PRACTICE PROBLEMS 2

1. Based on your knowledge of the first few hydrogenic eigenfunctions, deduce general formulas, in terms of \( n \) and \( \ell \), for (i) the number of radial nodes in an atomic orbital (ii) the number of angular nodes (iii) the total number of nodes

2. Recall that a filled or half-filled p, d or f shell has spherical symmetry. Accordingly, go through the periodic table from \( Z = 36 \) to \( Z = 54 \) and predict which atomic ground states will have spherically-symmetrical electronic distributions (multiplet-S term symbols).

3. Give the electronic configurations and term symbols of the first excited electronic states of the atoms up to \( Z = 10 \).

4. Using an optimized variational wavefunction of the form

\[
\psi(r_1, r_2) = e^{-\alpha(r_1+r_2)}
\]

estimate the ground-state energy of Li\(^+\).

5. Calculate the energy of the hypothetical 1s\(^3\) state of the Li atom using the optimized variational wavefunction

\[
\psi(1, 2, 3) = e^{-\alpha(r_1+r_2+r_3)}
\]

Neglect electron spin, of course. Compare with the experimental ground-state energy, \( E_0 = -7.478 \) hartrees. Comment on the applicability of the variational theorem.

6. After separation of variables in the \( H_2^+ \) problem, the function \( M(\mu) \) obeys the differential equation

\[
\frac{d}{d\mu}(\mu^2 - 1)\frac{dM}{d\mu} + \left( A + 2R\mu + \frac{1}{4}R^2E\mu^2 - \frac{\lambda^2}{\mu^2 - 1} \right)M(\mu) = 0
\]

where \( A \) is a constant, \( R \) is the internuclear distance, \( \lambda \) is the angular momentum quantum number, and \( E \) is the energy, a negative number for
bound states. Find the asymptotic solution of the above equation as \( \mu \to \infty \).

7. Predict the electronic configuration and term symbol for the ground state of the superoxide ion \( \text{O}_2^- \) and of the peroxide ion \( \text{O}_2^{2-} \).

8. Propose electron configurations and term symbols for the two lowest singlet excited states of \( \text{O}_2 \).

9. Give the electron configuration, term symbol and bond order for the ground state of each of the following species: \( \text{N}_2^+ \), \( \text{N}_2 \) and \( \text{N}_2^- \).

10. The overlap integral between a 1s and a 2p\( \sigma \) orbital on nuclei separated by a distance \( R \) (in bohr) is given by

\[
S = \left( R + R^2 + \frac{R^3}{3} \right) e^{-R}
\]

Determine the value of \( R \) which gives the maximum overlap. (It may be of interest that the internuclear distance in HF equals 0.916\( \text{Å} \).)

11. Carry out a Hückel calculation on the allyl radical

\[
\text{CH}_2 = \text{CH} - \text{CH}_2^\circ
\]

Determine, in terms of the empirical parameters \( \alpha \) and \( \beta \), the energies of the \( \pi \)-molecular orbitals, the resonance stabilization energy and the frequency of the lowest-energy electronic transition.
ANSWERS

1. Hydrogenic orbital $\psi_{n\ell}$ has $n - \ell - 1$ radial nodes, $\ell$ angular nodes, $n - 1$ total nodes.

2.

$\begin{align*}
Z=36 & \quad \text{Kr} \quad [\text{Kr}] \quad ^1S_0 \\
Z=37 & \quad \text{Rb} \quad [\text{Kr}]5s \quad ^2S_{1/2} \\
Z=38 & \quad \text{Sr} \quad [\text{Kr}]5s^2 \quad ^1S_0 \\
Z=42 & \quad \text{Mo} \quad [\text{Kr}]5s4d^5 \quad ^7S_3 \\
Z=43 & \quad \text{Tc} \quad [\text{Kr}]5s^24d^5 \quad ^6S_{5/2} \\
Z=46 & \quad \text{Pd} \quad [\text{Kr}]4d^{10} \quad ^1S_0 \\
Z=47 & \quad \text{Ag} \quad [\text{Kr}]5s4d^{10} \quad ^2S_{1/2} \\
Z=48 & \quad \text{Cd} \quad [\text{Kr}]5s^24d^{10} \quad ^1S_0 \\
Z=51 & \quad \text{Sb} \quad [\text{Kr}]5s^24d^{10}p^3 \quad ^4S_{3/2} \\
Z=54 & \quad \text{Xe} \quad [\text{Kr}]5s^24d^{10}p^6 \quad ^1S_0
\end{align*}$

3.

$\begin{align*}
Z=1 & \quad \text{H} \quad 2s \quad ^2S_{1/2} \quad \text{or} \quad \text{S} 2p \quad ^2P_{1/2} \\
Z=2 & \quad \text{He} \quad 1s2s \quad ^3S_1 \\
Z=3 & \quad \text{Li} \quad 1s^22p \quad ^2P_{1/2} \\
Z=4 & \quad \text{Be} \quad 1s^22s2p \quad ^3P_0 \\
Z=5 & \quad \text{B} \quad 1s^22s2p^2 \quad ^4P_{1/2} \\
Z=6 & \quad \text{C} \quad 1s^22s^22p^2 \quad ^1P_1 \quad \uparrow \downarrow
\end{align*}$
\[
\begin{align*}
Z = 7 & \quad \text{N} \quad 1s^22s^22p^3 \quad ^2S_{1/2} \quad \uparrow \uparrow \downarrow \\
Z = 8 & \quad \text{O} \quad 1s^22s^22p^4 \quad ^1P_1 \quad \downarrow \uparrow \downarrow \\
Z = 9 & \quad \text{F} \quad 1s^22s2p^6 \quad ^2S_{1/2} \\
Z = 10 & \quad \text{Ne} \quad 1s^22s^22p^53s \quad ^3P_0
\end{align*}
\]

4. Variational energy formula:

\[
E(\alpha) = \alpha^2 - 2Z - \frac{5}{8}\alpha
\]

Minimum for \( \alpha = Z - 5/16 \), \( E = -(Z - 5/16)^2 \). For \( Z = 3 \), \( E = -7.223 \) hartrees.

5. Components of above energy formula: each electron has KE = \( \alpha^2/2 \), nuclear attraction PE = \( -Z\alpha \). Each electron pair has repulsion PE = \( 5\alpha/8 \). For Li, with 3 electrons and 3 pairs,

\[
E(\alpha) = \frac{3}{2}\alpha^2 - 3Z\alpha + 3 \times \frac{5}{8}\alpha
\]

Minimum for \( \alpha = Z - 15/24 \) gives \( E = -8.4609 \) hartrees. Lower than \( E_0 = -7.478 \) but wavefunction is ILLEGAL!

6. As \( \mu \to \infty \) the largest terms are those containing \( \mu^2 \). Thus

\[
\mu^2 M''(\mu) + \frac{1}{4}R^2E\mu^2 M(\mu) \approx 0
\]

Cancel \( \mu^2 \) and find solution

\[
M(\mu) \approx \text{const} e^{-R\sqrt{-E\mu}/2}
\]

7. \( O_2 \) has configuration \( \ldots 3\sigma_g^21\pi_u^41\pi_g^2 \quad ^3\Sigma_g^- \)

\( O_2^- \) has configuration \( \ldots 3\sigma_g^21\pi_u^41\pi_g^3 \quad ^2\Pi_g \)
O$_2^{-2}$ has configuration \ldots 3\sigma_g^2\pi_u^4\pi_g^4 \Sigma_g^+$

8. Both excited states have same configuration as ground state, \ldots 3\sigma_g^2\pi_u^4\pi_g^2, but with the following occupancy of 1\pi_g orbitals:

\[
\begin{array}{cc}
\uparrow & \downarrow \\
1\Sigma_g^+ & \text{and} \\
\downarrow & \uparrow \\
1\Delta_g
\end{array}
\]

The plus superscript in the first term symbol is rather tricky. Don’t worry about it. But if you insist \ldots two-electron singlet spin state has anti-symmetric spin function, thus must have symmetric orbital function like \(\pi_x(1)\pi_y(2) + \pi_y(1)\pi_x(2)\) which doesn’t change sign upon transformation \(\phi \rightarrow -\phi\). Singlet oxygen and other active oxygen species are involved in biochemical lipid oxidations.

9. \(N_2 \ldots 1\pi_u^43\sigma_g^2 \Sigma_g^+ \text{BO}=3\)

\(N_2^+ \ldots 1\pi_u^43\sigma_g \Sigma_g^+ \text{BO}=2.5\)

\(N_2^- \ldots 1\pi_u^43\sigma_g^2\pi_g \Pi_g \text{BO}=2.5\)

10. Setting \(dS/dR = 0 \text{ find maximum at } R = 2.1038 \text{ Bohrs or } 2.1038 \times .593 = 1.115 \text{ } \AA\).

11. Secular determinant

\[
\begin{vmatrix}
x & 1 & 0 \\
1 & x & 1 \\
0 & 1 & x
\end{vmatrix} = x^3 - 2x = 0
\]

where \(x = (\alpha - E)/\beta\). Roots \(x = 0, \pm \sqrt{2}\), thus \(E = \alpha - \sqrt{2}\beta, \alpha, \alpha + \sqrt{2}\beta\). Remember both \(\alpha\) and \(\beta\) are negative. Ground state energy (3 electrons) = \(2(\alpha + \sqrt{2}\beta) + \alpha = 3\alpha + 2\sqrt{2}\beta\). One localized \(\pi\)-orbital plus one unpaired electron would have energy = \(2(\alpha + \beta) + \alpha = 3\alpha + 2\beta\). Resonance stabilization energy = \((2 - 2\sqrt{2})\beta = -.828\beta = .828|\beta|\). Lowest energy electronic transition given by

\[
\frac{hc}{\lambda} = \sqrt{2}|\beta|
\]