Second Quantization and a little bit of Green's function

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Contents

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 $\psi(\vec{x}_1, \cdots, \vec{x}_n)$? What's the space?
  - Could it be $\mathcal{H}^{\otimes N} = \mathcal{H} \otimes \cdots \otimes \mathcal{H}$?
  - For fermions, we have anti-symmetry:

$$\psi\left(\cdots, \vec{x}_i = \vec{a}, \cdots, \vec{x}_j = \vec{b}, \cdots\right) = -\psi\left(\cdots, \vec{x}_i = \vec{b}, \cdots, \vec{x}_j = \vec{a}, \cdots\right) \tag{13}$$

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

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

- In order to preserve the anti-symmetry:
  - if $P(n_1,\cdots,n_N)=(m_1,\cdots,m_N)$ is a permutation in S_N, then $c_{n_1,\cdots,n_N}=(-1)^P c_{m_1,\cdots,m_N}$.
  - if $n_i=n_j$, then $c_{n_1,\cdots,n_N}=0$.

- We introduce the Slater determinant:

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

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

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

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

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

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

  Under many circumstances, we will want to know

$$\langle\Phi_{n_1\cdots n_N}|\,\hat{O}\,|\Phi_{n_1'\cdots n_N'}\rangle \tag{17}$$

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

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

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

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

  (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?)

$$\langle\Phi_{n_1\cdots n_N}|\,\hat{O}\,|\Phi_{n_1'\cdots n_N'}\rangle = \sqrt{N!}\,\langle\phi_{n_1\cdots n_N}|\,\hat{O}\,|\Phi_{n_1'\cdots n_N'}\rangle \tag{20}$$

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

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

* Case 1: $(n_1, \cdots, n_N) = (n'_1, \cdots, n'_N)$.
  If $j \neq P(j)$, then $\left\langle \phi_{n_j} \middle| \phi_{n'_{P(j)}} \right\rangle = \left\langle \phi_{n_j} \middle| \phi_{n_{P(j)}} \right\rangle = 0$. Therefore the term is nonzero if and only if $P = I$, I is the identity permutation. Therefore we have:

$$\langle \Phi_{n_1 \cdots n_N} | \hat{O}_1 | \Phi_{n_1 \cdots n_N} \rangle = \sum_{i=1}^{N} \left\langle \phi_{n_i} \middle| \hat{h}(\vec{x}) \middle| \phi_{n_i} \right\rangle \tag{22}$$

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

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

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

$$\langle \Phi_{n_1 \cdots n_N} | \hat{O}_1 \left| \Phi_{n'_1 \cdots n'_N} \right\rangle = \left\langle \phi_{n_l} \middle| \hat{h}(\vec{x}) \middle| \phi_{m_l} \right\rangle \tag{23}$$

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

$$\langle \Phi_{n_1 \cdots n_N} | \hat{O}_1 \left| \Phi_{n'_1 \cdots n'_N} \right\rangle = 0 \tag{24}$$

- 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:

$$(\phi_1 \phi_2 | \phi_3 \phi_4) = \frac{1}{2} \int \mathrm{d}x_1 \mathrm{d}x_2 \phi_1^*(x_1) \phi_2^*(x_2) v(x_1, x_2) \phi_3(x_2) \phi_4(x_1) \tag{25}$$

  then similar as one-body operator, we have:

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

$$\langle \Phi_{n_1 \cdots n_N} | \hat{O}_2 | \Phi_{n_1 \cdots n_N} \rangle = \sum_{i \neq j}^{N} \left(\left(\phi_{n_i} \phi_{n_j} \middle| \phi_{n_j} \phi_{n_i} \right) - \left(\phi_{n_i} \phi_{n_j} \middle| \phi_{n_i} \phi_{n_j} \right) \right) \tag{26}$$

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

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

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

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

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

$$\langle \Phi_{n_1 \cdots n_N} | \hat{O}_2 \left| \Phi_{n'_1 \cdots n'_N} \right\rangle = 0 \tag{29}$$

2.2 Creation & annihilation operator

- We introduce a convenient notation for the Slater determinant:

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

- Scientifically, $|n_1 n_2 \cdots n_N\rangle$ means an N-particle state, occupying the n_1-th, $\cdots$ n_N-th orbitals. Note that for fermions, each orbital contains at most one electron, therefore the notation $|n_1 n_2 \cdots n_N\rangle$ 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:

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

- 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

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

  - $a_i^\dagger \, |0\rangle = |i\rangle$

- 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

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

  - $a_i \, |i\rangle = |0\rangle$

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

$$\mathcal{F} = \mathrm{Ant}\left(H^{\otimes 0}\right) \oplus \mathrm{Ant}\left(H^{\otimes 1}\right) \oplus \mathrm{Ant}\left(H^{\otimes 2}\right) \cdots \oplus \mathrm{Ant}\left(H^{\otimes N}\right) \oplus \cdots \tag{34}$$

  - Basis of $\mathcal{F}$:

$$|0\rangle, |n_i\rangle_{1 \le n_i < \infty}, |n_i n_j\rangle_{1 \le n_i < n_j < \infty}, |n_i n_j n_k\rangle_{1 \le n_i < n_j < n_k < \infty}, \cdots \tag{35}$$

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

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

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

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

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

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

- 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 $\left(a_i^\dagger a_i + a_i a_i^\dagger\right)|\cdots\rangle = |\cdots\rangle$
  * If $|\cdots\rangle$ does have the $i-$th orbital, similarly we have $\left(a_i^\dagger a_i + a_i a_i^\dagger\right)|\cdots\rangle = |\cdots\rangle$
- Other circumstances are similar.

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

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

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

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

- 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

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

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

$$\langle n_1 \cdots n_N | \hat{O}_1 |n_1' \cdots n_N'\rangle = \sum_{nm} h_{nm} \langle n_1 \cdots n_N | a_n^\dagger a_m |n_1' \cdots n_N'\rangle \tag{41}$$

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

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

which matches our previous calculation result.
  * Case 2: $(n_1, \cdots, n_N)$ and $(n_1', \cdots, n_N')$ is only different by one index:

$$\begin{aligned} &(n_1', \cdots, n_{l-1}', n_l', n_{l+1}', \cdots, n_N') \\ =&(n_1, \cdots, n_{l-1}, m_l, n_{l+1}, \cdots, n_N) \end{aligned}$$

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

$$\begin{aligned} \langle n_1 \cdots n_N | \hat{O}_1 |n_1' \cdots n_N'\rangle &= h_{n_l n_l'} \langle n_1 \cdots n_N | a_{n_l}^\dagger a_{n_l'} |n_1 \cdots n_N\rangle \\ &= h_{n_l n_l'} = \left\langle \phi_{n_l} \middle| \hat{h} \middle| \phi_{n_l'} \right\rangle \end{aligned} \tag{43}$$

which matches our previous calculation result.
  * Case 3: $(n_1, \cdots, n_N)$ and $(n_1', \cdots, n_N')$ 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

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

  The proof is very similar.

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

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

  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):

$$H_0 = \sum_{nm} t_{nm}a_n^\dagger a_m \tag{46}$$

  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

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

  - 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

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

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

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

    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.

$$t\varphi_k = \varphi_k\epsilon_k, \tag{49}$$

    * Construct new creation operator

$$c_k^\dagger = \sum_p a_p^\dagger\varphi_{pk} \tag{50}$$

    * Then the Hamitionian becomes (why?)

$$H = \sum_k \epsilon_k c_k^\dagger c_k \tag{51}$$

    * and the ground state is

$$|\Psi\rangle = c_1^\dagger\cdots c_N^\dagger|0\rangle \tag{52}$$

    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

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

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

- Why do we define these operators? Recall that

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

  Therefore

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

  Similarly, $\hat{O}_2$ is

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

  Therefore

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

- Anti-commutation rule:

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

2.5 Heisenberg picture of quantum mechanics

- The Schrodinger picture of quantum mechanics is that

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

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

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

- 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

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

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

- We have

$$\mathrm{i}\hbar\partial_t \hat{A}(t) = \left[\hat{A}(t), \hat{H}\right] = \hat{A}(t)\hat{H} - \hat{H}\hat{A}(t) \tag{62}$$

- In this way, we define

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

  with

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

- We can prove that

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

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

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

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

therefore

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

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 particle[2] Green's function $G(\mathbf{r},t;\mathbf{r}',t')$ is defined such that $\mathrm{i}\hbar G(\mathbf{r},t;\mathbf{r}',t')$ 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 $\exp(-\mathrm{i}\hat{H}(t-t')/\hbar)$) remove it at $(\mathbf{r},t)$(using $\hat{\psi}(\mathbf{r})$). Therefore , the Green's function is defined as followed at $t>t'$:

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

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:

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

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

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

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

Similarly, we have

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

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

which means propogating 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

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

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

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