**5. Concepts, Postulates and Techniques for Basic QM**

I find it quite amazing that in the space of about 30 years,

* the “failures” of Classical Physics (CP) had been resolved,
* a completely new way of looking into things had been developed and implemented,
* the details of chemical structure from then on could be examined, and
* spectroscopy (in its many forms) now could be explained and developed further.

The **significance of this era in science** can be gauged by the number of **Nobel Prizes won** by people associated with QM’s development – there were nearly **20** of them!

* “There was nothing else remotely comparable in the annals of science.” They were the “architects of modern physics and chemistry.” [Source now unknown]. See
* Solvay Conference picture with **18 Nobel Prize winners** – 15 in Physics & 3 in Chemistry.

**The Postulates of QM (Text Chapter 3)**

**Also** serve as a convenient framework for **summarizing the concepts of QM**.

* **Justification** for this postulate approach is that **it works!**

**1. The state of a QM system is completely specified by a time-dependent wavefunction Ψ(r, t) that is a function of the spatial coordinates (e.g., x, y, z) of the system and of time.**

**(If time is not a variable for the system, the state is specified by a time-independent wavefunction [ψ(r)]).**

**The probability that a particle will be found in the spatial interval dx dy dz centered at point r0 at time t0 is given by**

**P(r0, t0) = Ψ(r0, t0)\*Ψ(r0, t0) dx dy dz = ⎢Ψ(r0,t0) ⎢2 dx dy dz.**

Because of this **probability requirement**, a wavefunction **MUST** **be**

* a *single valued function* of the spatial coordinates,
* the *first derivative of a wavefunction must be continuous* so that the *second derivative can exists and be well behaved* (otherwise we could not set up the SWE), and
* a wave function *cannot have an infinite amplitude* over a finite interval (otherwise it could not be normalized).
  + - (e.g., Sin(x) can be a wavefunction but Tan(x) cannot because of discontinuities at x values where Tan(x) becomes infinite)

Note (a): The ***amplitude*** Ψ(**r0**, t0) has no physical meaning in QM; it is the **probability** that is related to the ***square*** of the magnitude of Ψ(r0, t0) **that has meaning**;

Note (b): **Ψ(r0, t0)** by itself can be **complex** or **negative**.

* It can be multiplied by –1 or its phase can be changed by multiplying it by a complex number of magnitude 1 (e.g., eiθ)
* ***All* *wavefunctions with only a different phase angle are******indistinguishable*** in that they generate the **same observable**. **[Fall 2021]**

Note (c): The **wavefunction is a complete description of the system** in that **any measurable property** (i.e., a physical “observable” such as its Energy) can be obtained from the wavefunction **by applying the appropriate QM operator**.

* Will see how to generator the appropriate QM operator in the next postulate.

**2. For every measurable property or observable of a system in CP (e.g., x, p, E), there exists a QM operator in QM which can be obtained by applying the following rules:**

**(i) Write the CP expression for the observable in terms of Cartesian coordinates & in terms of the components of linear momentum px, py, pz (≡ “conjugate momenta”);**

**(ii) Replace each Cartesian coordinate generically represented by q, by itself (≡ multiply by q; i.e., x, y, or z); & Replace each conjugate momentum component by **

* Saw that we can derive the Energy operator (called the Hamiltonian) in this way, i.e., we can use these two Rules to *convert from CP to QM.*

[Note: If  appears ≡

Note (a): **Operators act on wavefunctions from the left and the order of operation is important:**   necessarily.

Note (b): QM Operators must be **linear, i.e.,**  

Note (c): Simplest is the **identity** operator (≡ a do-nothing operator), 

Note (d): Since the measured values of observables are **real**, the **operators** corresponding to this property must yield **real eigenvalues**.

* This places a ***restriction*** on what QM operators can be:
* All QM operators must be **Hermitian operators** that have **real eigenvalues**.
* **Definition:** A **Hermitian operator**  has the property or following requirement:

For any well-behaved functions ψ and φ.



i.e., will get the same result (that must be the **same real value**) regardless of which way we determine the integral (i.e., by the ∫ on the left or by the ∫ on the right).

Proof: Suppose that in the above definition, ψ = φ and that 

but since  by definition, we must have a\* = a

proving that eigenvalues of Hermitian operators are real.

Note (e): **Eigenfunctions** of a Hermitian operator that have different eigenvalues of that operator are **orthogonal**. [Like the unit vectors in Cartesian coordinates].

Note (f): **Eigenfunctions** of a Hermitian operator can always be Normalized and so form an **orthonormal, complete set of functions**: i.e., 

Note (g): **Multiplication** of operators is **associative**  but is not necessarily **commutative** (i.e., you cannot generally switch the order of application and get the same result). Just as with matrices.

* Define the **commutator of 2 operators** as:

 & **if this equals 0**, the operators are said **to commute**.

Note (h): Some of the most important operators listed in the Text p. 39 of 1st, 41 of 2nd, (41 of 3rd), 69 of 4th Ed. The QM operator for **energy** is called the **Hamiltonian** operator.

**3. In any single measurement of the observable that corresponds to the operator, the only values that will ever be measured are the eigenvalues of that operator; i.e., the only possible values of an observable that ever can be observed are the eigenvalues of the corresponding operator.**

– E.g., when the energy of the H atom is measured, the only values obtained for the energy are the eigenvalues of the TI-SWE

Note (a): **Which** eigenvalue is obtained **depends on** whether the **current wavefunction** for the system is an eigenfunction of the corresponding QM operator:

* **If it is**, the value obtained is the **eigenvalue** of the **operator’s eigenvalue equation**.
* **If it is not**, the particular value measured will **still be** an **eigenvalue of the operator** but we **don’t know firsthand which particular *one* it will be**. We can determine the **average value** for such a measurement, however: the **average value** obtained for such a measurement can be determined by use of the next postulate.

**4. If the system is in a state described by the wavefunction Ψ(x, t), and the value of the observable a is measured once each for many identically prepared systems, the average value (also called the “expectation value”) of all of these measurements is given by**



If the wavefunction is Normalized, then the denominator is 1 (the ∫ ≡ Normalization integral).

E.g., if we are looking for the average energy of the system, it is given by



If the wavefunction Ψ(x, t) is actually ψn(x, t) which is an eigenfunction of with corresponding eigenvalue En, the result of this measurement is given by

 (i.e., an eigenvalue)

**So, what happens when the wavefunction Ψ(x, t) is NOT an eigenfunction of?**

* Suppose that the eigenfunctions of  are the complete set of eigenfunctions φi(x,t) so that φi = aiφi . Because these eigenfunctions form a complete set, the wavefunction Ψ(x, t) can be expanded in terms of those eigenfunctions, i.e., .

Since Ψ(x, t) and φi(x, t) are normalized, the average value of the observable

.

But because the eigenfunctions of  form an orthonormal set, the only values in this double sum for which the integral is not zero are the terms where m = n and the integral is 1 for those terms. Thus, the expression for  reduces to



where the values bm are the **expansion coefficients** of the wavefunction Ψ(x, t) in terms of the complete set of eigenfunctions of the operator .

* + **The individual coefficients bm are a measure of the extent to which the actual wavefunction “looks like” the mth eigenfunction of the operator .**

If Ψ(x, t) is one of the eigenfunctions of , say it is φn, the only value of bm that is non-zero is the one when m = n and then bn = 1 so  in this case.

Example: If only 3 of the bm values are non-zero, will be determined by the eigenvalues corresponding to those 3 eigenfunctions **but** the **expectation value** is **NOT simply an average** of those 3 eigenvalues: **it is a weighted average of those eigenvalues with the weighting factor |bm|2 each time being related to the contribution of that eigenfunction** φm **to wave function Ψ(x, t) in the expansion**.

Note: **3rd postulate specifies that the only possible result of a single measurement will be obtaining one of the eigenvalues** of the operator but it does not tell us which value will be measured.

Note: the **4th postulate specifies what will be measured** **from a large number of measurements**, each made only once on a large number of identically prepared systems.

* If the system’s eigenfunction is **not an eigenfunction** of the operator, there is no way of knowing the particular outcome of an individual measurement and the **outcomes** from measurement on identically prepared systems **are not the same!**
* The particular value measured in this case **could be any of the possible eigenvalues an** for which the corresponding bn in the expansion is non-zero. This is a **probabilistic outcome**.
* I.e., the **certainty of CP** – identically prepared systems all yield the same result (measurement outcome) – is **replaced in QM** by a **probabilistic outcome**.
  + - * In a sense, in QM **more** can be said about the outcome of a **large number** of measurements **than about** the outcome of a **single** measurement:
      * The ∑ equation above []

tells us that the **average value** resulting from a large number of measurements **is given by a sum containing the possible eigenvalues of the operator  weighted by |bm|2**, (which is the square of the expansion coefficient):

* + - * + the **bigger** the contribution of an **eigenfunction** φ(x,t) {an eigenfunction of operator } to Ψ(x,t), the **larger will be the weighting factor |bm|2** , and the **more probable** it is that the outcome of an individual measurement will be **am**, and **the more the am value will influence the average value **.
        + While there is **no way to tell which of the am will be found** in an individual measurement, if this same experiment is repeated many times on identically prepared systems, the **average value** can be predicted to **very high precision**.

**Example:** Suppose that Ψ(x,t) is a superposition of 3 functions φ1(x,t), φ2(x,t), φ3(x,t) which are eigenfunctions of operator  and the eigenvalues for these functions are a1, 4a1, and 9a1 respectively, and that the **superposition wavefunction** is (following expansion of Ψ(x,t) in terms of the eigenfunctions of the operator)

,

an individual measurement of property a will give only one of these eigenvalues (a1, or 4a1, or 9a1) **but the probability of obtaining a particular value** (e.g., 9a1, the eigenvalue for φ3(x,t)) will be given by the **square of the appropriate expansion coefficient** [i.e., (1/2)2 for φ3 in this case].

**Exercise: What is the average value for property a in the above example?**

**[Answer: 51/16 × a1].**

Now **Postulate 4** specified that the **measurement was to be carried out only once** on a large number of identically prepared systems.

We just learned that this 1st measurement will give **one of the eigenvalues** of the operator but that there is **no way** of predicting the **particular** outcome of this single measurement.

**What would the outcome be for a second measurement of the same observable?**

If a **successive measurement** is made on the same system, **exactly the same result will be obtained**(!) that was obtained in the 1st experiment and **further successive measurements** made on the same system would yield **exactly the same result as well;** i.e., for the **second and all subsequent measurements**, the results observed are exactly what would be expected if the system **were already in a particular eigenstate** of the operator [φ3(x, t) in our example] **and not in** **the original superposition state at all!!!**

*That is, the act of carrying out a QM measurement of a particular property appears to be to convert the wavefunction of a system to an eigenfunction of the operator corresponding to the measured property!*

**Probability in “CP”: Some Definitions**

In CP, the average value obtained for measuring property A will be obtained by averaging all the ai values found in a series of N measurements of that property, i.e.,



where nf is the number of times the value af is obtained and **pf = probability** of observing af as the value.

If f(x) = probability density such that f(x)⋅dx = probability that x lies between x and x + dx, **we define**

Probability, 

Average position, 

Second moment, 

**Probability in “QM”**

In QM, we deal with the current wavefunction for the system Ψ not being an eigenfunction of the operator  by expanding Ψ as a linear superposition of the eigenfunctions of the operator  (remembering that the eigenfunctions of an operator  form a complete set so that any other function in the same space e.g., Ψ, can be expanded in terms of them).

i.e.,  and since  we found that



where the values bm are the **expansion coefficients** for the wavefunction Ψ(x, t) in terms of the complete set of eigenfunctions of the operator  and each am is the eigenvalue corresponding to eigenfunction φm which is an eigenfunction of the operator.

Thus, the square of the expansion coefficient, ⎢bm ⎢2, is akin to the probability pm, (see the above definition) of getting am as the result.

**Now we can find the probability of getting a particular value** (e.g., am) when in state Ψ:



where bm is termed a **probability amplitude** which may be complex.

Thus, the **probability** = ⎢bm⎢2 which is **real**.

**Spread in the observable “a” values**

CP: The spread (or standard deviation) about the mean, σx = .

The **variance, σx2**, can then be related to the average value and second moment of variable x by the relation (straight statistics):

.

And this relationship will be used later in determining the spread in a result for QM. From this relation, if , there is no spread in the value being determined (see above).

We will find that the results found for a particular system (e.g., a particle in a box) will comply with those provided by the **Heisenberg Uncertainty Principle (HUP)**:

*For the HUP, the inequality can be written in the form  where  the standard deviations that would be obtained by analyzing the distribution of a large number of measured values of position (x) and the x-component of linear momentum (px).* [Note: if present,  ≡

**5. (Included for Completeness at this point). The evolution in time of a QM system is governed by the Time Dependent – SWE:**

*** where ***

Note: For wave functions that are solutions of the TI-SWE, we found that

. [Note: if present,  ≡

Note: In solving an eigenvalue equation for any operator  that is **not a function of time** , we can **ignore** the time-dependence.

E.g., if  where  is not varying with time, we can write

**

[Note: if present,  ≡

**→***Thus, we can* ***ignore*** *the time dependent function when the operator is time independent.*

**6. (We will use Postulate 6 later). The wavefunction of any system of electrons must be anti-symmetric with respect to the interchange of any two electrons.**

**E.g., if ψ(1,2) is used to represent the wave function for the atomic orbital of a helium atom where 1 and 2 denote the presence of the 2 electrons, this postulate requires that ψ(1,2) = −ψ(2,1) where the reversal of 1 and 2 implies the two electrons have been interchanged.**