Chapter 13: Atoms

13.1 Hydrogen-like states   (Fig. 13.5, 10, 14, 15, 16, 20, 23)

Ionic atom with 1 electron (-e) and a nucleus (+Z).

Note: force = - $Q_1 \cdot Q_2 / r^2$; potential energy = work = force * path = $\int dx \cdot F = Q_1 \cdot Q_2/r$

$V = -Z/r$, $T = p^2/2m_e = p_r{}^2/2m_e + \ell^2/2m_e r^2 = T_{rad} + T_{rot}$

In Cartesian coordinates: T is simple, V is complicated (1 over root);
In spherical coordinates: T looks complicated, V is simple.

$[\mathbf{V}(r) \cdot + \mathbf{T_{rad}}(r) + \ell^2(w)/2m_e r^2 - E] \cdot \psi(r,w) = 0$ (w = angles, 'Winkel' of electron position)

$\ell^2/2m_e r^2$ is the centrifugal potential, the centrifugal force is $\ell^2/m_e r^3$ (~mv^2/r):

Rule of variable separation: If the operator can be represented as a sum of terms of different variables, the eigenvalue is the respective sum, and the eigenfuction is a simple product.

Here a trick: to achieve separation of w and r, multiply with $2m_e r^2$:

$[2m_e r^2 (\mathbf{V}(r) \cdot + \mathbf{T_{rad}}(r) - E) + \ell^2(w)] \cdot \psi(r,w) = 0 \rightarrow \psi_{nlm} = R_{nl}(r) \cdot Y_{lm}(w)$

For (+Ze) – (–e) systems: $n = n_r + l$, n_r = no. of radial maxima , l = 0(s), 1(p), 2(d), 3(f) …

$E_{nl} = -Z^2 m_e/2n^2$; $<r>_{nl} = [3n^2 - l(l+1)]/2m_e Z$ (for low. levels of high-Z atoms: set $Z = Z_{eff}$)

$$R_{nl}(r) \sim \begin{cases} \text{large } r : \sim \exp(-r\sqrt{-2Em_e}) \\ \text{small } r : \sim r^l \end{cases}$$

(n = energy-, principal-, main-, Haupt- q.n.;
l = ang. mom., serial-, secondary-, Drall-, Neben- q.n.;
m = magnetic-, directional-q.n.;
m_e = mass of electron)

Spectrum: $h\nu = E_{nf,lf} - E_{ni,li}$ (i = initial, f = final; selection rule of Laporte $l_f = l_i \pm 1$) .

Note the differences between the physical concept of angular momentum ℓ, of its operator $\boldsymbol{\ell}$, its measurable or measured value $|\ell|$, and of the angular momentum quantum number *l*.

An s-orbital has its largest density in the nucleus, an s electron does not rotate, it is distributed in any direction from left to right through the nucleus. The highest orbital *point*-density is at the attractive nucleus. The largest amount of probability is in the outer spatial *shell*, about one order of magnitude less in each innermore spatial shell.

The outermost radial shell of an nl-orbital has number n with $r \sim n^2$. (For H-1s: *r* = 1.5 Bohr; $\sqrt{\langle r^2 \rangle} = \sqrt{3} = 1.75$ Bohr; $r_{max} = 1$ Bohr). The innermost spatial shell has main quantum number $l+1$.

The *real* linear combinations have *l* angular nodes. The subscript index represents the main Cartesian power of the angular behavior, for instance: $d_{z^2} \sim (2z^2 - x^2 - y^2)/r^2$. Any real function has zero average for all angular momentum components; only complex functions have non-vanishing ℓ_i and μ_i (magnetic moment).

13.2 Neutral many-electron atoms

$E_{nl} = -Z_{eff}{}^2/2(n-\delta_l)^2$ $<r>_{nl} \approx n^2/Z \cdot (n+l)$ (a very rough rule of thumb)

Z_{eff} = Z – no. of "inner" electrons – no. of "same" electrons / 3   (Fig. 13.21, 22)

δ_l = quantum defect: for s ~ 1, for p ~ ½   (screening, penetration or diving effect)
Concerning ionic or innermore orbitals, the energy order is less l-dependent (as in hydrogen).

Order of (shell and subshell) orbital ("one electron") *energies* in neutral! atoms with Z values

1-2	3-10	11-18	19-36	37-54	55-86	87-118 = Z
1s <<	2s<2p <<	3s<3p <<	3d≈4s<4p <<	4d≈5s<5p <<	4f≈5d≈6s<6p <<	5f≈6d≈7s<7p

Note: in cations, the higher the charge, the more hydrogen-like the order, $(n-1)f < nd < (n+1)s$.

Order of (shell and subshell) orbital *radii* : increase with n, and then with *l* (for valence orbitals note: $2s \approx 2p$, $ns < np$; $3d < 4s$, $nd \leq (n+1)s$; $4f < 5s$, $nf \approx (n+1)s$: secondary periodicity in the PS). If there are many occupied orbitals, the density minima of some of them are filled by the maxima of the others: the total density decreases very smoothly without pronounced visible radial shell structure. Valence density is very small. The x-ray experiment "sees" the electron density maximum at the nucleus.

13.3 The independent particle or orbital approximation

V contains Z–e attraction, and
e_1–e_2 Repulsion: $+1/\sqrt{(x_1-x_2)^2 + (y_1-y_2)^2 + (z_1-z_2)^2} \rightarrow$ no variable separation possible

Orbital-model: $\Psi(x_1,y_1,z_1,\theta_1,x_2,y_2,z_2,\theta_2) \approx R_a(r_1) \cdot Y_a(w_1) \cdot S_a(\theta_1) \cdot R_b(r_2) \cdot Y_b(w_2) \cdot S_b(\theta_2)$

$S(\theta)$ is the function describing the spin direction distribution. Note: different indices for electrons and orbitals; V contains no spin, but Ψ does; θ = spin angles.

A single electron has kinetic energy and feels attraction by the nucleus *and* repulsion by the other electrons. The so-called orbital energy E(orb) = T + V_{nuc} + Rep. Total Energy is not the sum of orbital energies, because that counts the repulsion twice.

$E_{total}(2e) \approx E_{total}(2orb) = (T+V_{nuc})_a + (T+V_{nuc})_b + Rep_{a,b} = E_a(orb) + E_b(orb) - Rep_{a,b}$
                                                         (note the signs of Rep)
Since there are no spin-energy contributions at the nonrelativistic level of approximation (very good for light atoms), the spin-variables are separable.

13.4 Symmetry

$H(1,2) = T(1) + T(2) + V_{nuc}(1) + V_{nuc}(2) + 1/|r_{12}| = H(2,1)$

The Hamiltonian does not change upon coordinate-permutation; H is **invariant against** this **coordinate-transformation**; the system described by H has a **symmetry**.

$H(1,2) \circ \Psi_\alpha(1,2) = \Psi_\alpha(1,2) \cdot E_\alpha$ From **symmetry**: $H(1,2) = H(2,1)$, there follows

$H(2,1) \circ \Psi_\beta(1,2) = \Psi_\beta(1,2) \cdot E_\beta$ for *nondegenerate* states: $E_\alpha = E_\beta$, $\Psi_\alpha = $ const $* \Psi_\beta$

If everything can be made real: $\Psi(1,2) = +$ or $- \Psi(2,1)$.
State function of several identical particles is either permutation-symmetric or permutation-antisymmetric.

13.5 Pauli Exclusion Principle

A relativistically acceptable two-particle wavefunction can only be constructed
for two equal fermions (s = 1/2: e,p,n)   if $\Psi(1,2) = -\Psi(2,1)$; $\Psi(1,2) = +\Psi(2,1)$ is excluded;
for two equal bosons (s = 0,1: ^{4}He, hν) if $\Psi(1,2) = +\Psi(2,1)$; $\Psi(1,2) = -\Psi(2,1)$ is excluded;
for two different particles, any combination $c_1\Psi(1,2) + c_2\Psi(2,1)$ is admissible.

Convention: 1 means x_1,y_1,z_1 (for s = 0)   or x_1,y_1,z_1,θ_1 (for s = 1/2)

Note: $\psi(x,y,z,\theta_s) = \psi_{nlm}(\theta_s) = \psi(x,y,z)_s = \psi_{nlms}$
where n = 1…∞, ℓ = 0…n–1, m = ℓ…–ℓ, s = 1/2, –1/2   and
x,y,z ∈ (-∞, +∞) or r ∈ [0, ∞], θ_r, θ_s ∈ [0, π], φ_r, φ_s ∈ [0,2π]

13.6 Consequence of Pauli exclusion principle within the orbital approximation

13.6.1 Two-particle wave functions

One orbital φ_a for two spinless particles: $\Psi = \varphi_a(1) \cdot \varphi_a(2)$, admissible for two bosons
Energy: $E = 2(T+V)_a + Rep(a^2,a^2)$

Two spin-orbitals φ_a, φ_b : $\Psi_+ = \varphi_a(1)\cdot\varphi_b(2) + \varphi_b(1)\cdot\varphi_a(2)$, admissible only for two bosons (photons)
Energy: $E = (T+V)_a + (T+V)_b + Rep(a^2,b^2) + Rep(ab,ab)$

or : $\Psi_- = \varphi_a(1) \cdot \varphi_b(2) - \varphi_b(1) \cdot \varphi_a(2)$, admissible only for two fermions (electrons)
Energy: $E = (T+V)_a + (T+V)_b + Rep(a^2,b^2) - Rep(ab,ab)$ (*'ab'* vanishes for different spins)

Note: φ_a and φ_b may be $\psi_a \cdot \alpha$ and $\psi_a \cdot \beta$; or $\psi_a \cdot \alpha$ and $\psi_b \cdot \alpha$; or $\psi_a \cdot \alpha$ and $\psi_b \cdot \beta$. Here ψ means a pure position function, and φ a spin-position function, a so-called spin-orbital.

The particle density of $(\varphi_a \cdot \varphi_b \pm \varphi_b \cdot \varphi_a)$ is, in both cases, $\varphi_a^2 + \varphi_b^2$. But the particle-*pair* density differs from $\varphi_a^2 \cdot \varphi_b^2 + \varphi_b^2 \cdot \varphi_a^2$ by $\pm 2 \cdot \varphi_a \varphi_b \cdot \varphi_a \varphi_b$. The so-called overlap density $\varphi_a \varphi_b$ of two usual orbitals of the same atom or molecule has positive and negative (i.e. increasing and decreasing) contributions, which exactly sum up to zero, $\langle \varphi_a | \varphi_b \rangle = 0$.

At the level of the nonrelativistic approximation, there is no spin-contribution to the energy! But, because of Pauli-exclusion, for 2 electrons: a symmetric position function product ($\psi_a \psi_a$ or $\psi_a \psi_b + \psi_b \psi_a$) must be combined with an antisymmetric spin direction function product ($\alpha\beta$ - $\beta\alpha$) or, vice versa, ($\varphi_a \varphi_b$ - $\varphi_b \varphi_a$; not $\varphi_a \varphi_a$) with ($\alpha\alpha$ or $\alpha\beta + \beta\alpha$ or $\beta\beta$).

13.6.2 Slater Determinants

Slater determinant is the simplest way to guarantee the Pauli principle. Let $\varphi_a, \varphi_b, \varphi_c$ be three spinposition-orbitals.

$$\frac{1}{\sqrt{3!}}\begin{vmatrix} \varphi_a(1) & \varphi_b(1) & \varphi_c(1) \\ \varphi_a(2) & \varphi_b(2) & \varphi_c(2) \\ \varphi_a(3) & \varphi_b(3) & \varphi_c(3) \end{vmatrix} = |abc|$$

$\rightarrow$ different orbitals
$\downarrow$ different electrons

Since electrons are completely indistinguishable (a nonclassical property) every electron appears in every orbital. n different electrons 1, 2, ... "in" n different orbitals a,b. ... with different indices!

$|a\alpha,a\beta|$: $E = 2h_a + J_{aa}$ (spin-singlet); $|a\alpha,b\alpha|$: $E = h_a + h_b + J_{ab} - K_{ab}$ (spin-triplet);

$|a\alpha,b\beta|$: $E = h_a + h_b + J_{ab} \pm K_{ab}$ ($|a\alpha,b\beta|$ $\pm$ $|b\alpha,a\beta|$ is spin-singlet and spin-triplet)

Coulomb repulsion between two **electrons** = Coulomb repulsion between two orbital clouds modified by + or – "exchange pair cloud" = so called Coulomb and exchange **orbital** integrals

Summary: Two-electron function at nonrelativistic approximation, where spin doesn't contribute to energy: either space-part symmetric and spin-part antisymmetric (higher Coulombic energy goes with singlet), or space-part antisymmetric and spin-part symmetric (lower Coulombic energy goes with triplet). 'Anti-pairing energy' is $2K_{ab}$. The + and – signs are a 'wave' phenomenon; the spatial pair-distribution determines the Coulomb energy; the connection between energy and spin comes via the Pauli exclusion.

The form (permutational symmetry) of the spatial two-electron function determines a) the energy (+ or – *K* correction of the e-e Coulomb repulsion), and b) the admissible spin-coupling ($\alpha_1\beta_2 \pm \beta_1\alpha_2$) through the Pauli principle: indirect relation between (lower) energy and (pseudo-parallel) spin coupling.

13.7 Aufbau principle and Hund's rule

If $\varepsilon_a \ll \varepsilon_b$: lowest energy for both electrons at level a, with ↙↗ spin

Hund's Rule for the orbital approximation

If $\varepsilon_a \approx \varepsilon_b$: lowest energy for both electrons at levels a and b with pseudoparallel spin

13.8 Magnetism

mass and mechanical spin: M and l; charge and magnetic spin moment: Q and μ with
$\mu / l = Q/M \cdot (g/2c)$ (magnetic/mechanical moment ~ charge/mass : gyromagnetic ratio)
g = 1 for "orbit motion", g = 2 for "spin motion"
The magnetic moments of orbiting and spinning electrons interact with a magnetic field:
$\Delta E_{para} \sim L \cdot B$
A moving charge is perturbed by a magnetic field: $\Delta E_{dia} \sim r^2 \cdot B^2$

13.9 Relativity

"Velocity of electrons near nucleus" is $v \approx Z$ au. Effective mass of electrons $m_{eff} = m_e/\sqrt{(1-v/c)^2}$ is relativistically increased by a fraction of $\frac{1}{2}(Z/c)^2$, where c = 137 au.

s-orbitals are relativistically contracted and stabilized by a fraction proportional to $(Z/c)^2$.

p-levels are split (spin-orbit coupling) into a lower p1/2 (spherical, complex orbital) and two higher p3/2 (nearly spherical orbitals).

d- and f-orbitals are better shielded by contracted s- and p1/2-orbitals: they are destabilized, expanded and split into two different levels.

This all is of eminent importance for the chemistry of medium and heavy elements (inorganic and metal organic chemistry), see modern textbooks of inorganic chemistry.

Learning objectives

After careful study of this chapter you should be able to:

(1) Describe the main features of the spectrum of atomic hydrogen and state the *Ritz combination principle*, Section 15.1(a).

(2) Write down the Schrödinger equation for the hydrogen atom in centre of mass coordinates, eqn (15.1.7), and show that it can be separated into radial and angular equations, eqn (15.1.8).

(3) State how the *energy levels* of hydrogen depend on the principal quantum number, eqn (15.1.22).

(4) Explain the significance of an *atomic orbital* and describe the shapes of s-, p-, and d-orbitals, Section 15.1(d).

(5) Define the *radial distribution function*, eqn (15.1.25), and explain its significance.

(6) State the *Bohr frequency condition*, eqn (15.1.26), and the *selection rules* for atomic transitions, Section 15.1(f).

(7) State the *Pauli principle* and the *Pauli exclusion principle*, Section 15.2(b).

(8) State and use the *Clebsch–Gordan series* for the coupling of angular momenta, eqn (15.2.1).

(9) State the rules of the *building-up principle and Hund's rule*, and use them to account for the electronic configurations of atoms, Section 15.2(d).

(10) Account for the variation of first ionization energies through the Periodic Table, Section 15.2(e).

(11) Describe the strategy for *self-consistent field* calculations of the electronic structures of many-electron atoms, Section 15.2(f).

(12) Describe the origin of *spin–orbit coupling*, and show how it is responsible for the *fine structure* of spectra, Section 15.3(a).

(13) Calculate the spin–orbit coupling constant from spectral information, Example 15.5.

(14) Describe the construction and significance of *term symbols*, Section 15.3(b).

(15) Describe *Russell–Saunders coupling*, and state the *selection rules* for many-electron atom spectra, Section 15.3(b).

(16) Write expressions relating the *magnetic moment* of an electron to its orbital and spin angular momenta, eqn (15.3.5), and for the energy of interaction with a magnetic field, eqns (15.3.6) and (15.3.7).

(17) Describe the meaning of *precession*, Fig. 15.22.

(18) Describe and explain the *Zeeman effect*, Section 15.3(c).