(1) (5 pts) Using the variation method for the standard 1-dimensional particle in a box problem, a student uses the trial function \( \phi = \alpha x (L - \alpha x) \) where \( \alpha \) is a variational parameter and the box is defined between \( x=0 \) and \( x=L \). Upon minimizing the trial energy with respect to \( \alpha \), s/he finds that the trial energy is lower than the exact ground state energy!! Certainly this can’t be right, but what is wrong? (be specific)

\[
\phi \text{ must satisfy the boundary conditions, but } \quad \phi(L) \neq 0
\]
(2) (30 pts) Consider the \( n = 2 \rightarrow 3 \) ro-vibrational band of the \(^{11}\text{B}^{19}\text{F}\) molecule within the harmonic oscillator, rigid-rotor approximation. The harmonic frequency and rotational constant of this isotopomer are equal to 1402.13 cm\(^{-1}\) and 1.50724 cm\(^{-1}\), respectively.

\[
[m^{(19)\text{F}}] = 18.9984 \text{ amu},
&m^{(11)\text{B}} = 11.0093 \text{ amu},
&m^{(10)\text{B}} = 10.0129 \text{ amu}
\]

(a) Determine the frequency (in cm\(^{-1}\)) of the P-branch transition with \( J = 4 \rightarrow 3 \).

\[
\frac{E_{nJ}}{\hbar c} = \frac{\tilde{\omega}_e (n + 1/2) + \tilde{b} J (J + 1)}{\hbar c} \]
\[
\Delta E = \tilde{\omega}_e \left[ \frac{3}{2} - \frac{5}{2} \right] + \tilde{b} \left[ 12 - 20 \right] = \tilde{\omega}_e - 8 \tilde{b}
\]
\[
= 1390.07 \text{ cm}^{-1}
\]

(b) Compared to your result of part (a), how would the use of a Morse potential function (instead of a harmonic oscillator) qualitatively change it?

The introduction of anharmonicity by the Morse potential would yield a lower transition frequency.

(c) Predict the harmonic frequency (in cm\(^{-1}\)) for the \(^{10}\text{B}^{19}\text{F}\) isotopomer.

\[
\tilde{\omega}_e \left( ^{10}\text{B}^{19}\text{F} \right) = \frac{\tilde{\omega}_e \left( ^{11}\text{B}^{19}\text{F} \right) \sqrt{\frac{\mu^{(11)\text{B}}}{\mu^{(10)\text{B}}}}}{6.55707 \text{ amu}}
\]
\[
= 1402.13 \sqrt{\frac{18.9984}{6.55707}} = 1445.62 \text{ cm}^{-1}
\]

(d) Predict the equilibrium bond length (in Å) of BF.

\[
\tilde{b} = \frac{\hbar}{8\pi^2 \mu c r^2} \quad \Rightarrow \quad \frac{r^2}{\hbar^2} = \frac{6.62608 \times 10^{-24}}{\left(8\pi^2\right)^2 \left(6.97018 \times 10^{-18}\right) \left(1.66054 \times 10^{-27}\right) \left(2.92792 \times 10^9\right) \times 1.50724}
\]
\[
= 1.6046 \times 10^{-20} \text{ m}^2
\]
\[
r = 1.2667 \times 10^{-10} \text{ m} = 1.2667 \text{ Å}
\]
(3) (15 pts.) A normalized trial function of the form (in atomic units) \( \phi = \left[ \frac{(2\beta)^7}{4\pi\beta^6} \right]^{1/2} r^2 e^{-\beta r} \), where \( \beta \) is an adjustable parameter, is used in the variation method to obtain the lowest possible energy for the hydrogen atom ground state. An intermediate result along this process is \( \int \phi H \phi d\tau = \frac{\beta^2}{10} - \frac{\beta}{3} \).

(a) Complete the variational calculation to obtain the optimal \( \beta \) and the best value of the trial energy.

\[
\text{minimize } E_{\text{trial}} \text{ wrt } \beta \quad \frac{\partial}{\partial \beta} \left[ \frac{\beta^2}{10} - \frac{\beta}{3} \right] = 0
\]

\[
\frac{2\beta}{10} - \frac{1}{3} = 0 \quad \Rightarrow \quad \beta_{\text{opt}} = \frac{5}{3}
\]

\[
E = \frac{1}{10} \left( \frac{5}{3} \right)^2 - \frac{1}{3} \left( \frac{5}{3} \right) = \frac{-25}{90} = \frac{-5}{18} \quad \text{a.u.}
\]

(b) What is the percent error in this result? Qualitatively, can you explain why this trial function maybe doesn’t perform so well?

exact result: \( E_n = -\frac{1}{2} \) a.u.  

\[
\% \text{ error} = -0.5 - (-0.2 \pi^2) \times 100 = 44.4 \%
\]

(4) (30 pts) Consider the C atom.

(a) Write the full hamiltonian operator for this atom using SI units. Feel free to use summation symbols but completely specify the limits.

\[
\hat{H} = -\frac{\hbar^2}{2m_e} \sum_{\alpha=1}^{6} \nabla^2_{\alpha} - \frac{6e^2}{4\pi\varepsilon_0} \sum_{\alpha=1}^{6} \frac{1}{r_\alpha} + \sum_{\alpha=1}^{6} \sum_{\beta \geq \alpha} \frac{e^2}{4\pi\varepsilon_0 r_{\alpha\beta}}
\]

(b) Consider its \( 1s^22s^22p^2 \) ground state configuration. What would you predict its ground state level to be? (give the term symbol)

\[
\begin{array}{ccc}
\text{max } S : & 1 & (\text{ triplet}) \\
\text{max } L : & 1 & (\text{ P}) \\
\text{min } J : & 0 & \\
\end{array}
\]

\[
\begin{array}{c}
\text{3P_0}
\end{array}
\]
(c) Now consider its \( 1s^22s^22p^13p^1 \) excited state configuration. What is the energy of this state within the independent particle approximation? (use atomic units)

\[
E_{\text{e.p.a.}} = 2E_{1s} + 2E_{2s} + E_{2p} + E_{3p} = \frac{-2}{2n^2} + \frac{-36}{2n^2} = -51.5 \text{ a.u.}
\]

(d) Now determine all the possible terms and levels of the excited configuration of part (c), i.e., find the term symbols. How many states are associated with each term?

\[
\begin{align*}
&l_1 = \frac{1}{2} \quad L = 2, 1, 0 \quad 3D, \quad 3P, \quad 3S, \quad 1D, \quad 1P, \quad 1S \quad \text{terms} \\
&l_2 = \frac{1}{2} \quad S = 1, 0 \\
&l_2 = -\frac{1}{2} \quad S = 1, 0
\end{align*}
\]

\[
3D_3, \quad 3D_2, \quad 3D_1, \quad 1D_2, \quad 1D_1, \quad 1P_2, \quad 1P_1, \quad 3P_1, \quad 3P_0, \quad 1S_1, \quad 1S_0
\]

3 + 1 = 4 states

(e) From your results of part (d), choose the level with the largest value of \( J \) and write a Slater determinant wavefunction for the state with \( M_J = +J \). Be as specific as possible in labeling the spin-orbitals chosen for your determinant. (Hint: remember that \( M_J = M_L + M_S \) and use this to determine which \( p_m \) orbitals are occupied) For half credit, you can just choose to write a Slater determinant for this electron configuration choosing any valid spin-orbital combination.

For \( J > 3 \), corresponding to \( 3D_3 \), need \( m_s = 1, \ m_L = 2 \)

\[
\begin{align*}
1s\alpha & \quad 1s\beta \\
2s\alpha & \quad \frac{1}{\sqrt{6!}} \\
2s\beta & \quad 2p_\uparrow \quad 2p_\downarrow \\
3p_\alpha & \quad 3p_\beta
\end{align*}
\]

\[
\begin{align*}
1s(1) & \quad - \quad - \quad - \quad - \quad - \quad 1s(6) \quad \alpha(1) \\
1s(1) & \quad - \quad - \quad - \quad - \quad - \quad 1s(6) \quad \beta(6) \\
2s(1) & \quad - \quad - \quad - \quad - \quad - \quad 2s(6) \quad \alpha(6) \\
2s(1) & \quad - \quad - \quad - \quad - \quad - \quad 2s(6) \quad \beta(6) \\
2p_\uparrow(1) & \quad - \quad - \quad - \quad - \quad - \quad 2p_\uparrow(6) \quad \alpha(6) \\
2p_\uparrow(1) & \quad - \quad - \quad - \quad - \quad - \quad 2p_\uparrow(6) \quad \beta(6) \\
3p_\uparrow(1) & \quad - \quad - \quad - \quad - \quad - \quad 3p_\uparrow(6) \quad \alpha(6) \\
3p_\uparrow(1) & \quad - \quad - \quad - \quad - \quad - \quad 3p_\uparrow(6) \quad \beta(6)
\end{align*}
\]
(5) (10 pts) Consider a hydrogen atom in a 2p excited state with a wavefunction given by:

\[ \psi_{2p_\ell} = R_{2,\ell}(r) Y_{1,0}(\theta, \phi), \text{ where (in atomic units) } R_{2,\ell} = \frac{1}{\sqrt{24}} r e^{-r/2} \text{ and } Y_{1,0} = \frac{1}{2} \sqrt{3} \cos \theta. \]

(a) What is the radial distribution function, \( P(r) \), for this state? (be specific)

\[ P(r) = |R_{2,1}|^2 r^2 = \frac{1}{24} r^4 e^{-r} \]

(b) Calculate the most probable distance (in a.u.) of the electron from the nucleus for this state.

\[ \frac{dP(r)}{dr} = 0 = -\frac{r^4}{24} e^{-r} + \frac{4}{24} r^3 e^{-r} \]

\[ = -r + 4 \]

\[ r_{mp} = 4 \text{ a.u.} \]

(6) (10 pts)

(a) Describe the major features of the Born-Oppenheimer approximation and its impact on solutions to the molecular Schrödinger equation.

Since the nuclei masses >> electron mass, their velocities are very different so the e⁻'s can instantaneously adapt to changes in the nuclear coordinates, leading to 2 separate S.E.'s: one for e⁻ motion (as function of nuclear coord) & one for nuclear motion.

(b) Define the the Pauli Principle as it applies to electrons.

The total (space + spin) wavefunction must be antisymmetric with respect to pairwise interchanges of electrons.