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1. Derive the commutator $[\hat{l}_x, \hat{l}_z]$.

$$[\hat{l}_x, \hat{l}_z] = [\hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \hat{x}\hat{p}_y - \hat{y}\hat{p}_x] \tag{1}$$
$$= [\hat{y}\hat{p}_z, \hat{x}\hat{p}_y] - [\hat{z}\hat{p}_y, \hat{x}\hat{p}_y] - [\hat{y}\hat{p}_z, \hat{y}\hat{p}_x] + [\hat{z}\hat{p}_y, \hat{y}\hat{p}_x] \tag{2}$$
$$= \hat{x}\hat{p}_z[\hat{y}, \hat{p}_y] - 0 - 0 + \hat{z}\hat{p}_x[\hat{p}_y, \hat{y}] \tag{3}$$
$$= i\hbar(\hat{x}\hat{p}_z - \hat{z}\hat{p}_x) = -i\hbar\hat{l}_y \tag{4}$$

2. Compute the Hückel molecular orbital energies of cyclobutadiene (*Hint*: remember that cyclobutadiene is cyclic so you have to consider atomic orbitals 1 and 4 as neighbors). If there are four electrons in cyclobutadiene, what is the total energy and how does it compare to the energy of four electrons in two localized π bonds ($2\times$ ethene)? What physical phenomenon is explained by the findings of Hückel theory?

The Hückel molecular orbitals are written as a linear combination of atomic p_z orbitals on each carbon atom:
$\psi = c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + c_4\phi_4$
The energies of each molecular orbital are obtained by solving the secular determinant:
$$\begin{vmatrix} \alpha - E & \beta & 0 & \beta \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ \beta & 0 & \beta & \alpha - E \end{vmatrix} = 0$$
Substituting terms in the determinant gives:
$$\begin{vmatrix} -x & 1 & 0 & 1 \\ 1 & -x & 1 & 0 \\ 0 & 1 & -x & 1 \\ 1 & 0 & 1 & -x \end{vmatrix} = 0$$
Expanding out the determinant gives
$$-x\begin{vmatrix} -x & 1 & 0 \\ 1 & -x & 1 \\ 0 & 1 & -x \end{vmatrix} - \begin{vmatrix} 1 & 1 & 0 \\ 0 & -x & 1 \\ 1 & 1 & -x \end{vmatrix} - \begin{vmatrix} 1 & -x & 1 \\ 0 & 1 & -x \\ 1 & 0 & 1 \end{vmatrix} = 0$$
$$-x\left(-x\begin{vmatrix} -x & 1 \\ 1 & -x \end{vmatrix} - \begin{vmatrix} 1 & 1 \\ 0 & -x \end{vmatrix}\right) - \left(\begin{vmatrix} -x & 1 \\ 1 & -x \end{vmatrix} - \begin{vmatrix} 0 & 1 \\ 1 & -x \end{vmatrix}\right) - \left(\begin{vmatrix} 1 & -x \\ 0 & 1 \end{vmatrix} + x\begin{vmatrix} 0 & -x \\ 1 & 1 \end{vmatrix} + \begin{vmatrix} 0 & 1 \\ 1 & 0 \end{vmatrix}\right) = 0$$
$-x(-x(x^2-1)-(-x))-((x^2-1)-(-1))-((1)+x(-x)+(-1)) = x^4-x^2-x^2-x^2+1+1-1-x^2-1 = 0$
$x^4 - 4x^2 = 0$, using $y = x^2$ we get $y^2 - 4y = 0$ so $y = 4, 0$ and $x = \pm 2, \pm 0$
$E_1 = \alpha + 2\beta$, $E_2 = E_3 = \alpha$, $E_4 = \alpha - 2\beta$
Total ground state energy from four electrons is $E = 2(\alpha + 2\beta) + 2(\alpha) = 4\alpha + 2\beta$
In the lectures we found the Hückel MO energies of ethene are $\alpha \pm \beta$ so the total ground state energy is $E = 2(\alpha + \beta) = 2\alpha + 2\beta$
Energy of two localized π bonds is $4\alpha + 4\beta$, which is lower than the energy of cyclobutadiene, rationalizing the observed anti-aromatic behavior.

3. This week will will connect molecular orbitals computed using electronic structure calculations on a computer with molecular orbitals from qualitative MO theory, followed by a more rigorous calculation of the Hückel model.

1 Computation and visualization of molecular orbitals and density

We are going to use Gaussian to determine the compute the electronic structure of atoms and molecules. We will then visualize the results in Gaussview and try to understand the nature of molecular orbitals as a linear combination of atomic orbitals. First log onto the CRC and write the following file using "vi hydrogen_atom.com":

```
%chk=hydrogen_atom.chk
#P

test

0 1
H
H 1 5.0
```

then run using "gsub hydrogen_atom.com" (see last weeks instructions for information about how to run Gaussian). Having run the calculation successfully, type "module load g16reva03_lcpu" followed by "module load gaussview6". Now type "gv &" and in the menu bar click "file→open" and select the file "hydrogen_atom.chk" and then go to "tools→MOs" and then in the MO viewer window click "visualize→update". Clicking the two molecular orbitals, you can see that the spatial structure of the lowest energy (-0.13234 a.u.) orbital is the sum of the two 1s orbitals, while the spatial structure of the highest energy (-0.02626 a.u.) orbital is the difference of the two orbitals. If you place the hydrogens sufficient distance apart you will find that the two molecular orbitals become degenerate (although we are talking very very large distances – try 10000 Å and you will see the two orbitals are still not quite degenerate, giving an idea of the distance over which atoms start to interact). Now change the distance to 1Å and rerun the calculation before visualizing the orbitals. Now you can see that even though the two molecular orbitals still comprise the sum and difference of atomic orbitals, the spatial structure of molecular orbitals no longer have the exact form of the underlying atomic orbitals, but appear distinct from the component parts, indicating the bonding and antibonding nature of the molecular orbitals. Now write the following file using "vi two_hydrogen_atoms.com":

```
%chk=two_hydrogen_atoms.chk
#P

test

0 1
```

```
H
H 1 1.0
H 1 R1 2 90.0
H 3 1.0 1 90.0 2 0.0

R1 = 5.0
```

Now one can see that each hydrogen molecule behaves exactly like when we computed the H_2 fragment in isolation, but the two H_2 molecules together couple in phase (lower energy) and out-of-phase (higher energy). Now change R1 to 1Å and examine how the two H_2 molecular orbitals distort as a result of the greater coupling. Now execute the input file:

```
%chk=NO.chk
#P rohf

test

0 2
N
O 1 1.2
```

and then visualize all orbitals in the MO viewer of Gaussview. Compare the molecular orbitals to the MO diagram of NO provided in the lecture notes. How do the molecular orbitals from the electronic structure calculations compare?

2   Hückel theory using intermediates from electronic structure calculations

In this weeks lectures and question 2, we used Hückel theory to compute the molecular orbitals of conjugated molecules. The approximations of the Hückel model are the separation of the σ and π spaces, that the overlap of atomic orbitals is 1 or 0, that the Hamiltonian matrix elements are α or β, and that there are no electron-electron interactions. Using computers, we can avoid the first three assumptions (although, as we will see later in the course, we use Gaussian radial functions instead of true hydrogenic wavefunctions, for purposes of computational efficiency when computing the integrals H_{ij} and S_{ij}). The treatment of electron-electron interactions is a difficult problem as the picture of electrons-in-orbitals breaks down (in fact, much of the remainder of the course is about treating the electron-electron interaction term). We will compute the molecular orbitals ignoring the electron-electron interaction term to examine the results of Hückel theory in more detail and examine if the resulting orbitals are in agreement with the pen-and-paper calculations.

Log onto the CRC and write the following file named two_p_orbitals.com:

```
%chk=two_p_orbitals.chk
#P gen output=matrix

test

0 1
C
C 1 R1

R1 = 5.0

C 0
SP 1 1.00
0.1478600533D+00   0.3995128261D+00   0.6076837186D+00
****

two_p_orbitals.mat
```

If you visualize the orbitals in Gaussview, you can see that there are eight molecular orbitals – s, p_x, p_y and p_z on each atom, and that the molecular orbitals are (in-phase and out-of-phase) linear combinations of these orbitals. Let's use MQC to explore further. Write a file named workshop_5.f03 and copy everything from last weeks code in workshop_4.f03 except for the lines regarding two-electron integrals. Replace the line "call wavefunction%print(6,'all')" with "call wavefunction%print(6,'overlap')" and on the subsequent three lines add "call wavefunction%print(6,'core hamiltonian')", "call wavefunction%print(6,'mo coefficients')", and "call wavefunction%print(6,'orbital energies')". Your code should now look like:

```
 1 program workshop_7
 2
 3 use mqc gaussian
 4 implicit none
 5
 6 character(len=:), allocatable :: fileName
 7 type(mqc_gaussian_unformatted_matrix_file)::matFile
 8 type(mqc_wavefunction)::wavefunction
 9 type(mqc_molecule_data)::molecule
10 type(mqc_scalar)::Vnn
11
12 call mqc_get_command_argument(1,fileName)
13 call matFile%load(fileName)
14 call matFile%getESTObj('wavefunction',wavefunction)
15 call matFile%getMolData(molecule)
16 Vnn = molecule%getNucRep()
17 call Vnn%print(6,'Nuclear Repulsion Energy (au)')
18 call molecule%print(6)
19 call wavefunction%print(6,'overlap')
```

```
20  call  wavefunction%print(6,'core hamiltonian')
21  call  wavefunction%print(6,'mo coefficients')
22  call  wavefunction%print(6,'orbital energies')
23
24 end program workshop_7
```

Compile and run the code using two_p_orbitals.mat (see last weeks instructions). The overlap matrix is S_{ij}. You can see that the diagonal elements are equal to one, while most of the off-diagonal elements are equal to zero. However, there are non-zero off-diagonal terms where Hückel assumed zero overlap. The core Hamiltonian is the matrix $H_{ij} = \langle \phi_i | \frac{1}{2}\hat{\nabla}^2 + \frac{1}{\mathbf{r}_1} + \frac{1}{\mathbf{r}_2} | \phi_j \rangle$ which is the Hamiltonian matrix element ignoring electron-electron interactions (kinetic energy plus electron-nuclear attraction). Looking at H_{ij}, we can see that the diagonal elements for orbitals orientated on the same axis are equal, which are the energies of an electron in that orbital, in agreement with Hückel's approximation of using α. The diagonal matrix elements of the p-orbitals along the internuclear axis are slightly larger in magnitude (lower energy) owing to the greater electrostatic interaction with the other nucleus from the nucleus on which the orbital is centered, while the energy of the s-orbital is lowest as would be expected from electron shielding arguments. The off-diagonal matrix elements (Hückel's β) describe the coupling between the orbitals as a result of the orbitals not corresponding to eigenfunctions of the system (determined by the electron-nuclear interaction). The molecular orbital coefficients are the c_i in the expansion of the molecular orbital as a linear combination of atomic orbitals $|\psi_p\rangle = \sum_i c_i |\phi_i\rangle$. These molecular orbitals come from a more advanced method of computing electronic structure than Hückel theory that takes account of electron-electron interactions (Hartree-Fock theory, which we will study in future lectures) and so it will be good to compare our results with these molecular orbitals later. Similarly the orbital energies are from calculations that try to take account of electron-electron repulsion.

To determine the molecular orbitals the variational theorem states that we must solve $|\mathbf{H} - E\mathbf{S}| = 0$ which is equivalent to diagonalizing using the formula $\mathbf{Hc} = \mathbf{ESc}$ to find the eigenvalues (orbital energies) and eigenvectors (molecular orbital coefficients). For Hückel theory, we want to treat the p_x orbitals orthogonal to the internuclear axis (either one will do) separately from the remaining space. Therefore, we must extract the relevant parts of the overlap and Hamiltonian corresponding to the p_x orbitals (orbitals 2 and 6). To do this in MQC we add the lines:

```
1 wavefunction%Overlap_Matrix = &
2     wavefunction%Overlap_Matrix%orbitals(alphaOrbsIn=[2,6],axis=1)
3 wavefunction%Overlap_Matrix = &
4     wavefunction%Overlap_Matrix%orbitals(alphaOrbsIn=[2,6],axis=2)
5 call  wavefunction%print(6,'overlap')
6 wavefunction%Core_Hamiltonian = &
7     wavefunction%Core_Hamiltonian%orbitals(alphaOrbsIn=[2,6],axis=1)
8 wavefunction%Core_Hamiltonian = &
9     wavefunction%Core_Hamiltonian%orbitals(alphaOrbsIn=[2,6],axis=2)
10 call  wavefunction%print(6,'core hamiltonian')
```

The "&" allow continuation of an expression onto the next line but are optional (although the compiler will not allow lines of lengths greater than 134 characters). Compile and run the code and you should see that the overlap and Hamiltonians are just two-by-two matrices. Now you could diagonalize this easily by hand, but we are going to use MQC. In the type declaration section add the lines "type(mqc_scf_eigenvalues)::energy" and then "type(mqc_scf_integral)::coefficients" which will store the eigenvalues **E** and the molecular orbital coefficients **c** computed using Hückel theory respectively. Now in the main body of the code add the lines
"call wavefunction%Core_Hamiltonian%eigensys(wavefunction%Overlap_Matrix,energy,coefficients)"
which does the diagonalization, followed by "call energy%print(6,'Huckel orbital energies')" and "call coefficients%print(6,'Huckel orbital coefficients')". The final code should look as follows:

```
 1 program workshop_7
 2
 3 use mqc gaussian
 4 implicit none
 5
 6 character(len=:),allocatable :: fileName
 7 type(mqc_gaussian_unformatted_matrix_file)::matFile
 8 type(mqc_wavefunction)::wavefunction
 9 type(mqc_molecule_data)::molecule
10 type(mqc_scalar)::Vnn
11  type(mqc_scf_eigenvalues):: energy
12  type(mqc_scf_integral)::  coefficients
13
14 call mqc_get_command_argument(1,fileName)
15 call matFile%load(fileName)
16 call matFile%getESTObj('wavefunction',wavefunction)
17 call matFile%getMolData(molecule)
18 Vnn = molecule%getNucRep()
19 call Vnn%print(6,'Nuclear Repulsion Energy (au)')
20 call molecule%print(6)
21 call wavefunction%print(6,'overlap')
22 call wavefunction%print(6,'core hamiltonian')
23 call wavefunction%print(6,'mo coefficients')
24 call wavefunction%print(6,'orbital energies')
25
26 wavefunction%Overlap_Matrix = &
27     wavefunction%Overlap_Matrix%orbitals(alphaOrbsIn=[2,6],axis=1)
28 wavefunction%Overlap_Matrix = &
29     wavefunction%Overlap_Matrix%orbitals(alphaOrbsIn=[2,6],axis=2)
30 call wavefunction%print(6,'overlap')
```

```
31  wavefunction%Core_Hamiltonian = &
32      wavefunction%Core_Hamiltonian%orbitals(alphaOrbsIn=[2,6],axis=1)
33  wavefunction%Core_Hamiltonian = &
34      wavefunction%Core_Hamiltonian%orbitals(alphaOrbsIn=[2,6],axis=2)
35  call  wavefunction%print(6,'core hamiltonian')
36
37  call  wavefunction%Core_Hamiltonian%eigensys(wavefunction%Overlap_Matrix,energy,coefficients)
38  call  energy%print(6,'Huckel orbital energies')
39  call    coefficients %print(6,'Huckel orbital   coefficients ')
40
41  end program workshop_7
```

Looking at the output, you notice that the orbital coefficients are in-phase (lower energy) and out-of-phase (higher energy). Comparing the orbital coefficients to those from Hartree-Fock (orbitals 6 and 7), and you will find identical results –Hückel's approximations appear to work fantastically well! However, compare the energies to those from Hartree-Fock and you will notice an enormous difference in the energy (around 3 Hartree which is ~ 1800 kcal mol^{-1}!). In addition, it turns out the agreement in molecular orbital coefficients was as a result of symmetry.

Now change the Gaussian input file to:

```
%chk=two_p_orbitals.chk
#P gen output=matrix

test

0 1
C
C 1 R1
C 2 R2 1 180.0
C 3 R3 2 180.0 1 0.0

R1 = 1.0
R2 = 1.1
R3 = 1.2

C 0
SP 1 1.00
0.1478600533D+00   0.3995128261D+00   0.6076837186D+00
****

two_p_orbitals.mat
```

and rerun. Update your code to include the new p_x atomic orbitals when extracting this set (orbitals 10 and 14) and then recompile and rerun you code using the new matrix file. Comparing you orbitals you will see the 'particle in a box' behavior, but now the orbital coefficients differ

between those that account for electron-electron repulsion and those that do not. However, even though the two sets of orbitals differ, despite the complete neglect of electron-electron repulsion, the orbital coefficients are qualitatively similar.