

KEY

2nd Exam (90 pts. possible)

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

$h = 6.62607 \times 10^{-34} \text{ J s}$	$1 \text{ \AA} = 1 \times 10^{-10} \text{ m}$	$m(^{11}\text{B}) = 11.00931 \text{ amu}$
$N_A = 6.02214 \times 10^{23} \text{ mol}^{-1}$	$1 \text{ amu} = 1.66054 \times 10^{-27} \text{ kg}$	$m(^{10}\text{B}) = 10.01294 \text{ amu}$
$c = 2.997925 \times 10^8 \text{ m/s}$	$B = h/(8\pi^2\mu r^2)$	$m(^{19}\text{F}) = 18.99840 \text{ amu}$

(1) (15 pts) Describe 3 out of the 5 Postulates of Quantum Mechanics. For each, use just a single sentence and perhaps a formula if needed.

- ① The physical state of a system is completely described by the wavefunction.
- ② A hermitian operator can be associated with any classical observable.
- ③ Wavefunctions satisfy the time dependent Schrödinger equation.
- ④ measurement of an observable can only yield one of the eigenvalues of its operator.
- ⑤ The expectation value is defined by
$$\frac{\int \psi^* \hat{B} \psi d\tau}{\int \psi^* \psi d\tau}$$

(2) (9 pts) Describe 3 major problems or inaccuracies inherent to using the harmonic oscillator approximation for diatomic vibrations. Be specific and concise.

- 1) evenly spaced energy levels
- 2) selection rules do not include $\Delta n \neq 1$
- 3) infinite number of vibrational levels since molecule can not dissociate.

(3) (15 pts) Given that the time dependent Schrödinger equation is given by $H\Psi = i\hbar \frac{\partial \Psi}{\partial t}$, where

$\Psi = \Psi(q, t)$, use the separation of variables technique to

(a) recover the time independent Schrödinger equation and

(b) show that the time dependence of Ψ is proportional to $e^{-iEt/\hbar}$.

For both (a) and (b) assume that H is a function only of the coordinates q . Explain/justify all steps.

$$\text{let } \Psi = \psi(q) \phi(t)$$

substitute:

$$\psi H \psi = i\hbar \psi \frac{\partial \phi}{\partial t}$$

divide by ψ

$$\frac{1}{\psi} H \psi = i\hbar \frac{1}{\phi} \frac{\partial \phi}{\partial t}$$

function of q only

function of t only

\Rightarrow both must equal a constant
let's call it E

$$\Rightarrow H\psi = E\psi \quad \checkmark$$

$$\Rightarrow i\hbar \frac{\partial \phi}{\partial t} = E\phi$$

$$\text{or } \frac{d\phi}{\phi} = \frac{E}{i\hbar} dt$$

$$\text{integrate: } \ln \phi = \frac{E}{i\hbar} t + C$$

$$\text{or } \phi = c' e^{-iEt/\hbar} \quad \checkmark$$

(4) (30 pts) Consider the first overtone vibrational band ($n = 0 \rightarrow 2$) 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.

(a) Determine the frequency (in cm^{-1}) of the $J = 5 \rightarrow 6$ R-branch transition in the 1st overtone.

$$\begin{aligned} \frac{E}{hc} &= \tilde{\omega}_e(n+1/2) + \tilde{B}J(J+1) \\ \frac{\Delta E}{hc} &= \tilde{\omega}_e \left[\frac{5}{2} - \frac{1}{2} \right] + \tilde{B} [6(7) - 5(6)] \\ &= 2\tilde{\omega}_e + 12\tilde{B}_e \\ &= 2(1402.13) + 12(1.50724) = 2822.35 \text{ cm}^{-1} \end{aligned}$$

(b) The ^{10}B isotope has a natural abundance of nearly 20%. Predict the frequency (in cm^{-1}) of the same transition as part (a) for the $^{10}\text{B}^{19}\text{F}$ isotopomer.

$$\tilde{\omega}_e(^{10}\text{B}) = \tilde{\omega}_e(^{11}\text{B}) \sqrt{\frac{\mu_{^{11}\text{B}}}}{\mu_{^{10}\text{B}}}} \quad \mu_{^{11}\text{B}} = \frac{(11.00931)(18.99840)}{11.00931 + 18.99840}$$

$$= 6.970185$$

$$\tilde{B}_e(^{10}\text{B}) = \tilde{B}_e(^{11}\text{B}) \cdot \frac{\mu_{^{11}\text{B}}}{\mu_{^{10}\text{B}}} \quad \mu_{^{10}\text{B}} = 6.55709$$

$$\tilde{\omega}_e(^{10}\text{B}) = (1402.13)(1.03102) = 1445.62 \text{ cm}^{-1}$$

$$\tilde{B}_e(^{10}\text{B}) = (1.50724)(1.06300) = 1.60220 \text{ cm}^{-1}$$

$$\nu(^{10}\text{BF}) = 2910.47 \text{ cm}^{-1}$$

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

$$B = \frac{h}{8\pi^2\mu r^2}$$

$$r = \sqrt{\frac{h}{8\pi^2\mu B}} = \sqrt{\frac{h}{8\pi^2\mu \tilde{B}_e}}$$

$$\begin{aligned} \mu &= 6.970185 \text{ amu} \times 1.66054 \times 10^{-27} \text{ kg/amu} \\ &= 1.15743 \times 10^{-26} \text{ kg} \end{aligned}$$

$$r = 1.2667 \times 10^{-10} \text{ m}$$

$$= 1.2667 \text{ \AA}$$

- (5) (16 pts) The physical state of a system under study is well-described as a superposition of particle-in-a-1-dimensional box eigenfunctions:

$$\psi = \frac{1}{\sqrt{2}}\phi_1 + \frac{1}{\sqrt{3}}\phi_2 + \frac{1}{\sqrt{6}}\phi_3$$

where $\phi_n = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right)$ with corresponding eigenvalues $E_n = \frac{n^2 h^2}{8mL^2}$.

- (a) What are the possible outcomes for a single measurement of the total energy E (in units of $\frac{h^2}{8mL^2}$) and what are the probabilities of obtaining each one?

E	prob = $ c_n ^2$
1	$\frac{1}{2}$
4	$\frac{1}{3}$
9	$\frac{1}{6}$

- (b) What is the expectation value of the total energy for this system?

$$\langle H \rangle = \frac{1}{2}(1) + \frac{1}{3}(4) + \frac{1}{6}(9) = \frac{10}{3} \frac{h^2}{8mL^2}$$

- (6) (5 pts) Consider a simple harmonic oscillator where its 1st excited state is represented by the wave function $\psi(x) = N\alpha^{1/2} x e^{-\alpha x^2/2}$, where both N and α are constants. Set up an expression that may be used to solve for N in such a way that $\psi(x)$ will be normalized. Simplify as much as possible but do not do any integrals.

$$\int |\psi|^2 dx = 1$$

$$N^2 \alpha \int_{-\infty}^{\infty} x^2 e^{-\alpha x^2/2} dx = 1$$

$$N = \sqrt{\frac{1}{2\alpha \int_0^{\infty} x^2 e^{-\alpha x^2/2} dx}}$$