10.1: Principles of quantum statistical mechanics

The problem of quantum statistical mechanics is the quantum mechanical treatment of an N-particle system. Suppose the corresponding N-particle classical system has Cartesian coordinates

$$q_1, \dots, q_{3N}$$

and momenta

$$p_1, \cdots, p_{3N}$$

and Hamiltonian

$$H = \sum_{i=1}^{3N} \frac{p_i^2}{2m_i} + U(q_1, \dots, q_{3N})$$

Then, as we have seen, the quantum mechanical problem consists of determining the state vector $|\Psi(t)\rangle$ from the Schrödinger equation

$$H|\Psi(t)\rangle = i\hbar \frac{\partial}{\partial t}|\Psi(t)\rangle$$

Denoting the corresponding operators, $Q_1, \cdots, Q_{3N}$ and $P_1, \cdots, P_{3N}$, we note that these operators satisfy the commutation relations:

$[Q_i, Q_j]$	$=$	$[P_i, P_j] = 0$
$[Q_i, P_j]$	$=$	$i\hbar I \delta_{ij}$

and the many-particle coordinate eigenstate $|q_1 \dots q_{3N}\rangle$ is a tensor product of the individual eigenstate $|q_1\rangle, \dots, |q_{3N}\rangle$:

$$|q_1 \dots q_{3N}\rangle = |q_1\rangle \cdots |q_{3N}\rangle$$

The Schrödinger equation can be cast as a partial differential equation by multiplying both sides by $\langle q_1 \dots q_{3N}|$:

$\langle q_1 \dots q_{3N}\|H\|\Psi(t)\rangle$	$=$	$\frac{\partial}{\partial t}\langle q_1 \dots q_{3N}\|\Psi(t)\rangle$	
$\left[-\sum_{i=1}^{3N} \frac{\hbar^2}{2m_i}\frac{\partial^2}{\partial q_i^2} + U(q_1, \dots, q_{3N})\right]\Psi(q_1, \dots, q_{3N}, t)$		$i\hbar\frac{\partial}{\partial t}\Psi(q_1, \dots, q_{3N}, t)$	

where the many-particle wave function is $\Psi(q_1, \dots., q_{3N}, t) = \langle q_1 \dots q_{3N}|\Psi(t)\rangle$. Similarly, the expectation value of an operator $A = A(Q_1, \dots, Q_{3N}, P_1, \dots, P_{3N})$ is given by

$$\langle A \rangle = \int dq_1 \cdots dq_{3N} \Psi^*(q_1, \dots, q_{3N}) A\left(q_1, \cdots, q_{3N}, \frac{\hbar}{i}\frac{\partial}{\partial q_1}, \cdots, \frac{\hbar}{i}\frac{\partial}{\partial q_{3N}}\right)\Psi(q_1, \dots, q_{3N})$$