Name_____

ME 501

Exam #1
23 October 2009
Prof. Lucht

1. POINT DISTRIBUTION

Choose two (2) of problems 1, 2, and 3:

Problem #1	**50 points**	_____
Problem #2	**50 points**	_____
Problem #3	**50 points**	_____

You are required to do two of the problems. Please indicate the problems you have chosen.

2. EXAM INSTRUCTIONS

- Write your name on each sheet.

- This exam is closed book and closed notes.

- Four equation sheets are attached.

- When working the problems, list all assumptions, and begin with the basic equations.

- If you do not have time to complete evaluation of integrals or of terms numerically, remember that the significant credit on each problem will be given for setting up the problem correctly and/or obtaining the correct analytical solution.

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1. **(50 points)** The system shown below has available energy levels of 0, 2, 4, and 8 units. The degeneracy of each of the four levels is 4. The thermodynamic assembly has 6 particles (N = 6) and a total system energy of 12 units (E = 12).

(a) For bosons, what are the available macrostates? (There are 6.) How many microstates are associated with each of these macrostates and what is the most probable macrostate? What is the entropy of the system? For Bose-Einstein statistics, the number of microstates for a given macrostate $\{N_j\}$ is given by:

$$W_{m,BE} = \prod_j W_{j,BE} = \prod_j \frac{(N_j + g_j - 1)!}{N_j!(g_j - 1)!}$$

Partial Answer: $\Omega = 3404$

(b) For fermions, what are the available macrostates? How many microstates are associated with each of these macrostates and what is the most probable macrostate? What is the entropy of the system? For Fermi-Dirac statistics, the number of microstates for a given macrostate $\{N_j\}$ is given by:

$$W_{m,FD} = \prod_j W_{j,FD} = \prod_j \frac{g_j!}{N_j! (g_j - N_j)!}$$

Partial Answer: $\Omega = 360$

(c) What is the entropy of an assembly of fermions that occupies the energy levels shown with N=16 and E = 56?

j	ε_j	g_j
3	8	4
2	4	4
1	2	4
0	0	4

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2.   The time-independent wavefunction $\psi_{n\ell m_\ell}(r,\theta,\phi)$ for the $n=2$, ℓ, m_ℓ state of the hydrogen atom is given by

$$\psi_{2\ell m_\ell}(r,\theta,\phi) = \frac{r\exp(-r/2a_0)}{8\sqrt{\pi}\,a_0^{5/2}} \sin\theta \,\exp(-i\phi)$$

$$R_{2\ell m_\ell}(r) = \frac{r\exp(-r/2a_0)}{8\sqrt{\pi}\,a_0^{5/2}} \qquad \Theta_{2\ell m_\ell}(\theta) = \sin\theta \qquad \Phi_{2\ell m_\ell}(\phi) = \exp(-i\phi)$$

The Bohr radius $a_0 = (4\pi\varepsilon_0\hbar^2)/(m_e e^2) = 0.52918\times10^{-10}$ m and the electron spin is neglected. (Note: In these formulas the factor ε_0 is the dielectric permittivity, <u>not</u> an energy).

(a)   Show that the wavefunction given above is normalized. Recall that for spherical coordinates $d\forall = r^2\sin\theta\,dr\,d\theta\,d\phi$ and that r can take on values from 0 to ∞, θ from 0 to π, and ϕ from 0 to 2π. The following definite integral relation will be needed

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

(b)   Using the result above, calculate the expectation value of the z-component of angular momentum, $\langle L_z\rangle$, where $L_{z,op} = -i\hbar\frac{\partial}{\partial\phi}$, and the expectation value of the square of total angular momentum $\langle L^2\rangle$, where $L_{op}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$. What are the quantum numbers ℓ and m_ℓ? [Hint: recall when a wavefunction ψ_k is an eigenstate for a particular operator A_{op}, $A_{op}\psi_k = a_k\psi_k$, where a_k is an eigenvalue. Part (b) should require little or no integration].

Answers: $\langle L_z\rangle = -\hbar$, $\langle L^2\rangle = 2\hbar^2$

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3.   A beam of infrared laser light passes through a cell filled with HF (hydrogen fluoride). A series of *P*- and *R*-branch absorption lines are observed when the laser frequency matches a vibration-rotation transition in HF. The laser excites the molecules from the v'' lower level to the $v' = v'' + 1$ upper vibrational level. For *P*-branch lines, $J' = J'' - 1$, where J' is the rotational quantum number of the upper level and $J'' = J$ is the rotational quantum number of the lower level.

(a) Develop a general formula for the frequency $\tilde{v}$ (cm-1) of the P-branch lines from lower level (J'', v'') to upper level $(J' = J'' - 1, v' = v'' + 1)$.

(b) Calculate the actual frequency (in cm^{-1}) of the $P(J'' = 10)$ rotational transition in the $v'' = 2 \rightarrow v' = 3$ vibrational band, accounting for anharmonicity, centrifugal stretching, and the dependence of the rotational constant B_v on vibrational level (neglect the dependence of D_v on vibrational level).   Answer: $\tilde{v} = 3156.60 \ cm^{-1}$

For HF,
$\omega_e = 4138.32 \ cm^{-1}$, $\omega_e x_e = 89.880 \ cm^{-1}$, $B_e = 20.956 \ cm^{-1}$, $\alpha_e = 0.798 \ cm^{-1}$, $D_e = 2.15 \times 10^{-3} \ cm^{-1}$,

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Equation Sheets

Schrödinger wave equation: $\quad i\hbar\dfrac{\partial\Psi(\vec{r},t)}{\partial t} = -\dfrac{\hbar^2}{2m}\nabla^2\Psi(\vec{r},t) + V(\vec{r},t)\,\Psi(\vec{r},t)$

Time-independent Schrödinger wave equation: $\quad -\dfrac{\hbar^2}{2m}\nabla^2\psi(\vec{r}) + V(\vec{r})\,\psi(\vec{r}) = \varepsilon\,\psi(\vec{r})$

Normalization Condition: $\quad 1 = \iiint_\forall \Psi^*(\vec{r},t)\,\Psi(\vec{r},t)\,d\forall \qquad three\text{-}dimensional\ \ form$

Dynamical Variable	Operator	
$\vec{r}$	$\vec{r}_{op} = \vec{r}$	
$\vec{p}$	$\vec{p}_{op} = -i\hbar\nabla$	$p_{x,op} = -i\hbar\dfrac{\partial}{\partial x}$
$\vec{p}^{\,2} = \vec{p}\bullet\vec{p}$	$\vec{p}_{op}^{\,2} = -\hbar^2\nabla^2$	
ε	$\varepsilon_{op} = i\hbar\dfrac{\partial}{\partial t}$	
$B(\vec{r},\vec{p})$	$B_{op} = B(\vec{r},-i\hbar\nabla)$	

$$\nabla = \hat{x}\,\frac{\partial}{\partial x} + \hat{y}\,\frac{\partial}{\partial y} + \hat{z}\,\frac{\partial}{\partial z} \quad Cartesian\ \ coord$$

$$\nabla = \hat{e}_r\,\frac{\partial}{\partial r} + \hat{e}_\theta\,\frac{1}{r}\frac{\partial}{\partial\theta} + \hat{e}_\varphi\,\frac{1}{r\sin\theta}\frac{\partial}{\partial\varphi} \quad spherical\ \ coord$$

$$\nabla^2\psi = \frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} \quad Cartesian\ \ coord$$

$$\nabla^2\psi = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} \quad Spherical\ \ coord$$

Expectation Values: $\quad \langle B\rangle = \iiint_\forall \Psi^*(\vec{r},t)\left[B_{op}\,\Psi(\vec{r},t)\right]d\forall \qquad three-dimensional\ \ form$

$$d\forall = dx\,dy\,dz \quad Cartesian\ \ coord,$$
$$d\forall = r^2\sin\theta\,dr\,d\theta\,d\phi \quad Spherical\ \ coord$$

$$\langle B\rangle = \int_{-\infty}^{+\infty}\Psi^*(x,t)\left[B_{op}\,\Psi(x,t)\right]dx \qquad one\text{-}dimensional\ \ form$$

$$\left\langle B^2 \right\rangle = \int_{-\infty}^{+\infty} \Psi^*(x,t) \left\{ B_{op} \left[B_{op} \Psi(x,t) \right] \right\} dx \qquad one-dimensional \;\; form$$

Molecular Energy Levels

$$\frac{\varepsilon_{vib}}{hc} = G(v) = \omega_e \left(v + \frac{1}{2} \right) - \omega_e x_e \left(v + \frac{1}{2} \right)^2 \qquad \text{with zero-point energy included}$$

$$\frac{\varepsilon_{vib}}{hc} = G(v) = \omega_e v - \omega_e x_e \left(v^2 + v \right) \qquad \text{zero-point energy subtracted, } G(0) = 0$$

$$\frac{\varepsilon_{rot}}{hc} = F_v(J) = B_v J(J+1) - D_v J^2 (J+1)^2$$

$$B_v = B_e - \alpha_e \left(v + \frac{1}{2} \right) \qquad\qquad D_e = \frac{4 B_e^3}{\omega_e^2} = D_v \quad for \;\; all \;\; v$$

<u>Degeneracies:</u> $\qquad g_{rot} = 2J + 1 \qquad\qquad g_{vib} = 1$

Rigid Rotator, Harmonic Oscillator

$$\frac{\varepsilon_{rot}}{hc} = F(J) = B_e J(J+1) \qquad \frac{\varepsilon_{rot}}{k_B} = \theta_{rot} J(J+1) \qquad \frac{\varepsilon_{vib}}{hc} = G(v) = \omega_e \left(v + \frac{1}{2} \right)$$

Characteristic Temperatures:

$$\theta_{rot} = \frac{hc}{k_B} B_e \qquad\qquad \theta_{vib} = \frac{hc}{k_B} \omega_e \qquad \frac{hc}{k_B} = 1.439 \; \frac{K}{cm^{-1}}$$

<u>Term Symbols Atomic:</u> $\quad {}^{2S+1}L_J, \qquad J = (L+S), (L+S-1), \ldots\ldots|L-S|$

		Term Symbol:	S	P	D	F	G....
		L:	0	1	2	3	4.....

<u>Term Symbols Molecular:</u> $\quad {}^{2S+1}\Lambda_{\Lambda+\Sigma}$

Term Symbol	Σ	Π	Δ	Φ	Γ
	0	1	2	3	4

$$\mu = \frac{m_A\, m_B}{m_A + m_B} = \textit{reduced mass}$$

<u>Boltzmann Relation:</u> $\quad S = k_B \ln\left(W_{tot}\right) \cong k_B \ln\left(W_{mp}\right)$

<u>Number of Microstates in a Macrostate for large g_j, N_j</u>

$$\ln(W_{m,CMB}) = \sum_j \left[N_j \ln\left(\frac{g_j}{N_j}\right) + N_j \right] = N + \sum_j N_j \ln\left(\frac{g_j}{N_j}\right)$$

$$\ln W_{m,FD} = \sum_j \left[N_j \ln\left(\frac{g_j - N_j}{N_j}\right) - g_j \ln\left(\frac{g_j - N_j}{g_j}\right) \right]$$

$$\ln W_{m,BE} = \sum_j \left[N_j \ln\left(\frac{g_j + N_j}{N_j}\right) + g_j \ln\left(\frac{g_j + N_j}{g_j}\right) \right]$$

<u>Integrals and Derivatives</u>

$$\int_{x1}^{x2} \int_{y1}^{y2} f(x)\, g(y)\, dx\, dy = \left[\int_{x1}^{x2} f(x)\, dx\right]\left[\int_{y1}^{y2} g(y)\, dy\right]$$

$$\int_{r1}^{r2} \int_{\theta1}^{\theta2} \int_{\phi1}^{\phi2} f(r)\, g(\theta)\, h(\phi)\, dr\, d\theta\, d\phi = \left[\int_{r1}^{r2} f(r)\, dr\right]\left[\int_{\theta1}^{\theta2} g(\theta)\, d\theta\right]\left[\int_{\phi1}^{\phi2} h(\phi)\, d\phi\right]$$

$$\frac{d\left[\sin(ax)\right]}{dx} = a\cos(ax) \qquad\qquad \frac{d\left[\cos(ax)\right]}{dx} = -a\sin(ax)$$

$$\int \sin^2(ax)\, dx = -\frac{1}{2a}\cos(ax)\sin(ax) + \frac{x}{2}$$

$$\int \cos^2(ax)\, dx = \frac{1}{2a}\cos(ax)\sin(ax) + \frac{x}{2}$$

$$\int \sin^3(ax)\, dx = -\frac{1}{3a}\cos(ax)\left(\sin^2(ax) + 2\right)$$

$$\int \sin(ax)\cos(ax)\, dx = \frac{1}{2a}\sin^2(ax)$$

$$\int \sin(ax) \cos^2(ax)\, dx = -\frac{1}{3a}\cos^3(ax)$$

$$\int \sin^2(ax) \cos(ax)\, dx = \frac{1}{3a}\sin^3(ax)$$

$$\int \sin(ax) \cos^3(ax)\, dx = -\frac{1}{4a}\cos^4(ax)$$

$$\int x\left[\sin^2(ax)\right] dx = \frac{x^2}{4} - \frac{x\sin(2ax)}{4a} - \frac{\cos(2ax)}{8a^2}$$

$$\int x^2\left[\sin^2(ax)\right] dx = \frac{x^3}{6} - \left(\frac{x^2}{4a} - \frac{1}{8a^3}\right)\sin(2ax) - \frac{x\cos(2ax)}{4a^2}$$

Constants and Conversion Factors

Universal gas constant
$$R_u = 8.314\,\frac{N-m}{(gmol)(K)} = 8.314\,\frac{J}{(gmol)(K)} = 8314\,\frac{J}{(kmol)(K)}$$

Pressure
$$1\ atm = 1.01325\ bars = 1.01325 \times 10^5\,\frac{N}{m^2} = 0.101325\ MPa$$

Speed of light
$$c = 2.998 \times 10^8\,\frac{m}{sec} = 2.998 \times 10^{10}\,\frac{cm}{sec}$$

Electron charge
$$e = 1.602 \times 10^{-19}\ coul$$

Electron mass
$$m_e = 9.11 \times 10^{-31}\ kg$$

Atomic mass unit
$$amu = 1.66 \times 10^{-27}\ kg$$

Planck's constant
$$h = 6.626 \times 10^{-34}\ J-sec\ ;\quad \hbar = \frac{h}{2\pi} = 1.055 \times 10^{-34}\ J-sec$$

Dielectric permittivity
$$\varepsilon_0 = 8.854 \times 10^{-12}\,\frac{coul^2}{J-m}$$

Avogadro constant
$$N_{Av} = 6.023 \times 10^{23}\ gmol^{-1}\quad or\quad N_{Av} = 6.023 \times 10^{26}\ kmol^{-1}$$

Boltzmann constant
$$k_B = 1.381 \times 10^{-23}\,\frac{J}{K}$$

$1\ J = 1\ kg\text{-}m^2/sec^2$

Quadratic solution

$$For\ the\ equation\quad ax^2 + bx + c = 0,\quad x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$