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`

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

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

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

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

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

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

We want to solve the electronic Schrödinger equation $\boxed{\hat{H}\Psi = E\Psi}$ 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) $\boxed{\Psi \equiv \Psi(\mathbf{r})}$ 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 $\left\{\varphi_K(X)\right\}$ 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

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

- 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:

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

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

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

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

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

the physical N-electron wave function of interest Ψ can be written as

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

"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": $|\text{vac}\rangle$ $\longleftarrow$ *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 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: $\boxed{\langle u|\hat{A}|v\rangle = \langle \hat{A}^\dagger u|v\rangle, \quad \left(\hat{A}^\dagger\right)^\dagger = \hat{A}, \quad \left(\hat{A}+\hat{B}\right)^\dagger = \hat{A}^\dagger + \hat{B}^\dagger, \quad \left(\hat{A}\hat{B}\right)^\dagger = \hat{B}^\dagger\hat{A}^\dagger, \quad \left(\alpha\hat{A}\right)^\dagger = \alpha^*\hat{A}^\dagger}$

"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:

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

- 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, $\hat{a}^\dagger_J \hat{a}^\dagger_I |\mathrm{vac}\rangle = -\hat{a}^\dagger_I \hat{a}^\dagger_J |\mathrm{vac}\rangle$,

  and Pauli's principle, $\hat{a}^\dagger_I \hat{a}^\dagger_I |\mathrm{vac}\rangle = 0$.

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

  $$\hat{a}_I \hat{a}^\dagger_J |\mathrm{vac}\rangle = \delta_{IJ} |\mathrm{vac}\rangle - \hat{a}^\dagger_J \hat{a}_I |\mathrm{vac}\rangle = \delta_{IJ} |\mathrm{vac}\rangle.$$

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

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

second quantization *first quantization*

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:* $\boxed{\sum_I |\varphi_I\rangle\langle\varphi_I| = \hat{\mathbb{1}}}$ $\longleftarrow |\varphi\rangle = \sum_I |\varphi_I\rangle C_I$, where $C_I = \langle\varphi_I|\varphi\rangle$

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

  where $\boxed{\langle\varphi_I|\hat{h}|\varphi_J\rangle = \int {\rm d}X\,\varphi_I^*(X)\times\Big(\hat{h}\varphi_J\Big)(X) \overset{notation}{=} h_{IJ}}$ 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: $\sum_{I,J}\langle\varphi_I|\hat{h}|\varphi_J\rangle\hat{a}_I^\dagger\hat{a}_J \overset{\text{one electron}}{\equiv} \sum_{I,J}\langle\varphi_I|\hat{h}|\varphi_J\rangle\hat{a}_I^\dagger|{\rm vac}\rangle\langle{\rm vac}|\hat{a}_J = \sum_{I,J}\langle\varphi_I|\hat{h}|\varphi_J\rangle|\varphi_I\rangle\langle\varphi_J| = \hat{h}$.

- 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.

- Two-electron operator representation in second quantization:

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

where

$$\langle \varphi_I \varphi_J | \hat{w}_{\rm ee} | \varphi_K \varphi_L \rangle = \int\!\!\int {\rm d}X_1 {\rm d}X_2 \, \varphi_I^*(X_1) \varphi_J^*(X_2) \times \hat{w}_{\rm ee} \Big(\varphi_K(X_1) \varphi_L(X_2) \Big) \overset{notation}{=} \langle IJ | KL \rangle$$

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

Indeed,

$$\frac{1}{2}\sum_{IJKL}\langle\varphi_I\varphi_J|\hat{w}_{\rm ee}|\varphi_K\varphi_L\rangle\;\hat{a}^\dagger_I\hat{a}^\dagger_J\hat{a}_L\hat{a}_K \overset{\text{two electrons}}{\equiv} \frac{1}{2}\sum_{IJKL}\langle\varphi_I\varphi_J|\hat{w}_{\rm ee}|\varphi_K\varphi_L\rangle\;\hat{a}^\dagger_I\hat{a}^\dagger_J|{\rm vac}\rangle\langle{\rm vac}|\hat{a}_L\hat{a}_K$$

$$= \frac{1}{2}\sum_{IJKL}\langle\varphi_I\varphi_J|\hat{w}_{\rm ee}|\varphi_K\varphi_L\rangle|\Phi_{IJ}\rangle\langle\Phi_{KL}|$$

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

$$\frac{1}{2}\sum_{IJKL}\langle\varphi_I\varphi_J|\hat{w}_{\rm ee}|\varphi_K\varphi_L\rangle\;\hat{a}^\dagger_I\hat{a}^\dagger_J\hat{a}_L\hat{a}_K \overset{\text{two electrons}}{\equiv} \frac{1}{\sqrt{2}}\sum_{I<J,KL}\langle\Phi_{IJ}|\hat{w}_{\rm ee}|\varphi_K\varphi_L\rangle|\Phi_{IJ}\rangle\langle\Phi_{KL}|$$

$$= \sum_{I<J,K<L}\langle\Phi_{IJ}|\hat{w}_{\rm ee}|\Phi_{KL}\rangle|\Phi_{IJ}\rangle\langle\Phi_{KL}|$$

$$= \left(\sum_{I<J}|\Phi_{IJ}\rangle\langle\Phi_{IJ}|\right)\hat{w}_{\rm ee}\left(\sum_{K<L}|\Phi_{KL}\rangle\langle\Phi_{KL}|\right)$$

$$\overset{\text{two electrons}}{\equiv} \hat{w}_{\rm ee}$$

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

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

thus leading to

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

$\hat{\Psi}^\dagger(X)$ $\hat{\Psi}(X)$ ← field operators

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

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

Some useful remarks

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

- $\hat{\Psi}(X)$ 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 Φ is evaluated as $n_\Phi(X) = \langle\Phi|\hat{n}(X)|\Phi\rangle$.

- The one-electron reduced *density matrix* (1RDM) of Φ 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:

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

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