MEST - Assignment 2

Due date: 04/03/2024
(For each solution, show your work through a set of important steps. Use Dirac Notation
for all questions)

Slater determinant, perturbation and Variation principle

1. Consider a system (for example, a molecule) consisting of three electrons with spins α, α, β occupying three different MOs ψ_1, ψ_2 and ψ_3 that are spatially different. (2 + 3 + 5 pts)
   a) List the possible Slater determinants (SDs) for this case.
   b) Are these SDs suitable approximate wave functions of such a system [Hint: check if they are pure spin states?]
   c) Construct suitable approximate wavefunctions that are pure spin states [Hint: try to diagonalize the S^2 matrix in this SD basis].

2. a) For a two electron system (e.g. He, H_2) express the wavefunction explicitly from the SD both for singlet and triplet cases. (3)
   b) Can it be separable into spin and spatial part for both the cases? If it does, which part will be symmetric and which part will be antisymmetric? (2)
   c) For the spatial portion, what will be the dimensionality of the nodal surface for the triplet wavefunction of He and H_2? Give justification of your answer [Hint: read the paper by Smolenskii et. al. attached in the notes folder]. (4)

3. Consider a charged particle in one-dimensional harmonic oscillator potential. Suppose we turn on a weak electric field (E) so that the potential is shifted by an amount $V' = -qEx$ (q is the charge of the particle). (3 + 3 pts)

   (a) Show that there is no first-order change in the energy levels and calculate the second order correction.

   (b) The Schrodinger equation can be solved exactly in this case by a change of variables. Find the exact energies and show that they are consistent with the perturbation theory approximation.

4. In relativistic theory the kinetic energy is given by the expression $T = \sqrt{p^2c^2 + m^2c^4} - mc^2$. This relativistic equation for kinetic energy reduces to classical result in nonrelativistic limit $p << mc$; expanding in powers of small number (p/mc) we have the lowest-order relativistic contribution to the Hamiltonian is $V' = -\frac{\hat{p}^4}{8m^3c^2}$ where p is momentum operator. This term is responsible for orbital contraction in elements (e.g Lanthanide contraction is partially attributed to relativistic effects) and shift the energy levels. Prove that the first order relativistic energy correction is given by:

$$E_r^{(1)} = -\frac{E_n^2}{2mc^2}\left[\frac{4n}{l + \frac{1}{2}} - 3\right]$$

(Use: $\langle \frac{1}{\hat{r}} \rangle = \frac{1}{an^2}$ and $\langle \frac{1}{\hat{r}^2} \rangle = \frac{1}{a^2 n^3 \left(l+\frac{1}{2}\right)}$) (5 pts)

5. Using a wavefunction based on hydrogenic orbitals the helium atom ground state energy differs by ≈ 0.15 a.u. from experimental values. This can be improved by treating the the nuclear charge, Z, as a variational parameter. Derive the general expression for energy expectation value in terms of Z for the ground-state wavefunction given by

$$\Psi(\bar{r}_1, \bar{r}_2) = \phi_{1s}(r_1)\phi_{1s}(r_2)\frac{1}{\sqrt{2}}\left[\alpha(\omega_1)\beta(\omega_2) - \alpha(\omega_2)\beta(\omega_1)\right] \tag{1}$$

To simplify the evaluation, use the spherical harmonic expansion of interelectronic repulsion term

$$\frac{1}{r_{12}} = \frac{1}{r_>}\sum_{l=0}^{\infty}\left(\frac{r_<}{r_>}\right)^l \frac{4\pi}{2l+1}\sum_{m=-l}^{l}Y_l^m(\theta_1, \phi_1)Y_l^m(\theta_2, \phi_2) \tag{2}$$

Here $r_> = \max(r_1, r_2)$ and $r_< = \min(r_1, r_2)$. Find the optimal Z value and the corresponding ground-state energy. (Hint: for the evaluation of this integral, split the integral into two parts corresponding to $(r_1 > r_2)$ and $(r_2 > r_1)$; and note that only l=0 contributes in the case of $1s$ orbitals). (10pts and you have taken the first steps in becoming a quantum chemist)

Total angular momentum, Term symbol and Spin-orbit coupling

1. Compute the following commutators given that $J(1)$ and $J(2)$ are individual angular momentum operators and J is total angular momentum operator (5 pts):

   (a) $[J(1) \cdot J(2), J]$
   (b) $[J(1) \cdot J(2), J^2]$
   (c) $[J^2, J(1)^2]$
   (d) $[J^2, J(1)_z]$
   (e) $[J^2, J_z]$

2. The spin-orbit coupling term is given by the expression $H_{SO} = \xi L.S$ where, ξ is spin-orbit constant and L and S are orbital and spin angular momentum. In class we have seen that emission line of atomic spectra of sodium split into closely spaced doublet having wavelength 5889.96 and 5895.93 angstrom. Calculate the spin orbit constant ξ and energy of ^2P level. (2 pts)

3. The shift in energy levels due to spin-orbit coupling (for $l > 0$) is given by expression:

$$\Delta E = \frac{(E_n)^2}{mc^2}\left(\frac{n\left[j(j+1) - l(l+1) - s(s+1)\right]}{l(l+1/2)(l+1)}\right)$$

where, E_n is nth bohr orbital energy $(2 + 2 + 2 + 2$ pts$)$

(a) Derive general expression for difference between the $j = l + 1/2$ and $j = l - 1/2$ levels

(b) Calculate the energy difference due to spin-orbit coupling between 3p $^2P_{1/2}$ and $^2P_{3/2}$ states of a hydrogen atom.

(c) Go online to the NIST Atomic Spectra Database (Energy Levels), retrieve the experimental energies for the two states (enter the keyword "H I" to get the energy levels for the neutral hydrogen atom), and compare the experimental difference to your calculated difference and comment on it.

(d) Calculate the wavelength of the transition 3p $(^2P_{1/2}) \rightarrow$ 1s $(^2S_{1/2})$ and 3p $(^2P_{3/2}) \rightarrow$ 1s $(^2S_{1/2})$. Briefly discuss their location in electromagnetic spectrum and their separation.