Lecture 4

Hydrogenic ions. Identical particles. The Helium atom.

A hydrogenic (or hydrogen-like) ion consists of a single electron orbiting a nucleus with Z protons. What are the corresponding energies?

Potential changes from $\quad V(r) = -\dfrac{e^2}{4\pi\varepsilon_0}\dfrac{1}{r}\quad$ to $\quad V(r) = -\dfrac{Ze^2}{4\pi\varepsilon_0}\dfrac{1}{r}$

so we just need to make substitution $e^2 \rightarrow Ze^2$ in all results.

Question for the class:
What is the ground state energy of hydrogen-like helium (Z=2)?

Hint: hydrogen energies are given by $\quad E = -\left[\dfrac{m_e}{2\hbar^2}\left(\dfrac{e^2}{4\pi\varepsilon_0}\right)^2\right]\dfrac{1}{n^2}$

Answer:

$$E = -\left[\frac{m_e}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\right]\frac{1}{n^2} \xrightarrow{e^2 \rightarrow Ze^2} E = -\left[\frac{m_e}{2\hbar^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2\right]\frac{1}{n^2}$$

$$E = -13.6\,eV\,\frac{Z^2}{n^2} \qquad \begin{array}{l} Z=2 \\ n=1 \end{array} \Rightarrow E = -13.6 \times 4\,eV = -54.4\,eV$$

Bohr radius $\quad a_0 \equiv \dfrac{4\pi\varepsilon_0 \hbar^2}{me^2} \rightarrow a = \dfrac{4\pi\varepsilon_0 \hbar^2}{Zme^2} = \dfrac{a_0}{Z} \Rightarrow$
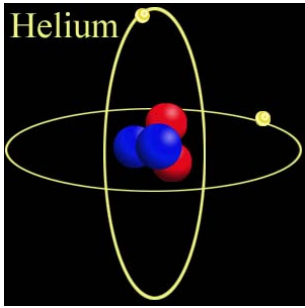
now put "o" label

Ground state wave function is

(H)

$$\psi_{100} = \frac{1}{\sqrt{\pi a_0^3}}\, e^{-r/a_0} \rightarrow$$

H-like He

$$\psi_{100} = \frac{1}{\sqrt{\pi a_0^3}}\sqrt{Z^3}\, e^{-rZ/a_0}$$

$$\boxed{Z=2}$$

$$\psi_{100} = \frac{2\sqrt{2}}{\sqrt{\pi a_0^3}}\, e^{-2r/a_0} \Bigg\rangle \; Z=2$$

Neutral Helium (Z=2), two electrons

Hamiltonian

$$H = \left\{ -\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{1}{4\pi\epsilon_0}\frac{2e^2}{r_1} \right\} + \left\{ -\frac{\hbar^2}{2m_2}\nabla_2^2 - \frac{1}{4\pi\epsilon_0}\frac{2e^2}{r_2} \right\}$$

(with Z indicated above the $2e^2$ term)

Two hydrogenic Hamiltonians (with Z=2), one for electron 1 and one for electron 2.

$$+ \frac{1}{4\pi\epsilon_0}\frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$$

Term that describes repulsion of two electrons.

What can we do to get some wave functions and energies?

In the lowest approximation, we can start by simply ignoring the second term. Then, the solution can be written simply as product of two hydrogen-like wave functions with Z=2:

$$\psi(\vec{r}_1, \vec{r}_2) = \psi_{n\ell m}(\vec{r}_1)\,\psi_{n\ell m}(\vec{r}_2).$$

Questions for the class:

Write ground state wave function of helium ignoring electron repulsion term in the Hamiltonian.

What is its energy?

Answer: The ground state is $\psi_0(\vec{r}_1, \vec{r}_2) = \psi_{100}(\vec{r}_1)\,\psi_{100}(\vec{r}_2) =$

$$= \frac{\sqrt{8}}{\sqrt{\pi a_0^3}}\, e^{-2r_1/a_0}\; \frac{\sqrt{8}}{\sqrt{\pi a_0^3}}\, e^{-2r_2/a_0} = \frac{8}{\pi a_0^3}\, e^{-2(r_1+r_2)/a_0}$$

a_0 is Bohr radius

The energy is just the sum of the energies of two electrons in this approximation:

$$E = 2\left(-13.6\,eV\,\frac{Z^2}{n^2}\right) = -109\,eV$$

$n = 1$
$Z = 2$

The actual experimentally determined energy is -78.975 eV, so while we got some reasonable number in this approximation, the interaction term is quite large. Now, we need to include spin in our description.

The two electrons of the He atom are identical particles. Let's review how to treat this.

Identical particles: bosons and fermions

If the particle one is in state $\psi_a(\vec{r})$ and particle two is in state $\psi_b(\vec{r})$, then the total state can be written as the simple product (we will ignore spin for now):

$$\psi(\vec{r}_1, \vec{r}_2) = \psi_a(\vec{r}_1)\, \psi_b(\vec{r}_2). \qquad Eq. (1)$$

> **Note of caution:** by no means assume that all two-particle states can be separated into simple product states. All entangled states can not be separated into product states. Here is example of the entangled state.
>
> Suppose each of two particles can be in spin state up $\uparrow$ or down $\downarrow$, then the following state can not be separated into product states:
>
> $$\psi_{12} = \frac{1}{\sqrt{2}} \left(\uparrow\downarrow - \downarrow\uparrow \right)$$
>
> with labels #1, #2, #1, #2 under the arrows.
>
> This state means that if the spin of one particle is up, then the spin of the other particle must be down. Such state can not be separated into the product state as neither particle is in definite state of being spin up or spin down.

Equation (1) above assumes that we can tell which particle is particle one and which particle is particle two. In classical mechanics, you can always identify which particle is which. In quantum mechanics, you simply can't say which electron is which as you can not put any labels on them to tell them apart.

There are two possible ways to deal with indistinguishable particles, i.e. to construct two-particle wave function that is non committal to which particle is in which state:

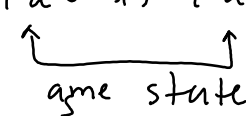$$\psi_+(\vec{r}_1, \vec{r}_2) = A\left[\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) + \psi_b(\vec{r}_1)\psi_a(\vec{r}_2) \right]$$

$$\psi_-(\vec{r}_1, \vec{r}_2) = A\left[\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) - \psi_b(\vec{r}_1)\psi_a(\vec{r}_2) \right].$$

Therefore, quantum mechanics allows for two kinds of identical particles: **bosons** (for the "+" sign) and **fermions** (for the "-" sign). In our non-relativistic quantum mechanics we accept the following statement as an axiom:

All particles with integer spin are bosons, all particles with half integer spin are fermions.

From the above, two identical fermions can not occupy the same state:

$$\psi_- (\vec{r}_1, \vec{r}_2) = A[\psi_a(\vec{r}_1)\psi_a(\vec{r}_2) - \psi_a(\vec{r}_2)\psi_a(\vec{r}_1)] = 0.$$

$\underbrace{\qquad\qquad\qquad}_{\text{same state}}$

It is called **Pauli exclusion principle**.

We introduce operator P that interchanges two particles (exchange operator)

If particles are identical
$$P f(\vec{r}_1, \vec{r}_2) = f(\vec{r}_2, \vec{r}_1). \qquad\qquad P^2 = 1$$
$$[P\ H] = 0 \qquad (PH - HP = 0)$$

Then, we can find solutions to Schrödinger equation that are either symmetric or antisymmetric:

$$\boxed{\psi(\vec{r}_1, \vec{r}_2) = \pm\psi(\vec{r}_2, \vec{r}_1).} \qquad (2)$$

Wave function is required to satisfy (2) for identical particles.

Electrons have spin $1/2$ and; therefore, are fermions. Total wave function has to be antisymmetric.

We already reviewed addition of two 1/2 spins. The result was as follows:

Three states $|s\ m\rangle$ with spin s = 1, m = 1, 0, -1

$$\begin{cases} |1 1\rangle = \uparrow\uparrow \\ |1 0\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow) \\ |1 -1\rangle = \downarrow\downarrow \end{cases} \quad S=1 \quad \begin{array}{l}\text{This is called a} \\ \textbf{triplet}\ \text{configuration.}\end{array}$$

and one state with spin s = 0, m = 0:

$$\left\{|0 0\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow)\right\} \quad S=0 \quad \begin{array}{l}\text{This is called a} \\ \textbf{singlet}\ \text{configuration.}\end{array}$$

Summary: Combination of two spin 1/2 particles can carry a total spin of s =1 or s = 0, depending on whether they occupy the triplet or singlet configuration.

Questions for the class

(a) Is ground state of helium triplet, singlet, or can be either one and can not be determined from the given information?

(b) The helium excited states have form $\psi_{100}\ \psi_{n\ell m}$,

one electron in the ground state and one electron in the excited state.
Do these states have to be singlet, triplet states, or can be both?

Answers:

(a) The total wave function has to be antisymmetric. The spatial wave function that we wrote before is symmetric:

$$\psi(\vec{r}_1,\vec{r}_2) = \frac{8}{\pi a_0^3}\, e^{-2(r_1+r_2)/a_0} \qquad\qquad \psi(\vec{r}_1,\vec{r}_2) = \psi(\vec{r}_2,\vec{r}_1).$$

Therefore, spin state has to be a singlet since it is antisymmetric since total wave function must be antisymmetric.

$$\chi = |00\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow) \implies$$

$$\chi(2,1) = \frac{1}{\sqrt{2}}(\downarrow\uparrow - \uparrow\downarrow) = -\chi(1,2)$$

(b) The excited state can be both triplet or singlet state since the electrons are in different states. We can constrict both symmetric and antisymmetric spatial wave functions. Symmetric spatial wave function will go with singlet spin state (parahelium) and antisymmetric one will be triplet (orthohelium).

Note: If your try to put both electrons in excited states, one of them will drop to the ground state and the released energy with be enough to ionize the other one. You will be left with helium ion He^{+} (hydrogen-like helium) with one electron.

Summary: He ground state is $1s^2$ with L=0 and S=0.
He excited states have configurations 1snl and can have either S=0 (singlet states) or S=1 (triplet states).
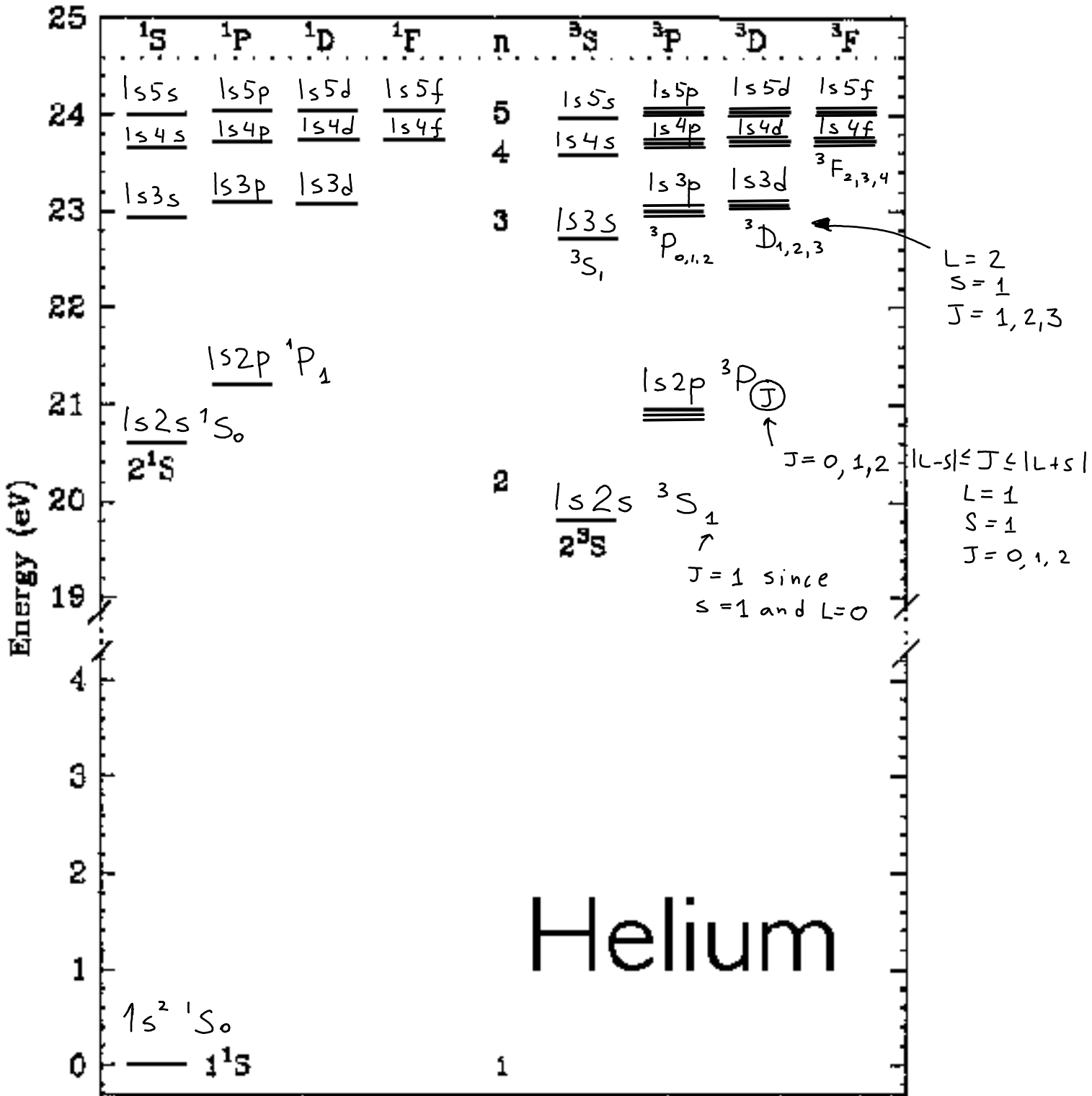
How do we label the atomic states in a general case?

The atomic state is described by its electronic configuration ($1s^2$, for example) and a "term" symbol that describes total S, L, and J of all electrons. The term symbol is always written as follows:

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

Numbers are used for S and J but letters S, P, D, F, etc. are used for L.

Helium energy level diagram

Energy (eV) (y-axis)

	^1S	^1P	^1D	^1F	n	^3S	^3P	^3D	^3F

25 —

— 1s5s   1s5p   1s5d   1s5f

24 —

— 1s4s   1s4p   1s4d   1s4f

5   1s5s   1s5p   1s5d   1s5f

4   1s4s   1s4p   1s4d   1s4f

$^3F_{2,3,4}$

— 1s3s   1s3p   1s3d

23 —

3   1s3s   1s3p   1s3d

$^3S_1$ $^3P_{0,1,2}$ $^3D_{1,2,3}$

22 —

L = 2
S = 1
J = 1, 2, 3

1s2p $^1P_1$

21 —

1s2s $^1S_0$

2^1S

1s2p ^3P_J

J = 0, 1, 2 $|L-S| \le J \le |L+S|$

L = 1
S = 1
J = 0, 1, 2

20 —

2   1s2s $^3S_1$

2^3S

J = 1 since
s = 1 and L = 0

19 —

4 —

3 —

2 —

Helium
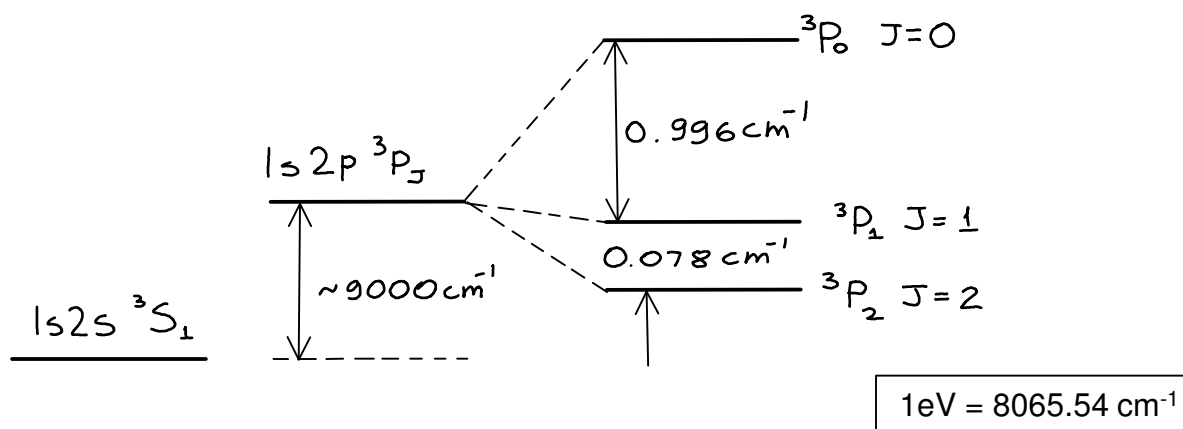
1 —

$1s^2 \; ^1S_0$

0 — 1^{1}S

1

$2S+1$

L_J

Helium ground state $1s^2$ $^1S_0$

Helium excited states 1snl ^1L_J or ^3L_J

He 1s2p fine structure, compared to 1s2s level position

$^3P_0$ J=0

0.996 cm^{-1}

1s2p ^3P_J

$^3P_1$ J=1

0.078 cm^{-1}

~9000 cm^{-1}

$^3P_2$ J=2

1s2s $^3S_1$

1eV = 8065.54 cm^{-1}

Units: due to variety of energy scales in atomic physics, you may see energies displayed in eV, cm^{-1}, Hz, atomic units, and Rydberg, so one needs to know how convert between quantities displayed in such various units. One of the most frequently used energy units is cm^{-1}. MHz and GHz are mostly frequently used for hyperfine structure.

Atomic units

In atomic units, electron mass m_e, electric charge e, reduced Planck's constant $\hbar = h/2\pi$, and Coulomb's constant $1/(4\pi\epsilon_0)$ all have numerical value of 1.

Derived atomic units & other quantities:

Length	Bohr radius	$a_0 = \dfrac{4\pi\epsilon_0 \hbar^2}{m_e e^2}$	5.29177×10^{-11}m
Energy	Hartree	$E_H = \dfrac{m_e e^4}{(4\pi\epsilon_0 \hbar)^2}$	4.359744×10^{-18}J = 27.21138eV
Time		$\hbar / E_H$	2.4188843×10^{-17}s
Electric dipole moment		$e a_0$	8.478353×10^{-30} C·m
Electric field		$E_H /(e a_0)$	5.1422065×10^{11} V/m
Magnetic moment		$2\mu_B = e\hbar/m_e$	1.854802×10^{-23}J/T
Magnetic field		$E_H / 2\mu_B$	2.350517×10^5 T
Speed of light	$c = 1/\alpha$	$4\pi\epsilon_0 \hbar c / e^2$	137.036
Temperature		E_H / k_B	3.1577464×10^5 K

Note that hydrogen energy levels are given by $E_n = -\dfrac{E_H}{2}\dfrac{1}{n^2}$ — Hartree, atomic unit of energy

Atomic unit of energy is 1a.u. = 27.211 eV (twice the binding energy of the 1s state of H)

Also, $E_n = -\frac{1}{n^2} hc\, Ry$ ← Ry has units of inverse length

value for infinitely heavy nucleus

Rydberg constant r (or Ry) has a numerical value $Ry_\infty = 109737.3157$ cm^{-1}

$Ry = Ry_\infty \dfrac{m_p}{m_e + m_p}$ for H

$E_n = -\frac{1}{n^2} E_R \Rightarrow E_H = 2E_R$

↖ 13.6 eV (1s H binding energy)

Since atomic unit of energy is E_H, to convert between energy atomic units and cm-1 multiply by 2R=219474.6314cm^{-1}.

1 a.u. (energy) $\Rightarrow$ 219474.6314 cm^{-1}
1 a.u. (energy) $\Rightarrow$ 27.21138 eV
1 eV $\Rightarrow$ 8065.54 cm^{-1}

Using $E = h\nu$, $\nu = E/h$, and plugging E_H and Planck's constant yields

equivalence of these energies in Hz:

1eV $\Rightarrow$ 2.41799×10^{14} Hz
1cm^{-1} $\Rightarrow$ 2.99792×10^{10} Hz

Note that when the energy interval between the two levels is expressed in cm^{-1} the wavelength in vacuum for the corresponding transition is just 1/E.

Example: Rb 5s-5p$_{1/2}$ energy difference is 12816.5 cm^{-1} and the wavelength of the 5s-5p$_{1/2}$ transition is (1/12816.5) cm = 780.24 nm [nm=10^{-9}m].