Quantum Mechanics 3 - Class Exercise 7

21.12.2022

Question 1

Consider two free particles with momentum $\vec{k}$, $\vec{k}'$. Find the probability density function for finding the particles at $\vec{r}_1$, $\vec{r}_2$ if

1. The particles are distinguishable.
2. The particles are spin-less bosons.
3. The particles are electrons in singlet state.
4. The particles are electrons in triplet state.

Solution to 1

The particles are distinguishable and so we know that one of them has momentum $\vec{k}$ while the other has momentum $\vec{k}'$. Therefore, their state is

$$|\psi\rangle = |\vec{k}\rangle|\vec{k}'\rangle, \tag{1}$$

and the wave-function is

$$\psi\left(\vec{r}_1, \vec{r}_2\right) = \langle\vec{r}_1|\langle\vec{r}_2| \cdot |\vec{k}\rangle|\vec{k}'\rangle = \langle\vec{r}_1|\vec{k}\rangle\langle\vec{r}_2|\vec{k}'\rangle = \frac{1}{L^{3/2}}\mathrm{e}^{i\left(\vec{k}\cdot\vec{r}_1+\vec{k}'\cdot\vec{r}_2\right)} \tag{2}$$

$$\implies \left|\psi\left(\vec{r}_1, \vec{r}_2\right)\right|^2 = \frac{1}{L^3}. \tag{3}$$

This distribution does not depend on the values of $\vec{r}_1$ and $\vec{r}_2$.

Solution to 2

The particles are spin-less bosons and their overall state has to be symmetric, therefore

$$|\psi\rangle = \frac{1}{\sqrt{2}}\left(|\vec{k}\rangle|\vec{k}'\rangle + |\vec{k}'\rangle|\vec{k}\rangle\right). \tag{4}$$

Thus

$$\psi\left(\vec{r}_1, \vec{r}_2\right) = \frac{1}{\sqrt{2}L^{3/2}}\left[\mathrm{e}^{i\left(\vec{k}\cdot\vec{r}_1+\vec{k}'\cdot\vec{r}_2\right)} + \mathrm{e}^{i\left(\vec{k}'\cdot\vec{r}_1+\vec{k}\cdot\vec{r}_2\right)}\right]. \tag{5}$$

$$\implies \left|\psi\left(\vec{r}_1, \vec{r}_2\right)\right|^2 = \frac{1}{2L^3}\left[1+1+2\,\mathrm{Re}\left(\mathrm{e}^{i\left(\vec{k}\cdot\vec{r}_1+\vec{k}'\cdot\vec{r}_2\right)}\mathrm{e}^{-i\left(\vec{k}'\cdot\vec{r}_1+\vec{k}\cdot\vec{r}_2\right)}\right)\right] \tag{6}$$

$$= \frac{1}{L^3}\left[1+\cos\left(\Delta\vec{k}\cdot\Delta\vec{r}\right)\right] = \frac{2}{L^3}\cos^2\left(\frac{\Delta\vec{k}\cdot\Delta\vec{r}}{2}\right), \tag{7}$$

where $\Delta\vec{r} \equiv \vec{r}_2 - \vec{r}_1$, $\Delta\vec{k} \equiv \vec{k} - \vec{k}'$. Notice it is fairly plausible to find the particles at $\Delta\vec{r} = 0$.

Solution to 3

The particles are electrons in singlet state which is anti-symmetric under the exchange of the electrons spins.

$$|\text{singlet}\rangle = \frac{1}{\sqrt{2}} \left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle \right). \tag{8}$$

Since the overall state of the electrons has to be anti-symmetric we know that it must be symmetric in momentum ,

$$|\psi\rangle = \frac{1}{\sqrt{2}} \left(|\vec{k}\rangle|\vec{k}'\rangle + |\vec{k}'\rangle|\vec{k}\rangle \right) \otimes |\text{singlet}\rangle. \tag{9}$$

Thus

$$\psi\left(\vec{r}_1, \vec{r}_2\right) = \frac{1}{\sqrt{2}L^{3/2}} \left[\mathrm{e}^{i\left(\vec{k}\cdot\vec{r}_1 + \vec{k}'\cdot\vec{r}_2\right)} + \mathrm{e}^{i\left(\vec{k}'\cdot\vec{r}_1 + \vec{k}\cdot\vec{r}_2\right)} \right]. \tag{10}$$

$$\begin{aligned} \Longrightarrow\ |\psi\left(\vec{r}_1, \vec{r}_2\right)|^2 &= \frac{1}{2L^3} \left[1 + 1 + 2\,\mathrm{Re}\left(\mathrm{e}^{i\left(\vec{k}\cdot\vec{r}_1 + \vec{k}'\cdot\vec{r}_2\right)} \mathrm{e}^{-i\left(\vec{k}'\cdot\vec{r}_1 + \vec{k}\cdot\vec{r}_2\right)} \right) \right] &(11)\\ &= \frac{1}{L^3} \left[1 + \cos\left(\Delta\vec{k}\cdot\Delta\vec{r} \right) \right] = \frac{2}{L^3} \cos^2\left(\frac{\Delta\vec{k}\cdot\Delta\vec{r}}{2} \right), &(12) \end{aligned}$$

As in the case of spin-less bosons, it is fairly plausible to find the particles at $\Delta\vec{r} = 0$.

Solution to 4

The particles are electrons in triplet state which is symmetric under the exchange of the electrons spins.

$$|\text{triplet}\rangle = \frac{1}{\sqrt{2}} \left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle \right) \quad \text{or} \quad |\uparrow\uparrow\rangle \quad \text{or} \quad |\downarrow\downarrow\rangle. \tag{13}$$

Since the overall state of the electrons has to be anti-symmetric we know that it must be anti-symmetric in momentum ,

$$|\psi\rangle = \frac{1}{\sqrt{2}} \left(|\vec{k}\rangle|\vec{k}'\rangle - |\vec{k}'\rangle|\vec{k}\rangle \right) \otimes |\text{triplet}\rangle. \tag{14}$$

Thus

$$\psi\left(\vec{r}_1, \vec{r}_2\right) = \frac{1}{\sqrt{2}L^{3/2}} \left[\mathrm{e}^{i\left(\vec{k}\cdot\vec{r}_1 + \vec{k}'\cdot\vec{r}_2\right)} - \mathrm{e}^{i\left(\vec{k}'\cdot\vec{r}_1 + \vec{k}\cdot\vec{r}_2\right)} \right]. \tag{15}$$

$$\begin{aligned} \Longrightarrow\ |\psi\left(\vec{r}_1, \vec{r}_2\right)|^2 &= \frac{1}{2L^3} \left[1 + 1 - 2\,\mathrm{Re}\left(\mathrm{e}^{i\left(\vec{k}\cdot\vec{r}_1 + \vec{k}'\cdot\vec{r}_2\right)} \mathrm{e}^{-i\left(\vec{k}'\cdot\vec{r}_1 + \vec{k}\cdot\vec{r}_2\right)} \right) \right] &(16)\\ &= \frac{1}{L^3} \left[1 - \cos\left(\Delta\vec{k}\cdot\Delta\vec{r} \right) \right] = \frac{2}{L^3} \sin^2\left(\frac{\Delta\vec{k}\cdot\Delta\vec{r}}{2} \right). &(17) \end{aligned}$$

It is now impossible to find the particles at $\Delta\vec{r} = 0$.

Question 2

Find the partition function for a system with N energy levels described by the Hamiltonian

$$\hat{H} = \sum_{i,j=1}^{N} \epsilon_{ij} \hat{a}_i^\dagger \hat{a}_j, \tag{18}$$

where $\hat{a}_i^\dagger$ and $\hat{a}_i$ are the creation and annihilation operators of the i'th state, and $\epsilon_{i,j}$ is a real symmetric matrix. Do it for

1. fermions.

2. bosons.

Solution to 1

The Hamiltonian is not diagonal in Fock basis. It would be convenient to diagonalize it for calculating the partition function. This is doable since $\epsilon_{i,j}$ is symmetric and real, and therefore it can be written as

$$\epsilon = U^{\mathrm{T}} E U \implies \epsilon_{ij} = \sum_{k=1}^{N} U_{ki} E_{kk} U_{kj}. \tag{19}$$

where E is a diagonal matrix and U is an orthogonal matrix ($UU^{\mathrm{T}} = \mathbb{I}$). Let us plug this definition in the Hamiltonian

$$\hat{H} = \sum_{i,j,k=1}^{N} U_{ki} E_{kk} U_{kj} \hat{a}_i^\dagger \hat{a}_j = \sum_{k=1}^{N} E_{kk} \sum_{i=1}^{N} U_{ki} \hat{a}_i^\dagger \sum_{j=1}^{N} U_{kj} \hat{a}_j = \sum_{k=1}^{N} E_{kk} \hat{b}_k^\dagger \hat{b}_k, \tag{20}$$

where we defined

$$\hat{b}_k \equiv \sum_{j=1}^{N} U_{kj} \hat{a}_j \qquad \hat{b}_k^\dagger \equiv \sum_{i=1}^{N} U_{ki} \hat{a}_i^\dagger \tag{21}$$

Let's verify that $\hat{b}_k^\dagger$ and $\hat{b}_k$ can be interpreted as creation and annihilation operators. For fermions we examine the anti-commutator relations

$$\begin{aligned} \left\{\hat{b}_i, \hat{b}_j^\dagger\right\} &= \left\{\sum_{k=1}^{N} U_{ik} \hat{a}_k, \sum_{l=1}^{N} U_{jl} \hat{a}_l^\dagger\right\} = \sum_{k,l=1}^{N} U_{ik} U_{jl} \left\{\hat{a}_k, \hat{a}_l^\dagger\right\} = \sum_{k,l=1}^{N} U_{ik} U_{jl} \delta_{k,l} \\ &= \sum_{k=1}^{N} U_{ik} U_{jk} = \left(UU^{\mathrm{T}}\right)_{ij} = \delta_{ij}. \end{aligned} \tag{22}$$

$$\left\{\hat{b}_i, \hat{b}_j\right\} = \left\{\sum_{k=1}^{N} U_{ik} \hat{a}_k, \sum_{l=1}^{N} U_{jl} \hat{a}_l\right\} = \sum_{k,l=1}^{N} U_{ik} U_{jl} \left\{\hat{a}_k, \hat{a}_l\right\} = 0 \tag{23}$$

$$\implies \left\{\hat{b}_i^\dagger, \hat{b}_j^\dagger\right\} = \left\{\hat{b}_i, \hat{b}_j\right\}^\dagger = 0 \tag{24}$$

We can now calculate the partition function

$$Z = \mathrm{Tr}\left(\mathrm{e}^{-\beta\hat{H}}\right) = \mathrm{Tr}\left(\mathrm{e}^{-\beta\sum_{k=1}^{N} E_{kk}\hat{b}_k^\dagger\hat{b}_k}\right) = \mathrm{Tr}\left(\prod_{k=1}^{N}\mathrm{e}^{-\beta E_{kk}\hat{b}_k^\dagger\hat{b}_k}\right), \tag{25}$$

where in the last equality I used $\mathrm{e}^{A+B} = \mathrm{e}^{A}\mathrm{e}^{B}$ if $[A,B]=0$, with $A = \hat{b}_i^\dagger\hat{b}_i$ and $B = \hat{b}_j^\dagger\hat{b}_j$ (convince yourself why $[\hat{b}_i^\dagger\hat{b}_i, \hat{b}_j^\dagger\hat{b}_j] = 0$). We now calculate the trace explicitly for fermions in Fock basis.

$$\begin{aligned} Z &= \sum_{n_1,n_2,\ldots n_N=0}^{1} \langle n_1, n_2, \ldots, n_N| \prod_{k=1}^{N} \mathrm{e}^{-\beta E_{kk}\hat{b}_k^\dagger\hat{b}_k} |n_1, n_2, \ldots, n_N\rangle \\ &= \sum_{n_1,n_2,\ldots n_N=0}^{1} \langle n_1, n_2, \ldots, n_N| \prod_{k=1}^{N} \mathrm{e}^{-\beta E_{kk} n_k} |n_1, n_2, \ldots, n_N\rangle \\ &= \sum_{n_1,n_2,\ldots n_N=0}^{1} \prod_{k=1}^{N} \mathrm{e}^{-\beta E_{kk} n_k} \overset{(*)}{=} \prod_{k=1}^{N}\left(1+\mathrm{e}^{-\beta E_{kk}}\right) = \det\left(\mathbb{I}+\mathrm{e}^{-\beta\hat{E}}\right) = \det\left(\mathbb{I}+\mathrm{e}^{-\beta\hat{\epsilon}}\right), \end{aligned} \tag{26}$$

where in the last step I used the fact that the determinant of a matrix is independent on the basis in which it is calculated.

While the equality sign $(*)$ in Eq. (26) is true, it is not very trivial. Let us see carefully why this equality holds.

$$\sum_{n_1,n_2,\ldots n_N=0}^{1}\prod_{k=1}^{N}\mathrm{e}^{-\beta E_{kk}n_k} = \sum_{n_1=0}^{1}\mathrm{e}^{-\beta E_{11}n_1}\sum_{n_2,\ldots n_N=0}^{1}\prod_{k=2}^{N}\mathrm{e}^{-\beta E_{kk}n_k} = \left(1+\mathrm{e}^{-\beta E_{11}}\right)\sum_{n_2,\ldots n_N=0}^{1}\prod_{k=2}^{N}\mathrm{e}^{-\beta E_{kk}n_k}. \tag{27}$$

By repeating the above procedure $N-1$ more times, it is easy to see that

$$\sum_{n_1,n_2,\ldots n_N=0}^{1}\prod_{k=1}^{N}\mathrm{e}^{-\beta E_{kk}n_k} = \left(1+\mathrm{e}^{-\beta E_{11}}\right)\left(1+\mathrm{e}^{-\beta E_{22}}\right)\cdots\left(1+\mathrm{e}^{-\beta E_{NN}}\right) = \prod_{k=1}^{N}\left(1+\mathrm{e}^{-\beta E_{kk}}\right). \tag{28}$$

Actually, we can easily generalize this relation for maximum M possible occupations:

$$\sum_{n_1,n_2,\ldots n_N=0}^{M}\prod_{k=1}^{N}\mathrm{e}^{-\beta E_{kk}n_k} = \prod_{k=1}^{N}\sum_{n_k=0}^{M}\mathrm{e}^{-\beta E_{kk}n_k}. \tag{29}$$

Thus, in some sense, the exponent allows us to switch the order of the sum and the product signs (this is not true in general!).

Solution to 2

For bosons we do the exact same calculations, but now each state can be occupied by up to $M \to \infty$ particles (instead of only one particle per state in the case of fermions). All of our calculations from the previous item are still valid so we can write

$$Z = \sum_{n_1,n_2,\dots n_N=0}^{\infty} \prod_{k=1}^{N} \mathrm{e}^{-\beta E_{kk} n_k} = \prod_{k=1}^{N} \sum_{n_k=0}^{\infty} \mathrm{e}^{-\beta E_{kk} n_k} = \prod_{k=1}^{N} \frac{1}{1-\mathrm{e}^{-\beta E_{kk}}} = \det\left[\left(\mathbb{I}-\mathrm{e}^{-\beta \hat{E}}\right)^{-1}\right] \tag{30}$$

$$= \det\left[\left(\mathbb{I}-\mathrm{e}^{-\beta \hat{\epsilon}}\right)^{-1}\right] = \left[\det\left(\mathbb{I}-\mathrm{e}^{-\beta \hat{\epsilon}}\right)\right]^{-1}. \tag{31}$$

Notice that we can write the partition function for both fermions and bosons as

$$\boxed{Z = \left[\det\left(\mathbb{I}\pm\mathrm{e}^{-\beta \hat{\epsilon}}\right)\right]^{\pm 1}}, \tag{32}$$

with + for fermions and − for bosons.

Question 3

Consider N interacting spin-less bosons in a box of volume L^3. The Hamiltonian is

$$\hat{H} = \sum_{\vec{k}} \frac{\hbar^2 k^2}{2m} \hat{a}^\dagger_{\vec{k}} \hat{a}_{\vec{k}} + \frac{1}{2L^3} \sum_{\vec{k},\vec{k}',\vec{q}} \tilde{V}(\vec{q})\, \hat{a}^\dagger_{\vec{k}+\vec{q}} \hat{a}^\dagger_{\vec{k}'-\vec{q}} \hat{a}_{\vec{k}'} \hat{a}_{\vec{k}}. \tag{33}$$

If $|\Phi_0\rangle$ is the ground state of the free system, compute $\langle \Phi_0 | \hat{H} | \Phi_0 \rangle$.

Solution

The free system is described by

$$\hat{H}_0 = \sum_{\vec{k}} \frac{\hbar^2 k^2}{2m} \hat{a}^\dagger_{\vec{k}} \hat{a}_{\vec{k}}. \tag{34}$$

From here it is easy to see that the ground state corresponds to all N bosons having zero momentum, i.e. $\vec{k} = 0$. The ground state can be constructed from the vacuum state,

$$|\Phi_0\rangle = \frac{1}{\sqrt{N!}} \hat{a}_0^{\dagger N} |0\rangle, \tag{35}$$

and has zero kinetic energy,

$$\langle \Phi_0 | \hat{H}_0 | \Phi_0 \rangle = 0. \tag{36}$$

Thus, we need to consider only the interaction term:

$$\langle \Phi_0 | \hat{H} | \Phi_0 \rangle = \frac{1}{2L^3} \sum_{\vec{k},\vec{k}',\vec{q}} \tilde{V}(\vec{q})\, \langle \Phi_0 | \hat{a}^\dagger_{\vec{k}+\vec{q}} \hat{a}^\dagger_{\vec{k}'-\vec{q}} \hat{a}_{\vec{k}'} \hat{a}_{\vec{k}} | \Phi_0 \rangle = \frac{1}{2L^3 N!} \sum_{\vec{k},\vec{k}',\vec{q}} \tilde{V}(\vec{q})\, \langle 0 | \hat{a}_0^N \hat{a}^\dagger_{\vec{k}+\vec{q}} \hat{a}^\dagger_{\vec{k}'-\vec{q}} \hat{a}_{\vec{k}'} \hat{a}_{\vec{k}} \hat{a}_0^{\dagger N} | 0 \rangle. \tag{37}$$

We need to calculate

$$\langle 0 | \hat{a}_0^N \hat{a}^\dagger_{\vec{k}+\vec{q}} \hat{a}^\dagger_{\vec{k}'-\vec{q}} \hat{a}_{\vec{k}'} \hat{a}_{\vec{k}} \hat{a}_0^{\dagger N} | 0 \rangle = \langle 0 | \left[\hat{a}_0^N, \hat{a}^\dagger_{\vec{k}+\vec{q}} \right] \hat{a}^\dagger_{\vec{k}'-\vec{q}} \hat{a}_{\vec{k}'} \left[\hat{a}_{\vec{k}}, \hat{a}_0^{\dagger N} \right] | 0 \rangle \tag{38}$$

We can now use the identity

$$\text{if } [A,[A,B]] = 0 \implies [f(A), B] = [A,B]\, f'(A), \tag{39}$$

to evaluate the commutators in Eq. (38):

$$\begin{aligned}
\langle 0 | \hat{a}_0^N \hat{a}^\dagger_{\vec{k}+\vec{q}} \hat{a}^\dagger_{\vec{k}'-\vec{q}} \hat{a}_{\vec{k}'} \hat{a}_{\vec{k}} \hat{a}_0^{\dagger N} | 0 \rangle &= N^2 \langle 0 | \underbrace{\left[\hat{a}_0, \hat{a}^\dagger_{\vec{k}+\vec{q}} \right]}_{\delta_{0,\vec{k}+\vec{q}}} \hat{a}_0^{N-1} \hat{a}^\dagger_{\vec{k}'-\vec{q}} \hat{a}_{\vec{k}'} \underbrace{\left[\hat{a}_{\vec{k}}, \hat{a}_0^\dagger \right]}_{\delta_{\vec{k},0}} \hat{a}_0^{\dagger N-1} | 0 \rangle \\
&= N^2 \langle 0 | \hat{a}_0^{N-1} \hat{a}^\dagger_{\vec{k}'-\vec{q}} \hat{a}_{\vec{k}'} \hat{a}_0^{\dagger N-1} | 0 \rangle \delta_{\vec{k},0} \delta_{0,\vec{k}+\vec{q}} = N^2 \langle 0 | \left[\hat{a}_0^{N-1}, \hat{a}^\dagger_{\vec{k}'} \right] \left[\hat{a}_{\vec{k}'}, \hat{a}_0^{\dagger N-1} \right] | 0 \rangle \delta_{\vec{k},0} \delta_{\vec{q},0} \\
&= N^2 (N-1)^2 \langle 0 | \underbrace{\left[\hat{a}_0, \hat{a}^\dagger_{\vec{k}'} \right]}_{\delta_{0,\vec{k}'}} \hat{a}_0^{N-2} \underbrace{\left[\hat{a}_{\vec{k}'}, \hat{a}_0^\dagger \right]}_{\delta_{\vec{k}',0}} \hat{a}_0^{\dagger N-2} | 0 \rangle \delta_{\vec{k},0} \delta_{\vec{q},0} \\
&= N^2 (N-1)^2 \langle 0 | \hat{a}_0^{N-2} \hat{a}_0^{\dagger N-2} | 0 \rangle \delta_{\vec{k},0} \delta_{\vec{q},0} \delta_{\vec{k}',0} = N^2 (N-1)^2 (N-2)!\, \delta_{\vec{k},0} \delta_{\vec{q},0} \delta_{\vec{k}',0}.
\end{aligned} \tag{40}$$

Plugging this result back in Eq. (37) yields

$$\boxed{\langle \Phi_0 | \hat{H} | \Phi_0 \rangle = \frac{N^2 (N-1)^2 (N-2)!}{2L^3 N!} \tilde{V}(\vec{q}=0) = \frac{N(N-1)}{2L^3} \tilde{V}(\vec{q}=0) = \binom{N}{2} \times \langle V(\vec{r}-\vec{r}') \rangle}. \tag{41}$$

The RHS is nothing but the mean potential energy between static boson pairs times the number of pairs (binomial coefficient of N over 2).