PHYS 614 – Spring 2021 – Problem set 1

Due Friday, Apr 9, 2021 at 8 pm on Canvas

1. Spin and rotational angular momentum: ortho/para Hydrogen (25 points)

(Based on Kardar 6.9)

Our discussion of the rotational degrees of freedom for diatomic molecules ignored the spin and the fermion nature of the nuclei, which constrains the allowed rotational states when the two atoms in the molecule are identical. For instance, the hydrogen molecule has two spin isomers, based on whether the proton nuclear spins are aligned parallel (orthohydrogen) or antiparallel (parahydrogen). The requirement that the combined wavefunction be antisymmetric upon swapping the nuclei restricts the allowed angular momentum eigenvalues for the two forms.

   i. In parahydrogen, the nuclear spins form a singlet state which is antisymmetric upon swapping the nuclei. To maintain overall antisymmetry of the wavefunction, only *even* values of the orbital, or azimuthal quantum number ℓ are allowed (these have symmetric wavefunctions) in the discrete Hamiltonian,
$$\mathcal{H} = \frac{\hbar^2}{2I}\ell(\ell+1), \qquad \ell = 0, 2, 4, ...$$
Find the rotational partition function Z_p of parahydrogen as an infinite sum. Evaluate its low- and high-temperature limits analytically.

   ii. In orthohydrogen, the nuclear spins are in a triply-degenerate symmetric state, so only *odd* values $\ell = 1, 3, 5, ...$ are allowed. Find the rotational partition function of orthohydrogen Z_o as an infinite sum (make sure to include a sum over all three degenerate states that the pair of nuclear spins can be in), and evaluate the low- and high-temperature limits analytically.

   iii. Assuming that all nuclear spin states are accessible, and ignoring any differences in energies of the nuclear spin states, what is the expected ratio of molecules in the ortho state to molecules in the para state for an equilibrium mixture of molecules at temperature T? First write your answer in terms of Z_p and Z_o, then evaluate it analytically in the low- and high-temperature limits.

   iv. Find the rotational contribution to the heat capacity of an equilibrium ideal gas of N hydrogen molecules in the low and high temperature limits.

   v. Using software of your choice, numerically evaluate the ratio $C_V/(Nk_B)$ as a function of rescaled temperature T/θ_rot where $\theta_\mathsf{rot} = \hbar^2/(2Ik_B)$. Generate a plot of $C_V/(Nk_B)$ versus T/θ_rot for the range $0 < T/\theta_\mathsf{rot} < 6$.
(One approach is to analytically express C_V in terms of infinite sums, with a singple parameter T/θ_rot, and evaluate those sums numerically with a sufficiently high number of terms. Another approach is to evaluate $\log Z$ numerically for sufficiently many discrete T values, and generate an interpolating function which can be differentiated to obtain C_V.)

   vi. (Bonus) Find an error in the sketch of the rotational contribution to C_V for the diatomic molecule (Figure 6.3 of Kardar).

2. Density matrix example: photons (10 points)

(Based on Sethna 7.5)

   i. A *pure state* can be thought of as an ensemble which contains only one state vector $|\Psi\rangle$. Show that a density matrix ρ corresponds to a pure state if, and only if, $\rho^2 = \rho$.

The space of polarization states for a photon is spanned by two states: vertical polarization $|V\rangle$ and horizontal polarization $|H\rangle$. These can be represented by the column vectors $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$ respectively.

   ii. In this basis, find ρ for the following:
- a vertically polarized photon in the pure state $|V\rangle$,
- a diagonally polarized photon in the pure state $\frac{1}{\sqrt{2}}(|V\rangle + |H\rangle)$
- unpolarized light, a mixed state of vertical and horizontal polarization in equal proportions

(Use the fact that the dual vectors are represented as row vectors: $\langle V| = (1\,0)$, etc. The operation $|a\rangle\langle b|$ is then a matrix multiplication that gives a 2×2 matrix.)

   iii. For the three density matrices in (ii.) evaluate $\mathrm{Tr}(\rho)$, $\mathrm{Tr}(\rho^2)$, and the von Neumann entropy $-k_B\mathrm{Tr}(\rho\log\rho)$. (You can look up what it means to take the logarithm of a matrix.) Explain differences, if any, in the values you find for the pure and the mixed states.

3. Canonical density matrix: electron spin (15 points)

Do Kardar 6.6 (Question 6 in)

Notes and hints:

- The density matrix in the quantum canonical ensemble is

$$\rho = \frac{e^{-\beta\mathcal{H}}}{\mathrm{Tr}(e^{-\beta\mathcal{H}})}.$$

- It might help to first prove the following property of the Pauli matrices:

$$e^{a\sigma_i} = \cosh(a\mathbf{I}) + \sinh(a\sigma_i),$$

where i is one of $\{x, y, z\}$; a is a scalar; and $\mathbf{I}$ is the 2×2 identity matrix. Note that the matrix exponential is defined in terms of its formal expansion in a power series: $e^{\mathbf{M}} = \sum_{k=0}^{\infty} \mathbf{M}^k/k!$, and similarly for $\cosh$ and $\sinh$.