

Quantum Chemistry
Midterm II Exam
November 18 2009



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Full credit will be given to correct answers only when ALL the necessary steps are shown.
DO NOT GUESS THE ANSWER.

This is a closed book and closed notes exam, and you are responsible to be sure that your exam has no missing pages (7 pages).

If you consider that there is not enough information to solve a problem, you have to specify the missing information and describe the problem solving procedure.

From "The Brothers K" by David James Duncan

"Vic Power, the Indians' Negro first baseman, is the hitter. It's weird to see a big black man like Power getting called an "Indian." Come to think of it, it's pretty strange to see a bunch of white guys running around calling themselves "Indians" too. How are real Indians supposed to feel about it? I mean, what if there was a team of Negroes and Indians called "the Cleveland White Guys"? I think a lot of pale-faced folks wouldn't be all that thrilled. That's one big advantage the Yankees have: black, red, brown, or white, they look like Yanks, and act like Yanks, and are Yanks. None of this cutesy Oriole or Cub or White-Indian crap for them"

Honor Statement

I have neither give nor received aid in this examination.

Full signature PD

Problem 1 (30 points)

a) Show that $\Psi(x) = \text{Exp}\left[-\frac{\alpha x^2}{2}\right]$ is an eigenfunction of $\hat{A} = \alpha^2 x^2 - \frac{d^2}{dx^2}$. What is its eigen value?

b) Show that $\hat{B}\Psi(x)$, where $\hat{B} = \alpha x - \frac{d}{dx}$, is another eigenfunction of \hat{A} . What is its eigenvalue?

c) Do \hat{A} and \hat{B} commute? Explain your answer.

$$\begin{aligned} \hat{A}\Psi &= (\alpha^2 x^2 \Psi - \frac{d^2 \Psi}{dx^2}) = \alpha^2 x^2 e^{-\frac{\alpha x^2}{2}} - \frac{d}{dx}(-\alpha x e^{-\frac{\alpha x^2}{2}}) \\ &= \alpha^2 x^2 e^{-\frac{\alpha x^2}{2}} + \alpha e^{-\frac{\alpha x^2}{2}} - (\alpha^2 x^2 e^{-\frac{\alpha x^2}{2}}) = \alpha e^{-\frac{\alpha x^2}{2}} \end{aligned}$$

$$\hat{A}\Psi = \alpha \Psi$$

eigenvalue = α

$$\hat{B}\Psi = \alpha x \Psi - \frac{d\Psi}{dx} = \alpha x e^{-\frac{\alpha x^2}{2}} - (-\alpha x e^{-\frac{\alpha x^2}{2}}) = 2\alpha x e^{-\frac{\alpha x^2}{2}}$$

$$\begin{aligned} \hat{A}(\hat{B}\Psi) &= 2\alpha(\alpha^2 x^2 x e^{-\frac{\alpha x^2}{2}}) - \frac{d}{dx}(2\alpha x e^{-\frac{\alpha x^2}{2}} - 2\alpha^2 x^2 e^{-\frac{\alpha x^2}{2}}) \\ &= 2\alpha^3 x^3 e^{-\frac{\alpha x^2}{2}} + 2\alpha^2 x e^{-\frac{\alpha x^2}{2}} - 2\alpha^3 x^3 e^{-\frac{\alpha x^2}{2}} + 4\alpha^2 x e^{-\frac{\alpha x^2}{2}} \\ &= 6\alpha^2 x e^{-\frac{\alpha x^2}{2}} = 3\alpha(\hat{B}\Psi) \end{aligned}$$

EIGENVALUE = 3α

$$\hat{A}(\hat{B}\Psi) = 3\alpha(\hat{B}\Psi)$$

$$\hat{B}(\hat{A}\Psi) = \alpha(\hat{B}\Psi)$$

$$[\hat{A}, \hat{B}]\Psi \neq 0$$

Do not commute.

Problem 2 (25 points)

$^1H^{127}I$ has a force constant of 314 N m^{-1} and a bond length of 160.92 pm . Calculate the frequency of the light corresponding to the **lowest energy pure vibrational** and **pure rotational transitions**. In what regions of the electromagnetic spectrum do the transitions lie?

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} = \frac{1}{2\pi} \sqrt{\frac{314 \text{ kg s}^{-2}}{\frac{1.008 \text{ amu} \times 126.9045 \text{ amu}}{1.008 \text{ amu} + 126.9045 \text{ amu}} \times \frac{1.661 \times 10^{-27} \text{ kg}}{\text{amu}}}}$$

$$= 6.92 \times 10^{13} \text{ s}^{-1}$$

This frequency lies in the infrared region of the electromagnetic spectrum.

The lowest energy transition is $J = 0 \rightarrow J = 1$.

$$I = \mu r_0^2 = \frac{1.008 \text{ amu} \times 126.9045 \text{ amu}}{1.008 \text{ amu} + 126.9045 \text{ amu}} \times \frac{1.661 \times 10^{-27} \text{ kg}}{\text{amu}} \times (160.92 \times 10^{-12} \text{ m})^2$$

$$= 4.30 \times 10^{-47} \text{ kg m}^2$$

$$\Delta E_{\text{rot}} = 2(J+1) \frac{\hbar^2}{2\mu r_0^2} = \frac{\hbar^2}{\mu r_0^2} = \frac{(1.055 \times 10^{-34} \text{ J s})^2}{4.30 \times 10^{-47} \text{ kg m}^2} = 2.59 \times 10^{-22} \text{ J}$$

$$\nu = \frac{\Delta E_{\text{rot}}}{h} = 3.91 \times 10^{11} \text{ s}^{-1}$$

Problem 3 (25 points)

Calculate the zero point energies ($n=0$) for $^1H^{35}Cl$ and $^2D^{35}Cl$ assuming a harmonic potential. Compare the difference in the zero point energies to $3kT/2$ at 300.0 K.

$$\nu_{HCl} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} = \frac{1}{2\pi} \sqrt{\frac{516 \text{ N m}^{-1}}{\frac{34.9688 \text{ amu} \times 1.0078 \text{ amu}}{34.9688 \text{ amu} + 1.0078 \text{ amu}} \times 1.6605 \times 10^{-27} \text{ kg amu}^{-1}}}}$$
$$= 8.97 \times 10^{13} \text{ s}^{-1}$$

$$\nu_{DCl} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} = \frac{1}{2\pi} \sqrt{\frac{516 \text{ N m}^{-1}}{\frac{34.9688 \text{ amu} \times 2.0140 \text{ amu}}{34.9688 \text{ amu} + 2.0140 \text{ amu}} \times 1.6605 \times 10^{-27} \text{ kg amu}^{-1}}}}$$
$$= 6.43 \times 10^{13} \text{ s}^{-1}$$

$$E_0^{HCl} = \frac{h\nu_{HCl}}{2} = 2.97 \times 10^{-20} \text{ J}$$

$$E_0^{DCl} = \frac{h\nu_{DCl}}{2} = 2.13 \times 10^{-20} \text{ J}$$

$$\frac{E_0^{HCl} - E_0^{DCl}}{kT} = \frac{(2.97 - 2.13) \times 10^{-20} \text{ J} \cdot 2}{(300. \text{ K} \times 1.381 \times 10^{-23} \text{ J K}^{-1}) \cdot 3} = \frac{2.03}{1.50} = 1.35$$

Problem 4 (10 points)

Using the Virial Theorem, one can prove for the harmonic oscillator the following relation among expectations:

$$\langle \hat{K} \rangle = \langle \hat{V} \rangle = \frac{1}{2} \langle \hat{H} \rangle.$$

Using this result prove the Heisenberg Uncertainty Principle for the harmonic oscillator for all values of the quantum number "n." Your final result should be expressed in term of the quantum number "n", and \hbar . You could use symmetry arguments to calculate $\langle \hat{x} \rangle$ and $\langle \hat{p} \rangle$. Hint: you really do not need to calculate any integrals.

FOR H.O. $\langle \hat{H} \rangle = h\nu \left(\frac{1}{2} + n\right)$

$$\langle \hat{K} \rangle = \left\langle \frac{\hat{p}^2}{2\mu} \right\rangle = \frac{1}{2\mu} \langle p^2 \rangle = \frac{1}{2} \langle \hat{H} \rangle = \frac{h\nu}{2} \left(\frac{1}{2} + n\right)$$

$$\boxed{\langle p^2 \rangle = \mu h\nu \left(\frac{1}{2} + n\right)}$$

$$\langle \hat{V} \rangle = \left\langle \frac{1}{2} k x^2 \right\rangle = \frac{1}{2} k \langle x^2 \rangle = \frac{h\nu}{2} \left(\frac{1}{2} + n\right)$$

$$\boxed{\langle x^2 \rangle = \frac{h\nu}{k} \left(\frac{1}{2} + n\right)}$$

$$\sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2$$

$$\sigma_p^2 = \langle p^2 \rangle - \langle p \rangle^2$$

BUT $\langle x \rangle = \langle p \rangle = 0$ DUE TO THE SYMMETRIC POTENTIAL

$$V(x) = V(-x)$$

$$\Delta x \Delta p = \sigma_x \sigma_p = \sqrt{\frac{\mu}{k} \nu^2 \hbar^2 \left(\frac{1}{2} + n\right)^2} = \sqrt{\hbar^2 \left(\frac{1}{2} + n\right)^2} = \hbar \left(\frac{1}{2} + n\right)$$

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

$$\boxed{\Delta x \Delta p = \hbar \left(\frac{1}{2} + n\right) \geq \frac{\hbar}{2}}$$

Problem 5 (10 points)

Within the rigid rotator-harmonic oscillator approximation, the rotational and vibrational energy for a diatomic molecule is given by the sum of both energies,

$$\tilde{E}_{n,J} = \tilde{\nu}(1/2 + n) + \tilde{B}J(J+1),$$

where $\tilde{\nu}$ and \tilde{B} are of the order of 10^3 cm^{-1} and 1 cm^{-1} , respectively. If the bond length in $^{12}\text{C}^{14}\text{N}$ is 117 pm and its force constant is 1630 N m^{-1} , predict the vibrational-rotational spectrum of $^{12}\text{C}^{14}\text{N}$. Consider only the $0 \rightarrow 1$ vibrational transition, but consider at least 3 rotational transitions for $\Delta J = +1$ and 3 for $\Delta J = -1$. Express your energies in wave numbers (cm^{-1}).

FOR $n=0 \rightarrow n=1$ AND $J \rightarrow J'$ WE GET

$$\Delta E = E_{1,J'} - E_{0,J} = h\nu^{\text{obs}} = \frac{hc}{\lambda} = hc \tilde{\nu}^{\text{obs}}$$

$$\tilde{\nu}^{\text{obs}} = \frac{\Delta E}{hc}$$

$$\Delta E = h\nu + hB[J'(J'+1) - J(J+1)]$$

$$\tilde{\nu}^{\text{obs}} = \tilde{\nu} + \frac{B}{c}[J'(J'+1) - J(J+1)]$$

$$\text{so } \tilde{\nu} = \frac{\nu}{c} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} = \frac{1}{2\pi \cdot 2.99 \times 10^{10} \text{ cm}^{-1} \text{ s}^{-1}} \sqrt{\frac{1630 \text{ N m}^{-1}}{\frac{(12)(14)}{26} \text{ amu}}} = 2076 \text{ cm}^{-1}$$

$$\tilde{B} = \frac{B}{c} = \frac{h}{8\pi^2 \mu r_0^2} = \frac{6.626 \times 10^{-34} \text{ J s}}{(2.99 \times 10^{10} \text{ cm}^{-1} \text{ s}^{-1})^2 \cdot \frac{(14)(12)}{26} \text{ amu} \cdot (117 \times 10^{-12} \text{ m})^2}$$

$$\boxed{\tilde{B} = 1.91 \text{ cm}^{-1}}$$

CONSIDER $J' = J+1$

$$\tilde{\nu}^{\text{obs}} = \tilde{\nu} + \tilde{B}[(J+1)(J+2) - J(J+1)] = \tilde{\nu} + \tilde{B}(J+1)2 \rightarrow 2 \rightarrow 3 \quad \tilde{\nu} + 6\tilde{B}$$

CONSIDER $J' = J-1$

$$\tilde{\nu}^{\text{obs}} = \tilde{\nu} + \tilde{B}[(J-1)J - J(J+1)] = \tilde{\nu} + \tilde{B}J(-2) \rightarrow 3 \rightarrow 2 \quad \tilde{\nu} - 6\tilde{B}$$

$0 \rightarrow 1$	$\tilde{\nu} + 2\tilde{B}$
$1 \rightarrow 2$	$\tilde{\nu} + 4\tilde{B}$
$2 \rightarrow 3$	$\tilde{\nu} + 6\tilde{B}$
$1 \rightarrow 0$	$\tilde{\nu} - 2\tilde{B}$
$2 \rightarrow 1$	$\tilde{\nu} - 4\tilde{B}$
$3 \rightarrow 2$	$\tilde{\nu} - 6\tilde{B}$

$$2064 \text{ cm}^{-1} \quad 2068 \text{ cm}^{-1} \quad 2072 \text{ cm}^{-1}, \quad 2080 \text{ cm}^{-1} \quad 2084 \text{ cm}^{-1} \quad 2088 \text{ cm}^{-1}$$

Bonus question (5 points)

Who won the 2009 Sub-17 world football cup?

Switzerland!