Summary of Chemistry 163A Ruminations on Quantum Mechanical Measurement

1. Postulate 3 (p 117-118 McQ)

> *In any measurement of an observable associated with the operator $\hat{A}$, the only values that will ever be observed (in individual measurements) are the eigenvalues, a_k of the operator $\hat{A}$:*

$$\hat{A}\psi_k = a_k\, \psi_k$$

2. If the wavefunction describing the system is an eigenfunction of some operator $\hat{Q}\psi_n = q_n\psi_n$, then every measurement of the observable (property) associated with $\hat{Q}$ gives the value q_n ; such a system would have a "fixed" value of the property Q. For example we often (almost always, so far, in Chem163A) deal with a stationary state of a system whose wavefunction satisfies the time-independent Schrödinger equation $\hat{H}\psi_n = E_n\,\psi_n$. For such a state, each time the energy is measured the same value E_n is obtained and $\sigma_E^2 = \langle E^2\rangle - \langle E\rangle^2 = 0$. However if, for this system, we do measurements for another property for which ψ_n is not an eigenfuntion of the operator associated with that property (e.g. $\hat{p}_x$), then a range of values will result from individual measurements of that property and $\sigma_p^2 = \langle p_x^2\rangle - \langle p_x\rangle^2 \neq 0$.

3. If a wavefunction ψ_k describes a system which has "fixed" (definite) values for **two observables** (properties) A and B, then ψ_k must be, simultaneously, an eigenfunction of both $\hat{A}\ and\ \hat{B}$:

$$\hat{A}\psi_k = a_k\,\psi_k \qquad and \qquad \hat{B}\psi_k = b_k\,\psi_k$$

In this case every measurement of A would give a_k and of B would always give b_k; thus both $\sigma_A=0$ and $\sigma_B = 0$.

4. The situation in #3 can occur only if $\hat{A}\ and\, \hat{B}\ commute,\ \left[\hat{A},\hat{B}\right] = 0$. More generally

$$\sigma_A^2\ \sigma_B^2\ \geq -\frac{1}{4}\left\{\int \psi^*\left[\hat{A},\hat{B}\right]\psi\, dx\right\}^2 \qquad \text{equation (4-75 McQ)}$$

An example where one wavefunction is simultaneously an eigenfunction of two operators is an atomic hydrogen orbital $\psi_{n\ell m}$ and the operators: $\hat{H}\ (energy)\quad and\, \hat{L}^2\,(magnitude\,of\,angular\,momentum)$

$$\left[\hat{H},\,\hat{L}^2\right] = 0 \quad consistent\,with \qquad \hat{H}\,\psi_{n\ell m} = \left[-\frac{Ze^2}{8\pi\varepsilon_0 a_0}\,\frac{1}{n^2}\right]\psi_{n\ell m} \quad and \quad \hat{L}^2\,\psi_{n\ell m} = \left[\ell\,(\ell+1)\hbar^2\right]\psi_{n\ell m}$$

Thus an electron in a hydrogen orbital will have "fixed" values for both energy (as determined by n) anf for the magnitude of angular momentum (as determined by ℓ).