Statistical Mechanics of the Quantum Harmonic Ensemble in Energy, Position, and Momentum Representations

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ABSTRACT

This paper investigates the statistical mechanics of a quantum harmonic oscillator ensemble. We begin by introducing the fundamental concepts, including the derivation of the energy eigenstates and eigenvalues of the quantum harmonic oscillator in the position basis. We also establish the connection between the partition function and the density matrix, outlining the relevant calculation methods. In this context, we derive the partition function and the density matrix of the quantum harmonic oscillator in the energy basis.

A unique aspect of this paper is the calculation of the partition function and density matrix of the quantum harmonic oscillator in both the position and momentum bases. While the position basis approach is less common due to the complexity of the calculations, the momentum basis offers a complementary perspective by representing the system in terms of momentum eigenstates. We demonstrate that the partition function remains unchanged across all bases, whereas the density matrix transforms according to the basis chosen. We carefully examine the implications of these density matrices, particularly in the quantum and classical limits, and discuss their physical significance.

Keywords: Quantum Harmonic Oscillator, Energy Eigenstates, Energy Eigenvalues, Position Basis, Hermite Polynomials, Quantum Statistical Ensemble, Partition Function, Density Matrix, Trace, Diagonal Elements, Mehler's Formula, Gaussian, Probability Density, Classical Limit, Quantum Limit, Molecular Systems.

I. INTRODUCTION

The quantum harmonic oscillator is a fundamental model in quantum mechanics, widely used to describe systems where the restoring force is proportional to displacement. Its importance extends beyond direct applications, as many potential energies can be approximated by harmonic potentials near equilibrium positions via a Taylor expansion. This makes the harmonic oscillator a universal tool in both classical and quantum mechanics.

In quantum mechanics, the discrete energy levels of the harmonic oscillator provide a clear illustration of energy quantization. It also plays a central role in quantum statistical mechanics, where it serves as a prototypical system for calculating thermodynamic properties such as free energy and entropy across different statistical ensembles.

This study investigates the quantum harmonic oscillator within the framework of quantum statistical mechanics, deriving the energy eigenstates and eigenvalues primarily in the position representation. We introduce the concept of quantum statistical ensembles, linking the partition function to the density matrix. The analysis then extends to the calculation of the partition function and density matrix expressed in multiple bases—energy, position, and momentum. While the position basis provides spatial intuition, the momentum basis offers a complementary perspective rooted in the system's momentum eigenstates. Key quantities such as the diagonal elements of the density matrix, the partition function, and probability densities are computed and compared across these bases. Finally, we examine the classical and quantum limits of the model, highlighting the physical insights gained from these different representations.

II. THEORETICAL BACKGROUND

A. Energy Eigenstates and Eigenvalues of the Quantum Harmonic Oscillator

The quantum harmonic oscillator is one of the most important systems in quantum mechanics. Its Hamiltonian in the position basis is given by

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2,$$

where $\hat{p} = -i\hbar\frac{d}{dx}$ is the momentum operator, and m and ω represent the mass and angular frequency of the oscillator, respectively. To derive the energy eigenstates and eigenvalues, we begin by writing the time-independent Schrödinger equation for the system:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + \frac{1}{2}m\omega^2x^2\psi(x) = E\psi(x).$$

This is a second-order differential equation for the wavefunction $\psi(x)$. To simplify the equation, we introduce a dimensionless variable $\xi = \sqrt{\frac{m\omega}{\hbar}}x$, which rescales the system in terms of the natural units of the harmonic oscillator. By expressing the derivatives in terms of this new variable, we get

$$\frac{d}{dx} = \sqrt{\frac{m\omega}{\hbar}}\frac{d}{d\xi} \quad \text{and} \quad \frac{d^2}{dx^2} = \frac{m\omega}{\hbar}\frac{d^2}{d\xi^2}.$$

Substituting these into the Schrödinger equation yields

$$-\frac{\hbar^2}{2m}\left(\frac{m\omega}{\hbar}\right)\frac{d^2\psi(\xi)}{d\xi^2} + \frac{1}{2}m\omega^2\left(\frac{\hbar}{m\omega}\xi^2\right)\psi(\xi) = E\psi(\xi),$$

which simplifies to

$$-\frac{\hbar\omega}{2}\frac{d^2\psi(\xi)}{d\xi^2} + \frac{\hbar\omega}{2}\xi^2\psi(\xi) = E\psi(\xi).$$

Dividing through by $\frac{\hbar\omega}{2}$ results in

$$-\frac{d^2\psi(\xi)}{d\xi^2} + \xi^2\psi(\xi) = \frac{2E}{\hbar\omega}\psi(\xi),$$

where we introduce a new parameter $\lambda = \frac{2E}{\hbar\omega}$. The equation now reads

$$-\frac{d^2\psi(\xi)}{d\xi^2} + \xi^2\psi(\xi) = \lambda\psi(\xi).$$

This is a standard form of the Schrödinger equation for the quantum harmonic oscillator in terms of the dimensionless variable ξ. To solve it, we first examine the asymptotic behavior of the solution. For large ξ, the ξ^2 term dominates, and we approximate the equation as

$$\frac{d^2\psi}{d\xi^2} \approx \xi^2\psi.$$

The general solution to this approximate equation is

$$\psi(\xi) \sim e^{\pm\xi^2/2}.$$

Since the wavefunction must be normalizable, we discard the exponentially growing solution $e^{+\xi^2/2}$ and retain only the decaying solution $e^{-\xi^2/2}$. Thus, the general form of the wavefunction is

$$\psi(\xi) = h(\xi)e^{-\xi^2/2},$$

where $h(\xi)$ is an unknown function that we will now determine.

Next, we substitute this expression for $\psi(\xi)$ into the Schrödinger equation. The first and second derivatives of $\psi(\xi)$ are:

$$\psi'(\xi) = h'(\xi)e^{-\xi^2/2} - \xi h(\xi)e^{-\xi^2/2},$$

and

$$\psi''(\xi) = h''(\xi)e^{-\xi^2/2} - 2\xi h'(\xi)e^{-\xi^2/2} + (\xi^2 - 1)h(\xi)e^{-\xi^2/2}.$$

Substituting $\psi(\xi)$ and $\psi''(\xi)$ into the Schrödinger equation and simplifying, we obtain

$$-\left[h''(\xi) - 2\xi h'(\xi) + (\xi^2 - 1)h(\xi)\right]e^{-\xi^2/2} + \xi^2h(\xi)e^{-\xi^2/2} = \lambda h(\xi)e^{-\xi^2/2}.$$

Canceling the common factor of $e^{-\xi^2/2}$, we are left with the equation

$$h''(\xi) - 2\xi h'(\xi) + (\lambda - 1)h(\xi) = 0.$$

This is a second-order linear differential equation for the function $h(\xi)$. We solve this equation by assuming a power series expansion for $h(\xi)$ of the form

$$h(\xi) = \sum_{n=0}^{\infty} a_n \xi^n.$$

Substituting this series into the differential equation leads to a recursion relation for the coefficients a_n. In order to obtain a physically acceptable, normalizable solution, we require that the series terminate, meaning that $h(\xi)$ must be a polynomial. This condition imposes a constraint on λ, yielding

$$\lambda = 2n + 1, \quad n = 0, 1, 2, \ldots.$$

This quantization condition gives the energy eigenvalues of the harmonic oscillator:

$$\boxed{E_n = \hbar\omega \left(n + \frac{1}{2}\right)} \tag{2.1}$$

The solutions for $h(\xi)$ are proportional to the Hermite polynomials $H_n(\xi)$, which are defined as

$$H_n(\xi) = (-1)^n e^{\xi^2} \frac{d^n}{d\xi^n} e^{-\xi^2}.$$

Thus, the normalized energy eigenfunctions of the quantum harmonic oscillator are given by

$$\boxed{\psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} \frac{H_n(\xi)}{\sqrt{2^n n!}} e^{-\frac{\xi^2}{2}}} \tag{2.2}$$

where

$$\xi = \sqrt{\frac{m\omega}{\hbar}} x.$$

B. Density Matrix and Partition Function

In quantum statistical mechanics, the density matrix $\hat{\rho}$ is a fundamental quantity used to describe the properties of a system in thermal equilibrium at temperature T. It not only encodes the quantum mechanical state of the system but also accounts for its interaction with a heat bath, making it a powerful tool for describing systems that may be in a mixed state rather than a pure state[1][2]. For a system described by the Hamiltonian $\hat{H}$, the density matrix in thermal equilibrium can be expressed in terms of the energy eigenstates $\{|\psi_k\rangle\}$ and their corresponding energy eigenvalues E_k.

We first consider the system within the canonical ensemble, which is a statistical description suitable for systems in contact with a heat bath. In this ensemble, the probability of the system being in a state $|\psi_k\rangle$ with energy E_k is given by the Boltzmann distribution:

$$\rho_k = \frac{e^{-\beta E_k}}{Q}$$

where $\beta = \frac{1}{k_B T}$ is the inverse temperature, and Q is the partition function, which acts as a normalization factor ensuring that the total probability over all possible states sums to 1[3].

Next, we can express the density matrix $\hat{\rho}$ as a weighted sum of the energy eigenstates $|\psi_k\rangle$, with weights given by the Boltzmann factor normalized by Q:

$$\hat{\rho} = \sum_k \rho_k |\psi_k\rangle\langle\psi_k| = \sum_k \frac{e^{-\beta E_k}}{Q} |\psi_k\rangle\langle\psi_k|$$

Since the energy eigenstates $|\psi_k\rangle$ are eigenstates of the Hamiltonian operator $\hat{H}$, satisfying $\hat{H}|\psi_k\rangle = E_k|\psi_k\rangle$, we can rewrite the Boltzmann factor $e^{-\beta E_k}$ in terms of the Hamiltonian operator itself, eliminating the need to explicitly sum over the index k. In this form, the summation over k acts only on the eigenstates, while the Boltzmann factor is rewritten as the exponential of the Hamiltonian:

$$\hat{\rho} = \frac{e^{-\beta\hat{H}}}{Q} \sum_k |\psi_k\rangle\langle\psi_k| = \frac{e^{-\beta\hat{H}}}{Q}$$

This expression shows that the density matrix is proportional to the exponential of the Hamiltonian operator $\hat{H}$, normalized by the partition function Q.

To compute the partition function Q, we apply the normalization condition of the density matrix, which requires that the trace of $\hat{\rho}$ equals 1:

$$\mathrm{Tr}\left(\frac{e^{-\beta\hat{H}}}{Q}\right) = \mathrm{Tr}(\hat{\rho}) = 1$$

Since Q is a constant, it can be factored out of the trace:

$$\frac{1}{Q}\text{Tr}(e^{-\beta\hat{H}}) = 1$$

which leads to the expression for the partition function:

$$Q = \text{Tr}(e^{-\beta\hat{H}})$$

The partition function plays a crucial role in determining the thermodynamic properties of the system, as it encodes a weighted sum over all possible energy states, with weights given by the Boltzmann factor. Finally, we obtain the canonical form of the density matrix:

$$\hat{\rho} = \frac{e^{-\beta\hat{H}}}{\text{Tr}\left(e^{-\beta\hat{H}}\right)}$$

This expression is of fundamental importance in quantum statistical mechanics, as it provides a compact representation of the system's state in thermal equilibrium. The trace condition ensures the proper normalization of the density matrix, while the exponential form incorporates the probability distribution of the system's energy states.

C. Partition Function and Density Matrix of the Quantum Harmonic Oscillator in Energy Basis

For the quantum harmonic oscillator, deriving the partition function and density matrix in the energy basis is a common and practical approach. This method simplifies the problem significantly compared to other representations, such as the position basis.

The partition function Q is defined as the trace of the operator $e^{-\beta\hat{H}}$, where $\hat{H}$ is the Hamiltonian of the system and $\beta = \frac{1}{k_B T}$ is the inverse temperature. In the energy basis, the eigenstates $|n\rangle$ of the Hamiltonian satisfy $\hat{H}|n\rangle = E_n|n\rangle$, with $E_n = \left(n + \frac{1}{2}\right)\hbar\omega$. The trace can then be expressed as:

$$Q = \text{Tr}\left(e^{-\beta\hat{H}}\right) = \sum_{n=0}^{\infty}\langle n|e^{-\beta\hat{H}}|n\rangle.$$

Since this operator is a function of the Hamiltonian, we are able to replace the Hamiltonian operator with energy eigenvalues, i.e. $\langle n|e^{-\beta\hat{H}}|n\rangle = e^{-\beta E_n}$. the partition function becomes:

$$Q = \sum_{n=0}^{\infty} e^{-\beta E_n} = \sum_{n=0}^{\infty} e^{-\beta\left(n+\frac{1}{2}\right)\hbar\omega}.$$

Factoring out the zero-point energy term (the energy when $n = 0$):

$$Q = e^{-\frac{\beta\hbar\omega}{2}}\sum_{n=0}^{\infty} e^{-\beta n\hbar\omega}.$$

This is a geometric series with the first term $a = e^{-\beta\hbar\omega}$ and common ratio $r = e^{-\beta\hbar\omega}$. The sum of this series is:

$$\sum_{n=0}^{\infty} e^{-\beta n\hbar\omega} = \frac{1}{1 - e^{-\beta\hbar\omega}}.$$

Thus, the partition function is:

$$\boxed{Q = \frac{e^{-\frac{\beta\hbar\omega}{2}}}{1 - e^{-\beta\hbar\omega}} = \frac{1}{2}\text{csch}\frac{\beta\hbar\omega}{2}} \tag{2.3}$$

The density matrix ρ in the canonical ensemble is given by:

$$\hat{\rho} = \frac{e^{-\beta\hat{H}}}{Q}.$$

In the energy basis, the Hamiltonian $\hat{H}$ is diagonal matrix, with eigenvalues E_n. Thus, the density matrix ρ becomes:

$$\hat{\rho} = \frac{1}{Q}\sum_{n=0}^{\infty} e^{-\beta E_n}|n\rangle\langle n|.$$

Substituting the energy eigenvalues $E_n = \left(n + \frac{1}{2}\right)\hbar\omega$, we get:

$$\begin{aligned}\hat{\rho} &= \frac{1}{Q}\sum_{n=0}^{\infty} e^{-\beta\left(n+\frac{1}{2}\right)\hbar\omega}|n\rangle\langle n| \\ &= \frac{e^{-\frac{\beta\hbar\omega}{2}}}{Q}\sum_{n=0}^{\infty} e^{-\beta n\hbar\omega}|n\rangle\langle n| \\ &= (1-e^{-\beta\hbar\omega})\sum_{n=0}^{\infty} e^{-\beta n\hbar\omega}|n\rangle\langle n| \\ &= \sum_{n=0}^{\infty} p_n|n\rangle\langle n|\end{aligned}$$

where the probability p_n of the system being in the n-th energy eigenstate is:

$$p_n = e^{-\beta n\hbar\omega}(1-e^{-\beta\hbar\omega}) = \frac{e^{-\beta n\hbar\omega}}{Q}.$$

This expression for the density matrix shows that the system has a thermal distribution over the energy eigenstates, with the probability of occupying the n-th state governed by the Boltzmann factor $e^{-\beta n\hbar\omega}$.

$$\boxed{\hat{\rho} = (1-e^{-\beta\hbar\omega})\sum_{n=0}^{\infty} e^{-\beta n\hbar\omega}|n\rangle\langle n|}$$

III. PARTITION FUNCTION AND DENSITY MATRIX OF THE QUANTUM HARMONIC OSCILLATOR IN POSITION BASIS

In the previous section, we calculated the partition function and density matrix of the quantum harmonic oscillator in the energy basis. In this section, we will calculate the partition function and density matrix in the position basis. This approach is relatively uncommon, as the calculations are more tedious. Since the eigenstates of the operator $e^{-\beta\hat{H}}$ are no longer the same as the basis for this calculation, we expect the density matrix in the position basis to be non-diagonal. We will derive the full expression of the density matrix in the position basis and discuss the physical significance of the non-diagonal terms.

The matrix elements of $e^{-\beta\hat{H}}$ are given by:

$$\begin{aligned}\langle x|e^{-\beta\hat{H}}|x'\rangle &= \sum_{n=0}^{\infty}\langle x|e^{-\beta\hat{H}}|\psi_n\rangle\langle\psi_n|x'\rangle \\ &= \sum_{n=0}^{\infty} e^{-\beta E_n}\psi_n(x)\psi_n^*(x')\end{aligned}$$

Since the harmonic oscillator wavefunctions are real, we have $\psi_n^*(x') = \psi_n(x')$. Therefore, the expression becomes:

$$\langle x|e^{-\beta\hat{H}}|x'\rangle = \sum_{n=0}^{\infty} e^{-\beta E_n}\psi_n(x)\psi_n(x')$$

Next, we substitute the expressions for the energy eigenstates (Equation 2.2) and eigenvalues (Equation 2.1), into the matrix element expression:

$$\begin{aligned}\langle x|e^{-\beta\hat{H}}|x'\rangle &= \sum_{n=0}^{\infty} e^{-\beta\left(n+\frac{1}{2}\right)\hbar\omega}\sqrt{\frac{m\omega}{\pi\hbar}}\frac{H_n(\xi)H_n(\xi')}{2^n n!}e^{-\frac{1}{2}\left(\xi^2+\xi'^2\right)} \\ &= \sqrt{\frac{m\omega}{\pi\hbar}}e^{-\frac{1}{2}\left(\xi^2+\xi'^2+\beta\hbar\omega\right)}\sum_{n=0}^{\infty} e^{-\beta n\hbar\omega}\frac{H_n(\xi)H_n(\xi')}{2^n n!}\end{aligned}$$

We now use the Mehler kernel[4], a closed-form expression derived from Mehler's Hermite formula, to evaluate the matrix element $\langle x|e^{-\beta\hat{H}}|x'\rangle$. This matrix element is the imaginary-time propagator of the quantum harmonic oscillator in the position basis, and it encodes the full quantum statistical behaviour of the system at temperature $T = 1/\beta$. Mehler's formula resums the infinite sum over energy eigenstates into a compact expression:

$$\boxed{\sum_{n=0}^{\infty}\left(\frac{w}{2}\right)^n\frac{H_n(x)H_n(y)}{n!} = \left(1-w^2\right)^{-\frac{1}{2}}\exp\left[\frac{2xyw-(x^2+y^2)w^2}{1-w^2}\right]}$$

Applying this formula to the harmonic oscillator's thermal operator leads to the Mehler kernel:

$$
\begin{aligned}
\langle x|e^{-\beta\hat{H}}|x'\rangle &= \sqrt{\frac{m\omega}{\pi\hbar}}\sqrt{\frac{1}{1-e^{-2\beta\hbar\omega}}}e^{-\frac{1}{2}\left(\xi^2+\xi'^2+\beta\hbar\omega\right)}\exp\left[\frac{2\xi\xi'-\left(\xi^2+\xi'^2\right)e^{-\beta\hbar\omega}}{e^{\beta\hbar\omega}-e^{-\beta\hbar\omega}}\right] \\
&= \sqrt{\frac{m\omega}{2\pi\hbar\sinh(\beta\hbar\omega)}}\exp\left[\frac{-\frac{1}{2}\left(\xi^2+\xi'^2\right)e^{\beta\hbar\omega}-\frac{1}{2}\left(\xi^2+\xi'^2\right)e^{-\beta\hbar\omega}+2\xi\xi'}{2\sinh(\beta\hbar\omega)}\right] \\
&= \sqrt{\frac{m\omega}{2\pi\hbar\sinh(\beta\hbar\omega)}}\exp\left[-\frac{m\omega}{4\hbar}\cdot\frac{\left(2x^2+2x'^2\right)e^{\beta\hbar\omega}+\left(2x^2+2x'^2\right)e^{-\beta\hbar\omega}-8xx'}{2\sinh(\beta\hbar\omega)}\right] \\
&= \sqrt{\frac{m\omega}{2\pi\hbar\sinh(\beta\hbar\omega)}}\exp\left[-\frac{m\omega}{4\hbar}\cdot\frac{\left(x^2+x'^2\right)\cosh(\beta\hbar\omega)-2xx'}{\sinh\frac{\beta\hbar\omega}{2}\cosh\frac{\beta\hbar\omega}{2}}\right] \\
&= \sqrt{\frac{m\omega}{2\pi\hbar\sinh(\beta\hbar\omega)}}\exp\left[-\frac{m\omega}{4\hbar}\cdot\frac{\left(x^2+x'^2\right)\left(\cosh^2\frac{\beta\hbar\omega}{2}+\sinh^2\frac{\beta\hbar\omega}{2}\right)-2xx'\left(\cosh^2\frac{\beta\hbar\omega}{2}-\sinh^2\frac{\beta\hbar\omega}{2}\right)}{\sinh\frac{\beta\hbar\omega}{2}\cosh\frac{\beta\hbar\omega}{2}}\right] \\
&= \sqrt{\frac{m\omega}{2\pi\hbar\sinh(\beta\hbar\omega)}}\exp\left\{-\frac{m\omega}{4\hbar}\left[(x+x')^2\tanh\frac{\beta\hbar\omega}{2}+(x-x')^2\coth\frac{\beta\hbar\omega}{2}\right]\right\}
\end{aligned}
$$

This is the simplified form of the matrix element expression. The diagonal elements of this matrix are the ones satisfying $x = x'$, which are relatively simply terms.

$$
\langle x|e^{-\beta\hat{H}}|x\rangle = \sqrt{\frac{m\omega}{2\pi\hbar\sinh(\beta\hbar\omega)}}\exp\left[-\frac{m\omega}{\hbar}x^2\tanh\frac{\beta\hbar\omega}{2}\right]
$$

The partition function $Q(\beta)$ is the trace of $e^{-\beta\hat{H}}$. This is equal to the summation of it's diagonal elements, or in this case, an integration over x. The partition function takes the form of a Gaussian curve, and its integration formula is used in the steps below.

$$
\begin{aligned}
Q(\beta) = \mathrm{Tr}\left(e^{-\beta\hat{H}}\right) &= \int_{-\infty}^{+\infty}\langle x|e^{-\beta\hat{H}}|x\rangle\,dx \\
&= \sqrt{\frac{m\omega}{2\pi\hbar\sinh(\beta\hbar\omega)}}\int_{-\infty}^{+\infty}\exp\left[-\frac{m\omega}{\hbar}x^2\tanh\frac{\beta\hbar\omega}{2}\right]dx \\
&= \sqrt{\frac{m\omega}{2\pi\hbar\sinh(\beta\hbar\omega)}}\cdot\sqrt{\frac{\pi\hbar}{m\omega\tanh\frac{\beta\hbar\omega}{2}}} \\
&= \frac{1}{2}\mathrm{csch}\frac{\beta\hbar\omega}{2}
\end{aligned}
$$

Notice that this is the same result as Equation (2.3). This is hardly surprising, as the partition function is a scalar quantity, and it is unaffected by the specific choice of basis. Now that we have the partition function, we can use it to obtain the elements of the density matrix.

$$
\begin{aligned}
\langle x|\hat{\rho}|x'\rangle &= \frac{1}{Q(\beta)}\langle x|e^{-\beta\hat{H}}|x'\rangle \\
&= 2\sinh\frac{\beta\hbar\omega}{2}\sqrt{\frac{m\omega}{2\pi\hbar\sinh(\beta\hbar\omega)}}\exp\left\{-\frac{m\omega}{4\hbar}\left[(x+x')^2\tanh\frac{\beta\hbar\omega}{2}+(x-x')^2\coth\frac{\beta\hbar\omega}{2}\right]\right\} \\
&= \sqrt{\frac{m\omega}{\pi\hbar}\tanh\frac{\beta\hbar\omega}{2}}\exp\left\{-\frac{m\omega}{4\hbar}\left[(x+x')^2\tanh\frac{\beta\hbar\omega}{2}+(x-x')^2\coth\frac{\beta\hbar\omega}{2}\right]\right\}
\end{aligned}
$$

In the case of the quantum harmonic oscillator, the off-diagonal elements of the density matrix, $\langle x|\rho|x'\rangle$, represent the quantum coherence between different position eigenstates. These elements describe the spatial extent of the wave packet associated with the particle in the QHO. Specifically, they capture the quantum superposition between two distinct positions x and x'. The off-diagonal elements measure the probability amplitude for the particle to be in a superposition of these positions, even though the positions cannot be observed simultaneously in a single measurement. This reflects the quantum nature of the system, where the particle can effectively "explore" multiple positions within the harmonic potential due to its wave-like properties.

The magnitude of the off-diagonal elements provides information about the spatial coherence of the wave packet. A larger magnitude indicates stronger coherence between the positions x and x', meaning the wave packet has significant overlap between these positions. This suggests that the particle's wave function is delocalized, with the positions being highly correlated. Conversely, smaller (or vanishing) off-diagonal elements indicate weaker coherence, implying that the wave packet is more localized around specific positions. The distance $|x - x'|$ between the positions also plays a role: as $|x - x'|$ increases, the coherence typically decreases, reflecting the reduced overlap of the wave function at widely separated points.

The diagonal elements $\langle x|\hat{\rho}|x\rangle$ represent the probability densities that the particle is found at position x in the thermal state described by the density matrix $\hat{\rho}$.

$$\boxed{\langle x|\hat{\rho}|x\rangle = \sqrt{\frac{m\omega}{\pi\hbar}\tanh\frac{\beta\hbar\omega}{2}}\exp\left\{-\frac{m\omega}{\hbar}x^2\tanh\frac{\beta\hbar\omega}{2}\right\}} \tag{3.1}$$

IV. PARTITION FUNCTION AND DENSITY MATRIX OF THE QUANTUM HARMONIC OSCILLATOR IN MOMENTUM BASIS

Following the calculation in the position basis, we now turn to the momentum basis. Similar to the position basis, this approach is less common than the energy basis due to the added complexity in evaluating the density matrix. Since the momentum eigenstates differ from the energy eigenstates, the density matrix expressed in the momentum basis will generally be non-diagonal. We will derive the explicit form of the density matrix in the momentum basis and analyse the implications of its off-diagonal elements. This provides complementary insights into the quantum harmonic oscillator by emphasising the system's behaviour in momentum space.

The normalized eigenfunctions of the quantum harmonic oscillator in the momentum basis are given by:

$$\phi_n(p) = \langle p|\psi_n\rangle = \frac{1}{(\pi\hbar m\omega)^{1/4}}\frac{1}{\sqrt{2^n n!}}H_n\left(\frac{p}{\sqrt{\hbar m\omega}}\right)\exp\left(-\frac{p^2}{2\hbar m\omega}\right)$$

where $H_n(y)$ are the Hermite polynomials. The energy eigenvalues are $E_n = \hbar\omega(n+\frac{1}{2})$. The imaginary-time propagator, or thermal kernel, in the momentum basis is:

$$\langle p|e^{-\beta\hat{H}}|p'\rangle = \sum_{n=0}^{\infty} e^{-\beta E_n}\phi_n(p)\phi_n^*(p')$$

Since $\phi_n(p)$ are real functions, $\phi_n^*(p') = \phi_n(p')$. Substituting the energy eigenvalues and the eigenfunctions:

$$\begin{aligned}
\langle p|e^{-\beta\hat{H}}|p'\rangle &= \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n+\frac{1}{2})}\left[\frac{1}{(\pi\hbar m\omega)^{1/4}}\frac{H_n\left(\frac{p}{\sqrt{\hbar m\omega}}\right)}{\sqrt{2^n n!}}\exp\left(-\frac{p^2}{2\hbar m\omega}\right)\right] \\
&\quad\times\left[\frac{1}{(\pi\hbar m\omega)^{1/4}}\frac{H_n\left(\frac{p'}{\sqrt{\hbar m\omega}}\right)}{\sqrt{2^n n!}}\exp\left(-\frac{p'^2}{2\hbar m\omega}\right)\right] \\
&= \frac{e^{-\beta\hbar\omega/2}}{\sqrt{\pi\hbar m\omega}}\exp\left(-\frac{p^2+p'^2}{2\hbar m\omega}\right)\sum_{n=0}^{\infty}\frac{e^{-n\beta\hbar\omega}}{2^n n!}H_n\left(\frac{p}{\sqrt{\hbar m\omega}}\right)H_n\left(\frac{p'}{\sqrt{\hbar m\omega}}\right)
\end{aligned}$$

We define the dimensionless momenta:

$$\xi_p \equiv \frac{p}{\sqrt{\hbar m\omega}}, \quad \xi_p' \equiv \frac{p'}{\sqrt{\hbar m\omega}}$$

and also define the substitution $w \equiv e^{-\beta\hbar\omega}$. The expression then becomes:

$$\langle p|e^{-\beta\hat{H}}|p'\rangle = \frac{w^{1/2}}{\sqrt{\pi\hbar m\omega}}\exp\left[-\frac{1}{2}(\xi_p^2+\xi_p'^2)\right]\sum_{n=0}^{\infty}\left(\frac{w}{2}\right)^n\frac{H_n(\xi_p)H_n(\xi_p')}{n!}$$

Again, we use Mehler's Hermite formula:

$$\sum_{n=0}^{\infty}\left(\frac{z}{2}\right)^n\frac{H_n(u)H_n(v)}{n!} = (1-z^2)^{-1/2}\exp\left[\frac{2uvz-(u^2+v^2)z^2}{1-z^2}\right]$$

With $u = \xi_p$, $v = \xi_p'$, and $z = w$:

$$\begin{aligned}
\langle p|e^{-\beta\hat{H}}|p'\rangle &= \frac{w^{1/2}}{\sqrt{\pi\hbar m\omega}}(1-w^2)^{-1/2}\exp\left[-\frac{1}{2}(\xi_p^2+\xi_p'^2)\right]\exp\left[\frac{2\xi_p\xi_p' w-(\xi_p^2+\xi_p'^2)w^2}{1-w^2}\right] \\
&= \frac{w^{1/2}}{\sqrt{\pi\hbar m\omega(1-w^2)}}\exp\left[\frac{-\frac{1}{2}(\xi_p^2+\xi_p'^2)(1-w^2)+2\xi_p\xi_p' w-(\xi_p^2+\xi_p'^2)w^2}{1-w^2}\right] \\
&= \frac{w^{1/2}}{\sqrt{\pi\hbar m\omega(1-w^2)}}\exp\left[\frac{-\frac{1}{2}(\xi_p^2+\xi_p'^2)+\frac{1}{2}w^2(\xi_p^2+\xi_p'^2)+2\xi_p\xi_p' w-w^2(\xi_p^2+\xi_p'^2)}{1-w^2}\right] \\
&= \frac{w^{1/2}}{\sqrt{\pi\hbar m\omega(1-w^2)}}\exp\left[\frac{-\frac{1}{2}(\xi_p^2+\xi_p'^2)(1+w^2)+2w\xi_p\xi_p'}{1-w^2}\right]
\end{aligned}$$

Let $X = \beta\hbar\omega$, and let $w = e^{-X}$. The prefactor coefficient is:

$$\frac{w^{1/2}}{\sqrt{\pi\hbar m\omega(1-w^2)}} = \frac{1}{\sqrt{\pi\hbar m\omega}}\sqrt{\frac{w}{1-w^2}}$$

Since $1 - w^2 = 1 - e^{-2X} = e^{-X}(e^X - e^{-X}) = 2e^{-X}\sinh X = 2w\sinh X$:

$$\frac{1}{\sqrt{\pi\hbar m\omega}}\sqrt{\frac{w}{2w\sinh X}} = \sqrt{\frac{1}{2\pi\hbar m\omega\sinh X}}$$

The argument of the exponential becomes:

$$\begin{aligned}
\text{ExpArg} &= \frac{-\frac{1}{2}(\xi_p^2 + \xi_p'^2)(1+w^2) + 2w\xi_p\xi_p'}{1-w^2} \\
&= \frac{1}{\hbar m\omega}\frac{-\frac{1}{2}(p^2 + p'^2)(1+w^2) + 2wpp'}{1-w^2} \\
&= \frac{1}{\hbar m\omega}\frac{-\frac{1}{2}(p^2 + p'^2)(2w\cosh X) + 2wpp'}{2w\sinh X} \\
&= -\frac{1}{2\hbar m\omega\sinh X}\left[(p^2 + p'^2)\cosh X - 2pp'\right]
\end{aligned}$$

This is one common form of the exponent. To express it using $\tanh(X/2)$ and $\coth(X/2)$, we use the identities:

$$\cosh X = \cosh^2(X/2) + \sinh^2(X/2)$$

$$(p+p')^2\tanh(X/2) + (p-p')^2\coth(X/2) = \frac{(p^2+p'^2)\cosh X - 2pp'}{\frac{1}{2}\sinh X}$$

Thus,

$$(p^2+p'^2)\cosh X - 2pp' = \frac{1}{2}\sinh X\left[(p+p')^2\tanh(X/2) + (p-p')^2\coth(X/2)\right]$$

Substituting this into the exponent argument:

$$\begin{aligned}
\text{ExpArg} &= -\frac{1}{2\hbar m\omega\sinh X}\left\{\frac{1}{2}\sinh X\left[(p+p')^2\tanh(X/2) + (p-p')^2\coth(X/2)\right]\right\} \\
&= -\frac{1}{4\hbar m\omega}\left[(p+p')^2\tanh\left(\frac{\beta\hbar\omega}{2}\right) + (p-p')^2\coth\left(\frac{\beta\hbar\omega}{2}\right)\right]
\end{aligned}$$

Thus, the closed-form kernel is:

$$\boxed{\langle p|e^{-\beta\hat{H}}|p'\rangle = \sqrt{\frac{1}{2\pi\hbar m\omega\sinh(\beta\hbar\omega)}}\exp\left\{-\frac{1}{4\hbar m\omega}\left[(p+p')^2\tanh\left(\frac{\beta\hbar\omega}{2}\right) + (p-p')^2\coth\left(\frac{\beta\hbar\omega}{2}\right)\right]\right\}}$$

Apart from the replacement $m\omega \to 1/(m\omega)$ in various places (overall prefactor and exponent coefficient), the functional form involving the combination of $(P+P')^2$ and $(P-P')^2$ (or $(X+X')^2$ and $(X-X')^2$) terms with $\tanh$ and $\coth$ is indeed analogous to the position-space result, reflecting the oscillator's x-p symmetry.

We can get the diagonal elements of the matrix by setting $p' = p$ in the kernel, which gives the thermal momentum distribution:

$$\begin{aligned}
\langle p|e^{-\beta\hat{H}}|p\rangle &= \sqrt{\frac{1}{2\pi\hbar m\omega\sinh(\beta\hbar\omega)}}\exp\left\{-\frac{1}{4\hbar m\omega}\left[(2p)^2\tanh\left(\frac{\beta\hbar\omega}{2}\right) + 0\right]\right\} \\
&= \sqrt{\frac{1}{2\pi\hbar m\omega\sinh(\beta\hbar\omega)}}\exp\left\{-\frac{p^2}{\hbar m\omega}\tanh\left(\frac{\beta\hbar\omega}{2}\right)\right\}
\end{aligned}$$

From this momentum kernel, one can compute $\langle p^2\rangle$ and all higher moments. The partition function $Z = \text{Tr}(e^{-\beta\hat{H}}) = \int dp\langle p|e^{-\beta\hat{H}}|p\rangle$.

$$\begin{aligned}
Z &= \int_{-\infty}^{\infty}\sqrt{\frac{1}{2\pi\hbar m\omega\sinh(\beta\hbar\omega)}}\exp\left\{-\frac{p^2}{\hbar m\omega}\tanh\left(\frac{\beta\hbar\omega}{2}\right)\right\}dp \\
&= \sqrt{\frac{1}{2\pi\hbar m\omega\sinh(\beta\hbar\omega)}}\sqrt{\frac{\pi\hbar m\omega}{\tanh(\beta\hbar\omega/2)}} \\
&= \sqrt{\frac{1}{4\sinh^2(X/2)}} = \frac{1}{2\sinh(\beta\hbar\omega/2)}
\end{aligned}$$

V. CLASSICAL AND QUANTUM LIMIT

In physical systems, whether the behaviour is classical or quantum depends on the temperature and density of the system. These conditions determine whether thermal energy or quantum effects play a more significant role in shaping the system's behaviour. Understanding this distinction helps explain why some systems, like gases at room temperature, can be described classically, while others, like electrons in a metal or particles at extremely low temperatures, require quantum mechanics.

At high temperatures and low densities, systems tend to behave classically. This is because the thermal energy of the particles is much larger than the energy differences between quantum states, causing particles to occupy a wide range of energy levels. As a result, quantum effects such as particle indistinguishability becomes negligible as the chances of particles occupying the same state is small. Additionally, at low densities, particles are far apart, reducing the likelihood of quantum interactions such as wavefunction overlap.

On the other hand, at low temperatures and high densities, quantum behaviour becomes essential. When the temperature is low, the thermal energy of particles is small compared to the spacing between quantum energy levels. This causes particles to occupy the lowest available quantum states, where quantum effects such as indistinguishability and Pauli exclusion principle can effect the statistics. At high densities, particles are packed closely together, leading to significant wavefunction overlap.

A. High Temperature (Classical) Limit in Position Basis

At high temperatures, $T \to +\infty$, which implies $\beta = 1/k_BT \to 0$. Note that $\lim_{x\to 0}\tanh x = x$ and $\lim_{x\to 0}\coth x = 1/x$.

$$\begin{aligned}\lim_{\beta\to 0}\langle x|\hat{\rho}|x'\rangle &= \lim_{\beta\to 0}\sqrt{\frac{m\omega}{\pi\hbar}\tanh\frac{\beta\hbar\omega}{2}}\exp\left\{-\frac{m\omega}{4\hbar}\left[(x+x')^2\tanh\frac{\beta\hbar\omega}{2}+(x-x')^2\coth\frac{\beta\hbar\omega}{2}\right]\right\}\\ &= \sqrt{\frac{m\omega}{\pi\hbar}\frac{\beta\hbar\omega}{2}}\exp\left\{-\frac{m\omega}{4\hbar}\left[(x+x')^2\frac{\beta\hbar\omega}{2}+(x-x')^2\frac{2}{\beta\hbar\omega}\right]\right\}\end{aligned}$$

It is evident that unless $(x-x')=0$, then the exponent would have an extremely large negative value, causing the matrix element to equate to 0. On the other hand, if $(x-x')=0$ (when $x=x'$), the diverging term cancels, and we are left with the following.

$$\boxed{\lim_{\beta\to 0}\langle x|\hat{\rho}|x\rangle = \sqrt{\frac{m\beta\omega^2}{2\pi}}\exp\left\{-\frac{m\beta\omega^2}{2}x^2\right\}} \tag{5.1}$$

Note that all non-diagonal elements disappear in the classical limit. This is hardly surprising as generally, the non-diagonal elements of a density matrix corresponds to quantum-mechanical effects. Also related is the complete disappearance of $\hbar$. Only the diagonal elements are left in the density matrix. Equation 5.1 describes the probability density distribution around x.

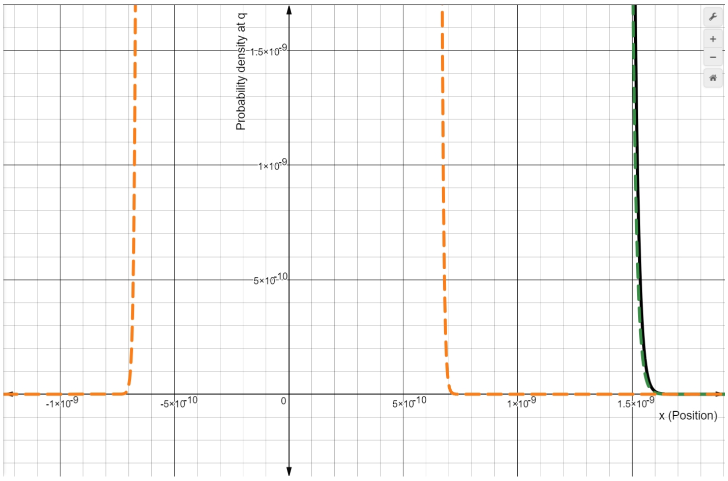

Figure 1: Probability density distribution (Black) vs High temperature approximation (Green) in position basis

B. Low Temperature (Quantum) Limit in Position Basis

At low temperatures, $T \to 0$, which implies $\beta = 1/k_BT \to +\infty$. Note that $\lim_{x\to\infty}\tanh x = 1$ and $\lim_{x\to\infty}\coth x = 1$.

$$
\begin{aligned}
\lim_{\beta\to\infty}\langle x|\hat{\rho}|x'\rangle &= \lim_{\beta\to\infty}\sqrt{\frac{m\omega}{\pi\hbar}\tanh\frac{\beta\hbar\omega}{2}}\exp\left\{-\frac{m\omega}{4\hbar}\left[(x+x')^2\tanh\frac{\beta\hbar\omega}{2}+(x-x')^2\coth\frac{\beta\hbar\omega}{2}\right]\right\}\\
&= \sqrt{\frac{m\omega}{\pi\hbar}}\exp\left\{-\frac{m\omega}{4\hbar}\left[(x+x')^2+(x-x')^2\right]\right\}\\
&= \sqrt{\frac{m\omega}{\pi\hbar}}\exp\left\{-\frac{m\omega}{2\hbar}\left(x^2+x'^2\right)\right\}
\end{aligned}
$$

Consider the diagonal elements, $x = x'$:

$$
\boxed{\lim_{\beta\to\infty}\langle x|\hat{\rho}|x\rangle = \sqrt{\frac{m\omega}{\pi\hbar}}\exp\left\{-\frac{m\omega}{\hbar}x^2\right\}} \tag{5.2}
$$

This result is purely quantum mechanical, and contains no thermal effects. The Boltzmann constant k_B, previously appearing as part of β, does not appear in the equation at all.

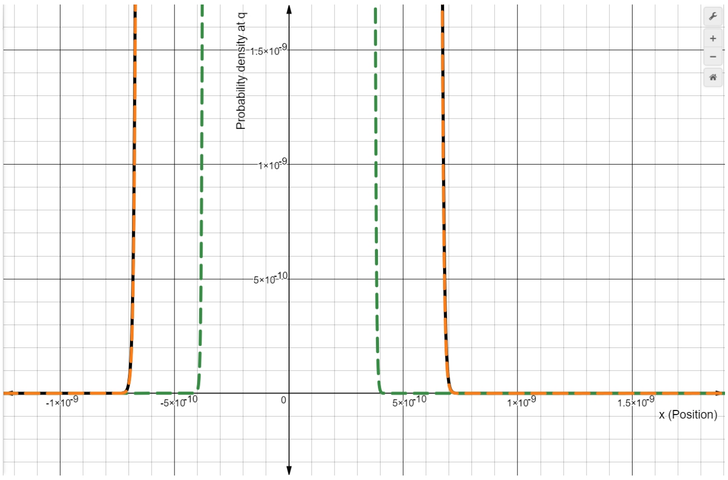

Figure 2: Probability density distribution (Black) vs Low temperature approximation (Orange) in position basis

VI. DISCUSSION AND OUTLOOK

The quantum harmonic ensemble typically refers to a single quantum harmonic oscillator in thermal equilibrium with a heat bath, described statistically via the canonical ensemble. In this context, the system is not in a fixed quantum state but rather in a statistical mixture of energy eigenstates, each weighted by the Boltzmann factor $e^{-\beta E_n}$, where $\beta = 1/(k_B T)$. The ensemble thus characterises how one quantum oscillator behaves on average at temperature T, capturing both quantum mechanical discreteness and thermal fluctuations. It is a minimal yet nontrivial model that allows one to study fundamental aspects of quantum statistical mechanics.

This single-particle model generalises naturally to many-particle systems, for instance, a collection of non-interacting harmonic oscillators. In such cases, the total Hamiltonian is a sum over the individual oscillator Hamiltonians, and the partition function becomes a product of the individual partition functions. This generalisation is relevant in various physical systems, including lattice vibrations (phonons) in solids, where each vibrational mode of the lattice behaves approximately like an independent quantum harmonic oscillator. Interactions between oscillators can also be incorporated perturbatively or via field-theoretic extensions.

The choice of basis—position or energy—affects how the thermal state is represented. In the energy basis, the density matrix is diagonal, with each element corresponding to the occupation probability of an energy eigenstate. This basis is natural for calculations involving partition functions and thermodynamic quantities. In contrast, in the position basis, the density matrix becomes a function $\rho(x, x')$, which encodes the probability amplitude of finding the particle at positions x and x'. Though more analytically involved, this representation reveals spatial coherence and allows one to visualise quantum statistical behaviour in position space, particularly in the classical limit where the density becomes approximately Gaussian.

Despite its simplicity, the quantum harmonic oscillator ensemble can model a wide range of physical phenomena. It underpins the quantisation of normal modes in molecules and solids, and serves as a foundational model in quantum optics, cavity QED, and statistical field theory. In particular, it models bosonic excitations such as phonons and photons, and appears as the basic unit in path integral formulations and quantum thermodynamic studies. Its analytic solvability makes it an essential tool for testing methods and exploring the quantum-classical crossover.

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IMAGE CREDITS

[1] Figure 1: From Zichen Luo, “Classical Approximation of Quantum Harmonic Ensemble in Position Basis,” `https://www.desmos.com/calculator/nkkkodldxf`, Desmos Graphing Calculator, 2025.

[2] Figure 2: From Zichen Luo, “Quantum Approximation of Quantum Harmonic Ensemble in Position Basis,” `https://www.desmos.com/calculator/nkkkodldxf`, Desmos Graphing Calculator, 2025.