

Mathematical foundations of quantum mechanics

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

$$\mathcal{F} = \mathcal{H}_0 \oplus \mathcal{H}_1 \oplus \mathcal{H}_1^{\otimes 2} \oplus \dots \mathcal{H}_1^{\otimes n} \oplus \dots \quad (\text{why } \textit{sum}?)$$

Vacuum state : ${}^0\Phi = |\rangle \neq 0$

Let us choose a normalized discrete basis set $\{\psi_1, \dots, \psi_i, \dots\}$ in \mathcal{H}_1

Then $\{{}^n\Phi_I\}$ with ${}^n\Phi_I \equiv |(\psi_{1_I} \dots \psi_{n_I})_-\rangle$ is a normalized basis of $\mathcal{H}_1^{\otimes n}$

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

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

Examples:

$$|(\psi_1 \dots \psi_n)_-\rangle = |\underbrace{1, \dots, 1}_n, 0, 0, \dots\rangle \quad |\rangle = |0, \dots, 0, \dots\rangle \quad (\text{bosons})$$

Annihilation operators

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

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

Examples:

$$\begin{aligned} \hat{a}_1 |1, n_2, \dots, n_i, \dots\rangle &= |0, n_2, \dots, n_i, \dots\rangle \\ \hat{a}_1 |0, n_2, \dots, n_i, \dots\rangle &= 0 \\ \hat{a}_2 |0, 1, \dots, n_i, \dots\rangle &= |0, 0, \dots, n_i, \dots\rangle \\ \hat{a}_2 |1, 1, \dots, n_i, \dots\rangle &= - |1, 0, \dots, n_i, \dots\rangle \end{aligned}$$

Slater determinant notation:

$$\begin{aligned} \hat{a}_i |(\psi_j \cdots \psi_i \cdots \psi_k)_-\rangle &= (-1)^{\nu_i} |(\psi_j \cdots \cancel{\psi_i} \cdots \psi_k)_-\rangle \\ \hat{a}_i |(\psi_j \cdots \cancel{\psi_i} \cdots \psi_k)_-\rangle &= 0 \end{aligned}$$

position number of $\psi_i - 1$

Creation operators

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

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

Examples: $\hat{a}_1^\dagger |0, n_2, \dots, n_i, \dots\rangle = |1, n_2, \dots, n_i, \dots\rangle$

$$\hat{a}_1^\dagger |1, n_2, \dots, n_i, \dots\rangle = 0$$

$$\hat{a}_2^\dagger |0, 0, \dots, n_i, \dots\rangle = |0, 1, \dots, n_i, \dots\rangle$$

$$\hat{a}_2^\dagger |1, 0, \dots, n_i, \dots\rangle = -|1, 1, \dots, n_i, \dots\rangle$$

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

Slater determinant notation: $\hat{a}_i^\dagger |(\psi_j \dots \cancel{\psi_i} \dots \psi_k)_-\rangle = (-1)^{\nu_i} |(\psi_j \dots \psi_i \dots \psi_k)_-\rangle$

$$\hat{a}_i^\dagger |(\psi_j \dots \cancel{\psi_i} \dots \psi_k)_-\rangle = |(\psi_i \psi_j \dots \psi_k)_-\rangle$$

$$\hat{a}_i^\dagger |(\psi_j \dots \psi_i \dots \psi_k)_-\rangle = 0$$

Adjointness relationship

\hat{a}_i^\dagger is the adjoint of \hat{a}_i :

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

$$(-1)^{\nu_i} n_i |n_1, \dots, 1 - n_i, \dots \rangle \qquad (-1)^{\nu'_i} (1 - n'_i) |n'_1, \dots, 1 - n'_i, \dots \rangle$$

$$(-1)^{\nu_i} n_i \delta_{n'_1, n_1} \dots \delta_{n'_i, 1 - n_i} \dots = (-1)^{\nu'_i} (1 - n'_i) \delta_{n'_1, n_1} \dots \delta_{1 - n'_i, n_i} \dots$$

This two expressions vanish unless $n'_1 = n_1, \dots, n'_i = 1 - n_i \dots$, in which case they coincide.

Number operators

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

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

$$\hat{n}_i |n_1, \dots, n_i, \dots\rangle = n_i |n_1, \dots, n_i, \dots\rangle$$

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

$$\hat{n} |n_1, \dots, n_i, \dots\rangle = \sum_i n_i |n_1, \dots, n_i, \dots\rangle = n |n_1, \dots, n_i, \dots\rangle$$

- \hat{n}_i are commuting *projection operators*

\hat{n}_i projects onto the subspace spanned by the many-electron basis vectors containing ψ_i .

- $\langle n_i \rangle_{n\Psi} = \langle {}^n\Psi | \hat{n}_i | {}^n\Psi \rangle = \left\langle \sum_I C_I {}^n\Phi_I \left| \hat{n}_i \right| \sum_J C_J {}^n\Phi_J \right\rangle = \sum_{IJ} C_I^* C_J \langle {}^n\Phi_I | \hat{n}_i | {}^n\Phi_J \rangle$
 $= \sum_{I, J \ni i} C_I^* C_J \langle {}^n\Phi_I | {}^n\Phi_J \rangle = \sum_{I \ni i} |C_I|^2 \leq 1$ (*populations*)

Anticommutation rules

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

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

$$\hat{a}_i\hat{a}_j = -\hat{a}_j\hat{a}_i \quad \hat{a}_i^\dagger\hat{a}_j^\dagger = -\hat{a}_j^\dagger\hat{a}_i^\dagger$$

$$\hat{a}_i\hat{a}_j^\dagger = \delta_{ij} - \hat{a}_j^\dagger\hat{a}_i \quad \begin{cases} \hat{a}_i\hat{a}_j^\dagger = -\hat{a}_j^\dagger\hat{a}_i & \text{for } i \neq j \\ \hat{a}_i\hat{a}_i^\dagger = 1 - \hat{a}_i^\dagger\hat{a}_i \end{cases}$$

$$\left(\hat{a}_i^\dagger\right)^2 = 0$$

Exercise

Use the second quantized form of 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.

Many-electron hamiltonian

- ▶ Standard expression (non-relativistic):

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

- ▶ Second quantized expression:

$$\hat{H} = \sum_{rs} h_{rs} \hat{a}_r^\dagger \hat{a}_s + \frac{1}{2} \sum_{rstu} g_{rstu} \hat{a}_r^\dagger \hat{a}_s^\dagger \hat{a}_u \hat{a}_t$$

$$h_{rs} = \left\langle \psi_r \left| \hat{h} \right| \psi_s \right\rangle \quad g_{rstu} = \left\langle \psi_r \psi_s \left| \frac{1}{r_{ij}} \right| \psi_t \psi_u \right\rangle$$

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

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

n does not appear explicitly, but it **is implied in the list of occupation numbers of** ${}^n\Phi_0 = |n_1, \dots, n_i, \dots\rangle$: $n = \sum_i n_i$

Same results previously obtained with Slater-Condon rules (slides 1.90 and 1.91); e. g.:

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

If $a \neq b$ then $\hat{a}_b |{}^n\Phi\rangle$ contains ψ_a so that $\hat{a}_a^\dagger \hat{a}_b |{}^n\Phi\rangle = 0$

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, ...).