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 Ψ_a and Ψ_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 Ψ_a at any given point. The function Ψ_a can then also be completely specified by the column vector

$$\mathbf{a} = \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_n \end{pmatrix}$$

By analogy, the function Ψ_b can be represented by the column vector **b**.

The norm of the function Ψ_a is the same as the absolute square of the vector **a** :

$$\langle \Psi_a | \Psi_a \rangle = \sum_k \sum_l a_k^* \langle \phi_k | \phi_l \rangle a_l$$

$$= \sum_k a_k^* a_k = \mathbf{a}^\dagger \cdot \mathbf{a} = |\mathbf{a}|^2$$

where $\mathbf{a}^\dagger$, the adjoint of **a**, is the row vector $\mathbf{a}^\dagger = \begin{pmatrix} a_1^* & a_2^* & \cdots & a_n^* \end{pmatrix}$

For the overlap integral between Ψ_a and Ψ_b :

$$\left\langle \Psi_a \middle| \Psi_b \right\rangle = \sum_k \sum_l a_k^* \left\langle \phi_k \middle| \phi_l \right\rangle b_l$$

$$= \sum_k a_k^* b_k = \mathbf{a}^\dagger \cdot \mathbf{b}$$

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

Now assume that application of some operator $\hat{\mathrm{A}}$ to Ψ_a results in the function Ψ_b :

$$\left| \Psi_b \right\rangle = \hat{\mathrm{A}} \left| \Psi_a \right\rangle$$

In terms of our basis set,

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

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

$$\sum_l \left\langle \phi_n \middle| \phi_l \right\rangle b_l = b_n$$

$$= \left\langle \phi_n \middle| \Psi_b \right\rangle = \sum_k \left\langle \phi_n \middle| \hat{\mathrm{A}} \middle| \phi_k \right\rangle a_k$$

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

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

Thus the operator $\hat{\mathrm{A}}$ 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 $\mathbf{A} = \mathbf{A}^\dagger$

Consider a 2nd operator $\hat{B}$ acting on Ψ_b to yield another function Ψ_c that can be represented by the vector **c** in our basis:

$$\left|\Psi_c\right\rangle = \hat{B}\left|\Psi_b\right\rangle = \hat{B}\hat{A}\left|\Psi_a\right\rangle$$

expansion gives:

$$\begin{aligned}\left|\Psi_c\right\rangle &= \sum_i \left|\phi_i\right\rangle c_i = \sum_l \hat{B}\left|\phi_l\right\rangle b_l \\ &= \sum_l \sum_k B\left|\phi_l\right\rangle\left\langle\phi_l\right|\hat{A}\left|\phi_k\right\rangle a_k\end{aligned}$$

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

$$\begin{aligned}c_j &= \left\langle\phi_j\middle|\Psi_c\right\rangle \\ &= \sum_l \sum_k \left\langle\phi_j\right|\hat{B}\left|\phi_l\right\rangle\left\langle\phi_l\right|\hat{A}\left|\phi_k\right\rangle a_k \\ &= \sum_l \sum_k B_{jl} A_{lk} a_k\end{aligned}$$

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, $\left\langle\phi_i\right|\hat{A}\hat{B}\left|\phi_j\right\rangle \neq \sum_{k-1}^{M}\left\langle\phi_i\right|\hat{A}\left|\phi_k\right\rangle\left\langle\phi_k\right|\hat{B}\left|\phi_j\right\rangle$. 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

$$\begin{aligned}\left\langle\Psi_a\right|\hat{A}\left|\Psi_a\right\rangle &= \sum_k \sum_l a_k^* \left\langle\phi_k\right|\hat{A}\left|\phi_l\right\rangle a_l \\ &= \mathbf{a}^\dagger\cdot\mathbf{A}\cdot\mathbf{a}\end{aligned}$$

Matrix element of $\hat{A}$

$$\begin{aligned}\left\langle\Psi_a\right|\hat{A}\left|\Psi_b\right\rangle &= \sum_k \sum_l a_k^* \left\langle\phi_k\right|\hat{A}\left|\phi_l\right\rangle b_l \\ &= \mathbf{a}^\dagger\cdot\mathbf{A}\cdot\mathbf{b}\end{aligned}$$

The unit operator (resolution of the identity) in a complete basis set:

$$\hat{\mathrm{I}} = \sum_k \left|\phi_k\right\rangle\left\langle\phi_k\right|$$

leads to the unit matrix **I** :

$$I_{ij} = \left\langle\phi_i\middle|\hat{\mathrm{I}}\middle|\phi_j\right\rangle = \sum_k \left\langle\phi_i\middle|\phi_k\right\rangle\left\langle\phi_k\middle|\phi_j\right\rangle = \delta_{ij}$$

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