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

$$\mathcal{F} = \mathcal{H}_0 \oplus \mathcal{H}_1 \oplus \mathcal{H}_1^{\otimes^a 2} \oplus \cdots \mathcal{H}_1^{\otimes^a n} \oplus \cdots$$ (why *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 $^n\Phi_I \equiv \left|(\psi_{1_I} \cdots \psi_{n_I})_-\right\rangle$ is a normalized basis of $\mathcal{H}_1^{\otimes^a n}$

and $\left\{^0\Phi, \left\{^1\Phi_I\right\}, \left\{^2\Phi_I\right\} \cdots \left\{^n\Phi_I\right\} \cdots\right\}$ is a normalized basis of $\mathcal{F}$

Occupation-number representation: $^n\Phi_I = |n_1, \cdots n_i, \cdots\rangle$ with $n = \sum_i n_{i_I}$

Examples:

$$\left|(\psi_1 \cdots \psi_n)_-\right\rangle = |\underbrace{1, \cdots 1}_{n}, 0, 0, \cdots\rangle \qquad |\rangle = |0, \cdots 0, \cdots\rangle$$

(bosons)

Annihilation operators

- *Annihilation operator* of an electron in the spin-orbital ψ_i:

$$\hat{a}_i \left| n_1, \cdots n_i, \cdots \right\rangle = (-1)^{\nu_i} n_i \left| n_1, \cdots 1 - n_i, \cdots \right\rangle \qquad \text{with} \qquad \nu_i = \sum_{j=1}^{i-1} n_j$$

Examples:

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

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

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

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

Slater determinant notation:

position number of ψ_i – 1 = number of transpositions to move ψ_i to the 1st position

$$\hat{a}_i \left| (\psi_j \cdots \psi_i \cdots \psi_k)_- \right\rangle = (-1)^{\nu_i} \left| (\psi_j \cdots \not{\psi_i} \cdots \psi_k)_- \right\rangle$$

$$\hat{a}_i \left| (\psi_j \cdots \not{\psi_i} \cdots \psi_k)_- \right\rangle = 0$$

Creation operators

- *Creation operator* of an electron in the spin-orbital ψ_i:

$$\widehat{a}_i^{\dagger} \left| n_1, \cdots n_i, \cdots \right\rangle = (-1)^{\nu_i} (1 - n_i) \left| n_1, \cdots 1 - n_i, \cdots \right\rangle$$

Examples:

$$\widehat{a}_1^{\dagger} \left| 0, n_2, \cdots n_i, \cdots \right\rangle = \left| 1, n_2, \cdots n_i, \cdots \right\rangle$$

$$\widehat{a}_1^{\dagger} \left| 1, n_2, \cdots n_i, \cdots \right\rangle = 0$$

$$\widehat{a}_2^{\dagger} \left| 0, 0, \cdots n_i, \cdots \right\rangle = \left| 0, 1, \cdots n_i, \cdots \right\rangle$$

$$\widehat{a}_2^{\dagger} \left| 1, 0, \cdots n_i, \cdots \right\rangle = - \left| 1, 1, \cdots n_i, \cdots \right\rangle$$

$$\left| n_1, \cdots n_i, \cdots \right\rangle = \left(\widehat{a}_1^{\dagger} \right)^{n_1} \cdots \left(\widehat{a}_i^{\dagger} \right)^{n_i} \cdots \left| 0, \cdots 0, \cdots \right\rangle$$

Slater determinant notation: $\widehat{a}_i^{\dagger} \left| (\psi_j \cdots \not{\psi_i} \cdots \psi_k)_- \right\rangle = (-1)^{\nu_i} \left| (\psi_j \cdots \psi_i \cdots \psi_k)_- \right\rangle$

$$\widehat{a}_i^{\dagger} \left| (\psi_j \cdots \not{\psi_i} \cdots \psi_k)_- \right\rangle = \left| (\psi_i \psi_j \cdots \psi_k)_- \right\rangle$$

$$\widehat{a}_i^{\dagger} \left| (\psi_j \cdots \psi_i \cdots \psi_k)_- \right\rangle = 0$$

Adjointness relationship

$\widehat{a_i}^\dagger$ is the adjoint of $\widehat{a_i}$:

$$\langle n_1', \cdots n_i', \cdots | \widehat{a_i} | n_1, \cdots n_i, \cdots \rangle = \left\langle \widehat{a_i}^\dagger (n_1', \cdots n_i', \cdots) \right| n_1, \cdots n_i, \cdots \right\rangle$$

$$(-1)^{\nu_i} n_i \, |n_1, \cdots 1 - n_i, \cdots\rangle \qquad\qquad (-1)^{\nu_i'} (1 - n_i') \, |n_1', \cdots 1 - n_i', \cdots\rangle$$

$$(-1)^{\nu_i} n_i \delta_{n_1',n_1} \cdots \delta_{n_i',1-n_i} \cdots = (-1)^{\nu_i'} (1 - n_i') \delta_{n_1',n_1} \cdots \delta_{1-n_i',n_i} \cdots$$

This two expressions vanish unless $n_1' = n_1, \cdots n_i' = 1 - n_i \cdots$, in which case they coincide.

Exercise

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

- Write Φ_i^k in terms of Φ by applying on this the proper creation and annihilation operators.
- Use the resulting expression to show that $\left\langle \Phi \middle| \Phi_i^k \right\rangle = 0$.

Exercise

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Solution

$$\hat{a}_k^+ \hat{a}_i \left|(\psi_1 \cdots \psi_i \cdots \psi_n)_-\right\rangle = \hat{a}_k^+ (-1)^{\nu_i} \left|(\psi_1 \cdots \not{\psi_i} \cdots \psi_n)_-\right\rangle =$$

$$= (-1)^{\nu_i}(-1)^{\nu_i} \left|(\psi_1 \cdots \psi_k \cdots \psi_n)_-\right\rangle = \left|(\psi_1 \cdots \psi_k \cdots \psi_n)_-\right\rangle = \Phi_i^k$$

↑ i-th position

$$\left\langle \Phi \middle| \Phi_i^k \right\rangle = \left\langle \Phi \middle| \hat{a}_k^+ \hat{a}_i \Phi \right\rangle = \left\langle \underbrace{\hat{a}_k \Phi}_{} \middle| \hat{a}_i \Phi \right\rangle = 0$$

0, since ψ_k is not in Φ

Number operators

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

$$\widehat{a}_i{}^\dagger \widehat{a}_i \left|n_1, \cdots n_i, \cdots\right\rangle = \widehat{a}_i{}^\dagger (-1)^{\nu_i} n_i \left|n_1, \cdots 1-n_i, \cdots\right\rangle = (-1)^{\nu_i} n_i (-1)^{\nu_i} (1-(1-n_i)) \left|n_1, \cdots n_i, \cdots\right\rangle$$

$$\widehat{n}_i \left|n_1, \cdots n_i, \cdots\right\rangle = n_i \left|n_1, \cdots n_i, \cdots\right\rangle$$

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

$$\widehat{n} \left|n_1, \cdots n_i, \cdots\right\rangle = \sum_i n_i \left|n_1, \cdots n_i, \cdots\right\rangle = n \left|n_1, \cdots n_i, \cdots\right\rangle$$

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

  $\widehat{n}_i$ projects onto the subspace spanned by the Slater determinants containing ψ_i

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

$$= \sum_{I,J \ni i} C_I^* C_J \langle {}^n\Phi_I | {}^n\Phi_J \rangle = \sum_{I \ni i} |C_I|^2 \leq 1 \qquad \textit{(populations)}$$

Anticommutation rules

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

$$\left[\widehat{a}_i,\widehat{a}_j{}^\dagger\right]_+ = \delta_{ij} \qquad \left[\widehat{a}_i,\widehat{a}_j\right]_+ = \left[\widehat{a}_i{}^\dagger,\widehat{a}_j{}^\dagger\right]_+ = 0$$

$$\widehat{a}_i\widehat{a}_j = -\widehat{a}_j\widehat{a}_i \qquad \widehat{a}_i{}^\dagger\widehat{a}_j{}^\dagger = -\widehat{a}_j{}^\dagger\widehat{a}_i{}^\dagger \quad \longrightarrow \quad \left(\widehat{a}_i{}^\dagger\right)^2 = 0$$

$$\widehat{a}_i\widehat{a}_j{}^\dagger = \delta_{ij} - \widehat{a}_j{}^\dagger\widehat{a}_i$$

$$\widehat{a}_i\widehat{a}_j{}^\dagger = -\widehat{a}_j{}^\dagger\widehat{a}_i \qquad \text{for } i \neq j$$

$$\widehat{a}_i\widehat{a}_i{}^\dagger = 1 - \widehat{a}_i{}^\dagger\widehat{a}_i$$

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

$$\langle (\psi_i\psi_j)_- | (\psi_k\psi_l)_- \rangle = \langle \hat{a}_i^+ \hat{a}_j^+ |\rangle | \hat{a}_k^+ \hat{a}_l^+ |\rangle\rangle =$$

$$= \langle | \hat{a}_j \hat{a}_i \hat{a}_k^+ \hat{a}_l^+ | \rangle = \delta_{ik} \langle | \hat{a}_j \hat{a}_l^+ | \rangle - \langle | \hat{a}_j \hat{a}_k^+ \hat{a}_i \hat{a}_l^+ | \rangle =$$

$\hat{a}_i \hat{a}_k^+ = \delta_{ik} - \hat{a}_k^+ \hat{a}_i$

$\hat{a}_j \hat{a}_l^+ |\rangle = \delta_{jl} - \hat{a}_l^+ \underbrace{\hat{a}_j |\rangle}_{0}$

$\hat{a}_i \hat{a}_l^+ |\rangle = (\delta_{il} - \hat{a}_l^+ \hat{a}_i)|\rangle$, with $\underbrace{\hat{a}_i |\rangle}_{0}$

$$= \delta_{ik}\delta_{jl} \underbrace{\langle | \rangle}_{1} - \delta_{il} \langle | \hat{a}_j \hat{a}_k^+ | \rangle = \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}$$

$\hat{a}_j \hat{a}_k^+ |\rangle = \delta_{jk} - \hat{a}_k^+ \underbrace{\hat{a}_j |\rangle}_{0}$

$\delta_{ik}\delta_{jl}$ and $\delta_{il}\delta_{jk}$: incompatible events

Many-electron hamiltonian

- Standard expression (non-relativistic):

$$ {}^{n}\widehat{H} = \sum_{i=1}^{n} h(i) + \sum_{i=1}^{n-1} \sum_{j=1}^{n} \frac{1}{r_{ij}} \qquad \widehat{h}(i) = -\frac{\nabla_i^2}{2} - \sum_{A=1}^{N} \frac{Z_A}{r_{iA}} $$

- Second quantized expression:

$$ \widehat{H} = \sum_{rs} h_{rs} \widehat{a_r}^{\dagger} \widehat{a_s} + \frac{1}{2} \sum_{rstu} g_{rstu} \widehat{a_r}^{\dagger} \widehat{a_s}^{\dagger} \widehat{a_u} \widehat{a_t} $$

$$ h_{rs} = \left\langle \psi_r \middle| \widehat{h}\, \psi_s \right\rangle \qquad g_{rstu} = \left\langle \psi_r \psi_s \middle| \frac{1}{r_{ij}}\, \psi_t \psi_u \right\rangle $$

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

$$\left\langle {}^{n}\Phi_0 \left| \widehat{H} \right| {}^{n}\Phi_0 \right\rangle = \sum_{ab}^{occ} h_{ab} \left\langle {}^{n}\Phi_0 \left| \widehat{a_a}^{\dagger} \widehat{a_b} \right| {}^{n}\Phi_0 \right\rangle + \frac{1}{2} \sum_{abcd}^{occ} g_{abcd} \left\langle {}^{n}\Phi_0 \left| \widehat{a_a}^{\dagger} \widehat{a_b}^{\dagger} \widehat{a_d} \widehat{a_c} \right| {}^{n}\Phi_0 \right\rangle$$

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.:

$$\sum_{rs} h_{rs} \left\langle \Phi \left| \widehat{a_r}^{\dagger} \widehat{a_s} \right| \Phi \right\rangle = \sum_{rs} h_{rs} \langle \widehat{a_r} \Phi | \widehat{a_s}\ \Phi \rangle = \sum_{ab}^{occ} h_{ab} \left\langle \Phi \left| \widehat{a_a}^{\dagger} \widehat{a_b} \right| \Phi \right\rangle = \sum_{a}^{occ} h_{aa}$$

If $a \neq b$ then $\widehat{a_b} |{}^{n}\Phi\rangle$ contains ψ_a so that $\widehat{a_a}^{\dagger} \widehat{a_b} |{}^{n}\Phi\rangle = 0$

Exercise

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

$$\widehat{F} = \frac{1}{n-1}\sum_{rstu} f_{rt}\delta_{su}\widehat{a_r}^{\dagger}\widehat{a_s}^{\dagger}\widehat{a_u}\widehat{a_t} = \frac{1}{n-1}\sum_{rstu} \delta_{rt}f_{su}\widehat{a_r}^{\dagger}\widehat{a_s}^{\dagger}\widehat{a_u}\widehat{a_t}$$

both being restricted to the n-electron subspace of the Fock space. *Hint*: use the anticommutation rules to bring $\widehat{a_t}$ next to $\widehat{a_r}^{\dagger}$ to obtain $\sum_{rt} f_{rt}\widehat{a_r}^{\dagger}\widehat{a_t} = \widehat{F}$; use also $\widehat{n} = \sum_s \widehat{n_s}$.

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

$$\widehat{H} = \sum_{rstu} w_{rstu}\widehat{a_r}^{\dagger}\widehat{a_s}^{\dagger}\widehat{a_u}\widehat{a_t} \quad \text{with} \quad w_{rstu} = \frac{1}{n-1}h_{rt}\delta_{su}\widehat{a_r}^{\dagger}\widehat{a_s}^{\dagger}\widehat{a_u}\widehat{a_t} + \frac{1}{2}g_{rstu}$$

Solution

$$\hat{A} = \frac{1}{n-1} \sum_{rstu} f_{rt}\, \delta_{su}\, \hat{a}_r^+ \hat{a}_s^+ \hat{a}_u \hat{a}_t =$$

($\times(-1)$; $u \to s$)

$$= \frac{-1}{n-1} \sum_{rst} f_{rt}\, \hat{a}_r^+ \underbrace{\hat{a}_s^+ \hat{a}_t}_{\delta_{st} - \hat{a}_t \hat{a}_s^+} \hat{a}_s =$$

$$= \frac{-1}{n-1} \Bigg(\underbrace{\sum_{rs} f_{rs}\, \hat{a}_r^+ \hat{a}_s}_{\hat{F}} - \underbrace{\sum_{rst} f_{rt}\, \hat{a}_r^+ \hat{a}_t \underbrace{\hat{a}_s^+ \hat{a}_s}_{\hat{n}_s}}_{\underbrace{\sum_{rt} f_{rt}\, \hat{a}_r^+ \hat{a}_t}_{\hat{F}} \underbrace{\sum_s \hat{n}_s}_{\hat{n}}} \Bigg) =$$

$$= \frac{-1}{n-1} \left(\hat{F}(1-\hat{n}) \right) = \hat{F}\, \frac{\hat{n}-1}{n-1}$$

El subespacio de estados n-electrónicos (del espacio de Fock) es propio de $\hat{n}$ con valor propio n; por lo tanto, el operador $\hat{A}$ restringido a dicho subespacio es:

$$^{n}\hat{A} = \hat{F}\, \frac{n-1}{n-1} = \hat{F}$$

The n-electron subspace of the Fock space is an eigenspace of $\hat{n}$ with eigenvalue n; thus, the operator $\hat{A}$ restricted to that subspace is: $^{n}\hat{A} = \hat{F}$

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 some-times used for finite systems (CI, CC, ...).