Foundations of quantum chemistry

Second quantization formalism

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Introduction

- Standard QM: time evolution preserves the norm of the state vector \( \rightarrow \) the number of particles is conserved.

- Why introduce operators that create or annihilate electrons? (QED, photons...)

- Practical reasons (many-electron developments, infinite systems, ...)}
The Fock space

\[ \mathcal{F} = \mathcal{H}_0 \oplus \mathcal{H}_1 \oplus \mathcal{H}_1^\otimes 2 \oplus \cdots \mathcal{H}_1^\otimes n \oplus \cdots \] (why \textit{sum}?)

Vacuum state: \( ^0\Phi = |\rangle \neq 0 \)

Let us choose a normalized discrete basis set \( \{\psi_1, \cdots \psi_i, \cdots\} \) in \( \mathcal{H}_1 \)

Then \( \{^n\Phi_I\} \) with \( ^n\Phi_I \equiv |(\psi_{I_1} \cdots \psi_{I_n})\rangle \) is a normalized basis of \( \mathcal{H}_1^\otimes n \)
and \( \{^0\Phi, \{^1\Phi_I\}, \{^2\Phi_I\}, \cdots \{^n\Phi_I\}, \cdots\} \) is a normalized basis of \( \mathcal{F} \)

**Occupation-number representation:** \( ^n\Phi_I = |n_1, \cdots n_i, \cdots\rangle \) with \( n = \sum_i n_i \)

**Examples:**

\( |(\psi_1 \cdots \psi_n)\rangle = |1, \cdots 1, 0, 0, \cdots\rangle \)

| \rangle = |0, \cdots 0, \cdots\rangle \) (bosons)
Annihilation operators

**Annihilation operator** of an electron in the spin-orbital $\psi_i$:

$$\hat{a}_i |n_1, \cdots n_i, \cdots \rangle = (-1)^{\nu_i} n_i |1 - n_i, \cdots \rangle$$

with

$$\nu_i = \sum_{j=1}^{i-1} n_j$$

**Examples:**

$$\hat{a}_1 |1, n_2, \cdots n_i, \cdots \rangle = |0, n_2, \cdots n_i, \cdots \rangle$$

$$\hat{a}_1 |0, n_2, \cdots n_i, \cdots \rangle = 0$$

$$\hat{a}_2 |0, 1, \cdots n_i, \cdots \rangle = |0, 0, \cdots n_i, \cdots \rangle$$

$$\hat{a}_2 |1, 1, \cdots n_i, \cdots \rangle = - |1, 0, \cdots n_i, \cdots \rangle$$

Slater determinant notation:

$$\hat{a}_i \left| (\psi_j \cdots \psi_i \cdots \psi_k) \right\rangle = (-1)^{\nu_i} \left| (\psi_j \cdots \psi_1 \cdots \psi_k) \right\rangle$$

$$\hat{a}_i \left| (\psi_j \cdots \psi_i \cdots \psi_k) \right\rangle = 0$$

position number of $\psi_i - 1$ = number of transpositions to move $\psi_i$ to the 1st position
Creation operators

**Creation operator** of an electron in the spin-orbital $\psi_i$:

$$\hat{a}^\dagger_i |n_1, \ldots n_i, \ldots\rangle = (-1)^{\nu_i} (1 - n_i) |n_1, \ldots 1 - n_i, \ldots\rangle$$

**Examples:**

$$\hat{a}^\dagger_1 |0, n_2, \ldots n_i, \ldots\rangle = |1, n_2, \ldots n_i, \ldots\rangle$$

$$\hat{a}^\dagger_1 |1, n_2, \ldots n_i, \ldots\rangle = 0$$

$$\hat{a}^\dagger_2 |0, 0, \ldots n_i, \ldots\rangle = |0, 1, \ldots n_i, \ldots\rangle$$

$$\hat{a}^\dagger_2 |1, 0, \ldots n_i, \ldots\rangle = - |1, 1, \ldots n_i, \ldots\rangle$$

$$|n_1, \ldots n_i, \ldots\rangle = (\hat{a}^\dagger_1)^{n_1} \ldots (\hat{a}^\dagger_i)^{n_i} \ldots |0, \ldots 0, \ldots\rangle$$

Slater determinant notation:  

$$\hat{a}^\dagger_i |(\psi_j \ldots \psi_i \ldots \psi_k)_\rangle = (-1)^{\nu_i} |(\psi_j \ldots \psi_i \ldots \psi_k)_\rangle$$

$$\hat{a}^\dagger_i |(\psi_j \ldots \psi_i \ldots \psi_k)_\rangle = |(\psi_i \psi_j \ldots \psi_k)_\rangle$$

$$\hat{a}^\dagger_i |(\psi_j \ldots \psi_i \ldots \psi_k)_\rangle = 0$$
\( \hat{a}_i^\dagger \) is the adjoint of \( \hat{a}_i \):

\[
\langle n'_1, \cdots n'_i, \cdots | \hat{a}_i | n_1, \cdots n_i, \cdots \rangle = \langle \hat{a}_i^\dagger (n'_1, \cdots n'_i, \cdots) | n_1, \cdots n_i, \cdots \rangle
\]

\[
(-1)^{\nu_i} n_i | n_1, \cdots 1 - n_i, \cdots \rangle
\]

\[
(-1)^{\nu'_i} (1 - n'_i) | n'_1, \cdots 1 - n'_i, \cdots \rangle
\]

\[
(-1)^{\nu_i} n_i \delta_{n'_1,n_1} \cdots \delta_{n'_i,1-n_i} \cdots = (-1)^{\nu'_i} (1 - n'_i) \delta_{n'_1,n_1} \cdots \delta_{1-n'_i,n_i} \cdots
\]

This two expressions vanish unless \( n'_1 = n_1, \cdots n'_i = 1 - n_i, \cdots \), in which case they coincide.
Exercise

Let $\Phi = |(\psi_1 \cdots \psi_i \cdots \psi_n)_\downarrow\rangle$ be the Hartree-Fock Slater determinant of an $n$-electron system and let $\Phi_i^k$ be the determinant that results upon changing in $\Phi$ the occupied spin-orbital $\psi_i$ by an empty one $\psi_k$. The spin-orbitals are assumed orthonormal.

- Write $\Phi_i^k$ in terms of $\Phi$ by applying on this the proper creation and annihilation operators.

- Use the resulting expression to show that $\langle \Phi | \Phi_i^k \rangle = 0$. 
Exercise
Let $\Phi = \left| (\psi_1 \cdots \psi_i \cdots \psi_n) \right\rangle$ be the Hartree-Fock Slater determinant of an $n$-electron system and let $\Phi_i^k$ be the determinant that results upon changing in $\Phi$ the occupied spin-orbital $\psi_i$ by an empty one $\psi_k$. The spin-orbitals are assumed orthonormal.

- Write $\Phi_i^k$ in terms of $\Phi$ by applying on this the proper creation and annihilation operators.

- Use the resulting expression to show that $\langle \Phi | \Phi_i^k \rangle = 0$.

Solution

\[ \hat{a}_k^+ \hat{a}_i \left| (\psi_1 \cdots \psi_i \cdots \psi_n) \right\rangle = \hat{a}_k^+ (-1)^{\delta_i^k} \left| \psi_1 \cdots \psi_{i-1} \psi_k \cdots \psi_n \right\rangle = (-1)^{\delta_i^k} (-1)^{\delta_i^k} \left| (\psi_1 \cdots \psi_k \cdots \psi_n) \right\rangle = \Phi_i^k \]

\[ \langle \Phi | \Phi_i^k \rangle = \langle \Phi | \hat{a}_k^+ \hat{a}_i \Phi \rangle = \langle \hat{a}_k^+ \hat{a}_i \Phi | \Phi \rangle = 0 \]

0, since $\psi_k$ is not in $\Phi$
Number operators

- **Occupation number operator** of the spin-orbital $\psi_i$: $\hat{a}_i^\dagger \hat{a}_i \equiv \hat{n}_i$

\[\hat{a}_i^\dagger \hat{a}_i |n_1, \cdots n_i, \cdots \rangle = \hat{a}_i^\dagger (-1)^{\nu_i} n_i |n_1, \cdots 1 - n_i, \cdots \rangle = (-1)^{\nu_i} n_i (-1)^{\nu_i} (1 - (1 - n_i)) |n_1, \cdots n_i, \cdots \rangle\]

\[\hat{n}_i |n_1, \cdots n_i, \cdots \rangle = n_i |n_1, \cdots n_i, \cdots \rangle\]

- **Electron number operator**: $\hat{n} = \sum_i \hat{n}_i$

\[\hat{n} |n_1, \cdots n_i, \cdots \rangle = \sum_i n_i |n_1, \cdots n_i, \cdots \rangle = n |n_1, \cdots n_i, \cdots \rangle\]

- $\hat{n}_i$ are commuting (non-orthogonal) projection operators

$\hat{n}_i$ projects onto the subspace spanned by the Slater determinants containing $\psi_i$

- $\langle n_i \rangle_{\Psi} = \langle ^n \Psi | \hat{n}_i ^n \Psi \rangle = \left\langle \sum_I C_I^n \Phi_I | \sum_J C_J^n \Phi_J \right\rangle = \sum_{IJ} C_I^* C_J \langle ^n \Phi_I | \hat{n}_i ^n \Phi_J \rangle$

\[= \sum_{I,J \ni i} C_I^* C_J \langle ^n \Phi_I | ^n \Phi_J \rangle = \sum_{I \ni i} |C_I|^2 \leq 1 \quad \text{(populations)}\]
Anticommutation rules

\[
\left[ \hat{A}, \hat{B} \right]_+ \equiv \hat{A}\hat{B} + \hat{B}\hat{A}
\]

\[
\left[ \hat{a}_i, \hat{a}^\dagger_j \right]_+ = \delta_{ij} \quad \left[ \hat{a}_i, \hat{a}_j \right]_+ = \left[ \hat{a}_i^\dagger, \hat{a}_j^\dagger \right]_+ = 0
\]

\[
\hat{a}_i\hat{a}_j = -\hat{a}_j\hat{a}_i \quad \hat{a}_i^\dagger\hat{a}_j^\dagger = -\hat{a}_j^\dagger\hat{a}_i^\dagger \quad \left( \hat{a}_i^\dagger \right)^2 = 0
\]

\[
\hat{a}_i\hat{a}_j^\dagger = \delta_{ij} - \hat{a}_j^\dagger\hat{a}_i \quad \hat{a}_i\hat{a}_j^\dagger = -\hat{a}_j^\dagger\hat{a}_i \quad \text{for } i \neq j
\]

\[
\hat{a}_i\hat{a}_i^\dagger = 1 - \hat{a}_i^\dagger\hat{a}_i
\]
Exercise

Use the occupation-number representation of the Slater determinants to show that

\[ \langle (\psi_i \psi_j)_- | (\psi_k \psi_l)_- \rangle = \delta_{ik} \delta_{jl} - \delta_{il} \delta_{jk} \]

*Hint:* Write the determinants as creation operators acting on the vacuum state; then move the creation operators from the left to the right-hand side of the scalar product and move the resulting annihilation operators to the right until they operate directly on the vacuum state.
Exercise

Use the occupation-number representation of the Slater determinants to show that

\[ \langle (\psi_i \psi_j)_- | (\psi_k \psi_l)_- \rangle = \delta_{ik} \delta_{jl} - \delta_{il} \delta_{jk} \]

Hint: Write the determinants as creation operators acting on the vacuum state; then move the creation operators from the left to the right-hand side of the scalar product and move the resulting annihilation operators to the right until they operate directly on the vacuum state.

Solution

\[
\begin{align*}
\langle (\psi_i \psi_j)_- | (\psi_k \psi_l)_- \rangle &= \langle \hat{a}_i^+ \hat{a}_j^+ | \hat{a}_k^+ \hat{a}_l^+ \rangle \\
&= \delta_{ik} \langle \hat{a}_j \hat{a}_l^+ | \hat{a}_k^+ \rangle - \delta_{il} \delta_{jk} \langle \hat{a}_j \hat{a}_l^+ | \hat{a}_k^+ \rangle \\
&= \delta_{ik} \delta_{jl} - \delta_{il} \delta_{jk} \\
&= \delta_{ik} \delta_{jl} \langle 1 \rangle - \delta_{il} \delta_{jk} \langle \hat{a}_j \hat{a}_l^+ \hat{a}_k^+ \rangle
\end{align*}
\]
Many-electron hamiltonian

- **Standard expression (non-relativistic):**
  \[ n \hat{H} = \sum_{i=1}^{n} h(i) + \sum_{i=1}^{n-1} \sum_{j=1}^{n} \frac{1}{r_{ij}} \]
  \[ \hat{h}(i) = -\frac{\nabla_i^2}{2} - \sum_{A=1}^{N} \frac{Z_A}{r_{iA}} \]

- **Second quantized expression:**
  \[ \hat{H} = \sum_{rs} h_{rs} \hat{a}_r \hat{a}_s^\dagger + \frac{1}{2} \sum_{rstu} g_{rstu} \hat{a}_r \hat{a}_s^\dagger \hat{a}_u \hat{a}_t \]
  \[ h_{rs} = \langle \psi_r | \hat{h} | \psi_s \rangle \quad g_{rstu} = \langle \psi_r \psi_s | \frac{1}{r_{ij}} | \psi_t \psi_u \rangle \]
  
  This expression is independent of \( n \).

- **Number of creation op. = number of annihil. op in fixed-particle quantum mechanics (exception for photons in spectroscopy).**
### Hartree-Fock energy

\[
\langle n \Phi_0 | \hat{H} | n \Phi_0 \rangle = \sum_{ab}^{\text{occ}} h_{ab} \langle n \Phi_0 | \hat{a}_a^\dagger \hat{a}_b | n \Phi_0 \rangle + \frac{1}{2} \sum_{abcd}^{\text{occ}} g_{abcd} \langle n \Phi_0 | \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_a \hat{a}_c | n \Phi_0 \rangle
\]

\(n\) does not appear explicitly, but it is implied in the list of occupation numbers of \(n \Phi_0 = |n_1, \cdots n_i, \cdots \rangle\): \(n = \sum_i n_i\)

Same results previously obtained with Slater-Condon rules (slide 1.107); e. g.:

\[
\sum_{rs} h_{rs} \langle \Phi | \hat{a}_r^\dagger \hat{a}_s | \Phi \rangle = \sum_{rs} h_{rs} \langle \hat{a}_r \Phi | \hat{a}_s \Phi \rangle = \sum_{ab}^{\text{occ}} h_{ab} \langle \Phi | \hat{a}_a^\dagger \hat{a}_b | \Phi \rangle = \sum_a^{\text{occ}} h_{aa}
\]

If \(a \neq b\) then \(\hat{a}_b |n \Phi \rangle\) contains \(\psi_a\) so that \(\hat{a}_a^\dagger \hat{a}_b |n \Phi \rangle = 0\)
Exercise

Use the anticommutation rules to show that a one-electron-type operator of an \( n \)-electron system, \( \hat{F} = \sum_{i=1}^{n} f(i) = \sum_{rs} f_{rs} \hat{a}_{r}^{\dagger} \hat{a}_{s} \), can be cast into the form of a two-electron-type operator:

\[
\hat{F} = \frac{1}{n-1} \sum_{rstu} f_{rt} \delta_{su} \hat{a}_{r}^{\dagger} \hat{a}_{s}^{\dagger} \hat{a}_{u} \hat{a}_{t} = \frac{1}{n-1} \sum_{rstu} \delta_{rt} f_{su} \hat{a}_{r}^{\dagger} \hat{a}_{s}^{\dagger} \hat{a}_{u} \hat{a}_{t}
\]

both being restricted to the \( n \)-electron subspace of the Fock space. \( \text{Hint:} \) use the anticommutation rules to bring \( \hat{a}_{t} \) next to \( \hat{a}_{r}^{\dagger} \) to obtain \( \sum_{rt} f_{rt} \hat{a}_{r}^{\dagger} \hat{a}_{t} = \hat{F} \); use also \( \hat{n} = \sum_{s} \hat{n}_{s} \).

Use this result to write the \( n \)-electron hamiltonian as a sum of two-electron operators:

\[
\hat{H} = \sum_{rstu} w_{rstu} \hat{a}_{r}^{\dagger} \hat{a}_{s}^{\dagger} \hat{a}_{u} \hat{a}_{t} \quad \text{with} \quad w_{rstu} = \frac{1}{n-1} h_{rt} \delta_{su} \hat{a}_{r}^{\dagger} \hat{a}_{s}^{\dagger} \hat{a}_{u} \hat{a}_{t} + \frac{1}{2} g_{rstu}
\]
Solution

\[ \hat{A} = \frac{1}{n-1} \sum_{rstn} \int_{rt} \hat{a}_r^\dagger \hat{a}_s \hat{a}_t \hat{a}_n \]

\[ = \frac{-1}{n-1} \sum_{rst} \int_{rt} \hat{a}_r^\dagger \hat{a}_t \hat{a}_s \hat{a}_n - \frac{\hat{a}_t}{\hat{\sigma}_{st} - \hat{a}_t \hat{a}_s} \]

\[ = \frac{-1}{n-1} \left( \sum_{rs} \int_{rs} \hat{a}_r^\dagger \hat{a}_s - \sum_{rst} \int_{rt} \hat{a}_r^\dagger \hat{a}_t \hat{a}_s \hat{a}_n \right) \]

\[ \hat{F} \]

\[ = \frac{-1}{n-1} \left( \hat{F} (1 - \hat{n}) \right) = \hat{F} \frac{\hat{n} - 1}{n - 1} \]

The subspace of states n-electron (of the space of Fock) is proper of \( \hat{n} \) with eigenvalue \( \hat{n} \); thus, the operator \( \hat{A} \) restricted to this subspace is:

\[ \hat{A} = \hat{F} \frac{n-1}{n-1} = \hat{F} \]
Particles and holes

- Creation and annihilation operators are sometimes referred to a *Fermi vacuum* or *Fermi sea*.

- Independent particle states are identified by specifying their occupation number differences with respect to that state (holes created in the Fermi sea and particles created above it).

- *Exciton*: a neutral pair formed by a hole (a quasi-particle with charge $e$) and an electron ($-e$).

- This language is common in solid-state theory, and it is also sometimes used for finite systems (CI, CC, ...).