Matrix Representations

C734b

A matrix is an array of numbers: $\{a_{ij}\} = \tilde{A}$

row (i), column (j)

Example:

$$\tilde{A} = \begin{pmatrix} 1 & 2 & 3 \\ 2 & 0 & 5 \\ -8 & -4 & 7 \end{pmatrix}$$

In general:

$$\tilde{A} = \begin{pmatrix} a_{11} & a_{12} & a_{13} & \cdots & a_{1n} \\ a_{21} & a_{22} & a_{23} & \cdots & a_{2n} \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ a_{m1} & a_{m2} & a_{m3} & \cdots & a_{mn} \end{pmatrix}$$

Indices m, n tells us the order of the matrix

Note: transpose of matrix ≡ $\tilde{A}^T = \{a_{ij}\}^T = \{a_{ji}\}$

Vectors in a p-dimensional space are specified by a p x 1 **column** vector.

Geometrical interpretation: they give the orthogonal coordinates of one end of the vector if the other end is at the origin of the coordinate system

Matrix Algebra

Matrices can be added, subtracted, multiplied and divided.

a) Addition and subtraction: $\tilde{A} \pm \tilde{B} = \tilde{C} \quad \Rightarrow c_{ij} = a_{ij} \pm b_{ij}$

b) Multiplication by a scalar α

$$\Rightarrow \alpha c_{ij} = \alpha a_{ij} \pm \alpha b_{ij}$$

c) Matrix multiplication: matrices must be **conformable**.

$\Rightarrow$ if $\tilde{C} = \tilde{A}\tilde{B}$ then the number of columns of **A** = number of rows of **B**

∴ if the order of **A** and **B** are (i x j) and (j x k), the order of **C** is:

(i x j)(j x k) = (i x k)

Each element in **C** can be computed by: $c_{i\ell} = \sum_k a_{ik} b_{k\ell}$

row column

Note: $\tilde{A}\tilde{B} \neq \tilde{B}\tilde{A}$ necessarily

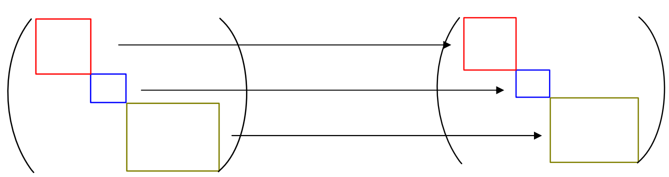
d) Matrix division $\frac{\widetilde{A}}{\widetilde{B}} = \widetilde{A}\widetilde{B}^{-1}$ where $\mathbf{B}^{-1}$ is the inverse of **B**

$$\Rightarrow \widetilde{B}\widetilde{B}^{-1} = \widetilde{B}^{-1}\widetilde{B} = \widetilde{E}$$

$$\widetilde{E} = \begin{pmatrix} 1 & 0 & 0 & \cdots \\ 0 & 1 & 0 & \cdots \\ 0 & 0 & 1 & \cdots \\ 0 & 0 & 0 & \ddots \end{pmatrix}$$

E = identity matrix which is often denoted by **I**.

If two matrices are block diagonal, the corresponding blocks of identical order can be multiplied individually



Definition:
For a square matrix its "character" or "trace", Χ ≡ sum of its diagonal elements

$$\chi = \sum_j a_{jj}$$

Properties:

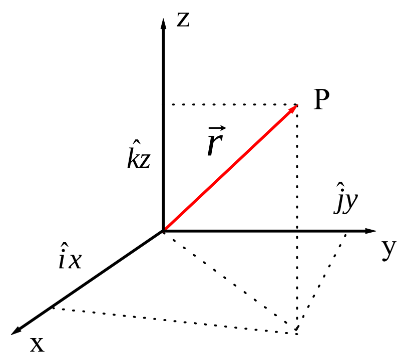
1.) if **C** = **A·B** and **D** = **B·A** $\Rightarrow \chi_{\tilde{C}} = \chi_{\tilde{D}}$

2.) Conjugate matrices related by a similarity transformation have identical characters

$$\Rightarrow \text{if } \tilde{A} = X^{-1}\tilde{B}X \Rightarrow \chi_{\tilde{A}} = \chi_{\tilde{B}}$$

3.) $\text{If } \tilde{C} = \tilde{A} \otimes \tilde{B} \Rightarrow \chi_{\tilde{C}} = \chi_{\tilde{A}} \cdot \chi_{\tilde{B}}$

Consider the vector shown below:



In general:

$$\vec{r} = \langle e_1, e_2, \ldots, e_n \,|\, r_1, r_2, \ldots, r_n \rangle = \langle e \,|\, r \rangle$$

bra: row matrix ≡ basis set

ket: column matrix ≡ coordinates

Both $\{e_i\}$ and $\{r_i\}$ may be complex

∴ define Hermitian scalar product of vectors **u** and **v** as:

$$\vec{u}^* \cdot \vec{v} = \langle e \,|\, u \rangle^+ \cdot \langle e \,|\, v \rangle$$

where superscript "+" denotes **adjoint** or transposed complex conjugate

$$\therefore \vec{u}^* \cdot \vec{v} = \langle u^* \,|\, e^* \rangle \cdot \langle e \,|\, v \rangle = \langle u^* \,|\, \tilde{M} \,|\, v \rangle = \sum_{i,j} u_i^* M_{ij} v_j$$

The square matrix $\tilde{M} = |e^*\rangle\langle e|$ ≡ **metric** of the linear vector space.

$$\tilde{M} = |e_1^*, e_2^*, \ldots, e_n^*\rangle\langle e_1, e_2, \ldots, e_n| = \begin{pmatrix} e_1^* \cdot e_1 & e_1^* \cdot e_2 & \cdots \\ e_2^* \cdot e_1 & e_2^* \cdot e_2 & \cdots \\ \vdots & \vdots & \vdots \end{pmatrix}$$

and $M_{ij} = e_i^* \cdot e_j = e_j \cdot e_i^* = (e_j^* \cdot e_i)^* = M_{ji}^*$

$\Rightarrow M = M^+$ (Hermitian or self-adjoint matrix)

If $M_{ij} = e_i^* \cdot e_j = \delta_{ij}$ $\Longrightarrow$ basis set is orthonormal or unitary and therefore

$$\tilde{M} = \tilde{E}$$

Configuration space ≡ 3-D space in which physical objects (atoms, molecules, crystals) exist

≡ R^3

Points in R^3 are described with respect to a system of right-handed orthogonal axes {0x, 0y, 0z}

Right-handed means a right-handed screw advancing from the origin; rotates x → y → z → x

Will use active representation: axes remain fixed but the whole of configuration space is rotated.

Rotation carries with it all vectors in configuration space including a set of coordinates {x, y, z} originally coincident with {**i**, **j**, **k**}.

Matrix Representation of Operators

Suppose a basis <e| is transformed to a new basis <e'| as a result of an operator R

$$\Rightarrow R\langle e| = \langle e'| = R\langle e_1, e_2, \cdots, e_n| = \langle e_1', e_2', \cdots, e_n'|$$

{e_j'} can be expressed in terms of the old set by writing e_j' as a sum of its projections:

$$e_j' = \sum_{i=1}^{n} e_i r_{ij} \qquad j = 1, \ldots, n$$

where r_{ij} ≡ component of e_j' along e_i

In matrix form: $\langle e_1', e_2', \cdots, e_n'| = \langle e_1, e_2, \cdots, e_n|\Gamma(R)$

$$\Gamma(R) = (r_{ij}) = \begin{pmatrix} r_{11} & r_{12} & \cdots & r_{1n} \\ r_{21} & r_{22} & \cdots & r_{2n} \\ \vdots & \vdots & \vdots & \vdots \\ r_{n1} & r_{n2} & \cdots & r_{nn} \end{pmatrix}$$

Γ(R) ≡ matrix representative of the operator R

In 3-D configuration space there are 5 operations to describe the transformation of a point or points in space: E, σ, i, C_n, and S_n

Each can be described by a matrix Γ(R) such that

$$\langle e'| = \langle e|\Gamma(R) \quad (e_2, e_2, e_3) = (\hat{i}, \hat{j}, \hat{k})$$

1.) Identity, E

$$\Rightarrow (e_1, e_2, e_3)\Gamma(E) = (e_1, e_2, e_3)$$

$$\Rightarrow \Gamma(E) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

2.) Reflection, σ

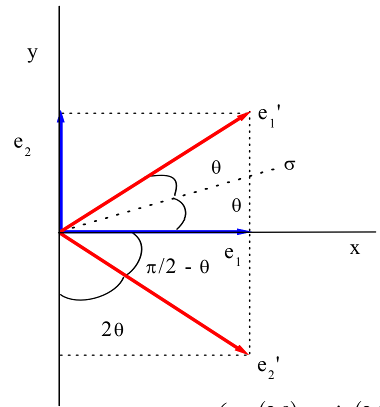
If the plane of reflection coincides with a principle Cartesian plane (xy, xz, or yz), reflection changes the sign of the coordinate ⊥ to plane but leaves the coordinate whose axes defines the plane unchanged.

$$\Rightarrow \sigma(xy) = \langle e| \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} = \langle e'| = (e_1, e_2, -e_3) = (e_1, e_2, \bar{e}_3)$$

Similarly:

$$\sigma(xz) = \langle e| \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \langle e'| = (e_1, -e_2, e_3) = (e_1, \bar{e}_2, e_3)$$

$$\sigma(yz) = \langle e| \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \langle e'| = (-e_1, e_2, e_3) = (\bar{e}_1, e_2, e_3)$$



In general using trigonometry:

$$\tilde{\sigma} = \begin{pmatrix} \cos(2\theta) & \sin(2\theta) & 0 \\ \sin(2\theta) & -\cos(2\theta) & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Θ = angle with respect to the xz plane

∴ when θ = π/2 $\Rightarrow \tilde{\sigma}_{yz} = \begin{pmatrix} \cos(\pi) & \sin(\pi) & 0 \\ \sin(\pi) & -\cos(\pi) & 0 \\ 0 & 0 & 1 \end{pmatrix}$

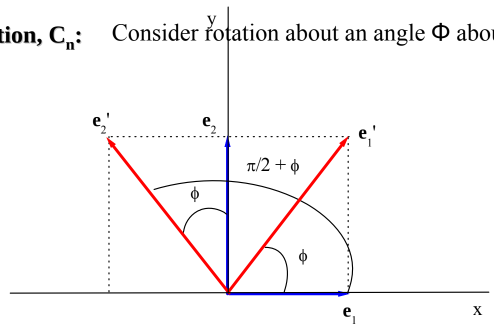
$$= \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \text{as before}$$

3.) Inversion, i: Here a point ($\mathbf{e}_1$, $\mathbf{e}_2$, $\mathbf{e}_3$) →(-$\mathbf{e}_1$, -$\mathbf{e}_2$, -$\mathbf{e}_3$)

∴ need a negative unit matrix

$$\Rightarrow \tilde{i} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

4.) Proper rotation, C_n: Consider rotation about an angle Φ about the 0z axis



$$\tilde{e}_1' = \tilde{e}_1\cos(\phi) + \tilde{e}_2\sin(\phi) + 0\tilde{e}_3$$

$$\tilde{e}_2' = \tilde{e}_1\cos\left(\frac{\pi}{2}+\phi\right) + \tilde{e}_2\cos(\phi) + 0\tilde{e}_3 = -\tilde{e}_1\sin(\phi) + \tilde{e}_2\cos(\phi) + 0\tilde{e}_3$$

$$\tilde{e}_3' = 0\tilde{e}_1 + 0\tilde{e}_2 + \tilde{e}_3$$

$$\therefore \tilde{C}_n = \begin{pmatrix} \cos(\phi) & -\sin(\phi) & 0 \\ \sin(\phi) & \cos(\phi) & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

5.) Improper rotation S_n: this is a C_n rotation followed by reflection σ_h.

Therefore, for the rotation in 4): $\mathbf{e}_3 \rightarrow -\mathbf{e}_3$

$$\therefore \tilde{S}_n = \begin{pmatrix} \cos(\phi) & -\sin(\phi) & 0 \\ \sin(\phi) & \cos(\phi) & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

Note: all Γ(R) for the symmetry operations are real orthogonal matrices.

$$\Rightarrow \Gamma(R)^T \Gamma(R) = \widetilde{E}$$

where $\Gamma(R)^T$ = transpose of Γ(R)

$\Longrightarrow \Gamma(R)^{-1} = \Gamma(R)^T$ is readily calculated.

Note: $\vec{r}' = R\vec{r} = R\langle e \mid r \rangle = \langle e' \mid r \rangle = \langle e' \mid \Gamma(R) \mid r \rangle = \langle e \mid r' \rangle$

Symmetry transformations are rigid. The length of all vectors and angles between them remain unchanged.

Aside: can show that if Γ(R) is complex then Γ(R) is a unitary matrix defined as

$$\Gamma(R)^{-1} = \Gamma(R)^{\dagger} = \Gamma(R)^{T*}$$

Proper and improper rotations can be distinguished by their determinant.

$$\Gamma(R)^T \Gamma(R) = \widetilde{E} = \Gamma(R)\Gamma(R)^T$$

$$\because \det\left(\widetilde{A}\widetilde{B}\right) = \det\left(\widetilde{A}\right)\det\left(\widetilde{B}\right)$$

$$\therefore \det\left(\Gamma(R)^T \Gamma(R)\right) = \det\left(\Gamma(R)^T\right)\det\left(\Gamma(R)\right)$$

$$= \left(\det\left(\Gamma(R)\right)\right)^2 = 1 \Rightarrow \det\left(\Gamma(R)\right) = \pm 1$$

Real orthogonal matrices with determinant = +1 imply proper rotations
≡ special orthogonal matrices
Those with determinant = -1 imply improper rotations

The effect of a symmetry operator **R**, on a point $\begin{pmatrix} x \\ y \\ z \end{pmatrix}$

$$\Rightarrow \tilde{R}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} \quad \equiv \text{mapping}$$

The result $\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix}$ is called a **Jones symbol**

A map ≡ (proper or improper) rotation of a basis with respect to fixed axes which carries all of R^3 and {**r**} in R^3 with it.

This is important since it means every point symmetry operator is equivalent to a proper or improper rotation.

⟹ Effect of a symmetry operator **R** on the components {x, y, z} of any vector 0P = **r** can be determined by finding Γ(R) of **R** from:

$$\langle e'| = \langle e|\Gamma(R)$$

and then use Γ(R) to calculate **r**' from **r** using:

$$\Gamma(r)|r\rangle = |r'\rangle$$

or

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \Gamma(R)\begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

Group Representations

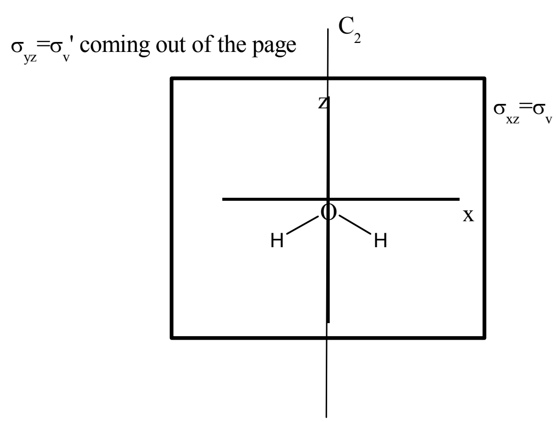
If {A, B, C, ….} for a group G then the set of matrix representatives {Γ(A), Γ(B), Γ(C),…} form an isomorphic group with G called a **group representation**.

and if AB = C then Γ(A)Γ(B) = Γ(C)

⟹ The matrix representatives obey the same multiplication table as the operators

Example: in C_{2v} the operations are E, C_2, σ_v, σ_v'

For H_2O place C_2 along the z-axis and let $\sigma_v = \sigma_{xz}$



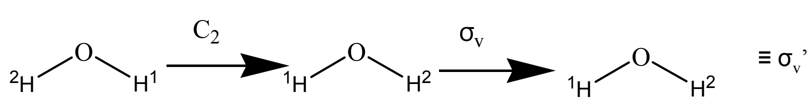
$$\therefore \sigma_v = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \sigma_v' = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

C_2: $\varphi = \pi$

$$\therefore C_2 = \begin{pmatrix} \cos(\pi) & \sin(\pi) & 0 \\ -\sin(\pi) & \cos(\pi) & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

and $$E = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Example: Consider the product $\sigma_v C_2 = \sigma_v$'



Now:

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$\sigma_v = \sigma_{xz}$ $\qquad$ C_2 $\qquad$ $\sigma_{v'} = \sigma_{yz}$

Transformation of Scalar Functions

Relevant for the understanding of how atomic orbitals transform under symmetry operations

If f = f(x, y, z), it means that f has a definite value at each point P(x, y, z) with coordinates x, y, z

Let (x, y, z) → {x} and (x', y', z') → {x'}

If an operator **T**, transforms P(x, y, z) → P(x', y', z')

$$\Rightarrow T\{x\} = \{x'\}$$

$$\Rightarrow |x'\rangle = \Gamma(T)|x\rangle$$

*But a symmetry operator leaves a system in an indistinguishable configuration. Therefore the properties of the system are unaffected by T

∴ **T** transforms f into a new function **T**f in such a way that:

$$\hat{T}f\left(\{x'\}\right) = f\left(\{x\}\right)$$

$\hat{T}$ ≡ function operator

Means: the value of the new function **T**f, evaluated at the transformed point {x'} is the same as the value of the original function at the original point {x}

Means: when a symmetry operator acts on a configuration, and function f is simultaneously transformed in to a new function **T**f.

Question: How to calculate **T**f?

Under symmetry operator **T**, point P → P'

that is: $TP(x, y, z) = P'(x', y', z')$

$$\Rightarrow T^{-1}P'(x', y', z') = P(x, y, z)$$

$$\therefore \hat{T}f\left(\{x'\}\right) = f\left(x\right) = f\left(T^{-1}\{x'\}\right)$$

Drop the primes since this applies to any point P'(x', y', z')

$$\Rightarrow \boxed{\hat{T}f\left(\{x\}\right) = f\left(T^{-1}\{x\}\right)}$$

Example: Let **T** = R(π/2, z) on d-orbital $d_{xy} = xyg(r)$

g(r) = function of r only and xy contains angular dependence

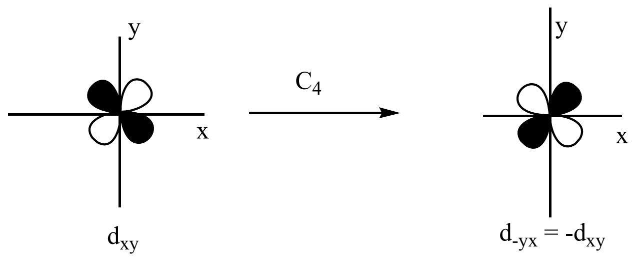
$$\Gamma(T = C_4) = \begin{pmatrix} \cos\left(\frac{\pi}{2}\right) & \sin\left(\frac{\pi}{2}\right) & 0 \\ -\sin\left(\frac{\pi}{2}\right) & \cos\left(\frac{\pi}{2}\right) & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\therefore [\Gamma(T)]^{-1} = [\Gamma(T)]^{T} = \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\therefore \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -y \\ x \\ z \end{pmatrix} = \begin{pmatrix} \bar{y} \\ x \\ z \end{pmatrix}$$

$$\therefore \hat{T}d_{xy} = d_{xy}\left(T^{-1}\{x\}\right) = d_{xy}\left(\bar{y}, x, z\right)$$

$$= -yxg(r) = -d_{xy}$$



Quantum Mechanical Considerations

a) Q.M. wavefunction Ψ({x}) strictly requires multiplication by a phase factor which is arbitrary. This phase factor has no effect on physical properties. Therefore, choose the phase factor = 1.

$$\therefore \hat{T}f\left(\{x\}\right) = f\left(T^{-1}\{x\}\right)$$

can be used for Q.M. wavefunctions

b) Function operators, **T**, corresponding to symmetry operators are unitary operators

$$\Rightarrow \hat{T}^{+}\hat{T} = \hat{T}\hat{T}^{+} = E$$

c) When **T** acts on a physical systems (atom, molecule, etc) a Q.M. operator **M** corresponding to a dynamical variable becomes:

$$\hat{M}' = \hat{T}M\hat{T}^{+}$$

Expectation values are invariant under symmetry operators.

$$\Rightarrow \hat{T}\hat{M}\hat{T}^{+} = \hat{M} \Rightarrow \left[\hat{T}, \hat{M}\right] = 0$$

Q.M. operator for the energy of a system is the Hamiltonian operator **H**.
This means **T** must commute with **H**.

The set of all function operators {**T**} that leaves **H** invariant and which form a group isomorphic with the symmetry operators {**T**} is known as "the group of the Hamiltonian" or "the group of the Schrodinger equation".

d) If the dynamical variable is an observable with operator **M**, this means Ψ is an eigenfunction of **M** with eigenvalue, m.

This means <M> = m ≡ value of physical quantity in state Ψ.

M is invariant under a symmetry operator **T**. Therefore, Ψ and **T**Ψ represent the same state; that is, they are degenerate.