Foundations of quantum chemistry
2. *Representations*

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Representation of a vector in a discrete basis set

Let $\{\phi_1, \ldots \phi_i, \ldots\}$ be a discrete basis of a Hilbert space. Any vector Ψ of the space can be expanded in that basis as

bold-face!

$$\Psi = \sum_i \phi_i c_i = \begin{pmatrix} \phi_1 & \ldots & \phi_i & \ldots \end{pmatrix} \begin{pmatrix} c_1 \\ \ldots \\ c_i \\ \ldots \end{pmatrix} = \boldsymbol{\phi}\mathbf{c}$$

The column matrix $\mathbf{c}$ *represents* vector Ψ in the basis $\boldsymbol{\phi}$.

Examples:

- Any state of a spin-less particle can be expanded in terms of the eigenvectors of a 3D harmonic oscillator hamiltonian: $\Psi = \sum_{n_x=0}^{\infty} \sum_{n_y=0}^{\infty} \sum_{n_z=0}^{\infty} \phi_{n_x n_y n_z} c_{n_x n_y n_z}$
- Exercise 1.8: $\psi_{1s\pm} = (\psi_{1s\alpha} \pm \psi_{1s\beta})/\sqrt{2}$

Scalar product in matrix notation

$$\langle \Psi | \Psi' \rangle = \left\langle \sum_i c_i \phi_i \middle| \sum_j c'_j \phi_j \right\rangle = \sum_i \sum_j c_i^* c'_j \langle \phi_i | \phi_j \rangle = \sum_i \sum_j c_i^* S_{ij} c'_j$$

$$= \begin{pmatrix} c_1^* & \cdots & c_i^* & \cdots \end{pmatrix} \begin{pmatrix} S_{11} & \cdots & S_{1j} & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ S_{i1} & \cdots & S_{ij} & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{pmatrix} \begin{pmatrix} c'_1 \\ \cdots \\ c'_j \\ \cdots \end{pmatrix} = \mathbf{c}^\dagger \mathbf{S} \mathbf{c}'$$

where $\mathbf{c}^\dagger$ is the *adjoint* of matrix $\mathbf{c}$: $\mathbf{c}^\dagger \equiv (\mathbf{c}^t)^*$

- In particular: $\|\Psi\|^2 = \langle \Psi | \Psi \rangle = \mathbf{c}^\dagger \mathbf{S} \mathbf{c} = \sum_i \sum_j c_i^* S_{ij} c_j$

- If $\{\psi_1, \ldots \psi_i, \ldots\}$ is *orthonormal* then $\mathbf{S} = \mathbf{1}$ and

$$\langle \Psi | \Psi' \rangle = \mathbf{c}^\dagger \mathbf{1} \mathbf{c}' = \mathbf{c}^\dagger \mathbf{c}' = \begin{pmatrix} c_1^* & \cdots & c_i^* & \cdots \end{pmatrix} \begin{pmatrix} c'_1 \\ \cdots \\ c'_i \\ \cdots \end{pmatrix} = \sum_i c_i^* c'_i$$

$$\langle \Psi | \Psi \rangle = \mathbf{c}^\dagger \mathbf{c} = \sum_i |c_i|^2$$

Representation of an operator in a discrete basis set

Any operator $\hat{A}$ can be specified by giving its effect on the basis vectors:

$$\hat{A}\,\psi_i = \sum_j \psi_j \mathcal{A}_{ji}\,, \qquad i = 1, 2, \ldots$$

$$\hat{A}\begin{pmatrix}\psi_1 & \ldots & \psi_i & \ldots\end{pmatrix} = \begin{pmatrix}\hat{A}\psi_1 & \ldots & \boxed{\hat{A}\psi_i} & \ldots\end{pmatrix}$$

$$= \left(\boxed{\psi_1 \quad \ldots \quad \psi_j \quad \ldots}\right)\begin{pmatrix}\mathcal{A}_{11} & \ldots & \mathcal{A}_{1i} & \ldots \\ \ldots & \ldots & \ldots & \ldots \\ \mathcal{A}_{j1} & \ldots & \mathcal{A}_{ji} & \ldots \\ \ldots & \ldots & \ldots & \ldots\end{pmatrix}$$

$$\boxed{\hat{A}\,\boldsymbol{\psi} = \boldsymbol{\psi}\,\boldsymbol{\mathcal{A}}}$$

The square matrix $\boldsymbol{\mathcal{A}}$ *represents* the operator $\hat{A}$ in the basis $\boldsymbol{\psi}$.

Examples: $\widehat{S_+}\beta = \hbar\alpha \quad \widehat{S_+}\alpha = 0 \quad \widehat{S_-}\alpha = \hbar\beta \quad \widehat{S_-}\beta = 0$

Representation of an operator in a discrete basis set

$\mathcal{A}$ provides the effect of the operator $\hat{A}$ on any vector:

$$\widehat{A}\Psi = \widehat{A}\sum_i \psi_i c_i = \sum_{ij} \psi_j \mathcal{A}_{ji} c_i$$

or, in matrix notation:

$$\widehat{A}\Psi = \widehat{A}\boldsymbol{\psi}\mathbf{c}$$

$$= \boldsymbol{\psi}\boldsymbol{\mathcal{A}}\mathbf{c} = \begin{pmatrix}\psi_1 & \dots & \psi_j & \dots\end{pmatrix}\begin{pmatrix}\mathcal{A}_{11} & \dots & \mathcal{A}_{1i} & \dots \\ \dots & \dots & \dots & \dots \\ \mathcal{A}_{j1} & \dots & \mathcal{A}_{ji} & \dots \\ \dots & \dots & \dots & \dots\end{pmatrix}\begin{pmatrix}c_1 \\ \dots \\ c_i \\ \dots\end{pmatrix}$$

Let's call $\Psi' \equiv \hat{A}\Psi$. Then it is clear that

$$\mathbf{c}' = \boldsymbol{\mathcal{A}}\mathbf{c}$$

$$\begin{pmatrix}c'_1 \\ \dots \\ c'_i \\ \dots\end{pmatrix} = \begin{pmatrix}\mathcal{A}_{11} & \dots & \mathcal{A}_{1i} & \dots \\ \dots & \dots & \dots & \dots \\ \mathcal{A}_{j1} & \dots & \mathcal{A}_{ji} & \dots \\ \dots & \dots & \dots & \dots\end{pmatrix}\begin{pmatrix}c_1 \\ \dots \\ c_i \\ \dots\end{pmatrix}$$

and (see <u>this</u> slide) $\langle \Psi | \hat{A}\Psi \rangle = \mathbf{c}^\dagger \mathbf{S} \boldsymbol{\mathcal{A}} \mathbf{c}$

Scalar-product representation

Scalar-product representation (**A**) of $\hat{A}$ on the basis $\boldsymbol{\psi}$:

$$\boxed{A_{ji} \equiv \langle \psi_j | \hat{A} \psi_i \rangle} = \sum_k \langle \psi_j | \psi_k \rangle \mathcal{A}_{ki} \qquad S_{jk} \equiv \langle \psi_j | \psi_k \rangle$$

TRUE representation

$$\boxed{\mathbf{A} = \mathbf{S}\,\boldsymbol{\mathcal{A}}}$$

$$\begin{pmatrix} A_{11} & \dots & A_{1i} & \dots \\ \dots & \dots & \dots & \dots \\ A_{j1} & \dots & \boxed{A_{ji}} & \dots \\ \dots & \dots & \dots & \dots \end{pmatrix} = \begin{pmatrix} S_{11} & \dots & S_{1k} & \dots \\ \dots & \dots & \dots & \dots \\ S_{j1} & \dots & S_{jk} & \dots \\ \dots & \dots & \dots & \dots \end{pmatrix} \begin{pmatrix} \mathcal{A}_{11} & \dots & \mathcal{A}_{1i} & \dots \\ \dots & \dots & \dots & \dots \\ \mathcal{A}_{k1} & \dots & \mathcal{A}_{ki} & \dots \\ \dots & \dots & \dots & \dots \end{pmatrix}$$

- **S** is the scalar-product representation of the *identity operator*:

$$(\mathbf{1})_{ij} = \langle \psi_i | \hat{1} \psi_j \rangle = S_{ij}$$

- Previous slide: $\boxed{\langle \Psi | \hat{A} \Psi \rangle = \mathbf{c}^\dagger \mathbf{S} \boldsymbol{\mathcal{A}} \mathbf{c} = \mathbf{c}^\dagger \mathbf{A} \mathbf{c}}$

- If the basis set is *orthonormal* ($\mathbf{S} = \mathbf{1}$) both representations coincide.

Matrix representations of operators

Exercise 2.1

Let $\{\chi_1, \chi_2, \chi_3\}$ be a basis set of a 3-dimensional Hilbert space and

$$\mathsf{S} = \begin{pmatrix} 1 & 1/2 & 1/2 \\ 1/2 & 1 & 1/2 \\ 1/2 & 1/2 & 1 \end{pmatrix}$$

the corresponding overlap matrix. $\hat{A}$ is an operator acting this way on the elements of that basis: $\hat{A}\chi_1 = \chi_2 + \chi_3$, $\hat{A}\chi_2 = \chi_1 + \chi_3$, $\hat{A}\chi_3 = \chi_1 + \chi_2$. Determine the true matrix representation of $\hat{A}$ in the basis $\{\chi_1, \chi_2, \chi_3\}$ and its scalar-product matrix representation.

Results: $\begin{pmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{pmatrix}$; $\begin{pmatrix} 1 & 3/2 & 3/2 \\ 3/2 & 1 & 3/2 \\ 3/2 & 3/2 & 1 \end{pmatrix}$.

Solution of the exercise 2.1

$$\{x_1, x_2, x_3\} \longrightarrow \mathbb{S} = \begin{pmatrix} 1 & 0.5 & 0.5 \\ 0.5 & 1 & 0.5 \\ 0.5 & 0.5 & 1 \end{pmatrix}$$

$$\hat{A}(x_1, x_2, x_3) = (x_1\ x_2\ x_3) \underbrace{\begin{pmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{pmatrix}}_{\mathcal{A}}$$

$$\mathbb{A} = \mathbb{S}\,\mathcal{A} = \begin{pmatrix} 1 & 0.5 & 0.5 \\ 0.5 & 1 & 0.5 \\ 0.5 & 0.5 & 1 \end{pmatrix} \begin{pmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{pmatrix} = \begin{pmatrix} 1 & 1{,}5 & 1{,}5 \\ 1{,}5 & 1 & 1{,}5 \\ 1{,}5 & 1{,}5 & 1 \end{pmatrix}$$

Definitions:

Adjoint matrix of **A**: $\mathbf{A}^\dagger = (\mathbf{A}^t)^* = (\mathbf{A}^*)^t$, so that $(\mathbf{A}^\dagger)_{ij} = A_{ji}^*$

A is *hermitian* $\Leftrightarrow$ $\mathbf{A}^\dagger = \mathbf{A}$, so that $A_{ij} = A_{ji}^*$

A is *unitary* $\Leftrightarrow$ $\mathbf{A}^\dagger = \mathbf{A}^{-1}$

A real and hermitian $\Leftrightarrow$ **A** *symmetric* ($\mathbf{A}^t = \mathbf{A}$ or $A_{ij} = A_{ji}$)

A real and unitary $\Leftrightarrow$ **A** *orthogonal* ($\mathbf{A}^t = \mathbf{A}^{-1}$)

Exercise 2.2 Prove the following statements.

a) If $\sum_k c_k \psi_k$ is the expression of a vector Ψ in a non-orthonormal basis set $\boldsymbol{\psi}$, then $\langle \psi_k | \Psi \rangle = (\mathbf{Sc})_k$

b) If $\hat{A}\hat{B} = \hat{C}$, $\mathcal{A}\,\mathcal{B} = \mathcal{C}$ but, in general, $\mathbf{AB} \neq \mathbf{C}$.

c) For any 2 matrices **A** and **B** such that the number of columns of **A** coincides with the number of rows of **B**, $(\mathbf{AB})^\dagger = \mathbf{B}^\dagger \mathbf{A}^\dagger$.

d) If $\hat{B} = \hat{A}^\dagger$, $\mathbf{B} = \mathbf{A}^\dagger$ but, in general, $\mathcal{B} \neq \mathcal{A}^\dagger$

e) The scalar-product representation of an hermitian operator is an hermitian matrix.

f) The columns of a unitary matrix can be considered "orthonormal" in the sense that $\sum_k A_{ki}^* A_{kj} = \delta_{ij}$

Solution of the exercise 2.2

a) $\langle \psi_k | \Phi \rangle = \langle \psi_k | \sum_j c_j \psi_j \rangle = \sum_j c_j \underbrace{\langle \psi_k | \psi_j \rangle}_{S_{kj}} = (\mathbb{S}\,\mathbf{c})_k$

b) $\widehat{\hat{A}\hat{B}\psi} = \widehat{\hat{A}\psi}\mathcal{B} = \psi\mathcal{A}\mathcal{B}$

$\hat{C}\psi = \psi\mathcal{C}$

$\psi\mathcal{A}\mathcal{B} = \psi\mathcal{C} \Rightarrow \psi(\underbrace{\mathcal{A}\mathcal{B} - \mathcal{C}}_{\overset{\shortparallel}{0}}) = 0$

$\{\psi_j\}$ linearly independent $\Rightarrow$

However:

$\mathbb{A}\mathbb{B} = \mathbb{S}\mathcal{A}\mathbb{S}\mathcal{B} \neq \mathbb{S}\mathcal{A}\mathcal{B} = \mathbb{S}\mathcal{C} = \mathbb{C}$

$\nwarrow$ in general

c) $[(\mathbb{A}\mathbb{B})^\dagger]_{ij} = (\mathbb{A}\mathbb{B})^*_{ji} = (\mathbb{A}^*\mathbb{B}^*)_{ji} = \sum_k A^*_{jk} B^*_{ki} = \sum_k (\mathbb{A}^\dagger)_{kj} (\mathbb{B}^\dagger)_{ik} = (\mathbb{B}^\dagger \mathbb{A}^\dagger)_{ij}$

d) $\hat{B} = \hat{A}^\dagger \Rightarrow B_{ij} = \langle \phi_i | \hat{A}^\dagger \phi_j \rangle = \langle \hat{A}\phi_i | \phi_j \rangle = \langle \phi_j | \hat{A}\phi_i \rangle^* = A^*_{ji} = (\mathbb{A}^\dagger)_{ij}$

$\Rightarrow \mathbb{B} = \mathbb{A}^\dagger$

$\mathcal{B} = \mathbb{S}^{-1}\mathbb{B} = \mathbb{S}^{-1}\mathbb{A}^\dagger$

$\mathcal{A}^\dagger = (\mathbb{S}^{-1}\mathbb{A})^\dagger = \mathbb{A}^\dagger(\mathbb{S}^{-1})^\dagger = \mathbb{A}^\dagger\mathbb{S}^{-1} \neq \mathbb{S}^{-1}\mathbb{A}^\dagger$ (in general matrices don't commute)

(see slide 21, can be omitted)

e) If $\hat{B} = \hat{A}$ in d) $\Rightarrow \mathbb{B} = \mathbb{A} = \mathbb{A}^\dagger$

f) $\mathbb{A}^\dagger = \mathbb{A}^{-1} \Rightarrow \mathbb{A}^\dagger\mathbb{A} = \mathbb{1} \Rightarrow \sum_k (\mathbb{A}^\dagger)_{ik} A_{kj} = \underbrace{\sum_k A^*_{ki} A_{kj}}_{(A_{1i} \cdots A_{ki} \cdots)^* \begin{pmatrix} A_{1j} \\ \vdots \\ A_{kj} \\ \vdots \end{pmatrix}} = \delta_{ij}$

Scalar-product matrix representation of projectors

- The scalar-product matrix representation of $|\phi_r\rangle\langle\phi_r|$ in any orthonormal basis set containing ϕ_r is readily seen to be

$$\begin{array}{cc} & \begin{array}{ccccc} & & \text{column } r & & \end{array} \\ \text{row } r \longrightarrow & \begin{pmatrix} 0 & \cdots & 0 & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & \cdots & 1 & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & \cdots & 0 & \cdots & 0 \end{pmatrix} \end{array} = \begin{array}{cc} \begin{pmatrix} 0 \\ \cdots \\ 1 \\ \cdots \\ 0 \end{pmatrix} & \text{row } r \end{array} \begin{array}{c} \begin{array}{ccccc} & & \text{column } r & & \end{array} \\ \begin{pmatrix} 0 & \cdots & 1 & \cdots & 0 \end{pmatrix} \end{array}$$

- More generally, the scalar-product matrix representation of $|\phi_r\rangle\langle\phi_s|$ in any orthonormal basis set containing ϕ_r and ϕ_s is

$$\begin{array}{cc} & \begin{array}{ccccc} & & \text{column } s & & \end{array} \\ \text{row } r \longrightarrow & \begin{pmatrix} 0 & \cdots & 0 & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & \cdots & 1 & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & \cdots & 0 & \cdots & 0 \end{pmatrix} \end{array} = \begin{array}{cc} \begin{pmatrix} 0 \\ \cdots \\ 1 \\ \cdots \\ 0 \end{pmatrix} & \text{row } r \end{array} \begin{array}{c} \begin{array}{ccccc} & & \text{column } s & & \end{array} \\ \begin{pmatrix} 0 & \cdots & 1 & \cdots & 0 \end{pmatrix} \end{array}$$

Operator expansion in an orthonormal basis set

- If $\{\phi_r\}$ is a denumerable orthonormal basis set then $\widehat{1} = \sum_r |\phi_r\rangle\langle\phi_r|$ and

$$\widehat{A} = \widehat{1}\,\widehat{A}\,\widehat{1} = \sum_r |\phi_r\rangle\langle\phi_r|\,\widehat{A}\,\sum_s |\phi_s\rangle\langle\phi_s|$$

$$= \sum_{rs} |\phi_r\rangle\langle\phi_r|\,\widehat{A}\,|\phi_s\rangle\langle\phi_s| = \sum_{rs} A_{rs}\,|\phi_r\rangle\langle\phi_s|$$

- If $\{\phi_r\}$ are eigenvectors of $\hat{A}$ this reduces to the spectral decomposition:

$$\widehat{A}\phi_{rj} = a_r\phi_{rj} \text{ with } \{\phi_{r1}\cdots\phi_{rd_r}\} \text{ orthonormal } \Rightarrow$$

$$\widehat{A} = \sum_{rj}\sum_{sk} a_r\delta_{rs}\delta_{jk}\,|\phi_{rj}\rangle\langle\phi_{sk}| = \sum_r a_r \sum_j^{d_r} |\phi_{rj}\rangle\langle\phi_{rj}| = \sum_r a_r \widehat{P}_{a_r}$$

Changes between discrete basis

Let us consider a change of basis: $\{\ldots\ \psi_i\ \ldots\} \rightarrow \{\ldots\ \psi'_r\ \ldots\}$

$$\psi'_r = \sum_i \psi_i L_{ir}$$

$$\begin{pmatrix}\psi'_1 & \ldots & \psi'_r & \ldots\end{pmatrix} = \begin{pmatrix}\psi_1 & \ldots & \psi_i & \ldots\end{pmatrix} \begin{pmatrix} L_{11} & \ldots & L_{1r} & \ldots \\ \ldots & \ldots & \ldots & \ldots \\ L_{i1} & \ldots & L_{ir} & \ldots \\ \ldots & \ldots & \ldots & \ldots \end{pmatrix}$$

$$\boxed{\boldsymbol{\psi}' = \boldsymbol{\psi}\, \mathbf{L}}$$

Transformation of vector coordinates:

linearly independent vectors

$$\Psi = \underline{\boldsymbol{\psi}\, \mathbf{c}} = \boldsymbol{\psi}'\, \mathbf{c}' = \underline{\boldsymbol{\psi}\, \mathbf{L}\, \mathbf{c}'} \qquad \boldsymbol{\psi}\underbrace{(\mathbf{c} - \mathbf{L}\, \mathbf{c}')}_{=\,\mathbf{0}} = 0 \qquad \boxed{\mathbf{c} = \mathbf{L}\, \mathbf{c}'}$$

If the inverse of matrix **L** exists (which happens whenever the two basis span the same space) then: $\mathbf{c}' = \mathbf{L}^{-1}\, \mathbf{c}$

Two basis in terms of a 3rd basis

Sometimes we are interested in a change between 2 basis sets $\boldsymbol{\phi}$ and $\boldsymbol{\phi}'$ –say 2 MO sets– that are, in turn, expressed in a 3rd basis set $\boldsymbol{\chi}$ –say an AO set.

Let's name $\mathbf{C}$ and $\mathbf{C}'$ the matrices expressing the changes from $\boldsymbol{\chi}$ to $\boldsymbol{\phi}$ and $\boldsymbol{\phi}'$:

$$\phi = \chi\mathbf{C} \qquad \phi' = \chi\mathbf{C}'$$

Then the matrix transforming $\boldsymbol{\phi}$ into $\boldsymbol{\phi}'$ can be readily obtained from $\mathbf{C}$ and $\mathbf{C}'$:

$$\phi' = \phi\mathbf{L} \quad \Rightarrow \quad \chi\mathbf{C}' = \chi\mathbf{C}\mathbf{L} \quad \Rightarrow \quad \chi(\mathbf{C}' - \mathbf{C}\mathbf{L}) = \mathbf{0}$$

and, since the elements of $\boldsymbol{\chi}$ are linearly independent,

$$\Rightarrow \quad \mathbf{C}' - \mathbf{C}\mathbf{L} = \mathbf{0} \quad \Rightarrow \quad \mathbf{C}' = \mathbf{C}\mathbf{L} \quad \Rightarrow \quad \boxed{\mathbf{L} = \mathbf{C}^{-1}\mathbf{C}'}$$

Changes between discrete basis

Let us consider a change of basis: $\boldsymbol{\psi}' = \boldsymbol{\psi}\,\mathbf{L}$

$$\hat{A}\,\underset{\substack{\uparrow\\ \mathbf{L}}}{\boldsymbol{\psi}} = \boldsymbol{\psi}\,\underset{\substack{\uparrow\\ \mathbf{L}}}{\boldsymbol{\mathcal{A}}} \qquad\qquad \hat{A}\,\boldsymbol{\psi}' = \boldsymbol{\psi}'\,\boldsymbol{\mathcal{A}}'$$

linearly independent vectors

(0, 0, … 0)

$$\boldsymbol{\psi}\underbrace{(\boldsymbol{\mathcal{A}}\,\mathbf{L} - \mathbf{L}\,\boldsymbol{\mathcal{A}}')}_{=\,\mathbf{0}} = 0$$

$$\boxed{\boldsymbol{\mathcal{A}}\,\mathbf{L} = \mathbf{L}\,\boldsymbol{\mathcal{A}}'}$$

If $\mathbf{L}^{-1}$ exists: $\boldsymbol{\mathcal{A}} = \mathbf{L}\,\boldsymbol{\mathcal{A}}'\,\mathbf{L}^{-1}$ $\qquad$ $\boldsymbol{\mathcal{A}}' = \mathbf{L}^{-1}\,\boldsymbol{\mathcal{A}}\,\mathbf{L}$

Changes between discrete basis

$$\boxed{\mathcal{A}\,\mathbf{L} = \mathbf{L}\,\mathcal{A}'} \longrightarrow \boxed{\mathbf{A}' = \mathbf{L}^{\dagger}\,\mathbf{A}\,\mathbf{L}} \qquad \mathcal{A}' = \mathbf{L}^{-1}\,\mathcal{A}\,\mathbf{L}$$

Exercise 2.3

Show that, if $\psi' = \psi\mathbf{L}$, then

a) $\mathbf{S}' = \mathbf{L}^{\dagger}\,\mathbf{S}\,\mathbf{L}$.

b) $\mathbf{A}' = \mathbf{L}^{\dagger}\,\mathbf{A}\,\mathbf{L}$ for any operator $\hat{A}$.

c) If ψ and ψ' are orthonormal then $\mathbf{L}$ is *unitary*.

d) The trace of a *true* matrix representation is invariant under *any* change of basis set.

e) The trace of an operator is the trace of its *true* matrix representation in any basis set.

f) The trace of a *scalar-product* matrix representation is invariant under any *unitary* change of basis set.

Hint: Use only matrix algebra for all the questions except for *a*).

Solution of the exercise 2.3

$$\boldsymbol{\psi}' = \boldsymbol{\psi}\,\mathbb{L} \;\Rightarrow\; \psi_i' = \sum_r \psi_r L_{ri}$$

a)
$$S'_{ij} = \langle \psi_i' | \psi_j' \rangle = \Big\langle \sum_r \psi_r L_{ri} \Big| \sum_s \psi_s L_{sj} \Big\rangle = \sum_{r,s} L_{ri}^{*} L_{sj} \overbrace{\langle \psi_r | \psi_s \rangle}^{S_{rs}} = (\mathbb{L}^{\dagger}\mathbb{S}\,\mathbb{L})_{ij}$$

b)
$$\underset{\uparrow\,\mathbb{L}^{\dagger}\mathbb{S}}{\mathcal{A}\mathbb{L}} = \underset{\uparrow\,\mathbb{L}^{\dagger}\mathbb{S}}{\mathbb{L}\mathcal{A}'} \;\Rightarrow\; \mathbb{L}^{\dagger}\underbrace{\mathbb{S}\mathcal{A}}_{\mathbb{A}}\mathbb{L} = \underbrace{\underbrace{\mathbb{L}^{\dagger}\mathbb{S}\,\mathbb{L}}_{\mathbb{S}'}\mathcal{A}'}_{\mathbb{A}'} \;\Rightarrow\; \mathbb{L}^{\dagger}\mathbb{A}\,\mathbb{L} = \mathbb{A}'$$

c) $\mathbb{S} = \mathbb{S}' = \mathbb{1}$ (orthonormality of $\boldsymbol{\psi}$ and $\boldsymbol{\psi}'$) $\Rightarrow$

$$\Big(\mathbb{1}' \underset{\nwarrow a)}{=} \mathbb{L}^{\dagger}\mathbb{1}\,\mathbb{L} = \mathbb{L}^{\dagger}\mathbb{L}\Big)\times\mathbb{L}^{-1} \;\Rightarrow\; \mathbb{L}^{-1} = \mathbb{L}^{\dagger}\underbrace{\mathbb{L}\,\mathbb{L}^{-1}}_{\mathbb{1}} = \mathbb{L}^{\dagger}$$

d)
$$\mathrm{Tr}(\mathcal{A}') = \mathrm{Tr}(\mathbb{L}^{-1}\mathcal{A}\,\mathbb{L}) = \mathrm{Tr}(\mathcal{A}\underbrace{\mathbb{L}\,\mathbb{L}^{-1}}_{\mathbb{1}}) = \mathrm{Tr}(\mathcal{A})$$

e)
$$\mathrm{Tr}\,\hat{A} = \mathrm{Tr}(\underset{\substack{\uparrow \\ \text{in any orthonormal} \\ \text{basis set}}}{\mathbb{A}}) = \mathrm{Tr}(\underset{\substack{\uparrow \\ \text{in the same} \\ \text{basis set}}}{\mathcal{A}}) \underset{\substack{\nwarrow \\ d)}}{=} \mathrm{Tr}(\underset{\substack{\uparrow \\ \text{in any other} \\ \text{basis set}}}{\mathcal{A}'})$$

f)
$$\mathrm{Tr}(\mathbb{A}') = \mathrm{Tr}(\mathbb{L}^{\dagger}\mathbb{A}\,\mathbb{L}) \underset{\substack{\uparrow \\ \mathbb{L}\text{ unitary}}}{=} \mathrm{Tr}(\mathbb{L}^{-1}\mathbb{A}\,\mathbb{L}) = \mathrm{Tr}(\mathbb{A}\underbrace{\mathbb{L}\,\mathbb{L}^{-1}}_{\mathbb{1}}) = \mathrm{Tr}(\mathbb{A})$$

Changes between discrete basis

Exercise 2.4

Let us make the following change of basis in the 3-dimensional Hilbert space considered in exercise 2.1:

$$\begin{aligned} \chi_1' &= \chi_1 + \chi_2 + \chi_3 \\ \chi_2' &= \chi_1 - \chi_3 \\ \chi_3' &= \chi_2 - \chi_3 \end{aligned}$$

a) Write the matrix of the basis change.

b) Write the matrices representing the vector $\phi = \chi_1 + \chi_2$ in the old and the new basis.

c) Calculate $\langle \chi_2' | \chi_3' \rangle$.

d) Write the true and the scalar-product matrix representations of the operator $\widehat{A}$ (defined in exercise 2.1) in the basis $\{\chi_1', \chi_2', \chi_3'\}$.

Hint: You can use any matrix calculation tool, such as the one provided in www.bluebit.gr/matrix-calculator/

Results:

a) $\begin{pmatrix} 1 & 1 & 0 \\ 1 & 0 & 1 \\ 1 & -1 & -1 \end{pmatrix}$; b) $\begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix}, \begin{pmatrix} 2/3 \\ 1/3 \\ 1/3 \end{pmatrix}$; c) 0.5; d) $\begin{pmatrix} 2 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \begin{pmatrix} 12 & 0 & 0 \\ 0 & -1 & -1/2 \\ 0 & -1/2 & -1 \end{pmatrix}$.

Solution of the exercise 2.4

a) $$(\chi_1' \; \chi_2' \; \chi_3') = (\chi_1 \; \chi_2 \; \chi_3) \overbrace{\begin{pmatrix} 1 & 1 & 0 \\ 1 & 0 & 1 \\ 1 & -1 & -1 \end{pmatrix}}^{\mathbb{L}}$$

b) Slide 11: $$\mathbb{C}' = \mathbb{L}^{-1}\mathbb{C} = \frac{1}{3}\begin{pmatrix} 1 & 1 & 1 \\ 2 & -1 & -1 \\ -1 & 2 & -1 \end{pmatrix} \underbrace{\begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix}}_{\mathbb{C}} = \begin{pmatrix} 2/3 \\ 1/3 \\ 1/3 \end{pmatrix}$$

(alternatively: $\mathbb{C} = \mathbb{L}\mathbb{C}' \Rightarrow \begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix} = \begin{pmatrix} 1 & 1 & 0 \\ 1 & 0 & 1 \\ 1 & -1 & -1 \end{pmatrix}\begin{pmatrix} c_1' \\ c_2' \\ c_3' \end{pmatrix} \Rightarrow \left.\begin{array}{l} 1 = c_1' + c_2' \\ 1 = c_1' - c_3' \\ 0 = c_1' - c_2' - c_3' \end{array}\right\} \Rightarrow \begin{array}{l} c_1' = \ldots \\ c_2' = \ldots \\ c_3' = \ldots \end{array}$)

c) Slide 3: $$\langle \chi_2' | \chi_3' \rangle = \mathbb{C}_2^{\dagger}\, \mathbb{S}\, \mathbb{C}_3 = (1 \; 0 \; -1) \underbrace{\begin{pmatrix} 1 & 1/2 & 1/2 \\ 1/2 & 1 & 1/2 \\ 1/2 & 1/2 & 1 \end{pmatrix}\begin{pmatrix} 0 \\ 1 \\ -1 \end{pmatrix}}_{\begin{pmatrix} 0 \\ 1/2 \\ -1/2 \end{pmatrix}} = 1/2$$

(alternatively: slide 14: $\mathbb{S}' = \mathbb{L}^{\dagger}\mathbb{S}\mathbb{L} \Rightarrow S'_{23} = \sum_{rs} L^*_{r2} S_{rs} L_{s3} = \ldots$)

d) Slide 13: $$\mathcal{A}' = \mathbb{L}^{-1}\mathcal{A}\,\mathbb{L} = \frac{1}{3}\begin{pmatrix} 1 & 1 & 1 \\ 2 & -1 & -1 \\ -1 & 2 & -1 \end{pmatrix}\begin{pmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{pmatrix}\begin{pmatrix} 1 & 1 & 0 \\ 1 & 0 & 1 \\ 1 & -1 & -1 \end{pmatrix} = \begin{pmatrix} 2 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

$$\mathbb{A}' = \mathbb{L}^{\dagger}\mathbb{A}\mathbb{L} = \begin{pmatrix} 1 & 1 & 1 \\ 1 & 0 & -1 \\ 0 & 1 & -1 \end{pmatrix}\begin{pmatrix} 1 & 3/2 & 3/2 \\ 3/2 & 1 & 3/2 \\ 3/2 & 3/2 & 1 \end{pmatrix}\begin{pmatrix} 1 & 1 & 0 \\ 1 & 0 & 1 \\ 1 & -1 & -1 \end{pmatrix} = \begin{pmatrix} 12 & 0 & 0 \\ 0 & -1 & -1/2 \\ 0 & -1/2 & -1 \end{pmatrix}$$

(you can check that
$$\mathbb{A}' = \mathbb{S}'\mathcal{A}' = \mathbb{L}^{\dagger}\mathbb{S}\mathbb{L}\mathcal{A}' = \begin{pmatrix} 6 & 0 & 0 \\ 0 & 1 & 1/2 \\ 0 & 1/2 & 1 \end{pmatrix}\begin{pmatrix} 2 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} = \begin{pmatrix} 12 & 0 & 0 \\ 0 & -1 & -1/2 \\ 0 & -1/2 & -1 \end{pmatrix}$$)

Eigenvalues and eigenvectors

$$\widehat{A}\psi_i = a_i\psi_i \qquad i = 1, \cdots i, \cdots$$

$$\widehat{A}\begin{pmatrix}\psi_1 & \ldots & \boxed{\psi_i} & \ldots\end{pmatrix} = \begin{pmatrix}\psi_1 & \ldots & \psi_i & \ldots\end{pmatrix}\begin{pmatrix} a_1 & \ldots & 0 & \ldots \\ \ldots & \ldots & \ldots & \ldots \\ 0 & \ldots & a_i & \ldots \\ \ldots & \ldots & \ldots & \ldots \end{pmatrix}$$

or, in matrix notation:

$$\widehat{A}\boldsymbol{\psi} = \boldsymbol{\psi}\mathbf{a}_\psi \qquad \text{with } \mathbf{a}_\psi \text{ diagonal:} \quad (\mathbf{a}_\psi)_{ij} = a_i\delta_{ij}$$

$\Rightarrow$ the true representation of an operator in the basis formed by its eigenvectors is *diagonal*.

Matrix diagonalization

The solution of the operator eigenvalue equation is *equivalent* to finding the basis change L that diagonalizes its true representation in any basis $\boldsymbol{\phi}$:

$$\text{solve} \quad \hat{A}\psi = \psi\mathbf{a}_\psi \quad \leftrightarrow \quad \text{find } \mathsf{L} \text{ such that } \quad \boxed{\mathcal{A}_\phi \mathsf{L} = \mathsf{L}\mathbf{a}_\psi}$$

$$\begin{pmatrix} \mathcal{A}_{\phi 11} & \cdots & \mathcal{A}_{\phi 1r} & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ \mathcal{A}_{\phi j1} & \cdots & \mathcal{A}_{\phi jr} & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{pmatrix} \begin{pmatrix} L_{11} & \cdots & L_{1i} & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ L_{r1} & \cdots & L_{ri} & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{pmatrix} = \begin{pmatrix} L_{11} & \cdots & L_{1i} & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ L_{j1} & \cdots & L_{ji} & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{pmatrix} \begin{pmatrix} a_1 & \cdots & 0 & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ 0 & \cdots & a_i & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{pmatrix}$$

The i^{th} column of the matrix products:

$$\begin{pmatrix} \mathcal{A}_{\phi 11} & \cdots & \mathcal{A}_{\phi 1r} & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ \mathcal{A}_{\phi j1} & \cdots & \mathcal{A}_{\phi jr} & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{pmatrix} \begin{pmatrix} L_{1i} \\ \cdots \\ L_{ri} \\ \cdots \end{pmatrix} = \begin{pmatrix} L_{11} & \cdots & L_{1i} & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ L_{j1} & \cdots & L_{ji} & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{pmatrix} \begin{pmatrix} 0 \\ \cdots \\ a_i \\ \cdots \end{pmatrix} = \begin{pmatrix} L_{1i}a_i \\ \cdots \\ L_{ji}a_i \\ \cdots \end{pmatrix} = a_i \begin{pmatrix} L_{1i} \\ \cdots \\ L_{ji} \\ \cdots \end{pmatrix}$$

gives the *matrix eigenvalue equation:*

$$\boxed{\mathcal{A}_\phi \mathsf{l}_i = a_i \mathsf{l}_i} \quad \rightarrow \quad (\mathcal{A}_\phi - a_i\mathbf{1})\mathsf{l}_i = \mathbf{0} \quad \rightarrow \quad |\mathcal{A}_\phi - a_i\mathbf{1}| = 0 \quad \cdots$$

Matrix diagonalization

By expressing the eigenvector basis in terms of the original basis set:

$$\begin{pmatrix}\psi_1 & \dots & \boxed{\psi_i} & \dots\end{pmatrix} = \begin{pmatrix}\phi_1 & \dots & \phi_r & \dots\end{pmatrix}\begin{pmatrix} L_{11} & \dots & L_{1i} & \dots \\ \dots & \dots & \dots & \dots \\ L_{r1} & \dots & L_{ri} & \dots \\ \dots & \dots & \dots & \dots \end{pmatrix}$$

we see that the column $\mathbf{l}_i$ of $\mathbf{L}$ contains the coefficients of an eigenvector ψ_i with eigenvalue a_i:

$$\psi_i = \sum_r \phi_r L_{ri}$$

so that the eigenvectors of $\boldsymbol{\mathcal{A}}_\phi$ *represent* the eigenvectors of $\hat{A}$ (as expected).

Scalar-product matrix diagonalization

For the *scalar-product representation* the operator eigenvalue equation takes a more complicated form:

$$\underset{\mathbf{S}_\phi}{\underset{\uparrow}{}}\mathcal{A}_\phi\,\mathbf{L} = \underset{\mathbf{S}_\phi}{\underset{\uparrow}{}}\mathbf{L}\,\mathbf{a}_\psi \quad\longrightarrow\quad \boxed{\mathbf{A}_\phi\,\mathbf{L} = \mathbf{S}_\phi\,\mathbf{L}\,\mathbf{a}_\psi}$$

$$\begin{pmatrix} A_{\phi 11} & \cdots & A_{\phi 1r} & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ A_{\phi j1} & \cdots & A_{\phi jr} & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{pmatrix} \begin{pmatrix} L_{11} & \cdots & L_{1i} & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ L_{r1} & \cdots & L_{ri} & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{pmatrix} = \begin{pmatrix} S_{\phi 11} & \cdots & S_{\phi 1r} & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ S_{\phi j1} & \cdots & S_{\phi jr} & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{pmatrix} \begin{pmatrix} L_{11}a_1 & \cdots & L_{1i}a_i & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ L_{r1}a_1 & \cdots & L_{ri}a_i & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{pmatrix}$$

$$\mathbf{A}_\phi \mathbf{l}_i = a_i \mathbf{S}_\phi \mathbf{l}_i \quad\longrightarrow\quad (\mathbf{A}_\phi - a_i \mathbf{S}_\phi)\mathbf{l}_i = \mathbf{0} \quad\longrightarrow\quad |\mathbf{A}_\phi - a_i \mathbf{S}_\phi| = 0 \quad \cdots$$

T3 $\Rightarrow$ If $\hat{A}$ is *hermitian* its eigenvectors can be chosen *orthonormal* ($\mathbf{S}_\psi = \mathbf{1}$).
If, moreover, the starting basis $\{\ldots\phi_i\ldots\}$ is also orthonormal, then $\mathbf{L}$ is *unitary* (ex. 2.3.c).

Eigenvalues and eigenvectors in matrix form

Exercise 2.5

Verify that the new basis vectors introduced in exercise 2.4:

$$\begin{aligned}\chi_1' &= \chi_1 + \chi_2 + \chi_3 \\ \chi_2' &= \chi_1 - \chi_3 \\ \chi_3' &= \chi_2 - \chi_3\end{aligned}$$

are eigenvectors of the operator $\widehat{A}$ defined in exercise 2.1, so that the corresponding true matrix representation of this operator is diagonal. Note that its scalar-product matrix representation is non-diagonal (see exercise 2.4 d).

Results: $\widehat{A}\chi_1' = 2\chi_1'$; $\widehat{A}\chi_2' = -\chi_2'$; $\widehat{A}\chi_3' = -\chi_3'$.

Solution of the exercise 2.5

a) $\hat{A}\mathbf{x}' = \mathbf{x}'\mathbb{A}'$

ex 2,1

$$\hat{A}x_1' = \hat{A}(x_1 + x_2 + x_3) = (x_2 + x_3) + (x_1 + x_3) + (x_1 + x_2) = 2x_1'$$

$$\hat{A}x_2' = \hat{A}(x_1 - x_3) = (\cancel{x_2} + x_3) - (x_1 + \cancel{x_2}) = -(x_1 - x_3) = -x_2'$$

$$\hat{A}x_3' = \hat{A}(x_2 - x_3) = (\cancel{x_1} + x_3) - (\cancel{x_1} + x_2) = -(x_2 - x_3) = -x_3'$$

$\Rightarrow$ x_1', x_2', x_3' are eigenvectors of $\hat{A}$, and $\mathbb{A}' = \begin{pmatrix} 2 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$

(a result already found in 2.4d)

Functions of matrices

Let $\boxed{f(\hat{A}) = \sum_{k=0}^{\infty} f_k \hat{A}^k}$ (slide 1.38): what is the representation of $f(\hat{A})$ in an *orthonormal* discrete basis $\{\ldots \phi_i \ldots\}$?

$$\begin{aligned}\langle \phi_i | f(\hat{A}) | \phi_j \rangle &= \sum_{k=0}^{\infty} f_k \langle \phi_i | \hat{A}^k | \phi_j \rangle \\ &= \sum_{k=0}^{\infty} f_k \underline{\sum_l} \sum_m \cdots \sum_p \langle \phi_i | \hat{A} \underline{| \phi_l \rangle \langle \phi_l |} \hat{A} | \phi_m \rangle \ldots \langle \phi_p | \hat{A} | \phi_j \rangle \\ &= \sum_{k=0}^{\infty} f_k (\mathbf{A}^k)_{ij} \\ &= [\, f(\mathbf{A})\,]_{ij} \,,\end{aligned}$$

where we have defined the function f of matrix **A** as $\boxed{f(\mathbf{A}) \equiv \sum_{k=0}^{\infty} f_k \mathbf{A}^k}$

- $[f(\mathbf{A})]^\dagger = \sum_k (f_k \mathbf{A}^k)^\dagger = \sum_k f_k^* (\mathbf{A}^\dagger)^k$

  $\Rightarrow$ a real function of an hermitian matrix is an hermitian matrix: $[f(\mathbf{A})]^\dagger = f(\mathbf{A})$

- Convergence of the Taylor expansion is sometimes slow

  (Python: scipy.linalg → linalg.expm3 to calculate exp(A) → trigonometric, hyperbolic ...)

Functions of matrices

f(**A**) can be calculated from **A** by diagonalizing this matrix and using **A = LaL**$^{-1}$ (slide 2.11 + orthonormal basis set):

$$f(\mathbf{A}) = \sum_{k=0}^{\infty} f_k \mathbf{A}^k = \sum_{k=0}^{\infty} f_k (\mathbf{LaL}^{-1}) \cdots (\mathbf{LaL}^{-1}) = \mathbf{L} \underbrace{\sum_{k=0}^{\infty} f_k \mathbf{a}^k}_{f(\mathbf{a})} \mathbf{L}^{-1}$$

$$(\mathbf{a}^2)_{ij} = \sum_{l=1}^{n} a_{il} a_{lj} = \sum_{l=1}^{n} a_i \delta_{il}\, a_j \delta_{lj} = a_i^2 \delta_{ij} \quad \Rightarrow \quad (\mathbf{a}^k)_{ij} = a_i^k \delta_{ij}$$

$$\Rightarrow \quad (f(\mathbf{a}))_{ij} = \left(\sum_{k=0}^{\infty} f_k \mathbf{a}^k \right)_{ij} = \sum_{k=0}^{\infty} f_k a_i^k \delta_{ij} = \left(\sum_{k=0}^{\infty} f_k a_i^k \right) \delta_{ij} = f(a_i) \delta_{ij}$$

Procedure: **A** → **a** → f(**a**) → f(**A**)

(Fortran: LAPACK to diagonalize. Python: scipy.linalg → linalg.expm2 to calculate exp(A) or linalg.expm (uses scaling and a Padé approximation for exp(x))

Orthonormalization

Given a *non-orthonormal basis* **ψ** we look for **L** such that **ψ′** = **ψL** with **S'=1**

- *Schmidt method*:

  (asymmetric)

$$\chi_1' = N_1\chi_1 = \chi_1/\langle\chi_1|\chi_1\rangle^{1/2}$$
$$\chi_2' = N_2\{\chi_2 - \langle\chi_1'|\chi_2\rangle\chi_1'\}$$
$$\chi_3' = N_3\{\chi_3 - \langle\chi_1'|\chi_3\rangle\chi_1' - \langle\chi_2'|\chi_3\rangle\chi_2'\}$$
$$\text{etc.}$$

- *Löwdin method*:

$$\mathbf{L} = \mathbf{S}^{-1/2} \Rightarrow \mathbf{S}' = \mathbf{L}^\dagger\,\mathbf{S}\,\mathbf{L} = (\mathbf{S}^{-1/2})^\dagger\,\mathbf{S}\,\mathbf{S}^{-1/2} = \mathbf{S}^{-1/2}\,\mathbf{S}\,\mathbf{S}^{-1/2} = \mathbf{1}$$

(there has to be no linear dependencies between the basis vectors)

Canonical othonormalization

- *Canonical method:* $\mathbf{L} = \mathbf{U}\mathbf{s}^{-1/2}$ with $\mathbf{U}^\dagger\mathbf{S}\mathbf{U} = \mathbf{s} \Rightarrow \mathbf{L}^\dagger\,\mathbf{S}\,\mathbf{L} = \mathbf{s}^{-1/2}\,\mathbf{U}^\dagger\mathbf{S}\mathbf{U}\mathbf{s}^{-1/2} = \mathbf{1}$

This diagonal matrix can be truncated if necessary: $\overline{\mathbf{L}} \equiv \overline{\mathbf{U}}\ \overline{\mathbf{s}^{-1/2}}$

$$\begin{pmatrix} L_{11} & \cdots & L_{1,n-k} \\ \cdots & \cdots & \cdots \\ L_{n-k,1} & \cdots & L_{n-k,n-k} \\ \cdots & \cdots & \cdots \\ L_{n,1} & \cdots & L_{n,n-k} \end{pmatrix} = \begin{pmatrix} U_{11} & \cdots & U_{1,n-k} \\ \cdots & \cdots & \cdots \\ U_{n-k,1} & \cdots & U_{n-k,n-k} \\ \cdots & \cdots & \cdots \\ U_{n,1} & \cdots & U_{n,n-k} \end{pmatrix} \begin{pmatrix} s_1^{-1/2} & \cdots & 0 \\ \cdots & \cdots & \cdots \\ 0 & \cdots & s_{n-k}^{-1/2} \end{pmatrix}$$

$$\begin{pmatrix} \psi_1 & \cdots & \psi_{n-k} \end{pmatrix} = \begin{pmatrix} \phi_1 & \cdots & \phi_{n-k} & \cdots & \phi_n \end{pmatrix} \begin{pmatrix} L_{11} & \cdots & L_{1,n-k} \\ \cdots & \cdots & \cdots \\ L_{n-k,1} & \cdots & L_{n-k,n-k} \\ \cdots & \cdots & \cdots \\ L_{n,1} & \cdots & L_{n,n-k} \end{pmatrix}$$

3 birds with 1 stone:

- orthonormal basis
- shorter dimension
- faster convergence of SCF (HF, DFT,...)

Canonical othonormalization

Exercise 2.6

a) Use the canonical method to ortonormalize a basis of a real 3-dimensional Hilbert space with the following overlap matrix:

$$\mathbf{S} = \begin{pmatrix} 1 & 0.5 & 0.8 \\ 0.5 & 1 & 0.2 \\ 0.8 & 0.2 & 1 \end{pmatrix}$$

b) Which vector of the new basis could be omitted with a least lost of "basis quality"?

Results: *a*) $\chi_1'(s = 2.04) = 0.47\chi_1 + 0.31\chi_2 + 0.42\chi_3$, $\chi_2'(s = 0.82) = 0.11\chi_1 - 0.94\chi_2 + 0.56\chi_3$, $\chi_3'(s = 0.14) = 1.99\chi_1 - 0.76\chi_2 - 1.66\chi_3$; *b*) the third.

(using www.bluebit.gr/matrix-calculator/)

Solution of the exercise 2.6

```
     1.0  0.5  0.8
S =  0.5  1.0  0.2
     0.8  0.2  1.0

     0.6706  0.7351  0.0996
U =  0.4372 -0.2832 -0.8536
     0.5993 -0.6159  0.5113

     2.0410  0.0000  0.0000
s =  0.0000  0.1371  0.0000
     0.0000  0.0000  0.8219

         0.7000  0.0000  0.0000
s-1/2 =  0.0000  2.7007  0.0000
         0.0000  0.0000  1.1031

               0.4694  1.9853  0.1099
L = U s-1/2 =  0.3060 -0.7648 -0.9416
               0.4195 -1.6634  0.5640

          0.4694  0.1099
Ltrunc =  0.3060 -0.9416
          0.4195  0.5640
```

Truncated "basis" sets

Let $\bar{\boldsymbol{\chi}} = \{\chi_1 \ldots \chi_{n\text{-}k}\}$ an *incomplete* set or *truncated* "basis" set and $\{\chi_{n\text{-}k+1} \ldots \chi_n\}$ a basis of its orthogonal complement, so that $\boldsymbol{\chi} = \{\chi_1 \ldots \chi_{n\text{-}k} \ldots \chi_n\}$ is a complete set.

- The true matrix representation of $\hat{A}$ in $\{\chi_1 \ldots \chi_{n\text{-}k} \ldots \chi_n\}$ is:

$$\widehat{A}\,\boldsymbol{\chi} = \left(\widehat{A}\,\chi_1 \cdots \widehat{A}\,\chi_{n-k} \cdots \widehat{A}\,\chi_n\right)$$

$$= (\chi_1 \cdots \chi_{n-k} \cdots \chi_n) \begin{pmatrix} \mathcal{A}_{11} & \ldots & \mathcal{A}_{1,n-k} & \cdots & \mathcal{A}_{1,n} \\ \ldots & \ldots & \ldots & \ldots & \ldots \\ \mathcal{A}_{n-k,1} & \ldots & \mathcal{A}_{n-k,n-k} & \ldots & \mathcal{A}_{n-k,n} \\ \ldots & \ldots & \ldots & \ldots & \ldots \\ \mathcal{A}_{n,1} & \ldots & \mathcal{A}_{n,n-k} & \ldots & \mathcal{A}_{n,n} \end{pmatrix}$$

- and the true matrix representation of the projection of $\hat{A}$ onto $\bar{\boldsymbol{\chi}}$ is:

$$\widehat{P_{\bar{\chi}}}\widehat{A}\widehat{P_{\bar{\chi}}}\,\boldsymbol{\chi} = \left(\widehat{P_{\bar{\chi}}}\widehat{A}\,\chi_1 \cdots \widehat{P_{\bar{\chi}}}\widehat{A}\,\chi_{n-k} \cdots 0\right)$$

$$= (\chi_1 \cdots \chi_{n-k} \cdots \chi_n) \begin{pmatrix} \mathcal{A}_{11} & \ldots & \mathcal{A}_{1,n-k} & \cdots & 0 \\ \ldots & \ldots & \ldots & \ldots & \ldots \\ \mathcal{A}_{n-k,1} & \ldots & \mathcal{A}_{n-k,n-k} & \ldots & 0 \\ \ldots & \ldots & \ldots & \ldots & \ldots \\ 0 & \ldots & 0 & \ldots & 0 \end{pmatrix}$$

Truncated "basis" sets

The *n-k* x *n-k* submatrix $\bar{\boldsymbol{\mathcal{A}}}$ represents $\widehat{P_{\bar{\chi}}}\,\widehat{A}\widehat{P_{\bar{\chi}}}$ in the truncated basis $\bar{\boldsymbol{\chi}}$:

$$\widehat{P_{\bar{\chi}}}\,\widehat{A}\widehat{P_{\bar{\chi}}}\,\boldsymbol{\chi} = \left(\widehat{P_{\bar{\chi}}}\,\widehat{A}\,\chi_1 \cdots \widehat{P_{\bar{\chi}}}\,\widehat{A}\,\chi_{n-k}\right)$$
$$= (\chi_1 \cdots \chi_{n-k}) \begin{pmatrix} \mathcal{A}_{11} & \cdots & \mathcal{A}_{1,n-k} \\ \cdots & \cdots & \cdots \\ \mathcal{A}_{n-k,1} & \cdots & \mathcal{A}_{n-k,n-k} \end{pmatrix}$$

and the elements of the corresponding scalar-product *n-k* x *n-k* matrix representation $\bar{\mathbf{A}} = \bar{\mathbf{S}}\bar{\boldsymbol{\mathcal{A}}}$ are

$$\bar{\mathsf{A}}_{ji} = \langle \chi_j |\, \widehat{P_{\bar{\chi}}}\,\widehat{A}\widehat{P_{\bar{\chi}}}\,\chi_i \rangle = \langle\, \widehat{P_{\bar{\chi}}}\chi_j \Big|\, \widehat{A}\widehat{P_{\bar{\chi}}}\,\chi_i \rangle = \langle \chi_j |\, \widehat{A}\,\chi_i \rangle, \quad i,j = 1, \cdots n-k$$

Separation theorem

Is there any relationship between the eigenvalues of $\hat{A}$ and those of $\widehat{P_{\bar{\chi}}}\hat{A}\widehat{P_{\bar{\chi}}}$:

$$\hat{A}\psi_i = a_i\psi_i \qquad \widehat{P_{\bar{\chi}}}\hat{A}\widehat{P_{\bar{\chi}}}\,\bar{\psi}_i = \bar{a}_i\,\bar{\psi}_i$$

or, equivalently, between the eigenvalues of $\boldsymbol{\mathcal{A}}$ and those of $\bar{\boldsymbol{\mathcal{A}}}$:

$$\boldsymbol{\mathcal{A}}\mathbf{c}_i = a_i\mathbf{c}_i \qquad \bar{\boldsymbol{\mathcal{A}}}\bar{\mathbf{c}}_i = \bar{a}_i\bar{\mathbf{c}}_i$$

or, equivalently,

$$\mathbf{A}\mathbf{c}_i = a_i\mathbf{S}\mathbf{c}_i \qquad \bar{\mathbf{A}}\bar{\mathbf{c}}_i = \bar{a}_i\bar{\mathbf{S}}\bar{\mathbf{c}}_i \qquad ?$$

- **T12** (*separation* or *interleaving theorem*): if we add an additional vector to the truncated basis the new *n–k* lowest eigenvalues are lower or equal than the corresponding old ones (and the new highest eigenvalue is higher than all the old ones), which is the basis of the *linear variation method*. By further adding vectors one should tend to completeness, so the eigenvalues of $\bar{\boldsymbol{\mathcal{A}}}$ are higher (or equal) than the corresponding ones of $\boldsymbol{\mathcal{A}}$: $\bar{a}_i \geq a_i \quad \forall i = 1,\ldots n-k$

Continuous "basis" sets

If we choose a basis set made of eigenvectors of observables with *continuous* spectrum the coefficients representing any vector state will be *functions* of the corresponding continuous eigenvalues (*wave functions*).

- *E. g.*: x and p are 2 CSCO for a one-dimensional spin-less particle:

$$\Psi(x) = \langle \psi_x | \Psi \rangle \equiv \langle x | \Psi \rangle \qquad \tilde{\Psi}(p) = \langle \psi_p | \Psi \rangle \equiv \langle p | \Psi \rangle$$

According to the third postulate $|\Psi(x)|^2$ y $|\Psi(p)|^2$ are probability densities

- Scalar products in the (continuous) position representation:

$$\langle \Psi | \Psi' \rangle = \langle \Psi | \boxed{\int_{-\infty}^{\infty} | x \rangle \langle x | dx} | \Psi' \rangle = \int_{-\infty}^{\infty} \Psi^*(x)\, \Psi'(x)\, dx = \int_{-\infty}^{\infty} \Psi^*(p)\, \Psi'(p)\, dp$$

- Matrix representation in position repr.: $A(x, x') = \langle \psi_x | \hat{A}\, \psi_{x'} \rangle = \langle x | \hat{A} | x' \rangle$

A *diagonal* matrix representation: $\langle x | \hat{x} | x' \rangle = x\, \delta(x' - x)$

Position representation

Definition of the *Dirac delta* (one among many): $\int_{-\infty}^{\infty} \delta(x'-x)f(x')dx' = f(x)$

$$(\widehat{x}\Psi)(x) = \langle x\,|\widehat{x}\;\Psi\rangle = \langle x\,|\widehat{x}\left(\int_{-\infty}^{\infty} |x'\rangle\langle x'|\,dx'\right)\Psi\rangle$$

$$= \int_{-\infty}^{\infty} x\delta(x'-x)\Psi(x')dx' = x\Psi(x)$$

so the effect of the position operator in the position representation is:

$$\widehat{x}\Psi(x) = x\Psi(x)$$

Position representation of $\widehat{p}$

The momentum operator in the position representation can be chosen (among other more complicate choices) as:

$$\widehat{p_x}\Psi(x) = -i\hbar\frac{d}{dx}\Psi(x)$$

This operator is said to be *local*, because we only need to know $\Psi(x)$ in the vicinity of x to obtain $\widehat{p_x}\Psi(x)$.
Diagonal operators $\hat{A}$ are local operators for which only its value at x is needed to obtain $\hat{A}\Psi(x)$).

Exercise 2.7

(a) Show that the position-representation operator $\widehat{p_x} = -i\hbar\frac{d}{dx}$ satisfies the second postulate.

(b) Show that $\psi_p(x) = (2\pi\hbar)^{-1/2}exp(ipx/\hbar)$ is an eigenfunction of $\widehat{p_x}$ with real eigenvalue for any real number p.

Solution of the exercise 2.7

a) $$[\hat{x},\hat{p}_x]\Psi(x) = \cancel{x\left(-i\hbar\frac{d}{dx}\Psi(x)\right)} - \left(\underbrace{-i\hbar\frac{d}{dx}\,x\,\Psi(x)}_{\Psi(x)+\cancel{x\frac{d}{dx}\Psi(x)}}\right) = i\hbar\,\Psi(x)$$

Since this applies to any $\Psi(x)\in\mathcal{H}$ we conclude that $[\hat{x},\hat{p}_x] = i\hbar$

b) $$-i\hbar\frac{d}{dx}(2\pi\hbar)^{-1/2}\exp(i\underset{\text{real}}{p}x/\hbar) = \underbrace{-i\hbar\frac{ip}{\hbar}}_{p\in\mathbb{R}}(2\pi\hbar)^{-1/2}\exp(ipx/\hbar)$$

Non-local or *integral* operators

In the general case:

$$\left(\widehat{A}\Psi\right)(x) \equiv \widehat{A}\Psi(x) = \langle x \left| \widehat{A} \; \Psi \right\rangle = \boxed{\langle x \left| \widehat{A} \left(\int_{-\infty}^{\infty} |x'\rangle \right.\right.} \langle x' | \, dx' \Bigg) \; \Psi \rangle$$

$$= \int_{-\infty}^{\infty} \underbrace{\boxed{A(x, x')}}_{\text{kernel of } \hat{A}} \Psi(x') dx'$$

Examples:

1. The position representation of the Coulomb operator: $\widehat{j}_l(\vec{r}_1)\phi(\vec{r}_1) = \left\{ \int_{\vec{r}_2} [\phi_l(\vec{r}_2)]^* \frac{1}{r_{12}} \phi_l(\vec{r}_2) d\vec{r}_2 \right\} \phi(\vec{r}_1)$ is diagonal.

2. The position representation of the exchange operator: $\widehat{k}_l(\vec{r}_1)\phi(\vec{r}_1) = \left\{ \int_{\vec{r}_2} \underbrace{\boxed{[\phi_l(\vec{r}_2)]^* \frac{1}{r_{12}}}}_{\text{kernel}} \phi(\vec{r}_2) d\vec{r}_2 \right\} \phi_l(\vec{r}_1)$ is of integral type.

Changes between continuous representations

Position representation of a momentum eigenvector: $\hat{p}(x)\,\psi_p(x) = p\,\psi_p(x)$

$$\psi_p(x) = (2\pi\hbar)^{-1/2}\exp(ipx/\hbar) \qquad \langle p\,|\,p'\rangle = (2\pi\hbar)^{-1}\int_{-\infty}^{\infty}\exp[i(p'-p)x/\hbar]\,dx = \delta(p-p')$$

$$\tilde{\Psi}(p) = \langle p|\left(\int_{-\infty}^{\infty}|x\rangle\langle x|\,dx\right)|\Psi\rangle = \int_{-\infty}^{\infty}\langle p|x\rangle\langle x|\Psi\rangle\,dx = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty}\exp(-ipx/\hbar)\,\Psi(x)\,dx$$

(*Fourier transform*)

$$\Psi(x) = \int_{-\infty}^{\infty}\langle x|p\rangle\langle p|\Psi\rangle\,dp = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty}\exp(ipx/\hbar)\,\tilde{\Psi}(p)\,dp$$

Direct products of vectors → normal products of functions:

$$|\psi(1)\rangle\otimes|\phi(2)\rangle \quad\rightarrow\quad \langle x_1\otimes x_2|\,\psi(1)\otimes\phi(2)\rangle = \langle x_1|\,\psi(1)\rangle\,\langle x_2|\,\phi(2)\rangle = \psi(x_1)\phi(x_2)$$

Notation

$\vec{x}_i \equiv i$ space+spin coordinates of electron i

$\psi_j(\vec{x}_i) = \langle \vec{x}_i | \psi_j \rangle$ spin-orbital $\qquad \psi_j(\vec{x}_i) = \phi_j(\vec{r}_i)\,\alpha(\omega_i)$

$\phi_j(\vec{r}_i) = \langle \vec{r}_i | \phi_j \rangle$ orbital $\qquad \alpha(\omega_i) = \langle m_{si} | \alpha \rangle = \delta_{m_{si},\,1/2}$

$\beta(\omega_i) = \langle m_{si} | \beta \rangle = \delta_{m_{si},\,-1/2}$

$\chi_\mu(\vec{r}_i)$ "basis" function (atomic orbital)

$$\phi_j(\vec{r}_i) = \sum_{\mu=1}^{n} \chi_\mu(\vec{r}_i)\, c_{\mu i}$$

$\Psi(\vec{x}_1, \ldots \vec{x}_N) = \langle \vec{x}_1 \ldots \vec{x}_N | \Psi \rangle$ N-electron wave function

$$\begin{aligned} |\psi_1 \ldots \psi_N| &= \left\langle \vec{x}_1 \ldots \vec{x}_N \middle| (\psi_1 \ldots \psi_N)_- \right\rangle \\ &= \sqrt{N!}\, \hat{\mathcal{A}} \left(\psi_1(\vec{x}_1) \ldots \psi_N(\vec{x}_N)\right) \\ &= \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\vec{x}_1) & \ldots & \psi_N(\vec{x}_1) \\ \ldots & \ldots & \ldots \\ \psi_1(\vec{x}_N) & \ldots & \psi_N(\vec{x}_N) \end{vmatrix} \end{aligned}$$

Slater determinant built from orthogonal spin-orbitals

To avoid a too cumbersome wording we will also use the terms "orbital", "spin-orbital" and "Slater determinant" to refer to the corresponding state vectors.

Notation

$\vec{x}_i \equiv i$ space+spin coordinates of electron i

$$\left\langle \psi_i \middle| \hat{f}\, \psi_j \right\rangle = \sum_{\omega=-1/2}^{1/2} \int_{\mathcal{R}^3} \psi_i^*(\vec{x})\, \hat{f}(\vec{x})\, \psi_j(\vec{x})\, d\vec{r} \qquad \left\langle \psi_i \middle| \hat{f}\, \psi_j \right\rangle = \int \psi_i^*(\vec{x})\, \hat{f}(\vec{x})\, \psi_j(\vec{x})\, d\vec{x}$$

$$\left\langle \phi_i \middle| \hat{h}\, \phi_j \right\rangle = \int_{\mathcal{R}^3} \phi_i^*(\vec{r})\, \hat{h}(\vec{r})\, \phi_j(\vec{x})\, d\vec{r}$$

$$\left\langle \psi_i\, \psi_j \middle| \frac{1}{r_{12}}\, \psi_k\, \psi_l \right\rangle = \sum_{\omega_1,\omega_2=-1/2}^{1/2} \int_{\mathcal{R}^6} \psi_i^*(\vec{x}_1)\, \psi_j^*(\vec{x}_2)\, \frac{1}{r_{12}}\, \psi_k(\vec{x}_1)\, \psi_l(\vec{x}_2)\, d\vec{r}_1\, d\vec{r}_2$$

$$= \int \psi_i^*(\vec{x}_1)\, \psi_j^*(\vec{x}_2)\, \frac{1}{r_{12}}\, \psi_k(\vec{x}_1)\, \psi_l(\vec{x}_2)\, d\vec{x}_1\, d\vec{x}_2 \ :$$

$$\left\langle \phi_i\, \phi_j \middle| \frac{1}{r_{12}}\, \phi_k\, \phi_l \right\rangle = \int_{\mathcal{R}^6} \phi_i^*(\vec{r}_1)\, \phi_j^*(\vec{r}_2)\, \frac{1}{r_{12}}\, \phi_k(\vec{r}_1)\, \phi_l(\vec{r}_2)\, d\vec{r}_1\, d\vec{r}_2 \equiv (\phi_i\, \phi_k \,|\, \phi_j\, \phi_l\,)$$