

NORTH CAROLINA STATE UNIVERSITY

Department of Chemistry

Name _____

CH 795T

Molecular Spectroscopy

Problem Set #3

Sept. 21, 2007

Due Date: Oct. 1, 2007

1. The uncertainty principle arises from the relationship among conjugate variables in a Fourier transform. For example, $x \leftrightarrow k$ and $t \leftrightarrow \omega$ are related. In quantum mechanics we can define operators that commute and variables that do not commute.

Definition: mathematically we can define two operators that commute as

$$[A,B] = AB - BA = 0$$

This statement means that it does not matter what order I use to apply the operators. If two operators do NOT commute then

$$[A,B] = AB - BA \neq 0$$

An example two operators that do not commute are the position, x and momentum, p_x . The momentum along x is defined as $p_x = -i\hbar\partial/\partial x$.

A. Consider the wave function e^{ikx} . Prove that x and p_x do not commute.

B. The definition of the uncertainty principle is:

$$\Delta_\psi A \Delta_\psi B \geq \frac{1}{2} |\langle [A,B] \rangle_\psi|$$

where

$$\langle X \rangle_\psi = \langle \Psi | X | \Psi \rangle \quad \text{and} \quad \Delta_\psi X = \sqrt{\langle X^2 \rangle_\psi - \langle X \rangle_\psi^2}$$

Derive the uncertainty principle for position and momentum based on these definitions.

If we assume that $\Psi = e^{ikx}$ as above we find that:

$$\Delta_\psi A \Delta_\psi B \geq \frac{1}{2} |i\hbar|$$

$$|i\hbar| = \sqrt{i\hbar(-i\hbar)} = \hbar$$

$$\Delta_\psi A \Delta_\psi B \geq \frac{\hbar}{2}$$

This is the formal statement of the Uncertainty Principle.

Now start using the vibrational wavefunction for the $v = 0$ state and calculate the uncertainty.

$$\chi(Q) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha Q^2/2}$$

Show that a Gaussian wave function provides the minimum value of the uncertainty.

$$\Delta p_Q \Delta Q = \frac{\hbar}{2}$$

In other words show that the equal sign applies rather than the greater than sign.

C. The time-energy commutator is:

$$\begin{aligned}
[t, H]e^{i\omega t} &= t\left(i\hbar\frac{\partial}{\partial t}\right)e^{i\omega t} - \left(i\hbar\frac{\partial}{\partial t}\right)te^{i\omega t} \\
&= -\hbar\omega te^{i\omega t} - \left(i\hbar e^{i\omega t} - \hbar\omega te^{i\omega t}\right) \\
&= -i\hbar e^{i\omega t} \\
\therefore [t, H] &= -i\hbar
\end{aligned}$$

Show that the Gaussian line shape function:

$$G(\omega) = \left(\frac{\Gamma^2}{4\pi}\right)^{1/4} e^{-\Gamma^2(\omega - \omega_0)^2/4}$$

satisfies the minimum uncertainty condition:

$$\Delta E \Delta t = \hbar \Delta \omega \Delta t = \frac{\hbar}{2}$$

D. Compare the Lorentzian function to the Gaussian function. Calculate the time-energy uncertainty for the function:

$$L(\omega) = \frac{1}{\pi} \frac{\Gamma}{\Gamma^2 + (\omega - \omega_0)^2}$$

estimate the product using the Half-Width at Half Maximum for a Lorentzian for $\Delta\omega$ and the half-life for t . Using these definitions how much larger is the $\Delta\omega\Delta t$ product for $L(\omega)$ than for $G(\omega)$?

2. A. Convert the limits of the visible spectrum, 390 nm to 780 nm to kJ/mol, eV and cm^{-1} .
- B. Given that the temperature at the surface of the sun is 5600 K, calculate the wavelength and wavenumber of the peak of the solar emission spectrum.
- C. Using a typical value of the intensity of solar radiation in the upper atmosphere (1000 W/m^2), calculate the amplitude of the electric field of sunlight.
- D. Using the wavelength of maximum emission of the sun, find the photon flux (number of photons per unit area per unit time) that corresponds to the intensity of 1000 W/m^2 .
3. If a dipole moment has the components $x = 3 \text{ D}$, $y = 4 \text{ D}$, where D is in units of Debyes, calculate its magnitude and the angle the dipole moment has with respect to the x-axis.
4. Consider four charge, equal in magnitude. Two positive charges are located at $(x,y) = (3,3)$ and $(-3,-3)$ and two negative charges are at $(3,-3)$ and $(-3,3)$. Calculate the nonzero components of the Cartesian quadrupole tensor, using arbitrary units. Then find a new coordinate system for these charges that diagonalizes the quadrupole tensor.
5. The molar absorptivity of the dye rhodamine 6G is about 10^5 L/mol-cm at 540 nm. Estimate ϵ'' for a 10^{-3} solution of this dye in ethanol.