Problem Set 0 – Linear Algebra Review and the Matrix Representation of Quantum Mechanics

Show all work for full credit.

1) Exercise 1.4 a, b, c, d, and f (skip e) on page 7 of Szabo and Ostlund.

2) Exercise 1.6 on page 8 of Szabo and Ostlund.

3) Exercise 1.8 on page 14 of Szabo and Ostlund.

4) Consider a one-electron homonuclear diatomic molecule (e.g. H_2^+). If we choose a basis of atomic orbitals, the electronic Hamiltonian for such a system can be approximated to be

$$\mathbf{H} = \begin{bmatrix} E_{atom} & V \\ V & E_{atom} \end{bmatrix}$$

where E_{atom} is the energy of a one-electron atom, and V is the coupling between the orbitals on the left and right atoms. (Extraneous information: If we were starting from scratch, these matrix elements would be computed

$$E_{atom} = \langle \phi_l | \hat{H} | \phi_l \rangle = \langle \phi_r | \hat{H} | \phi_r \rangle$$

$$V = \langle \phi_l | \hat{H} | \phi_r \rangle = \langle \phi_r | \hat{H} | \phi_l \rangle$$

where $|\phi_r\rangle$ and $|\phi_l\rangle$ are orbitals that solve the atomic Schrodinger equation for the right and left atoms respectively, and $\hat{H}$ is the Hamiltonian operator.)

a) Find the eigenvalues and normalized eigenvectors of this Hamiltonian by finding the unitary transformation that diagonalizes the Hamiltonian by hand.

b) Assume that $|\phi_r\rangle$ and $|\phi_l\rangle$ correspond to *s* orbitals. Draw a picture of the two states corresponding to the two eigenvectors. In general chemistry language, what are these two states?

c) Derive the condition under which the two states are degenerate (have the same energy). In physical terms, when do you think that this would be true?