Now we commute to the density to the left

$$\langle 0|\hat{\psi}(x_1)\dots\hat{\rho}(x')\hat{\psi}(x_j)\dots\hat{\psi}(x_N)|\Psi\rangle =$$

$$= \sum_{\ell<j} \delta(x'-x_\ell)\langle 0|\hat{\psi}(x_1)\dots\hat{\psi}(x_N)|\Psi\rangle$$

As a result, we get many-body Sch. eq

$$\boxed{i\hbar\partial_t \Psi = \left(\sum_{j=1}^{N} H_j^{(0)} + \sum_{\ell<j} V_{\ell j}\right)\Psi}$$

The final result does not depend on quantum statistics

Grand canonical ensemble from 2nd quantization

Grand canonical ensemble – a system is in contact with heat bath which it can exchange energy and particles.

Probability of being in a state λ of energy E_λ and particle number N_λ

$$\boxed{p_\lambda = \frac{1}{Z} e^{-\beta(E_\lambda - \mu N_\lambda)}}, \quad \beta = 1/k_B T$$

$$Z = \sum_\lambda e^{-\beta(E_\lambda - \mu N_\lambda)} \rightsquigarrow \text{normalization constant}$$

partition function

We can extract all thermodynamic properties from Z:

$$N = \frac{\sum_\lambda N e^{-\beta(E_\lambda - \mu N_\lambda)}}{Z} = \frac{1}{\beta}\frac{\partial}{\partial \mu} \log Z$$

or if we introduce free energy

$$Z = e^{-\beta\Omega} \Rightarrow \Omega = -\beta^{-1}\log Z$$

$$N = -\frac{\partial \Omega}{\partial \mu}$$

following similar arguments

$$P = -\frac{\partial\Omega}{\partial V} \qquad S = -\frac{\partial \Omega}{\partial T}$$

Using second quantization:

$$\boxed{\begin{aligned} Z &= \sum_\lambda \langle \lambda | e^{-\beta(\hat{H}-\mu\hat{N})} | \lambda \rangle \\ &= \mathrm{Tr}\left(e^{-\beta(\hat{H}-\mu\hat{N})}\right) \end{aligned}}$$

energy eigenstates

basis-independent form

Expectation values of observables:

$\hat{A}$ – observable diagonal in λ-basis

$$\langle \hat{A} \rangle = \sum_\lambda p_\lambda \langle \lambda | \hat{A} | \lambda \rangle = \mathrm{Tr}(\hat{\rho}\hat{A})$$

where we introduced density matrix

$$\hat{\rho} = \sum_\lambda |\lambda\rangle p_\lambda \langle \lambda| = Z^{-1} e^{-\beta(\hat{H}-\mu\hat{N})}$$

It turns out that $\langle \hat{A} \rangle = \mathrm{Tr}(\hat{\rho}\hat{A})$ for all observables $\hat{A}$ (not only diagonal in λ basis)

Grand canonical partition function for independent particles.

Imagine
$$\hat{H} = \sum_i \varepsilon_i \hat{n}_i$$
$$\hat{N} = \sum_i \hat{n}_i$$

i can be for example momentum $\vec{p}$

$$\hat{H} - \mu \hat{N} = \sum_i (\varepsilon_i - \mu)\hat{n}_i$$

$$Z = \mathrm{Tr}\left(\prod_i e^{-\beta(\varepsilon_i-\mu)\hat{n}_i}\right)$$

$$= \prod_i \mathrm{tr}\, e^{-\beta(\varepsilon_i-\mu)\hat{n}_i} = \prod_i Z_i$$

$$Z_i = \begin{cases} 1 + e^{-\beta(\varepsilon_i-\mu)} & \leftarrow \text{fermions} \\ 1 + e^{-\beta(\varepsilon_i-\mu)} + e^{-2\beta(\varepsilon_i-\mu)} + \dots = \dfrac{1}{1-e^{-\beta(\varepsilon_i-\mu)}} & \leftarrow \text{bosons} \end{cases}$$

as a result

$$\boxed{\Omega = -\beta^{-1}\log Z = \mp \beta^{-1}\sum_i \log\left(1 \pm e^{-\beta(\varepsilon_i-\mu)}\right)}$$

where upper sign $\to$ fermions
lower sign $\to$ bosons

$$N = -\frac{\partial\Omega}{\partial\mu} = \pm\beta^{-1}\sum_i \frac{\pm\beta\, e^{-\beta(\varepsilon_i-\mu)}}{1 \pm e^{-\beta(\varepsilon_i-\mu)}}$$

$$= \sum_i \frac{1}{e^{\beta(\varepsilon_i-\mu)} \pm 1}$$

we got <u>FD and BE distributions</u>