

# Second quantization

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

Slides used in the video: [https://quantique.u-strasbg.fr/lib/exe/fetch.php?media=en:pageperso:ef:istpc2021\\_second\\_quantization.pdf](https://quantique.u-strasbg.fr/lib/exe/fetch.php?media=en:pageperso:ef:istpc2021_second_quantization.pdf)

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

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

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

$$\hat{T} = \sum_{i=1}^N \hat{t}(i) \quad \text{where} \quad \hat{t}(i) \equiv -\frac{1}{2} \nabla_{\mathbf{r}_i}^2 \quad \rightarrow \quad \text{kinetic energy}$$

$$\hat{V}_{\text{ne}} = \sum_{i=1}^N \hat{v}_{\text{ne}}(i) \quad \text{where} \quad \hat{v}_{\text{ne}}(i) \equiv - \sum_A^{\text{nuclei}} \frac{Z_A}{|\mathbf{r}_i - \mathbf{R}_A|} \times \quad \rightarrow \quad \text{electron-nuclei attraction}$$

$$\hat{W}_{\text{ee}} = \frac{1}{2} \sum_{i \neq j}^N \hat{w}_{\text{ee}}(i, j) \quad \text{where} \quad \hat{w}_{\text{ee}}(i, j) \equiv \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \times \quad \rightarrow \quad \text{electron-electron repulsion}$$

### 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:

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

- 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  $\{\varphi_K(X)\}_K$  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**

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

- 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

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

- One may decompose  $\Psi$  in a basis of Slater determinants  $\{\Phi_\xi\}$ :

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

### “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”:  $|\text{vac}\rangle \leftarrow$  *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:

$$\hat{a}_J^\dagger \hat{a}_I^\dagger |\text{vac}\rangle \equiv |\Phi_{IJ}\rangle = |\varphi_I \varphi_J\rangle.$$

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

*second quantization*
*first quantization*

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- In the following, we will use the notation  $|I_1 I_2 \dots I_{N-1} I_N\rangle = \hat{a}_{I_1}^\dagger \hat{a}_{I_2}^\dagger \dots \hat{a}_{I_{N-1}}^\dagger \hat{a}_{I_N}^\dagger |\text{vac}\rangle$ .

## Second quantization

**EXERCISE:** (1) Show that  $|I_1 I_2 \dots I_{N-1} I_N\rangle$  is **normalized**.

(2) Let us consider another state  $|J_1 J_2 \dots J_{N-1} J_N\rangle$  and assume that at least one of the occupied spin-orbitals (let us denote it  $\varphi_{J_k}$ ) is not occupied in  $|I_1 I_2 \dots I_{N-1} I_N\rangle$ . Show that the two states are **orthogonal**.

(3) The "counting" operator  $\hat{N}$  is defined as  $\hat{N} = \sum_I \hat{n}_I$  where  $\hat{n}_I = \hat{a}_I^\dagger \hat{a}_I$ . Show that

$$\begin{aligned} \hat{n}_I |I_1 I_2 \dots I_{N-1} I_N\rangle &= |I_1 I_2 \dots I_{N-1} I_N\rangle & \text{if } I = I_k \quad 1 \leq k \leq N \\ &= 0 & \text{otherwise} \end{aligned}$$

and conclude that  $\hat{N} |I_1 I_2 \dots I_{N-1} I_N\rangle = N |I_1 I_2 \dots I_{N-1} I_N\rangle$ .

(4) Explain why states corresponding to different numbers of electrons are automatically orthogonal.

(5) Explain why any normalized state  $|\Psi\rangle$  fulfills the condition  $0 \leq \langle \Psi | \hat{n}_I | \Psi \rangle \leq 1$ .

## One-electron operators in second quantization

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

- Resolution of the identity:* 
$$\sum_I |\varphi_I\rangle\langle\varphi_I| = \hat{\mathbf{1}},$$

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

- Second-quantized representation:**

$$\hat{h} \equiv \sum_{I,J} \langle\varphi_I|\hat{h}|\varphi_J\rangle \hat{a}_I^\dagger \hat{a}_J$$

Indeed,

$$\begin{aligned} \left( \sum_{I,J} \langle\varphi_I|\hat{h}|\varphi_J\rangle \hat{a}_I^\dagger \hat{a}_J \right) |\varphi_K\rangle &= \left( \sum_{I,J} \langle\varphi_I|\hat{h}|\varphi_J\rangle \hat{a}_I^\dagger \hat{a}_J \right) \hat{a}_K^\dagger |\text{vac}\rangle = \left( \sum_{I,J} \langle\varphi_I|\hat{h}|\varphi_J\rangle \hat{a}_I^\dagger \delta_{JK} \right) |\text{vac}\rangle \\ &= \sum_I \langle\varphi_I|\hat{h}|\varphi_K\rangle |\varphi_I\rangle = \hat{h}|\varphi_K\rangle \end{aligned}$$

## 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.

**EXERCISE:** Let us consider another orthonormal basis  $\{\tilde{\varphi}_K(X)\}_K$  of spin-orbitals that we decompose in the current basis as follows,  $|\tilde{\varphi}_P\rangle = \sum_Q U_{QP} |\varphi_Q\rangle$ .

- (1) Show that the matrix  $U$  is unitary ( $U^\dagger = U^{-1}$ ).
- (2) Explain why  $\hat{a}_{\tilde{P}}^\dagger = \sum_Q U_{QP} \hat{a}_Q^\dagger$  and show that  $\sum_{I,J} \langle \tilde{\varphi}_I | \hat{h} | \tilde{\varphi}_J \rangle \hat{a}_{\tilde{I}}^\dagger \hat{a}_{\tilde{J}} \equiv \hat{h}$ .
- (3) Show that the diagonalization of  $\hat{h}$  in the one-electron space leads automatically to the diagonalization in the  $N$ -electron space (see the previous exercise).

### Two-electron contributions to the second-quantized Hamiltonian

- The total electronic Hamiltonian reads in second quantization as follows *[see the complements]*,

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

where  $\langle \varphi_I | \hat{h} | \varphi_J \rangle = \int dX \varphi_I^*(X) \times (\hat{h} \varphi_J)(X)$  ← one-electron integrals

$\langle \varphi_I \varphi_J | \hat{w}_{ee} | \varphi_K \varphi_L \rangle = \int \int dX_1 dX_2 \varphi_I^*(X_1) \varphi_J^*(X_2) \times (\hat{w}_{ee} \varphi_K \varphi_L)(X_1, X_2)$  ← two-electron integrals

- Note that this expression is also valid for a **relativistic** Hamiltonian. Two or four-component **spinors** should be used rather than spin-orbitals in conjunction with the **Dirac** (Breit) Coulomb Hamiltonian.
- The standard (**non-relativistic**) Hamiltonian will be used in the following.

### EXERCISE:

At the non-relativistic level, **real algebra** can be used,  $\varphi_I(X) = \varphi_{i\sigma}(\mathbf{r}, \tau) = \phi_i(\mathbf{r})\delta_{\sigma\tau}$ ,

$$\hat{h} \equiv -\frac{1}{2}\nabla_{\mathbf{r}}^2 + v_{\text{ne}}(\mathbf{r}) \times \quad \text{and} \quad \hat{w}_{\text{ee}} \equiv \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \times .$$

Show that the Hamiltonian, that is here a spin-free operator, can be rewritten in the basis of the molecular orbitals  $\{\phi_p(\mathbf{r})\}_p$  as follows

$$\hat{H} = \sum_{p,q} h_{pq} \hat{E}_{pq} + \frac{1}{2} \sum_{p,q,r,s} \langle pr|qs \rangle \left( \hat{E}_{pq} \hat{E}_{rs} - \delta_{qr} \hat{E}_{ps} \right)$$

where  $\hat{E}_{pq} = \sum_{\sigma} \hat{a}_{p,\sigma}^{\dagger} \hat{a}_{q,\sigma}$ ,  $h_{pq} = \langle \phi_p | \hat{h} | \phi_q \rangle$  and

$$\langle pr|qs \rangle = \int \int d\mathbf{r}_1 d\mathbf{r}_2 \phi_p(\mathbf{r}_1) \phi_r(\mathbf{r}_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_q(\mathbf{r}_1) \phi_s(\mathbf{r}_2) = (pq|rs).$$

**EXERCISE:**

For any normalized  $N$ -electron wavefunction  $\Psi$ , we define the one-electron (1) and two-electron (2) **reduced density matrices** (RDM) as follows,

$$D_{pq} = \langle \Psi | \hat{E}_{pq} | \Psi \rangle \quad \text{and} \quad D_{pqrs} = \langle \Psi | \hat{E}_{pq} \hat{E}_{rs} - \delta_{qr} \hat{E}_{ps} | \Psi \rangle.$$

(1) Show that the **1RDM is symmetric** and that  $\forall p$ , the **occupation**  $n_p = D_{pp}$  of the orbital  $p$  fulfills the inequality  $0 \leq n_p \leq 2$ . Show that the trace of the 1RDM equals  $N$ .

(2) Explain why the expectation value for the **energy**  $\langle \Psi | \hat{H} | \Psi \rangle$  can be **determined from the 2RDM**.

**Hint:** show that  $D_{pq} = \frac{1}{N-1} \sum_r D_{pqrr}$ .

(3) Let us consider the particular case  $|\Psi\rangle \rightarrow |\Phi\rangle = \prod_{i=1}^{N/2} \prod_{\sigma} \hat{a}_{i,\sigma}^{\dagger} |\text{vac}\rangle$ . Explain why both density matrices are non-zero only in the occupied-orbital space.

Show that  $D_{ij} = 2\delta_{ij}$  and  $D_{ijkl} = 4\delta_{ij}\delta_{kl} - 2\delta_{jk}\delta_{il}$  and ...

... deduce the corresponding energy expression:

$$\langle \Phi | \hat{H} | \Phi \rangle = 2 \sum_{i=1}^{N/2} h_{ii} + \sum_{i,j=1}^{N/2} \left( 2 \langle ij | ij \rangle - \langle ij | ji \rangle \right).$$

(4) Let  $i, j$  and  $a, b$  denote occupied and unoccupied (virtuals) orbitals in  $\Phi$ , respectively. Explain why  $\hat{E}_{ai}$  and  $\hat{E}_{ai}\hat{E}_{bj}$  are referred to as **single** excitation and **double excitation operators**, respectively.

**Hint:** derive simplified expressions for  $|\Phi_i^a\rangle = \frac{1}{\sqrt{2}}\hat{E}_{ai}|\Phi\rangle$  and  $|\Phi_{ij}^{ab}\rangle = \frac{1}{2}\hat{E}_{ai}\hat{E}_{bj}|\Phi\rangle$  with  $i < j, a < b$ .



## Why “second” quantization?

- Let us focus on the (one-electron) electron-nuclei **local potential operator** which, in second

quantization, reads  $\hat{V}_{\text{ne}} = \sum_{i=1}^N \hat{v}_{\text{ne}}(i) \equiv \sum_{IJ} \langle \varphi_I | \hat{v}_{\text{ne}} | \varphi_J \rangle \hat{a}_I^\dagger \hat{a}_J$  where

$$\langle \varphi_I | \hat{v}_{\text{ne}} | \varphi_J \rangle = \int dX v_{\text{ne}}(\mathbf{r}) \varphi_I^*(X) \varphi_J(X),$$

thus leading to

$$\hat{V}_{\text{ne}} \equiv \int dX v_{\text{ne}}(\mathbf{r}) \underbrace{\left( \sum_I \varphi_I^*(X) \hat{a}_I^\dagger \right)}_{\hat{\Psi}^\dagger(X)} \underbrace{\left( \sum_J \varphi_J(X) \hat{a}_J \right)}_{\hat{\Psi}(X)} = \boxed{\int d\mathbf{r} v_{\text{ne}}(\mathbf{r}) \sum_{\sigma} \hat{\Psi}^\dagger(\mathbf{r}, \sigma) \hat{\Psi}(\mathbf{r}, \sigma) \equiv \hat{V}_{\text{ne}}}$$

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

- For a **single electron** occupying the spin-orbital  $\Psi(X) = \Psi(\mathbf{r}, \sigma)$ , the corresponding expectation value for the electron-nuclei potential energy equals

$$\langle \Psi | \hat{v}_{\text{ne}} | \Psi \rangle = \int dX v_{\text{ne}}(\mathbf{r}) \Psi^*(X) \Psi(X) = \int d\mathbf{r} v_{\text{ne}}(\mathbf{r}) \sum_{\sigma} \Psi^*(\mathbf{r}, \sigma) \Psi(\mathbf{r}, \sigma).$$

### *Complements*

## Two-electron operators in second quantization

- Let  $\hat{w}$  denote a **two-electron** operator: it acts on two-electron states  $|\varphi_I\varphi_J\rangle = |1: \varphi_I, 2: \varphi_J\rangle$ .
- A **complete anti-symmetrized basis** should be used for describing the two electrons:

$$|IJ\rangle = \frac{1}{\sqrt{2}} \left( |\varphi_I\varphi_J\rangle - |\varphi_J\varphi_I\rangle \right) \equiv \hat{a}_I^\dagger \hat{a}_J^\dagger |\text{vac}\rangle \quad \text{with } I < J.$$

Consequently, any two-electron anti-symmetrized state  $|\Psi\rangle$  should fulfill the condition

$$\hat{P}_\mathcal{A}|\Psi\rangle = |\Psi\rangle \quad \text{where} \quad \hat{P}_\mathcal{A} = \sum_{I < J} |IJ\rangle\langle IJ| \quad \longleftarrow \text{projection operator!}$$

- Projection of the two-electron operator onto the space of anti-symmetrized states:

$$\hat{w}_\mathcal{A} = \hat{P}_\mathcal{A} \hat{w} \hat{P}_\mathcal{A} = \sum_{I < J, K < L} \langle IJ | \hat{w} | KL \rangle |IJ\rangle\langle KL|$$

## Two-electron operators in second quantization

**EXERCISE:** Prove that  $\hat{w}_A \equiv \frac{1}{2} \sum_{IJKL} \langle \varphi_I \varphi_J | \hat{w} | \varphi_K \varphi_L \rangle \hat{a}_I^\dagger \hat{a}_J^\dagger \hat{a}_L \hat{a}_K$

**hint:** apply  $\hat{w}_A$  and the proposed second-quantized representation to  $|PQ\rangle \equiv \hat{a}_P^\dagger \hat{a}_Q^\dagger |\text{vac}\rangle$  ( $P < Q$ ).  
Conclude.

- What is convenient is that this second-quantized representation is **valid for any number  $N$  of electrons** and includes the projection onto **anti-symmetrized** states:

$$\frac{1}{2} \sum_{i \neq j}^N \hat{w}(i, j) \equiv \frac{1}{2} \sum_{IJKL} \langle \varphi_I \varphi_J | \hat{w} | \varphi_K \varphi_L \rangle \hat{a}_I^\dagger \hat{a}_J^\dagger \hat{a}_L \hat{a}_K \equiv \hat{w}$$

- **Physical interpretation** of the field operators:

$$\hat{\Psi}^\dagger(\mathbf{X})|\text{vac}\rangle = \sum_I \varphi_I^*(\mathbf{X}) \hat{a}_I^\dagger |\text{vac}\rangle = \sum_I \varphi_I^*(\mathbf{X}) |\varphi_I\rangle = \sum_I |\varphi_I\rangle \langle \varphi_I | \mathbf{X} \rangle = \boxed{|\mathbf{X}\rangle = \hat{\Psi}^\dagger(\mathbf{X})|\text{vac}\rangle},$$

which means that  $\hat{\Psi}^\dagger(\mathbf{X}) = \hat{\Psi}^\dagger(\mathbf{r}, \sigma)$  creates an electron at position  $\mathbf{r}$  with spin  $\sigma$ .

- Consequently, the **density operator** reads in second quantization  $\hat{n}(\mathbf{r}) = \sum_{\sigma} \hat{\Psi}^\dagger(\mathbf{r}, \sigma) \hat{\Psi}(\mathbf{r}, \sigma)$ ,

and the **electron density** associated with the normalized  $N$ -electron wavefunction  $\Psi$  is simply calculated as follows,

$$n_{\Psi}(\mathbf{r}) = \langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle.$$

- **Anticommutation rules:**  $[\hat{\Psi}(\mathbf{X}), \hat{\Psi}(\mathbf{X}')]_+ = \sum_{IJ} \varphi_J(\mathbf{X}) \varphi_I(\mathbf{X}') [\hat{a}_J, \hat{a}_I]_+ = 0$  and

$$\begin{aligned} [\hat{\Psi}(\mathbf{X}), \hat{\Psi}^\dagger(\mathbf{X}')]_+ &= \sum_{IJ} \varphi_J(\mathbf{X}) \varphi_I^*(\mathbf{X}') [\hat{a}_J, \hat{a}_I^\dagger]_+ = \sum_{IJ} \varphi_J(\mathbf{X}) \varphi_I^*(\mathbf{X}') \delta_{IJ} \\ &= \sum_I \langle \mathbf{X} | \varphi_I \rangle \langle \varphi_I | \mathbf{X}' \rangle = \langle \mathbf{X} | \mathbf{X}' \rangle = \delta(\mathbf{X} - \mathbf{X}'). \end{aligned}$$

## Model Hamiltonians: example of the Hubbard Hamiltonian

$$h_{ij} \longrightarrow -t(\delta_{i,j-1} + \delta_{i,j+1}) + \varepsilon_i \delta_{ij}$$

$$\langle ij|kl \rangle \longrightarrow U \delta_{ij} \delta_{ik} \delta_{lj}$$

$$\hat{E}_{ik} \hat{E}_{jl} - \delta_{kj} \hat{E}_{il} \longrightarrow \hat{n}_i \hat{n}_i - \hat{n}_i$$

where  $\hat{n}_i = \hat{E}_{ii} = \hat{n}_{i\uparrow} + \hat{n}_{i\downarrow}$  so that  $\hat{n}_i \hat{n}_i = 2\hat{n}_{i\uparrow} \hat{n}_{i\downarrow} + \hat{n}_i$

$$\hat{H} \longrightarrow \underbrace{-t \sum_{\langle i,j \rangle} \sum_{\sigma=\uparrow,\downarrow} \hat{a}_{i,\sigma}^\dagger \hat{a}_{j,\sigma}}_{\hat{\mathcal{T}} \text{ (hopping)}} + \underbrace{U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}}_{\text{on-site repulsion}} + \underbrace{\sum_i \varepsilon_i \hat{n}_i}_{\text{local potential}}$$

## Second quantization

