

## Second quantization

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YouTube video: <https://www.youtube.com/watch?v=FQBrEI57pDA>

YouTube slides: [https://lcqs.unistra.fr/wordpress/wp-content/uploads/dlm\\_uploads/2023/10/istpc2021\\_second\\_quantization.pdf](https://lcqs.unistra.fr/wordpress/wp-content/uploads/dlm_uploads/2023/10/istpc2021_second_quantization.pdf)

### Electronic Hamiltonian in (so-called) *first quantization*

$N$ -electron Hamiltonian within the Born–Oppenheimer approximation:

$$\hat{H} = \hat{T} + \hat{V}_{\text{ne}} + \hat{W}_{\text{ee}}$$

$$\hat{T} = \sum_{i=1}^N \hat{t}(i)$$

where  $\hat{t}(i) \equiv -\frac{1}{2} \nabla_{\mathbf{r}_i}^2 \rightarrow$  kinetic energy

$$\hat{V}_{\text{ne}} = \sum_{i=1}^N \hat{v}_{\text{ne}}(i)$$

where  $\hat{v}_{\text{ne}}(i) \equiv - \sum_A^{\text{nuclei}} \frac{Z_A}{|\mathbf{r}_i - \mathbf{R}_A|} \times \rightarrow$  electron-nuclei attraction

$$\hat{W}_{\text{ee}} = \frac{1}{2} \sum_{i \neq j}^N \hat{w}_{\text{ee}}(i, j)$$

where  $\hat{w}_{\text{ee}}(i, j) \equiv \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \times \rightarrow$  electron-electron repulsion

We want to solve the electronic Schrödinger equation  $\hat{H}\Psi = E\Psi$  for fixed nuclei positions  $\{\mathbf{R}_A\}$ .

### Quantum theory of a single electron

- Let us start with *Schrödinger's theory*: the quantum state of a single electron is described by a wave function (referred to as **orbital**)  $\Psi \equiv \Psi(\mathbf{r})$  which is a function of the electronic space coordinates  $\mathbf{r}$ .
- In *Pauli's theory*, the **spin**  $\sigma = \alpha, \beta$  (also denoted  $\sigma = \uparrow, \downarrow$ ) of the electron is an additional degree of freedom. The quantum state of a single electron is now described by a wave function  $\Psi \equiv \Psi(\mathbf{r}, \sigma)$  which is a function of both space coordinates **and spin**.

- In the following we denote  $X \equiv (\mathbf{r}, \sigma)$  and  $\Psi \equiv \Psi(X)$ .

- *Normalization* condition:

$$\langle \Psi | \Psi \rangle = 1 = \sum_{\sigma=\alpha,\beta} \int d\mathbf{r} |\Psi(\mathbf{r}, \sigma)|^2 \stackrel{\text{notation}}{=} \int dX |\Psi(X)|^2$$

- In the **non-relativistic** case, a single electron will have a spin  $\sigma_0$  which is either up or down. The corresponding wave function  $\Psi_{\sigma_0}$  can then be written as a **spin-orbital**  $\Psi_{\sigma_0}(\mathbf{r}, \sigma) = \Psi(\mathbf{r})\delta_{\sigma\sigma_0}$ .

### Quantum theory of two electrons

- The quantum state of two electrons is described by the following wave function:

$$\Psi \equiv \Psi(X_1, X_2),$$

where  $X_1$  and  $X_2$  are the space-spin coordinates of the first and second electron, respectively.

- Normalization condition:

$$\int dX_1 \int dX_2 |\Psi(X_1, X_2)|^2 = 1.$$

- Electrons are *indistinguishable* particles:

$$|\Psi(X_1, X_2)|^2 = |\Psi(X_2, X_1)|^2 \quad \overset{\text{real algebra}}{\iff} \quad \Psi(X_1, X_2) = \pm \Psi(X_2, X_1)$$

- Electrons are fermionic particles. Therefore, they fulfill *Pauli's exclusion principle*  $|\Psi(X, X)|^2 = 0$ .
- **Conclusion:** a physical two-electron wave function must fulfill the *anti-symmetrization principle*

$$\Psi(X_1, X_2) = -\Psi(X_2, X_1)$$

### Slater determinants

- Let  $\{\varphi_K(X)\}$  denote an **orthonormal** basis of (molecular) spin-orbitals. Two electrons that occupy the spin-orbitals  $\varphi_I(X)$  and  $\varphi_J(X)$  will be described by the (normalized) **Slater determinant**

$$\Phi_{IJ}(X_1, X_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_I(X_1) & \varphi_I(X_2) \\ \varphi_J(X_1) & \varphi_J(X_2) \end{vmatrix} = \frac{1}{\sqrt{2}} \left( \varphi_I(X_1)\varphi_J(X_2) - \varphi_I(X_2)\varphi_J(X_1) \right) \stackrel{\text{Dirac notation}}{\equiv} |\Phi_{IJ}\rangle$$

- Note that Slater determinants and, consequently, linear combinations of Slater determinants are **anti-symmetric**.
- Therefore, Slater determinants are convenient "**building blocks**" for computing the electronic wavefunction.
- Still, we may wonder if we really need this **complicated** expression obtained from the determinant (obviously things get worse for a larger number of electrons).
- Another drawback of the current formulation: Both Slater determinant and Hamiltonian expressions **depend on the number of electrons**.

### Many-electron wave functions and Dirac notation

- An  $N$ -electron system will be described by the following wave function:

$$\Psi \equiv \Psi(X_1, X_2, \dots, X_N).$$

- In this (more general) case, the anti-symmetrization principle reads as

$$\Psi(X_1, X_2, \dots, X_i, \dots, X_j, \dots, X_N) \stackrel{X_i \leftrightarrow X_j}{=} -\Psi(X_1, X_2, \dots, X_j, \dots, X_i, \dots, X_N)$$

- If we consider a *basis of* (orthonormal and anti-symmetric)  $N$ -electron *Slater determinants*

$$\left\{ \Phi_\xi(X_1, \dots, X_N) = \frac{1}{\sqrt{N!}} \det \left[ \{ \varphi_{I_i}(X_j) \}_{1 \leq i, j \leq N} \right] \right\}_{\xi \equiv (I_1, I_2, \dots, I_N)}$$

the physical  $N$ -electron wave function of interest  $\Psi$  can be written as

$$\Psi(X_1, X_2, \dots, X_N) = \sum_{\xi} C_{\xi} \underbrace{\Phi_{\xi}(X_1, X_2, \dots, X_N)}_{\text{representation of } |\Phi_{\xi}\rangle} \quad \overset{\text{Dirac notation}}{\iff} \quad \boxed{|\Psi\rangle = \sum_{\xi} C_{\xi} |\Phi_{\xi}\rangle}$$

### “What is occupied?” rather than “Who occupies what?”

- Since electrons are **indistinguishable**, there is no need to know that electron 1 occupies  $\varphi_I$  and electron 2 occupies  $\varphi_J$  or the other way around...
- The important information is that spin-orbitals  $\varphi_I$  and  $\varphi_J$  are **occupied** and the remaining ones are **empty**.
- **Second quantization** is a formalism that relies on this idea. Let me tell you a story...
- At the beginning there was “nothing”:  $|\text{vac}\rangle \longleftarrow$  *normalized “vacuum state”, i.e.,  $\langle \text{vac} | \text{vac} \rangle = 1$ .*
- Then came the idea of introducing the quantum operator  $\hat{a}_I^\dagger$  that *creates* an electron occupying  $\varphi_I$ :  $\hat{a}_I^\dagger |\text{vac}\rangle \equiv |\varphi_I\rangle$ .
- We can also *annihilate* an electron occupying  $\varphi_I$  with the quantum operator  $\hat{a}_I$ , which is the *adjoint* of  $\hat{a}_I^\dagger$ .

Math toolbox:  $\langle u | \hat{A} | v \rangle = \langle \hat{A}^\dagger u | v \rangle, \quad (\hat{A}^\dagger)^\dagger = \hat{A}, \quad (\hat{A} + \hat{B})^\dagger = \hat{A}^\dagger + \hat{B}^\dagger, \quad (\hat{A}\hat{B})^\dagger = \hat{B}^\dagger\hat{A}^\dagger, \quad (\alpha\hat{A})^\dagger = \alpha^*\hat{A}^\dagger$

### “What is occupied?” rather than “Who occupies what?”

- Applying to the vacuum *two creation operators successively* leads to another representation of a two-electron Slater determinant:

$$\hat{a}_I^\dagger \hat{a}_J^\dagger |\text{vac}\rangle \stackrel{\text{notation}}{\equiv} |\Phi_{IJ}\rangle = \frac{1}{\sqrt{2}} \left( \underbrace{|\varphi_I \varphi_J\rangle}_{\text{not anti-symmetrized}} - |\varphi_J \varphi_I\rangle \right).$$

- If we interpret  $\hat{a}_I^\dagger \hat{a}_I$  as the *occupation operator* for the spin-orbital  $\varphi_I$ , then we should have

$$\langle \text{vac} | \hat{a}_I^\dagger \hat{a}_I | \text{vac} \rangle = 0 \quad \Leftrightarrow \quad \boxed{\hat{a}_I | \text{vac} \rangle = 0 \quad \text{(rule 1)}}$$

- In order to have a representation that is equivalent to the one used in first quantization, we only need two more rules:

$$\boxed{\forall I, J, \quad \hat{a}_I \hat{a}_J = -\hat{a}_J \hat{a}_I} \quad \text{(rule 2)} \quad \longrightarrow \quad \hat{a}_I^\dagger \hat{a}_J^\dagger = -\hat{a}_J^\dagger \hat{a}_I^\dagger$$

$$\boxed{\forall I, J, \quad \hat{a}_I \hat{a}_J^\dagger = \delta_{IJ} - \hat{a}_J^\dagger \hat{a}_I} \quad \text{(rule 3)} \quad \longrightarrow \quad \hat{a}_J^\dagger \hat{a}_I = \delta_{IJ} - \hat{a}_I \hat{a}_J^\dagger$$



“What is occupied?” rather than “Who occupies what?”

- **Rule 2** describes the indistinguishability of the electrons,  $\hat{a}_J^\dagger \hat{a}_I^\dagger |\text{vac}\rangle = -\hat{a}_I^\dagger \hat{a}_J^\dagger |\text{vac}\rangle$ ,

and Pauli's principle,  $\hat{a}_I^\dagger \hat{a}_I^\dagger |\text{vac}\rangle = 0$ .

- **Rule 3** ensures that you can only annihilate what has already been created:

$$\hat{a}_I \hat{a}_J^\dagger |\text{vac}\rangle = \delta_{IJ} |\text{vac}\rangle - \hat{a}_J^\dagger \hat{a}_I |\text{vac}\rangle = \delta_{IJ} |\text{vac}\rangle.$$

- It is now very easy to generate representations of Slater determinants for an **arbitrary number  $N$  of electrons** through products of creation operators!

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$$|\Phi_\xi\rangle \equiv \hat{a}_{I_1}^\dagger \hat{a}_{I_2}^\dagger \cdots \hat{a}_{I_{N-1}}^\dagger \hat{a}_{I_N}^\dagger |\text{vac}\rangle \quad \equiv \quad \frac{1}{\sqrt{N!}} \det \left[ \{ \varphi_{I_i}(X_j) \}_{1 \leq i, j \leq N} \right] = \Phi_\xi(X_1, \dots, X_N)$$

*second quantization*  *first quantization*

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## One-electron operators in second quantization

- Let  $\hat{h}$  denote a **one-electron** operator ( $\hat{t} + \hat{v}_{ne}$  for example): it acts on the one-electron states  $|\varphi_I\rangle$ .

- Resolution of the identity:  $\boxed{\sum_I |\varphi_I\rangle\langle\varphi_I| = \hat{1}}$   $\leftarrow |\varphi\rangle = \sum_I |\varphi_I\rangle C_I$ , where  $C_I = \langle\varphi_I|\varphi\rangle$

which leads to the **conventional representation**  $\hat{h} = \hat{1} \hat{h} \hat{1} = \sum_{I,J} \langle\varphi_I|\hat{h}|\varphi_J\rangle |\varphi_I\rangle\langle\varphi_J|$ ,

where  $\boxed{\langle\varphi_I|\hat{h}|\varphi_J\rangle = \int dX \varphi_I^*(X) \times (\hat{h}\varphi_J)(X) \stackrel{\text{notation}}{=} h_{IJ}}$  are the *one-electron* integrals.

- Second-quantized representation:**  $\boxed{\hat{h} \equiv \sum_{I,J} \langle\varphi_I|\hat{h}|\varphi_J\rangle \hat{a}_I^\dagger \hat{a}_J}$

Proof:  $\sum_{I,J} \langle\varphi_I|\hat{h}|\varphi_J\rangle \hat{a}_I^\dagger \hat{a}_J \stackrel{\text{one electron}}{=} \sum_{I,J} \langle\varphi_I|\hat{h}|\varphi_J\rangle \hat{a}_I^\dagger |\text{vac}\rangle \langle\text{vac}|\hat{a}_J = \sum_{I,J} \langle\varphi_I|\hat{h}|\varphi_J\rangle |\varphi_I\rangle\langle\varphi_J| = \hat{h}$ .

## Second quantization

- What is convenient is that this second-quantized representation is **valid for any number  $N$  of electrons**:

$$\sum_{i=1}^N \hat{h}(i) \equiv \sum_{I,J} \langle \varphi_I | \hat{h} | \varphi_J \rangle \hat{a}_I^\dagger \hat{a}_J \equiv \hat{h}$$

The information about  $N$  has been completely transferred to the states. It **does not appear in the operator** anymore.

- **Two-electron operator** representation in second quantization:

$$\hat{W}_{ee} = \frac{1}{2} \sum_{IJKL} \langle \varphi_I \varphi_J | \hat{w}_{ee} | \varphi_K \varphi_L \rangle \hat{a}_I^\dagger \hat{a}_J^\dagger \hat{a}_L \hat{a}_K$$

where

$$\langle \varphi_I \varphi_J | \hat{w}_{ee} | \varphi_K \varphi_L \rangle = \int \int dX_1 dX_2 \varphi_I^*(X_1) \varphi_J^*(X_2) \times \hat{w}_{ee}(\varphi_K(X_1) \varphi_L(X_2)) \stackrel{\text{notation}}{=} \langle IJ | KL \rangle$$

are the *(non-antisymmetrized) two-electron integrals*.

## Second quantization

Indeed,

$$\begin{aligned}
 \frac{1}{2} \sum_{IJKL} \langle \varphi_I \varphi_J | \hat{w}_{ee} | \varphi_K \varphi_L \rangle \hat{a}_I^\dagger \hat{a}_J^\dagger \hat{a}_L \hat{a}_K &\stackrel{\text{two electrons}}{\equiv} \frac{1}{2} \sum_{IJKL} \langle \varphi_I \varphi_J | \hat{w}_{ee} | \varphi_K \varphi_L \rangle \hat{a}_I^\dagger \hat{a}_J^\dagger | \text{vac} \rangle \langle \text{vac} | \hat{a}_L \hat{a}_K \\
 &= \frac{1}{2} \sum_{IJKL} \langle \varphi_I \varphi_J | \hat{w}_{ee} | \varphi_K \varphi_L \rangle |\Phi_{IJ}\rangle \langle \Phi_{KL}|
 \end{aligned}$$

where  $|\Phi_{IJ}\rangle \equiv \frac{1}{\sqrt{2}} (|\varphi_I \varphi_J\rangle - |\varphi_J \varphi_I\rangle) = -|\Phi_{JI}\rangle$  and  $|\Phi_{KL}\rangle = -|\Phi_{LK}\rangle$  (*redundancies*), thus leading to

$$\begin{aligned}
 \frac{1}{2} \sum_{IJKL} \langle \varphi_I \varphi_J | \hat{w}_{ee} | \varphi_K \varphi_L \rangle \hat{a}_I^\dagger \hat{a}_J^\dagger \hat{a}_L \hat{a}_K &\stackrel{\text{two electrons}}{\equiv} \frac{1}{\sqrt{2}} \sum_{I < J, KL} \langle \Phi_{IJ} | \hat{w}_{ee} | \varphi_K \varphi_L \rangle |\Phi_{IJ}\rangle \langle \Phi_{KL}| \\
 &= \sum_{I < J, K < L} \langle \Phi_{IJ} | \hat{w}_{ee} | \Phi_{KL} \rangle |\Phi_{IJ}\rangle \langle \Phi_{KL}| \\
 &= \left( \sum_{I < J} |\Phi_{IJ}\rangle \langle \Phi_{IJ}| \right) \hat{w}_{ee} \left( \sum_{K < L} |\Phi_{KL}\rangle \langle \Phi_{KL}| \right) \\
 &\stackrel{\text{two electrons}}{\equiv} \hat{w}_{ee}
 \end{aligned}$$

### Full second-quantized Hamiltonian

- The total electronic Hamiltonian reads in second quantization as follows,

$$\hat{H} = \sum_{IJ} h_{IJ} \hat{a}_I^\dagger \hat{a}_J + \frac{1}{2} \sum_{IJKL} \langle IJ|KL \rangle \hat{a}_I^\dagger \hat{a}_J^\dagger \hat{a}_L \hat{a}_K$$

- Note that the above expression holds for **relativistic** Hamiltonians. Two- or four-component **spinors** should be used instead of spin-orbitals.
- In **four-component** relativistic quantum chemical calculations, the **Dirac** (Breit) Coulomb Hamiltonian is employed.

## Why “second” quantization?

- Let us consider a one-electron **local (i.e. multiplicative) potential operator** (the electron-nuclei one, for example) which, in second quantization, reads  $\hat{V} = \sum_{i=1}^N \hat{v}(i) \equiv \sum_{IJ} \langle \varphi_I | \hat{v} | \varphi_J \rangle \hat{a}_I^\dagger \hat{a}_J$  where

$$\langle \varphi_I | \hat{v} | \varphi_J \rangle = \int dX v(X) \varphi_I^*(X) \varphi_J(X),$$

thus leading to

$$\hat{V} \equiv \int dX v(X) \underbrace{\left( \sum_I \varphi_I^*(X) \hat{a}_I^\dagger \right)}_{\hat{\Psi}^\dagger(X)} \underbrace{\left( \sum_J \varphi_J(X) \hat{a}_J \right)}_{\hat{\Psi}(X)} = \boxed{\int dX v(X) \hat{\Psi}^\dagger(X) \hat{\Psi}(X) \equiv \hat{V}}$$

$\hat{\Psi}^\dagger(X) \quad \hat{\Psi}(X) \quad \leftarrow \text{field operators}$

- For a **single electron** occupying the spin-orbital  $\Psi(X)$ , the corresponding expectation value for  $\hat{v}$  equals

$$\langle \Psi | \hat{v} | \Psi \rangle = \int dX v(X) \Psi^*(X) \Psi(X).$$

### Some useful remarks

- $\hat{\Psi}^\dagger(X) = \hat{\Psi}^\dagger(\mathbf{r}, \sigma)$  *creates* an electron at position  $\mathbf{r}$  with spin  $\sigma$ .
- $\hat{\Psi}(X)$  is the corresponding *annihilation* operator.
- $\hat{n}(X) = \hat{\Psi}^\dagger(X)\hat{\Psi}(X) = \hat{n}(\mathbf{r}, \sigma)$  is the (spin) *density operator*.
- The electron (spin) *density*  $n_\Phi(X) = n_\Phi(\mathbf{r}, \sigma)$  of any normalized  $N$ -electron wave function  $\Phi$  is evaluated as  $n_\Phi(X) = \langle \Phi | \hat{n}(X) | \Phi \rangle$ .
- The one-electron reduced *density matrix* (1RDM) of  $\Phi$  is defined as  $\gamma_\Phi(X, X') = \langle \Phi | \hat{\Psi}^\dagger(X)\hat{\Psi}(X') | \Phi \rangle$
- *Time-dependent field operators* can be constructed as follows:

$$\hat{\Psi}^\dagger(X_1, t_1) \equiv \hat{\Psi}^\dagger(1) = e^{+i\hat{H}t_1} \hat{\Psi}^\dagger(X_1) e^{-i\hat{H}t_1}.$$

- The latter are the key ingredients in the definition of the one- and more-electron *Green functions*.