MJC-12: Physical Chemistry: Quantum Chemistry

Elementary Quantum Mechanics:

Postulates of Quantum Mechanics, quantum mechanical operators, properties of operator, Hermitian operator, Schrödinger wave equation and its importance, physical interpretation of wave function, probability distribution function, nodal properties, particle in one dimensional box, particle in three dimensionalbox, concept of degeneracy and zero point energy, Schrödinger wave equation for hydrogen atom, separation of variables, hydrogen like wave functions.

Operators and Quantum Mechanics:

In quantum mechanics, physical observables (e.g., energy, momentum, position, etc.) are represented mathematically by operators. For instance, the operator corresponding to energy is the Hamiltonian operator.

$$\hat{H} = -\frac{\hbar^2}{2}\sum_i \frac{1}{m_i}\nabla_i^2 + V$$

where i is an index over all the particles of the system.

Basic Properties of Operators

Most of the properties of operators are obvious, but they are summarized below for completeness.

- The **sum** and **difference** of two operators $\hat{A}$ and $\hat{B}$ are given by

$$\begin{aligned}(\hat{A}+\hat{B})f &= \hat{A}f + \hat{B}f \\ (\hat{A}-\hat{B})f &= \hat{A}f - \hat{B}f\end{aligned}$$

- The **product** of two operators is defined by

$$\hat{A}\hat{B}f \equiv \hat{A}[\hat{B}f]$$

- Two operators are **equal** if

$$\hat{A}f = \hat{B}f$$

  for all functions f.

- The **identity operator** $\hat{1}$ does nothing (or multiplies by 1)

$$\hat{1}f = f$$

A common mathematical trick is to write this operator as a sum over a complete set of states (more on this later).

$$\sum_i |i\rangle\langle i|f = f$$

- The **associative law** holds for operators

$$\hat{A}(\hat{B}\hat{C}) = (\hat{A}\hat{B})\hat{C}$$

The commutative law does not generally hold for operators.

$$\hat{A}\hat{B} \neq \hat{B}\hat{A}.$$

It is convenient to define the quantity

$$[\hat{A},\hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}$$

which is called the **commutator** of $\hat{A}$ and $\hat{B}$. Note that the order matters, so that $[\hat{A},\hat{B}] = -[\hat{B},\hat{A}]$. If $\hat{A}$ and $\hat{B}$ happen to commute, then $[\hat{A},\hat{B}] = 0$.

- The **n-th power** of an operator $\hat{A}^n$ is defined as n successive applications of the operator, e.g.

$$\hat{A}^2 f = \hat{A}\hat{A}f \tag{41}$$

- The **exponential** of an operator $e^{\hat{A}}$ is defined via the power series

$$e^{\hat{A}} = \hat{1} + \hat{A} + \frac{\hat{A}^2}{2!} + \frac{\hat{A}^3}{3!} + \cdots \tag{42}$$