

Chemistry 346
Spring, 2005
Final Exam

1 (20 points). A cell contains 1 Torr of argon atoms at room temperature.

A. Provide an order of magnitude estimate of how many collisions each atom undergoes in one second. Explain any assumptions that you made to arrive at your answer.

B. Use the previous result to estimate the average distance an atom travels between collisions.

2 (15 points). Consider a sample of NO molecules adsorbed onto a graphite surface at temperature T. The atoms are confined to a plane but are free to move around on that plane.

A. Write down the speed distribution function for these molecules. It is not necessary to normalize this function.

B. Determine the most probable value of the speed. You may express your answer as a multiple of the quantity $a = (2kT/m)^{1/2}$.

3 (20 points). A sample of molecules is excited with a laser to an electronically excited state. The molecules are observed to spontaneously emit photons, so that after 1.0 sec half of the molecules have returned to the ground state. How long after the laser is fired will it take until 90% of the molecules have returned to the ground state? Give a numerical value.

4 (20 points). In this problem we will compare the properties of some elementary systems in quantum mechanics. Copy this page into your exam book, and fill in the boxes for each system:

System	Spacing between energy levels increases, remains the same, or decreases with increasing energy. (Select one.)	Value of the zero-point energy. If it is zero, write "0".
Particle in a box		
Rigid Rotor		
Harmonic oscillator		
Anharmonic oscillator		
Hydrogen Atom		

5 (30 points). In this problem we explore different ways in which probability is used in quantum mechanics. We will use a harmonic oscillator as a case study.

- A. Suppose you have a mixture of oxygen molecules in thermal equilibrium at a temperature of 1,000 K. The vibrational frequency of oxygen is $1,580 \text{ cm}^{-1}$. What is the ratio of the number of molecules in the $\nu=1$ state vs. the number in the $\nu=0$ state?
- B. Suppose instead that the molecules are in a superposition state with the following wave function:

$$\mathbf{y}(y) = \frac{1}{2}\mathbf{y}_0(y) + \frac{\sqrt{3}}{2}\mathbf{y}_1(y),$$

- where $\mathbf{y}_\nu(y)$ is the ν^{th} eigenfunction of the Hamiltonian, and y is a reduced distance. Suppose further that a measurement is made of the energy of the molecules. What are the possible outcomes of such a measurement, and what is the probability of obtaining each outcome?
- C. Continuing with the superposition state in part B, suppose a measurement is made of the oscillator stretch, y . What is the relative probability of obtaining a value $y = -1$ compared with $y = 1$? (A table of harmonic oscillator eigenfunctions is provided.)

6 (20 points). In this problem we explore some of the spatial properties of the hydrogen atom. The radial wave function for the ground state atom is given by

$$y(r) = \frac{2}{a_0^{3/2}} e^{-r/a_0}$$

where a_0 is the Bohr radius.

- A. At what point in space is the electron most likely to be found? Give the Cartesian coordinates of that point.
- B. Write down the probability distribution function for finding the electron at a radial distance between r and $r + dr$.
- C. At what radial distance r is the electron most likely to be found? Express your answer as a multiple of a_0 .

7 (20 points). The spin-orbit operator is given by

$$H_{so} = \frac{Ze^2}{2mc^2} \frac{1}{r^3} \hat{L} \cdot \hat{S}$$

where \hat{L} and \hat{S} are the vector operators for orbital and spin angular momentum. Use perturbation theory to calculate the energy difference between the ${}^2P_{1/2}$ and the ${}^2P_{3/2}$ states of the hydrogen atom. The 2p radial wave function is

$$R_{2p} = \frac{1}{2\sqrt{6}} \frac{1}{a_0^{5/2}} r e^{-r/2a_0}$$

Hint: Your answer should contain two factors, one for the radial part of the operator, and the other for the angular momentum part. You will be given equal credit for each factor.

8 (15 points). Consider the spin of an electron.

- A. What is the length of the spin angular momentum vector?
- B. What angle does the angular momentum vector make with the z-axis?

9 (20 points). Use the following table from Herzberg to calculate the wavelength for the transition from $X^3\Sigma_g^-(v''=0, J''=10)$ to $b^1\Sigma_g^+(v'=3, J'=9)$ for the oxygen molecule. Find first the transition energy in cm^{-1} and then find the wavelength in nm. Include in your calculation the effects of anharmonicity, centrifugal distortion, and vibration-rotation interaction. (Note: T_e refers to the energy at the minimum of the associated potential energy curve. All quantities are in cm^{-1} , unless indicated otherwise. Use $B_e = 1.44563$ for the X state.)

State	T_e	ω_e	$\omega_e x_e$	B_e	α_e	D_e (10^{-6}cm^{-1})	r_e (Å)	Observed Transitions		References
								Design.	ν_{00}	
¹⁶ O ₂ (continued)										
b $^1\Sigma_g^+$	13195.1	1432.77 ^a	± 14.00 ^a	1.40037 ^a	0.01820 ^a	5.351 ^b	1.22688	b→a, c	5238.5	(40)
								b→X, d ₀ R	13120.91 ^c	(12)*
								Atmospheric oxygen b.		
a $^1\Delta_g$	7918.1	[1483.5 ₀]	± (12.9)	1.4264	0.0171	[4.86]	1.2156 ₃	a ^d →X, h ₀ R	7882.39	(10)*
								IR atmosph. oxygen b.		
X $^3\Sigma_g^-$	0	1580.19 ₃	± 11.98 ₁ ⁱ	[1.4376766] ^j B ₀ = 1.44563	0.0159 ₃ ^{kl}	[4.839] ^{kl}	1.20752	Rot.-vibr. sp. (collision induced)		(12a)(75a) (142)
								Rotation sp. ^m		(94)(105)
								Spin reorientation (fine structure) sp. ^{no}		(20)(41)(76) (120)(159)
								Raman sp. ^p		(38)* (124)* (162)(183)*
								EPR sp.		(25)(138)(154)

10 (20 points). In class we worked out the possible term symbols for two equivalent p electrons. Now do the same thing for **three equivalent p electrons**. Use the attached work sheet to guide you, and hand it in with your exam book. Your entire answer should be on that sheet. A spare work sheet is provided in case you need it.

General data and fundamental constants

Quantity	Symbol	Value	Power of ten	Units
Speed of light	c	2.997 924 58*	10^8	m s^{-1}
Elementary charge	e	1.602 176	10^{-19}	C
Faraday constant	$F = N_A e$	9.648 53	10^4	C mol^{-1}
Boltzmann constant	k	1.380 65	10^{-23}	J K^{-1}
Gas constant	$R = N_A k$	8.314 47		$\text{J K}^{-1} \text{mol}^{-1}$
		8.314 47	10^{-2}	$\text{L bar K}^{-1} \text{mol}^{-1}$
		8.205 74	10^{-2}	$\text{L atm K}^{-1} \text{mol}^{-1}$
		6.236 37	10	$\text{L Torr K}^{-1} \text{mol}^{-1}$
Planck constant	h	6.626 08	10^{-34}	J s
	$\hbar = h/2\pi$	1.054 57	10^{-34}	J s
Avogadro constant	N_A	6.022 14	10^{23}	mol^{-1}
Atomic mass unit	u	1.660 54	10^{-27}	kg
Mass				
electron	m_e	9.109 38	10^{-31}	kg
proton	m_p	1.672 62	10^{-27}	kg
neutron	m_n	1.674 93	10^{-27}	kg
Vacuum permittivity	$\epsilon_0 = 1/c^2 \mu_0$	8.854 19	10^{-12}	$\text{J}^{-1} \text{C}^2 \text{m}^{-1}$
	$4\pi\epsilon_0$	1.112 65	10^{-10}	$\text{J}^{-1} \text{C}^2 \text{m}^{-1}$
Vacuum permeability	μ_0	$4\pi^*$	10^{-7}	$\text{J s}^2 \text{C}^{-2} \text{m}^{-1} (= \text{T}^2 \text{J}^{-1} \text{m}^2)$
Magneton				
Bohr	$\mu_B = e\hbar/2m_e$	9.274 01	10^{-24}	J T^{-1}
nuclear	$\mu_N = e\hbar/2m_p$	5.050 78	10^{-27}	J T^{-1}
g value	g_e	2.002 32		
Bohr radius	$a_0 = 4\pi\epsilon_0\hbar^2/m_e e^2$	5.291 77	10^{-11}	m
Fine-structure constant	$\alpha = \mu_0 e^2 c/2h$	7.297 35	10^{-3}	
	α^{-1}	1.370 36	10^3	
Second radiation constant	$c_2 = hc/k$	1.438 78	10^{-2}	m K
Stefan-Boltzmann constant	$\sigma = 2\pi^5 k^4/15h^3 c^2$	5.670 51	10^{-8}	$\text{W m}^{-2} \text{K}^{-4}$
Rydberg constant	$R = m_e e^4/8h^3 c \epsilon_0^2$	1.097 37	10^7	cm^{-1}
Standard acceleration of free fall	g	9.806 65*		m s^{-2}
Gravitational constant	G	6.673	10^{-11}	$\text{N m}^2 \text{kg}^{-2}$

* Exact value

TABLE A.5 Integrals

$$\int x \sin bx \, dx = \frac{1}{b^2} \sin bx - \frac{x}{b} \cos bx \quad (\text{A.1})$$

$$\int \sin^2 bx \, dx = \frac{x}{2} - \frac{1}{4b} \sin (2bx) \quad (\text{A.2})$$

$$\int x \sin^2 bx \, dx = \frac{x^2}{4} - \frac{x}{4b} \sin (2bx) - \frac{1}{8b^2} \cos (2bx) \quad (\text{A.3})$$

$$\int x^2 \sin^2 bx \, dx = \frac{x^3}{6} - \left(\frac{x^2}{4b} - \frac{1}{8b^3} \right) \sin (2bx) - \frac{x}{4b^2} \cos (2bx) \quad (\text{A.4})$$

$$\int x e^{bx} \, dx = \frac{e^{bx}}{b^2} (bx - 1) \quad (\text{A.5})$$

$$\int x^2 e^{bx} \, dx = e^{bx} \left(\frac{x^2}{b} - \frac{2x}{b^2} + \frac{2}{b^3} \right) \quad (\text{A.6})$$

$$\int_0^{\infty} x^n e^{-qx} \, dx = \frac{n!}{q^{n+1}}, \quad n > -1, q > 0 \quad (\text{A.7})$$

$$\int_0^{\infty} e^{-bx^2} \, dx = \frac{1}{2} \left(\frac{\pi}{b} \right)^{1/2}, \quad b > 0 \quad (\text{A.8})$$

$$\int_0^{\infty} x^{2n} e^{-bx^2} \, dx = \frac{1 \cdot 3 \cdots (2n-1)}{2^{n+1}} \left(\frac{\pi}{b^{2n+1}} \right)^{1/2}, \quad b > 0, n = 1, 2, 3, \dots \quad (\text{A.9})$$

$$\int_t^{\infty} z^n e^{-az} \, dz = \frac{n!}{a^{n+1}} e^{-at} \left(1 + at + \frac{a^2 t^2}{2!} + \cdots + \frac{a^n t^n}{n!} \right), \quad n = 0, 1, 2, \dots, a > 0 \quad (\text{A.10})$$

$$\int_0^{\infty} x^{2n+1} e^{-bx^2} \, dx = \frac{n!}{2b^{n+1}}$$

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C.2. Energy Equivalences

	Wave Number	Frequency	Energy	Energy	Molar Energy	Molar Energy
	(cm ⁻¹)	MHz	eV	hartrees	kJ / mol	kcal / mol
1 (cm⁻¹)	1	2.99793E+04	1.23984E-04	4.55634E-06	1.19627E-02	2.85914E-03
1 MHz	3.33564E-05	1	4.13567E-09	1.151983E-10	3.99031E-07	9.53708E-08
1 eV	8.06554E+03	2.41799E+08	1	3.67493E-02	9.64853E+01	2.30605E+01
1 hartree	2.19475E+05	6.57968E+09	2.72114E+01	1	2.62550E+03	6.27510E+02
1 kJ/mol	8.35935E+01	2.50607E+06	1.03643E-02	3.80880E-04	1	2.39006E-01
1 kcal/mol	3.49755E+02	1.04854E+07	4.33641E-02	1.59360E-03	4.18400E+00	1

$$1 \text{ cm}^{-1} = 1.4388 \text{ K}$$

$$\psi_v(x) = N_v H_v(y) \exp\left[-\frac{y^2}{2}\right], \quad (12.148)$$

where $y = \alpha^{1/2} x$, with $\alpha = (\mu k)^{1/2}/\hbar$. The normalization constant is given by

$$N_v = \left[\left(\frac{1}{\pi} \right)^{1/2} \frac{1}{2^v v!} \right]^{1/2}. \quad (12.149)$$

In Eq. 12.148, $H_v(y)$ is a polynomial in y whose leading power is y^v . $H_v(y)$ is called a *Hermite polynomial*. Hermite polynomials and their associated vibrational-energy eigenvalues are listed in Table 12.2.

Table 12.2 Energy eigenvalues and Hermite polynomials for the harmonic oscillator

v	E_v	$H_v(y)$
0	$\frac{1}{2}h\nu_0$	1
1	$\frac{3}{2}h\nu_0$	$2y$
2	$\frac{5}{2}h\nu_0$	$4y^2 - 2$
3	$\frac{7}{2}h\nu_0$	$8y^3 - 12y$
4	$\frac{9}{2}h\nu_0$	$16y^4 - 48y^2 + 12$
5	$\frac{11}{2}h\nu_0$	$32y^5 - 160y^3 + 120y$
6	$\frac{13}{2}h\nu_0$	$64y^6 - 480y^4 + 720y^2 - 120$

Note: $\nu_0 =$ classical vibration frequency $= (1/2\pi)(k/\mu)^{1/2}$.

1. A $\lambda = v \sigma v$

$$v = 1.29 \times 10^4 \sqrt{\frac{1}{M}} = 3.5 \times 10^4 \text{ cm/s}$$

$$\sigma \approx 1 \text{ \AA}^2 = 10^{-16} \text{ cm}^2$$

$$PV = NRT, \quad \frac{N}{V} = \frac{P}{RT} = \frac{1}{62.36 \times 310} \frac{\text{mole}}{\text{liter}} = 5.34 \times 10^{-6} \frac{\text{mole}}{\text{cm}^3}$$

$$= 3.22 \times 10^{16} \text{ molecules/cm}^3$$

$$\lambda = 3.5 \times 10^4 \times 10^{-16} \times 3.22 \times 10^{16} = 1.1 \times 10^5 \text{ s}^{-1}$$

B. $\lambda = v/\lambda = 0.32 \text{ cm}$

2. A. $\phi(x) = N v e^{-v^2/2} \propto x e^{-x^2}$

B. $\frac{d\phi}{dx} = 1 - 2x^2 = 0, \quad x = \frac{1}{\sqrt{2}}, \quad N_{\text{mp}} = \alpha/\sqrt{2}$

3. $N/N_0 = e^{-t/\tau}$

$$\frac{1}{2} = e^{-t/\tau}$$

$$\ln 2 = t/\tau, \quad \tau = 1.4427 \text{ s}$$

$$N/N_0 = 0.1 = e^{-t/\tau}$$

$$2.302 = t/\tau, \quad \Rightarrow \quad t = \frac{3.322}{\tau} = 3.322 \tau$$

4. See Table

5. A. $P_1/P_0 = e^{-h\nu/kT}$

$$h\nu = 1580 \text{ cm}^{-1}, \quad kT = 695.0 \text{ cm}^{-1}$$

$$P_1/P_0 = e^{-1580/695} = 0.103 = e^{-2.27}$$

B. $E_0 = \frac{1}{2} h\nu, \quad P_0 = \frac{1}{4}; \quad E_1 = \frac{3}{2} h\nu, \quad P_1 = \frac{3}{4}$

C. $\psi(y) = \frac{1}{\sqrt{\pi}} \pi^{-1/4} e^{-y^2/2} + \frac{\sqrt{2}}{\sqrt{\pi}} \pi^{-1/4} \sqrt{\frac{1}{2}} \cdot 2y e^{-y^2/2}$

$$P(y) = \psi^2 = \frac{1}{\sqrt{\pi}} e^{-y^2} \left[\frac{1}{2} + \sqrt{\frac{2}{\pi}} y \right]^2$$

$$P(-1)/P(1) = \left[\frac{\frac{1}{2} - \sqrt{\frac{2}{\pi}}}{\frac{1}{2} + \sqrt{\frac{2}{\pi}}} \right]^2 = 0.177$$

6 A. $r=0$ or $x=0, y=0, z=0$

B. $\rho(r) = \frac{Qr^2}{a_0^3} e^{-2r/a_0}$

C. $\rho = r/a_0 \Rightarrow \rho(r) \propto r^2 e^{-2r}$

$$\frac{d\rho}{dr} = 2r - 2r^2 = 0 \Rightarrow r=1, \quad r = a_0$$

7. $\langle \frac{1}{r^3} \rangle = \frac{1}{4 \cdot 6 a_0^5} \int_0^\infty \frac{r^4}{r^3} e^{-r/a_0} dr = \frac{1}{24 a_0^3}$

$$\vec{J}^2 = (\vec{L} + \vec{S})^2 = L^2 + S^2 + 2\vec{L} \cdot \vec{S}$$

$$2\langle \vec{L} \cdot \vec{S} \rangle = [J(J+1) - L(L+1) - S(S+1)] \hbar^2$$

$$J=3/2, L=1, S=1/2, \quad \langle \vec{L} \cdot \vec{S} \rangle = \frac{\hbar^2}{2} \left[\frac{3}{2} \cdot \frac{5}{2} - 2 \cdot \frac{3}{2} \right] = \frac{\hbar^2}{2}$$

$$J=1/2, \quad \langle \vec{L} \cdot \vec{S} \rangle = \frac{\hbar^2}{2} \left[\frac{3}{4} - 2 \cdot \frac{3}{4} \right] = -\frac{\hbar^2}{2}$$

$$\Delta E_{s_0} = \frac{e^2}{2mc^2} \frac{1}{24a_0^3} \frac{3}{2} \hbar^2$$

8. A. $\sqrt{S(S+1)} \hbar = \sqrt{\frac{3}{4}} \hbar$

B. $\cos \theta = \frac{3/4}{\sqrt{3/4}} = \sqrt{\frac{1}{3}}, \quad \theta = 54.7^\circ$

9. X state, $B_0 = 1.44563 - 0.01593 \times \frac{1}{2} = 1.437665$

$$E_x = \frac{1}{2}(1560193) - \frac{1}{4}(11.96) + 1.437665 \times 10111 - 4.639 \times 10^{-6} \times 100 \times 121 = 961.11751 \text{ cm}^{-1}$$

b state, $B_2 = 1.40037 - 3.5(0.0182) = 1.33667$

$$E_b = 3.5(1432.77) - (3.5)^2(14.00) + 1.33667 \times 9 \times 10 - 5.3517 \times 10^{-6} \times 81 \times 100 = 4963.5386 \text{ cm}^{-1}$$

$$\Delta E = 13195.1 + 4963.5 - 961.1 = 17197.5 \text{ cm}^{-1}$$

$$\lambda = 581.48 \text{ nm}$$