Statistical Mechanics / Quantum Mechanics

General Exam Questions for January, 2005

Instructions

Answer two out of problems 1–3, and four out of problems 4–8, for a total of six problems. Put each of your solutions in a separate answer book. Make sure that you label and sign your name on the cover of each book.

Possibly Useful Information

$$\nabla^2 \;=\; \frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2} \;=\; \frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}+\frac{1}{r^2}\frac{\partial^2}{\partial \theta^2}+\frac{\cos\theta}{r^2\sin\theta}\frac{\partial}{\partial\theta}+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

$$\int_0^\infty dx\; e^{-a^2x^2} = \frac{\pi^{1/2}}{2a}, \qquad \int_0^\infty dx\; xe^{-a^2x^2} = \frac{1}{2a^2},$$

$$\text{Hermite polynomial} \;=\; H_n(x) \;=\; (-1)^n e^{x^2}\frac{d^n}{dx^n}e^{-x^2}$$

$$\text{associated Laguerre} \;=\; L_{n+l}^{2l+1}(r) \;=\; \sum_{k=0}^{n-l-1}(-1)^{k+2l+1}\frac{[(n+l)!]^2 r^k}{(n-l-1-k)!(2l+1+k)!k!}$$

$$\text{Legendre polynomial} \;=\; P_l(w) \;=\; \frac{1}{2^l l!}\frac{d^l}{dw^l}(w^2-1)^l$$

$$\text{associated Legendre polynomial} \;=\; P_l^m(w) \;=\; (1-w^2)^{|m|/2}\frac{d^{|m|}}{dw^{|m|}}P_l(w)$$

$$\text{spherical harmonic} \;=\; Y_l^m(\theta,\,\phi) \;=\; (-1)^m\left[\frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!}\right]^{1/2} P_l^m(\cos\theta)e^{im\phi}$$

$$\text{spherical Bessels}: \quad j_l(r) \;=R_l(r)\frac{\sin r}{r}+S_l(r)\frac{\cos r}{r}, \qquad n_l(r) \;=R_l(r)\frac{\cos r}{r}-S_l(r)\frac{\sin r}{r},$$

$$\text{where} \quad R_l(r)+iS_l(r) \;=\; \sum_{s=0}^{l}\frac{i^{s-l}(l+s)!}{2^s s!(l-s)!}r^{-s},$$

and with asymptotic behavior $j_\ell(r)\to\dfrac{\sin(r-\ell\pi/2)}{r}$, $n_\ell(r)\to\dfrac{\cos(r-\ell\pi/2)}{r}$.

Harmonic oscillator energies and wave functions:

$$E_n = \left(n+\frac{1}{2}\right)\hbar\omega \;,\; \psi_n(x) = \frac{1}{\sqrt{2^n n!}}\left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} e^{-\xi^2/2}\; H_n(\xi) \;,\; \text{with } \xi = \sqrt{\frac{m\omega}{\hbar}}x$$

Hydrogenic energies and expectation values:

$$E_n = \frac{-Z^2e^2}{2n^2a_0} \;,\langle r\rangle = \left(\frac{a_0}{2Z}\right)[3n^2-\ell(\ell+1)] \;,\langle r^2\rangle = \left(\frac{a_0^2n^2}{2Z^2}\right)[5n^2+1-3\ell(\ell+1)].$$

STATISTICAL MECHANICS

Solve any two out of the following three problems.

Problem 1

In the isothermal-isobaric ensemble, the system is considered to be in contact with a large bath of enthalpy $H = E + PV$.

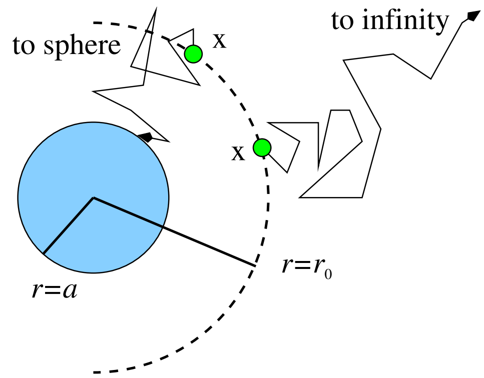
a) Assuming the states accessible to the system have energies E_r and volumes V_r, write down the isothermal-isobaric partition function $\Delta_N(T, P)$?

b) Express the mean square fluctuations of the enthalpy $\langle H^2 \rangle - \langle H \rangle^2$ in terms of the isobaric heat capacity $C_P = \left(\frac{\partial}{\partial T} \langle H \rangle \right)_{N,P}$.

c) Express the mean square fluctuations of the energy E in terms of the isochoric heat capacity C_V and the thermal expansion coefficient α_P, and compare them to the energy fluctuations in the canonical ensemble.

Problem 2

A sphere of radius a is placed in a homogeneous medium. The medium contains also molecules of type x which undergo diffusion. Any molecule which touches the surface of the sphere is captured (tied to the surface or simply disappears). A particular molecule of type x is initially located at a distance $r = r_0$ ($r_0 > a$) from the center of the sphere (see figure beside). You are asked to find the probability that it will ultimately be captured by the sphere.



To do this problem, consider a steady state disctribution $n(\mathbf{r})$ which satisfies the diffusion equation

$$\nabla^2 n(\mathbf{r}) = 0 \text{ except at } r = r_0,$$

with $n(\mathbf{r}) = 0$ at $r \to \infty$ and $r \to a$.

(a) Find the solution for $n(\mathbf{r})$ in the region $a \leq r < r_0$ and in the region $r \geq r_0$. Assume the $n(\mathbf{r}_0) = n_0$ and note that $n(\mathbf{r})$ is continuous (but not necessarily its derivative).

(b) Find the flux S_a of particles onto the surface at $r = a$. Note that

$$S = \oint \mathbf{j} \cdot d\mathbf{A}$$

where $\mathbf{j} = -D\nabla n$, ignoring external forces, and D is the diffusion coefficient.

(c) Find the flux S_∞ of particles into $r \to \infty$.

(d) Give an expression for the probability that the particle eventually be captured by the sphere in terms of S_a and S_∞. What is it in terms of a and r_0 ?

Problem 3

Consider the free photon gas in a cavity of volume V. The energy of a photon of momentum $\mathbf{p} = \hbar\mathbf{k}$ is $e_k = \hbar c|\mathbf{k}|$. The photon also has two transverse polarizations $\alpha = 1, 2$. The partition function for the gas is

$$Q = \sum_{n_{\mathbf{k},\alpha}} e^{-\beta \sum_{\mathbf{k},\alpha} \hbar e_k n_{\mathbf{k},\alpha}}$$

where $n_{\mathbf{k},\alpha} = 0, 1, 2...$ is the number of photons with wave number $\mathbf{k}$ and polarization α.

a) What is the chemical potential for this gas? Explain.

b) Calculate the average occupation number $\langle n_{\mathbf{k},\alpha} \rangle$ as a function of temperature.

c) Show that the internal energy of the system in the infinite volume limit is given by

$$\frac{U}{V} = \frac{\hbar}{\pi^2 c^3} \int_0^\infty d\epsilon \frac{\epsilon^3}{e^{\beta\hbar\epsilon} - 1}$$

d) What is the "utraviolet catastrophe" of the classical theory of radiation, and how do you see it in the classical limit of c?

QUANTUM MECHANICS

Solve any <u>four</u> out of the following five problems.

Problem 4

Consider two hydrogen atoms A and B in their ground states, separated along the z axis by a distance R. We will assume that $R \gg a_0$, where a_0 is the Bohr radius.

a) Show that the dipole-dipole interaction between the two atoms can be written as
$$W_d = \frac{e^2}{4\pi\epsilon_0 R^3}(x_A x_B + y_A y_B - 2z_A z_B),$$
where e is the elementary charge, and $\mathbf{r}_A = (x_A, y_A, z_A)$ is the position vector of the electron in atom A relative to its nucleus.

b) Show that the first-order correction to the energy of the system A,B due to the perturbation in part (a) vanishes.

c) Write down the leading correction to the energy of the system, and show that it is of the form $\epsilon_2 = -\frac{C}{R^6}$, where $C > 0$.

d) Making use of the closure relation, find an approximate value for the constant C. To estimate C, neglect the contribution of continuum states. You should also approximate the energies of all bound excited states by zero.

Problem 5

Consider quantum particle moving in the static potential in one dimension

$$H = \frac{p^2}{2M} + \frac{1}{2}M\omega^2 x^2 + \lambda x^4$$

a) Treating λx^4 as a small perturbation, calculate the energy of the ground state to first order in λ.

b) You can improve on perturbative results at not-so-small λ with the help of variational calculation. Take the following set of wave functions as your variational ansatz:

$$\psi(x) = A\exp\{-\frac{\mu^2 x^2}{2\hbar}\}$$

with μ as a variational parameter. Write down the variational equation.

c) Find the solution to the variational equation and calculate the energy of the best variational state in the limit $\hbar\lambda \ll M^2\omega^3$. Compare the result with the one obtained on a).

d) Find the solution and the ground state energy for $\hbar\lambda \gg M^2\omega^3$. What do you think better approximates the energy of the anharmonic oscillator in this limit, d) or a)? Explain.

Problem 6

Consider the system of two degrees of freedom with the Hamiltonian

$$H = \frac{P_1^2}{2M_1} + \frac{P_2^2}{2M_2} + V_1(x_1) + V_2(x_2) + U(x_1, x_2)$$

The potentials V_1 and V_2 are such that in the absence of the interaction ($U = 0$) the energy level spacings for the first particle are much larger than for the second.

The Born-Oppenheimer approximation for solving such system is the following. One looks for a solution of the Schrödinger equation in the general form

$$\psi_{n,m}(x_1, x_2) = \xi_m(x_2)\chi_n(x_1, x_2)$$

. The dependence of the second factor χ on the "slow" coordinate x_2 is considered to be parametric. One then first solves the equation

$$[\frac{P_1^2}{2M_1} + V_1(x_1) + U(x_1, x_2)]\chi_n = \epsilon_n(x_2)\chi_n$$

The eigenvalues ϵ depend on the value of the coordinate x_2. In the next step one solves the equation

$$[\frac{P_2^2}{2M_2} + V_2(x_2) + \epsilon_n(x_2)]\xi_m(x_2) = E_{nm}\xi_m(x_2)$$

This procedure gives the spectrum of approximate energy eigenvalues E_{mn}.

a) Consider the system of two quantum oscillators coupled through a non-linear coupling

$$H = -\frac{\hbar^2}{2M}\frac{d^2}{dR^2} - \frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \frac{1}{2}M\Omega^2 R^2 + \frac{1}{2}m\omega^2 r^2 + \lambda R^2 r^2$$

such that $\Omega \gg \omega$, and also $\lambda \ll Mm\Omega^2\omega$. Solve this system (find energy eigenvalues and eigenfunctions) using the Born-Oppenheimer approximation (hint: use an expansion in λ *where appropriate*).

b) Describe the general structure of the spectrum E_{mn}. Does the approximation hold equally well for all energy levels? If not, explain when and why it breaks down.

Problem 7

Consider two particles interacting through a potential $V(r)$ that depends only on the relative distance between them. The time independent Schrödinger equation describing the collision reduces to the radial differential equation

$$\left[\frac{d^2}{dr^2} + k^2 - \frac{\ell(\ell+1)}{r^2} - U(r)\right] y_\ell(k,r) = 0 \ ,$$

where $E = \hbar^2 k^2/2m$ and $U(r) = 2mV(r)/\hbar^2$. The wave function is

$$\psi_{\ell m} = \frac{y_\ell(kr)}{r} Y^\ell_m(\hat{r}) \ .$$

For large values of r, if $V(r) \to 0$ faster than $1/r$, its asymptotic behavior is given by

$$y_\ell(k,r) \approx \frac{1}{k} \sin\left(kr - \ell\frac{\pi}{2} + \delta_\ell(k)\right) \ .$$

Consider a hard-sphere potential

$$V(r) = \begin{cases} +\infty & , \quad r < a \\ 0 & , \quad r > a \end{cases} \ .$$

a) Write down the general solution $y_\ell(k,r)$ for all separation $r \geq a$ in terms of the phase shift $\delta_\ell(k)$.

[Hint: at large distance, $j_\ell(kr) = \sin(kr - \ell\pi/2)/kr$ and $n\ell(kr) = -\cos(kr - \ell\pi/2)/kr$.]

b) Find the phase shift $\delta_\ell(k)$ by matching the appropriate boundary conditions. Show that in the limit of small k (i.e $ka \ll 1$), the leading term is

$$\tan\delta_\ell(k) \approx -\frac{(ka)^{2\ell+1}}{(2\ell+1)!!(2\ell-1)!!} \ .$$

[Hint: for small x, $j_\ell(x) \approx x^\ell/(2\ell+1)!!$ and $n_\ell(x) \approx -(2\ell-1)!!/x^\ell$.]

c) Give the value of the scattering length defined by $\alpha_\ell = -\lim_{k\to 0} \frac{\tan\delta_\ell(k)}{k}$. Finally, find the zero energy elastic scattering cross section $\sigma(0)$ from the expression

$$\sigma(k) = \frac{4\pi}{k^2} \sum_{\ell=0}^{\infty} (2\ell+1)\sin^2\delta_\ell(k) \ .$$

d) Discuss how $\sigma(0)$ will change if $V = V_0$ (instead of ∞) for $r < a$?

Problem 8

Consider the harmonic oscillator described by the Hamiltonian

$$H = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2 = \hbar\omega(a^\dagger a + 1/2) \ ,$$

where a and $a^\dagger$ are the annihilation and creation operators, respectively.

a) Show the the coherent state

$$\langle z| = \langle 0| e^{za} \qquad , \text{ with } \qquad z = x_0 \sqrt{\frac{m\omega}{2\hbar}} \ ,$$

is the ground state of the oscillator with a displaced equilibrium position

$$H = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 (x - x_0)^2 \ .$$

[Hint: use the identities $e^{\eta a^\dagger} a = (a - \eta) e^{\eta a^\dagger}$ and $e^{\eta a} a^\dagger = (a^\dagger - \eta) e^{\eta a}$, where η is a complex number.]

b) Calculate $\langle z|z\rangle$. [Hint: $e^A e^B = e^{A+B} e^{\frac{1}{2}[A,B]} = e^B e^A e^{[A,B]}$.]

c) Calculate $\psi(x) = \langle z|x\rangle$.