ENERGY LEVEL STRUCTURE OF He

The He atom has two electrons and we can extend – in principle – the structure observed for the H atom to two electrons filling the Hydrogen like level structure.

The set of quantum numbers describing the state of one electron in the extended Bohr – Schrödinger picture (including spin, that is) is given by

$$Q \equiv (n, \ell, m_\ell, m_s) \quad \text{where} \quad \begin{aligned} n &= (1, 2, \dots \quad) \\ \ell &= (0, 1, \dots \; n-1) \\ m_\ell &= (-\ell, \dots 0, \dots +\ell) \\ m_s &= -\tfrac{1}{2}, +\tfrac{1}{2} \end{aligned}$$

For two electrons in the ground state, the set of quantum numbers would be $Q = (1, 0, 0, \pm\frac{1}{2})$. It is found that we can only have

$$\left.\begin{aligned} n_1 = 1, \; \ell_1 = 0, \; m_{s_1} = +\tfrac{1}{2} \\ n_2 = 1, \; \ell_2 = 0, \; m_{s_2} = -\tfrac{1}{2} \end{aligned}\right\} \text{only one allowed combinations}$$

but never $m_{s_1} = m_{s_2}$; the two spins have to be opposite. This leads the generalisation by Pauli, the Pauli exclusion principle: No two electrons can have all quantum numbers identical.

For $n = 2$ $(\ell_{+} = 0, m_{s_{+}} = 1/2)$, $(\ell = 1, m_s = 1/2)$, $(\ell = 1, m_s = -\frac{1}{2})$ and $(\ell = 0, m_s = -1/2)$ are all allowed combinations. ~~That is if one electron~~ That is ${}^4C_2 = 6$ states arise from this combination of quantum numbers.

In fact, it is found that the level scheme for He, or any two electron system splits into two systems, called the singlet system and the triplet system and transitions only occur either within the triplet system or within the singlet system, never from one to the other

These systems are distinguished by the value of $m_{s_1} + m_{s_2}$ being 0 or 1

$m_{s_1} + m_{s_2} = 0 \rightarrow$ singlet system $\quad m_{s_1} + m_{s_2} = 1 \rightarrow$ triplet system.

The scheme for populating Bohr-like levels would be
(1s 1s), (1s 2s), (1s 2p), (1s 3s), (1s 3p), (1s 3d) etc
(2s 2s), (2s 2p), (2s 3s), (2s 3p), (2s 3d) etc

These occupancies are further classified based on the
(a) the spins $m_{s_1} + m_{s_2} \equiv S$
evidently S can only take the values 0, 1
(b) the orbital angular momenta $\vec{l}_1 + \vec{l}_2 = \vec{L}$
(c) the total angular momentum $\vec{J} = \vec{L} + \vec{S}$

Each of the resulting allowed occupancies are called terms, and each term is designated by the term symbol $^{2S+1}L_J$

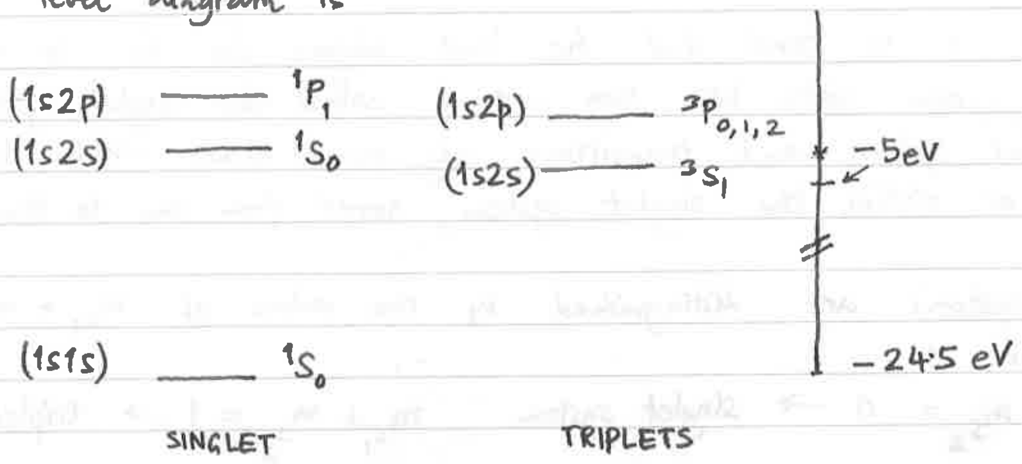
Thus, we have for

(1s1s): $l_1 = 0$, $l_2 = 0$, $m_{s_1} = \frac{1}{2}$, $m_{s_2} = -\frac{1}{2}$
$\Rightarrow$ $S = 0$, $L = 0$, $J = 0$ $\longrightarrow$ $^1S_0$

(1s2s): $l_1 = 0$, $l_2 = 0$, $m_{s_1} = \frac{1}{2}$, $m_{s_2} = \frac{1}{2}, -\frac{1}{2}$
$\Rightarrow$ (1) $L = 0$, $S = 0$, $J = 0$ $\longrightarrow$ $^1S_0$
$\Rightarrow$ (2) $L = 0$, $S = 1$, $J = 1$ $\longrightarrow$ $^3S_1$

(1s2p): $l_1 = 0$ $l_2 = 1$, $m_{s_1} = \frac{1}{2}$, $m_{s_2} = \frac{1}{2}, -\frac{1}{2}$
$\Rightarrow$ (1) $L = 1$, $S = 0$, $J = 1$ $\longrightarrow$ $^1P_1$
$\Rightarrow$ (2) $L = 1$, $S = 1$, $J = 0, 1, 2$ $\longrightarrow$ $^3P_{0,1,2}$

The level diagram is



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Transitions within the singlet system lie in the UV, visible and infrared whereas transition within the triplet system are in the IR, vis. The triplet system spans ~ 5eV, singlet system spans ~ 25eV

The most dominant line is the 1s2p $^1P_1 \rightarrow$ 1s1s $^1S_0$ [~21eV, 54nm]

The type of coupling of orb. angular momentum and spin seen in Helium is an example of L-S coupling which is seen in low Z ($Z \lesssim 30$) atoms. L-S coupling is valid when the ~~$\vec{L}\cdot\vec{S}$~~ $\vec{l}\cdot\vec{s}$ interaction is weaker (for an individual electron) than the coupling between the orbital angular momenta of a pair of electrons.

[The L-S coupling energy is

$$\frac{\mu_0}{4\pi}\,\frac{Ze^2}{2m_e^2 r^3}\,\vec{L}\cdot\vec{S}$$
]

[While the orbit-orbit coupling energy is

$$\frac{\mu_0}{4\pi}\,\frac{Ze}{m r_{12}^3}\,\vec{l}_1 \cdot \frac{e}{2m}\,\vec{l}_2$$
]

We first add the $\vec{l}_i$ to give $\vec{L} = \Sigma \vec{l}_i$ and $\vec{S} = \Sigma \vec{s}_i$; we then set $\vec{J} = \vec{L} + \vec{S}$

This scheme applies to $\geqslant 2$ electrons also. However if a shell is filled then the ground state is the one in which the filled shells have $J=0$, $L=0$, $S=0$

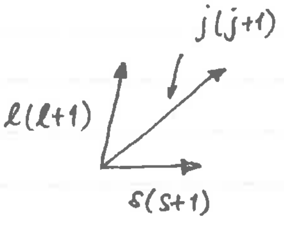
Only the electrons in non-closed shells need be considered for determining the angular momentum state of the atom.

A different coupling scheme arises, if the individual electron $\vec{l}\cdot\vec{s}$ coupling is comparable to ~~the~~ or greater than the $\vec{l}_i\cdot\vec{l}_j$ or $\vec{s}_i\cdot\vec{s}_j$ coupling between two arbitrary electrons.

Clearly, this situation arises for atoms with large Z, since the $\vec{l}\cdot\vec{s}$ coupling depends on the strength of the magnetic field of the nucleus experienced by the orbiting electron.

This second scheme is called j-j coupling since $\vec{l}_i$ and $\vec{s}_i$ first couple to form $\vec{j}_i$ for the ith electron and the j_i and j_k terms of different electrons interact with each other at the next order.

In this coupling scheme it only makes sense to talk about the total angular momentum $\vec{J} = \Sigma \vec{j}_i$, but not of the orbital momenta $\vec{l}_i$ or their sum $\vec{L}$, Addition of $\vec{l}$, $\vec{s}$,



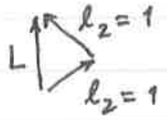
l, ~~s~~, ~~j~~ are all integers, $s = \frac{1}{2}$

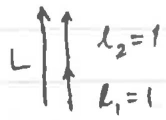
$j = l \pm \frac{1}{2}$ for $l \neq 0$

$= \frac{1}{2}$ for $l = 0$

Addition of $\vec{l}_i$ $\vec{l}_j$

$l_1 = 1$ ↑↓ $l_2 = 1$





L=0, 'S' term L=1, 'P' term L=2, 'D' term

ENERGY LEVELS

The angular momentum coupling schemes indicate existence of fine structure, but does not tell us anything about the energy levels. To obtain those we need to solve the Schrödinger equation for the electrostatic part of the Hamiltonian first.

However, even for the simplest case — the Helium atom — the multielectron Hamiltonian has no exact solutions. The Hamiltonian is

$$\hat{H} = -\frac{1}{2}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{r_{12}} \qquad \left[\begin{matrix}\text{in atomic}\\ \text{units}\end{matrix}\right]$$

In the crudest approximation we may treat the $1/r_{12}$ term as the perturbation : $\hat{H} = \hat{H}_0 + 1/r_{12}$

The hamiltonian $\hat{H}_0$ has exact solutions, which are simply products of one electron wavefunctions

$$\Psi = \Psi_1 \psi_2 \qquad \psi(\vec{r}_1, \vec{r}_2) = \Psi_1(r_1)\,\psi_2(r_2)$$

individually, these are hydrogen atom solutions with Z = 2

The ground state energy would be

$$E_0 = \langle \Psi_1^0(r_1)\,\psi_2^0(r_2) | \hat{H}_0 | \psi_1^0(r_1)\psi_2^0(r_2) \rangle$$

where $\psi^0_{1,2}(r_{1,2})$ are the hydrogen-like ground state functions with $Z=2$

Evidently $$E_0 = \left(-\frac{1}{2}Z^2\right) \times 2$$

$$= -4 \text{ (atomic units)}$$ — This is 108·8 eV, when in fact the value is 79 eV or −2·90 at·units.

We can do slightly better than this by treating the two electrons step by step:

- Treat the first electron as bound "directly" to the nucleus ie with $Z = 2$, so that $E_{0(1)} = -\frac{1}{2}Z^2 = -2$ a.u.
- Treat the second electron as bound to an "screened" nucleus, i.e. for the second electron alone, $Z = 1$, so that $E_{0(2)} = -\frac{1}{2}$

The net binding energy would then be

$$E_0 = E_{0(1)} + E_{0(2)}$$
$$= -2 - \frac{1}{2} = -\frac{5}{2}$$ which closer to the actual value than the previous one, but on the "wrong" side, that is more +ve

As a less drastic attempt at accounting for the screening we may set the screening term as $(Z-\epsilon)$ where $\epsilon < 1$, so that the binding energy as calculated above matches the actual value

$$E_0 = -\frac{1}{2} Z^2 - \frac{1}{2} (Z-\epsilon)^2 = E_{actual}$$

putting $Z=2$ and $E_{actual} = -2{\cdot}90$ gives $\epsilon = 0{\cdot}656$.

As an aside we also note, that if we set the same screening constant for calculating the binding of the second electron and equate it to the known 1st ionisation potential, we get an exact match : $-\frac{1}{2}(Z-\epsilon)^2 = -\frac{1}{2}(2-0{\cdot}656)^2 = -0{\cdot}9 \equiv 24{\cdot}5$ eV.

NOTE : for He
double ionisation energy = binding energy of two electrons = 79eV = −2·90au
single — " — = — " — on electron = 24·5 eV = −0·9 au

PERTURBATIVE APPROX. TO THE GROUND STATE ENERGY

We can include the $1/r_{12}$ term in the helium atom hamiltonian as a perturbative correction to the wavefunction obtained for the non-interacting hamiltonian $\hat{H}_0$:

$$\hat{H}_0 = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2}$$

which has solutions $\Psi(\vec{r}_1, \vec{r}_2) = \psi_1(r_1)\,\psi_2(r_2)$, in which $\psi_i(r_i)$ is a hydrogenic wave function. The energy eigenvalue is $(-\frac{1}{2}Z^2) \times 2$ for the G.S.
First order perturbation theory gives the correction

$$E_0^{(1)} = \langle \Psi(\vec{r}_1, \vec{r}_2) | \frac{1}{r_{12}} | \Psi(\vec{r}_1, \vec{r}_2) \rangle$$

To solve this we note that $\Psi(\vec{r}_1, \vec{r}_2) = (Z^3/\pi)\, e^{-Z(r_1+r_2)}$ and

① $$\frac{1}{r_{12}} = \frac{1}{(r_1^2 + r_2^2 - 2r_1 r_2 \cos\chi_{12})^{1/2}},$$ where χ_{12} is the free angle between $\vec{r}_1$ & $\vec{r}_2$

② $$\cos\chi_{12} = \cos\theta_1 \cos\theta_2 + \sin\theta_1 \sin\theta_2 \cos(\phi_2 - \phi_1)$$

① can be written as $$\sum_{l=0}^{\infty} \frac{r_<^l}{r_>^{l+1}} P_l(\cos\chi_{12})$$ where $r_<$ and $r_>$ represent the smaller or larger of r_1 and r_2 at the point of interest

Thus $$E_0^{(1)} = \frac{Z^6}{\pi^2} \iint r_1^2 dr_1\, d\Omega_1\, r_2^2 dr_2\, d\Omega_2\, e^{-2Z(r_1+r_2)} \sum_0^{\infty} \frac{r_<^l}{r_>^l} P_l \cos(\chi_{12})$$

From the properties of spherical harmonics we have

$$P_l(\cos\chi_{12}) = \sum_{m=-l}^{l} Y_{lm}^*(\theta_1, \phi_1)\, Y_{lm}(\theta_2, \phi_2) \cdot \frac{4\pi}{(2l+1)}$$

{ the addition theorem for spherical harmonics }

$$E_0^{(1)} = \frac{Z^6}{\pi^2} \iint d\tau_1\, d\tau_2\, e^{-2Z(r_1+r_2)} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{4\pi}{(2l+1)} Y_{lm}^*(1)\, Y_{lm}(2) \cdot \frac{r_<^l}{r_>^{l+1}}$$

The integrand has no θ or ϕ dependence other than the Y_{lm}s. Since Y_{lm}

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of different $\ell, m,$ are orthogonal to each other and since $Y_{00} = (4\pi)^{-1/2}$ is independent of θ, ϕ we can re write the integral as

$$E_0^{(1)} = \frac{Z^6}{\pi^2} \iint d\tau_1\, d\tau_2\, e^{-2Z(r+r_2)} \frac{(4\pi)^2}{2\ell+1} \sum_{\ell} \sum_{m} Y_{00}(\theta_1, \phi_1)\, Y_{\ell m}^{*}(\theta_1, \phi_1)$$

and exploit the orthogonality to get

$$\times\, Y_{00}(\theta_2, \phi_2)\, Y_{\ell m}^{*}(\theta_2, \phi_2)\, \frac{r_{\cancel{2}<}^{\ell}}{r_{\cancel{2}>}^{\ell}}$$

$$= \frac{Z^6}{\pi^2} \iint_{r_1, r_2 = 0}^{\infty} r_1^2 dr_1\, r_2^2 dr_2\, e^{-2Z(r_1+r_2)} \frac{(4\pi)^2}{2\ell+1} \frac{r_<^{\ell}}{r_>^{\ell+1}} \delta_{\ell 0}\, \delta_{m0}$$

$$= 16\cancel{\pi} Z^6 \iint r_1^2 dr_1\, r_2^2 dr_2\, e^{-2Z(r_1+r_2)} \frac{r_<^{0}}{r_>^{\cancel{\ell}1}} \qquad (\because \ell = 0 \text{ is the only term})$$

$$= 16 Z^6 \int_{r_1=0}^{\infty} r_1^2 dr_1\, e^{-2Zr_1} \left[\int_{r_2=0}^{r_1} e^{-2Zr_2} \frac{1}{r_1} r_2^2 dr + \int_{r_2=r_1}^{\infty} e^{-2Zr_2} \frac{1}{r_2} r_2^2 dr \right]$$

$$= 16 Z^6 \int_{r_1=0}^{\infty} r_1^2 dr_1\, e^{-2Zr_1} \left[\frac{1}{r_1} \int_{0}^{r_1} e^{-2Zr_2} r_2^2 dr + \int_{r_1}^{\infty} e^{-2Zr_2} r_2\, dr \right]$$

$$= +\frac{5}{8} Z$$

As expected, this correction is positive since it corresponds to electron-electron repulsion.

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Thus the G.S. energy correct to first order in perturbation theory is

$$\cancel{E_0^{(1)}}\ E_0 = E_0^{(0)} + E_0^{(1)}$$

$$= \left(-\frac{1}{2} Z^2\right) \times 2 + \frac{5}{8} \times 2$$

$$= \cancel{\frac{-1/2}{8}} -4 + \frac{5}{4} = -\frac{11}{4} = -2.75 \text{ a.u.}$$

This is to be compared with -2.90 (exact).

VARIATIONAL CALCULATION

So far we have taken the unperturbed wavefunction to be a product of hydrogenic wavefunctions : $\Psi = e^{-Z(r_1+r_2)}$ (where $Z=2$)

If instead, we take a trial wavefunction of the form

$$\Psi_{trial}(\vec{r}_1, \vec{r}_2) = \exp\left[-\alpha(r_1+r_2)\right]$$

which while still being spherically symmetric, has an adjustable parameter α that can be detrmined by the variational principle: This wavefn. may be seen as a "screened" nucleus wavefunction, with the screening determined variationally. In this method, the adjustable parameter is determined by the minimisation of the expectation value of the energy corresponding to the ~~unper~~ complete hamiltonian and the trial wavefunction.

That is, we find

$$\langle E \rangle = \langle \Psi_{trial} | \hat{H} | \Psi_{trial} \rangle$$

where $\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}$

and finally minimise $\langle E \rangle$ w.r.t. variation in α.

These expectation values of the various terms are

$$\left\langle -\frac{1}{2}\nabla_1^2 \right\rangle = \left\langle -\frac{1}{2}\nabla_2^2 \right\rangle = +\frac{1}{2}\alpha^2$$

$$\left\langle -\frac{1}{r_1} \right\rangle = \left\langle -\frac{1}{r_2} \right\rangle = -2\alpha \qquad \{\text{or in general } -Z\alpha\}$$

not 2

$$\left\langle \frac{1}{r_{12}} \right\rangle = +\frac{5}{8}\alpha$$

Thus $\langle E \rangle = \alpha^2 \cancel{+} - 4\alpha + \frac{5}{8}\alpha$

$\partial\langle E \rangle / \partial\alpha = 2\alpha \cancel{+} - \frac{27}{8}$; So $\alpha = \frac{27}{16}$

an $\langle E \rangle = \left(\frac{27}{16}\right)^2 - 4\left(\frac{27}{16}\right) + \frac{5}{8}\left(\frac{27}{16}\right)$ $\left\{ \text{NOT } -\frac{\alpha^2}{2} \,! \right\}$

$= -\left(\frac{27}{16}\right)^2 \simeq -2.85$ a.u.

This is considerably closer to the actual (within < 2%.)

The trial wavefunction that we considered was spherically symmetric and did not explicitly include any r_{12} containing term. Since the $1/r_{12}$ term does explicilty enter the hamiltonian it is reasonable to take a trial wavefunction to be

$$\Psi_{\text{trial}} = e^{-\alpha(r_1 + r_2)} \left[1 + \beta r_{12} + \cdots \right]$$

The variationally calculated energy with this trial function gives $E = -2.89$. with one term in r_{12}.

It should be noted that this trial wavefunction yields an even better value than the best possible value obtained using single particle wavefunctions (by the so-called self-consistent field method of Hartree). We say that the $1/r_{12}$ term gives us the "correlation energy"

Comparison of various E_0 estimates

Simple hydrogenic	$(-Z^2/2) \times 2$	-4	
Successive hydrogenic	$-Z^2/2 + (Z-1)^2/2$	$-5/2$	$(= -2.5)$
"Screened" variational	$\alpha = 27/16$	$-(27/16)^2$	$(= -2.85)$
variational with r_{12}		-2.89	
Simple hydrogenic + perturbative		-2.75	

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PAULI EXCLUSION PRINCIPLE, SPIN ORBITALS, OCCUPATION OF LEVELS

For Applying the exclusion principle, we need to consider spatial and spin ~~we say that the~~ wavefunctions of a single electron, ~~is~~ to be specified as

$$\phi(1) = \psi(1)\,\alpha(1) \quad \text{or} \quad \psi(1)\,\beta(1)$$

where (1) ~~is~~ is a label numbering the electron
$\psi(1)$ is the spatial part of the wavefunction ($\equiv$ hydrogenic in the simplest form)
$\alpha(1)$ is a spin-up wavefn
$\beta(1)$ is a spin-down wavefn.

For brevity we write the spin-orbitals as $\phi_a(1)$ where 'a' represents the set of 4 quantum numbers n, l, m_l, m_s

Thus, in this designation of the spin orbitals, for a two-electron system, the orbitals $\phi_a(1)$ and $\phi_b(2)$ must be distinct in accordance with Pauli's principle.

The two electron spin orbital wavefunction is a product of $\phi_a(1)\,\phi_b(2)$
However, in addition there is also the possibility of exchange of coordinates that does not affect the probability distribution, so the correct 2-electron spin-orbital wavefunction would be

$$\Psi(1,2) = \frac{1}{\sqrt{2}}\left[\phi_a(1)\,\phi_b(2) - \phi_a(2)\,\phi_b(1)\right]$$

which vanishes when $a = b$ (i.e. when all quantum numbers are identical) as required by the exclusion principle
This function is antisymmetric under exchange of coordinates

$$\Psi(1,2) = -\Psi(2,1)$$

The other possibility, $\Psi = [\phi_a(1)\phi_b(2) + \phi_a(2)\phi_b(1)]/\sqrt{2}$ is a symmetric wavefunction that does not satisfy the exclusion principle.

Thus the anti-symmetry of the wavefunction is an expression of the exclusion principle.

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For later reference, i.e. for multielectron (≥ 2) case, it is useful to write $\Psi(1,2)$ as a determinant

$$\Psi_{\cancel{12}}(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_a(1) & \phi_b(1) \\ \phi_a(2) & \phi_b(2) \end{vmatrix} \downarrow \text{electrons}$$

$$\longrightarrow \text{orbitals}$$

$1s^2$ STATE

For the $1s^2$ state $\psi(1) = \psi_{1s}$ $\psi_{\cancel{2}}(2) = \psi_{1s}$. (both hydrogenic)
Hence we ~~can~~ ~~write~~ must have the spins opposite, and allow for antisymmetry

Thus:

$$\Psi(1,2) = \psi_{1s}(1)\,\psi_{1s}(2) \cdot \underbrace{\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \alpha(2)\beta(1)\right]}_{\sigma_{S,M_S}(1,2)}$$

σ_{S,M_S} is the spin part of the two electrons with S and M_S denoting the total Spin quanta (value of $\sqrt{S(S+1)}$ and $S_z = M_S$)
In the above case $S=0$, $M_S=0$ for opp. spins, so $\sigma_{S,M_S} \equiv \sigma_{00}$

OTHER STATES

Although not for the $1s^2$ state, it is possible to have another spin wave functions if the spatial quantum numbers are not all identical:
This set of spin wavefunctions is ~~anti~~ symmetric w.r.t. exchange:

$$\sigma_{11}(1,2) = \alpha(1)\alpha(2) \qquad \text{Both up so } M_S = 1,\ S = 1$$

$$\sigma_{10}(1,2) = \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) + \beta(1)\alpha(2)\right] \qquad$$ ~~One up One down opposite~~

$$\sigma_{1-1}(1,2) = \cancel{\frac{1}{\sqrt{2}}}\ \beta(1)\,\beta(2) \qquad \text{Both down so } M_S = -1 \quad S = 1$$

These ~~trip~~ three possibilities encode the triplet state that we saw earlier in the spectroscopy context. Clearly these spin state ~~are~~ must be associated with non-identical spatial wavefunctions of the two electrons in the hydrogenic basis, e.g. for $1s2s$, $1s2p$ etc configurations

Swabeshi

In particular, for the (1s 2s) configuration the wavefunctions will be

$$\Psi^{+}(1,2) = \frac{1}{\sqrt{2}}\left[\psi_{1s}(1)\psi_{2s}(2) + \psi_{1s}(2)\psi_{2s}(1)\right]\sigma_{00}(1,2)$$

normalisation for spatial part

2 terms since spatial orbitals can also be exchanged, unlike the $1s^2$ state

NOTE: σ also has a $\frac{1}{\sqrt{2}}$ factor in its definition

$$\Psi^{-}(1,2) = \frac{1}{\sqrt{2}}\left[\psi_{1s}(1)\psi_{2s}(2) - \psi_{1s}(2)\psi_{2s}(1)\right]\begin{array}{l}\sigma_{1,1}(1,2)\\ \sigma_{1,0}(1,2)\\ \sigma_{1,-1}(1,2)\end{array}$$

The energies corresponding to the singlet (Ψ^{+}) and triplet (Ψ^{-}) states are different and can be computed from

$$\langle E^{\pm}\rangle = \iint \Psi^{\pm *}\,\hat{H}\,\Psi^{*}\,d\tau_1\,d\tau_2$$

which is conveniently written in the form of

$$\langle E^{\pm}\rangle = I(1s) + I(2s) + J(1s,2s) \pm K(1s,2s)$$

where

$$I(a) = \int \psi_a(\vec{r})\left(-\frac{1}{2}\nabla^2 - \frac{Z}{r}\right)\psi_a(\vec{r})\,d\tau$$

(1-electron hamiltonian)

$$J(a,b) = \iint |\psi_a(\vec{r}_1)|^2\,\frac{1}{r_{12}}\,|\psi_b(\vec{r}_2)|^2\,d\tau_1\,d\tau_2$$

$$K(a,b) = \iint \psi_a(\vec{r}_1)\,\psi_b(r_1)\,\frac{1}{r_{12}}\,\psi_a(\vec{r}_2)\,\psi_b(\vec{r}_2)\,d\tau_1\,d\tau_2$$

These are, respectively, called the direct, coulomb and exchange integrals
The direct integral corresponds to the single particle energy (in nuclear field)
coulomb integral correnponds to the electrostatic repulsion between 2 elec
exchange integral has no classical analogue ↔ related to exclusion principle.