

UNIT A: QUANTUM MECHANICS

- 1) Systems of identical particles, fermions and bosons. Pauli exclusion principle for fermions. Helium atom. Exchange interaction. Multielectron atoms and periodic table.
- 2) Diatomic molecules and molecular binding. Molecular orbitals. The simplest molecule H_2^+ , Born-Oppenheimer approximation, electronic, vibrational and rotational spectra of diatomic molecules.
- 3) Charged particle in an external magnetic field. Gauge invariance. Landau levels.
- 4) Heisenberg formulation of quantum mechanics. Example: 1D harmonic oscillator, creations and annihilation operators.
- 5) The path integration method. Feynman formulation of quantum mechanics.
- 6) Relativistic wave equations. The Klein-Gordon and Dirac equations.
- 7) Potential scattering. Scattering amplitude and scattering phases. Optical theorem
- 8) Born approximation. Scattering of slow particles. Virtual levels, resonances, Breit-Wigner formula.
- 9) Inelastic scattering. $1/v$ law, neutron capture. Scattering of electrons by atoms.
- 10) Electromagnetic transitions and Quantization of the Electromagnetic Field.

Books:

- E. S. Abers, Quantum Mechanics. Pearson Education Inc. 2004.
R. L. Liboff, Introductory Quantum Mechanics. Pearson Education Inc. 2003.
S. Gasiorowicz, Quantum Physics, John Willey, 2003

PART 1

Identical particles, fermions and bosons, Pauli exclusion principle, Slater determinant.

Variational method.

He atom.

Multielectron atoms, effective potential.

Exchange interaction

Identical particles and quantum statistics.

Consider two identical particles.

- 2 electrons
- 2 protons
- 2 ¹²C nuclei
- 2 photons
- ...

$$\Psi = \Psi(\vec{r}_1, \vec{s}_1, \vec{t}_1; \vec{r}_2, \vec{s}_2, \vec{t}_2 \dots)$$

r_1, s_1, t_1, \dots variables of the 1st particle.

$r_2, s_2, t_2 \dots$ variables of the 2nd particle.

r - coordinate

s - spin

t - isospin

\dots - other internal quantum numbers, if any

omit isospin for now.

The particles are identical \Rightarrow the state is not changed under permutation. (2)

$$\Psi(\Gamma_2, S_2; \Gamma_1, S_1) = R \Psi(\Gamma_1, S_1; \Gamma_2, S_2)$$

R is a coefficient.

Double permutation = 1 \Rightarrow

$$\Rightarrow R^2 = 1 \Rightarrow R = \pm 1.$$

The spin-statistics theorem claims that

Particles with integer spin have $R = 1$, they are called bosons
(Bose-Einstein statistics)

Particles with half-integer spins have $R = -1$, they are called Fermions
(Fermi-Dirac statistics)

The spin-statistics theorem can be proven in relativistic quantum mechanics. Technically the theorem is based on the fact that due to the structure of the Lorentz transformation the wave equation for a particle with spin $\frac{1}{2}$ is of the first order in time derivative (see Dirac eq later in the course).

At the same time the wave equation for a particle with integer spin is of the second order in time derivative.

For example Maxwell's eq. for vector potential in electrodynamics (the wave eq. for photon, $s=1$) reads

$$\left[\frac{1}{c^2} \frac{\partial^2}{\partial t^2} - \nabla^2 \right] \vec{A} = 4\pi \vec{J}$$

↑ second derivative.

Comment: Do not mix permutation with parity, these are different operations

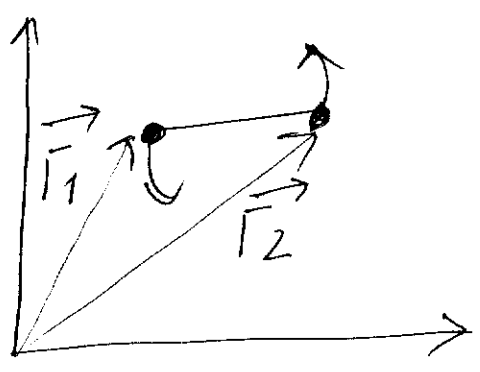
permutation: $\Psi(\Gamma_1, S_1; \Gamma_2, S_2) \rightarrow \Psi(\Gamma_2, S_2; \Gamma_1, S_1)$

space reflection: $\Psi(\Gamma_1, S_1; \Gamma_2, S_2) \rightarrow \Psi(-\Gamma_1, S_1; -\Gamma_2, S_2)$

Example: Statistics influence rotational spectra of diatomic molecules.

Consider rotational spectrum of the C_2 molecule that consists of two ^{12}C .

A ^{12}C nucleus has spin $S=0$ hence it is a boson.



$$\Psi(1,2) = U\left(\frac{\vec{r}_1 + \vec{r}_2}{2}\right) V(\vec{r}_1 - \vec{r}_2) \psi_1 \psi_2$$

↑↑
spin wave functions

U is the wave function of the center of mass motion

V is the wave function of the relative motion

Spin $s=0 \Rightarrow \psi_1 = \psi_2 = 1$

$V(\vec{r}_1 - \vec{r}_2) = \chi(|\vec{r}_1 - \vec{r}_2|) Y_{lm}(\vec{r}_1 - \vec{r}_2)$
permutation

$$\begin{aligned} V(2,1) &= \chi(|\vec{r}_2 - \vec{r}_1|) Y_{lm}(\vec{r}_2 - \vec{r}_1) = \\ &= (-1)^l \chi(|\vec{r}_1 - \vec{r}_2|) Y_{lm}(\vec{r}_1 - \vec{r}_2) = \\ &= (-1)^l V(1,2) \end{aligned}$$

I've used the ^{mathematical} relation $Y_{lm}(-\vec{r}) = (-1)^l Y_{lm}(\vec{r})$

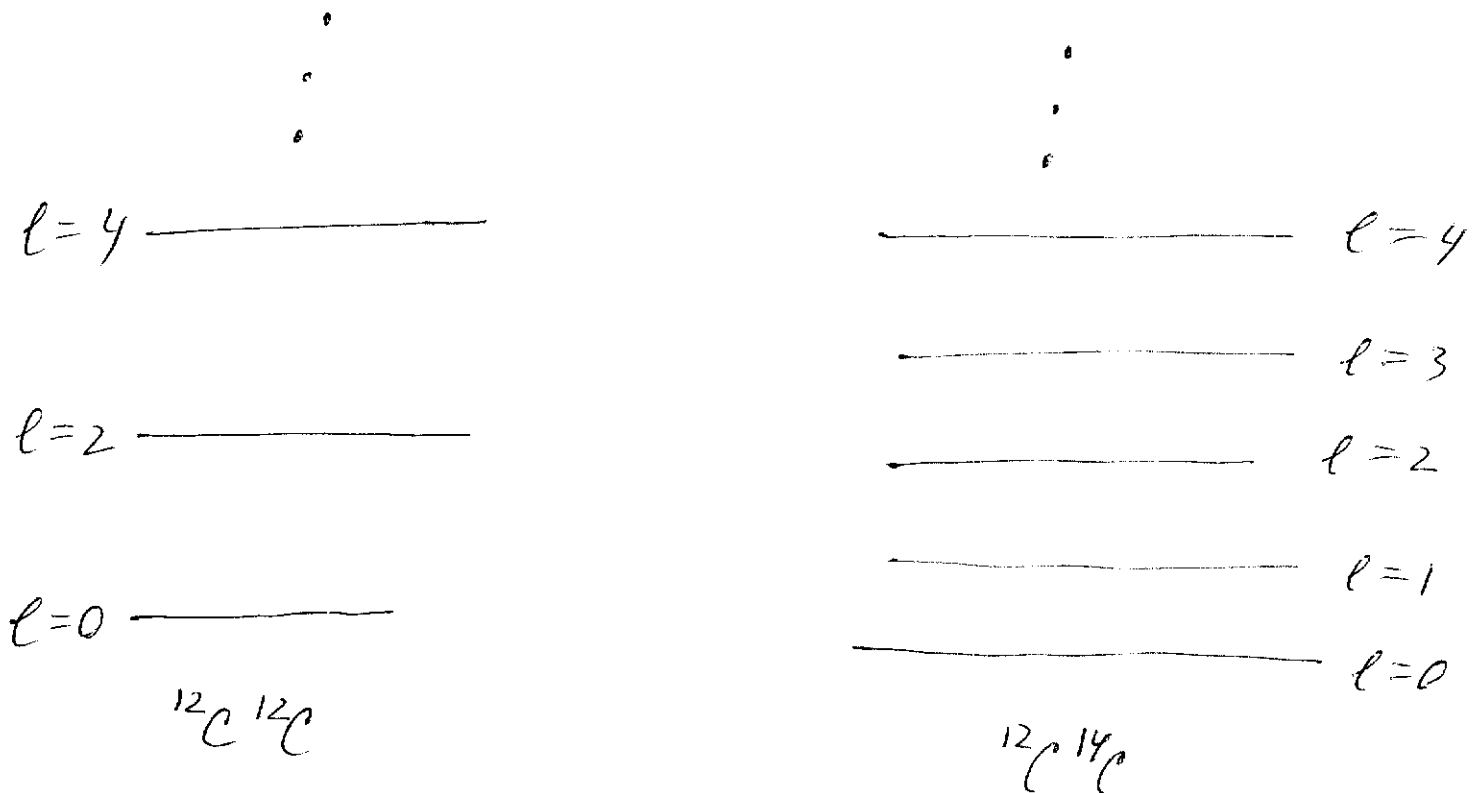
Requirement of Bose statistics:

$$\psi(1,2) = \psi(2,1)$$

Hence only even values of l are allowed in the rotational spectrum of C_2 consisting of two ^{12}C isotopes.

If we take a molecule consisting of two different isotopes, say

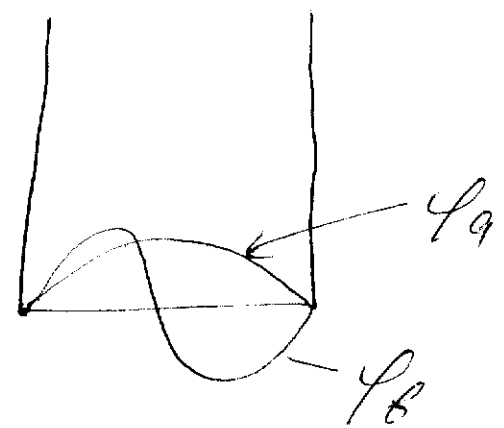
$^{12}C^{13}C$ or $^{12}C^{14}C$ then all values of l are allowed



Two noninteracting fermions in an external potential.

Any external potential: Coulomb field of a nucleus, a potential well, ...

Let ψ_a and ψ_b are single particle states in the potential. For infinite potential well



Let us put two electrons with parallel spins in the potential

Requirement of Fermi statistics:
 $\psi(1,2) = -\psi(2,1)$

Therefore the many-body wave function is

$$\Psi(1,2) = \frac{1}{\sqrt{2}} [\psi_a(r_1)\psi_b(r_2) - \psi_a(r_2)\psi_b(r_1)] | \uparrow \rangle_1 | \uparrow \rangle_2$$

if $\psi_a = \psi_b$ then $\underline{\Psi \equiv 0}$

Thus, one cannot put two fermions in the same single-particle quantum state.

This is Pauli exclusion principle

If spins of the electrons are opposite then the single particle states are different, $\psi_a \uparrow$ and $\psi_a \downarrow$, even if the coordinate states are identical.

So such two-electron state is possible

$$\Psi(1,2) = \psi_a(r_1)\psi_a(r_2) \frac{1}{\sqrt{2}} (|\uparrow\rangle_1 |\downarrow\rangle_2 - |\downarrow\rangle_1 |\uparrow\rangle_2)$$

Slater determinant

Let us introduce spin in the definition of the single particle orbitals, and let us enumerate these orbitals by index i ;

In these notations orbitals of the previous example are

$$\psi_1(r, s) = \psi_{a\uparrow} \equiv \psi_a(r) |\uparrow\rangle$$

$$\psi_2(r, s) = \psi_{a\downarrow} \equiv \psi_a(r) |\downarrow\rangle$$

$$\psi_3(r, s) = \psi_{b\uparrow} \equiv \psi_b(r) |\uparrow\rangle$$

$$\psi_4(r, s) = \psi_{b\downarrow} \equiv \psi_b(r) |\downarrow\rangle$$

Then the wave function on page 7 can be written as

$$\Psi(1, 2) = \frac{1}{\sqrt{2}} [\psi_1(1)\psi_3(2) - \psi_1(2)\psi_3(1)] \equiv$$

$$\equiv \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_1(1) & \psi_1(2) \\ \psi_3(1) & \psi_3(2) \end{vmatrix}$$

↑ determinant.

Similarly, the wave function on page 8 can be written as

$$\Psi(1, 2) = \frac{1}{\sqrt{2}} [\psi_1(1)\psi_2(2) - \psi_1(2)\psi_2(1)] \equiv$$

$$\equiv \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_1(1) & \psi_1(2) \\ \psi_2(1) & \psi_2(2) \end{vmatrix}$$

↖ determinant.

Once more, the notation is

$$\psi_i(X)$$

i enumerates orbitals

X shows coordinates (spacial, spin, etc) of a particle.

Using these notations we can write the many-body wave function for arbitrary number of fermions

$$\Psi(1, 2, \dots, N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(1) & \psi_1(2) & \dots & \psi_1(N) \\ \psi_2(1) & \psi_2(2) & \dots & \psi_2(N) \\ \vdots & \vdots & \dots & \vdots \\ \psi_N(1) & \psi_N(2) & \dots & \psi_N(N) \end{vmatrix}$$

This form was suggested by Slater and it is called Slater determinant. Permutation of two particles is equivalent to permutation of two columns.

For example

$$\begin{aligned} \Psi(2, 1, 3, \dots, N) &= \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(2) & \psi_1(1) & \dots & \psi_1(N) \\ \psi_2(2) & \psi_2(1) & \dots & \psi_2(N) \\ \vdots & \vdots & \dots & \vdots \\ \psi_N(2) & \psi_N(1) & \dots & \psi_N(N) \end{vmatrix} \\ &= -\Psi(1, 2, 3, \dots, N). \end{aligned}$$

(12)

So, the statistics requirement is automatically satisfied.

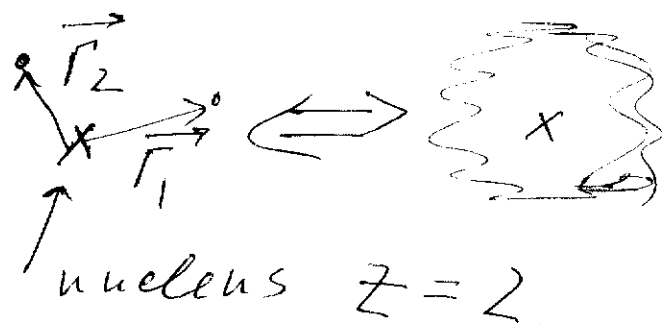
If two orbitals in the determinant coincide: $i=j$, then the determinant vanishes because there are two identical lines. This is the Pauli exclusion principle.

Slater determinant is a very convenient form for the wave function.

Unfortunately this form is exact only for noninteracting fermions.

Interacting fermions. Variational (13) solution for He atom ground state

He atom



$$\hat{H} = \frac{\vec{p}_1^2}{2m} + \frac{\vec{p}_2^2}{2m} - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$$

Schrodinger eq

$$H \psi(1, 2) = E \psi(1, 2).$$

Can be solved exactly numerically
but:

- 1) the solution is very involved technically.
- 2) there is no exact solution for three (Li atom) and more electrons.

So, we need an approximate but relatively simple method.

Variational method

Energy of the system:

$$\langle \psi | \hat{H} | \psi \rangle = \int \psi^* \hat{H} \psi d\tau_1 d\tau_2 \dots$$

constraint (normalization)

$$\langle \psi | \psi \rangle = \int \psi^* \psi d\tau_1 d\tau_2 \dots = 1$$

Let us find min of energy with respect to variation of ψ^* .

To account for the constraint let us use Lagrange multiplier method

$$\frac{\delta}{\delta \psi^*(x)} [\langle \psi^* \hat{H} | \psi \rangle - \lambda \langle \psi^* | \psi \rangle] = 0$$

$$\Rightarrow \hat{H} \psi - \lambda \psi = 0 \Rightarrow \hat{H} \psi = \lambda \psi \Rightarrow$$

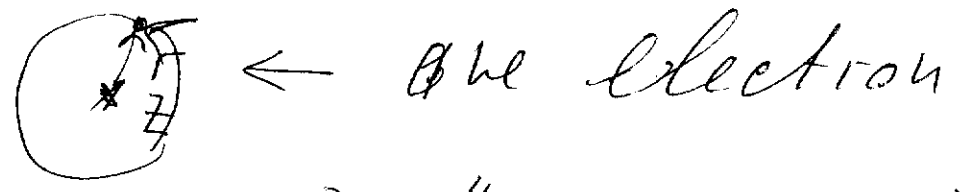
$$\Rightarrow \lambda = E$$

In this case the number of variational parameters = ∞ [$\psi^*(x)$ at each point x] and the variational method is equivalent to Schrodinger eq.

For practical applications we choose a finite number of parameters and hence the variational method gives an approximate answer.

He ground state

1) Hydrogen like situation



$$\left\{ \begin{aligned} \mathcal{E} &= -\frac{Z^2 m e^4}{2 \hbar^4} ; \psi = A e^{-Zr/a_B} \\ a_B &= \frac{\hbar^2}{m e^2} & A &= \sqrt{\frac{Z^3}{\pi a_B^3}} \text{ - normalization} \\ \hat{h} &= \frac{p^2}{2m} - \frac{e^2}{r} \end{aligned} \right.$$

atomic units

$$\left. \begin{aligned} E &\rightarrow \frac{E}{(m e^4 / \hbar^4)} = 27.2 \text{ eV} \\ r &\rightarrow \frac{r}{a_B} = 0.53 \cdot 10^{-8} \text{ cm} \end{aligned} \right\}$$

He Hamiltonian in atomic units

$$\hat{H} = -\frac{\Delta_1}{2} - \frac{\Delta_2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{|r_1 - r_2|}$$

$$\Psi = \varphi(1)\varphi(2) \underbrace{\frac{1}{\sqrt{2}} [|\uparrow\downarrow\rangle_1 |\downarrow\rangle_2 - |\downarrow\rangle_1 |\uparrow\rangle_2]}_{\text{spin part} = \phi_s}$$

$$\varphi_{\frac{1}{2}}(r) = \sqrt{\frac{Z_{\text{eff}}^3}{\pi}} e^{-Z_{\text{eff}} r}$$

Z_{eff} is a variational parameter.



$$\langle \Psi | H | \Psi \rangle = -\frac{1}{2} \langle \Psi | \Delta_1 + \Delta_2 | \Psi \rangle - \langle \Psi | \frac{Z}{r_1} + \frac{Z}{r_2} | \Psi \rangle + \langle \Psi | \frac{1}{|r_1 - r_2|} | \Psi \rangle$$

$$\langle \Psi | \Delta_1 | \Psi \rangle = \int \phi_s^* \varphi^*(2) \varphi_{\frac{1}{2}}^*(1) \Delta_1 \varphi_{\frac{1}{2}}(1) \varphi(2) \phi_s d^3r_1 d^3r_2$$

$$= \underbrace{\langle \phi_s^* | \phi_s \rangle}_{=1} \underbrace{\int \varphi^*(2) \varphi(2) d^3r_2}_{=1} \underbrace{\int \varphi^*(1) \Delta_1 \varphi(1) d^3r_1}_{\text{assignment } - Z_{\text{eff}}}$$

$$\Delta = \frac{1}{r^2} \frac{d}{dr} r^2 \frac{d}{dr}$$

(17)

$$\begin{aligned} \left\langle \frac{Z}{r_1} \right\rangle &= \int \phi_s^* \psi^*(2) \psi^*(1) \frac{Z}{r_1} \psi(1) \psi^*(2) \phi_s d\tau_1^3 d\tau_2^3 \\ &= \underbrace{\langle \phi_s^* | \phi_s \rangle}_{=1} \underbrace{\int \psi^*(2) \psi(2) d\tau_2^3}_{=1} \underbrace{\int \psi^*(1) \frac{Z}{r_1} \psi(1) d\tau_1^3}_{Z Z_{eff}} \end{aligned}$$

assignment

$$\begin{aligned} \left\langle \psi \left| \frac{1}{|r_1 - r_2|} \right| \psi \right\rangle &= \int \phi_s^* \psi^*(2) \psi^*(1) \frac{1}{|r_1 - r_2|} \psi(1) \psi(2) \phi_s d\tau_1^3 d\tau_2^3 \\ &= \langle \phi_s^* | \phi_s \rangle \int \psi^*(2) \psi^*(1) \frac{1}{|r_1 - r_2|} \psi(1) \psi(2) d\tau_1^3 d\tau_2^3 \end{aligned}$$

assignment

$$\frac{6}{\pi^2} \int e^{-2Z_{eff} r_1} e^{-2Z_{eff} r_2} \frac{1}{|r_1 - r_2|} r_1^2 dr_1 d\Omega_1 r_2^2 dr_2 d\Omega_2$$

= $\frac{5}{8} Z_{eff}$

All together

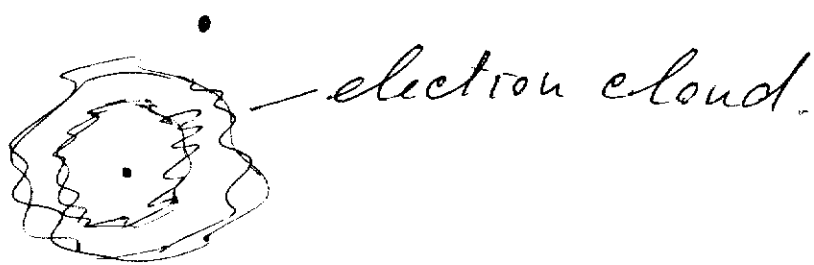
$$\langle \psi | H | \psi \rangle = Z_{eff}^2 - 2Z Z_{eff} + \frac{5}{8} Z_{eff}$$

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

$$E = \langle \psi | H | \psi \rangle = - \left(Z - \frac{5}{16} \right)^2 \left| \begin{array}{l} \rightarrow -77.38 eV \\ Z=2 \end{array} \right.$$

Experiment: $E = -78.9 eV$

Multi-electron atom and effective self-consistent potential

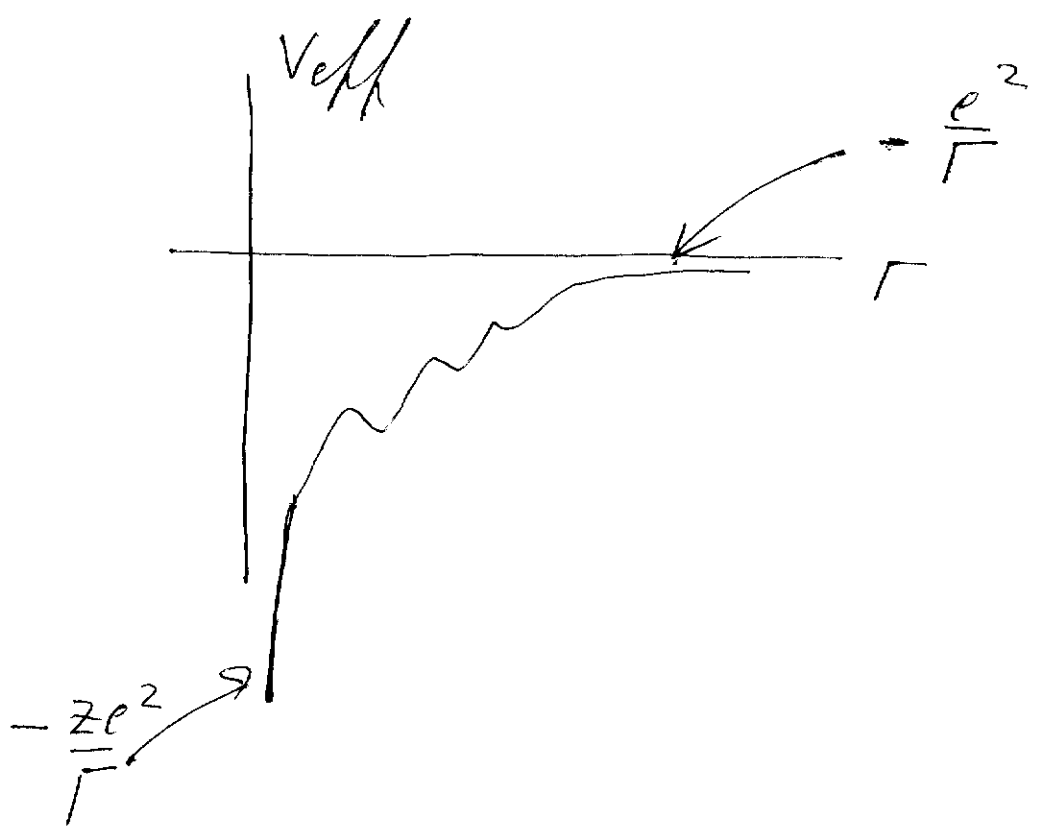


$H_{many-body} \rightarrow H_{single-particle}$

$$H_{sp} = \frac{p^2}{2m} + V_{eff}(r)$$

↑
simple
particle

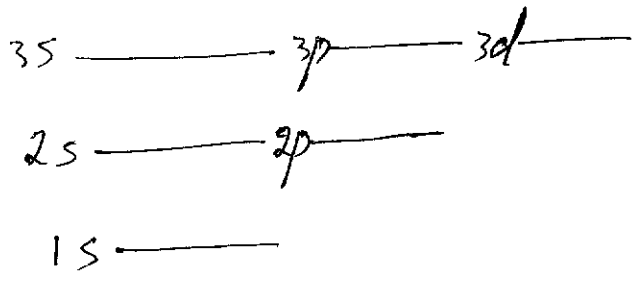
$$\left\{ \begin{array}{l} r \ll \frac{a_B}{Z} : V_{eff} = -\frac{Ze^2}{r} \\ r \gg a_B : V_{eff} = -\frac{e^2}{r} \end{array} \right.$$



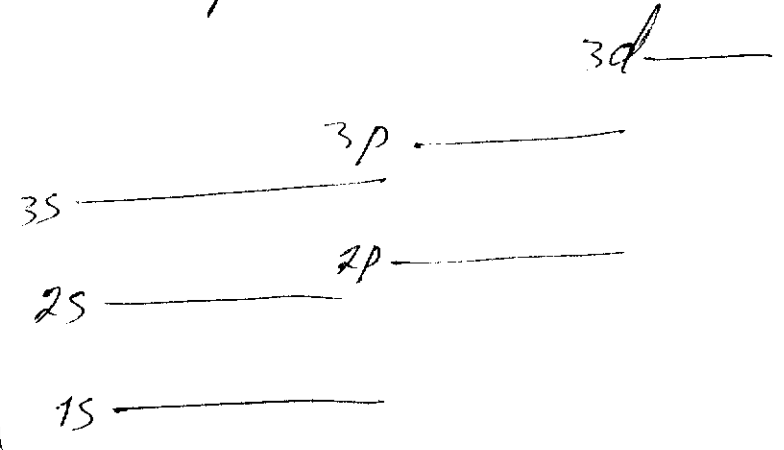
The effective potential is different from that of a point-like nucleus.

Therefore the degeneracy of states with the same principal quantum numbers is lifted

Coulomb potential



Effective atomic potential



Exchange interaction

Consider two lowest excitations of He atom. Experimental spectrum is as follows

	spectroscopic notation	Energy
_____	$1s2s\ ^1S_0$	20.62eV
_____	$1s2s\ ^3S_1$	19.82eV
ground state _____	$1s^2\ ^1S_0$	0

The spectroscopic notation is

$$2S+1, L, J, \quad \frac{1}{J} = \frac{1}{L} + \frac{1}{S}$$

for example 1S_0 means that:

$$S^1 \Rightarrow L = 0$$

$$1 \Rightarrow 2S+1 = 1 \Rightarrow S = 0 \text{ spin}$$

$$0 \Rightarrow J = L + S = 0 + 0 = 0$$

The states $|1s2s, ^1S_0\rangle$ and $|1s2s, ^3S_1\rangle$ differ by total spin only,

$$S = \begin{cases} 0 \\ 1 \end{cases}$$

Question: the interaction is spin independent (Coulomb). Why the states have different energies???

single particle orbitals

$$\left. \begin{aligned} \psi_1(r) \equiv \psi_{1s}(r) &= \sqrt{\frac{Z_{eff}^3}{\pi}} e^{-Z_{eff}r} \\ \psi_2(r) = \psi_{2s}(r) &= \text{some function with one node} \end{aligned} \right\}$$

two particle states

$$|1s2s, ^1S_0\rangle = \frac{1}{\sqrt{2}} [\psi_1(r_1)\psi_2(r_2) + \psi_1(r_2)\psi_2(r_1)] \otimes \frac{1}{\sqrt{2}} [|\uparrow\rangle_1 |\downarrow\rangle_2 - |\downarrow\rangle_1 |\uparrow\rangle_2] \leftarrow \Phi_0(s)$$

$$|1s2s, ^3S_1\rangle = \frac{1}{\sqrt{2}} [\psi_1(r_1)\psi_2(r_2) - \psi_1(r_2)\psi_2(r_1)] \underbrace{[|\uparrow\rangle_1 |\uparrow\rangle_2]}_{\Phi_1(s)}$$

Let us calculate contributions to energies that come from interaction between electrons

$$\begin{aligned}
 E_{^1S_0} &= \langle ^1S_0 | \frac{1}{|\vec{r}_1 - \vec{r}_2|} | ^1S_0 \rangle = \\
 &= \frac{1}{2} \int [\psi_1^*(1)\psi_2^*(2) + \psi_1^*(2)\psi_2^*(1)] \frac{1}{|\vec{r}_1 - \vec{r}_2|} [\psi_1(1)\psi_2(2) + \psi_1(2)\psi_2(1)] \\
 &= \int \frac{|\psi_1(\vec{r}_1)|^2 |\psi_2(\vec{r}_2)|^2}{|\vec{r}_1 - \vec{r}_2|} d^3r_1 d^3r_2 + \int \frac{\psi_1^*(1)\psi_1(2)\psi_2^*(2)\psi_2(1)}{|\vec{r}_1 - \vec{r}_2|} d^3r_1 d^3r_2
 \end{aligned}$$

+

$$\begin{aligned}
 E_{^3S_1} &= \langle ^3S_1 | \frac{1}{|\vec{r}_1 - \vec{r}_2|} | ^3S_1 \rangle = \\
 &= \frac{1}{2} \int [\psi_1^*(1)\psi_2^*(2) - \psi_1^*(2)\psi_2^*(1)] \frac{1}{|\vec{r}_1 - \vec{r}_2|} [\psi_1(1)\psi_2(2) - \psi_1(2)\psi_2(1)] = \\
 &= \int \frac{|\psi_1(\vec{r}_1)|^2 |\psi_2(\vec{r}_2)|^2}{|\vec{r}_1 - \vec{r}_2|} d^3r_1 d^3r_2 - \int \frac{\psi_1^*(1)\psi_1(2)\psi_2^*(2)\psi_2(1)}{|\vec{r}_1 - \vec{r}_2|} d^3r_1 d^3r_2
 \end{aligned}$$

-

Thus the energy is

$$E = \begin{array}{c} 1 \quad 1 \\ \text{---} \\ \text{ } \\ \text{ } \\ \text{---} \\ 1 \quad 1 \end{array} + \begin{array}{c} 1 \quad 2 \\ \text{---} \\ \text{ } \\ \text{ } \\ \text{---} \\ 2 \quad 1 \end{array}$$

↑ direct contribution
exchange contribution

Due to statistics the exchange term depends on total spin in spite of the fact that the interaction is spin independent.

Comparing with exp. data on He we find.

$$2 \otimes \begin{array}{c} 1 \quad 2 \\ \text{---} \\ \text{ } \\ \text{ } \\ \text{---} \\ 2 \quad 1 \end{array} = 0.76 \text{ eV}$$

Comment: magnetism in solids is due to exchange interaction.