Plan of lectures

- 1 15.04.2015 Preliminary Discussion / Introduction

- 2 22.04.2015 Experiments (discovery of the positron, formation of antihydrogen, ...)
- 3 29.04.2015 Experiments (Lamb shift, hyperfine structure, quasimolecules and MO spectra)
- 4 06.05.2015 Theory (from Schrödinger to Dirac equation, solutions with negative energy)
- 5 13.05.2015 Theory (bound-state solutions of Dirac equation, quantum numbers)
- 6 20.05.2015 Theory (bound-state Dirac wavefunctions, QED corrections)

- 7 27.05.2015 Experiment (photoionization, radiative recombination, ATI, HHG...)
- 8 03.06.2015 Theory (description of the light-matter interaction)
- 9 10.06.2015 Experiment (Kamiokande, cancer therapy, ….)
- 10 17.06.2015 Theory (interaction of charged particles with matter)

- 11 24.06.2015 Experiment (Auger decay, dielectronic recombination, double ionization)
- 12 01.06.2015 Theory (interelectronic interactions, extension of Dirac (and Schrödinger) theory for the description of many-electron systems, approximate methods)
- 13 08.07.2015 Theory (many-electron atoms)

- 14 15.07.2015 Experiment (Atomic physics PNC experiments (Cs,...), heavy ion PV research)

Many-electron ions (part 2)

(Spectra of many-electron atom, coupling schemes and advanced many-electron methods)

08 July 2015

Plan of lecture

- Central field approximation for *N*-electron system
- Spectra of many-electron ions: Perturbative approach
  - jj coupling
  - LS coupling
- Variational methods: Hartree-Fock and Dirac-Fock approaches

Central field approximation for *N* electrons

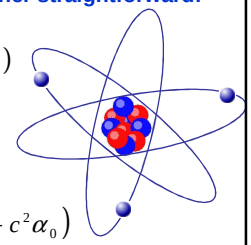
(reminder from the last lecture)

- Generalization of the central field approximation (and, as its particular case, the independent particle model) for the system of *N* electrons is rather straightforward:

$$\left[\sum_k \left(-ic\boldsymbol{\alpha}\cdot\nabla_k - \frac{Z}{r_k} + c^2\alpha_0\right) + \sum_{k<i}\frac{1}{r_{ki}}\right]\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2,...) = E\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2,...)$$

$$\Downarrow$$

$$\left(\hat{H}_0 + \hat{H}'\right)\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2,...) = E\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2,...)$$



- where central field Hamiltonian: $\hat{H}_0 = \sum_k \left(-ic\boldsymbol{\alpha}\cdot\nabla_k + V(r_k) + c^2\alpha_0\right)$
- and remaining (non-spherical) part is: $\hat{H}' = \sum_{k<i}\frac{1}{r_{ki}} - \sum_k\left(\frac{Z}{r_k} + V(r_k)\right)$

⇒ By neglecting first the non-spherical part, we find solution of H_0

$$\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2,...) = \frac{1}{\sqrt{N!}}\sum_{\mu_a,\mu_b,\mu_c...} \underbrace{d(j_a\mu_a, j_b\mu_b, j_c\mu_c,...:JM)}_{\text{angular coupling coefficients}} \begin{vmatrix} \psi_{n_a j_a\mu_a}(\boldsymbol{r}_1) & \psi_{n_b j_b\mu_b}(\boldsymbol{r}_1) & \psi_{n_c j_c\mu_c}(\boldsymbol{r}_1) & ... \\ \psi_{n_a j_a\mu_a}(\boldsymbol{r}_2) & \psi_{n_b j_b\mu_b}(\boldsymbol{r}_2) & \psi_{n_c j_c\mu_c}(\boldsymbol{r}_2) & ... \\ \psi_{n_a j_a\mu_a}(\boldsymbol{r}_3) & \psi_{n_b j_b\mu_b}(\boldsymbol{r}_3) & \psi_{n_c j_c\mu_c}(\boldsymbol{r}_3) & ... \\ ... & ... & ... & ... \\ ... & ... & ... & ... \end{vmatrix}$$

Central field approximation for *N* electrons

(reminder from the last lecture)

- **Since the many-electron wavefunction:**

$$\Psi(\mathbf{r}_1,\mathbf{r}_2,\ldots)=\frac{1}{\sqrt{N!}}\sum_{\mu_a,\mu_b,\mu_c,\ldots} d(j_a\mu_a,\, j_b\mu_b,\, j_c\mu_c,\ldots : JM)\begin{vmatrix} \psi_{n_a j_a\mu_a}(\mathbf{r}_1) & \psi_{n_b j_b\mu_b}(\mathbf{r}_1) & \psi_{n_c j_c\mu_c}(\mathbf{r}_1) & \ldots \\ \psi_{n_a j_a\mu_a}(\mathbf{r}_2) & \psi_{n_b j_b\mu_b}(\mathbf{r}_2) & \psi_{n_c j_c\mu_c}(\mathbf{r}_2) & \ldots \\ \psi_{n_a j_a\mu_a}(\mathbf{r}_3) & \psi_{n_b j_b\mu_b}(\mathbf{r}_3) & \psi_{n_c j_c\mu_c}(\mathbf{r}_3) & \ldots \\ \ldots & \ldots & \ldots & \ldots \\ \ldots & \ldots & \ldots & \ldots \end{vmatrix}$$

- **is obtained as a solution of central-field Hamiltonian:**

$$\hat{H}_0=\sum_k\left(-ic\boldsymbol{\alpha}\cdot\nabla_k+V(r_k)+c^2\alpha_0\right)$$

- **the total energy of the N-electron ion is given by:** $E=E_{n_a j_a}+E_{n_b j_b}+E_{n_c j_c}+\ldots.$

- **where:** $\left(-ic\boldsymbol{\alpha}\cdot\nabla_k+V(r_k)+c^2\alpha_0\right)\psi_{nj\mu}=E_{nj}\,\psi_{nj\mu}$

- **For central filed Hamiltonians the total energy of the system is entirely determined by the *electron configuration!!!* (i.e. by the way how electrons "sit down" in atom/ion).**

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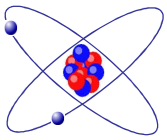
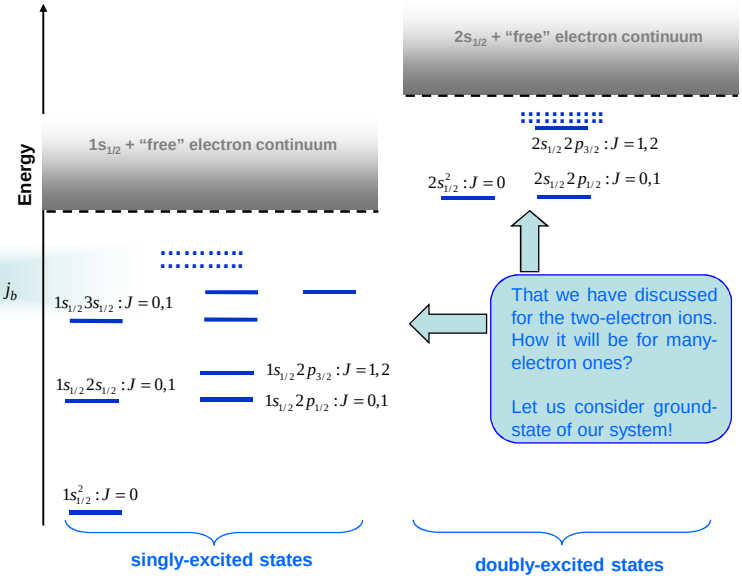
Central field approximation for He-like ions

(energy levels)



$E=E_{n_a j_a}+E_{n_b j_b}$



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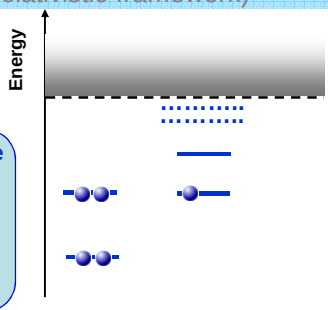
Ground states of many-electron ions

(relativistic framework)

- **Let us start "filling" our ion with electrons!**
- **But don't forget Pauli principle!**



- **Only (2j+1) electrons may occupy the same *subshell* (i.e. have the same *n* and *j*).**
- **For given total momentum *j*:**
  - **μ_j = -*j*, ... +*j* (magnetic)**

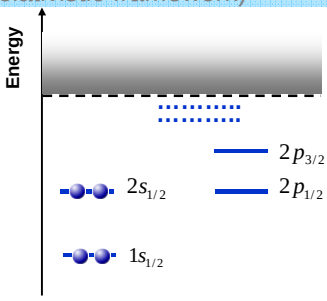
n	*j*	$(-1)^l$	notation	
1	1/2	+	$1s_{1/2}$	2 electrons
2	1/2	+	$2s_{1/2}$	2 electrons
2	1/2	-	$2p_{1/2}$	2 electrons
2	3/2	-	$2p_{3/2}$	4 electrons
3	1/2	+	$3s_{1/2}$	2 electrons
			.....	

By following these rules we can easily "build" ground state of heavy many-electron ion.

Ground states of many-electron ions

(relativistic framework)

- **Let us start "filling" our ion with electrons!**
- **But don't forget Pauli principle!**



n	*j*	$(-1)^l$	notation	
1	1/2	+	$1s_{1/2}$	2 electrons
2	1/2	+	$2s_{1/2}$	2 electrons
2	1/2	-	$2p_{1/2}$	2 electrons
2	3/2	-	$2p_{3/2}$	4 electrons
3	1/2	+	$3s_{1/2}$	2 electrons
			.....	

So far: energy levels are independent on total J.

$1s_{1/2}$	H-like ion
$1s^2_{1/2}$	He-like ion
$1s^2_{1/2}\ 2s_{1/2}$	Li-like ion
$1s^2_{1/2}\ 2s^2_{1/2}$	Be-like ion

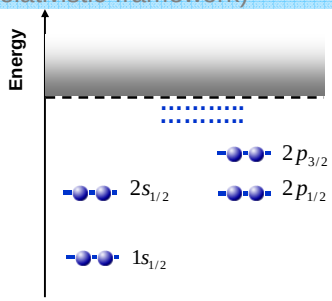
Excited states of many-electron ions

(relativistic framework)

- **Of course, we may also fill electrons into excited states of ions/atom.**
- **Pauli principle is anyway has to be satisfied!**

n	*j*	*(-1)^l*	notation	
1	1/2	+	$1s_{1/2}$	2 electrons
2	1/2	+	$2s_{1/2}$	2 electrons
2	1/2	-	$2p_{1/2}$	2 electrons
2	3/2	-	$2p_{3/2}$	4 electrons
3	1/2	+	$3s_{1/2}$	2 electrons

.....



So far: energy levels are independent on total J.

Please, remind yourself: there is splitting of energy levels with different J if "perturbation" is taken into account.

Let us consider, for example, C-like ion:

$1s^2_{1/2}\ 2s^2_{1/2}\ 2p^2_{1/2}$ ground state

$1s^2_{1/2}\ 2s^2_{1/2}\ 2p_{1/2}\ 2p_{3/2}$ excited state

$1s^2_{1/2}\ 2s^2_{1/2}\ 2p^2_{3/2}$ excited state

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Central field approximation for *N* electrons

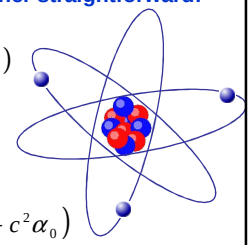
(reminder from the last lecture)

- **Generalization of the central field approximation (and, as its particular case, the independent particle model) for the system of *N* electrons is rather straightforward:**

$$\left[\sum_k\left(-ic\boldsymbol{\alpha}\cdot\nabla_k-\frac{Z}{r_k}+c^2\alpha_0\right)+\sum_{k<i}\frac{1}{r_{ki}}\right]\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots)=E\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots)$$

$$\Downarrow$$

$$\left(\hat{H}_0+\hat{H}'\right)\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots)=E\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots)$$



- **where central field Hamiltonian:** $\hat{H}_0=\sum_k\left(-ic\boldsymbol{\alpha}\cdot\nabla_k+V(r_k)+c^2\alpha_0\right)$
- **and remaining (non-spherical) part is:** $\hat{H}'=\sum_{k<i}\frac{1}{r_{ki}}-\sum_k\left(\frac{Z}{r_k}+V(r_k)\right)$

⇒ By neglecting first the non-spherical part, we find solution of H_0

$$\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots)=\frac{1}{\sqrt{N!}}\sum_{\mu_a,\mu_b,\mu_c,\ldots}\underbrace{d(j_a\mu_a,\,j_b\mu_b,\,j_c\mu_c,\ldots:JM)}_{\text{angular coupling coefficients}}\begin{vmatrix}\psi_{n_aj_a\mu_a}(\boldsymbol{r}_1) & \psi_{n_bj_b\mu_b}(\boldsymbol{r}_1) & \psi_{n_cj_c\mu_c}(\boldsymbol{r}_1) & \ldots\\ \psi_{n_aj_a\mu_a}(\boldsymbol{r}_2) & \psi_{n_bj_b\mu_b}(\boldsymbol{r}_2) & \psi_{n_cj_c\mu_c}(\boldsymbol{r}_2) & \ldots\\ \psi_{n_aj_a\mu_a}(\boldsymbol{r}_3) & \psi_{n_bj_b\mu_b}(\boldsymbol{r}_3) & \psi_{n_cj_c\mu_c}(\boldsymbol{r}_3) & \ldots\\ \ldots & \ldots & \ldots & \ldots\\ \ldots & \ldots & \ldots & \ldots\end{vmatrix}$$

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Excited states of many-electron ions

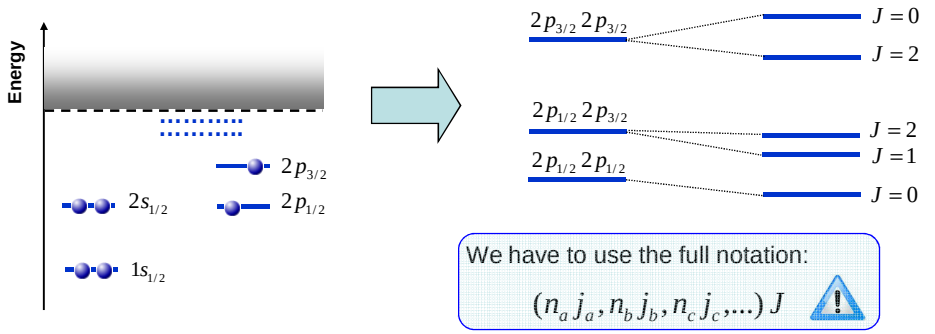
(carbon-like ions)

- **We make use of perturbation theory to take into account "non-central" term:**

$$\hat{H}' = \sum_{k<i} \frac{1}{r_{ki}} - \sum_k \left(\frac{Z}{r_k} + V(r_k) \right)$$

- **And to find energy shift:**

$$E' = \langle \gamma J M_J | \hat{H}' | \gamma J M_J \rangle \equiv \int \Psi^*_{JM_J}(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3, ...) \hat{H}' \Psi_{JM_J}(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3, ...) d\boldsymbol{r}_1 d\boldsymbol{r}_2 d\boldsymbol{r}_3 ...$$



We have to use the full notation:

$$(n_a j_a, n_b j_b, n_c j_c, ...) J$$

jj-coupling

- **All the results which we have discussed before have been obtained in assumption that the electron-electron interactions are weaker comparing to relativistic ones.**

$$\left(\hat{H}_0 + \hat{H}'\right) \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, ..) = E \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, ...)$$

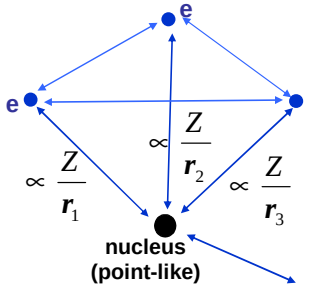
$$\hat{H}_0 = \sum_k \left(-ic\boldsymbol{\alpha} \cdot \nabla_k + V(r_k) + c^2 \alpha_0 \right)$$

sum of one-electron (relativistic) Hamiltonians

$$\hat{H}' = \sum_{k<i} \frac{1}{r_{ki}} - \sum_k \left(\frac{Z}{r_k} + V(r_k) \right)$$

perturbation (includes e-e terms)

- **But all this is true only for heavy ions!**
- **What shall we do for low-*Z* elements?**



Task 1

Assuming that j-j coupling holds, list the possible terms $(n_1 j_1, n_2 j_2, \ldots)\, J$ for the following electronic configurations:

$$1s^2$$

$$1s\ 2s$$

$$1s^2 2s^2 2p$$

$$1s^2 2s^2 2p^5$$

Plan of lecture

- Central field approximation for *N*-electron system
- Spectra of many-electron ions: Perturbative approach
  - jj coupling
  - LS coupling
- Variational methods: Hartree-Fock and Dirac-Fock approaches

Back to Schrödinger equation

(non-relativistic theory with spin included)

- **Please, remind yourself: we have already included spin into non-relativistic consideration also and got simple model:**

$$\psi_{nlm_l sm_s}(\boldsymbol{r}) = \psi_{nlm_l sm_s}(r,\theta,\varphi,\sigma) = R_{nl}(r)Y_{lm_l}(\theta,\varphi)\chi_{sm_s}(\sigma)$$

Note: there is no need to couple l and s since there is no spin-orbit coupling in non-relativistic case.

- **This wavefunction is solution of Schrödinger equation:**

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\boldsymbol{r}) + V(r)\psi(\boldsymbol{r}) = E\psi(\boldsymbol{r})$$

- **with some central potential.**

Why some? We have discussed until now
only Coulomb case for Schrödinger equation!

Central field approximation

(non-relativistic case)

- **Similarly to relativistic case, we may build up central field approximation for the Schrödinger equation:**

$$\left(\hat{H}_c + \hat{H}_1\right)\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2,..) = E\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2,...)$$

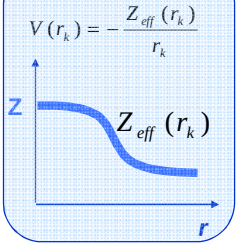
- **where:**

$$\hat{H}_c = \sum_k \tilde{h}_k = \sum_k \left(-\frac{1}{2}\nabla_k^2 + V(r_k)\right)$$

Each electron sees an identical (not necessary Coulomb) potential that is only a function of its distance from the nucleus

Quite often:

$$V(r_k) = -\frac{Z_{eff}(r_k)}{r_k}$$



- **and remaining non-central part is:**

$$\hat{H}_1 = \sum_{k<i}\frac{1}{r_{ki}} - \sum_k\left(\frac{Z}{r_k} + V(r_k)\right)$$

By neglecting for the moment this remaining part we again find solution of the Hamiltonian:

$$\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2,...) = \frac{1}{\sqrt{N!}}\begin{vmatrix}\psi_a(\boldsymbol{r}_1) & \psi_b(\boldsymbol{r}_1) & \cdots\\ \psi_a(\boldsymbol{r}_2) & \psi_b(\boldsymbol{r}_2) & \cdots\\ \cdots & \cdots & \cdots\end{vmatrix}$$

where $|a\rangle = |n_a l_a m_{l_a} s_a m_{s_a}\rangle$

Central field approximation

(non-relativistic case)

- **Similarly to relativistic case, we may build up central field approximation for the Schrödinger equation:**

$$\left(\hat{H}_c + \hat{H}_1\right)\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, ..) = E\,\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, ...)$$

- **where:**

$$\hat{H}_c = \sum_k \tilde{h}_k = \sum_k \left(-\frac{1}{2}\nabla_k^{\,2} + \underbrace{V(r_k)}_{} \right)$$

Each electron sees an identical (not necessary Coulomb) potential that is only a function of its distance from the nucleus

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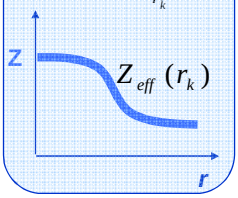


- **and remai**

Please, note: we did not couple electron momenta so far!

$$\ldots - \sum_{k<i} \frac{}{r_{ki}} \sum_k \left(\frac{}{r_k} + V(r_k) \right)$$

By neglecting for the ment this remaining part we again find solution of the Hamiltonian:

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, ...) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_a(\boldsymbol{r}_1) & \psi_b(\boldsymbol{r}_1) & \cdots \\ \psi_a(\boldsymbol{r}_2) & \psi_b(\boldsymbol{r}_2) & \cdots \\ \cdots & \cdots & \cdots \end{vmatrix}$$

where $|a\rangle = |n_a l_a m_{l_a} s_a m_{s_a}\rangle$

Central field approximation

(non-relativistic case)

- **Again, since the for the moment we just consider wavefunction:**

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, ...) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_a(\boldsymbol{r}_1) & \psi_b(\boldsymbol{r}_1) & \cdots \\ \psi_a(\boldsymbol{r}_2) & \psi_b(\boldsymbol{r}_2) & \cdots \\ \cdots & \cdots & \cdots \end{vmatrix}$$

- **which is eigenfunction of the central-field Hamiltonian:**

$$\hat{H}_c = \sum_k \tilde{h}_k = \sum_k \left(-\frac{1}{2}\nabla_k^{\,2} + V(r_k) \right)$$

- **The total energy of the ion (atom) is completely determined by the *electron configuration*:**

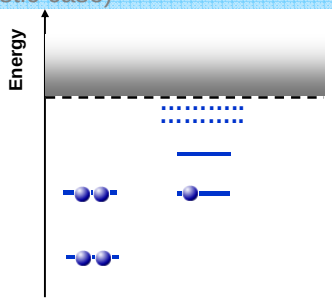
$$E = \sum_k E_k$$

What is the difference here from the relativistic case?

Electronic configuration

(non-relativistic case)

- Let us start "filling" our ion with electrons!
- But don't forget Pauli principle!
  - Only 2(2l+1) electrons may occupy the same *subshell* (i.e. have the same *n* and *l*).
  - For given orbital momentum *l*:
    - m_l = -*l*, …. +*l* (magnetic)
    - m_s = +1/2, -1/2 (spin)



n	*l*	$(-1)^l$	notation	
1	0	+	1s	2 electrons
2	0	+	2s	2 electrons
2	1	-	2p	6 electrons
3	0	+	3s	2 electrons
3	1	-	3p	6 electrons
			…..	

By following these rules we can easily "build" ground state of heavy many-electron ion.

Electronic configuration

(non-relativistic case)

n	*l*	$(-1)^l$	notation	
1	0	+	1s	2 electrons
2	0	+	2s	2 electrons
2	1	-	2p	6 electrons
3	0	+	3s	2 electrons
3	1	-	3p	6 electrons
			…..	

- Let us start "filling" our ion with electrons! (This time without animation.)
- Everything looks very similar to relativistic case.

Element	Total Electrons	Orbital Diagram 1s	2s	2p	3s	Electron Configuration
H	1	↑				$1s^1$
He	2	↑↓				$1s^2$
Li	3	↑↓	↑			$1s^2\,2s^1$
Be	4	↑↓	↑↓			$1s^2\,2s^2$
B	5	↑↓	↑↓	↑		$1s^2\,2s^2\,2p^1$

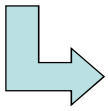
Picture from: http://www.mikeblaber.org/

Electronic configuration

(non-relativistic case)

n	*l*	$(-1)^l$	notation	
1	0	+	1s	2 electrons
2	0	+	2s	2 electrons
2	1	-	2p	6 electrons
3	0	+	3s	2 electrons
3	1	-	3p	6 electrons
			.....	

- **Let us start "filling" our ion with electrons! (This time without animation.)**
- **Everything looks very similar to relativistic case.**
- **But...**



Element	Total Electrons	Orbital Diagram (1s 2s 2p 3s)	Electron Configuration
C	6	↿⇂ ↿⇂ ↿ ↿	$1s^2\,2s^2\,2p^2$
N	7	↿⇂ ↿⇂ ↿ ↿ ↿	$1s^2\,2s^2\,2p^3$
Ne	10	↿⇂ ↿⇂ ↿⇂ ↿⇂ ↿⇂	$1s^2\,2s^2\,2p^6$
Na	11	↿⇂ ↿⇂ ↿⇂ ↿⇂ ↿⇂ ↿	$1s^2\,2s^2\,2p^6\,3s^1$

Picture from: http://www.mikeblaber.org/

Hund's law: for degenerate orbitals, the lowest energy is attained when the number of electrons with the same spin is maximized.

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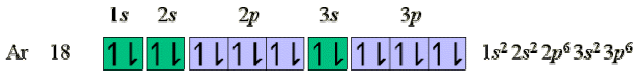
Electronic configuration

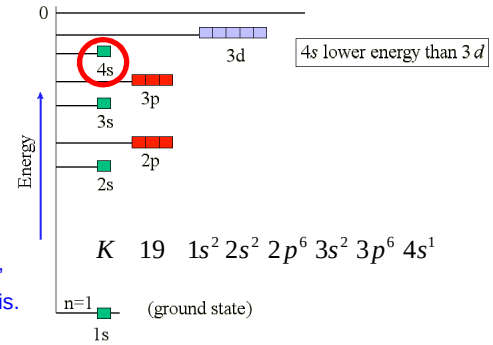
(non-relativistic case)

n	*l*	$(-1)^l$	notation
1	0	+	1s
2	0	+	2s
2	1	-	2p
3	0	+	3s
3	1	-	3p
3	2	+	3d
4	0	+	4s
4	1	-	4p
4	2	+	4d

- **What is going on after Argon?**



- **At Potassium a "natural order" of filling the orbitals ends up.**



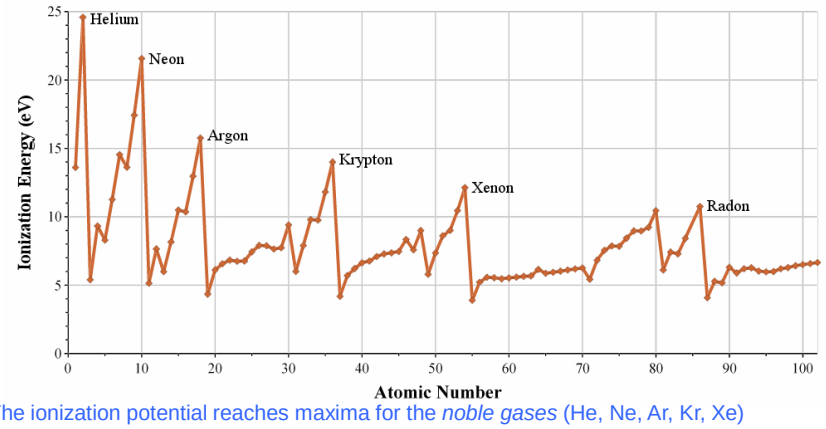
This departure from the "natural order" of filling requires more detailed analysis.

Picture from: http://www.mikeblaber.org/

08 July 2015

Ionization potential of neutral atoms

- **By using our knowledge on electronic configurations of many-electron atoms we may understand *Z*-behaviour of ionization potential.**



Picture from: http://www.wikipedia.org

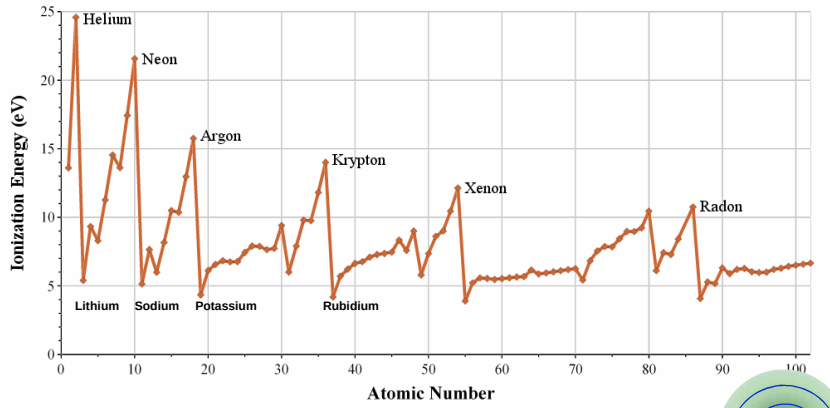
The ionization potential reaches maxima for the *noble gases* (He, Ne, Ar, Kr, Xe)

$He \quad 2 \quad 1s^2$ $\qquad$ $Ar \quad 18 \quad 1s^2 2s^2 2p^6 3s^2 3p^6$

$Ne \quad 10 \quad 1s^2 2s^2 2p^6$ $\qquad$ $Kr \quad 36 \quad [Ar] 4s^2 3d^{10} 4p^6$

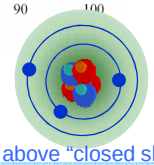
Ionization potential of neutral atoms

- **By using our knowledge on electronic configurations of many-electron atoms we may understand *Z*-behaviour of ionization potential.**



Picture from: http://www.wikipedia.org

The ionization potential is smallest for the *alkalis* (Li, Na, K, Rb, Cs)

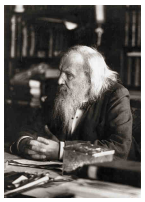


$Li \quad 3 \quad 1s^2 2s$ $\qquad$ $K \quad 19 \quad 1s^2 2s^2 2p^6 3s^2 3p^6 4s$

$Na \quad 11 \quad 1s^2 2s^2 2p^6 3s^1$ $\qquad$ $Rb \quad 37 \quad [Kr] 5s$

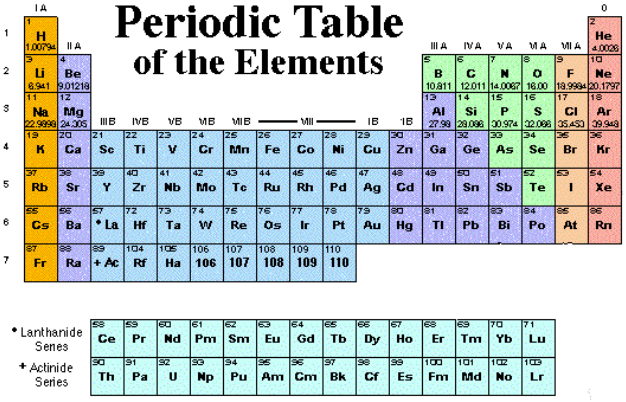
One electron above "closed shell"

Periodic table of elements



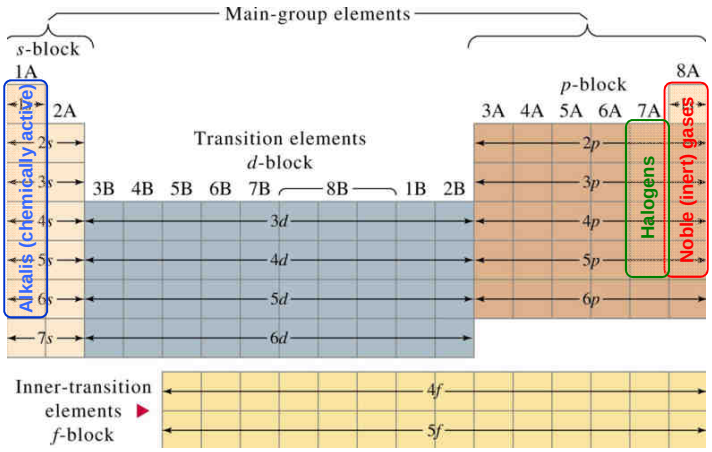
Dmitry Mendeleev

Lothar Meyer



- **Periodic table (in its "final" form) has been proposed by Dmitry Mendeleev and Lothar Meyer in 1869! (More than 50 years prior to Quantum Mechanics).**

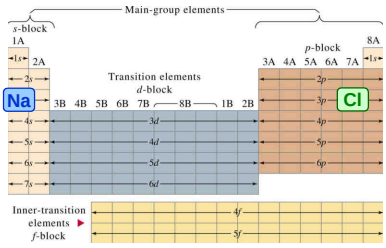
Periodic table of elements



Picture from: http://www.wikipedia.org

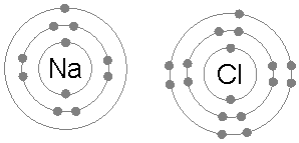
- **The periodic table is structured so that elements with the same type (symmetry) of valence electron configuration are arranged in columns.**
- **Chemical properties follow electronic configuration of atoms.**

Ionic bonding



$$Na + Cl \rightarrow Na^{+} + Cl^{-} \rightarrow Na\,Cl$$

- **Ionic bonding is one of the types of chemical bonding that can form, for example, between alkali atom and halogen through electrostatic attraction.**
- **Example is sodium chloride (Na Cl): When sodium (Na) and chlorine (Cl) are combined, the sodium atoms each lose an electron, forming a cation (Na^+), and the chlorine atoms each gain an electron to form an anion (Cl^-). These ions are then attracted to each other in a 1:1 ratio to form sodium chloride (NaCl).**



Picture from: http://www.wikipedia.org

Taking correlations into account

- **Up to now we have discussed solutions of the central field potential:**

$$\hat{H}_c = \sum_k \tilde{h}_k = \sum_k \left(-\frac{1}{2}\nabla_k^{\,2} + V(r_k) \right)$$

- **Similar to the relativistic case, we have to include now non-central part into account:**

$$\hat{H}_1 = \sum_{k<i} \frac{1}{r_{ki}} - \sum_k \left(\frac{Z}{r_k} + V(r_k) \right)$$

- **Indeed, we may again use perturbation theory! But in which basis?**

So far our wavefunctions are:

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_a(\boldsymbol{r}_1) & \psi_b(\boldsymbol{r}_1) & \ldots \\ \psi_a(\boldsymbol{r}_2) & \psi_b(\boldsymbol{r}_2) & \ldots \\ \ldots & \ldots & \ldots \end{vmatrix}$$

Shall we couple electron momenta?
But which?

⇨ Let us answer a question: what are the commuting operators in our case?

LS (Russel-Saunders) coupling

- **Since the non-relativistic Hamiltonian commutes with operators of total angular momentum *L* and total spin *S* its eigenfunction (which we still have to find) are also eigenfunctions of these operators!**
- **For perturbation procedure it makes sense to couple our "unperturbed" wavefunctions:**

$$\left|\gamma L M_L S M_S\right\rangle \equiv \left|n_a l_a s_a, n_b l_b s_b, \ldots : L M_L S M_S\right\rangle$$

- **where:** $\hat{\boldsymbol{L}} = \sum_k \hat{\boldsymbol{l}}_k$ and $\hat{\boldsymbol{S}} = \sum_k \hat{\boldsymbol{s}}_k$

Energy levels corresponding to definite values of *L* and *S* are called terms and are denoted as:

^{2S+1}L

***L*=0 ⇨S**
***L*=1 ⇨P**
***L*=2 ⇨D**
....

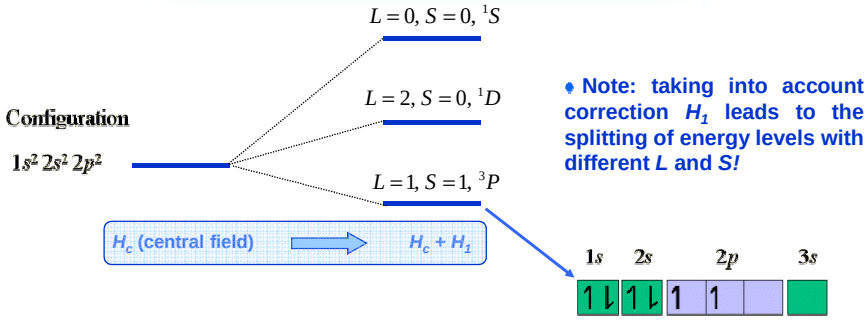
Henry Norris Russell

08 July 2015

Taking correlations into account

- **Now, in the new coupled basis we may apply perturbation theory:**

$$\Delta E = \left\langle \gamma L S M_L M_S \left| \hat{H}_1 \right| \gamma L S M_L M_S \right\rangle$$



- **Note: taking into account correction H_1 leads to the splitting of energy levels with different *L* and *S!***

- **The term with the largest possible value of S (for a given configuration) has the lowest energy.** } Hund's law

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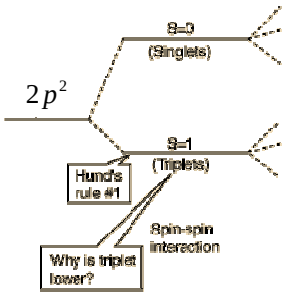
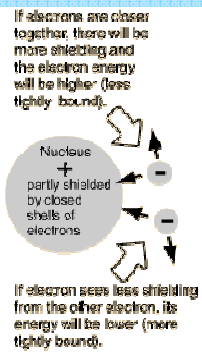
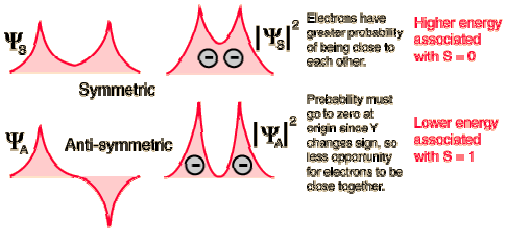
Few words about Hund's law





Picture from:http://hyperphysics.phy-astr.gsu.edu



Taking relativistic effects into account

- **By making use of the perturbation approach, we were able to obtain eigenvalues and eigenfunctions of the non-relativistic Hamiltonian:**

$$\left(\hat{H}_c + \hat{H}_1\right)\Psi\left(\boldsymbol{r}_1, \boldsymbol{r}_2, ...\right) = E\Psi\left(\boldsymbol{r}_1, \boldsymbol{r}_2, ...\right)$$

- **where** $\hat{H}_c = \sum_k \tilde{h}_k = \sum_k \left(-\frac{1}{2}\nabla_k^2 + V(r_k)\right)$ **and** $\hat{H}_1 = \sum_{k<i} \frac{1}{r_{ki}} - \sum_k \left(\frac{Z}{r_k} + V(r_k)\right)$

⇨ But, by increasing nuclear charge Z we expect relativistic effects (in particular spin-orbit coupling) become more sizable.

How to take these effects into account?

To come back to the fully-relativistic (jj) framework? But what if the e-e interaction effects are still stronger than the relativistic ones?

We can use perturbation theory second time! (Now, our unperturbed basis is provided by eigenfunctions of $H_c + H_1$ Hamiltonian!)

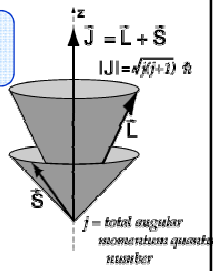
Taking relativistic effects into account

- **Now, we write our Hamiltonian as:**

$$\left(\underbrace{\hat{H}_c + \hat{H}_1}_{\text{non-relativistic terms}} + \underbrace{\hat{H}_2}_{\text{perturbation: relativistic terms}}\right)\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, ..) = E\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, ...)$$

- **where:** $\hat{H}_2 \propto \hat{\boldsymbol{L}}\hat{\boldsymbol{S}}$ ⟹ *L* and *S* are not good quantum numbers anymore! We need to build new basis!

$$|\gamma L S J M_J\rangle = \sum_{M_L M_S} (L M_L \; S M_S | J M_J) | \gamma L M_L \; S M_S \rangle$$

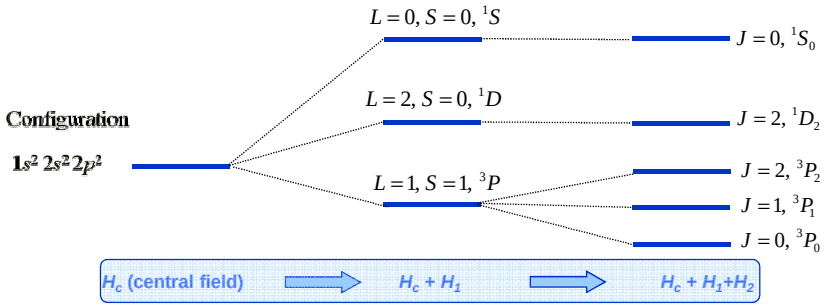


- **By using this basis and the first-order perturbation theory:**

$$\langle \gamma L S J M_J | H_2 | \gamma L S J M_J \rangle \approx A \langle \gamma L S J M_J | \boldsymbol{LS} | \gamma L S J M_J \rangle$$

New notation for the term symbol: $^{2S+1}L_J$

Ground-state configuration of carbon

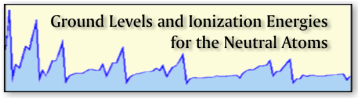


- **Due to the perturbation H_2 term ^{2S+1}L splits into a number of fine-structure components, characterized by the value of the total angular momentum *J*.**
- **The various fine structure components are said to form a *multiplet*.**

Ground-state configuration of carbon

Ground levels and ionization energies for the neutral atoms

Z	Element	Ground-state configuration	Ground level	Ionization energy (eV)	Reference for ionization energy
1	H	Hydrogen	$1s$	$^2S_{1/2}$	13.5984	(1983), (1985)
2	He	Helium	$1s^2$	$^1S_0$	24.5874	(1997), (1998)
3	Li	Lithium	$1s^2\ 2s$	$^2S_{1/2}$	5.3917	Lorenzen & Niemax (1982)
4	Be	Beryllium	$1s^2\ 2s^2$	$^1S_0$	9.3227	Beigman et al. (1983)
5	B	Boron	$1s^2\ 2s^2\ 2p$	$^2P^o_{1/2}$	8.2980	(1970), (1974)
6	C	Carbon	$1s^2\ 2s^2\ 2p^2$	$^3P_0$	11.2603	Johnson (1966)
7	N	Nitrogen	$1s^2\ 2s^2\ 2p^3$	$^4S^o_{3/2}$	14.5341	Eriksson & Pettersson (1971)
8	O	Oxygen	$1s^2\ 2s^2\ 2p^4$	$^3P_2$	13.6181	Eriksson & Ederer (1968)
9	F	Fluorine	$1s^2\ 2s^2\ 2p^5$	$^2P^o_{3/2}$	17.4228	(1949), (1969)
10	Ne	Neon	$1s^2\ 2s^2\ 2p^6$	$^1S_0$	21.5645	Kaufman & Minnhagen (1972)
11	Na	Sodium	[Ne] $3s$	$^2S_{1/2}$	5.1391	(1992), (1998)
12	Mg	Magnesium	[Ne] $3s^2$	$^1S_0$	7.6462	(1987), (1991)
13	Al	Aluminum	[Ne] $3s^2\ 3p$	$^2P^o_{1/2}$	5.9858	(1990), (1991)
14	Si	Silicon	[Ne] $3s^2\ 3p^2$	$^3P_0$	8.1517	Martin & Zalubas (1983)
15	P	Phosphorus	[Ne] $3s^2\ 3p^3$	$^4S^o_{3/2}$	10.4867	Sugar & Musgrove (1990)
16	S	Sulfur	[Ne] $3s^2\ 3p^4$	$^3P_2$	10.3600	Martin et al. (1990)
17	Cl	Chlorine	[Ne] $3s^2\ 3p^5$	$^2P^o_{3/2}$	12.9676	Kaufman & Kaufman (1999)
18	Ar	Argon	[Ne] $3s^2\ 3p^6$	$^1S_0$	15.7596	Velchev et al. (1999)
19	K	Potassium	[Ar] $4s$	$^2S_{1/2}$	4.3407	(1983), (1985)
20	Ca	Calcium	[Ar] $4s^2$	$^1S_0$	6.1132	Sugar & Corliss (1985)
21	Sc	Scandium	[Ar] $3d\ 4s^2$	$^2D_{3/2}$	6.5615	Sugar & Corliss (1985)
22	Ti	Titanium	[Ar] $3d^2\ 4s^2$	$^3F_2$	6.8281	Sansonetti et al. (1990)
23	V	Vanadium	[Ar] $3d^3\ 4s^2$	$^4F_{3/2}$	6.7462	Sansonetti et al. (1994)
24	Cr	Chromium	[Ar] $3d^5\ 4s$	$^7S_3$	6.7665	Sugar & Corliss (1985)
25	Mn	Manganese	[Ar] $3d^5\ 4s^2$	$^6S_{5/2}$	7.4340	Sugar & Corliss (1985)
26	Fe	Iron	[Ar] $3d^6\ 4s^2$	$^5D_4$	7.9024	Sugar & Corliss (1985)
27	Co	Cobalt	[Ar] $3d^7\ 4s^2$	$^4F_{9/2}$	7.8810	Pinnington et al. (1995)
28	Ni	Nickel	[Ar] $3d^8\ 4s^2$	$^3F_4$	7.6398	Pinnington et al. (1995)
29	Cu	Copper	[Ar] $3d^{10}\ 4s$	$^2S_{1/2}$	7.7264	(1948), (1980), (1999)
30	Zn	Zinc	[Ar] $3d^{10}\ 4s^2$	$^1S_0$	9.3942	Brown et al. (1975)



http://physics.nist.gov/

Energy levels corresponding to definite values of L and S are called terms and are denoted as:

$$^{2S+1}L_J$$

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LS and jj coupling schemes

(summary)

- **In general, we have dealt with the Hamiltonian:**

$$\left(\hat{H}_c + \hat{H}_1 + \hat{H}_2\right)\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, ...) = E\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, ...)$$

e-e terms relativistic terms

- **And we discussed a perturbative approach of how to take these terms into account**

$$\langle \Psi | H_1 + H_2 | \Psi \rangle$$

LS (or Russel-Saunders) coupling

$|H_1| >> |H_2|$

- Relativistic effects are small (usually for Z<30).
- Spin *s* and orbital momentum *l* is rather "decoupled" from each other.

$|H_1| \approx |H_2|$

intermediate coupling

jj coupling

$|H_1| << |H_2|$

- Relativistic effects are strong (for high-Z).
- Spin *s* and orbital momentum *l* are coupled into total spin *j*.

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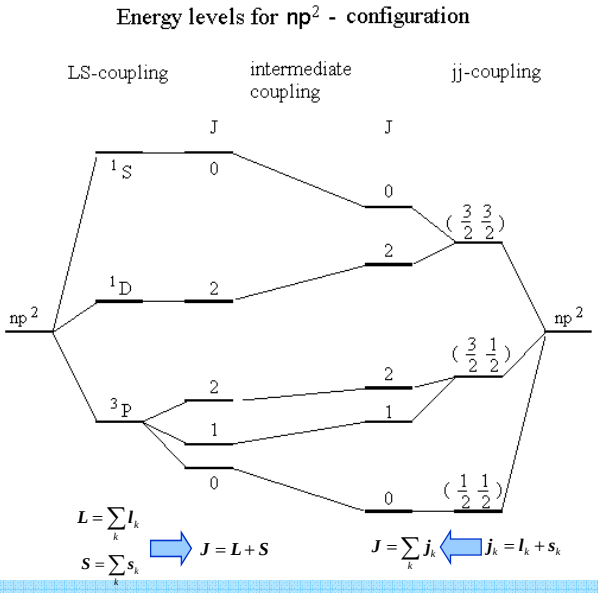
LS and jj coupling schemes
(summary)



Plan of lecture

- Central field approximation for *N*-electron system
- Spectra of many-electron ions: Perturbative approach
  - jj coupling
  - LS coupling
- Variational methods: Hartree-Fock and Dirac-Fock approaches

Many-electron systems: variational approach

(Hartree-Fock/Dirack-Fock methods)

- **The starting point of this approach is again model of independent electrons:**

$$\Psi(q_1,q_2)=\frac{1}{\sqrt{2}}\begin{vmatrix} u_a(q_1) & u_b(q_1) \\ u_a(q_2) & u_b(q_2)\end{vmatrix}$$

$u_a(q), u_b(q)$ are not anymore hydrogenic functions

Douglas Rayner Hartre

- **We again wish to evaluate functional:** $E[\Psi]=\langle\Psi|H|\Psi\rangle$
- **With the "real" Hamiltonian:** $\hat{H}=\sum_{k=1,2}\hat{h}_k+\frac{1}{r_{12}}$

$$\hat{h}_k=-\frac{1}{2}\nabla_k^2-\frac{Z}{r_k}$$

- **After some algebra, we may obtain:**

$$E[\Psi]=\sum_\lambda I_\lambda+\frac{1}{2}\sum_\lambda\sum_\mu\left[J_{\lambda\mu}-K_{\lambda\mu}\right]$$

Vladimir Fock

08 July 2015

Many-electron systems: variational approach

(Hartree-Fock/Dirack-Fock methods)

- **After some algebra, we obtained for the functional:**

$$E[\Psi]=\sum_\lambda I_\lambda+\frac{1}{2}\sum_\lambda\sum_\mu\left[J_{\lambda\mu}-K_{\lambda\mu}\right]$$

- **Where:**
  - **One-electron operator:** $I_\lambda=\langle u_\lambda(q)|h|u_\lambda(q)\rangle$ Don't forget: *u*(q) are not hydrogenic functions anymore!
  - **Two-electron operator (direct term):** $J_{\lambda\mu}=\left\langle u_\lambda(q_1)u_\mu(q_2)\left|\frac{1}{r_{12}}\right|u_\lambda(q_1)u_\mu(q_2)\right\rangle$
  - **Two-electron operator (exchange term):**

$$K_{\lambda\mu}=\left\langle u_\lambda(q_1)u_\mu(q_2)\left|\frac{1}{r_{12}}\right|u_\lambda(q_2)u_\mu(q_1)\right\rangle$$

Having obtained the functional *E* we now proceed to the second step of calculations…

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Many-electron systems: variational approach

(Hartree-Fock/Dirack-Fock methods)

- **We shall express that functional *E* stationary with respect to variations of the orbitals $u_\lambda(q)$.**

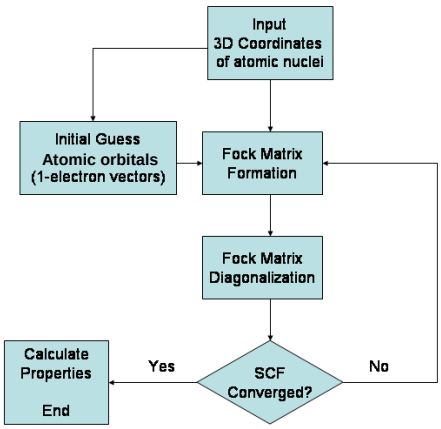
$$E[\Psi] = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad \Rightarrow \quad \delta E[\Psi] = 0$$

Hartree-Fock (Dirac-Fock) equations
(system of coupled integro-differential equations from which one can find orbitals $u_\lambda(r)$)

$$\left[-\frac{1}{2}\nabla_{r_i}^2 - \frac{Z}{r_i} \right] u_\lambda(q_i) + \left[\sum_\mu \int u_\mu^*(q_j) \frac{1}{r_{ij}} u_\mu(q_j) dq_j \right] u_\lambda(q_i)$$

$$- \sum_\mu \left[\int u_\mu^*(q_j) \frac{1}{r_{ij}} u_\lambda(q_j) dq_j \right] u_\mu(q_i) = E_\lambda u_\lambda(q_i)$$

Self-consistent calculations



From: www.wikipedia.org

A number of computer programs are available nowadays to deal with HF/DF methods in atomic and molecular physics.

Configuration interaction

- **HF/DF is very powerful method in atomic physics but the energies obtained from these methods are still not exact ones:**

$$E_{exact} = E_{HF/DF} + E_{corr}$$

Still, part of e-e interactions!

- **How to take the correlation effects into account? Of course, we may again use perturbation approach with HF/DF functions.**
- **But there is an alternative way to use variational method with a new trial function which is built as (here, in relativistic notations):**

$$|\Phi\rangle = \sum_r c_r |\gamma_r J P M_J\rangle$$

variational parameters; different electronic configurations

Muticonfiguration Dirac-Fock (Hartree-Fock) approaches are widely used nowadays in atomic structure and dynamics calculations.

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Task 2

Use variational method to find ground-state energy of non-relativistic Helium atom:

$$\hat{H} = \sum_{k=1,2}\left(-\frac{1}{2}\nabla_k^2 - \frac{Z}{r_k}\right) + \frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|}$$

As a trial function take: $\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \psi_1(\boldsymbol{r}_1, \beta)\psi_2(\boldsymbol{r}_2, \beta)$

Where: $\psi_i(\boldsymbol{r}_i, \beta) = \frac{\beta^{3/2}}{\sqrt{\pi}} \exp(-\beta r_i)$

Use: $$\frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} = \begin{cases} \frac{4\pi}{r_1}\sum_{lm}\frac{1}{2l+1}\left(\frac{r_2}{r_1}\right)^l Y^*_{lm}(\theta_1,\varphi_1)Y_{lm}(\theta_2,\varphi_2) & r_1 > r_2 \\ \frac{4\pi}{r_2}\sum_{lm}\frac{1}{2l+1}\left(\frac{r_1}{r_2}\right)^l Y^*_{lm}(\theta_1,\varphi_1)Y_{lm}(\theta_2,\varphi_2) & r_1 < r_2 \end{cases}$$

08 July 2015

Plan of lectures

- 1 15.04.2015 Preliminary Discussion / Introduction

- 2 22.04.2015 Experiments (discovery of the positron, formation of antihydrogen, ...)
- 3 29.04.2015 Experiments (Lamb shift, hyperfine structure, quasimolecules and MO spectra)
- 4 06.05.2015 Theory (from Schrödinger to Dirac equation, solutions with negative energy)
- 5 13.05.2015 Theory (bound-state solutions of Dirac equation, quantum numbers)
- 6 20.05.2015 Theory (bound-state Dirac wavefunctions, QED corrections)

- 7 27.05.2015 Experiment (photoionization, radiative recombination, ATI, HHG...)
- 8 03.06.2015 Theory (description of the light-matter interaction)
- 9 10.06.2015 Experiment (Kamiokande, cancer therapy, ….)
- 10 17.06.2015 Theory (interaction of charged particles with matter)

- 11 24.06.2015 Experiment (Auger decay, dielectronic recombination, double ionization)
- 12 01.06.2015 Theory (interelectronic interactions, extension of Dirac (and Schrödinger) theory for the description of many-electron systems, approximate methods)
- 13 08.07.2015 Theory (many-electron atoms)

- 14 15.07.2015 Experiment (Atomic physics PNC experiments (Cs,...), heavy ion PV research)