

Second Quantization and a little bit of Green's function

2021-05-02

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2 Second Quantization

2.1 Fermionic N particle wavefunction

In this part, we talk about fermionic N particle wavefunction, which is mostly a review of things that we already know.

- Single particle wavefunction $\psi(\vec{x}), \vec{x} \in \mathbb{R}^3, \psi \in \mathcal{H}, \mathcal{H}$ is a Hilbert space.
- How to describe the N particle wavefunction $\psi(\vec{x}_1, \dots, \vec{x}_n)$? What's the space?
 - Could it be $\mathcal{H}^{\otimes N} = \mathcal{H} \otimes \dots \otimes \mathcal{H}$?
 - For fermions, we have anti-symmetry:

$$\psi(\dots, \vec{x}_i = \vec{a}, \dots, \vec{x}_j = \vec{b}, \dots) = -\psi(\dots, \vec{x}_i = \vec{b}, \dots, \vec{x}_j = \vec{a}, \dots) \quad (13)$$

- Assume that $\{\phi_n(x)\}_{n=1}^{\infty}$ is a complete orthogonal basis of \mathcal{H} , then we have the following expansion:

$$\psi(\vec{x}_1, \dots, \vec{x}_n) = \sum_{1 \leq n_1, \dots, n_N < \infty} c_{n_1, \dots, n_N} \phi_{n_1}(\vec{x}_1) \phi_{n_2}(\vec{x}_2) \cdots \phi_{n_N}(\vec{x}_N) \quad (14)$$

- In order to preserve the anti-symmetry:

- if $P(n_1, \dots, n_N) = (m_1, \dots, m_N)$ is a permutation in S_N , then $c_{n_1, \dots, n_N} = (-1)^P c_{m_1, \dots, m_N}$.
- if $n_i = n_j$, then $c_{n_1, \dots, n_N} = 0$.

- We introduce the Slater determinant:

$$\Phi_{n_1 n_2 \dots n_N}(\vec{x}_1, \dots, \vec{x}_n) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_{n_1}(\vec{x}_1) & \phi_{n_1}(\vec{x}_2) & \dots & \phi_{n_1}(\vec{x}_N) \\ \phi_{n_2}(\vec{x}_1) & \phi_{n_2}(\vec{x}_2) & \dots & \phi_{n_2}(\vec{x}_N) \\ \dots & \dots & \dots & \dots \\ \phi_{n_N}(\vec{x}_1) & \phi_{n_N}(\vec{x}_2) & \dots & \phi_{n_N}(\vec{x}_N) \end{vmatrix} \quad (15)$$

- All the Slater Determinant forms a complete orthogonal basis of the space of fermionic N particle wavefunction:

$$\psi(\vec{x}_1, \dots, \vec{x}_n) = \sum_{1 \leq n_1 < \dots < n_N < \infty} c_{n_1, \dots, n_N} \Phi_{n_1 n_2 \dots n_N}(\vec{x}_1, \dots, \vec{x}_N)$$

- Now we discuss the mathematical property of the Slater determinant.

Let $\Phi_{n_1 \dots n_N}, \Phi_{n'_1 \dots n'_N}$ be two Slater Determinant. Let $\phi_{n_1 \dots n_N}(\vec{x}_1, \dots, \vec{x}_n) = \phi_{n_1}(\vec{x}_1) \cdots \phi_{n_N}(\vec{x}_n)$. Then we have

$$\Phi_{n_1 \dots n_N}(\vec{x}_1, \dots, \vec{x}_n) = \frac{1}{\sqrt{N!}} \sum_{P \in S_N} (-1)^P \phi_{n_{P(1)} \dots n_{P(N)}}(\vec{x}_1, \dots, \vec{x}_n) \quad (16)$$

Under many circumstances, we will want to know

$$\langle \Phi_{n_1 \dots n_N} | \hat{O} | \Phi_{n'_1 \dots n'_N} \rangle \quad (17)$$

which is the matrix element of the operator \hat{O} . Mostly, \hat{O} is invariant under permutation, for example the one-body operator

$$\hat{O}_1 = \sum_{i=1}^N \hat{h}(\vec{x}_i) \quad (18)$$

(maybe $\hat{h}(\vec{x}) = -\frac{\hbar^2}{2m} \Delta_x + V(\vec{x})$) and the two-body operator

$$\hat{O}_2 = \frac{1}{2} \sum_{i \neq j} \hat{v}(\vec{x}_i, \vec{x}_j) \quad (19)$$

(maybe $\hat{v}(\vec{x}_i, \vec{x}_j) = \frac{1}{|\vec{x}_i - \vec{x}_j|}$). Mostly we deal with only one-body and two-body operator. Actually for operator \hat{O} that is invariant under permutation, we have (why?)

$$\langle \Phi_{n_1 \dots n_N} | \hat{O} | \Phi_{n'_1 \dots n'_N} \rangle = \sqrt{N!} \langle \phi_{n_1 \dots n_N} | \hat{O} | \phi_{n'_1 \dots n'_N} \rangle \quad (20)$$

- For one-body operator $\hat{O}_1 = \sum_{i=1}^N \hat{h}(\vec{x}_i)$:

$$\begin{aligned} \langle \Phi_{n_1 \dots n_N} | \hat{O}_1 | \Phi_{n'_1 \dots n'_N} \rangle &= \sqrt{N!} \langle \phi_{n_1 \dots n_N} | \hat{O}_1 | \phi_{n'_1 \dots n'_N} \rangle \\ &= \sum_{i=1}^N \sqrt{N!} \langle \phi_{n_1 \dots n_N} | \hat{h}(\vec{x}_i) | \phi_{n'_1 \dots n'_N} \rangle \\ &= \sum_{i=1}^N \sqrt{N!} \frac{1}{\sqrt{N!}} \sum_{P \in S_N} (-1)^P \langle \phi_{n_1 \dots n_N} | \hat{h}(\vec{x}_i) | \phi_{n'_{P(1)} \dots n'_{P(N)}} \rangle \\ &= \sum_{i=1}^N \sum_{P \in S_N} (-1)^P \langle \phi_{n_1} | \phi_{n'_{P(1)}} \rangle \langle \phi_{n_2} | \phi_{n'_{P(2)}} \rangle \cdots \langle \phi_{n_i} | \hat{h}(\vec{x}_i) | \phi_{n'_{P(i)}} \rangle \cdots \langle \phi_{n_N} | \phi_{n'_{P(N)}} \rangle \end{aligned} \quad (21)$$

* Case 1: $(n_1, \dots, n_N) = (n'_1, \dots, n'_N)$.

If $j \neq P(j)$, then $\langle \phi_{n_j} | \phi_{n'_{P(j)}} \rangle = \langle \phi_{n_j} | \phi_{n_{P(j)}} \rangle = 0$. Therefore the term is nonzero if and only if $P = I$, I is the identity permutation. Therefore we have:

$$\langle \Phi_{n_1 \dots n_N} | \hat{O}_1 | \Phi_{n_1 \dots n_N} \rangle = \sum_{i=1}^N \langle \phi_{n_i} | \hat{h}(\vec{x}) | \phi_{n_i} \rangle \quad (22)$$

* Case 2: (n_1, \dots, n_N) and (n'_1, \dots, n'_N) is only different by one index:

$$\begin{aligned} & (n'_1, \dots, n'_{l-1}, n'_l, n'_{l+1}, \dots, n'_N) \\ & = (n_1, \dots, n_{l-1}, m_l, n_{l+1}, \dots, n_N) \end{aligned}$$

Because of $m_l \neq n_l$, therefore the only term that doesn't cancel is:

$$\langle \Phi_{n_1 \dots n_N} | \hat{O}_1 | \Phi_{n'_1 \dots n'_N} \rangle = \langle \phi_{n_l} | \hat{h}(\vec{x}) | \phi_{m_l} \rangle \quad (23)$$

* Case 3: (n_1, \dots, n_N) and (n'_1, \dots, n'_N) is different by more than one index, then

$$\langle \Phi_{n_1 \dots n_N} | \hat{O}_1 | \Phi_{n'_1 \dots n'_N} \rangle = 0 \quad (24)$$

– For two-body operator $\hat{O}_2 = \frac{1}{2} \sum_{i \neq j} \hat{v}(\vec{x}_i, \vec{x}_j)$, we define two-electron integral, well known in quantum chemistry:

$$(\phi_1 \phi_2 | \phi_3 \phi_4) = \frac{1}{2} \int d\mathbf{x}_1 d\mathbf{x}_2 \phi_1^*(\mathbf{x}_1) \phi_2^*(\mathbf{x}_2) v(\mathbf{x}_1, \mathbf{x}_2) \phi_3(\mathbf{x}_2) \phi_4(\mathbf{x}_1) \quad (25)$$

then similar as one-body operator, we have:

* Case 1: $(n_1, \dots, n_N) = (n'_1, \dots, n'_N)$:

$$\langle \Phi_{n_1 \dots n_N} | \hat{O}_2 | \Phi_{n_1 \dots n_N} \rangle = \sum_{i \neq j}^N ((\phi_{n_i} \phi_{n_j} | \phi_{n_j} \phi_{n_i}) - (\phi_{n_i} \phi_{n_j} | \phi_{n_i} \phi_{n_j})) \quad (26)$$

* Case 2: (n_1, \dots, n_N) and (n'_1, \dots, n'_N) is only different by one index: $n_l \neq n'_l = m_l$

$$\langle \Phi_{n_1 \dots n_N} | \hat{O}_2 | \Phi_{n'_1 \dots n'_N} \rangle = \sum_{i=1, i \neq l}^N ((\phi_{n_i} \phi_{n_l} | \phi_{m_l} \phi_{n_i}) - (\phi_{n_i} \phi_{n_l} | \phi_{n_i} \phi_{m_l})) \quad (27)$$

* Case 3: (n_1, \dots, n_N) and (n'_1, \dots, n'_N) is different by two index: $n_l \neq n'_l = m_l, n_{l'} \neq n'_{l'} = m_{l'}$

$$\langle \Phi_{n_1 \dots n_N} | \hat{O}_2 | \Phi_{n'_1 \dots n'_N} \rangle = (\phi_{n_l} \phi_{n_{l'}} | \phi_{m_{l'}} \phi_{m_l}) - (\phi_{n_l} \phi_{n_{l'}} | \phi_{m_l} \phi_{m_{l'}}) \quad (28)$$

* Case 4: (n_1, \dots, n_N) and (n'_1, \dots, n'_N) is different by more than two index:

$$\langle \Phi_{n_1 \dots n_N} | \hat{O}_2 | \Phi_{n'_1 \dots n'_N} \rangle = 0 \quad (29)$$

2.2 Creation & annihilation operator

• We introduce a convenient notation for the Slater determinant:

$$\frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_{n_1}(\vec{x}_1) & \phi_{n_1}(\vec{x}_2) & \dots & \phi_{n_1}(\vec{x}_N) \\ \phi_{n_2}(\vec{x}_1) & \phi_{n_2}(\vec{x}_2) & \dots & \phi_{n_2}(\vec{x}_N) \\ \dots & \dots & \dots & \dots \\ \phi_{n_N}(\vec{x}_1) & \phi_{n_N}(\vec{x}_2) & \dots & \phi_{n_N}(\vec{x}_N) \end{vmatrix} \leftrightarrow |n_1 n_2 \dots n_N\rangle \quad (30)$$

• Scientifically, $|n_1 n_2 \dots n_N\rangle$ means an N -particle state, occupying the n_1 -th, \dots n_N -th orbitals. Note that for fermions, each orbital contains at most one electron, therefore the notation $|n_1 n_2 \dots n_N\rangle$ is not confusing at all. (Let's not worry about spin at the current moment.)

• Now we have an expression for wavefunctions of arbitrary particle number N . For the state that has no particle (why would we care about this?), we denote it as $|vac\rangle$ or $|0\rangle$.

- In a word, $|n_1 n_2 \cdots n_N\rangle$ means $\Phi_{n_1 \cdots n_N}$ (Slater Determinant), or more precisely:

$$\langle x_1 \cdots x_N | n_1 n_2 \cdots n_N \rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_{n_1}(\vec{x}_1) & \phi_{n_1}(\vec{x}_2) & \cdots & \phi_{n_1}(\vec{x}_N) \\ \phi_{n_2}(\vec{x}_1) & \phi_{n_2}(\vec{x}_2) & \cdots & \phi_{n_2}(\vec{x}_N) \\ \cdots & \cdots & \cdots & \cdots \\ \phi_{n_N}(\vec{x}_1) & \phi_{n_N}(\vec{x}_2) & \cdots & \phi_{n_N}(\vec{x}_N) \end{vmatrix} \quad (31)$$

- creation operator a_i^\dagger : creates an electron on i -th orbital
 - a_i^\dagger maps an N -fermion state into an $(N+1)$ -fermion state;
 - $a_i^\dagger |n_1 n_2 \cdots n_N\rangle = |n_1 n_2 \cdots n_N i\rangle$, if $i \notin \{n_1, \cdots, n_N\}$
 - $a_i^\dagger |n_1 n_2 \cdots n_N\rangle = 0$, if $i \in \{n_1, \cdots, n_N\}$
 - How to understand this? a_i^\dagger does something like this

$$\frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_{n_1}(\vec{x}_1) & \cdots & \phi_{n_1}(\vec{x}_N) \\ \cdots & \cdots & \cdots \\ \phi_{n_N}(\vec{x}_1) & \cdots & \phi_{n_N}(\vec{x}_N) \end{vmatrix} \rightarrow \frac{1}{\sqrt{(N+1)!}} \begin{vmatrix} \phi_{n_1}(\vec{x}_1) & \cdots & \phi_{n_1}(\vec{x}_N) & \phi_{n_1}(\vec{x}_{N+1}) \\ \cdots & \cdots & \cdots & \cdots \\ \phi_{n_N}(\vec{x}_1) & \cdots & \phi_{n_N}(\vec{x}_N) & \phi_{n_N}(\vec{x}_{N+1}) \\ \phi_i(\vec{x}_1) & \cdots & \phi_i(\vec{x}_N) & \phi_i(\vec{x}_{N+1}) \end{vmatrix} \quad (32)$$

- $a_i^\dagger |0\rangle = |i\rangle$
- annihilation operator a_i : annihilates an electron on i -th orbital
 - a_i maps an $(N+1)$ -fermion state into an N -fermion state;
 - $a_i |n_1 \cdots i \cdots\rangle = (-1)^r |n_1 \cdots \cancel{i} \cdots\rangle$, if $i \in \{n_1, \cdots\}$ (why $(-1)^r$?)
 - $a_i |n_1 \cdots\rangle = 0$, if $i \notin \{n_1, \cdots, n_N\}$
 - How to understand this? a_i does something like this

$$\frac{1}{\sqrt{(N+1)!}} \begin{vmatrix} \phi_{n_1}(\vec{x}_1) & \cdots & \phi_{n_1}(\vec{x}_N) & \phi_{n_1}(\vec{x}_{N+1}) \\ \cdots & \cdots & \cdots & \cdots \\ \phi_{n_N}(\vec{x}_1) & \cdots & \phi_{n_N}(\vec{x}_N) & \phi_{n_N}(\vec{x}_{N+1}) \\ \phi_i(\vec{x}_1) & \cdots & \phi_i(\vec{x}_N) & \phi_i(\vec{x}_{N+1}) \end{vmatrix} \rightarrow \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_{n_1}(\vec{x}_1) & \cdots & \phi_{n_1}(\vec{x}_N) \\ \cdots & \cdots & \cdots \\ \phi_{n_N}(\vec{x}_1) & \cdots & \phi_{n_N}(\vec{x}_N) \end{vmatrix} \quad (33)$$

- $a_i |i\rangle = |0\rangle$
- How to understand creation and annihilation operator mathematically?
 - More importantly, on what space is a_i^\dagger and a_i defined?
 - Let $\text{Ant}(H^{\otimes N})$ be the anti-symmetric part of $H^{\otimes N}$, i.e. the space of fermionic N particle wavefunction.
 - a_i^\dagger and a_i are not defined on $\text{Ant}(H^{\otimes N})$ for any specific N ; actually it's rather defined on some kind of direct sum of $\text{Ant}(H^{\otimes N})$ (for all N).
 - We define the Fock space \mathcal{F} , as

$$\mathcal{F} = \text{Ant}(H^{\otimes 0}) \oplus \text{Ant}(H^{\otimes 1}) \oplus \text{Ant}(H^{\otimes 2}) \cdots \oplus \text{Ant}(H^{\otimes N}) \oplus \cdots \quad (34)$$

- Basis of \mathcal{F} :

$$|0\rangle, |n_i\rangle_{1 \leq n_i < \infty}, |n_i n_j\rangle_{1 \leq n_i < n_j < \infty}, |n_i n_j n_k\rangle_{1 \leq n_i < n_j < n_k < \infty}, \cdots \quad (35)$$

- a_n^\dagger could be viewed as an operator on Fock space, with matrix element being

$$\begin{cases} 1 \text{ (or maybe } -1\text{) on } (|n_1 \cdots n_l\rangle \text{ row}, |n_1 \cdots n_l\rangle \text{ column}) \\ 0, \text{ otherwise} \end{cases} \quad (36)$$

- a_n could be viewed as an operator on Fock space, with matrix element being

$$\begin{cases} 1 \text{ (or maybe } -1\text{) on } (|n_1 \cdots n_l\rangle \text{ row}, |n_1 \cdots n_l n\rangle \text{ column}), \\ 0, \text{ otherwise} \end{cases} \quad (37)$$

- Anti-commutation relation: the anti-commutation relation is

$$\{a_i, a_j\} = 0, \quad \{a_i^\dagger, a_j^\dagger\} = 0, \quad \{a_i^\dagger, a_j\} = \delta_{ij} \quad (38)$$

– for $i \neq j$, why $a_i a_j + a_j a_i = 0$? Try to look at this, we have $|\cdots ij\rangle = -|\cdots ji\rangle$, then :

$$(a_i a_j + a_j a_i) |\cdots ij\rangle = a_i a_j |\cdots ij\rangle + a_j a_i |\cdots ij\rangle = a_i a_j |\cdots ij\rangle - a_j a_i |\cdots ji\rangle = |\cdots\rangle - |\cdots\rangle = 0$$

– why $a_i^\dagger a_i + a_i a_i^\dagger = 1$?

* If $|\cdots\rangle$ doesn't have the i -th orbital, then $a_i a_i^\dagger |\cdots\rangle = a_i |\cdots i\rangle = |\cdots\rangle$, while $a_i^\dagger a_i |\cdots\rangle = a_i^\dagger (a_i |\cdots\rangle) = 0$, therefore $(a_i^\dagger a_i + a_i a_i^\dagger) |\cdots\rangle = |\cdots\rangle$

* If $|\cdots\rangle$ does have the i -th orbital, similarly we have $(a_i^\dagger a_i + a_i a_i^\dagger) |\cdots\rangle = |\cdots\rangle$

– Other circumstances are similar.

• number operator $a_i^\dagger a_i$: Note that

$$a_i^\dagger a_i |n_1 \cdots n_N\rangle = \begin{cases} |n_1 \cdots n_N\rangle & \text{if } i \in \{n_1, \dots, n_N\} \\ 0 & \text{if } i \notin \{n_1, \dots, n_N\} \end{cases} \quad (39)$$

therefore the operator $a_i^\dagger a_i$ is called the number operator, which measures the number of electrons on the i -th orbital.

2.3 Operators under second quantization

Recall that for fermionic N -particle wavefunction, we have

$$|\psi\rangle = \sum_{1 \leq n_1 < n_2 < \cdots < n_N} c_{n_1 \cdots n_N} |n_1 \cdots n_N\rangle = \sum_{1 \leq n_1 < n_2 < \cdots < n_N} c_{n_1 \cdots n_N} a_{n_1}^\dagger \cdots a_{n_N}^\dagger |0\rangle$$

• Operators under second quantization

– One-body operator $\hat{O}_1 = \sum_{i=1}^N \hat{h}(\vec{x}_i)$: we'll prove that under second quantization, $\hat{O}_1 = \sum_{i=1}^N \hat{h}(\vec{x}_i)$ becomes

$$\hat{O}_1 = \sum_{n,m} h_{nm} a_n^\dagger a_m, \quad h_{nm} = \langle \phi_n | \hat{h} | \phi_m \rangle \quad (40)$$

We'll prove that the matrix element is exactly the same as what we have calculated before.

If $\hat{O}_1 = \sum_{n,m} h_{nm} a_n^\dagger a_m$, then the matrix element is

$$\langle n_1 \cdots n_N | \hat{O}_1 | n'_1 \cdots n'_N \rangle = \sum_{nm} h_{nm} \langle n_1 \cdots n_N | a_n^\dagger a_m | n'_1 \cdots n'_N \rangle \quad (41)$$

* Case 1: $(n_1, \dots, n_N) = (n'_1, \dots, n'_N)$, for $\langle n_1 \cdots n_N | a_n^\dagger a_m | n_1 \cdots n_N \rangle$, it's zero unless $m = n \in \{n_1, \dots, n_N\}$ (why?), therefore

$$\begin{aligned} \langle n_1 \cdots n_N | \hat{O}_1 | n_1 \cdots n_N \rangle &= \sum_{i=1}^N h_{n_i n_i} \langle n_1 \cdots n_N | a_{n_i}^\dagger a_{n_i} | n_1 \cdots n_N \rangle \\ &= \sum_{i=1}^N h_{n_i n_i} = \sum_{i=1}^N \langle \phi_{n_i} | \hat{h} | \phi_{n_i} \rangle \end{aligned} \quad (42)$$

which matches our previous calculation result.

* Case 2: (n_1, \dots, n_N) and (n'_1, \dots, n'_N) is only different by one index:

$$\begin{aligned} &(n'_1, \dots, n'_{l-1}, n'_l, n'_{l+1}, \dots, n'_N) \\ &= (n_1, \dots, n_{l-1}, n_l, n_{l+1}, \dots, n_N) \end{aligned}$$

Similarly we know that if and only if $n = n_l, m = n'_l$ the term is nonzero, therefore we have:

$$\begin{aligned} \langle n_1 \cdots n_N | \hat{O}_1 | n'_1 \cdots n'_N \rangle &= h_{n_l n'_l} \langle n_1 \cdots n_N | a_{n_l}^\dagger a_{n'_l} | n_1 \cdots n_N \rangle \\ &= h_{n_l n'_l} = \langle \phi_{n_l} | \hat{h} | \phi_{n'_l} \rangle \end{aligned} \quad (43)$$

which matches our previous calculation result.

* Case 3: (n_1, \dots, n_N) and (n'_1, \dots, n'_N) is different by more than one index, then all term are zero, which also matches previous calculation result.

- for two-body operator $\hat{O}_2 = \frac{1}{2} \sum_{i \neq j} \hat{v}(\vec{x}_i, \vec{x}_j)$, under second quantization it becomes

$$\hat{O}_2 = \frac{1}{2} \sum_{nm lk} (nm|lk) a_n^\dagger a_m^\dagger a_l a_k \quad (44)$$

The proof is very similar.

- Hamiltonian under second quantization: The Hamiltonian under second quantization often looks like something below:

$$H = \sum_{nm} t_{nm} a_n^\dagger a_m + \frac{1}{2} \sum_{pqrs} v_{pqrs} a_p^\dagger a_q^\dagger a_r a_s \quad (45)$$

The quadratic part is the one-body term and the quatic part is the two-body term.

- Non-interacting picture (only have one-body term):

$$H_0 = \sum_{nm} t_{nm} a_n^\dagger a_m \quad (46)$$

Here

$$t_{nm} = \langle \phi_n | \hat{T} | \phi_m \rangle = \int \phi_n^*(\vec{x}) \hat{T} \phi_m(\vec{x}), \quad \hat{T} = -\frac{\hbar^2}{2m} \Delta_{\vec{x}} + V(\vec{x})$$

- This non-interacting hamiltonian in first quantization is

$$H_0 = \sum_{n=1}^N \left(-\frac{\hbar^2}{2m} \Delta_{\vec{x}_i} + V(\vec{x}_i) \right) \quad (47)$$

- Finding N particle ground state using first quantization:

- * For one particle operator $\hat{T} = -\frac{\hbar^2}{2m} \Delta_{\vec{x}} + V(\vec{x})$, let its eigenpairs be

$$(E_1, \psi_1), \dots, (E_N, \psi_N), \dots, \quad E_1 < \dots < E_N < \dots, \quad \psi_1, \dots, \psi_N, \in \mathcal{H}$$

- * It's not difficult to prove that the N particle ground state is:

$$\Psi(\vec{x}_1, \dots, \vec{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\vec{x}_1) & \dots & \psi_1(\vec{x}_N) \\ \dots & & \dots \\ \psi_N(\vec{x}_1) & \dots & \psi_N(\vec{x}_N) \end{vmatrix} \quad (48)$$

Scientifically, we can say that in the non-interacting case, the N electrons simply occupy the N lowest energy single-particle orbitals.

- How to find N particle ground state using second quantization?

- * Solve the eigenvalue problem of matrix t : here ϵ_k is the k -th smallest eigenvalue, φ_k is the eigenvector.

$$t\varphi_k = \epsilon_k \varphi_k, \quad (49)$$

- * Construct new creation operator

$$c_k^\dagger = \sum_p a_p^\dagger \varphi_{pk} \quad (50)$$

- * Then the Hamiltonian becomes (why?)

$$H = \sum_k \epsilon_k c_k^\dagger c_k \quad (51)$$

- * and the ground state is

$$|\Psi\rangle = c_1^\dagger \dots c_N^\dagger |0\rangle \quad (52)$$

which is equivalent to the result that we get using first quantization. (why?)

2.4 Quantum field operator $\hat{\psi}(x), \hat{\psi}^\dagger(x)$

- We define $\hat{\psi}(\vec{x}), \hat{\psi}^\dagger(\vec{x})$ as

$$\hat{\psi}(\vec{x}) = \sum_n \phi_n(\vec{x}) a_n, \quad \hat{\psi}^\dagger(\vec{x}) = \sum_n \phi_n^*(\vec{x}) a_n^\dagger \quad (53)$$

which means annihilating or creating an electron at \vec{x} .

- Why do we define these operators? Recall that

$$\hat{O}_1 = \sum_{n,m} h_{nm} a_n^\dagger a_m, \quad h_{nm} = \langle \phi_n | \hat{h} | \phi_m \rangle \quad (54)$$

Therefore

$$\begin{aligned} \hat{O}_1 &= \sum_{n,m} h_{nm} a_n^\dagger a_m = \sum_{n,m} \langle \phi_n | \hat{h} | \phi_m \rangle a_n^\dagger a_m = \sum_{n,m} \int d\vec{x} \phi_n^*(\vec{x}) \hat{h}(\vec{x}) \phi_m(\vec{x}) a_n^\dagger a_m \\ &= \int d\vec{x} \left(\sum_n \phi_n^*(\vec{x}) a_n^\dagger \right) \hat{h}(\vec{x}) \left(\sum_m \phi_m(\vec{x}) a_m \right) \\ &= \int d\vec{x} \hat{\psi}^\dagger(\vec{x}) \hat{h}(\vec{x}) \hat{\psi}(\vec{x}) \end{aligned} \quad (55)$$

Similarly, \hat{O}_2 is

$$\hat{O}_2 = \int d\vec{x}_1 d\vec{x}_2 \psi^\dagger(\vec{x}_1) \psi^\dagger(\vec{x}_2) v(\vec{x}_1, \vec{x}_2) \psi(\vec{x}_2) \psi(\vec{x}_1) \quad (56)$$

Therefore

$$\hat{H} = \hat{O}_1 + \hat{O}_2 = \int d\vec{x} \hat{\psi}^\dagger(\vec{x}) \hat{h}(\vec{x}) \hat{\psi}(\vec{x}) + \int d\vec{x}_1 d\vec{x}_2 \psi^\dagger(\vec{x}_1) \psi^\dagger(\vec{x}_2) v(\vec{x}_1, \vec{x}_2) \psi(\vec{x}_2) \psi(\vec{x}_1) \quad (57)$$

- Anti-commutation rule:

$$\begin{aligned} \psi(\vec{x}) \psi(\vec{x}') + \psi(\vec{x}') \psi(\vec{x}) &= 0 \\ \psi^\dagger(\vec{x}) \psi^\dagger(\vec{x}') + \psi^\dagger(\vec{x}') \psi^\dagger(\vec{x}) &= 0 \\ \psi(\vec{x}) \psi^\dagger(\vec{x}') + \psi^\dagger(\vec{x}') \psi(\vec{x}) &= \delta(\vec{x} - \vec{x}') \end{aligned} \quad (58)$$

2.5 Heisenberg picture of quantum mechanics

- The Schrodinger picture of quantum mechanics is that

$$i\hbar \partial_t |\psi(t)\rangle = \hat{H} |\psi(t)\rangle \Rightarrow |\psi(t)\rangle = \exp(-i\hat{H}t/\hbar) |\psi_0\rangle \quad (59)$$

Therefore for the operator \hat{A} , the observable of \hat{A} satisfies the equation:

$$\langle \psi(t) | \hat{A} | \psi(t) \rangle = \langle \psi_0 | \exp(i\hat{H}t/\hbar) \hat{A} \exp(-i\hat{H}t/\hbar) | \psi_0 \rangle \quad (60)$$

- The Heisenberg picture of quantum mechanics postulates that the state vector $|\psi(t)\rangle$ doesn't change and remains to be $|\psi_0\rangle$, while the operator \hat{A} at time t are defined as

$$\hat{A}(t) = \exp(i\hat{H}t/\hbar) \hat{A} \exp(-i\hat{H}t/\hbar) \quad (61)$$

so that $\langle \psi(t) | \hat{A} | \psi(t) \rangle = \langle \psi_0 | \hat{A}(t) | \psi_0 \rangle$

- We have

$$i\hbar \partial_t \hat{A}(t) = [\hat{A}(t), \hat{H}] = \hat{A}(t) \hat{H} - \hat{H} \hat{A}(t) \quad (62)$$

- In this way, we define

$$\hat{\psi}(x, t) = \exp(i\hat{H}t/\hbar) \hat{\psi}(x) \exp(-i\hat{H}t/\hbar), \quad \hat{\psi}^\dagger(x, t) = \exp(i\hat{H}t/\hbar) \hat{\psi}^\dagger(x) \exp(-i\hat{H}t/\hbar) \quad (63)$$

with

$$\hat{H} = \hat{O}_1 + \hat{O}_2 = \int dx \hat{\psi}^\dagger(\vec{x}) \hat{h}(\vec{x}) \hat{\psi}(\vec{x}) + \int d\vec{x}_1 d\vec{x}_2 \psi^\dagger(\vec{x}_1) \psi^\dagger(\vec{x}_2) v(\vec{x}_1, \vec{x}_2) \psi(\vec{x}_2) \psi(\vec{x}_1) \quad (64)$$

- We can prove that

$$i\hbar \frac{\partial}{\partial t} \hat{\psi}(\vec{x}, t) = [\hat{\psi}(\vec{x}, t), \hat{H}] = \hat{h}(\vec{x}) \hat{\psi}(\vec{x}, t) + \int v(\vec{x}, \vec{x}_2) \hat{\psi}^\dagger(\vec{x}_2, t) \hat{\psi}(\vec{x}_2, t) \hat{\psi}(\vec{x}, t) d\vec{x}_2 \quad (65)$$

$$i\hbar \frac{\partial}{\partial t} \hat{\psi}^\dagger(\vec{x}, t) = [\hat{\psi}^\dagger(\vec{x}, t), \hat{H}] = -\hat{h}(\vec{x}) \hat{\psi}^\dagger(\vec{x}, t) + \int v(\vec{x}, \vec{x}_2) \hat{\psi}^\dagger(\vec{x}, t) \hat{\psi}^\dagger(\vec{x}_2, t) \hat{\psi}(\vec{x}_2, t) d\vec{x}_2 \quad (66)$$

The key point for the proof is that using anti-commutation rules we have

$$\begin{aligned} [\hat{\psi}(\vec{x}), \hat{\psi}^\dagger(\vec{y}) \hat{h}(\vec{y}) \hat{\psi}(\vec{y})] &= \hat{\psi}(\vec{x}) \hat{\psi}^\dagger(\vec{y}) \hat{h}(\vec{y}) \hat{\psi}(\vec{y}) - \hat{\psi}^\dagger(\vec{y}) \hat{h}(\vec{y}) \hat{\psi}(\vec{y}) \hat{\psi}(\vec{x}) \\ &= \hat{\psi}(\vec{x}) \hat{\psi}^\dagger(\vec{y}) \hat{h}(\vec{y}) \hat{\psi}(\vec{y}) + \hat{\psi}^\dagger(\vec{y}) \hat{\psi}(\vec{x}) \hat{h}(\vec{y}) \hat{\psi}(\vec{y}) \\ &= \{\hat{\psi}(\vec{x}), \hat{\psi}^\dagger(\vec{y})\} \hat{h}(\vec{y}) \hat{\psi}(\vec{y}) = \delta(\vec{x} - \vec{y}) \hat{h}(\vec{y}) \hat{\psi}(\vec{y}) \end{aligned} \quad (67)$$

therefore

$$\begin{aligned} \left[\hat{\psi}(\vec{x}, t), \int d\vec{y} \hat{\psi}^\dagger(\vec{y}) \hat{h}(\vec{y}) \hat{\psi}(\vec{y}) \right] &= \left[\exp(i\hat{H}t/\hbar) \hat{\psi}(\vec{x}) \exp(-i\hat{H}t/\hbar), \int d\vec{y} \hat{\psi}^\dagger(\vec{y}) \hat{h}(\vec{y}) \hat{\psi}(\vec{y}) \right] \\ &= \exp(i\hat{H}t/\hbar) \left(\int d\vec{y} [\hat{\psi}(\vec{x}), \hat{\psi}^\dagger(\vec{y}) \hat{h}(\vec{y}) \hat{\psi}(\vec{y})] \right) \exp(-i\hat{H}t/\hbar) \\ &= \exp(i\hat{H}t/\hbar) \left(\int d\vec{y} \delta(\vec{x} - \vec{y}) \hat{h}(\vec{y}) \hat{\psi}(\vec{y}) \right) \exp(-i\hat{H}t/\hbar) \\ &= \exp(i\hat{H}t/\hbar) \hat{h}(\vec{x}) \hat{\psi}(\vec{x}) \exp(-i\hat{H}t/\hbar) = \hat{h}(\vec{x}) \hat{\psi}(\vec{x}, t) \end{aligned} \quad (68)$$

In a similar way we can get the second term.

3 Green's function

3.1 Definition of single particle Green's function

The single particle² Green's function $G(\mathbf{r}, t; \mathbf{r}', t')$ is defined such that $i\hbar G(\mathbf{r}, t; \mathbf{r}', t')$ is the probability amplitude for the propagation of an additional electron from (\vec{r}', t') to (\vec{r}, t) , i.e. from the ground state Ψ_0^N creates a particle at (\mathbf{r}', t') (using $\hat{\psi}^\dagger(\mathbf{r}')$) and then after $(t - t')$ time (using operator $\exp(-i\hat{H}(t - t')/\hbar)$) remove it at (\mathbf{r}, t) (using $\hat{\psi}(\mathbf{r})$). Therefore, the Green's function is defined as followed at $t > t'$:

$$\begin{aligned} G^e(\mathbf{r}, t; \mathbf{r}', t') &= -\frac{i}{\hbar} \left\langle \Psi_0^N(t) \left| \hat{\psi}(\mathbf{r}) \exp\left(-\frac{i}{\hbar} \hat{H}(t - t')\right) \hat{\psi}^\dagger(\mathbf{r}') \right| \Psi_0^N(t') \right\rangle \theta(t - t') \\ &= -\frac{i}{\hbar} \left\langle \exp\left(-\frac{i}{\hbar} \hat{H}t\right) \Psi_0^N \left| \hat{\psi}(\mathbf{r}) \exp\left(-\frac{i}{\hbar} \hat{H}(t - t')\right) \hat{\psi}^\dagger(\mathbf{r}') \right| \exp\left(-\frac{i}{\hbar} \hat{H}t'\right) \Psi_0^N \right\rangle \theta(t - t') \\ &= -\frac{i}{\hbar} \left\langle \Psi_0^N \left| \exp\left(\frac{i}{\hbar} \hat{H}t\right) \hat{\psi}(\mathbf{r}) \exp\left(-\frac{i}{\hbar} \hat{H}t\right) \exp\left(\frac{i}{\hbar} \hat{H}t'\right) \hat{\psi}^\dagger(\mathbf{r}') \exp\left(-\frac{i}{\hbar} \hat{H}t'\right) \right| \Psi_0^N \right\rangle \theta(t - t') \\ &= -\frac{i}{\hbar} \left\langle \Psi_0^N \left| \hat{\psi}(\mathbf{r}, t) \hat{\psi}^\dagger(\mathbf{r}', t') \right| \Psi_0^N \right\rangle \theta(t - t') \end{aligned} \quad (69)$$

Here from the first line to the last line, we change from the Schrodinger picture to the Heisenberg picture. $\theta(t - t')$ is the Heaviside step function:

$$\theta(t - t') = \begin{cases} 1 & \text{if } t > t' \\ 0 & \text{if } t < t' \end{cases} \quad (70)$$

and $\hat{\psi}(\mathbf{r}, t), \hat{\psi}^\dagger(\mathbf{r}, t)$ is defined as

$$\hat{\psi}(\mathbf{r}, t) = \exp\left(\frac{i}{\hbar} \hat{H}t\right) \hat{\psi}(\mathbf{r}) \exp\left(-\frac{i}{\hbar} \hat{H}t\right) \quad (71)$$

$$\hat{\psi}^\dagger(\mathbf{r}, t) = \exp\left(\frac{i}{\hbar} \hat{H}t\right) \hat{\psi}^\dagger(\mathbf{r}) \exp\left(-\frac{i}{\hbar} \hat{H}t\right) \quad (72)$$

Similarly, we have

$$G^h(\mathbf{r}', t', \mathbf{r}, t) = -\frac{i}{\hbar} \left\langle \Psi_0^N \left| \hat{\psi}^\dagger(\mathbf{r}', t') \hat{\psi}(\mathbf{r}, t) \right| \Psi_0^N \right\rangle \theta(t' - t) \quad (73)$$

²Note that these are all many body objects. The Green function is *single-particle* in the sense that it only propagates one particle.

which means propagating a hole (what's a hole?) from (\mathbf{r}, t) to (\mathbf{r}', t') . As a matter of convenience, we combine the two expressions in one time-ordered Green function

$$G(\mathbf{r}, t, \mathbf{r}', t') = G^e(\mathbf{r}, t, \mathbf{r}', t') - G^h(\mathbf{r}', t', \mathbf{r}, t) = -\frac{i}{\hbar} \left\langle \Psi_0^N \left| \hat{T} \left[\hat{\psi}(\mathbf{r}, t) \hat{\psi}^\dagger(\mathbf{r}', t') \right] \right| \Psi_0^N \right\rangle \quad (74)$$

This equation describes either electron ($t > t'$) or hole ($t < t'$) propagation depending on the time ordering operator \hat{T} :

$$\hat{T}(A(t)B(t')) = \begin{cases} A(t)B(t') & \text{if } t > t' \\ -B(t')A(t) & \text{if } t < t' \end{cases} \quad (75)$$