Quantum Chemistry Postulates
Chapter 14

Quantum theory can be formulated with to a few ***postulates***, which are theoretical principles based on experimental observations.

For a physical system consisting of a particle(s) there are associated mathematical functions known as ***wave functions***. A wave function carries 'information' about everything that *can be known* (observable/measurable) about the system.

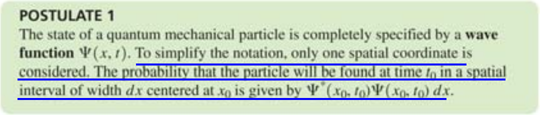
Every observable property is associated with an ***operator***.

Operating on the wave functions with the relevant operator of an observable property, would produce the *values* of the observable property of the system.

Postulate 1. The state of a quantum mechanical system is completely specified by a *function* Ψ(r,t) that depends on the coordinates, r (x, y, z) of the particle(s) and on time, t. This function, called the wave function or state function, has the property that *Ψ*(r,t) Ψ(r,t)* ***dτ*** *is the probability that the particle lies in the volume element* ***dτ*** *located at r at time t*.

Probability density

$$P(r,t) = \Psi^*(r,t)\Psi(r,t)d\tau = |\Psi(r,t)|^2 d\tau$$



POSTULATE 1

The state of a quantum mechanical particle is completely specified by a **wave function** $\Psi(x,t)$. To simplify the notation, only one spatial coordinate is considered. The probability that the particle will be found at time t_0 in a spatial interval of width dx centered at x_0 is given by $\Psi^*(x_0,t_0)\Psi(x_0,t_0)\,dx$.

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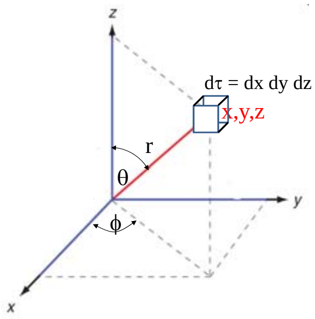
A wavefunction is a mathematical function and it contains a complete description of the system.



Cartesian *volume element* dτ = dx dy dz
Polar coordinate *volume element* $d\tau = r^2 \sin\theta \, d\theta \, d\phi \, dr$

Normalization

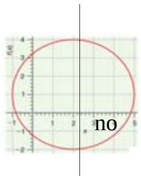
Because of the *probabilistic interpretation* the wave function Ψ(r,t) must satisfy, for a single particle the probability of finding it somewhere in space is unity (normalization).

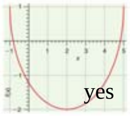
$$\int_0^\infty \Psi^*(r,t)\Psi(r,t)d\tau = 1$$

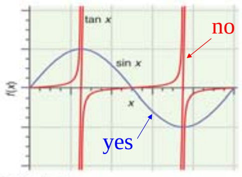
It is routine to normalize wavefunctions, Ψ(r,t) .

The wavefunction may and often have imaginary terms, thus the need to use the complex conjugate Ψ*(r,t) .

A *well behaved (meaningful) wavefunction* must be *single-valued* in r coordinate (because there can be only one probability value at a given position), *continuous* (so that a second derivative can exist and well behaved) and *finite* (to be able to normalize the wave function, Ψ, *integrable*).
For a function to be normalized the function has to be well behaved.







Operators in Quantum Mechanics:

Operators represent experimentally observable properties such as position, momentum, energy…

Operators enables the extraction of the values of the property of the system that the operator represents.

operator

$$\frac{d}{dx}\sin x = \cos x \qquad \frac{d^2}{dx^2}\sin x = (-1)\sin x \quad \textit{function regenerated}$$

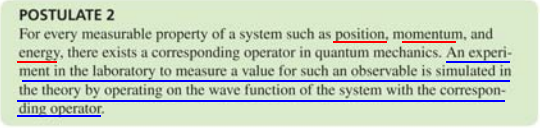
eigenvalue eigenfunction

$$\boxed{\text{Operator (eigenfunction)} = \text{eigenvalue} \times \text{eigenfunction}}$$

Postulate 2. For every *observable property* there exists an operator corresponding to that property. It is a *Hermitian operator*, a necessary condition to get *real* *(non-complex) value for dynamic observables* in quantum mechanics.

Hermitian operator, $\hat{A}$, has the property;

$$\int \Psi^*[\hat{A}\Psi(r)]d\tau = \int \Psi[\hat{A}\Psi(r)]^* d\tau$$


POSTULATE 2
For every measurable property of a system such as position, momentum, and energy, there exists a corresponding operator in quantum mechanics. An experiment in the laboratory to measure a value for such an observable is simulated in the theory by operating on the wave function of the system with the corresponding operator.

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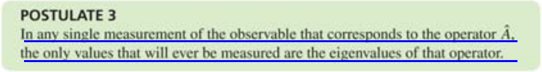
Result of an individual measurement

Postulate 3. In any *single measurement* of the observable associated with an operator $\hat{A}$, the only values that will ever be observed are the eigenvalues a, which satisfy the eigen value equation;

$$\hat{A}\psi = a\psi \qquad a = \frac{\int_{all\_space} \psi^* \hat{A}\psi \, d\tau}{\int_{all\_space} \psi^* \psi \, d\tau} \qquad \psi\text{, un-normalized}$$

If the system is in an eigenstate of $\hat{A}$ with eigen value a, then any measurement of the quantity A will yield a.


POSTULATE 3
In any single measurement of the observable that corresponds to the operator $\hat{A}$, the only values that will ever be measured are the eigenvalues of that operator.

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Wave functions yields values of measurable properties of a quantum system. Value of the property A can be predicted theoretically by operating with the operator $\hat{A}$.
Wave functions would be that satisfy of an operation so that,

$$\hat{A}\psi_n = a_n\psi_n$$

value eigen-function

are termed ***eigefunctions***.

Multiple measurements of a property A would yield the same value, a_n, *always;* are termed ***eigenvalues; discrete values.***

Eigenfunctions are orthogonal. Wave functions that are normalized and orthogonal are termed ***orthonormal***.

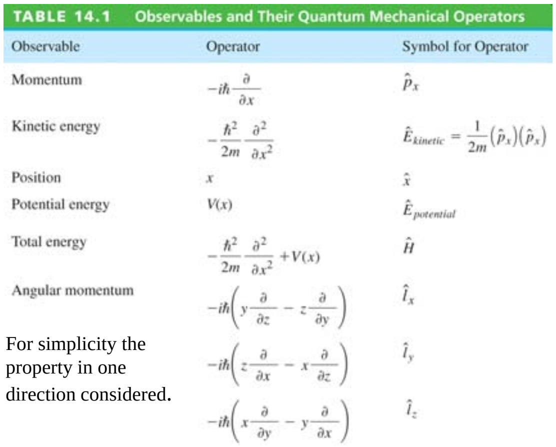


TABLE 14.1 Observables and Their Quantum Mechanical Operators

Observable	Operator	Symbol for Operator
Momentum	$-i\hbar\frac{\partial}{\partial x}$	$\hat{p}_x$
Kinetic energy	$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$	$\hat{E}_{kinetic} = \frac{1}{2m}(\hat{p}_x)(\hat{p}_x)$
Position	x	$\hat{x}$
Potential energy	$V(x)$	$\hat{E}_{potential}$
Total energy	$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V(x)$	$\hat{H}$
Angular momentum	$-i\hbar\left(y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y}\right)$	$\hat{l}_x$
	$-i\hbar\left(z\frac{\partial}{\partial x}-x\frac{\partial}{\partial z}\right)$	$\hat{l}_y$
	$-i\hbar\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right)$	$\hat{l}_z$

For simplicity the property in one direction considered.

Observable Name	Observable Symbol	Operator Symbol	Operation
Position	$\underline{r}$	$\hat{r}$	Multiply by $\underline{r}$
Momentum	p	$\hat{p}$	$-i\hbar\left(\hat{i}\frac{\partial}{\partial x}+\hat{j}\frac{\partial}{\partial y}+\hat{k}\frac{\partial}{\partial z}\right)$
Kinetic energy	T	$\hat{T}$	$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)$
Potential energy	$V(r)$	$\hat{V}(r)$	Multiply by $V(r)$
Total energy	$E=T+V$	$\hat{H}$	$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+V(\mathbf{r})$
Angular momentum	l_x	$\hat{l}_x$	$-i\hbar\left(y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y}\right)$
	l_y	$\hat{l}_y$	$-i\hbar\left(z\frac{\partial}{\partial x}-x\frac{\partial}{\partial z}\right)$
	l_z	$\hat{l}_z$	$-i\hbar\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right)$

Operators act on the wave function from immediate left,

$$\underset{\substack{\uparrow\\ 2^{\text{nd}}}}{\hat{A}}\underset{\substack{\uparrow\\ 1^{\text{st}}}}{\hat{B}}\Psi$$

and the order of operation is important because,

$$\hat{A}\hat{B}\Psi \neq \hat{B}\hat{A}\Psi \quad \text{in general.}$$

Operators are linear; $\hat{A}(\phi_1+\phi_2)=\hat{A}\phi_1+\hat{A}\phi_2$

and $\hat{A}(k\phi_1)=k\hat{A}\phi_1$ where k = constant

For most system the wavefunctions cannot be determined as analytically precise mathematical functions (eigenfunctions).

That is, all well behaved wave functions may not be eigenfunctions of an operator.

Such wavefunctions however can be constructed as a weighted sum of *eigenfunctions*. Such *eigenfunctions* of an operator forms a complete set.

Concept: Linear combination of eigenfunctions.

Multiple measurements of a property of a system described by such a wavefunction would yield *more than one value for that property.*

Expectation (average) Value of measurements:

Postulate 4. If a system is in a state described by a *wave function* Ψ (which is not an eigenfunction), then the average value of the observable value of *a* is given by the expectation value <*a*>;

$$\langle a\rangle = \frac{\int_{all\_space}\Psi^*\hat{A}\Psi\,d\tau}{\boxed{\int_{all\_space}\Psi^*\Psi\,d\tau}} \qquad \text{if } \Psi \text{ is un-normalized.}$$

$$\longrightarrow 1$$

$$\langle a\rangle = \int_{all\_space}\Psi^*\hat{A}\Psi\,d\tau \qquad \text{if } \Psi \text{ is normalized.}$$

(to be continued)

Although measurements yields an eigenvalues,
a state does not have to be an eigenstate of $\hat{A}$ *initially*.

A wavefunction for a state Ψ, can be constructed from *n eigen-functions* selected from a complete set of *eigenfunctions* {ψ_i} (vectors) of an operator $\hat{A}$, as;

$$\hat{A}\psi_i = a_i\psi_i$$

$$\Psi = \sum_i^n b_i\psi_i. \qquad \text{Basis set} = \{\psi_i\}$$

Ψ, however, is not an eigenfunction of $\hat{A}$.
Note, b_i is how much Ψ resembles ψ_i.

$$\Psi = \sum_i^n b_i\psi_i. \qquad \text{Basis set} = \{\psi_i\}$$

In this case we only know that the measurement of *A* will yield *one* of the values of a_i (*contribution from* ψ_i), but we don't know which one. ({ψ_i} is orthonormal).

However, we do know the *probability* that eigenvalue will occur for a single measurement of a_i is $|b_i|^2$.

$$\sum_i^n b_i^2 = 1 \qquad \text{(to be continued)}$$

$$\langle a\rangle = |b_1^2|a_1+|b_2^2|a_2+|b_3^2|a_3+....$$

i. e. $\langle a\rangle = \sum_i |b_i^2|a_i$

Basis sets and completeness.

Eigenfunctions of an operator will form a *basis set* which is said to be a *complete set*. *Orthogonality* of wave functions allows them to form a basis set.

e.g. in the Cartesian coordinate system, unit or "basis" set (vectors) are unit vectors ***i, j, k*** along the x, y and z direction. It (***i, j, k)*** is a complete basis set.

Any arbitrary vector can be constructed in terms of the unit vectors (in terms of the complete basis set; ***i, j, k***) as a linear combination of the basis set, with appropriate weighing coefficients *a, b, c* that corresponds to the basis set.

$$\boldsymbol{r} = a\,\boldsymbol{i} + b\,\boldsymbol{j} + c\,\boldsymbol{k}$$

Basis sets and completeness.

Eigenfunctions of an operator forms a complete set $\{\psi_i\}$.

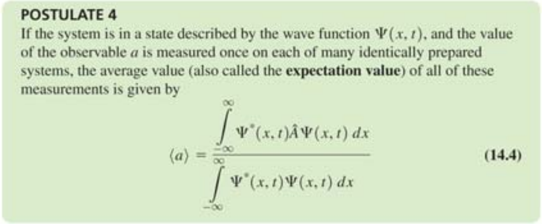
Now;

$$\widehat{A}\psi_i = a_i\psi_i \quad \Rightarrow \psi_1, \psi_2, \psi_3, \ldots \psi_n \quad \text{– complete basis set}$$

An arbitrary wave function can be constructed as a linear combination of the basis functions with appropriate weighing factors b_i associated with the basis functions, ψ_i ;

$$\psi = \sum_i^n b_i\psi_i .$$

Linear combination of eigenfunctions ψ_i .



POSTULATE 4

If the system is in a state described by the wave function $\Psi(x, t)$, and the value of the observable a is measured once on each of many identically prepared systems, the average value (also called the **expectation value**) of all of these measurements is given by

$$\langle a \rangle = \frac{\int_{-\infty}^{\infty} \Psi^*(x,t)\hat{A}\Psi(x,t)\,dx}{\int_{-\infty}^{\infty} \Psi^*(x,t)\Psi(x,t)\,dx} \qquad (14.4)$$

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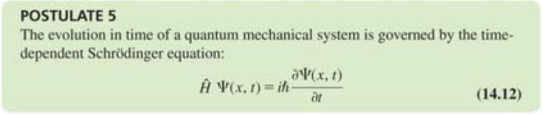
Postulate 5. The wave function or state function of a system evolves in time according to the time-dependent Schrödinger equation;

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



POSTULATE 5

The evolution in time of a quantum mechanical system is governed by the time-dependent Schrödinger equation:

$$\hat{H}\ \Psi(x,t) = i\hbar\frac{\partial\Psi(x,t)}{\partial t} \qquad (14.12)$$

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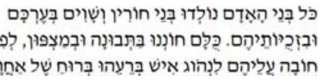
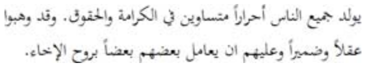
Consecutive Operators; order

$$\underset{\longleftarrow}{\widehat{A}_3\,\widehat{A}_2\,\widehat{A}_1}\ \Psi$$



כׇּל בְּנֵי הָאָדָם נוֹלְדוּ בְּנֵי חוֹרִין וְשָׁוִים בְּעֶרְכָּם
וּבִזְכֻיּוֹתֵיהֶם. כֻּלָּם חוֹנְנוּ בַּתְּבוּנָה וּבְמַצְפּוּן, לְפִיכָךְ
חוֹבָה עֲלֵיהֶם לִנְהוֹג אִישׁ בְּרֵעֵהוּ בְּרוּחַ שֶׁל אַחֲוָה.



يولد جميع الناس أحراراً متساوين في الكرامة والحقوق. وقد وهبوا
عقلاً وضميراً وعليهم ان يعامل بعضهم بعضاً بروح الإخاء.

Preserve the order of the operators.