E618: Pertubation theory for Helium atom

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The problem:

The Helium Atom includes 2 electrons with half spin. In this problem, the interaction between the electrons should be treated as a pertubation

(1) Write the Hamiltonian that describes the electrons in the atom.
(2) Find the stable states of the atom, neglecting the interaction between the electrons.
(3) What is the Ionization energy of the Helium atom in the zeroth order of the pertubation theory?
(4) What is the first order correction for the ionization energy?
(5) What is the leading order correction for the bound excited states?

The solution:

(1) The unpertubed hamiltonian of the helium atom includes the interactins between the two electrons and the nuclei. the interaction between the electrons is refered to as a pertubation. the total hamiltonian looks like that:

$$H = \frac{{P_1}^2}{2M} + \frac{{P_2}^2}{2M} - \frac{\alpha}{\boldsymbol{r}_1} - \frac{\alpha}{\boldsymbol{r}_2} + \frac{e^2}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|}$$

while $\alpha = ze^2$ and $z = 2$ for Helium.

(2) first let us define the base we are working in:

$$base = |\nu_1 l_1 m_1 \sigma_1\rangle \otimes |\nu_2 l_2 m_2 \sigma_2\rangle$$

These are the same quntum numbers that describe the electron in the hydrogen atom, only here we have two electrons. the eigen functions are thus, the same like in those of hydrogen:

$$\varphi^{\nu l m}(r, \Omega) = \langle r\Omega | lm\nu\rangle = R^{l\nu}(r) Y^{lm}(\Omega)$$

The energies of the unpertubed hamiltonian will be:

$$E_{l1m1\nu1, l2m2\nu2} = -M\alpha^2 \left(\frac{1}{(l_1 + \nu_1)^2} + \frac{1}{(l_2 + \nu_2)^2} \right)$$

The stable states are those with the energies between $E_{ground} = -M\alpha^2(1+1)$ and$E_\infty = -M\alpha^2(1+0)$ as above E_∞, the atom can be ionized (one of the electrons is taken to infinity). all the states below E_∞ are stable, and all the states above it belong to the continum. Thus, the stable states are those with at least one electron in the ground state ($l + \nu = 1$) if we have, for example, two electrons in the excited state, this is not a stable state, as the energy is greater than E_∞.

(3) The ionzation energy in the zeroth order will thus be:

$$E_{ionization} = E_\infty - E_{ground} = M\alpha^2$$

(4) The first order correction of the energy is:

$$\Delta E = \langle \Psi | V | \Psi \rangle$$

And in the ground state:

$$\Psi = [|l = 0, \nu = 1\rangle \otimes |l = 0, \nu = 1\rangle] \otimes [singlet]$$

When $singlet = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$ is the unsymetric spin state. The reason we took only the singlet state (and not the triplet) is that the "'general"' wave function has to be unsymetric to the exchange of the electrons (fermions),

and as the orbital function is symetric, the spin function has to be unsymetric.The pertubation is:$V = \frac{e^2}{|r_1 - r_2|}$ The correction to the energy will thus be calculated by the integral on the Radial functions:

$$\Delta E = \frac{e^2}{\pi^2} \int d\boldsymbol{r}_1 d\boldsymbol{r}_2 [R^{01}(r_1)R^{01}(r_2)]^* \frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} R^{01}(r_1)R^{01}(r_2)$$

$$\Delta E = (\frac{1}{\pi})^2 (\frac{z}{a_0})^6 e^2 \int dr_1 r_1^2 \mathrm{e}^{-\frac{zr_1}{a_0}} \int dr_2 r_2^2 \mathrm{e}^{-\frac{zr_2}{a_0}} \int d\Omega_1 d\Omega_2 \frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|}$$

when we use spherical coordinatesand,and the eigen function are those of the hydrogen atom. $a_0 = \frac{1}{me^2}$ is radius Bhor. first, we have to solve the integral over Ω

$$\int d\Omega_1 d\Omega_2 \frac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} = 4\pi \cdot 2\pi \int_{-1}^{1} dcos(\theta) \frac{1}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 cos(\theta)}}$$

$$= 8\pi^2 \frac{2}{2r_1 r_2} \sqrt{r_1^2 + r_2^2 - 2r_1 r_2 cos(\theta)}$$

$$= \frac{8\pi^2}{r_1 r_2} (r_1 + r_2 - |r_1 - r_2|)$$

$$= 16\pi^2 \cdot \frac{1}{r_>}$$

$$\Delta E = 16 \frac{z^6 e^2}{a_0^6} \int_0^\infty dr_1 r_1^2 \mathrm{e}^{-\frac{2zr_1}{a_0}} \int_0^\infty dr_2 r_2^2 \mathrm{e}^{-\frac{2zr_2}{a_0}} \frac{1}{r_>}$$

we divide the integral over r_1 into two integrals. one for $r_1 < r_2$, and one for $r_1 > r_2$. we then get

$$\Delta E = 16 \frac{z^6 e^2}{a_0^6} \int_0^\infty dr_2 r_2^2 \mathrm{e}^{-\frac{2zr_2}{a_0}} \cdot \left[\int_0^{r_2} dr_1 \frac{r_1^2}{r_2} \mathrm{e}^{-\frac{2zr_1}{a_0}} + \int_{r_2}^\infty dr_1 \frac{r_1^2}{r_1} \mathrm{e}^{-\frac{2zr_1}{a_0}} \right]$$

$$= -\frac{8z^5 e^2}{a_0^5} \int_0^\infty dr_2 r_2^2 \mathrm{e}^{-\frac{2zr_2}{a_0}} \cdot \left[\mathrm{e}^{-\frac{2zr_2}{a_0}} (r_2 + \frac{a_0}{z} + \frac{a_0^2}{2zr_2}) - \frac{a_0^2}{2zr_2} - \mathrm{e}^{-\frac{2zr_2}{a_0}} (r_2 + \frac{a_0}{2z}) \right]$$

$$= -\frac{4z^4 e^2}{a_0^4} \int_0^\infty dr_2 r_2^2 \mathrm{e}^{-\frac{4zr_2}{a_0}} + \frac{a_0}{z} r_2 \mathrm{e}^{-\frac{4zr_2}{a_0}} - \frac{a_0}{z} \mathrm{e}^{-\frac{2zr_2}{a_0}}$$

$$= -\frac{4z^4 e^2}{a_0^4} \cdot \left[2(\frac{-a_0}{4z})^3 + \frac{a_0}{z} (\frac{-a_0}{4z})^2 - \frac{a_0}{z} (\frac{-a_0}{2z})^2 \right]$$

$$\Delta E = \frac{5}{8} \frac{ze^2}{a_0} = \frac{5}{8} M\alpha^2.$$

(5) In the first excited state of helium, one of the electrons has $n = l + \nu = 2$ the other one got $n = 1$. The $n = 2$ electron can have both $l = 1$ and $l = 0$ states. first we deal the case in which both of the electrons got $l = 0$. The symetrical and unsymetrycal states will be:

$$\Psi_+ = \frac{1}{\sqrt{2}} (|l = 0, \nu = 2\rangle \otimes |l = 0, \nu = 1\rangle + |l = 0, \nu = 1\rangle \otimes |l = 0, \nu = 2\rangle) \otimes [singlet](degeneration = 1)$$

$$\Psi_- = \frac{1}{\sqrt{2}}\left(|l=0,\nu=2\rangle \otimes |l=0,\nu=1\rangle - |l=0,\nu=1\rangle \otimes |l=0,\nu=2\rangle\right) \otimes [triplet](degeneration=3)$$

and one can notice we attached a singlet (unsymetric) to the symetric orbital function and a triplet to the unsymetric orbital function in order to keep the general wave function unsymetric. in the case that 1 electron has $l=1$ and the other has $l=0$ we get:

$$\Psi_+ = \frac{1}{\sqrt{2}}\left(|l=1,m,\nu=1\rangle \otimes |l=0,\nu=1\rangle + |l=0,\nu=1\rangle \otimes |l=1,m,\nu=1\rangle\right) \otimes [singlet](degeneration=3)$$

$$\Psi_- = \frac{1}{\sqrt{2}}\left(|l=1,m,\nu=1\rangle \otimes |l=0,\nu=1\rangle - |l=0,\nu=1\rangle \otimes |l=1,m,\nu=1\rangle\right) \otimes [triplet](degeneration=9)$$

we will now want to calculate the change in the energy due to pertubation:

$$\Delta E = \langle \Psi | V | \Psi \rangle$$

and thus:

$$\Delta E = \int d\boldsymbol{r}_1 d\boldsymbol{r}_2 \left(\varphi^{100}(r_1,\Omega_1)\varphi^{\nu lm}(r_2,\Omega_2) \pm \varphi^{100}(r_2,\Omega_2)\varphi^{\nu lm}(r_1,\Omega_1)\right)^* \frac{1}{|\boldsymbol{r}_1 - _2|}\varphi^{100}(r_1,\Omega_1)\varphi^{\nu lm}(r_2,\Omega_2) \pm$$

$$\pm\varphi^{100}(r_2,\Omega_2)\varphi^{\nu lm}(r_1,\Omega_1) = J \pm K$$

when $\varphi^{\nu lm}(r,\Omega)$ was defined in section 2 and $\varphi^{100}(r,\Omega)$ goes for the electron in the ground state. J and K are the self and exchange integral that were discussed in class. note that this is just a general form and we get different J and K values for different quantum numbers. All together we get a 16×16 diagonal matrix. the reason that we got a diagonal matrix relates to our choice of base (two particles base) where between two states, atleast one of the quantum numbers is different. in a one particle base we would have got off diagonal elements.