

Quantum Chemistry
Midterm 2 Exam
November 20, 2008



Name _____

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 (6 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.

No one can make you feel inferior without your consent

- Eleanor Roosevelt -

Honor Statement

I have neither give nor received aid in this examination.

Full signature _____

Problem 1 (25 points)

Evaluate the commutator

$$\left[\frac{d}{dx} - x, \frac{d}{dx} + x \right]$$

by applying the operators to an arbitrary function $f(x)$.

$$\begin{aligned} \left[\frac{d}{dx} - x, \frac{d}{dx} + x \right] f(x) &= \left(\frac{d}{dx} - x \right) \left(\frac{d}{dx} + x \right) f(x) - \left(\frac{d}{dx} + x \right) \left(\frac{d}{dx} - x \right) f(x) \\ &= \left(\frac{d}{dx} - x \right) \left(\frac{df(x)}{dx} + xf(x) \right) - \left(\frac{d}{dx} + x \right) \left(\frac{df(x)}{dx} - xf(x) \right) \\ &= \frac{d^2 f(x)}{dx^2} + f(x) + x \frac{df(x)}{dx} - x \frac{df(x)}{dx} - x^2 f(x) - \frac{d^2 f(x)}{dx^2} + f(x) + x \frac{df(x)}{dx} - x \frac{df(x)}{dx} + x^2 f(x) \\ &= 2f(x) \text{ Therefore,} \end{aligned}$$

$$\left[\frac{d}{dx} - x, \frac{d}{dx} + x \right] = 2$$

Problem 2 (25 points)

The moment of inertia of $^1H^{35}Cl$ is $2.644 \times 10^{-47} \text{ kg m}^2$. Calculate E_{rot}/kT for $J = 0, 5, 10, 20$ at 298 K. For which of these values of J is $E_{rot}/kT \approx 1$.

$$E = \frac{\hbar^2}{2I} J(J+1) = \frac{\hbar^2}{2I} 1(1+1) = \frac{(1.055 \times 10^{-34} \text{ J s})^2}{2 \times 2.644 \times 10^{-47} \text{ kg m}^2} J(J+1) = 2.089 \times 10^{-22} J(J+1)$$

$$E_{J=0} = 0$$

$$E_{J=5} = 30 \times 2.089 \times 10^{-22} \text{ J} = 6.267 \times 10^{-21} \text{ J}$$

$$\frac{E_{J=5}}{kT} = \frac{6.267 \times 10^{-21} \text{ J}}{1.381 \times 10^{-23} \text{ J K}^{-1} \times 298 \text{ K}} = 1.51$$

$$E_{J=10} = 110 \times 2.089 \times 10^{-22} \text{ J} = 2.297 \times 10^{-20} \text{ J}$$

$$\frac{E_{J=10}}{kT} = \frac{2.528 \times 10^{-20} \text{ J}}{1.381 \times 10^{-23} \text{ J K}^{-1} \times 298 \text{ K}} = 5.55$$

$$E_{J=20} = 20 \times 21 \times 2.089 \times 10^{-22} \text{ J} = 8.774 \times 10^{-20} \text{ J}$$

$$\frac{E_{J=20}}{kT} = \frac{8.774 \times 10^{-20} \text{ J}}{1.381 \times 10^{-23} \text{ J K}^{-1} \times 298 \text{ K}} = 21.2$$

$$\frac{E_{rot}}{kT} \approx 1 \text{ for } J = 5.$$

Problem 3 (25 points)

The rigid rotator model can be improved by recognizing that in a realistic anharmonic potential, the bond length increases with the vibrational quantum number n , and it can be shown that $B_n = B - (n + q/2) \alpha$, where B is the rigid rotator value. The constant α can be obtained from experimental spectra. For $^1H^{79}Br$, $B = 8.473 \text{ cm}^{-1}$ and $\alpha = 0.226 \text{ cm}^{-1}$. Using this more accurate formula for B_n , calculate the bond length for $^1H^{79}Br$ in the ground state and for $n = 3$.

For $n=0$

$$B = \frac{h}{8\pi^2 \mu r_0^2}; \quad r_0 = \sqrt{\frac{h}{8\pi^2 \mu B_n}}$$

$$r_0 = \sqrt{\frac{6.6260755 \times 10^{-34} \text{ J s}}{8\pi^2 \times \frac{1.0078250 \times 78.918336 \text{ amu}}{1.0078250 + 78.918336} \times 1.6605402 \times 10^{-27} \text{ kg amu}^{-1} \times \left(8.473 - \frac{0.226}{2}\right) \text{ cm}^{-1} \times 2.99792458 \times 10^{10} \text{ cm s}^{-1}}}$$

$$r_0 = 1.424 \times 10^{-10} \text{ m}$$

For $n=3$

$$B = \frac{h}{8\pi^2 \mu r_0^2}; \quad r_0 = \sqrt{\frac{h}{8\pi^2 \mu B}}$$

$$r_0 = \sqrt{\frac{6.6260755 \times 10^{-34} \text{ J s}}{8\pi^2 \times \frac{1.0078250 \times 78.918336 \text{ amu}}{1.0078250 + 78.918336} \times 1.6605402 \times 10^{-27} \text{ kg amu}^{-1} \times \left(8.472 - \frac{3 \times 0.226}{2}\right) \text{ cm}^{-1} \times 2.99792458 \times 10^{10} \text{ cm s}^{-1}}}$$

$$r_0 = 1.443 \times 10^{-10} \text{ m}$$

Problem 4 (25 points)

Calculate the expectation value $\langle (r - \langle r \rangle)^2 \rangle$ if the He^+ atom wave function is Ψ_{100} .

Estimate the percentage error in the measurement of $\langle r \rangle$ by calculation the standard

deviation $\sigma_r = \sqrt{\langle (r - \langle r \rangle)^2 \rangle}$.

For H

$$\psi_{100}(r).$$

$$\langle (r - \langle r \rangle)^2 \rangle = \langle r^2 - 2r\langle r \rangle + \langle r \rangle^2 \rangle = \langle r^2 \rangle - 2\langle r \rangle^2 + \langle r \rangle^2 = \langle r^2 \rangle - \langle r \rangle^2$$

$$\langle r \rangle = \frac{1}{\pi a_0^3} \int_0^{2\pi} d\phi \int_0^\pi \sin\theta d\theta \int_0^\infty r^3 e^{-\frac{2r}{a_0}} dr$$

$$\langle r \rangle = \frac{4}{a_0^3} \int_0^\infty r^3 e^{-\frac{2r}{a_0}} dr$$

Using the standard integral $\int_0^\infty r^n e^{-\alpha r} = \frac{n!}{\alpha^{n+1}}$

$$\langle r \rangle = \frac{4}{a_0^3} \frac{6a_0^4}{16} = \frac{3}{2} a_0$$

$$\langle r^2 \rangle = \frac{1}{\pi a_0^3} \int_0^{2\pi} d\phi \int_0^\pi \sin\theta d\theta \int_0^\infty r^4 e^{-\frac{2r}{a_0}} dr$$

$$\langle r^2 \rangle = \frac{4}{a_0^3} \int_0^\infty r^4 e^{-\frac{2r}{a_0}} dr$$

Using the standard integral $\int_0^\infty r^n e^{-\alpha r} = \frac{n!}{\alpha^{n+1}}$

$$\langle r^2 \rangle = \frac{4}{a_0^3} \frac{4!}{(2/a_0)^5} = 3(a_0)^2$$

Therefore, $\langle (r - \langle r \rangle)^2 \rangle = \langle r^2 \rangle - \langle r \rangle^2 = 3(a_0)^2 - \left(\frac{3}{2}a_0\right)^2 = \frac{3}{4}(a_0)^2$.

For any hydrogen-like atom substitute $1/a_0$ for Z/a_0 , so the final result for the He^+ atom is given by $Z=2$

$$\langle r \rangle = \frac{3}{4} a_0 = 0.75 a_0$$

$$\langle (r - \langle r \rangle)^2 \rangle = \frac{3}{16} a_0^2$$

$$\sigma_r = \frac{\sqrt{3}}{4} a_0 = 0.43 a_0$$

Therefore the percentage error is equal to $(\sigma_r / \langle r \rangle) \times 100$ or 58% !

Bonus (5 points)

What do Mexicans celebrate today?

The 1910 Revolution.