

KEY

Chem 332: Third Exam (100 pts. possible)

Friday, April 19, 2013

Please budget your time carefully and show all work for partial credit. Read each problem carefully!

$h = 6.62608 \times 10^{-34} \text{ J s}$	$1 \text{ \AA} = 1 \times 10^{-10} \text{ m} = 0.1 \text{ nm}$	$\int_0^{\infty} x^n e^{-ax} dx = \frac{n!}{a^{n+1}}$
$N_A = 6.02214 \times 10^{23} \text{ mol}^{-1}$	$1 \text{ amu} = 1.66054 \times 10^{-27} \text{ kg}$	
$c = 2.99792 \times 10^8 \text{ m/s}$	$m_e = 9.10939 \times 10^{-31} \text{ kg}$	
$k_B = 1.38065 \times 10^{-23} \text{ J K}^{-1}$	$e^{\pm i\theta} = \cos\theta \pm i\sin\theta$	$\int_0^{\infty} x^2 e^{-ax^2} dx = \frac{1}{4a} \left(\frac{\pi}{a}\right)^{1/2}$
$E_n = -\frac{Z^2}{2n^2} \text{ (a.u.)}$	$[\ell_x, \ell_y] = i\hbar\ell_z$	$E_J = \hbar B J(J+1)$
$B = \frac{\hbar}{8\pi^2\mu r^2}$	$E_n = \hbar \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \left(n + \frac{1}{2}\right)$	$E_n = \frac{n^2 \hbar^2}{8mL^2}$
$\psi_n(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} H_n e^{-\alpha x^2/2}$	$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right)$	$\psi_k(\phi) = \frac{1}{\sqrt{2\pi}} e^{ik\phi}$
$\ell^2 Y_{l,m_l} = l(l+1)\hbar^2 Y_{l,m_l}$ $\ell_z Y_{l,m_l} = m_l \hbar Y_{l,m_l}$	$-\frac{\hbar^2}{2m} \nabla^2 + \frac{1}{2} kx^2$	$\ell_z = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$

- (1) (5 pts) Using the variation method for the standard 1-dimensional particle in a box problem, a student uses the trial function $\phi = \alpha x(L - \alpha x)$ where α is a variational parameter and the box is defined between $x=0$ and $x=L$. Upon minimizing the trial energy with respect to α , s/he finds that the trial energy is lower than the exact ground state energy!! Certainly this can't be right, but what is wrong? (be specific)

ϕ must satisfy the boundary conditions, but
 $\phi(L) \neq 0$

- (2) (30 pts) Consider the $n = 2 \rightarrow 3$ ro-vibrational band of the $^{11}\text{B}^{19}\text{F}$ molecule within the harmonic oscillator, rigid-rotor approximation. The harmonic frequency and rotational constant of this isotopomer are equal to 1402.13 cm^{-1} and 1.50724 cm^{-1} , respectively.

$$[m(^{19}\text{F}) = 18.9984 \text{ amu}, m(^{11}\text{B}) = 11.0093 \text{ amu}, m(^{10}\text{B}) = 10.0129 \text{ amu}]$$

- (a) Determine the frequency (in cm^{-1}) of the P-branch transition with $J = 4 \rightarrow 3$.

$$\begin{aligned} \frac{E_{n,J}}{hc} &= \tilde{\omega}_e (n + 1/2) + \tilde{B} J(J+1) \\ \Delta E &= \tilde{\omega}_e [7/2 - 5/2] + \tilde{B} [12 - 20] = \tilde{\omega}_e - 8\tilde{B} \\ &= 1390.07 \text{ cm}^{-1} \end{aligned}$$

- (b) Compared to your result of part (a), how would the use of a Morse potential function (instead of a harmonic oscillator) qualitatively change it?

The introduction of anharmonicity by the Morse potential would yield a lower transition ~~energy~~ frequency.

- (c) Predict the harmonic frequency (in cm^{-1}) for the $^{10}\text{B}^{19}\text{F}$ isotopomer.

$$\mu(^{11}\text{B}) = \frac{(11.0093)(18.9984)}{11.0093 + 18.9984} = 6.97018 \text{ a.u.}$$

$$\omega_e \propto \frac{1}{\sqrt{\mu}}$$

$$\mu(^{10}\text{B}) = 6.55707 \text{ amu}$$

$$\tilde{\omega}_e(^{10}\text{BF}) = \tilde{\omega}_e(^{11}\text{BF}) \sqrt{\frac{\mu(^{11}\text{B})}{\mu(^{10}\text{B})}} = 1402.13 \sqrt{\frac{6.97018}{6.55707}} = 1445.62 \text{ cm}^{-1}$$

- (d) Predict the equilibrium bond length (in \AA) of BF.

$$\begin{aligned} \tilde{B} &= \frac{h}{8\pi^2 \mu c r^2} & r^2 &= \frac{6.62608 \times 10^{-34}}{(8)(\pi)^2 (6.97018)(1.66054 \times 10^{-27})(2.99792 \times 10^{10}) \times 1.50724} \\ & & &= 1.6046 \times 10^{-20} \text{ m}^2 \\ r &= 1.2667 \times 10^{-10} \text{ m} = 1.2667 \text{ \AA} \end{aligned}$$

- (3) (15 pts.) A normalized trial function of the form (in atomic units) $\phi = \left[\frac{(2\beta)^7}{4\pi 6!} \right]^{1/2} r^2 e^{-\beta r}$, where β is an adjustable parameter, is used in the variation method to obtain the lowest possible energy for the hydrogen atom ground state. An intermediate result along this process is $\int \phi H \phi d\tau = \frac{\beta^2}{10} - \frac{\beta}{3}$.

- (a) Complete the variational calculation to obtain the optimal β and the best value of the trial energy.

$$\text{minimize } E_{\text{trial}} \text{ wrt to } \beta \quad ; \quad \frac{\partial}{\partial \beta} \left[\frac{\beta^2}{10} - \frac{\beta}{3} \right] = 0$$

$$\frac{2\beta}{10} - \frac{1}{3} = 0 \quad \beta_{\text{opt}} = 5/3$$

$$\therefore E = \frac{1}{10} \left(\frac{5}{3} \right)^2 - \frac{1}{3} \left(\frac{5}{3} \right) = -\frac{25}{90} = -\frac{5}{18} \text{ a.u.}$$

- (b) What is the percent error in this result? Qualitatively, can you explain why this trial function maybe doesn't perform so well?

$$\text{exact result: } E_n = \frac{-1^2}{2 \cdot 1^2} = -\frac{1}{2} \text{ a.u.}$$

$$\% \text{ error} = \frac{-0.5 - (-0.278)}{-0.5} \times 100 = 44.4\%$$

this ϕ has an r^2 factor which does not appear in exact 4. Wrong behavior at origin.

- (4) (30 pts) Consider the C atom.

- (a) Write the full hamiltonian operator for this atom using SI units. Feel free to use summation symbols but completely specify the limits.

$$\hat{H} = \frac{-\hbar^2}{2m_e} \sum_{i=1}^6 \nabla_i^2 - \frac{6e^2}{4\pi\epsilon_0} \sum_{i=1}^6 \frac{1}{r_i} + \sum_{i=1}^6 \sum_{j>i}^6 \frac{e^2}{4\pi\epsilon_0 r_{ij}}$$

- (b) Consider its $1s^2 2s^2 2p^2$ ground state configuration. What would you predict its ground state level to be? (give the term symbol)

$$m_s \quad - \quad \uparrow \quad \uparrow \\ -1 \quad 0 \quad 1$$

$$\text{max } S : 1 \text{ (triplet)}$$

$$\text{max } L : 1 \text{ (P)}$$

$$\text{min } J : 0$$

$$\boxed{3P_0}$$

- (c) Now consider its $1s^2 2s^2 2p^1 3p^1$ excited state configuration. What is the energy of this state within the independent particle approximation? (use atomic units)

$$E_{\text{IPA}} = 2E_{1s} + 2E_{2s} + E_{2p} + E_{3p} \quad E_n = \frac{-Z^2}{2n^2} = \frac{-36}{2n^2}$$

$$= 2\left(\frac{-36}{2}\right) + 3\left(\frac{-36}{8}\right) + \frac{-36}{18} = -51.5 \text{ a.u.}$$

- (d) Now determine all the possible terms and levels of the excited configuration of part (c), i.e., find the term symbols. How many states are associated with each term?

$$\left. \begin{array}{l} l_1 = 1 \\ l_2 = 1 \end{array} \right\} L = 2, 1, 0 \quad {}^3D, {}^3P, {}^3S, {}^1D, {}^1P, {}^1S \text{ terms}$$

$$\left. \begin{array}{l} s_1 = 1/2 \\ s_2 = 1/2 \end{array} \right\} S = 1, 0 \quad {}^3D_3, {}^3D_2, {}^3D_1, {}^1D_2 \quad 7+5+3+5 = 20 \text{ states}$$

$${}^3P_2, {}^3P_1, {}^3P_0, {}^1P_1 \quad 5+3+1+3 = 12 \text{ states}$$

$${}^3S_1, {}^1S_0 \quad 3+1 = 4 \text{ states}$$

- (e) From your results of part (d), choose the level with the largest value of J and write a Slater determinant wavefunction for the state with $M_J = +J$. Be as specific as possible in labeling the spin-orbitals chosen for your determinant. (Hint: remember that $M_J = M_L + M_S$ and use this to determine which p_m orbitals are occupied) For half credit, you can just choose to write a Slater determinant for this electron configuration choosing any valid spin-orbital combination.

For $J=3$, corresponding to 3D_3
 need $m_s = 1, m_L = 2$

$$\psi = \frac{1}{\sqrt{6!}}$$

$1s\alpha$	$1s(1)\alpha(1)$...	$1s(6)\alpha(6)$
$1s\beta$	$1s(1)\beta(1)$...	$1s(6)\beta(6)$
$2s\alpha$	$2s(1)\alpha(1)$...	$2s(6)\alpha(6)$
$2s\beta$	$2s(1)\beta(1)$...	$2s(6)\beta(6)$
$2p_1\alpha$	$2p_1(1)\alpha(1)$...	$2p_1(6)\alpha(6)$
$3p_1\alpha$	$3p_1(1)\alpha(1)$...	$3p_1(6)\alpha(6)$

(5) (10 pts) Consider a hydrogen atom in a $2p$ excited state with a wavefunction given by:

$$\psi_{2p_0} = R_{2,1}(r)Y_{1,0}(\theta, \phi), \text{ where (in atomic units) } R_{2,1} = \frac{1}{\sqrt{24}}re^{-r/2} \text{ and } Y_{1,0} = \frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta.$$

(a) What is the radial distribution function, $P(r)$, for this state? (be specific)

$$P(r) = |R_{n\ell}|^2 r^2 = \frac{1}{24} r^4 e^{-r}$$

(b) Calculate the most probable distance (in a.u.) of the electron from the nucleus for this state.

for r_{mp}

$$\begin{aligned} \frac{\partial P(r)}{\partial r} = 0 &= -\frac{r^4}{24} e^{-r} + \frac{4}{24} r^3 e^{-r} \\ &= -r + 4 \end{aligned}$$

$$r_{mp} = 4 \text{ a.u.}$$

(6) (10 pts)

(a) Describe the major features of the Born-Oppenheimer approximation and its impact on solutions to the molecular Schrödinger equation.

Since the nuclei masses \gg electron mass, their velocities are very different. So the e^- 's can instantaneously adapt to changes in the nuclear coordinates. Leads to 2 separate S.E.s: one for e^- motion (as function of nuclear coord) & one for nuclear motion.

(b) Define the the Pauli Principle as it applies to electrons.

The total (space + spin) wavefunction must be antisymmetric with respect to pairwise interchanges of electrons.