1. The angular momentum operators, $\hat{l}_y$ and $\hat{l}_z$, for a 3D rigid rotor are shown in Engel eq. 7.29 (p. 115). Calculate $[\hat{l}_z, \hat{l}_y]$ using Cartesian coordinates.

**Solution:**

$$[\hat{l}_z, \hat{l}_y] = \hat{l}_z \hat{l}_y - \hat{l}_y \hat{l}_z$$

$$= [-i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x}\right)] \left[-i\hbar \left(z \frac{\partial}{\partial z} - x \frac{\partial}{\partial x}\right)\right] - \left[-i\hbar \left(z \frac{\partial}{\partial z} - x \frac{\partial}{\partial x}\right)\right] \left[-i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x}\right)\right]$$

At this point it is possible to introduce some small simplification by performing the multiplications involving $-i\hbar$. It is also necessary to introduce a dummy function, $f$, for the operators to work on.

$$\frac{[\hat{l}_z, \hat{l}_y]}{-\hbar} = \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x}\right) \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z}\right)f - \left(z \frac{\partial}{\partial z} - x \frac{\partial}{\partial x}\right) \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x}\right)f$$

Four terms can be cancelled immediately.

$$= x \frac{\partial}{\partial y} z \frac{\partial f}{\partial x} - y \frac{\partial}{\partial x} z \frac{\partial f}{\partial z} - x \frac{\partial}{\partial x} x \frac{\partial f}{\partial y} + y \frac{\partial}{\partial y} x \frac{\partial f}{\partial z} - z \frac{\partial}{\partial z} x \frac{\partial f}{\partial y} + x \frac{\partial}{\partial z} x \frac{\partial f}{\partial z} - z \frac{\partial}{\partial x} y \frac{\partial f}{\partial x} - y \frac{\partial}{\partial x} y \frac{\partial f}{\partial x}$$

The second and third terms require use of the product rule.

$$= x \frac{\partial}{\partial y} z \frac{\partial f}{\partial x} + y \left(\frac{\partial f}{\partial z} + x \frac{\partial^2 f}{\partial z \partial x}\right) - z \left(\frac{\partial f}{\partial y} + x \frac{\partial^2 f}{\partial x \partial y}\right) - x \frac{\partial}{\partial z} y \frac{\partial f}{\partial x}$$

All of the double differentials in this formula cancel.

$$\frac{[\hat{l}_z, \hat{l}_y]}{-\hbar} = y \frac{\partial f}{\partial z} - z \frac{\partial f}{\partial y}$$

$$[\hat{l}_z, \hat{l}_y] = -i\hbar \left[-i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y}\right)\right]$$
\[ [\hat{l}_z, \hat{l}_y] = -i \hbar \hat{l}_x \]

**Comment:** Engel, p. 115, states \([\hat{l}_y, \hat{l}_z] = i \hbar \hat{l}_x\) which agrees with the result given above (switching the order of operators in the commutator reverses the sign of the commutator).

2. Write \(\hat{l}^2\) for the 3D rigid rotor in spherical polar coordinates.

**Solution:** Engel, p. 112 shows the formula for \(\hat{H}\). \(\hat{l}^2\) is \(2 \hat{l} \cdot \hat{H}\) so Engel's formula can be used to generate the desired operator.

\[
\hat{l}^2 = -\hbar^2 \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]
\]

3. Determine whether \(\sin^2 \theta \ e^{2i\phi} + 2 \sin \theta \cos \theta \ e^{i\phi}\) is an eigenfunction of \(\hat{l}^2\). If it is, give its eigenvalue.

**Solution:** The operator obtained in problem 2 combines two terms. One involves a single differential with respect to \(\theta\), the other a double differential with respect to \(\phi\). I apply these terms separately to the function, \(f\), to generate two results, \(f_1\) and \(f_2\), and then I combine these terms and divide by the original function to obtain the eigenvalue.

\[
\text{Clear}[f] \\
f = \sin[\theta]^2 \ e^{2i\phi} + 2 \sin[\theta] \cos[\theta] \ e^{i\phi} \\
2 \ e^{i\phi} \cos[\theta] \sin[\theta] + e^{2i\phi} \sin[\theta]^2
\]
Clear[f1]
f1 = \partial_\phi f
f1 = Sin[\theta] * f1
f1 = \partial_\theta f1
f1 = f1 / Sin[\theta]

\[ 2 e^{i\phi} \cos[\theta]^2 + 2 e^{2i\phi} \cos[\theta] \sin[\theta] - 2 e^{i\phi} \sin[\theta]^2 \]

\[ \sin[\theta] (2 e^{i\phi} \cos[\theta]^2 + 2 e^{2i\phi} \cos[\theta] \sin[\theta] - 2 e^{i\phi} \sin[\theta]^2) \]

\[ \cos[\theta] (2 e^{i\phi} \cos[\theta]^2 + 2 e^{2i\phi} \cos[\theta] \sin[\theta] - 2 e^{i\phi} \sin[\theta]^2) + 
   \sin[\theta] (2 e^{2i\phi} \cos[\theta]^2 - 8 e^{i\phi} \cos[\theta] \sin[\theta] - 2 e^{2i\phi} \sin[\theta]^2) \]

Clear[f2]
f2 = \partial_\phi f
f2 = \partial_\phi f2
f2 = \frac{f2}{\sin[\theta]^2}

\[ 2 i e^{i\phi} \cos[\theta] \sin[\theta] + 2 i e^{2i\phi} \sin[\theta]^2 \]

\[ -2 e^{i\phi} \cos[\theta] \sin[\theta] - 4 e^{2i\phi} \sin[\theta]^2 \]

\[ \csc[\theta]^2 (-2 e^{i\phi} \cos[\theta] \sin[\theta] - 4 e^{2i\phi} \sin[\theta]^2) \]

Clear[f12]
f12 = f1 + f2

\[ \csc[\theta]^2 (-2 e^{i\phi} \cos[\theta] \sin[\theta] - 4 e^{2i\phi} \sin[\theta]^2) + 
   \csc[\theta] (\cos[\theta] (2 e^{i\phi} \cos[\theta]^2 + 2 e^{2i\phi} \cos[\theta] \sin[\theta] - 2 e^{i\phi} \sin[\theta]^2) + 
   \sin[\theta] (2 e^{2i\phi} \cos[\theta]^2 - 8 e^{i\phi} \cos[\theta] \sin[\theta] - 2 e^{2i\phi} \sin[\theta]^2)) \]
The \( \hat{J}^2 \) operator includes a \(-\hbar^2\) term that I failed to use in my work. Including this terms gives the eigenvalue, \( 6\hbar^2 \). If you compare the original function with the \( \hat{J}^2 \) eigenfunctions listed in Engel, p. 116, you will see that the original function is a linear combination of two functions with \( l = 2 \), i.e., it combines degenerate eigenfunctions of \( \hat{J}^2 \). The eigenvalues of this operator (eq. 7.28, p. 114) are \( \hbar^2 (l + 1) \) or \( 6\hbar^2 \).

4. Determine whether \( \sin^2 \theta \ e^{2i\phi} + 2 \sin \theta \cos \theta \ e^{i\phi} \) is an eigenfunction of \( \hat{J}_z \). If it is, give its eigenvalue.

**Solution:** Engel p. 115 (eq. 7.30) shows the operator. Applying it to the function gives:
This function clearly is not an eigenfunction of $\hat{I}_z$. Differentiating with respect to $\phi$ multiplies the first term of the function by $i$ and the second term by $2i$.

**Extra credit.** How is possible that the function that appears in problems 3 and 4 can be an eigenfunction of $\hat{I}^2$ and not $\hat{I}_z$? If you compare the function with the eigenfunctions shown in Engel, p. 116, you will see that the function is a linear combination of eigenfunctions with identical $l$ quantum numbers, but different $m_l$ quantum numbers.

5. The $n = 0$ $n = 3$ transition for the harmonic oscillator is not IR active. Demonstrate this by showing that the transition dipole moment, $\mu_{30}$, vanishes. **Note:** You need to set up and evaluate two integrals to solve this problem (see Engel eq. 8.8, p. 137), and you need use explicit formulas for two harmonic oscillator wave functions (see Engel eq. 7.5, p. 105).

**Solution.** The two integrals have the general form: $\int \psi_3^* \psi_0 \, dx$ and $\int \psi_3^* x \psi_0 \, dx$. The first one should be zero because we know that the eigenfunctions of a Hermitian operator are orthogonal, but you must still demonstrate this.
Both integrals vanish if the real part of $\alpha$ is positive. Engel p. 105 (2nd line) states $\alpha = \sqrt{k \mu / \hbar^2}$. hbar and $\mu$ are guaranteed to be positive real quantities. The force constant, $k$, is positive for a harmonic oscillator (more generally, $k$ is positive for the geometry corresponding to any potential energy minimum). Therefore, $\alpha$ is real and positive, and the two integrals vanish.

6. The following rotational transitions (in MHz) have been observed for the $^{12}\text{C}^{32}\text{S}$ molecule (ground vibration state). (Note: exact masses for these isotopes can be found in Engel, inside back cover.)

<table>
<thead>
<tr>
<th>Transition</th>
<th>Frequency (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>J = 1 — 0</td>
<td>48 990.978</td>
</tr>
<tr>
<td>J = 2 — 1</td>
<td>97 980.950</td>
</tr>
<tr>
<td>J = 3 — 2</td>
<td>146 969.033</td>
</tr>
<tr>
<td>J = 4 — 3</td>
<td>195 954.226</td>
</tr>
</tbody>
</table>

**Part A.** Calculate $B$, the rotational constant, in cm$^{-1}$

**Solution:** According to Engel, Table 8.5, p. 144, the transition frequencies are $2cB$, $4cB$, $6cB$, and $8cB$, respectively. Let's see if the observed frequencies for CS actually follow this pattern.
The values for $B$ vary slightly (this is to be expected because the bond distance changes slightly for different rotational states), but the variation is small.

**Part B.** Calculate the equilibrium bond distance in pm.

**Solution.** Engel, p. 143, gives a formula that connects $B$ with the reduced mass, $\mu$, and equilibrium bond distance, $r_0$: $B = \frac{\hbar^2}{8\pi^2\mu r_0^2}$
Clear[amu, C12, S32, μ]
amu = 1.6605 \times 10^{-27} \text{ kg}
C12 = 12. \text{ amu}
S32 = 31.9721 \text{ amu}
μ = \frac{C12 \times S32}{C12 + S32}
B = B \mu

1.6605 \times 10^{-27} \text{ kg}

1.9926 \times 10^{-26} \text{ kg}

5.30897 \times 10^{-26} \text{ kg}

1.44882 \times 10^{-26} \text{ kg}

\left\{ \frac{4.22894 \times 10^{19}}{\text{m}^2}, \frac{4.2289 \times 10^{19}}{\text{m}^2}, \frac{4.2283 \times 10^{19}}{\text{m}^2}, \frac{4.22874 \times 10^{19}}{\text{m}^2} \right\}

The value of “B” at this point in the calculation is $r_0^{-2}$.

Clear[r0]
r0 = \sqrt{1/B}

\left\{ 1.53774 \times 10^{-10} \sqrt{\text{m}^2}, 1.53775 \times 10^{-10} \sqrt{\text{m}^2},
1.53776 \times 10^{-10} \sqrt{\text{m}^2}, 1.53778 \times 10^{-10} \sqrt{\text{m}^2} \right\}

$r_0 = 1.53774$ angstroms or 153.774 pm. The NIST Chemistry web book lists the equilibrium bond distance of CS as 153.48 pm (http://physics.nist.gov/PhysRefData/MolSpec/Diatomic/Html/Tables/CS.html)