## More matrix algebra

let $\psi = \sum_{i=1}^{N} c_i \phi_i$ $\quad \{\phi_i\}$ is the set of N basis functions

$$\Rightarrow \widetilde{A} = \left\langle \psi \,|\, \hat{A} \,|\, \psi \right\rangle = \sum_{i=1}^{N} \sum_{j=1}^{N} c_i^* A_{ij} c_j \qquad \sum_{i=1}^{N} c_i^* c_i = 1 \qquad \Psi \text{ normal}$$

$$A_{ij} = < \phi_i \,|\, \hat{A} \,|\, \phi_j > = \text{matrix element}$$

In matrix notation

$$\overline{A} = \widetilde{c}^{\,+} \widetilde{A} \widetilde{c} \qquad \widetilde{c}^{\,+} \widetilde{c} = 1$$

where

$$\widetilde{c} = \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_N \end{pmatrix} \text{ column vector} \qquad \widetilde{c}^{\,+} = \begin{pmatrix} c_1^* & c_2^* & \dots & c_N^* \end{pmatrix} \text{ row vector}$$

**Determinants**

$$\left|\tilde{A}\right| = \sum_i (-1)^{i+j} a_{ij} \left|A_{ij}\right|$$

For a 2x2 matrix:

$$\left|\tilde{A}\right| = \begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} = a_{11}a_{22} - a_{21}a_{22}$$

For a 3x3 matrix: label each matrix element in the following way (in your mind)

$$\tilde{A} = \begin{pmatrix} \underset{(+)}{a_{11}} & \underset{(-)}{a_{12}} & \underset{(+)}{a_{13}} \\ \underset{(-)}{a_{21}} & \underset{(+)}{a_{22}} & \underset{(-)}{a_{23}} \\ \underset{(+)}{a_{31}} & \underset{(-)}{a_{32}} & \underset{(+)}{a_{33}} \end{pmatrix}$$

The +/- are the signs of the cofactors

Can expand the determinant along any row or column. Using the first row:

$$\left|\tilde{A}\right| = a_{11}(-1)^{1+1}\begin{vmatrix} a_{22} & a_{23} \\ a_{32} & a_{33} \end{vmatrix} + a_{12}(-1)^{1+2}\begin{vmatrix} a_{21} & a_{23} \\ a_{31} & a_{33} \end{vmatrix} + a_{13}(-1)^{1+3}\begin{vmatrix} a_{21} & a_{22} \\ a_{31} & a_{32} \end{vmatrix}$$

$$\Rightarrow \left|\tilde{A}\right| = a_{11}\begin{vmatrix} a_{22} & a_{23} \\ a_{32} & a_{33} \end{vmatrix} - a_{12}\begin{vmatrix} a_{21} & a_{23} \\ a_{31} & a_{33} \end{vmatrix} + a_{13}\begin{vmatrix} a_{21} & a_{22} \\ a_{31} & a_{32} \end{vmatrix}$$

For a diagonal matrix where all off-diagonal elements are zero:

$$\tilde{A} = \begin{pmatrix} a_{11} & 0 & 0 \\ 0 & a_{22} & 0 \\ 0 & 0 & a_{33} \end{pmatrix} \Rightarrow \left|\tilde{A}\right| = a_{11}a_{22}a_{33}$$

**Further properties of determinants:**

$$\left|\tilde{A}^{T}\right| = \left|\tilde{A}\right|$$

$$\left|\tilde{A}^{*}\right| = \left|\tilde{A}\right|^{*}$$

$$\left|\tilde{A}^{+}\right| = \left|\tilde{A}^{*}\right| = \left|\tilde{A}\right|^{*}$$

## More Theorems

1.) A Hermitian matrix **H** has "real" eigenvalues

2.) A Hermitian matrix can be diagonalized by a unitary transformation; that is, there is a matrix **S** such that:

$$\tilde{S}\tilde{H}\tilde{S}^{-1} = \tilde{D}$$

3.) $$\left|\tilde{S}\tilde{H}\tilde{S}^{-1}\right| = \left|\tilde{D}\right|$$

This means the eigenvalues of **H** and $\mathbf{SHS}^{-1}$ are equal; that is, the physical content is unaffected by the unitary transformation

4.) If two Hermitian matrices $\mathbf{H}_1$ and $\mathbf{H}_2$ commute then they can be simultaneously diagonalized (no proof give). This means there is a **S** such that:

$$\tilde{S}\tilde{H}_1\tilde{S}^{-1} = \tilde{D}_1$$
$$\tilde{S}\tilde{H}_2\tilde{S}^{-1} = \tilde{D}_2$$

Solution of the eigenvalue problem using complete sets

## = Matrix Mechanics

$$\hat{M}\psi_i = m_i\psi_i \quad \text{or} \quad \hat{M}\psi = m\psi \qquad (1)$$

Could take **M** = **H**; m = E, etc.

In the Schrodinger approach, **M** is a differential equation which we solve for the eigenfunctions and eigenvalues. These can involve relatively hard calculus methods.

In the Heisenberg approach, **M** is a matrix which we solve for the eigenvectors and eigenvalues by relatively easy linear algebra methods.

Either approach is valid and give the same answers.

Let $\{\Omega_i\}$ be a convenient complete basis set $\{\Omega_i\}$ in the space of the problem. We need a complete set so all the standard problems covered in C374a are useful. These include the particle-in-a box wave functions, harmonic oscillator functions, rigid-rotor functions, H-atom orbitals, etc.

Which do you choose? It depends on the problem. If the Hamiltonian for example is a distorted particle-in-a box type problem, use a normal particle-in-a box basis set to construct the matrix operators.

In general:

$$\langle \Omega_i \mid \Omega_j \rangle = \delta_{ij}$$

(orthonormal)

Write: $$\psi = \sum_{i=1}^{N} c_i \Omega_i \qquad (2)$$

N = infinity to be rigorous; in practice it isn't.

Substitute (2) into (1).

$$\Rightarrow \sum_{i=1}^{N} c_i \hat{M} \Omega_i = m\left(\sum_{i=1}^{N} c_i \Omega_i\right)$$

Multiply by $\Omega_k^{\star}$ and integrate. (k = 1,2,3, …, N)

$$\therefore \sum_{i=1}^{N} c_i \underbrace{\left\langle \Omega_k \mid \hat{M} \mid \Omega_i \right\rangle}_{M_{ki}} = m \sum_{i=1}^{N} c_i \underbrace{\left\langle \Omega_k \mid \Omega_i \right\rangle}_{\delta_{ki}} = mc_k$$

Matrix elements in $\{\Omega_i\}$;
known

$$\therefore \sum_{i=1}^{N} M_{ki} c_i = mc_k$$

$$\Rightarrow \sum_{i=1}^{N} \left[M_{ki} - m\,\delta_{ki}\right] c_i = 0 \;;\; (k = 1,2,3,\ldots, N) \qquad (3)$$

(3) Is a set of N simultaneous homogenous linear equations in N unknowns: $\{c_i\}$ I = 1,2,3,…,N once {m} are known.

A trivial solution, $c_i = 0$ for all I will satisfy (3) (but not us).

A non-trivial solution exist only if the determinant of the coefficients of the unknowns is zero

$$\left| M_{ki} - m\delta_{ki} \right| = 0 \qquad (4)$$

Expanding (4) out yields a polynomial of degree N for m since the $M_{ki}$ are known.

→ N roots: $m_i$ i=1,2,3,…,N

Let's see what these results look like in matrix notation.

(3) Written in long hand for k=1,2,3,…,N

$$k=1: M_{11}c_1 + M_{12}c_2 + M_{13}c_3 + \cdots + M_{1N}c_N = mc_1$$
$$k=2: M_{21}c_1 + M_{22}c_2 + M_{23}c_3 + \cdots + M_{2N}c_N = mc_2$$
$$k=3: M_{31}c_1 + M_{32}c_2 + M_{33}c_3 + \cdots + M_{3N}c_N = mc_3$$
$$\vdots$$
$$k=N: M_{N1}c_1 + M_{N2}c_2 + M_{N3}c_3 + \cdots + M_{NN}c_N = mc_N$$

This is the same as: $\tilde{M}\tilde{c} = m\tilde{c}$ eigenvalue problem in matrix form where:

$$\tilde{M} = \begin{pmatrix} M_{11} & M_{12} & M_{13} & \ldots & M_{1N} \\ M_{21} & M_{22} & M_{23} & \ldots & M_{2N} \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ M_{N1} & M_{N2} & M_{N3} & \ldots & M_{NN} \end{pmatrix} \qquad \tilde{c} = \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_N \end{pmatrix}$$

N x N square matrix

N x 1 column matrix or column vector