
This is a set of problems for you to practice on. No need to hand it in. It covers material in Mathchapter H, Chapter 9, and Sections 11.6-11.8. It is all material that will be covered on the final exam.

We will have a first look at many-electron systems (atoms) and this requires the consideration of spin. The spin operators $\hat{S}_x, \hat{S}_y, \hat{S}_z$ satisfy the usual angular momentum commutation relations, and this leads us to consider the common eigenfunctions of $\hat{S}^2$ and $\hat{S}_z$. The one-electron spin functions $\alpha$ and $\beta$ have half-integer quantum numbers ($g_{1/2,1/2}$ and $g_{1/2,-1/2}$ in the notation of the lecture notes on angular momentum). Another important concept that is introduced is the Pauli principle that states that the overall wavefunction has to be antisymmetric under an interchange of electronic coordinates. Slater determinants are the analog of a product wave function, which is antisymmetrized by creating the determinant. In an antisymmetric Slater determinant constructed from spin-orbitals, each spin-orbital is at most singly occupied. The many-electron wavefunctions for atoms (spherically symmetric) are eigenfunctions of the operators $\hat{L}^2$ and $\hat{S}^2$. In the absence of spin-orbit coupling (a very small effect) many-electron wavefunctions for atoms are also eigenfunctions of $\hat{L}_z$ and $\hat{S}_z$. This leads to a classification of the eigenstates that is qualitatively correct (notations like $^3D, ^1P$). To describe the final small splitting due to spin-orbit coupling the total angular momentum operator $\hat{J} = \hat{L} + \hat{S}$ will be introduced. This lifts the $(2L+1)(2S+1)$-fold degeneracy and leads to an additional quantum number $J$ that has values ranging from $L+\ldots\left|L-S\right|$. These eigenstates are no longer eigenstates of $\hat{L}_z$ and $\hat{S}_z$. Hund's rules predict the overall lowest state in a given configuration.

The fact that we can use different descriptions (localized orbitals vs. delocalized MO theory) illustrates that orbitals are not unique. Many-electron wavefunctions and determinants are well-defined, however. Hückel $\pi$ electron theory for conjugated molecules introduces delocalized MOs that are closely related to particle-in-a-box / particle-on-a-ring functions. The frontier orbitals (HOMO and LUMO) are linear combinations of $2p_z$ atomic orbitals in conjugated molecules with $sp^2$ hybridized carbons. These AOs are identical, as a first approximation, and have identical overlaps with neighbors. This enabled Hückel to obtain many important results decades before reliable all-electron MO calculations were feasible.

Suggested problems:

H-2, H-3
11-30, 11-37, 11-38, 11-44, 11-46
See problem below.
Hückel model for cyclobutadiene: more Jahn-Teller distortions (final 2010)

Cyclobutadiene has four $\pi$-electrons and four sp$^2$ carbons.

We consider a square geometry in part (a) and a rectangle in part (b). Questions:

(a) For square C$_4$H$_4$, set up the Hückel determinant and show that the orbital energies $\alpha + 2\beta$, $\alpha$ (twice), and $\alpha - 2\beta$ are solutions to the Hückel problem. Sketch the $\pi$-MOs (indicating the phases) corresponding to the orbital energies. Use orbitals that are either symmetric or asymmetric under reflection in the x- and y-axis (see figure). Make an orbital level diagram and show the MO occupations for the lowest triplet and the lowest singlet of the neutral molecule (pick one), and also for the ground state of the anion.

(b) Now consider rectangular C$_4$H$_4$ with bond lengths $a$ between C1-C2 and C3-C4 and bond length $b$ between C2-C3 and C1-C4. Consider the case $a < b$ and draw the orbital levels you expect now, also sketching the respective orbitals. Again show the MO occupations of the lowest triplet and singlet of the neutral molecule and the ground state of the anion. Do you expect the geometry of the singlet to be square or rectangular? What about the anion and the triplet state? Which state do you expect to differ most from a square? In all cases clearly indicate your reasoning.