

Atomic Systems

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Central Field Approximation

The Hamiltonian between two interacting particles takes the form

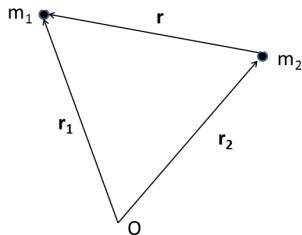
$$\mathbf{H} = -\frac{\hbar^2}{2m_1}\Delta_1 + -\frac{\hbar^2}{2m_2}\Delta_2 + U(r)$$

where $U(r)$ is the interacting potential.
If we introduce the variables

$$\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1 \quad \mathbf{R} = (m_1\mathbf{r}_1 + m_2\mathbf{r}_2)/(m_1 + m_2)$$

the Hamiltonian can be written

$$\mathbf{H} = -\frac{\hbar^2}{2(m_1 + m_2)}\Delta_R + -\frac{\hbar^2}{2\mu}\Delta_r + U(r)$$



where μ is the reduced mass. The wave function is then separable

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \varphi(\mathbf{R})\psi(\mathbf{r}) .$$

$\psi(\mathbf{r})$ describes the movement of a particle of mass μ in a central field $U(r)$.

The CFA reduces the SE to a one dimension

The Schrödinger equation (SE) for a central field is

$$\Delta\Psi + (2\mu/\hbar^2)[E - U(r)]\Psi = 0 .$$

Since angular momentum is conserved, it determines its angular dependence and solutions are of the type

$$\Psi = \frac{P_\ell(r)}{r} Y_{\ell m}(\theta, \phi)$$

where $Y_{\ell m}(\theta, \phi)$ are the spherical harmonics. The SE is reduced to a one dimension

$$\frac{d^2 P}{dr^2} + \frac{2\mu}{\hbar^2} \left[E - U(r) - \frac{\hbar^2}{2\mu} \frac{\ell(\ell+1)}{r^2} \right] P = 0$$

where the potential now contains a *centrifugal term*. The wave function is completely determined by $\{E, \ell, m\}$.

In CFA, wave functions are expanded in partial waves

The spectroscopic notation is usually used to denote values of ℓ :

$$\ell = \{0, 1, 2, 3, 4, 5, 6, 7\} = \{s, p, d, f, g, h, i, k\} .$$

A plane wave can be expanded in *partial waves*

$$\exp(ikz) = \frac{1}{kr} \sum_{\ell=0}^{\infty} i^{\ell} (2\ell + 1) P_{\ell}(\cos \theta) \sin(kr - \ell\pi/2) \quad (r \rightarrow \infty)$$

where P_{ℓ} are the Legendre polynomials.

For a Coulomb field ($U = \pm Z/r$) and $E \leq 0$ (bound spectrum),

$$E_n = -\frac{Z^2}{2n^2} \quad n \geq \ell + 1$$

where n is the *principal quantum number* (integer). For $E > 0$ (continuum spectrum)

$$R_{k\ell} \sim \frac{2}{r} \sin(kr + \log(2kr)/k - \ell\pi/2 + \delta_{\ell}) \quad (r \rightarrow \infty)$$

where $\delta_{\ell} = \arg\Gamma(\ell + 1 - i/k)$ is known as the *Coulomb phase*.

Parity conservation: even or odd

Besides invariance to displacement and rotation, the Hamiltonian of a closed system is also invariant to inversion which leads to a QM conservation law: *parity conservation* (space symmetry under reflexion). If \mathbf{P} is the inversion operator

$$\mathbf{P}\psi(r) = \psi(-r) ,$$

its eigenvalues are given by the equation

$$\mathbf{P}\psi(r) = P\psi(r) .$$

If we take into consideration that

$$\mathbf{P}^2\psi = P^2\psi = \psi ,$$

then $P = \pm 1$. That is, eigenfunctions are either of even or odd parity.

Parity conservation: even or odd

The angular momentum operator is also invariant under inversion (i.e. \mathbf{P} and \mathbf{L} commute). Therefore, the system has a definite parity established simultaneously with the definite values of L and M .

For a single particle, it may be shown that

$$P = (-1)^\ell ,$$

and for a system of particles in a CFA where the mutual interaction between particles is assumed weak, the total parity is given by

$$P_{\text{tot}} = (-1)^{\sum_i \ell_i} .$$

Spin leads to the Exclusion Principle

The total angular momentum of a particle contains two components

$$\mathbf{j} = \mathbf{l} + \mathbf{s} .$$

Let us consider a system of two identical particles at coordinates $\mathbf{x}_i = \{\mathbf{r}_i, \sigma_i\}$. If the particles are exchanged, the wave functions obey

$$\psi(\mathbf{x}_1, \mathbf{x}_2) = \pm \psi(\mathbf{x}_2, \mathbf{x}_1)$$

Symmetric wave functions are obeyed by particles with integer spin (bosons)

$$\psi(x_1, x_2) = \frac{1}{\sqrt{2}} [\psi_1(x_1)\psi_2(x_2) + \psi_1(x_2)\psi_2(x_1)]$$

and anti-symmetric wave functions are obeyed by particles with half-integer spin (fermions)

$$\psi(x_1, x_2) = \frac{1}{\sqrt{2}} [\psi_1(x_1)\psi_2(x_2) - \psi_1(x_2)\psi_2(x_1)] .$$

If $\psi_1 = \psi_2$, $\Rightarrow \psi(x_1, x_2) = 0$ (Pauli Exclusion Principle).

Spin leads to the exchange interaction

Although the SE does not take into account particle spin, its prediction power is not invalidated as the Coulomb interaction is not spin dependent in the non-relativistic limit. The wave function for two particles can be then be written

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \varphi(\mathbf{r}_1, \mathbf{x}_2)\chi(\sigma_1, \sigma_2)$$

There is, however, a peculiar energy dependence on spin which originates in particle exchange. If the two particles are fermions (spin $1/2$), the complete wave function $\psi = \varphi\chi$ must be anti-symmetric with respect to exchange. Therefore, if φ is symmetric, χ must be anti-symmetric and vice-versa. The energy levels with a symmetric $\varphi(r_1, r_2)$ only occur for total spin 0 ($\uparrow\downarrow$). Level energies with anti-symmetric $\varphi(r_1, r_2)$ must have a total spin of 1 ($\uparrow\uparrow$). This interaction is referred to as the *exchange interaction*.

Multi-electron atoms are also treated with the CFA

The starting point for the computations of multi-electron systems is the *central field approximation*: each electron moves in an effective spherically symmetric potential $V(r)$ resulting from the nucleus and the rest of the electrons. For a system with nuclear charge Z and N electrons we must take into account:

1. The kinetic energy of the electrons and the potential energy of the attractive, electrostatic Coulombic field of the nucleus (assumed punctual and infinitely massive).
2. The electrostatic Coulombic repulsion between the electrons.
3. The magnetic interaction of the electronic spin with their orbit.
4. A collection of small effects: two-body magnetic interactions (e.g. spin–spin), other relativistic effects (e.g. mass corrections), radiative corrections, nuclear corrections.

Multi-electron atoms

Neglecting relativistic interactions, the atomic Hamiltonian is

$$\mathbf{H} = \sum_i^N \left(-\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \right) + \sum_{i < j}^N \frac{1}{r_{ij}}$$

and the SE

$$\mathbf{H}\Psi(q_1, q_2, \dots, q_n) = E\Psi(q_1, q_2, \dots, q_n)$$

where $q_i = \{\mathbf{r}_i, \sigma_i\}$. $\Psi(q_1, q_2, \dots, q_n)$ must be completely anti-symmetric with respect to exchange. Since \mathbf{H} is spin independent

$$\Psi(q_1, q_2, \dots, q_n) = \psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \chi(\sigma_1, \sigma_2, \dots, \sigma_N)$$

$$\Rightarrow \mathbf{H}\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = E\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) .$$

The SE is a non-separable partial differential equation in 3D.

Multi-electron atoms

Slater and Hartree proposed as a starting point an independent-particle model in a central field approximation. Since $1/r_{ij}$ contains a fairly large spherically symmetric component (screening)

$S(r) = \sum_i S_i(r)$, we define the potential

$$V(r) \equiv -\frac{Z}{r} + S(r) .$$

The Hamiltonian can then be written

$$\mathbf{H} = \mathbf{H}_c + \mathbf{H}_1$$

where

$$\mathbf{H}_c = \sum_i^N h_i = \sum_i^N -\frac{1}{2} \nabla_i^2 + V(r_i) .$$

$$\mathbf{H}_1 = \sum_{i < j}^N \frac{1}{r_{ij}} - \sum_i^N S(r_i)$$

Multi-electron atoms

If we obviate \mathbf{H}_1 , the SE reduces to

$$\mathbf{H}_c \psi_c = \sum_i^N -\frac{1}{2} \nabla_i^2 + V(r_i) = E_c \psi_c$$

which is separable in N equations. The solution takes the form of an electron *configuration*

$$\psi_c = u_{a1}(\mathbf{r}_1) u_{a2}(\mathbf{r}_2) \dots u_N(\mathbf{r}_{aN})$$

with $a_i = \{n_i \ell_i m_i\}$ and $u_{n\ell m} = P_{n\ell}(r) r^{-1} Y_{\ell m}(\theta, \varphi)$.

$$n = 1, 2, 3, \dots \quad (1)$$

$$\ell = 0, 1, 2, \dots, n-1 \quad (2)$$

$$m = -\ell, -\ell+1, \dots, 0, \dots, +\ell-1, +\ell \quad (3)$$

$$E_c = \sum_i^N E_{n_i \ell_i} \quad (4)$$

Multi-electron atoms: corrections to the CFA

Electron correlation

The most important correction to \mathbf{H}_c is

$$\mathbf{H}_1 = \sum_{i < j}^N \frac{1}{r_{ij}} - \sum_i^N S(r_i)$$

which gives rise to electron correlation effects. It is dealt with by the method of *configuration interaction*

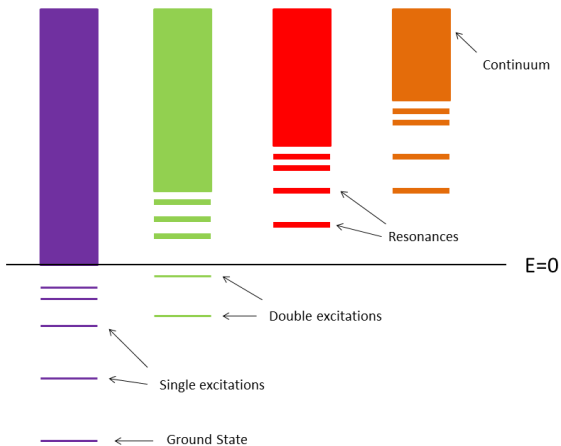
$$\Psi(LS\pi) = \sum_j \Phi_j(SL\pi)$$

where $\Phi_j(SL\pi)$ represents a configuration function of the appropriate symmetry. Similarly, for a mixture of bound and continuum states, the *close coupling* expansion is used

$$\Psi(LS\pi) = \sum_i \chi_i \theta_i + \sum_j \Phi_j(SL\pi)$$

where χ_i are the target eigenfunctions.

Multi-electron atoms: corrections to the CFA



Multi-electron atoms: corrections to the CFA

Breit–Pauli relativistic corrections

A relativistic corrected Hamiltonian can be written

$$\mathbf{H} = \mathbf{H}_c + \mathbf{H}_1 + \mathbf{H}_{1B} + \mathbf{H}_{2B}$$

The one-body relativistic operators

$$H_{1B} = \sum_i^N f_i(\text{mass}) + f_i(\text{d}) + f_i(\text{so}) \quad (5)$$

represent the spin–orbit interaction, $f_i(\text{so})$, the non-fine-structure mass variation, $f_i(\text{mass})$, and one-body Darwin correction, $f_i(\text{d})$.

Multi-electron atoms: corrections to the CFA

Breit–Pauli relativistic corrections

The two-body Breit operators are given by

$$H_{2B} = \sum_{i < j} g_{ij}(\text{so}) + g_{ij}(\text{ss}) + g_{ij}(\text{css}) + g_{ij}(\text{d}) + g_{ij}(\text{oo})$$

where the fine-structure terms are $g_{ij}(\text{so})$ (spin-other-orbit and mutual spin-orbit) and $g_{ij}(\text{ss})$ (spin-spin), and the non-fine-structure counterparts are $g_{ij}(\text{css})$ (spin-spin contact), $g_{ij}(\text{d})$ (two-body Darwin), and $g_{ij}(\text{oo})$ (orbit-orbit).

In a relativistic-correct context, L and S are no longer good quantum numbers but the total angular momentum

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

is still conserved and J is a good quantum number. The relativistic corrections lead to *fine structure*.

He-like systems (Figure from Porquet & Dubau 2000)

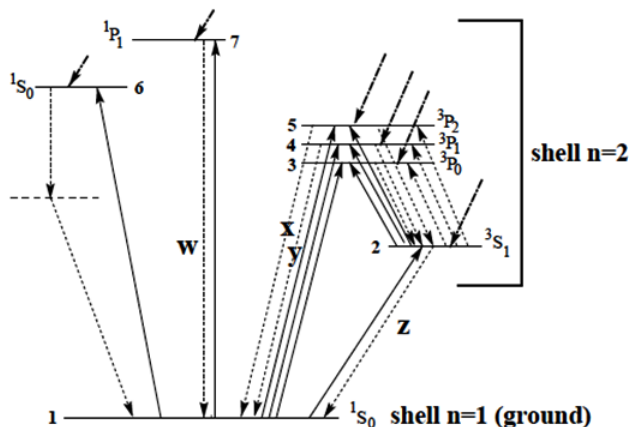
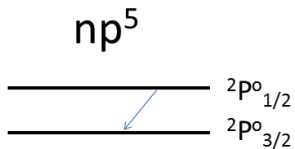
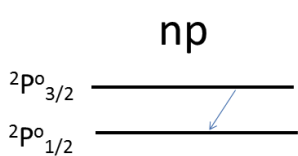
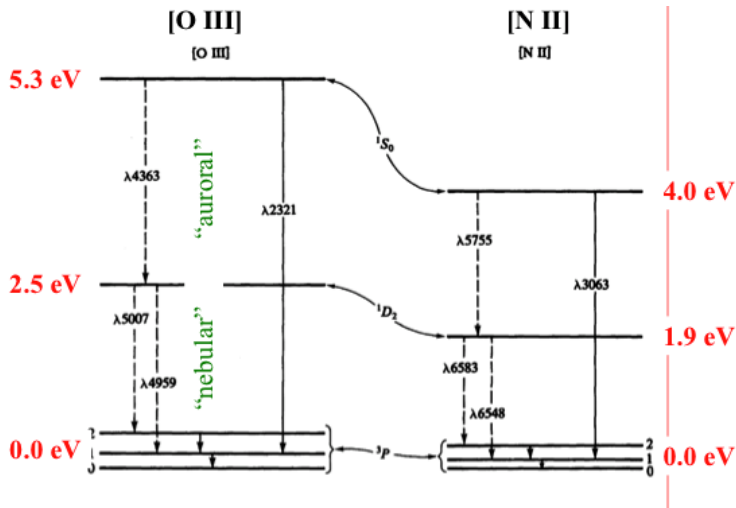


Fig. 1. Simplified Gotrian diagram for He-like ions. w , x , y and z correspond respectively to the resonance, intercombination and forbidden lines. *Full curves*: collisional excitation transitions, *broken curves*: radiative transitions and *thick dot-dashed curves*: recombination (radiative and dielectronic). *Note*: the broken arrow ($1S_0$ to the ground level) correspond to the 2-photon continuum

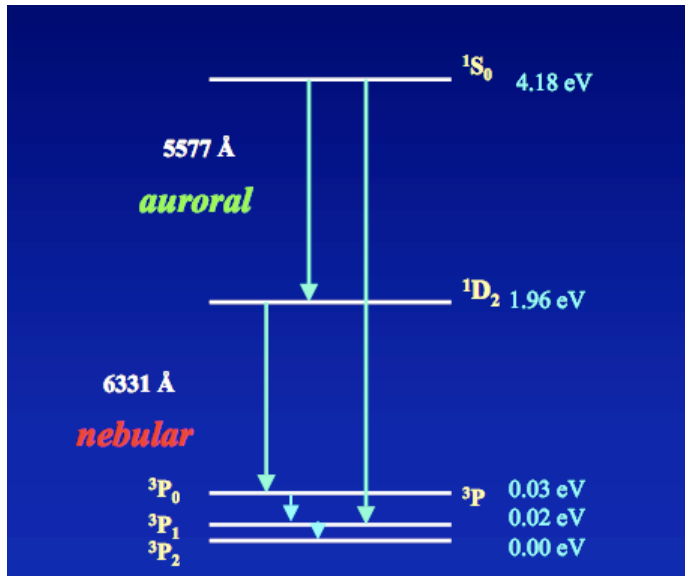
$np^{1,5}$ configurations



$np^{2,4}$ configurations (Fig. from Osterbrock & Ferland 2005)



$np^{2,4}$ configurations: level structure of O I



np^3 configurations (Fig. from Osterbrock & Ferland 2005)

