

# Advanced Physical Chemistry (fizkemhk17em)

## Electronic Structure

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## Electronic structure of atoms

*The Hamiltonian in atomic units:*

$$\hat{H} = \underbrace{-\frac{1}{2} \sum_i^{\text{electrons}} \Delta_i}_{\text{kinetic energy of electrons}} \underbrace{- \sum_i^{\text{electrons}} \frac{Z_A}{r_{iA}}}_{\text{electron-nuclei attraction}} \underbrace{+ \sum_i^{\text{electrons}} \sum_{j < i}^{\text{electrons}} \frac{1}{r_{ij}}}_{\text{electron-electron repulsion}}$$

- $Z_A$  being the charge of nucleus  $A$ ;
- $r_{ij}$  being the distance of electrons  $i$  and  $j$ ;
- $r_{iA}$  is the distance of electron  $i$  and nucleus  $A$ ;

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Wave function of the many electron system

$$\begin{aligned} \Psi &= \Psi(x_1, y_1, z_1, \sigma_1, x_2, y_2, z_2, \sigma_2, \dots, x_n, y_n, z_n, \sigma_n) \\ &\equiv \Psi(1, 2, \dots, n) \end{aligned}$$

i.e. a function with  $4n$  variables.

# The Independent Particle Approximation

a) Hartree-method: Approximation of the wave function in a product form

$$\underbrace{\Psi(r_1, r_2, \dots, r_n)}_{\text{wave function}} = \underbrace{\phi_1(r_1) \cdot \phi_2(r_2) \dots \cdot \phi_n(r_n)}_{\text{product of spin orbitals}}$$

In this case the Schrödinger equation reduces to one-electron equations:

$$\begin{aligned} \hat{H}\Psi = E\Psi \quad \Rightarrow \quad \hat{h}_1(r_1)\phi_1(r_1) &= \varepsilon_1\phi_1(r_1) \\ \hat{h}_2(r_2)\phi_2(r_2) &= \varepsilon_2\phi_2(r_2) \\ &\dots \\ \hat{h}_n(r_n)\phi_n(r_n) &= \varepsilon_n\phi_n(r_n) \end{aligned}$$

One n-electron equation  $\Rightarrow$  system of n one-electron equations

$$\hat{h}_i \quad \rightarrow \quad \hat{h}_i^{eff} = -\frac{1}{2}\Delta_i - \frac{Z_A}{r_{iA}} + V_i^{eff}$$

where  $V_i^{eff}$  is the interaction of electron  $i$  with all other electrons.

# Pauli principle and the Slater determinant

b) Hartree-Fock-method:

To fulfill anti-symmetry of the wave function, use determinant (*Slater determinant*):

$$\Psi(r_1, r_2, \dots, r_n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_1(r_1) & \phi_2(r_1) & \cdots & \phi_n(r_1) \\ \phi_1(r_2) & \phi_2(r_2) & \cdots & \phi_n(r_2) \\ \vdots & \vdots & \vdots & \vdots \\ \phi_1(r_n) & \phi_2(r_n) & \cdots & \phi_n(r_n) \end{vmatrix}$$

To fulfill the indistinguishability, use the same operator (Fock operator) for all electrons:

$$\hat{h}_i^{eff} \rightarrow \hat{f}(r_i) = -\frac{1}{2}\Delta_i - \frac{Z_A}{r_{iA}} + U^{HF}$$

with  $U^{HF}$  being an averaged (Hartree-Fock) potential.

The Hartree-Fock equation:

$$\hat{f}(r_i)\varphi_i(r_i) = \varepsilon_i\varphi_i(r_i) \quad i = 1, \dots, n$$

## Electronic structure of atoms

In the Independent Particle Approximation the equations to solve:

$$\begin{aligned}\hat{h}(i)\phi_i &= \varepsilon_i\phi_i \\ \hat{h}(i) &= -\frac{1}{2}\Delta_i - \frac{1}{r} + V\end{aligned}$$

Since  $\hat{h}$  is similar to the Hamiltonian of the hydrogen atom, the solutions will also be similar:

The *angular part* of the wave functions will be the SAME. Therefore we can again classify the orbitals as  $1s$ ,  $2s$ ,  $2p_0$ ,  $2p_1$ ,  $2p_{-1}$ , etc.

The *radial part*:  $R(r)$  will differ, since the potential is different here than for the H atom: since it is not a simple Coulomb-potential, the degeneracy according to  $l$  quantum number will be lifted, i.e. the orbital energies will depend not only on  $n$  but also on  $l$  ( $\varepsilon = \varepsilon_{nl}$ ).

## Electronic structure of atoms: angular momentum

$$\begin{array}{l} \text{one particle:} \quad \hat{l}^2 \quad \hat{l}_z \quad \hat{s}^2 \quad \hat{s}_z \\ \text{many particle:} \quad \hat{L}^2 \quad \hat{L}_z \quad \hat{S}^2 \quad \hat{S}_z \end{array}$$

The angular momentum of the system is given by the sum of the individual angular momentum of the particles ( so called vector model or Sommerfeld model):

$$\begin{aligned} \underline{\hat{L}} &= \sum_i \underline{\hat{l}}(i) \\ \underline{\hat{S}} &= \sum_i \underline{\hat{s}}(i) \end{aligned}$$

It follows that the  $z$  component of  $\underline{\hat{L}}$  and  $\underline{\hat{S}}$  is simply the sum of the  $z$  component of the individual vectors:

$$M_L = \sum_i m(i) \quad M_S = \sum_i m_s(i)$$

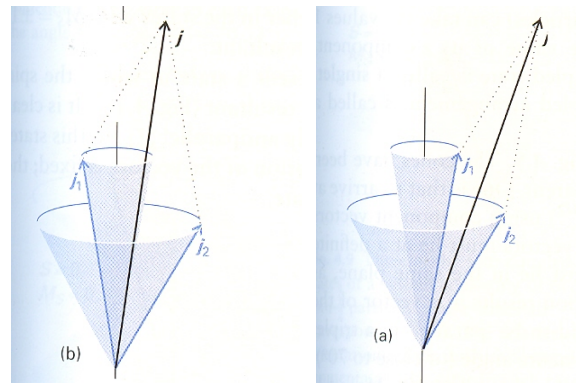
# Electronic structure of atoms: angular momentum

$$\underline{\hat{L}} = \sum_i \underline{\hat{l}}(i) \qquad \underline{\hat{S}} = \sum_i \underline{\hat{s}}(i)$$

The length of the vector is much more complicated: due to the quantizations and uncertainty principle, we can get different results: For example for two particles:

$$L = (l(1) + l(2)), (l(1) + l(2) - 1), \dots, |l(1) - l(2)|$$

$$S = (s(1) + s(2)), (s(1) - s(2))$$





## Classification and notation of the atomic states

The Hamiltonian commutes with  $\hat{L}^2$ ,  $\hat{L}_z$ ,  $\hat{S}^2$  and  $\hat{S}_z$  operators  $\Rightarrow$  we can classify the atomic states by the corresponding quantum numbers of the angular momentum operators:

$$\Psi_{L,M_L,S,M_S} = |L, M_L, S, M_S\rangle$$

The latter notation is more popular.

In analogy to the hydrogen atom, the *states* can be classified according to the quantum numbers:

		Angular momentum:						
L=		0	1	2	3	4	5	...
notation:		S	P	D	F	G	H	...
degeneracy		1	3	5	7	9	11	...
		<hr/> <hr/>						
		Spin momentum:						
S=		0	$\frac{1}{2}$	1	$\frac{3}{2}$	2	...	
multiplicity (2S+1):		1	2	3	4	...		
denomination:		singlet	doublet	triplet	quartet	...		

# Classification and notation of the atomic states

In the full notation one takes the notation of the above table for the given  $L$  and writes the multiplicity as superscript before it:

Examples:

$L = 0, S = 0$ :  $^1S$  read: singlet S

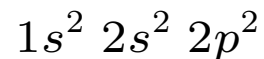
$L = 2, S = 1$ :  $^3D$  read: triplet D

Total degeneracy is  $(2S+1)(2L+1)$ -fold!!

## Construction of the atomic states

Since there is a high-level degeneracy, degenerate orbitals are often not fully occupied  $\rightarrow$  configuration is not sufficient to represent the states.

Example: carbon atom



$2p$  is open subshell, since only two electrons are there for six possible places on the  $2p$  subshell.

What are the possibilities to put the two electrons onto these orbitals?

spatial part:  $2p_0, 2p_1, 2p_{-1}$

spin part:  $\alpha, \beta$

These gives altogether six spin orbitals which allow to construct  $\binom{6}{2} = 15$  determinants, i.e. we have 15 different states.

## Construction of the atomic states

Let us construct the states by summing the angular momenta:

$$l(1) = 1, l(2) = 1 \rightarrow L = (l(1) + l(2)), (l(1) + l(2) - 1), \dots, |l(1) - l(2)| = 2, 1, 0$$

$$s(1) = \frac{1}{2}, s(2) = \frac{1}{2} \rightarrow S = (s(1) + s(2)), (s(1) - s(2)) = 1, 0$$

Possible states:

$${}^1S \quad {}^1P \quad {}^1D$$

$${}^3S \quad {}^3P \quad {}^3D$$

Considering the degeneracy there are 36 states. But we can have only 15, as was shown above!

## Construction of the atomic states

We also have to consider *Pauli principle*, which says that two electrons can not be in the same state.

If we consider this, too, the following states will be allowed:

$${}^1S \quad {}^3P \quad {}^1D$$

These give exactly 15 states, so that everything is round now!

# Construction of the atomic states

Summarized: carbon atom in the  $2p^2$  configuration has three energy levels.

What is the order of these states?

Hund's rule (from experiment; „Nun, einfach durch Anstieren der Spektren“):

- the state with the maximum multiplicity is the most stable (there is an interaction called „exchange” which exists only between same spins);
- if multiplicities are the same, the state with larger  $L$  value is lower in energy;

In case of the carbon atom:

$$E_{3P} < E_{1D} < E_{1S}$$

## Spin-orbit interaction, total angular momentum

As in case of the hydrogen atom, orbital and spin angular momenta interact. The Hamiltonian changes according to these interaction as:

$$\hat{H} \rightarrow \hat{H} + \sum_i \zeta \hat{l}(i) \cdot \hat{s}(i)$$

Consequence:  $\hat{L}^2$  and  $\hat{S}^2$  do not commute with  $\hat{H}$  anymore, thus  $L$  and  $S$  will not be suitable to label the states („not good quantum numbers”). One can, however, define the *total angular momentum* operator as:

$$\underline{\hat{J}} = \underline{\hat{L}} + \underline{\hat{S}}$$

which

$$[\hat{H}, \hat{J}^2] = 0 \quad [\hat{H}, \hat{J}_z] = 0$$

i.e. the eigenvalues of  $\hat{J}^2$  and  $\hat{J}_z$  are good quantum numbers.

## Spin-orbit interaction, total angular momentum

These eigenvalues again follow the same pattern than in case of other angular momentum-type operators we have already observed:

$$\hat{J}^2 \rightarrow J(J + 1) [\hbar^2]$$

$$\hat{J}_z \rightarrow M_J [\hbar]$$

The quantum numbers  $J$  and  $M_J$  of the total angular momentum operators follow the same summation rule which was discussed above, i.e.

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

Energy depends on  $J$  only, therefore degenerate energy level might split!!



# Spin-orbit interaction, total angular momentum

Notation: even though  $L$  and  $S$  are not good quantum numbers, we keep the notation but we extend it with a subscript giving the value of  $J$ .

Example I: carbon atom,  $^3P$  state:

$$L = 1, S = 1 \rightarrow J = 2, 1, 0$$
$$^3P \rightarrow ^3P_2, ^3P_1, ^3P_0$$

Energy splits into three levels!

Example II: carbon atom  $^1D$  state:

$$L = 2, S = 0 \rightarrow J = 2$$
$$^1D \rightarrow ^1D_2$$

There is no splitting of energy here,  $J$  can have only one value. This should not be a surprise since  $S = 0$  means zero spin momentum, therefore no spin-orbit interaction!!!

## Electronic structure of atom: magnetic field

Considering the total angular momentum, the change of energy in magnetic field reads:

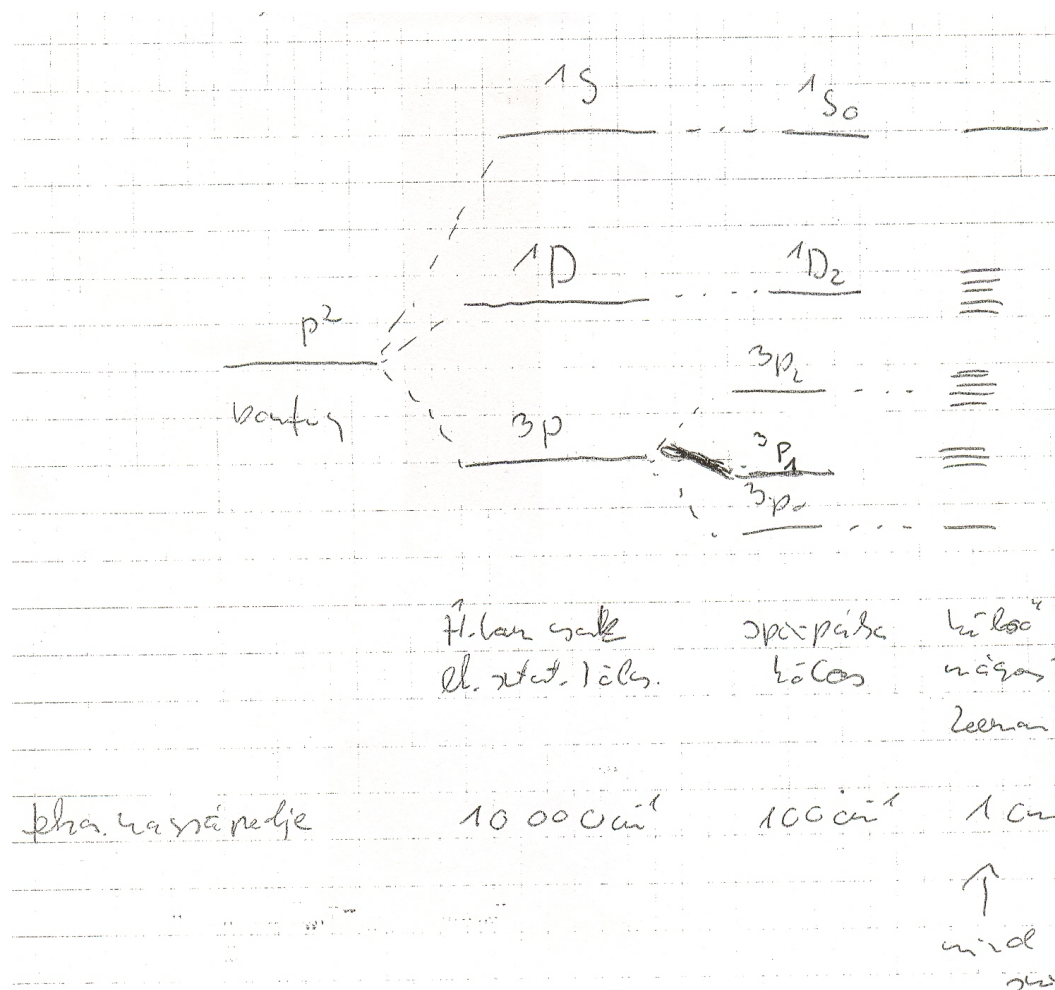
$$\Delta E = M_J \cdot \mu_B \cdot B_z$$

$$M_J = -J, -J + 1, \dots, J$$

This means, levels will split into  $2J + 1$  sublevels!

# Electronic states of atoms: summary

Carbon atom in  $2p^2$  configuration:



## Electronic states of atoms: summary

Other configuration for  $p$  shell:

$p^1$	and	$p^5$	$^2P$	B, F
$p^2$	and	$p^4$	$^3P, ^1D, ^1S$	C, O
$p^3$			$^4S, ^2D, ^2P$	N
$p^6$	(closed shell)		$^1S$	Ne