QUALIFYING EXAMINATION, Part 2

Solutions

Problem 1: Quantum Mechanics I

(a) Take $|n\rangle$ to be the true energy eigenstates of H

$$H|n\rangle = E_n|n\rangle \ ,$$

with eigenvalues E_n $(n = 0, 1, \ldots)$. Since E_0 is the ground-state energy, $E_0 \leq E_n$. Then

$$\langle\psi|H|\psi\rangle = \sum_n E_n |\langle n|\psi\rangle|^2 \geq E_0 \sum_n |\langle n|\psi\rangle|^2 = E_0 \ ,$$

where we have used the fact that ψ is normalized, $\sum_n |\langle n|\psi\rangle|^2 = 1$.

(b) The trial wave function is spherically symmetric and thus has $l = 0$. The Hamiltonian of the hydrogen atom is rotationally invariant, and thus l is a good quantum number. In using the variational method, it is advantageous to choose a trial wave function that has the same values of the good quantum numbers as the exact ground state. Since the true ground state has l=0, we choose a trial wave function that also has good $l = 0$.

(c) The expectation value of V is

$$\langle\psi|V|\psi\rangle = \frac{1}{N^2}\int_0^\infty \left(-\frac{e^2}{r}\right) e^{-2\alpha r^2} r^2 dr = -\frac{1}{N^2}\frac{e^2}{4\alpha} \ ,$$

where

$$N^2 = \int_0^\infty e^{-2\alpha r^2} r^2 dr = \frac{1}{8\alpha}\sqrt{\frac{\pi}{2\alpha}} \ .$$

Using the given result for the expectation value of T, we find

$$E(\alpha) = \langle\psi|T|\psi\rangle + \langle\psi|V|\psi\rangle = \frac{3\hbar^2\alpha}{2m} - 2e^2\sqrt{\frac{2\alpha}{\pi}} \ .$$

(d) To find the best variational estimate for the given Gaussian trial wave function, we minimize $E(\alpha)$ with respect to α. The first derivative

$$\frac{dE}{d\alpha} = \frac{3\hbar^2}{2m} - e^2\sqrt{\frac{2}{\pi\alpha}}$$

vanishes for

$$\alpha = \alpha_{\min} = \frac{8}{9\pi}\left(\frac{me^2}{\hbar^2}\right)^2 .$$

It is easy to verify that $\frac{d^2E(\alpha)}{d\alpha^2} = e^2\sqrt{\frac{1}{2\pi\alpha^3}} > 0$, and thus $E(\alpha)$ has a minimum at $\alpha_{\min}$. The variational estimate for the energy is then

$$E_{\min} = E\left(\alpha_{\min}\right) = -\frac{8}{3\pi}\frac{me^4}{2\hbar^2} .$$

This value differs from the exact ground-state energy of $-\frac{me^4}{2\hbar^2}$ by only a factor of $\frac{8}{3\pi} \approx 0.85$.

Problem 2: Quantum Mechanics II

(a) We have

$$\hat{H}_{JC} |0,g\rangle = \left(\hat{H}_o + \hat{H}_a + \hat{H}_{int}\right) |0,g\rangle = \left(\frac{1}{2}\hbar\omega_o + 0 + 0\right) |0,g\rangle = \frac{1}{2}\hbar\omega_o |0,g\rangle \ .$$

Thus $|0,g\rangle$ is an eigenstate of $\hat{H}_{JC}$ with eigenvalue $\frac{1}{2}\hbar\omega_o$.

(b) To show that $\hat{N}$ is conserved, we verify that it commutes with $\hat{H}_{JC}$

$$\begin{aligned}\left[\hat{H}_{JC}, \hat{N}\right] &= \left[\hat{H}_o, \hat{N}\right] + \left[\hat{H}_a, \hat{N}\right] + \left[\hat{H}_{int}, \hat{N}\right] \\ &= 0 + 0 + \kappa\hat{a}\left[\hat{\sigma}^+, |e\rangle\langle e|\right] + \kappa\hat{a}^\dagger\left[\hat{\sigma}^-, |e\rangle\langle e|\right] + \kappa\left[\hat{a}, \hat{n}\right]\hat{\sigma}^+ + \kappa\left[\hat{a}^\dagger, \hat{n}\right]\hat{\sigma}^- \\ &= -\kappa\hat{a}\hat{\sigma}^+ + \kappa\hat{a}^\dagger\hat{\sigma}^- + \kappa\hat{a}\hat{\sigma}^+ - \kappa\hat{a}^\dagger\hat{\sigma}^- = 0 \ .\end{aligned}$$

(c) We verify that $|n,g\rangle$ and $|n,e\rangle$ are eigenstates of $\hat{N}$

$$\begin{aligned}\hat{N}|n,g\rangle &= \Lambda_{n,g}|n,g\rangle \\ \hat{N}|n,e\rangle &= \Lambda_{n,e}|n,e\rangle \ ,\end{aligned}$$

with eigenvalues $\Lambda_{n,g} = n$ and $\Lambda_{n,e} = n+1$ for $n = 0, 1, \cdots$.

For the eigenvalue $\Lambda_{0,g} = 0$, there is only one eigenstate $|0,g\rangle$. For the eigenvalue $\Lambda_{n,g} = \Lambda_{n-1,e} = n$ with $n = 1, 2 \ldots$, there is a two-fold degeneracy associated with eigenstates $|n,g\rangle$ and $|n-1,e\rangle$.

(d) Since $\left[\hat{H}_{JC}, \hat{N}\right] = 0$, $\hat{H}_{JC}$ can be represented as a block diagonal matrix in the eigenbasis associated with $\hat{N}$. More specifically, $\hat{H}_{JC}$ has the block diagonal form

$$\hat{H}_{JC} = \begin{pmatrix} (H_0)_{1\times1} & & & & & \\ & (H_1)_{2\times2} & & & & \\ & & (H_2)_{2\times2} & & & \\ & & & \ddots & & \\ & & & & (H_k)_{2\times2} & \\ & & & & & \ddots \end{pmatrix}$$

in the basis of $\{|0,g\rangle, |0,e\rangle, |1,g\rangle, |1,e\rangle, \cdots\}$. According to part (a), we have $H_0 = \frac{1}{2}\hbar\omega_o$. For $n = 1, 2, \ldots$, the 2×2 diagonal block associated with the basis states $\{|n-1,e\rangle, |n,g\rangle\}$ is

$$\begin{aligned}(H_n)_{2\times2} &= \begin{pmatrix} \left(n-\frac{1}{2}\right)\hbar\omega_o + \hbar\omega_a & \hbar\kappa\sqrt{n} \\ \hbar\kappa\sqrt{n} & \left(n+\frac{1}{2}\right)\hbar\omega_o \end{pmatrix} \\ &= \begin{pmatrix} n\hbar\omega_o + \frac{1}{2}\hbar\omega_a & 0 \\ 0 & n\hbar\omega_o + \frac{1}{2}\hbar\omega_a \end{pmatrix} + \begin{pmatrix} -\frac{1}{2}\hbar\delta & \hbar\kappa\sqrt{n} \\ \hbar\kappa\sqrt{n} & +\frac{1}{2}\hbar\delta \end{pmatrix},\end{aligned}$$

with $\delta = \omega_o - \omega_a$.

The eigenvalues of $\hat{H}_{JC}$ can be computed by finding the eigenvalues of these 2×2 matrices.

Statistical Mechanics I

(a) There are $\frac{N!}{n_1!n_2!}$ many-particle states with n_1 particles in the state with energy 0 and n_2 particles in the excited state ϵ. The energy of each such many-particle state is $n_1 \cdot 0 + n_2\epsilon = n_2\epsilon$ The partition function Z is then given by

$$Z = \sum_{\substack{n_1, n_2 \\ n_1+n_2=N}} \frac{N!}{n_1!n_2} e^{-\beta n_2 \epsilon} = (1 + e^{-\beta\epsilon})^N \ ,$$

where $\beta = 1/k_B T$. This result can also be derived from $Z = z^N$, where $z = \sum_i e^{-\beta\epsilon_i}$ is the single-particle partition function (this holds for a system of N non-interacting distinguishable particles). The given system has two levels, 0 and ϵ, so that $z = 1 + e^{-\beta\epsilon}$.

(b) The energy of the system is found from

$$E = -\frac{\partial \ln Z}{\partial \beta} = N \frac{\epsilon}{e^{\beta\epsilon} + 1} \ .$$

The heat capacity is then

$$C = \frac{dE}{dT} = N k_B \left(\frac{\epsilon}{k_B T} \right)^2 \frac{e^{\beta\epsilon}}{(e^{\beta\epsilon} + 1)^2} \ .$$

In the high-temperature limit $kT \gg \epsilon$, $\beta\epsilon \to 0$ and

$$C \approx \frac{1}{4} N k_B \left(\frac{\epsilon}{kT} \right)^2 \ .$$

(c) The entropy can be calculated from $S = -\partial F/\partial T$, where $F = -k_B T \ln Z$ is the free energy. Using $F = -N k_B T \ln(1 + e^{-\beta\epsilon})$, we find

$$\begin{aligned} S &= N k_B \ln(1 + e^{-\beta\epsilon}) + \frac{N k_B T e^{-\beta\epsilon}}{1 + e^{-\beta\epsilon}} \epsilon \frac{1}{k_B T^2} \\ &= N k_B \ln(1 + e^{-\beta\epsilon}) + \frac{N\epsilon}{T} \frac{e^{-\beta\epsilon}}{1 + e^{-\beta\epsilon}} = N k_B \left[\ln(1 + e^{-\beta\epsilon}) + \beta\epsilon \frac{e^{-\beta\epsilon}}{1 + e^{-\beta\epsilon}} \right] \ . \end{aligned}$$

Another way to calculate the entropy is to use $F = E - TS$ and the known expressions for F and E.

At the high-temperature limit, $\beta\epsilon \to 0$, and

$$S = N k_B \ln 2 \ .$$

This entropy is just $k_B \ln \Omega$ where $\Omega = 2^N$ is the total number of states.

In the limit $T \to 0$, $\beta\epsilon \to \infty$, $(\beta\epsilon)e^{-\beta\epsilon} \to 0$ and

$$S = 0 \, .$$

At $T = 0$, the system is in its non-degenerate ground state and $S = 0$.

(d) To calculate $\langle n_2 \rangle$, we use

$$\langle n_2 \rangle = -\frac{\partial}{\partial(\beta\epsilon)} \ln Z = N \frac{e^{-\beta\epsilon}}{1 + e^{-\beta\epsilon}} \, .$$

$\langle n_1 \rangle$ is determined from $\langle n_1 \rangle = N - \langle n_2 \rangle$. We find

$$\langle n_1 \rangle = N \frac{1}{1 + e^{-\beta\epsilon}} \, .$$

Using the expression for the entropy in part (c) and the above expressions for the occupations, one finds after some algebra

$$S = -N k_B \left(\frac{\langle n_1 \rangle}{N} \ln \frac{\langle n_1 \rangle}{N} + \frac{\langle n_2 \rangle}{N} \ln \frac{\langle n_2 \rangle}{N} \right) \, .$$

Problem 4: Statistical Mechanics II

(a) A photon with momentum $\vec{p} = \hbar\vec{k}$ has energy $\epsilon_{\vec{k}} = \hbar\omega_{\vec{k}} = \hbar c|\vec{k}|$. Imposing periodic boundary conditions, the allowed values of $\vec{k}$ are $\vec{k} = \frac{2\pi}{L}\vec{n}$ with $\vec{n} = (n_x, n_y)$ having integer components. Thus, $\omega_{\vec{k}} = c\frac{2\pi}{L}\sqrt{n_x^2 + n_y^2}$.

To determine the density of states, we consider the number of possible photon states in a volume $d^2\vec{k}$ of momentum space. The number of allowed momentum values between $\vec{k}$ and $\vec{k} + d\vec{k}$ are

$$\frac{L^2}{(2\pi)^2} d^2\vec{k} = \frac{L^2}{2\pi} k dk = \frac{L^2}{2\pi c^2}\omega d\omega.$$

Thus the density of states of photons with frequency ω is

$$g(\omega) = \frac{A}{2\pi c^2}\omega.$$

(b) Writing $\beta = 1/k_B T$, the grand-canonical quantum partition function is

$$Z(T) = \prod_{\vec{k}} \sum_{n_{\vec{k}}=0}^{\infty} e^{-\beta\epsilon_{\vec{k}} n_{\vec{k}}} = \prod_{\vec{k}} \frac{1}{1 - e^{-\beta\epsilon_{\vec{k}}}},$$

where $n_{\vec{k}}$ is the number of photons with wavenumber $\vec{k}$, giving

$$\ln Z(T) = -\sum_{\vec{k}} \ln(1 - e^{-\beta\epsilon_{\vec{k}}}).$$

This is just the partition function of non-interacting bosons with a chemical potential $\mu = 0$. For photons $\mu = 0$ since their number N is not fixed a priori but is determined from the equilibrium condition $\mu = \partial F/\partial N|_{T,A} = 0$.

For large area, the photon spectrum becomes quasi-continuous, and the sum above can be approximated as an integral over ω using the density of states:

$$\ln Z(T) \approx -\int_0^\infty d\omega g(\omega) \ln(1 - e^{-\beta\hbar\omega}) = -\frac{A}{2\pi c^2}\int_0^\infty d\omega\omega \ln(1 - e^{-\beta\hbar\omega}).$$

(c) The total energy is

$$U = -\frac{\partial \ln Z}{\partial \beta} = \frac{\hbar A}{2\pi c^2}\int_0^\infty d\omega \frac{\omega^2 e^{\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}}.$$

The total energy can also be derived from

$$U = \sum_{\vec{k}} \epsilon_{\vec{k}} \langle n_{\vec{k}} \rangle \approx \int_0^\infty d\omega g(\omega)\hbar\omega \langle n_\omega \rangle \ ,$$

where

$$\langle n_\omega \rangle = -\frac{\partial}{\partial(\beta\hbar\omega)} \ln Z(T) = \frac{1}{e^{\beta\hbar\omega} - 1}$$

is the average occupation in a photon state with frequency ω.

Thus, in two dimensions the spectral energy density is

$$u(\omega, T) = \frac{\hbar}{2\pi c^2} \frac{\omega^2}{e^{\beta\hbar\omega} - 1}.$$

Substituting in the integral $x = \beta\hbar\omega$, the total energy density is

$$\frac{U}{A} = \frac{k_B^3 T^3}{2\pi c^2 \hbar^2} \int_0^\infty dx \frac{x^2}{e^x - 1} = \frac{k_B^3}{\pi c^2 \hbar^2} \zeta(3) T^3,$$

where we have represented the dimensionless integral using the Riemann ζ function

$$\zeta(n+1) = \frac{1}{n!} \int_0^\infty dx \frac{x^n}{e^x - 1}.$$

(d) First derivation of entropy: at fixed area

$$dS = \frac{1}{T} dU = \frac{1}{T} \left(\frac{3Ak_B^3 \zeta(3)}{\pi c^2 \hbar^2} \right) T^2 dT,$$

so the total entropy is given by integrating

$$S = \left(\frac{3Ak_B^3 \zeta(3)}{\pi c^2 \hbar^2} \right) \int T dT = \left(\frac{3Ak_B^3 \zeta(3)}{2\pi c^2 \hbar^2} \right) T^2.$$

Here we have fixed the constant of integration by demanding that the entropy vanishes at $T = 0$, since the system has a unique ground state.

Second derivation of entropy: consider the free energy $F = -k_B T \ln Z$, in which case

$$\begin{aligned} S &= -\left.\frac{\partial F}{\partial T}\right|_A = -\frac{\partial}{\partial T} \frac{Ak_B T}{2\pi c^2} \int_0^\infty d\omega \omega \ln(1 - e^{-\beta\hbar\omega}) \\ &= -\frac{\partial}{\partial T} \frac{Ak_B^3 T^3}{2\pi c^2 \hbar^2} \int_0^\infty dx x \ln(1 - e^{-x}) = \left(\frac{3Ak_B^3 T^2}{2\pi c^2 \hbar^2} \right) \left[-\int_0^\infty dx x \ln(1 - e^{-x}) \right] \end{aligned}$$

where the integral in brackets in also equal to $\zeta(3)$ upon integration by parts.

On the other hand, the total number of photons is given by

$$N \approx \int_0^\infty d\omega g(\omega) \langle n_\omega \rangle = \frac{A}{2\pi c^2} \int_0^\infty d\omega \omega \frac{1}{e^{\beta\hbar\omega} - 1} = \frac{A}{2\pi \beta^2 c^2 \hbar^2} \int_0^\infty dx \frac{x}{e^x - 1} = \frac{A}{2\pi \beta^2 c^2 \hbar^2} \zeta(2).$$

Then the entropy per photon is given by

$$\frac{S}{N} = \left(\frac{3Ak_B^3 \zeta(3) T^2}{2\pi c^2 \hbar^2} \right) \left(\frac{Ak_B^2 \zeta(2) T^2}{2\pi c^2 \hbar^2} \right)^{-1} = 3 \frac{\zeta(3)}{\zeta(2)} k_B.$$