Plan of lectures

Many-electron ions

(Independent particle model and central field approximation)
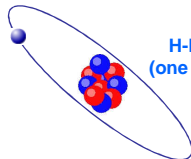
01 July 2015

1

Plan of lecture

- **From one- to two-electron ions (atoms)**

- **Symmetry properties of the two-electron wavefunctions**

- **Independent particle model (IPM)**

- **Corrections to IPM: Screening and coupling**

- **Central field approximation**

- **From two- to many-electron ions (atoms)**

01 July 2015

Solutions for one-electron ions

Erwin Schrödinger

H-like ion (one electron)

Paul Dirac

- **Schrödinger equation (a.u.):**

$$\left(-\frac{1}{2}\nabla^2 + V(\mathbf{r})\right)\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

- **Dirac equation (a.u.):**

$$\left(-ic\,\boldsymbol{\alpha}\cdot\nabla + V(\mathbf{r}) + c^2\alpha_0\right)\psi(\mathbf{r})$$
$$= E\psi(\mathbf{r})$$

- **(Bound-state) energy values:**

$$E_n = -\frac{Z^2}{2n^2}$$

- **(Bound-state) energy values:**

$$E_{nj} = c^2 \left/ \sqrt{1 + \left(\frac{Z\alpha}{n - |j+1/2| + \sqrt{(j+1/2)^2 - (Z\alpha)^2}}\right)^2}\right.$$

- **Wavefunctions:**

$$\psi_{nlm}(\mathbf{r}) = R_{nl}(r)Y_{lm}(\theta,\varphi)$$

- **Wavefunctions:**

$$\psi_{n(\varepsilon)ljm_j}(\mathbf{r}) = \frac{1}{r}\begin{pmatrix} g_{n(\varepsilon)j}(r)\,\Omega_{ljm_j}(\hat{\mathbf{r}}) \\ i\,f_{n(\varepsilon)j}(r)\,\Omega_{l'jm_j}(\hat{\mathbf{r}}) \end{pmatrix}$$

01 July 2015

Solutions for one-electron ions

Erwin Schrödinger

**H-like ion
(one electron)**

Paul Dirac

- **Schrödinger equation (a.u.):**

$$\left(-\frac{1}{2}\nabla^2 + V(\mathbf{r})\right)\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

- **Dirac equation (a.u.):**

$$\left(-ic\,\boldsymbol{\alpha}\cdot\nabla + V(\mathbf{r}) + c^2\alpha_0\right)\psi(\mathbf{r})$$

- **(Bound-state)**

**Note: both energies and wavefunctions are
known for one-electron case analytically!**

$$E_n = -\frac{Z^2}{2n^2}$$

$$E_{nj} = c^2 \Big/ \sqrt{1 + \left(\frac{Z\alpha}{n - |j+1/2| + \sqrt{(j+1/2)^2 - (Z\alpha)^2}}\right)^2}$$

- **Wavefunctions:**

$$\psi_{nlm}(\mathbf{r}) = R_{nl}(r)Y_{lm}(\theta,\varphi)$$
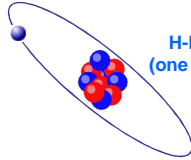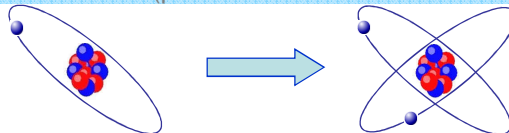
- **Wavefunctions:**

$$\psi_{n(\varepsilon)ljm_j}(\mathbf{r}) = \frac{1}{r}\begin{pmatrix} g_{n(\varepsilon)j}(r)\,\Omega_{ljm_j}(\hat{\mathbf{r}}) \\ i\,f_{n(\varepsilon)j}(r)\,\Omega_{l'jm_j}(\hat{\mathbf{r}}) \end{pmatrix}$$

01 July 2015

From one- to many-electron ions
(particular case of helium-like systems)

- **(Stationary) Dirac equation for the two-electron ions is given by:**

$$\left(\sum_{k=1,2} h_k + V_{12}\right)\Psi(\mathbf{r}_1,\mathbf{r}_2) = E\,\Psi(\mathbf{r}_1,\mathbf{r}_2)$$

- **Here the one-particle Hamiltonians (in atomic units):**

$$h_k = -ic\,\boldsymbol{\alpha}\cdot\nabla_k - \frac{Z}{r_k} + c^2\alpha_0$$

- **And the electron-electron interaction term:**

$$V_{12} = \frac{1}{r_{12}}$$
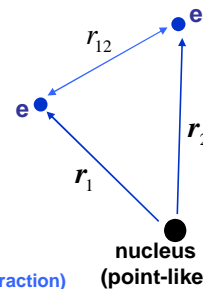
(for the moment we don't consider relativistic corrections to Coulomb interaction)

e

r_{12}

e

r_2

r_1

**nucleus
(point-like)**

01 July 2015

From one- to many-electron ions
(particular case of helium-like systems)

- Our task now is to find solution for the two-electron Dirac equation:
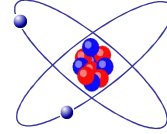
$$\left(\sum_{k=1,2} h_k + V_{12} \right) \Psi(r_1, r_2) = E \Psi(r_1, r_2)$$

- In other words: we have to find energy E and wavefunction $\Psi(r_1, r_2)$

Bad news: analytical solutions for this equation do not exist!

We have to apply *approximate* methods!

- First, let us discuss the general properties of the solutions.

01 July 2015

Plan of lecture

- **From one- to two-electron ions (atoms)**

- **Symmetry properties of the two-electron wavefunctions**

- **Independent particle model (IPM)**

- **Corrections to IPM: Screening and coupling**

- **Central field approximation**

- **From two- to many-electron ions (atoms)**

01 July 2015

Symmetry properties of many-electron wavefunctions

- **Few-electron ions contain a number of electrons which are *identical*!**

- **The Hamiltonian, therefore, must be symmetric with respect to any interchange of the spin and space coordinates of the particle.**

- **Thus an interchange operator commutes with the Hamiltonian:**

$$\left[\hat{P}_{12}, \hat{H}\right] = 0$$

- **As a result, solutions of Dirac equation are - at the same time – eigenfunctions of permutation operator:**

$$\hat{P}_{12}\Psi\left(r_1, r_2\right) = \Psi\left(r_2, r_1\right) = \varepsilon\,\Psi\left(r_1, r_2\right)$$

- **How to find eigenvalues ε?** $\quad P_{12}^2\Psi\left(r_1, r_2\right) = P_{12}\left(\varepsilon\,\Psi\left(r_1, r_2\right)\right) = \varepsilon^2\,\Psi\left(r_1, r_2\right)$

- **Since two successive interchanges shall bring the system back to the original configuration:**

$$\varepsilon = \pm 1$$

Symmetric wavefunction (ε = 1)	Antisymmetric wavefunction (ε = -1)
$\Psi\left(r_2, r_1\right) = \Psi\left(r_1, r_2\right)$	$\Psi\left(r_2, r_1\right) = -\Psi\left(r_1, r_2\right)$

01 July 2015

Symmetrization postulate

- **To our present knowledge: all systems of identical particles in nature could be described by either totally symmetric or totally asymmetric wavefunctions.**

Bosons (particles with zero or integer spin)	Fermions (particles with half-integer spin)
$\Psi\left(r_2, r_1\right) = \Psi\left(r_1, r_2\right)$	$\Psi\left(r_2, r_1\right) = -\Psi\left(r_1, r_2\right)$

Bosons and fermions satisfy different kinds of statistics!
(Statistics depends on spin!)

- **Let us briefly remember two types of statistics!**

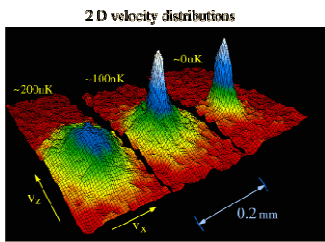01 July 2015

Bose-Einstein statistics
(just few words)

- **To our present knowledge: all systems of identical particles in nature could be described by either totally symmetric or totally asymmetric wavefunctions.**

Bosons
(particles with zero or integer spin)

$$\Psi\left(r_2, r_1\right) = \Psi\left(r_1, r_2\right)$$

Carriers of interaction (γ, W, Z, g), complex particles with total spin J =0,1,2...

Picture from: JILA, University of Colorado, Boulder

2 D velocity distributions

The Bose-Einstein distribution describes the statistical behavior of integer spin particles (bosons).

$$n(E) = \frac{1}{A\,e^{E/kT} - 1}$$

Average population number

At low temperatures, an unlimited number of bosons can collect into the same energy state, a phenomenon called "condensation".
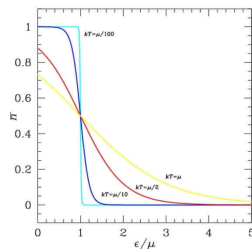
01 July 2015

Fermi-Dirac statistics
(just few words)

- **To our present knowledge: all systems of identical particles in nature could be described by either totally symmetric or totally asymmetric wavefunctions.**

The Fermi-Dirac distribution applies to fermions, particles with half-integer spin which must obey the Pauli exclusion principle.

$$n(E) = \frac{1}{e^{(E - E_F)/kT} + 1}$$

Fermions
(particles with half-integer spin)

$$\Psi\left(r_2, r_1\right) = -\Psi\left(r_1, r_2\right)$$

Leptons, quarks, complex particles with total spin J=1/2, 3/2, ...

Pauli exclusion principle!

Wolfgang Pauli

01 July 2015

Symmetrization postulate

- **To our present knowledge: all systems of identical particles in nature could be described by either totally symmetric or totally asymmetric wavefunctions.**

Bosons
(particles with zero or integer spin)
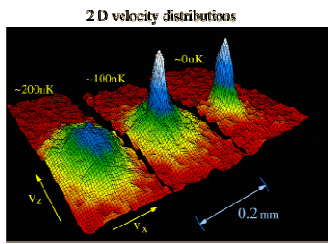
$$\Psi(r_2, r_1) = \Psi(r_1, r_2)$$

Carriers of interaction (γ, W, Z, g), complex particles with total spin J =0,1,2...

Fermions
(particles with half-integer spin)

$$\Psi(r_2, r_1) = -\Psi(r_1, r_2)$$

Leptons, quarks, complex particles with total spin J=1/2, 3/2, ...

Pauli exclusion principle!

Wolfgang Pauli

2 D velocity distributions

~0nK

~100nK

~200nK

v_z

v_x

0.2 mm

01 July 2015

---

01 July 2015

7

Back to the two-electron wavefunction

- **To our present knowledge: all systems of identical particles in nature could be described by either totally symmetric or totally asymmetric wavefunctions.**

Fermions
(particles with half-integer spin)

$$\Psi\left(r_2, r_1\right) = -\Psi\left(r_1, r_2\right)$$

Leptons, quarks, complex particles with total spin J=1/2, 3/2, ...

Pauli exclusion principle!

Wolfgang Pauli

|a>

|b>
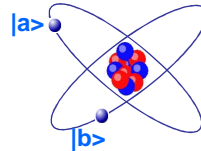
How to build wavefunction of helium-like ion?

$$\left(\sum_{k=1,2} h_k + V_{12}\right)\Psi\left(r_1, r_2\right) = E\Psi\left(r_1, r_2\right)$$

- **Let us build the two-electron wavefunction in terms of one-electron ones:**

$$\Psi\left(r_1, r_2\right) = \psi_a\left(r_1\right)\psi_b\left(r_2\right)$$

- **Good! But does not fit to Pauli principle!**

01 July 2015

Two-electron wavefunction
(symmetry structure)

- **After discussing symmetry properties of the system of indistinguishable electrons (fermions) we may write down the two-electron wavefunction:**

$$\Psi\left(r_1, r_2\right) = \boxed{\frac{1}{\sqrt{2}}}\left(\psi_a\left(r_1\right)\psi_b\left(r_2\right) - \psi_b\left(r_1\right)\psi_a\left(r_2\right)\right)$$

normalization constant
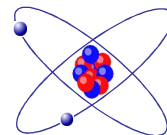
- **It is very convenient to express this function in terms of Slater determinant:**

$$\Psi\left(r_1, r_2\right) = \frac{1}{\sqrt{2}}\begin{vmatrix} \psi_a\left(r_1\right) & \psi_b\left(r_1\right) \\ \psi_a\left(r_2\right) & \psi_b\left(r_2\right) \end{vmatrix}$$

- **(It is straightforward later to extend this expression for describing 3-, 4- ... electron systems.)**

Important question: what are the one-electron functions here?

John C. Slater

01 July 2015

8

Two-electron wavefunction
(symmetry structure)

- After discussing symmetry properties of the system of indistinguishable
  el...

  Please, note: by using Slater determinants it is straightforward to construct N-electron antisymmetrized wavefunction:

$$\Psi(r_1, r_2, \ldots) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_a(r_1) & \psi_b(r_1) & \psi_c(r_1) & \ldots \\ \psi_a(r_2) & \psi_b(r_2) & \psi_c(r_2) & \ldots \\ \psi_a(r_3) & \psi_b(r_3) & \psi_c(r_3) & \ldots \\ \ldots & \ldots & \ldots & \ldots \\ \ldots & \ldots & \ldots & \ldots \end{vmatrix}$$

-

$$\frac{1}{\sqrt{2}} \begin{vmatrix} \psi_a(r_2) & \psi_b(r_2) \end{vmatrix}$$

- **(It is straightforward later to extend this expression for describing 3-, 4- ... electron systems.)**

  Important question: what are the one-electron functions here?

  John C. Slater

Plan of lecture

- **From one- to two-electron ions (atoms)**

- **Symmetry properties of the two-electron wavefunctions**

- **Independent particle model (IPM)**

- **Corrections to IPM: Screening and coupling**

- **Central field approximation**

- **From two- to many-electron ions (atoms)**

Independent particle model

- **Simple, but rather efficient approximation is just to take hydrogenic orbitals as one-particle wave functions:**

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_a(\boldsymbol{r}_1) & \psi_b(\boldsymbol{r}_1) \\ \psi_a(\boldsymbol{r}_2) & \psi_b(\boldsymbol{r}_2) \end{vmatrix} \qquad \begin{aligned} \psi_a(\boldsymbol{r}) &= \psi_{n_a j_a \mu_a}(\boldsymbol{r}) \\ \psi_b(\boldsymbol{r}) &= \psi_{n_b j_b \mu_b}(\boldsymbol{r}) \end{aligned}$$

solutions of Dirac (Schrödinger) equation

- **The wavefunction in IPM is solution of two-electron Dirac equation while neglecting electron-electron interaction:**

$$\left(\sum_{k=1,2} \hat{h}_k + \varnothing \right) \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = E \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) \qquad \propto \frac{1}{r_{12}}$$

IPM can be applied for high-Z ions since the electron-electron interaction scales like 1/Z when compared with electron nucleus interaction.

$$\propto \frac{Z}{r_1} \qquad \propto \frac{Z}{r_2}$$

nucleus (point-like)
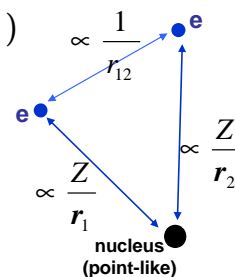
01 July 2015

Independent particle model

(spectroscopy of levels)

- **The wavefunction in IPM**
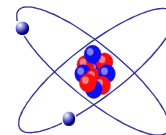
$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_{n_a j_a \mu_a}(\boldsymbol{r}_1) & \psi_{n_b j_b \mu_b}(\boldsymbol{r}_1) \\ \psi_{n_a j_a \mu_a}(\boldsymbol{r}_2) & \psi_{n_b j_b \mu_b}(\boldsymbol{r}_2) \end{vmatrix}$$

- **is solution of two-electron Dirac equation while neglecting electron-electron interaction:**

$$\sum_{k=1,2} \hat{h}_k \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = E \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2)$$

- **The energy of the (two-electron) ion:** $\quad E = E_{n_a j_a} + E_{n_b j_b}$

- **Within the Independent Particle Model the total energy of the system is entirely determined by the *electron configuration!!!***

For example, one may say that He-like ion can be in the states: $1s_{1/2}^2, 1s_{1/2}2s_{1/2}, 2s_{1/2}2s_{1/2}, \dots$

01 July 2015

10

Independent particle model
(energy levels)

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

2s$_{1/2}$ + "free" electron continuum

1s$_{1/2}$ + "free" electron continuum

$2s_{1/2} 2p_{3/2}$

$2s_{1/2}^2$ $2s_{1/2} 2p_{1/2}$

$1s_{1/2} 3s_{1/2}$

$1s_{1/2} 2s_{1/2}$ $1s_{1/2} 2p_{3/2}$

$1s_{1/2} 2p_{1/2}$

$1s_{1/2}^2$

Energy

singly-excited states   **doubly-excited states**

Independent particle model

- **The wavefunction in IPM is solution of two-electron Dirac equation while neglecting electron-electron interaction:**

$$\left(\sum_{k=1,2} \hat{h}_k + \cancel{V_{12}} \right) \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = E \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2)$$

- **The energy of the (two-electron) ion:** $E = E_{n_a j_a} + E_{n_b j_b}$

➡ **Example: ground-state energy of He-like ions**

$\propto \dfrac{Z}{r_1}$ $\propto \dfrac{Z}{r_2}$

nucleus (point-like)

101 %

1 %

Ion	IPM energy	"exact" energy
H$^-$	-1	-0.528
He	-4	-2.904
C^{4+}	-36	-32.41
U^{90+}	-9722	-9605

Independent particle model

- **The wavefunction in IPM is solution of two-electron Dirac equation while neglecting electron-electron interaction:**

$$\left(\sum \ldots \right) \Psi(\ldots) = E \Psi(\ldots)$$

Not bad (especially for heavy He-like ions)! But can we improve our simple model?

- **The e**

Example: ground-state energy of He-like ions

$$\propto \frac{1}{r_{12}}$$

$$\propto \frac{Z}{r_2}$$

$$\propto \frac{Z}{r_1}$$

nucleus (point-like)

101 %

1 %
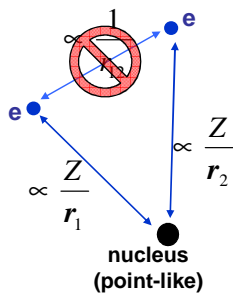
Ion	IPM energy	"exact" energy
H⁻	-1	-0.528
He	-4	-2.904
C^{4+}	-36	-32.41
U^{90+}	-9722	-9605

01 July 2015

Plan of lecture

- ◆ **From one- to two-electron ions (atoms)**

- ◆ **Symmetry properties of the two-electron wavefunctions**

- ◆ **Independent particle model (IPM)**

- ◆ **Corrections to IPM: Screening and coupling**

- ◆ **Central field approximation**

- ◆ **From two- to many-electron ions (atoms)**

01 July 2015

Screening of nucleus
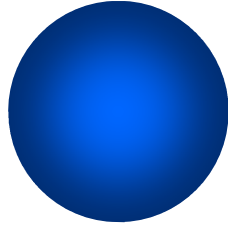
- **In helium-like ions electrons *screen* nucleus from each other!**

- **Each electron already does not "see" the nuclear charge Z but some smaller charge Z_{eff}.**

- **How to estimate "effective charge" Z_{eff}?**

- **We may consider nuclear charge as a parameter and apply variational principle:**

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

- **By varying nuclear charge Z it was found (for non-relativistic systems):**

$$Z_{eff} = Z - \frac{5}{16}$$

"effective charge"   charge of the nucleus

01 July 2015

Independent particle model
(taking screening into account)

- **After taking screening into account, we obtain the wavefunction in IPM:**

$$\Psi(r_1, r_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_{n_a j_a \mu_a}(r_1) & \psi_{n_b j_b \mu_b}(r_1) \\ \psi_{n_a j_a \mu_a}(r_2) & \psi_{n_b j_b \mu_b}(r_2) \end{vmatrix}$$

- **But where one-electron wavefunctions are solutions of Dirac equation:**

$$\left(-ic\,\boldsymbol{\alpha} \cdot \nabla_k - \frac{Z_{eff}}{r_k} + c^2 \alpha_0 \right) \psi_{n_a \kappa_a \mu_a}(r_k) = E_{n_a j_a} \psi_{n_a \kappa_a \mu_a}(r_k)$$

We end up with new energies:

$$E = E_{n_a j_a}(Z_{eff}) + E_{n_b j_b}(Z_{eff})$$

Are further improvements possible?

11 %

0.4 %

Ion	IPM energy with Z_{eff}	"exact" energy
H$^-$	-0.473	-0.528
He	-2.84	-2.904
C^{4+}	-32.36	-32.41
U^{90+}	-9645	-9605

01 July 2015

13

Coupling of angular momenta
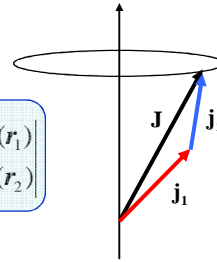
$$\Psi(r_1, r_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_{n_a j_a \mu_a}(r_1) & \psi_{n_b j_b \mu_b}(r_1) \\ \psi_{n_a j_a \mu_a}(r_2) & \psi_{n_b j_b \mu_b}(r_2) \end{vmatrix}$$

Electrons are characterized by their total angular momenta (and parities).

- **Atom (ion) is also characterized by the <u>total angular momentum J</u>.**

- **To find this momentum we need to *couple* together individual electron momenta.**

$$\Psi_{JM_J}(r_1, r_2) = N \cdot \sum_{\mu_a \mu_b} \left(j_a \mu_a \ j_b \mu_b \middle| JM_J \right) \begin{vmatrix} \psi_{n_a j_a \mu_a}(r_1) & \psi_{n_b j_b \mu_b}(r_1) \\ \psi_{n_a j_a \mu_a}(r_2) & \psi_{n_b j_b \mu_b}(r_2) \end{vmatrix}$$

Clebsch-Gordan coefficients

J   **j₂**   **j₁**

Please, remind yourself: we coupled already orbital momentum *l* and spin *s* to the total momentum *j*.

01 July 2015

Normalization of many-electron wavefunctions
(coupled basis)

⚠️ **In contrast to "uncoupled" basis it is not so straightforward now with normalization!**

- **We wish now to find normalization constant *N* for the wavefunction:**

$$\Psi_{JM_J}(r_1, r_2) = N \cdot \sum_{\mu_a \mu_b} \left(j_a \mu_a \ j_b \mu_b \middle| JM_J \right) \begin{vmatrix} \psi_{n_a j_a \mu_a}(r_1) & \psi_{n_b j_b \mu_b}(r_1) \\ \psi_{n_a j_a \mu_a}(r_2) & \psi_{n_b j_b \mu_b}(r_2) \end{vmatrix}$$

- **By assuming "standard" normalization condition for the bound-state wavefunction:**

$$\left\langle JM_J \middle| JM_J \right\rangle = \int \Psi_{JM_J}^*(r_1, r_2) \Psi_{JM_J}(r_1, r_2) dr_1 dr_2$$

- **We obtain (by using properties of Clebsch-Gordan coefficients):**

$$N = \frac{1}{\sqrt{2}}, \text{ if } n_a \neq n_b \text{ or/and } j_a \neq j_b$$

$$N = \frac{1}{2}, \text{ if } n_a = n_b \text{ and } j_a = j_b$$

01 July 2015

Independent particle model
(energy levels)

Energy

$2s_{1/2}$ + "free" electron continuum

$1s_{1/2}$ + "free" electron continuum

$2s_{1/2} 2p_{3/2} : J = 1,2$

$2s_{1/2}^2 : J = 0$ $2s_{1/2} 2p_{1/2} : J = 0,1$

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

$1s_{1/2} 3s_{1/2} : J = 0,1$

$1s_{1/2} 2s_{1/2} : J = 0,1$ $1s_{1/2} 2p_{3/2} : J = 1,2$

$1s_{1/2} 2p_{1/2} : J = 0,1$

Note degeneracy in total angular momentum J.

$1s_{1/2}^2 : J = 0$

singly-excited states   **doubly-excited states**

01 July 2015
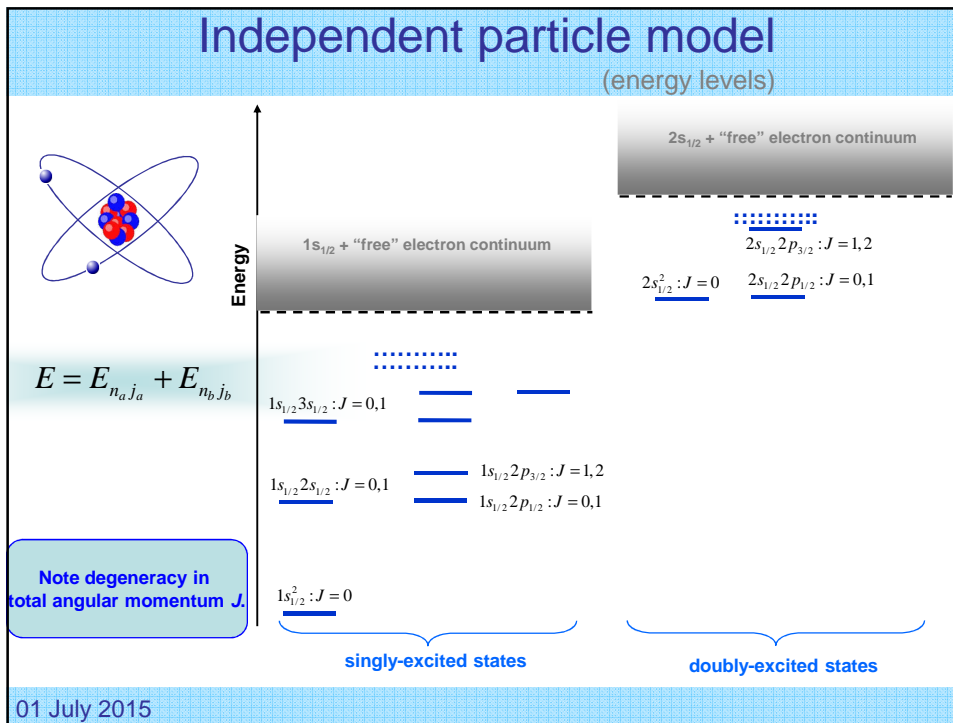
Coupling of angular momenta
(important comment)

- **We have built two-electron wavefunction within the framework of Independent Particle Model:**

$$\Psi_{JM_J}(r_1, r_2) = N \cdot \sum_{\mu_a \mu_b} \left(j_a \mu_a \; j_b \mu_b \middle| JM_J \right) \begin{vmatrix} \psi_{n_a j_a \mu_a}(r_1) & \psi_{n_b j_b \mu_b}(r_1) \\ \psi_{n_a j_a \mu_a}(r_2) & \psi_{n_b j_b \mu_b}(r_2) \end{vmatrix}$$

- **But! Within the IPM individual angular momenta are still good quantum numbers (since we "switched-off" interelectronic interaction).**

- **However, there are two important arguments *pro* making coupling here:**

  1) **IPM wavefunction is good starting point for building more "advanced" wavefunctions.**

  2) **"IPM with coupling" is very often enough for understanding the physics of various collision processes and basics of the structure of heavy ions.**

01 July 2015

Independent particle model: Summary

● **We have built two-electron wavefunction within the framework of Independent Particle Model:**

$$\Psi_{JM_J}\left(r_1, r_2\right) = N \cdot \sum_{\mu_a \mu_b} \left(j_a \mu_a \; j_b \mu_b \big| JM_J\right) \begin{vmatrix} \psi_{n_a j_a \mu_a}(r_1) & \psi_{n_b j_b \mu_b}(r_1) \\ \psi_{n_a j_a \mu_a}(r_2) & \psi_{n_b j_b \mu_b}(r_2) \end{vmatrix}$$
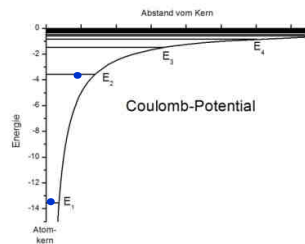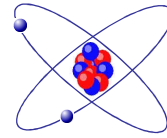
● **This simple model takes into account:**

✓ **Pauli principle (antisymmetrization)**
✓ **Momentum coupling**
✓ **Part of e-e interaction effects (screening)**

Again: IPM is rather good approximation for analyzing many processes involving heavy ions.

But: electrons do not interact with each other directly!

Plan of lecture

♦ **From one- to two-electron ions (atoms)**

♦ **Symmetry properties of the two-electron wavefunctions**

♦ **Independent particle model (IPM)**

♦ **Corrections to IPM: Screening and coupling**

♦ **Central field approximation**
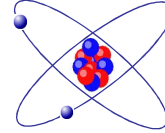
♦ **From two- to many-electron ions (atoms)**

Central field approximation

(derivation from "exact" Dirac equation)

● **Let us again start from the two-electron Dirac equation:**

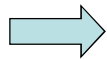$$\left[\sum_k \left(-ic\,\boldsymbol{\alpha}\cdot\nabla_k - \frac{Z}{r_k} + c^2\alpha_0 \right) + \frac{1}{r_{12}} \right] \Psi(\boldsymbol{r}_1,\boldsymbol{r}_2) = E\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2)$$

● **And re-write it in the form:**

central potential!

$$\left[\underbrace{\sum_k \left(-ic\,\boldsymbol{\alpha}\cdot\nabla_k + V(r_k) + c^2\alpha_0 \right)}_{\hat{H}_0} + \underbrace{\left(\frac{1}{r_{12}} + \sum_k \left(-V(r_k) - \frac{Z}{r_k} \right) \right)}_{\hat{H}'} \right] \Psi(\boldsymbol{r}_1,\boldsymbol{r}_2) = E\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2)$$

$\hat{H}_0$
new "unperturbed" Hamiltonian
(still sum of one-electron Hamiltonians)

$\hat{H}'$
perturbation
(chosen to be small)

By neglecting for the moment perturbation term $\hat{H}'$ we may obtain solutions in the central field approximation:

$$\hat{H}_0 \Psi(\boldsymbol{r}_1,\boldsymbol{r}_2) = E\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2)$$

01 July 2015

Central field approximation

(wavefunctions)

● **Solutions of the new central field Hamiltonian:**

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

● **Read again as:**

$$\Psi_{JM_J}(\boldsymbol{r}_1,\boldsymbol{r}_2) = N \cdot \sum_{\mu_a\mu_b} \left(j_a\mu_a\; j_b\mu_b \middle| JM_J \right) \begin{vmatrix} u_{n_a j_a \mu_a}(\boldsymbol{r}_1) & u_{n_b j_b \mu_b}(\boldsymbol{r}_1) \\ u_{n_a j_a \mu_a}(\boldsymbol{r}_2) & u_{n_b j_b \mu_b}(\boldsymbol{r}_2) \end{vmatrix}$$

⬧ **Please, note that *u(r)* functions are not anymore solutions of Dirac-Coulomb equation but:**

$$\left(-ic\,\boldsymbol{\alpha}\cdot\nabla + V(r_k) + c^2\alpha_0 \right) u_{n_a\kappa_a\mu_a}(\boldsymbol{r}_k) = E u_{n_a\kappa_a\mu_a}(\boldsymbol{r}_k)$$

⬧ **Since potential V(r) is central:**

$$u_{nljm_j}(\boldsymbol{r}) = \frac{1}{r} \begin{pmatrix} \tilde{g}_{n\kappa}(r)\,\Omega_{ljm_j}(\hat{\boldsymbol{r}}) \\ i\,\tilde{f}_{n\kappa}(r)\,\Omega_{l'jm_j}(\hat{\boldsymbol{r}}) \end{pmatrix}$$

But radial components (in general case) have to be found numerically! (Depending on the particular form of central potential *V(r)*)

01 July 2015

17

Finding solutions for central field approximation

✦ **Please, note that _u(r)_ functions are not anymore solutions of Dirac-Coulomb equation but:**

$$\left(- ic\,\boldsymbol{\alpha}\cdot\nabla + V(r_k) + c^2\alpha_0\right)u_{n_a\kappa_a\mu_a}(\boldsymbol{r}_k) = E\,u_{n_a\kappa_a\mu_a}(\boldsymbol{r}_k)$$

✦ **Since potential V(r) is central:**

$$u_{nljm_j}(\boldsymbol{r}) = \frac{1}{r}\left(\begin{array}{c} \tilde{g}_{n\kappa}(r)\,\Omega_{ljm_j}(\hat{\boldsymbol{r}}) \\ i\,\tilde{f}_{n\kappa}(r)\,\Omega_{l'jm_j}(\hat{\boldsymbol{r}}) \end{array}\right)$$

✦ **Radial components can be found by <u>numerical solution</u> of the system of coupled equations:**

$$\left(\frac{d\,\tilde{f}_{n\kappa}(r)}{dr} - \frac{\kappa}{r}\,\tilde{f}_{n\kappa}(r)\right) = -\left(E - V(r) - c^2\right)\tilde{g}_{n\kappa}(r)$$

$$\left(\frac{d\tilde{g}_{n\kappa}(r)}{dr} + \frac{\kappa}{r}\,\tilde{g}_{n\kappa}(r)\right) = \left(E - V(r) + c^2\right)\tilde{f}_{n\kappa}(r)$$

Indeed, particular form of the radial components depends on the choice of potential.

01 July 2015

Choice of effective potential

● **Indeed, there are many ways to choose effective (central) potential in:**

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

● **Quite often, people make use of the** $V(r_k) = -\dfrac{Z_{eff}(r_k)}{r_k}$

$$Z_{eff}(r_k) = \begin{cases} Z & r_k \to 0 \\ Z-1 & r_k \to \infty \end{cases}$$
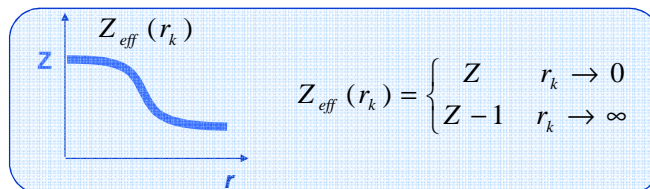
➡ **How to find "effective" nuclear charge?**

One may, for example, apply Poisson's equation: $\Delta V = -4\pi\rho$

01 July 2015

18

Central field approximation
(taking perturbation into account)

- **We have "found" solutions of the new central field Hamiltonian:**

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

- **Which can be given in terms of Slater determinants:**

$$\Psi_{JM_J}(\boldsymbol{r}_1,\boldsymbol{r}_2) = N\cdot\sum_{\mu_a\mu_b}\left(j_a\mu_a\;j_b\mu_b\,|\,JM_J\right)\begin{vmatrix} u_{n_a j_a \mu_a}(\boldsymbol{r}_1) & u_{n_b j_b \mu_b}(\boldsymbol{r}_1) \\ u_{n_a j_a \mu_a}(\boldsymbol{r}_2) & u_{n_b j_b \mu_b}(\boldsymbol{r}_2) \end{vmatrix}$$

- **In order to find solutions of "exact" Hamiltonian:**

$$\left[\underbrace{\sum_k \left(-ic\,\boldsymbol{\alpha}\cdot\nabla_k + V(r_k) + c^2\alpha_0 \right)}_{\hat{H}_0} + \underbrace{\left(\frac{1}{r_{12}} + \sum_k \left(-V(r_k) - \frac{Z}{r_k} \right) \right)}_{\hat{H}'} \right]\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2) = E\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2)$$

- **For relativistic ions (for which relativistic interactions are stronger than interelectronic ones) we may apply perturbation theory in order to take $\hat{H}'$ into account!**

01 July 2015

Central field approximation
(taking perturbation into account)

- **By making use of the first-order perturbation theory we may find energy correction to the central-field energy result:**
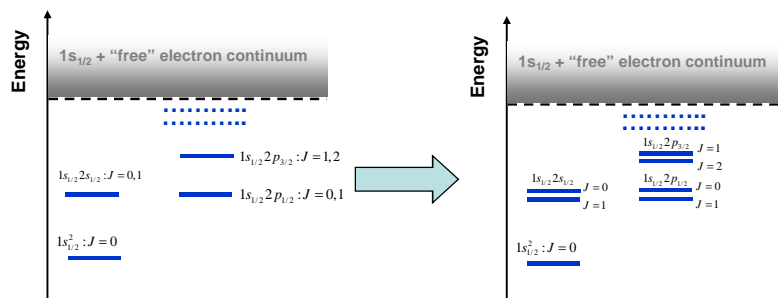
$$E' = \left\langle \gamma\,J\,M_J\,\middle|\,\hat{H}'\,\middle|\,\gamma\,J\,M_J \right\rangle \equiv \int \Psi_{JM_J}^{*}(\boldsymbol{r}_1,\boldsymbol{r}_2)\,\hat{H}'\,\Psi_{JM_J}(\boldsymbol{r}_1,\boldsymbol{r}_2)\,d\boldsymbol{r}_1 d\boldsymbol{r}_2$$

⚠ **Taking e-e interaction into account leads to a splitting of energy levels with different J.**

Pay your attention to notation:

$$\left| \gamma\,J\,M_J \right\rangle = \left| n_1 j_1, n_2 j_2 : J M_J \right\rangle$$

01 July 2015

Plan of lecture

◆ **From one- to two-electron ions (atoms)**

◆ **Symmetry properties of the two-electron wavefunctions**

◆ **Independent particle model (IPM)**

◆ **Corrections to IPM: Screening and coupling**

◆ **Central field approximation**

◆ **From two- to many-electron ions (atoms)**
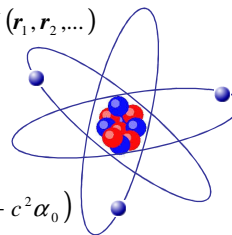

Central field approximation
(generalization to N-electron case)

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

$$\left[\sum_k \left(-ic\boldsymbol{\alpha} \cdot \nabla_k - \frac{Z}{r_k} + c^2 \alpha_0 \right) + \sum_{k<i} \frac{1}{r_{ki}} \right] \Psi(r_1, r_2, ...) = E\Psi(r_1, r_2, ...)$$

$$\left(\hat{H}_0 + \hat{H}' \right) \Psi(r_1, r_2, ...) = E\Psi(r_1, r_2, ...)$$

● **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
... and may use later perturbation theory to include rest terms H'.

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