Ay126: Homework 2

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I. Total Potential Energy of Helium Atom. The Schrodinger equation is $\hat{H}\psi = E\psi$. For the Helium atom it is

$$\left(-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \right)\psi(\mathbf{r_1}, \mathbf{r_2}) = E\psi(\mathbf{r_1}, \mathbf{r_2}). \tag{1}$$

The "orbital" approach consists of using unperturbed wavefunctions as a starting point. For this calculation, you are not aware of the Pauli exclusion principle. Thus, your trial wave function, for each of the two electrons is the $1s$ wave function but for a $Z = 2$ Hydrogen-like atom:

$$\psi(\mathbf{r_1}, \mathbf{r_2}) = \psi_{1s}(r_1)\psi_{1s}(r_2) \propto Z^3 \exp[-Z(r_1 + r_2)] \tag{2}$$

You, however (as a part of the "variational" approach) allow for the screening of the nucleus by replacing Z in the above equation by α (but *not in the Hamiltonian*, naturally). The eigen-energy is given by

$$E = \frac{\int \psi(r_1, r_2)\hat{H}\psi(r_1, r_2)dv_1 dv_2}{\int \psi(r_1, r_2)\psi(r_1, r_2)dv_1 dv_2} \tag{3}$$

where dv_j is a volume element. The resulting eigen-energy[1] is a function of Z and α. Minimize it with respect to α find $E = -(Z - 5/16)^2 = -2.847$ Hartree. This can be compared with the experimental value of -2.90372 Hartree. The discrepancy arises of not accounting for the repulsion of electrons. [2]

II. Spectroscopic Terms: Pair of Electrons with the same n, l. In the class we worked out the spectroscopic terms of the ground state of carbon, $1s^2 2s^2 2p^2$. We noted that each electron is specified by (n, l, m_l, m_s). The possible number of quantum number sets for each p electron is thus $(2l + 1)(2s + 1) = 6$. With Pauli's exclusion principle and noting that electrons are not distinguishable we find that there are 15 possible combinations

[1] It may help review/consult a QM textbook on various integrals related to Legendre expansion of the r_{12}^{-1}.

[2] The breakthrough was undertaken by E. Hylleraas; see §A

of pairs of sets of quantum numbers or *microstates*. We worked out, with some effort, that the fifteen microstates mapped to three spectroscopic terms: ^1S, ^3P and ^1D. The purpose of this problem is to develop a program which, given a number of identical electrons will produce the spectroscopic terms.

A. Consider an atom with the valence (open shell) electrons being two d electrons, each in a different energy quantum level, n. How many pairs of microstates does this atoms have? List the resulting 10 spectroscopic terms. [5points]

B. Consider the case of Titanium ($Z = 22$). The electronic configuration is Ar$4s^2 3d^2$. Apply "Trick 1" (see SRK Notes) to the previous answer and show that the ground state of Ti has five spectroscopic terms: three singlet (^1S, ^1D and ^1G) and two triplets (^3P and ^3F). [5 points]

C. Apply your computer program and reproduce the above result. [10 points]

D: Optional. Expand the capabilities of your computer program to accept three electrons. Show that the spectroscopic terms of the ground state of nitrogen, $1s^2 2s^2 2p^3$ are ^2P, ^2D and ^4S. Using Hund's rule order the 3 spectroscopic terms in energy. Research and find a Grotrian diagram of NI. Admire the beautiful Grotrian diagram of Nitrogen. [15 points]

III. Far-infrared lines of abundant elements. Nitrogen and Oxygen are amongst the most abundant metals. However, astronomers do not seem to talk about the fine structure lines of NI or OII. Research and explain. [5 points]

IV. Fine Structure Lines of Highly Ionized Species. Using the simple formulation discussed in the class compute the energy of the fine structure line of NeV. Compare this to the measured value. [5 points]

V. Fine Structure Lines from the IGM/CGM. Speculate about the possibility of detecting fine structure lines from the IGM/CGM. Feel free to talk to students and post-docs working on IGM/CGM and also those involved in far-infrared astronomy. Assuming you could detect lines from major metals what unique diagnostics would you these lines provide. [10 points]

A Hylleraas solution

Egil Hylleraas, a self-taught young man from a farming family in Finland, solved the problem using only three coordinates: $s = r_1 + r_2$, $t = r_2 - r_1$ and $u = |\mathbf{r_1} - \mathbf{r_2}|$. His trial solution was $\psi = \exp(-\alpha r_1 - \alpha r_2)(1 + bu)$. Notice that as $u \to 0$ the additional contribution to ψ^2 goes to zero and thus reduces the probability of two electrons coming close to each other. Hylleraas found $\alpha = 1.849$ and $b = 0.364$ minimizes the eigen-energy. The resulting value of $E = -2.8913$ Hartree is within 0.42% of the measured value. Incidentally, Hylleraas was one of the founders of CERN.