**In class, no-calculations mini-exam 2: Chem 6854 Spring 2016**

Your name: \_\_\_\_\_\_\_\_\_answers\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ \_\_\_/36 pts

2 pts/problem

1. **If φ = Ceikx, express <φ\*|φ> as an integral over all space from 0🡪L. (Don’t evaluate: just set up)**

\*

1. **If we were to `normalize φ’ above, what must the expression above be set equal to ??**

1

1. **Briefly explain why spherical (r, θ,φ) rather than Cartesian (x,y,z) coordinates are used to solve the**

**Hydrogen atom Schrödinger equation.**

***If we use Cartesian coordinates, the distance between electron and proton mus be written as a radical***

***(x2 +y2 +z2)1/2. This is a function which is impossible to separate variables with. The alternativwe spherical coordinate system expresses r as a separate variable and allows re-writing Ψ(r,θ,φ)=R(r)Θ(θ) Φ(φ), and so reduces the intractable single three variable eigen value problem Ψ=EΨ to three (easier) one variable eigen value problems.***

1. **The energy of an H atom is proportional to:**
2. -n2 b) -L(L+1)/n2 c) –mL2(L)(L+1)/n2 d) -L2/n2 e) -1/n2
3. **If = kinetic energy operator and +½ kx2 = the potential operator for a harmonic oscillator system, E = the eigen energy and ψ the wave function write down the basic form of the Schrödinger eigenvalue problem we need to solve.**

**+½ kx2Ψ(x) = EΨ(x)**

1. **The quantum energy of a rigid rotor varies with:**
2. **J(J+1)**  b) 1/J c) J d) J2/(1+J) e) J-1
3. **The correct expression for the energy of a quantum harmonic oscillator is: (**ω **=f/2**π **radians)**
4. En = hωn b)En = hω(n +1) c) En = h(n + ½ )/ω d) En = hω(n + ½) e) En = μr2n(n+1)
5. **Given that n=2 for an H atom, what are possible values of L ?**
6. 2,1,0 b) 2,1,0,-1,2 c) 1,0 d)1,0,-1 e) 2
7. **If L= 1, what are the possible values of mL ?**
8. 1,0 b) 1,0,-1 c) 2,1,0 d) 0,-1 e) 0
9. **If L=3, what corresponding orbital equivalent are we talking about ?**
10. s orbits b) p orbits c) d orbits d) f orbits
11. **Which term below represents the main reason an exact quantum solution to multi-electron systems of either atoms or molecules is essentially impossible:**
12. **electron-nuclear interaction b) nuclear-nuclear interaction c) electron-electron interaction d) kinetic E**
13. **In the variational method of approximation used in the Hartree-Fock calculations you carried out with the Spartan QChem program, what critical basis set is used throughout:**
14. **Roothan-Hall wavefunctions b) Slater orbitals (STO) c) H1s orbitals d)Laguerre polynomials**
15. **Given that an approximated wave function ψapprox =ψ has the form below, what does the variational method**

**minimize? ψapprox = c1φ1(r1,θ1 ) + c2φ2(r2,θ2)**

1. <ψ|ψ>/dE =0 c) dφ1/dc1= dφ2/dc2 =0
2. (<ψ|ψ>/<ψ|ψ>)/dc1= d(<ψ|ψ>/<ψ|ψ>)/dc2= 0 ) d) dψ/dr1 = dψ/dr2 = 0

**14) The secular equation for a two basis element ( φ1 and φ2) approximation of Ψ for a given quantum Hamiltonian is written below :**

det

= 0

**a) define H11= H11 using bra-ket notation (1 pt)**

**H11 = <φ1|φ1> an energy Hamiltonian**

**b) define S12= S12 using standard integral notation. Assume the integration range is 0🡪∞. (1 pt)**

**S12 = an overlap integral**

**c) The secular equation above arises from solving the matrix problem below :**

0

0

C1

C2

=

**Why is the determinant (det) of the matrix set =0 ? (2 pts)**

det

**c1=**

**det**

**Since the upper determinant =0, for finite values of c1 to occur, the denominator must =0 so that**

**We have a `indeterminant’ solution via a zero divide. This basically means c1 and c2 are dependent on each other rather than independent.**

1. **Briefly describe the `correlation’ problem inherent in the Hartree-Fock methodology used in our Spartan QChem program**

**The correlation problem is essentially that we ignore dynamic interactions of electrons with other electrons and simply assume an average field.**

1. **Recalling Professor Simpson’s two lectures, what prime advantage does the DFT approach to quantum calculation have over other post Hartree-Fock methods ?**
2. The Universal function is known

b) Computation time goes up only as N3, N=# basis elements (cheaper)

c) DFT leaves out electron-electron interactions

d) The Born-Oppenheimer approximation is not applied

1. **How many angels can dance on the head of a pin ?**
2. get bent, Fong b) cats rule, you drool c) 4n+2 d) Nookie !