1. Consider a linear conjugate hydrocarbon $C_3$. According to the LCAO - MO theory, the molecular orbital can be approximated with a combination of three linearly-independent real functions $\phi_1, \phi_2, \phi_3$:

$$\psi = c_1\phi_1 + c_2\phi_2 + c_3\phi_3$$

where $\psi$ is the trial variation function and the coefficient $c_j$ are parameters to be optimized by minimizing the variational integral:

$$W(c_1, c_2, c_3) = \frac{\int \psi^* \hat{H} \psi d\tau}{\int \psi^* \psi d\tau}$$

(A) Please show that

$$W(c_1, c_2, c_3) = \frac{\int \psi^* \hat{H} \psi d\tau}{\int \psi^* \psi d\tau} = \sum_{j=1}^{3} \sum_{k=1}^{3} c_j c_k H_{jk}$$

$$\sum_{j=1}^{3} \sum_{k=1}^{3} c_j c_k S_{jk}$$

where $H_{jk} = \int \phi_j \hat{H} \phi_k d\tau$ and $S_{jk} = \int \phi_j \phi_k d\tau$ (8%)

(B) A necessary condition for a minimum in a function $W(c_1, c_2, c_3)$ of three variables is that its partial derivatives with respect to each variable must be zero at the minimum:

$$\frac{\partial W(c_1, c_2, c_3)}{\partial c_i} = 0 \quad i = 1, 2, 3$$

The result in (a) can be rearranged and becomes

$$W(c_1, c_2, c_3) \cdot \sum_{j=1}^{3} \sum_{k=1}^{3} c_j c_k S_{jk} = \sum_{j=1}^{3} \sum_{k=1}^{3} c_j c_k H_{jk}$$

Please show that

$$\sum_{i=1}^{3} [(H_{ik} - S_{ik}) \cdot c_i] = 0 \quad i = 1, 2, 3$$

(6%)

(C) A system of $n$ linear homogeneous equations in $n$ unknowns has a nontrivial solution if and only if the determinant of the coefficients is zero:

$$\det(H_{kk} - S_{kk} W) = 0$$

What is the secular equation for a linear conjugate hydrocarbon $C_3$? (6%)
2. The energy level of a particle in a box can be expressed as \[ E_n = \frac{n^2 \hbar^2}{8mL^2} \]

\((n=1, 2, 3, \ldots)\) where \(L\) is the width of the box, \(m\) is the mass of the particle, \(\hbar\) is the Planck's constant, and \(n\) is the quantum number.

(A) What is the energy released when a transition from \(n = 3\) to \(n = 1\) states occurs? (5%)

(B) What is the wavelength of the radiation if the energy is released as an emission of photons? (5%)  

*Note: Express your result in terms of the variables defined above.*

3. (A) Please construct the wavefunctions for the 1s and 2p\(_y\) orbitals with the information provided in the table. (5%)

(B) Please sketch these two orbitals. Make sure you clearly label your x, y, and z coordinates? (5%)

<table>
<thead>
<tr>
<th>TABLE 1.2 Hydrogen Wavefunctions (Atomic Orbitals), (\phi = R)</th>
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</thead>
<tbody>
<tr>
<td>(a) Radial wavefunctions, (R_n(r))</td>
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<td>(n)</td>
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</table>

*Note: In each case, \(a_0 = \text{s}m_t \text{nm}^2\), or close to 52.9 pm, for hydrogen itself, \(Z = 1\).  
*In all cases except \(m_l = 0\), the orbitals are sums and differences of orbitals with specific values of \(m_l\).  

4. Employing Raman spectroscopy on biomolecules or polymers is quite challenging because the background fluorescence from impurities almost inevitably overwhelms the much weaker Raman signals. To overcome this, the difference is taken of two emission spectra obtained with excitation
frequencies differing by a few wavenumbers (spectra A and B). The fluorescence background is essentially unaffected by the shift in excitation frequency and, thus, disappears in the difference spectrum, leaving only a Raman difference spectrum (spectrum D).

Please use an energy-level diagram (Jablonski diagram) to illustrate the idea and explain the underlined paragraph. (10%)

5. Evaluate the value of

\[
\left( \frac{\partial S}{\partial P} \right)_V \left( \frac{\partial T}{\partial V} \right)_P - \left( \frac{\partial T}{\partial P} \right)_V \left( \frac{\partial S}{\partial V} \right)_P
\]

where P, V, T, S are, respectively, the pressure, volume, temperature and entropy of the system. (10%)

6. Molecules with molecular mass m and diameter d are confined within a box at temperature T and pressure P.

(a) Find the collision frequency of a molecule colliding with the other molecules. (10%)

(b) Find the mean free path of the molecules. (10%)
7. A gas obeys the equation of state \( P(\bar{V} - b) = RT \), and has its molar heat capacity at constant pressure \( \overline{C_v}(T) = c + dT \). Here \( P, \bar{V}, T \) are pressure, molar volume and temperature, respectively, and \( b, c, d \) are constants.

(a) Find an expression for molar heat capacity at constant volume, \( \overline{C_v} \). (10%)  

(b) Find the entropy change when the gas undergoes a process from \( (T_1, P_1) \) to \( (T_2, P_2) \). (10%)