

Independent and indistinguishable particles

MSE 421 - Ceriotti

- A quantum mechanical (micro)state is characterized in terms of the eigenstates of a complete set of commuting observables
- An ensemble can be seen as the set of probabilities of finding the system in one of such eigenstates
- The density matrix provides a formally elegant solution to computing ensemble averages in quantum mechanics. E.g. the canonical density matrix is

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

- The partition function is the trace of ρ

$$\text{Tr } \rho = \sum_{\nu} \langle \nu | e^{-\beta \hat{H}} | \nu \rangle = \sum_{\nu} e^{-\beta E_{\nu}} = Q$$

- The value of any observable can be obtained as a trace

$$\frac{1}{Q} \text{Tr } \rho \hat{A} = \frac{1}{Q} \sum_{\nu} \langle \nu | e^{-\beta \hat{H}} \hat{A} | \nu \rangle = \frac{1}{Q} \sum_{\nu} A_{\nu} e^{-\beta E_{\nu}} = \langle A \rangle$$

- Consider the quantum mechanical partition function in the position representation

$$Q = \text{Tr} e^{-\beta \hat{H}} = \int d\mathbf{q} \langle \mathbf{q} | e^{-\beta \hat{H}} | \mathbf{q} \rangle$$

- Now, let's pretend that $[\hat{T}, \hat{V}] = 0$, so we can write $e^{-\beta \hat{H}} = e^{-\beta \hat{T}} e^{-\beta \hat{V}}$

$$\int d\mathbf{q} \langle \mathbf{q} | e^{-\beta \hat{T}} e^{-\beta \hat{V}} | \mathbf{q} \rangle = \int d\mathbf{q} e^{-\beta V(\mathbf{q})} \langle \mathbf{q} | e^{-\beta \hat{T}} | \mathbf{q} \rangle$$

- We need to insert a $\mathbf{p}$ projector $\int d\mathbf{p} |\mathbf{p}\rangle \langle \mathbf{p}|$

$$\int d\mathbf{q} \int d\mathbf{p} e^{-\beta V(\mathbf{q})} \langle \mathbf{q} | e^{-\beta \hat{T}} | \mathbf{p} \rangle \langle \mathbf{p} | \mathbf{q} \rangle = \int d\mathbf{q} \int d\mathbf{p} e^{-\beta \left[V(\mathbf{q}) + \frac{p^2}{2m} \right]} \langle \mathbf{q} | \mathbf{p} \rangle \langle \mathbf{p} | \mathbf{q} \rangle$$

- We are left with the *classical* canonical partition function. QM behavior arises from non-commuting operators!

Remember: $\langle \mathbf{p} | \mathbf{q} \rangle \propto e^{i\mathbf{p} \cdot \mathbf{q}}$, so $\langle \mathbf{q} | \mathbf{p} \rangle \langle \mathbf{p} | \mathbf{q} \rangle = \text{cnst.}$

- Let's look at the canonical partition function of two non-interacting subsystems considered as a whole
 - Let ν_i^A and ν_i^B be the microstates of subsystems A and B respectively, so

$$Q^A = \sum_i e^{-\beta E_i^A}, \quad Q^B = \sum_i e^{-\beta E_i^B}$$

now, if we consider the composite system, its states correspond to the Cartesian product of $\{\nu_i^A\} \times \{\nu_j^B\}$, so

$$Q^{AB} = \sum_{ij} e^{-\beta E_i^A} e^{-\beta E_j^B} = Q^A Q^B$$

- The observables of the composite systems are similarly easy to obtain,

$$\langle E \rangle = \langle E^A \rangle + \langle E^B \rangle$$

and observables of individual systems are uncorrelated as they should

$$\langle E^A E^B \rangle = \frac{1}{Q} \sum_{ij} E_i^A E_j^B e^{-\beta(E_i^A + E_j^B)} = \frac{\left[\sum_i E_i^A e^{-\beta E_i^A} \right] \left[\sum_j E_j^B e^{-\beta E_j^B} \right]}{Q_A Q_B} = \langle E^A \rangle \langle E^B \rangle$$

- Consider a system with N particles. They will be described by the many-body wavefunction

$$\langle \mathbf{x}_1, \mathbf{x}_2, \dots \mathbf{x}_N | \nu \rangle = \Psi_\nu (\mathbf{x}_1, \mathbf{x}_2, \dots \mathbf{x}_N)$$

- This is a formidable problem! How are we going to write this wavefunction, and to label states??
- In many cases we can make a factorization ansatz, that is equivalent to assuming that (quasi)particles behave independently of each other

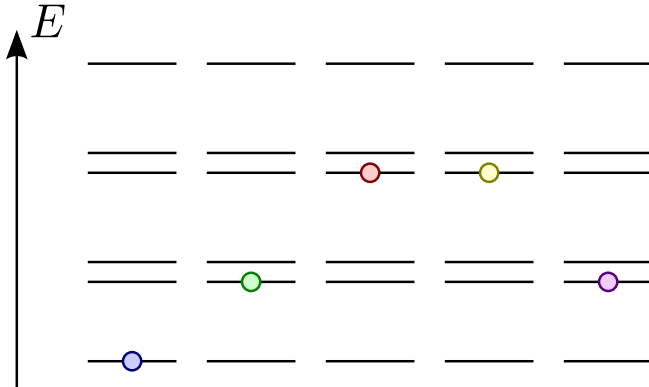
$$\Psi_\nu (\mathbf{x}_1, \mathbf{x}_2, \dots \mathbf{x}_N) = \prod_{i=1}^N \psi_{\nu_i}^{(i)} (\mathbf{x}_i)$$

- If the particles are all subject to a sum of single-particle Hamiltonians, then everything pans out nicely, and the density matrix and partition function are just products of single-particle DM and PF

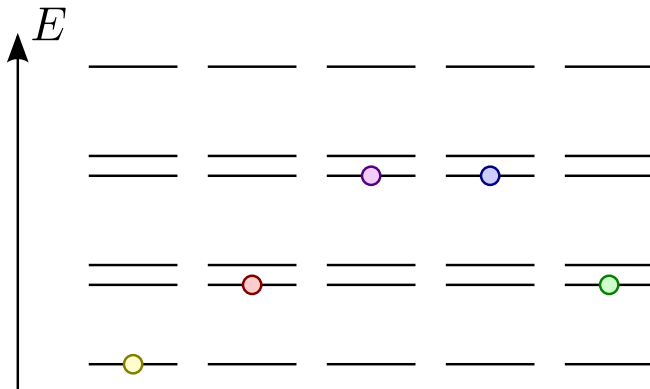
$$\rho = e^{-\beta \hat{H}} = e^{-\beta \sum_i \hat{H}_i} = \prod_i e^{-\beta \hat{H}_i} = \prod_i \rho_i$$

$$Q = \text{Tr} e^{-\beta \hat{H}} = \prod_i \sum_{\nu_i} \langle \nu_i | e^{-\beta \hat{H}_i} | \nu_i \rangle = \prod_i Q_i$$

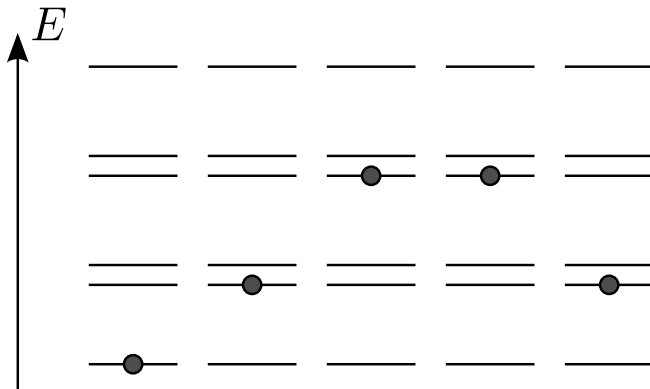
- Now consider what should happen if all the Hamiltonians are identical, but the different particles are somehow distinguishable (e.g. because they are very far from each other)
- If particles are all the same, some states are indistinguishable, and we must avoid double-counting!
- A very effective formalism: using *occupation numbers* for the different levels



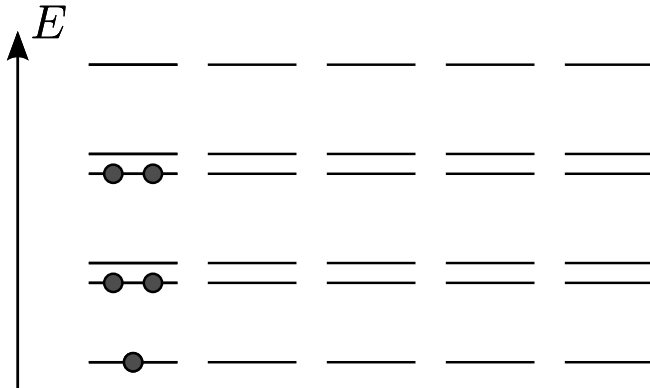
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- Quantum mechanically, the observables must not change if we swap indices of identical particles, e.g.

$$|\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)|^2 = |\Psi(\mathbf{x}_2, \mathbf{x}_1, \dots, \mathbf{x}_N)|^2$$

in fact, there are only two possibilities:

- 1 bosons: $\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \Psi(\mathbf{x}_2, \mathbf{x}_1, \dots, \mathbf{x}_N)$

$$\Psi = \frac{1}{\sqrt{N!}} \sum_{\pi} \prod_{i=1}^N \psi_{\nu_{\pi_i}}(\mathbf{x}_{\pi_i})$$

- 2 fermions: $\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = -\Psi(\mathbf{x}_2, \mathbf{x}_1, \dots, \mathbf{x}_N)$

$$\Psi = \frac{1}{\sqrt{N!}} \sum_{\pi} \text{sign } \pi \prod_{i=1}^N \psi_{\nu_{\pi_i}}(\mathbf{x}_{\pi_i})$$

- Exclusion principle: Ψ_F is zero if two systems are in the same quantum state, so each state can be occupied at most once!

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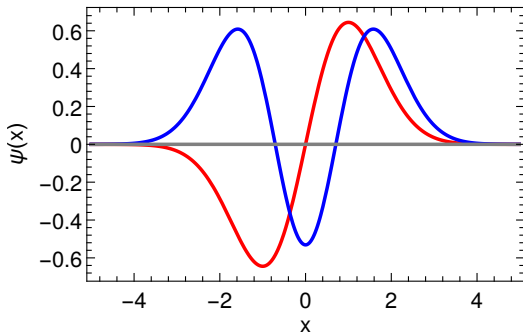
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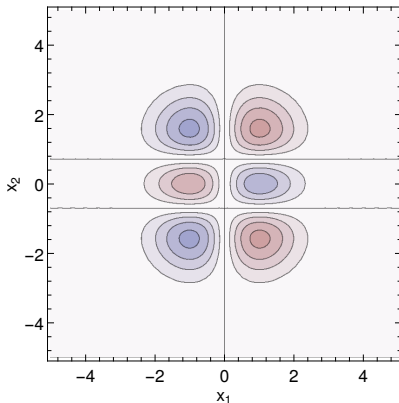
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- Two identical oscillators, resp. in the first and second excited states
- Product ansatz is not invariant to particle exchanges
- Symmetrized wavefunctions introduce new correlations



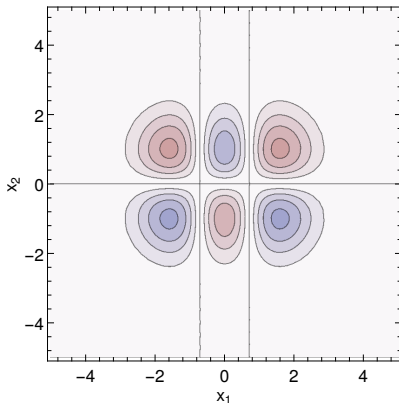
$\psi_1(x), \quad \psi_2(x)$

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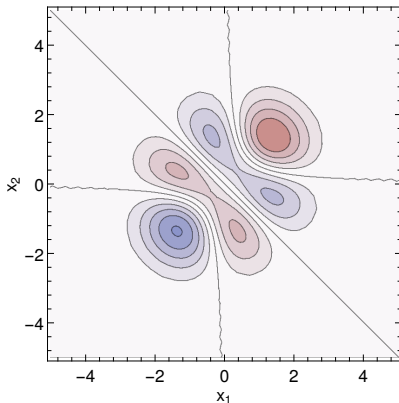
$$\Psi(x_1, x_2) = \psi_1(x_1) \psi_2(x_2)$$

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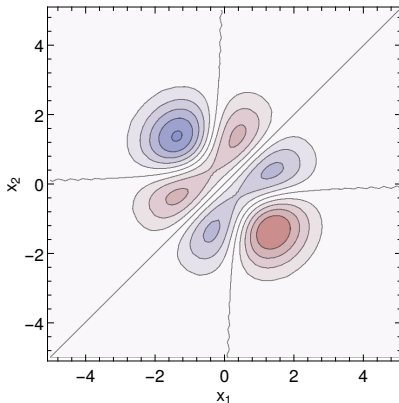
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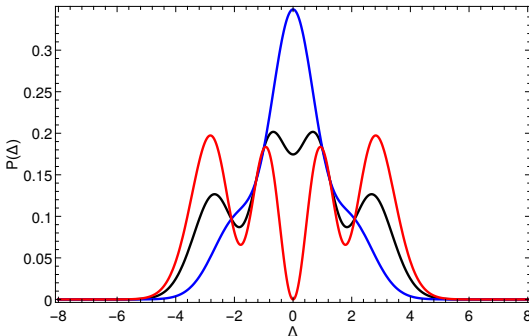
$$\Psi(x_1, x_2) = \frac{1}{\sqrt{2}} [\psi_1(x_1) \psi_2(x_2) + \psi_1(x_2) \psi_2(x_1)]$$

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$$\Psi(x_1, x_2) = \frac{1}{\sqrt{2}} [\psi_1(x_1) \psi_2(x_2) - \psi_1(x_2) \psi_2(x_1)]$$

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$$P(\Delta) = \int |\Psi(x, x + \Delta)|^2 dx$$

- For N *distinguishable* particles with single-particle energy levels ϵ_i

$$Q = q^N = \left[\sum_i e^{-\beta \epsilon_i} \right]^N$$

where q is the partition function for a single particle

- For indistinguishable particles it is better to work in terms of the occupation numbers $\{n_\nu\}$

➊ bosons: $Q = \sum_{\{n_i\}} \delta \left(\sum_i n_i - N \right) e^{-\beta \sum_i n_i \epsilon_i}$

➋ fermions $Q = \sum_{\{n_i\}} \delta \left(\sum_i n_i - N \right) \left[\prod_i (\delta_{n_i 0} + \delta_{n_i 1}) \right] e^{-\beta \sum_i n_i \epsilon_i}$

- It is far from trivial to work analytically in constant- N ensembles

- How about we use the grand-canonical formalism?

$$\Xi = \sum_{\{n_i\}} e^{-\beta [\sum_i n_i \epsilon_i - \mu \sum_i n_i]} = \sum_{\{n_i\}} \prod_i e^{-\beta n_i (\epsilon_i - \mu)} = \prod_i \sum_{n_i=0}^{\infty} e^{-\beta n_i (\epsilon_i - \mu)}$$

- Summing up the geometric series we get

$$\Xi = \prod_i \frac{1}{1 - e^{-\beta(\epsilon_i - \mu)}}, \quad \ln \Xi = - \sum_i \ln \left(1 - e^{-\beta(\epsilon_i - \mu)} \right)$$

from which we get mean occupation numbers

$$\langle n_j \rangle = - \frac{\partial \ln \Xi}{\partial (\beta \epsilon_j)} = \frac{e^{-\beta(\epsilon_j - \mu)}}{1 - e^{-\beta(\epsilon_j - \mu)}} = \frac{1}{e^{\beta(\epsilon_j - \mu)} - 1}$$

- Total particle number can be enforced by computing $\langle N \rangle$ and self-consistently adjusting μ

- Also when considering Fermions it helps working grand-canonical

$$\Xi = \sum_{\{n_i\}} e^{-\beta [\sum_i n_i \epsilon_i - \mu \sum_i n_i]} = \sum_{\{n_i\}} \prod_i e^{-\beta n_i (\epsilon_i - \mu)} = \prod_i \sum_{n_i=0}^1 e^{-\beta n_i (\epsilon_i - \mu)}$$

- Getting the PF is a piece of cake

$$\Xi = \prod_i (1 + e^{-\beta (\epsilon_i - \mu)}), \quad \ln \Xi = \sum_i \ln (1 + e^{-\beta (\epsilon_i - \mu)})$$

and so is obtaining the mean occupation numbers

$$\langle n_j \rangle = - \frac{\partial \ln \Xi}{\partial (\beta \epsilon_j)} = \frac{e^{-\beta (\epsilon_j - \mu)}}{1 + e^{-\beta (\epsilon_j - \mu)}} = \frac{1}{e^{\beta (\epsilon_j - \mu)} + 1}$$

- Also in this case, in the thermodynamic limit, constant- $\langle N \rangle$ can be set by adjusting μ

- Re-consider the distinguishable particles case in the grand-canonical ensemble

$$\Xi = \sum_N q^N e^{\beta\mu N} = \frac{1}{1 - qe^{\beta\mu}}, \quad \ln \Xi = -\ln 1 - qe^{\beta\mu}$$

- It is easy to get $\langle n_j \rangle$ by differentiating the G-C PF

$$\langle n_j \rangle = -\frac{\partial \ln \Xi}{\partial \beta \epsilon_j} = \frac{e^{\beta\mu} (\partial q / \beta \epsilon_j)}{1 - qe^{\beta\mu}} = \frac{e^{\beta\mu} e^{-\beta \epsilon_j}}{1 - qe^{\beta\mu}} = \frac{e^{-\beta(\epsilon_j - \mu)}}{1 - e^{\beta\mu} q} = \frac{e^{-\beta \epsilon_j}}{e^{-\beta\mu} - q}$$

- Guess how you can enforce the desired value for $\langle N \rangle \dots$

- In the high- T limit, for a system with an infinite number of energy levels, the number of levels gets much larger than $\langle N \rangle$. Then,

$$\langle n_j \rangle = \frac{1}{e^{\beta(\epsilon_j - \mu)} \pm 1} \ll 1$$

which implies that $e^{\beta(\epsilon_j - \mu)} \gg 1$.

- Then, one can write $\langle n_j \rangle \approx e^{-\beta(\epsilon_j - \mu)}$, so

$$\langle N \rangle = \sum_j \langle n_j \rangle = e^{\beta\mu} \sum_j e^{-\beta\epsilon_j} \rightarrow \beta\mu = \ln \langle N \rangle - \ln \sum_j e^{-\beta\epsilon_j}$$

- Let's now apply a few thermodynamic relations
- The high-temperature partition function equals the Boltzmann case, with a correction to account for the indistinguishability of particles

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