Theoretical Statistical Physics

Solution to Exercise Sheet 10

1 Trace of linear operators (3 points)

The trace of an operator A on a Hilbert space $\mathcal{H}$ is defined as

$$\mathrm{tr}(A) = \sum_n \langle e_n|A|e_n\rangle \tag{1}$$

where $(e_n)_{n\in\mathbb{N}}$ is an orthonormal basis of $\mathcal{H}$.

a) Show that the trace is independent of the orthonormal basis.

b) Show that for all operators A and B on $\mathcal{H}$

$$\mathrm{tr}(AB) = \mathrm{tr}(BA). \tag{2}$$

What is the analogous formula for $\mathrm{tr}(ABC)$?

c) Show that $\mathrm{tr}(UAU^\dagger) = \mathrm{tr}(A)$ if U is unitary.

d) Find the general form of the density operator for spin-$\frac{1}{2}$ systems.
Hint: Spin-$\frac{1}{2}$ means that $\mathcal{H} \simeq \mathbb{C}^2$, so a density operator ρ is a 2×2-matrix. Express this operator using Pauli matrices. Use the conditions on a density operator to constrain the form of ρ.

a) Let $(b_n)_{n\in\mathbb{N}}$ be another orthonormal basis of $\mathcal{H}$ distinct from $(e_n)_{n\in\mathbb{N}}$, then $(b_n)_{n\in\mathbb{N}}$ forms a complete set of states, i.e.

$$\sum_n |b_n\rangle\langle b_n| = \mathbb{1}_{\mathcal{H}}. \tag{3}$$

Inserting two such sets into (1) left and right of A gives

$$\begin{aligned}\sum_n \langle e_n|A|e_n\rangle &= \sum_n \sum_{i,j} \langle e_n|b_i\rangle\langle b_i|A|b_j\rangle\langle b_j|e_n\rangle = \sum_{i,j}\langle b_i|A|b_j\rangle \underbrace{\sum_n \langle b_j|e_n\rangle\langle e_n|b_i\rangle}_{\langle b_j|b_i\rangle = \delta_{ij}} \\ &= \sum_i \langle b_i|A|b_i\rangle.\end{aligned} \tag{4}$$

b) By definition,

$$\mathrm{tr}(AB) = \sum_n \langle e_n|AB|e_n\rangle = \sum_{m,n}\langle e_n|A|e_m\rangle\langle e_m|B|e_n\rangle = \sum_{m,n}\langle e_m|B|e_n\rangle\langle e_n|A|e_m\rangle = \mathrm{tr}(BA). \tag{5}$$

In the case of three operators, (5) implies cyclicity of the trace, i.e.

$$\mathrm{tr}(ABC) = \mathrm{tr}(CAB) = \mathrm{tr}(BCA). \tag{6}$$

c) U unitary means $U^\dagger = U^{-1}$. Thus, using (6),

$$\mathrm{tr}(UAU^\dagger) = \mathrm{tr}(U^\dagger UA) = \mathrm{tr}(A). \tag{7}$$

d) The 2×2-unit matrix and the Pauli matrices are linearly independent, so they form a basis of $\mathbb{C}^2$, a vector space with four (real) dimensions. We can thus write the density operator

$$\begin{aligned}\rho = \sum_{i=0}^{3} a_i \sigma_i &= a_0 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + a_1 \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} + a_2 \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} + a_3 \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \\ &= \begin{pmatrix} a_0 + a_3 & a_1 - i a_2 \\ a_1 + i a_2 & a_0 - a_3 \end{pmatrix},\end{aligned} \tag{8}$$

Any density operator must satisfy

i) $\rho^\dagger = \rho$,

ii) $\mathrm{tr}(\rho) = 1$,

iii) $\rho \geq 0$.

i) allows us to restrict the coefficients a_i to the real numbers. ii) requires $a_0 = \frac{1}{2}$, so (8) becomes[1]

$$\rho = \frac{1}{2}\big(\mathbb{1}_2 + \boldsymbol{a} \cdot \boldsymbol{\sigma}\big), \tag{9}$$

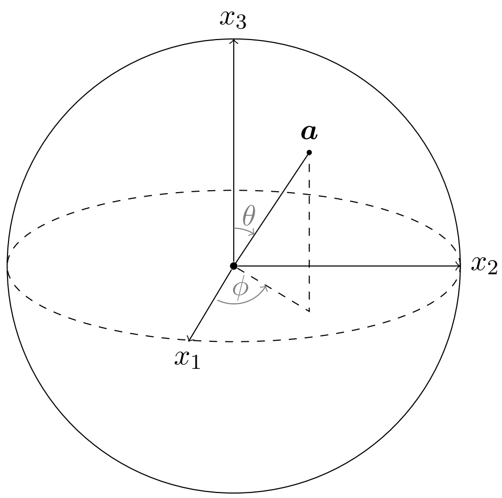
where $\boldsymbol{a} \in \mathbb{R}^3$ is known as the Bloch vector. For a given density matrix, it can be calculated as the expectation value of the Pauli matrices,

$$\langle \sigma_i \rangle = \mathrm{tr}(\sigma_i\, \rho) = \frac{1}{2} \underbrace{\mathrm{tr}(\sigma_i)}_{0} + \frac{1}{2} \sum_{j=1}^{3} a_j \underbrace{\mathrm{tr}(\sigma_i \sigma_j)}_{2\,\delta_{ij}} = a_i, \qquad \text{i.e. } \boldsymbol{a} = \langle \boldsymbol{\sigma} \rangle. \tag{10}$$

Since the Pauli matrices have eigenvalues $\lambda_\sigma = \pm 1$, ρ as in (9) has eigenvalues

$$\lambda_\pm = \frac{1}{2}\big(1 \pm |\boldsymbol{a}|\big). \tag{11}$$

iii) requires that $\lambda_\pm \geq 0$, so $\boldsymbol{a}$ must satisfy $|\boldsymbol{a}| \leq 1$. Thus all spin-$\frac{1}{2}$ density matrices lie on or within the so-called *Bloch sphere* of radius $|\boldsymbol{a}| = 1$ and are fully determined by the Bloch vector $\boldsymbol{a}$.



For ρ to describe a pure state, we must have $\rho^2 = \rho$. Squaring (9) and using $\boldsymbol{\sigma}^2 = \mathbb{1}_2$ gives

$$\rho^2 = \frac{1}{4}\big(\mathbb{1}_2^2 + 2\,\mathbb{1}_2\, \boldsymbol{a} \cdot \boldsymbol{\sigma} + \boldsymbol{a}^2\, \mathbb{1}_2\big), \tag{12}$$

which is equal to ρ only if $|\boldsymbol{a}| = 1$, so all pure states lie directly on the Bloch sphere. We can infer that the length of the Bloch vector indicates the mixedness, or in a language more suitable to this problem, the polarization of an ensemble. For $|\boldsymbol{a}| = 1$, ρ describes a pure state that is completely polarized, whereas for $\boldsymbol{a} = 0$, the state is mixed and unpolarized.

[1] In (9), we rescaled the $a_i \to \frac{a_i}{2}$ for $i \in \{1, 2, 3\}$.

2 Statistical mixture of spin states (3 points)

In a neutron beam, the spin of half of the particles is polarized in positive x-direction, and that of the other half in y-direction.

a) Find the density operator ρ corresponding to this situation.

b) Calculate the expectation value of the spin operator in the state given by ρ.

c) Calculate the eigenvalues $p_\pm$ and eigenvectors of ρ.

d) Determine the spin polarization

$$\pi = \frac{p_+ - p_-}{p_+ + p_-}. \tag{13}$$

a) Neutrons are spin-$\frac{1}{2}$ particles. As such, they occupy states in a Hilbert space $\mathcal{H} \simeq \mathbb{C}^2$, meaning all considerations concerning density operators and Bloch vectors from exercise 1.d) apply. The Bloch vector for a beam containing equal parts x- and y-polarized neutrons reads $\boldsymbol{a} = \left(\frac{1}{2}, \frac{1}{2}, 0\right)$ which results in a density operator

$$\rho \overset{(9)}{=} \frac{1}{2}\left(\mathbb{1}_2 + \tfrac{1}{2}\sigma_1 + \tfrac{1}{2}\sigma_2\right) = \frac{1}{2}\begin{pmatrix} 1 & \frac{1}{2} - \frac{i}{2} \\ \frac{1}{2} + \frac{i}{2} & 1 \end{pmatrix}. \tag{14}$$

b) Recalling eq. (10), we can immediately state the spin operator's expectation value,

$$\langle \boldsymbol{s} \rangle = \frac{\hbar}{2}\langle \boldsymbol{\sigma} \rangle = \frac{\hbar}{2}\boldsymbol{a} = \frac{\hbar}{4}\begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix}. \tag{15}$$

c) ρ as defined in (14) has eigenvalues

$$p_\pm = \frac{1}{4}\left(2 \pm \sqrt{2}\right), \tag{16}$$

belonging to the eigenvectors

$$\boldsymbol{b}_\pm = \frac{1}{2}\begin{pmatrix} \pm(1-i) \\ \sqrt{2} \end{pmatrix}. \tag{17}$$

d) Inserting (16) into (13) results in a spin polarization of $\pi = \frac{1}{\sqrt{2}}$.

3 Entropy of the microcanonical ensemble (2 points)

Calculate the von Neumann entropy for the microcanonical ensemble of quantum statistical mechanics, and show that it equals Boltzmann's constant times the logarithm of the microcanonical partition function.

The von Neumann definition of entropy is

$$S = -k_\mathrm{B}\,\mathrm{tr}_\mathcal{H}[\rho \ln(\rho)] \tag{18}$$

where the density operator is given by $\rho = \sum_n p_n |n\rangle\langle n|$ and n sums over a complete set of states of the Hilbert space $\mathcal{H}$. The microcanonical ensemble consists of all states $|n\rangle$ whose energy lie within a small interval of uncertainty $E_n \in I_\Delta = [E - \Delta, E]$ around the macroscopically observed energy E.[2] Since all accessible states are weighted equally, $p_n = 1/Z_m^\Delta$, where the

[2] Δ takes into account thermal and quantum fluctuations which prevent us from knowing the energy with absolute certainty for any finite sized system. It vanishes in the thermodynamic limit, reducing the interval to a point.

partition function Z_m^Δ counts the total number of states. Thus, a density operator for the microcanonical ensemble takes the form

$$\rho_m = \sum_{\{n|E_n \in I_\Delta\}} \frac{1}{Z_m^\Delta} |n\rangle\langle n| = \frac{1}{Z_m^\Delta} P_\Delta, \tag{19}$$

where P_Δ defined as

$$P_\Delta = \sum_{\{n|E_n \in I_\Delta\}} |n\rangle\langle n| \tag{20}$$

projects onto the subspace of accessible microstates $\mathcal{H}_\Delta \subset \mathcal{H}$. It follows from the density operator's normalization condition $\mathrm{tr}(\rho) \overset{!}{=} 1$ that $Z_m^\Delta = \mathrm{tr}[P_\Delta]$. Inserting (19) into (18) yields

$$S = -k_\mathrm{B}\,\mathrm{tr}\left[\frac{1}{Z_m^\Delta} P_\Delta \ln\left(\frac{1}{Z_m^\Delta} P_\Delta\right)\right] = k_\mathrm{B}\,\frac{1}{Z_m^\Delta} \ln(Z_m^\Delta)\,\underbrace{\mathrm{tr}[P_\Delta]}_{=Z_m^\Delta} - \frac{k_B}{Z_m^\Delta}\,\mathrm{tr}[P_\Delta \ln(P_\Delta)]. \tag{21}$$

As we showed in exercise 1, the trace is basis independent. We may therefore evaluate the second term using an energy eigenbasis in which P_Δ has diagonal form with eigenvalue one for every state that lies in $\mathcal{H}_\Delta$ and zero else. The logarithm of a diagonal matrix is just the logarithm of the eigenvalues. Thus, $\ln(P_\Delta)$ will feature a zero where ever P_Δ has unit entry and vice versa. Hence, the product $P_\Delta \ln(P_\Delta)$ is traceless and the von Neumann entropy (21) simplifies to

$$S = k_\mathrm{B} \ln(Z_m^\Delta). \tag{22}$$

4 Partition function (2 points)

Given a Hamiltonian H with discrete spectrum $E_0 < E_1 < E_2 < \dots$, where for all n, E_n is a $(n+1)$-fold degenerate eigenvalue,

a) express the canonical partition function Z_c in terms of a sum over n,

b) for $E_n = \hbar\omega\big(n + \frac{1}{2}\big)$, $\omega > 0$, calculate Z_c and the expectation value of the energy.

a) The canonical partition function sums over all states weighted by their energy. Since states in quantum mechanics furnish a Hilbert space $\mathcal{H}$, the partition function can be written very elegantly as the trace of the weighting factor,

$$Z_c = \mathrm{tr}_\mathcal{H}\big(e^{-\beta H}\big). \tag{23}$$

Since the trace is basis-independent, we make a convenient choice and evaluate it in a normalized eigenbasis of the Hamiltonian H. Different eigenstates are linearly independent - even if they correspond to the same degenerate eigenvalue. Thus the Hilbert space of a Hamiltonian with eigenvalues running up to E_n, each of degeneracy $n+1$, has dimension

$$d = \sum_{i=0}^{n} i + 1 = \frac{1}{2}(n+2)(n+1). \tag{24}$$

To form a complete[3] eigenbasis of H, we need d eigenstates. In general, d is not finite and then neither is the cardinality of the basis.[4] Denoting the basis vectors $|\psi_{mj}\rangle$, where

[3] Completeness here means that the span of basis vectors includes (in fact coincides with) the whole space.

[4] We are working with separable Hilbert spaces which contain countable dense subsets, meaning even if the number of basis states becomes infinite, they will always be countable.

$m \in \{0, \dots, n\} \subset \mathbb{N}_0$ counts the eigenvalues and $j \in \{1, \dots, m+1\}$ their degeneracy, (23) can be written

$$\begin{aligned} Z_c &= \sum_{m=0}^{n} \sum_{j=1}^{m+1} \langle \psi_{mj} | \underbrace{e^{-\beta H} |\psi_{mj}\rangle}_{e^{-\beta E_m}|\psi_{mj}\rangle} = \sum_{m=0}^{n} e^{-\beta E_m} \sum_{j=1}^{m+1} \underbrace{\langle \psi_{mj} | \psi_{mj} \rangle}_{1} \\ &= \sum_{m=0}^{n} (m+1)\, e^{-\beta E_m}. \end{aligned} \tag{25}$$

b) For $E_m = \hbar\omega\big(m + \frac{1}{2}\big)$, $\omega > 0$ and $n \to \infty$, (25) becomes

$$Z_c = \sum_{m=0}^{\infty} (m+1)\, e^{-\beta\hbar\omega\left(m+\frac{1}{2}\right)} = e^{-\frac{\varepsilon}{2}} \sum_{m=0}^{\infty} (m+1)\, e^{-m\varepsilon} = e^{-\frac{\varepsilon}{2}} (1 - \partial_\varepsilon) \sum_{m=0}^{\infty} e^{-m\varepsilon}, \tag{26}$$

where we defined the ratio of oscillatory and thermal energy $\varepsilon = \frac{\hbar\omega}{k_\mathrm{B} T} > 0$. Since $e^{-\varepsilon} < 1$, by the geometric series we have

$$Z_c = e^{-\frac{\varepsilon}{2}} (1 - \partial_\varepsilon) \frac{1}{1 - e^{-\varepsilon}} = e^{-\frac{\varepsilon}{2}} \left(\frac{1}{1 - e^{-\varepsilon}} + \frac{e^{-\varepsilon}}{(1 - e^{-\varepsilon})^2} \right) = \frac{e^{\frac{3}{2}\varepsilon}}{(e^{\varepsilon} - 1)^2}. \tag{27}$$

The expected energy follows immediately from the partition function,

$$\langle E \rangle = -\frac{1}{Z_c} \partial_\beta Z_c = -\frac{1}{Z_c} \left(\frac{3}{2} \hbar\omega - 2\,\hbar\omega \frac{e^{\epsilon}}{e^{\epsilon} - 1} \right) Z_c = \frac{\hbar\omega}{2} \left(1 + \frac{4}{e^{\beta\omega\hbar} - 1} \right), \tag{28}$$

which approaches the ground state energy of the harmonic oscillator $\frac{1}{2}\hbar\omega$ for $\beta \to \infty$, i.e. $T \to 0$. Interestingly, as can be seen from the right-hand plot below, the expected energy is not a monotonous function of ω but rather decreases at first for increasing angular frequency before approaching a linear relation. In the static case $\omega \to 0$, we find

$$\lim_{\omega \to 0} \langle E \rangle = \lim_{\omega \to 0} \frac{2\hbar\omega}{e^{\beta\omega\hbar} - 1} = 2 k_\mathrm{B} T. \tag{29}$$