Quantum Chemistry
Midterm I Exam
October 7, 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)**
If an electron passes through an electrical potential difference of 1 volt (V), it has energy of 1 electron-volt (eV). What potential difference must it pass through in order to have a wavelength of 0.100 nm? Electrons with this wavelength can be used to determine molecular structures by diffraction. Calculate the speed of an electron for which the wavelength is equal to a typical bond length, namely 0.100 nm.

$$E = |e|V \qquad E = \frac{p^2}{2m} \Rightarrow p = \sqrt{2mE}$$

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE}}$$

$$\lambda^2 = \frac{h^2}{2mE} = \frac{h^2}{2m|e|V} \Rightarrow \boxed{|e|V = \frac{h^2}{2m\lambda^2}}$$

$$|e|V = \frac{(6.626\times10^{-34}\,Js)^2}{2(9.109\times10^{-31}\,Kg)(10^{-10}\,m)^2} = \frac{2.41\times10^{-17}\,J}{1.602\times10^{-19}\,J}\,|e|V$$

$$= 150.\ eV \Rightarrow \boxed{V = 150 \text{ volts}}$$

$$p = \frac{h}{\lambda} \Rightarrow mv = \frac{h}{\lambda} \Rightarrow \boxed{v = \frac{h}{\lambda m}}$$

$$\boxed{v = \frac{(6.626\times10^{-34}\,Js)}{(10^{-10}\,m)(9.109\times10^{-31}\,Kg)} = 7.27\times10^{6}\,\frac{m}{s}}$$

Problem 2 **(25 points)**

Consider the following operator and function:

$$\hat{O} = \frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr} + \frac{2}{r}$$

$$f(r) = B\,e^{-d\,r}$$

Find the result of operating $\hat{O}$ on $f(r)$. What must the values of B and d be to make $f(r)$ an eigenfunction of the operator?

$$\hat{O} f(r) = \frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{df}{dr}\right) + \frac{2}{r} f$$

$$= \frac{1}{r^2}\left[2r\frac{df}{dr} + r^2\frac{d^2f}{dr^2}\right] + \frac{2}{r} f$$

$$= \frac{2}{r}\frac{d}{dr}Be^{-dr} + \frac{d^2}{dr^2}Be^{-dr} + \frac{2}{r} f$$

$$= -\frac{2}{r}Bd\,e^{-dr} + Bd^2 e^{-dn} + \frac{2}{r}Be^{-dr}$$

$$= \left[-\frac{2}{r}d + d^2 + \frac{2}{r}\right]Be^{-dr}$$

$$= \left[\left(\frac{2}{r}\right)(1-d) + d^2\right] f(r)$$

$d = 1 \Rightarrow \hat{O} f = f$ with $\lambda = 1$, $d = 1$

No restrictions on B.

Problem 3 (25 points)
The function

$$\Psi(x) = A\, x^2\, (x-a)^2$$

is an acceptable wave function for the particle in the one dimensional infinite depth box of length a. Calculate the normalization constant A, and the expectation values $< x >$ and $< x^2 >$.

$$1 = \int_0^a |\Psi(x)|^2 dx = \int_0^a A^2 x^4 (x-a)^4 dx = A^2 \int_0^a x^4 (x-a)^4 dx$$

$$= A^2 \int_0^a \left\{ x^4 \left[x^4 - 4x^3 a + 6x^2 a^2 - 4xa^3 + a^4 \right] dx \right.$$

$$= A^2 \int_0^a \left\{ x^8 - 4ax^7 + 6a^2 x^6 - 4a^3 x^5 + a^4 x^4 \right\} dx$$

$$= A^2 \left[\frac{1}{9} x^9 - \frac{4a}{8} x^8 + \frac{6a^2}{7} x^7 - \frac{4a^3}{6} x^6 + \frac{a^4}{5} x^5 \right]_0^a$$

$$= A^2 \left[\frac{a^9}{9} - \frac{1}{2} a^9 + \frac{6}{7} a^9 - \frac{2}{3} a^9 + \frac{1}{5} a^9 \right] \qquad CD = 9 \cdot 2 \cdot 7 \cdot 5 = 630$$

$$= A^2 \left[70 - 315 + 540 - 420 + 126 \right] \frac{a^9}{630} = \frac{A^2 a^9}{630}$$

$$\boxed{A = \sqrt{\frac{630}{a}} \frac{1}{a^4}}$$

$$\langle x \rangle = A^2 \int_0^a x^5 (x-a)^4 dx = A^2 \int_0^a \left[x^9 - 4ax^8 + 6a^2 x^7 - 4a^3 x^6 + a^4 x^5 \right] dx$$

$$= A^2 \left\{ \frac{1}{10} x^{10} - \frac{4a}{9} x^9 + \frac{6a^2}{8} x^8 - \frac{4a^3}{7} x^7 + \frac{a^4}{6} x^6 \right]_0^a$$

$$\langle x\rangle = A^2\left[\frac{1}{10}-\frac{4}{9}+\frac{6}{8}-\frac{4}{7}+\frac{1}{6}\right]a^{10} = \left(\frac{630}{a^9}\right)\frac{a^{10}}{2\cdot 630} = \frac{a}{2}\,!$$

$$\langle x^2\rangle = A^2\int_0^a x^6(x-a)^4\,dx = A^2\int_0^a\left[x^{10}-4ax^9+6a^2x^8-4a^3x^7+a^4x^6\right]dx$$

$$= A^2\left[\frac{1}{11}-\frac{4}{10}+\frac{6}{9}-\frac{4}{8}+\frac{1}{7}\right]a^{11}$$

$$= \left(\frac{\cancel{630}}{\cancel{a^9}}\right)\frac{12\,a^{\cancel{11}\,2}}{4\cdot\cancel{630}\cdot 11} = \boxed{\frac{3}{11}a^2 = \langle x^2\rangle}$$

$$\sqrt{\langle x^2\rangle} = \sqrt{\frac{3}{11}}\,a$$

Problem 4 (25 points)
Generally, the quantization of translational motion is not significant for atoms because of their mass. However, this conclusion depends on the dimensions of the space to which they are confined. Zeolites are structure with small pore that we can describe by a cube with edge length 1nm. Calculate the energy of an $Ar(g)$ molecule with $n_x = n_y = n_z = 10$. Compare the difference of this energy level with its adjacent level, $\Delta E_{j+1,j}$, to kT at T=300 K. Is classical or quantum description appropriate?

$$E_{n_x n_y n_z} = \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2 + n_z^2\right) = \frac{h^2}{8ma^2}(3\times10^2)$$

$$= \frac{(6.626\times10^{-34}\,Js)^2\,300}{8(39.95\,amu)(1.661\times10^{-27}\,Kg\,amu^{-1})(10^{-9}m)^2}$$

$$= 2.48\times10^{-22}\,J$$

$$\Delta E = E_{\alpha+1} - E_{\alpha} \quad \text{where } \alpha = \sqrt{300}$$

$$= \frac{h^2}{8ma^2}\left[(\alpha+1)^2 - \alpha^2\right] = \frac{h^2(2\alpha+1)}{8ma^2}$$

$$= \frac{(6.626\times10^{-34}\,Js)^2(2\sqrt{300}+1)}{8(39.95\,amu)(1.661\times10^{-27}\,kg\,amu^{-1})(10^{-9}m)^2}$$

$$= 1.51\times10^{-23}\,J$$

$$kT = 1.361\times10^{-23}\,JK^{-1}\;298K = 4.06\times10^{-21}\,J$$

$$\frac{\Delta E}{kT} = \frac{1.51\times10^{-23}\,J}{4.06\times10^{-21}\,J} = 3.72\times10^{-3} \ll 1$$

$$\simeq 0.4\%$$

CLASSICAL DESCRIPTION IS OK

Bonus (15 points)
Two Japanese and one US physicists won the 2008 Nobel in physics. Why?

Spontaneous symmetry breaking mechanism in particle physics.