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

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

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

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

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

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

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

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) $\boxed{\Psi \equiv \Psi(\mathbf{r})}$ 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 $\boxed{\Psi \equiv \Psi(\mathbf{r}, \sigma)}$ which is a function of both space coordinates and spin.

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

- *Normalization* condition:

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

- In the non-relativistic case, a single electron will have a spin σ_0 which is either up or down. The corresponding wave function Ψ_{σ_0} can then be written as a spin-orbital $\boxed{\Psi_{\sigma_0}(\mathbf{r}, \sigma) = \Psi(\mathbf{r}) \delta_{\sigma\sigma_0}}$.

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:

$$\int \mathrm{d}X_1 \int \mathrm{d}X_2 \, |\Psi(X_1, X_2)|^2 = 1.$$

- Electrons are *indistinguishable* particles:

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

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

$$\boxed{\Psi(X_1, X_2) = -\Psi(X_2, X_1)}$$

Slater determinants

- Let $\left\{\varphi_K(X)\right\}_K$ 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

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

- 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:

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

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

$$\Psi(X_1, X_2, \ldots, X_i, \ldots, X_j, \ldots) \overset{X_i \leftrightarrow X_j}{=} -\Psi(X_1, X_2, \ldots, X_j, \ldots, X_i, \ldots)$$

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

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

"What is occupied?" rather than "Who occupies what?"

- Since electrons are indistinguishable, there is no need to know that electron 1 occupies φ_I and electron 2 occupies φ_J or the other way around...

- The important information is that spin-orbitals φ_I and φ_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": $|\text{vac}\rangle$ ⟵ *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 φ_I: $\hat{a}_I^\dagger|\text{vac}\rangle \equiv |\varphi_I\rangle$.

- We can also *annihilate* an electron occupying φ_I with the quantum operator $\hat{a}_I$, which is the *adjoint* of $\hat{a}_I^\dagger$.

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

"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 φ_I, then we should have

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

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

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

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

"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!

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

second quantization *first quantization*

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

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

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

$$\hat{n}_I |I_1 I_2 \ldots I_{N-1} I_N\rangle = |I_1 I_2 \ldots I_{N-1} I_N\rangle \qquad \text{if} \quad I = I_k \qquad 1 \leq k \leq N$$

$$= 0 \qquad\qquad\qquad\qquad \text{otherwise}$$

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

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

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

One-electron operators in second quantization

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

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

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

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

  Indeed,

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

$$= \sum_I \langle\varphi_I|\hat{h}|\varphi_K\rangle |\varphi_I\rangle = \hat{h}|\varphi_K\rangle$$

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

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

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 $\left\{ \tilde{\varphi}_K(X) \right\}_K$ 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 $\mathbf{U}$ is unitary ($\mathbf{U}^\dagger = \mathbf{U}^{-1}$).

(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]*,

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

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

$\langle \varphi_I \varphi_J | \hat{w}_{\rm ee} | \varphi_K \varphi_L \rangle = \int \int \mathrm{d}X_1 \mathrm{d}X_2 \, \varphi_I^*(X_1) \varphi_J^*(X_2) \times \Big(\hat{w}_{\rm ee} \varphi_K \varphi_L \Big)(X_1, X_2)$ ←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, $\varphi_I(X) = \varphi_{i\sigma}(\mathbf{r},\tau) = \phi_i(\mathbf{r})\delta_{\sigma\tau}$,

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

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

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

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

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

EXERCISE:

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

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

(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 $D_{pq} = \dfrac{1}{N-1} \sum_r D_{pqrr}$.

(3) Let us consider the particular case $|\Psi\rangle \rightarrow |\Phi\rangle = \prod_{i=1}^{N/2} \prod_{\sigma} \hat{a}^{\dagger}_{i,\sigma} |\text{vac}\rangle$. 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:

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

(4) Let i, j and a, b denote occupied and unoccupied (virtuals) orbitals in Φ, 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 $\hat{V}_{\rm ne} = \sum_{i=1}^{N} \hat{v}_{\rm ne}(i) \equiv \sum_{IJ} \langle \varphi_I | \hat{v}_{\rm ne} | \varphi_J \rangle \hat{a}_I^\dagger \hat{a}_J$ where

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

thus leading to

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

$\hat{\Psi}^\dagger(X)$ $\hat{\Psi}(X)$ $\leftarrow$ 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

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

Complements

Two-electron operators in second quantization

- Let $\hat{w}$ denote a two-electron operator: it acts on two-electron states $|\varphi_I \varphi_J\rangle = |1\text{: } \varphi_I, 2\text{: } \varphi_J\rangle$.

- A complete anti-symmetrized basis should be used for describing the two electrons:

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

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

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

- 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 $\hat{w}_{\mathcal{A}} \equiv \frac{1}{2} \sum_{IJKL} \langle \varphi_I \varphi_J | \hat{w} | \varphi_K \varphi_L \rangle \, \hat{a}_I^\dagger \hat{a}_J^\dagger \hat{a}_L \hat{a}_K$

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

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

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

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

  and the electron density associated with the normalized N-electron wavefunction Ψ is simply calculated as follows,

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

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

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

Model Hamiltonians: example of the Hubbard Hamiltonian

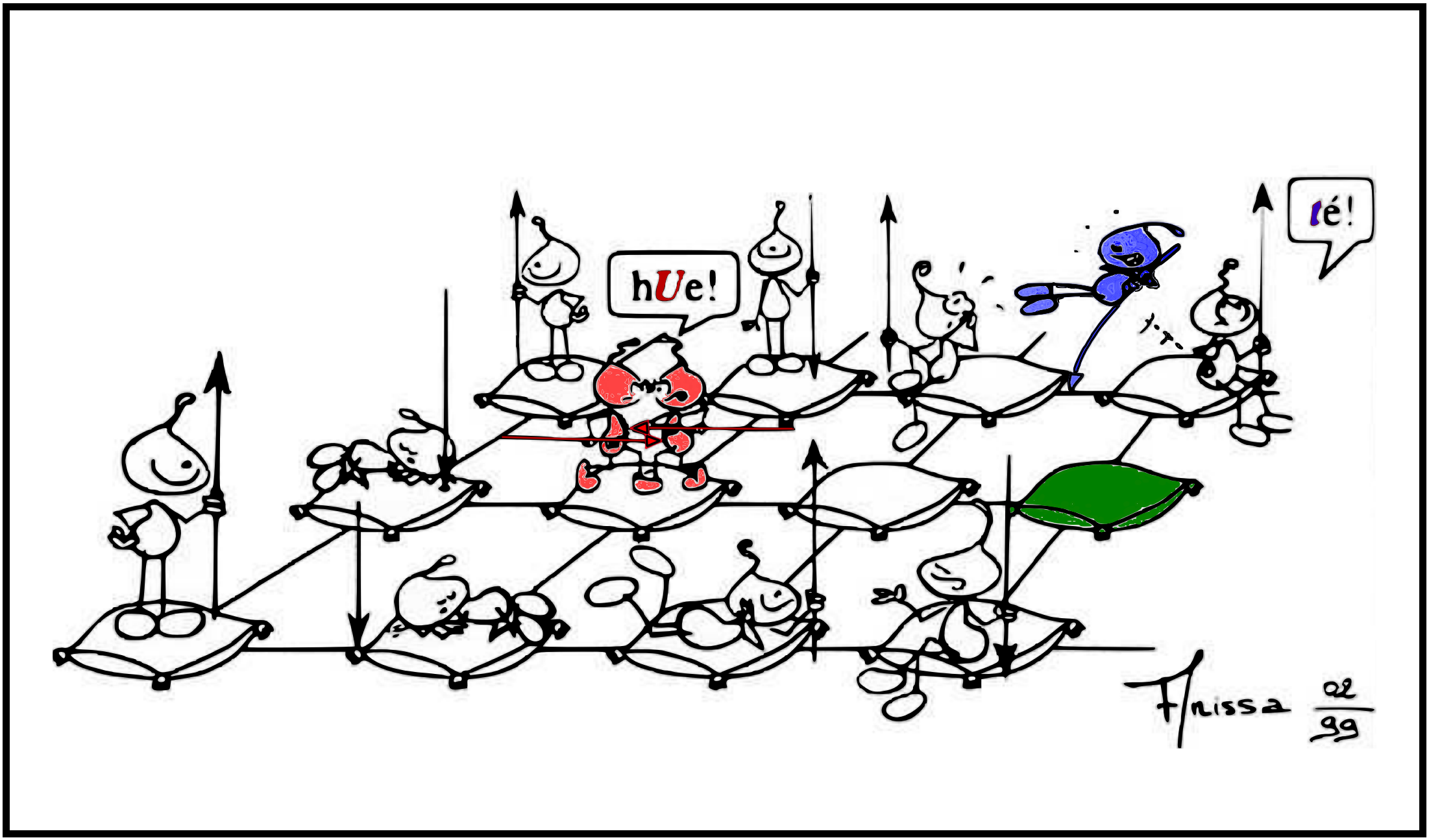
$$h_{ij} \longrightarrow -t\left(\delta_{i,j-1} + \delta_{i,j+1}\right) + \varepsilon_i \delta_{ij}$$

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

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

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

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