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CH101

Classes 2; Physical Chemistry

Postulates of Quantum Mechanics

Postulate 1.

The state of a quantum mechanical system is completely specified by a wavefunction $\Psi(r,t)$, that depends on the coordinates of the particle(s) and on time.

The probability that the particle lies in the volume element dτ located at r and at time t is given by

$$\Psi^*(r,t)\ \Psi(r,t)\ \mathrm{d}\tau$$

For a single particle, since the total probability of finding it somewhere in space is 1,

$$\int_{-\infty}^{\infty} \Psi^*(r,t)\ \Psi(r,t)\ \mathrm{d}\tau = 1$$

This is also the normalization condition.
The wavefunction must also be single-valued, continuous, and finite.

Postulate 2.

In the results of the measurement of the observable associated with operator $\hat{\mathbf{A}}$, the only values that will ever be observed are the eigenvalues a, which satisfy the following equation

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

This postulate essentially states the central point of quantum mechanics, which is that the values of dynamical variables are quantized.

It is also possible that an arbitrary state can be expanded as

$\mathbf{\Psi} = \sum_{i}^{n} c_i \Psi_i$ **,** which represents a complete set of eigenvectors with n possibly going up to infinity.

Also,

$$\mathbf{\hat{A}}\Psi_{\mathrm{i}} = a_i\,\Psi_{\mathrm{i}}$$

Each measurement will yield only single value of a_i. However, the probability that the eigenvalue a_i will occur is $\left|c_i\right|^2$

Postulate 3.

When $\mathbf{\Psi}$ represents the state that a system is in, the average value of the observable corresponding to $\hat{\mathrm{A}}$ is given by

$$\langle A\rangle = \int_{-\infty}^{\infty} \Psi^* \hat{\mathrm{A}} \Psi d\tau$$

Postulate 4.

For every observable in classical mechanics, there is a corresponding linear, Hermitian operator in quantum mechanics.

If the expectation value of the operator $\mathbf{\hat{A}}$ is real, then $\mathbf{\hat{A}}$ must be Hermitian.

Hermitian Operator: $$\int_{-\infty}^{\infty} \Psi^* \hat{\mathrm{A}} \Psi d\tau = \int_{-\infty}^{\infty} (\hat{\mathrm{A}}\Psi)^* \Psi d\tau$$

Some common physical observables of classical mechanics and their corresponding quantum operators

Physical observables and their corresponding quantum operators (single particle)			
Observable	Observable	Operator	Operator
Name	Symbol	Symbol	Operation
Position	r	$\hat{r}$	Multiply by **r**
Momentum	p	$\hat{p}$	$-ih\left(\hat{i}\frac{\partial}{\partial x}+\hat{j}\frac{\partial}{\partial y}+\hat{k}\frac{\partial}{\partial z}\right)$
Kinetic energy	T	$\hat{T}$	$-\frac{h^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)$
Potential energy	$V(r)$	$\hat{V}(r)$	Multiply by $V(r)$
Total energy	E	$\hat{H}$	$-\frac{h^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+V(r)$
Angular momentum	l_x	$\hat{i}_x$	$-ih\left(y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y}\right)$
	l_y	$\hat{l}_y$	$-ih\left(z\frac{\partial}{\partial x}-x\frac{\partial}{\partial z}\right)$
	l_z	$\hat{l}_z$	$-ih\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right)$

Postulate 5.

The evolution of the wavefunction or state function of a system is given by the time-dependent Schrödinger equation

$$\hat{H}\Psi(r,t) = i\hbar \frac{\partial \Psi}{\partial t}$$

This is the central equation of quantum mechanics.

The additional postulate

Postulate 6.

For a bound electron which is a Fermion, the total wavefunction must be antisymmetric with respect to the interchange of all coordinates of one fermion with those of another. Electronic spin has to be included in this set of coordinates.

This is the Pauli exclusion principle and is a direct result of this *antisymmetry principle*.

** *It must be mentioned here that Postulate 6 is not generally referred to as a postulate in Quantum Mechanics.*