Helium Atom

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1 Schrodinguer equation

In any system of various particles with no external forces we can separate the solution in terms of mass center and relative coordinates. The Schrodinguer equation is:

$$\left[-\frac{\hbar^2}{2(m_N + 2m_e)} \nabla_R^2 - \frac{\hbar^2}{2\mu} \sum_{i=1}^{2} \nabla_{r_i}^2 - \frac{\hbar^2}{m_N} \vec{\nabla}_{r_1} \cdot \vec{\nabla}_{r_2} + V(\vec{r}_1, \vec{r}_2) \right] \Psi_{tot}(\vec{R}, \vec{r}_1, \vec{r}_2) = E_{tot} \Psi_{tot}(\vec{R}, \vec{r}_1, \vec{r}_2)$$

(1.1)

where:

$$\vec{R} = \frac{1}{m_N + 2m_e}(m_N \vec{R_N} + m_e \vec{r}_1 + m_e \vec{r}_2) \qquad \vec{r}_i = \vec{R}_i - \vec{R}_N$$

(1.2)

where $\vec{R}_i$ and $\vec{R}_N$ are the coordinates of the electrons and the nucleus in some coordinate system. The reduced mass μ in eq.[1.1] is:

$$\mu = \frac{m_e m_N}{m_e + m_N}$$

(1.3)

The third term in eq.[1.1] is a kinetic term due to nuclear motion. This equation admits separable solutions in terms of the center of the mass coordinates and the relatives coordinates:

$$\Psi_{tot}(\vec{R}, \vec{r}_1, \vec{r}_2) = U(\vec{R}) \Psi(\vec{r}_1, \vec{r}_2)$$

(1.4)

Inserting this solution in eq.[1.1] leads us to two independent equation. One is for the center of the mass which does not include a potential, it is the dynamics of a free particle, therefore we are not interested in it. The second one describe the relative motion of the particles involved:

$$\left[-\frac{\hbar^2}{2\mu} \sum_{i=1}^{2} \nabla_{r_i}^2 - \frac{\hbar^2}{m_N} \vec{\nabla}_{r_1} \cdot \vec{\nabla}_{r_2} + V(\vec{r}_1, \vec{r}_2) \right] \Psi(\vec{r}_1, \vec{r}_2) = E \Psi(\vec{r}_1, \vec{r}_2)$$

(1.5)

and we have that:

$$E_{tot} = E_{CM} + E$$

(1.6)

The potential we consider is the Coulombian interaction between the particles:

$$V(\vec{r}_1, \vec{r}_2) = -\frac{Ze^2}{4\pi\epsilon_0} \sum_{i=1}^{2} \frac{1}{r_i} + \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_{12}}$$

(1.7)

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2 Infinitely heavy nucleus

We can consider $M \to \infty$ so the polarisation term can be omitted and the reduced mass is then $\mu \to m_e$. Now our Schrodinguer equation is:

$$\left[-\frac{\hbar^2}{2\mu} \sum_{i=1}^{2} \nabla_{r_i}^2 - \frac{Ze^2}{4\pi\epsilon_0} \sum_{i=1}^{2} \frac{1}{r_i} + \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_{12}} \right] \Psi(\vec{r}_1, \vec{r}_2) = E\Psi(\vec{r}_1, \vec{r}_2) \tag{2.1}$$

We have that this hamiltonian conmutes with the interchange operator P_{12}. That means we can find a set of eigenfunctions of H which are simultaneously eigenfunctions of P_{12}:

$$P_{12}\Psi(\vec{r}_1, \vec{r}_2) = \lambda\Psi(\vec{r}_1, \vec{r}_2) \tag{2.2}$$

Applyng two times the operator we have:

$$P_{12}^2\Psi(\vec{r}_1, \vec{r}_2) = \Psi(\vec{r}_1, \vec{r}_2) = \lambda^2\Psi(\vec{r}_1, \vec{r}_2) \tag{2.3}$$

so $\lambda = \pm 1$. Therefore we can classify the eigenfunctions based on that sign:

$$P_{12}\Psi(\vec{r}_1, \vec{r}_2) = \pm\Psi(\vec{r}_1, \vec{r}_2) \tag{2.4}$$

when the sign is plus it is called spacially symmetric (also called para states) Ψ_+, when the sign is minus it is called spacially antisymmetric (also called orto states) Ψ_-.

2.1 Spin

Because the hamiltonian does not depend on the spins of the particles we can choose the spin part of the eigenfunction as we wish:

$$\Psi(1,2) = \Psi(\vec{r}_1, \vec{r}_2)\chi(\sigma_1, \sigma_2) \tag{2.5}$$

where χ can be any normalizes combination of the states $\alpha(\sigma)$ or $\beta(\sigma)$ in a product (for example $\chi = \alpha(\sigma_1)\beta(\sigma_2)$. α denotes a state with third component of spin $+1/2$ and β denotes a state with third component of spin $-1/2$. Anyway you choose χ it is always a eigenfunction of $S_z = (S_z)_1 + (S_z)_2$

But let's suppose we are interested only in a set of eigenfunctions which are eigenfunctions of P_{12}. There are four combinations of α and β which leads us to this kind of states. They are:

$$\chi_{00} = \frac{1}{\sqrt{2}} \left[\alpha(\sigma_1)\beta(\sigma_2) - \beta(\sigma_1)\alpha(\sigma_2) \right] \tag{2.6}$$

$$\chi_{10} = \frac{1}{\sqrt{2}} \left[\alpha(\sigma_1)\beta(\sigma_2) + \beta(\sigma_1)\alpha(\sigma_2) \right] \tag{2.7}$$

$$\chi_{11} = \alpha(\sigma_1)\alpha(\sigma_2) \tag{2.8}$$

$$\chi_{1-1} = \beta(\sigma_1)\beta(\sigma_2) \tag{2.9}$$

where χ_{1M_S} are spacially symmetric and χ_{00} are spacially antisymmetric. We describe this functions as χ_{SM_S}, all of the are eigenfunctions of operators S^2 and S_z.

So our eigenfunctions simultaneously eigenfunctions of S^2, S_z and P_12 are:

$$\Psi_+(1,2) = \Psi_+(\vec{r}_1,\vec{r}_2)\chi_{1M_S}(\sigma_1,\sigma_2) \tag{2.10}$$

and:

$$\Psi_-(1,2) = \Psi_-(\vec{r}_1,\vec{r}_2)\chi_{00}(\sigma_1,\sigma_2) \tag{2.11}$$

2.2 Independent particle model

We split our hamiltonian shown in eq.[2.1] as:

$$H = H_0 + H' \tag{2.12}$$

where H_0 is:

$$H_0 = -\frac{\hbar^2}{2\mu}\sum_{i=1}^{2}\nabla_{r_i}^2 - \frac{Ze^2}{4\pi\epsilon_0}\sum_{i=1}^{2}\frac{1}{r_i} = \sum_{i=1}^{2}h_i \tag{2.13}$$

where h_i is:

$$h_i = -\frac{\hbar^2}{2\mu}\nabla_{r_i}^2 - \frac{Ze^2}{4\pi\epsilon_0}\frac{1}{r_i} \tag{2.14}$$

so the hamiltonian is separable in terms of the relative coordinates of the electrons that means we can express the eigenfunctions as:

$$\Psi(1,2) = \psi_{\nu_1}(1)\psi_{\nu_2}(2) \tag{2.15}$$

where $\psi(i)$ are the single-particle eigenfunctions which follows the single-particle eigenvalues equation:

$$h_i\psi_\nu(i) = \epsilon_\nu\psi_\nu(i) \tag{2.16}$$

which is the hydrogenoid equation which solutions are known. This h hamiltonian commutes with l and l_z and its eigenstates are characterized by a radial quantum number n:

$$\psi_{nlm_l}(\vec{r}) = R_{nl}(r)Y_{lm_l}(\theta,\varphi) \tag{2.17}$$

The total energy (eigenvalue of H_0) is the sum of the single-particle energies:

$$E^0_{n1n2} = \sum_{i=1}^{2}\epsilon_{n_i} \tag{2.18}$$

where:

$$\epsilon_n = -\frac{1}{n^2}\left[\frac{m}{2\hbar^2}\left(\frac{Ze^2}{4\pi\epsilon_0}\right)^2\right] = -\frac{1}{n^2}\left[\frac{mc^2}{2}\left(\frac{Ze^2}{4\pi\epsilon_0\hbar c}\right)^2\right] \tag{2.19}$$

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and:

$$R_{nl}(r) = \left[\left(\frac{2Z}{na_\mu} \right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3} \right]^{1/2} e^{-\rho} (2\rho)^l \left[L_{n-l-1}^{2l+1}(2\rho) \right] \tag{2.20}$$

with:

$$\rho = \frac{Zr}{na_\mu} \qquad a_\mu = \frac{4\pi\epsilon_0 \hbar c}{e^2} \frac{\hbar c}{\mu c^2} \tag{2.21}$$

Impossing being eigenfunctions of P_{12} we have:

$$\Psi_\pm^0(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} \left[\psi_{n_1 l_1 m_1}(\vec{r}_1) \psi_{n_2 l_2 m_2}(\vec{r}_2) \pm \psi_{n_2 l_2 m_2}(\vec{r}_1) \psi_{n_1 l_1 m_1}(\vec{r}_2) \right] \tag{2.22}$$

This is only taking into account the spacial part, globally we have:

$$\Psi_+^0(1,2) = \Psi_+^0(\vec{r}_1, \vec{r}_2) \chi_{1M_s}(\sigma_1, \sigma_2) \qquad \Psi_-^0(1,2) = \Psi_-^0(\vec{r}_1, \vec{r}_2) \chi_{00}(\sigma_1, \sigma_2) \tag{2.23}$$

The energy levels in eq.[2.18] depend on n_1 and n_2.

2.3 Ground State

2.3.1 Perturbation theory

The perturbative hamiltonian H' in eq.[2.12] is:

$$H' = \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_{12}} \tag{2.24}$$

In this case the spatial part ot the wavefunction can only be spacially symmetric, otherwise it nullifies. And the spin part must be antisymmetric in order to have a global antisymmetric function to follow Pauli's principle. Then we have:

$$\Psi_0^0(\vec{r}_1, \vec{r}_2, \sigma_1, \sigma_2) = [\psi_{1s}(\vec{r}_1) \psi_{1s}(\vec{r}_2)] \chi_{00}(\sigma_1, \sigma_2) \tag{2.25}$$

So the ground state is not degenerate using H_0. So the first correction to the energy using perturbation theory is:

$$E_0^{(1)} = \int \psi_{1s}^*(\vec{r}_1) \psi_{1s}^*(\vec{r}_2) \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_{12}} \psi_{1s}(\vec{r}_1) \psi_{1s}(\vec{r}_2) dV_1 dV_2 \sum_{\sigma_1, \sigma_2} \chi_{00}^*(\sigma_1, \sigma_2) \chi_{00}(\sigma_1, \sigma_2) \tag{2.26}$$

where $\sum_{\sigma_1, \sigma_2} \chi_{00}^*(\sigma_1, \sigma_2) \chi_{00}(\sigma_1, \sigma_2) = 1$ (this is a representation in coordinates of $< 00|00 >$).

Therefore we have:

$$E_0^{(1)} = \frac{e^2}{4\pi\epsilon_0} \int |\psi_{1s}(\vec{r}_1)|^2 \frac{1}{r_{12}} |\psi_{1s}(\vec{r}_2)|^2 dV_1 dV_2 \tag{2.27}$$

The wavefunctions are:

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$$\psi_{1s}(\vec{r}) = R_{1s}(r)Y_{00} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a}\right)^{3/2}e^{-\frac{Zr}{a}} \tag{2.28}$$

Then we have:

$$E_0^{(1)} = \frac{e^2}{4\pi\epsilon_0}\frac{Z^6}{\pi^2}\int e^{-2Z(r_1+r_2)/a}\frac{1}{r_{12}}dV_1dV_2 \tag{2.29}$$

and we can express $\frac{1}{r_{12}}$ as:

$$\frac{1}{r_{12}} = \sum_{l=0}^{\infty}\sum_{m_l=-l}^{l}\frac{4\pi}{2l+1}\frac{(r_<)^l}{(r_>)^{l+1}}Y_{lm}^*(\theta_1,\varphi_1)Y_{lm}(\theta_2,\varphi_2) \tag{2.30}$$

Inserting the expression in the energy integral we have:

$$E_0^{(1)} = \frac{e^2}{4\pi\epsilon_0}\frac{Z^6}{\pi^2}\sum_{l=0}^{\infty}\sum_{m_l=-l}^{l}\frac{4\pi}{2l+1}\left[\int\frac{(r_<)^l}{(r_>)^{l+1}}e^{-2Z(r_1+r_2)/a}(r_1)^2(r_2)^2dr_1dr_2\right]4\pi$$
$$\left[\int Y_{lm}^*(\theta_1,\varphi_1)Y_{00}d\Omega_1\int Y_{00}^*Y_{lm}(\theta_2,\varphi_2)d\Omega_2\right] \tag{2.31}$$

Spherical harmonics are orthonormal with respect l and m_l so we have:

$$E_0^{(1)} = \frac{e^2}{4\pi\epsilon_0}\frac{Z^6}{\pi^2}\sum_{l=0}^{\infty}\sum_{m_l=-l}^{l}\frac{(4\pi)^2}{2l+1}\left[\int\frac{(r_<)^l}{(r_>)^{l+1}}e^{-2Z(r_1+r_2)/a}(r_1)^2(r_2)^2dr_1dr_2\right]\delta_{l0}\delta_{m_l0} =$$
$$= \frac{e^2}{4\pi\epsilon_0}16Z^6\left[\int\frac{(r_<)^l}{(r_>)^{l+1}}e^{-2Z(r_1+r_2)/a}(r_1)^2(r_2)^2dr_1dr_2\right] \tag{2.32}$$

The integrand depends on the values of the two variables:

$$E_0^{(1)} = \frac{e^2}{4\pi\epsilon_0}16Z^6\int_0^{\infty}r_1^2e^{-2Zr_1/a}dr_1\left[\frac{1}{r_1}\int_0^{r_1}r_2^2e^{-2Zr_2/a}dr_2+\int_{r_1}^{\infty}r_2e^{-2Zr_2/a}dr_2\right] \tag{2.33}$$

Let's rewrite the expression as:

$$E_0^{(1)} = \frac{e^2}{4\pi\epsilon_0}16Z^6\int_0^{\infty}r_1^2e^{-\gamma r_1}dr_1\left[\frac{1}{r_1}\int_0^{r_1}r_2^2e^{-\gamma r_2}dr_2+\int_{r_1}^{\infty}r_2e^{-\gamma r_2}dr_2\right] \tag{2.34}$$

One can get the final result which is:

$$E_0^{(1)} = \frac{e^2}{4\pi\epsilon_0}\frac{5Z}{8a} \tag{2.35}$$

Using 2.18 we have that:

$$E_0^{(0)} = -\frac{1}{a}\frac{e^2}{4\pi\epsilon_0}Z^2 \tag{2.36}$$

Therefore, using first order perturbation theory the energy for the ground state is:

$$E_0 = \frac{1}{a}\frac{e^2}{4\pi\epsilon_0}\left(-Z^2+\frac{5Z}{8}\right) \tag{2.37}$$

2.3.2 Variational Method

We know that being E_0 the eigenvalue of our total hamiltonian for the ground state we have:

$$E_0 < \frac{\langle \phi | H | \phi \rangle}{\langle \phi | \phi \rangle} \equiv E[\phi] \tag{2.38}$$

for any trial wavefunction ϕ.

The trial wavefunction we use here is:

$$\phi(\vec{r}_1, \vec{r}_2) = \frac{Z_e^3}{\pi} e^{-Z_e(\vec{r}_1 + \vec{r}_2)/a} \tag{2.39}$$

The variational parameter is Z_e, the wave function is separable in the single-particle coordinates because it has the form $\phi_{1s}^{Z_e}(\vec{r}_1)\phi_{1s}^{Z_e}(\vec{r}_2)$.

$$E[\phi] = < \phi | T_1 + T_2 - \frac{e^2}{4\pi\epsilon_0} \frac{Z}{r_1} - \frac{e^2}{4\pi\epsilon_0} \frac{Z}{r_2} + \frac{e^2}{4\pi\epsilon_0} \frac{Z}{r_{12}} | \phi > \tag{2.40}$$

We take advantage of the virial theorem to determina the kinetic energy expected value. Viarial theorem establishes:

$$\langle T \rangle = -\frac{1}{2} \langle V \rangle \tag{2.41}$$

and for one-electron functions we have:

$$\left\langle \phi_{nlm}^{Z_e} | T_i | \phi_{nlm}^{Z_e} \right\rangle = -E_n(Z_e) \tag{2.42}$$

where we have used that $< nlmZ_e | V | nlmZ_e > = 2E_n$, this is a known result. We use also that:

$$< nlmZ_e | \frac{Z}{r_i} | nlmZ_e > = \frac{ZZ_e}{an^2} \qquad < \phi | \frac{1}{r_{12}} | \phi > = \frac{5}{8a} Z_e \tag{2.43}$$

Therefore we get to the following expression:

$$E[\phi] = \frac{1}{a} \frac{e^2}{4\pi\epsilon_0} \left[Z_e^2 - 2ZZ_e + \frac{5}{8} Z_e \right] \tag{2.44}$$

The value of Z_e which minimize the function $E[\phi]$ is:

$$Z_e^{min} = Z - \frac{5}{16} \tag{2.45}$$

Introducing this value in eq.[2.44] we have:

$$E[\phi]_{min} = \frac{1}{a} \frac{e^2}{4\pi\epsilon_0} \left(-Z^2 - \frac{5}{8} Z - \frac{25}{256} \right) \tag{2.46}$$

As we can see this is a better result than using first order perturbation theory.

2.4 Excited states

2.4.1 Perturbation theory

In order to study the excited states using perturbation theory we are interested in the matrix elements of the perturbative hamiltonian H' in the base of eigenfunctions of the non-perturbative hamiltonian H_0 that we call $|n_1 l_1 m_{l_1}\rangle |n_2 l_2 m_{l_2}\rangle \chi_{SM_S}$.

First of all, notice that because H' does not depend on the spins we have:

$$\langle \Psi_{a+}(1,2) | H' | \Psi_{b-}(1,2)\rangle = \langle \Psi_{a+}(\vec{r}_1, \vec{r}_2) | H' | \Psi_{b-}(\vec{r}_1, \vec{r}_2)\rangle \langle S=0 M_S=0 | S=1 M_S\rangle = 0 \tag{2.47}$$

and

$$\langle \Psi_{a-}(1,2) | H' | \Psi_{b+}(1,2)\rangle = \langle \Psi_{a-}(\vec{r}_1, \vec{r}_2) | H' | \Psi_{b+}(\vec{r}_1, \vec{r}_2)\rangle \langle S=1 M_S | S=0 M_S=0\rangle = 0 \tag{2.48}$$

for any set of quantum numbers $n_1, l_1, m_{l_1}, n_2, l_2, m_{l_2}$ which describe the radial functions that we symbolize with the letters a and b. In total, taking into account the spacial symmetry of the eigenfunctions we have:

$$\langle \Psi_{a\pm}(1,2) | H' | \Psi_{b\mp}(1,2)\rangle = 0 \qquad \langle \Psi_{a\pm}(1,2) | H' | \Psi_{b\pm}(1,2)\rangle = \langle \Psi_{a\pm}(\vec{r}_1, \vec{r}_2) | H' | \Psi_{b\pm}(\vec{r}_1, \vec{r}_2)\rangle \tag{2.49}$$

Then we only focus on matrix elements with same spacial symmetry. Now we wonder about any set of the single-particle quantum numbers. Let's describe then as:

$$|\Psi_{a\pm}(\vec{r}_1, \vec{r}_2)\rangle = |n_{1a} l_{1a} m_{l_{1a}}\rangle |n_{2a} l_{2a} m_{l_{2a}}\rangle \pm |n_{2a} l_{2a} m_{l_{2a}}\rangle |n_{1a} l_{1a} m_{l_{1a}}\rangle$$

$$\equiv |1a\rangle 2a\rangle \pm |2a\rangle 1a\rangle \tag{2.50}$$

Then we can express the expected value as:

$$\langle \Psi_{a\pm}(\vec{r}_1, \vec{r}_2) | H' | \Psi_{b\pm}(\vec{r}_1, \vec{r}_2)\rangle = \langle 1a2a | H' | 1b2b\rangle + \langle 2a1a | H' | 2b1b\rangle \pm \langle 1a2a | H' | 2b1b\rangle \pm \langle 2a1a | H' | 1b2b\rangle \tag{2.51}$$

So we are interested in determining any of the summings $\langle 1a2a | H' | 1b2b\rangle$ and that's what we are going to develope here:

$$\langle n_{1a} l_{1a} m_{l_{1a}} | \langle n_{2a} l_{2a} m_{l_{2a}} | | H' | n_{1b} l_{1b} m_{l_{1b}}\rangle |n_{2b} l_{2b} m_{l_{2b}}\rangle =$$

$$= \frac{e^2}{4\pi\epsilon_0} \int R^*_{n_{1a} l_{1a}}(r_1) Y^*_{l_{1a} m_{l_{1a}}}(\theta_1, \varphi_1) R^*_{n_{2a} l_{2a}}(r_1) Y^*_{l_{2a} m_{l_{2a}}}(\theta_2, \varphi_2) \frac{1}{r_{12}}$$

$$R_{n_{1b} l_{1b}}(r_1) Y_{l_{1b} m_{l_{1b}}}(\theta_1, \varphi_1) R_{n_{2b} l_{2b}}(r_2) Y_{l_{2b} m_{l_{2b}}}(\theta_2, \varphi_2) r_1^2 r_2^2 dr_1 dr_2 d\Omega_1 d\Omega_2 \tag{2.52}$$

Let's focus on the angular part of the integral. We have:

$$\int Y^*_{l_{1a} m_{l_{1a}}}(\theta_1, \varphi_1) Y^*_{lm}(\theta_1, \varphi_1) Y_{l_{1b} m_{l_{1b}}}(\theta_1, \varphi_1) d\Omega_1 \int Y^*_{l_{2a} m_{l_{2a}}}(\theta_2, \varphi_2) Y_{lm}(\theta_2, \varphi_2) Y_{l_{2b} m_{l_{2b}}}(\theta_2, \varphi_2) d\Omega_2 \tag{2.53}$$

Now let's suppose we are interested in the first excited states, that's it, the degenerate subspace is the corresponding to $n_1 = 1 n_2 = n$. That means in the independent model we keep one electron in $1s$ level and give freedom to the other electron to be in any other level n. This means the integrals we are interested in are:

$$\langle 100| \langle nl_{2a}m_{l_{2a}}| \, |H'| \, 100\rangle |nl_{2b}m_{l_{2b}}\rangle \tag{2.54}$$

and

$$\langle 100| \langle nl_{2a}m_{l_{2a}}| \, |H'| \, nl_{2b}m_{l_{2b}}\rangle |100\rangle \tag{2.55}$$

Now let's evaluate the part in eq. [2.53] of eq.[2.54]. For the first coordinate we have:

$$Y_{00}^2 \int Y_{lm}^*(\theta_1, \varphi_1) d\Omega_1 \tag{2.56}$$

which is zero unless $l = 0$ (and $m_l = 0$). So for the second integral we have:

$$Y_{00} \int Y_{l_{2a}m_{l_{2a}}}^*(\theta_2, \varphi_2) Y_{l_{2b}m_{l_{2b}}}(\theta_2, \varphi_2) d\Omega_2 = Y_{00}\delta_{l_{2a}l_{2b}}\delta_{m_{l_{2a}}m_{l_{2b}}} \tag{2.57}$$

therefore for that integral not to be zero we have that $l_{2a} = l_{2b}$ and $m_{l_{2a}} = m_{l_{2b}}$.

Now we evaluate eq.[2.55]. The first part of the integral eq.[2.53] is:

$$\int Y_{00}^*(\theta_1, \varphi_1) Y_{lm}^*(\theta_1, \varphi_1) Y_{l_{2b}m_{l_{2b}}}(\theta_1, \varphi_1) d\Omega_1 \tag{2.58}$$

the slection rules lead us to $m = m_{l_{2b}}$ and $l = l_{2b}$ in order to be non-zero. Now in the second integral we have:

$$Y_{00} \int Y_{l_{2a}m_{l_{2a}}}^*(\theta_2, \varphi_2) Y_{l_{2b}m_{l_{2b}}}(\theta_2, \varphi_2) d\Omega_2 = Y_{00}\delta_{l_{2a}l_{2b}}\delta_{m_{l_{2a}}m_{l_{2b}}} \tag{2.59}$$

therefore for that integral not to be zero we have that $l_{2a} = l_{2b}$ and $m_{l_{2a}} = m_{l_{2b}}$, exactly the same condition as before. This means that for this subspace H' does not couple states with different l and m_l. Therefore the first order energy correction is just:

$$E_{exc}^1 = \langle \Psi_{nlm\pm}(\vec{r}_1, \vec{r}_2) \, |H'| \, \Psi_{nlm\pm}(\vec{r}_1, \vec{r}_2)\rangle \tag{2.60}$$

where $\Psi_{nlm\pm}$ are:

$$|\Psi_{nlm\pm}\rangle = \frac{1}{\sqrt{2}} \left(|100\rangle|nlm\rangle \pm |nlm\rangle|100\rangle \right) |SM_S\rangle \tag{2.61}$$

Inserting in the expression above we have that:

$$E_{exc}^1 = \frac{1}{2} \left[\langle 100nlm \, |H'| \, 100nlm\rangle + \langle nlm100 \, |H'| \, nlm100\rangle \pm \langle 100nlm \, |H'| \, nlm100\rangle \pm \langle nlm100 \, |H'| \, 100nlm\rangle \right]$$

$$= \langle 100| \langle nlm \, |H'| \, 100\rangle |nlm\rangle \pm \langle 100| \langle nlm \, |H'| \, nlm\rangle |100\rangle \tag{2.62}$$

Let's define the real quantities J_{nl} and K_{nl} as:

$$J_{nl} = \langle 100| \langle nlm \, |H'| \, 100\rangle |nlm\rangle \qquad K_{nl} = \langle 100| \langle nlm \, |H'| \, nlm\rangle |100\rangle \tag{2.63}$$

The sign in front of K_{nl} depends inderectly on the spin-coupling of the electrons. Plus is for the triplet state and minus is for the single state so symbollicaly we can express this first orden energy as:

$$E_{exc}^1 = J_{nl} - \frac{1}{2}\left(1 + 4\vec{S}_1 \cdot \vec{S}_2\right)K_{nl} \tag{2.64}$$

Let's develope both expressions and you can see wht they are labeled with nl:

$$J_{nl} = \frac{e^2}{4\pi\epsilon_0}\sum_{k=0}^{\infty}\sum_{q=-k}^{k}\frac{4\pi}{2k+1}\int\frac{(r_<)^k}{(r_>)^{k+1}}\left|R_{10}(r_1)\right|^2\left|R_{nl}(r_2)\right|^2 r_1^2 r_2^2 dr_1 dr_2$$

$$\left|Y_{00}\right|^2\int Y_{kq}^*(\theta_1,\varphi_1)d\Omega_1\int\left|Y_{lm}(\theta_2,\varphi_2)\right|^2 Y_{kq}(\theta_2,\varphi_2)d\Omega_2 \tag{2.65}$$

where from the integral over Ω_1 we can notice that only the term of the sum with $k = 0$ and $q = 0$ is non-zero. Therefore we have:

$$J_{nl} = \frac{e^2}{4\pi\epsilon_0}\int\frac{1}{(r_>)}\left|R_{10}(r_1)\right|^2\left|R_{nl}(r_2)\right|^2 r_1^2 r_2^2 dr_1 dr_2$$

$$= \frac{e^2}{4\pi\epsilon_0}\int_0^{\infty}\left|R_{10}(r_1)\right|^2 r_1^2 dr_1\left[\frac{1}{r_1}\int_0^{r_1}\left|R_{nl}(r_2)\right|^2 r_2^2 dr_2 + \int_{r_1}^{\infty}\left|R_{nl}(r_2)\right|^2 r_2 dr_2\right] \tag{2.66}$$

Now we study K_{nl}:

$$K_{nl} = \frac{e^2}{4\pi\epsilon_0}\sum_{k=0}^{\infty}\sum_{q=-k}^{k}\frac{4\pi}{2l+1}\int\frac{(r_<)^k}{(r_>)^{k+1}}R_{10}^*(r_1)R_{nl}^*(r_2)R_{nl}(r_1)R_{10}(r_2)r_1^2 r_2^2 dr_1 dr_2$$

$$= \left|Y_{00}\right|^2\int Y_{kq}^*(\theta_1,\varphi_1)Y_{lm(\theta_1,\varphi_1)}d\Omega_1\int Y_{lm}^*(\theta_2,\varphi_2)Y_{kq}(\theta_2,\varphi_2)d\Omega_2 \tag{2.67}$$

The integrals over Ω_1 and Ω_2 are zero unless $k = l$ and $q = m$, therefore we have:

$$K_{nl} = \frac{e^2}{4\pi\epsilon_0}\frac{1}{2l+1}\int\frac{(r_<)^l}{(r_>)^{l+1}}R_{10}^*(r_1)R_{nl}(r_1)R_{nl}^*(r_2)R_{10}(r_2)r_1^2 r_2^2 dr_1 dr_2 =$$

$$= \frac{e^2}{4\pi\epsilon_0}\frac{1}{2l+1}\int_0^{\infty}R_{10}^*(r_1)R_{nl}(r_1)r_1^2 dr_1$$

$$\left[\frac{1}{(r_1)^{l+1}}\int_0^{r_1}(r_2)^l R_{nl}^*(r_2)R_{10}(r_2)r_2^2 dr_2 + (r_1)^l\int_{r_1}^{\infty}\frac{1}{(r_2)^{l+1}}R_{nl}^*(r_2)R_{10}(r_2)r_2^2 dr_2\right] \tag{2.68}$$

2.4.2 Handling the integrals

It is advantageous to express all the terms in the integrals as dimensionless quantities and not having to handle quantities as a, the Bohr radius, in the integrands for numerical reasons. We have integrals of the form:

$$I = \frac{e^2}{4\pi\epsilon_0}\int R_{n'l'}(r_1)R_{nl}(r_1)R_{n'l'}(r_2)R_{nl}(r_2)r_1^2 r_2 dr_2 dr_1 \tag{2.69}$$

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or interchanging r_1 with r_2.

If we extract the factor $a^{-3/2}$ from all the radial functions and make the change of variables $r' = \frac{r}{a}$ we have:

$$I = \frac{e^2}{4\pi\epsilon_0} \frac{1}{a^6} \int \int R_{n'l'}^{a=1}(r_1') R_{nl}^{a=1}(r_1') R_{n'l'}^{a=1}(r_2') R_{nl}^{a=1}(r_2') a^3 r_1'^2 r_2' a^2 dr_2' dr_1' =$$

$$= \frac{e^2}{4\pi\epsilon_0} \frac{1}{a} \int \int R_{n'l'}^{a=1}(r_1') R_{nl}^{a=1}(r_1') R_{n'l'}^{a=1}(r_2') R_{nl}^{a=1}(r_2') r_1'^2 r_2' dr_2' dr_1' \quad (2.70)$$

where $R^{a=1}$ are the radial equations with $a = 1$.

$$R_{nl}^{a=1}(r) = \left[\left(\frac{2Z}{n} \right)^3 \frac{(n-l-1)!}{2n[(n+l)!]} \right]^{1/2} e^{-\rho} (2\rho)^l \left[L_{n-l-1}^{2l+1}(2\rho) \right] \quad (2.71)$$

where ρ:

$$\rho = \frac{Zr'}{n} \quad (2.72)$$

This way we perform the integral numerically using a program we code:

$$I' = \int \int R_{n'l'}^{a=1}(r_1') R_{nl}^{a=1}(r_1') R_{n'l'}^{a=1}(r_2') R_{nl}^{a=1}(r_2') r_1'^2 r_2' dr_2' dr_1' \quad (2.73)$$

without any quantity with dimensions. And finally we do:

$$I = \frac{e^2}{4\pi\epsilon_0} \frac{1}{a} I' \quad (2.74)$$

Besides we can extract the normalization factors from the wavefunctions:

$$R_{nl}(r) = N_{nl}^{a=1} H(r) \qquad H(\rho) = e^{-\rho} (2\rho)^l \left[L_{n-l-1}^{2l+1}(2\rho) \right] \quad (2.75)$$

and

$$N_{nl}^{a=1} = \left[\left(\frac{2Z}{n} \right)^3 \frac{(n-l-1)!}{2n[(n+l)!]} \right]^{1/2} \quad (2.76)$$

Then defining:

$$I'' = \int \int H_{n'l'}^{a=1}(r_1') H_{nl}^{a=1}(r_1') H_{n'l'}^{a=1}(r_2') H_{nl}^{a=1}(r_2') r_1'^2 r_2' dr_2' dr_1' \quad (2.77)$$

we have:

$$I = \frac{e^2}{4\pi\epsilon_0} \frac{1}{a} (N_{nl}^{a=1})^2 (N_{n'l'}^{a=1})^2 I'' \quad (2.78)$$