# Lecture 2 - Algebra



1. 3-dimensional vector algebra.
2. Matrices.
3. Determinants.
4. Operators.
5. Basis sets.
6. The eigenvalue problem.
7. Orthogonal functions and Eigenfunctions.
8. The variation principle.

Use Chapter 16 of Jensen's book, p. 514.

# 3-dimensional Vector Algebra



1. Point in space represented by $[x, y, z]$ or $[r, \theta, \phi]$.
2. Complex numbers: visualised by points on a plane.
3. Quaternions: hypercomplex numbers, express a rotation in 3D space, more convenient than Euler angles.
4. Assuming $E(\{R_j\})$, gradient of energy wrt nuclear coordinates is a vector $[\{\partial E/\partial R_j\}]E$. Second derivatives are a Hessian matrix.
5. Change of the coordinate system: multiplication by a unitary matrix. Translation: add an extra dimension to the matrix.

# Matrices



$$A = \begin{bmatrix} a_{11} & a_{12} & \cdots & a_{1N} \\ a_{21} & a_{22} & \cdots & a_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ a_{N1} & a_{N2} & \cdots & a_{NN} \end{bmatrix}$$

- Transpose operation: $A = B^T$, $a_{pq} = b_{qp}$.
- Matrix multiplication: $A := B * C$, $a_{pq} = b_{pi} c_{iq}$.
- Matrix trace: $\mathrm{Tr} A = \sum_i a_{ii}$

# Matrix Inverse



- It is rarely worth to form the inverse matrix explicitly.
- Multiplication by an inverse is equivalent to solving a linear set of equations: $\vec{b} = A^{-1}\vec{a} \Leftrightarrow A\vec{b} = \vec{a}$

# Other Transformations



- Unitary matrix: $UU^T = I$

Vector rotation: multiplication by an unitary matrix:

$$\vec{v}' = U\vec{v}$$

Similarity transformation (basis change) for a matrix.

$$A' = UAU^T$$

Similarity transformation does not change the trace of the matrix.

# Determinants

Example:

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

In general, determinant has $N!$ terms.

- Interchanging two rows/columns changes the sign of the determinant (wave-function antisymmetry).
- adding a row to another does not change the determinant.
- determinant is zero if two rows are identical except for an multiplicative constant.

# Operators



**function** produces scalar from another scalar or a set of scalars.

**functional** produces a scalar from a function.

**operator** produces a function from another function.

# Basis Sets



- Basis sets make it possible to represent an analytical function/operator on a computer.
- Functions are replaced with vectors of expansion coefficients, Operators: with matrices.

$$f(\vec{r}) \quad \Rightarrow \quad f_a(\vec{r}) = \sum_i c_i b_i(\vec{r}) \tag{1}$$

$$g(\vec{r}) = \hat{a} f(\vec{r}) \quad \Rightarrow \quad g_a(\vec{r}) = \sum_j a_{ji} \sum_i c_i b_i(\vec{r}) \tag{2}$$

# The Eigenvalue Problem



Perform an similarity transformation that the matrix becomes diagonal

$$\varepsilon = UAU^{-1} \Leftrightarrow Ax = \varepsilon x$$

Any $N \times N$ Hermitian matrix can be similarity-transformed to diagonal form with real eigenvalues.
Applications: orbital energies, vibrational frequencies.

- Number of nonzero eigenvalues: rank of the matrix.
- Condition number $\frac{\max|\epsilon|}{\min|\epsilon|}$

# Orthogonal Functions and Eigenfunctions



- Eigenfunctions are orthogonal – a convenient basis set!
- In discrete space: associated matrix becomes diagonal, making the interpretation – and calculations! – easier.
- Orbital energies, vibrational modes.
- Transformation of generalized eigenproblem to orthogonal basis with help of $S^{-1/2}$ – or Cholesky factors $U, S = UU^T$

# The Variational Principle



**Variational Principle**: approximate wave function has an energy that is above or equal to the exact ground state energy:

$$W = \frac{\langle \tilde{\Phi} | H | \tilde{\Phi} \rangle}{\langle \tilde{\Phi} | \tilde{\Phi} \rangle} \geq E_0$$

# Exercise



*Show how Cholesky factors $U$, $S = LL^T$ can be used to transform the generalized eigenproblem $FC = SC\varepsilon$ to standard eigenproblem $F'C' = C'\varepsilon$. What is the similarity transformation matrix $U$?*

The standard way to perform such transformation is to obtain the transformation by computing $S^{-1/2}$ via diagonalization. This becomes very time consuming for large systems and much faster Cholesky decomposition is preferred.
Both ways have problems when the overlap matrix is ill-conditioned.