Atoms with More Than One electron

In atoms with more than one electron additional problems that are caused by mutual electrostatic and magnetic interaction between the electrons.

~~We will Est~~
In addition to this, we are now confronted with new symmetry principle that are valid if two electrons are exchanged. Then shows that electrons can not be distinguished from each other

It we will study these phenomenon for the helium atoms, which represents the simplest system with two electrons

The Helium ~~Atom~~

The helium atom consist of a nucleus with charge $+Ze = +2e$, and mass $m_k \simeq 4m_H$ and charge of each electron $(e) = -e$
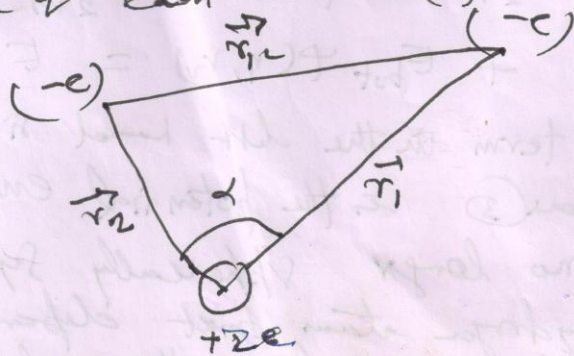
The spatial distribution of the two electrons depends on their wave functions $\psi(r_1, r_2)$, which is the function of the special coordinates $r_1 = (x_1, y_1, z_1)$ and $r_2 = (x_2, y_2, z_2)$.

$$r_1 = |\vec{r_1}|, \quad r_2 = |\vec{r_2}|, \quad r_{12} = |\vec{r_1} - \vec{r_2}|.$$

The potential energy of the electrons

$$\hat{E}_{pot} = \frac{-e^2}{4\pi\varepsilon_0}\left[\frac{2}{r_1} + \frac{2}{r_2} - \frac{1}{r_{12}}\right] \quad \text{①}$$

$$\hat{E}_{kin} = -\frac{\hbar^2}{2\mu}\left[\Delta_1(r_1) + \Delta_2(r_2)\right] \quad \text{②}$$

with $\mu = \frac{m_e m_k}{m_e + m_k}$

Since $m_k \approx 7300\, m_e$, using the approximation $\mu \approx m_e \approx m$, the Schrödinger equation

$$-\frac{\hbar^2}{2m}\Delta_1(\psi(r_1, r_2) - \frac{\hbar^2}{2m}\Delta_2\,\psi(r_1, r_2)$$

$$+ \hat{E}_{pot}\,\psi(r_1, r_2) = E\,\psi(r_1, r_2) \quad \text{③}$$

the 2nd term in the left hand side of the equation ③ is the potential energy, which is no longer spherically symmetric as in the hydrogen atom, but depends on the angle α between the values r_1 & r_2 of the

the electrons we can write it as ⑭ ③

$$r_{12} = |\vec{r_1} - \vec{r_2}|$$

$$r_{12}^2 = r_1^2 + r_2^2 - 2 r_1 r_2 \cos\theta$$ ④

we can not separate the total wave function into radial part and an angular part, as we could in the the case of one-electron system. This implies that schrödinger equation ③ is no longer solvable analytically and we have to use approximation ~~methods~~

Approximation Models

Because of the mutual repulsion, the charge distribution of the electrons will be such that the total energy becomes minimum.

i.e. KE + PE, due to the e-e repulsion and attraction between the electrons and nucleus becomes minimum. in this two average is

~~⟨r₁₂⟩ > ⟨r₁⟩~~

$$\langle r_{12} \rangle > \langle r_1 \rangle = \langle r_2 \rangle \quad ---$$

In a first approximation, we can neglect the last term in ①, then we can separate this wave function a $\psi(r_1, r_2) = \psi_1(r_1) \psi_2(r_2)$ ⑤

putting ⑤ in the schrödinger eqn. no. ③

yields two separate equations from the two electrons

$$-\frac{\hbar^2}{2m} \Delta_1 \psi_1(r_1) - \frac{e^2}{4\pi\epsilon_0} \frac{Z}{r_1} \psi_1(r_1) = \epsilon_1 \psi_1(r_1) \tag{6}$$

$$-\frac{\hbar^2}{2m} \Delta_2 \psi_2(r_2) - \frac{e^2}{4\pi\epsilon_0} \frac{Z}{r_2} \psi_2(r_2) = \epsilon_2 \psi_2(r_2) \tag{6'}$$

with $E = \epsilon_1 + \epsilon_2$. Each of these equations is itself identical to the schrödinger equation of

$$\boxed{-\frac{\hbar^2}{2m} \Delta\psi + \epsilon_{pot}(r) \psi = \epsilon \psi} \tag{7}$$

with $E = \epsilon_1 + \epsilon_2$. These equation is identical to the schrödinger equation for one electron and can be solved accordingly

with $Z = 2$, we obtain in this approximation

for the energy of the two electrons

in the lowest state with $n=1$

$$E_{He}(1S) = -2Z^2 E_H = -2 \times 4 \times 13.6 \, eV$$

$$\boxed{E_{He}(1S) = -108.8 \, eV}$$

The experimental value for this

~~it is necessary~~ energy to remove the two ~~electron~~ both the electrons from the atoms (it means to convert the He atom into the doubly charged ion He_2^{++}) is

~~there~~ $E_{exp} = -78.9 \, eV$

$$\begin{bmatrix} -78 - 61 \\ \epsilon_{rr} = 78.9 - (-108.9) \\ 78.9\% \\ \approx 40\% \end{bmatrix}$$

$$\boxed{\epsilon_{rms} \approx 8 \, \epsilon_H. \, 40\%}$$

Another much better approximation is obtained by a model that assumes that each of the two electrons moves in the Coulomb potential of the nucleus, shielded by the charge distribution of other electron (which is assumed to have spherically symmetric time average). The resulting potential for each electron is then a spherically symmetric potential generated by
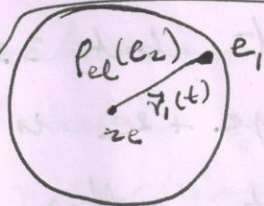

[Fig 2]. Partial shielding of the nuclear charge $+2e$ by the negative charge distribution $\rho_{el}(r_2)$

$$= -e\,|\psi_{1s}(r_2)|^2$$

of a 1s electron

$$= -e\,\psi_{1s}^{*}\cdot\psi_{1s}\cdot e$$

the electronic charge

$$q_{eff} = (z - s)\,e \quad \text{---} \quad 8$$

$s \rightarrow$ shielding const $0 \leq s \leq 1$

For the total shielding $s = 1$ and one need the energy E_H to remove the 1st electron from the atom. The remaining ion He^+ now has the nuclear charge $+2e$ and the B.E. of the second electron $\varepsilon_2 = -2^2 E_H = -4E_H$, atom is th...

The total ionization energy of the He atom is

$$E_i = -4E_H = -5E_H \approx -68\ eV \quad \text{...5)}$$

which comes much closer to the experiment
values. $E_{He} = -78.983$ ev.

For shielding constant $S = 0.656$ the experimental
value is exactly reproduced.

In our model the correct energy
is therefore obtained for taking an
effective nuclear charge of $z_{eff} = +1.344 e$.
This implies that about 33% of the real
nuclear charge $+2e$ is shielding for one
electron by the other electron in the
1s state.

Note: The shielding for an electron in
      higher energy state (for example 2s or 2p
      state) by an 1s electron can be much
      larger, ~~state~~ because the special charge
      distribution for the higher state has only
      small values within the 1s distribution
      of the shielding electron.

The spacial charge distribution of the shielding electron in the 1s state is given by

$$\rho_{el} = -e\, \psi_2^{*}(1s)\, \psi_2(1s) \qquad —⑨$$

The potential energy of the other electron is then

$$E_{pot}(r_1) = -\frac{e^2}{4\pi\epsilon_0}\left(\frac{2}{r_1} - \iiint_{0}^{\infty}\frac{\psi_2^{*}\psi_2}{r_{12}}\, d\tau_2\right) \quad —⑩$$

In a first approximation we can assume that the charge distribution of the shielding electron is not changed much by the presence of the second electron.

This means that we can take the unperturbed hydrogenic wave function for its spherically symmetric spatial distribution. This yields for the potential energy

$$E_{pot}(r_1) = -\frac{e^2}{4\pi\epsilon_0}\left(\frac{2}{r_1} - \frac{1}{\pi}\left(\frac{2}{a_0}\right)^3 \int_{r_2}\frac{e^{-2Zr_2/a_0}}{r_{12}}\, d\tau_2\right)$$

with $d\tau_2 = r_2^2 \sin\eta_2\, d\eta_2\, d\phi_2$ $\qquad —⑪$

After solving ⑪, we have

$$E_{pot}(r_1) = \frac{e^2}{4\pi\epsilon_0}\left[\frac{2-1}{r_1} + \left(\frac{2}{a_0} + \frac{1}{r_1}\right)e^{-2Zr_1/a_0}\right] \quad ⑫$$

For $Z=2$, $E_{pot}(r_1) = \frac{e^2}{4\pi\epsilon_0}\left[\frac{1}{r_1} + \left(\frac{2r_1}{a_0} + 1\right)e^{-4r_1/a_0}\right] \quad —⑬$

energy values (13) into the schrodinger
equation gives much better value for
the energy of the He ground state
than by inserting the shielding factor

$$S = 1.$$

In addition the shielding is now
dependent on the distance r_1 of electron
e_1 from the nucleus. This is reasonable
because the more the electron e_1
penetrates into the charge distribution
of e_2, the lower the shielding
by e_2 becomes.

Symmetry of the two wave functions

Here we will label the two electrons
e_1 and e_2. The two functions $\psi_1(n_1, l_1, ml_1)$
and $\psi_2(n_2, l_2, ml_2)$ of the seperated wave
function $\psi(r_1, r_2) = \psi(r_1) \times \psi(r_2)$ of the depend
on the three quantum nos (n, l, m_l) of the two
electrons. we fit we will abbreviate then
$a = (n_1, l_1, ml_1)$ and $b = (n_2, l_2, ml_2)$,
The Probability $\Rightarrow$ $p(a, b) = |\psi_{ab}(r_1, r_2)|^2$ —— ①
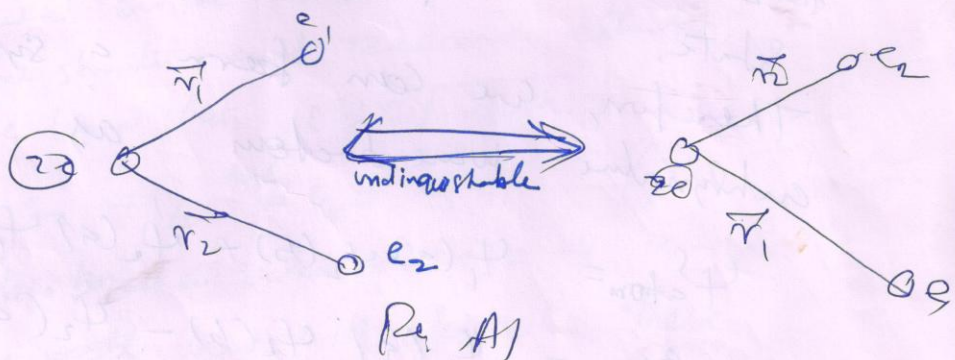
that the atomic state (a, b) is realized.
this means that e_1 is in the state a & e_2 in
the state b, and can be expressed in the
approximate model of independent electrons

i.e $\left(\dfrac{e^2}{r_{12}} \text{ may be neglected} \right)$ by

the absolute square of the product
function i.e

$$\Psi_{ab}^{I} = \Psi_1(a)\, \Psi_2(b) \qquad ②$$

If we change the two electron (Fig A)
i.e e_1 now in state b & e_2 now in state a
Now our product function becom

$$\Psi_{ab}^{II} = \Psi_2(a)\, \Psi_1(b) \qquad ③$$

Fig A)

However, the two electrons are indistinguishable.
This means that the charge distribution of
the total atom should not be changed
changed under the exchange of the
two electron. We can can write this

as

$$|\Psi'_{ab}|^2 = |\Psi''_{ab}|^2 \implies \Psi'_{ab} = e^{i\varphi}\, \Psi^2_{ab}$$ — ④

Applying the permutation of the two electrons twice bring the state back into its original configuration. This demands $\varphi = 0$ or $\varphi = \pi \implies$

$$\Psi'_{ab} = \pm \, \Psi^{II}_{ab}$$ — ⑤

Neither the two functions Ψ^{I} & Ψ^{II} fulfull this condition. They therefore can not represent the correct eigenfunctions for the description of the atomic state.

Therefore, we can form a symmetric & antisymmetric wave functions as

$$\Psi^s_{atom} = \Psi_1(a)\, \Psi_2(b) + \Psi_2(a)\, \Psi_1(b)$$ — ⑥

$$\Psi^a_{atom} = \Psi_1(a)\, \Psi_2(b) - \Psi_2(a)\, \Psi_1(b)$$ — ⑨

Note:- Ψ^s & Ψ^a represents the probability amplitudes for the configuration that one electron in state a & other in state b. However, we do not know which of the two electron in a & which

rb.

If both electrons are in the same
State $a=b$, the

$$\psi^a_{am} = 0$$

i.e. The probability to find the two
electrons with parallel spin in
the same state $(n, \ell, m_\ell) = $ is zero

Two electrons with same quantum
nos. (n, ℓ, m_ℓ) are described by the
symmetric spatial wave function ψ_{sym}

consideration of Electron spin.

based on the experimetal facts
(fine structure and zeeman effects),
we know that $\langle S \rangle = \sqrt{s(s+1)}\hbar$

$$S_z + \frac{1}{2} \text{ and } S_z = m_s \hbar \qquad —①$$

spin projection quantum no. $m_s = +\frac{1}{2}$ or $-\frac{1}{2}$

Here we will describe these
two possible orientation by
spin function $\chi^+ (m_s = \frac{1}{2})$ or $\chi^- (m_s = -\frac{1}{2})$
The spin state of the atom where both
electron have parallel spins must
be described by the symmetric wave

functions. There 3 possible ways to form the symmetric wave function

$$X_1^S(1,2) = C_1 X^+(1) X^+(2) \longrightarrow ①$$

$$X_2^S(1,2) = C_2 X^{-1}(1) X^-(2) \longrightarrow ②$$

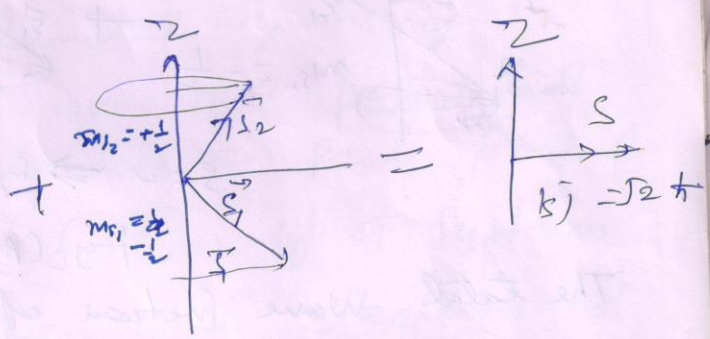$$X_3^S(1,2,3) = C_3 [X^+(1)\cdot X^-(2) + X^-(1) X^{+}(2)] \longrightarrow ③$$
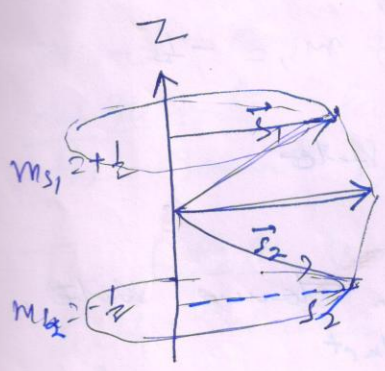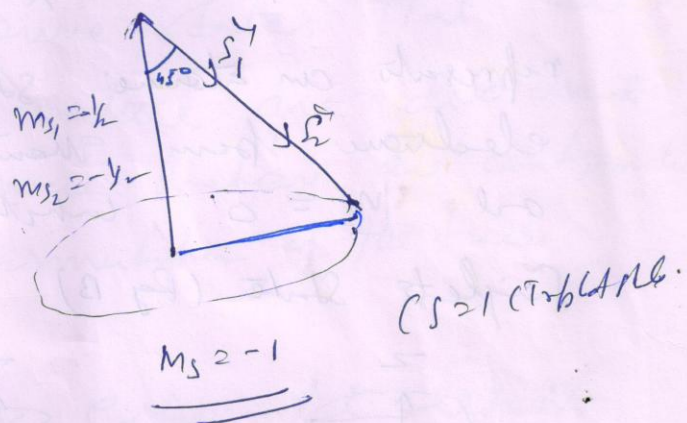
which remain the unchanged, when the two electrons are exchanged.

If we normalised the spin wave functions ($|X^*X|^2 = 1$, the coefficients of Eqs ①-③, become $C_1 = C_2 = 1$, $C_3 = \frac{1}{\sqrt{2}}$
This gives the three normalized symmetric wave functions.

$$
\begin{cases}
X_1^S(1,2) = X^+(1) X^+(2); & M_s = m_{s_1} + m_{s_2} = +1 \\
X_2^S(1,2) = X^-(1) X^-(2); & = M_s = m_{s_1} + m_{s_2} = -1 \\
X_3^S(1,2) = \frac{1}{\sqrt{2}} [X^+(1) X^-(2) + X^+(2) X^-(1)]; & M_s = 0
\end{cases}
$$

This is show in the figure ④

$M_S = +1$

$m_{s_1} = +\frac{1}{2}$

$45°$ $\vec{S_2}$

$m_{s_2} = +\frac{1}{2}$

$M_S = +1$

$m_s = +\frac{1}{2}$

$S = 1$ Triplet State

$45°$ $\vec{S_1}$

$m_{s_1} = -\frac{1}{2}$

$\vec{S_2}$

$m_{s_2} = -\frac{1}{2}$

$(S = 1 (Triblt State.$

$M_S = -1$

$m_{s_1} = +\frac{1}{2}$

$\vec{S_1}$

$\vec{S_2}$

$m_{s_2} = -\frac{1}{2}$

$+$

$sm_{s_2} = +\frac{1}{2}$ $\vec{S_2}$

$m_{s_1} = \frac{+\frac{1}{2}}{-\frac{1}{2}}$

$\vec{S_1}$

$=$

S

$\vec{S} = \sqrt{2}\, \hbar$
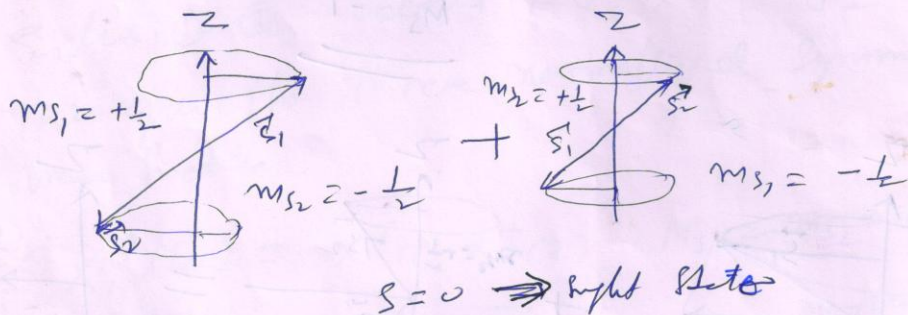
$M_S = 0$

(single state)
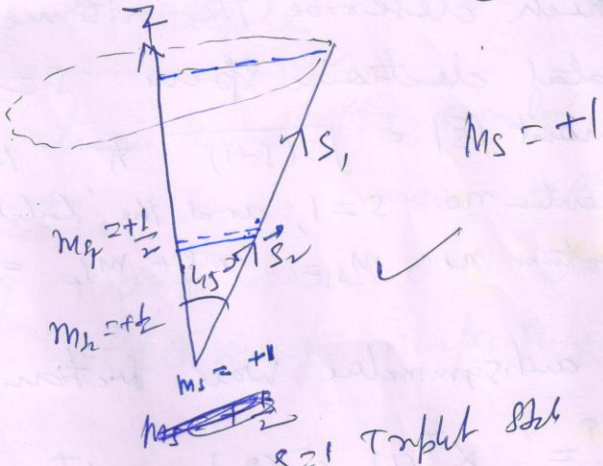
which describe the atomic states with
total electron spin $S = S_1 + S_2$, its
amount $|\vec{S}| = \sqrt{S(S+1)}\, \hbar$ the total spin
quantum no. $S = 1$, and the total spin projection
quantum no. $M_S = m_{s_1} + m_{s_2} = 0, \pm 1$

The antisymmetric wave function

$$\chi^a = \chi^+(1)\,\chi^-(2) - \chi^+(2)\,\chi^-(1) \quad —\text{⑥}$$

represents an atomic state with total
electron spin quantum no. $S = 0$
and $M_S = 0$, which is called the

Singlet State (Fig. B)

$S = 0 \Rightarrow$ Singlet State

Fig (B)

The total wave function of an atomic state
can now be written as the product

$$\Psi_{total} = \Psi_{ab}(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2) \cdot \chi(S, M_S)$$

of the spacial wave function $\Psi(r, \theta, \phi)$ that is $—\text{⑦}$
determined by the two sets of quantum nos $a = (n_1, l_1, m_1)$ and
$b = (n_2, l_2, m_2)$ and the spin wave function $\chi(S, M_S)$.

The Pauli Principle

The observation and the analysis of the spectrum and many other atoms having more than one electron brought the following surprising result.

The only atomic states that are observed in nature are described by the total wave function are antisymmetric against the permutation of the two electrons.

Based on these experimental results and on fundamental symmetry arguments Pauli (1900 – 1958) postulated the general symmetry rule = Pauli Principle

The total wave function of a system with more than one electron is always antisymmetric with respect to an exchange of two electrons

"Two electrons with the same quantum nos n, l, m_l; must have different spin projection quantum no $m_{s_1} \neq m_{s_2}$, when we will describe the atomic state by four

quantum nos (n, l, m_l, m_s) for each electron

~~when we choose the state~~

We formulate the Pauli principle as

$n=1, l=0, m_l=0$	
$\bar{S}_{1s}\uparrow$ $\downarrow \bar{S}_{2s}$	$\bar{S}_{1s}\uparrow$ $\uparrow \bar{S}_{1s}$
$m_s=0$ Allowed	$m_s=1$ Forbidden

Ground State $^1S_0$ of the He atom with

$$n=1 \quad l=0 \quad m_l=0, \quad m_s=0$$

β—16

Lamb Shift

In 1938, Pasternack, pointed out that the discrepancy in the separation between the main components of H_α line could be explained by assuming that the state $2\,^2S_{1/2}$ to be about $0.03\,cm^{-1}$ higher than $2\,^2P_{1/2}$ in contradiction to Dirac's theory. which had shown them to have exactly the same energy. In 1947, Rutherford & Lamb proved the correctness of this assumption they performed a microwave experiment on the hydrogen atom and showed that the hydrogen. like atoms the state of a particular n value having terms with the same J value but different l values such as $2\,^2P_{1/2}$ and $2\,^2S_{1/2}$ are not degenerate but are separated. This is called the Lamb Shift

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If both effects, relativistic & of
the electron and spin-orbit coupling are
taken into account. Then we obtain
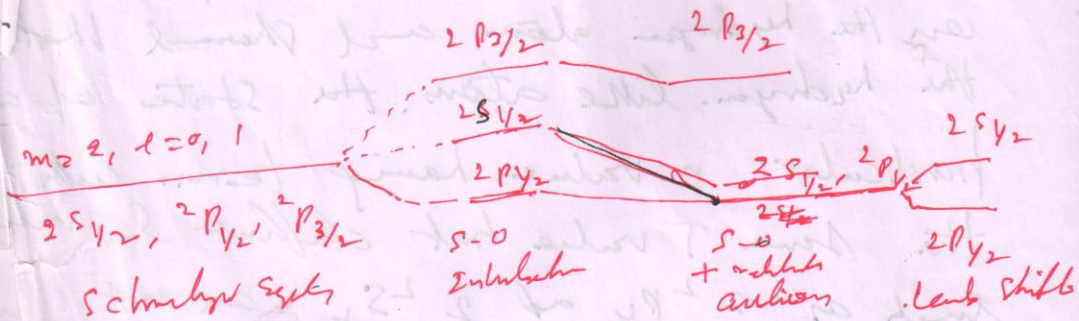the energy of a fine structure coulomb's
Adding (16) & (17)

$$E = E_{00} - \frac{R_y Z^2}{n^2}\left(1 + \frac{Z^2 \alpha^2}{n}\left(\frac{1}{(j+\frac{1}{2})} - \frac{3}{4n}\right)\right)$$

$$= E_{nr}\left[1 + \frac{Z^2 \alpha^2}{n}\left(\frac{1}{(j+\frac{1}{2})} - \frac{3}{4n}\right)\right]$$

$$E_{nj} = E_{nr}\left(1 + \frac{Z^2 \alpha^2}{n}\left(\frac{1}{(j+\frac{1}{2})} - \frac{3}{4n}\right)\right)$$

$$\text{---} \quad (18)$$

where $E_{nr} = E_{nr} = -\frac{R_y Z^2}{n^2}$

$m = 2, l = 0, 1$

$^2S_{1/2}, \; ^2P_{1/2}, \; ^2P_{3/2}$ S-0   S-0 $2P_{1/2}$
Schrödinger Eqution   Coulomb   + relativistic   Lamb Shift
                                              corrections

Energys of the levels $n=1, l=0, s=\frac{1}{2}$
of H atom within schrödinger theory
and including different relativistic effect