Answers to Problem Set 7
On commutators, constants of the motion, the uncertainty principle

1. (a) Average distance of the electron from the nucleus in the state described by $\Psi_{1s} = \{1/\sqrt{\pi}\} \{Z/a_0\}^{3/2} \exp[-Zr/a_0]$. Use Postulate 3, the expectation value is

$\langle r \rangle = \iiint \Psi_{1s}^* \, r \, \Psi_{1s} \, r^2 dr \, \sin\theta d\theta d\phi =$

$\iiint \{1/\sqrt{\pi}\} \{Z/a_0\}^{3/2} \exp[-Zr/a_0] \, r \, \{1/\sqrt{\pi}\} \{Z/a_0\}^{3/2} \exp[-Zr/a_0] \, r^2 dr \, \sin\theta d\theta d\phi$

$\langle r \rangle = 4\pi(1/\pi) \{Z/a_0\}^3 \int r^3 \exp[-2Zr/a_0] dr$

This integral is of the form,

$\int_0^\infty x^n \exp(-ax)dx = n!/a^{n+1}$ for $a > 0$, n positive integer; here n=3, a=2Z/a_0

$\langle r \rangle = 4\pi(1/\pi) \{Z/a_0\}^3 \, 3!(2Z/a_0)^{-4} = 4 \cdot 3!(2)^{-4}(Z/a_0)^{-1} = (3/2) \, a_0$

(b) Probability for finding the electron at any one position is given by $\Psi^*\Psi$. The probability of finding the electron within a spherical shell between r and r+dr is given by $4\pi r^2\Psi_{1s}^* \, \Psi_{1s}$. To get maximum probability, need to find the distance at which the derivative of this probability is zero. First differentiate $4\pi r^2 \, \Psi_{1s}^* \, \Psi_{1s}$, then set the derivative to zero, then solve for r.

Probability of finding the electron within a spherical shell, between r and r+ dr, is = $\{(1/\pi) (Z/a_0)^3 \, 4\pi r^2 \exp[-2Zr/a_0]\}$ dr.

$d/dr\{ 4 (Z/a_0)^3 \, r^2\exp[-2Zr/a_0] \} = 4 (Z/a_0)^3 \, \exp[-2Zr/a_0][(-2Z/a_0)r^2 + 2r] = 0$

answer: $r = a_0/Z$

(c) Outcomes of measurements are the eigenvalues. The eigenvalues of the operator $L_z = (\hbar/i)\partial/\partial\varphi$ are given by $m = 0, \pm\hbar, \pm 2\hbar, ...$ For the state whose function is $\Psi_{1s} = \{1/\sqrt{\pi}\} \{Z/a_0\}^{3/2} \exp[-Zr/a_0]$, m=0.
Therefore measurements of L_z on this state can yield only the eigenvalue 0.

(d) The average value of a series of measurements of L_z will be the average of a string of zeroes, which is zero.

(e) $\mathcal{H} = -(\hbar^2/2m)\nabla^2 - Ze^2/r$, $\qquad L_z = (\hbar/i)\partial/\partial\varphi$

$\nabla^2 = \partial^2/\partial r^2 + (2/r) \, \partial/\partial r + \{r^2\sin\theta\}^{-1}\partial/\partial\theta(\sin\theta \, \partial/\partial\theta) + r^2\sin^2\theta)^{-1}(\partial^2/\partial\phi^2)$

$\partial/\partial\varphi$ commutes with any terms in r or θ, and $\partial/\partial\varphi$ commutes with $(\partial^2/\partial\phi^2)$.
Therefore, $[\mathcal{H}, L_z] = 0$

We have derived in lecture, $(d/dt) \langle S \rangle = (i/\hbar)\langle [\mathcal{H}, L_z] \rangle + (\partial/\partial t) S$

When $(d/dt) \langle S \rangle = 0$ then S is said to be a constant of the motion.

For $S = L_z$: $(\partial/\partial t) (\hbar/i)\partial/\partial\varphi = 0$, no explicit t in the operator.

And we have already seen that $[\mathcal{H}, L_z] = 0$. Therefore, $(d/dt) \langle L_z \rangle = 0$; L_z is a constant of the motion.

2.

(a) We can use the Uncertainty Principle for the conjugate variables: position x and the x component p_x of the linear momentum,

$$\sigma_x \sigma_{px} \geq \hbar/2$$

If the diameter of the nucleus is 10^{-12} cm, then the position of a proton in the nucleus is known to be within this value. So we set $\sigma_x = 10^{-12}$ cm. If so, then the linear momentum of the proton has to be $\geq (\hbar/2)/10^{-12}$.
How is this related to kinetic energy? kinetic energy $= p^2/2m$. Then the kinetic energy of the proton has to be $\geq [(\hbar/2)/10^{-12}]^2/2m$ or at least $[6.62618 \times 10^{-27}/2 \times 10^{-12}]^2/2 \times 1.67262158 \times 10^{-24} = 3.281 \times 10^{-6}$ erg,

using mass of a proton $= 1.67262158 \times 10^{-24}$ g ; erg $=$ g cm^2 s^{-2}

(b) Similarly, for an electron in an atom of 10^{-8} cm diameter. The uncertainty in the position of the electron is of the same order of magnitude as the diameter of the atom itself. As long as the electron is bound to the atom, we will not be able to say much more about its position than that it is in the atom.
$[6.62618 \times 10^{-27}/2 \times 10^{-8}]^2/2 \times 9.10938188 \times 10^{-28} = 0.60248 \times 10^{-10}$ erg
using electron mass $= 9.10938188 \times 10^{-28}$ grams
This minimum kinetic energy is the same order of magnitude as the energy for an electron in a ground state H atom, 0.218×10^{-10} erg
T+V$= -0.218 \times 10^{-10}$ erg So V has to be at least -0.82×10^{-10} erg
(c) We can use the Uncertainty Principle

$$\sigma_E \sigma_t \geq \hbar/2$$

From lecture, we saw that we can also write this as

$$4\pi\sigma_v \, \sigma_t \geq 1$$

For a Lorentzian line, full width at half maximum is $4\pi\sigma_v = 2\sigma_\omega$ the natural linewidth in rad s^{-1}, where the lifetime of the state is σ_t. Here the lifetime of the excited state was given, 10^{-8} s, which gives a full width at half maximum equal to 10^8 rad s^{-1}.
We use $hc/\lambda = h\omega/2\pi$; $\sigma_\omega = 2\pi c \, \sigma_\lambda/\lambda^2$
Substituting, we get,
10^8 rad s$^{-1} = 2\pi 3 \times 10^{10}$cm s$^{-1}\sigma_\lambda$ cm $/(5000 \times 10^{-8})^2$;
$\sigma_\lambda = 10^8 \, 25 \times 10^{-10}/2\pi 3 \times 10^{10} = 1.33 \times 10^{-12}$ cm $=$ half-width at half maximum peak height

3 4 & 5. For questions 3,4 and 5, the approach is the same:

When the individual conformations are long lived, they can be distinguished and each individually observed as a separate peak. The spectral separation then provides the energy or Hertz or cm^{-1} difference between the two conformations. At the point (a given temperature) when the peaks just coalesce, the peak for one conformation is indistinguishable from the other, we can use the Uncertainty Principle

$$\sigma_E \sigma_t \geq \hbar/2$$

We may rewrite this, using $\sigma_E = h\sigma_v$, to get $hc\sigma_v\sigma_t \geq \hbar/2$,

$$\sigma_v\sigma_t \geq [4\pi]^{-1} \quad \sigma_t \geq [4\pi\sigma_v]^{-1}$$

or else, if in wavenumbers, $\sigma_E = hc\sigma_{v\sim}$, $hc\sigma_{v\sim}\sigma_t \geq \hbar/2$ or

$$\sigma_{v\sim}\sigma_t \geq [4\pi c]^{-1}$$
$$\sigma_t \geq [4\pi c\sigma_{v\sim}]^{-1}$$

At coalescence, the uncertainty principle provides a <u>LOWER LIMIT to the lifetime</u> of each conformation (lower limit because of the $\geq$ in the inequality). This lower limit will be obtained from $\sigma_{v\sim}$ the wavenumber cm^{-1} separation, for example, by calculating

$$\sigma_t \text{ (seconds)} = [4\pi c\sigma_{v\sim}]^{-1}$$

If conversion occurs every σ_t (seconds), for a first order kinetic process, the rate constant has units of 1/time. Thus, the UPPER limit to the rate constant for the process is $4\pi c\sigma_{v\sim}$.

Now that we have an upper limit to the rate constant, we can use Eyring's absolute rate theory:

$$k = (k_B T/h) \exp[-\Delta G^{\ddagger}/k_B T] \quad \text{where } k = \text{rate constant, s}^{-1}$$

k_B = Boltzmann's constant = 1.987 cal mol^{-1} deg^{-1}

k_B = Boltzmann's constant = 1.38 x10^{-16} erg deg^{-1}

h = Planck's constant = 6.62618x10^{-27} erg s

find an approximate value for $\Delta G\ddagger$, the free energy barrier to inversion, in Kcal mol^{-1}. Using the upper limit for the rate constant, gives the LOWER LIMIT for $\Delta G^{\ddagger}$, the free energy barrier for the process. Aside: Of course there is an accurate way of determining the free energy barrier for the process from a temperature dependent study, but this exercise is to show that the Uncertainty Principle alone can provide a good limiting value.

3. Given here from the NMR spectrum, $\sigma_v = 30.5$ Hz from which $[4\pi\sigma_v]^{-1} = [4\pi\ 30.5\ \text{s}^{-1}]^{-1} = 0.0026$ seconds, the lower limit for the lifetime of each conformer at -135°C or 138 K.

From this we get the upper limit for the rate constant, the reciprocal of the lifetime, $k = 383$ s^{-1}

383 $s^{-1} =$

$$\frac{1.38 \times 10^{-16} \text{ erg deg}^{-1} \bullet 138 \text{ deg}}{6.62618 \times 10^{-27} \text{ erg s}} \quad \exp[-\Delta G^{\ddagger}/1.987 \text{ cal mol}^{-1} \text{ deg}^{-1} 138 \text{ deg}]$$

$-\Delta G^{\ddagger}$ cal mol^{-1}/1.987$\bullet$138 = ln $[12.59 \times 10^{11}]$

gives the lower limit for $\Delta G^{\ddagger}$, the free energy barrier for the process.

4. Given here from the NMR spectrum, $\sigma_v = 9.2$ Hz from which $[4\pi\sigma_v]^{-1} = [4\pi\ 9.2\ s^{-1}]^{-1} = 0.0086$ seconds, the lower limit for the lifetime of each conformer at -44°C or 229 K. From this we get the upper limit for the rate constant, the reciprocal of the lifetime, $k = 116$ s^{-1}

116 $s^{-1} =$

$$\frac{1.38 \times 10^{-16} \text{ erg deg}^{-1} \bullet 229 \text{ deg}}{6.62618 \times 10^{-27} \text{ erg s}} \quad \exp[-\Delta G^{\ddagger}/1.987 \text{ cal mol}^{-1} \text{ deg}^{-1} 229 \text{ deg}]$$

$-\Delta G^{\ddagger}$ cal mol^{-1}/1.987$\bullet$229 = ln $[2.43 \times 10^{11}]$

gives the lower limit for $\Delta G^{\ddagger}$, the free energy barrier for the process.

5. Given here from the IR spectrum, $\sigma_{\tilde{v}} = 15$ cm^{-1} from which $[4\pi c \sigma_{\tilde{v}}]^{-1} = [4\pi\ 3 \times 10^{10}\ \text{cm s}^{-1}\ 15\ \text{cm}^{-1}]^{-1} = 1.8 \times 10^{-13}$ seconds, the lower limit for the lifetime of each conformer. From this we get the upper limit for the rate constant, the reciprocal of the lifetime, $k = 5.65 \times 10^{12}$ s^{-1}

5.65×10^{12} $s^{-1} =$

$$\frac{1.38 \times 10^{-16} \text{ erg deg}^{-1} \bullet 293 \text{ deg}}{6.62618 \times 10^{-27} \text{ erg s}} \quad \exp[-\Delta G^{\ddagger}/1.987 \text{ cal mol}^{-1} \text{ deg}^{-1} 293 \text{ deg}]$$

$-\Delta G^{\ddagger}$ cal mol^{-1}/1.987$\bullet$293 = ln 0.926

gives the lower limit for $\Delta G^{\ddagger}$, the free energy barrier for the process.