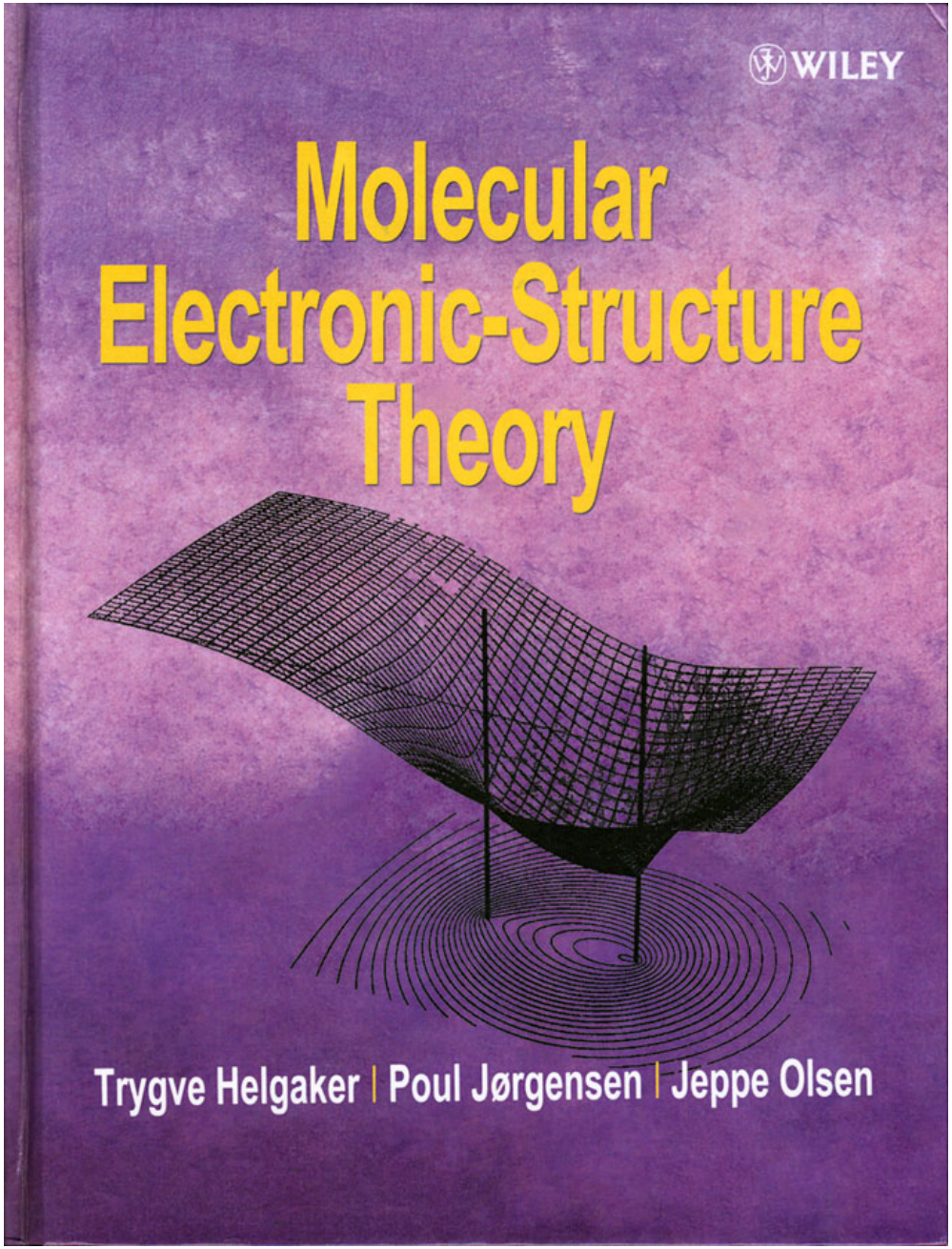
Second quantization

Emmanuel Fromager

Laboratoire de Chimie Quantique, Institut de Chimie de Strasbourg,
Université de Strasbourg, Strasbourg, France.

Textbook


WILEY
Molecular Electronic-Structure Theory
Trygve Helgaker | Poul Jørgensen | Jeppe Olsen

Outline

- **Standard (first quantization) formalism**

  Atomic *orbitals*, molecular *spin-orbitals*, Slater *determinants*.

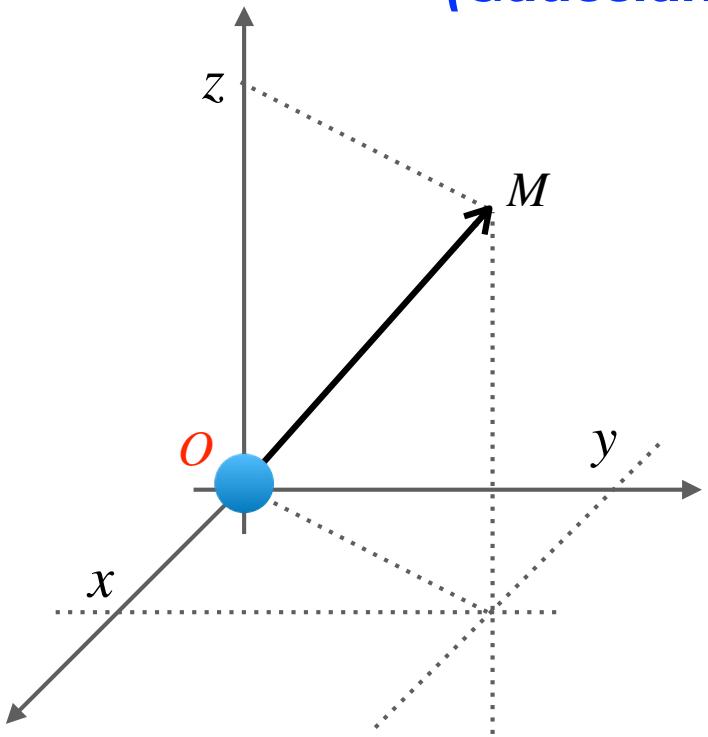
- **Second quantization formalism**

  Vacuum state, *creation* operators, *annihilation* operators,
  excitation operators, one- and two-electron *Hamiltonian* operators.

- **Why “second” quantization?**

  Field operators, *density* operator, one-electron reduced *density matrix*,
  and one-electron *Green function*.

(Gaussian) atomic orbitals



$$\overrightarrow{OM} = \mathbf{r} \equiv (x, y, z)$$

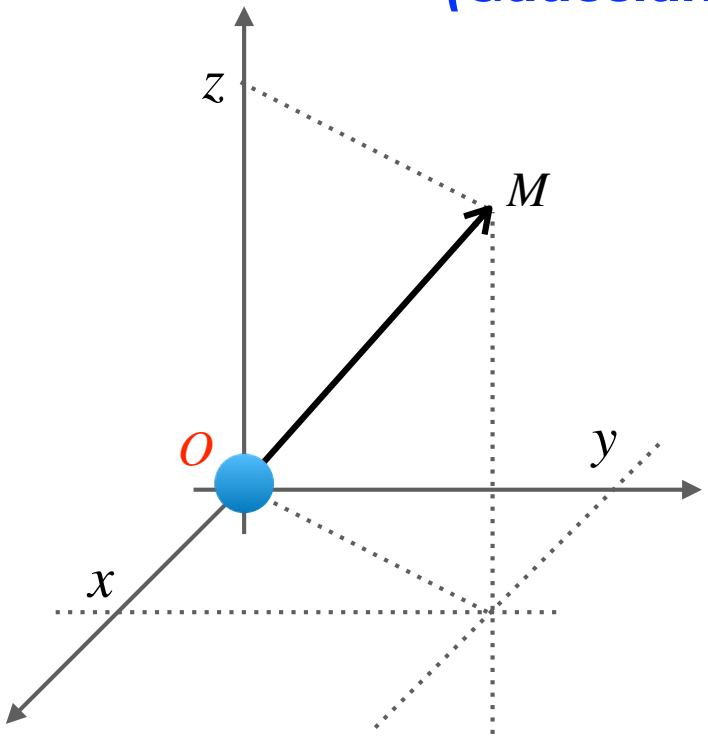
$$\chi(\mathbf{r}) \sim x^m y^n z^p \, e^{-\alpha(x^2+y^2+z^2)}$$

integers

Exponent

Atomic orbital

(Gaussian) atomic orbitals



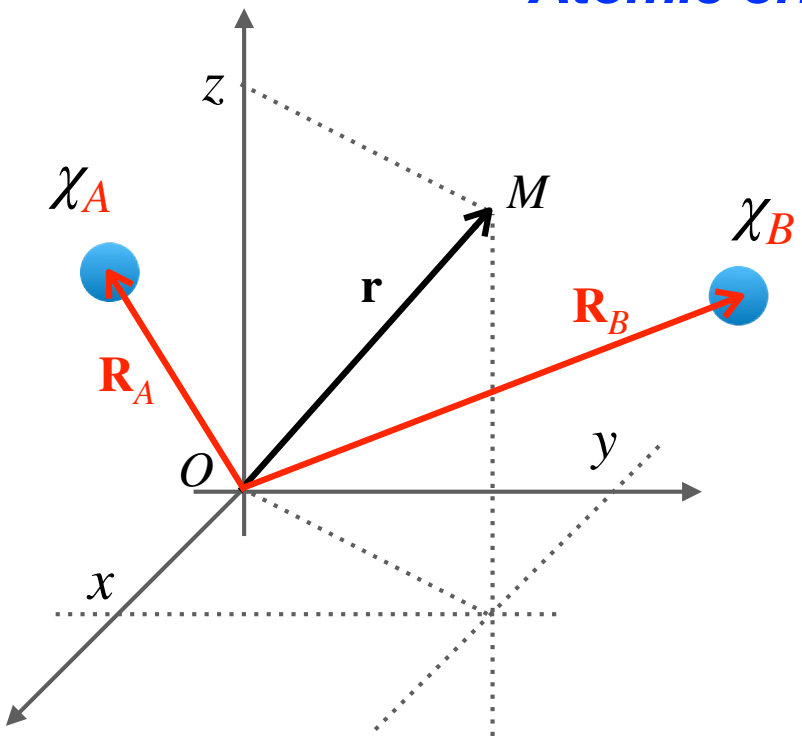
$$\overrightarrow{OM} = \mathbf{r} \equiv (x, y, z)$$

$$\chi(\mathbf{r}) \overset{s\ orbital}{\sim} e^{-\alpha(x^2+y^2+z^2)}$$

$$\chi(\mathbf{r}) \overset{p_x\ orbital}{\sim} x\, e^{-\alpha(x^2+y^2+z^2)}$$

$$\chi(\mathbf{r}) \overset{d_{yz}\ orbital}{\sim} yz\, e^{-\alpha(x^2+y^2+z^2)}$$

Atomic orbital basis

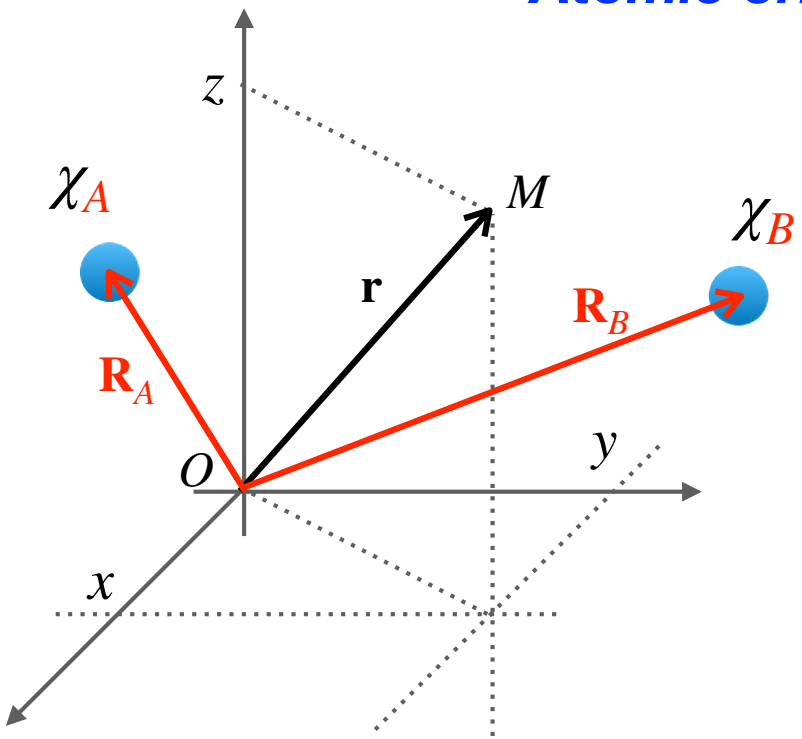


"Paving space with atomic orbitals"

$$\chi_A(\mathbf{r}) = \chi\left(\mathbf{r}-\mathbf{R}_A\right)$$

$$\chi_B(\mathbf{r}) = \chi\left(\mathbf{r}-\mathbf{R}_B\right)$$

Atomic orbital basis

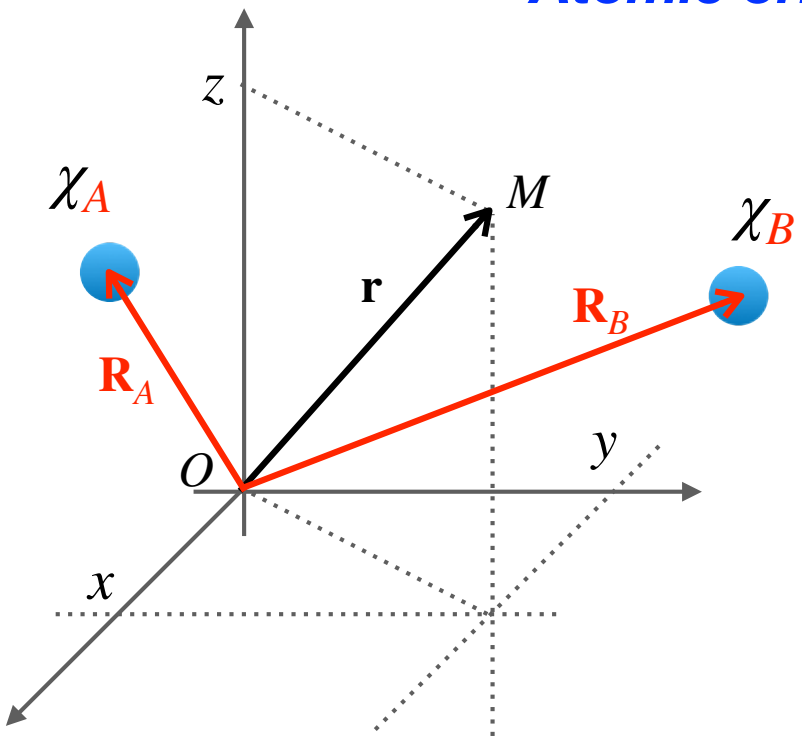


"Paving space with atomic orbitals"

$$\chi_A(\mathbf{r}) = \chi\left(\mathbf{r}-\mathbf{R}_A\right)$$

$$p_x \text{ orbital} \sim \left(x-X_A\right)\ e^{-\alpha\left((x-X_A)^2+(y-Y_A)^2+(z-Z_A)^2\right)}$$

Atomic orbital basis



"Paving space with atomic orbitals"

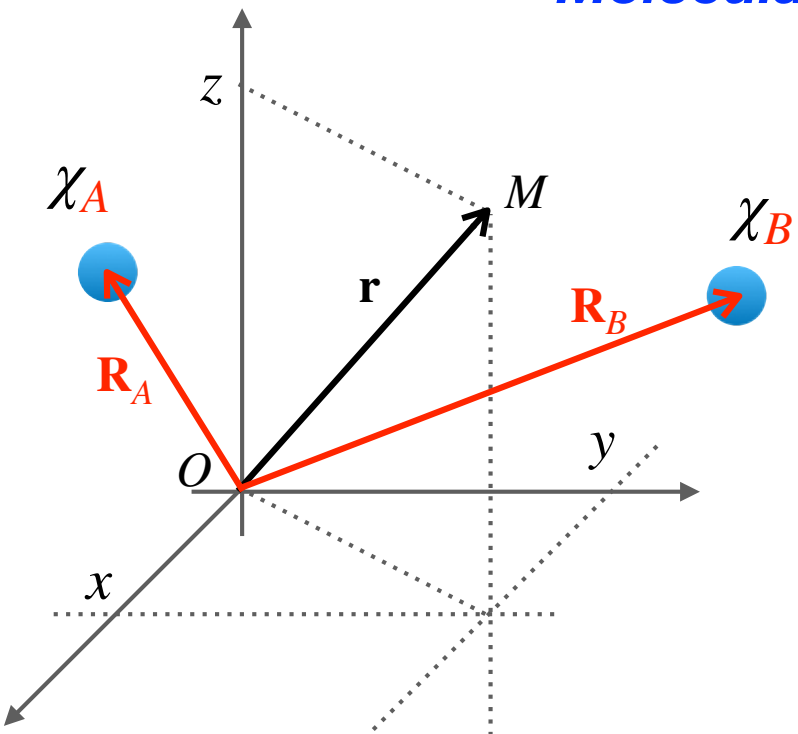
$$\chi_A(\mathbf{r}) = \chi\left(\mathbf{r}-\mathbf{R}_A\right) \qquad \chi_B(\mathbf{r}) = \chi\left(\mathbf{r}-\mathbf{R}_B\right)$$

Overlap

$$\langle \chi_A | \chi_B \rangle = \int d\mathbf{r}\, \chi_A(\mathbf{r})\chi_B(\mathbf{r}) \neq 0$$

Non-orthonormal *basis!*

Molecular orbitals

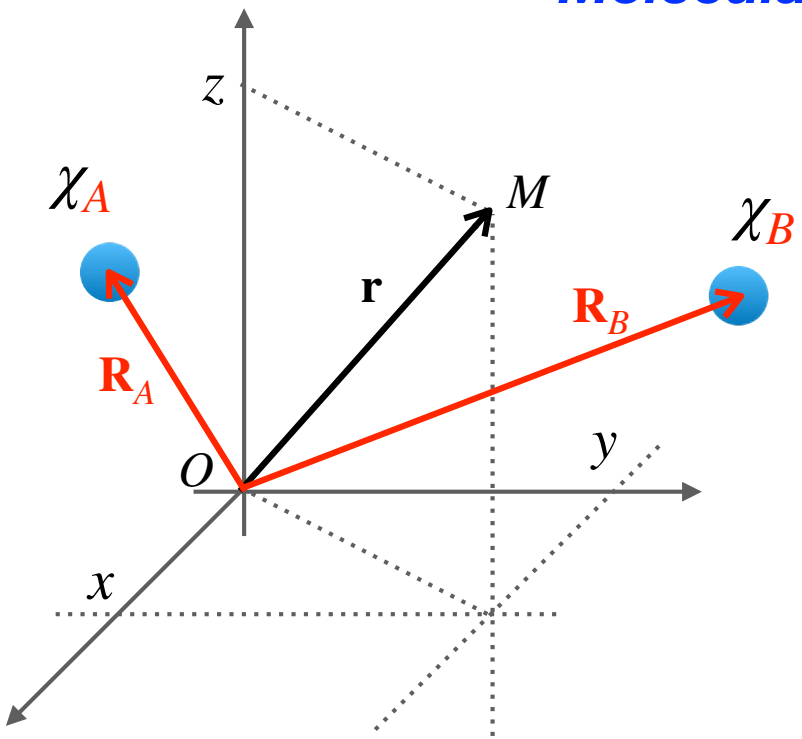


Coefficients of the Molecular Orbital (CMOs)

$$\varphi_p(\mathbf{r}) = C_{Ap}\,\chi_A(\mathbf{r}) + C_{Bp}\,\chi_B(\mathbf{r})$$

***Label** of the molecular orbital (bonding, anti-bonding, HOMO, LUMO, etc…)*

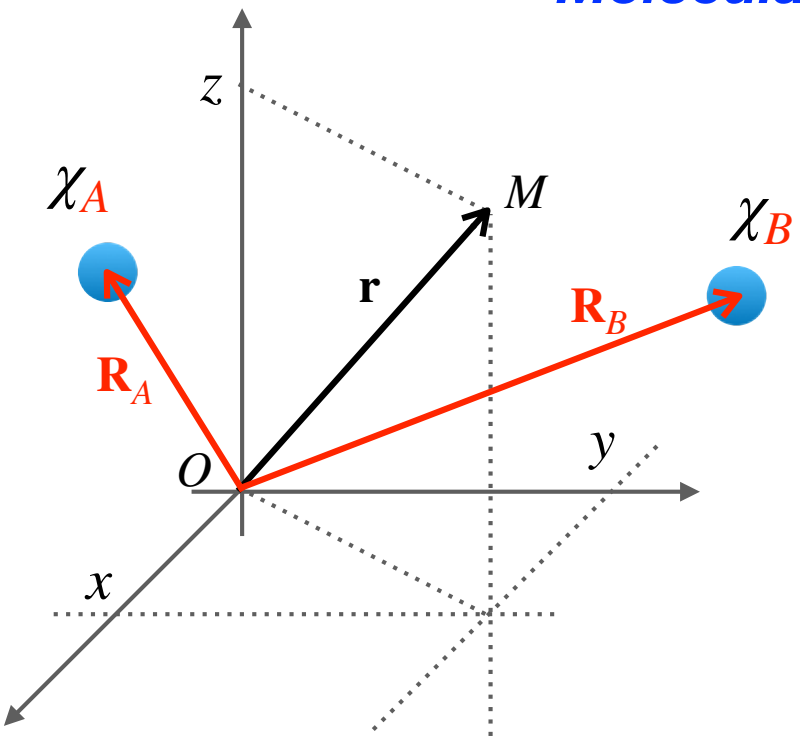
Molecular orbitals



$$\varphi_p(\mathbf{r}) = C_{Ap}\,\chi_A(\mathbf{r}) + C_{Bp}\,\chi_B(\mathbf{r})$$

$$\overset{notation}{\equiv} \sum_{\mu} C_{\mu p}\chi_{\mu}(\mathbf{r})$$

Molecular orbitals



$$\langle \varphi_p \,|\, \varphi_q \rangle = \int d\mathbf{r}\, \varphi_p(\mathbf{r}) \varphi_q(\mathbf{r}) = \delta_{pq}$$

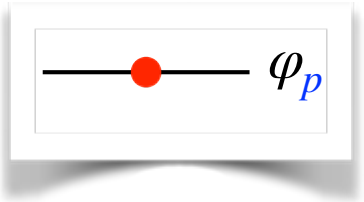
Kronecker delta
(=1 if $p = q$, 0 otherwise)

Eigenfunctions
of some hermitian operator
(Fock operator, for example)

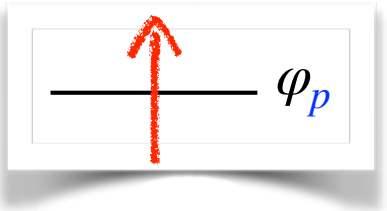
Orthonormal
basis!

Molecular spin-orbitals

$\varphi_p(\mathbf{r})$

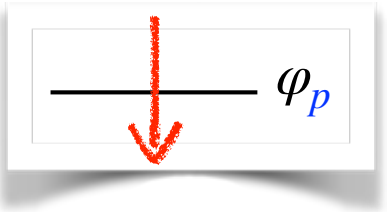


$$\varphi_{p,\alpha}(\mathbf{r},\sigma) = \varphi_p(\mathbf{r}) \times \delta_{\sigma\alpha}$$



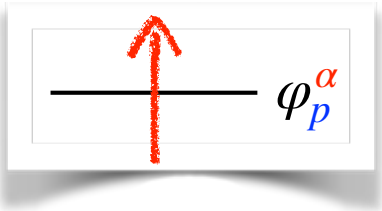
Spin variable

$$\varphi_{p,\beta}(\mathbf{r},\sigma) = \varphi_p(\mathbf{r}) \times \delta_{\sigma\beta}$$



Molecular spin-orbitals

$$\varphi_{p,\alpha}(\mathbf{r},\sigma) = \varphi_p^{\alpha}(\mathbf{r}) \times \delta_{\sigma\alpha}$$



Unrestricted *formalism*

$$\varphi_{p,\beta}(\mathbf{r},\sigma) = \varphi_p^{\beta}(\mathbf{r}) \times \delta_{\sigma\beta}$$

Molecular spin-orbitals

$$\mathbf{x} \overset{notation}{\equiv} (\mathbf{r}, \sigma)$$

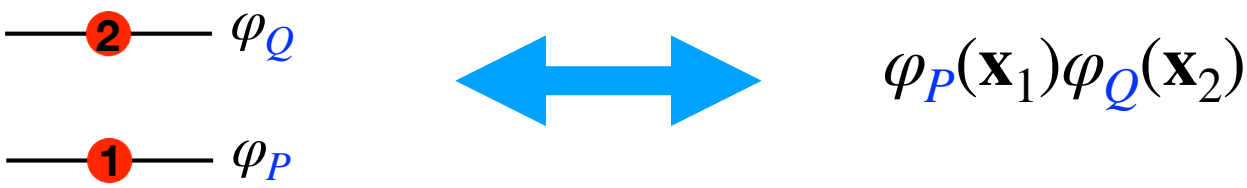
$$\varphi_P(\mathbf{x}) \overset{notation}{\equiv} \varphi_{p,\tau}(\mathbf{r}, \sigma) \quad \longleftarrow \quad \tau = \alpha \text{ or } \beta$$

$$\int d\mathbf{x} \overset{notation}{\equiv} \sum_{\sigma=\alpha,\beta} \int d\mathbf{r}$$

$$\langle \varphi_P \,|\, \varphi_Q \rangle = \int d\mathbf{x}\; \varphi_P^*(\mathbf{x}) \varphi_Q(\mathbf{x}) = \delta_{PQ}$$

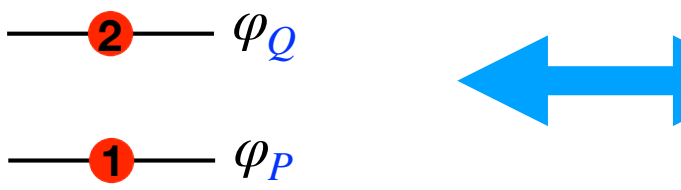
Orthonormal basis!

Two-electron wave functions



$$\varphi_P(\mathbf{x}_1)\varphi_Q(\mathbf{x}_2)$$

Two-electron wave functions

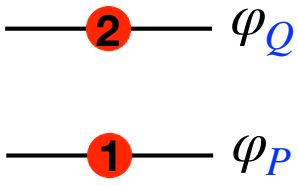


$$\varphi_P(\mathbf{x}_1)\varphi_Q(\mathbf{x}_2)$$

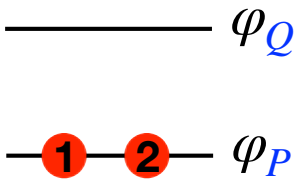
Hartree product

*I **distinguish** the first electron from the second one*

Two-electron wave functions

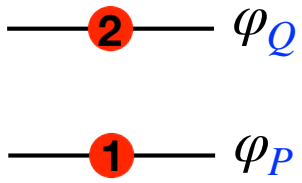


$$\varphi_P(\mathbf{x}_1)\varphi_Q(\mathbf{x}_2)$$

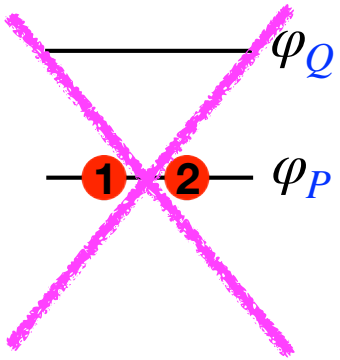


$$\varphi_P(\mathbf{x}_1)\varphi_P(\mathbf{x}_2) \neq 0$$

Two-electron wave functions



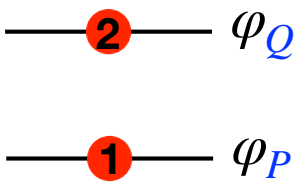
$$\varphi_P(\mathbf{x}_1)\varphi_Q(\mathbf{x}_2)$$

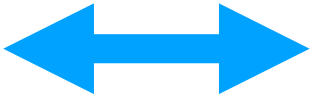


$$\varphi_P(\mathbf{x}_1)\varphi_P(\mathbf{x}_2) \neq 0$$

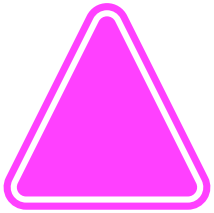
Violates the Pauli principle!

Two-electron wave functions



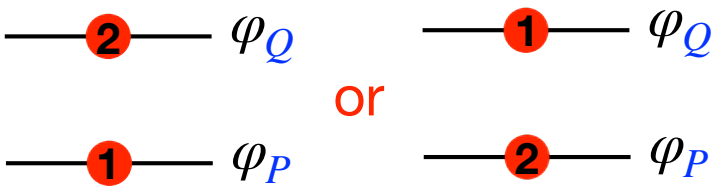


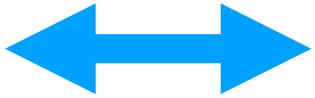
$$\varphi_P(\mathbf{x}_1)\varphi_Q(\mathbf{x}_2)$$



Unphysical!

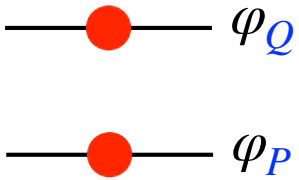
Slater determinants



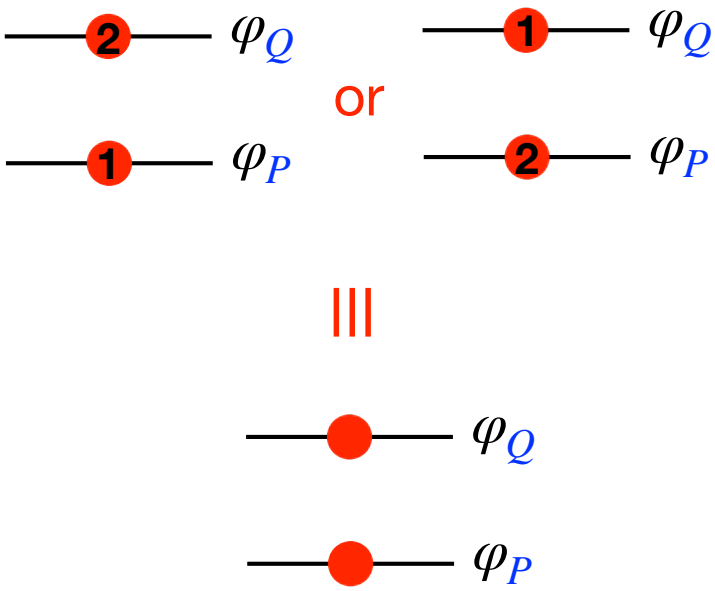


$$\frac{1}{\sqrt{2}}\left(\varphi_P(\mathbf{x}_1)\varphi_Q(\mathbf{x}_2) - \varphi_P(\mathbf{x}_2)\varphi_Q(\mathbf{x}_1)\right)$$

|||



Slater determinants



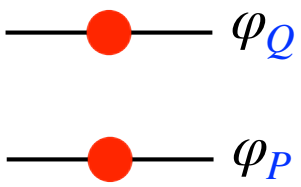
$$\frac{1}{\sqrt{2}}\left(\varphi_P(\mathbf{x}_1)\varphi_Q(\mathbf{x}_2) - \varphi_P(\mathbf{x}_2)\varphi_Q(\mathbf{x}_1)\right)$$

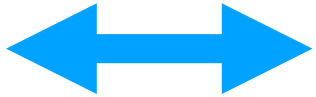
||

$$\frac{1}{\sqrt{2}}\begin{vmatrix}\varphi_P(\mathbf{x}_1) & \varphi_P(\mathbf{x}_2)\\ \varphi_Q(\mathbf{x}_1) & \varphi_Q(\mathbf{x}_2)\end{vmatrix}$$

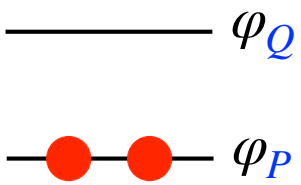
Slater determinant

Slater determinants



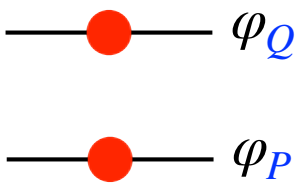


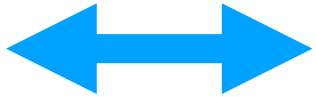
$$\frac{1}{\sqrt{2}}\left(\varphi_P(\mathbf{x}_1)\varphi_Q(\mathbf{x}_2) - \varphi_P(\mathbf{x}_2)\varphi_Q(\mathbf{x}_1)\right)$$



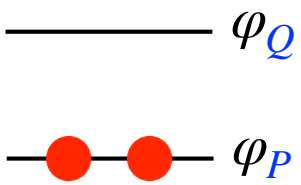
$$0$$

Slater determinants





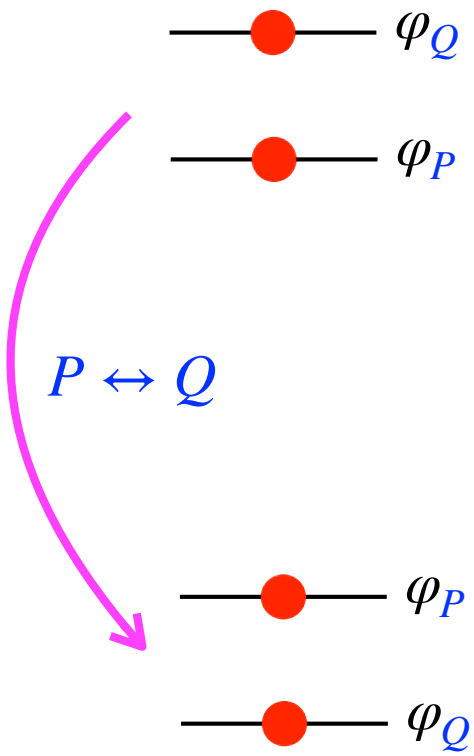
$$\frac{1}{\sqrt{2}}\left(\varphi_P(\mathbf{x}_1)\varphi_Q(\mathbf{x}_2) - \varphi_P(\mathbf{x}_2)\varphi_Q(\mathbf{x}_1)\right)$$



$$0$$

Pauli principle fulfilled!

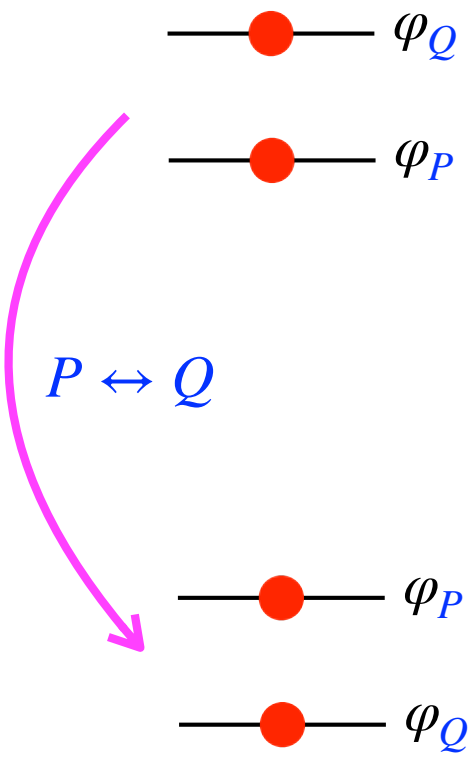
Slater determinants



$$\frac{1}{\sqrt{2}}\left(\varphi_P(\mathbf{x}_1)\varphi_Q(\mathbf{x}_2) - \varphi_P(\mathbf{x}_2)\varphi_Q(\mathbf{x}_1)\right)$$

$$-\frac{1}{\sqrt{2}}\left(\varphi_P(\mathbf{x}_1)\varphi_Q(\mathbf{x}_2) - \varphi_P(\mathbf{x}_2)\varphi_Q(\mathbf{x}_1)\right)$$

Slater determinants



$$\frac{1}{\sqrt{2}}\left(\varphi_P(\mathbf{x}_1)\varphi_Q(\mathbf{x}_2) - \varphi_P(\mathbf{x}_2)\varphi_Q(\mathbf{x}_1)\right)$$

$$-\frac{1}{\sqrt{2}}\left(\varphi_P(\mathbf{x}_1)\varphi_Q(\mathbf{x}_2) - \varphi_P(\mathbf{x}_2)\varphi_Q(\mathbf{x}_1)\right)$$

***anti**symmetric*

Outline

- **Standard (first quantization) formalism**

  Atomic *orbitals*, molecular *spin-orbitals*, Slater *determinants*.

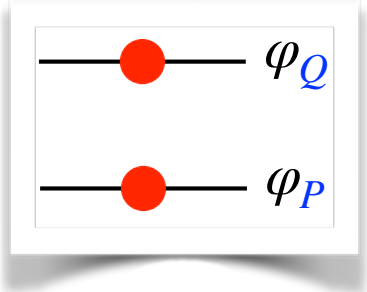
- **Second quantization formalism**

  Vacuum state, *creation* operators, *annihilation* operators,
  excitation operators, one- and two-electron *Hamiltonian* operators.

- **Why “second” quantization?**

  Field operators, *density* operator, one-electron reduced *density matrix*,
  and one-electron *Green function*.

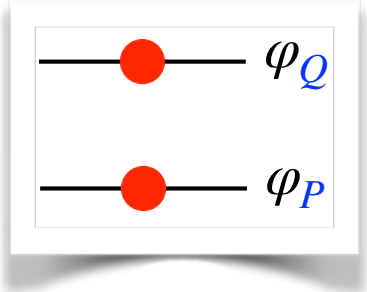
From first to second quantization



$$\frac{1}{\sqrt{2}}\left(\varphi_P(\mathbf{x}_1)\varphi_Q(\mathbf{x}_2) - \varphi_P(\mathbf{x}_2)\varphi_Q(\mathbf{x}_1)\right)$$

Representation
in **first** quantization

From first to second quantization



$$\frac{1}{\sqrt{2}}\left(\varphi_P(\mathbf{x}_1)\varphi_Q(\mathbf{x}_2) - \varphi_P(\mathbf{x}_2)\varphi_Q(\mathbf{x}_1)\right)$$

Representation
in **first** quantization

$$\hat{a}_P^\dagger \hat{a}_Q^\dagger \,|\,\mathrm{vac}\rangle$$

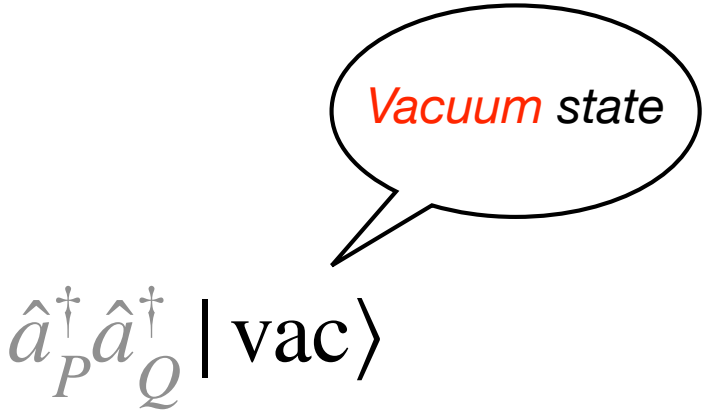
Representation
in **second** quantization

Deciphering the second quantisation formalism

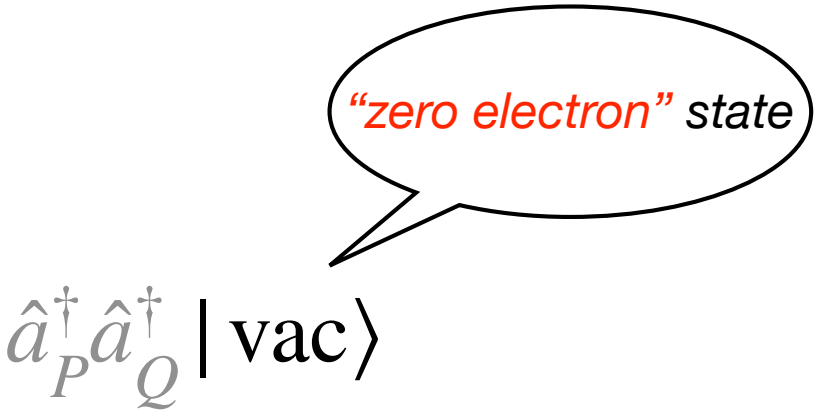
$$\hat{a}_P^\dagger \hat{a}_Q^\dagger \,|\,\mathrm{vac}\rangle$$

Read from right to left

Deciphering the second quantisation formalism



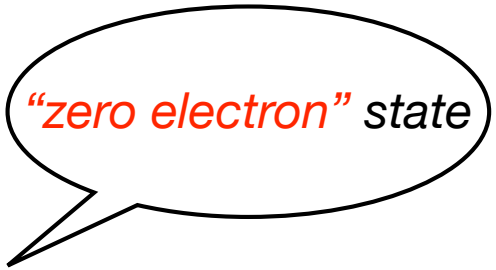
Deciphering the second quantisation formalism



$$\langle \mathrm{vac} \,|\, \mathrm{vac} \rangle = 1$$

*This is **not** the zero vector (whose square norm is **zero**)*
of the Hilbert space of many-electron quantum states

Deciphering the second quantisation formalism



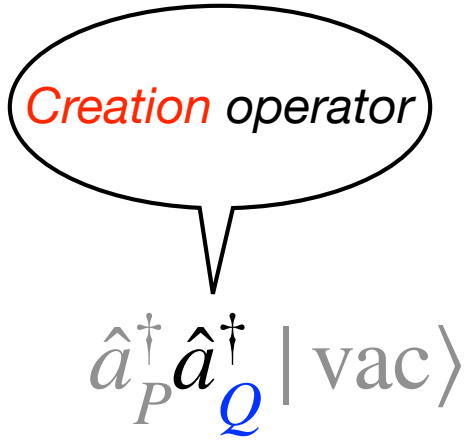
$$\hat{a}_P^\dagger \hat{a}_Q^\dagger \,|\,\mathrm{vac}\rangle$$

$$\langle \mathrm{vac} \,|\, \mathrm{vac} \rangle = 1$$

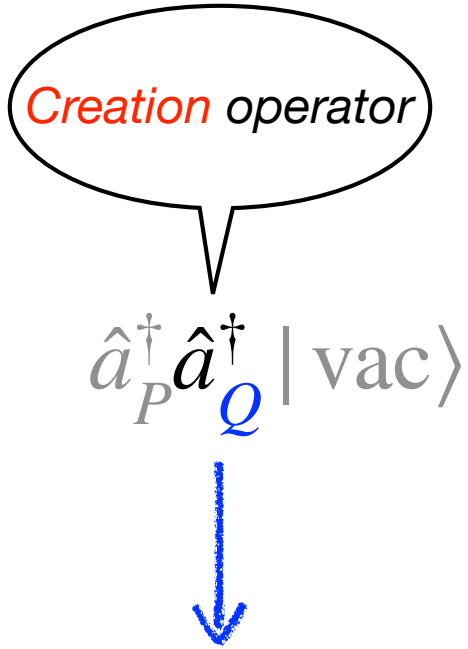
This is not the zero vector (whose square norm is zero)
of the ***Hilbert space of many-electron*** *(zero, one, two, three, etc.)*
quantum states

Fock space

Deciphering the second quantisation formalism



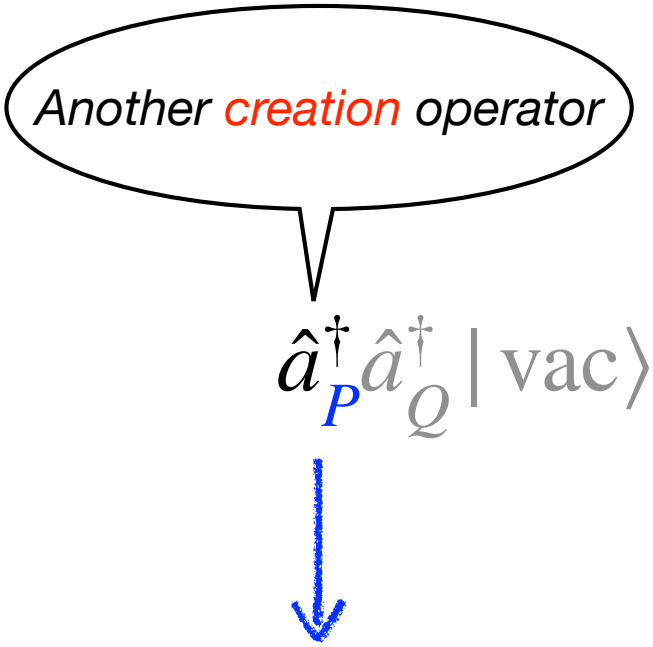
Deciphering the second quantisation formalism



Creates an electron

that occupies the spin-orbital φ_Q

Deciphering the second quantisation formalism



Creates an electron

that occupies the spin-orbital φ_P

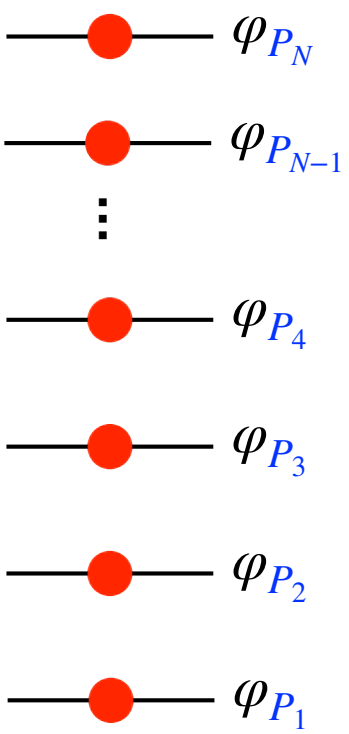
Deciphering the second quantisation formalism

$$\hat{a}_P^\dagger \hat{a}_Q^\dagger |\,\mathrm{vac}\rangle = \hat{a}_P^\dagger \left(\hat{a}_Q^\dagger |\,\mathrm{vac}\rangle \right)$$

The ***product*** of two creation operators describes the ***composition*** of two creations (one after the other)

Exploring the Fock space

Encoding a Slater determinant for an arbitrary number *N* of electrons:



$$\hat{a}^\dagger_{P_1}\hat{a}^\dagger_{P_2}\ldots\hat{a}^\dagger_{P_{N-1}}\hat{a}^\dagger_{P_N}|\mathrm{vac}\rangle$$

Anti-commutation rules

$$\hat{a}^\dagger_P \hat{a}^\dagger_Q = -\hat{a}^\dagger_Q \hat{a}^\dagger_P$$

$P \leftrightarrow Q$

Anti-commutation rules

$$\hat{a}^\dagger_P \hat{a}^\dagger_Q = -\hat{a}^\dagger_Q \hat{a}^\dagger_P$$

$P \leftrightarrow Q$

$$\hat{a}^\dagger_P \hat{a}^\dagger_Q |\,\mathrm{vac}\rangle = -\hat{a}^\dagger_Q \hat{a}^\dagger_P |\,\mathrm{vac}\rangle$$

Anti-commutation rules

$$\hat{a}_P^\dagger \hat{a}_Q^\dagger = -\hat{a}_Q^\dagger \hat{a}_P^\dagger$$

$P \leftrightarrow Q$

$$\hat{a}_P^\dagger \hat{a}_Q^\dagger |\,\mathrm{vac}\rangle = -\hat{a}_Q^\dagger \hat{a}_P^\dagger |\,\mathrm{vac}\rangle$$

$P = Q$

$$2\hat{a}_P^\dagger \hat{a}_P^\dagger |\,\mathrm{vac}\rangle = 0$$

Zero vector
of the Fock space

Anti-commutation rules

$$\hat{a}_P^\dagger \hat{a}_Q^\dagger = -\hat{a}_Q^\dagger \hat{a}_P^\dagger$$

$P \leftrightarrow Q$

$$\hat{a}_P^\dagger \hat{a}_Q^\dagger |\,\mathrm{vac}\rangle = -\hat{a}_Q^\dagger \hat{a}_P^\dagger |\,\mathrm{vac}\rangle$$

$P = Q$

$$\hat{a}_P^\dagger \hat{a}_P^\dagger |\,\mathrm{vac}\rangle = 0 \quad \leftarrow \quad \textit{Pauli principle!}$$

Annihilation operators

$\hat{a}_P^\dagger$ Creation operator

Annihilation operators

Creation operator

$\hat{a}_P^\dagger$ is the ***adjoint*** of the operator $\hat{a}_P$

Annihilation operators

"dagger" *symbol*

Creation operator

$\hat{a}_P^\dagger$ is the ***adjoint*** of the operator $\hat{a}_P$

$$\langle \hat{a}_P^\dagger \Psi \,|\, \Phi \rangle = \langle \Psi \,|\, \hat{a}_P \Phi \rangle$$

Bra **Ket**

Annihilation operators

$\hat{a}_P^\dagger$ Creation operator

What is the physical meaning of $\hat{a}_P$*?*

Annihilation operators

$\hat{a}_P^\dagger$ Creation operator

Exercise:

$$1 = \langle \varphi_P \,|\, \varphi_P \rangle$$

Annihilation operators

$\hat{a}_P^\dagger$ Creation operator

Exercise:

$$1 = \langle \varphi_P | \varphi_P \rangle \equiv \langle \hat{a}_P^\dagger \mathrm{vac} | \hat{a}_P^\dagger \mathrm{vac} \rangle$$

First quantization

Second quantization

Annihilation operators

$\hat{a}_P^\dagger$ Creation operator

$$\langle \hat{a}_P^\dagger \Psi \,|\, \Phi \rangle = \langle \Psi \,|\, \hat{a}_P \Phi \rangle$$

Mathematical definition of the adjoint

Exercise:

$$1 = \langle \varphi_P \,|\, \varphi_P \rangle \equiv \langle \hat{a}_P^\dagger \underbrace{\text{vac}}_{\Psi} \,|\, \hat{a}_P^\dagger \underbrace{\text{vac}}_{\Phi} \rangle = \langle \underbrace{\text{vac}}_{\Psi} \,|\, \hat{a}_P \hat{a}_P^\dagger \underbrace{\text{vac}}_{\Phi} \rangle$$

First quantization

Second quantization

Annihilation operators

$\hat{a}_P^\dagger$ Creation operator

Exercise:

$$1 = \langle \varphi_P \,|\, \varphi_P \rangle \equiv \langle \hat{a}_P^\dagger \mathrm{vac} \,|\, \hat{a}_P^\dagger \mathrm{vac} \rangle = \langle \mathrm{vac} \,|\, \hat{a}_P \, \hat{a}_P^\dagger \mathrm{vac} \rangle = 1 = \langle \mathrm{vac} \,|\, \mathrm{vac} \rangle$$

First quantization

Second quantization

Annihilation operators

$\hat{a}_P^\dagger$ Creation operator

Exercise:

$$1 = \langle \varphi_P | \varphi_P \rangle \equiv \langle \hat{a}_P^\dagger \text{vac} | \hat{a}_P^\dagger \text{vac} \rangle = \langle \text{vac} | \hat{a}_P \hat{a}_P^\dagger \text{vac} \rangle = 1 = \langle \text{vac} | \text{vac} \rangle$$

First quantization

Second quantization

Annihilation operators

$\hat{a}_P^\dagger$ Creation operator

Conclusion:

$$\langle \text{vac} \,|\, \hat{a}_P \hat{a}_P^\dagger \text{vac} \rangle = \langle \text{vac} \,|\, \text{vac} \rangle$$

Annihilation operators

$\hat{a}_P^\dagger$ Creation operator

Conclusion:

$$\langle \text{vac} | \hat{a}_P \hat{a}_P^\dagger \text{vac} \rangle = \langle \text{vac} | \text{vac} \rangle$$

$\hat{a}_P$ **Annihilation** operator

Removes an electron

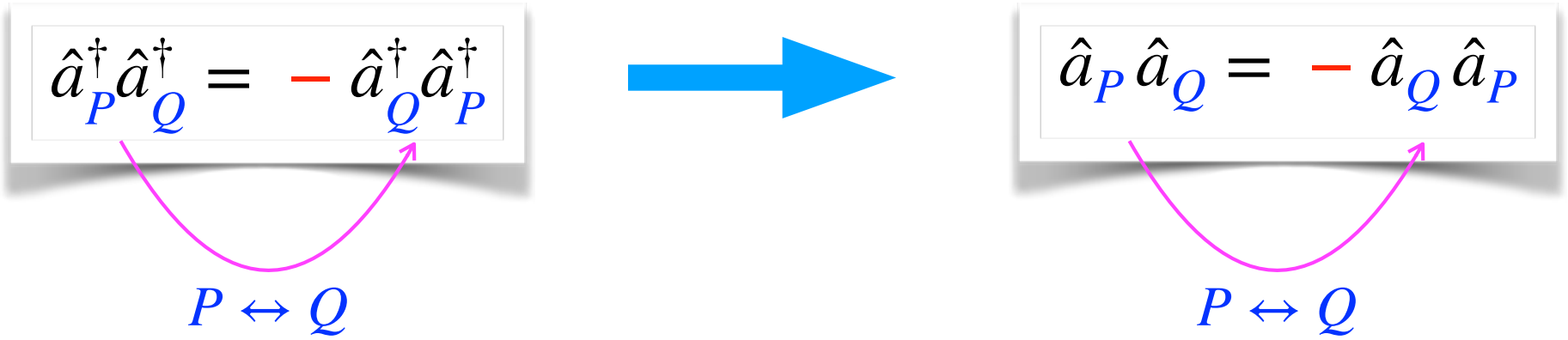
that occupies the spin-orbital φ_P

Annihilation operators

$$\hat{a}_P \,|\,\mathrm{vac}\rangle = 0$$

← ***Zero vector*** *of the Fock space*

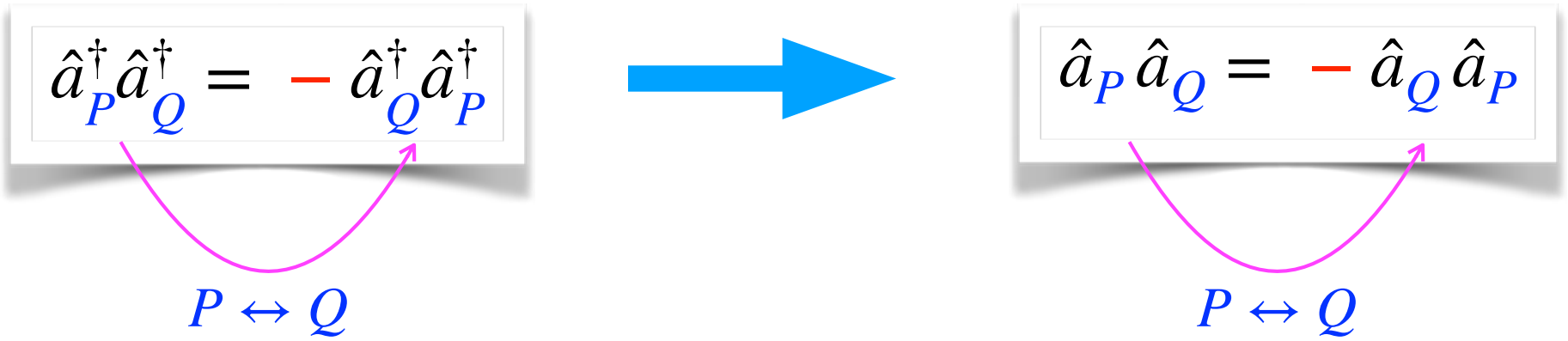
Anti-commutation rules



Creation/creation operators

Annihilation/annihilation operators

Anti-commutation rules



We need one more rule:

Annihilation/creation operators

Anti-commutation rules

$$\hat{a}^\dagger_P \hat{a}^\dagger_Q = -\hat{a}^\dagger_Q \hat{a}^\dagger_P$$

$P \leftrightarrow Q$

$$\Rightarrow \quad \hat{a}_P \hat{a}_Q = -\hat{a}_Q \hat{a}_P$$

$P \leftrightarrow Q$

We need one more rule:

$$\hat{a}_P \hat{a}^\dagger_Q = \delta_{PQ} - \hat{a}^\dagger_Q \hat{a}_P$$

Annihilation/creation operators

Anti-commutation rules

$$\hat{a}_P \hat{a}^\dagger_Q = \delta_{PQ} - \hat{a}^\dagger_Q \hat{a}_P$$

"You can only annihilate what has been created"

Second quantization, 20th century AD.

Anti-commutation rules

$$\hat{a}_P \hat{a}_Q^\dagger = \delta_{PQ} - \hat{a}_Q^\dagger \hat{a}_P$$

"You can only annihilate what has been created"

Second quantization, 20th century AD.

Exercise:

$$\hat{a}_P \hat{a}_Q^\dagger |\,\mathrm{vac}\rangle = \left(\delta_{PQ} - \hat{a}_Q^\dagger \hat{a}_P\right)|\,\mathrm{vac}\rangle = \delta_{PQ}|\,\mathrm{vac}\rangle - \hat{a}_Q^\dagger \hat{a}_P |\,\mathrm{vac}\rangle = \delta_{PQ}|\,\mathrm{vac}\rangle$$

Anti-commutation rules

$$\hat{a}_P \hat{a}_Q^\dagger = \delta_{PQ} - \hat{a}_Q^\dagger \hat{a}_P$$

"You can only annihilate what has been created"

Second quantization, 20th century AD.

Conclusion:

$$\hat{a}_P \hat{a}_Q^\dagger |\,\mathrm{vac}\rangle \overset{P \neq Q}{=} 0$$

$$\hat{a}_P \hat{a}_P^\dagger |\,\mathrm{vac}\rangle = |\,\mathrm{vac}\rangle$$

Anti-commutation rules

$$\hat{a}_P \hat{a}_Q^\dagger = \delta_{PQ} - \hat{a}_Q^\dagger \hat{a}_P$$

This has something to do with the ***orthonormality*** *of the spin-orbital basis*

Anti-commutation rules

$$\hat{a}_P \hat{a}_Q^\dagger = \delta_{PQ} - \hat{a}_Q^\dagger \hat{a}_P$$

Exercise:

$$\langle \varphi_P | \varphi_Q \rangle = \langle \hat{a}_P^\dagger \text{vac} | \hat{a}_Q^\dagger \text{vac} \rangle = \langle \text{vac} | \hat{a}_P \hat{a}_Q^\dagger \text{vac} \rangle$$

$$= \delta_{PQ} \underbrace{\langle \text{vac} | \text{vac} \rangle}_{1} - \langle \text{vac} | \hat{a}_Q^\dagger \underbrace{\hat{a}_P \text{vac}}_{0} \rangle$$

$$= \delta_{PQ}$$

Anti-commutation rules

$$\hat{a}_P \hat{a}_Q^\dagger = \delta_{PQ} - \hat{a}_Q^\dagger \hat{a}_P$$

Exercise:

$$\langle \varphi_P | \varphi_Q \rangle = \langle \hat{a}_P^\dagger \mathrm{vac} | \hat{a}_Q^\dagger \mathrm{vac} \rangle = \langle \mathrm{vac} | \hat{a}_P \hat{a}_Q^\dagger \mathrm{vac} \rangle$$

$$= \delta_{PQ} \underbrace{\langle \mathrm{vac} | \mathrm{vac} \rangle}_{1} - \langle \mathrm{vac} | \hat{a}_Q^\dagger \underbrace{\hat{a}_P \mathrm{vac}}_{0} \rangle$$

$$= \delta_{PQ}$$

Summary of what you should memorise

$$\langle \text{vac} \,|\, \text{vac} \rangle = 1$$

$$\hat{a}_P \,|\, \text{vac} \rangle = 0$$

$$\hat{a}_P \hat{a}_Q + \hat{a}_Q \hat{a}_P = \hat{a}_P^\dagger \hat{a}_Q^\dagger + \hat{a}_Q^\dagger \hat{a}_P^\dagger \equiv 0$$

$$\hat{a}_P \hat{a}_Q^\dagger + \hat{a}_Q^\dagger \hat{a}_P \equiv \delta_{PQ}$$

Anti-commutation rules

Encoding a many-body wave function in second quantisation

We want to solve the electronic Schrödinger equation:

$$\hat{H}\,|\Psi\rangle = E\,|\Psi\rangle$$

Encoding a many-body wave function in second quantisation

We want to solve the electronic Schrödinger equation:

$$\hat{H}|\Psi\rangle = E|\Psi\rangle$$

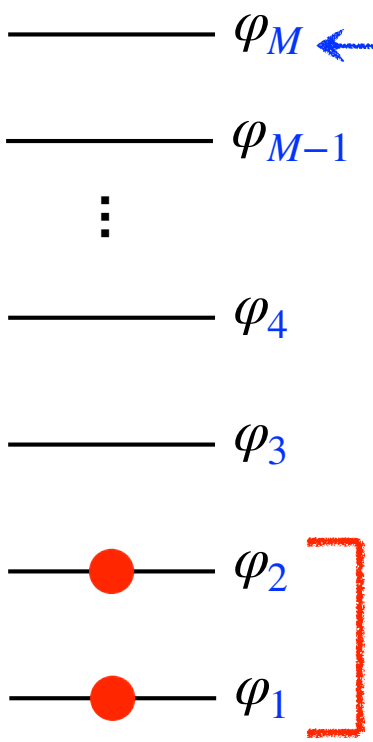
$$|\Psi\rangle \approx \sum_{P_1<P_2<\ldots<P_N} C_{P_1P_2\ldots P_N}\, \hat{a}^\dagger_{P_1}\hat{a}^\dagger_{P_2}\ldots\hat{a}^\dagger_{P_{N-1}}\hat{a}^\dagger_{P_N}|\mathrm{vac}\rangle$$

Configuration Interaction (CI) **coefficient**

Slater determinants used as **basis**

to be determined!

Two-electron configuration interaction (CI)

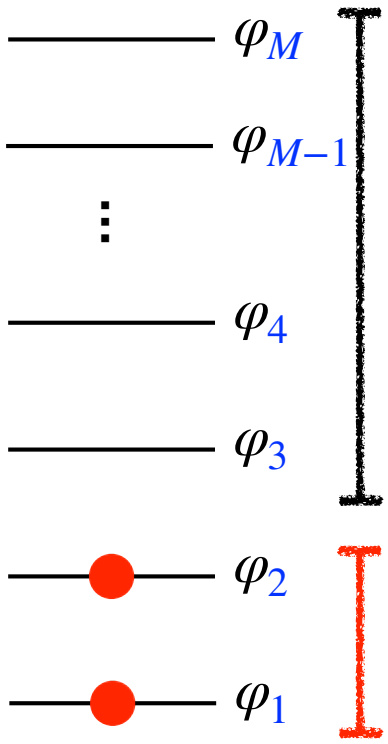


M: **dimension** of the spin-orbital basis

Reference Slater determinant
(typically Hartree-Fock)

$$|\Phi_0\rangle = \hat{a}_1^\dagger \hat{a}_2^\dagger |\text{vac}\rangle$$

Two-electron configuration interaction (CI)

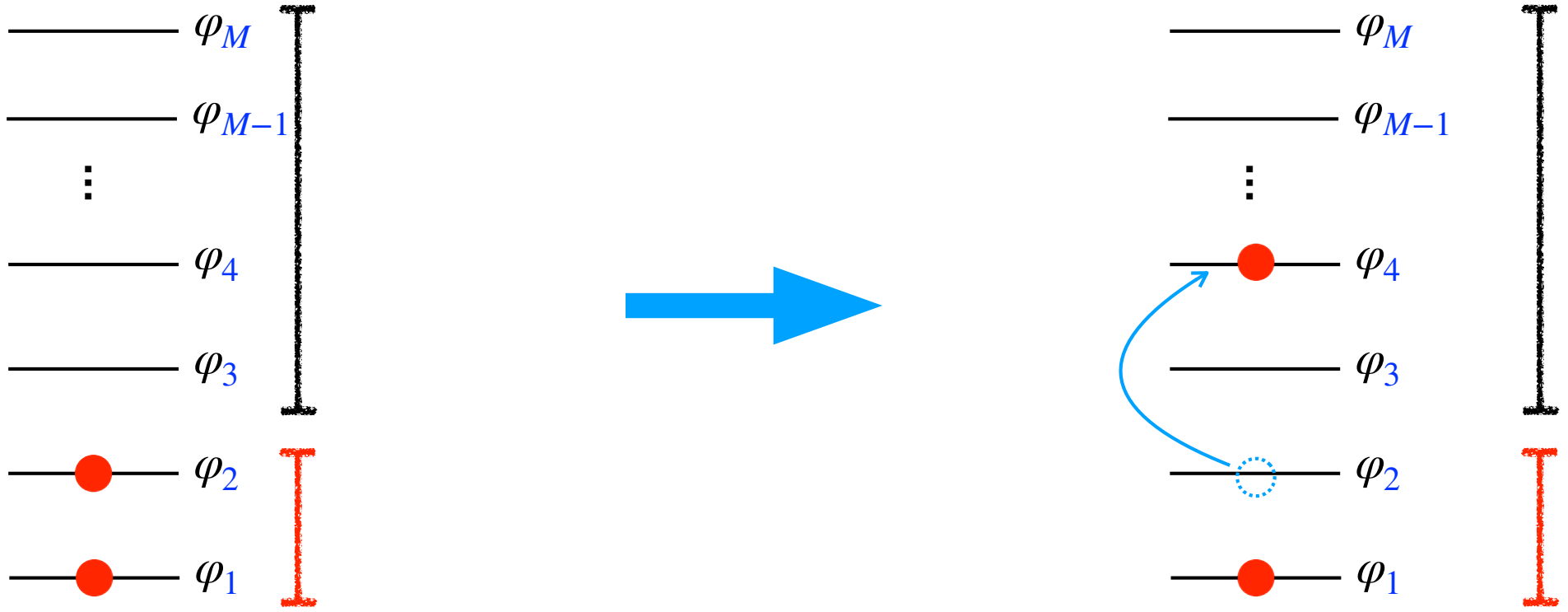


$3 \leq A, B \leq M$ **virtual** orbitals

$1 \leq I, J \leq 2$ **occupied** orbitals

Reference

Two-electron configuration interaction (CI)



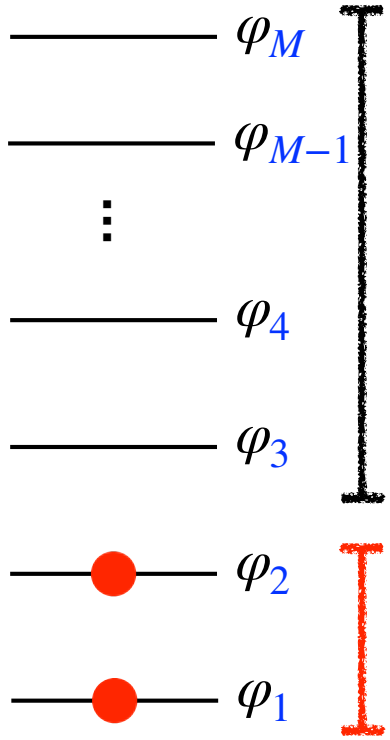
$$|\Phi_0\rangle = \hat{a}_1^\dagger \hat{a}_2^\dagger |\text{vac}\rangle$$

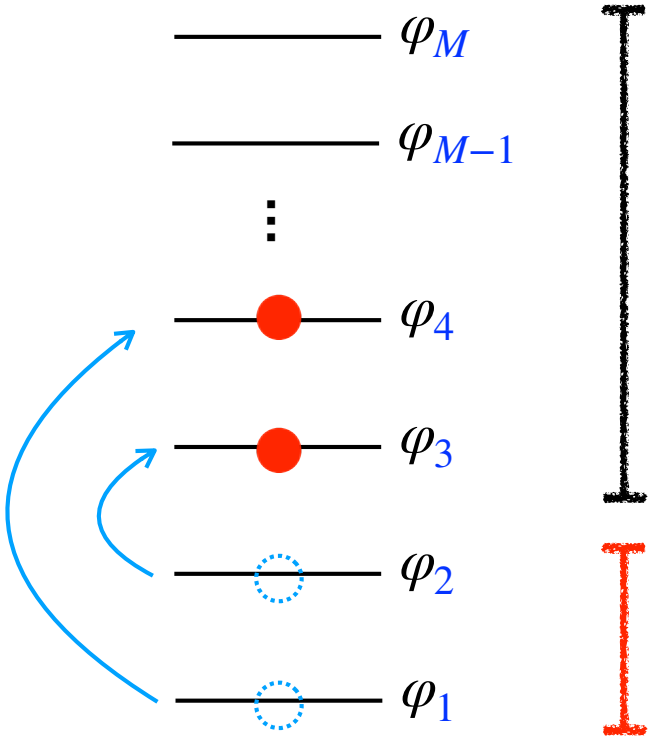
Reference

$$|\Phi_2^4\rangle = \hat{a}_4^\dagger \hat{a}_2 |\Phi_0\rangle$$

Single excitation

Two-electron configuration interaction (CI)





$$|\Phi_0\rangle = \hat{a}_1^\dagger \hat{a}_2^\dagger |\text{vac}\rangle$$

Reference

$$|\Phi_{12}^{34}\rangle = \hat{a}_3^\dagger \hat{a}_2 \hat{a}_4^\dagger \hat{a}_1 |\Phi_0\rangle$$

Double excitation

Configuration interaction (CI) expansion of many-body wave functions

We want to solve the electronic Schrödinger equation:

$$\hat{H}|\Psi\rangle = E|\Psi\rangle$$

"triples", "quadruples", ...

$$|\Psi\rangle \approx \left(1 + \sum_{I,A} C_I^A \hat{a}_A^\dagger \hat{a}_I + \sum_{I<J,A<B} C_{IJ}^{AB} \hat{a}_B^\dagger \hat{a}_J \hat{a}_A^\dagger \hat{a}_I + \ldots\right)|\Phi_0\rangle$$

"singles" *"doubles"*

Configuration interaction (CI) expansion of many-body wave functions

We want to solve the electronic Schrödinger equation:

$$\hat{H}\,|\Psi\rangle = E\,|\Psi\rangle$$

to-be-determined CI coefficients

$$|\Psi\rangle \approx \left(1 + \sum_{I,A} C_I^A\, \hat{a}_A^\dagger \hat{a}_I + \sum_{I<J,A<B} C_{IJ}^{AB}\, \hat{a}_B^\dagger \hat{a}_J \hat{a}_A^\dagger \hat{a}_I + \ldots\right) |\Phi_0\rangle$$

Electronic Hamiltonian in first quantisation *(in atomic units)*

$$\hat{H} \equiv \sum_{i=1}^{N} \hat{h}(i) + \frac{1}{2} \sum_{i \neq j}^{N} \hat{g}(i,j)$$

One-electron part **Two-electron part**

$$\hat{h}(i) \equiv -\frac{1}{2}\nabla_{\mathbf{r}_i}^2 + v_{\text{ext}}(\mathbf{r}_i) \times$$

$$\hat{g}(i,j) \equiv \frac{1}{\mathbf{r}_i - \mathbf{r}_j} \times$$

Kinetic energy+nuclear attraction

Electronic repulsion

One-electron Hamiltonian in second quantisation

Let's show that $\hat{h}$ can be expressed in terms of creation and annihilation operators.

Matrix representation of the one-electron Hamiltonian

one-electron integrals

$$\langle \varphi_P | \hat{h} | \varphi_R \rangle = \int d\mathbf{x}\, \varphi_P^*(\mathbf{x})\, \hat{h} \varphi_R(\mathbf{x})$$

$$\hat{h} \equiv \{h_{PR}\} \equiv \begin{bmatrix} \langle \varphi_1 | \hat{h} | \varphi_1 \rangle & \langle \varphi_1 | \hat{h} | \varphi_2 \rangle & \cdots & \langle \varphi_1 | \hat{h} | \varphi_R \rangle & \cdots \\ \langle \varphi_2 | \hat{h} | \varphi_1 \rangle & \langle \varphi_2 | \hat{h} | \varphi_2 \rangle & \cdots & \langle \varphi_2 | \hat{h} | \varphi_R \rangle & \cdots \\ \langle \varphi_3 | \hat{h} | \varphi_1 \rangle & \langle \varphi_3 | \hat{h} | \varphi_2 \rangle & \cdots & \langle \varphi_3 | \hat{h} | \varphi_R \rangle & \cdots \\ \vdots & \vdots & \cdots & \vdots & \cdots \\ \langle \varphi_P | \hat{h} | \varphi_1 \rangle & \langle \varphi_P | \hat{h} | \varphi_2 \rangle & \cdots & \langle \varphi_P | \hat{h} | \varphi_R \rangle & \cdots \\ \vdots & \vdots & \cdots & \vdots & \cdots \end{bmatrix}$$

Matrix representation of the one-electron Hamiltonian

$$\hat{h}\,|\varphi_R\rangle = \sum_P \langle\varphi_P|\hat{h}|\varphi_R\rangle\,|\varphi_P\rangle$$

$$\hat{h} \equiv \{h_{PR}\} \equiv \begin{bmatrix} \langle\varphi_1|\hat{h}|\varphi_1\rangle & \langle\varphi_1|\hat{h}|\varphi_2\rangle & \cdots & \langle\varphi_1|\hat{h}|\varphi_R\rangle & \cdots \\ \langle\varphi_2|\hat{h}|\varphi_1\rangle & \langle\varphi_2|\hat{h}|\varphi_2\rangle & \cdots & \langle\varphi_2|\hat{h}|\varphi_R\rangle & \cdots \\ \langle\varphi_3|\hat{h}|\varphi_1\rangle & \langle\varphi_3|\hat{h}|\varphi_2\rangle & \cdots & \langle\varphi_3|\hat{h}|\varphi_R\rangle & \cdots \\ \vdots & \vdots & \cdots & \vdots & \cdots \\ \langle\varphi_P|\hat{h}|\varphi_1\rangle & \langle\varphi_P|\hat{h}|\varphi_2\rangle & \cdots & \langle\varphi_P|\hat{h}|\varphi_R\rangle & \cdots \\ \vdots & \vdots & \cdots & \vdots & \cdots \end{bmatrix}$$

One-electron Hamiltonian in second quantisation

Exercise:

$$\hat{h}\,|\varphi_R\rangle = \sum_P \langle\varphi_P|\hat{h}|\varphi_R\rangle\,|\varphi_P\rangle$$

One-electron Hamiltonian in second quantisation

Exercise:

$$\hat{h}\,|\varphi_R\rangle = \sum_P \langle\varphi_P|\hat{h}|\varphi_R\rangle\,|\varphi_P\rangle = \sum_{PQ} \langle\varphi_P|\hat{h}|\varphi_Q\rangle\,\delta_{QR}\,|\varphi_P\rangle$$

One-electron Hamiltonian in second quantisation

Exercise:

$$\hat{h}\,|\varphi_R\rangle = \sum_P \langle\varphi_P|\hat{h}|\varphi_R\rangle\,|\varphi_P\rangle = \sum_{PQ} \langle\varphi_P|\hat{h}|\varphi_Q\rangle\,\delta_{QR}\,|\varphi_P\rangle$$

$$= \sum_{PQ} \langle\varphi_P|\hat{h}|\varphi_Q\rangle\,\delta_{QR}\,\hat{a}_P^\dagger\,|\mathrm{vac}\rangle$$

One-electron Hamiltonian in second quantisation

Exercise:

$$\hat{h}\,|\varphi_R\rangle = \sum_P \langle\varphi_P|\hat{h}|\varphi_R\rangle\,|\varphi_P\rangle = \sum_{PQ} \langle\varphi_P|\hat{h}|\varphi_Q\rangle\,\delta_{QR}\,|\varphi_P\rangle$$

$$= \sum_{PQ} \langle\varphi_P|\hat{h}|\varphi_Q\rangle\,\delta_{QR}\,\hat{a}_P^\dagger|\,\mathrm{vac}\rangle$$

$$= \sum_{PQ} \langle\varphi_P|\hat{h}|\varphi_Q\rangle\,\hat{a}_P^\dagger\,\delta_{QR}\,|\,\mathrm{vac}\rangle$$

One-electron Hamiltonian in second quantisation

Exercise:

$$\hat{h}\,|\varphi_R\rangle = \sum_P \langle\varphi_P|\hat{h}|\varphi_R\rangle\,|\varphi_P\rangle = \sum_{PQ} \langle\varphi_P|\hat{h}|\varphi_Q\rangle\,\delta_{QR}\,|\varphi_P\rangle$$

$$= \sum_{PQ} \langle\varphi_P|\hat{h}|\varphi_Q\rangle\,\delta_{QR}\,\hat{a}_P^\dagger\,|\mathrm{vac}\rangle$$

$$= \sum_{PQ} \langle\varphi_P|\hat{h}|\varphi_Q\rangle\,\hat{a}_P^\dagger\,\delta_{QR}\,|\mathrm{vac}\rangle$$

Anti-commutation rule

$$= \sum_{PQ} \langle\varphi_P|\hat{h}|\varphi_Q\rangle\,\hat{a}_P^\dagger\left(\hat{a}_Q\hat{a}_R^\dagger + \hat{a}_R^\dagger\hat{a}_Q\right)|\mathrm{vac}\rangle$$

One-electron Hamiltonian in second quantisation

Exercise:

$$\hat{h}\,|\varphi_R\rangle = \sum_P \langle\varphi_P|\hat{h}|\varphi_R\rangle\,|\varphi_P\rangle = \sum_{PQ} \langle\varphi_P|\hat{h}|\varphi_Q\rangle\,\delta_{QR}\,|\varphi_P\rangle$$

$$= \sum_{PQ} \langle\varphi_P|\hat{h}|\varphi_Q\rangle\,\delta_{QR}\,\hat{a}_P^\dagger\,|\mathrm{vac}\rangle$$

$$= \sum_{PQ} \langle\varphi_P|\hat{h}|\varphi_Q\rangle\,\hat{a}_P^\dagger\,\delta_{QR}\,|\mathrm{vac}\rangle$$

$$= \sum_{PQ} \langle\varphi_P|\hat{h}|\varphi_Q\rangle\,\hat{a}_P^\dagger\,\left(\hat{a}_Q\hat{a}_R^\dagger + \hat{a}_R^\dagger\hat{a}_Q\right)|\mathrm{vac}\rangle$$

$\hat{a}_R^\dagger\hat{a}_Q\,|\mathrm{vac}\rangle \rightarrow 0$

One-electron Hamiltonian in second quantisation

Exercise:

$$\hat{h}\,|\varphi_R\rangle = \sum_P \langle\varphi_P|\hat{h}|\varphi_R\rangle\,|\varphi_P\rangle = \sum_{PQ} \langle\varphi_P|\hat{h}|\varphi_Q\rangle\,\delta_{QR}\,|\varphi_P\rangle$$

$$= \sum_{PQ} \langle\varphi_P|\hat{h}|\varphi_Q\rangle\,\delta_{QR}\,\hat{a}_P^\dagger\,|\mathrm{vac}\rangle$$

$$= \sum_{PQ} \langle\varphi_P|\hat{h}|\varphi_Q\rangle\,\hat{a}_P^\dagger\,\delta_{QR}\,|\mathrm{vac}\rangle$$

$$= \sum_{PQ} \langle\varphi_P|\hat{h}|\varphi_Q\rangle\,\hat{a}_P^\dagger\,\left(\hat{a}_Q\hat{a}_R^\dagger + \cancel{\hat{a}_R^\dagger\hat{a}_Q}\right)|\mathrm{vac}\rangle$$

$$= \sum_{PQ} \langle\varphi_P|\hat{h}|\varphi_Q\rangle\,\hat{a}_P^\dagger\hat{a}_Q\,\hat{a}_R^\dagger\,|\mathrm{vac}\rangle$$

One-electron Hamiltonian in second quantisation

Exercise:

$$\hat{h}\,|\varphi_R\rangle = \sum_P \langle\varphi_P|\hat{h}|\varphi_R\rangle\,|\varphi_P\rangle = \sum_{PQ} \langle\varphi_P|\hat{h}|\varphi_Q\rangle\,\delta_{QR}\,|\varphi_P\rangle$$

$$= \sum_{PQ} \langle\varphi_P|\hat{h}|\varphi_Q\rangle\,\delta_{QR}\,\hat{a}_P^\dagger\,|\mathrm{vac}\rangle$$

$$= \sum_{PQ} \langle\varphi_P|\hat{h}|\varphi_Q\rangle\,\hat{a}_P^\dagger\,\delta_{QR}\,|\mathrm{vac}\rangle$$

$$= \sum_{PQ} \langle\varphi_P|\hat{h}|\varphi_Q\rangle\,\hat{a}_P^\dagger\left(\hat{a}_Q\hat{a}_R^\dagger + \hat{a}_R^\dagger\hat{a}_Q\right)|\mathrm{vac}\rangle$$

$$= \sum_{PQ} \langle\varphi_P|\hat{h}|\varphi_Q\rangle\,\hat{a}_P^\dagger\hat{a}_Q\,\hat{a}_R^\dagger\,|\mathrm{vac}\rangle$$

$\hat{a}_R^\dagger\,|\mathrm{vac}\rangle = |\varphi_R\rangle$

One-electron Hamiltonian in second quantisation

Exercise:

$$\hat{h}\,|\varphi_R\rangle = \sum_P \langle\varphi_P|\hat{h}|\varphi_R\rangle\,|\varphi_P\rangle = \sum_{PQ} \langle\varphi_P|\hat{h}|\varphi_Q\rangle\,\delta_{QR}\,|\varphi_P\rangle$$

$$= \sum_{PQ} \langle\varphi_P|\hat{h}|\varphi_Q\rangle\,\delta_{QR}\,\hat{a}_P^\dagger\,|\mathrm{vac}\rangle$$

$$= \sum_{PQ} \langle\varphi_P|\hat{h}|\varphi_Q\rangle\,\hat{a}_P^\dagger\,\delta_{QR}\,|\mathrm{vac}\rangle$$

$$= \sum_{PQ} \langle\varphi_P|\hat{h}|\varphi_Q\rangle\,\hat{a}_P^\dagger\left(\hat{a}_Q\hat{a}_R^\dagger + \hat{a}_R^\dagger\hat{a}_Q\right)|\mathrm{vac}\rangle$$

$$= \sum_{PQ} \langle\varphi_P|\hat{h}|\varphi_Q\rangle\,\hat{a}_P^\dagger\hat{a}_Q\hat{a}_R^\dagger\,|\mathrm{vac}\rangle$$

$$\hat{h}\,|\varphi_R\rangle = \left(\sum_{PQ} \langle\varphi_P|\hat{h}|\varphi_Q\rangle\,\hat{a}_P^\dagger\hat{a}_Q\right)|\varphi_R\rangle$$

One-electron Hamiltonian in second quantisation

$$\hat{h} = \sum_{PQ} \langle \varphi_P | \hat{h} | \varphi_Q \rangle \, \hat{a}_P^\dagger \hat{a}_Q$$

One-electron Hamiltonian in second quantisation

$$\hat{h} = \sum_{PQ} \langle \varphi_P | \hat{h} | \varphi_Q \rangle \, \hat{a}_P^\dagger \hat{a}_Q \equiv \sum_{i=1}^{N} \hat{h}(i)$$

*Valid over the **entire** Fock space!*

Two-electron repulsion operator in second quantisation

$$\sum_{i=1}^{N} \hat{h}(i) \equiv \sum_{PQ} \langle \varphi_P | \hat{h} | \varphi_Q \rangle \, \hat{a}_P^\dagger \hat{a}_Q$$

One-electron operator

$$\frac{1}{2} \sum_{i \neq j}^{N} \hat{g}(i,j) \equiv \frac{1}{2} \sum_{PQRS} \langle \varphi_P \varphi_Q | \hat{g} | \varphi_R \varphi_S \rangle \, \hat{a}_P^\dagger \hat{a}_Q^\dagger \hat{a}_S \hat{a}_R$$

Two-electron operator

Two-electron repulsion operator in second quantisation

$$\sum_{i=1}^{N} \hat{h}(i) \equiv \sum_{PQ} \langle \varphi_P | \hat{h} | \varphi_Q \rangle \hat{a}_P^\dagger \hat{a}_Q$$

One-electron operator

$$\frac{1}{2} \sum_{i \neq j}^{N} \hat{g}(i,j) \equiv \frac{1}{2} \sum_{PQRS} \langle \varphi_P \varphi_Q | \hat{g} | \varphi_R \varphi_S \rangle \hat{a}_P^\dagger \hat{a}_Q^\dagger \hat{a}_S \hat{a}_R$$

Two-electron operator

Two-electron repulsion operator in second quantisation

$$\frac{1}{2}\sum_{i\neq j}^{N}\hat{g}(i,j) \equiv \frac{1}{2}\sum_{PQRS}\langle\varphi_P\varphi_Q\,|\,\hat{g}\,|\,\varphi_R\varphi_S\rangle\,\hat{a}_P^\dagger\hat{a}_Q^\dagger\hat{a}_S\hat{a}_R$$

Two-electron integrals $\equiv (PR, QS)$

in Vincent Robert's lecture

$$\int d\mathbf{x}_1 \int d\mathbf{x}_2\; \varphi_P^*(\mathbf{x}_1)\varphi_Q^*(\mathbf{x}_2)\frac{1}{|\,\mathbf{r}_1-\mathbf{r}_2\,|}\varphi_R(\mathbf{x}_1)\varphi_S(\mathbf{x}_2)$$

Total Hamiltonian in second quantisation

$$\hat{H} \equiv \sum_{PQ} \langle \varphi_P | \hat{h} | \varphi_Q \rangle \, \hat{a}_P^\dagger \hat{a}_Q + \frac{1}{2} \sum_{PQRS} \langle \varphi_P \varphi_Q | \hat{g} | \varphi_R \varphi_S \rangle \, \hat{a}_P^\dagger \hat{a}_Q^\dagger \hat{a}_S \hat{a}_R$$

Outline

- **Standard (first quantization) formalism**

  Atomic *orbitals*, molecular *spin-orbitals*, Slater *determinants*.

- **Second quantization formalism**

  Vacuum state, *creation* operators, *annihilation* operators,
  excitation operators, one- and two-electron *Hamiltonian* operators.

- **Why “second” quantization?**

  Field operators, *density* operator, one-electron reduced *density matrix*,
  and one-electron *Green function*.

Why “second” quantisation?

Exercise:

$$\hat{h} = \sum_{PQ} \langle \varphi_P | \hat{h} | \varphi_Q \rangle \, \hat{a}^\dagger_P \hat{a}_Q$$

Why “second” quantisation?

Exercise:

$$\hat{h} = \sum_{PQ} \langle \varphi_P | \hat{h} | \varphi_Q \rangle \hat{a}_P^\dagger \hat{a}_Q$$

one-electron integrals

$$= \sum_{PQ} \int d\mathbf{x}\, \varphi_P^*(\mathbf{x}) \left(-\frac{1}{2}\nabla_{\mathbf{r}}^2 + v_{\text{ext}}(\mathbf{r}) \right) \varphi_Q(\mathbf{x})\, \hat{a}_P^\dagger \hat{a}_Q$$

Why “second” quantisation?

Exercise:

$$\hat{h} = \sum_{PQ} \langle \varphi_P | \hat{h} | \varphi_Q \rangle \, \hat{a}_P^\dagger \hat{a}_Q$$

$$= \sum_{PQ} \int d\mathbf{x} \, \varphi_P^*(\mathbf{x}) \left(-\frac{1}{2} \nabla_{\mathbf{r}}^2 + v_{\text{ext}}(\mathbf{r}) \right) \varphi_Q(\mathbf{x}) \, \hat{a}_P^\dagger \hat{a}_Q$$

$$= \int d\mathbf{x} \sum_P \varphi_P^*(\mathbf{x}) \hat{a}_P^\dagger \left(-\frac{1}{2} \nabla_{\mathbf{r}}^2 + v_{\text{ext}}(\mathbf{r}) \right) \sum_Q \varphi_Q(\mathbf{x}) \hat{a}_Q$$

Why "second" quantisation?

Exercise:

$$\hat{h} = \sum_{PQ} \langle \varphi_P | \hat{h} | \varphi_Q \rangle \, \hat{a}_P^\dagger \hat{a}_Q$$

$$= \sum_{PQ} \int d\mathbf{x} \, \varphi_P^*(\mathbf{x}) \left(-\frac{1}{2}\nabla_{\mathbf{r}}^2 + v_{\text{ext}}(\mathbf{r}) \right) \varphi_Q(\mathbf{x}) \, \hat{a}_P^\dagger \hat{a}_Q$$

$$= \int d\mathbf{x} \left(\sum_P \varphi_P^*(\mathbf{x}) \hat{a}_P^\dagger \right) \left(-\frac{1}{2}\nabla_{\mathbf{r}}^2 + v_{\text{ext}}(\mathbf{r}) \right) \left(\sum_Q \varphi_Q(\mathbf{x}) \hat{a}_Q \right)$$

Notation

Notation

$$= \int d\mathbf{x} \, \hat{\Psi}^\dagger(\mathbf{x}) \left(-\frac{1}{2}\nabla_{\mathbf{r}}^2 + v_{\text{ext}}(\mathbf{r}) \right) \hat{\Psi}(\mathbf{x})$$

Why "second" quantisation?

$$\hat{h} = \int d\mathbf{x}\, \hat{\Psi}^{\dagger}(\mathbf{x}) \left(-\frac{1}{2}\nabla^2_{\mathbf{r}} + v_{\text{ext}}(\mathbf{r}) \right) \hat{\Psi}(\mathbf{x})$$

Why "second" quantisation?

We learn in textbooks that, for a ***single*** electron,

$$\langle \Psi | \hat{h} | \Psi \rangle = \int d\mathbf{x}\, \Psi^*(\mathbf{x}) \left(-\frac{1}{2}\nabla^2_{\mathbf{r}} + v_{\text{ext}}(\mathbf{r}) \right) \Psi(\mathbf{x})$$

$$\hat{h} = \int d\mathbf{x}\, \hat{\Psi}^\dagger(\mathbf{x}) \left(-\frac{1}{2}\nabla^2_{\mathbf{r}} + v_{\text{ext}}(\mathbf{r}) \right) \hat{\Psi}(\mathbf{x})$$

Why "second" quantisation?

Quantum theory of a single particle

$\Psi(\mathbf{x})$

Wave function
(complex number)

"Quantised" version of the single particle quantum theory

$\hat{\Psi}(\mathbf{x})$

(so-called) **field operator**

$$= \sum_Q \varphi_Q(\mathbf{x})\hat{a}_Q$$

Density operator

Quantum theory of a single particle

$$n(\mathbf{x}) = \Psi^*(\mathbf{x})\Psi(\mathbf{x})$$

Density of probability

(real number)

"Quantised" version of the single particle quantum theory

$$\hat{n}(\mathbf{x}) = \hat{\Psi}^\dagger(\mathbf{x})\hat{\Psi}(\mathbf{x})$$

Density operator

Electron density

If Φ is a *many-body wave function* encoded in second quantization, its ***density*** can be evaluated as follows:

$$n_\Phi(\mathbf{x}) = \langle \Phi | \hat{n}(\mathbf{x}) | \Phi \rangle = \langle \Phi | \hat{\Psi}^\dagger(\mathbf{x}) \hat{\Psi}(\mathbf{x}) | \Phi \rangle$$

Electron density

If Φ is a *many-body wave function* encoded in second quantization, its density can be evaluated as follows:

$$n_\Phi(\mathbf{x}) = \langle \Phi | \hat{n}(\mathbf{x}) | \Phi \rangle = \langle \Phi | \hat{\Psi}^\dagger(\mathbf{x}) \hat{\Psi}(\mathbf{x}) | \Phi \rangle$$

$$= \sum_P \varphi_P^*(\mathbf{x}) \varphi_Q(\mathbf{x}) \langle \Phi | \hat{a}_P^\dagger \hat{a}_Q | \Phi \rangle$$

$$\hat{\Psi}(\mathbf{x}) = \sum_Q \varphi_Q(\mathbf{x}) \hat{a}_Q$$

If we return to the spin-orbital basis…

Density operator

If Φ is a *many-body wave function* encoded in second quantization, its density can be evaluated as follows:

$$n_\Phi(\mathbf{x}) = \langle \Phi | \hat{n}(\mathbf{x}) | \Phi \rangle = \langle \Phi | \hat{\Psi}^\dagger(\mathbf{x}) \hat{\Psi}(\mathbf{x}) | \Phi \rangle$$

$$= \sum_P \varphi_P^*(\mathbf{x}) \varphi_Q(\mathbf{x}) \langle \Phi | \hat{a}_P^\dagger \hat{a}_Q | \Phi \rangle$$

One-electron reduced ***density matrix*** *elements*

$$\gamma_{PQ}$$

One-electron reduced density matrix *(in real space)*

If Φ is a many-body wave function encoded in second quantization, its ***density matrix*** can be evaluated as follows:

$$\gamma(\mathbf{x}_1, \mathbf{x}_2) = \langle \Phi \,|\, \hat{\Psi}^\dagger(\mathbf{x}_1)\hat{\Psi}(\mathbf{x}_2) \,|\, \Phi \rangle$$

One-electron Green function *(in real space)*

$$\hat{\Psi}^{\dagger}(\mathbf{x}_1) \quad \Rightarrow \quad \hat{\Psi}^{\dagger}(1) \equiv \hat{\Psi}^{\dagger}(\mathbf{x}_1, t_1) = e^{\mathrm{i}\hat{H}t_1}\hat{\Psi}^{\dagger}(\mathbf{x}_1)e^{-\mathrm{i}\hat{H}t_1}$$

One-electron Green function *(in real space)*

$$\hat{\Psi}^{\dagger}(\mathbf{x}_1) \quad \Rightarrow \quad \hat{\Psi}^{\dagger}(1) \equiv \hat{\Psi}^{\dagger}(\mathbf{x}_1, t_1) = e^{\mathrm{i}\hat{H}t_1}\, \hat{\Psi}^{\dagger}(\mathbf{x}_1)\, e^{-\mathrm{i}\hat{H}t_1}$$

$\mathrm{i}^2 = -1$

One-electron Green function *(in real space)*

$$\hat{\Psi}^{\dagger}(\mathbf{x}_1) \quad \Rightarrow \quad \hat{\Psi}^{\dagger}(1) \equiv \hat{\Psi}^{\dagger}(\mathbf{x}_1, t_1) = e^{\mathrm{i}\hat{H}t_1}\,\hat{\Psi}^{\dagger}(\mathbf{x}_1)\,e^{-\mathrm{i}\hat{H}t_1}$$

$$\hat{\Psi}(\mathbf{x}_2) \quad \Rightarrow \quad \hat{\Psi}(2) \equiv \hat{\Psi}(\mathbf{x}_2, t_2) = e^{\mathrm{i}\hat{H}t_2}\,\hat{\Psi}(\mathbf{x}_2)\,e^{-\mathrm{i}\hat{H}t_2}$$

$$\gamma(\mathbf{x}_1, \mathbf{x}_2) \quad \Rightarrow \quad \langle \Phi \,|\, \hat{\Psi}^{\dagger}(1)\hat{\Psi}(2) \,|\, \Phi \rangle \overset{t_1 > t_2}{\equiv} -\mathrm{i}G(2,1)$$

Time-ordered one-electron Green function

One-electron Green function *(in real space)*

$$\hat{\Psi}^{\dagger}(\mathbf{x}_1) \quad \Rightarrow \quad \hat{\Psi}^{\dagger}(1) \equiv \hat{\Psi}^{\dagger}(\mathbf{x}_1, t_1) = e^{\mathrm{i}\hat{H}t_1}\,\hat{\Psi}^{\dagger}(\mathbf{x}_1)\,e^{-\mathrm{i}\hat{H}t_1}$$

$$\hat{\Psi}(\mathbf{x}_2) \quad \Rightarrow \quad \hat{\Psi}(2) \equiv \hat{\Psi}(\mathbf{x}_2, t_2) = e^{\mathrm{i}\hat{H}t_2}\,\hat{\Psi}(\mathbf{x}_2)\,e^{-\mathrm{i}\hat{H}t_2}$$

$$\gamma(\mathbf{x}_1, \mathbf{x}_2) \quad \Rightarrow \quad \langle \Phi \,|\, \hat{\Psi}^{\dagger}(1)\hat{\Psi}(2) \,|\, \Phi \rangle \overset{t_1 > t_2}{\equiv} -\mathrm{i}G(2,1)$$