = 2), \quad J = 1/2, 3/2$$

So the term are $^2P_{1/2}$ and $^2P_{3/2}$.

Excited state of Na splits to 2 sublevels because of the interaction between spin and orbital angular momenta (spin-orbit coupling, a relativistic effect)

Energy

$$E_{L,S,J} = (1/2)hcA[J(J+1) - L(L+1) - S(S+1)]$$

A is the coupling constant that increases with $\sim Z^4$, so spin-orbit coupling becomes more important for heavy atoms.

Splitting:

$$\begin{aligned}\Delta\tilde{\nu} &= \frac{\Delta E}{hc} = \frac{1}{2}A[J(J+1) - J'(J'+1)] \\ &= \frac{1}{2} \times 17.2\text{cm}^{-1} \left[\frac{3}{2} \left(\frac{3}{2} + 1 \right) - \frac{1}{2} \left(\frac{1}{2} + 1 \right) \right] = 11.5\text{cm}^{-1}\end{aligned}$$

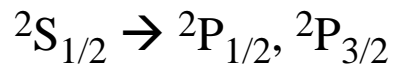
Selection rules

$$\Delta S = 0$$

$$\Delta L = 0, \pm 1 \text{ with } \Delta l = \pm 1$$

$$\Delta J = 0, \pm 1 \text{ but } J = 0 \text{ cannot combine with } J = 0$$

Fine structure of the Na D lines



$$\Delta S = 0, \Delta L = 1, \Delta J = 0, 1 \quad (\text{allowed})$$