

Chem 361  
Quantum Chemistry  
Midterm Exam  
November 15, 2006



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 (5 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 \_\_\_\_\_

**Problem 1 (25 Points)**

**P19.24)** Selection rules in the dipole approximation are determined by the integral  $\mu_x^{mn} = \int \psi_m^*(\tau) \mu_x(\tau) \psi_n(\tau) d\tau$ . If this integral is nonzero, the transition will be observed in an absorption spectrum. If the integral is zero, the transition is “forbidden” in the dipole approximation. It actually occurs with low probability because the dipole approximation is not exact. Consider the particle in the one-dimensional box and set  $\mu_x = -ex$ .

a) Calculate  $\mu_x^{12}$  and  $\mu_x^{13}$  in the dipole approximation. Can you see a pattern and discern a selection rule? You may need to evaluate a few more integrals of the type  $\mu_x^{lm}$ . The standard integral

$$\int x \sin \frac{\pi x}{a} \sin \frac{n\pi x}{a} dx = \frac{1}{2} \left( \frac{a^2 \cos \frac{(n-1)\pi x}{a}}{(n-1)^2 \pi^2} + \frac{(n-1) a x \sin \frac{(n-1)\pi x}{a}}{(n-1)\pi} \right) - \frac{1}{2} \left( \frac{a^2 \cos \frac{(n+1)\pi x}{a}}{(n+1)^2 \pi^2} + \frac{a x \sin \frac{(n+1)\pi x}{a}}{(n+1)\pi} \right)$$

is useful for solving this problem.

b) Determine the ratio  $\mu_x^{12}/\mu_x^{14}$ . On the basis of your result, would you modify the selection rule that you determined in part (a)?

**Problem 2 (25 Points)**

**P20.7)** In this problem, you will calculate the probability density of finding the electron within a sphere of radius  $r$  for the H atom in its ground state.

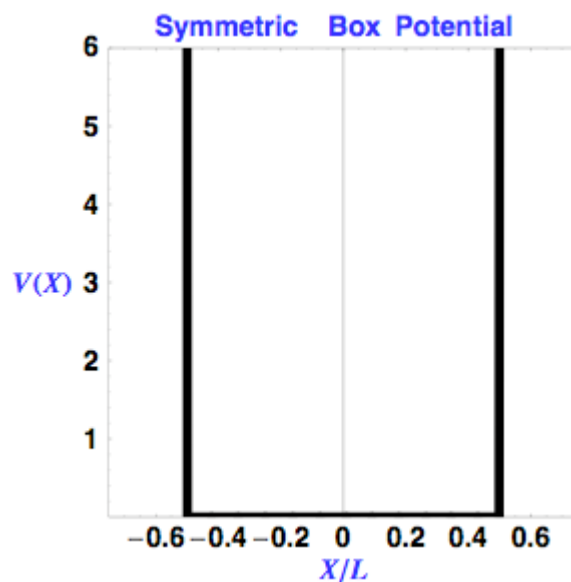
a) Show using integration by parts,  $\int u dv = uv - \int v du$ , that

$$\int r^2 e^{-\frac{r}{a}} dr = e^{-\frac{r}{a}} (-2a^3 - 2a^2 r - ar^2)$$

c) Evaluate this probability density for  $r = 0.10 a_0$ ,  $r = 1.0$

**Problem 3 (25 Points)**

Solve the Schrödinger equation for a particle in a symmetric box.

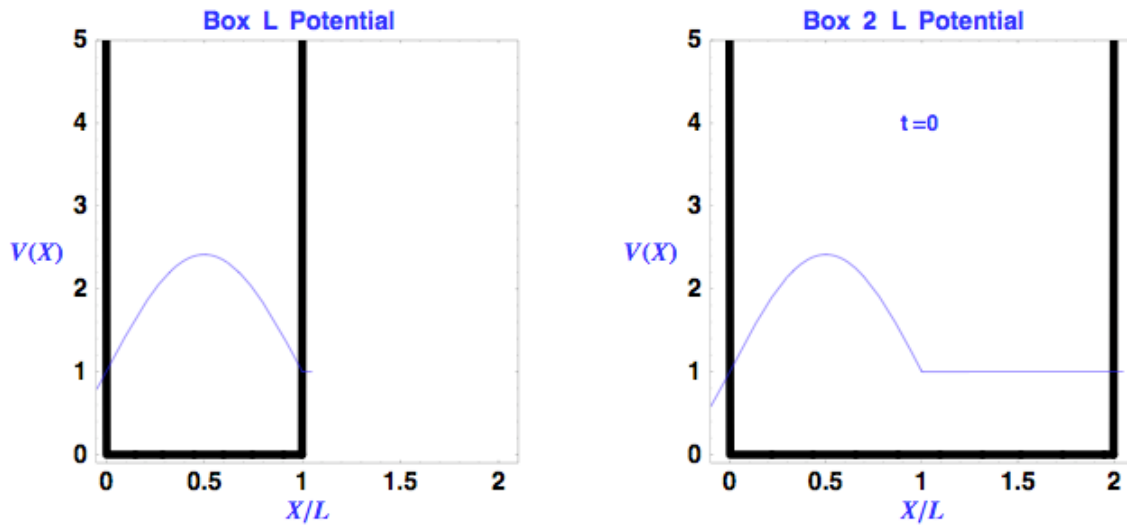


Notice that the boundary conditions are at  $x=-L/2$  and  $x=L/2$ .

- Find a general expression for the normalized eigenfunctions.
- Find the energy levels.

**Problem 4 (25 Points)****Nonadiabatic transition and superposition principle**

Sudden changes in the potential may be so fast that the system is not able to adjust instantaneously, as in the case illustrated below, where a box of size  $L$  is change to size  $2L$ . Before the change, the system is in its ground state, but after the change the initial function is not an eigenfunction of the bigger box. In particular notice that the function is zero for  $L < x < 2L$ .



After the change, if we measure the energy the system would collapse into one of the new eigenstates. What is the probability of finding the state in the ground state, and first excited state of the new potential?