Unit 3-3: Particle in a Box States, the Two Particle Density Matrix

Particles in a Box

For free particles we will often consider the quantum single particle states to be *particle in a box* states.

We take our system to have length L in each direction $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, and $\hat{\mathbf{z}}$. The volume is $V = L^3$. We will also use *periodic boundary conditions*, defined by,

$$\phi(x + L, y, z) = \phi(x, y, z), \quad \phi(x, y + L, z) = \phi(x, y, z), \quad \phi(x, y, z + L) = \phi(x, y, z) \tag{3.3.1}$$

The single particle energy eigenstates can then be written as,

$$\phi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}} \qquad \text{with energy} \quad \epsilon_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m} \tag{3.3.2}$$

Here $\hbar = h/2\pi$, with h being Planck's constant.

Periodic boundary conditions require,

$$\phi_{\mathbf{k}}(x + L, y, z) = \frac{1}{\sqrt{V}} e^{ik_x(x+L)} e^{ik_y y} e^{ik_z z} = \phi_{\mathbf{k}}(x, y, z) = \frac{1}{\sqrt{V}} e^{ik_x x} e^{ik_y y} e^{ik_z z} \tag{3.3.3}$$

This requires,

$$e^{ik_x L} = 1 \quad \Rightarrow \quad k_x = \frac{2\pi}{L} n_x \quad \text{with} \quad n_x = 0, \pm 1, \pm 2, \ldots \text{ integer} \tag{3.3.4}$$

and similarly,

$$k_y = \frac{2\pi}{L} n_y \quad \text{and} \quad k_z = \frac{2\pi}{L} n_z, \quad \text{with} \quad n_x, n_y = 0, \pm 1, \pm 2, \ldots \tag{3.3.5}$$

The spacing between allowed values of k_x (or k_y or k_z) is $\Delta k = \frac{2\pi}{L}$.

Non-Interacting Two Particle System

Here we will compute $\langle \mathbf{r}_1, \mathbf{r}_2 | \hat{\rho}_2 | \mathbf{r}_1, \mathbf{r}_2 \rangle$, the diagonal elements of the two particle density matrix $\hat{\rho}_2$ in the position basis. This gives the probability density that one particle is at position $\mathbf{r}_1$ and the other is at $\mathbf{r}_2$. The goal is to see how the BE vs the FD statistics affect the probability that the two particles will be near each other.

The single particle wavefunctions are $\phi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}}$ with $\epsilon_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m}$.

For free, non-interaction, particles, the energy eigenstates of the two particle system are specified by two wavevectors $\mathbf{k}_1$ and $\mathbf{k}_2$ and have energy $E = \frac{\hbar^2}{2m}(k_1^2 + k_2^2)$. We will denote these energy eigenstates as $|\mathbf{k}_1, \mathbf{k}_2\rangle$. The symmetrized two particle wavefunctions for the energy eigenstates are therefore,

$$\psi_{\mathbf{k}_1, \mathbf{k}_2}(\mathbf{r}_1, \mathbf{r}_2) \equiv \langle \mathbf{r}_1, \mathbf{r}_2 | \mathbf{k}_1, \mathbf{k}_2 \rangle = \frac{1}{\sqrt{2!}(\sqrt{V})^2} \left[e^{i(\mathbf{k}_1\cdot\mathbf{r}_1 + \mathbf{k}_2\cdot\mathbf{r}_2)} \pm e^{i(\mathbf{k}_1\cdot\mathbf{r}_2 + \mathbf{k}_2\cdot\mathbf{r}_1)} \right] \qquad \text{with } + \text{ for BE and } - \text{ for FD} \tag{3.3.6}$$

Then,

$$\langle \mathbf{r}_1, \mathbf{r}_2 | \hat{\rho}_2 | \mathbf{r}_1, \mathbf{r}_2 \rangle = \langle \mathbf{r}_1, \mathbf{r}_2 | \frac{e^{-\beta\hat{\mathcal{H}}}}{Q_2} | \mathbf{r}_1, \mathbf{r}_2 \rangle = \sum_{|\mathbf{k}_1, \mathbf{k}_2\rangle} \langle \mathbf{r}_1, \mathbf{r}_2 | \mathbf{k}_1, \mathbf{k}_2 \rangle \frac{e^{-\beta\hbar^2(k_1^2 + k_2^2)/2m}}{Q_2} \langle \mathbf{k}_1, \mathbf{k}_2 | \mathbf{r}_1, \mathbf{r}_2 \rangle \tag{3.3.7}$$

$$= \frac{1}{Q_2} \sum_{|\mathbf{k}_1, \mathbf{k}_2\rangle} e^{-\beta\hbar^2(k_1^2 + k_2^2)/2m} |\langle \mathbf{r}_1, \mathbf{r}_2 | \mathbf{k}_1, \mathbf{k}_2 \rangle|^2 \tag{3.3.8}$$

Note, if we take $\mathbf{k}_1 \leftrightarrow \mathbf{k}_2$, then $\langle \mathbf{r}_1, \mathbf{r}_2 | \mathbf{k}_1, \mathbf{k}_2 \rangle = \pm \langle \mathbf{r}_1, \mathbf{r}_2 | \mathbf{k}_2, \mathbf{k}_1 \rangle$. But since this matrix element is squared in the above sum, any sign change is canceled out. Thus, in taking the sum over all eigenstates, we can replace $\displaystyle\sum_{|\mathbf{k}_1, \mathbf{k}_2\rangle}$ by independent sums on $\mathbf{k}_1$ and $\mathbf{k}_2$, provided we multiply by $1/2!$ so as not to double count $|\mathbf{k}_1, \mathbf{k}_2\rangle$ and $|\mathbf{k}_2, \mathbf{k}_1\rangle$ which represent the same physical state. Thus,

$$\langle \mathbf{r}_1, \mathbf{r}_2 | e^{-\beta \hat{\mathcal{H}}} | \mathbf{r}_1, \mathbf{r}_2 \rangle = \frac{1}{2!} \sum_{\mathbf{k}_1, \mathbf{k}_2} e^{-\beta \hbar^2 (k_1^2 + k_2^2)/2m} |\langle \mathbf{r}_1, \mathbf{r}_2 | \mathbf{k}_1, \mathbf{k}_2 \rangle|^2 \tag{3.3.9}$$

Now from Eq. (3.3.6) we have,

$$|\langle \mathbf{r}_1, \mathbf{r}_2 | \mathbf{k}_1, \mathbf{k}_2 \rangle|^2 = \frac{2 \pm e^{i\mathbf{k}_1 \cdot \mathbf{r}_{12}} e^{-\mathbf{k}_2 \cdot \mathbf{r}_{12}} \pm e^{-i\mathbf{k}_1 \cdot \mathbf{r}_{12}} e^{i\mathbf{k}_2 \cdot \mathbf{r}_{12}}}{2V^2} \qquad \text{where } \mathbf{r}_{12} \equiv \mathbf{r}_1 - \mathbf{r}_2 \tag{3.3.10}$$

$$= \frac{1 \pm \mathrm{Re}\left[e^{i\mathbf{k}_1 \cdot \mathbf{r}_{12}} e^{-i\mathbf{k}_2 \cdot \mathbf{r}_{12}}\right]}{V^2} \tag{3.3.11}$$

For convenience, let $\alpha = \beta \hbar^2 / m$. Then,

$$\langle \mathbf{r}_1, \mathbf{r}_2 | e^{-\beta \hat{\mathcal{H}}} | \mathbf{r}_1, \mathbf{r}_2 \rangle = \frac{1}{2!V^2} \sum_{\mathbf{k}_1, \mathbf{k}_2} e^{-\alpha k_1^2/2} e^{-\alpha k_2^2/2} \left(1 \pm \mathrm{Re}\left[e^{i\mathbf{k}_1 \cdot \mathbf{r}_{12}} e^{-i\mathbf{k}_2 \cdot \mathbf{r}_{12}}\right] \right) \tag{3.3.12}$$

Now for large $V = L^3$ we have small $\Delta k = 2\pi/L$. We can then approximate,

$$\frac{1}{V} \sum_{\mathbf{k}} = \frac{1}{V(\Delta k)^3} \sum_{\mathbf{k}} (\Delta k)^3 = \frac{1}{V} \left(\frac{L}{2\pi}\right)^3 \int d^3k = \frac{1}{(2\pi)^3} \int d^3k \tag{3.3.13}$$

We thus have,

$$\langle \mathbf{r}_1, \mathbf{r}_2 | e^{-\beta \hat{\mathcal{H}}} | \mathbf{r}_1, \mathbf{r}_2 \rangle = \frac{1}{2(2\pi)^6} \int d^3k_1 \int d^3k_2 \, e^{-\alpha k_1^2/2} e^{-\alpha k_2^2/2} \left(1 \pm \mathrm{Re}\left[e^{i\mathbf{k}_1 \cdot \mathbf{r}_{12}} e^{-i\mathbf{k}_2 \cdot \mathbf{r}_{12}}\right] \right) \tag{3.3.14}$$

To evaluate the above, we will need the following integrals,

$$\int_{-\infty}^{\infty} d^3k \, e^{-\alpha k^2/2} = \left(\frac{2\pi}{\alpha}\right)^{3/2} \tag{3.3.15}$$

which follows from the familiar Gaussian integration $\int_{-\infty}^{\infty} dx \, e^{-x^2/2\sigma^2} = \sqrt{2\pi\sigma^2}$.

We also need,

$$\int_{-\infty}^{\infty} d^3k \, e^{-\alpha k^2/2 + i\mathbf{k} \cdot \mathbf{r}} \tag{3.3.16}$$

which we will do by "completing the square." We have,

$$-\frac{\alpha}{2} k^2 + i\mathbf{k} \cdot \mathbf{r} = -\frac{\alpha}{2} \left(k^2 - \frac{2i}{\alpha} \mathbf{k} \cdot \mathbf{r} \right) = -\frac{\alpha}{2} \left[\left(\mathbf{k} - \frac{i\mathbf{r}}{\alpha} \right)^2 + \frac{r^2}{\alpha^2} \right] = -\frac{\alpha}{2} \tilde{k}^2 - \frac{r^2}{2\alpha} \tag{3.3.17}$$

where $\tilde{\mathbf{k}} \equiv \mathbf{k} - \dfrac{i\mathbf{r}}{\alpha}$. We can now do the integral,

$$\int_{-\infty}^{\infty} d^3k \, e^{-\alpha k^2/2 + i\mathbf{k} \cdot \mathbf{r}} = \int d^3\tilde{k} \, e^{-\alpha \tilde{k}^2/2} \, e^{-r^2/2\alpha} = \left(\frac{2\pi}{\alpha}\right)^{3/2} e^{-r^2/2\alpha} \tag{3.3.18}$$

where in the integral over $\tilde{\mathbf{k}}$, the integration over $\tilde{k}_\mu$ takes place along the contour $k_\mu - ir_\mu/\alpha$, in the lower half of the complex $\tilde{k}_\mu$ plane, parallel to the real $\tilde{k}_\mu$ axis, as in the sketch below. However, since the region between the real axis

and this contour encloses no poles of the integrand, we can move the integration back to the real $\tilde{k}_\mu$ axis and evaluate as a normal real Gaussian integral to get the final result.
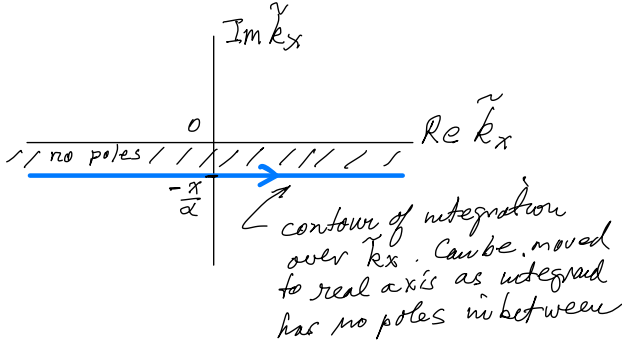
So doing the integrals in Eq. (3.3.14) we now get,

$$\langle \mathbf{r}_1, \mathbf{r}_2 | \, e^{-\beta \hat{\mathcal{H}}} \, | \mathbf{r}_1, \mathbf{r}_2 \rangle = \frac{1}{2(2\pi)^6} \left(\frac{2\pi}{\alpha} \right)^3 \left[1 \pm e^{-r_{i2}^2/\alpha} \right] = \frac{1}{2(2\pi\alpha)^3} \left[1 \pm e^{-r_{12}^2/\alpha} \right] \tag{3.3.19}$$

It is customary to introduce the thermal wavelength λ that we saw already in Eq. (2.19.23),

$$\lambda^2 = 2\pi\alpha = \frac{2\pi\beta\hbar^2}{m} = \frac{2\pi\hbar^2}{k_B T m} = \frac{h^2}{2\pi m k_B T} \tag{3.3.20}$$

only here the constant h, which classically was arbitrary, is now specifically Planck's constant. We now have,

$$\langle \mathbf{r}_1, \mathbf{r}_2 | \, e^{-\beta \hat{\mathcal{H}}} \, | \mathbf{r}_1, \mathbf{r}_2 \rangle = \frac{1}{2\lambda^6} \left[1 \pm e^{-2\pi r_{12}^2/\lambda^2} \right] \tag{3.3.21}$$

To finish the calculation of $\langle \mathbf{r}_1, \mathbf{r}_2 | \, \hat{\rho}_2 \, | \mathbf{r}_1, \mathbf{r}_2 \rangle$, we now need to compute Q_2,

$$Q_2 = \text{Tr}[e^{-\beta \hat{\mathcal{H}}}] = \int d^3 r_1 \int d^3 r_2 \, \langle \mathbf{r}_1, \mathbf{r}_2 | \, e^{-\beta \hat{\mathcal{H}}} \, | \mathbf{r}_1, \mathbf{r}_2 \rangle = \frac{1}{2\lambda^6} \int d^3 r_1 \int d^3 r_2 \left[1 \pm e^{-2\pi r_{12}^2/\lambda^2} \right] \tag{3.3.22}$$

Define the average coordinate of the two particles $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$ and their separation $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2 = \mathbf{r}_{12}$. We can then do a transformation of integration variables to change the integration from $d^3 r_1 d^3 r_2$ to $d^3 R d^3 r$.

$$Q_2 = \frac{1}{2\lambda^6} \int d^3 R \int d^3 r \left[1 \pm e^{-2\pi r^2/\lambda^2} \right] = \frac{V}{2\lambda^6} \left[V \pm \int_0^\infty dr \, 4\pi r^2 \, e^{-2\pi r^2/\lambda^2} \right] \tag{3.3.23}$$

where the integration over $d^3 R$ gives the overall factor of V. Continuing to do the integral over dr we get,

$$Q_2 = \frac{1}{2} \left(\frac{V}{\lambda^3} \right)^2 \left[1 \pm \frac{1}{2^{3/2}} \left(\frac{\lambda^3}{V} \right) \right] \approx \frac{1}{2} \left(\frac{V}{\lambda^3} \right)^2 \qquad \text{as } V \to \infty \text{ in the thermodynamic limit} \tag{3.3.24}$$

So finally, we can put all the pieces together. Using our results from Eqs. (3.3.21) and (3.3.24) we get,

$$\langle \mathbf{r}_1, \mathbf{r}_2 | \, \hat{\rho}_2 \, | \mathbf{r}_1, \mathbf{r}_2 \rangle = \frac{\dfrac{1}{2\lambda^6} \left[1 \pm e^{-2\pi r_{12}^2/\lambda^2} \right]}{\dfrac{1}{2} \left(\dfrac{V}{\lambda^3} \right)^2} \tag{3.3.25}$$

$$\boxed{\langle \mathbf{r}_1, \mathbf{r}_2 | \, \hat{\rho}_2 \, | \mathbf{r}_1, \mathbf{r}_2 \rangle = \frac{1}{V^2} \left[1 \pm e^{-2\pi r_{12}^2/\lambda^2} \right]} \qquad \text{with} \quad \begin{array}{l} + \text{ for BE} \\ - \text{ for FD} \end{array} \tag{3.3.26}$$

We can now compare the above result to what we would expect for two classical non-interacting particles in a box of volume V. Since the positions of these particles are uncorrelated (since they are non-interacting), and each particle is equally likely to be anywhere in the box, the probability density to find one at $\mathbf{r}_1$ and the other at $\mathbf{r}_2$ is just,

$$\rho_2(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{V^2} \tag{3.3.27}$$

Thus it is the $\pm e^{-2\pi r_{12}^2/\lambda^2}$ term in Eq. (3.3.26) that gives the quantum corrections to this classical result. We see that the quantum correction introduces spatial correlations between the two particles. This is due entirely to the required symmetry of the two-particle wavefunction rather than any direct interaction between the particles.

For BE statistics, using the $+$ sign, we see that the probability for the particles to be separated a distance r_{12} is *larger* that it is classically. BE statistics give an effective *attraction* between the particles.

For FD statistics, using the $-$ sign, we see that the probability for the particles to be separated a distance r_{12} is *smaller* that it is classically. FD statistics give an effective *repulsion* between the particles.

The length scale on which the quantum correction is important is $r_{12} \lesssim \lambda$, the thermal wavelength. We can now give the physical meaning of the thermal wavelength of Eq. (3.3.20). Since $k_B T$ is roughly the thermal energy of a typical particle in a gas in equilibrium at temperature T, then the de Broglie wavenumber k of such a particle would be given by $k_B T \sim \hbar^2 k^2/2m$. With $k = 2\pi/\lambda$ and $\hbar = h/2\pi$ we then get $k_B T \sim h^2/2m\lambda^2$. We thus see that the thermal wavelength $\lambda = \sqrt{h^2/2\pi m k_B T}$ is roughly the de Broglie wavelength of a typical particle in a gas at temperature T. Thus, when two particles are separated on a length scale $r_{12} \gg \lambda$, it is reasonable to expect they see no quantum effects. However, when the particles are separated on a length scale $r_{12} \lesssim \lambda$, so that their wavepackets overlap, then quantum effects will be important!

To get a better feeling for the quantum correlation induced between the two particles by their quantum statistics, we can ask what classical interaction between the two particles would give rise to the same correlation?

Suppose two classical particles have a pairwise interaction potential $v(|\mathbf{r}_1 - \mathbf{r}_2|) = v(r_{12})$. Then the classical probability density to have one particle at $\mathbf{r}_1$ and the other at $\mathbf{r}_2$ would be,

$$\rho_2(\mathbf{r}_1, \mathbf{r}_2) = \frac{\sum\limits_{\mathbf{p}_1, \mathbf{p}_2} e^{-\beta \mathcal{H}[\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2]}}{\sum\limits_{\mathbf{p}_1, \mathbf{p}_2} \sum\limits_{\mathbf{r}_1, \mathbf{r}_2} e^{-\beta \mathcal{H}[\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2]}} = \frac{\sum\limits_{\mathbf{p}_1, \mathbf{p}_2} e^{-\beta\left[\frac{p_1^2}{2m} + \frac{p_2^2}{2m} + v(r_{12})\right]}}{\sum\limits_{\mathbf{p}_1, \mathbf{p}_2} \sum\limits_{\mathbf{r}_1, \mathbf{r}_2} e^{-\beta\left[\frac{p_1^2}{2m} + \frac{p_2^2}{2m} + v(r_{12})\right]}} = \frac{e^{-\beta v(r_{12})}}{\sum\limits_{\mathbf{r}_1, \mathbf{r}_2} e^{-\beta v(r_{12})}} \tag{3.3.28}$$

Transforming to center of mass and difference coordinates as before, $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$ and $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2 = \mathbf{r}_{12}$, for large V and assuming $v(r_{12}) \to 0$ as $r_{12} \to \infty$, we get.

$$\sum_{\mathbf{r}_1, \mathbf{r}_2} e^{-\beta v(r_{12})} = \sum_{\mathbf{R}} \sum_{\mathbf{r}} e^{-\beta v(r)} = V \sum_{\mathbf{r}} e^{-\beta v(r)} \approx V^2 \tag{3.3.29}$$

The last step follows because, as r gets large, $v(r) \to 0$ and $e^{-\beta v(r)} \to 1$. So the fraction of the volume V for which $e^{-\beta v(r)}$ is significantly different from unity becomes negligibly small once $L = V^{1/3}$ is much larger than the range of the interaction $v(r)$.

We thus have for the classical two-particle probability density,

$$\rho_2(\mathbf{r}_1, \mathbf{r}_2) = \frac{e^{-\beta v(r_{12})}}{V^2} \tag{3.3.30}$$

Comparing to Eq. (3.3.26), the effective classical interaction potential $v(r_{12})$ that would reproduce the quantum correlations, is,
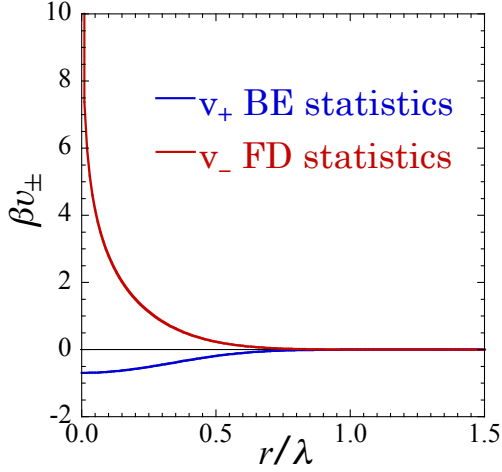
$$v_{\pm}(r) = -k_B T \ln\left[1 \pm e^{-2\pi r^2/\lambda^2}\right] \qquad \begin{array}{l} + \text{ for BE} \\ - \text{ for FD} \end{array} \qquad (3.3.31)$$

To summarize, we found that BE statistics lead to an effective *attraction* between otherwise non-interacting particles, while FD statistics lead to an effective *repulsion*.

These quantum correlations become noticeable on particle separations $r \lesssim \lambda$, where $\lambda = \sqrt{h^2/2\pi m k_B T}$ is the thermal wavelength.

N-Particle Partition Function in the Position Representation

For those who enjoy this sort of thing, we can also compute the N-particle partition function Q_N using the position representation.

The eigenstates are,

$$\langle \mathbf{r}_1, \ldots, \mathbf{r}_N | \mathbf{k}_1, \ldots, \mathbf{k}_N \rangle = \frac{1}{\sqrt{N!V^N}} \sum_{\mathbb{P}} (\pm 1)^P e^{i \sum_i (\mathbb{P}\mathbf{r}_i) \cdot \mathbf{k}_i} \qquad + \text{ for BE}, - \text{ for FD} \qquad (3.3.32)$$

where $\mathbb{P}\mathbf{r}_i$ is a permutation of the positions $\mathbf{r}_i$, i.e. if $\mathbb{P}(123) = 231$, then $\mathbb{P}1 = 2$, $\mathbb{P}2 = 3$, and $\mathbb{P}(3) = 1$, and we sum over all $N!$ possible permutations.

Now,

$$\langle \mathbf{r}_1, \ldots, \mathbf{r}_N | e^{-\beta \hat{\mathcal{H}}} | \mathbf{r}_1, \ldots, \mathbf{r}_N \rangle = \sum_{|\mathbf{k}_1, \ldots, \mathbf{k}_N\rangle} e^{-\frac{\beta \hbar^2}{2m}(k_1^2 + \cdots + k_N^2)} |\langle \mathbf{r}_1, \ldots, \mathbf{r}_N | \mathbf{k}_1, \ldots, \mathbf{k}_N \rangle|^2 \qquad (3.3.33)$$

and

$$|\langle \mathbf{r}_1, \ldots, \mathbf{r}_N | \mathbf{k}_1, \ldots, \mathbf{k}_N \rangle|^2 = \frac{1}{N!V} \sum_{\mathbb{P}} \sum_{\mathbb{P}'} (\pm 1)^{P+P'} e^{i \sum_i [\mathbb{P}\mathbf{r}_i - \mathbb{P}'\mathbf{r}_i] \cdot \mathbf{k}_k} \qquad (3.3.34)$$

Now we can write

$$[\mathbb{P}\mathbf{r}_i - \mathbb{P}'\mathbf{r}_i] \cdot \mathbf{k}_i = \left[\mathbb{P}\left(\mathbf{r}_i - \mathbb{P}^{-1}\mathbb{P}'\mathbf{r}_i\right)\right] \cdot \mathbf{k}_i = \left(\mathbf{r}_i - \mathbb{P}^{-1}\mathbb{P}'\mathbf{r}_i\right) \cdot \mathbb{P}^{-1}\mathbf{k}_i \qquad (3.3.35)$$

where $\mathbb{P}^{-1}$ is the inverse permutation of $\mathbb{P}$; also, the order P of $\mathbb{P}^{-1}$ is the same as that of $\mathbb{P}$. Therefore we have,

$$|\langle \mathbf{r}_1, \ldots, \mathbf{r}_N | \mathbf{k}_1, \ldots, \mathbf{k}_N \rangle|^2 = \frac{1}{N!V} \sum_{\mathbb{P}} \sum_{\mathbb{P}''} (\pm 1)^{P''} e^{i \sum_i (\mathbf{r}_i - \mathbb{P}''\mathbf{r}_i) \cdot \mathbb{P}^{-1}\mathbf{k}_k} \qquad (3.3.36)$$

where $\mathbb{P}'' = \mathbb{P}^{-1}\mathbb{P}'$ and $P'' = P + P'$.

Now when we sum over the energy eigenstates $|\mathbf{k}_1, \ldots, \mathbf{k}_N\rangle$ in Eq. (3.3.33), we sum over all the $\mathbf{k}_i$. Since $\mathbf{k}_i$ is a dummy index in the sum, it does not matter whether we label it $\mathbf{k}_i$ or $\mathbb{P}^{-1}\mathbf{k}_i$. So in the above, each term in the $\sum_{\mathbb{P}}$ contributes an equal amount. We can therefore replace $\sum_{\mathbb{P}}$ by $N!$ times the one term $\mathbb{P} = \mathbb{I}$, the identity. Similarly, when we do the sum on the eigenstates $\sum_{|\mathbf{k}_1, \ldots, \mathbf{k}_N\rangle}$ we can do independent sums on $\mathbf{k}_1, \ldots, \mathbf{k}_N$ provided we add a factor $1/N!$ to prevent double counting.

The result is,

$$\langle \mathbf{r}_1, \ldots, \mathbf{r}_N | \, e^{-\beta \hat{\mathcal{H}}} \, | \mathbf{r}_1, \ldots, \mathbf{r}_N \rangle = \frac{1}{N! V^N} \sum_{\mathbf{k}_1, \ldots, \mathbf{k}_N} e^{-\frac{\beta \hbar^2}{2m}(k_1^2 + \cdots + k_N^2)} \sum_{\mathbb{P}} (\pm 1)^P e^{i \sum_i \mathbf{k}_i \cdot (\mathbf{r}_i - \mathbb{P}\mathbf{r}_i)} \tag{3.3.37}$$

$$= \frac{1}{N!(2\pi)^{3N}} \sum_{\mathbb{P}} (\pm 1)^P \prod_{i=1}^{N} \left[\int d^3 k_i \, e^{-\frac{\beta \hbar^2}{2m} k_i^2 + i\mathbf{k}_i \cdot (\mathbf{r}_i - \mathbb{P}\mathbf{r}_i)} \right] \tag{3.3.38}$$

This integral we already did when we considered the two particle problem. With $\alpha \equiv \beta \hbar^2 / 2m$, we have,

$$\langle \mathbf{r}_1, \ldots, \mathbf{r}_N | \, e^{-\beta \hat{\mathcal{H}}} \, | \mathbf{r}_1, \ldots, \mathbf{r}_N \rangle = \frac{1}{N!(2\pi)^{3N}} \sum_{\mathbb{P}} (\pm 1)^P \prod_{i=1}^{N} \left[\left(\frac{2\pi}{\alpha} \right)^{3/2} e^{-(\mathbf{r}_i - \mathbb{P}\mathbf{r}_i)^2 / 2\alpha} \right] \tag{3.3.39}$$

$$= \frac{1}{N!(2\pi)^{3N}} \left(\frac{2\pi}{\alpha} \right)^{3/2} \sum_{\mathbb{P}} (\pm 1)^P \prod_{i=1}^{N} f(\mathbf{r} - \mathbb{P}\mathbf{r}_i) \tag{3.3.40}$$

$$= \frac{1}{N! \lambda^{3N}} \sum_{\mathbb{P}} (\pm 1)^P \prod_{i=1}^{N} f(\mathbf{r} - \mathbb{P}\mathbf{r}_i) \tag{3.3.41}$$

where $\lambda^2 = 2\pi\alpha$, and $f(r) = e^{-r^2/2\alpha} = e^{-\pi r^2/\lambda^2}$ with $f(0) = 1$.

The N-particle partition function is then,

$$Q_N = \int d^3 r_1 \cdots \int d^3 r_N \, \langle \mathbf{r}_1, \ldots, \mathbf{r}_N | \, e^{-\beta \hat{\mathcal{H}}} \, | \mathbf{r}_1, \ldots, \mathbf{r}_N \rangle \tag{3.3.42}$$

$$= \frac{1}{N! \lambda^{3N}} \sum_{\mathbb{P}} (\pm 1)^P \int d^3 r_1 \cdots \int d^3 r_N \, f(\mathbf{r}_1 - \mathbb{P}\mathbf{r}_1) f(\mathbf{r}_2 - \mathbb{P}\mathbf{r}_2) \ldots f(\mathbf{r}_N - \mathbb{P}\mathbf{r}_N) \tag{3.3.43}$$

The leading term in the sum on $\mathbb{P}$ is when $\mathbb{P} = \mathbb{I}$ the identity. Then $\mathbb{P}\mathbf{r}_i = \mathbf{r}_i$ and all the terms $f(\mathbf{r}_i - \mathbb{P}\mathbf{r}_i) = f(0) = 1$.

The next most leading terms are those corresponding to permutations involving only a singe pair exchange, say $\mathbb{P}\mathbf{r}_i = \mathbf{r}_j$ and $\mathbb{P}\mathbf{r}_j = \mathbf{r}_i$, while all other $\mathbb{P}\mathbf{r}_k = \mathbf{r}_k$. In this case there are only two of the $f(\mathbf{r}_i - \mathbb{P}\mathbf{r}_i)$ factors that are not unity.

The next order are terms from permutations involving an exchange of only three particles, $\mathbb{P}\mathbf{r}_i = \mathbf{r}_j$, $\mathbb{P}\mathbf{r}_j = \mathbf{r}_k$, and $\mathbb{P}\mathbf{r}_k = \mathbf{r}_i$. The next order are terms from permutations involving exchanges of four particles, etc.

We thus have,

$$\begin{aligned} Q_N = \frac{V^N}{N! \lambda^{3N}} \Bigg\{ 1 &\pm \sum_{i<j} \int \frac{d^3 r_i}{V} \int \frac{d^3 r_j}{V} \, f(\mathbf{r}_i - \mathbf{r}_j) \, f(\mathbf{r}_j - \mathbf{r}_i) \\ &+ \sum_{i<j<k} \int \frac{d^3 r_i}{V} \int \frac{d^3 r_j}{V} \int \frac{d^3 r_k}{V} \, f(\mathbf{r}_i - \mathbf{r}_j) \, f(\mathbf{r}_j - \mathbf{r}_k) \, f(\mathbf{r}_k - \mathbf{r}_i) \quad \pm \quad \ldots \Bigg\} \end{aligned} \tag{3.3.44}$$

The leading term $\dfrac{V^N}{N! \lambda^{3N}}$ is just the classical result, provided we take the phase space parameter h to be Planck's constant. Note, we *automatically* get the Gibbs $1/N!$ factor for identical particles.

The higher order terms are the quantum corrections that arise from 2-particle, 3-particle, etc., exchanges. For BE the terms all add with + signs. For FD the terms add with alternating signs.