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ME 501

Exam #1
October 16, 2007
Prof. Lucht
ME 255

1. POINT DISTRIBUTION

Problem #1	**30 points**	____________________
Problem #2	**30 points**	____________________
Problem #3	**40 points**	____________________

2. EXAM INSTRUCTIONS

- Write your name on each sheet.
- This exam is closed book and closed notes.
- Three 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. **(30 points)** The system shown below has available energy levels of zero, one, two, and three units. The degeneracies of the four levels are 1, 2, 3, and 4, respectively. The thermodynamic state has five particles (N = 5) and a total system energy of eight units (E = 8).

(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:

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

Answer: $\Omega = 201$

(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:

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

Answer: $\Omega = 31$

j	ε_j	g_j
3	3	4
2	2	3
1	1	2
0	0	1

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2. **(30 points)** An electron is confined on the surface of a copper crystal by a square wall of iron atoms to a region $0 \le x \le L, 0 \le y \le L$. The <u>normalized</u> wavefunction for the electron is given by

$$\Psi(x, y, t) = \frac{2}{L} \sin\left(\frac{n_1 \pi x}{L}\right) \sin\left(\frac{n_2 \pi y}{L}\right) \exp\left[-i \frac{(\varepsilon_1 + \varepsilon_2)t}{\hbar}\right] \quad \text{for } 0 \le x \le L, 0 \le y \le L$$

$$\Psi(x, y, t) = 0 \qquad x \text{ or } y < 0 \text{ , } x \text{ or } y > L \qquad \varepsilon_1 = \frac{h^2 n_1^2}{8 m_e L^2} \qquad \varepsilon_2 = \frac{h^2 n_2^2}{8 m_e L^2}$$

The dimension $L = 10^{-9}$ m for this quantum box, and the electron has the quantum numbers $n_1 = 3$, $n_2 = 1$. Determine the expectation value for the square of the momentum in the x-direction $\langle p_x^2 \rangle = \iint \Psi^*(x, y, t)\{p_{x,op}[p_{x,op}\Psi(x, y, t)]\}\,dx\,dy$ (You need to put the correct limits on this integral). What is the mean electron speed $\sqrt{\langle p_x^2 \rangle}/m_e$?

Answer: $\text{v}_e = 1.091 \times 10^6 \ m/s$

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3. **(40 points)** A nitrogen molecule is in a superposition state of two vibrational eigenstates. The wavefunction for the vibrational mode is given by

$$\Psi(x,t) = C_0 \psi_0(x) \exp\left(-i\frac{2\pi \varepsilon_0 t}{h}\right) + C_1 \psi_1(x) \exp\left(-i\frac{2\pi \varepsilon_1 t}{h}\right)$$

$$C_0 = 1/2 \quad ; \quad C_1 = \sqrt{3}/2$$

$$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} \exp\left(-\frac{\alpha x^2}{2}\right) \quad ; \quad \psi_1(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} \sqrt{2\alpha}\; x \exp\left(-\frac{\alpha x^2}{2}\right)$$

$$\alpha = \frac{4\pi \mu c \omega_e}{h} \qquad \mu = \frac{m_1 m_2}{m_1 + m_2} \qquad mass\ of\ N\ nucleus = 14\ amu$$

$$\frac{\varepsilon_0}{hc} = \frac{\omega_e}{2} \quad ; \quad \frac{\varepsilon_1}{hc} = \frac{3\omega_e}{2} \quad ; \quad \omega_e = 2330\, cm^{-1} \quad ; \quad c = 2.998\times 10^{10}\ cm/s$$

(a) Show that the wavefunction $\Psi(x,t)$ is normalized. The definite integral relations that you will need are

$$\int_0^\infty \exp\left(-b x^2\right) dx = \frac{1}{2}\sqrt{\frac{\pi}{b}}$$

$$\int_0^\infty x^{2n} \exp\left(-b x^2\right) dx = \frac{1\times 3\times 5\times\cdots(2n-1)}{2^{n+1}\, b^n}\sqrt{\frac{\pi}{b}} \qquad for \quad n \ge 1$$

The range of integration to be considered is from x = -∞ to x = +∞. Remember to think about whether the integrands are even or odd.

(b) Derive an equation for the expectation value $\langle x\rangle(t)$ of the internuclear spacing for the superposition wavefunction. The equation will have the form $\langle x\rangle(t) = A\cos(Bt)$. Determine the numerical values and units of A and B. Hints: This expectation value for the superposition state will be a function of time, but the expectation values for the pure eigenstates will both be zero: $\langle x\rangle_0 = \langle x\rangle_1 = 0$.

Answer: $\langle x\rangle = \left(4.94\times 10^{-12}\ m\right)\cos\left[\left(4.389\times 10^{14}\ s^{-1}\right)t\right]$

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Equation Sheet #1

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

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

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

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

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

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

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

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

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

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

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

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

Equation Sheet #2

Boltzmann Relation: $S = k_B \ln\left(W_{tot}\right) \cong k_B \ln\left(W_{mp}\right)$

Integrals and Derivatives

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

$$\int_{r1}^{r2}\int_{\theta 1}^{\theta 2}\int_{\phi 1}^{\phi 2} f(r)\, g(\theta)\, h(\phi)\, dr\, d\theta\, d\phi = \left[\int_{r1}^{r2} f(r)\, dr\right]\left[\int_{\theta 1}^{\theta 2} g(\theta)\, d\theta\right]\left[\int_{\phi 1}^{\phi 2} h(\phi)\, d\phi\right]$$

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

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

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

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

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

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

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

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

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

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

Equation Sheet #3

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 $1 \ atm = 1.01325 \ bars = 1.01325x10^5 \frac{N}{m^2} = 0.101325 \ MPa$

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

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-m^2/sec^2

Molecular Energy Levels

$$\frac{\varepsilon_{vib}}{hc} = G(\mathrm{v}) = \omega_e\left(\mathrm{v}+\frac{1}{2}\right) - \omega_e x_e\left(\mathrm{v}+\frac{1}{2}\right)^2$$

$$\frac{\varepsilon_{rot}}{hc} = F_{\mathrm{v}}(J) = B_{\mathrm{v}}\, J(J+1) - D_{\mathrm{v}}\, J^2(J+1)$$

$$B_{\mathrm{v}} = B_e - \alpha_e\left(\mathrm{v}+\frac{1}{2}\right) \qquad\qquad D_e = \frac{4B_e^3}{\omega_e^2}$$