

Worksheet 4B Solutions

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1. Absolute Energies

- (a) The energy for the rigid rotor is given by $E_J = \frac{\hbar^2}{2I} J(J+1)$. What is J in this expression? What values can J have?
 J is the angular momentum quantum number and can have integer values (0,1,2...).
- (b) What is the lowest value of J ? What is the energy E_J for this level? **The lowest value of J is 0 and the energy is 0.**
- (c) What is the next lowest value for J ? What is the energy?
The next lowest value of J . The corresponding energy, E_1 , is $\frac{\hbar^2}{I}$.
- (d) What is the zero point energy for a rigid rotor?
The zero point energy is 0.

2. Energy Differences

- (a) In the laboratory, we cannot measure absolute energy levels. Instead we measure transitions between the energy levels. What is the general expression for the energy associated with a transition from rotational from a particular energy level, E_J , to the next higher energy level, E_{J+1} ?

$$E_{J+1} - E_J = \Delta E = \frac{\hbar^2}{2I}(J+1)(J+2) - \frac{\hbar^2}{2I}J(J+1) = \frac{\hbar^2}{I}(J+1) \quad (1)$$

- (b) It is much more common to refer to the frequency of a rotational spectroscopic transition than to use energy. If the energy of a transition is given by $\Delta E = h\nu$, modify your general expression for the energy associated with a rotational transition that you wrote above with an expression that only refers to the frequency.

$$\nu = \frac{h}{4\pi^2 I}(J+1) \quad (2)$$

- (c) Usually we use the rotational constant $B = \frac{h}{8\pi I}$ to describe rotational transitions and spectroscopy. With $I = \mu r^2$, as the moment of inertia. Rewrite your expression for the frequency of a rotational spectroscopic transition using B .

$$\nu = \frac{2B}{\pi}(J+1) \quad (3)$$

- (d) Generally, spectral transitions for rotations are only allowed when $\Delta J = \pm 1$. Use the diagram below to draw where you would expect to see spectral lines in a rotational spectrum of a generic diatomic molecule. Label your axes with *units* and *values*.
The spectrum peaks should peaks spaced apart by $2(J+1)B$ for each value of J .

- (e) How do the rotational spectra for HCl and HBr differ? How do spectra of HCl and DCl differ?

The differences arise in the behavior of the reduced mass, $\frac{m_1 m_2}{m_1 + m_2}$ in the denominator with varying masses. The larger the mass difference, the more the reduced mass converges to the value of the smaller mass. This means the spacing for HBr increases due to the lower reduced mass relative to HCl. When the mass difference becomes lower, the reduced mass asymptotes to half the average mass. In DCl, the reduced mass increases, which shrinks the spacing between the peaks compared with HCl.

3. Degeneracy of Eigenstates

- (a) The eigenstates of a rigid rotor are degenerate (i.e., multiple eigenstates correspond to the same energy) with a set of $2J + 1$ for each energy of E_J . How many different transitions from one specific eigenstate to another coexist in the lowest energy line in a microwave spectrum (i.e., the $J = 0 \rightarrow J = 1$ line) if there were no selection rules limiting the options. **We can count the transitions by considering the combinations of starting states with final states. In the $J = 0$ state, there is only one level to start at, while there are three states in the $J = 1$ state to arrive at. This makes the number of transitions 3.**