Introduction to second quantization

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Electronic Hamiltonian in first quantization

N-electron Hamiltonian within the Born-Oppenheimer approximation:

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

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

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

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

One-electron wavefunction

- Let us start with Schrödinger theory: the quantum state of a single electron is written as

$$|\Psi\rangle = \int \mathrm{d}\mathbf{r}\ \Psi(\mathbf{r})|\mathbf{r}\rangle$$

where $\Psi(\mathbf{r})$ is the one-electron wavefunction (orbital) and $|\mathbf{r}\rangle$ denotes the quantum state "the electron is at position $\mathbf{r}$". In other words, $\boxed{\hat{\mathbf{r}}|\mathbf{r}\rangle = \mathbf{r}|\mathbf{r}\rangle.}$

- This choice of basis is known as "$\mathbf{r}$ representation".

- Orthonormalization condition: $\langle\mathbf{r}'|\mathbf{r}\rangle = \delta(\mathbf{r}'-\mathbf{r})$ ⟵ Dirac distribution

Useful formulas: **(1)** "$\forall f$", $\displaystyle\int \mathrm{d}\mathbf{r}\ f(\mathbf{r})\delta(\mathbf{r}'-\mathbf{r}) = f(\mathbf{r}')$

(2) $$\delta(\mathbf{r}'-\mathbf{r}) = \frac{1}{(2\pi)^3}\int \mathrm{d}\mathbf{k}\ e^{\mathrm{i}\mathbf{k}.(\mathbf{r}'-\mathbf{r})}$$

- In this representation, the momentum vector operator is defined as follows,

$$\hat{\mathbf{p}}|\Psi\rangle = -\mathrm{i}\int \mathrm{d}\mathbf{r}\,\boldsymbol{\nabla}_{\mathbf{r}}\Psi(\mathbf{r})|\mathbf{r}\rangle$$

- "k representation": $|\mathbf{k}\rangle = \dfrac{1}{(2\pi)^{3/2}}\displaystyle\int \mathrm{d}\mathbf{r}\; e^{\mathrm{i}\mathbf{k}.\mathbf{r}}|\mathbf{r}\rangle$

Note that $\boxed{\hat{\mathbf{p}}|\mathbf{k}\rangle = \mathbf{k}|\mathbf{k}\rangle}$ and $\langle\mathbf{k}'|\mathbf{k}\rangle = \delta(\mathbf{k}'-\mathbf{k})$ ⟵ use formula **(2)** !

- Pauli theory: the spin of the electron is now considered as an additional degree of freedom. The quantum state of a single electron is then written as

$$|\Psi\rangle = \int \mathrm{d}\mathbf{r} \sum_{\sigma=\alpha,\beta} \Psi(\mathbf{r},\sigma)|\mathbf{r},\sigma\rangle$$

where $|\mathbf{r},\alpha\rangle$ denotes the quantum state "electron at position $\mathbf{r}$ with spin up" and $|\mathbf{r},\beta\rangle$ corresponds to the state "electron at position $\mathbf{r}$ with spin down"

Two-electron wavefunction

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

- With the notations $X = (\mathbf{r},\sigma)$ and $\int \mathrm{d}X = \int \mathrm{d}\mathbf{r} \sum_{\sigma=\alpha,\beta}$,

  a one-electron quantum state in Pauli theory is simply written as

$$|\Psi\rangle = \int \mathrm{d}X\, \Psi(X)|X\rangle$$

- Two-electron case:

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

  where the two-electron quantum state $|1\colon X_1, 2\colon X_2\rangle$ corresponds to "electron 1 in state $|X_1\rangle$ and electron 2 in state $|X_2\rangle$"

- Anti-symmetrization principle: a physical two-electron wavefunction should fulfill the condition

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

thus leading to

$$|\Psi\rangle=-\int\!\!\int \mathrm{d}X_1\mathrm{d}X_2\,\Psi(X_2,X_1)|1\colon \boxed{X_1},2\colon X_2\rangle=\underbrace{-\int\!\!\int \mathrm{d}X_1\mathrm{d}X_2\,\Psi(X_1,X_2)|1\colon X_2,2\colon \boxed{X_1}\rangle}_{|\Psi_{1\leftrightarrow 2}\rangle}$$

and

$$|\Psi\rangle=\frac{1}{2}\int\!\!\int \mathrm{d}X_1\mathrm{d}X_2\,\underbrace{\Big[\Psi(X_1,X_2)-\Psi(X_2,X_1)\Big]}_{0\quad\text{if}\quad X_1=X_2}|1\colon X_1,2\colon X_2\rangle$$

Conclusion: the anti-symmetrization of the wavefunction ensures that electrons are indistinguishable and that they cannot be in the same quantum state (Pauli principle).

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

$$\Phi_{IJ}(X_1,X_2)=\frac{1}{\sqrt{2}}\begin{vmatrix}\varphi_I(X_1) & \varphi_I(X_2)\\ \varphi_J(X_1) & \varphi_J(X_2)\end{vmatrix}=\frac{1}{\sqrt{2}}\Big(\varphi_I(X_1)\varphi_J(X_2)-\varphi_I(X_2)\varphi_J(X_1)\Big)$$

- 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

"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.

- At the beginning, there was "nothing" ... $|\text{vac}\rangle$ $\longleftarrow$ normalized "vacuum state"

- ... then was introduced the concept of annihilation of an electron occupying φ_I , that would obviously give zero when applied to the vacuum state: $\boxed{\forall\, I, \quad \hat{a}_I|\text{vac}\rangle = 0}$ **(rule 1)**

- ... and then came the concept of creation of an electron occupying φ_I: $\hat{a}_I^\dagger|\text{vac}\rangle \equiv |\varphi_I\rangle$

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

- ... and then came the idea to create another electron occupying φ_J: $\hat{a}^\dagger_J \hat{a}^\dagger_I |\text{vac}\rangle \equiv |\Phi_{IJ}\rangle$

- Note that the creation operator $\hat{a}^\dagger_I$ is the adjoint of the annihilation operator $\hat{a}_I$. This ensures, in particular, that one-electron and vacuum states are orthogonal:

$$\langle \varphi_I|\text{vac}\rangle = \langle \hat{a}^\dagger_I \text{vac}|\text{vac}\rangle = \langle \text{vac}|\hat{a}_I|\text{vac}\rangle = 0$$

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

$$\boxed{\forall\, I, J, \quad [\hat{a}_I, \hat{a}_J]_+ = \hat{a}_I\hat{a}_J + \hat{a}_J\hat{a}_I = 0} \qquad \textbf{(rule 2)} \qquad \longrightarrow \qquad \left[\hat{a}^\dagger_I, \hat{a}^\dagger_J\right]_+ = [\hat{a}_J, \hat{a}_I]^\dagger_+ = 0$$

$$\boxed{\forall\, I, J, \quad \left[\hat{a}_I, \hat{a}^\dagger_J\right]_+ = \hat{a}_I\hat{a}^\dagger_J + \hat{a}^\dagger_J\hat{a}_I = \delta_{IJ}} \qquad \textbf{(rule 3)}$$

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

- **Rule 2** contains 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 the Pauli 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: multiply more creation operators !

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

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

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

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

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 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: $\displaystyle\sum_I |\varphi_I\rangle\langle\varphi_I| = \hat{\mathbb{1}}$,

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

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

  Indeed,

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

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

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

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

  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 $\hat{a}^{\dagger}_{\tilde{P}} = \sum_{Q} U_{QP}\,\hat{a}^{\dagger}_{Q}$ and show that $\hat{h} \equiv \sum_{I,J}\langle\tilde{\varphi}_I|\hat{h}|\tilde{\varphi}_J\rangle\hat{a}^{\dagger}_{\tilde{I}}\hat{a}_{\tilde{J}}$.

(3) Show how the diagonalization of $\hat{h}$ in the one-electron space leads automatically to the diagonalization in the N-electron space (use exercise page 11).

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:

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

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

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

- 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 $\hat{w}_{\mathcal{A}} \equiv \dfrac{1}{2} \displaystyle\sum_{IJKL} \langle \varphi_I \varphi_J | \hat{w} | \varphi_K \varphi_L \rangle \; \hat{a}^\dagger_I \hat{a}^\dagger_J \hat{a}_L \hat{a}_K$

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

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

Summary

- In summary, the electronic Hamiltonian can be written in second quantization as follows,

$$\hat{H} = \sum_{IJ} \langle \varphi_I | \hat{h} | \varphi_J \rangle \hat{a}^\dagger_I \hat{a}_J + \frac{1}{2} \sum_{IJKL} \langle \varphi_I \varphi_J | \hat{w}_{\mathrm{ee}} | \varphi_K \varphi_L \rangle \; \hat{a}^\dagger_I \hat{a}^\dagger_J \hat{a}_L \hat{a}_K$$

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

$\langle \varphi_I \varphi_J | \hat{w}_{\mathrm{ee}} | \varphi_K \varphi_L \rangle = \int \int \mathrm{d}X_1 \mathrm{d}X_2 \, \varphi^*_I(X_1) \varphi^*_J(X_2) \Big(\hat{w}_{\mathrm{ee}} \varphi_K \varphi_L \Big)(X_1, X_2)$ ←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:

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

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

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

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

where $\hat{E}_{pq} = \sum_\sigma \hat{a}^\dagger_{p,\sigma}\hat{a}_{q,\sigma}$, $\quad h_{pq} = \langle\phi_p|\hat{h}|\phi_q\rangle$ 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 $|\Phi_i^a\rangle = \dfrac{1}{\sqrt{2}}\hat{E}_{ai}|\Phi\rangle$ and $|\Phi_{ij}^{ab}\rangle = \dfrac{1}{2}\hat{E}_{ai}\hat{E}_{bj}|\Phi\rangle$ with $i < j,\ a < b$.

Why "second" quantization ?

- Let us consider a single electron occupying the spin-orbital $\Psi(X) = \Psi(\mathbf{r}, \sigma)$. The corresponding expectation value for the nuclear potential energy equals

$$\langle \Psi | \hat{v}_{\mathrm{ne}} | \Psi \rangle = \int \mathrm{d}X \; \Psi^*(X) v_{\mathrm{ne}}(\mathbf{r}) \Psi(X) = \int \mathrm{d}\mathbf{r} \, v_{\mathrm{ne}}(\mathbf{r}) \underbrace{\sum_{\sigma} \Psi^*(\mathbf{r}, \sigma) \Psi(\mathbf{r}, \sigma)}_{n(\mathbf{r}): \quad \text{density}}$$

- For an arbitrary number of electrons: $\hat{V}_{\mathrm{ne}} = \sum_{i=1}^{N} \hat{v}_{\mathrm{ne}}(i) \equiv \sum_{p,q} \langle \phi_p | \hat{v}_{\mathrm{ne}} | \phi_q \rangle \hat{E}_{pq}$

- Change of basis: $\{ |\phi_p\rangle \}_p \quad \longrightarrow \quad \{ |\mathbf{r}\rangle \}_{\mathbf{r} \in \mathbb{R}^3},$

$$\langle \phi_p | \hat{v}_{\mathrm{ne}} | \phi_q \rangle \quad \longrightarrow \quad \langle \mathbf{r}' | \hat{v}_{\mathrm{ne}} | \mathbf{r} \rangle = v_{\mathrm{ne}}(\mathbf{r}) \delta(\mathbf{r}' - \mathbf{r})$$

$$\hat{a}^\dagger_{p,\sigma} \quad \longrightarrow \quad \hat{a}^\dagger_{\mathbf{r},\sigma} = \hat{\Psi}^\dagger(\mathbf{r}, \sigma)$$

thus leading to $\boxed{\hat{V}_{\text{ne}} = \displaystyle\int \text{d}\mathbf{r}\, v_{\text{ne}}(\mathbf{r})\, \hat{n}(\mathbf{r})}$ $\longleftarrow$ local potential operator !

where the density operator equals $\hat{n}(\mathbf{r}) = \displaystyle\sum_{\sigma} \hat{\Psi}^{\dagger}(\mathbf{r},\sigma)\hat{\Psi}(\mathbf{r},\sigma).$

- Note that the electron density associated with the normalized N-electron wavefunction Ψ equals $n_{\Psi}(\mathbf{r}) = \langle \Psi|\hat{n}(\mathbf{r})|\Psi\rangle$.

- Note also that $\displaystyle\int \text{d}\mathbf{r}\, \hat{n}(\mathbf{r}) = \hat{N} \quad \longrightarrow \quad \int \text{d}\mathbf{r}\, n_{\Psi}(\mathbf{r}) = \langle \Psi|\hat{N}|\Psi\rangle = N$

- In practice, the density is usually obtained from the molecular orbitals and the 1RDM:

$$|\mathbf{r},\sigma\rangle = \sum_{p} |\phi_p,\sigma\rangle\langle\phi_p|\mathbf{r}\rangle = \sum_{p} \phi_p(\mathbf{r})|\phi_p,\sigma\rangle \quad \longrightarrow \quad \hat{n}(\mathbf{r}) = \sum_{pq} \phi_p(\mathbf{r})\phi_q(\mathbf{r})\hat{E}_{pq}$$

$$\longrightarrow \quad n_{\Psi}(\mathbf{r}) = \sum_{pq} \phi_p(\mathbf{r})\phi_q(\mathbf{r})D_{pq}$$

EXERCISE:

(1) Show that the kinetic energy operator is written as follows in the **k** representation:

$$\hat{T}=\sum_{i=1}^{N}\frac{1}{2}\widehat{\mathbf{p}^2}(i)\equiv\int \mathrm{d}\mathbf{k}\,\frac{k^2}{2}\sum_{\sigma}\hat{\Psi}^{\dagger}(\mathbf{k},\sigma)\hat{\Psi}(\mathbf{k},\sigma)\qquad\text{where}\quad \hat{\Psi}^{\dagger}(\mathbf{k},\sigma)=\hat{a}^{\dagger}_{\mathbf{k},\sigma}.$$

(2) Explain why $\hat{\Psi}^{\dagger}(\mathbf{k},\sigma)=\dfrac{1}{(2\pi)^{3/2}}\displaystyle\int \mathrm{d}\mathbf{r}\,e^{\mathrm{i}\mathbf{k}.\mathbf{r}}\;\hat{\Psi}^{\dagger}(\mathbf{r},\sigma)$ and

$$\hat{\Psi}^{\dagger}(\mathbf{r},\sigma)=\frac{1}{(2\pi)^{3/2}}\int \mathrm{d}\mathbf{k}\,e^{-\mathrm{i}\mathbf{k}.\mathbf{r}}\;\hat{\Psi}^{\dagger}(\mathbf{k},\sigma)$$

(3) Conclude that

$$\boxed{\hat{T}\equiv-\frac{1}{2}\int \mathrm{d}\mathbf{r}\sum_{\sigma}\hat{\Psi}^{\dagger}(\mathbf{r},\sigma)\nabla^2_{\mathbf{r}}\hat{\Psi}(\mathbf{r},\sigma)}$$

(4) Let $\hat{n}_1(\mathbf{r}',\mathbf{r}) = \sum_\sigma \hat{\Psi}^\dagger(\mathbf{r}',\sigma)\hat{\Psi}(\mathbf{r},\sigma)$ denote the one-electron density matrix operator. Deduce from question **(3)** the standard expression

$$\hat{T} \equiv -\frac{1}{2}\int\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\,\delta(\mathbf{r}'-\mathbf{r})\nabla^2_{\mathbf{r}}\hat{n}_1(\mathbf{r}',\mathbf{r})$$

(5) Show that the one-electron density matrix operator is connected with the $\hat{E}_{pq}$ operators as follows,

$$\hat{n}_1(\mathbf{r}',\mathbf{r}) = \sum_{pq}\phi_p(\mathbf{r}')\phi_q(\mathbf{r})\hat{E}_{pq}$$

(6) The one-electron density matrix associated with the wavefunction Ψ is defined as
$n_1(\mathbf{r}',\mathbf{r}) = \langle\Psi|\hat{n}_1(\mathbf{r}',\mathbf{r})|\Psi\rangle$.

We already know that the 1RDM enables to compute the electron density. Is it possible to restore the 1RDM from the electron density alone ?

Hint: show that the full one-electron density matrix is required for constructing each elements of the 1RDM.

Pair density operator

- Two-electron repulsion operator in the **r** representation:

$$\hat{E}_{pq} \longrightarrow \sum_{\sigma} \hat{\Psi}^{\dagger}(\mathbf{r}_1,\sigma)\hat{\Psi}(\mathbf{r}_2,\sigma)$$

$$\langle pr|qs\rangle \longrightarrow \langle \mathbf{r}_1\mathbf{r}_2|\hat{w}_{\mathrm{ee}}|\mathbf{r}_3\mathbf{r}_4\rangle = \frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\delta(\mathbf{r}_1-\mathbf{r}_3)\delta(\mathbf{r}_2-\mathbf{r}_4)$$

$$\hat{W}_{\mathrm{ee}} = \frac{1}{2}\sum_{p,q,r,s}\langle pr|qs\rangle\Big(\hat{E}_{pq}\hat{E}_{rs} - \delta_{qr}\hat{E}_{ps}\Big) \longrightarrow \boxed{\hat{W}_{\mathrm{ee}} = \frac{1}{2}\int\int \mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2\,\frac{\hat{n}_2(\mathbf{r}_1,\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}}$$

where $\hat{n}_2(\mathbf{r}_1,\mathbf{r}_2) = \hat{n}(\mathbf{r}_1)\hat{n}(\mathbf{r}_2) - \delta(\mathbf{r}_1-\mathbf{r}_2)\hat{n}(\mathbf{r}_1)$ $\longleftarrow$ pair density operator !

Pair density operator

- Expectation value for the two-electron repulsion:

$$\langle\Psi|\hat{W}_{\mathrm{ee}}|\Psi\rangle = \frac{1}{2}\int\int \mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2\,\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\Big(\langle\Psi|\hat{n}(\mathbf{r}_1)\hat{n}(\mathbf{r}_2)|\Psi\rangle - \delta(\mathbf{r}_1-\mathbf{r}_2)n_\Psi(\mathbf{r}_1)\Big)$$

- If Ψ is the ground-state wavefunction of an interacting electronic system ($\hat{w}\neq 0$), it is usual in density-functional theory (DFT) to consider the Kohn–Sham (KS) Slater determinant Φ^{KS} that is the ground-state wavefunction of the non-interacting system ($\hat{w}=0$) that has exactly the same electron density:

$$n_{\Phi^{\mathrm{KS}}}(\mathbf{r}_1) = n_\Psi(\mathbf{r}_1),$$

thus leading to

$$\langle\Psi|\hat{W}_{\mathrm{ee}}|\Psi\rangle - \langle\Phi^{\mathrm{KS}}|\hat{W}_{\mathrm{ee}}|\Phi^{\mathrm{KS}}\rangle = \frac{1}{2}\int\int \mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2\,\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\Big[\langle\Psi|\hat{n}(\mathbf{r}_1)\hat{n}(\mathbf{r}_2)|\Psi\rangle - \langle\Phi^{\mathrm{KS}}|\hat{n}(\mathbf{r}_1)\hat{n}(\mathbf{r}_2)|\Phi^{\mathrm{KS}}\rangle\Big]$$

- This expression can be used in the calculation of the correlation energy (adiabatic connection fluctuation-dissipation theorem)

Hubbard Hamiltonian

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

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

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

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

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

Spin operators

- Spin vector operator in second quantization:

$$\hat{\mathbf{S}} = \sum_{i=1}^{N} \hat{\mathbf{s}}(i) \quad \equiv \quad \sum_{pq,\sigma\sigma'} \underbrace{\langle \phi_p, \sigma | \hat{\mathbf{s}} | \phi_q, \sigma' \rangle}\, \hat{a}^\dagger_{p,\sigma} \hat{a}_{q,\sigma'}$$

$$\langle \phi_p, \sigma | \phi_q, \hat{\mathbf{s}}\, \sigma' \rangle = \delta_{pq} \langle \sigma | \hat{\mathbf{s}} | \sigma' \rangle = \delta_{pq} \mathbf{s}_{\sigma\sigma'}$$

with $\hat{s}^{\mathrm{x}} \equiv \frac{1}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$, $\hat{s}^{\mathrm{y}} \equiv \frac{1}{2}\begin{bmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{bmatrix}$, $\hat{s}^{\mathrm{z}} \equiv \frac{1}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$,

thus leading to $\boxed{\hat{\mathbf{S}} \equiv \sum_p \hat{\mathbf{S}}_p}$ where

$$\hat{S}_p^{\mathrm{x}} = \frac{1}{2}\left(\hat{a}^\dagger_{p,\uparrow}\hat{a}_{p,\downarrow} + \hat{a}^\dagger_{p,\downarrow}\hat{a}_{p,\uparrow}\right), \quad \hat{S}_p^{\mathrm{y}} = \frac{1}{2\mathrm{i}}\left(\hat{a}^\dagger_{p,\uparrow}\hat{a}_{p,\downarrow} - \hat{a}^\dagger_{p,\downarrow}\hat{a}_{p,\uparrow}\right), \quad \hat{S}_p^{\mathrm{z}} = \frac{1}{2}\left(\hat{a}^\dagger_{p,\uparrow}\hat{a}_{p,\uparrow} - \hat{a}^\dagger_{p,\downarrow}\hat{a}_{p,\downarrow}\right).$$

EXERCISE:

(1) Show that $\left[\hat{A},\hat{B}\hat{C}\right]=\left[\hat{A},\hat{B}\right]\hat{C}+\hat{B}\left[\hat{A},\hat{C}\right]=\left[\hat{A},\hat{B}\right]_{+}\hat{C}-\hat{B}\left[\hat{A},\hat{C}\right]_{+}.$

(2) Deduce from **(1)** that $\left[\hat{a}^{\dagger}_{p,\sigma}\hat{a}_{q,\sigma'},\hat{a}^{\dagger}_{r,\tau}\hat{a}_{s,\tau'}\right]=\delta_{rq}\delta_{\tau\sigma'}\hat{a}^{\dagger}_{p,\sigma}\hat{a}_{s,\tau'}-\delta_{sp}\delta_{\tau'\sigma}\hat{a}^{\dagger}_{r,\tau}\hat{a}_{q,\sigma'}.$

We suggest to use in the following the notation $\hat{\mathbf{S}}_p=\sum_{\sigma\sigma'}\mathbf{s}_{\sigma\sigma'}\hat{a}^{\dagger}_{p,\sigma}\hat{a}_{p,\sigma'}.$

(3) Explain why $\left[\hat{S}^{\mathrm{x}},\hat{S}^{\mathrm{y}}\right]=\sum_{p}\left[\hat{S}^{\mathrm{x}}_{p},\hat{S}^{\mathrm{y}}_{p}\right].$

(4) Prove that $\left[\hat{S}^{\mathrm{x}}_{p},\hat{S}^{\mathrm{y}}_{p}\right]=\mathrm{i}\,\hat{S}^{\mathrm{z}}_{p}.$ **Hint**: use **(2)** and the equality $[\hat{s}^{\mathrm{x}},\hat{s}^{\mathrm{y}}]=\mathrm{i}\,\hat{s}^{\mathrm{z}}.$

(5) Conclude that $\hat{\mathbf{S}}$ is an angular momentum operator: $\boxed{\left[\hat{S}^{\mathrm{x}},\hat{S}^{\mathrm{y}}\right]=\mathrm{i}\,\hat{S}^{\mathrm{z}}}.$

Spin operators

- Another important model Hamiltonian is the Heisenberg Hamiltonian:

$$\hat{H} \quad \longrightarrow \quad -J \sum_{p} \hat{\mathbf{S}}_{p} \,.\, \hat{\mathbf{S}}_{p+1}$$