

Helium atom and the origin of ferromagnetism by Werner Heisenberg

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In 1926, Heisenberg was able to account for the helium atom problem using the Schrödinger equation with the use of the Pauli's exclusion principle and Hund's rule for the total spin. Pauli's exclusion principle is the anti-symmetric property of the total wavefunction. In Hund's rule, the lowest energy state has the maximum value of total spin S .

In helium atom, there are two electrons outside the nucleus (two protons and two neutrons). These electrons are identical fermions. Note that the Hamiltonian of helium atom is totally independent of spins. The first-order perturbation theory is applied to the degenerate orbital states. The repulsive Coulomb interactions between two electrons is regarded as perturbation. The total wavefunction of two electrons consists of a product of the orbital wavefunction and spin wavefunction. According to the Pauli's exclusion principle, the total wavefunction should be antisymmetric under the interchange of particles. For the spin wavefunction, the triplet state of two $1/2$ -spins is symmetric ($S = 1$) and the singlet state is antisymmetric ($S = 0$) under the interchange of particles. According to the Hund's rule, the energy level of the symmetric state ($S = 1$) should be lower than that of the antisymmetric state ($S = 0$) for typically a $(1s)(2s)$ electron configuration. The energy level of the doubly degenerate state is split into two separated states. For the low energy state, the orbital wavefunction is antisymmetric ($S = 1$, the **orthohelium**) under the interchange of two particles, while the orbital wavefunction is symmetric ($S = 0$, the **parahelium**). Heisenberg found that the separation between two separated energy is a spectral term and is much larger than conventional magnetic dipole-dipole interaction. Using the Dirac spin exchange operator, the effective spin Hamiltonian can be expressed in terms of a Heisenberg exchange interaction with very large exchange interaction (it is on the order of the spectral term). For the first time, Heisenberg gave a clear explanation for the origin of the ferromagnetism; the spectral term of two electron systems. According to the book of Cassidy, this work had enabled Heisenberg's Nobel Prize-winning work (Nobel laureate in physics in 1932). It is amazing that Heisenberg used the Schrödinger equation to solve the two-body problem of helium atom, while Heisenberg debated with Schrödinger whether the Heisenberg's matrix formulation is much more fundamental to quantum mechanics, compared to the Schrödinger formulation. When the number of identical particles change from one to two, new concepts should be required for understanding the quantum mechanics. We need to take into account of interaction between two particles, time independent perturbation (degenerate and nondegenerate cases), Pauli exclusion principle, Hund's law, and so on.

When I taught on the physics of helium atom (identical particle) in Phys.422 (Quantum Mechanics II) in the Spring, 2022, I became so interested in the experimental data of exchange

integrals from helium spectra. Finally, I found the experimental data of helium atom, so-called NIST Data (National Institute of Standard and Technology). Next step, I calculated the Coulomb integrals and the exchange integrals (which are seen in many standard textbooks on quantum mechanics) by using Mathematica. The main motivation of this article is to compare the theoretical values of exchange integral based on the first-order perturbation to the degenerate system, with those derived from the NIST Data. In order to do this, I collected information related to the exchange integrals of helium atom, from standard textbooks of quantum mechanics.

Here, we present the Heisenberg's theory on helium atom. We use Mathematica for the calculation of Coulomb integral and exchange integral. The symmetric and antisymmetric wavefunctions, can be constructed from the orbital wavefunctions of hydrogen atom with one electron. The first-order perturbation theory of the degenerate system is applied, where the repulsive Coulomb interaction is treated as a perturbation. Calculated values are compared with the experimental values obtained from NIST Atomic Spectra Data base levels Form.

https://physics.nist.gov/PhysRefData/ASD/levels_form.html

The second element in the periodic table provides our first example of a quantum-mechanical problem which *cannot* be solved exactly. Nevertheless, as we will show, approximation methods applied to helium can give accurate solutions in perfect agreement with experimental results. In this sense, it can be concluded that quantum mechanics is correct for atoms more complicated than hydrogen. By contrast, the Bohr theory failed miserably in attempts to apply it beyond the hydrogen atom.

We do not have to take into account of the spin-orbit coupling in helium since it is actually extremely small because of small Z ($=2$). Note that the magnitude of the spin-orbit interaction is proportional to the atomic number Z . Note that the value of Z may be reduced from 2 to 1.6875 because of the polarization effect in the ground state $(1s)(1s)$ electron configuration.



Fig.1 At the University of Chicago. 1929. Front row from left to right: Werner Heisenberg, Paul Dirac, Robert Millikan, and Friedrich Hund.

From the book of **D. Cassidy, Beyond Uncertainty; Heisenberg, Quantum Physics, and the Bomb** (Bellevue Literary Press, 2009).

((**Prof. Werner K. Heisenberg**))

Werner Karl Heisenberg (Würzburg, Kingdom of Bavaria, German Empire; 5 December 1901 – Munich, Bavaria, Germany; 1 February 1976) was a German theoretical physicist and one of the key pioneers of quantum mechanics. He published his work in 1925 in a breakthrough paper. In the subsequent series of papers with Max Born and Pascual Jordan, during the same year, his matrix formulation of quantum mechanics was substantially elaborated. He is known for the uncertainty principle, which he published in 1927. Heisenberg was awarded the 1932 Nobel Prize in Physics "for the creation of quantum mechanics".

https://en.wikipedia.org/wiki/Werner_Heisenberg



Fig.2 Prof. Werner K. Heisenberg in 1933

((C.P. Enz))

Heisenberg's application of quantum mechanics (1926-1933) or the settling of the new land [Helvetica Physica Acta 56, 993 (1983)]

We find a very interesting article of C.P. Enz in the introduction, which clearly explained that Werner Heisenberg played a significant role of the development in the quantum mechanics (1926 – 1933).

The discovery of quantum mechanics between 1925 and 1926 was almost simultaneously followed by the setting out for the new land to explore the new theory with respect to the physical interpretation and its formal structure. Heisenberg played a important part in both these stages. In his exploratory role, Heisenberg mainly contributed as co-author of the 3-man paper (with Born and Jordan), but also as partner of Pauli in an exchange of letters on the development of a formalism of action and angle variables. This endeavor was never published because of the problem had just been solved in a most elegant way as Dirac. In a third stage devoted to the 'settling of the new land' quantum mechanics was applied to the physical problems left unexplained by the old quantum theory. Here again Heisenberg made important contributions which are described in this paper. Prominent among the unsolved physical problems was the anomalous Zeeman effect with which Heisenberg had struggled since the beginning of his scientific career and whose solution he got at last in 1926. A more difficult problem, because it involves two electrons, was the singlet-triplet splitting in the spectrum of the Helium atom which Heisenberg solved in the same year. The third application concerned an old many-electron problem, namely the explanation of ferromagnetism; it was settled by Heisenberg in 1928.

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1. Overview: Origin of ferromagnet (Heisenberg)

In helium atom (denoted as He I) there are two electrons (identical particles) near the nucleus consisting of two protons and two neutrons. There is a repulsive Coulomb interaction between two electrons, in addition to attractive Coulomb interaction between two protons and each electron. The energy level of electrons in helium atom was first discussed by Werner Heisenberg. The total

wavefunction is a product of orbital wavefunction and spin wavefunction. The singlet spin is antisymmetric, while the triplet spin is symmetric with respect to interchange of particles.

The system of two electrons in helium atom is closely related to the origin of ferromagnetism which was found by Werner Heisenberg in 1926. It is amazing that the origin of ferromagnetism can be derived from the application of quantum mechanics to two electrons in helium atom. It was finally recognized in the early days of quantum mechanics that the Heisenberg's exchange interaction probably valid between all neighboring atoms. The development of his research on the origin of ferromagnet and He atom is well described by C.P. Enz [Helvetica Physics Acta 56, 993-1001 (1983); Heisenberg's applications of quantum mechanics (1926-33) or the settling of the new land

<https://www.e-periodica.ch/cntmng?pid=hpa-001%3A1983%3A56%3A%3A1314>

2. Identical particles fo helium atom and Pauli's principle of exclusion

As a typical example of identical particles, we discuss the energy levels of two electrons around the nucleus (two protons) in helium (He) atom. Since electrons are fermion with a spin $1/2$, the total wavefunction of the two electrons should be antisymmetric under the interchange of two particles. These wavefunctions are the product of the orbital wavefunction and spin wavefunction. The spin wavefunction is antisymmetric for $S = 0$ (singlet), while it is symmetric for $S = 1$ (triplet).

$$D_{1/2} \times D_{1/2} = D_1 + D_0.$$

Correspondingly, the orbital wavefunction should be symmetric for $S = 0$, while it should be symmetric for $S = 1$. Thanks to NIST (National Institute of Standard and Technology, we can obtain the atomic spectra data of He I and He II from the web site; NIST (National Institute of Technology) atomic spectra data base levels form. Here the energy levels of two electrons in He atom will be discussed using the symmetric and antisymmetric orbital wavefunctions and then compared with the NIST data which are the best among experimentally reliable ones: https://physics.nist.gov/PhysRefData/ASD/levels_form.html

Although the Hamiltonian of two electrons in helium atom does not include any interaction dependent on spins. The total wavefunction should be antisymmetric under the interchange of two particles in the unperturbed degenerate system. When the repulsive Coulomb interaction between two electrons is applied to the unperturbed system, the resultant energy levels split into two levels; energy level with the symmetric spin state ($S = 1$; triplet) and the energy (antisymmetric spin state ($S = 0$, singlet), leading to the effective spin Hamiltonian, so called Heisenberg's exchange interaction. Thus, the origin of ferromagnetism was explained from the exchange interaction between spins. The final form of the effective spin Hamiltonian is expressed as

$$\hat{H}_{eff} = (I - \frac{1}{2}K)\hat{1} - \frac{2K}{\hbar^2}\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2, \quad (\text{Heisenberg model})$$

which is called as Heisenberg's exchange interaction; interaction between $\hat{\mathbf{S}}_1$ and $\hat{\mathbf{S}}_2$, where J is the Coulomb integral and K is the exchange integral. In some books, the notations I and K are used instead of K and J , respectively. Note that the permutation operator is expressed by the Dirac spin exchange operator $\hat{P}_{12}^\sigma$ as

$$\hat{P}_{12}^\sigma = \frac{1}{2}(\hat{1} + \frac{4}{\hbar^2} \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2) = \frac{1}{2}(\hat{1} + \hat{\boldsymbol{\sigma}}_1 \cdot \hat{\boldsymbol{\sigma}}_2). \quad (\text{Dirac spin exchange operator})$$

After Heisenberg's paper, Dirac also published a paper on the apparent spin-spin interaction. He derives the spin-spin interaction ingeniously by considering the interchange of particles (in general, permutation) as a physical quantity.

((Tomonaga, Sin-itiro))

From the book of S. Tomonaga, The Story of Spin (University of Chicago)

We found a very interesting article on the origin ferromagnetism by Heisenberg (Nobel prize in physics, 1932), in Tomonaga's book [The Story of Spins by S. Tomonaga (University of Chicago, 1997)]: The content of this article is as follows. We note that Prof. Sin-itiro Tomonaga (Nobel prize on physics, 1965, sharing with J. Schwinger and R.P. Feynman) collaborated with Prof. Heisenberg at Leipzig University in Germany, during the period between 1937 and 1939. In 1929, both Heisenberg and Dirac were invited to Japan in 1929, When Heisenberg and Dirac visited Japan in the September of 1929, they gave six lectures each on their works on quantum mechanics at Tokyo Imperial University (current University of Tokyo) and Riken. Tomonaga was strongly influenced by their lectures, facing newly developed quantum mechanics in Europe.

The effect of the apparently large interaction between electron spins is not limited to spectral term values. In order to explain the ferromagnetism of iron (Fe), as you may know, Pierre Weiss proposed long ago that there is a large interaction between molecular magnets based on the then-accepted concept of the molecular magnet. By using this idea, Weiss could explain a wide variety of experimental results related to ferromagnetism. However, the origin of such a strong interaction between molecular magnets was entirely unknown.

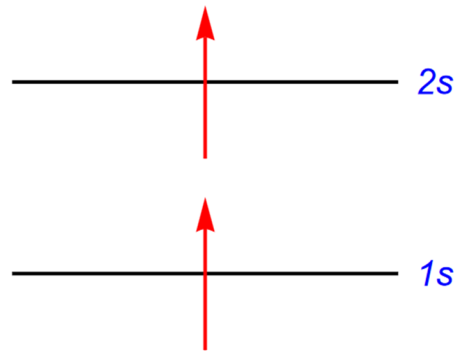
Then, there appeared the new interpretation of the spectral terms of alkaline earth (but not Helium). This new interpretation was given by Werner Heisenberg in 1926., he not only discovered that the symmetry property of the wavefunction has a close connection to a particle's statistics in a many-electron system but also found that it plays an important role in variety of problems and for the first time gave a clear explanation of the spectral terms of two-electron systems. Furthermore, immediately after this work he applied the same idea to the problem of ferromagnetism.

Ferromagnetism occurs because electron spins outside all the Fe atomic cores point in the same direction over an entire macroscopic crystal of Fe. The apparently very strong spin-spin interaction just discussed, plays the role of orienting spins in the same direction. Therefore, the subtle property of electron spin appears directly in the everyday macroscopic phenomenon of a magnet interacting iron, and this is related to wholly transcendent facts such as the symmetry property of wavefunctions and the electron being a fermion (obeying the Pauli's exclusion principle). This is one good example of transcendent theory appearing directly in ordinary phenomena.

3. Hund' rule

We consider the total spin angular momentum for the electron configuration, $(1s)(2s)$, by using the Hund's rule

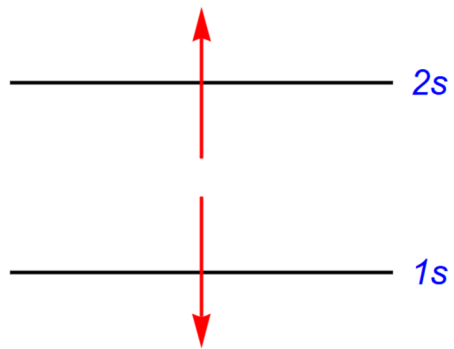
$$|+z, +z\rangle \quad (S = 1, m = 1)$$



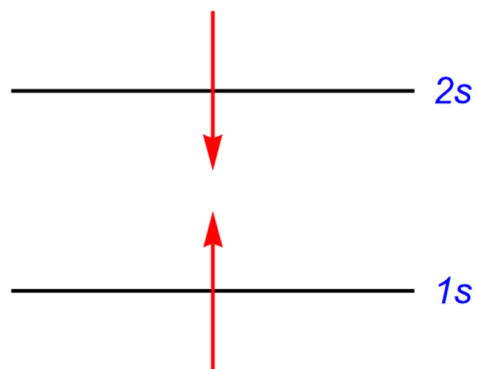
(a)

$$\frac{1}{\sqrt{2}}[|+z, -z\rangle + |-z, +z\rangle] \quad (S = 1, m = 0)$$

$$\frac{1}{\sqrt{2}}[|+z, -z\rangle - |-z, +z\rangle] \quad (S = 0, m = 0)$$



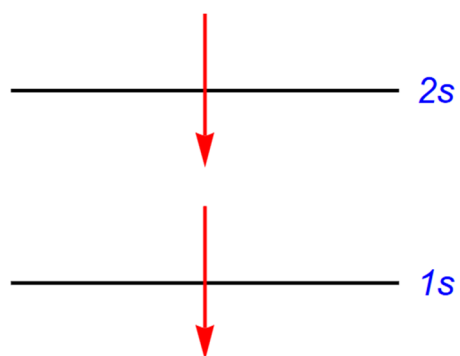
(b)



(c)

$|-z, -z\rangle$

$(S = 1, m = -1)$



(d)

Fig.3 (a)-(d) Occupancy of electron spins with spin $1/2$ in the $(1s)(2s)$ electron configuration of helium atom. $S = 1$ (the lowest energy, triplet). $S = 0$ (singlet).

((Hund's rule))

In atomic physics, **Hund's rules** refers to a set of rules that German physicist Friedrich Hund formulated around 1927, which are used to determine the term symbol that corresponds to the ground state of a multi-electron atom. The first rule is especially important in chemistry, where it is often referred to simply as Hund's rule.

The three rules are as follows.

- (a) For a given electron configuration, the term with maximum multiplicity has the lowest energy. The multiplicity is equal to $2S + 1$ where S is the total spin angular momentum for all electrons. The multiplicity is also equal to the number of unpaired electrons plus one. Therefore, the term with lowest energy is also the term with maximum and maximum number of unpaired electrons.
- (b) For a given multiplicity, the term with the largest value of the total orbital angular momentum quantum number has the lowest energy.
- (c) For a given term, in an atom with outermost subshell half-filled or less, the level with the lowest value of the total angular momentum quantum number (for the operator $\mathbf{J} = \mathbf{L} + \mathbf{S}$ lies lowest in energy. If the outermost shell is more than half-filled, the level with the highest value of J is lowest in energy.

((Hund's rule)) The Hund's rule is applied to the present case as follows.

Hund's rule-I:

The lowest energy state should have maximum in S . It means that the exchange energy has a minimum.

Hund's rule-II:

With the maximum S , the value of L has maximum. It means that the Coulomb energy has a minimum.

The triplet levels and the singlet levels do not combine optically with each other. Hund's rule suggests that the triplet spin state is lower energy than the singlet spin state is lower energy than the singlet spin state.

((Spin-orbit interaction)) H.A Bethe and E.E. Salpeter

In a purely nonrelativistic theory, the energy eigenvalues of all the ortho-state are degenerate. If the relativistic interaction between spin and orbital angular momentum is taken into account,

however, this degeneracy is partially removed. Each nonrelativistic (ortho) level is split into a triplet, the energy being slightly different for the three values of the quantum number j .

A symmetric spatial wavefunction (para-state), on the other hand, must be multiplied by the single antisymmetric spin wave function. For a fixed value of l , the total quantum number J must then be equal to 1, since $s = 0$. Thus, even if the spin-orbit interaction is included, each nonrelativistic energy level the para-system remains unsplit.

4. Dirac spin exchange operator

$\hat{P}_{12}^\sigma$ is the Dirac exchange operator for spins. It is the permutation operator for spins. The detail of the definition will be discussed later.

$$\hat{P}_{12}^\sigma | +z \rangle_1 \otimes | +z \rangle_2 = | +z \rangle_1 \otimes | +z \rangle_2,$$

$$\hat{P}_{12}^\sigma | +z \rangle_1 \otimes | -z \rangle_2 = | -z \rangle_1 \otimes | +z \rangle_2,$$

$$\hat{P}_{12}^\sigma | -z \rangle_1 \otimes | +z \rangle_2 = | +z \rangle_1 \otimes | -z \rangle_2,$$

$$\hat{P}_{12}^\sigma | -z \rangle_1 \otimes | -z \rangle_2 = | -z \rangle_1 \otimes | -z \rangle_2.$$

We note that the matrix of $\hat{P}_{12}^\sigma$ under the basis of four states $| +z \rangle_1 \otimes | +z \rangle_2$, $| +z \rangle_1 \otimes | -z \rangle_2$, $| -z \rangle_1 \otimes | +z \rangle_2$, and $| -z \rangle_1 \otimes | -z \rangle_2$ is expressed by

$$\hat{P}_{12}^\sigma = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

$| +z \rangle_1 \otimes | +z \rangle_2$ and are the eigenstate of $\hat{P}_{12}^\sigma$ with the eigenvalue 1. We consider the matrix of $\hat{P}_{12}^\sigma$ under the sub-basis, $| +z \rangle_1 \otimes | -z \rangle_2$ and $| -z \rangle_1 \otimes | +z \rangle_2$

$$\hat{P}_{12}^\sigma (\text{subspace}) = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \rightarrow \hat{\sigma}_x.$$

So that, the eigenkets and eigenvalues are obtained as

$$\frac{1}{\sqrt{2}}[|+z\rangle_1 \otimes |-z\rangle_2 + |-z\rangle_1 \otimes |+z\rangle_2], \quad (\text{eigenvalue 1, symmetric state})$$

and

$$\frac{1}{\sqrt{2}}[|+z\rangle_1 \otimes |-z\rangle_2 - |-z\rangle_1 \otimes |+z\rangle_2], \quad (\text{eigenvalue 0, anti-symmetric state})$$

In conclusion, we have triplet state and singlet;

Triplet state (symmetric state) with the total spin $S = 1$

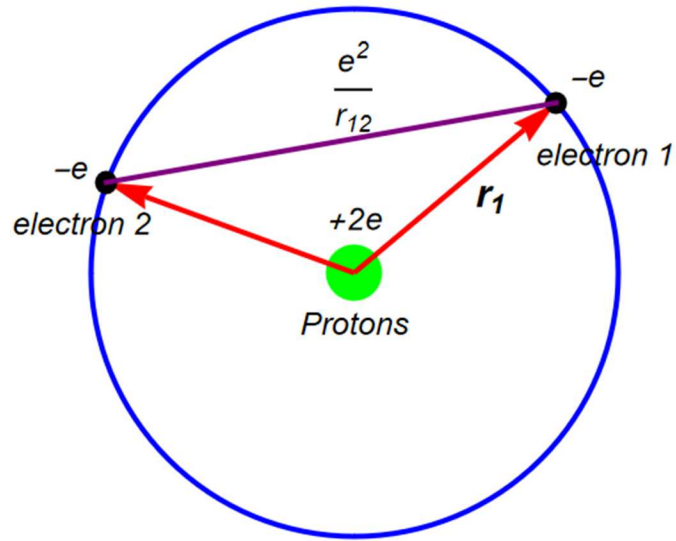
$$\begin{aligned} & |+z\rangle_1 \otimes |+z\rangle_2 \\ & \frac{1}{\sqrt{2}}[|+z\rangle_1 \otimes |-z\rangle_2 + |-z\rangle_1 \otimes |+z\rangle_2], \\ & |-z\rangle_1 \otimes |-z\rangle_2 \end{aligned}$$

Singlet state (antisymmetric state) with the total spin $S = 0$

$$\frac{1}{\sqrt{2}}[|+z\rangle_1 \otimes |-z\rangle_2 - |-z\rangle_1 \otimes |+z\rangle_2]$$

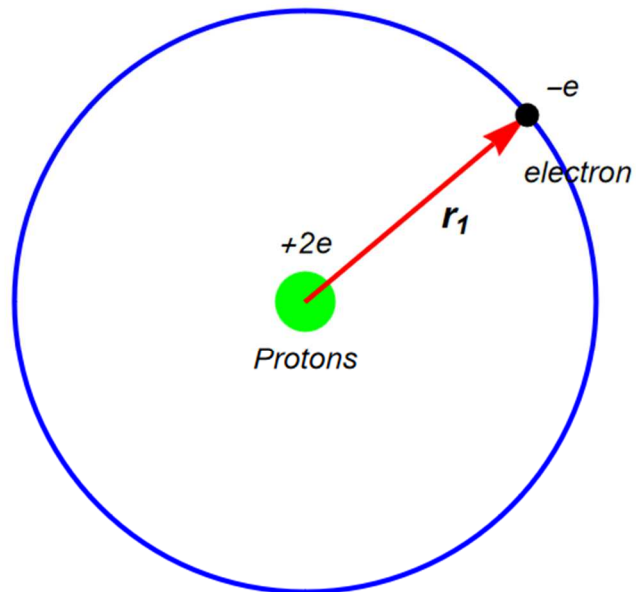
5. Model of helium atom. Definition of He I and He II

The helium atom consists of two electrons in orbit around a nucleus containing two protons and two neutrons.



Helium I

Fig.4 Helium I. Two electrons (at the position vectors r_1 and r_2) around the nucleus with two protons in the nucleus at the origin. As a perturbation there is a weak repulsive Coulomb interaction.



Helium II

Fig.5 Helium II (He^+), where one electron is removed from the original helium atom (He I).

There is one electron outside the He nucleus (2 protons).

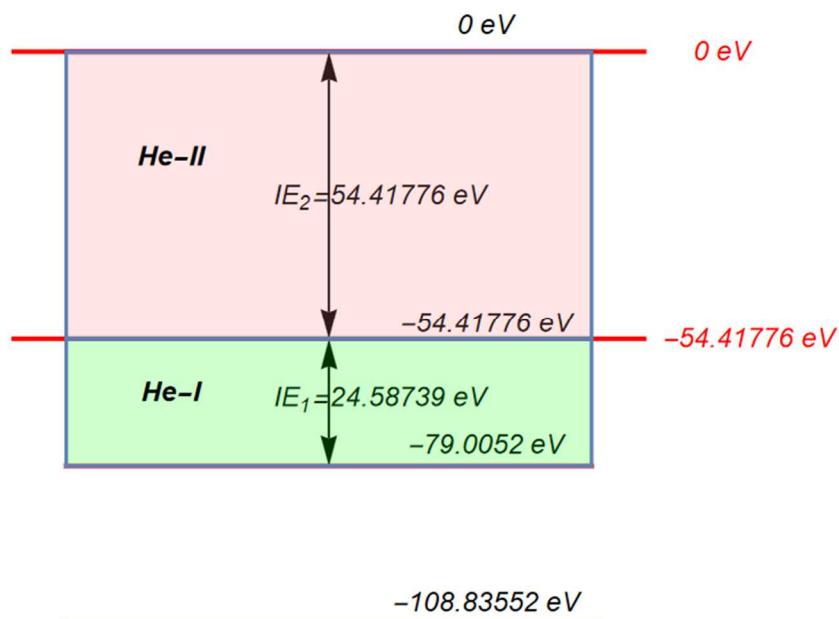
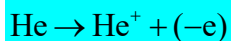


Fig.6 The region of energy diagram for He I (the green region) and He II (the pink region), where there is one e electron around the He nuclear core (two protons). The ionization energy is $IE_1 = 24.5873890 \text{ eV}$ for He-I, and $IE_2 = 54.4177631 \text{ eV}$ for He-II.

The helium atom has two electrons bound to a nucleus with charge $Z = 2$. The successive removal of the two electrons can be diagrammed as

(a)



with

$$IE_1 = \text{first ionization energy} = 24.5873890 \text{ eV}$$

The first ionization energy IE_1 is the minimum energy required to remove the first electron from helium.

(b)



with

$$IE_2 = \text{second ionization energy} = 54.4177631 \text{ eV}$$

The second ionization energy IE_2 is the minimum energy required to remove the second electron from He^+ ion.

The energy level diagram in He atom consists of two regions, He I and He II. For He I, there are two electrons around the He nucleus. For He II, there is only one electron around the He nucleus. He II is denoted as He^+ (ion). We show the energy level diagram for He atom below; the pink region (He-II; between -54.41776 eV and 0 eV) and the green region (He I; between -79.0052 eV and -54.41776 eV). The total ground state energy for the (1s)(1s) state is

$$E_G(1s, 1s) = -IE_1 - IE_2 = -79.0051521 \text{ eV}.$$

The value of the second ionization energy I_2 can be calculated exactly since He^+ is a hydrogen-like ion.

$$IE_2 = -E_{1s}(\text{He}^+) = RyZ^2 = 4Ry = 54.4177631 \text{ eV}$$

where

$$\begin{array}{ll} Ry = 13.605693122994 \text{ eV} & (\text{Rydberg constant}) \\ \text{Hartree} = 2Ry & (\text{Hartree energy}) \end{array}$$

6. Hamiltonian of two electron in helium atom: commutation relation

We looked at a very crude model of the helium atom, in which we ignored the interaction between the two electrons. In that model, the spatial wave function for helium is just the product of two hydrogen-like functions. In all but the ground state, we can construct totally symmetric and totally antisymmetric combinations of the wave functions. Since a system composed of two fermions (which the electrons are) must have an overall antisymmetric wave function, we need to combine symmetric spatial functions with antisymmetric spin functions, and vice versa. States with an antisymmetric spin function are known as parahelium, and states with a symmetric spin

function are known as orthohelium. Since the ground state always has a symmetric spatial function, it is always parahelium, but the excited states all come in both forms. Because of the exchange force, the average distance between two identical particles in a symmetric spatial state is less than for an antisymmetric spatial state. Since two electrons have a higher interaction energy if they are closer together, we'd expect parahelium (symmetric spatial and anti-symmetric spin) energies to be higher than the corresponding orthohelium (antisymmetric spatial and symmetric spin) states, and this is, in fact, observed experimentally.

The total wavefunction of the system consisting of two identical particles (electrons in the present case) is expressed by a product of orbital wavefunction $|\phi^{orbital}\rangle$ and spin wavefunction $|\chi^{spin}\rangle$ as

$$|\psi^{total}\rangle = |\phi^{orbital}\rangle \otimes |\chi^{spin}\rangle.$$

Here we define the permutation operator for the total system as.

$$\hat{P}_{12}^{total} = \hat{P}_{12}^{orbital} \otimes \hat{P}_{12}^{spin} = \hat{P}_{12} \otimes \hat{P}_{12}^{\sigma}$$

where for the sake of convenience, we use the notations

$$\hat{P}_{12}^{orbital} = \hat{P}_{12}, \quad \hat{P}_{12}^{spin} = \hat{P}_{12}^{\sigma}$$

So that we have

$$\begin{aligned} \hat{P}_{12} |\psi^{total}\rangle &= (\hat{P}_{12} \otimes \hat{P}_{12}^{\sigma}) (|\phi^{space}\rangle \otimes |\chi^{spin}\rangle) \\ &= \hat{P}_{12} |\phi^{space}\rangle \otimes \hat{P}_{12}^{\sigma} |\chi^{spin}\rangle \end{aligned}$$

Now we start with the unperturbed system without Coulomb interaction between two electrons. We consider only the orbital wavefunction, since the Hamiltonian of the unperturbed system is independent of spins

$$\hat{H}_0(1,2) = \hat{H}_0(2,1) = \hat{H}_0(1) \otimes \hat{1}_2 + \hat{1}_1 \otimes \hat{H}_0(2)$$

With

$$\hat{H}_0(1) = \frac{\hat{\mathbf{p}}_1^2}{2m} - \frac{Ze^2}{|\hat{\mathbf{r}}_1|}, \quad \hat{H}_0(2) = \frac{\hat{\mathbf{p}}_2^2}{2m} - \frac{Ze^2}{|\hat{\mathbf{r}}_2|}$$

$$\hat{H}_{in}(1,2) = \frac{e^2}{|\hat{\mathbf{r}}_1 - \hat{\mathbf{r}}_2|} = \hat{H}_{in}(2,1)$$

The total Hamiltonian

$$\hat{H}(1,2) = \hat{H}(2,1) = \hat{H}_0(1) \otimes \hat{I}_2 + \hat{I}_1 \otimes \hat{H}_0(2) + \hat{H}_{in}(1,2)$$

since

$$\begin{aligned} \hat{H}(2,1) &= \hat{H}_0(2) \otimes \hat{I}_1 + \hat{I}_2 \otimes \hat{H}_0(1) + \hat{H}_{in}(2,1) \\ &= \hat{I}_1 \otimes \hat{H}_0(2) + \hat{H}_0(1) \otimes \hat{I}_2 + \hat{H}_{in}(1,2) \\ &= \hat{H}(1,2) \end{aligned}$$

The permutation operator for the orbital wavefunction

$$\hat{P}_{12} \hat{H}(1,2) \hat{P}_{12} = \hat{H}(2,1) = \hat{H}(1,2)$$

$$[\hat{P}_{12}, \hat{H}(1,2)] = [\hat{P}_{12}, \hat{H}_0(1,2) + \hat{H}_{in}(1,2)] = 0$$

where

The wavefunction for $|\phi_a\rangle_1 \otimes |\phi_b\rangle_2$

$$\begin{aligned} \hat{H}_0(1,2) |\phi_a\rangle_1 \otimes |\phi_b\rangle_2 &= (\hat{H}_0(1) \otimes \hat{I}_2 + \hat{I}_1 \otimes \hat{H}_0(2)) |\phi_a\rangle_1 \otimes |\phi_b\rangle_2 \\ &= (\hat{H}_0(1) \otimes \hat{I}_2) (|\phi_a\rangle_1 \otimes |\phi_b\rangle_2) + (\hat{I}_1 \otimes \hat{H}_0(2)) (|\phi_a\rangle_1 \otimes |\phi_b\rangle_2) \\ &= \hat{H}_0(1) |\phi_a\rangle_1 \otimes \hat{I}_2 |\phi_b\rangle_2 + (\hat{I}_1 |\phi_a\rangle_1 \otimes \hat{H}_0(2) |\phi_b\rangle_2) \\ &= E_a^{(0)} |\phi_a\rangle_1 \otimes |\phi_b\rangle_2 + (\hat{I}_1 |\phi_a\rangle_1 \otimes E_b^{(0)} |\phi_b\rangle_2) \\ &= (E_a^{(0)} + E_b^{(0)}) |\phi_a\rangle_1 \otimes |\phi_b\rangle_2 \end{aligned}$$

Similarly,

$$\begin{aligned}
\hat{H}_0(1,2)|\phi_b\rangle_1 \otimes |\phi_a\rangle_2 &= (\hat{H}_0(1) \otimes \hat{1}_2 + \hat{1}_1 \otimes \hat{H}_0(2))|\phi_b\rangle_1 \otimes |\phi_a\rangle_2 \\
&= (\hat{H}_0(1) \otimes \hat{1}_2)(|\phi_b\rangle_1 \otimes |\phi_a\rangle_2) + (\hat{1}_1 \otimes \hat{H}_0(2))(|\phi_b\rangle_1 \otimes |\phi_a\rangle_2) \\
&= \hat{H}_0(1)|\phi_b\rangle_1 \otimes \hat{1}_2|\phi_a\rangle_2 + (\hat{1}_1|\phi_b\rangle_1 \otimes \hat{H}_0(2)|\phi_a\rangle_2) \\
&= E_b^{(0)}|\phi_b\rangle_1 \otimes |\phi_a\rangle_2 + (\hat{1}_1|\phi_b\rangle_1 \otimes E_a^{(0)}|\phi_a\rangle_2) \\
&= (E_b^{(0)} + E_a^{(0)})|\phi_b\rangle_1 \otimes |\phi_a\rangle_2
\end{aligned}$$

or

$$\hat{H}_0[C_1|\phi_a\rangle_1 \otimes |\phi_b\rangle_2 + C_2|\phi_b\rangle_1 \otimes |\phi_a\rangle_2] = (E_a^{(0)} + E_b^{(0)})[C_1|\phi_a\rangle_1 \otimes |\phi_b\rangle_2 + C_2|\phi_b\rangle_1 \otimes |\phi_a\rangle_2]$$

where C_1 and C_2 are arbitrary constants. So that, the linear combination of $|\phi_b\rangle_1 \otimes |\phi_a\rangle_2$ and $|\phi_a\rangle_1 \otimes |\phi_b\rangle_2$ are the eigenkets of the unperturbed Hamiltonian $\hat{H}_0$ with the energy eigenvalue $E_a^{(0)} + E_b^{(0)}$

((Note))

$$\begin{aligned}
\hat{P}_{12}\hat{H}_0(1,2)\hat{P}_{12}|\phi_a\rangle_1 \otimes |\phi_b\rangle_2 &= \hat{P}_{12}\hat{H}_0(1,2)|\phi_b\rangle_1 \otimes |\phi_a\rangle_2 \\
&= (E_b^{(0)} + E_a^{(0)})\hat{P}_{12}|\phi_b\rangle_1 \otimes |\phi_a\rangle_2 \\
&= (E_a^{(0)} + E_b^{(0)})|\phi_a\rangle_1 \otimes |\phi_b\rangle_2
\end{aligned}$$

where

$$\begin{aligned}
\hat{H}_0(1,2)|\phi_b\rangle_1 \otimes |\phi_a\rangle_2 &= (\hat{H}_0(1) \otimes \hat{1}_2 + \hat{1}_1 \otimes \hat{H}_0(2))|\phi_b\rangle_1 \otimes |\phi_a\rangle_2 \\
&= (\hat{H}_0(1) \otimes \hat{1}_2)(|\phi_b\rangle_1 \otimes |\phi_a\rangle_2) + (\hat{1}_1 \otimes \hat{H}_0(2))(|\phi_b\rangle_1 \otimes |\phi_a\rangle_2) \\
&= \hat{H}_0(1)|\phi_b\rangle_1 \otimes \hat{1}_2|\phi_a\rangle_2 + \hat{1}_1|\phi_b\rangle_1 \otimes \hat{H}_0(2)|\phi_a\rangle_2 \\
&= E_b^{(0)}|\phi_b\rangle_1 \otimes |\phi_a\rangle_2 + |\phi_b\rangle_1 \otimes E_a^{(0)}|\phi_a\rangle_2 \\
&= (E_b^{(0)} + E_a^{(0)})|\phi_b\rangle_1 \otimes |\phi_a\rangle_2
\end{aligned}$$

Noting that

$$\hat{H}_0(2,1)|\phi_a\rangle_1 \otimes |\phi_b\rangle_2 = (E_b^{(0)} + E_a^{(0)})|\phi_a\rangle_1 \otimes |\phi_b\rangle_2$$

Thus, we have

$$\hat{P}_{12}\hat{H}_0(1,2)\hat{P}_{12}|\phi_a\rangle_1\otimes|\phi_b\rangle_2=(E_a^{(0)}+E_b^{(0)})|\phi_a\rangle_1\otimes|\phi_b\rangle_2=\hat{H}_0(2,1)|\phi_a\rangle_1\otimes|\phi_b\rangle_2$$

leading to

$$\hat{P}_{12}\hat{H}_0(1,2)\hat{P}_{12}=\hat{H}_0(2,1)=\hat{H}_0(1,2)$$

Using the property that $(\hat{P}_{12})^2=\hat{1}$, we get the commutation relation

$$\hat{P}_{12}\hat{H}_0(1,2)=\hat{H}_0(1,2)\hat{P}_{12}$$

7. Energy level for helium atom: He I and He II from analogy from hydrogen atom

We consider the energy level for helium, without any perturbation including repulsive Coulomb interaction.

There are two electrons around two protons ($Z=2$). One electron is in the orbital state (n_1) and the other electron is in the orbital state (n_2). Based on the Bohr model, the total energy of electron is

$$\begin{aligned} E_0(n_1, n_2) &= -\frac{Z^2}{n_1^2} Ry - \frac{Z^2}{n_2^2} Ry \\ &= -2^2 Ry \left(\frac{1}{n_1^2} + \frac{1}{n_2^2} \right) \text{ eV} \end{aligned}$$

Note that

$(n_1=1, n_2=1)$	-108.84554984 eV	
$(1s, 1s)_G$	-79.0051521 eV	(0 eV, ground state)
$(1, 2)$	-68.0284656 eV	(-13.6056931 eV)
$(1, 3)$	-60.46974721 eV	(-6.04697472 eV)

where the observed energy level of the ground state $(1s, 1s)_G$,

$$\begin{aligned} (1s, 1s)_G &= (1, 1) + \langle 1s, 1s | H_{in} | 1s, 1s \rangle_{obs} \\ &= -108.84554984 \text{ eV} + 28.83032 \text{ eV} \\ &= -79.0052 \text{ eV} \end{aligned}$$

$$\langle 1s, 1s | H_{in} | 1s, 1s \rangle = 29.83032 \text{ eV} \quad (\text{repulsive Coulomb interaction}).$$

Recently we found the experimental data on the energy level diagram of He I and He II from the NIST Data. Unlike the situation in 1928, we already have reliable experimental results.

The energy level without perturbation: He I region

(1s)(2s)	-13.6057 eV
(1s)(2p)	-13.6057 eV
(1s)(3s)	-6.04697 eV

8. The energy level diagram of helium I (NIST)

Here are the energy level data of He I which are obtained from NIST, where the units of energy in (eV). In the NIST Data, the energy of ground state is chosen to be zero.

((Definition of energy level for He I))

We use a new notation for the energy level for convenience as

$$E(1s, nl)_{our} = E(1s, nl)_{NIST} - IE_1,$$

$$E(1s, 1s)_{our} = E(1s, 1s)_{NIST} - IE_1 = -IE_1 = -24.587389 \text{ eV}.$$

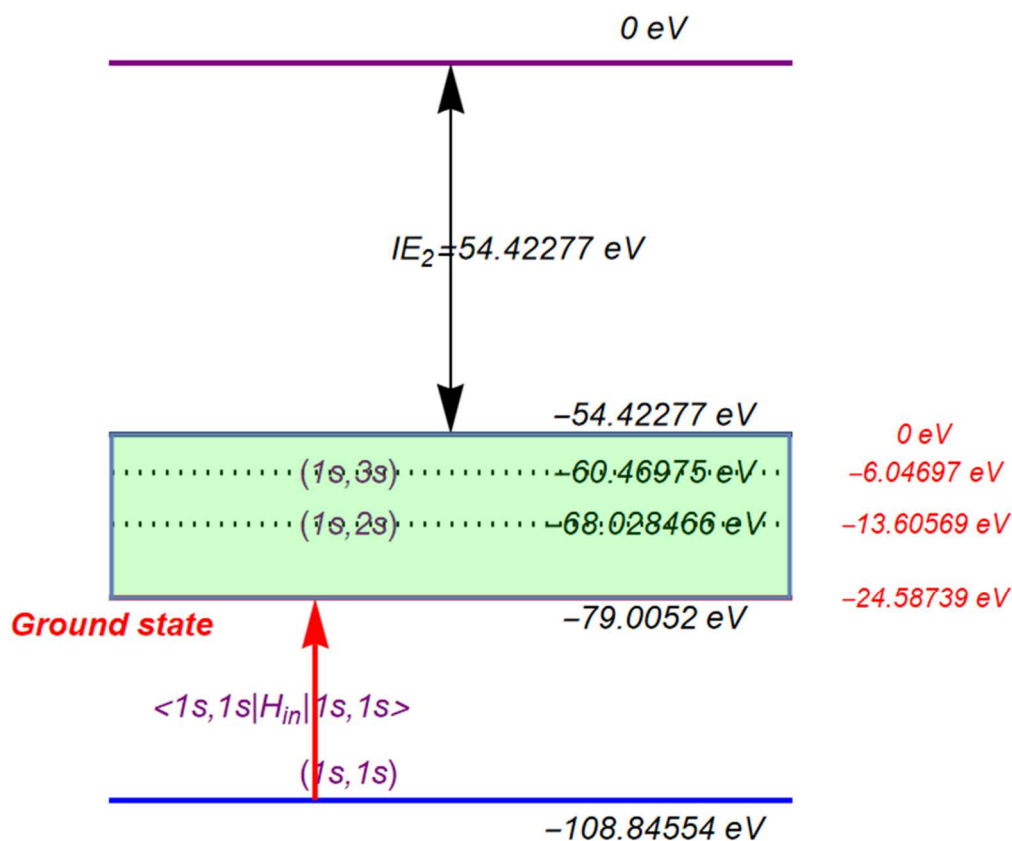


Fig.7 The energy level diagram of electron in He I (the green region).

((NIST data))

https://physics.nist.gov/PhysRefData/ASD/levels_form.html

NIST Atomic Spectra Data base levels Form

Table I Energy level for He I (2 electron outside the He nucleus with 2 protons).

			NIST (eV)	Our notation (eV)
1s1s	¹ S	$j=0$	0.0000000	-24.5873890
1s2s	³ S	1	19.81961484203	-4.76777415797
1s2s	¹ S	0	20.6157751334	-3.9716138666
1s2p	³ P	2	20.96408720675	-3.62330179325
		1	20.96409668230	-3.6232923177
		0	20.96421916817	-3.62316983183

1s2p	¹ P	1	21.2180230218	-3.3693659782
1s3s	³ S	1	22.718466742	-1.868922258
1s3s	¹ S	0	22.920317682	-1.667071318
1s3p	³ P	2	23.0070734673	-1.5803155327
		1	23.0070761918	-1.5803128082
		0	23.0071097475	-1.5802792525
1s3d	³ D	3	23.07365102990	-1.5137370701
		2	23.07365134140	-1.5137376586
		1	23.07365682165	-1.51373217835
1s3p	¹ P	1	23.0870188528	-1.5003701472
1s4s	³ S	1	23.593959036	-0.993429964
1s4s	¹ S	0	23.6735709133	-0.9138180867
1s4p	³ P	2	23.7078915511	-0.8794974489
		1	23.7078926664	-0.8794963336
		0	23.7079063452	-0.8794826548
1s4d	³ D	3	23.73609051247	-0.85129848753
		2	23.73609066143	-0.85129833857
		1	23.73609295768	-0.85129822857
1s4d	¹ D	2	23.73633535786	-0.8510536421
1s4f	³ F	3	23.737007130074	-0.850381869926
		4	23.737008015292	-0.850380984708
		2	23.737009083833	-0.850379916167
1s4f	¹ F	3	23.737010045198	-0.850378954802

1s4p	¹ P	1	23.7420703918	-0.8453186082
1s5s	³ S	1	23.9719717413	-0.6154172587
1s5s	¹ S	0	24.0112153129	-0.5761736871
1s5p	³ P	2	24.0282253870	-0.559163613
		1	24.0282259477	-0.5591630523
		0	24.0282328220	-0.5591561780

9. The energy level diagram of Helium II (NIST)

Here are the energy level data of He II which are obtained from NIST, where the units of energy in (eV). In our notation (here), the energy of ground state [(1s)(1s) state] is taken to be zero.

NIST Data,

https://physics.nist.gov/PhysRefData/ASD/levels_form.html

NIST Atomic Spectra Data base levels Form

Ground state energy: -54,417760 eV. (1s; ²S_{1/2})

for He⁺ ion (only one electron surrounding the two protons at the nucleus)

((Definition of the energy level for He-II)

$$E(nl)_{our} = E(nl)_{NIST} - I_2$$

$$E(1s)_{our} = E(1s)_{NIST} - I_2 = 0 - I_2 = -I_2$$

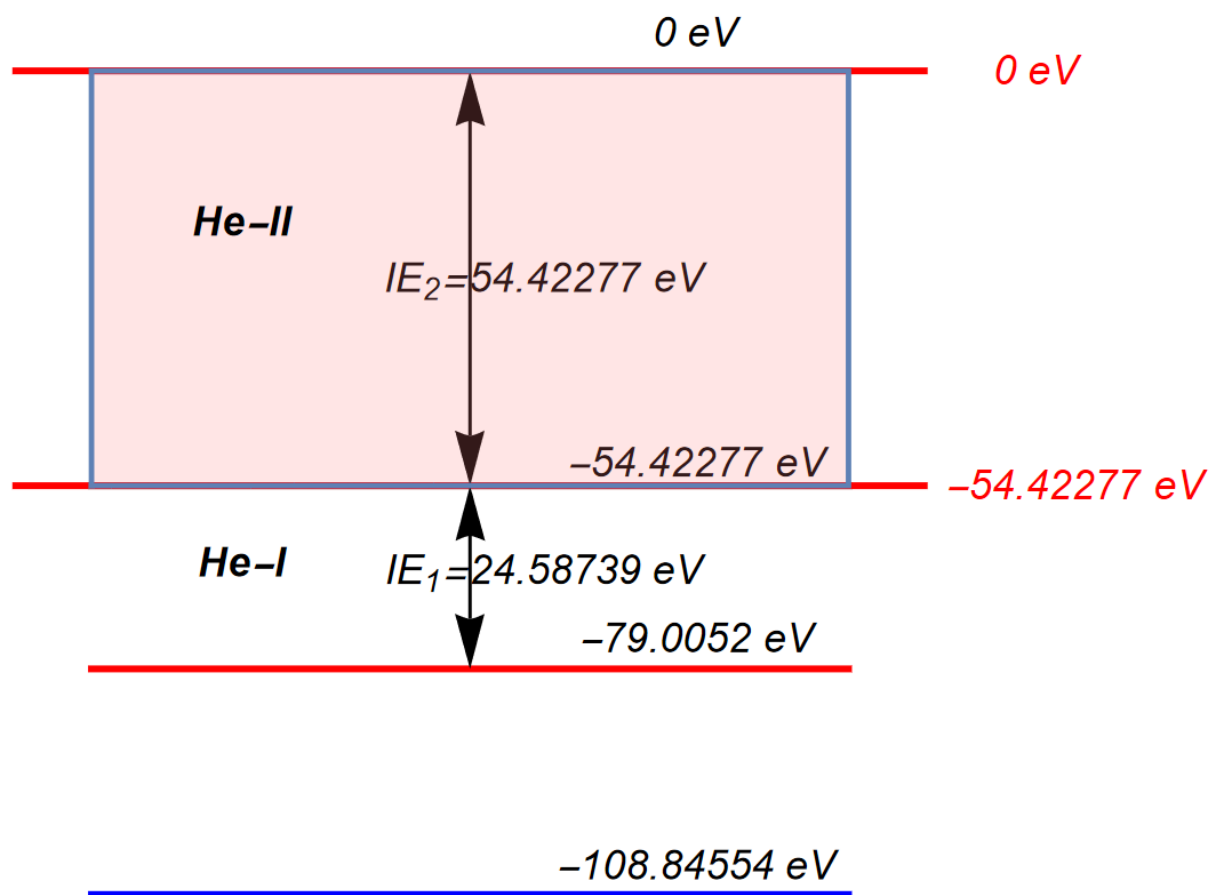


Fig.8 The energy level diagram of electron in He II (the pink region).

3s	-6.04645 eV	$j = 1/2$
3p	-6.04625 eV	$3/2$
	-6.04646 eV	$1/2$
2s	-13.6047 eV	$1/2$
2p	-13,604 eV	$3/2$
	-13.6047 eV	$1/2$
1s	-54.41776 eV	$1/2$

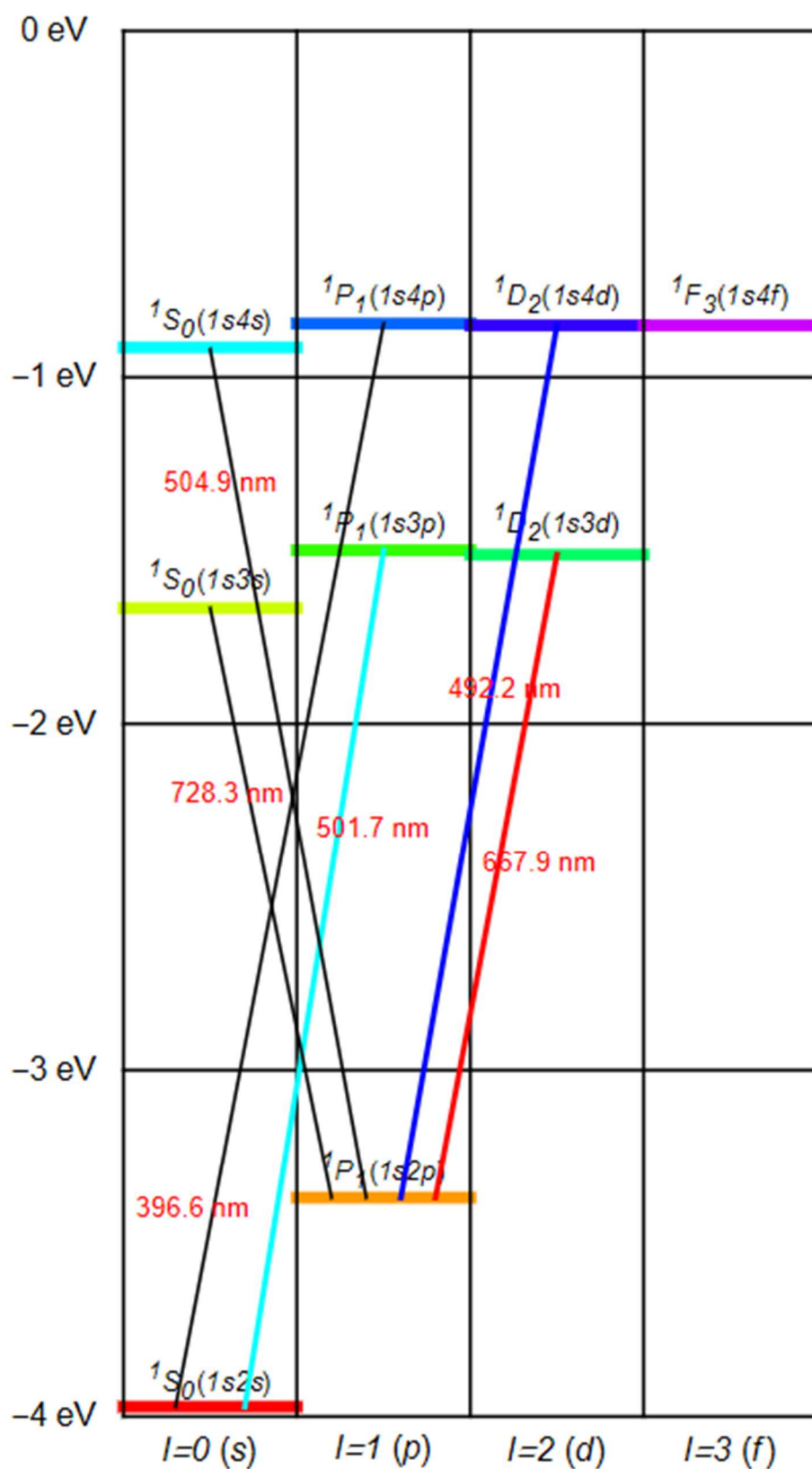
Helium II (NIST Data)

		j	NIST	Our notation
1s	2S	1/2	0.0000 (eV)	-54.422772492 (eV)
2p	2P	1/2	40.8130308564	-13.6097416358
		3/2	40.8137570515	-13.6090154405
2s	2S	1/2	40.813030889283	-13.60968356368
3p	2P	1/2	48.37129741757	-6.05147509198
		3/2	48.37151258731	-6.05125990498
3s	2S	1/2	48.3713147192	-6.05145777298
3d	2D	3/2	48.371512233303	-6.05126025867
		5/2	48.37151583949701	-6.05118854228
4p	2P	1/2	51.01666119611	-3.406111295876
		3/2	51.01675197039	-3.40602052159
4s	2S	1/2	51.01666951092	-3.406102981056
4d	2D	3/2	51.016751892	-3.406020599976
		5/2	51.0167820747	-3.40599041796
4f	2F	5/2	51.0167820202	-3.405990471776
		7/2	51.0167971475	-3.405975344476

Table II Energy level for He II (1 electron outside the He nucleus with 2 protons). If the ground state is set to be -54.422772 eV and the vacuum level is set to be 0 eV, the energy for 3s state (for example) is evaluated as -54.422722+48.3713 = -6.052 eV.

10. Energy level diagram for He I (summary of experimental results)

$S=0$ (singlet)



$S=1$ (triplet)

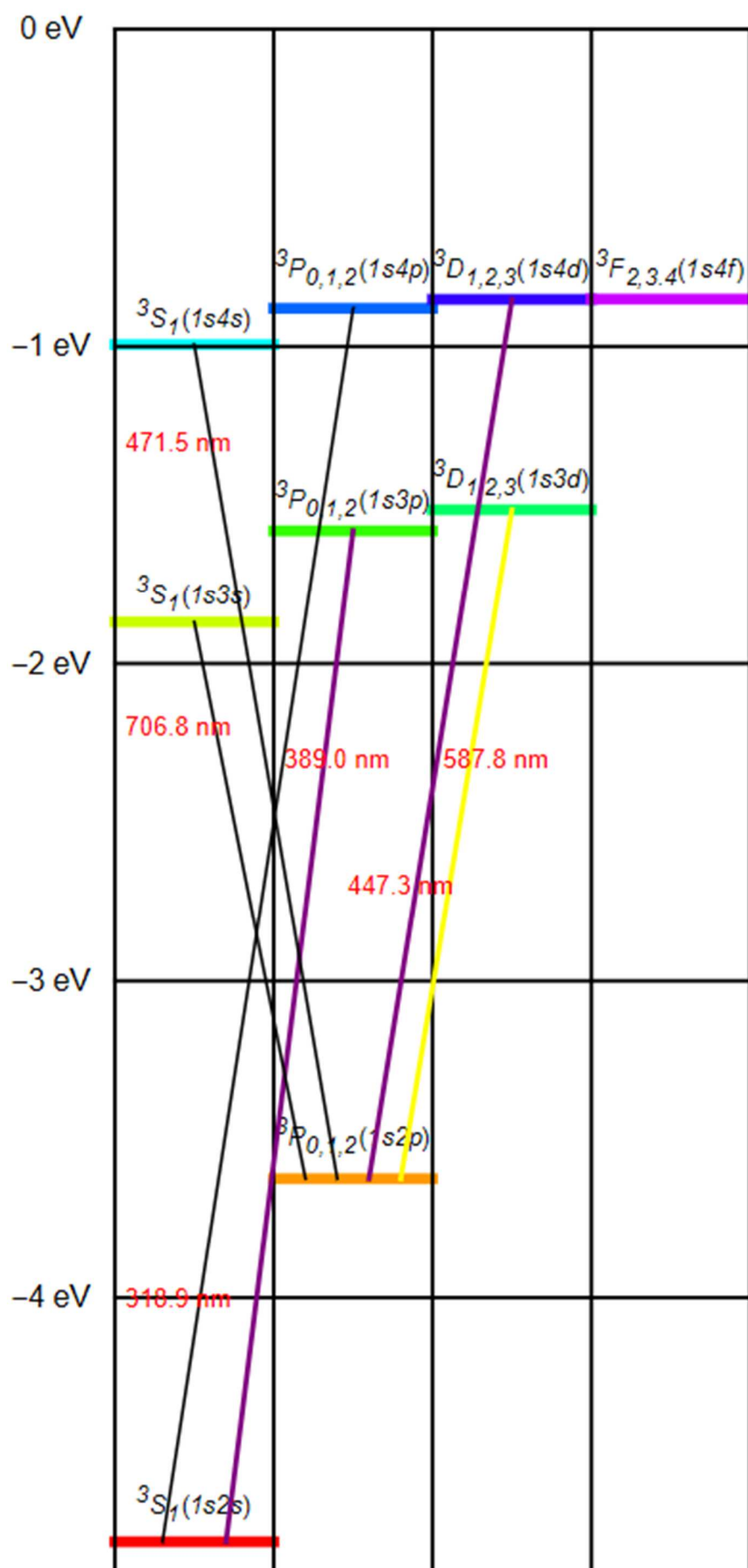
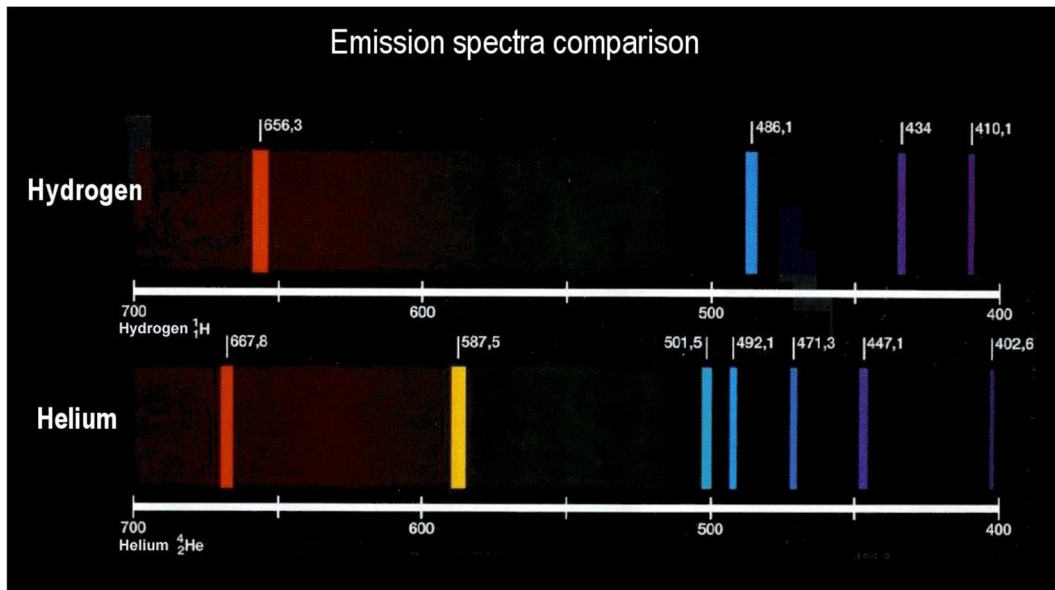


Fig.9

Energy levels and transitions in helium. $S=0$ (parahelium). $S=1$ (orthohelium). The singlet and triplet levels are grouped separately, because the transitions between singlet and triplet levels would violate the $\Delta S = 0$ selection rule. See the on-line data base compiled by the National Institute of Standards and Technology (NIST). https://physics.nist.gov/PhysRefData/ASD/levels_form.html

11. Helium-I spectra (experimental results)

**Fig.10**

Spectrum of helium atom, Intensity vs wavelength.

http://www.ice-age-ahead-iaa.ca/scrp_absolute_climate/tcca021.htm

((Helium spectra))

728.1 nm

$$^1S_0 (1s3s) \quad E_1 = -1.66707 \text{ eV}$$

$$^1P_1 (1s2p) \quad E_2 = -3.36937 \text{ eV}$$

$$\Delta E = E_1 - E_2 = 1.7023 \text{ eV}, \quad \lambda = \frac{2\pi\hbar c}{\Delta E} = 728.333 \text{ nm}.$$

706.765 nm

$$\begin{array}{ll}
^3S_1 (1s3s) & E_1=-1.86892 \text{ eV} \\
^3P_0 (1s2p) & E_2=-3.62317 \text{ eV}
\end{array}$$

$$\Delta E = E_1 - E_2 = 1.75425 \text{ eV}, \quad \lambda = \frac{2\pi\hbar c}{\Delta E} = 706.765 \text{ nm.}$$

667.997 nm

$$\begin{array}{ll}
^1D_2 (1s3d) & E_1=-1.51331 \text{ eV} \\
^1P_1 (1s2p) & E_2=-3.36937 \text{ eV}
\end{array}$$

$$\Delta E = E_1 - E_2 = 1.85606 \text{ eV}, \quad \lambda = \frac{2\pi\hbar c}{\Delta E} = 667.997 \text{ nm.}$$

587.759 nm

$$\begin{array}{ll}
^3D_1 (1s3d) & E_1=-1.51373 \text{ eV} \\
^3P_0 (1s2p) & E_2=-3.62317 \text{ eV}
\end{array}$$

$$\Delta E = E_1 - E_2 = 2.10944 \text{ eV}, \quad \lambda = \frac{2\pi\hbar c}{\Delta E} = 587.759 \text{ nm.}$$

501.708 nm

$$\begin{array}{ll}
^1P_1 (1s3p) & E_1=-1.50037 \text{ eV} \\
^1S_0 (1s2s) & E_2=-3.97161 \text{ eV}
\end{array}$$

$$\Delta E = E_1 - E_2 = 2.47124 \text{ eV}, \quad \lambda = \frac{2\pi\hbar c}{\Delta E} = 501.708 \text{ nm.}$$

492.198 nm

$$\begin{array}{ll}
^1D_2 (1s4d) & E_1=-0.850379 \text{ eV} \\
^1P_1 (1s2p) & E_2=-3.36937 \text{ eV}
\end{array}$$

$$\Delta E = E_1 - E_2 = 2.518991 \text{ eV}, \quad \lambda = \frac{2\pi\hbar c}{\Delta E} = 492.198 \text{ nm.}$$

471.460 nm

$$\begin{array}{ll} {}^3S_1 (1s4s) & E_1=-0.99343 \text{ eV} \\ {}^3P_0 (1s2p) & E_2=-3.62317 \text{ eV} \end{array}$$

$$\Delta E = E_1 - E_2 = 2.62974 \text{ eV}, \quad \lambda = \frac{2\pi\hbar c}{\Delta E} = 492.198 \text{ nm.}$$

447.306 nm

$$\begin{array}{ll} {}^3D_1 (1s4d) & E_1=-0.851296 \text{ eV} \\ {}^3P_0 (1s2p) & E_2=-3.62317 \text{ eV} \end{array}$$

$$\Delta E = E_1 - E_2 = 2.771874 \text{ eV}, \quad \lambda = \frac{2\pi\hbar c}{\Delta E} = 447.306 \text{ nm.}$$

388.971 nm

$$\begin{array}{ll} {}^3P_0 (1s3p) & E_1=-1.58028 \text{ eV} \\ {}^3S_1 (1s2s) & E_2=-4.76777 \text{ eV} \end{array}$$

$$\Delta E = E_1 - E_2 = 3.18749 \text{ eV}, \quad \lambda = \frac{2\pi\hbar c}{\Delta E} = 388.971 \text{ nm.}$$

12. Symmetry of the total wave function for helium atom

The Hamiltonian is given by

$$\hat{H} = \hat{H}_0 + \hat{H}_{in}$$

$$\hat{H}_0 = \frac{1}{2\mu}(\hat{\mathbf{p}}_1^2 + \hat{\mathbf{p}}_2^2) - Ze^2\left(\frac{1}{|\hat{\mathbf{r}}_1|} + \frac{1}{|\hat{\mathbf{r}}_2|}\right)$$

$$\hat{H}_{in} = \frac{e^2}{|\hat{\mathbf{r}}_1 - \hat{\mathbf{r}}_2|} \quad (\text{perturbation, repulsive Coulomb interaction})$$

where $Z = 2$, and $\hat{H}_{in}$ contains only the Coulombic term and no spin dependent term.

The Hamiltonian $\hat{H}$ does not include any spin operators. We note that

$$[\hat{P}_{12}, \hat{H}] = [\hat{P}_{12}, \hat{H}_0 + \hat{H}_{in}] = 0$$

It seems that the wavefunction consists of orbital parts.

$$\hat{H}|\psi_{orbital}\rangle = E|\psi_{orbital}\rangle.$$

However, it is required that the total wavefunction is given by

$$|\psi_{total}\rangle = |\psi_{orbital}\rangle \otimes |\chi_{spin}\rangle.$$

The permutation operator for the total system is defined by

$$\hat{P}_{12}^{total} = \hat{P}_{12} \otimes \hat{P}_{12}^{\sigma}.$$

For the fermion system, we have

$$\hat{P}_{12}^{total} |\psi_{tot}\rangle = -|\psi_{tot}\rangle \quad (\text{anti-symmetric})$$

where $\hat{P}_{12}$ is the orbital permutation operator and $\hat{P}_{12}^{\sigma}$ is the spin permutation operator.

13. Symmetry of spin part in wavefunction

Spin (two spins state)

(a) $S = 1$ (Symmetric state)

$$\begin{cases} | +z \rangle_1 \otimes | +z \rangle_2 & (M_s = 1) \\ \frac{1}{\sqrt{2}} [| +z \rangle_1 \otimes | -z \rangle_2 + | -z \rangle_1 \otimes | +z \rangle_2] & (M_s = 0) \\ | -z \rangle_1 \otimes | -z \rangle_2 & (M_s = -1) \end{cases}$$

(b) $S = 0$ (Anti-symmetric state)

$$\frac{1}{\sqrt{2}} [| +z \rangle_1 \otimes | -z \rangle_2 - | -z \rangle_1 \otimes | +z \rangle_2] \quad (M_s = 0),$$

or

$$\hat{P}_{12}^{\sigma} |S=1; M_S=1, 0, -1\rangle = |S=1; M_S=1, 0, -1\rangle,$$

$$\hat{P}_{12}^{\sigma} |S=0; M_S=0\rangle = -|S=0; M_S=0\rangle.$$

We need to get the antisymmetric wavefunction. Using the antisymmetrizer

$$\begin{aligned}\hat{A}^{total} &= \frac{1}{2}(\hat{1} - \hat{P}_{12}^{total}) \\ &= \frac{1}{\sqrt{2}}(\hat{1} - \hat{P}_{12} \otimes \hat{P}_{12}^{\sigma})\end{aligned}$$

we get

$$|\psi_{total}\rangle = |\psi_{orbital}\rangle \otimes |\chi_{spin}\rangle,$$

or

$$\hat{A}^{total} |\psi_{total}\rangle = \frac{1}{\sqrt{2}}(\hat{1} - \hat{P}_{12} \otimes \hat{P}_{12}^{\sigma}) |\psi_{orbital}\rangle \otimes |\chi_{spin}\rangle.$$

(a) $|\chi_{spin}\rangle = |\chi_{S=1}^S\rangle$ (triplet, $S=1$)

$$\begin{aligned}\hat{A}^{total} |\psi_{total}\rangle &= \frac{1}{\sqrt{2}}(\hat{1} - \hat{P}_{12} \otimes \hat{P}_{12}^{\sigma}) |\psi_{orbital}\rangle \otimes |\chi_{S=1}^S\rangle \\ &= \frac{1}{\sqrt{2}}(\hat{1} - \hat{P}_{12}) |\psi_{orbital}\rangle \otimes |\chi_{S=1}^S\rangle \\ &= |\psi_{orbital}^A\rangle \otimes |\chi_{S=1}^S\rangle\end{aligned}$$

with

$$\begin{aligned}|\psi_{orbital}^A\rangle &= \frac{1}{\sqrt{2}}(\hat{1} - \hat{P}_{12}) |\psi_{orbital}\rangle \\ &= \hat{A} |\psi_{orbital}\rangle\end{aligned}$$

(symmetric orbital wavefunction)

and

$$\hat{A} = \frac{1}{\sqrt{2}}(\hat{1} - \hat{P}_{12}).$$

The resultant wavefunction $|\psi_{orbital}^A\rangle \otimes |\chi_{S=1}^S\rangle$ is clearly antisymmetric under the interchange of particle.

(b) $|\chi_{spin}\rangle = |\chi_{S=0}\rangle$ (singlet, $S = 0$)

$$\begin{aligned}\hat{A}^{total}|\psi_{total}\rangle &= \frac{1}{\sqrt{2}}(\hat{1} - \hat{P}_{12}\hat{P}_{12}^\sigma)|\psi_{orbital}\rangle \otimes |\chi_{S=0}^A\rangle \\ &= \frac{1}{\sqrt{2}}(\hat{1} + \hat{P}_{12})|\psi_{orbital}\rangle \otimes |\chi_{S=0}^A\rangle \\ &= |\psi_{orbital}^S\rangle \otimes |\chi_{S=0}^A\rangle\end{aligned}$$

with

$$\begin{aligned}|\psi_{orbital}^S\rangle &= \frac{1}{\sqrt{2}}(\hat{1} + \hat{P}_{12})|\psi_{orbital}\rangle \\ &= \hat{S}|\psi_{orbital}\rangle\end{aligned}$$

(symmetric orbital wavefunction)

and

$$\hat{S} = \frac{1}{\sqrt{2}}(\hat{1} + \hat{P}_{12}).$$

The resultant wavefunction $|\psi_{orbital}^S\rangle \otimes |\chi_{S=0}^A\rangle$ is clearly antisymmetric under the interchange of particle.

We now consider two orbital states

$$|\phi_a\rangle, \quad |\phi_b\rangle$$

Symmetric orbital function is form as

$$\frac{1}{\sqrt{2}}[|\phi_a\rangle_1 \otimes |\phi_b\rangle_2 + |\phi_b\rangle_1 \otimes |\phi_a\rangle_2]$$

Antisymmetric orbital function can also be formed as

$$\frac{1}{\sqrt{2}}[|\phi_a\rangle_1 \otimes |\phi_b\rangle_2 - |\phi_b\rangle_1 \otimes |\phi_a\rangle_2].$$

((**Note**)) Pauli's principle of exclusion

When $|\phi_a\rangle = |\phi_b\rangle$ (same state)

Symmetric orbital state.

$$|\phi_a\rangle_1 \otimes |\phi_b\rangle_2$$

But no antisymmetric state is allowed (Pauli's exclusion principle). We note that the orbital wavefunctions used here are orthogonal ones, just like the case of hydrogen atom.

Orbital (different from hydrogen atom)

One-electron energy diagram (He^+ , He atom but one electron lost))

We need to use the perturbation theory (degenerate case). According to Sakurai and Napolitano, we define

$$\hat{A} = \frac{1}{\sqrt{2}}(\hat{1} - \hat{P}_{12}).$$

$$\hat{S} = \frac{1}{\sqrt{2}}(\hat{1} + \hat{P}_{12}).$$

$$\hat{P}_{12}^+ = \hat{P}_{12} \quad \hat{P}_{12}^{-1} = \hat{P}_{12}.$$

$$\hat{P}_{12}^2 = \hat{1}.$$

$$\begin{aligned} \hat{S}\hat{A} &= \frac{1}{2}(\hat{1} + \hat{P}_{12})(\hat{1} - \hat{P}_{12}) \\ &= \frac{1}{2}(\hat{1} - \hat{P}_{12} + \hat{P}_{12} - \hat{P}_{12}^2) \\ &= 0 \end{aligned}$$

$$\begin{aligned} \hat{A}\hat{S} &= \frac{1}{2}(\hat{1} - \hat{P}_{12})(\hat{1} + \hat{P}_{12}) \\ &= \frac{1}{2}(\hat{1} + \hat{P}_{12} - \hat{P}_{12} - \hat{P}_{12}^2) \\ &= 0 \end{aligned}$$

$$\hat{P}_{12}\hat{O}(1,2)\hat{P}_{12}^{-1} = \hat{O}(2,1); \quad \hat{O}(2,1) \text{ is a general operator}$$

$$|\psi_A\rangle = \hat{A}|\phi\rangle, \quad |\psi_S\rangle = \hat{S}|\phi\rangle.$$

The matrix

$$\langle\psi_A|\hat{H}_{in}|\psi_A\rangle = \langle\phi|\hat{A}^+\hat{H}_{in}\hat{A}|\phi\rangle,$$

$$\langle\psi_S|\hat{H}_{in}|\psi_S\rangle = \langle\phi|\hat{S}^+\hat{H}_{in}\hat{S}|\phi\rangle,$$

$$\langle\psi_S|\hat{H}_{in}|\psi_A\rangle = \langle\phi|\hat{S}^+\hat{H}_{in}\hat{A}|\phi\rangle,$$

$$\langle\psi_A|\hat{H}_{in}|\psi_S\rangle = \langle\phi|\hat{A}^+\hat{H}_{in}\hat{S}|\phi\rangle.$$

Suppose that
$$\hat{H}_{in} = \hat{H}_{in}(1,2) = \hat{H}_{in}(2,1) = \frac{e^2}{|\mathbf{r} - \mathbf{r}'|}.$$

$$\hat{P}_{12}\hat{H}_{in}\hat{P}_{12}^{-1} = \hat{H}_{in} \quad \hat{P}_{12}\hat{H}_{in} = \hat{H}_{in}\hat{P}_{12}$$

$$\hat{H}_{in} = \hat{P}_{12}\hat{H}_{in}\hat{P}_{12}$$

$$\begin{aligned} \hat{S}^+\hat{H}_{in}\hat{A} &= \frac{1}{2}(\hat{1} + \hat{P}_{12})^+\hat{H}_{in}(\hat{1} - \hat{P}_{12}) \\ &= \frac{1}{2}(\hat{1} + \hat{P}_{12})\hat{H}_{in}(\hat{1} - \hat{P}_{12}) \\ &= \frac{1}{2}(\hat{1} + \hat{P}_{12})(\hat{H}_{in} - \hat{H}_{in}\hat{P}_{12}) \\ &= \frac{1}{2}(\hat{H}_{in} - \hat{H}_{in}\hat{P}_{12} + \hat{P}_{12}\hat{H}_{in} - \hat{P}_{12}\hat{H}_{in}\hat{P}_{12}) \\ &= \frac{1}{2}(-\hat{H}_{in}\hat{P}_{12} + \hat{P}_{12}\hat{H}_{in}) \\ &= 0 \end{aligned}$$

We note that

$$(\hat{S}^+ \hat{H}_{in} \hat{A})^+ = \hat{A}^+ \hat{H}_{in}^+ \hat{S} = \hat{A}^+ \hat{H}_{in} \hat{S} = 0$$

$$\begin{aligned} \hat{S}^+ \hat{H}_{in} \hat{S} &= \frac{1}{2} (\hat{1} + \hat{P}_{12})^+ \hat{H}_{in} (\hat{1} + \hat{P}_{12}) \\ &= \frac{1}{2} (\hat{1} + \hat{P}_{12}) \hat{H}_{in} (\hat{1} + \hat{P}_{12}) \\ &= \frac{1}{2} (\hat{1} + \hat{P}_{12}) (\hat{H}_{in} + \hat{H}_{in} \hat{P}_{12}) \\ &= \frac{1}{2} (\hat{H}_{in} + \hat{H}_{in} \hat{P}_{12} + \hat{P}_{12} \hat{H}_{in} + \hat{P}_{12} \hat{H}_{in} \hat{P}_{12}) \\ &= (\hat{H}_{in} + \hat{P}_{12} \hat{H}_{in}) \end{aligned}$$

$$\begin{aligned} \hat{A}^+ \hat{H}_{in} \hat{A} &= \frac{1}{2} (\hat{1} - \hat{P}_{12})^+ \hat{H}_{in} (\hat{1} - \hat{P}_{12}) \\ &= \frac{1}{2} (\hat{1} - \hat{P}_{12}) \hat{H}_{in} (\hat{1} - \hat{P}_{12}) \\ &= \frac{1}{2} (\hat{1} - \hat{P}_{12}) (\hat{H}_{in} - \hat{H}_{in} \hat{P}_{12}) \\ &= \frac{1}{2} (\hat{H}_{in} - \hat{H}_{in} \hat{P}_{12} - \hat{P}_{12} \hat{H}_{in} + \hat{P}_{12} \hat{H}_{in} \hat{P}_{12}) \\ &= \hat{H}_{in} - \hat{P}_{12} \hat{H}_{in} \end{aligned}$$

$$\langle \phi | \hat{S}^+ \hat{H}_{in} \hat{S} | \phi \rangle = \langle \phi | \hat{H}_{in} + \hat{P}_{12} \hat{H}_{in} | \phi \rangle = J + K$$

$$\langle \phi | \hat{A}^+ \hat{H}_{in} \hat{A} | \phi \rangle = \langle \phi | \hat{H}_{in} - \hat{P}_{12} \hat{H}_{in} | \phi \rangle = J - K$$

14. Definition of Coulomb Integral and Exchange Integral

Here we define the Coulomb integral

$$\begin{aligned} I &= \langle \phi | \hat{H}_{in} | \phi \rangle \\ &= \iint d\mathbf{r}_1 d\mathbf{r}_2 \langle \mathbf{r}_1 | \phi_{1s} \rangle^* \langle \mathbf{r}_2 | \phi_{2s} \rangle^* \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \langle \mathbf{r}_1 | \phi_{1s} \rangle \langle \mathbf{r}_2 | \phi_{2s} \rangle, \\ &= e^2 \iint d\mathbf{r}_1 d\mathbf{r}_2 \frac{|\langle \mathbf{r}_1 | \phi_{1s} \rangle|^2 |\langle \mathbf{r}_2 | \phi_{2s} \rangle|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \end{aligned}$$

and the exchange integral

$$\begin{aligned}
K &= \langle \phi | \hat{P}_{12} \hat{H}_{in} | \phi \rangle \\
&= \iint d\mathbf{r}_1 d\mathbf{r}_2 \langle \mathbf{r}_1 | \phi_{1s} \rangle^* \langle \mathbf{r}_2 | \phi_{2s} \rangle^* \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \langle \mathbf{r}_1 | \phi_{2s} \rangle \langle \mathbf{r}_2 | \phi_{1s} \rangle \\
&= e^2 \iint d\mathbf{r}_1 d\mathbf{r}_2 \frac{\langle \mathbf{r}_1 | \phi_{1s} \rangle^* \langle \mathbf{r}_2 | \phi_{2s} \rangle \langle \mathbf{r}_1 | \phi_{2s} \rangle \langle \mathbf{r}_2 | \phi_{1s} \rangle}{|\mathbf{r}_1 - \mathbf{r}_2|}
\end{aligned}$$

where

$$\langle \mathbf{r}_1, \mathbf{r}_2 | \phi \rangle = \langle \mathbf{r}_1 | \phi_{1s} \rangle \langle \mathbf{r}_2 | \phi_{2s} \rangle,$$

$$\langle \mathbf{r}_1, \mathbf{r}_2 | \hat{P}_{12} | \phi \rangle = \langle \mathbf{r}_1 | \phi_{2s} \rangle \langle \mathbf{r}_2 | \phi_{1s} \rangle,$$

$$\hat{H}_{in} = \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

Thus, we have

$$\begin{pmatrix} \langle \psi_S | \hat{H}_{in} | \psi_S \rangle & \langle \psi_S | \hat{H}_{in} | \psi_A \rangle \\ \langle \psi_A | \hat{H}_{in} | \psi_S \rangle & \langle \psi_A | \hat{H}_{in} | \psi_A \rangle \end{pmatrix} = \begin{pmatrix} I + K & 0 \\ 0 & I - K \end{pmatrix}$$

or

$$\hat{H}_{in} | \psi_S \rangle = (I + K) | \psi_S \rangle$$

$$\hat{H}_{in} | \psi_A \rangle = (I - K) | \psi_A \rangle$$

So that, $| \psi_S \rangle$ is the eigenket of $\hat{H}_{in}$ with eigenvalue $I + K$, and $| \psi_A \rangle$ is the eigenket of $\hat{H}_{in}$ with eigenvalue $I - K$.

15. Formula of Coulomb integral

$$\begin{aligned}
& \iint d\mathbf{r}_1 d\mathbf{r}_2 \phi_{1s}^*(\mathbf{r}_1) \phi_{2s}^*(\mathbf{r}_2) \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_{1s}(\mathbf{r}_1) \phi_{2s}(\mathbf{r}_2) \\
&= \int r_1^2 dr_1 R_{1s}^2(r_1) \int r_2^2 dr_2 R_{2s}^2(r_2) \sum_{l=0}^{\infty} \sum_{m=-l}^l G_l(r_1, r_2) \left(\frac{1}{\sqrt{4\pi}}\right)^4 \int d\Omega_1 Y_l^m(\theta_1, \phi_1) \int dY_l^{m*}(\theta_2, \phi_2) \\
&= \int r_1^2 dr_1 R_{1s}^2(r_1) \int r_2^2 dr_2 R_{2s}^2(r_2) \sum_{l=0}^{\infty} \sum_{m=-l}^l G_l(r_1, r_2) \left(\frac{1}{\sqrt{4\pi}}\right)^2 \delta_{l,0} \delta_{m,0} \\
&= \frac{1}{4\pi} \int r_1^2 dr_1 R_{1s}^2(r_1) \int r_2^2 dr_2 R_{2s}^2(r_2) G_l(r_1, r_2) \big|_{l=0} \\
&= \int_0^{\infty} r_1^2 dr_1 R_{1s}^2(r_1) \left[\frac{1}{r_1} \int_0^{r_1} r_2^2 dr_2 R_{2s}^2(r_2) + \int_{r_1}^{\infty} r_2 dr_2 R_{2s}^2(r_2) \right]
\end{aligned}$$

where

$$\frac{G_{l=0}(r_1, r_2)}{4\pi} = \frac{F_{l=0}(r_1, r_2)}{2l+1} \bigg|_{l=0} = \begin{cases} \frac{1}{r_1} & r_1 > r_2 \\ \frac{1}{r_2} & r_2 > r_1 \end{cases}$$

or

$$F_{l=0}(r_1, r_2) = \frac{1}{r_1} u(r_1 - r_2) + \frac{1}{r_2} u(r_2 - r_1)$$

Note that $u(r)$ is the step function.

16. Formula of Exchange Integral

$$\begin{aligned}
& \iint d\mathbf{r}_1 d\mathbf{r}_2 \phi_{1s}^*(\mathbf{r}_1) \phi_{2s}^*(\mathbf{r}_2) \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_{2s}(\mathbf{r}_1) \phi_{1s}(\mathbf{r}_2) \\
&= \int r_1^2 dr_1 R_{1s}(r_1) R_{2s}(r_1) \int r_2^2 dr_2 R_{2s}(r_2) R_{1s}(r_2) \sum_{l=0}^{\infty} \sum_{m=-l}^l G_l(r_1, r_2) \left(\frac{1}{\sqrt{4\pi}}\right)^4 \int d\Omega_1 Y_l^m(\theta_1, \phi_1) \int d\Omega_2 Y_l^{m*}(\theta_2, \phi_2) \\
&= \left(\frac{1}{\sqrt{4\pi}}\right)^2 \int r_1^2 dr_1 R_{1s}(r_1) R_{2s}(r_1) \int r_2^2 dr_2 R_{2s}(r_2) R_{1s}(r_2) \sum_{l=0}^{\infty} \sum_{m=-l}^l G_l(r_1, r_2) \delta_{l,0} \delta_{m,0} \\
&= \frac{1}{4\pi} \int r_1^2 dr_1 R_{1s}(r_1) R_{2s}(r_1) \int r_2^2 dr_2 R_{2s}(r_2) R_{1s}(r_2) G_l(r_1, r_2) \big|_{l=0} \\
&= \frac{1}{4\pi} \int r_1^2 dr_1 R_{1s}(r_1) R_{2s}(r_1) \int r_2^2 dr_2 R_{2s}(r_2) R_{1s}(r_2) G_{l=0}(r_1, r_2) \\
&= \int r_1^2 dr_1 R_{1s}(r_1) R_{2s}(r_1) \int r_2^2 dr_2 R_{2s}(r_2) R_{1s}(r_2) F_l(r_1, r_2) \big|_{l=0} \\
&= \int_0^{\infty} r_1^2 dr_1 R_{1s}(r_1) R_{2s}(r_1) \left[\frac{1}{r_1} \int_0^{r_1} r_2^2 dr_2 R_{2s}(r_2) R_{1s}(r_2) + \int_{r_1}^{\infty} r_2 dr_2 R_{2s}(r_2) R_{1s}(r_2) \right]
\end{aligned}$$

17. Calculation of Coulomb integral using radial wavefunction

Using the orbital wavefunction,

$$\phi_{2p}(\mathbf{r}) = R_{21}(r) Y_1^{m'}(\theta, \phi) \text{ with the state } |l=1, m'\rangle,$$

we calculate the Coulomb integral given by

$$\begin{aligned}
& \iint d\mathbf{r}_1 d\mathbf{r}_2 \phi_{1s}^*(\mathbf{r}_1) \phi_{2p}^*(\mathbf{r}_2) \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_{1s}(\mathbf{r}_1) \phi_{2p}(\mathbf{r}_2) \\
&= \left(\frac{1}{\sqrt{4\pi}}\right)^2 \int r_1^2 dr_1 R_{1s}^2(r_1) \int r_2^2 dr_2 R_{2p}^2(r_2) \sum_{l=0}^{\infty} \sum_{m=-l}^l G_l(r_1, r_2) \int d\Omega_1 Y_l^m(\theta_1, \phi_1) \int d\Omega_2 Y_l^{m*}(\theta_2, \phi_2) Y_l^{m'}(\theta_2, \phi_2) Y_l^{m*}(\theta_2, \phi_2) \\
&= \frac{1}{4\pi} \int r_1^2 dr_1 R_{1s}^2(r_1) \int r_2^2 dr_2 R_{2p}^2(r_2) \sum_{l=0}^{\infty} \sum_{m=-l}^l G_l(r_1, r_2) \delta_{l,0} \delta_{m,0} \int d\Omega_2 Y_l^{m*}(\theta_2, \phi_2) Y_l^{m'}(\theta_2, \phi_2) Y_l^{m*}(\theta_2, \phi_2) \\
&= \frac{1}{\sqrt{4\pi}} \int r_1^2 dr_1 R_{1s}^2(r_1) \int r_2^2 dr_2 R_{2p}^2(r_2) \sum_{l=0}^{\infty} \sum_{m=-l}^l G_l(r_1, r_2) \delta_{l,0} \delta_{m,0} \int d\Omega_2 Y_l^{m*}(\theta_2, \phi_2) Y_l^{m'}(\theta_2, \phi_2) Y_l^{m*}(\theta_2, \phi_2) \\
&= \frac{1}{\sqrt{4\pi}} \int r_1^2 dr_1 R_{1s}^2(r_1) \int r_2^2 dr_2 R_{2p}^2(r_2) G_{l=0}(r_1, r_2) \int d\Omega_2 Y_l^{m*}(\theta_2, \phi_2) Y_l^{m'}(\theta_2, \phi_2) Y_l^{0*}(\theta_2, \phi_2) \\
&= \frac{1}{4\pi} \int r_1^2 dr_1 R_{1s}^2(r_1) \int r_2^2 dr_2 R_{2p}^2(r_2) G_{l=0}(r_1, r_2) \int d\Omega_2 Y_l^{m*}(\theta_2, \phi_2) Y_l^{m'}(\theta_2, \phi_2) \\
&= \int r_1^2 dr_1 R_{1s}^2(r_1) \int r_2^2 dr_2 R_{2p}^2(r_2) F_{l=0}(r_1, r_2) \\
&= \int_0^{\infty} r_1^2 dr_1 R_{1s}^2(r_1) \left[\frac{1}{r_1} \int_0^{r_1} r_2^2 dr_2 R_{2p}^2(r_2) + \int_{r_1}^{\infty} r_2 dr_2 R_{2p}^2(r_2) \right]
\end{aligned}$$

where

$$G_l(r_1, r_2) = \frac{F_l(r_1, r_2)}{2l+1}$$

and

$$\int d\Omega Y_l^m(\theta, \phi) = \sqrt{4\pi} \delta_{l,0} \delta_{m,0}$$

18. Coulomb integral: calculation by Mathematica

We calculate the Coulomb integrals with the combination of (1s) (nl).

$$\iint d\mathbf{r}_1 d\mathbf{r}_2 \phi_{1s}^*(\mathbf{r}_1) \phi_{2p}^*(\mathbf{r}_2) \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_{1s}(\mathbf{r}_1) \phi_{2p}(\mathbf{r}_2)$$

by using Mathematica.

(1s)(nl) electron configuration

n	l	Coulomb integral
-----	-----	------------------

1	0	$\frac{5}{8} \frac{Ze^2}{a} = 34.0142 \text{ eV}$
2	0	$\frac{17}{81} \frac{Ze^2}{a} = 11.4221 \text{ eV}$
2	1	$\frac{8}{243} \frac{Ze^2}{a} = 1.7917 \text{ eV}$
3	0	$\frac{815}{8192} \frac{Ze^2}{a} = 5.41437 \text{ eV}$
3	1	$\frac{469}{49152} \frac{Ze^2}{a} = 0.515293 \text{ eV}$
3	2	$\frac{9}{81920} \frac{Ze^2}{a} (-263937 + 1835008 \ln 2 - 917504 \ln 3) = 0.0744525 \text{ eV}$

where a is the Bohr radius of hydrogen atom;

$$a = a_B = \frac{\hbar^2}{me^2} = \frac{\hbar}{mc\alpha} = \frac{\tilde{\lambda}}{\alpha} = 0.529177210903(80) \text{ \AA},$$

α is a fine structure constant,

$$\alpha = \frac{e^2}{\hbar c} = \frac{1}{137.035999084(21)},$$

and $\tilde{\lambda}$ is the reduced Compton wavelength of electron;

$$\tilde{\lambda} = \frac{\lambda}{2\pi} = \frac{\hbar}{mc} = 3.8615926800 \times 10^{-11} \text{ cm}.$$

((MATHEMATICA PROGRAM-I))

Coulomb Integral

Coulomb integral

$\phi(1s), \phi(nL)$

```

Clear["Global`*"];
rwave[n_, l_, r_] :=
  1 / (Sqrt[n + l]!)
  (21+l a-l-3/2 e-Zr/an n-l-2 Zl+3/2 rl Sqrt[n - l - 1]! ×
    LaguerreL[-1 + n - l, 1 + 2 l, (2 Z r) / (a n)]);
F1[r1_, r2_, L_] :=
  1 / (2 L + 1)
  ( (r2/r1)L 1/r1 UnitStep[r1 - r2] +
    (r1/r2)L 1/r2 UnitStep[r2 - r1] );
Coulomb[N1_, L1_] :=
  Module[{g1, g2},
    g1 = e2 r22 rwave[N1, L1, r2]2 F1[r1, r2, L1];
    G1[r1_] := Integrate[g1, {r2, 0, ∞},
      Assumptions → {r1 > 0, Z > 0, a > 0, e > 0}];
  ]

```

```

g2 = Integrate[r12 rwave[1, 0, r1]2 G1[r1],
  {r1, 0, ∞},
  Assumptions → {Z > 0, a > 0, e > 0}]]];

rule1 = {Z → 2, e → 1, a →  $\frac{1}{2 \times 13.605693122}$ };

Coulomb[1, 0]

$$\frac{5 e^2 Z}{8 a}$$


% //. rule1
34.0142

Coulomb[2, 0]

$$\frac{17 e^2 Z}{81 a}$$


% //. rule1
11.4221

```

Coulomb[2, 1]

$$\frac{8 e^2 Z}{243 a}$$

% //. **rule1**

1.7917

Coulomb[3, 0]

$$\frac{815 e^2 Z}{8192 a}$$

% //. **rule1**

5.41437

Coulomb[3, 1]

% //. **rule1**

$$\frac{469 e^2 Z}{49152 a}$$

0.519293

```
Coulomb[3, 2] // Simplify
```

$$\frac{9 e^2 Z (-263 937 + 1 835 008 \operatorname{Log}[2] - 917 504 \operatorname{Log}[3])}{81 920 a}$$

```
% //. rule1
```

```
0.0744525
```

```
Coulomb[4, 0] // Simplify
```

$$\frac{22 513 e^2 Z}{390 625 a}$$

```
Coulomb[5, 0] // Simplify
```

$$\frac{756 167 e^2 Z}{20 155 392 a}$$

```
Coulomb[6, 0] // Simplify
```

$$\frac{364 627 393 e^2 Z}{13 841 287 201 a}$$

19. Another calculation for Coulomb integral (example)

Here we calculate the Coulomb integral in a little different way. This approach can be seen in many standard textbooks.

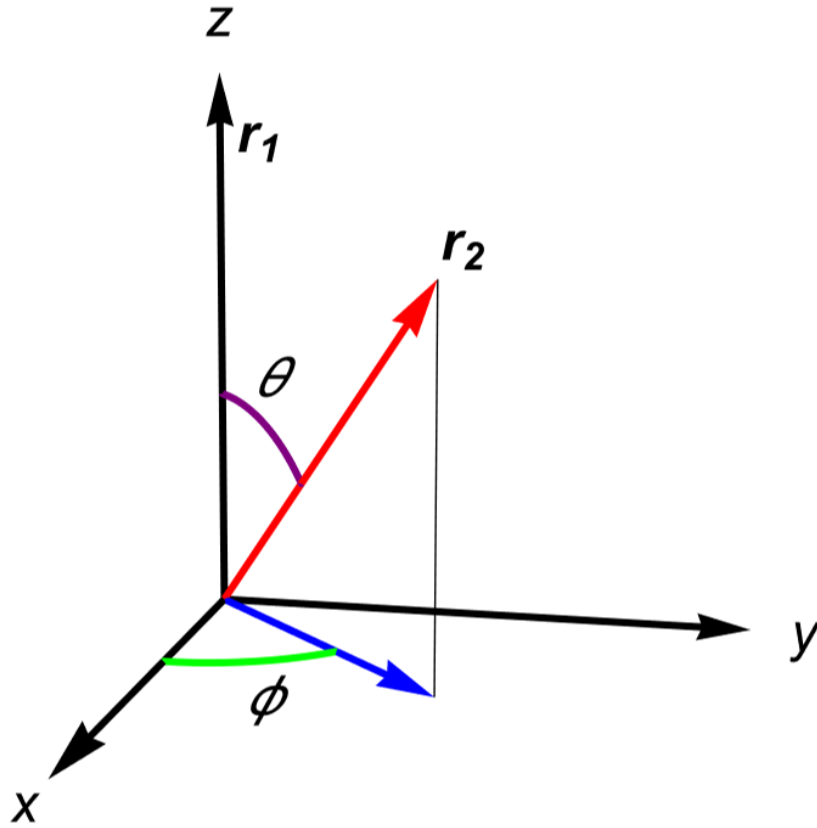


Fig.11 The position vectors $\mathbf{r}_1$ and $\mathbf{r}_2$ in the 3D real space.

$$|\mathbf{r}_1 - \mathbf{r}_2| = \sqrt{r_1^2 + r_2^2 - 2r_1r_2 \cos \theta}$$

We start with a Coulomb integral defined by

$$I = e^2 \iint d\mathbf{r}_1 d\mathbf{r}_2 \frac{|\phi_{1s}(\mathbf{r}_1)|^2 |\phi_{1s}(\mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

Note that

$$|\phi_{1s}(\mathbf{r}_1)|^2 |\phi_{1s}(\mathbf{r}_2)|^2 = \frac{1}{\pi^2} \left(\frac{Z}{a_B} \right)^6 \exp\left[-\frac{2Z(r_1 + r_2)}{a_B}\right]$$

and

$$|\mathbf{r}_1 - \mathbf{r}_2| = r_{12} = \sqrt{r_1^2 + r_2^2 - 2r_1r_2 \cos \theta}$$

Thus, we get

$$\begin{aligned}
I_1 &= e^2 \frac{1}{\pi^2} \left(\frac{Z}{a_B}\right)^6 \iint d\mathbf{r}_1 d\mathbf{r}_2 \frac{1}{r_{12}} \exp\left[-\frac{2Z(r_1 + r_2)}{a_B}\right] \\
&= e^2 \frac{1}{\pi^2} \left(\frac{Z}{a_B}\right)^6 4\pi \int_0^\infty r_1^2 \exp\left(-\frac{2Zr_1}{a_B}\right) dr_1 \int_0^\infty r_2^2 \exp\left(-\frac{2Zr_2}{a_B}\right) dr_2 \int_0^{2\pi} d\phi \int_0^\pi \frac{\sin \theta d\theta}{\sqrt{r_1^2 + r_2^2 - 2r_1r_2 \cos \theta}} \\
&= e^2 \frac{1}{\pi^2} \left(\frac{Z}{a_B}\right)^6 8\pi^2 \int_0^\infty r_1^2 \exp\left(-\frac{2Zr_1}{a_B}\right) dr_1 \int_0^\infty r_2^2 \exp\left(-\frac{2Zr_2}{a_B}\right) dr_2 \int_0^\pi \frac{\sin \theta d\theta}{\sqrt{r_1^2 + r_2^2 - 2r_1r_2 \cos \theta}} \\
&= 8e^2 \left(\frac{Z}{a_B}\right)^6 \int_0^\infty r_1^2 \exp\left(-\frac{2Zr_1}{a_B}\right) dr_1 K(r_1) \\
&= \frac{5Ze^2}{8a_B} \\
&= \frac{5Z}{4} Ry
\end{aligned}$$

where

$$\begin{aligned}
\int_0^\pi \frac{\sin \theta d\theta}{\sqrt{r_1^2 + r_2^2 - 2r_1r_2 \cos \theta}} &= \frac{r_1 + r_2 - |r_1 - r_2|}{r_1 r_2} \\
&= \begin{cases} 2/r_1 & r_1 > r_2 \\ 2/r_2 & r_1 < r_2 \end{cases}
\end{aligned}$$

and

$$\begin{aligned}
K(r_1) &= \int_0^\infty r_2^2 \exp\left(-\frac{2Zr_2}{a_B}\right) dr_2 \frac{r_1 + r_2 - |r_1 - r_2|}{r_1 r_2} \\
&= \int_0^{r_1} r_2^2 \exp\left(-\frac{2Zr_2}{a_B}\right) dr_2 \frac{r_1 + r_2 - |r_1 - r_2|}{r_1 r_2} + \int_{r_1}^\infty r_2^2 \exp\left(-\frac{2Zr_2}{a_B}\right) dr_2 \frac{r_1 + r_2 - |r_1 - r_2|}{r_1 r_2} \\
&= \int_0^{r_1} \frac{2}{r_1} r_2^2 \exp\left(-\frac{2Zr_2}{a_B}\right) dr_2 + \int_{r_1}^\infty 2r_2 \exp\left(-\frac{2Zr_2}{a_B}\right) dr_2
\end{aligned}$$

$$Ry = \frac{e^2}{2a_B} \quad (\text{in units of c,g,s,})$$

The above integral can be evaluated using the following Mathematica.

((MATHEMATICA PROGRAM-II))

Coulomb integral

```
Clear["Global`*"];
```

```
F1[θ_] := 
$$\frac{\text{Sin}[\theta]}{\sqrt{r1^2 + r2^2 - 2 r1 r2 \text{Cos}[\theta]}};$$

```

```
F1[α]
```

$$\frac{\text{Sin}[\alpha]}{\sqrt{r1^2 + r2^2 - 2 r1 r2 \text{Cos}[\alpha]}}$$

```
Integrate[F1[θ], {θ, 0, π},  
Assumptions → {r1 > 0, r2 > 0}]
```

$$\frac{r1 + r2 - \text{Abs}[r1 - r2]}{r1 r2} \quad \text{if } r1 \neq r2$$

$$\begin{aligned}
 K1 &= \text{Integrate}\left[2 \frac{r2^2}{r1} \text{Exp}\left[-\frac{2 Z r2}{aB}\right], \right. \\
 &\quad \{r2, 0, r1\}, \\
 &\quad \left. \text{Assumptions} \rightarrow \{r1 > 0, Z > 0, aB > 0\}\right] \\
 &= \frac{aB \left(aB^2 - e^{-\frac{2 r1 Z}{aB}} \left(aB^2 + 2 aB r1 Z + 2 r1^2 Z^2 \right) \right)}{2 r1 Z^3}
 \end{aligned}$$

$$\begin{aligned}
 K2 &= \text{Integrate}\left[2 r2 \text{Exp}\left[-\frac{2 Z r2}{aB}\right], \right. \\
 &\quad \{r2, r1, \infty\}, \\
 &\quad \left. \text{Assumptions} \rightarrow \{r1 > 0, Z > 0, aB > 0\}\right] \\
 &= \frac{aB e^{-\frac{2 r1 Z}{aB}} (aB + 2 r1 Z)}{2 Z^2}
 \end{aligned}$$

$$K12 = K1 + K2 // \text{Simplify}$$

$$\frac{aB^2 e^{-\frac{2 r1 Z}{aB}} \left(aB \left(-1 + e^{\frac{2 r1 Z}{aB}} \right) - r1 Z \right)}{2 r1 Z^3}$$

$$\begin{aligned}
 J1 &= \frac{8 Z^6}{aB^6} r1^2 \text{Exp}\left[-\frac{2 Z r1}{aB}\right] K12 // \text{Simplify} \\
 &= -\frac{4 e^{-\frac{4 r1 Z}{aB}} r1 Z^3 \left(aB - aB e^{\frac{2 r1 Z}{aB}} + r1 Z \right)}{aB^4}
 \end{aligned}$$

$$\begin{aligned}
 &\text{Integrate}[J1, \{r1, 0, \infty\}, \\
 &\quad \text{Assumptions} \rightarrow \{Z > 0, aB > 0\}]
 \end{aligned}$$

$$\frac{5 Z}{8 aB}$$

20. Exchange integral

Using the orbital wavefunction,

$$\phi_{2p}(\mathbf{r}) = R_{21}(r)Y_1^{m'}(\theta, \phi) \text{ with the state } |l=1, m'\rangle$$

we calculate the exchange integral given by

$$\begin{aligned} & \iint d\mathbf{r}_1 d\mathbf{r}_2 \phi_{1s}^*(\mathbf{r}_1) \phi_{2p}^*(\mathbf{r}_2) \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_{1s}(\mathbf{r}_2) \phi_{2p}(\mathbf{r}_1) \\ &= \left(\frac{1}{\sqrt{4\pi}}\right)^2 \int r_1^2 dr_1 R_{1s}(r_1) R_{2p}(r_1) \int r_2^2 dr_2 R_{1s}(r_2) R_{2p}(r_2) \\ & \times \sum_{l=0}^{\infty} \sum_{m=-l}^l G_l(r_1, r_2) \int d\Omega_1 Y_l^m(\theta_1, \phi_1) Y_1^{m'*}(\theta_1, \phi_1) \int d\Omega_2 Y_1^{m'}(\theta_2, \phi_2) Y_l^{m*}(\theta_2, \phi_2) \\ &= \left(\frac{1}{\sqrt{4\pi}}\right)^2 \int r_1^2 dr_1 R_{1s}(r_1) R_{2p}(r_1) \int r_2^2 dr_2 R_{1s}(r_2) R_{2p}(r_2) \sum_{l=0}^{\infty} \sum_{m=-l}^l G_l(r_1, r_2) \delta_{l,1} \delta_{m,m'} \\ &= \frac{1}{4\pi} \int r_1^2 dr_1 R_{1s}(r_1) R_{2p}(r_1) \int r_2^2 dr_2 R_{1s}(r_2) R_{2p}(r_2) G_l(r_1, r_2) |_{l=1} \\ &= \int r_1^2 dr_1 R_{1s}(r_1) R_{2p}(r_1) \int r_2^2 dr_2 R_{1s}(r_2) R_{2p}(r_2) F_l(r_1, r_2) |_{l=1} \\ &= \int_0^{\infty} r_1^2 dr_1 R_{1s}(r_1) R_{2p}(r_1) \left[\frac{1}{3r_1^2} \int_0^{r_1} r_2^3 dr_2 R_{1s}(r_2) R_{2p}(r_2) + \frac{r_1}{3} \int_{r_1}^{\infty} dr_2 R_{1s}(r_2) R_{2p}(r_2) \right] \end{aligned}$$

where

$$\frac{G_l(r_1, r_2)}{4\pi} = \frac{F_l(r_1, r_2)}{2l+1} = \begin{cases} \frac{1}{2l+1} \frac{1}{r_1} \left(\frac{r_2}{r_1}\right)^l & r_1 > r_2 \\ \frac{1}{2l+1} \frac{1}{r_2} \left(\frac{r_1}{r_2}\right)^l & r_2 > r_1 \end{cases}$$

or

$$F_l(r_1, r_2) = \frac{1}{2l+1} \left[\frac{1}{r_1} \left(\frac{r_2}{r_1}\right)^l u(r_1 - r_2) + \frac{1}{r_2} \left(\frac{r_1}{r_2}\right)^l u(r_2 - r_1) \right]$$

$$P_l(\cos \theta) = \frac{4\pi}{2l+1} \sum_{m=-l}^l Y_l^m(\theta_1, \phi_1) Y_l^{m*}(\theta_2, \phi_2)$$

$$\begin{aligned} \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} &= \sum_{l=0}^{\infty} F_l(r_1, r_2) P_l(\cos \theta) \\ &= 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{F_l(r_1, r_2)}{2l+1} Y_l^m(\theta_1, \phi_1) Y_l^{m*}(\theta_2, \phi_2) \end{aligned}$$

$$\langle l', m' | l, m \rangle = \delta_{l,l'} \delta_{m,m'} = \int d\Omega \langle l', m' | \mathbf{n} \rangle \langle \mathbf{n} | l, m \rangle$$

$$\begin{aligned} \langle 0, 0 | l, m \rangle &= \delta_{l,0} \delta_{m,0} \\ &= \int d\Omega \langle 0, 0 | \mathbf{n} \rangle \langle \mathbf{n} | l, m \rangle \\ &= \frac{1}{\sqrt{4\pi}} \int d\Omega \langle \mathbf{n} | l, m \rangle \end{aligned}$$

or

$$\int d\Omega \langle \mathbf{n} | l, m \rangle = \sqrt{4\pi} \delta_{l,0} \delta_{m,0}.$$

21. Exchange Integral: calculation by Mathematica

We calculate the exchange integrals with the combination of (1s) (nl).

$$K(1s, nl) = \iint d\mathbf{r}_1 d\mathbf{r}_2 \phi_{1s}^*(\mathbf{r}_1) \phi_{nl}^*(\mathbf{r}_2) \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_{nl}(\mathbf{r}_1) \phi_{1s}(\mathbf{r}_2)$$

by using Mathematica.

(1s) (nl) electron configuration

Result

n	l	$K(1s, nl)$
2	0	$\frac{16}{729} \frac{Ze^2}{a} = 1.19446 \text{ eV}$

2	1	$\frac{112}{6561} \frac{Ze^2}{a} = 0.929028 \text{ eV}$
3	0	$\frac{189}{32768} \frac{Ze^2}{a} = 0.313901 \text{ eV}$
3	1	$\frac{297}{65536} \frac{Ze^2}{a} = 0.246636 \text{ eV}$
3	2	$\frac{81}{327680} \frac{Ze^2}{a} = 0.0134529 \text{ eV}$
4	0	$\frac{22848}{9765625} \frac{Ze^2}{a} = 0.127329 \text{ eV}$
4	1	$\frac{90048}{48828125} \frac{Ze^2}{a} = 0.100366 \text{ eV}$
4	2	$\frac{32192}{244140625} \frac{Ze^2}{a} = 0.0071761 \text{ eV}$
4	3	$\frac{704}{341796875} \frac{Ze^2}{a} = 0.000112095 \text{ eV}$
5	0	$\frac{213475}{181398528} \frac{Ze^2}{a} = 0.0640463 \text{ eV}$
5	1	$\frac{2274875}{2448880128} \frac{Ze^2}{a} = 0.0505558 \text{ eV}$
5	2	$\frac{19975}{272097792} \frac{Ze^2}{a} = 0.00399524 \text{ eV}$
5	3	$\frac{12625}{7618738176} \frac{Ze^2}{a} = 0.0000901839 \text{ eV}$
5	4	$\frac{325}{29386561536} \frac{Ze^2}{a} = 6.01887 \times 10^{-7} \text{ eV}$

((MATHEMATICA PROGRAM-III)) Exchange integral K

Exchange integral

$\phi(1s), \phi(nL)$

```
Clear["Global`*"];
rwave[n_, l_, r_] :=
  1 / (Sqrt[n + l]!) ×
  (21+l a-l-3/2 e-Zr/a n-l-2 Zl+3/2 rl Sqrt[n - l - 1]! ×
    LaguerreL[-1 + n - l, 1 + 2 l, (2 Z r) / (a n)]);

F1[r1_, r2_, L_] :=
  1 / (2 L + 1)
  ( (r2/r1)L 1/r1 UnitStep[r1 - r2] +
    (r1/r2)L 1/r2 UnitStep[r2 - r1] );

Exchange[N1_, L1_] :=
  Module[{g1, g2},
    g1 = r22 rwave[1, 0, r2] × rwave[N1, L1, r2] ×
      F1[r1, r2, L1];
    G1[r1_] := Integrate[g1, {r2, 0, ∞},
      Assumptions → {r1 > 0, Z > 0, a > 0}];
    g2 = Integrate[e2 r12 rwave[1, 0, r1] ×
      rwave[N1, L1, r1] × G1[r1], {r1, 0, ∞},
      Assumptions → {Z > 0, a > 0, e > 0}];
```

$$\text{rule1} = \left\{ \text{Z} \rightarrow 2, \text{e} \rightarrow 1, \text{a} \rightarrow \frac{1}{2 \times 13.605693122} \right\};$$

h1 = Exchange[1, 0]

$$\frac{5 \text{ e}^2 \text{ Z}}{8 \text{ a}}$$

h1 = Exchange[2, 0]

$$\frac{16 \text{ e}^2 \text{ Z}}{729 \text{ a}}$$

h1 /. rule1

1.19446

h2 = Exchange[2, 1]

$$\frac{112 \text{ e}^2 \text{ Z}}{6561 \text{ a}}$$

h2 /. rule1

0.929028

h3 = Exchange[3, 0]

$$\frac{189 \text{ e}^2 \text{ Z}}{32768 \text{ a}}$$

h3 /. rule1

0.313901

h4 = Exchange[3, 1]

$$\frac{297 e^2 Z}{65 536 a}$$

h4 /. rule1

0.246636

h5 = Exchange[3, 2]

$$\frac{81 e^2 Z}{327 680 a}$$

h5 //. rule1

0.0134529

h6 = Exchange[4, 0]

$$\frac{22 848 e^2 Z}{9 765 625 a}$$

h6 //. rule1

0.127329

h7 = Exchange [4, 1]

$$\frac{90\,048\,e^2\,Z}{48\,828\,125\,a}$$

h7 /. rule1

0.100366

h8 = Exchange [4, 2]

$$\frac{32\,192\,e^2\,Z}{244\,140\,625\,a}$$

h8 /. rule1

0.0071761

h9 = Exchange [4, 3]

$$\frac{704\,e^2\,Z}{341\,796\,875\,a}$$

h9 /. rule1

0.000112095

h10 = Exchange [5, 0]

$$\frac{213\,475\,e^2\,Z}{181\,398\,528\,a}$$

h10 /. rule1

0.0640463

h11 = Exchange[5, 1]

$$\frac{2\,274\,875\,e^2\,Z}{2\,448\,880\,128\,a}$$

h11 /. rule1

0.0505558

h12 = Exchange[5, 2]

$$\frac{19\,975\,e^2\,Z}{272\,097\,792\,a}$$

h12 /. rule1

0.00399524

h13 = Exchange[5, 3]

$$\frac{12\,625\,e^2\,Z}{7\,618\,738\,176\,a}$$

h13 // . rule1

0.0000901839

h14 = Exchange [5, 4]

$$\frac{325 \text{ e}^2 Z}{29\,386\,561\,536 \text{ a}}$$

h14 // . rule1

6.01887×10^{-7}

22. Helium ground state; first-order perturbation for non-degenerate case

We consider the first-order perturbation theory to evaluate the ground state energy for the (1s)(1s) electron configuration. We start with a unperturbed wavefunction for (1s)(1s) electron configuration,

$$\psi_0 = \phi_{1s}(1)\phi_{1s}(2) = \frac{1}{\pi} \left(\frac{Z}{a_B}\right)^3 \exp\left[-\frac{Z(r_1 + r_2)}{a_B}\right]$$

The ground state energy (unperturbed system H_0);

$$E_{G0} = 2Z^2 E_H = 2 \cdot 2^2 (-Ry) = -8 \times 13.605693122 \text{ eV} = -108.8455 \text{ eV}$$

where $E_H = -13.605693122 \text{ eV}$ (ground state energy of hydrogen atom)

H_{in} (perturbation) is given by

$$H_{in} = \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}.$$

The first-order perturbation:

$$\begin{aligned}
E_G^{(1)} &= \langle \psi_0 | \hat{H}_{in} | \psi_0 \rangle \\
&= -\frac{5}{4} Z E_H \\
&= -\frac{5}{4} \times 2 \times (-13.605693122 \text{ eV}) \\
&= 34.014233 \text{ eV}
\end{aligned}$$

where $Z = 2$. So that, we have

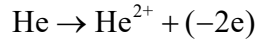
$$E_G = E_G^{(0)} + E_G^{(1)} = -108.8455 \text{ eV} + 34.014233 \text{ eV} = -74.8313 \text{ eV}$$

Experimentally, we have $E_G = E_G^{(0)} + E_G^{(1)} = -79.0051521 \text{ eV}$

Ionization energy:



or



From the second ionization,

$$I_2 = -Z^2 E_H = 4 \times 13.605693122 = 54.422772 \text{ eV}$$

Thus, we get

$$I_1 + I_2 = 79.0051521 \text{ eV}$$

or

$$I_1 = 79.0051521 - 54.4177631 = 24.587389 \text{ eV}$$

23. Ground state (1s)(1s): variational method

We use the variational method with a simple trial function. Here we choose a trial wave function to obtain an upper limit for the energy of the ground state of the helium atom. For this

end, we assume a radial function which is a real function, taking into account the screening effect. We choose a radial function for 1s electron as

$$\tilde{R}_{1,0}(r) = 2\left(\frac{\alpha}{a}\right)^{3/2} e^{-\alpha r/a},$$

where $\tilde{R}_{1,0}^*(r) = \tilde{R}_{1,0}(r)$ (we assume the real function) and α is a constant, but not a fine structure constant. So, the normalized wavefunction is given by

$$\begin{aligned}\psi_{1s}(\mathbf{r}) &= \frac{1}{\sqrt{4\pi}} \tilde{R}_{1,0}(r) \\ &= \frac{1}{\sqrt{4\pi}} 2\left(\frac{\alpha}{a}\right)^{3/2} e^{-\alpha r/a} \\ &= \frac{1}{\sqrt{\pi}} \left(\frac{\alpha}{a}\right)^{3/2} e^{-\alpha r/a}\end{aligned}$$

using the spherical harmonics of $Y_{l=0}^{m=0}(\theta, \phi) = \frac{1}{\sqrt{4\pi}}$. Note that the radial trial function satisfies the condition of normalization,

$$\int_0^\infty \tilde{R}_{1,0}(r) \tilde{R}_{1,0}(r) r^2 dr = 1.$$

The orbital (symmetric wavefunction) is

$$\begin{aligned}\tilde{R}_{1,0}(r_1) \tilde{R}_{1,0}(r_2) &= [2\left(\frac{\alpha}{a}\right)^{3/2} e^{-\alpha r_1/a}] [2\left(\frac{\alpha}{a}\right)^{3/2} e^{-\alpha r_2/a}] \\ &= 4\left(\frac{\alpha}{a}\right)^3 e^{-\alpha(r_1+r_2)/a}\end{aligned}$$

where the spin state is antisymmetric; $S = 0$.

We start with the Hamiltonian,

$$\hat{H} = \hat{H}_0 + \hat{H}_{in} = \left(\frac{\hat{\mathbf{p}}_1^2}{2m} - \frac{Ze^2}{|\hat{\mathbf{r}}_1|} + \frac{\hat{\mathbf{p}}_2^2}{2m} - \frac{Ze^2}{|\hat{\mathbf{r}}_2|} \right) + \frac{e^2}{|\hat{\mathbf{r}}_1 - \hat{\mathbf{r}}_2|}.$$

We calculate the average energy of the ground state as

$$E_G = \langle \psi_0 | \hat{H}_0 + \hat{H}_{\text{int}} | \psi_0 \rangle$$

with the trial function

$$\begin{aligned} \psi_0(\mathbf{r}_1, \mathbf{r}_2) &= \tilde{\psi}_{1s}(\mathbf{r}_1) \tilde{\psi}_{1s}(\mathbf{r}_2) \\ &= \frac{1}{4\pi} \tilde{R}_{1,0}(r_1) \tilde{R}_{1,0}(r_2) \\ &= \frac{1}{4\pi} 4 \left(\frac{\alpha}{a} \right)^3 e^{-\alpha(r_1+r_2)/a} \end{aligned}$$

The energy average is as follows.

$$\begin{aligned} \langle H_0 \rangle &= \iint d\mathbf{r}_1 d\mathbf{r}_2 \tilde{\psi}_{1,s}^*(\mathbf{r}_1) \tilde{\psi}_{1,s}^*(\mathbf{r}_2) \left(\frac{\mathbf{p}_1^2}{2m} - \frac{Ze^2}{r_1} \right) \tilde{\psi}_{1,s}(\mathbf{r}_1) \tilde{\psi}_{1,s}(\mathbf{r}_2) \\ &\quad + \iint d\mathbf{r}_1 d\mathbf{r}_2 \tilde{\psi}_{1,s}^*(\mathbf{r}_1) \tilde{\psi}_{1,s}^*(\mathbf{r}_2) \left(\frac{\mathbf{p}_2^2}{2m} - \frac{Ze^2}{r_2} \right) \tilde{\psi}_{1,s}(\mathbf{r}_1) \tilde{\psi}_{1,s}(\mathbf{r}_2) \\ &= \int d\mathbf{r}_1 \tilde{\psi}_{1,s}^*(\mathbf{r}_1) \left(\frac{\mathbf{p}_1^2}{2m} - \frac{Ze^2}{r_1} \right) \tilde{\psi}_{1,s}(\mathbf{r}_1) \int d\mathbf{r}_2 \tilde{\psi}_{1,s}^*(\mathbf{r}_2) \tilde{\psi}_{1,s}(\mathbf{r}_2) \\ &\quad + \int d\mathbf{r}_2 \tilde{\psi}_{1,s}^*(\mathbf{r}_2) \left(\frac{\mathbf{p}_2^2}{2m} - \frac{Ze^2}{r_2} \right) \tilde{\psi}_{1,s}(\mathbf{r}_2) \int d\mathbf{r}_1 \tilde{\psi}_{1,s}^*(\mathbf{r}_1) \tilde{\psi}_{1,s}(\mathbf{r}_1) \\ &= \int d\mathbf{r}_1 \tilde{\psi}_{1,s}^*(\mathbf{r}_1) \left(\frac{\mathbf{p}_1^2}{2m} - \frac{Ze^2}{r_1} \right) \tilde{\psi}_{1,s}(\mathbf{r}_1) \\ &\quad + \int d\mathbf{r}_2 \tilde{\psi}_{1,s}^*(\mathbf{r}_2) \left(\frac{\mathbf{p}_2^2}{2m} - \frac{Ze^2}{r_2} \right) \tilde{\psi}_{1,s}(\mathbf{r}_2) \\ &= 2 \int d\mathbf{r} \tilde{\psi}_{1,s}^*(\mathbf{r}) \left(\frac{\mathbf{p}^2}{2m} - \frac{Ze^2}{r} \right) \tilde{\psi}_{1,s}(\mathbf{r}) \end{aligned}$$

or

$$\begin{aligned} \langle H_0 \rangle &= 2 \frac{1}{4\pi} \int_0^\infty r^2 dr \hat{R}_{1,s}^*(r) \left(\frac{\mathbf{p}^2}{2m} - \frac{Ze^2}{r} \right) \hat{R}_{1,s}(r) \int_0^\pi 2\pi \sin \theta d\theta \\ &= 2 \int_0^\infty \tilde{R}_{1,0}(r) \left(\frac{p_r^2}{2m} - \frac{Ze^2}{r} \right) \tilde{R}_{1,0}(r) r^2 dr \\ &= \frac{e^2}{a} \alpha (-2Z + \alpha) \end{aligned}$$

noting that

$$\begin{aligned}
\mathbf{p}^2 &= p_r^2 + \frac{\mathbf{L}^2}{r^2} \\
&= \frac{\hbar}{ir} \frac{\partial}{\partial r} \left(r \frac{\hbar}{ir} \frac{\partial}{\partial r} r \right) + \frac{\hbar^2 l(l+1)}{r^2} \\
&= -\frac{\hbar^2}{r} \frac{\partial^2}{\partial r^2} r + \frac{\hbar^2 l(l+1)}{r^2}
\end{aligned}$$

When $l = 0$ for 1s state, we have $\mathbf{p}^2 = -\frac{\hbar^2}{r} \frac{\partial^2}{\partial r^2} r$. We also need to calculate the exchange interaction defined by

$$\begin{aligned}
\langle H_{in} \rangle &= \iint d\mathbf{r}_1 d\mathbf{r}_2 \tilde{\psi}_0^*(\mathbf{r}_1, \mathbf{r}_2) \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \tilde{\psi}_0^*(\mathbf{r}_1, \mathbf{r}_2) \\
&= \iint d\mathbf{r}_1 d\mathbf{r}_2 \tilde{\psi}_{1s}^*(\mathbf{r}_1) \tilde{\psi}_{1s}^*(\mathbf{r}_2) \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \hat{\psi}_{1s}(\mathbf{r}_1) \hat{\psi}_{1s}(\mathbf{r}_2) \\
&= \iint d\mathbf{r}_1 d\mathbf{r}_2 |\tilde{\psi}_{1s}(\mathbf{r}_1)|^2 \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} |\hat{\psi}_{1s}(\mathbf{r}_2)|^2
\end{aligned}$$

The above derivation will be discussed later in detail. The integral can be done by using Mathematica.

$$\begin{aligned}
\langle H_{in} \rangle &= \int r_1^2 dr_1 \tilde{R}_{1,0}(r_1) \tilde{R}_{1,0}(r_1) \int r_2^2 dr_2 \hat{R}_{1,0}(r_2) \hat{R}_{1,0}(r_2) F_{l=0}(r_1, r_2) \\
&= \frac{5}{8} \frac{e^2 \alpha}{e}
\end{aligned}$$

where

$$F_{l=0}(r_1, r_2) = \frac{1}{r_1} u(r_1 - r_2) + \frac{1}{r_2} u(r_2 - r_1),$$

with $u(r)$ is the step function. Thus, we get the average energy as

$$\begin{aligned}
E(\alpha) &= \langle H \rangle \\
&= \langle H_0 \rangle + \langle H_{in} \rangle \\
&= \frac{e^2}{2a} [2\alpha(-2Z + \alpha) + \frac{5\alpha}{4}] \\
&= 2Ry \alpha(\alpha - 2Z + \frac{5}{8})
\end{aligned}$$

where

$$\frac{e^2}{2a} = Ry \quad (\text{Rydberg constant})$$

$$Ry = 13.605693122994(26) \text{ eV},$$

The minimization of $E(\alpha)$,

$$\frac{\partial E(\alpha)}{\partial \alpha} = 0,$$

yields

$$\alpha = \alpha_0 = Z - \frac{5}{16}.$$

So, the ground state energy is

$$E(\alpha_0) = -\frac{1}{128}(5-16Z)^2 Ry$$

By substituting $Z = 2$, we have

$$\alpha_0 = 2 - \frac{5}{16} = \frac{27}{16} = 1.6875$$

$$E_{\min} = -\frac{729}{128} Ry = -5.6953125 Ry = -77.48867411455 \text{ eV}$$

So, we get the real ground state energy as

$$E_G \leq E_{\min}$$

Note that the observed value of E_G is -79.00521521 eV. This value of E_G is the minimum energy required to remove both electrons from a helium atom. The result that the trial wave function gives the best energy value when $Z_{\text{eff}} = 27/16$ rather than 2 indicates that each electron screens the nucleus from the other electron, the effective nuclear charge being reduced by 5/16 of an electronic charge. The wavefunction shows that the second electron does not see a charge Ze , but a lower charge $\alpha_0 = 1.6875$.

The average radius is evaluated as

$$\begin{aligned} \langle r \rangle &= \int_0^{\infty} dr r^3 [\tilde{R}_{1,0}(r)]^2 \\ &= \int_0^{\infty} dr r^3 4 \left(\frac{\alpha}{a} \right)^3 e^{-2\alpha r/a} \\ &= \frac{3a}{2\alpha} \end{aligned}$$

When α changes from $\alpha = Z = 2$ to $\alpha = \alpha_0 = Z_{\text{eff}} = 1.6875$, the average radius from $0.75 a$ to $0.889 a$, favoring the screen effect.

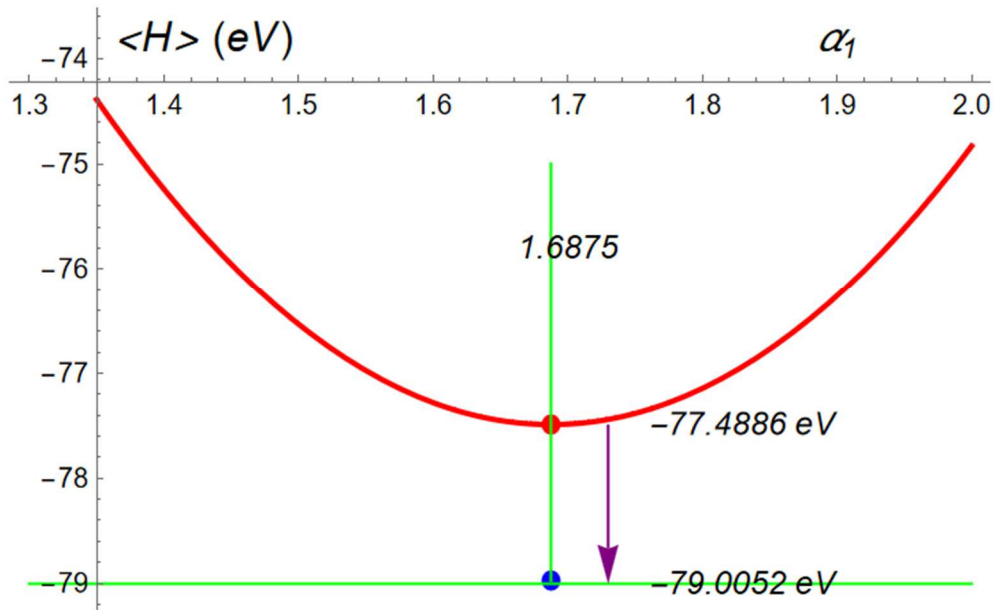


Fig.12 The average energy $\langle H \rangle = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle}$ as a function of the parameter α_1 . The minimum energy is -77.4886 eV at $\alpha_1 = 1.6875$, which is a little higher than the experimental value; -79.0052 eV, which is consistent with the prediction derived from the variation method.

((Comment by F. Seitz))

F. Seitz, *The Modern Theory of Solids*, 1st edition (McGraw Hill, 1940).

One important fact that may be gained from this investigation is that the method of one-electron functions yields an energy which is in error by about 0.5 eV per electron, because it does not involve the necessary correlations. Since the binding energy of many solids is of the order of 1 eV per electron, we may expect that the cohesive energies derived from on-electron functions will often have a relatively high percentage of error.

((MATHEMATICA PROGRAM-IV))

Variation method for the determination of the ground state of He atom

```
Clear["Global`*"];
rule1 = {e2 → 2 a Ry};
rwave[r_] := 2  $\frac{\alpha_1^{3/2}}{a^{3/2}}$  e- $\frac{r \alpha_1}{a}$ ;
F1[r1_, r2_, L_] :=
 $\frac{1}{2L+1} \left( \left( \frac{r2}{r1} \right)^L \frac{1}{r1} \text{UnitStep}[r1 - r2] + \left( \frac{r1}{r2} \right)^L \frac{1}{r2} \text{UnitStep}[r2 - r1] \right);$ 
```

Normalization of wavefunction R(n=1,l=0) = rwave[r]; s-wave function

```
T1 = Integrate[rwave[r]2 r2, {r, 0, ∞},
Assumptions → {a > 0, α1 > 0}]
```

1

Formulation of Exchange term $\langle H_{\text{exchsng}} \rangle$

```

Exchange := Module[{g1, g2},
  g1 = r2^2 rwave[r2] × rwave[r2] × F1[r1, r2, 0];
  G1[r1_] := Integrate[g1, {r2, 0, ∞},
    Assumptions → {r1 > 0, a > 0, α1 > 0}];
  g2 = Integrate[e^2 r1^2 rwave[r1] × rwave[r1] × G1[r1],
    {r1, 0, ∞}, Assumptions → {a > 0, e > 0, α1 > 0}];

```

Radial linear momentum

```

pr :=  $\frac{\hbar}{i r}$  D[r #, r] &;

```

```

K1 = rwave[r]  $\left( \frac{1}{2 m} \text{pr}[\text{pr}[\text{rwave}[r]]] - \frac{Z e^2}{r} \text{rwave}[r] \right)$  // Simplify;

```

Average energy of H0; $\langle H_0 \rangle$

```

K11 = Integrate[2 r^2 K1, {r, 0, ∞}, Assumptions → {a > 0, α1 > 0}]

```

$$\frac{\alpha 1 \left(-2 a e^2 m Z + \alpha 1 \hbar^2 \right)}{a^2 m}$$

$$E1 = K11 /. \{\hbar^2 \rightarrow a m e^2\} // Simplify$$

$$\frac{e^2 \alpha 1 (-2 Z + \alpha 1)}{a}$$

Average energy of Hexchange; $\langle H_{\text{exchange}} \rangle$

$$E2 = \text{Exchange}$$

$$\frac{5 e^2 \alpha 1}{8 a}$$

$\langle H \rangle = \langle H_0 \rangle + \langle \text{Hexchange} \rangle$ as a function of a parameter $\alpha 1$

Ry = 13.605693122994 eV (Rydberg constant)

$$ET = (E1 + E2) /. \text{rule1} // Simplify$$

$$\frac{1}{4} \text{Ry } \alpha 1 (5 - 16 Z + 8 \alpha 1)$$

Finding the minimum of the average energy

```
eq1 = D[ET,  $\alpha 1$ ] // Simplify; eq2 = Solve[eq1 == 0,  $\alpha 1$ ] // Simplify
```

$$\left\{ \left\{ \alpha 1 \rightarrow -\frac{5}{16} + Z \right\} \right\}$$

```
ET1 = ET /. eq2[[1]] // Simplify
```

$$-\frac{1}{128} \text{Ry} (5 - 16 Z)^2$$

```
ET2 = ET1 /. Z -> 2
```

$$-\frac{729 \text{Ry}}{128}$$

```
ET3 = ET2 /. { Ry -> 13.605693122994 }
```

$$-77.4887$$

24. Ground state energy (1s)(1s) electron configuration

$$(1s) \quad l = 0, \quad m = 0$$

$$(1s) \quad l = 0, \quad m = 0$$

Total angular momentum

$$D_0 \times D_0 = D_0 \quad (L = 0)$$

Orbital wavefunction

$$|\phi_{1s}\rangle_1 \otimes |\phi_{1s}\rangle_2$$

Note that the wavefunction should be symmetric. No antisymmetric orbital state is allowed. Since the total wavefunction should be antisymmetric, the spin wavefunction should be antisymmetric.

$$S = 0 \quad (\text{singlet})$$

The total angular momentum is $J = 0$;

$$D_{L=0} \times D_{S=0} = D_0$$

The ground state is

$$^{2S+1}S_{J=0} = {}^1S_0$$

with $L = 0$, $S = 0$ and $J = 0$.

(1s)(1s) electron configuration

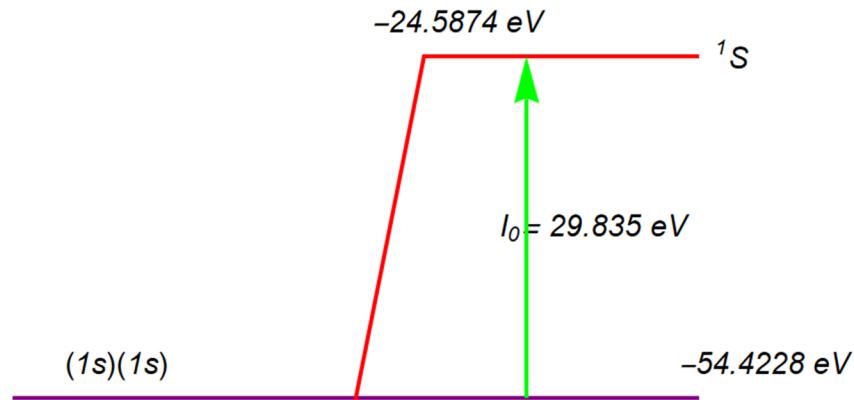


Fig.13 Ground state for He I: (1s)(1s) electron configuration.

$${}^1S_0 \quad -24.5873890 \text{ eV} \quad (\text{spin singlet})$$

for the ground state (1S_0 ; singlet). Then we get

$$I_0(\text{exp}) = -24.5873890 \text{ eV} + 54.4228 \text{ eV} = 29.835 \text{ eV}$$

$$I_0(\text{cal}) = 34.0112 \text{ eV}$$

((Ground state 1s1s)) Hund's rule

The electron configuration $(1s)^2$ is the ground state with $S = 0$ (singlet spin state) since the orbital wavefunction should be symmetric. In this case, the average of spin over the ground state is zero.

The helium ground state consists of **two identical 1s electrons**. The energy required to remove one of them is the highest ionization energy of any atom in the periodic table: 24.5874 eV.

The system is in the so-called singlet state with overall spin zero. Hence, the ground state of helium atom has overall electron spin zero.

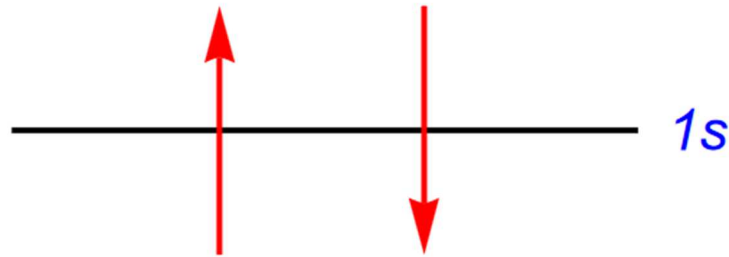


Fig.14 Occupancy of two spins in the (1s) orbital state with $|+z\rangle$ spin state and with (1s) orbital state with $|-z\rangle$ spin state. The spin state is antisymmetric with $S = 0$ (singlet), since the orbital wavefunction is symmetric.

Using the Hund's rule, we have $S = 0$. The orbital wavefunction for (1s)(1s) electron configuration should be even under the interexchange of particles. So that, we have singlet spin state ($S = 0$). The ground state is singlet.

((Kanamori))

When the ground state is the singlet state, no Curie law can be obtained.

25. Energy level diagram for the (1s)(2s) electron configuration

$$(1s) \quad l = 0, \quad m = 0$$

$$(2s) \quad l = 0, \quad m = 0$$

Total orbital angular momentum

$$D_0 \times D_0 = D_0 \quad (L = 0)$$

(a) Symmetric orbital state

Orbital wavefunction;

$$|\psi_s\rangle = \frac{1}{\sqrt{2}} [|\phi_{1s}\rangle_1 \otimes |\phi_{2s}\rangle_2 + |\phi_{2s}\rangle_1 \otimes |\phi_{1s}\rangle_2]$$

Spin state: antisymmetric state

$$S = 0 \quad (\text{singlet})$$

The total angular momentum is $J = 0$;

$$D_{L=0} \times D_{S=0} = D_0$$

So that, we have

$${}^{2S+1=1}S_{J=0} = {}^1S_0 \quad (L = 0, S = 0, J = 0)$$

(b) Antisymmetric orbital state

$$|\psi_A\rangle = \frac{1}{\sqrt{2}} [|\phi_{1s}\rangle_1 \otimes |\phi_{2s}\rangle_2 - |\phi_{2s}\rangle_1 \otimes |\phi_{1s}\rangle_2]$$

Spin state: symmetric state

$$S = 1 \quad (\text{triplet}, M_s = 1, 0, -1)$$

Since $L = 0$, the total angular momentum is $J = 1$

$$D_{L=0} \times D_{S=1} = D_1$$

So that, we have

$${}^{2S+1=3}S_{J=1} = {}^3S_1 \quad (L = 0, S = 1, J = 1)$$

The energy of the system which is the sum of the unperturbed system and perturbation is

$$J_1 + K_1 = -3.97161 \text{ eV}, \quad J_1 - K_1 = -4.761777 \text{ eV}$$

where J_1 is defined as $J_1 = -13.6057 \text{ eV} + I_1$.

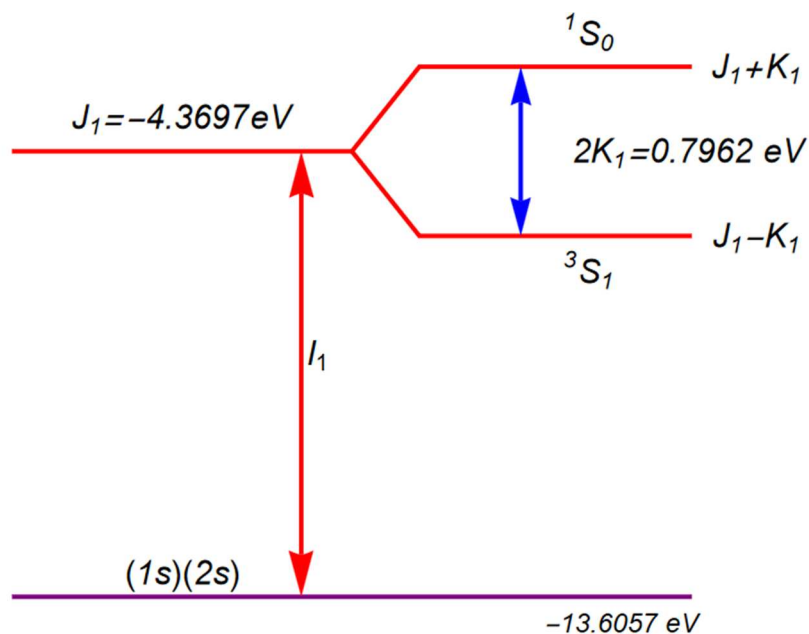


Fig.15 Energy level diagram for the (1s)(2s) electron configuration. The energy level of (1s)(2s) is the one as a result of perturbation, in addition to the one of unperturbed system. $K_1 = K(1s,2s)$. $J_1 = J(1s,2s)$ (definition).

$$J_1(\text{exp}) = -13.6057 \text{ eV} + I_1(\text{exp}) = -4.3697 \text{ eV}.$$

$$I_1(\text{exp}) = 9.236 \text{ eV}.$$

$$K_1(\text{exp}) = 0.3981 \text{ eV}.$$

$$I_1(\text{cal}) = 11.4221 \text{ eV}.$$

$$K_1(\text{cal}) = 1.19446 \text{ eV}.$$

$$J_1 + K_1 = -3.97161 \text{ eV} \quad (\text{spin singlet, } {}^1S_0).$$

$$J_1 - K_1 = -4.761777 \text{ eV} \quad (\text{spin triplet, } {}^3S_1)$$

((Note))

1s2s	3S	1	-4.76777415797 eV	(S = 1, orthohelium)
1s2s	1S	0	-3.9716138666 eV	(S = 0, parahelium)

((Hind's law))

In the helium atom, Hund's first rule correctly predicts that the 1s2s triplet state (3S) is lower than the 1s2s singlet (1S). This is an almost universal generalization and contributes to Hund's rule.

26. Heisenberg's spin exchange interaction (origin)

Here we use the Pauli spin operators $\hat{\sigma}$;

$$\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 = \frac{\hbar^2}{4} \hat{\mathbf{e}}_1 \cdot \hat{\mathbf{e}}_2$$

with the Pauli matrices,

$$\hat{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \hat{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \hat{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

The Dirac spin exchange operator is defined as

$$\hat{P}_{12}^\sigma = \frac{1}{2}(\hat{1} + \hat{\mathbf{e}}_1 \cdot \hat{\mathbf{e}}_2),$$

and

$$\frac{1}{\hbar^2} \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 = \frac{1}{4} (2\hat{P}_{12}^\sigma - 1).$$

For $S = 1$

$$\begin{aligned} \frac{1}{\hbar^2} \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 |S = 1, M_s\rangle &= \frac{1}{4} (2\hat{P}_{12}^\sigma - 1) |S = 1, M_s\rangle \\ &= \frac{1}{4} |S = 1, M_s\rangle \end{aligned}$$

For $S = 0$

$$\begin{aligned} \frac{1}{\hbar^2} \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 |S = 0, M_s = 0\rangle &= \frac{1}{4} (2\hat{P}_{12}^\sigma - 1) |S = 0, M_s = 0\rangle \\ &= -\frac{3}{4} |S = 0, M_s = 0\rangle \end{aligned}$$

We consider the effective spin Hamiltonian as

$$\hat{H}_{eff} = (I + \alpha K) \hat{1} + \frac{\beta K}{\hbar^2} \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2$$

with constant α and β to be determined.

For $|S=1, M_s\rangle$ (spin triplet)

$$\begin{aligned}\hat{H}_{eff} |S=1, M_s\rangle &= [(I + \alpha K)\hat{1} + \frac{\beta K}{\hbar^2} \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2] |S=1, M_s\rangle \\ &= (I + \alpha K + \frac{\beta}{4} K) |S=1, M_s\rangle \\ &= (I - K) |S=1, M_s\rangle\end{aligned}$$

For $|S=0, M_s=0\rangle$ (spin singlet),

$$\begin{aligned}\hat{H}_{eff} |S=0, M_s=0\rangle &= [(I + \alpha K)\hat{1} + \frac{\beta K}{\hbar^2} \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2] |S=0, M_s=0\rangle \\ &= (I + \alpha K - \frac{3\beta}{4} K) |S=0, M_s=0\rangle \\ &= (I + K) |S=0, M_s=0\rangle\end{aligned}$$

From these two equations, we get

$$\alpha + \frac{1}{4}\beta = -1, \quad \alpha - \frac{3}{4}\beta = 1,$$

leading to $\alpha = -\frac{1}{2}$ and $\beta = -2$. Then we have the final form of the effective spin

Hamiltonian as

$$\hat{H}_{eff} = (I - \frac{1}{2}K)\hat{1} - \frac{2K}{\hbar^2} \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2,$$

which is called as Heisenberg's exchange interaction; interaction between $\hat{\mathbf{S}}_1$ and $\hat{\mathbf{S}}_2$. When $K > 0$, the system becomes ferromagnet. This Hamiltonian is considered to be responsible for spin-ordering in ferromagnets. Note that parahelium atoms ($S=0$) have no magnetic moment and form a diamagnetic behavior. On the other hand, orthohelium atoms ($S=1$) have a magnetic moment and show a paramagnetic behavior. The difference between two systems is due to the degeneracy of the states. The singlet ground state has no magnetic moment since $S=0$.

((Note))

Note that Heisenberg's exchange interaction holds precisely as Dirac's vector model when the following conditions are satisfied (**Kubo and Nagamiya**)

- (a) The orbital wavefunctions are mutually orthogonal [each atomic orbital contains one electrons is equal to that of orbitals].
- (b) The eigenstates are determined only with respect to the spin state,

27. Energy level diagram for the (1s)(2p) electron configuration

$$(1s); \quad l = 0 \quad (m = 0)$$

$$(2p); \quad l = 1 \quad (m = 1, 0, -1)$$

Total angular momentum:

$$D_1 \times D_0 = D_1 \quad L = 1$$

Note that the total spin angular momentum is

$$D_{1/2} \times D_{1/2} = D_1 + D_0$$

$$S = 1 \quad (\text{triplet, symmetric})$$

$$S = 0 \quad (\text{singlet, antisymmetric})$$

The total angular momentum J

For $S = 1$ (triplet, symmetric), and $L = 1$,

$$D_1 \times D_1 = D_2 + D_1 + D_0$$

leading to $J = 2, 1$, and 0 .

The notation: ${}^3P_2, {}^3P_1, {}^3P_0$

So that, the orbital wavefunction should be antisymmetric;

$$|\psi_A\rangle = \frac{1}{\sqrt{2}} [|\phi_{1s}\rangle_1 \otimes |\phi_{2p}\rangle_2 - |\phi_{2p}\rangle_1 \otimes |\phi_{1s}\rangle_2]$$

For $S = 0$ (singlet, antisymmetric) and $L = 0$,

$$D_1 \times D_0 = D_1$$

leading to $J = 1$.

The notation: 1P_1 .

So that, the orbital wavefunction should be symmetric;

$$|\psi_S\rangle = \frac{1}{\sqrt{2}} [|\phi_{1s}\rangle_1 \otimes |\phi_{2p}\rangle_2 + |\phi_{2p}\rangle_1 \otimes |\phi_{1s}\rangle_2]$$

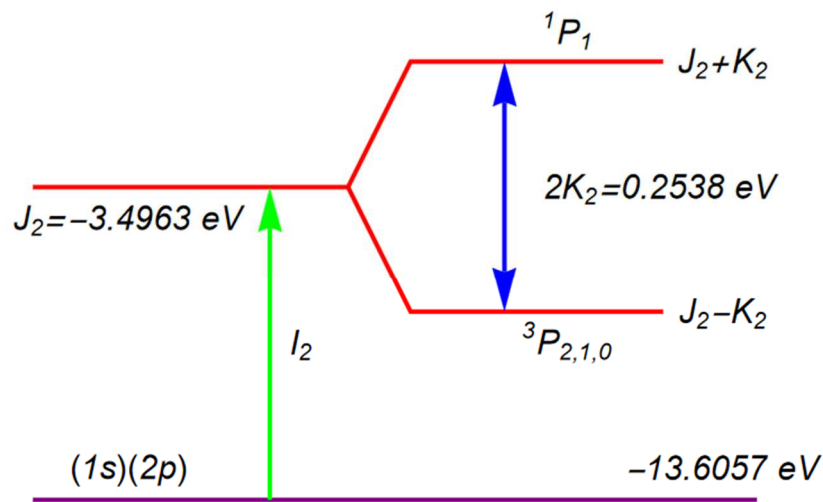


Fig.16 Energy level diagram for the (1s)(2p) electron configuration.

$K_2 = K(1s,2p)$. $J_2 = J(1s,2p)$. (definition).

$J_2(\text{exp}) = -13.6057 \text{ eV} + I_2(\text{exp}) = -3.4963 \text{ eV}$.

$I_2(\text{exp}) = 10.1094 \text{ eV}$.

$K_2(\text{exp}) = 0.1269 \text{ eV}$.

$I_2(\text{cal}) = 1.7917 \text{ eV}$.

$K_2(\text{cal}) = 0.929028 \text{ eV}$

(1s)(2p) electron configuration (experimental result)

1P_1 -3.36937 eV ($S = 0$)

3P_0 -3.6233 eV ($S = 1$)

3P_1	-3.62329 eV
3P_2	-3.62317 eV

((Note)) Heisenberg's principle of uncertainty

Using the Heisenberg's principle of uncertainty, the relaxation time is related to the exchange integrals as

$$\tau = \frac{\hbar}{2K} = 2.59 \times 10^{-15} \text{ (s)}.$$

using the value $K_{\text{exp}}(1s, 2p) = 0.1269 \text{ eV}$.

28. Possible degenerate case for (1s)(2s) and (1s)(2p) electron configuration

I found an interesting problem in the book of L.I. Schiff. It is reasonable to assume that the unperturbed energy level of (1s)(2s) electron configuration is the same as that of (1s)(2p) electron configuration. If so and the repulsive Coulomb interaction is applied as a perturbation we need to apply the degenerate perturbation theory (the first order) to determine the energy shift. The matrix element

((L.I. Schiff)) L.I. Schiff, Quantum Mechanics, 3rd edition (McGraw-Hill, 1968).

Show that the (1s)(2p) configurations in helium can be treated separately from the (1s)(2s) configurations so far as the first-order energy-level calculation.

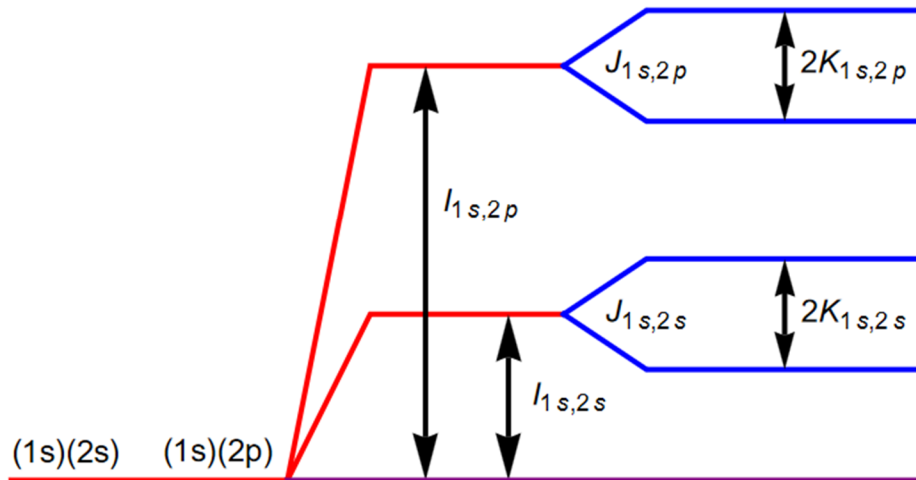


Fig.17 Possibility of the degenerate states of (1s)(2s) and (1s)(2p) electron configuration. The shift in energy levels of the electron configurations, (1s)(2s), and (1s)(2p), in

the presence of perturbation, Coulomb repulsive interaction. Note that the energy level of (1s)(2s) and (1s)(2p) are degenerate in the unperturbed Hamiltonian.

We consider the four states (degenerate states); 4 independent states with the same energy. For simplicity, here we use

$$|\psi_1\rangle_S = \hat{S}|\phi_{1s,2s}\rangle = \frac{1}{\sqrt{2}}(\hat{1} + \hat{P}_{12})|\phi_{1s,2s}\rangle,$$

$$|\psi_1\rangle_A = \hat{A}|\phi_{1s,2s}\rangle = \frac{1}{\sqrt{2}}(\hat{1} - \hat{P}_{12})|\phi_{1s,2s}\rangle$$

$$|\psi_2\rangle_S = \hat{S}|\phi_{1s,2p}\rangle = \frac{1}{\sqrt{2}}(\hat{1} + \hat{P}_{12})|\phi_{1s,2p}\rangle,$$

$$|\psi_2\rangle_A = \hat{A}|\phi_{1s,2p}\rangle = \frac{1}{\sqrt{2}}(\hat{1} - \hat{P}_{12})|\phi_{1s,2p}\rangle$$

where

$$|\psi_1\rangle = |\phi_{1s,2s}\rangle = |\phi_{1s}\rangle_1 \otimes |\phi_{2s}\rangle_2$$

$$|\psi_2\rangle = |\phi_{1s,2p}\rangle = |\phi_{1s}\rangle_1 \otimes |\phi_{2p}\rangle_2$$

In the presence of the Coulomb repulsive interaction

$$\hat{H}_{in} = \frac{e^2}{|\hat{\mathbf{r}}_1 - \hat{\mathbf{r}}_2|}$$

we need to evaluate the matrix elements of this perturbation over the four states, since the four states are energetically degenerate. We show that

$$\begin{pmatrix}
{}_S\langle\psi_1|\hat{H}_{in}|\psi_1\rangle_S & {}_S\langle\psi_1|\hat{H}_{in}|\psi_1\rangle_A & {}_S\langle\psi_1|\hat{H}_{in}|\psi_2\rangle_S & {}_S\langle\psi_1|\hat{H}_{in}|\psi_2\rangle_A \\
{}_A\langle\psi_1|\hat{H}_{in}|\psi_1\rangle_S & {}_A\langle\psi_1|\hat{H}_{in}|\psi_1\rangle_A & {}_A\langle\psi_1|\hat{H}_{in}|\psi_2\rangle_S & {}_A\langle\psi_1|\hat{H}_{in}|\psi_2\rangle_A \\
{}_S\langle\psi_2|\hat{H}_{in}|\psi_1\rangle_S & {}_S\langle\psi_2|\hat{H}_{in}|\psi_1\rangle_A & {}_S\langle\psi_2|\hat{H}_{in}|\psi_2\rangle_S & {}_S\langle\psi_2|\hat{H}_{in}|\psi_2\rangle_A \\
{}_A\langle\psi_2|\hat{H}_{in}|\psi_1\rangle_S & {}_A\langle\psi_2|\hat{H}_{in}|\psi_1\rangle_A & {}_A\langle\psi_2|\hat{H}_{in}|\psi_2\rangle_S & {}_A\langle\psi_2|\hat{H}_{in}|\psi_2\rangle_A
\end{pmatrix}
= \begin{pmatrix}
J_1 + K_1 & 0 & 0 & 0 \\
0 & J_1 - K_1 & 0 & 0 \\
0 & 0 & J_2 + K_2 & 0 \\
0 & 0 & 0 & J_2 - K_2
\end{pmatrix}$$

$$\begin{aligned}
{}_S\langle\psi_2|\hat{H}_{in}|\psi_1\rangle_S &= \langle\phi_{1s,2p}|\hat{S}\hat{H}_{in}\hat{S}|\phi_{1s,2s}\rangle \\
&= \frac{1}{2}\langle\phi_{1s,2p}|\hat{H}_{in} + \hat{H}_{in}\hat{P}_{12}|\phi_{1s,2s}\rangle \\
&= \frac{1}{2}[\langle\phi_{1s,2p}|\hat{H}_{in}|\phi_{1s,2s}\rangle + \langle\phi_{1s,2p}|\hat{H}_{in}|\phi_{2s,1s}\rangle]
\end{aligned}$$

$$\begin{aligned}
{}_A\langle\psi_2|\hat{H}_{in}|\psi_1\rangle_A &= \langle\phi_{1s,2p}|\hat{A}\hat{H}_{in}\hat{A}|\phi_{1s,2s}\rangle \\
&= \langle\phi_{1s,2p}|\hat{H}_{in} + \hat{H}_{in}\hat{P}_{12}|\phi_{1s,2s}\rangle \\
&= \langle\phi_{1s,2p}|\hat{H}_{in}|\phi_{1s,2s}\rangle + \langle\phi_{1s,2p}|\hat{H}_{in}|\phi_{2s,1s}\rangle
\end{aligned}$$

$${}_A\langle\psi_2|\hat{H}_{in}|\psi_1\rangle_S = \langle\phi_{1s,2p}|\hat{A}\hat{H}_{in}\hat{S}|\phi_{1s,2s}\rangle = 0$$

$${}_S\langle\psi_2|\hat{H}_{in}|\psi_1\rangle_A = \langle\phi_{1s,2p}|\hat{S}\hat{H}_{in}\hat{A}|\phi_{1s,2s}\rangle = 0$$

where

$$\begin{aligned}
\hat{A}\hat{H}_{in}\hat{S} &= \frac{1}{2}(\hat{1} - \hat{P}_{12})\hat{H}_{in}(\hat{1} + \hat{P}_{12}) \\
&= \frac{1}{2}(\hat{H}_{in} + \hat{H}_{in}\hat{P}_{12} - \hat{P}_{12}\hat{H}_{in} - \hat{P}_{12}\hat{H}_{in}\hat{P}_{12}) \\
&= 0
\end{aligned}$$

$$(\hat{S}\hat{H}_{in}\hat{A})^+ = \hat{A}^+\hat{H}_{in}^+\hat{S}^+ = \hat{A}\hat{H}_{in}\hat{S} = 0$$

$$\begin{aligned}
\hat{S}\hat{H}_{in}\hat{S} &= \frac{1}{2}(\hat{1} + \hat{P}_{12})\hat{H}_{in}(\hat{1} + \hat{P}_{12}) \\
&= \frac{1}{2}(\hat{1} + \hat{P}_{12})\hat{H}_{in}(\hat{1} + \hat{P}_{12}) \\
&= \hat{H}_{in} + \hat{H}_{in}\hat{P}_{12}
\end{aligned}$$

$$\begin{aligned}
\hat{A}\hat{H}_{in}\hat{A} &= \frac{1}{2}(\hat{1} - \hat{P}_{12})\hat{H}_{in}(\hat{1} - \hat{P}_{12}) \\
&= \frac{1}{2}(\hat{1} - \hat{P}_{12})\hat{H}_{in}(\hat{1} - \hat{P}_{12}) \\
&= \hat{H}_{in} - \hat{H}_{in}\hat{P}_{12}
\end{aligned}$$

We show now

$$\langle \phi_{1s,2p} | \hat{H}_{in} | \phi_{1s,2s} \rangle = 0$$

$$\langle \phi_{1s,2p} | \hat{H}_{in} | \phi_{2s,1s} \rangle = 0$$

((Proof))

$$\langle \mathbf{r}_1, \mathbf{r}_2 | \phi_{1s,2s} \rangle = \phi_{1s}(\mathbf{r}_1)\phi_{2s}(\mathbf{r}_1)$$

$$\langle \mathbf{r}_1, \mathbf{r}_2 | \phi_{1s,2p} \rangle = \phi_{1s}(\mathbf{r}_1)\phi_{2p}(\mathbf{r}_2)$$

where

$$\phi_{1s}(\mathbf{r}) = R_{n=1,l=0}(r)Y_{l=0,m=0}(\theta, \phi) = R_{1,0}(r)\frac{1}{\sqrt{4\pi}}$$

$$\phi_{2s}(\mathbf{r}) = R_{20}(r)Y_{l=0,m=0}(\theta, \phi) = R_{20}(r)\frac{1}{\sqrt{4\pi}}$$

$$\phi_{2p}(\mathbf{r}) = R_{n=2,l=1}(r)Y_{1,m}(\theta, \phi) = R_{2,1}(r)Y_{1,m}(\theta, \phi)$$

Parity operator $\hat{\pi}$:

$$\hat{\pi} |l, m\rangle = (-1)^l |l, m\rangle$$

$$\langle \mathbf{n} | \hat{\pi} | l, m \rangle = \langle -\mathbf{n} | l, m \rangle = (-1)^l \langle \mathbf{n} | l, m \rangle$$

So that $\langle \mathbf{n} | l, m \rangle$ has an even parity for $l = 0$ and odd parity for $l = 1$.

$$J_A = \langle \phi_{1s,2p} | \hat{H}_{in} | \phi_{1s,2s} \rangle = \iint d\mathbf{r}_1 d\mathbf{r}_2 \phi_{1s}^*(\mathbf{r}_1) \phi_{2p}^*(\mathbf{r}_2) \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_1|} \phi_{1s}(\mathbf{r}_1) \phi_{2s}(\mathbf{r}_2)$$

$$J_B = \langle \phi_{1s,2p} | \hat{H}_{in} | \phi_{2s,1s} \rangle = \iint d\mathbf{r}_1 d\mathbf{r}_2 \phi_{1s}^*(\mathbf{r}_1) \phi_{2p}^*(\mathbf{r}_2) \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_{2s}(\mathbf{r}_1) \phi_{1s}(\mathbf{r}_2)$$

These integrals remain unchanged under the change of parity;

$$\begin{aligned} J_A &= \langle \phi_{1s,2p} | \hat{H}_{in} | \phi_{1s,2s} \rangle \\ &= \frac{1}{2} \iint d\mathbf{r}_1 d\mathbf{r}_2 [\phi_{1s}^*(\mathbf{r}_1) \phi_{2p}^*(\mathbf{r}_2) \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_{1s}(\mathbf{r}_1) \phi_{2s}(\mathbf{r}_2) \\ &\quad + \phi_{1s}^*(-\mathbf{r}_1) \phi_{2p}^*(-\mathbf{r}_2) \frac{e^2}{|-\mathbf{r}_1 + \mathbf{r}_2|} \phi_{1s}(-\mathbf{r}_1) \phi_{2s}(-\mathbf{r}_2)] \\ &= \frac{1}{2} \iint d\mathbf{r}_1 d\mathbf{r}_2 [\phi_{1s}^*(\mathbf{r}_1) \phi_{2p}^*(\mathbf{r}_2) \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_{1s}(\mathbf{r}_1) \phi_{2s}(\mathbf{r}_2) \\ &\quad - \phi_{1s}^*(\mathbf{r}_1) \phi_{2p}^*(\mathbf{r}_2) \frac{e^2}{|-\mathbf{r}_1 + \mathbf{r}_2|} \phi_{1s}(\mathbf{r}_1) \phi_{2s}(\mathbf{r}_2)] \\ &= 0 \end{aligned}$$

and

$$\begin{aligned}
J_B &= \langle \phi_{1s,2p} | \hat{H}_{in} | \phi_{2s,1s} \rangle \\
&= \frac{1}{2} \iint d\mathbf{r}_1 d\mathbf{r}_2 [\phi_{1s}^*(\mathbf{r}_1) \phi_{2p}^*(\mathbf{r}_2) \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_{2s}(\mathbf{r}_1) \phi_{1s}(\mathbf{r}_2) \\
&\quad + \phi_{1s}^*(-\mathbf{r}_1) \phi_{2p}^*(-\mathbf{r}_2) \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_{2s}(-\mathbf{r}_1) \phi_{1s}(-\mathbf{r}_2)] \\
&= \frac{1}{2} \iint d\mathbf{r}_1 d\mathbf{r}_2 [\phi_{1s}^*(\mathbf{r}_1) \phi_{2p}^*(\mathbf{r}_2) \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_{2s}(\mathbf{r}_1) \phi_{1s}(\mathbf{r}_2) \\
&\quad - \phi_{1s}^*(\mathbf{r}_1) \phi_{2p}^*(\mathbf{r}_2) \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_{2s}(\mathbf{r}_1) \phi_{1s}(\mathbf{r}_2)] \\
&= 0
\end{aligned}$$

since

$$\phi_{1s}(-\mathbf{r}_1) = \phi_{1s}(\mathbf{r}_1), \quad (\text{even function, } l=0)$$

$$\phi_{2s}(-\mathbf{r}_1) = \phi_{2s}(\mathbf{r}_1) \quad (\text{even function, } l=0)$$

$$\phi_{2p}(-\mathbf{r}_1) = -\phi_{2p}(\mathbf{r}_1), \quad (\text{odd function, } l=1)$$

$$\begin{aligned}
\langle \mathbf{r} | n, l, m \rangle &= R_{nl}(r) Y_{l,m}(\theta, \phi) \\
&= R_{nl}(r) \langle \mathbf{n} | l, m \rangle
\end{aligned}$$

We note that for the parity operator $\hat{\pi}$,

$$\hat{\pi} |l, m\rangle = (-1)^l |l, m\rangle$$

$$\hat{\pi} |\mathbf{n}\rangle = |-\mathbf{n}\rangle, \quad \text{or} \quad \langle \mathbf{n} | \hat{\pi}^\dagger = \langle \mathbf{n} | \hat{\pi} = \langle -\mathbf{n} |$$

For $\mathbf{r} \rightarrow -\mathbf{r}$, we have

$$\begin{aligned}
\langle -\mathbf{r} | n, l, m \rangle &= \langle \mathbf{r} | \hat{\pi} | n, l, m \rangle \\
&= (-1)^l R_{nl}(r) \langle \mathbf{n} | l, m \rangle \\
&= (-1)^l \langle \mathbf{r} | n, l, m \rangle
\end{aligned}$$

In other words, the wavefunction has an odd parity for $l=0, 2, 4, \dots$, and an even parity for $l=1, 3, 5, \dots$

$$\phi_{nlm}(\mathbf{r}) = \langle \mathbf{r} | n, l, m \rangle$$

$$\phi_{nlm}(-\mathbf{r}) = (-1)^l \phi_{nlm}(\mathbf{r})$$

((Peeble)) Quantum mechanics

Since in atomic hydrogen the 2s and 2p energy levels are degenerate (apart from small relativistic corrections), it is not surprising that the states approximated by the 1s2s configuration have energies fairly close to the 1s2p configuration. The latter has the higher energy (less tight binding energy), because the angular momentum contribution to the effective potential suppresses the 2p wavefunction near the nucleus ($\phi_{2p} \propto r$ at small r , ϕ_{2s} is nonzero at $r = 0$). In a classical picture, the 2s orbit with no angular momentum plunges toward the nucleus, while the orbits with nonzero angular momentum avoid the nucleus. Either way, we see that the 1s electron is more effective at screening a 2p electron from the attractive charge of the nucleus than it is at screening a 2s electron, because the 2p electron is less likely to be found near the nucleus. Thus, the 1s2p configuration is less tightly bound.

29. Energy level diagram for the (1s)(3s) electron configuration

(1s)(3s) electron configuration (experimental result)

1S_0	-1.66707 eV	(spin singlet)
3S_1	-1.86892 eV	(spin triplet)

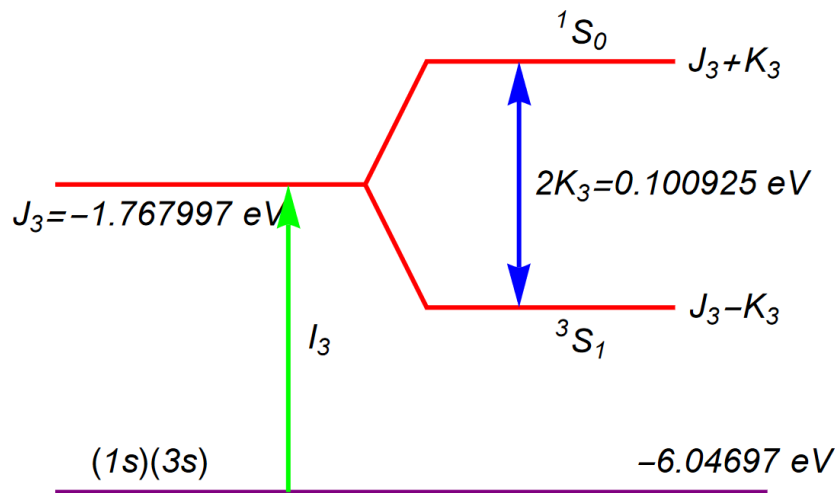


Fig.18 Energy level diagram for the (1s)(3s) electron configuration. $K_3 = K(1s,3s)$. $J_3 = J(1s,3s)$. (definition).

$$-6.04697 \text{ eV} + I_3(\text{exp}) = -1.767997 \text{ eV}$$

$$I_3(\text{exp}) = 4.27897 \text{ eV},$$

$$K_3(\text{exp}) = 0.0504625 \text{ eV}$$

30. Energy level diagram for the (1s)(3p) electron configuration

Energy level diagram for the (1s)(3p) electron configuration.

$$^1P_1 \quad -1.50037 \text{ eV} \quad (S=0)$$

$$^3P_0 \quad -1.58028 \text{ eV} \quad (S=1)$$

$$^3P_1 \quad -1.58031 \text{ eV}$$

$$^3P_2 \quad -1.58032 \text{ eV}$$

$$J_4(\text{cal}) = 0.519293 \text{ eV}.$$

$$K_4(\text{cal}) = 0.246636 \text{ eV}.$$

$$-6.04697 \text{ eV} + J_4(\text{exp}) = -1.540325 \text{ eV}$$

$$J_4(\text{exp}) = 4.506645 \text{ eV},$$

$$K_4(\text{exp}) = 0.03997 \text{ eV}$$

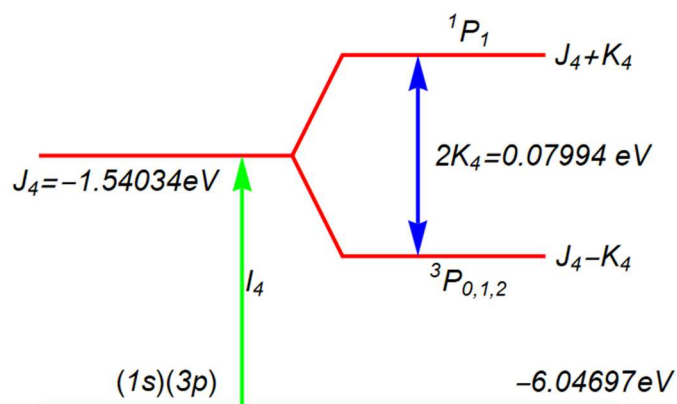


Fig.19 Energy level diagram for the (1s)(3p) electron configuration. $K_4 = K(1s,3p)$. $J_4 = J(1s,3p)$. (definition).

31. Experimental results of exchange integral K from NIST Data comparison with those predicted from the calculations.

Experimental results from NIST Data

1s2s

1S_0	-3.97161 eV	($S=0$),
3S_1	-4.76777 eV	($S=1$)

leading to

$$K(1s, 2s) \approx 0.3981 \text{ eV}$$

1s2p

1P_1	-3.36937 eV	($S=0$)
3P_0	-3.62317 eV	
3P_1	-3.62329 eV	($S=1$)
3P_2	-3.6233 eV	

leading to

$$K(1s, 2p) = 0.1269 \text{ eV}$$

which the difference between the energy (3P_1 , denoted by yellow, the intermediate value) and energy (1P_1 , denoted by yellow).

1s3s

1S_0	-1.66707 eV	($S=0$)
3S_1	-1.86892 eV	($S=1$)

leading to

$$K(1s, 3s) = 0.100925 \text{ eV}$$

1s3p

$$^1P_1 \quad -1.50037 \text{ eV} \quad (S=0)$$

$$^3P_0 \quad -1.58028 \text{ eV}$$

$$^3P_1 \quad -1.58031 \text{ eV} \quad (S=1)$$

$$^3P_2 \quad -1.58032 \text{ eV}$$

leading to

$$K(1s, 3p) \approx 0.03997 \text{ eV}$$

1s3d

$$^1D_2 \quad -1.51331 \text{ eV} \quad (S=0)$$

$$^3D_1 \quad -1.51373$$

$$^3D_2 \quad -1.51374 \quad (S=1)$$

$$^3D_3 \quad -1.51374 \text{ eV}$$

leading to

$$K(1s, 3d) = 0.000215 \text{ eV}$$

1s4s

$$^1S_0 \quad -0.913818 \text{ eV} \quad (S=0)$$

$$^3S_1 \quad -0.99343 \text{ eV} \quad (S=1)$$

leading to

$$K(1s, 4s) = 0.039806 \text{ eV}$$

1s4p

1P_1	-0.845319 eV	($S=0$)
3P_0	-0.879483 eV	
3P_1	-0.879496 eV	($S=1$)
3P_2	-0.879497 eV	

leading to

$$K(1s, 4p) = 0.017089 \text{ eV}$$

1s4d

1D_2	-0.850379 eV	($S=0$)
3D_1	-0.851296 eV	
3D_2	-0.851298 eV	($S=1$)
3D_3	-0.851298 eV	

leading to

$$K(1s, 4d) = 0.0004595 \text{ eV}$$

1s4f

1F_3	-0.850379 eV	($S=0$)
3F_2	-0.850380 eV	
3F_3	-0.850381 eV	($S=1$)
3F_4	-0.850381 eV	

$$K(1s, 4f) = 2.0 \times 10^{-6} \text{ eV}$$

1s5s

$$^1S_0 \quad -0.5761736871 \text{ eV} \quad (S = 0)$$

$$^3S_1 \quad -0.6154172587 \text{ eV} \quad (S = 1)$$

$$K(1s, 5s) = 0.019621786 \text{ eV}$$

1s5p

$$^1P_1 \quad -0.5415882703 \text{ eV} \quad (S = 0)$$

$$^3P_2 \quad -0.559163613 \text{ eV}$$

$$^3P_1 \quad -0.5591630523 \text{ eV} \quad (S = 1)$$

$$^3P_0 \quad -0.559156178 \text{ eV}$$

$$K(1s, 5p) = 8.787391 \times 10^{-3} \text{ eV}$$

1s5d

$$^1D \quad -0.54458526507 \text{ eV} \quad (S = 0)$$

$$^3D_3 \quad -0.544726435181 \text{ eV}$$

$$^3D_2 \quad -0.54472635569 \text{ eV} \quad (S = 1)$$

$$^3D_1 \quad -0.544725182979 \text{ eV}$$

leading to

$$K(1s, 5d) = 7.054531 \times 10^{-5} \text{ eV}$$

1s5f

$$^1F_3 \quad -0.54423302844 \text{ eV} \quad (S = 0)$$

$$^3F_3 \quad -0.54423459272 \text{ eV}$$

3F_4	-0.544234211052 eV	(S = 1)
3F_2	-0.544233664238 eV	

leading to

$$K(1s, 5f) = 5.91306 \times 10^{-7} \text{ eV}$$

1s5g

1G_4	-0.5441721457584 eV	(S = 0)
3G_4	-0.544173011709 eV	(S = 1)
3G_5	-0.544172668208 eV	
3G_3	-0.54417235591 eV	

leading to

$$K(1s, 5g) = 2.612248 \times 10^{-7}$$

Calculated values of the exchange integral obtained by Mathematica

$n = 2$

$$K(1s, 2s)_{cal} = 1.19446 \text{ eV}$$

$$K(1s, 2p)_{cal} = 0.929028 \text{ eV}$$

$n = 3$

$$K(1s, 3s)_{cal} = 0.313901 \text{ eV}$$

$$K(1s, 3p)_{cal} = 0.246636 \text{ eV}$$

$$K(1s, 3d)_{cal} = 0.0134529 \text{ eV}$$

$n = 4$

$$K(1s,4s)_{cal} = 0.127329 \text{ eV}$$

$$K(1s,4p)_{cal} = 0.100366 \text{ eV}$$

$$K(1s,4d)_{cal} = 0.0071761 \text{ eV}$$

$$K(1s,4f)_{cal} = 0.000112095 \text{ eV}$$

$n = 5$

$$K(1s,5s)_{cal} = 0.0640463 \text{ eV}$$

$$K(1s,5p)_{cal} = 0.0505558 \text{ eV}$$

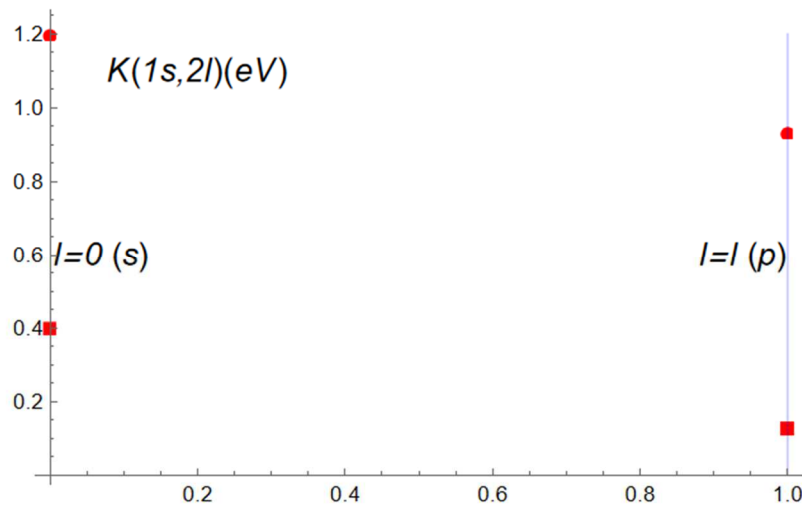
$$K(1s,5d)_{cal} = 3.99524 \times 10^{-3} \text{ eV}$$

$$K(1s,5f)_{cal} = 9.01839 \times 10^{-5} \text{ eV}$$

$$K(1s,5g)_{cal} = 6.01887 \times 10^{-7} \text{ eV}$$

32. Exchange integral $K(1s, nl)$

We make a plot of the exchange integral $K(1s, nl)$ as a function of l for experimental results (NIST Data) and calculated values, where $n = 2$, $n = 3$, $n = 4$, and $n = 5$.



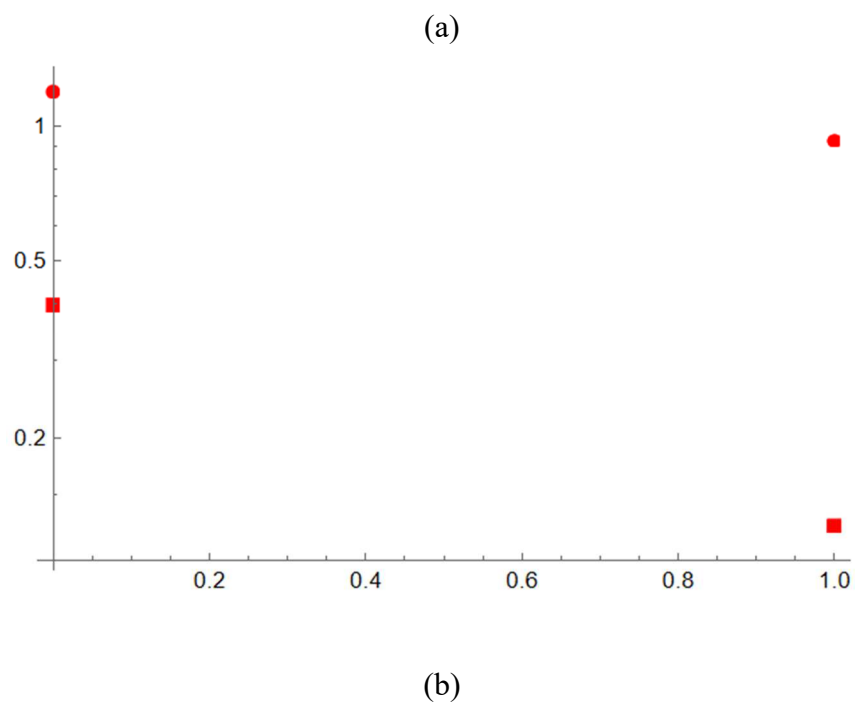
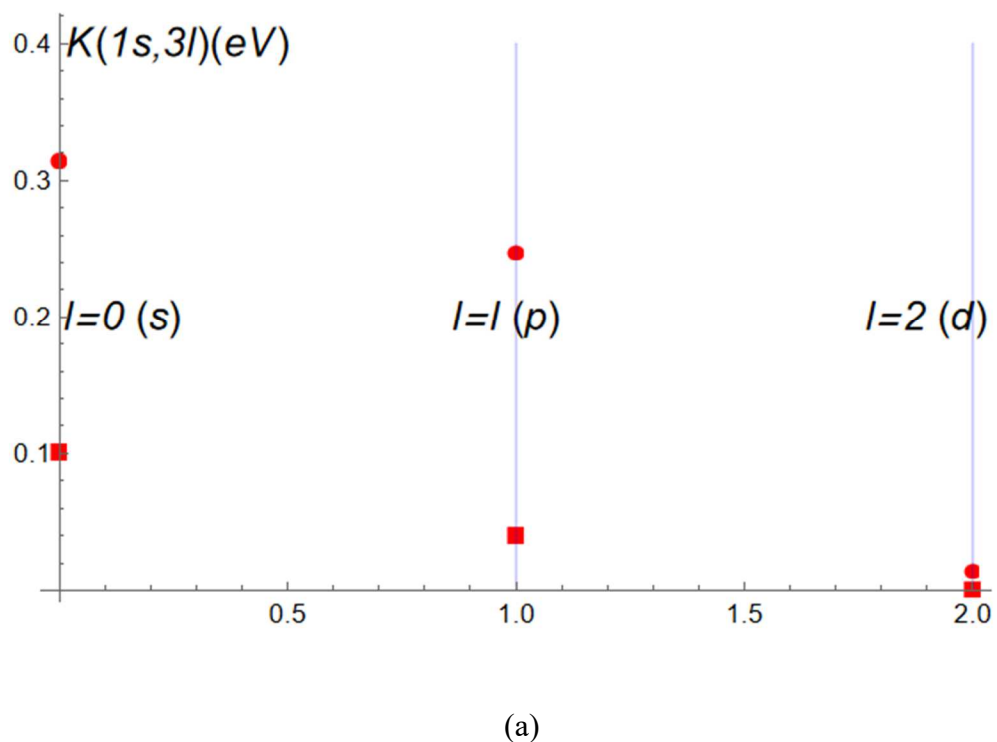
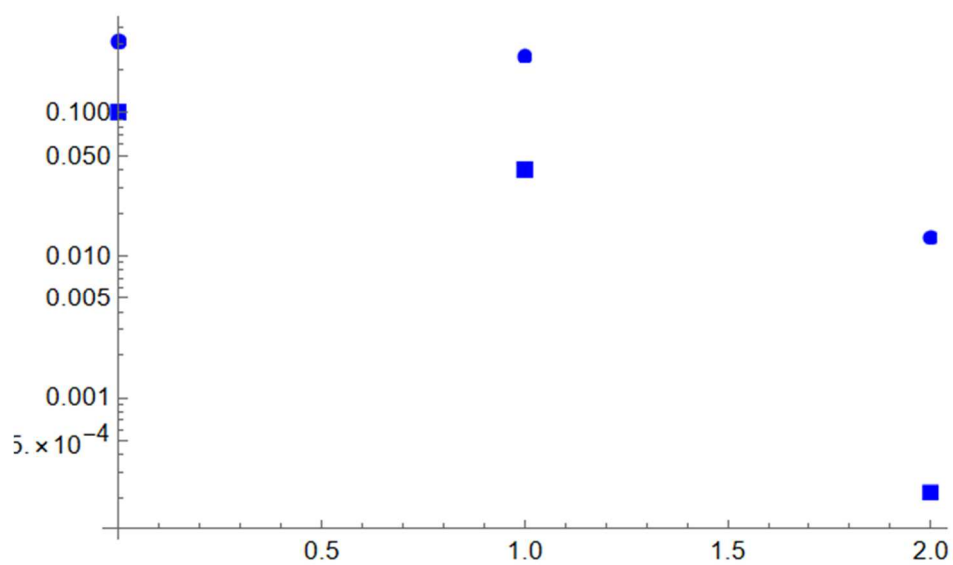


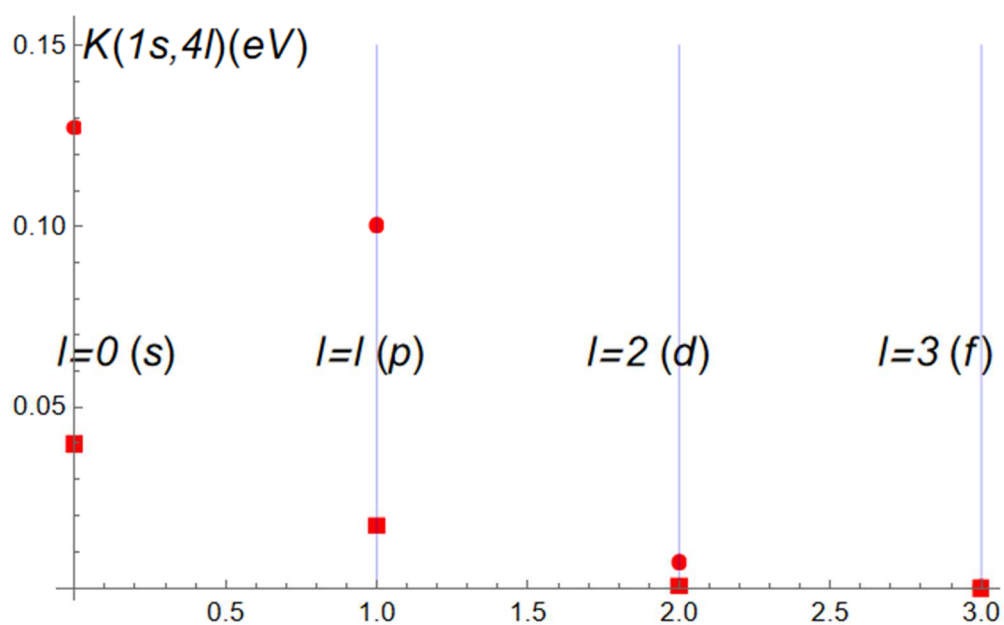
Fig.20 (a) linear plot. (b) linear log plot. The exchange integral $K(1s, 2l)$ vs l . $l=0$ (s), and $l=1$ (p). Calculated values of K (red solid circles) and the experimental values (red solid square).





(b)

Fig.21 (a) linear plot. (b) linear log plot. The exchange integral $K(1s, 3l)$ vs l . $l=0$ (s), 1 (p), and 2 (d). Calculated values (blue solid circle) and the experimental values (blue solid square).



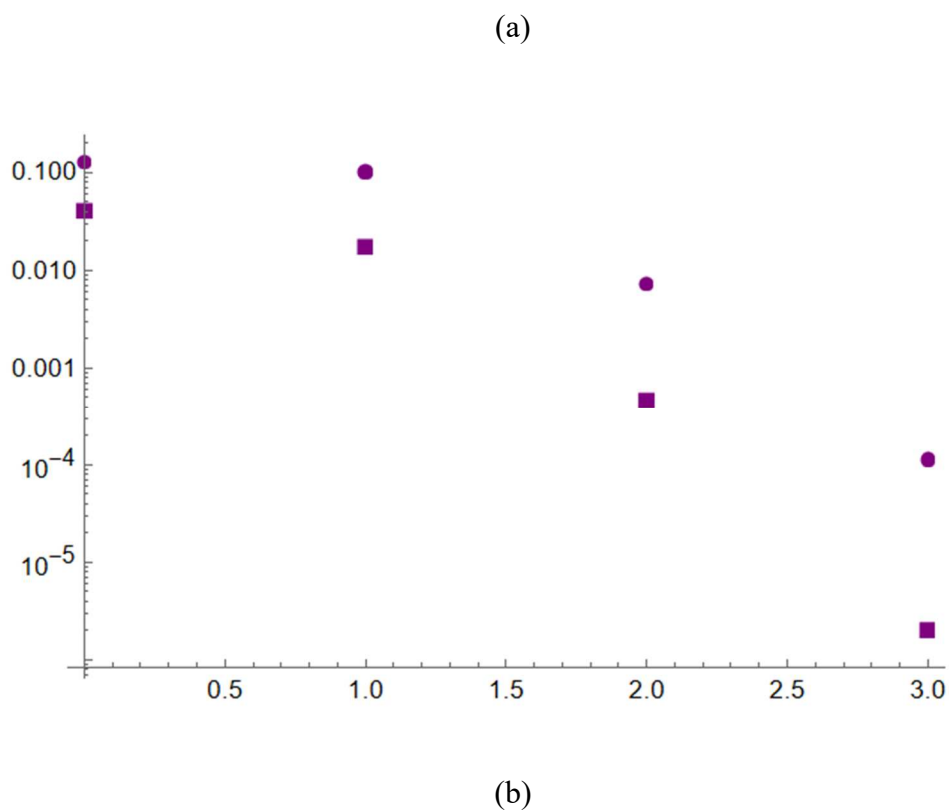
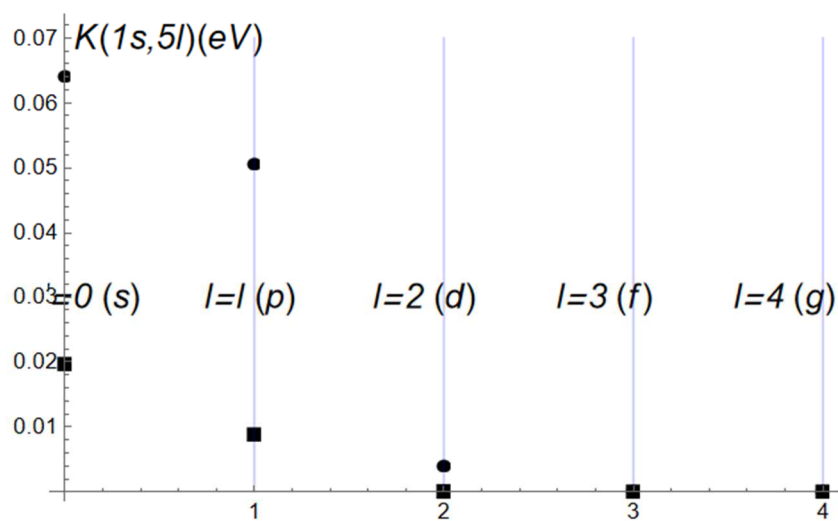


Fig.22 (a) linear plot. (b) linear log plot. The exchange integral $K(1s, 4l)$ vs l . $l=0$ (s), 1 (p), 2 (d), and 3 (f). Calculated values (purple solid circle) and the experimental values (purple solid square).



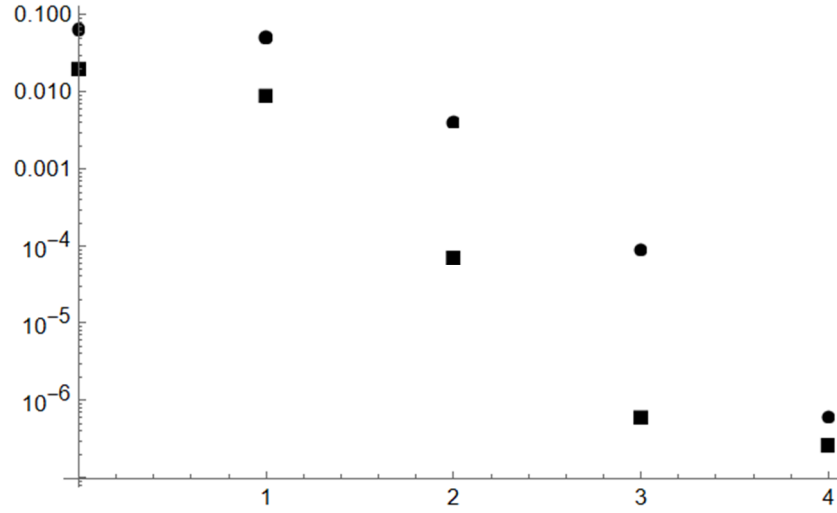


Fig.23 (a) linear plot. (b) linear log plot. The exchange integral $K(1s, 5l)$ vs l . $l=0$ (s), 1 (p), 2 (d), 3 (f), and 4 (g). Calculated values (black solid circle) and the experimental values (black solid square).

33. Scaling plot of $\log[n^3 K(1s, nl)]$ as a function of l

It is noted that the experimental values of the exchange integral $K(1s, nl)$ drastically decreases with increasing the orbital angular momentum l . The first-order calculation values of the exchange path integral are rather larger than the experimental values for the same n and l , although they also tend to decrease drastically with increasing l . According to the book of **H.A. Bethe and R. Jackiw**, (Intermediate Quantum mechanics) it is predicted that the exchange integral can be expressed by a scaling form as

$$K(1s, nl) = \frac{1}{n^3} G(Z, l), \quad (\text{scaling relation by Bethe and Jackiw})$$

where $G(Z, l)$ is a scaling function of Z and l , falls off quickly for large l . In other words, $n^3 K(1s, nl) = G(Z, l)$ should depend only on l , if Z is given. We make a scaling plot of $\log_{10}[n^3 K(1s, nl)]$ as a function of l for both experimental values and the first-order calculated values.

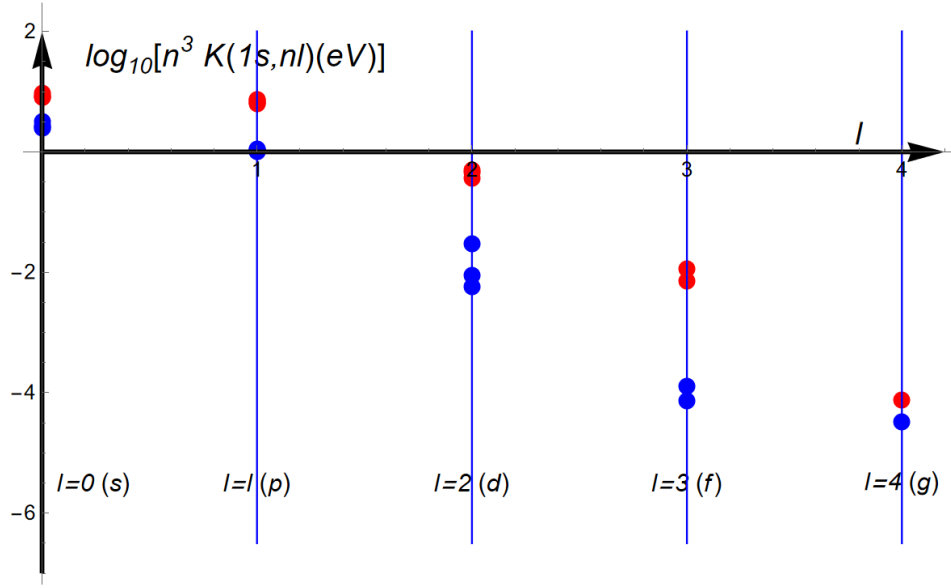


Fig.24 Scaling plot of $\log_{10}[n^3 K(1s, nl)(\text{eV})]$ as a function of l for experimental values (denoted by blue solid circles) and first-order calculated values (denoted by red solid circles). All data are plotted in this figure where $[n = 1 (l = 0), n = 2 (l = 0, 1), n = 3 (l = 0, 1, 2), n = 4 (l = 0, 1, 2, 3), \text{ and } n = 5 (l = 0, 1, 2, 3, 4)]$,

As shown in **Fig.24**, it seems that all the experimental data fall on a certain curve, suggesting the validity of scaling relation predicted by Bethe and Jackiw. We also note that the first-order calculated values nearly fall on a different scaling curve, except for the data at $l = 2$. In **Fig.25**, we make a plot of $-C + \log[n^3 K(1s, nl)(\text{eV})]$ as a function of l , where we choose $C = 1.2$ for the first-order calculated values and $C = 0$ for the experimental values.

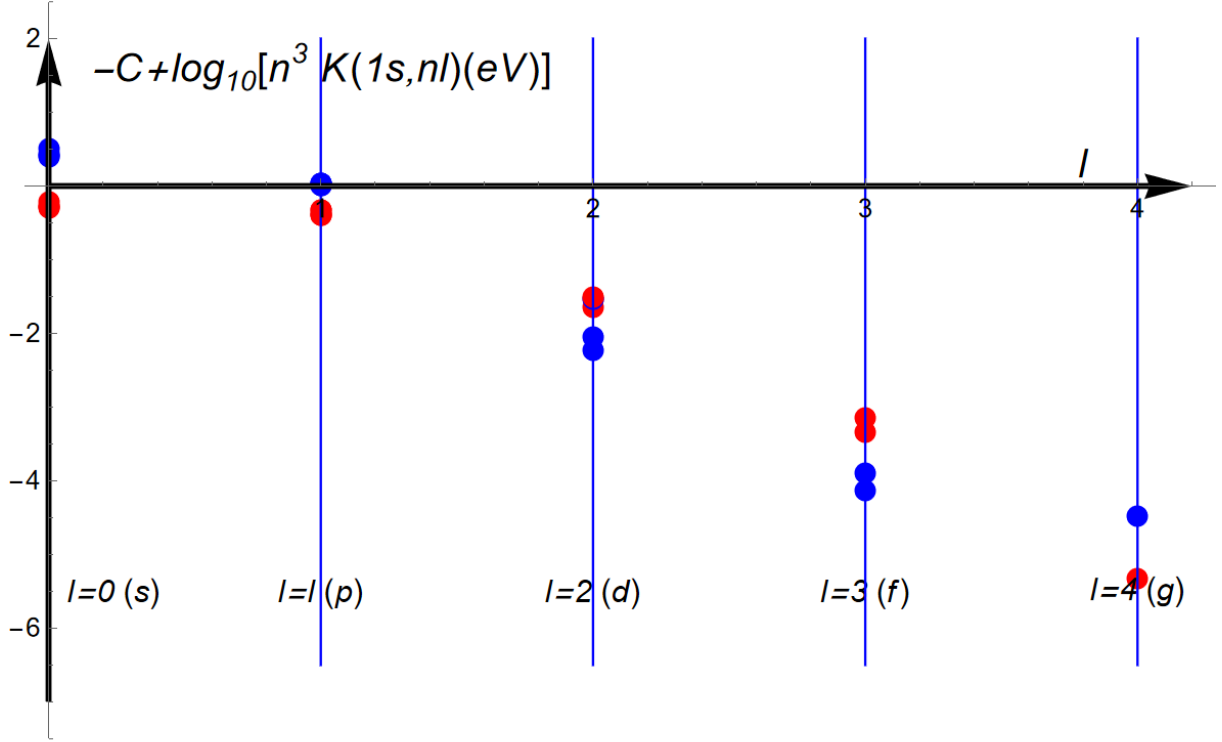


Fig.25 Scaling plot of $-C + \log[n^3 K(1s, nl)(\text{eV})]$ as a function of l for experimental values ($C = 0$, denoted by blue solid circles) and first-order calculated values ($C = 1.2$, denoted by red solid circles). All data are plotted in this figure where $[n = 1 (l = 0), n = 2 (l = 0, 1), n = 3 (l = 0, 1, 2), n = 4 (l = 0, 1, 2, 3), \text{ and } n = 5 (l = 0, 1, 2, 3, 4)]$.

We choose $C = 1.2$, so that the theoretical curve seems to overlap with the experimental data. If this assumption is correct, we may get the result as

$$-C + \log[n^3 K_{th}(1s, nl)] = \log[n^3 K_{exp}(1s, nl)],$$

or

$$\log\left[\frac{K_{exp}(1s, nl)}{K_{th}(1s, nl)}\right] = -C,$$

leading to the final result as

$$\frac{K_{exp}(1s, nl)}{K_{th}(1s, nl)} = 10^{-C} = 10^{-1.2} = 0.063.$$

What is the cause for such a ratio of K (≈ 0.063) between experimental and theoretical values? It may be partly due to the polarization effect. In reality, the correct helium wavefunctions cannot be exactly of this simple form (the product of two independent single-particle wavefunctions), since the presence of one electron at a particular position affects the wavefunction of the other. The Coulomb repulsion due to one electron polarizes the charge distribution of the other such as to increase their mutual separation.

Note that conventional second order perturbation theory would take account of the perturbation of the zero-order wavefunction, and hence of polarization. A rigorous second-order treatment is, however, much too tedious (**Bethe and Salpeter**).

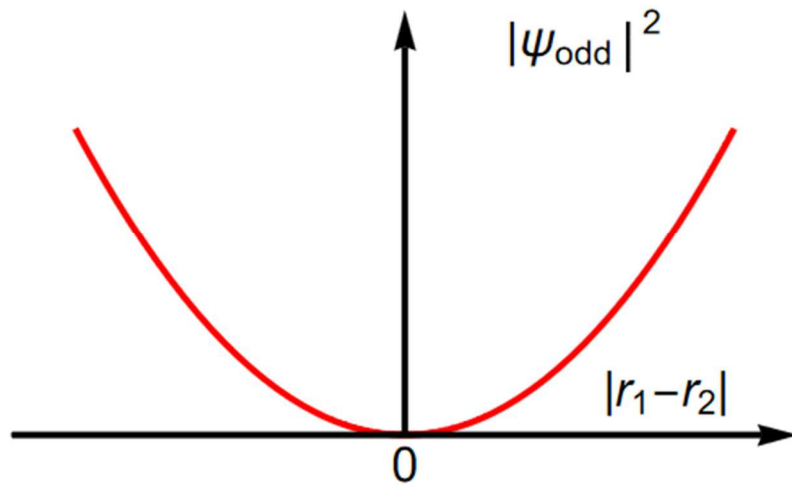
34. Probability density for the symmetric and antisymmetric orbital wavefunctions

((David Bohm))

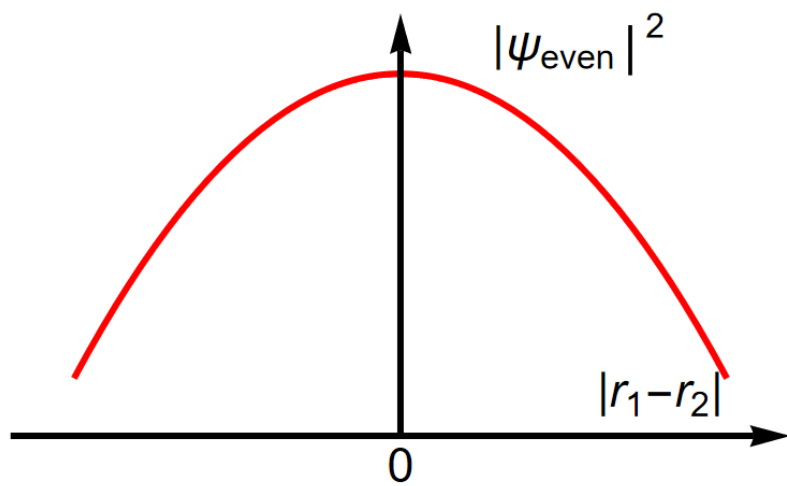
From the book of D. Bohm, Quantum Theory

The physical meaning of the exchange integral can be understood in terms of correlations between electronic positions that are inevitably present whenever the wave function is symmetric or antisymmetric. To demonstrate the existence of such correlations, we note that for the symmetric function, ψ_S , the wave function is a maximum when $r_1 = r_2$, while for the antisymmetric function, ψ_A , the wave function is zero for $r_1 = r_2$ and very small when r_1 is close to r_2 . Thus, a symmetric wave function implies an unusually large probability that the two electrons will be close together, and an antisymmetric function implies an unusually small probability that they will be close together.

How are we to interpret the correlations in electronic position which are, as we have seen, associated with the symmetry of the orbital wavefunction? The interpretation is that for an antisymmetric wave function, the two electrons tend to be on opposite sides of the nucleus with a higher probability than would be present in a random distribution, whereas for a symmetric wave function, there is a statistical tendency to favor their being on the same side of the nucleus. Since the Coulomb energy of interaction between electrons, $e^2 / |\mathbf{r}_{12}|$, depends on the interelectronic distance, we see that for a symmetric wave function, this energy must be larger than for an antisymmetric wave function. Because the energy difference between symmetric and antisymmetric wave functions is $2K_{12}$, we conclude that the exchange integral, K_{12} , is positive for a Coulomb potential. Moreover, we see also that the so-called "exchange energy" is merely a part of the usual Coulomb energy, resulting from the quantum-mechanical correlations of the relative positions of the two electrons.



(a)



(b)

Fig.26 Schematic diagram for the probability as a function of the relative distance $|r_1 - r_2|$ for the 1D case. (a) Antisymmetric case. Two electrons tend to be present on opposite sides with a higher probability. (b) Symmetric case. Two electrons tend to be present on the same sides with a higher probability.

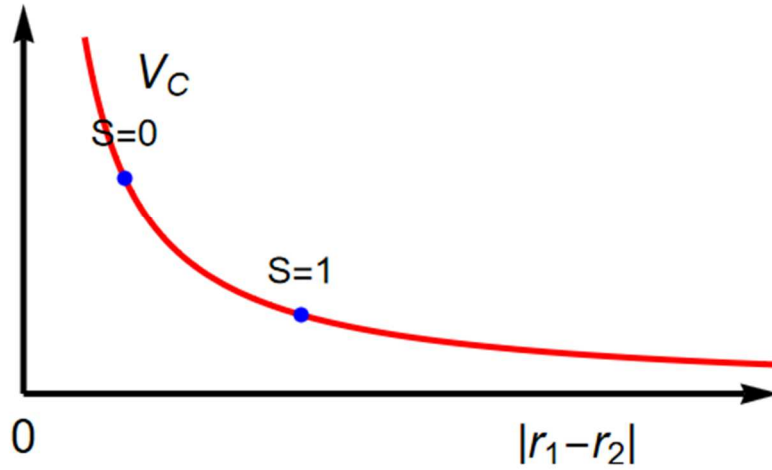


Fig.27 Schematic diagram on the repulsive Coulomb potential V_C between two electrons, as a function of relative distance $|r_1 - r_2|$ for the 1D case. The energy for the triplet spin state ($S = 1$) [antisymmetric orbital wavefunction] is lower than that for the singlet spin state ($S = 0$) [symmetric orbital wavefunction], as is predicted from the Hund' rule.

We now discuss the probability density of the symmetric wavefunction and antisymmetric wavefunction. We start with the antisymmetric orbital wavefunction.

$$\begin{aligned}\langle \mathbf{r}', \mathbf{r}'' | \hat{A} | \phi \rangle &= \frac{1}{\sqrt{2}} \langle \mathbf{r}', \mathbf{r}'' | \hat{1} - \hat{P}_{12} | \phi \rangle \\ &= \frac{1}{\sqrt{2}} [\langle \mathbf{r}', \mathbf{r}'' | \phi \rangle - \langle \mathbf{r}', \mathbf{r}'' | \hat{P}_{12} | \phi \rangle]\end{aligned}$$

$$\begin{aligned}\langle \mathbf{r}', \mathbf{r}'' | \hat{S} | \phi \rangle &= \frac{1}{\sqrt{2}} \langle \mathbf{r}', \mathbf{r}'' | \hat{1} + \hat{P}_{12} | \phi \rangle \\ &= \frac{1}{\sqrt{2}} [\langle \mathbf{r}', \mathbf{r}'' | \phi \rangle + \langle \mathbf{r}', \mathbf{r}'' | \hat{P}_{12} | \phi \rangle]\end{aligned}$$

Suppose that

$$|\phi\rangle = |\phi_s\rangle \otimes |\phi_{n,l}\rangle,$$

with

$$\phi_{1s}(\mathbf{r}') = Y_0^0(\mathbf{n}') R_{1,0}(r') = \frac{1}{\sqrt{4\pi}} R_{1,0}(r'), \quad \phi_{n,;}(\mathbf{r}') = Y_l^m(\mathbf{n}') R_{n,0}(r').$$

We also use the formula

$$\int d\Omega Y_{l'}^{m'*}(\theta, \phi) Y_l^m(\theta, \phi) = \int d\Omega Y_{l'}^{m'*}(\mathbf{n}) Y_l^m(\mathbf{n}) = \delta_{l,l'} \delta_{m,m'}.$$

Using

$$Y_{l'}^{m'*}(\theta, \phi) = Y_0^0(\theta, \phi) = \frac{1}{\sqrt{4\pi}}.$$

We get the formula

$$\int d\Omega Y_0^{0'*}(\theta, \phi) Y_l^m(\theta, \phi) = \delta_{l,0} \delta_{m,0},$$

or

$$\int d\Omega Y_l^m(\theta, \phi) = \sqrt{4\pi} \delta_{l,0} \delta_{m,0},$$

or

$$\int d\Omega Y_l^{m*}(\theta, \phi) = \sqrt{4\pi} \delta_{l,0} \delta_{m,0}.$$

$$\langle \mathbf{r}', \mathbf{r}'' | \hat{A} | \phi \rangle = \frac{1}{\sqrt{2}} [\phi_{1s}(\mathbf{r}') \phi_{n,l}(\mathbf{r}'') - \phi_{n,l}(\mathbf{r}') \phi_{1s}(\mathbf{r}'')]$$

$$\begin{aligned} \langle \mathbf{r}', \mathbf{r}'' | \hat{S} | \phi \rangle &= \frac{1}{\sqrt{2}} [\phi_{1s}(\mathbf{r}') \phi_{n,l}(\mathbf{r}'') + \phi_{n,l}(\mathbf{r}') \phi_{1s}(\mathbf{r}'')] \\ &= \frac{1}{2\sqrt{2\pi}} [Y_l^m(\mathbf{n}'') R_{10}(r') R_{n,l}(r'') + Y_l^m(\mathbf{n}') R_{n,l}(r') R_{10}(r'')] \end{aligned}$$

$$\begin{aligned}
\left| \langle \mathbf{r}', \mathbf{r}'' | \hat{S} | \phi \rangle \right|^2 &= \frac{1}{8\pi} [Y_l^{m*}(\mathbf{n}'') R_{10}(r') R_{n,l}(r'') + Y_l^{m*}(\mathbf{n}') R_{n,l}(r') R_{10}(r'')] \\
&\quad [Y_l^m(\mathbf{n}'') R_{10}(r') R_{n,l}(r'') + Y_l^m(\mathbf{n}') R_{n,l}(r') R_{10}(r'')] \\
&= \frac{1}{8\pi} [|Y_l^m(\mathbf{n}'')|^2 R_{10}^2(r') R_{n,l}^2(r'') + |Y_l^m(\mathbf{n}')|^2 R_{n,l}^2(r') R_{10}^2(r'') \\
&\quad + Y_l^{m*}(\mathbf{n}'') Y_l^m(\mathbf{n}') R_{10}(r') R_{10}(r'') R_{n,l}(r') R_{n,l}(r'') \\
&\quad + Y_l^{m*}(\mathbf{n}') Y_l^m(\mathbf{n}'') R_{10}(r') R_{10}(r'') R_{n,l}(r') R_{n,l}(r'')]
\end{aligned}$$

$$\begin{aligned}
r'^2 r''^2 \int d\Omega' \int d\Omega'' \left| \langle \mathbf{r}', \mathbf{r}'' | \hat{S} | \phi \rangle \right|^2 &= \frac{1}{8\pi} r'^2 r''^2 \int d\Omega' \int d\Omega'' [|Y_l^m(\mathbf{n}'')|^2 R_{10}^2(r') R_{n,l}^2(r'') \\
&\quad + |Y_l^m(\mathbf{n}')|^2 R_{n,l}^2(r') R_{10}^2(r'') \\
&\quad + Y_l^{m*}(\mathbf{n}'') Y_l^m(\mathbf{n}') R_{10}(r') R_{10}(r'') R_{n,l}(r') R_{n,l}(r'') \\
&\quad + Y_l^{m*}(\mathbf{n}') Y_l^m(\mathbf{n}'') R_{10}(r') R_{10}(r'') R_{n,l}(r') R_{n,l}(r'')] \\
&= \frac{1}{8\pi} r'^2 r''^2 \{ 4\pi R_{10}^2(r') R_{n,l}^2(r'') \\
&\quad + 4\pi R_{n,l}^2(r') R_{10}^2(r'') \\
&\quad + [\int d\Omega' Y_l^{m*}(\mathbf{n}'') \int d\Omega'' Y_l^m(\mathbf{n}') \\
&\quad + \int d\Omega' Y_l^{m*}(\mathbf{n}') \int d\Omega'' Y_l^m(\mathbf{n}'')] R_{10}(r') R_{10}(r'') R_{n,l}(r') R_{n,l}(r'') \} \\
&= \frac{1}{2} r'^2 r''^2 [R_{10}^2(r') R_{n,l}^2(r'') \\
&\quad + R_{n,l}^2(r') R_{10}^2(r'') \\
&\quad + 2\delta_{l,0} \delta_{m,0} R_{10}(r') R_{10}(r'') R_{n,l}(r') R_{n,l}(r'')]
\end{aligned}$$

We now consider the case of $l = 0$ and $m = 0$. The probability density is

$$\begin{aligned}
P_S &= r'^2 r''^2 \int d\Omega' \int d\Omega'' \left| \langle \mathbf{r}', \mathbf{r}'' | \hat{S} | \phi \rangle \right|^2 \\
&= \frac{1}{2} r'^2 r''^2 [R_{10}(r') R_{n,l}(r'') + R_{10}(r'') R_{n,l}(r')]^2
\end{aligned}$$

Similarly for the antisymmetric case, we have the spatial wavefunction for the symmetric case

$$\begin{aligned}
\left| \langle \mathbf{r}', \mathbf{r}'' | \hat{A} | \phi \rangle \right|^2 &= \frac{1}{8\pi} [|Y_l^m(\mathbf{n}'')|^2 R_{10}^2(r') R_{n,l}^2(r'') + |Y_l^m(\mathbf{n}')|^2 R_{n,l}^2(r') R_{10}^2(r'') \\
&\quad - Y_l^{m*}(\mathbf{n}'') Y_l^m(\mathbf{n}') R_{10}(r') R_{10}(r'') R_{n,l}(r') R_{n,l}(r'') \\
&\quad - Y_l^{m*}(\mathbf{n}') Y_l^m(\mathbf{n}'') R_{10}(r') R_{10}(r'') R_{n,l}(r') R_{n,l}(r'')]
\end{aligned}$$

The probability density is

$$\begin{aligned}
P_A &= r'^2 r''^2 \int d\Omega' \int d\Omega'' \left| \langle \mathbf{r}', \mathbf{r}'' | \hat{A} | \phi \rangle \right|^2 \\
&= \frac{1}{2} r'^2 r''^2 [R_{10}^2(r') R_{n,l}^2(r'') \\
&\quad + R_{n,l}^2(r') R_{10}^2(r'') \\
&\quad - 2\delta_{l,0} \delta_{m,0} R_{10}(r') R_{10}(r'') R_{n,l}(r') R_{n,l}(r'')]
\end{aligned}$$

We now consider the case of $l = 0$ and $m = 0$. The probability density is

$$P_A = r'^2 r''^2 \int d\Omega' \int d\Omega'' \left| \langle \mathbf{r}', \mathbf{r}'' | \hat{A} | \phi \rangle \right|^2 = \frac{1}{2} r'^2 r''^2 [R_{10}(r') R_{n,0}(r'') - R_{10}(r'') R_{n,0}(r')]^2$$

((Probability density))

In the one-particle case, the probability is defined as

$$\begin{aligned}
\int d\mathbf{r} |\psi|^2 &= \iint |\psi|^2 r^2 d\Omega \\
&= \int r^2 |R_{nl}(r)|^2 \int |Y_l^m(\mathbf{n})|^2 d\Omega
\end{aligned}$$

In the present case (two particles), we define the probability as

$$\int d\mathbf{r}' \int d\mathbf{r}'' |\psi_A|^2 = \int r'^2 dr' \int r''^2 dr'' \int d\Omega' \int d\Omega'' |\psi_A|^2,$$

for the anti-symmetric case. We note that

$$P_A = r'^2 r''^2 \int d\Omega' \int d\Omega'' |\psi_A|^2,$$

is the probability of finding the system in the region of $(r'$ to $r' + dr'$) and $(r''$ to $r'' + dr''$). We can also call this term as **the probability density**. Similarly, we det the probability density for the symmetric orbital wave function as

$$P_S = r'^2 r''^2 \int d\Omega' \int d\Omega'' |\psi_S|^2.$$

We make a ContourPlot of P_S and P_A in the (r', r'') plane with $r' > 0$ and $r'' > 0$, using Mathematica. The probability density for the (1s)(2s) electron configuration, can be evaluated as

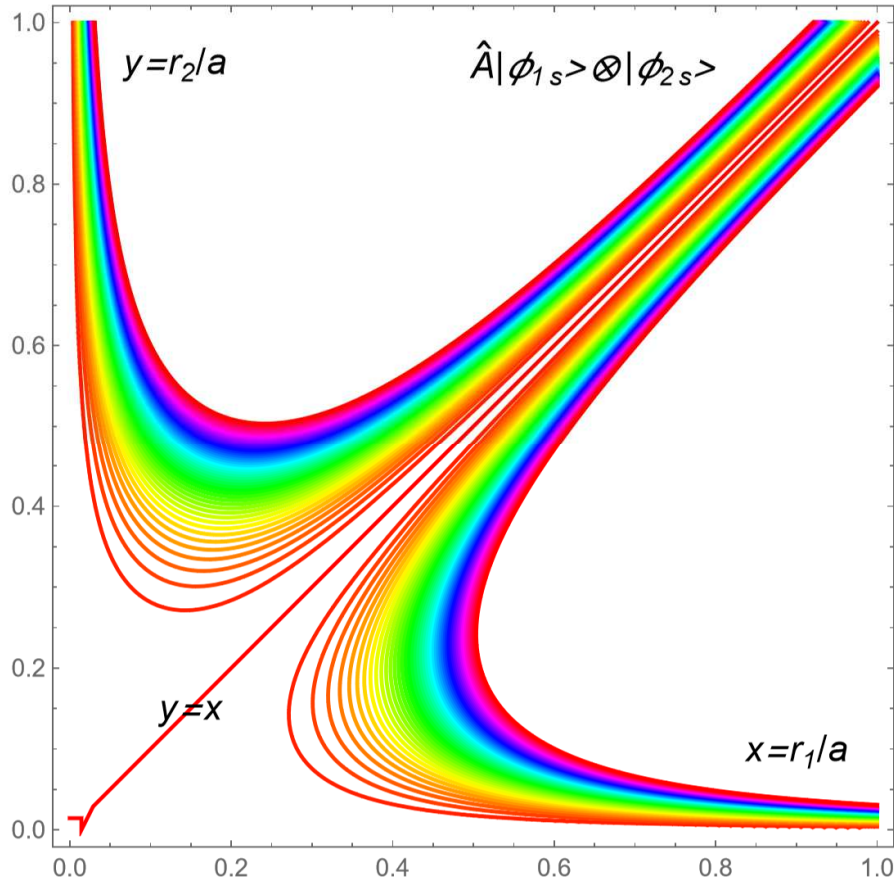
$$P_A =$$

$$\frac{e^{-\frac{2(r_1+r_2)Z}{a}} r_1^2 r_2^2 Z^6 \left(e^{\frac{r_1 Z}{2a}} (-2a + r_1 Z) + e^{\frac{r_2 Z}{2a}} (2a - r_2 Z) \right)^2}{2a^8}$$

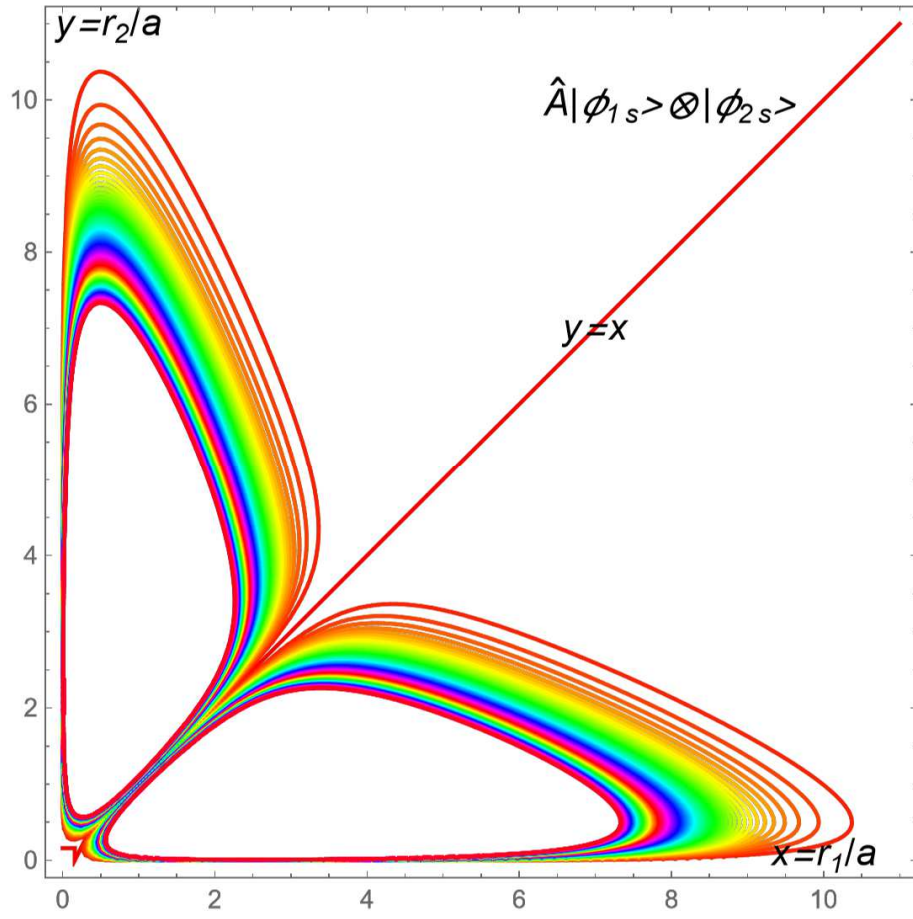
$$P_S =$$

$$\frac{e^{-\frac{2(r_1+r_2)Z}{a}} r_1^2 r_2^2 Z^6 \left(e^{\frac{r_1 Z}{2a}} (-2a + r_1 Z) + e^{\frac{r_2 Z}{2a}} (-2a + r_2 Z) \right)^2}{2a^8}$$

where we use $r' = r_1$ and $r'' = r_2$ for the convenience.



(b)



(b)

Fig.28

(a) and (b). ContourPlot of the probability density P_A for the $(1s)(2s)$ electron configuration in the (x, y) plane. $x = r_1/a$. $y = r_2/a$. $l=0$ for 2s electron configuration. Note that $P_A = 0$ for $y = x$.

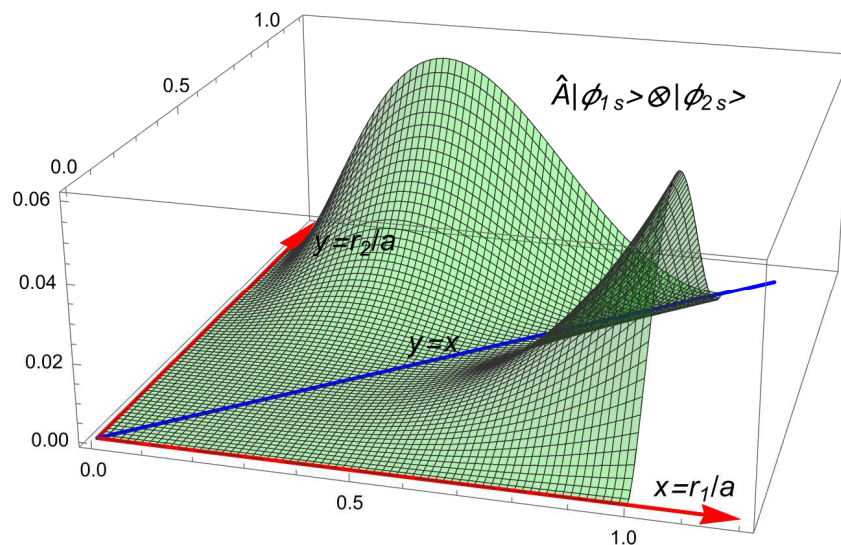
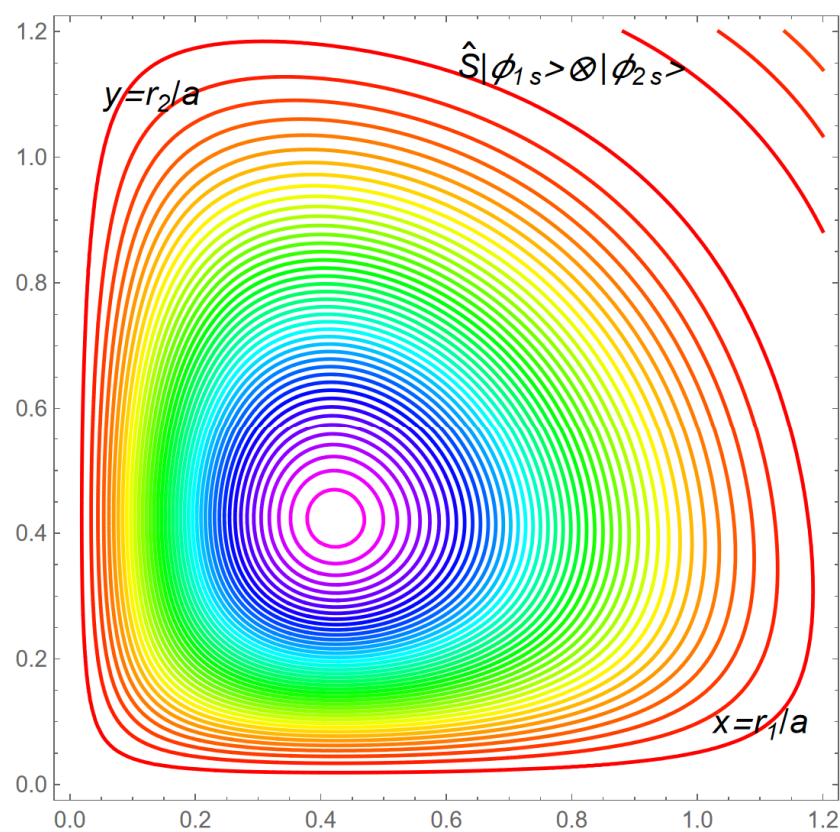
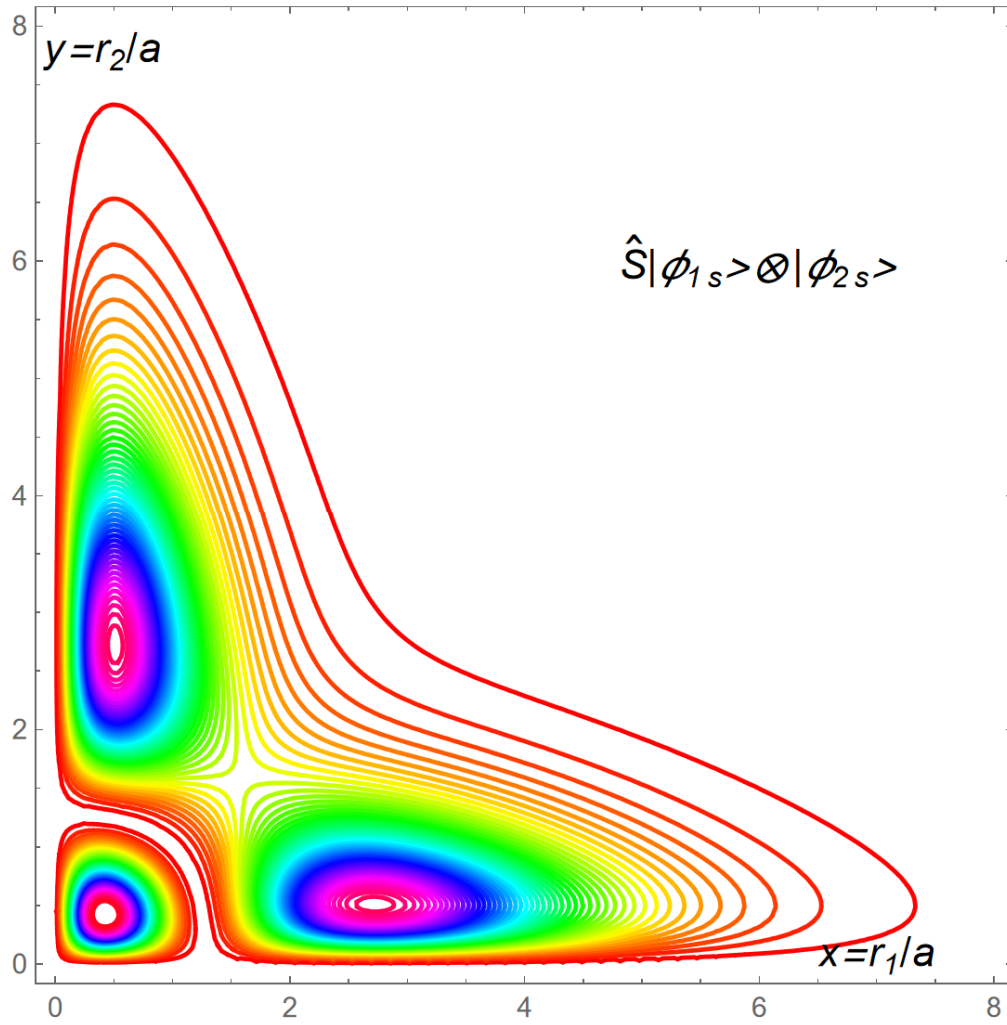


Fig.29 Plot3D of the probability density P_A for the (1s)(2s) electron configuration in the (x,y) plane. $x=r_1/a$. $y=r_2/a$. $l=0$ for 2s electron configuration. Note that $P_A=0$ for $y=x$.



(a)



(b)

Fig.30

(a) and (b). ContourPlot of the probability density P_S for the (1s)(2s) electron configuration in the (x, y) plane. $x = r_1/a$. $y = r_2/a$. $l=0$ for 2s electron configuration. Note that P_S has a maximum on the line $y = x = 0.42$.

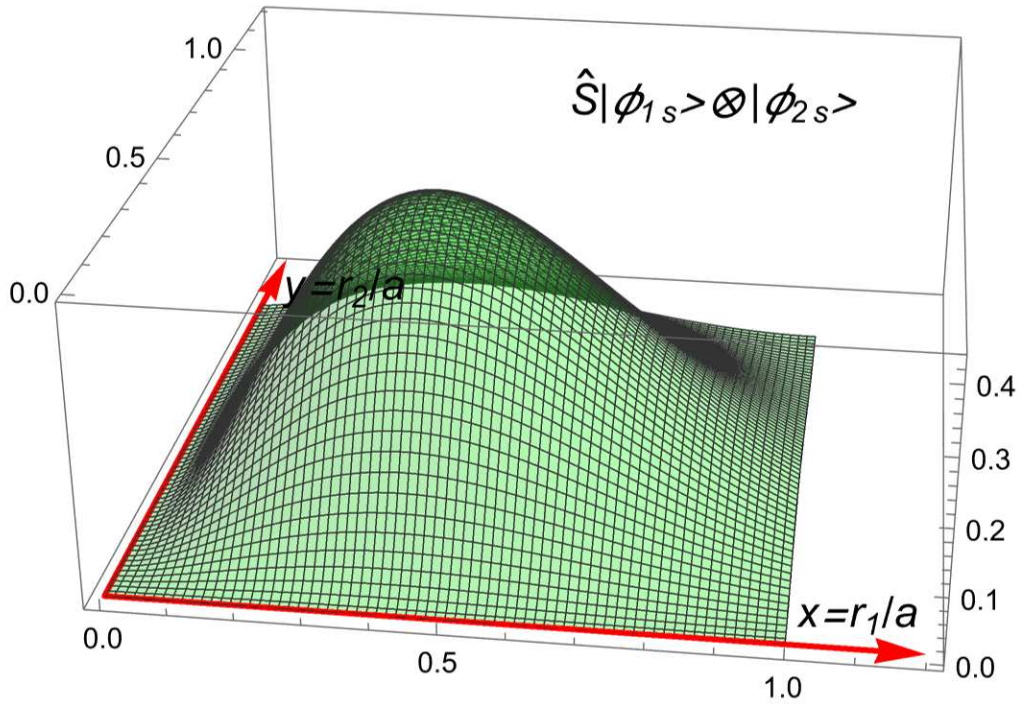


Fig.31 DensityPlot 3D of the probability density P_s for the (1s)(2s) electron configuration in the (x, y) plane. $x = r_1 / a$. $y = r_2 / a$. $l = 0$ for 2s electron configuration. Note that P_s has a maximum on the line $y = x = 0.42$.

35 Interaction between magnetic dipole moments

The ordered state of magnetic moment can be caused by the interaction between magnetic moment of atoms. The origin of such phenomenon is the exchange interaction due to the combination of electrostatic Coulomb force and the Pauli's exclusion principle. In classical physics, the possible origin is considered to be the interaction between magnetic (dipole) moment

$$\frac{1}{r_{12}^3} \boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2 - \frac{3}{r_{12}^5} (\boldsymbol{\mu}_1 \cdot \mathbf{r}_{12})(\boldsymbol{\mu}_2 \cdot \mathbf{r}_{12}),$$

where $\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_2$ are the two magnetic moment and $\mathbf{r}_{12}$ is a positional vector connecting between $\mathbf{r}_1$ and $\mathbf{r}_2$. The magnitude of this interaction can be estimated as 1 K (at most) when μ_1 and μ_2 are on the order of Bohr magneton and the distance r_{12} is on the order of $2\text{\AA}$. On the other hand, the Curie temperature (ferromagnet) or Neel temperature (antiferromagnet), which are the transition temperature from disordered state to the ordered state, is a measure for the energy difference (per atom). It is over 1000 K. So that, such a

large difference can be explained by classical physics. The origin of ferromagnetism is understood only based on the quantum mechanics. The answer for this was clearly given by Heisenberg based on the quantum mechanics, for the first time.

36. Heisenberg model in magnetism: Origin of exchange interaction

The exchange field gives an approximate representation of the quantum-mechanical exchange interaction

$$E_{ex} = -2\tilde{J} \sum_{i < j} \mathbf{S}_i \cdot \mathbf{S}_j ,$$

where the sum is over nearest neighbor pairs. $\tilde{J}$ is the exchange interaction and is related to the overlap of the charge distribution of spins i, j . This equation is called the Heisenberg model. The interaction related to the i -th spin is given by

$$E_{ex} = -2\tilde{J}z \langle \mathbf{S} \rangle \cdot \mathbf{S}_i = -(g\mu_B \mathbf{S}_i) \cdot \mathbf{B}(i) ,$$

where z is the number of nearest-neighbor spins and $\mathbf{B}(i)$ is the exchange field seen by the i -th spin,

$$\mathbf{B}(i) = -\frac{2\tilde{J}z}{g\mu_B} \langle \mathbf{S} \rangle .$$

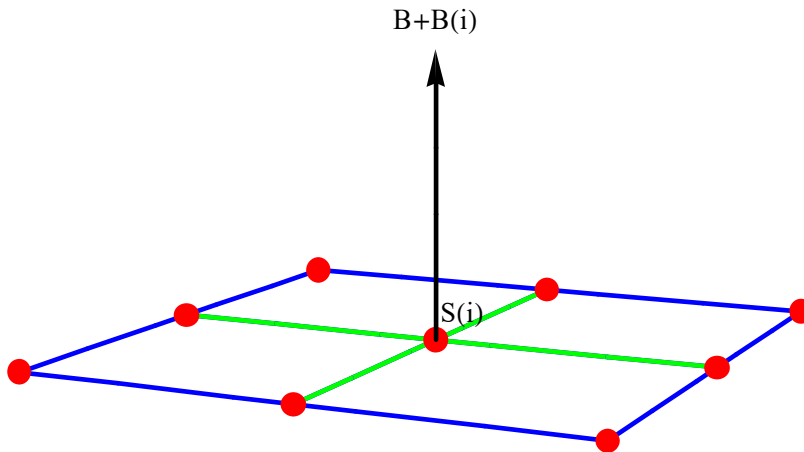


Fig.32 Mean field (molecular field) $\mathbf{B}(i)$ applied to the spin $\mathbf{S}_i$ (at the center in this Fig), arising from the exchange interaction with the surrounding spins (in this case, $z = 4$). $\mathbf{B}$ is the applied magnetic field.

The magnetization $\mathbf{M}$ is given by

$$\mathbf{M} = -g\mu_B N_A \langle \mathbf{S} \rangle .$$

Then the exchange field is

$$\mathbf{B}(i) = -\frac{2\tilde{J}z}{g\mu_B} \frac{\mathbf{M}}{(-g\mu_B N_A)} = \frac{2z\tilde{J}}{g^2\mu_B^2 N_A} \mathbf{M} = A\mathbf{M},$$

which means that

$$A = \frac{2z\tilde{J}}{g^2\mu_B^2 N_A}.$$

In the presence of a mean field, the molar magnetization can be described by

$$M = \frac{C_M}{T} [B + AM],$$

where C_M is the Curie constant and is given by

$$C_M = \frac{N_A g^2 \mu_B^2 S(S+1)}{3k_B}.$$

From this equation M can be derived as

$$M = \frac{C_M}{T - C_M A} B.$$

The corresponding susceptibility is

$$\chi_M = \frac{M}{B} = \frac{C_M}{T - C_M A} = \frac{C_M}{T - \Theta}.$$

The Curie-Weiss temperature Θ is given by

$$\Theta = C_M A = \frac{N_A g^2 \mu_B^2 S(S+1)}{3k_B} \frac{2z\tilde{J}}{g^2 \mu_B^2 N_A} = \frac{2z\tilde{J}}{3k_B} S(S+1).$$

Note that Θ is positive for ferromagnetic exchange interaction ($\tilde{J} > 0$) and Θ is negative for antiferromagnetic interaction ($\tilde{J} < 0$). From this equation $\tilde{J}$ is expressed in terms of Θ as

$$\tilde{J} = \frac{3k_B \Theta}{2zS(S+1)}.$$

From this expression, one can evaluate the value of exchange interaction between the nearest neighbor interactions.

The dipole-dipole interaction was considered to be the main origin of magnetism before the appearance of Heisenberg's theory. The magnitude of this interaction is on the order of $\mu_B^2 / \text{\AA}^3 = 0.0537 \text{ meV}$. On the other hand, the exchange integral is on the order of $k_B T_c = 86.17 \text{ meV}$ for the Curie temperature $T_c = 1000 \text{ K}$.

((Note)) $1 \text{ meV} = 11.60451812 \text{ K}$.

37. Impact on Japanese young students from lectures by Heisenberg and Dirac to Japan (1929)

Dr. Yoshio Nishina had returned to Japan in December 1928, after seven years of studying in Europe, six years of them at Bohr's institute in Copenhagen, where he had done important theoretical research with Oskar Klein (Klein-Nishina formula, constituting one of the first successful application of the Dirac equation). He had joined in 1918 at the Institute for Physical and Chemical Research (Riken) in Tokyo, where he began studying physics under Hantaro Nagaoka. He had financed his stay abroad from Riken between 1921 and 1928.

Heisenberg and Dirac's visit in September of 1929 would be the first major opportunity for Japanese physicists to meet highly successful European physicists who directly contributed to the birth of the new quantum mechanics, and Nishina made every effort to make their visit successful. He knew through his Copenhagen connections that Heisenberg and Dirac would give lectures at American Universities in the Spring of 1929, and asked them whether they could visit Japan to give some lectures before returning to Europe.

From September 2 to 7 of 1929, Heisenberg and Dirac each gave six lectures at Riken and Tokyo Imperial University (currently, University of Tokyo). They presented their lectures on recent developments in physics. Details of these lectures are provided in **Table III**. These lectures profoundly influenced many young Japanese physicists, including Tomonaga (Sin-itiro) and Yukawa (Hideki).

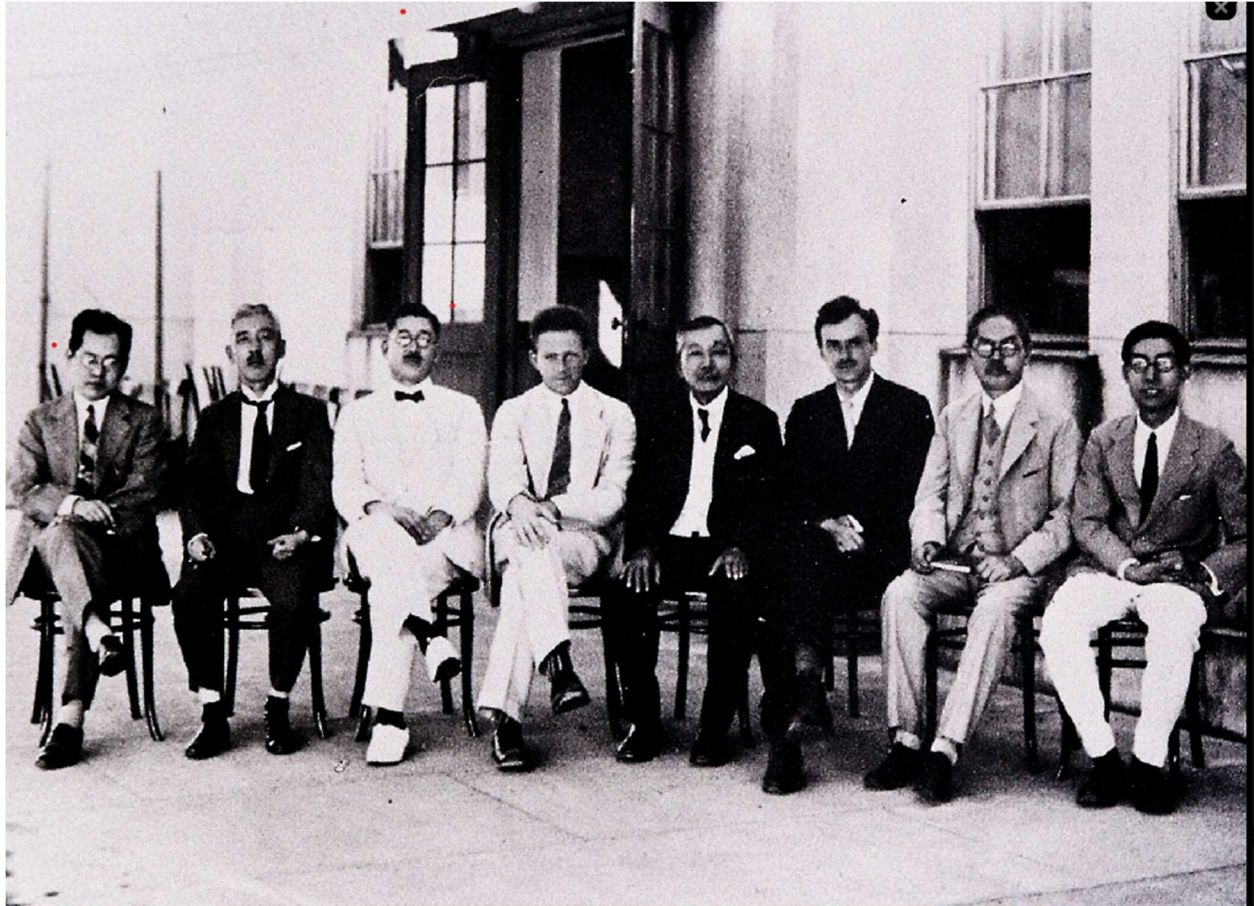


Fig.33 Werner Heisenberg (fourth from the left) and Paul Dirac (third from the right) who visited Japan in the Fall of 1929. Their lectures on new quantum mechanics stimulated the minds of young Japanese physicists. Yoshio Nishina (first from the left) carefully arranged their visit, translated their lectures for Japanese audiences, and later edited a book containing these translations. From left to right, Yoshio Nishina, Masao Katayama, Masatoshi Okouchi, Heisenberg, Hantaro Nagaoka, Dirac, Koutaro Honda, and Yoshikatsu Sugiura. All these Japanese scientists in this picture, had experience for study (research) abroad in Europe before 1929. **From the book of Dong-Won Kim, Yoshio Nishina: Father of Modern Physics in Japan (Taylor& Francis, 2007)**

During the six days of lectures, Nishina stood beside Heisenberg and Dirac, translating their lectures into Japanese and adding explanations when necessary.

Table III List of titles of lectures given by Heisenberg and Dirac at Tokyo Imperial University and Riken in September of 1929.

September 02, 1929 (Monday)

Riken

Heisenberg: The indeterminacy (uncertainty)-relations and the physical Principles of quantum theory.
 Dirac: The principles of superposition and the two-dimensional harmonic oscillator.

September, 03, 1929 (Tuesday) **Tokyo Imperial University** (currently, University of Tokyo)

Heisenberg: **Theory of ferromagnetism (helium atom).**
 Dirac: The basic of statistical mechanics (density operator)

September, 04, 1929 (Wednesday) **Tokyo Imperial University**

Heisenberg: **Theory of ferromagnetism (helium atom, continued)**
 Dirac: Quantum mechanics of many-electrons system

September, 05, 1929 (Thursday) **Tokyo Imperial University**

Heisenberg: Theory of conduction (Bloch theorem by F. Bloch)
 Dirac: Quantum mechanics of many-electrons system (continued)

September, 06, 1929 (Friday) **Tokyo Imperial University**

Heisenberg: Retarded potential in the quantum theory (with W. Pauli)
 Dirac: Relativity theory of electron

September, 07, 1929 (Saturday) **Tokyo Imperial University**

Heisenberg: Retarded potential in the quantum theory (with W. Pauli, continued)
 Dirac: Relativity theory of electron (continued)

Young physicists including Hideki Yukawa (Nobel laureate in Physics, 1949) and Sin-ichiro Tomonaga (Nobel laureate in physics, 1965) were strongly impressed by their lectures on the developments of quantum mechanics. When Werner Heisenberg and Paul Dirac visited Japan in September, 1929, Tomonaga was 23 years old and Yukawa was 22 years old, while Heisenberg was 27 years old and Dirac was 26 years old. Both Tomonaga and Yukawa (physics students at Kyoto University) attended the lectures of Heisenberg and Dirac in Tokyo, Japan (University of Tokyo and Riken). According to the book of Tomonaga, Quantum Mechanics and me, In Japanese), both Heisenberg and Dirac presented the following lectures at the University of Tokyo and Riken

at that time. Note that as collaborators of Heisenberg, W. Pauli was 29 years old, and F. Bloch was 23 years old.

((Hideki Yukawa))

From the book of H. Yukawa, *Tabibito (The Traveler)*, translated by L. Brown and R.

Yoshida from Japanese to English (World Scientific, 1982)

Although I (Hideki Yukawa) was only 22 years old, I was not lacking in years. At that time, most of the physicists who were contributing to the development of quantum mechanics were in their twenties, some only five or six years older than I. Four of the most outstanding scientists: Heisenberg, Dirac, Pauli, and Fermi were all born in the period 1900 - 1902, and they all had attained major achievements by about 23 or 24 years of age. In the Fall of 1929, Heisenberg and Dirac both visited Japan; attending their lectures was a great stimulus to me,

((S. Schweber))

From the book of Schweber, *QED*

As undergraduate students of Kyoto University, Tomonaga (Sin-itiro) and Yukawa (Hideki) embarked on a project to learn quantum mechanics. They read the papers of Heisenberg, Dirac, Jordan, Schrödinger, and Pauli that had laid the foundations of quantum mechanics, and explained them to each other. Shortly after their graduation from Kyoto University, the two traveled to Tokyo to attend the lectures that Heisenberg and Dirac gave at Riken and the Tokyo Imperial University (University of Tokyo) during their visit to Japan in 1929. These lectures made a strong impression on Tomonaga and Yukawa.

((D. Cassidy))

From the book of D. Cassidy, *Beyond Uncertainty; Heisenberg, Quantum Physics, and the Bomb* (Bellevue Literary Press, 2009). p.184.

As a condition for accepting the appointment to Leipzig in 1927, Heisenberg had negotiated an eight-month leave of absence in order to accept a series of lecture invitations from abroad. With bookings at MIT and the University of Chicago, and then in Japan and India, Heisenberg boarded a ship at Bremerhaven in early March 1929 for his first trans-Atlantic trip. He eagerly anticipated the journey, which would ultimately take him around the world; and he looked forward to meeting fellow visitors Sommerfeld, Dirac, and Hund “over there among the wild Americans.” But less than a day out to sea, the ship was trapped for several days by an early spring fog and a solid sheet of ice. Adrift in the unending fog prison, Heisenberg began to entertain second thoughts. He wrote to Bohr of how much he would rather spend his holiday in his usual fashion, with his youth group at their Bavarian ski hut “instead of traveling all the way to America—but one has to try everything.”

The trip must have been exhausting for the 27-year-old. After delivering the MIT and Chicago lectures, Heisenberg traveled to Washington for a few days to lead a session on atomic structure and spectral lines at the American Physical Society meeting. From there he went west to climb in

the Rocky Mountains, writing excitedly of the unanticipated beauty of the mountain landscape, which reminded him of home; then through Colorado and Arizona to the Grand Canyon; on to Pasadena for a week of lectures at the California Institute of Technology and touring in the Sierras; then back to Chicago by June. From Chicago he wrote to Bohr that in this “unsettled life” he traveled 1,000 kilometers (620 miles) per week—and in those

In Chicago, Heisenberg stayed with German-American physicist Carl Eckart. When not lecturing and working, he sailed and swam in Lake Michigan, went on a fishing expedition to the northern Wisconsin lakes with Barton Hoag, a Chicago experimentalist, stopped in Madison, (Wisconsin), to see Dirac, and engaged in tennis and music with numerous other physicists. On July 20, he described for Pauli the rest of his exhausting schedule: he would meet Dirac in Yellowstone National Park in mid-August and leave for Hawaii and Japan, where they would stay and lecture until mid-September. While Dirac headed from Japan through Siberia to Moscow, Heisenberg would travel through China to India to lecture, tour, and visit the Himalayas, finally arriving back in Leipzig in time to begin the winter semester in November 1929. “Then I hope to be able to really do physics once again.”

Aside from mountaintops, the series of ten lectures that Heisenberg delivered to the University of Chicago in March and April 1929 were the high point of his tour. The lectures were the basis of his textbook, *The Physical Principles of the Quantum Theory*, which was probably the most influential and widely read early account of the Copenhagen doctrine and the inspirations behind it. In Eckart’s translation from the German, the text also marked the transition of the name of his famous principle in English usage from “indeterminacy” to “uncertainty.”

38. Conclusion

Using the quantum mechanics which was established in 1920’s, Heisenberg (one of the founders of quantum mechanics) tried to calculate the energy levels of helium atom using the Schrödinger equation. There are two electrons outside the nucleus (two protons and two neutrons). The problem is much complicated compared to the energy level of hydrogen atom where there are one electron outside the nucleus (one proton). There is a repulsive Coulomb interaction between two electrons. These two electrons are fermion with spin $1/2$. According to Pauli’s exclusion principle, the total wave functions of two electrons should be antisymmetric under the exchange of two particles. This wavefunction is the product of spin part and spatial part (orbital). The spin part is symmetric for the total spin $S = 1$ (ortho-helium), while it is anti-symmetric for spin $S = 0$ (para-helium). Correspondingly, the orbital wavefunction of two particles should be symmetric for $S = 0$, while it should be anti-symmetric for $S = 1$. The Hamiltonian does not include any terms related to the spin interactions. Heisenberg showed that the energy levels of the symmetric orbital wavefunction is different from that of the antisymmetric orbital wavefunction. Such a large difference between these energy levels originates from the electrostatic energy. Taking into account of the spin-dependence on the energy level, Heisenberg reached a striking conclusion that the origin of ferromagnet is from the Coulomb electrostatic interactions (spectral term). Finally,

the origin of the extremely large molecular field (the Weiss field) can be understood in terms of quantum mechanics.

Heisenberg interpreted the Weiss field as an exchange effect. An exchange force is essentially caused by a static Coulomb interaction, and its magnitude can be much larger than that of the magnetic interaction. This exchange force appears in the form of a spin-spin interaction because the orbital states of the electrons naturally impose a limitation on the spin states according to the Pauli's exclusion principle. If it is a good approximation to assume that the electron carrying magnetism in a crystal have orbitals localized on the atom, then it is reasonable to think that their exchange effect can be expressed as the following sum

$$\hat{H}_{exch} = -2 \sum_{i,j} J_{ij} \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j . \quad (1)$$

This is precisely what Heisenberg assumed in his theory of ferromagnetism. If we consider that the spin of each atom containing a number of electrons obeys Hund' rule, then S_i in Eq.(1) is the atomic spin in this sense. We note that Eq.(1) holds precisely as Dirac's vector model when the following conditions are satisfied (**Kubo and Nagamiya**)

- (a) The orbital wavefunctions are **mutually orthogonal** [each atomic orbital contains one electron is equal to that of orbitals].
- (b) The eigenstates are determined only with respect to the spin state,

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APPENDIX-A Properties of spherical harmonics

We note that

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \sum_{l=0}^{\infty} F_l(r_1, r_2) P_l(\cos \theta)$$

where

$$F_l(r_1, r_2) = \begin{cases} \frac{1}{r_1} \left(\frac{r_2}{r_1} \right)^l & r_1 > r_2 \\ \frac{1}{r_2} \left(\frac{r_1}{r_2} \right)^l & r_2 > r_1 \end{cases}$$

and

$$\cos \theta = \frac{\mathbf{r}_1 \cdot \mathbf{r}_2}{r_1 r_2}$$

$P_l(\cos \theta)$ is called the Legendre polynomial.

$$P_l(\cos \theta) = \sum_{m=-l}^l \frac{(l-m)!}{(l+m)!} P_l^{|m|}(\cos \theta_1) P_l^{|m|}(\cos \theta_2) \exp[im(\phi_1 - \phi_2)]$$

and

$$\begin{aligned} P_l(\cos \theta) &= \frac{4\pi}{2l+1} \sum_{m=-l}^l Y_l^m(\theta_1, \phi_1) Y_l^{m*}(\theta_2, \phi_2) \\ &= \frac{4\pi}{2l+1} \sum_{m=-l}^l \langle \mathbf{n}_1 | l, m \rangle \langle \mathbf{n}_2 | l, m \rangle^* \end{aligned}$$

We also note that

$$Y_l^{m*}(\theta, \phi) = (-1)^m Y_l^{-m}(\theta, \phi)$$

$$Y_l^{-m}(\theta, \phi) = (-1)^m Y_l^{m*}(\theta, \phi)$$

from the relation

$$\hat{\Theta} |l, m\rangle = (-1)^m |l, m\rangle \quad (\text{time reversal operator})$$

or

$$\langle \mathbf{n} | \hat{\Theta} |l, m\rangle = (-1)^m \langle \mathbf{n} | l, m\rangle$$

or

$$\langle \mathbf{n} | \hat{\Theta} | l, m \rangle = (-1)^m \langle \mathbf{n} | l, -m \rangle$$

We use the formula

$$\begin{aligned} \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} &= 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{F_l(r_1, r_2)}{2l+1} Y_l^m(\theta_1, \phi_1) Y_l^{m*}(\theta_2, \phi_2) \\ &= 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^l G_l(r_1, r_2) Y_l^m(\theta_1, \phi_1) Y_l^{m*}(\theta_2, \phi_2) \end{aligned}$$

with

$$G_l(r_1, r_2) = \frac{F_l(r_1, r_2)}{2l+1}$$

$$\begin{aligned} \sum_{m=-l}^l Y_l^m(\theta_1, \phi_1) Y_l^{m*}(\theta_2, \phi_2) &= Y_l^0(\theta_1, \phi_1) Y_l^{0*}(\theta_2, \phi_2) \\ &\quad + \sum_{m=1}^l Y_l^m(\theta_1, \phi_1) Y_l^{m*}(\theta_2, \phi_2) + \sum_{m=-l}^{-1} Y_l^m(\theta_1, \phi_1) Y_l^{m*}(\theta_2, \phi_2) \\ &= Y_l^0(\theta_1, \phi_1) Y_l^{0*}(\theta_2, \phi_2) \\ &\quad + \sum_{m=1}^l Y_l^m(\theta_1, \phi_1) Y_l^{m*}(\theta_2, \phi_2) + \sum_{m=1}^l Y_l^{-m}(\theta_1, \phi_1) Y_l^{-m*}(\theta_2, \phi_2) \\ &= Y_l^0(\theta_1, \phi_1) Y_l^{0*}(\theta_2, \phi_2) \\ &\quad + \sum_{m=1}^l Y_l^m(\theta_1, \phi_1) Y_l^{m*}(\theta_2, \phi_2) + \sum_{m=1}^l Y_l^{m*}(\theta_1, \phi_1) Y_l^m(\theta_2, \phi_2) \\ &= Y_l^0(\theta_1, \phi_1) Y_l^{0*}(\theta_2, \phi_2) + 2 \sum_{m=1}^l \text{Re}[Y_l^m(\theta_1, \phi_1) Y_l^{m*}(\theta_2, \phi_2)] \end{aligned}$$

since

$$\begin{aligned} \sum_{m=1}^l Y_l^{-m}(\theta_1, \phi_1) Y_l^{-m*}(\theta_2, \phi_2) &= \sum_{m=1}^l (-1)^{2m} Y_l^{m*}(\theta_1, \phi_1) Y_l^m(\theta_2, \phi_2) \\ &= \sum_{m=1}^l Y_l^{m*}(\theta_1, \phi_1) Y_l^m(\theta_2, \phi_2) \end{aligned}$$

The associate Legendre polynomial

$$Y_l^m(\theta, \phi) = (-1)^m \sqrt{\frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!}} P_l^m(\cos \theta) e^{im\phi}$$

$$Y_l^{m=0}(\theta, \phi) = \sqrt{\frac{2l+1}{4\pi}} P_l(\cos \theta)$$

$$\begin{aligned} P_l(\cos \theta) &= \frac{4\pi}{2l+1} \{Y_l^0(\theta_1, \phi_1) Y_l^{0*}(\theta_2, \phi_2) + 2 \sum_{m=1}^l \operatorname{Re}[Y_l^m(\theta_1, \phi_1) Y_l^{m*}(\theta_2, \phi_2)]\} \\ &= P_l(\cos \theta_1) P_l(\cos \theta_2) + \frac{8\pi}{2l+1} \sum_{m=1}^l \operatorname{Re}[Y_l^m(\theta_1, \phi_1) Y_l^{m*}(\theta_2, \phi_2)] \\ &= P_l(\cos \theta_1) P_l(\cos \theta_2) + 2 \sum_{m=1}^l \frac{(l-m)!}{(l+m)!} P_l^m(\cos \theta_1) P_l^m(\cos \theta_2) \operatorname{Re}[e^{im(\phi_1 - \phi_2)}] \\ &= P_l(\cos \theta_1) P_l(\cos \theta_2) + 2 \sum_{m=1}^l \frac{(l-m)!}{(l+m)!} P_l^m(\cos \theta_1) P_l^m(\cos \theta_2) \cos[m(\phi_1 - \phi_2)] \end{aligned}$$

$$\begin{aligned} P_l(\cos \theta) &= \frac{4\pi}{2l+1} \sum_{m=-l}^l Y_l^m(\theta, \phi) Y_l^{m*}(\theta, \phi) \\ &= \frac{4\pi}{2l+1} \sum_{m=-l}^l \langle \mathbf{n}_1 | l, m \rangle \langle \mathbf{n}_2 | l, m \rangle^* \end{aligned}$$

$$\int d\Omega Y_l^{m'*}(\theta, \phi) Y_l^m(\theta, \phi) = \delta_{l,l'} \delta_{m,m'}$$

When $Y_l^{m'*}(\theta, \phi) = Y_0^0(\theta, \phi) = \frac{1}{\sqrt{4\pi}}$

$$\int d\Omega Y_0^{0'*}(\theta, \phi) Y_l^m(\theta, \phi) = \delta_{l,0} \delta_{m,0}$$

$$Y_0^0(\theta, \phi) = \frac{1}{\sqrt{4\pi}}$$

$$\int d\Omega Y_l^m(\theta, \phi) = \sqrt{4\pi} \delta_{l,0} \delta_{m,0}$$

and

$$\int d\Omega Y_l^{m*}(\theta, \phi) = \sqrt{4\pi} \delta_{l,0} \delta_{m,0}$$

$$\begin{aligned} \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} &= \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{4\pi F_l(r_1, r_2)}{2l+1} Y_l^m(\theta_1, \phi_1) Y_l^{m*}(\theta_2, \phi_2) \\ &= \sum_{l=0}^{\infty} \sum_{m=-l}^l G_l(r_1, r_2) Y_l^m(\theta_1, \phi_1) Y_l^{m*}(\theta_2, \phi_2) \end{aligned}$$

where

$$\frac{4\pi F_l(r_1, r_2)}{2l+1} = G_l(r_1, r_2)$$

APPENDIX-II	Spherical Harmonics	$Y_l^m(\theta, \phi)$
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$$Y_l^{-m}(\theta, \phi) = (-1)^m Y_l^{m*}(\theta, \phi) \quad \text{with } m > 0.$$

$l = 0, m = 0$

L	M	Y [L, m, θ, ϕ]
0	0	$\frac{1}{2\sqrt{\pi}}$

$l = 1, m = 0, 1$

L	M	Y [L, m, θ, ϕ]
1	0	$\frac{1}{2} \sqrt{\frac{3}{\pi}} \text{Cos} [\theta]$
1	1	$-\frac{1}{2} e^{i\phi} \sqrt{\frac{3}{2\pi}} \text{Sin} [\theta]$

$l = 2, m = 2, 1, 0$

L	M	$Y[L, m, \theta, \phi]$
2	0	$\frac{1}{4} \sqrt{\frac{5}{\pi}} (-1 + 3 \cos[\theta]^2)$
2	1	$-\frac{1}{2} e^{i\phi} \sqrt{\frac{15}{2\pi}} \cos[\theta] \sin[\theta]$
2	2	$\frac{1}{4} e^{2i\phi} \sqrt{\frac{15}{2\pi}} \sin[\theta]^2$

$l = 3, m = 0, 1, 2, 3$

L	M	$Y[L, m, \theta, \phi]$
3	0	$\frac{1}{4} \sqrt{\frac{7}{\pi}} (-3 \cos[\theta] + 5 \cos[\theta]^3)$
3	1	$-\frac{1}{8} e^{i\phi} \sqrt{\frac{21}{\pi}} (-1 + 5 \cos[\theta]^2) \sin[\theta]$
3	2	$\frac{1}{4} e^{2i\phi} \sqrt{\frac{105}{2\pi}} \cos[\theta] \sin[\theta]^2$
3	3	$-\frac{1}{8} e^{3i\phi} \sqrt{\frac{35}{\pi}} \sin[\theta]^3$

$l = 4, m = 0, 1, 2, 3, 4$

L	M	$Y[L, m, \theta, \phi]$
4	0	$\frac{3 (3 - 30 \cos[\theta]^2 + 35 \cos[\theta]^4)}{16 \sqrt{\pi}}$
4	1	$-\frac{3}{8} e^{i\phi} \sqrt{\frac{5}{\pi}} \cos[\theta] (-3 + 7 \cos[\theta]^2) \sin[\theta]$
4	2	$\frac{3}{8} e^{2i\phi} \sqrt{\frac{5}{2\pi}} (-1 + 7 \cos[\theta]^2) \sin[\theta]^2$
4	3	$-\frac{3}{8} e^{3i\phi} \sqrt{\frac{35}{\pi}} \cos[\theta] \sin[\theta]^3$
4	4	$\frac{3}{16} e^{4i\phi} \sqrt{\frac{35}{2\pi}} \sin[\theta]^4$

$l = 5, m = 5, 4, 3, 2, 1, 0$

L	M	$Y[L, m, \theta, \phi]$
5	0	$\frac{1}{16} \sqrt{\frac{11}{\pi}} (15 \cos[\theta] - 70 \cos[\theta]^3 + 63 \cos[\theta]^5)$
5	1	$-\frac{1}{16} e^{i\phi} \sqrt{\frac{165}{2\pi}} (1 - 14 \cos[\theta]^2 + 21 \cos[\theta]^4) \sin[\theta]$
5	2	$\frac{1}{8} e^{2i\phi} \sqrt{\frac{1155}{2\pi}} \cos[\theta] (-1 + 3 \cos[\theta]^2) \sin[\theta]^2$
5	3	$-\frac{1}{32} e^{3i\phi} \sqrt{\frac{385}{\pi}} (-1 + 9 \cos[\theta]^2) \sin[\theta]^3$
5	4	$\frac{3}{16} e^{4i\phi} \sqrt{\frac{385}{2\pi}} \cos[\theta] \sin[\theta]^4$
5	5	$-\frac{3}{32} e^{5i\phi} \sqrt{\frac{77}{\pi}} \sin[\theta]^5$

APPENDIX-III	Radial wavefunction	$R_{n,l}(r)$
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$l = n-1, n-2, \dots, 0.$

$n = 1.$ $l = 0 (s)$

n	L	rwave [n, L, r]
1	0	$\frac{2 e^{-\frac{rZ}{a}} Z^{3/2}}{a^{3/2}}$

$n = 2.$ $l = 0 (s), 1(p)$

n	L	rwave [n, L, r]
2	0	$\frac{e^{-\frac{rZ}{2a}} Z^{3/2} \left(2 - \frac{rZ}{a}\right)}{2 \sqrt{2} a^{3/2}}$
2	1	$\frac{e^{-\frac{rZ}{2a}} r Z^{5/2}}{2 \sqrt{6} a^{5/2}}$

$n = 3.$ $l = 0 (s), 1(p), 2 (d)$

n	L	rwave [n, L, r]
3	0	$\frac{2 e^{-\frac{r Z}{3 a}} Z^{3/2} (27 a^2 - 18 a r Z + 2 r^2 Z^2)}{81 \sqrt{3} a^{7/2}}$
3	1	$\frac{\sqrt{\frac{2}{3}} e^{-\frac{r Z}{3 a}} r Z^{5/2} (4 - \frac{2 r Z}{3 a})}{27 a^{5/2}}$
3	2	$\frac{2 \sqrt{\frac{2}{15}} e^{-\frac{r Z}{3 a}} r^2 Z^{7/2}}{81 a^{7/2}}$

n = 4. l = 0 (s), 1(p), 2 (d), 3 (f)

n	L	rwave [n, L, r]
4	0	$\frac{e^{-\frac{r Z}{4 a}} Z^{3/2} (192 a^3 - 144 a^2 r Z + 24 a r^2 Z^2 - r^3 Z^3)}{768 a^{9/2}}$
4	1	$\frac{e^{-\frac{r Z}{4 a}} r Z^{5/2} (80 a^2 - 20 a r Z + r^2 Z^2)}{256 \sqrt{15} a^{9/2}}$
4	2	$\frac{e^{-\frac{r Z}{4 a}} r^2 Z^{7/2} (6 - \frac{r Z}{2 a})}{384 \sqrt{5} a^{7/2}}$
4	3	$\frac{e^{-\frac{r Z}{4 a}} r^3 Z^{9/2}}{768 \sqrt{35} a^{9/2}}$

n = 5. l = 0 (s), 1(p), 2 (d), 3 (f), 4 (g)

n	L	rwave [n, L, r]
5	0	$\frac{2 e^{-\frac{rZ}{5a}} Z^{3/2} (9375 a^4 - 7500 a^3 r Z + 1500 a^2 r^2 Z^2 - 100 a r^3 Z^3 + 2 r^4 Z^4)}{46875 \sqrt{5} a^{11/2}}$
5	1	$\frac{2 \sqrt{\frac{2}{15}} e^{-\frac{rZ}{5a}} r Z^{5/2} (3750 a^3 - 1125 a^2 r Z + 90 a r^2 Z^2 - 2 r^3 Z^3)}{46875 a^{11/2}}$
5	2	$\frac{2 \sqrt{\frac{2}{35}} e^{-\frac{rZ}{5a}} r^2 Z^{7/2} (525 a^2 - 70 a r Z + 2 r^2 Z^2)}{46875 a^{11/2}}$
5	3	$\frac{\sqrt{\frac{2}{35}} e^{-\frac{rZ}{5a}} r^3 Z^{9/2} (8 - \frac{2 r Z}{5 a})}{9375 a^{9/2}}$
5	4	$\frac{2 \sqrt{\frac{2}{35}} e^{-\frac{rZ}{5a}} r^4 Z^{11/2}}{140625 a^{11/2}}$

APPENDIX-IV Selection rule for the transition between states

We have the selection rule for the transition between electron energy levels

$$\Delta L = \pm 1, \quad \Delta S = 0$$

The latter means that only transitions (singlet $\rightarrow$ singlet, and triplet $\rightarrow$ triplet) occur. No transition is allowed between the singlet and triplet spin states. So that, it is believed that there exist two kinds of helium, orthohelium (triplet) and parahelium (singlet).

In order to get the section rule for $\Delta L = \pm 1$ and $\Delta S = 0$ we start with the transition matrix elements

$$\langle l', m' | \hat{\mathbf{r}} | l, m \rangle,$$

and

$$\langle S', m_{S'} | \hat{\mathbf{r}} | S, m_S \rangle$$

for the orbital angular momentum and spin angular momentum. Note that the perturbation Hamiltonian is due to an electric dipole moment (proportional to $\hat{\mathbf{r}}$). Clearly, the perturbation is independent of the spin operator. So that, we have the selection rule

$$\Delta S = S' - S = 0 \quad \text{for the spin states.}$$

How about the selection rule $\Delta l = l' - l$ for the orbital angular momentum? Using the properties of the parity operator, we have

$$\hat{\pi} |l, m\rangle = (-1)^l |l, m\rangle,$$

or

$$\langle l, m | \hat{\pi} = \langle l, m | (-1)^l = \langle l, m | \frac{(-1)^l}{(-1)^{2l}} = \langle l, m | (-1)^{-l},$$

or

$$\langle l, m | = (-1)^{-l} \langle l, m | \hat{\pi},$$

with

$$\hat{\pi}^2 = \hat{1}$$

and

$$\hat{\pi} \hat{\mathbf{r}} \hat{\pi} = -\hat{\mathbf{r}} \quad (\hat{\mathbf{r}}; \text{odd parity})$$

Thus, we have

$$\begin{aligned} \langle l', m' | \hat{\mathbf{r}} | l, m \rangle &= (-1)^{-l'} \langle l', m' | \hat{\pi} \hat{\mathbf{r}} \hat{\pi} | l, m \rangle \\ &= (-1)^l (-1)^{-l'} \langle l', m' | \hat{\pi} \hat{\mathbf{r}} \hat{\pi} | l, m \rangle \\ &= (-1)^{l-l'+1} \langle l', m' | \hat{\mathbf{r}} | l, m \rangle \end{aligned}$$

leading to the selection rule; .

$$\Delta l = l' - l = \pm 1$$

((Selection rule))

We start with

$$\begin{aligned}
\hat{\mathbf{r}} &= \hat{x} \mathbf{e}_x + \hat{y} \mathbf{e}_y + \hat{z} \mathbf{e}_z \\
&= (\mathbf{e}_x + i\mathbf{e}_y)\hat{A}_+ + (\mathbf{e}_x - i\mathbf{e}_y)\hat{A}_- + \mathbf{e}_z\hat{A}_z \\
&= (\hat{A}_+ + \hat{A}_-)\mathbf{e}_x + i(\hat{A}_+ - \hat{A}_-)\mathbf{e}_y + \mathbf{e}_z\hat{A}_z
\end{aligned}$$

leading to

$$\begin{aligned}
\hat{A}_+ + \hat{A}_- &= \hat{x} \\
\hat{A}_+ - \hat{A}_- &= -i\hat{y} \\
\hat{A}_z &= \hat{z}
\end{aligned}$$

or

$$\begin{aligned}
\hat{A}_z &= \hat{z} \\
\hat{A}_+ &= \frac{1}{2}(\hat{x} - i\hat{y}) \\
\hat{A}_- &= \frac{1}{2}(\hat{x} + i\hat{y})
\end{aligned}$$

Thus, we have

$$\begin{aligned}
\hat{\mathbf{r}} &= (\mathbf{e}_x + i\mathbf{e}_y)\frac{1}{2}(\hat{x} - i\hat{y}) + (\mathbf{e}_x - i\mathbf{e}_y)\frac{1}{2}(\hat{x} + i\hat{y}) + \mathbf{e}_z\hat{z} \\
&= \frac{(\mathbf{e}_x + i\mathbf{e}_y)}{\sqrt{2}}\frac{1}{\sqrt{2}}(\hat{x} - i\hat{y}) + \frac{(\mathbf{e}_x - i\mathbf{e}_y)}{\sqrt{2}}\frac{1}{\sqrt{2}}(\hat{x} + i\hat{y}) + \mathbf{e}_z\hat{z} \\
&= \left[-\frac{(\mathbf{e}_x + i\mathbf{e}_y)}{\sqrt{2}}\right]\left[-\frac{1}{\sqrt{2}}(\hat{x} - i\hat{y})\right] + \frac{(\mathbf{e}_x - i\mathbf{e}_y)}{\sqrt{2}}\frac{1}{\sqrt{2}}(\hat{x} + i\hat{y}) + \mathbf{e}_z\hat{z}
\end{aligned}$$

Spherical harmonics

$$x = r \sin \theta \cos \phi, \quad y = r \sin \theta \sin \phi, \quad z = r \cos \theta$$

$$x + iy = r \sin \theta e^{i\phi}, \quad x - iy = r \sin \theta e^{-i\phi}, \quad z = r \cos \theta$$

Spherical harmonics

$$rY_1^1 = -\sqrt{\frac{3}{8\pi}} r \sin \theta e^{i\phi} = -\sqrt{\frac{3}{8\pi}} (x + iy) = \langle \mathbf{n} | l=1, m=1 \rangle$$

$$rY_1^0 = \sqrt{\frac{3}{4\pi}} r \cos \theta = \sqrt{\frac{3}{4\pi}} z = \langle \mathbf{n} | l=1, m=0 \rangle$$

$$rY_1^{-1} = \sqrt{\frac{3}{8\pi}} r \sin \theta e^{-i\phi} = \sqrt{\frac{3}{8\pi}} (x - iy) = \langle \mathbf{n} | l=1, m=-1 \rangle$$

or

$$-(\frac{x+iy}{\sqrt{2}}) = \sqrt{\frac{4\pi}{3}} \langle \mathbf{n} | l=1, m=1 \rangle$$

$$\frac{x-iy}{\sqrt{2}} = \sqrt{\frac{4\pi}{3}} \langle \mathbf{n} | l=1, m=-1 \rangle$$

$$z = \sqrt{\frac{4\pi}{3}} \langle \mathbf{n} | l=1, m=0 \rangle$$

Spherical tensor

$$\hat{T}_{q=1}^{(k=1)} = \sqrt{\frac{3}{4\pi}} (-\frac{\hat{x} + i\hat{y}}{\sqrt{2}}) \quad \sqrt{\frac{4\pi}{3}} \hat{T}_{q=1}^{(k=1)} = -\frac{\hat{x} + i\hat{y}}{\sqrt{2}}$$

$$\hat{T}_{q=0}^{(k=1)} = \sqrt{\frac{3}{4\pi}} \hat{z} \quad \sqrt{\frac{4\pi}{3}} \hat{T}_{q=0}^{(k=1)} = \hat{z}$$

$$\hat{T}_{q=-1}^{(k=1)} = \sqrt{\frac{3}{4\pi}} (\frac{\hat{x} - i\hat{y}}{\sqrt{2}}) \quad \sqrt{\frac{4\pi}{3}} \hat{T}_{q=-1}^{(k=1)} = \frac{\hat{x} - i\hat{y}}{\sqrt{2}}$$

$$\hat{\mathbf{r}} = \sqrt{\frac{4\pi}{3}} \left[\frac{(\mathbf{e}_x + i\mathbf{e}_y)}{\sqrt{2}} \hat{T}_{q=-1}^{(k=1)} - \frac{(\mathbf{e}_x - i\mathbf{e}_y)}{\sqrt{2}} \hat{T}_{q=1}^{(k=1)} + \mathbf{e}_z \hat{T}_{q=0}^{(k=1)} \right]$$

Note that

$$\text{Re}[E_0 e^{i(kz - \omega t)} (\frac{\mathbf{e}_x + i\mathbf{e}_y}{\sqrt{2}})] = \frac{E_0}{\sqrt{2}} [\cos(kz - \omega t)\mathbf{e}_x - \sin(kz - \omega t)\mathbf{e}_y]$$

(Right-hand polarized state)

$$\text{Re}[E_0 e^{i(kz - \omega t)} (\frac{\mathbf{e}_x - i\mathbf{e}_y}{\sqrt{2}})] = \frac{E_0}{\sqrt{2}} [\cos(kz - \omega t)\mathbf{e}_x + \sin(kz - \omega t)\mathbf{e}_y]$$

(Left-hand polarized state)

$$\text{Re}[E_0 e^{i\omega t} \mathbf{e}_z] = E_0 \cos(\omega t) \mathbf{e}_z$$

(linearly polarized state)

The matrix element:

$$\begin{aligned} \langle l', m' | \hat{\mathbf{r}} | l, m \rangle &= \sqrt{\frac{4\pi}{3}} \left[\frac{(\mathbf{e}_x + i\mathbf{e}_y)}{\sqrt{2}} \langle l', m' | \hat{T}_{q=-1}^{(k=1)} | l, m \rangle \right. \\ &\quad \left. - \frac{(\mathbf{e}_x - i\mathbf{e}_y)}{\sqrt{2}} \langle l', m' | \hat{T}_{q=1}^{(k=1)} | l, m \rangle + \mathbf{e}_z \langle l', m' | \hat{T}_{q=0}^{(k=1)} | l, m \rangle \right] \\ &= \sqrt{\frac{4\pi}{3}} [\mathbf{e}_+ \langle l', m' | \hat{T}_{q=-1}^{(k=1)} | l, m \rangle + \mathbf{e}_+ \langle l', m' | \hat{T}_{q=1}^{(k=1)} | l, m \rangle + \mathbf{e}_z \langle l', m' | \hat{T}_{q=0}^{(k=1)} | l, m \rangle] \end{aligned}$$

where

$$\mathbf{e}_+ = \frac{\mathbf{e}_x + i\mathbf{e}_y}{\sqrt{2}}, \quad \mathbf{e}_- = -\frac{(\mathbf{e}_x - i\mathbf{e}_y)}{\sqrt{2}}$$

$$\begin{aligned} \langle l', m' | \boldsymbol{\varepsilon} \cdot \hat{\mathbf{r}} | l, m \rangle &= \sqrt{\frac{4\pi}{3}} [\boldsymbol{\varepsilon} \cdot \mathbf{e}_+ \langle l', m' | \hat{T}_{q=-1}^{(k=1)} | l, m \rangle \\ &\quad + \boldsymbol{\varepsilon} \cdot \mathbf{e}_+ \langle l', m' | \hat{T}_{q=1}^{(k=1)} | l, m \rangle + \boldsymbol{\varepsilon} \cdot \mathbf{e}_z \langle l', m' | \hat{T}_{q=0}^{(k=1)} | l, m \rangle] \end{aligned}$$

We use the Wigner-Eckart to find the selection rules

$$\langle l', m' | \hat{T}_q^{(k)} | l, m \rangle \neq 0$$

only if

$$m' = m + q$$

$$l' = l + k, l + k - 1, \dots, |l - k| \quad (\text{triangle inequality})$$

((Note))

$$k = 1$$

$$q = 1, 0, -1$$

$$m' = m, m + 1, m - 1$$

$$l' = l + 1, l, l - 1 \quad (\text{triangle inequality})$$

Since $\hat{T}_q^{(1)}$ is the odd parity, the transition for $l' = l$ is not allowed.