

**Problem set 3: Performing small model calculations on atoms and H₂.
(Peruse lecture notes on limitations of the MO model, angular momentum theory).**

Using the Slater rules to evaluate the Hamiltonian matrix elements over the Slater determinants we discuss some model problems, in particular H₂ in a minimal basis, and a model for atomic ground and excited states.

Calculations of atomic energy levels.

In the following *two problems* we will solve some small CI problems for the C and N atoms, and consider configurations that differ in the occupation of the p_x, p_y, p_z spin-orbitals. We will neglect the explicit interactions with the s-orbitals, which can be included by a redefinition of the 1-electron matrix elements. It is most convenient if you set up the matrices in Mathcad (or other package), using symbolic notation. Then you can easily perform the diagonalization. We will use the following non-zero integrals, defined over the spatial orbitals. Integrals that are related by permutational / Hermitian symmetry are present also, but other integrals are zero by symmetry. Every integral needs to have an even number of x, y and z indices. If the integrand has for example only one x-index the integrand is odd under reflection in the yz plane and the integral vanishes. Here is a list of the symmetry unique integrals:

$$\begin{aligned}h_{xx} &= h_{yy} = h_{zz} \equiv h \\ \langle xx | xx \rangle &= \langle yy | yy \rangle = \langle zz | zz \rangle \equiv D \\ \langle xy | xy \rangle &= \langle xz | xz \rangle = \langle yz | yz \rangle \equiv J \\ \langle xy | yx \rangle &= \langle xz | zx \rangle = \langle yz | zy \rangle = \langle xx | yy \rangle = \langle xx | zz \rangle = \langle yy | zz \rangle \equiv K\end{aligned}$$

4. Consider the carbon atom with 2-electrons in the p orbitals, and build the CI Hamiltonian matrix over the $M_s = 0$ determinants. What is the dimension of the CI space? What is the degeneracy of the eigenvalues you expect to get out of the diagonalization (use what you know from angular momentum)? Diagonalize the

matrix (using Mathcad or Maple), in symbolic notation, and list the eigenvalues.

Consider next the $M_S = 1$ state $|p_x p_y\rangle$. What is the energy expectation value of this state? Is it an eigenstate of the Hamiltonian (within the basis of the p-orbitals)? Why or why not? Can you label the symmetry of the states you have found up to now? In order to find the proper degeneracies of the 1D state you have to assume a definite relation for the D integral in terms of J and K. Show that the relation $D = J + 2K$ leads to the proper result. Can you rationalize the relative magnitude of the matrix elements D, J and K ? Rationalize the energy ordering of the states you found, and argue the validity of Hund's rules for the carbon atom.

5. Consider the Nitrogen atom, and the above set of integrals in symbolic form. Set up the variational 3x3 CI problem for the following basis states:

$|p_x p_y \bar{p}_z\rangle, |p_x \bar{p}_y p_z\rangle, |\bar{p}_x p_y p_z\rangle$. All three determinants have $M_S = \frac{1}{2}$. Diagonalize the CI matrix and list the eigenvalues. What are the corresponding eigenvectors? Compare the energies from the CI to the energy of $|p_x p_y p_z\rangle$. Also set up the 2x2 CI problem for the determinants $|p_x \bar{p}_x p_y\rangle, |p_z \bar{p}_z p_y\rangle$. These determinants fall in a separate symmetry, as they have a single p_y orbital. Consider the other types of small CI's that you could do in the space of states that have $M_S = \frac{1}{2}$, and list the multiplets by energy and indicate their degeneracies. As in the previous question you will need the same relation $D = J + 2K$ to find the proper degeneracies. Give the term symbols, as we discussed in the section on angular momentum theory. Again verify Hund's rule which states that the state with the highest S value is lowest in energy, and only after this the rule applies that if states have the same S-value, the state that has the highest L-value is lowest in energy.

6. In this problem we will calculate the Potential Energy Curve of ground and excited states for the H_2 molecule for a variety of methods, but all in a minimal basis set. The required integrals are given in Szabo and Ostlund on page 459. In these tables you

find the orbital energies ε_1 and ε_2 , rather than the one electron matrix elements h_{11}, h_{22} . They are related as $\varepsilon_1 = h_{11} + J_{11}$; $\varepsilon_2 = h_{22} + 2J_{12} - K_{12}$, and this allows you to extract the one-electron matrix-elements. Use a math program (or excel ?) to do the problem.

Questions:

- a. Set up the variational 2x2 CI problem for the ground state. Calculate and plot the potential energy curve for the ground state as a function of bond distance, using Maple/Mathcad.
- b. Calculate the potential energy curve at the restricted Hartree-Fock level, and plot it in the same graph as the CI curve.
- c. Plot the ground state energy at the Hartree-Fock + second order perturbation theory (see exercise S&O 2.18), again in the same graph. You will see that perturbation theory is a disaster at larger distances. Can you track the source of the problem?
- d. Set up the variational problem for the singly excited singlet and the $M_s = 0$ component of the triplet states, and plot the potential energy curves. Show analytically that in the asymptotic region of large internuclear distance the ground state and the triplet state are degenerate, and verify this result from your plots.