Atomic structure

- Review of the Schrödinger equation
- Wavefunctions of one electron in a central field
- Hydrogenic atoms
- Multielectron systems
- Spectroscopic terms

References. Books: G.B., Rybicki, A.P. Lightman, *Radiative processes in Atsrophysics*, chapter 9;
B. H. Bransden, C. J. Joachain, *Physics of Atoms and Molecules*, J. Wiley & Sons, (2003)
R. Fitzpatrick, *Introductory Quantum mechanics*, LibreText;
Lecture notes provided during the course.

Quantum operators- commutation rules

$[x_i, p_j] = i\hbar\delta_{ij}$

$\mathbf{p} = -i\hbar\nabla$

$\mathbf{L} = \mathbf{x} \times \mathbf{p}$

$\mathbf{L} \times \mathbf{L} = i\hbar\mathbf{L}$

$\mathbf{S} \times \mathbf{S} = i\hbar\mathbf{S}$

$[\mathbf{L}_i, \mathbf{S}_j] = 0$

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

$\mathbf{J} \times \mathbf{J} = i\hbar\,\mathbf{J}$

$\mathbf{J}^2 = J_x^2 + J_y^2 + J_z^2$

$[\mathbf{J}^2, \mathbf{L}^2] = [\mathbf{J}^2, \mathbf{S}^2] = 0$

$[\mathbf{J}^2, \mathbf{L}_z] \neq 0\,,\ [\mathbf{J}^2, \mathbf{S}_z] \neq 0$

$[\mathbf{J}_z, \mathbf{L}_z] = 0\,,\ [\mathbf{J}_z, \mathbf{S}_z] = 0$

A review of the Schrödinger equation

The classical theory of radiation is unable to treat those physical situations in which the matter-radiation interaction takes place by means of a single (or a few) photon. We now review the main principles of atomic structure.

Erwin Schrödinger
(1887-1961)
Nobel Prize 1933

Neglecting spin, relativistic effects and nuclear effects, The time-independent Hamilitonian for the Hydrogenic atoms (nucleus and electron, $Z = 1$ for Hydrogen) is $(\mathbf{p} = -i\hbar\boldsymbol{\nabla})$:

$$H = \underbrace{-\frac{\hbar^2}{2m_n}\nabla_n^2}_{\text{Kinetic nucleus}} \underbrace{-\frac{\hbar^2}{2m_e}\nabla_e^2}_{\text{Kinetic electron}} \underbrace{-\frac{Ze^2}{|\mathbf{r}_e-\mathbf{r}_n|}}_{\text{Coulomb potential}}$$

Since this Hamiltonian does not depend on time, the time dependence of the wave functions is in a phase factor:

$\Psi(\mathbf{r}_e, \mathbf{r}_n, t) = \Psi(\mathbf{r}_e, \mathbf{r}_n)\, e^{iEt/\hbar}$. The time-independent Schrödinger equation (nucleus and electron) $i\hbar\frac{\partial\Psi}{\partial t} = H\Psi$ becomes:

$$\left(-\frac{\hbar^2}{2m_n}\nabla_n^2 - \frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{Ze^2}{|\mathbf{r}_e-\mathbf{r}_n|}\right)\Psi(\mathbf{r}_e, \mathbf{r}_n) = E\,\Psi(\mathbf{r}_e, \mathbf{r}_n)$$

Define new coordinates: $\mathbf{r} = \mathbf{r}_e - \mathbf{r}_n$ (electron-nucleus distance vector) and $\mathbf{R} = \frac{m_n\mathbf{r}_n + m_e\mathbf{r}_e}{m_n+m_e}$ (center of mass – c.o.m.- position):

$$\left(-\frac{\hbar^2}{2(m_n+m_e)}\nabla_R^2 - \frac{\hbar^2(m_n+m_e)}{2m_nm_e}\nabla_r^2 - \frac{ze^2}{|\mathbf{r}|}\right)\Psi(\mathbf{R}, \mathbf{r}) = E\Psi(\mathbf{R}, \mathbf{r}) \quad \Rightarrow \quad \left(\underbrace{-\frac{\hbar^2}{2M}\nabla_R^2}_{\text{c.o.m.}} \underbrace{-\frac{\hbar^2}{2\mu}\nabla_r^2 - \frac{Ze^2}{|\mathbf{r}|}}_{\text{electron}}\right)\Psi(\mathbf{R}, \mathbf{r}) = E\Psi(\mathbf{R}, \mathbf{r})$$

with $M = m_n + m_e$, $\mu = \frac{m_nm_e}{m_n+m_e}$ = reduced mass.

We can separate the variables, $\Psi(\mathbf{R},\mathbf{r})=\psi_{\mathrm{r}}(\mathbf{r})\psi_R(\mathbf{R})$ obtaining two independent equations:

$$-\frac{\hbar^2}{2M}\nabla_R^2\,\psi_R(\mathbf{R}) = E_R\,\psi_R(\mathbf{R}) \qquad \text{and} \qquad \left(-\frac{\hbar^2}{2\mu}\nabla_r^2 - \frac{Ze^2}{|\mathbf{r}|}\right)\psi_{\mathrm{r}}(\mathbf{r}) = E_r\,\psi_{\mathrm{r}}(\mathbf{r}) \quad .$$

The solutions of the first equation are simple plane waves of the center-of-mass motion (with a constant momentum $\mathbf{P}=\hbar\mathbf{k}$) : $\psi_R(\mathbf{R}) = \mathbf{e}^{\,i\,\mathbf{k}\cdot\mathbf{R}}$.

The solutions of the second equation are the Hydrogen orbitals (centered at r=0) for the relative motion: $\psi_{\mathrm{r}}(\mathbf{r})=\psi_{nlm_l}(r,\theta,\varphi)$

We will, from now on, omit the subscript «r» . Note that $\mu \approx m_e$. We will only refer to the wavefunction of the electron(s) as a function of the position with respect to the nucleus, and to the electron energies.

- When the atom has more than one electron, in a nucleus of charge $+Ze$, we add the Coulomb repulsive energy between the electrons. Neglecting spin and relativistic effects, the Hamiltonian of the system of electrons and the corresponding time independent wavefunction are:

$$H = -\frac{\hbar^2}{2m_e}\nabla_r^2 - \frac{Ze^2}{|\mathbf{r}|} \quad \rightarrow -\frac{\hbar^2}{2m_e}\sum_j \nabla_j^2 - Ze^2\sum_j\frac{1}{r_j} + \sum_{i>j}\frac{e^2}{r_{ij}}$$

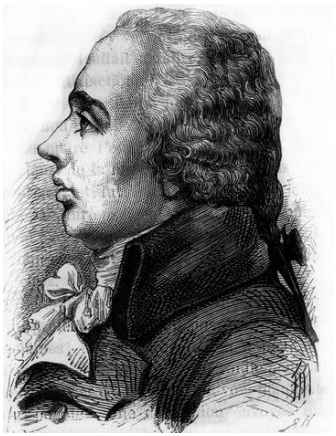
$$\left(-\frac{\hbar^2}{2m_e}\sum_j \nabla_j^2 - Ze^2\sum_j\frac{1}{r_j} + \sum_{i>j}\frac{e^2}{r_{ij}}\right)\psi = E\,\psi$$

Even in such multi-electron systems, it is useful to consider single electron states, assuming that each electron moves in the potential of the nucleus plus the averaged potential due to the other *N-1* electrons (self-consistent field approximation). When this averaged potential is assumed to be spherically symmetric, each electron feels a Coulomb-like, central potential representing the nuclear charge shielded by the other electrons. This is the central field approximation, useful as a starting point for treating electron interactions as perturbations.

Wave functions of one electron in a central field.

As in classical mechanics, a central potential implies conservation of angular momentum, $[H, L_z] = [H, \boldsymbol{L}^2] = 0$. If H depends only on the magnitude of $\mathbf{r}$, we can *separate the spatial dependence* into radial and an angular factors. In spherical coordinates,

$$\left[-\frac{\hbar^2}{2}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{\mathbf{L}^2}{2\mu r^2}-\frac{Ze^2}{r}\right]\psi(r,\vartheta,\varphi) = E\psi(r,\vartheta,\varphi)$$



Adrien-Marie Legendre
1752-1833

with $\psi(r,\theta,\varphi) = \mathcal{R}(r)\, Y(\theta,\varphi)$.

The functions $Y(\theta,\varphi)$ are the spherical harmonics, $Y_{lm}(\theta,\varphi) = \left[\frac{(l-|m|)!}{(l+|m|)!}\,\frac{2l+1}{4\pi}\right]^{\frac{1}{2}}(-1)^{\frac{m+|m|}{2}}P_l^{|m|}(\cos\theta)e^{im\varphi}$

where P_l^m is the associated Legendre function, and l, m are the azimuthal quantum number and the magnetic quantum number, both are integers. Orthonormality condition:

$\int Y^*_{l'm'}(\theta,\varphi)Y_{lm}(\theta,\varphi)\, d\Omega = \delta_{l,l'}\delta_{m,m'}$

The spherical harmonics are eigenfunctions of the orbital angular momentum operator $\mathbf{L} = \mathbf{r}\times\mathbf{p}$:

$\mathbf{L}^2\, Y_{lm}(\theta,\varphi) = \hbar^2 l(l+1)\, Y_{lm}(\theta,\varphi)$

$\boldsymbol{L_z}\, Y_{lm}(\theta,\varphi) = \hbar\, m Y_{lm}(\theta,\varphi)$

The values of l are $l =$ 0,1,2 … called s states, p states, d states, and so on . The value of m ranges from $-l$ to $+l$ in integer steps.

We see that the eigenvalues of the Hamitonian do not depend on m.

The angular eigenfunctions are independent of the form of the potential, as long as it is a central one (spherically symmetric).

Legendre polynomials, defined for $-1 \leq x \leq 1$:

$$P_n(x) = (2^n n!)^{-1} \frac{d^n}{dx^n}[(x^2-1)^n]$$

Orthogonality property: $\int_{-1}^{1} P_n(x)\, P_m(x) = \frac{2}{2n+1}\delta_{nm}$

Associated Legendre polynomials:

For $0 \leq m \leq l$ $\quad P_l^m(u) = (1-u^2)^{\frac{m}{2}} \frac{d^m}{du^m} P_l(u) =$

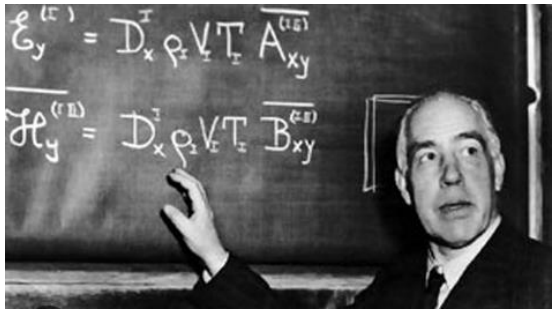
$$= \frac{(-1)^l}{2^l l!}(1-u^2)^{m/2} \frac{d^{l+m}}{du^{l+m}}(1-u^2)^l$$

This definition is extended to negative values of m:

$$P_l^{-m}(u) = (-1)^m \frac{(l-m)!}{(l+m)!} P_l^m\,(u)$$

The radial part of the wavefunction satisfies the equation

$$\left[-\frac{\hbar^2}{2}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{\hbar^2 l(l+1)}{2\mu r^2}-\frac{Ze^2}{r}\right]\mathcal{R}(r)=E\mathcal{R}(r)$$



Niels H.D. Bohr, 1885-1962

Defining $\mathcal{R}(r)=X(r)/r$ (*)

$$\left[-\frac{\hbar^2}{2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{\hbar^2 l(l+1)}{2\mu r^2}-\frac{Ze^2}{r}\right]X(r)=EX(r)$$

Notice that $\frac{\hbar^2 l(l+1)}{2\mu r^2}-\frac{Ze^2}{r}$ represents an effective nuclear potential shielded by the centrifugal force of the electron if $l\neq 0$.

We see that $X(r)$ depends on l but not on m. Boundary condition: $X(r)\to 0$ as $r\to 0$ ($because\ V(0)\to\infty$)

The solutions of the radial equation are *analytical* and can be written with the associate Laguerre polynomials $\mathcal{L}$.

They are labeled with the values of the principal quantum number n and the orbital quantum number l:

$$X_{n,l}(r)=-\left\{\frac{Z(n-l-1)!}{n^2[(n+l)!]^3}\right\}\rho^{l+1}e^{-\frac{\rho}{2}}\mathcal{L}_{n+l}^{2l+1}(\rho)$$

Rydberg constant=12.6 eV

where $\rho=\frac{2Zr\mu}{n\,a_0 m_e}$ and with $\boxed{E_n=-\mu c^2 Z^2\alpha^2/2n^2=-\frac{\mu}{m}\mathrm{R}_\infty\frac{Z^2}{n^2}}$ $\alpha=\frac{e^2}{\hbar c}$, $a_0=\frac{\hbar}{m_e c\alpha}$ = Bohr radius (innermost H orbit)~5×10^{-13}cm

The radial functions normalization is: $\int_0^\infty X_{nl}(r)X_{n'l'}(r)=\delta_{n'n}$.

In addition to these discrete eigenfunctions, there is also a continuous set of eigenfunctions correponding to unbound states.

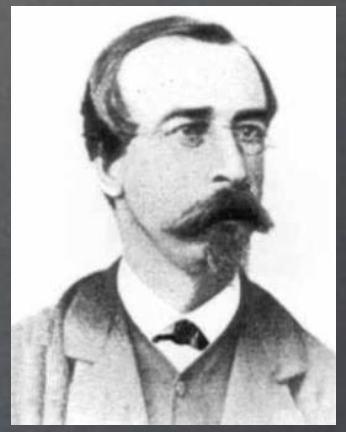
(*) Note. In the Rybicki Lightman book, $R(r)$ is what we call $X(r)$.

Laguerre polynomials, defined for $-1 \leq x \leq 1$:

$$\mathcal{L}_n(x) = \frac{e^x}{n!}\frac{d^n}{dx^n}[e^{-x}x^n] \qquad n = 0,1,2,3 \ldots$$

Associated Laguerre polynomials:

$$\mathcal{L}_n^{(\alpha)}(x) = \frac{x^{-\alpha}e^x}{n!}\frac{d^n}{dx^n}[e^{-x}x^{n+\alpha}]$$



Edmond Nicholas Laguerre
1834-1886

The quantity $X_{nl}^2 = \mathcal{R}_{nl}^2 \; r^2$ is the probability that the electron is between r and $r + dr$.

Including the electron spin, the time-independent electron wavefunction is defined by four quantum numbers related by:

$n = 1,2,3 \ldots$	$\rightarrow$ *energy*
$l = 0, \ldots, n-1$	$\rightarrow$ *shape*
$m_l = -l, -l+1, \ldots, l-1, l$	$\rightarrow$ *orbital orientation*
$m_s = \pm\frac{1}{2}$	$\rightarrow$ *spin orientation*

$$\psi(\mathbf{q}) = \chi_{s,m_s}\Psi_{n,l,m_l}(\boldsymbol{r}) = \chi_{s,m_s}\mathcal{R}_{n,l}(r)Y_{l,m_l}(\theta,\varphi)$$

The electron spatial wavefunctions are then defined by four quantum numbers, n, l, m, m_s.

All these states are degenerate in the central field approximation, since the eigenvalues of the Hamiltonian depend on n only.

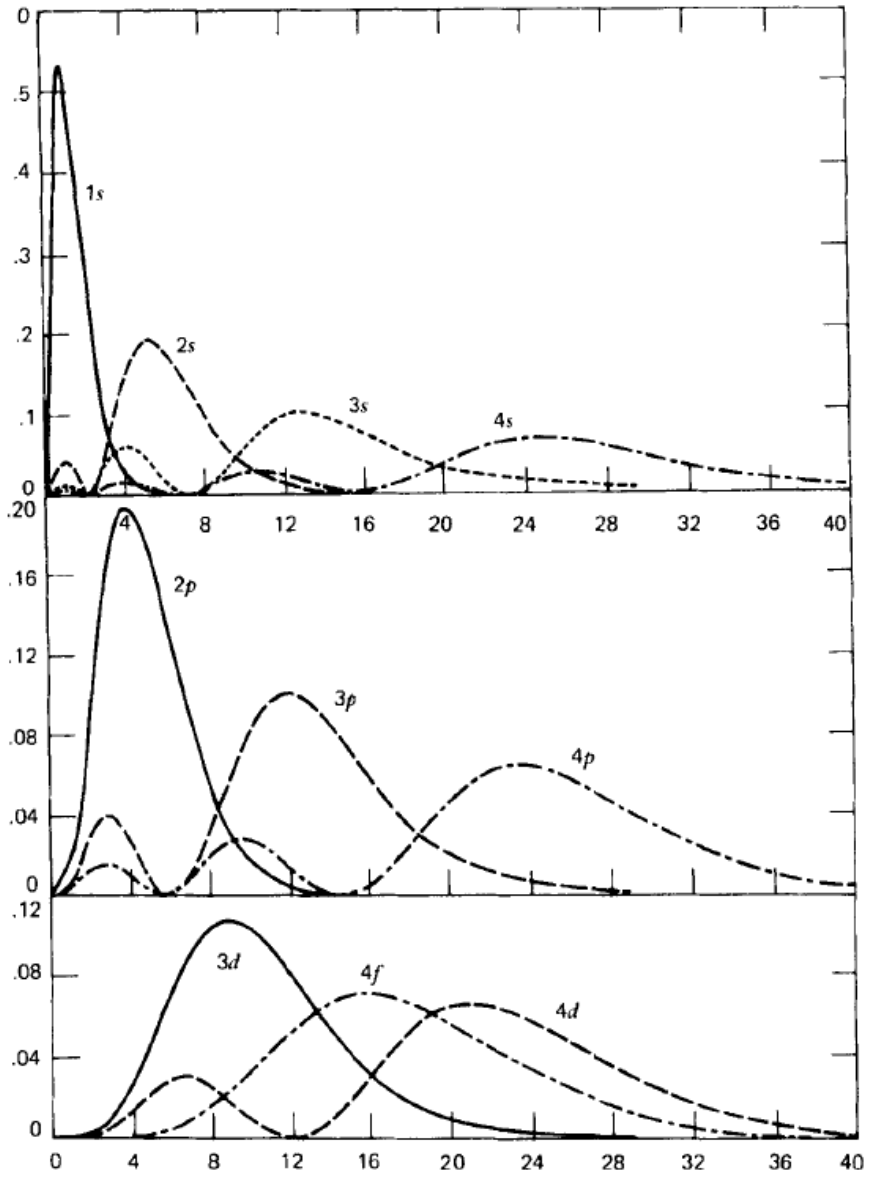


Figure 9.1 Radial probability distribution for an electron in several of the lowest levels of hydrogen. The abscissa is the radius in atomic units. (Taken from Condon, E. and Shortley, G. 1963, The Theory of Atomic Spectra, Cambridge, Cambridge University Press.)

The general solution for the Hydrogen-like atom is (for $\mu \approx m_e$):

$$\Psi_{n,l,m}(r,\theta,\varphi) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n(n+l)!}}\, e^{-\frac{Zr}{a_0 n}} \left(\frac{2r}{na_0}\right)^l \mathcal{L}_{n-l-1}^{2l+1}(2r/na_0)\, Y_{lm}(\theta,\varphi)$$

Examples:

$$\Psi_{1,0,0}(r,\theta,\varphi) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$$

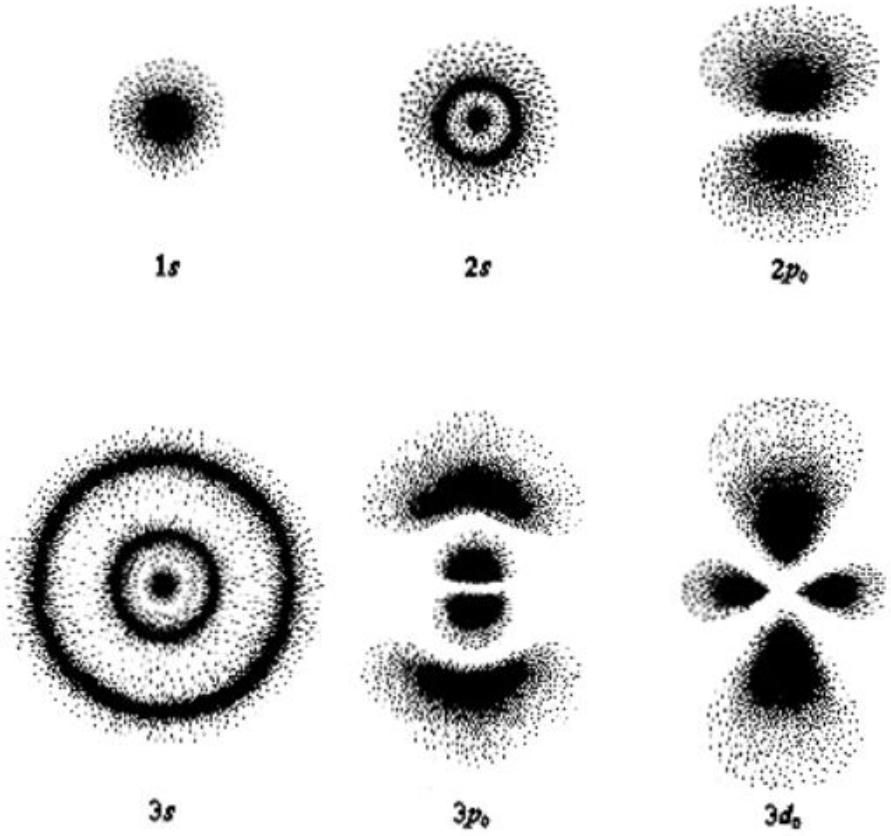
$$\Psi_{2,0,0}(r,\theta,\varphi) = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2-\frac{Zr}{a_0}\right) e^{-Zr/2a_0}$$

s orbitals

$$\Psi_{2,1,0}(r,\theta,\varphi) = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \frac{Zr}{a_0}\, e^{-Zr/2a_0} \cos\theta$$

$$\Psi_{2,1,\pm1}(r,\theta,\varphi) = \frac{1}{8\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \frac{Zr}{a_0}\, e^{-Zr/2a_0} \sin\theta\, e^{\pm i\varphi}$$

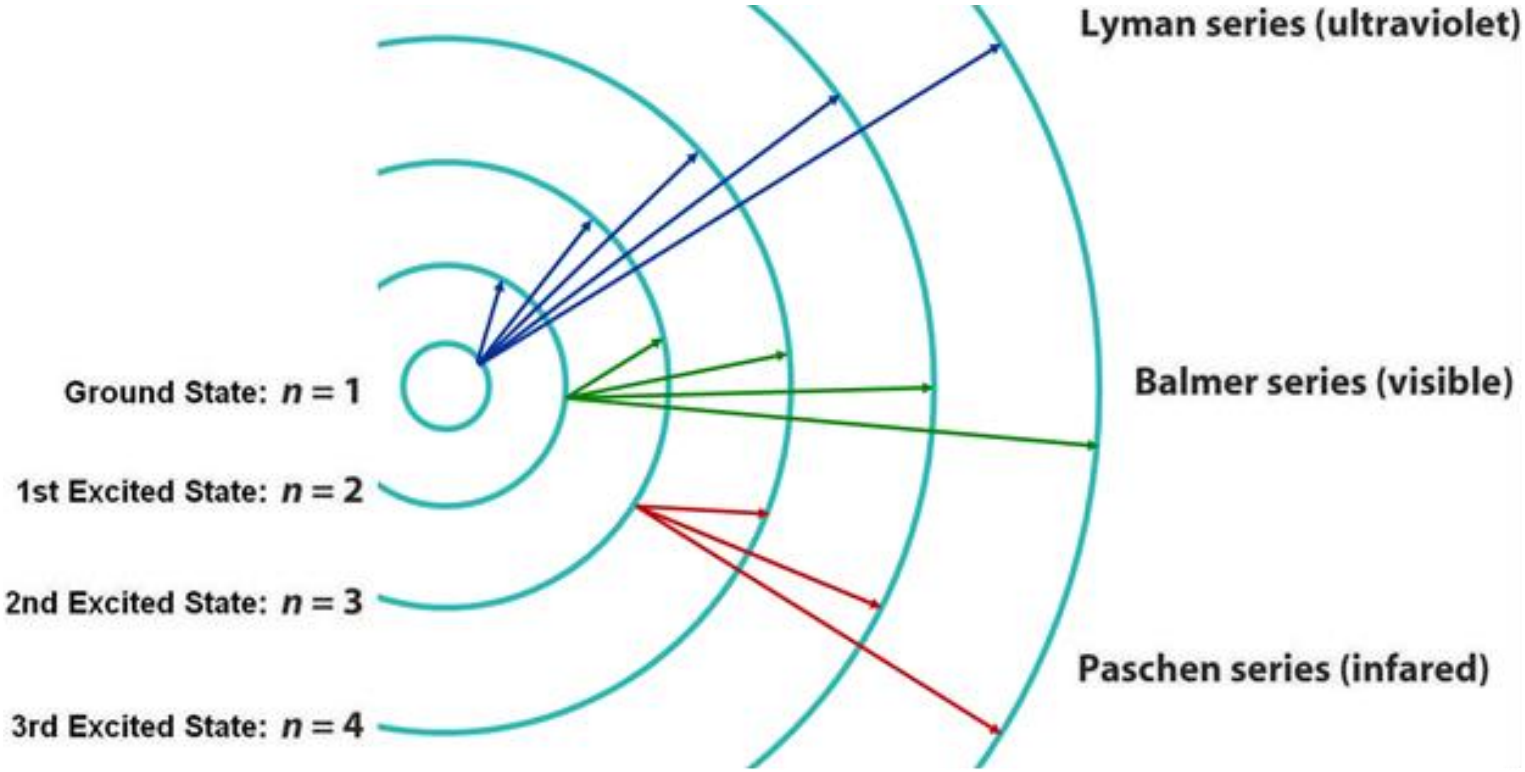
p orbitals

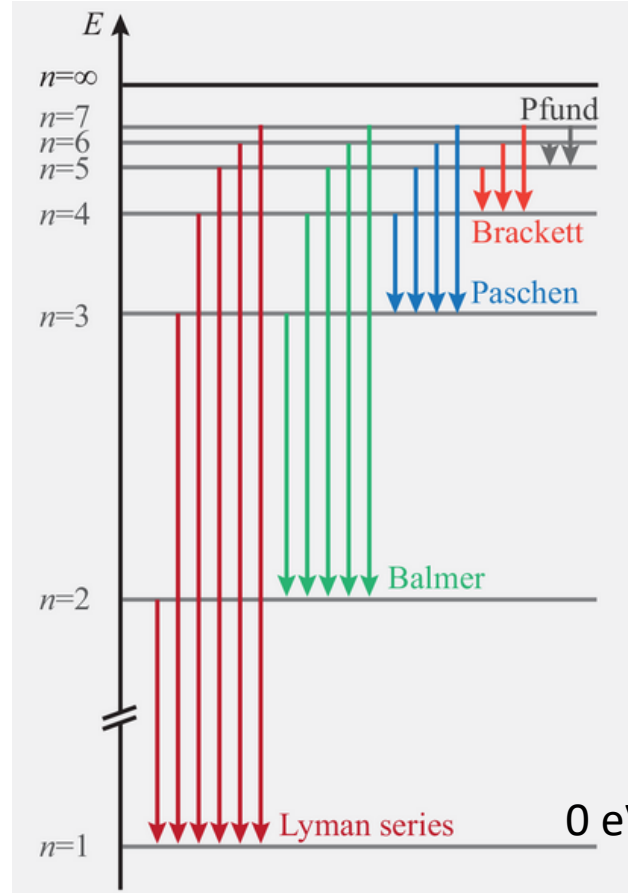


At the origin, $r \to 0$ the radial wavefunction $\mathcal{R}_{nl}(r)$ vanishes for $l > 0$, and goes to a finite constant for $l = 0$ (s *orbitals*) .

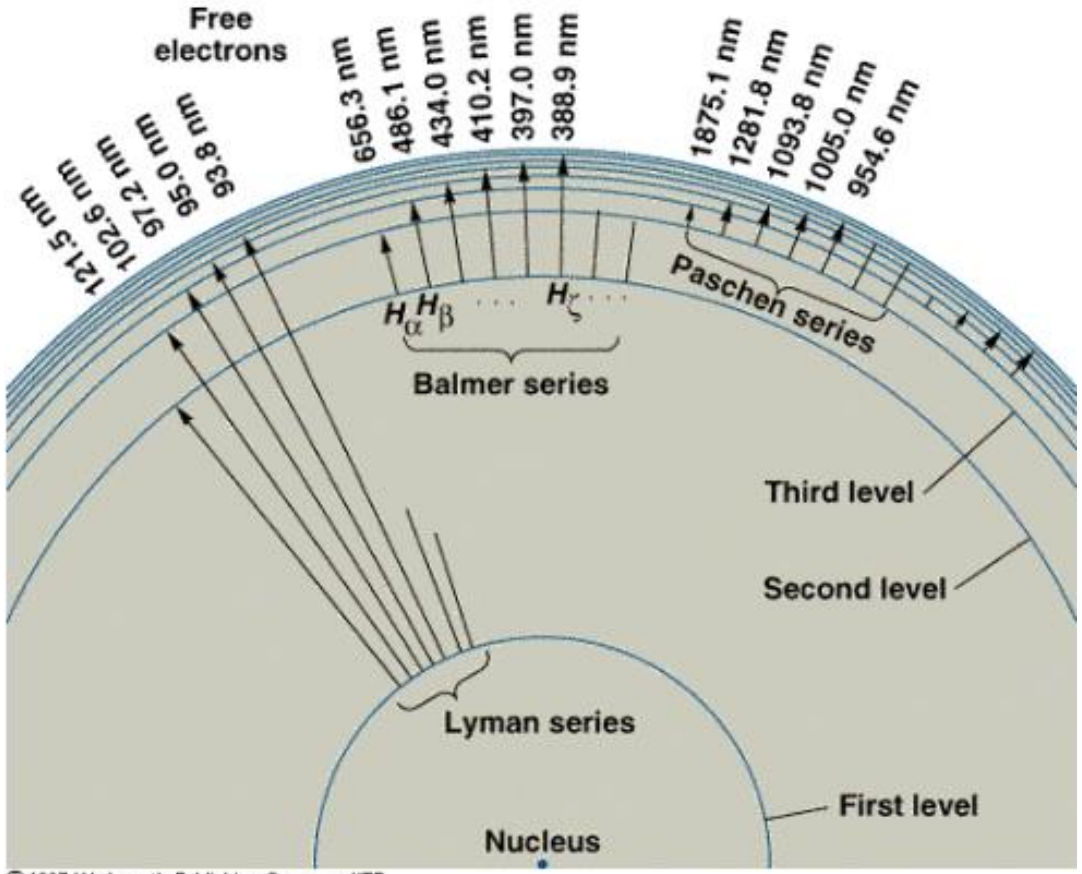
However, the corresponding probability of finding the electron in the origin between $r = 0$ and $r = 0 + dr$, is proportional to $|\mathcal{R}_{nl}(r)|^2\, r^2 dr = X_{nl}^2\, dr$ and it is null also for s orbitals.

Atomic Hydrogen spectrum





Atomic Hydrogen spectrum



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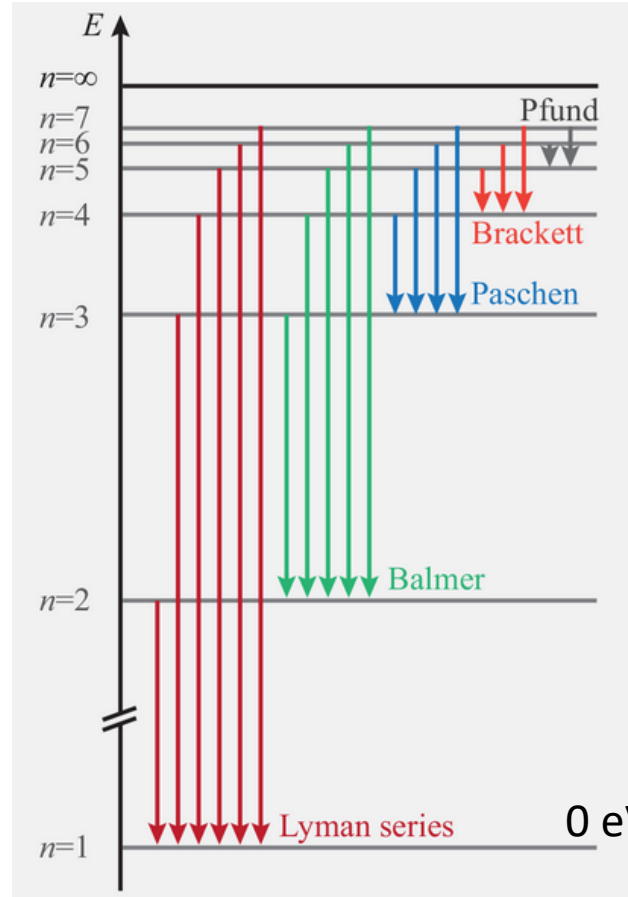
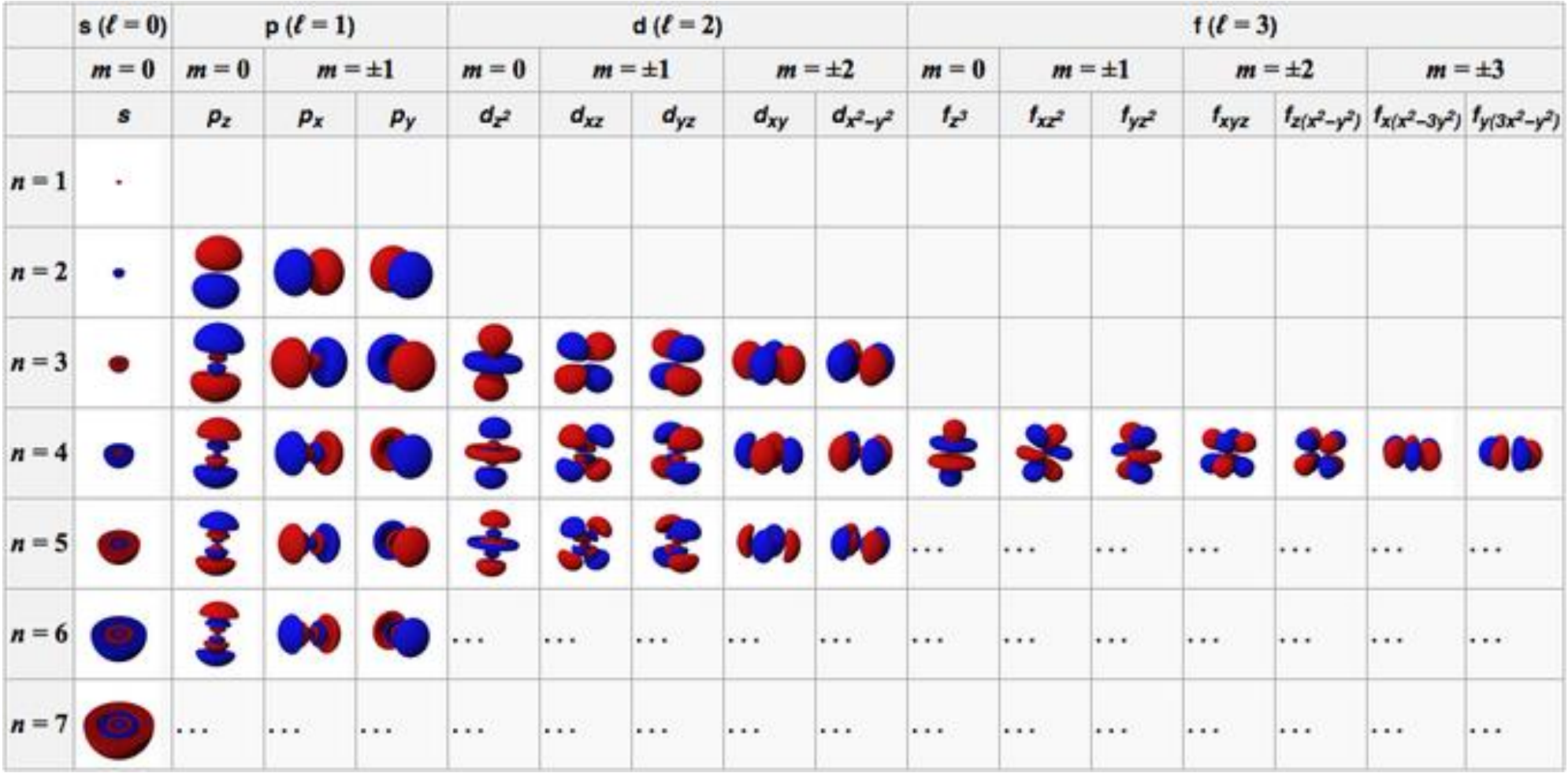




Relationship between three of the four quantum numbers to the orbital shape of simple electronic configuration atoms up through Radium (Ra, atomic number 88). The fourth quantum number, the spin, is a property of individual electrons within a particular orbital. Each orbital may hold up to two electrons with opposite spin directions.

Fine structure of Hydrogenic atoms

The fine structure describes the splitting of the atomic energy levels due to electron spin and relativistic corrections to the Hamiltonian. For hydrogenic atoms, the gross structure energy levels only depend on n. Introducing relativistic and spin effects, we break the degeneracy of the E_n.

Relativistic corrections. In the Hamiltonian $H = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{Ze^2}{\boldsymbol{r}} = \frac{p^2}{2m_e} + V(r)$, we replace the kinetic term $\frac{p^2}{2m_e}$ with its **relativistic expression**:

$E_{Kinetic} = m_e c^2\gamma - m_e c^2 = m_e c^2(\gamma - 1) \approx \frac{p^2}{2m_e} - \frac{p^4}{8m_e^3c^2} + \ldots$ and we consider the term in p^4 as a perturbation to the Hamiltonian:

$H_1 = -\frac{p^4}{8m_e^3c^2}$. The first order energy corrections due to relativistic effect are then $E_n^{(1)} = \langle\psi_0|H_1|\psi_0\rangle = -\frac{E_n^2}{2m_ec^2}\left(\frac{4n}{l+1/2} - 3\right)$

The order of magnitude of this correction is -9.056×10^{-4} eV.

Spin-orbit coupling. Also called LS coupling or Russell-Saunders coupling. In the ERF, the nucleus orbits around the electron, generating an effective **current loop** and thus a magnetic field **B**. This interacts with the electron magnetic moment $\boldsymbol{\mu}_s$(due to the spin, intrinsic angular momentum), producing an energy correction of the form: $H_{SO} = Ze^2\left(\frac{1}{2m_e^2c^2}\right)\frac{\mathbf{L}\cdot\mathbf{S}}{r^3}$

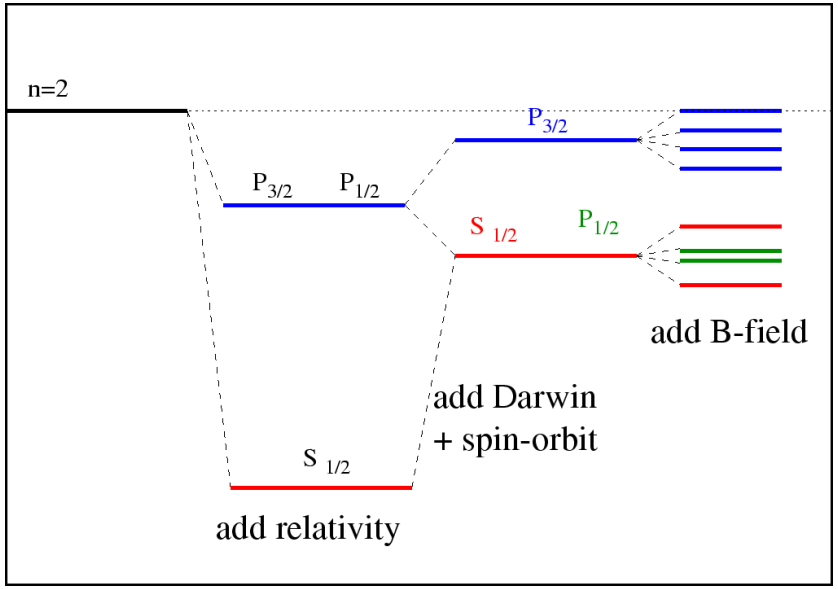
Noting that $\mathbf{J}^2 = (\mathbf{L}+\mathbf{S})\cdot(\mathbf{L}+\mathbf{S}) = \mathbf{L}^2 + \mathbf{S}^2 + 2\mathbf{L}\cdot\mathbf{S}$, $H_{SO} \propto (\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2)$

$E_{SO} = \frac{E_n^2}{m_ec^2}\, n\, \frac{j(j+1)-l(l+1)-3/4}{l\left(l+\frac{1}{2}\right)(l+1)}$ The order of magnitude of this corrections is $E_{SO} \sim \frac{Z^4}{n^3(j+\frac{1}{2})}10^{-5}$ eV

Darwin term

In a relativistic treatment of an electron, its Compton wavelength is relevant, being the shortest distance an electron can be physically localized. We can imagine it as if the electron is not point-like, but it is like a "ball" with radius of the order of its Compton wavelength, $\frac{\hbar}{m_e c} = 0.0243\text{Å}$. The potential energy by the nucleus is obtained as a weighted integral over the «extended» electron.

It affects only the s orbitals, because it is proportional to $\delta(\mathbf{r})$, but the wavefunction of an electron with $l > 0$ vanishes at the origin, thus the delta function has no effect. The correction Hamiltonian term is $H_{Darwin} = \frac{\hbar^2}{8m_e^2c^2}\nabla^2 V$. The Darwin correction is $E_{n,Darwin} = \frac{2n}{m_e c^2}E_n^2$. E.g. the energy difference introduce by this effect between the 2s and the 2p orbitals (otherwise degenerate) is of the order of 9×10^{-5} Ev.



The eigenvalues E_n of the *zeroth order* Hamiltonian are n^2 degenerate. E.g, the $n = 3$ level contains 9 orbitals (one 3s orbital, three 3p orbitals, five 3d orbitals), all with the same energy.

The fact that energy eigenvalues of a hydrogenlike atom - in non relativistic description - depend only on n and not on l is referred to as **accidental degeneracy.**

Many-electron systems

Statistics: the Pauli's principle

A set of single-particles states, specified by (n, l, m, m_s) is called orbital. An atom or ion with a single electron can have its electron in any of the allowed orbitals or wave functions. To construct the states of a whole system of multi-electron atoms, let us indicate with $a, b, c \ldots k$ the sets of values (n, l, m, m_s) and with 1,2,…N the space and spin coordinates for the 1°,2°,…, Nth particle. Be u the product of a spatial wavefunction with the spin part. We want to have a complete set (a basis) of functions to represent the whole system. It is clear, that a simple product as $u_a(1)\, u_b(2)\, u_c(3) \ldots u_k(N)$ fails to account for the Principle of Identity (e.g. the state $u_a(1)\, u_b(2)$ is undistinguishable from the state $u_a(2)\, u_b(1)$).

We can then build an antisymmetrized linear combination of those products of orbitals, conveniently written as the Slater determinant:

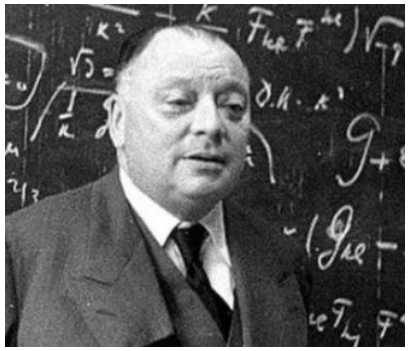
$N!$ permutations of the particles among the orbitals

$$\frac{1}{\sqrt{N!}} \begin{vmatrix} u_a(1) & u_a(2) & u_a(3) & \ldots & u_a(N) \\ u_b(1) & u_b(2) & u_b(3) & \ldots & u_b(N) \\ \vdots & & & & \\ u_k(1) & u_k(2) & u_k(3) & \ldots & u_k(N) \end{vmatrix} = \text{Basis states for the system}$$

In this form, when two electrons occupy the same orbital, the determinant vanishes ⇒

Pauli's principle: no two electrons can occupy the same orbital.

Particles with this symmetry for their wavefunctions are called fermions. There is complete antisymmetry of the total wavefunction under interchange of two particles (=interchange of two columns of the above determinant changes the determinant sign).



W. Pauli, 1900-1958

Configurations

Implementing the Pauli's priciple corresponds to writing Schroedinger equation for each orbital, which contain two types of potential:

1) a term representing the electrostatic potential of the nucleus and of the averaged charge density of all other electrons;

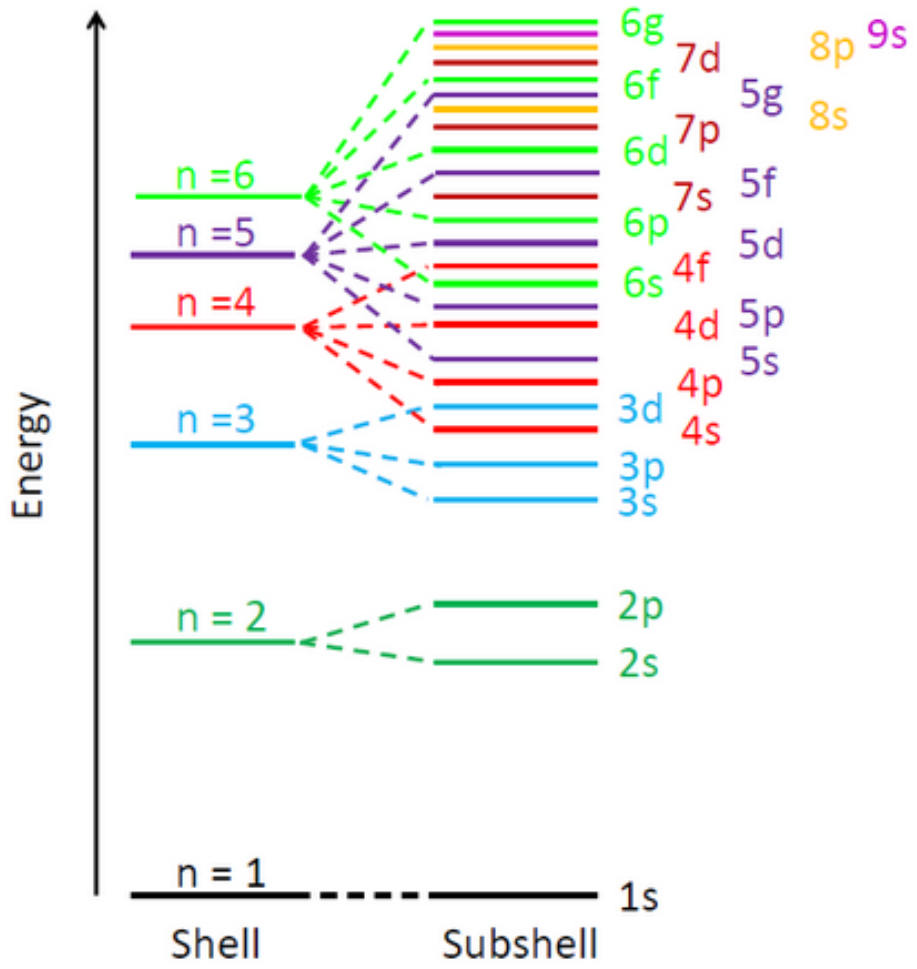
2) a term with no classical analogue, called exchange potential, manifesting itself as an effective repulsion term between electrons with the same spin. It does not correspond to a real potential.

For **many** electrons atoms, for Pauli exclusion principle, there can be at most $2(2l+1)$ electrons in a given subshell nl:

- s subshell can contain at most 2 electrons
- p subshell can contain at most 6 electrons
- d subshell can contain at most 10 electrons.

The orbitals in order of increasing energy are $1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s$ and so on.

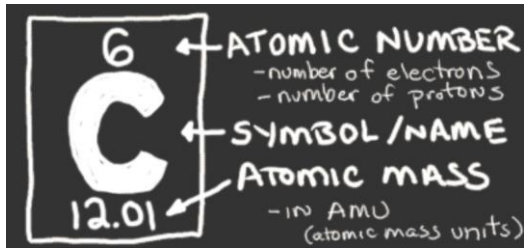
Filling the orbitals



More binding energy close to the nucleus

Closed shells not much influenced by changes in the outer, partially filled shells. We usually specify the configuration of the outer shell only, mostly affected by radiative transitions (at least at optical frequencies)

Example. The atomic Carbon, with 6 electrons, has a ground state configuration with 2 electrons in the 1s subshell, 2 electrons in the 2s, and the remaining electrons in the 2p subshell. This is designated as $1s^2 2s^2 2p^2$. *or* (He) $2s^2 2p^2$



	Element		Electron configuration ($3d^5$ = five $3d$ electrons, *etc.*)	Ground state $^{2S+1}L_J$	Ionization energy (eV)
1	H	Hydrogen	$1s$	$^2S_{1/2}$	13.5984
2	He	Helium	$1s^2$	$^1S_0$	24.5874
3	Li	Lithium	(He) $2s$	$^2S_{1/2}$	5.3917
4	Be	Beryllium	(He) $2s^2$	$^1S_0$	9.3227
5	B	Boron	(He) $2s^2$ $2p$	$^2P_{1/2}$	8.2980
6	C	Carbon	(He) $2s^2$ $2p^2$	$^3P_0$	11.2603
7	N	Nitrogen	(He) $2s^2$ $2p^3$	$^4S_{3/2}$	14.5341
8	O	Oxygen	(He) $2s^2$ $2p^4$	$^3P_2$	13.6181
9	F	Fluorine	(He) $2s^2$ $2p^5$	$^2P_{3/2}$	17.4228
10	Ne	Neon	(He) $2s^2$ $2p^6$	$^1S_0$	21.5645
11	Na	Sodium	(Ne) $3s$	$^2S_{1/2}$	5.1391
12	Mg	Magnesium	(Ne) $3s^2$	$^1S_0$	7.6462
13	Al	Aluminum	(Ne) $3s^2$ $3p$	$^2P_{1/2}$	5.9858
14	Si	Silicon	(Ne) $3s^2$ $3p^2$	$^3P_0$	8.1517
15	P	Phosphorus	(Ne) $3s^2$ $3p^3$	$^4S_{3/2}$	10.4867
16	S	Sulfur	(Ne) $3s^2$ $3p^4$	$^3P_2$	10.3600
17	Cl	Chlorine	(Ne) $3s^2$ $3p^5$	$^2P_{3/2}$	12.9676
18	Ar	Argon	(Ne) $3s^2$ $3p^6$	$^1S_0$	15.7596
19	K	Potassium	(Ar) $4s$	$^2S_{1/2}$	4.3407
20	Ca	Calcium	(Ar) $4s^2$	$^1S_0$	6.1132
21	Sc	Scandium	(Ar) $3d$ $4s^2$	$^2D_{3/2}$	6.5615
22	Ti	Titanium	(Ar) $3d^2$ $4s^2$	$^3F_2$	6.8281

Electrostatic interaction; LS coupling and terms.

In the multi-electron atom with nucleus $+Ze$, we add the Coulomb repulsive energy between the electrons and the spin effects. The Hamiltonian of the system of electrons and the corresponding time independent wavefunction are (neglecting relativistic corrections):

$$H = \underbrace{\frac{\hbar^2}{2m_e}\sum_j \nabla_j^2}_{\text{kinetic}} - \underbrace{Ze^2 \sum_j \frac{1}{r_j}}_{\text{Coulomb field electron-nucleus}} + \underbrace{\sum_{i>j} \frac{e^2}{r_{ij}}}_{\text{Mutual electron repulsion}} + \underbrace{H_{so}}_{\text{Spin-orbit}} = \frac{\hbar^2}{2m_e}\sum_j \nabla_j^2 - Ze^2 \sum_j \frac{1}{r_j} + \underbrace{\sum_j V_j(r_j) - \sum_j V_j(r_j)}_{\pm\text{Central field potentials due to the smeared-out electrons}} + \sum_{i>j} \frac{e^2}{r_{ij}} + H_{so} = H_0 + H_1$$

where we have added and subtracted a term representing the effect of the averaged charge density of all other electrons. We regard this as a perturbative problem, with:

$$H_0 = \frac{\hbar^2}{2m_e}\sum_j \nabla_j^2 - Ze^2 \sum_j \frac{1}{r_j} + \sum_j V_j(r_j)$$ → electrons in effective central potentials

$$H_1 = \sum_{i>j} \frac{e^2}{r_{ij}} - \sum_j V_j(r_j) + H_{so} \equiv H_{es} + H_{so}$$ → perturbation describing the interactions between electrons and the spin-orbit.

The central field approximation assumes that the averaged potential $V_j(r_j)$ is spherically symmetric, so that each electron feels a Coulomb-like, central potential, representing the nuclear charge shielded by the other electrons: *Shielded potential felt by single electron at* $r_j = -\frac{e^2}{r_j} + V_j(r_j)$.

Thus, H_0 is the zeroth-order Hamiltonian, whose **states and configurations** we have been discussing. Its eigenvalues are n^2 degenerate.

Focus on the perturbation term H_1 .

Residual electrostatic energy

The term $H_{es} = \sum_{i>j} \frac{e^2}{r_{ij}} - \sum_j V_j(r_j)$ is the residual electrostatic interaction between the electrons, after the averaged central field has been subtracted. We call it electrostatic interaction. To apply perturbation theory to degenerate eigenstates, we must choose a basis for our degenerate subspace that diagonalizes the perturbing Hamiltonian. Under the H_{es} interaction, the individual orbital angular momenta will not remain constant, although the total $\mathbf{L} = \sum_i \mathbf{l}_i$ and $\mathbf{S} = \sum_i \mathbf{s}_i$ will be constant. The perturbing Hamiltonian necessarily commutes with $\mathbf{L}$ and $\mathbf{L_z}$, as the total orbital angular momentum of electrons is not coupled to any other torque. Similarly, the perturbation commutes with $\mathbf{S}$ and $\mathbf{S_z}$.

So we choose the basis to be states with well defined quantum numbers L, S, M_l and M_s. The net effect of the perturbation is to split the configurations into terms of well defined L and S. These terms are still degenerate with respect to M_l and M_s, as there is no preferred direction for the atom.

In this framework, named *LS coupling*, or *Russell-Saunders* coupling, the electrostatic interaction is the dominant splitting source, and the remaining spin-orbit splitting is much smaller.

Hund's rules (based on Pauli's):

- terms with larger S have lower energy (large S implies alignment of individual spins: for Pauli's, electrons are further apart on average).
- for the same S, larger L have lower energy (large L implies alignment of individual l: for Pauli's, electrons are further apart, on average, when they orbit in the same direction). This effect is smaller than the preceding.

Spin-Orbit

In the all-electron system, the **total quantum numbers** for orbital L, spin S, and total J angular momenta are all good quantum numbers , which are conserved. The result of the Russell-Saunders approach is presented as an *atomic term symbol* , or *spectroscopic term,* which has the form:

$^{2S+1}\mathcal{L}_J$. At given L,S, energy can be splitted further due to Spin-Orbit coupling, $H_{SO} \propto \mathbf{S} \cdot \mathbf{L}$. It can be interpreted as in the ERF, the electron moving in a central electrostatic force field (by the shielded nuclear charge) perceives it as having a magnetic field $\mathbf{B} = -\frac{1}{c}\,\mathbf{v} \times \mathbf{E}$, interacting with its intrinsic magnetic moment.

The individual shift is proportional to J(J+1). Therefore,

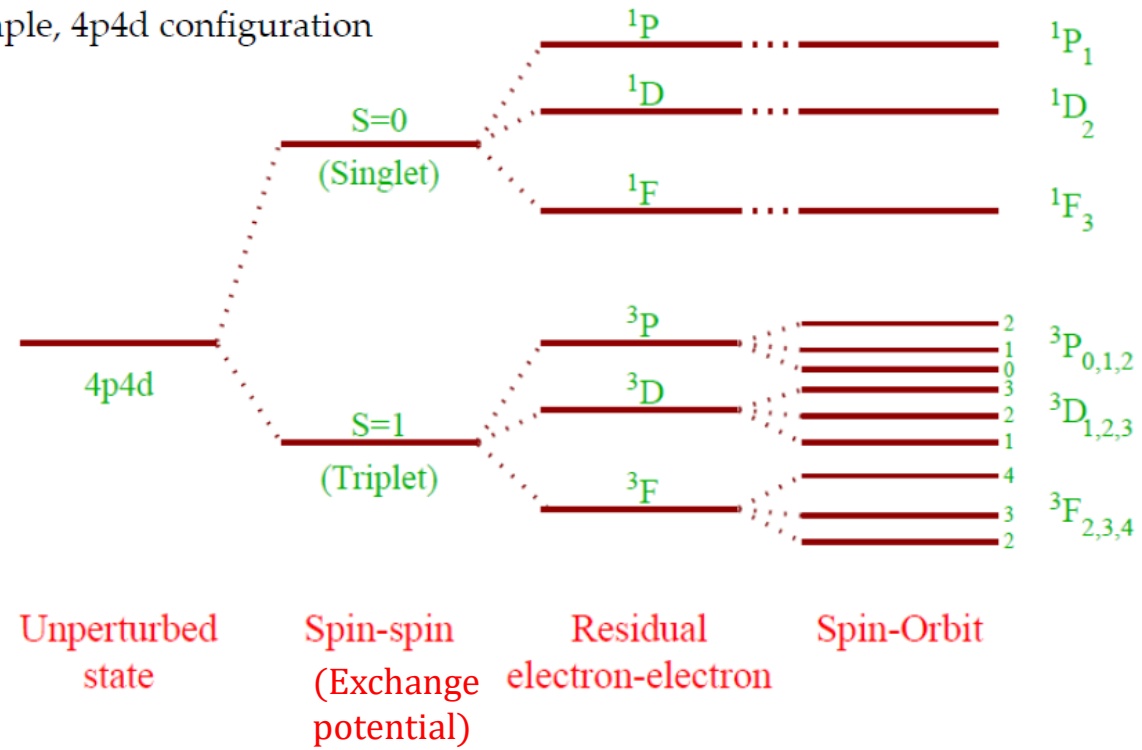
$E_{J+1} - E_J \propto C[(J+1)(J+2) - J(J+1)] = C(J+1)$

where $C > 0$ if shell less than half-full (normal term) and $C < 0$ if shell more than half-full (inverted term).

These levels can be splitted further in an external magnetic field, depending on the value of M_J, producing the *hyperfine* structure of the levels .

Hyperfine splitting also due to the electron magnetic moment interaction with the magnetic moment of the nucleus, which has its own spin.

Example, 4p4d configuration



Spectroscopic terms

An orbital n, l can contain $2(2l+1)$ electrons. If an orbital has more than one electron and less than $4l+1$ electrons, there is more than one way in which the spin and orbital angular momentum of the electrons can add. **LS** coupling vectorially adds the spin and orbital angular momenta, to give a total angular momentum **J**. Each allowed combination (L, S) is referred to as a term: ${}^{2S+1}\mathcal{L}_{\mathrm{J}}$.

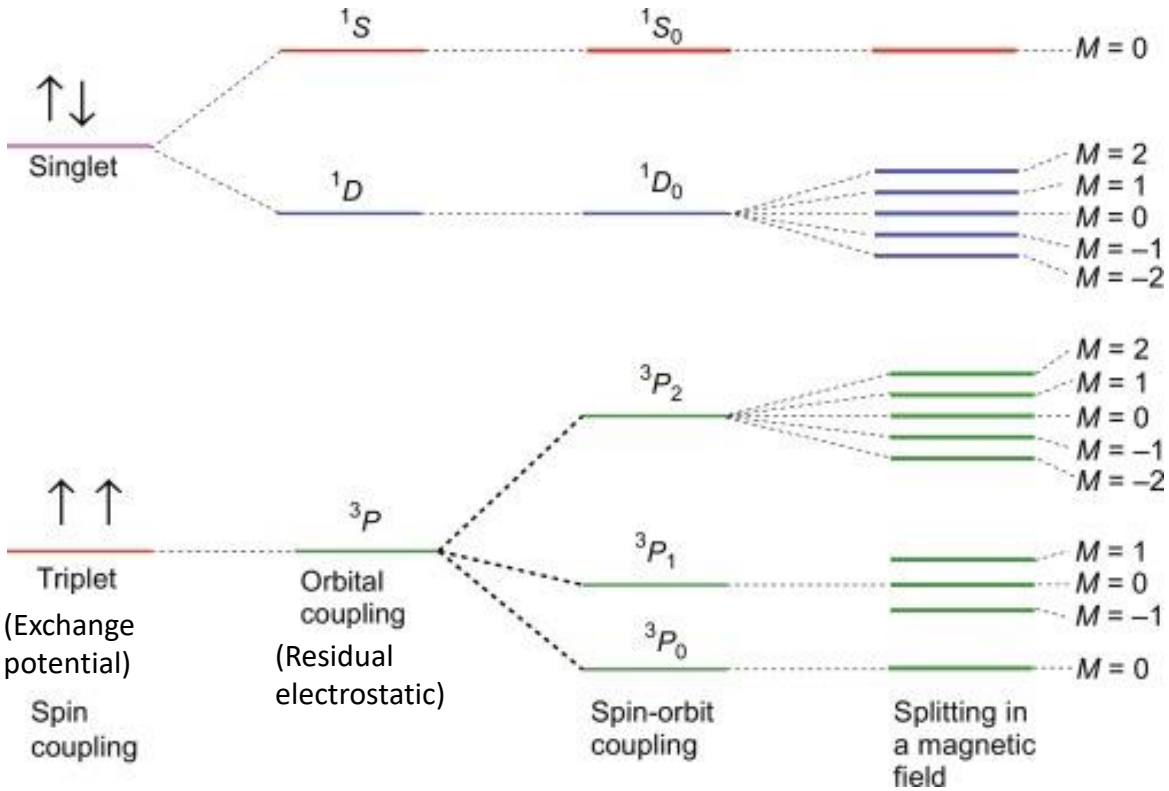
Different terms have significantly different energies (up to few eV).

When $L > 0$ and $S > 0$, there is more than ne way to add L and S to give **J**= **L**+**S**.

For given L, S, the allowed J values are $|L-S| \leq J \leq |L+S|$.

For example, the ^{3}P term $(S=1, L=1)$ can have $J = 0,1,2$, leading to fine structure spin-orbit splitting between the three different fine structure levels of the term: ${}^3\mathrm{P}_0$, ${}^3\mathrm{P}_1$, ${}^3\mathrm{P}_2$.

Because of the possibility of multiple values of J for a given (L,S), terms are also called multiplets (singlets, doublets, triplets etc, depending on the number of possible J values).



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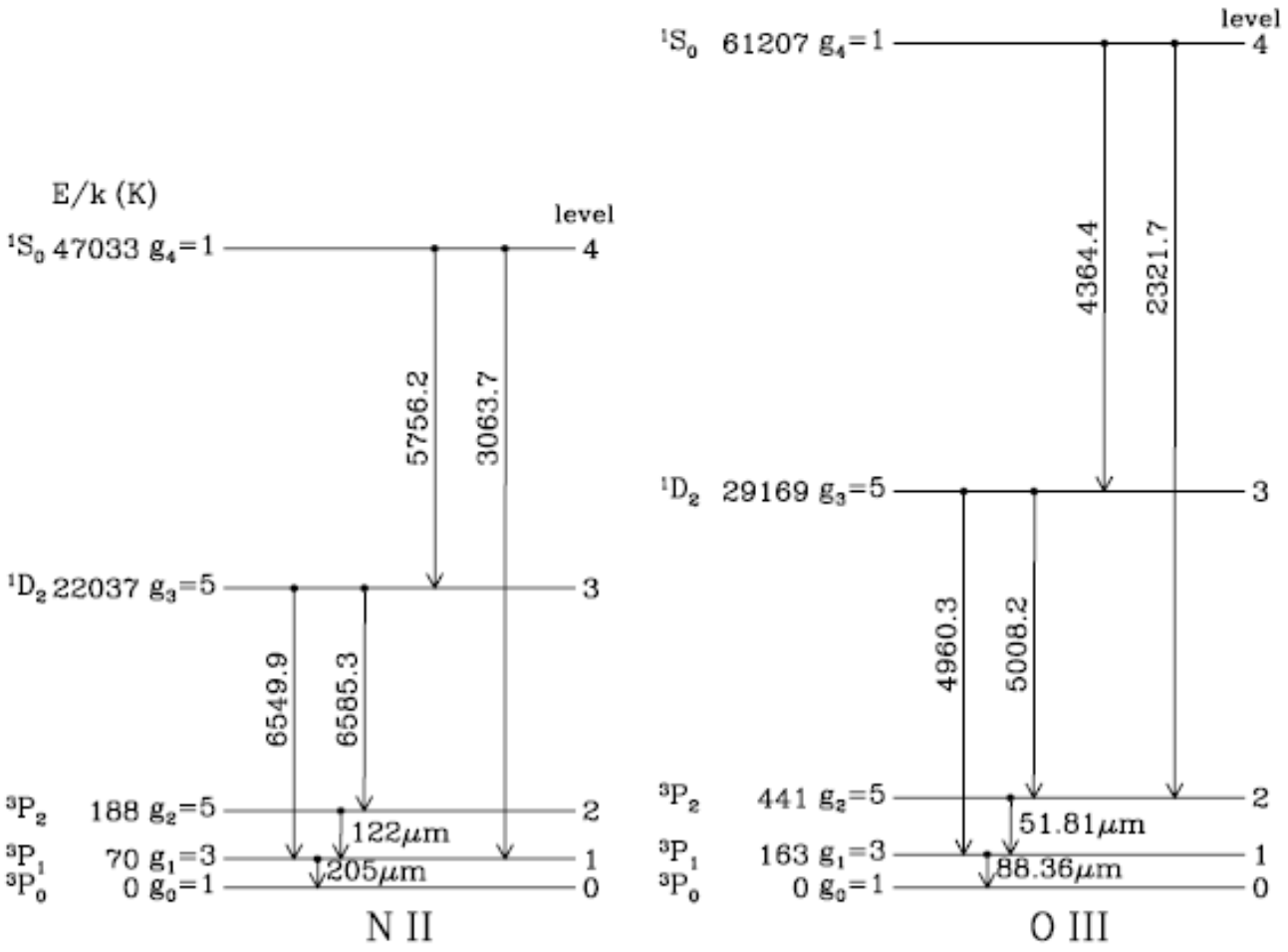
Terms for ns and np Subshells

Ground configuration	Terms (in order of increasing energy)	Examples
$\ldots ns^1$	${}^2\mathrm{S}_{1/2}$	H I, He II, C IV, N V, O VI
$\ldots ns^2$	${}^1\mathrm{S}_0$	He I, C III, N IV, O V
$\ldots np^1$	${}^2\mathrm{P}^{\mathrm{o}}_{1/2,3/2}$	C II, N III, O IV
$\ldots np^2$	${}^3\mathrm{P}_{0,1,2}$, ${}^1\mathrm{D}_2$, ${}^1\mathrm{S}_0$	C I, N II, O III, Ne V, S III
$\ldots np^3$	${}^4\mathrm{S}^{\mathrm{o}}_{3/2}$, ${}^2\mathrm{D}^{\mathrm{o}}_{3/2,5/2}$, ${}^2\mathrm{P}^{\mathrm{o}}_{1/2,3/2}$	N I, O II, Ne IV, S II, Ar IV
$\ldots np^4$	${}^3\mathrm{P}_{2,1,0}$, ${}^1\mathrm{D}_2$, ${}^1\mathrm{S}_0$	O I, Ne III, Mg V, Ar III
$\ldots np^5$	${}^2\mathrm{P}^{\mathrm{o}}_{3/2,1/2}$	Ne II, Na III, Mg IV, Ar IV
$\ldots np^6$	${}^1\mathrm{S}_0$	Ne I, Na II, Mg III, Ar III

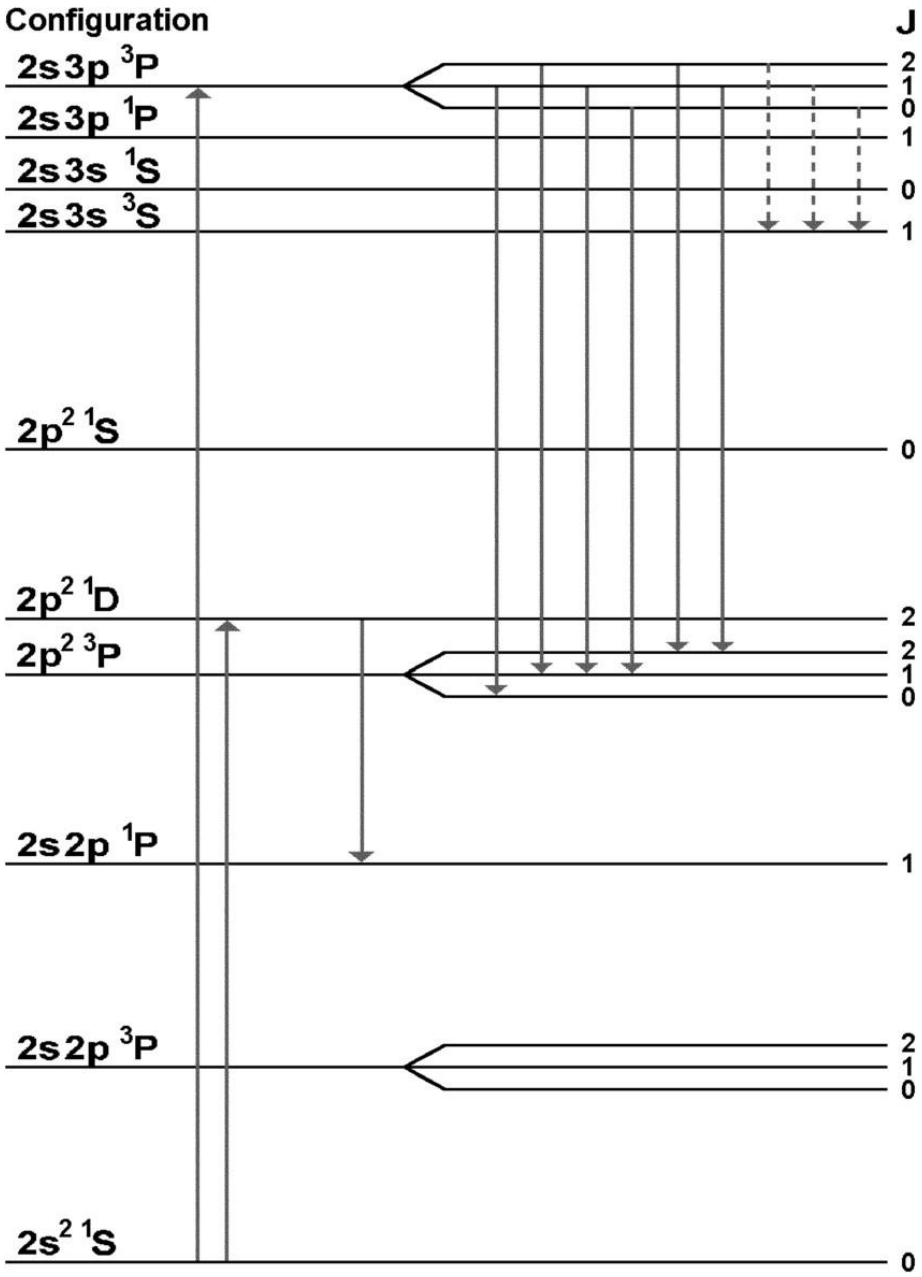
Fine-structure splitting for ^3P



Energy-level diagram for the ground configuration of the $2p^2$ ions N II and O III. (Fine-structure splitting is exaggerated for clarity.) Forbidden transitions connecting these levels are shown, with wavelengths in vacuo.

Table 2

Species	f	$\leftarrow$	i	λ(Å)	$A_{ul}(s^{-1})$	ΔJ	Parity†	ΔS	Δl
NII	$2p^2\ {}^3P_0^e$	$\leftarrow$	$2p3s\ {}^3D_1^o$	1084.0	2.18×10^8	-1	$o \rightarrow e$	0	-1
CIII]	$2s^2\ {}^1S_0^e$	$\leftarrow$	$2s2p\ {}^3P_1^o$	1908.7	114	$+1$	$o \rightarrow e$	-1	-1
[CIII]	$2s^2\ {}^1S_0^e$	$\leftarrow$	$2s2p\ {}^3P_2^o$	1906.7	0.0052	$+2$	$o \rightarrow e$	-1	-1



Allowed transitions for the 2s3p P and 2p D levels of the CIII ion. Upward lines indicate the excitation from the ground level and the downward lines the radiative transitions. Dotted lines represent emissions in the visible spectra and solid lines emissions in the VUV spectra.

Machida M., IEEE Trans. Plasma Sci. 33, 1961-1967

electron distribution. Using the vector $\mathbf{u}$ to define position relative to the center P of the electron, and letting $\rho(\mathbf{u})$ denote the position dependent charge density, we have

$$\widetilde{V}(\mathbf{r}) \;=\; \int_{\text{electron}} d^3\mathbf{u}\,\rho(\mathbf{u})\mathbf{\Phi}(\mathbf{r}+\mathbf{u})\,, \tag{2.4.26}$$

where, as shown in the Figure, $\mathbf{r}+\mathbf{u}$ is the position of the integration point, measured relative to the proton at the origin. It is convenient to write the charge density in terms of a normalized function ρ_0:

$$\rho(\mathbf{u}) \;=\; -e\,\rho_0(\mathbf{u}) \quad \rightarrow \quad \int_{\text{electron}} d^3\mathbf{u}\,\rho_0(\mathbf{u}) = 1\,, \tag{2.4.27}$$

which guarantees that the integral of ρ over the electron is indeed $(-e)$. Recalling that $-e\Phi(\mathbf{r}+\mathbf{u}) = V(\mathbf{r}+\mathbf{u})$ we now rewrite (2.4.26) as

$$\widetilde{V}(\mathbf{r}) \;=\; \int_{\text{electron}} d^3\mathbf{u}\,\rho_0(\mathbf{u})V(\mathbf{r}+\mathbf{u})\,. \tag{2.4.28}$$

This equation has a clear interpretation: the potential energy is obtained as a weighted integral of potential due to the proton over the extended electron. If the electron charge would be perfectly localized, $\rho_0(\mathbf{u}) = \delta(\mathbf{u})$ and $\tilde{V}(\mathbf{r})$ would just be equal to $V(\mathbf{r})$. We will assume that the distribution of charge is spherically symmetric, so that

$$\rho_0\,(\mathbf{u}) = \rho_0(u)\,. \tag{2.4.29}$$