

1. The state of a single particle is described as fully as possible by an appropriate function, $\Psi(x, y, z, t)$, which may be expressed for stationary energy states as the product of a time-independent amplitude function, $\psi(x, y, z)$, and a time-dependent function, $f(t)$. Both functions, Ψ and ψ , must be single valued, continuous, finite and square integrable for all values of the coordinates.

2.a. The possible state functions $\Psi(x, y, z, t)$ for a single particle are given by solutions to the time-dependent Schrödinger equation:

$$\frac{\hbar}{i} \frac{\partial}{\partial t} \Psi = \hat{H} \Psi = \left[-\frac{\hbar^2}{2m} \nabla^2 + V(x, y, z, t) \right] \Psi$$

2.b. In the special case of a conservative system, where V is not a function of time, and $\Psi(x, y, z, t) = \psi(x, y, z) e^{-iEt/\hbar}$, the possible time-independent amplitude functions $\psi(x, y, z)$ for a single particle are given by solutions to the time independent Schrödinger equation:

$$\hat{H} \psi = \left[-\frac{\hbar^2}{2m} \nabla^2 + V(x, y, z) \right] \psi = E \psi$$

3.a. For every physically observable dynamical variable, \mathbf{A} , there is a corresponding linear Hermitian operator, $\hat{\mathbf{A}}$. If the variable is capable of exact experimental determination, its only possible exact values, a , are those given by the eigenvalues of the equation:

$$\hat{\mathbf{A}} \Psi = a \Psi$$

3.b. In conservative systems and time-independent operators, the only possible exact values of the variable are given by:

$$\hat{\mathbf{A}} \psi = a \psi$$

4.a. The term $|\Psi|^2 d\tau = \Psi^* \Psi d\tau$ is the time-dependent probability that a single particle exists at a given time t in the space element $d\tau$, i.e. between (x, y, z) and $(x+dx, y+dy, z+dz)$.

4.b. In conservative systems (in which the single particle is restricted to an energy eigenstate), the time independent probability that the particle exists in the space element $d\tau$ is $|\psi|^2 d\tau = \psi^* \psi d\tau$.

Chemistry 4507 - Physical Chemistry I

Lecture Handout

The Postulates of Quantum Mechanics

5.a. The expected mean value, $\langle a \rangle$, of a series of measurements of variable \mathbf{A} made over a large number of particles each in the state Ψ is:

$$\langle a \rangle = \frac{\int_{-\infty}^{+\infty} \Psi^* \hat{\mathbf{A}} \Psi d\tau}{\int_{-\infty}^{+\infty} |\Psi|^2 d\tau}$$

where $\hat{\mathbf{A}}$ is the quantum mechanical operator for the variable.

5.b. For conservative systems, this equation becomes:

$$\langle a \rangle = \frac{\int_{-\infty}^{+\infty} \psi^* \hat{\mathbf{A}} \psi d\tau}{\int_{-\infty}^{+\infty} |\psi|^2 d\tau}$$

and, when the time-independent functions are normalized, this further reduces to:

$$\langle a \rangle = \int_{-\infty}^{+\infty} \psi^* \hat{\mathbf{A}} \psi d\tau$$

6. The operators corresponding to the position and the linear momentum are:

$$\hat{\mathbf{x}} = x \cdot \quad \text{and} \quad \hat{\mathbf{p}}_x = \frac{\hbar}{i} \frac{d}{dx}$$

respectively.