Name____________________________

ME 501

Exam #1
18 October 2013
Prof. Lucht

1. POINT DISTRIBUTION

Problem #1	**30 points**	________________
Problem #2	**35 points**	________________
Problem #3	**35 points**	________________

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. **(30 points)** The system shown below has available five energy levels of 0, 1, 4, 10, and 15 units. The degeneracy of the levels is 10, 10, 3, 3, and 2 as shown. The thermodynamic assembly has 6 particles (N = 6) and a total system energy of 45 units (E = 45).

(a) For bosons, what are the available macrostates? (There are at least 4.) 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:

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

(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:

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

j	ε_j	g_j
4	15	2
3	10	3
2	4	3
1	1	10
0	0	10

(a) For bosons the available macrostates are:

N=6, E=45

j	ε_j	g_j	A	B	C	D	E	F	G	H	I
4	15	2	3	2	1	0					
3	10	3	0	1	3	4					
2	4	3	0	1	0	1					
1	1	10	0	1	0	1					
0	0	10	3	1	2	0					

+8

$$W_A = \prod_j \frac{(N_j + g_j - 1)!}{N_j!(g_j - 1)!} = \left(\frac{4!}{3!1!}\right)\left(\frac{2!}{0!2!}\right)\left(\frac{2!}{0!2!}\right)\left(\frac{9!}{0!9!}\right)\left(\frac{12!}{3!9!}\right) = 4\times1\times1\times1\times\frac{12\times11\times10}{3\times2} = 880$$

$$W_B = \left(\frac{3!}{2!1!}\right)\left(\frac{3!}{1!2!}\right)\left(\frac{3!}{1!2!}\right)\left(\frac{10!}{1!9!}\right)\left(\frac{10!}{1!9!}\right) = 3\times3\times3\times10\times10 = 2700$$

$$W_C = \left(\frac{2!}{1!1!}\right)\left(\frac{5!}{3!2!}\right)\left(\frac{2!}{0!2!}\right)\left(\frac{9!}{0!9!}\right)\left(\frac{11!}{2!9!}\right) = 2\times\frac{5\times4}{2}\times1\times1\times\frac{11\times10}{2} = 1100$$

$$W_D = \left(\frac{1!}{0!1!}\right)\left(\frac{6!}{4!2!}\right)\left(\frac{3!}{1!2!}\right)\left(\frac{10!}{1!9!}\right)\left(\frac{9!}{0!9!}\right) = 1\times\frac{6\times5}{2}\times3\times10\times1 = 450 \quad \boxed{+8}$$

$W_{tot} = W_A + W_B + W_C + W_D = 880 + 2700 + 1100 + 450 = 5130$ +1

$S = k_B \ln W_{tot} = 8.543 k_B = 1.18\times10^{-22}\ J/K$ +2

B = most probable macrostate +1

(b) for fermions, macrostates A and D are excluded because $N_j > g_j$ +2 .

$$W_B = \prod_j \frac{g_j!}{N_j!\,(g_j - N_j)!} = \left(\frac{2!}{2!0!}\right)\left(\frac{3!}{1!2!}\right)\left(\frac{3!}{1!2!}\right)\left(\frac{10!}{1!9!}\right)\left(\frac{10!}{1!9!}\right) = 1\times3\times3\times10\times10 = 900$$

$$W_C = \left(\frac{2!}{1!1!}\right)\left(\frac{3!}{3!0!}\right)\left(\frac{3!}{0!3!}\right)\left(\frac{10!}{0!10!}\right)\left(\frac{10!}{2!8!}\right) = 2\times1\times1\times1\times\frac{10\times9}{2} = 90 \quad \boxed{+4}$$

$W_{tot} = W_B + W_C = 990$ +1

$S = k_B \ln W_{tot} = 6.898 k_B = 9.526\times10^{-23}\ J/K$ +2

B = most probable macrostate +1

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2. **(35 points)** An electron is confined on the surface of copper by a wall of iron atoms to a region $0 \le x \le L,\ \ L = 10^{-8}\ m$; the y-dimension of the box is much larger and we will ignore that dimension. The electron is in a superposition of two quantum states. i.e., a linear superposition of the eigenstates A and B with quantum numbers $n_{1A} = 2$ and $n_{1B} = 5$, respectively. The normalized wavefunction $\Psi(x,t)$ for the particle is given by

$$\Psi(x,t) = c_A \Psi_A(x,t) + c_B \Psi_B(x,t) = c_A \sin\left(\frac{2\pi x}{L}\right)\exp\left(-i\frac{\varepsilon_A t}{\hbar}\right) + c_B \sin\left(\frac{5\pi x}{L}\right)\exp\left(-i\frac{\varepsilon_B t}{\hbar}\right)$$

$$where \quad c_A = \sqrt{\frac{7}{5L}} \qquad c_B = \sqrt{\frac{3}{5L}}$$

for $0 \le x \le L$. For $x < 0$ or $x > L$, $\Psi(x,t) = 0$. The energies ε_A and ε_B are given by

$$\varepsilon_A = \frac{h^2 n_{1A}^2}{8 m L^2} \qquad \varepsilon_B = \frac{h^2 n_{1B}^2}{8 m L^2}$$

where again L = 10^{-8} m for this quantum box. Determine the expectation value $\langle \varepsilon \rangle$ for electron energy (in *J*) and calculate the mean electron speed $\langle \mathrm{v}_e \rangle$ from $\langle \varepsilon \rangle = \dfrac{m_e \langle \mathrm{v}_e \rangle^2}{2}$?

Solution:

Prove that the wavefunction is normalized (not asked for)

$$1 = \int_0^L \Psi^*(x,t)\Psi(x,t)\,dx = \int_0^L P(x,t)\,dx$$

$$P(x,t) = \Psi^*(x,t)\Psi(x,t) = c_A c_A^* \sin^2\left(\frac{2\pi x}{L}\right) + c_A c_B^* \sin\left(\frac{2\pi x}{L}\right)\sin\left(\frac{5\pi x}{L}\right)\exp\left[-i\frac{(\varepsilon_A - \varepsilon_B)t}{\hbar}\right]$$

$$+ c_A^* c_B \sin\left(\frac{2\pi x}{L}\right)\sin\left(\frac{5\pi x}{L}\right)\exp\left[-i\frac{(\varepsilon_B - \varepsilon_A)t}{\hbar}\right] + c_B c_B^* \sin^2\left(\frac{5\pi x}{L}\right)$$

$$1 = c_A c_A^* \int_0^L \sin^2\left(\frac{2\pi x}{L}\right)dx + c_A c_B^* \exp\left[-i\frac{(\varepsilon_A - \varepsilon_B)t}{\hbar}\right]\int_0^L \sin\left(\frac{2\pi x}{L}\right)\sin\left(\frac{5\pi x}{L}\right)dx$$

$$+ c_A^* c_B \exp\left[-i\frac{(\varepsilon_B - \varepsilon_A)t}{\hbar}\right]\int_0^L \sin\left(\frac{2\pi x}{L}\right)\sin\left(\frac{5\pi x}{L}\right)dx + c_B c_B^* \int_0^L \sin^2\left(\frac{5\pi x}{L}\right)dx$$

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

$$\int_0^L \sin^2\left(\frac{2\pi x}{L}\right)dx = \left[\frac{1}{2}x - \frac{L}{8\pi}\sin\left(\frac{4\pi x}{L}\right)\right]_0^L = \frac{L}{2}$$

$$\int_0^L \sin^2\left(\frac{5\pi x}{L}\right)dx = \left[\frac{1}{2}x - \frac{L}{20\pi}\sin\left(\frac{10\pi x}{L}\right)\right]_0^L = \frac{L}{2}$$

$$\int \sin(ax)\sin(bx)\,dx = \frac{\sin\left[(a-b)x\right]}{2(a-b)} - \frac{\sin\left[(a+b)x\right]}{2(a+b)}$$

$$\int_0^L \sin\left(\frac{2\pi x}{L}\right)\sin\left(\frac{5\pi x}{L}\right)dx = \left[\frac{1}{6}\sin\left(\frac{3\pi x}{L}\right) - \frac{1}{14}\sin\left(\frac{8\pi x}{L}\right)\right]_0^L = 0$$

$$1 = c_A c_A^* \frac{L}{2} + c_A c_B^*(0) + c_A^* c_B(0) + c_B c_B^* \frac{L}{2} = \left(c_A c_A^* + c_B c_B^*\right)\frac{L}{2} = \left(\frac{7}{5L} + \frac{3}{5L}\right)\frac{L}{2} = 1$$

Energy:

$$\langle \varepsilon \rangle = \int_0^L \Psi^*(x,t)\,\varepsilon_{op}\Psi(x,t)\,dx \quad \boxed{+3}$$

$$\varepsilon_{op}\Psi(x,t) = \varepsilon_A c_A \Psi_A(x,t) + \varepsilon_B c_B \Psi_B(x,t) \quad \boxed{+3}$$

$$\langle \varepsilon \rangle = \int_0^L \left[c_A^*\Psi_A^*(x,t) + c_B^*\Psi_B^*(x,t)\right]\left[\varepsilon_A c_A \Psi_A(x,t) + \varepsilon_B c_B \Psi_B(x,t)\right]dx$$

$$= \varepsilon_A c_A^* c_A \int_0^L \Psi_A^*(x,t)\Psi_A(x,t)\,dx + \varepsilon_A c_B^* c_A \int_0^L \Psi_B^*(x,t)\Psi_A(x,t)\,dx$$

$$+ \varepsilon_B c_A^* c_B \int_0^L \Psi_A^*(x,t)\Psi_B(x,t)\,dx + \varepsilon_B c_B^* c_B \int_0^L \Psi_B^*(x,t)\Psi_B(x,t)\,dx \quad \boxed{+6}$$

$$\int_0^L \Psi_A^*(x,t)\Psi_A(x,t)\,dx = \int_0^L \left[\sin\left(\frac{2\pi x}{L}\right)\exp\left(+i\frac{\varepsilon_A t}{\hbar}\right)\right]\left[\sin\left(\frac{2\pi x}{L}\right)\exp\left(-i\frac{\varepsilon_A t}{\hbar}\right)\right]dx$$

$$= \int_0^L \sin^2\left(\frac{2\pi x}{L}\right)dx = \left[\frac{1}{2}x - \frac{L}{8\pi}\sin\left(\frac{4\pi x}{L}\right)\right]_0^L = \frac{L}{2} \quad \boxed{+3}$$

$$\int_0^L \Psi_B^*(x,t)\Psi_B(x,t)\,dx = \int_0^L \left[\sin\left(\frac{5\pi x}{L}\right)\exp\left(+i\frac{\varepsilon_B t}{\hbar}\right)\right]\left[\sin\left(\frac{5\pi x}{L}\right)\exp\left(-i\frac{\varepsilon_B t}{\hbar}\right)\right]dx$$

$$= \int_0^L \sin^2\left(\frac{5\pi x}{L}\right)dx = \left[\frac{1}{2}x - \frac{L}{20\pi}\sin\left(\frac{10\pi x}{L}\right)\right]_0^L = \frac{L}{2} \quad \boxed{+3}$$

$$\int_0^L \Psi_A^*(x,t)\Psi_B(x,t)\,dx = \int_0^L \left[\sin\left(\frac{2\pi x}{L}\right)\exp\left(+i\frac{\varepsilon_A t}{\hbar}\right)\right]\left[\sin\left(\frac{5\pi x}{L}\right)\exp\left(-i\frac{\varepsilon_B t}{\hbar}\right)\right]dx$$

$$= \exp\left[+i\frac{(\varepsilon_A-\varepsilon_B)t}{\hbar}\right]\int_0^L \sin\left(\frac{2\pi x}{L}\right)\sin\left(\frac{5\pi x}{L}\right)dx$$

$$= \exp\left[+i\frac{(\varepsilon_A-\varepsilon_B)t}{\hbar}\right]\left[\frac{1}{6}\sin\left(\frac{3\pi x}{L}\right)+\frac{1}{14}\sin\left(\frac{7\pi x}{L}\right)\right]_0^L = 0 \qquad \boxed{+4}$$

Similarly, $\int_0^L \Psi_B^*(x,t)\Psi_A(x,t)\,dx = 0$

Therefore,

$$\langle\varepsilon\rangle = \int_0^L \left[c_A^*\Psi_A^*(x,t)+c_B^*\Psi_B^*(x,t)\right]\left[\varepsilon_A c_A\Psi_A(x,t)+\varepsilon_B c_B\Psi_B(x,t)\right]dx$$

$$= \varepsilon_A c_A^* c_A\left(\frac{L}{2}\right) + \varepsilon_B c_B^* c_B\left(\frac{L}{2}\right) = \varepsilon_A\left(\frac{7}{5L}\right)\left(\frac{L}{2}\right)+\varepsilon_B\left(\frac{3}{5L}\right)\left(\frac{L}{2}\right) = \frac{7}{10}\varepsilon_A+\frac{3}{10}\varepsilon_B \qquad \boxed{+5}$$

$$\langle\varepsilon\rangle = \left(\frac{7}{10}\right)\frac{h^2}{8mL^2}(2)^2+\left(\frac{3}{10}\right)\frac{h^2}{8mL^2}(5)^2 = \frac{h^2}{8mL^2}\left[\frac{28}{10}+\frac{75}{10}\right] = 10.3\frac{h^2}{8mL^2} \qquad \boxed{+2}$$

$$\langle\varepsilon\rangle = 10.3\frac{\left(6.626\times10^{-34}\ J-s\right)^2}{8\left(9.11\times10^{-31}\ kg\right)\left(10^{-8}\ m\right)^2} = 6.205\times10^{-21}\ \frac{J^2 s^2}{kg\,m^2} \qquad \boxed{+3}$$

$$\boxed{\langle\varepsilon\rangle = 6.205\times10^{-21}\ J}$$

$$\langle v_e\rangle = \sqrt{\frac{2\langle\varepsilon\rangle}{m}} = \sqrt{\frac{2\left(6.205\times10^{-21}\ \frac{kg\,m^2}{s^2}\right)}{\left(9.11\times10^{-31}\ kg\right)}} = 1.167\times10^5\ \frac{m}{s} \qquad \boxed{+3}$$

$$\boxed{\langle v_e\rangle = 1.167\times10^5\ \frac{m}{s}}$$

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3. Short Answer Section

(a) **(12 points)** An atom has an electron configuration of $1s^2 2s^2 2p^6 3p^2$. Write out all possible spectroscopic terms $^{2S+1}L_J$ and list the degeneracy of each term.

$\ell_1 = 1,\ \ell_2 = 1 \ \Rightarrow\ L = 0,1,2 \qquad S, P, D \ \ terms$ +2

$s_1 = \frac{1}{2},\ s_2 = \frac{1}{2} \ \Rightarrow\ S = 0,1 \qquad 2S+1 = 1,3$ +2

$J = L+S,\ L+S-1, \ldots |L-S|$

$S \ \ Terms:$

$^3S_1 \quad g = 2J+1 = 3$

$^1S_0 \quad g = 2J+1 = 1$ +2

$P\, terms:$

$^3P_2 \quad g = 2J+1 = 5$

$^3P_1 \quad g = 2J+1 = 3$

$^3P_0 \quad g = 2J+1 = 1$

$^1P_1 \quad g = 2J+1 = 3$ +3

$D \ \ terms:$

$^3D_3 \quad g = 2J+1 = 7$

$^3D_2 \quad g = 2J+1 = 5$

$^3D_1 \quad g = 2J+1 = 3$

$^1D_2 \quad g = 2J+1 = 5$ +3

(b) **(10 points)** Including zero-point energy and the first-order correction terms for vibrational anharmonicity, vibration-rotation coupling, and centrifugal stretching, calculate the energy in cm^{-1} of the J=41, v=2 level of the CO molecule.

For CO, $\omega_e = 2169.814\ cm^{-1},\ \omega_e x_e = 13.288\ cm^{-1},$
$B_e = 1.9313\ cm^{-1},\ \alpha_e = 1.750\times10^{-2}\ cm^{-1},\ D_e = 6.121\times10^{-6}\ cm^{-1}$

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

$$G(2) = (2169.814)(2.5) - (13.288)(2.5)^2 = 5341.49\ cm^{-1}$$ +3

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

$$B_2 = 1.9313 - 2.5(0.0175) = 1.8876\ cm^{-1}$$ +2

For the J=41 level:

$$F_2(J=41) = B_2 J(J+1) - D_e (J)^2 (J+1)^2 = (1.8876\ cm^{-1})(41)(42) - (6.121\times10^{-6}\ cm^{-1})(41)^2(42)^2$$
$$= 3250.55 - 18.15 = 3232.30\ cm^{-1}$$ +3

$$\boxed{\frac{\varepsilon}{hc} = \left[F_2(J=41) + G(\mathrm{v}=2)\right] = 3232.30 + 5341.59 = 8573.89 cm^{-1}}$$ +2

(c) **(13 points)** Atomic hydrogen is in the quantum state described by the following wavefunction:

$$\psi_{n\ell m_\ell}(r,\theta,\phi)=\frac{\left(\frac{r}{a_0}\right)^2\exp\left(-\frac{r}{3a_0}\right)}{162\sqrt{\pi}\,a_0^{3/2}}\sin^2\theta\exp(+2i\phi)=R(r)\sin^2\theta\exp(+2i\phi)$$

Recall that if a physical quantity A is a precisely defined eigenvalue of a wavefunction, then $A_{op}\psi=a\psi$, where a is a constant. Prove that the squared magnitude of angular momentum is precisely defined for the given wavefunction, and determine the value of $\langle L^2\rangle$ in units of $\hbar^2$.

$$L_{op}^2=-\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

Hint: $\cos^2\theta=(1-\sin^2\theta)$ $\quad\frac{\partial\sin\theta}{\partial\theta}=\cos\theta$ $\quad\frac{\partial\cos\theta}{\partial\theta}=-\sin\theta$

Solution:

$$L_{op}^2\psi=-\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right] \quad \boxed{+3}$$

$$=-\hbar^2R(r)\left[\frac{\exp(2i\phi)}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\sin^2\theta}{\partial\theta}\right)+\frac{\sin^2\theta}{\sin^2\theta}\frac{\partial^2\exp(2i\phi)}{\partial\phi^2}\right] \quad \boxed{+2}$$

$$=-\hbar^2R(r)\exp(2i\phi)\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta(2\sin\theta\cos\theta)\right)+(2i)^2\right]$$

$$=-\hbar^2R(r)\exp(2i\phi)\left[\frac{2}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin^2\theta\cos\theta\right)-4\right]$$

$$=-\hbar^2R(r)\exp(2i\phi)\left[\frac{2}{\sin\theta}\left(2\sin\theta\cos^2\theta-\sin^3\theta\right)-4\right] \quad \boxed{+4}$$

$$=-\hbar^2R(r)\exp(2i\phi)\left[\frac{2}{\sin\theta}\left(2\sin\theta(1-\sin^2\theta)-\sin^3\theta\right)-4\right]$$

$$=-\hbar^2R(r)\exp(2i\phi)\left[4-\left(\frac{2}{\sin\theta}3\sin^3\theta\right)-4\right]=6\hbar^2R(r)\sin^2\theta\exp(2i\phi) \quad \boxed{+3}$$

$$=6\hbar^2\psi \quad \boxed{+1}$$

$$\langle L^2\rangle=6\hbar^2$$

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Equation Sheets

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: $1 = \iiint_{\forall} \Psi^*(\vec{r},t)\,\Psi(\vec{r},t)\;d\forall$ *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	$\varepsilon_{op} = i\hbar\frac{\partial}{\partial t}$	
$B(\vec{r},\vec{p})$	$B_{op} = B(\vec{r}, -i\hbar\nabla)$	

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

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

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

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

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

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

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

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

Molecular Energy Levels

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

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

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

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

Degeneracies: $g_{rot} = 2J + 1$ $\qquad g_{vib} = 1$

Rigid Rotator, Harmonic Oscillator

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

Characteristic Temperatures:

$$\theta_{rot} = \frac{hc}{k_B} B_\mathrm{e} \qquad \theta_{vib} = \frac{hc}{k_B} \omega_\mathrm{e} \qquad \frac{hc}{k_B} = 1.439 \frac{K}{cm^{-1}}$$

Term Symbols Atomic: $^{2S+1}L_J$, J = (L+S), (L+S-1), ...|L-S|

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

Term Symbols Molecular: $^{2S+1}\Lambda_{\Lambda+\Sigma}$

Term Symbol	Σ	Π	Δ	Φ	Γ
	0	1	2	3	4

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

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

Number of Microstates in a Macrostate for large g_j, N_j

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

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

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

Integrals and Derivatives

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

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

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

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

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

$$\int \sin\left(ax\right)\sin\left(bx\right)dx = \frac{\sin\left[\left(a-b\right)x\right]}{2\left(a-b\right)} - \frac{\sin\left[\left(a+b\right)x\right]}{2\left(a+b\right)}$$

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

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

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

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

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

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

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

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	$1\ atm = 1.01325\,bars = 1.01325x10^5\ \frac{N}{m^2} = 0.101325\ MPa$
Speed of light	$c = 2.998\times10^8\ \frac{m}{sec} = 2.998\times10^{10}\ \frac{cm}{sec}$
Electron charge	$e = 1.602\times10^{-19}\ coul$
Electron mass	$m_e = 9.11\times10^{-31}\ kg$
Atomic mass unit	$amu = 1.66\times10^{-27}\ kg$
Planck's constant	$h = 6.626\times10^{-34}\ J-sec\ ;\ \hbar = \frac{h}{2\pi} = 1.055\times10^{-34}\ J-sec$
Dielectric permittivity	$\varepsilon_0 = 8.854\times10^{-12}\ \frac{coul^2}{J-m}$
Avogadro constant	$N_{Av} = 6.023\times10^{23}\ gmol^{-1}\ \ or\ \ N_{Av} = 6.023\times10^{26}\ kmol^{-1}$
Boltzmann constant	$k_B = 1.381\times10^{-23}\ \frac{J}{K}$

1 J = 1 kg-m^2/sec^2

Quadratic solution

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