**Supplement 3: Chemistry 6854**

**Physical Chemistry Alfred State College**

**Schrodinger’s 5 Quantum Postulates with *Play-by-Play* Notes**

**Postulate 1:**

**ψ(x), the source code for quantum systems (pg 116)**

**The state of a quantum mechanical system is completely specified (*at any given time t*) by the function**

**ψ(x) where x is the position of the system *(can be also in x,y,z*). All information about the particle is *stored in ψ(x)* and can be retrieved using the appropriate quantum operators and given that the probability of the system being at any particular x ± dx is the product: ψ\*(x)ψ(x)dx. *(ψ(x) is often called the stationary state wave function, or, the time-independent wave function).***

*Note: It is common to include as an addendum to the above postulate that a specific requirement on ψ(x) is that it be `normalized’ so that:*

<ψ\*|ψ> = 1

*which is mathematically compact way of saying that if we integrate over all possible x, the system exists with a 100 % probability.*

**Postulate 2:**

**Connecting classical quantities with quantum operators (pp 118-119, 130 )**

**Every classically observed physical quantity can be re-expressed in the quantum domain with an appropriate linear (*Hermitian)* operator ( *specified by the recipes on page 119, table 4.1 attached here*).**

*Note 1: a linear operator Â has the `distributive’ property, e.g. (see also: pg 79)*

*Â\*(c1 f(x) + c2g(x)) = c1 Âf(x) + c2Âg(x)*

*d/dx is an example of a linear operator: d/dx(c1f(x) + c2(g(x))= c1df(x)/dx + c2dg(x)/dx*

*√ is an example of a non-linear operator: √(f(x) +g(x) ≠ √f(x) + √g(x)*

*Linearity also means that if two different functions f(x) and g(x) result in the same `eigenvalue’* **α** *for a physical quantity like energy, then their linear combination is also a solution (eigen function) of Â.*

*e.g. c1 f(x) + c2g(x) is also a solution to Âψ(x) =* ***α****ψ (see page 121)*

*Note 2: a Hermitian, linear operator Â has the additional property that:*

*∫ψn (x)\*Âψm (x) dx = ∫ψm (x)[(|Â|ψn (x)]\*dx (see also, eq. 4.31 page 129)*

*or equivalently :<ψn \*|Â|ψm> = <ψm |(Â|ψn \*>*

*where ψn and ψm are any two solutions (or the same solution***: ψn=ψm***) to the eigenvalue problem.*

*This will guarantee that the eigen values of Â will be real numbered, and, that different wave function solutions to Â, ψ1 and ψ2 corresponding to different allowed eigen values have the (lovely) property that:*

*<ψ1|ψ2> = 0*

*which means ψ1 and ψ2 are `orthonormal’- a term meant to imply that the two wave functions are like Cartesian (perpendicular) coordinate axes helping to define the `space’ of possible states for the system.*

**Postulate 3:**

**Finding physical quantities in the quantum world- Schrodinger’s eigenvalue formulation (p 122)**

**In any measurement of an observable associated with an operator Â, the only values that can be observed for this operator are the `eigenvalues’, a, which are real numbers that satisfy the eigenvalue equation:**

**Âψn = anψn**

*Note: As a practical matter, the chief `* **Â** *‘ we focus on is* ***Hop*** *, the quantum Hamiltonian, whose analysis in the above leads to the wave function* **ψ(x)** *defined in postulate 1.* *The inclusion of a subscript n reflects our experience in chapter 3 that quantum mechanical solutions involve integers n= 1,2,3….which arise from the accompanying boundary conditions applied to the eigenvalue problem. As already noted from Postulate 2, the separate ψn are orthonormal. Postulate 2 and 3 let us deduce that Â must be Hermitian and <ψm\*| ψn> = 0 if n ≠m.*

**Postulate 4:**

**How we compute average behavior of quantities in the quantum world (page 122)**

**If ψn(x) is an allowed and normalized state function for a quantum system, then the average of the observable A associated with any allowed quantum operator Â *(table 4.1, pg 119), is given by:***

**<ψn\*|Â|ψ > = <A>**

*Note: this is the quantum equivalent of what was described in Homework 3 and in Math supplement B of the text, e.g. that an* ***average*** *of any quantity y= ∫y P(y) dx = <y>.*

**Postulate 5:**

**Recipe for finding the time variation of quantum systems (pg. 125)**

**Let Ψ(x,t) be the composite wave function of x and t (which may contain ψ(x)) . Let Hop be a (possibly) time-containing Hamiltonian energy operator. To find the more general, non-stationary Ψ(x,t) we must solve the `time*-dependent’ Schrodinger equation:***

***Hop Ψ(x,t) = i ħ ∂Ψ(x,t)***

***∂t***

*Note: Often* ***Hop*** *will not contain any time variable and we can write, as we did with the classical wave equation, Ψ(x,t)= ψ(x)\*T(t) and separate* variables so that (after some algebra…)

***H****ψ(x) = Eψ(x) stationary state Schrodinger equation*

*dT(t) = -i ET(t)*

*dt* ***ħ***

*The latter differential equation is easily solved so that T(t)= Ce-iEt/ħ, which has the exact form to that determined for the classical wave equation’s T(t). If this is the case, then the probability:*

***Ψ(x,t)\*Ψ(x,t) dx =(T(t)*** *ψ(x)) \*(T(t) ψ(x))dx= (T(t)\*T(t)) X(x)\*X(x)dx*

*= C2e+ iEt/ħe- iEt/ħX(x)\*X(x)dx*

*=C2\*1\* X(x)\*X(x)dx*

*Which means that if t is not part of Hop , then the probability density is also time-independent.*

