CHM 6480 – Take home exam 2
Due date: Wednesday, December 2nd (by 11:59pm)
Do all of the following problems. Show your work.

1) The particle in a sphere TISE has the following potential

$$V(r) = 0 \qquad 0 \le r \le a \qquad (1.1)$$
$$V(r) = \infty \qquad r > a$$

where a is the radius of the sphere.

a) Write down the TISE for the above system. Use spherical polar coordinates.

b) The wavefunction for the above system is clearly $\phi(r) = 0$ outside the sphere ($r > a$). Consider the following trial wavefunction for inside the sphere

$$\phi(r) = a - r \qquad 0 \le r \le a \qquad (1.2)$$

Find the energy corresponding to the above trial wavefunction.

2) In a calculation using the linear variational method the following 2 x 2 matrix was obtained

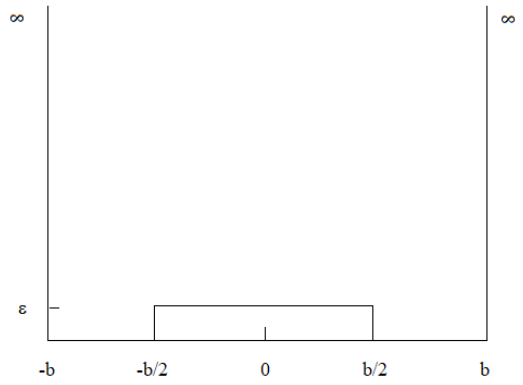
$$\det \begin{vmatrix} 4 - W & -3 \\ -3 & 6 - W \end{vmatrix} = 0$$

where W is the variational energy, and energy is given in units of E_0.

Find the two roots to the above equation, corresponding to the two possible values for the variational energy W. Which root corresponds to the ground state variational energy?

3) Consider the following perturbed particle in an infinite box system. This corresponds to the following potential energy

$V = \infty \quad |x| > b$
$V = 0 \quad b > |x| > b/2$
$V = \varepsilon \quad b/2 > |x| > 0$



Find the first order correction to the energy for this system for the n = 1 and n = 2 state.

4) Titanium (Z = 22) has the electron configuration [Ar] $4s^2$ $3d^2$, and is the smallest atom containing two electrons in a d-orbital in its ground state electron configuration. The term symbols for a d^2 state are (not including values for J) are

$$^1G,\ ^3F,\ ^1D,\ ^3P,\ ^1S \qquad (4.1)$$

a) Using Hund's rules, place the above electronic states in order from lowest energy to highest energy.

b) For each of the above electroic states find the possible values for J, the quantum number for spin+orbital angular momentum).

c) The formula for the energy for spin-orbit coupling, based on first order perturbation theory, is

$$E_{SO} = a\,[J(J+1) - L(L+1) - S(S+1)] \qquad (4.2)$$

where L, S, and J are quantum numbers and a is a constant.

For the ^3F state of titanium there are three possible values for J. Using the highest and lowest J value and the data at the NIST website below, find the experimental value for a. The NIST website is

https://physics.nist.gov/PhysRefData/ASD/levels_form.html

Enter "Ti I" in the box labeled "Spectrum" (this corresponds to the states for a neutral titanium atom).

d) Using your value for a in part c of this problem, find the energy predicted for the third value for J for the 3F state. Compare your result to the experimental result. If they differ, explain why they are different.