1. Use Maple to find the lowest three solutions to the bouncing-neutron problem described in class, using the linear variational method and a basis set of particle in a 1D box wavefunctions. The potential energy function is \( V(z \geq 0) = m_n g z, \) \( V(z < 0) = \infty. \) The classical turning point \( z_{\text{max}} \) for each state is the height such that \( V(z_{\text{max}}) = E. \) Note that \( z_{\text{max}} \) will be different for each eigenstate. You can choose the length \( l \) of the box for your basis, but all of your basis functions must use the same value of \( l \) and your eigenvalues should be accurate to three significant digits.

<table>
<thead>
<tr>
<th>state</th>
<th>eigenvalue (J)</th>
<th>( z_{\text{max}} ) (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.26 \cdot 10^{-31}</td>
<td>8.13 \cdot 10^{-6}</td>
</tr>
</tbody>
</table>

2. Use Gaussian to calculate the geometry and harmonic vibrational constants of \( \text{H}_3^+. \) Use the B3LYP DFT method and a cc-pVQZ basis set. **Solution:**

- \( R_{\text{AB}} = 0.880 \) Å
- \( R_{\text{AB}} = 0.880 \) Å
- \( R_{\text{AB}} = 0.880 \) Å
- \( \omega_c = 2694 \) cm\(^{-1}\), 2694 cm\(^{-1}\), 3381 cm\(^{-1}\)

3. Show that if any two degenerate states have an identical interaction with a third state, their degeneracy is removed. Accomplish this by finding analytical expressions for the eigenvalues and eigenvectors of the matrix

\[
\begin{pmatrix}
  a & c & 0 \\
  c & b & c \\
  0 & c & a
\end{pmatrix}
\]

in which states 1 and 3 are not directly coupled, but both interact with state 2. **Solution:** If we subtract the diagonal energies \( a \) of the two non-interacting states from the diagonal of the matrix, setting \( b' = b - a \), then we find the roots of the determinant

\[
\begin{vmatrix}
  -\lambda & c & 0 \\
  c & b' - \lambda & c \\
  0 & c & -\lambda
\end{vmatrix} = \lambda^3 - b'\lambda^2 - 2c^2\lambda = 0
\]

\[
\lambda = 0, \quad \frac{b'}{2} \pm \sqrt{1 + 8 \left( \frac{c}{b'} \right)^2}
\]

The final eigenvalues need to have that diagonal contribution in \( a \) added back in:

\[
E = a, \quad \frac{b + a}{2} + \frac{b - a}{2} \left[ 1 \pm \sqrt{1 + 8 \left( \frac{c}{b - a} \right)^2} \right]
\]

Checking a couple of limits, we can verify that

\[
\lim_{c \to 0} E = \lim_{(b-a) \to \infty} E = a, \ a, \ b
\]

which makes sense for turning off the interactions between the states, and in the opposite limit

\[
\lim_{(b-a) \to 0} E = a, \ \frac{b + a}{2} \pm \sqrt{2c},
\]
which makes sense if we think of one state as being equally repelled by the two others, while the others shift up and down in proportion to the off-diagonal element \( c \). One other simple limit is \( b - a = c \), for which the eigenvalues are \( a, a - b, a + 2b \). In this case the \( E = a \) state has eigenvector \((|1\rangle - |3\rangle)/\sqrt{2}\), so is an equal mixture of the two “non-interacting” states.

4. The IR spectra of ketones are characterized by a strong absorption at about 1760 cm\(^{-1}\) associated with the C=O carbonyl stretch.

(a) Treat this vibration as an O atom vibrating against an infinitely massive molecule. Calculate the reduced mass (in amu) for this motion, and then the force constant (in N/m) for the C=O bond. **Solution:** \( \mu = 16 \) amu, \( k \approx 2830 \) N/m.

(b) Using this force constant, calculate the reduced masses in amu for symmetric (1333 cm\(^{-1}\)) and antisymmetric (2349 cm\(^{-1}\)) stretches in CO\(_2\). If your values look reasonable, offer a qualitative explanation why the values are what they are. **Solution:** \( \mu(2349 \text{ cm}^{-1}) \approx 8.7 \) amu, \( \mu(1333 \text{ cm}^{-1}) \approx 27 \) amu. The qualitative argument is that the symmetric stretch is like two oxygen atoms pushing against the carbon (so roughly twice the mass of one O atom) while the antisymmetric stretch is like a lone carbon atom swinging between two oxygens, with a reduced mass of \((m_Cm_{O_2})/(m_C + m_{O_2}) = 8.7 \) amu.

5. The size consistency problem was described in class for a system A+B of non-interacting molecules A and B, CISD calculations would lead to the erroneous result

\[
E_{\text{CISD}}(A + B) > E_{\text{CISD}}(A) + E_{\text{CISD}}(B).
\]

CISD only takes single and double substitutions into account. Full CI includes all possible substitutions of all the electrons into all of the available orbitals. Show by proof or by example that CI is size consistent in the limit of full CI. **Solution:** Let there be \( M_A \) electrons and \( N_A \) basis functions for A by itself, and \( M_B \) electrons and \( N_B \) basis functions for B by itself. The total number of functions in the full CI wavefunction for A by itself is then \( N_A(N_A-1)(N_A-2)\ldots(N_A-M_A) \), and for B is \( N_B(N_B-1)(N_B-2)\ldots(N_B-M_B) \). The sum of these is the same as the total number of A+B functions for which A and B are neutral molecules.