

Self-consistent methods for many electron atoms

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1 Central Field Approximation

$$\hat{H} = \sum_{i=1}^N \left(-\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Ze^2}{r_i} + \sum_{j>i}^N \frac{e^2}{r_{ij}} \right) \quad (1)$$

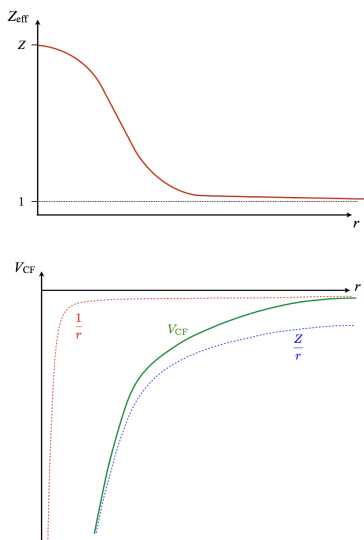


Figure 1: (Top): Effective charge at radius, r . (Bottom): V_{CF} .

The central-field (cf) approximation consists of replacing the electrostatic potential by a purely radial potential, applicable to all electrons:

$$V_{\text{CF}}(r) = -\frac{Ze^2}{r} + S(r). \quad (2)$$

The first term on the RHS is due to the attraction between an electron, located at radius r and the nucleus. The second term is the “screening” potential from $N - 1$ electrons. Close

to the nucleus $V_{cf} \approx -Ze^2/r$ and increases to $-e^2/r$ in the outer reaches of the atom (see Figure 1).

Thus the principal Hamiltonian is

$$H_{CF}(r_1, r_2, \dots, r_N) = \sum_{i=1}^N -\frac{1}{2} \nabla_i^2 + V_{CF}(r_i) \quad (3)$$

and the perturbing Hamiltonian is

$$H' = \sum_{j>i}^N \frac{1}{r_{ij}} - \sum_{i=1}^N S(r_i) \quad (4)$$

Schrodinger's equation with the principal Hamiltonian

$$H_{CF}\psi_{CF} = E_{CF}\psi_{CF} \quad (5)$$

yields the eigen-energy, E_{CF} . Note that $\psi_{CF} = \psi(r_1)\psi(r_2)\dots\psi(r_N)$ is separable because there are no cross-terms in the Hamiltonian. Equation 5 leads to N equations, all of which are "Hydrogen" like (with the polar and azimuthal part the same as that of Hydrogen but the radial part given by the differential equation of the sort given below:

$$\left[-\frac{1}{2} \nabla_r^2 + V_{CF}(r) \right] \psi_{nlm_l}(r) = E_{nl} \psi_{nlm_l}(r) \quad (6)$$

The total energy of the system, $E_{CF} = \sum_{i=1}^N E_{n_i l_i}$. Each of these wave function is called as an "orbital".

The Hartree Method: For a given V_{CF} one obtains ψ_{nlm_l} by numerically solving Equation 6. V_{CF} is recomputed given that we know the probability distribution of electrons. Equation 6 is resolved and a new V_{CF} is obtained. The process is stopped once convergence is achieved. The Hartree wave function not satisfy Pauli's Principle. In the case of Helium we constructed the wave functions by hand. A method due to Slater allows the construction of a wave functions using linear algebra. The Hartree-Fock method uses these wave functions.

Once the spin is incorporated the wavefunctions are called as "spin-orbitals". These wavefunctions are then applied to H' (residual electrostatic potential) to compute the corrections to the energy levels. The total angular momentum, L and the total spin angular momentum, S , are conserved separately. So these are good quantum numbers. Thus, spin-orbitals can be described by n, L, S . Note that L and S are still degenerated with their projections, m_l and m_s .

2 Periodic Table

The success of approximating multi-electron atom/ion via the orbital approach and Pauli's exclusion principle sets the stage for a physical understanding of the periodic table. Briefly, each electron has four quantum numbers: n , l , m_l and m_s (spin). As with hydrogen for a given n , the angular momentum quantum number for an orbital ranges from 0 to $n - 1$. For a given l , m_l ranges from $-l$ to $+l$. Finally, m_s can be either $\pm 1/2$.

The electron configurations are built up using the "Aufbau" (German for build up) principle. The framework is the following. (1) Orbitals are filled up in increasing $n+l$ value; see Figure 2 (2) For the same $n+l$ value, the lower n value is filled first. (3) Within the same shell (i.e. given $n+l$ value) the sub-shells (i.e. differing m_l) are first occupied according to the "bus rule" (in a bus with several rows passengers prefer to sit in a row all by themselves. After all the rows are occupied by one passenger subsequent passenger reluctantly sit to another passenger). Pauli principle will ensure that the wave functions are anti-symmetric (so that no two electrons can have the same set of quantum numbers).

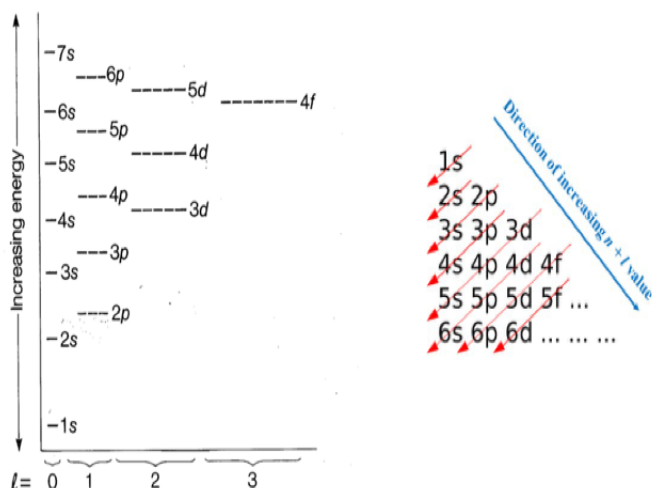


Figure 2: (Left): Energy levels of successive shells. (Right): The Madelung mnemonic.

The sequence is $1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s$ and so on; see chart. The electron configuration for the first few elements of the periodic table are as follows: H ($1s^1$), He ($1s^2$), Li ($1s^2 2s^1$), Be ($1s^2 2s^2$), B ($1s^2 2s^2 2p^1$), C ($1s^2 2s^2 2p^2$) and so on. See also [PeriodicTable.html](#)

There are deviations as you go to high Z elements (e.g. For Copper we expect the electronic structure to be $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^9$ but its is instead ... $4s^1 3d^{10}$. This is

attributed to the "Rule of Stability": A sub-shell (e.g. $2p^3$) is particularly stable if it is half full or full. Given two configurations, the atom would "choose" the more stable one.

In the specific example of Copper: $4s^2 3d^9$ is unstable because $3d^9$ is only one electron shy of being full. So the electron jumps and the new arrangement is $3d^{10}4s^1$. In this case, $4s^1$ is stable because it half filled and $3d$ is stable because it is fully filled. However, $4s^1$ is more energetic relative to $3d$ since the latter is full, whence $3d^{10}4s^1$.