Review Sheet

Concepts and definitions you should know and understand:

well-behaved function
normalization
eigenfunction
eigenvalue
operator
observable
linear momentum
kinetic energy
potential energy
Hamiltonian
Laplacian
Schrödinger equation
expectation value
the postulate on operators
the postulate on eigenvalues
the postulate on expectation values
separation of variables
polar coordinates
degenerate eigenfunctions
particle on a circle
given a Hamiltonian, how to find the eigenfunctions
particle on a line
probability density
energy level diagram
complete set of eigenfunctions of an operator
orthogonal
orthonormal
superposition of states
linear operators
Hermitian operators
commutator
commuting operators have simultaneous eigenfunctions
standard deviation of a series of measurements
uncertainty principle
natural linewidth
standard deviation of energy and linewidth

time-dependent Schrödinger equation
stationary state
constant of the motion
when is the average value of an observable invariant with time?
derivation of Newton's equations from quantum mechanics
angular momentum
cross product of two vectors
derive commutation rules for angular momentum
spherical polar coordinates
particle on a sphere
numerical solution of the theta equation
spherical harmonics
rigid rotor
center of mass coordinates
reduced mass
the hydrogen atom
a particle in a Coulomb field
the quantum numbers for a hydrogen atom
radial distribution function
Bohr radius
the characteristics of the eigenfunctions of the H atom
central field approximation for many-electron atoms
raising and lowering operators
derive commutation rules of raising and lowering operators
the result of applying the ladder operators on the eigenfunctions of angular momentum
bra ket notation for angular momentum functions
vector sum of two angular momenta
commutation rules for coupled angular momenta
intrinsic (spin) angular momentum of a particle
spin orbit coupling
term symbol

Common mistakes in this class: (Get it right for the final exam)

DIMENSIONAL ANALYSIS:
Check the expressions you are using by making sure the dimensions are correct. If it is supposed to be equal to a length, then the units for the whole expression must be in units of length.

VECTORS:

1. The vector **A** is not equal to $A_x + A_y + A_z$. The correct relation is $\mathbf{A} = A_x\mathbf{i} + A_y\mathbf{j} + A_z\mathbf{k}$, where **i**, **j**, **k** are unit vectors along the x,y,z Cartesian axes.

2. The square of vector **A** is a scalar quantity equal to $\mathbf{A}\bullet\mathbf{A} = A_x^2 + A_y^2 + A_z^2$.

CALCULUS:

1. After integration over all variables, *the result is a number*, the result can **not** still have *the variable* left. Remember that an integral corresponds to a <u>sum</u> over infinitesimal slivers (volume elements) weighted by the value of the integrand function in that sliver of integration space.

2. The meaning of a double integral: The various parts of the function within the integrand can not be separately integrated if there are variables in common. That is,

$$\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}F(\theta,\phi)^*\cos\phi\ G(\theta,\phi)\ \sin\theta\ d\theta d\phi$$
$$\neq \int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}F(\theta,\phi)^*G(\theta,\phi)d\theta d\phi\bullet\int_{\theta=0}^{\pi}\sin\theta\ d\theta\bullet\int_{\phi=0}^{2\pi}\cos\phi\ d\phi.$$

One must do <u>all the θ</u> parts in one integral and <u>all the ϕ</u> parts in another integral.

POSTULATE 3:

If the operator *Op* is known for <u>any observable</u>, and the function which describes the state of the system is known to be Ψ(1,2,3,..),
then the average value that will be observed is given by

$$\iiint\ldots\int \Psi(1,2,3,..)^*\ Op\ \Psi(1,2,3,..)\ d\tau_1 d\tau_2 d\tau_3\ldots$$

Op does not have to be related to energy and Ψ does not have to be an eigenfunction of anything, it just has to be normalized.

HYDROGEN ATOM:

1. $x = r\sin\theta\cos\phi$ corresponds to the position of the electron relative to the nucleus sitting at the origin of a Cartesian axis system.

2. $dxdydz = r^2dr\ \sin\theta d\theta\ d\phi$ is the correct volume element for integration for a hydrogen atom system. The limits are $r = 0\rightarrow\infty$, $\theta = 0\rightarrow \pi$, $\phi = 0\rightarrow 2\pi$.

3. Know the significance of every coordinate involved in the wavefunction of the hydrogen atom and where it came from. Know the meaning of every symbol used. We did all of this in great detail!

4. The energy of a hydrogen atom is $E = -(Z/n)^2(e^2/2a)$. Negative! The energy is proportional to Z^2. The zero of energy is for the electron at infinite distance from the nucleus.

5. In this expression e is the magnitude of charge of the electron, and $a = \hbar^2/\mu e^2$, in which $(1/\mu) = (1/m_{electron}) + (1/m_{nucleus})$. On the other hand, the Bohr radius $a_0 = \hbar^2/me^2$

Here m, the mass of the electron, is used alone because a_0 corresponds to $(1/\mu) = (1/m_{electron}) + (1/m_{nucleus})$ where $m_{nucleus}$ is taken to be infinite, leaving $(1/\mu) = (1/m_{electron})$.

In general $a = \hbar^2/\mu e^2$ [where the reduced mass μ is given by $(1/\mu) = (1/m_{electron}) + (1/m_{nucleus})$] appears in the energy eigenvalues and in the eigenfunctions $R_{n\ell}(r)$ of the hydrogen atom. I have explained this in lecture and told you that isotope shifts in atomic spectra clearly are due to slightly different reduced masses for different masses of nuclei. Your textbook makes this distinction between the Rydberg constant for the infinitely heavy nucleus and for the real nucleus.

MANY-ELECTRON ATOMS:

1. Understand separation of variables! This is what permits the writing of a sum of $[Z_{eff}(i)/n_i]^2 \cdot(e^2/2a_0)$, one for each electron, in order to get the energy for the whole atom.

2. $Z_{eff}(i) = Z - s_{n\ell}$, for the i^{th} electron in the $n_i\ell_i$ subshell.

$s_{n\ell}$ comes from the screening effect of all the other electrons. Have to figure out the value of $s_{n\ell}$ for each electron by counting. For example, using Slater's rules

Z = 5, configuration $1s^2 2s 3p 3d$:

electron	$n_i\ell_i$	1s	1s	2s	3p	3d	for the ith electron $s_{n\ell}$	for the ith electron $(Z - s_{n\ell})_i$
i=1	1s	–	0.3	0	0	0	0.3	4.7
i=2	1s	0.3	–	0	0	0	0.3	4.7
i=3	2s	0.85	0.85	–	0	0	1.7	3.3
i=4	3p	1.00	1.00	0.85	–	0	2.85	2.15
i=5	3d	1.00	1.00	1.00	1.00	–	4	1.0

EIGENFUNCTIONS OF AN OPERATOR:

Understand the principles,

"The eigenfunctions of an operator that can represent an observable (a Hermitian operator) form a complete orthonormal set."

Do not simply copy results without thinking, in evaluating integrals such as the following:

(1) $\int\int \Psi_i(\theta,\phi)^* \Psi_i(\theta,\phi)\, d\tau = 1$ always, for normalization of a function that describes a physical system. Normalization is very general, $\Psi_i(\theta,\phi)$ does not have to be an eigenfunction of anything.

(2) $\int\int \Psi_i(\theta,\phi)^* \Psi_k(\theta,\phi)\, d\tau = 0$ <u>if</u> Ψ_i and Ψ_k are eigenfunctions of a Hermitian operator corresponding to different eigenvalues, in which case they are orthogonal. *Otherwise*, if Ψ_i and Ψ_k are any two different functions, the integral could be any number; it is simply the overlap between the two functions.

(3) $\int\int \Psi_i(\theta,\phi)^* \mathrm{Op}\, \Psi_k(\theta,\phi)\, d\tau = 0$ only if Ψ_i and Ψ_k are eigenfunctions of Op itself, in which case,

$\int\int \Psi_i(\theta,\phi)^* \underline{\mathrm{Op}\, \Psi_k(\theta,\phi)} d\tau = \int\int \Psi_i(\theta,\phi)^* \underline{a_k \Psi_k(\theta,\phi)} d\tau = a_k \int\int \Psi_i(\theta,\phi)^* \Psi_k(\theta,\phi) d\tau = 0$ because Ψ_i and Ψ_k are eigenfunctions corresponding to different eigenvalues, they are orthogonal. *Otherwise* , when Ψ_i and Ψ_k are any two different functions, the integral could be any number; it is simply the overlap between the function Ψ_i and the new function resulting from $\mathrm{Op}\Psi_k$.

(4) $\int\int \Psi_i(\theta,\phi)^* \mathrm{Op}\, \Psi_i(\theta,\phi)\, d\tau = a_i$ only if Ψ_i is an eigenfunction of Hermitian operator Op with the eigenvalue a_i . *Otherwise*, if Ψ_i is not an eigenfunction of Op, but is an eigenfunction of some other operator Op′ then one needs to carry out the operation $\mathrm{Op}\Psi_i$ to find out what is the result, that is, to find out if any part of the result has a non-zero overlap with the old function Ψ_i . For example, if Ψ_i is an eigenfunction of the Hamiltonian,

$\int\int \Psi_i(\theta,\phi)^* \mathrm{Op}\, \Psi_i(\theta,\phi)\, d\tau \neq E_i$. To get the result, one must do the operation $\underline{\mathrm{Op}\, \Psi_i(\theta,\phi)}$ which will of course result in some function which can be written as a linear combination of the complete orthonormal set of Hamiltonian eigenfunctions. Thus

$\mathrm{Op}\, \Psi_i(\theta,\phi) = c_1\Psi_1(\theta,\phi) + c_2\Psi_2(\theta,\phi) + c_3\Psi_3(\theta,\phi) + c_4\Psi_4(\theta,\phi) + ...$

Now, since the eigenfunctions of the Hamiltonian form an orthonormal set, then $\int\int\Psi_i (\theta,\phi)^*Op\ \Psi_i (\theta,\phi)\ d\tau = c_i$ since only the i^{th} function is not orthogonal and it has the coefficient c_i in front of it.

On the other hand if it is stated that $\Psi_i (\theta,\phi)$ is a function that describes the state of the system, and Op is a Hermitian operator, then the integral $\int\int\Psi_i (\theta,\phi)^*Op\ \Psi_i (\theta,\phi)\ d\tau$ is merely the average value of the observable for which Op is the operator. This is a statement of Postulate 3.