Matrix Representation of Wavefunctions and Operators in Quantum Chemistry

The following is a consequence of expanding a general wavefunction in a complete set of eigenfunctions

For a complete, orthonormal basis set \( \{ \phi_n \} \), \( \langle \phi_i | \phi_j \rangle = \delta_{ij} \)

For general state functions \( \Psi_a \) and \( \Psi_b \), one can then exactly write:

\[
|\Psi_a\rangle = \sum_k |\phi_k\rangle a_k
\]
\[
|\Psi_b\rangle = \sum_l |\phi_l\rangle b_l
\]

Furthermore, for a specified basis set it is sufficient to know just the coefficients \( a_k \) in order to calculate the function \( \Psi_a \) at any given point. The function \( \Psi_a \) can then also be completely specified by the column vector

\[
a = \begin{pmatrix}
a_1 \\
a_2 \\
\vdots \\
a_n
\end{pmatrix}
\]

By analogy, the function \( \Psi_b \) can be represented by the column vector \( b \).

The norm of the function \( \Psi_a \) is the same as the absolute square of the vector \( a \):

\[
\langle \Psi_a | \Psi_a \rangle = \sum_k \sum_l a_k^* \langle \phi_k | \phi_l \rangle a_l
\]
\[
= \sum_k a_k^* a_k = a^\dagger a = |a|^2
\]

where \( a^\dagger \), the adjoint of \( a \), is the row vector \( a^\dagger = \left( a_1^*, a_2^*, \ldots, a_n^* \right) \)
For the overlap integral between $\Psi_a$ and $\Psi_b$:

$$
\langle \Psi_a | \Psi_b \rangle = \sum_k \sum_l a_k^* \langle \phi_k | \phi_l \rangle b_l \\
= \sum_k a_k^* b_l = a^l \cdot b
$$

Thus integration in this basis representation will be replaced by a scalar or inner product.

Now assume that application of some operator $\hat{A}$ to $\Psi_a$ results in the function $\Psi_b$:

$$
|\Psi_b\rangle = \hat{A}|\Psi_a\rangle
$$

In terms of our basis set,

$$
|\Psi_b\rangle = \sum_l |\phi_l\rangle b_l = \sum_k \hat{A}|\phi_k\rangle a_k
$$

A particular coefficient $b_n$ in the definition of $\Psi_b$ is obtained by multiplication on the left by $\langle \phi_n |$:

$$
\sum_l \langle \phi_n | \phi_l \rangle b_l = b_n
$$

$$
= \langle \phi_n | \Psi_b \rangle = \sum_k \langle \phi_n | \hat{A}|\phi_k\rangle a_k
$$

$$
= \sum_k A_{nk} a_k
$$

or in matrix notation: $b = A \cdot a$

Thus the operator $\hat{A}$ becomes the matrix $A$ in the basis representation with matrix elements $A_{ij}$, and the effect of an operator acting on a function is transformed to a matrix-vector multiplication.

A hermitian operator corresponds to a hermitian matrix with the property

$$
A_{ij} = A_{ji}^*
$$

or $A = A^\dagger$
Consider a 2nd operator \( \hat{B} \) acting on \( \Psi_b \) to yield another function \( \Psi_c \) that can be represented by the vector \( \mathbf{c} \) in our basis:

\[
|\Psi_c\rangle = \hat{B}|\Psi_b\rangle = \hat{B}|\Psi_a\rangle
\]

expansion gives:

\[
|\Psi_c\rangle = \sum_i |\phi_i\rangle c_i = \sum_l \hat{B} |\phi_l\rangle b_l = \sum_{l,k} B |\phi_l\rangle \langle \hat{A} |\phi_k\rangle a_k
\]

The coefficients \( c_j \) are obtained by multiplication on the left with \( \langle \phi_j | \) :

\[
c_j = \langle \phi_j | \Psi_c \rangle = \sum_l \sum_k \langle \phi_j | \hat{B} |\phi_l\rangle \langle \phi_l | \hat{A} |\phi_k\rangle a_k = \sum_l \sum_k B_{jl} A_{lk} a_k
\]

which in matrix notation is: \( \mathbf{c} = \mathbf{B} \cdot \mathbf{b} = \mathbf{B} \cdot \mathbf{A} \cdot \mathbf{a} \)

So the operator product \( \hat{B} \hat{A} \) becomes the matrix product \( \mathbf{B} \cdot \mathbf{A} \) in the matrix representation.

Of course all of the above is strictly valid only for complete basis sets. For a finite basis set of \( M \) functions, \( \langle \phi_k | \hat{A} \hat{B} |\phi_j\rangle \neq \sum_{k-1}^M \langle \phi_k | \hat{A} |\phi_j\rangle \langle \phi_j | \hat{B} |\phi_k\rangle \). The usage of finite basis sets in approximate methods of quantum chemistry will be discussed later in this course.

Expectation values in the matrix representation

\[
\langle \Psi_a | \hat{A} |\Psi_a\rangle = \sum_k \sum_l a_k^* \langle \phi_k | \hat{A} |\phi_l\rangle a_l = \mathbf{a}^\dagger \cdot \mathbf{A} \cdot \mathbf{a}
\]

Matrix element of \( \hat{A} \)

\[
\langle \Psi_a | \hat{A} |\Psi_b\rangle = \sum_k \sum_l a_k^* \langle \phi_k | \hat{A} |\phi_l\rangle b_l = \mathbf{a}^\dagger \cdot \mathbf{A} \cdot \mathbf{b}
\]
The unit operator (resolution of the identity) in a complete basis set:

\[ \hat{I} = \sum_k |\phi_k\rangle \langle \phi_k| \]

leads to the unit matrix \( I \):

\[ I_{ij} = \langle \phi_i | \hat{I} | \phi_j \rangle = \sum_k \langle \phi_i | \phi_k \rangle \langle \phi_k | \phi_j \rangle = \delta_{ij} \]

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