An Invitation to Quantum Statistical Mechanics

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Quantum Many Particle Systems

$\Omega \subset \mathbb{R}^d$ (for us $d=3$ $\Omega = \mathbb{R}^3 / [-\frac{L}{2}, \frac{L}{2}]^3$)

N particles in Ω

- wave function $\Psi_N \in L^2(\Omega^N, dx_1 \dots dx_N) \simeq L^2(\Omega)^{\otimes N}$, $\|\Psi_N\| = 1$
- $\mathcal{A}$ represented by s.a. operator A on $L^2(\Omega^N)$

$$P(\mathcal{A} \in I : \Psi_N) = \langle \Psi_N, E_A(I) \Psi_N \rangle_{L^2(\Omega^N)} \quad \forall I \subset \mathbb{R}$$

· evolution

$$\begin{cases} i\hbar\,\partial_t \Psi_N(x_1,\dots,x_N;t) = H_N \Psi_N(x_1\dots x_N;t) \\ \Psi_N(x_1\dots x_N;0) = \Psi_{N,0}(x_1\dots x_N) \end{cases}$$

↳ Typically

$$H_N = \underbrace{\sum_{j=1}^{N} h_j}_{\text{one-particle}} + \underbrace{\sum_{i<j} V_{ij}(x_i - x_j)}_{\text{two-particle}}$$

ex: $h_j = -\Delta_{x_j} + V_{ext}(x_j)$

Indistinguishable Particles

We can't distinguish identical particles!

All observables are invariant under permutation:

$\pi \in S_N$ we define the unitary operator $U_\pi : L^2(\Omega^N) \to L^2(\Omega^N)$

$$\left(U_\pi \Psi_N\right)(x_1 .. x_N) = \Psi_N\left(x_{\pi(1)}, .., x_{\pi(N)}\right)$$

$$\Rightarrow [A, U_\pi] = 0 \quad \forall \pi \in S_N$$

$$\hookrightarrow U_\pi^* A U_\pi = A$$

$[A, B] = AB - BA$ commutator of A and B

In particular $[H_N, U_\pi] = 0 \;\forall \pi \in S_N$

$$h_j = \mathbb{1} \otimes \dots \otimes \underbrace{\mathbb{1} \otimes h}_{\text{position } j} \otimes \mathbb{1} \otimes \dots \otimes \mathbb{1} \quad \text{and} \quad V_{ij}(x_i - x_j) = V(x_i - x_j)$$

Assume $[A, U_\pi] = 0 \;\forall \pi$

$$\langle U_\pi \underline{\Psi}_N, A\, U_\pi \underline{\Psi}_N \rangle = \langle \underline{\Psi}_N, \underbrace{U_\pi^* A\, U_\pi}_{A} \underline{\Psi}_N \rangle = \langle \underline{\Psi}_N, A\, \underline{\Psi}_N \rangle$$

and $\| U_\pi \underline{\Psi}_N \| = 1$

$\Rightarrow \underline{\Psi}_N$ and $U_\pi \underline{\Psi}$ are the same state $\forall \pi \in S_N$

$$U_\pi \underline{\Psi}_N = e^{i\alpha_\pi} \underline{\Psi}_N \qquad \forall \pi \in S_N$$

so that $|\underline{\Psi}_N|^2 = |U_\pi \underline{\Psi}_N|^2$

1 $\; U_\pi \underline{\Psi}_N = \underline{\Psi}_N \quad \forall \pi \in S_N \rightsquigarrow \underline{\Psi}_N$ bosonic wave function

$L^2_s(\Omega^N) = \{ \underline{\Psi}_N \in L^2(\Omega^N) : 1 \text{ holds} \}$

2 $\; U_\pi \underline{\Psi}_N = \underbrace{\delta_\pi}_{=\pm 1} \underline{\Psi}_N$ where δ_π is the sign of π

$\rightsquigarrow \underline{\Psi}_N$ fermionic wave function

$L^2_a(\Omega^N) = \{ \underline{\Psi}_N \in L^2(\Omega^N) : 2 \text{ holds} \}$

Examples

Let $\varphi \in L^2(\Omega)$

$\Rightarrow \varphi^{\otimes N} \in L^2_s(\Omega^N)$

$\hookrightarrow \varphi^{\otimes N}(x_1 \dots x_N) = \prod_{j=1}^{N} \varphi(x_j)$

rmk $\{\varphi_j\}$ is onb of $L^2(\Omega)$

Then

$\{P_N^S(\varphi_{j_1} \otimes \dots \otimes \varphi_{j_N})\}$

onb of $L^2_s(\Omega^N)$

In general if we have $\{\varphi_j\} \subset L^2(\Omega)$

$$P_N^S(\varphi_1 \otimes \dots \otimes \varphi_N) := \frac{1}{\sqrt{N!\, \ell_1! \dots \ell_k!}} \sum_{\pi \in S_N} \varphi_{j_1}(x_{\pi(1)}) \dots \varphi_{j_N}(x_{\pi(N)})$$

if $\{j_1 \dots j_N\}$ contains k indices with multiplicity $\ell_1 \dots \ell_k$ respectively

$(\ell_1 + \dots + \ell_k = N)$

$$P_N^A(\varphi_{j_1} \otimes \cdots \otimes \varphi_{j_N}) = \frac{1}{\sqrt{N!}} \sum_{\pi \in S_N} \delta_\pi \, \varphi_{j_1}(x_{\pi(1)}) \cdots \varphi_{j_N}(x_{\pi(N)})$$

⚠ $P_N^A(\varphi_{j_1} \otimes \cdots \otimes \varphi_{j_N}) = 0$ unless $\{\varphi_j\}$ are linearly independent

(in particular $= 0$ when $\varphi_{j_i} = \varphi_{j_k}$ for $j_i \neq j_k$ $\rightsquigarrow$ Pauli Principle)

$$P_N^A(\varphi_{j_1} \otimes \cdots \otimes \varphi_{j_N}) = \frac{1}{\sqrt{N!}} \det \begin{vmatrix} \varphi_{j_1}(x_1) & \cdots & \varphi_{j_N}(x_1) \\ \vdots & & \vdots \\ \varphi_{j_1}(x_N) & & \varphi_{j_N}(x_N) \end{vmatrix}$$

Slater determinant

<u>rmk</u> $\{\varphi_j\}$ onb of $L^2(\Omega)$

$$\Rightarrow \left\{ P_N^A(\varphi_{j_1} \otimes \cdots \otimes \varphi_{j_N}) \right\} \text{ onb of } L^2_a(\Omega^N)$$

Pure and Mixed States

$\Psi_N \in L^2(\Omega^N)$, $\|\Psi_N\| = 1$

We can define $\gamma_N = |\Psi_N \rangle\langle \Psi_N|$

↳ bra-ket notation

$$\gamma_N f_N = \langle \Psi_N, f_N \rangle \Psi_N$$

$$\Rightarrow \langle \Psi_N, A \Psi_N \rangle = \mathrm{Tr}(A\gamma_N)$$

↳ $\mathrm{Tr}(A\gamma_N) = \sum_k \langle \Phi_{N,k}, A\gamma_N \Phi_{N,k} \rangle$ $\quad \{\Phi_{N,k}\}$ onb

$$= \sum_k \langle \Phi_{N,k}, A\Psi_N \rangle \langle \Psi_N, \Phi_{N,k} \rangle$$

$$= \langle \underbrace{\sum_k \langle \Psi_N, \Phi_{N,k} \rangle \Phi_{N,k}}_{\Psi_N}, A\Psi_N \rangle = \langle \Psi_N, A\Psi_N \rangle$$

$\Rightarrow$ All information on Ψ_N are encoded in γ_N

We can generalise γ_N to consider

$$(*) \quad \gamma_N = \sum_j \lambda_j |\Psi_{N,j} \rangle\langle \Psi_{N,j}| , \quad 0 \le \lambda_j \le 1 , \quad \sum_j \lambda_j = 1$$

$\hookrightarrow$ prob to find the system in the state $\Psi_{N,j}$

γ_N of the form $(*)$ is a mixed state $\leadsto$ Trace class operator γ_N non-negative and s.t. $\mathrm{Tr}\, \gamma_N = 1$

$\gamma_N = |\Psi_N \rangle\langle \Psi_N|$ is a pure state

γ_N is called density matrix

<u>rmk</u> bosonic/fermionic density matrix analogous def on $L^2_s(\Omega^N) / L^2_a(\Omega^N)$

- Expectation of the observable A on the state γ_N is

$\mathrm{Tr}(A\gamma_N)$

- evolution :

$$\begin{cases} i\hbar\,\partial_t \gamma_N(t) = [H, \gamma_N(t)] \\ \gamma_N(0) = \gamma_N \end{cases}$$

Von Neumann equation

⚠ Differs from the Heisenberg eq by a minus sign

$\Psi_N, \Phi_N \in L^2(\Omega^N)$ normalized

we can consider $\dfrac{\Psi_N + \Phi_N}{\sqrt{2}} \longleftrightarrow \gamma_{N,\text{pure}} = \dfrac{1}{2}\Big[|\Psi_N \rangle\langle \Psi_N| + |\Phi_N\rangle\langle\Phi_N| + |\Psi_N\rangle\langle\Phi_N|$
$+ |\Phi_N\rangle\langle\Psi_N| \Big]$

or $\gamma_{N,\text{mixed}} = \dfrac{|\Psi_N\rangle\langle\Psi_N|}{2} + \dfrac{|\Phi_N\rangle\langle\Phi_N|}{2}$

$\mathrm{Tr}(A\gamma_{N,\text{pure}}) = \dfrac{1}{2}\Big[\langle \Psi_N A \Psi_N\rangle + \langle\Phi_N, A\Phi_N\rangle + \langle\Psi_N, A\Phi_N\rangle + \langle\Phi_N, A\Psi_N\rangle \Big]$

$\hookrightarrow$ produce interference

$\mathrm{Tr}(A\gamma_{N,\text{mixed}}) = \dfrac{1}{2}\Big[\langle\Psi_N, A\Psi_N\rangle + \langle\Phi_N, A\Phi_N\rangle \Big]$

Reduced density Matrices

γ_N bosonic / fermionic density matrix

We define the operator $\gamma_N^{(k)}$ on the k-particle space with integral kernel

$$\gamma_N^{(k)}(x_1 .. x_k ; y_1 .. y_k) = \frac{N!}{(N-k)!} \int_{\Omega^{N-k}} dz_{k+1} .. dz_N \; \gamma_N(x_1 .. x_k \, z_{k+1} .. z_N ; y_1 .. y_k \, z_{k+1} .. z_N)$$

$\hookrightarrow \gamma_N(\vec{x}_N ; \vec{y}_N)$ integral kernel of γ_N

$\gamma_N^{(k)}$ is the k-particle reduced density

$\gamma_N^{(k)}$ contains less information than γ_N

BUT if we have a permutation symmetric k-particle operator

$$\mathcal{O} = \frac{1}{(N-k)!} \sum_{\pi \in S_N} \mathcal{O}^{(k)}_{\pi(1) \,..\, \pi(k)}$$

↳ acts non-trivially on particles $\pi(1) \,..\, \pi(k)$

[ex $(-\Delta)$ one particle operator $\mathcal{O} = \sum_{j=1}^{N} (-\Delta_{x_j})$]

$$\mathrm{Tr}(\mathcal{O}\gamma_N) = \frac{1}{(N-k)!} \sum_{\pi} \mathrm{Tr}\left(\mathcal{O}^{(k)}_{\pi(1) \,..\, \pi(k)} \gamma_N\right)$$

$$= \frac{1}{(N-k)!} \sum_{\pi} \mathrm{Tr}\left(\mathcal{O}^{(k)}_{1 \,..\, k} \gamma_N\right) = \cancel{\frac{N!}{(N-k)!}} \mathrm{Tr}_{1 \,..\, k}\Big(\mathcal{O}^{(k)}_{1 \,..\, k} \underbrace{\mathrm{Tr}_{k+1 \,..\, N} \gamma_N}_{\cancel{\frac{(N-k)!}{N!}} \gamma_N^{(k)}}\Big)$$

$$= \mathrm{Tr}\left(\mathcal{O}^{(k)} \gamma_N^{(k)}\right)$$

In particular

$$H_N = H_1 + H_2 = \sum_{j=1}^{N} \left(-\Delta_{x_j} + V_{ext}(x_j) \right) + \frac{1}{2} \sum_{i \neq j} V(x_i - x_j)$$

$$\mathrm{Tr}(H_N \gamma_N) = \mathrm{Tr}\left[(-\Delta + V_{ext}) \gamma_N^{(1)} \right] + \mathrm{Tr}\left(\frac{1}{2} V \gamma_N^{(2)} \right)$$

We would like to find

$$\inf \mathrm{Tr}(H_N \gamma_N) \rightsquigarrow \inf \left[\mathrm{Tr}(h \gamma_N^{(1)}) + \mathrm{Tr}\left(\frac{1}{2} V \gamma_N^{(2)} \right) \right]$$

seems simpler ...

<u>Problem</u> : We can't characterise all $\gamma^{(2)}$ which are two particle reduced density matrix of some γ_N (N-representability problem)

<u>rmk</u> Necessary and sufficient conditions are known for $\gamma^{(1)}$