

# Foundations of Chemical Kinetics Lecture 6: Introduction to quantum chemical calculations with Gaussian

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# Molecular orbitals

- Because electrons are much lighter than the nuclei, we can generally use the **Born-Oppenheimer approximation** according to which we can treat the nuclei as quasi-static. This allows us to separate the quantum mechanical problem into an electronic problem solved at different (fixed) nuclear positions, and a nuclear problem in which the nuclei only experience an average field from the electrons.
- A further approximation (but supported by, e.g., photoelectron spectroscopy) is that the electrons occupy **molecular orbitals**. An orbital is a one-electron wavefunction. Because of the Pauli exclusion principle, a pair of electrons may occupy an orbital.

# How molecular orbitals are computed

Problem 1: How do you represent an MO?

- Suppose that I have a machine that calculates values of a function of one variable,  $f(x)$ , slowly but accurately.
- I want an approximation that is going to be faster to compute.
- You might say “let’s fit a polynomial using a few function values”.

$$f_k(x) \approx a_0 + a_1x + a_2x^2 + \dots + a_kx^k$$

- Given a number of function values  $n > k$ , you would find the best coefficients for the polynomial by minimizing

$$\text{error} = \sum_{i=0}^n [f(x_i) - f_k(x_i)]^2$$

- Provided  $k$  is large enough and the function isn’t badly behaved, this is guaranteed to work because the set of **basis functions**  $(1, x, x^2, \dots)$  is **complete**, i.e. if I take enough of

# How molecular orbitals are computed

How do you represent an MO?

- You should have previously learned a simple MO theory built on making linear combinations of atomic orbitals (LCAOs).
- That is not quite right because the electron distribution around an atom won't have the spherical symmetry of the electron distribution around a lone atom.
- To solve this, we can use additional functions that look like atomic orbitals but have different orbital exponents (equivalent to different nuclear charges being "mixed in"). In other words, we enlarge the **basis set** with functions that have only a passing relationship to the atomic orbitals.

# How molecular orbitals are computed

How do you represent an MO? (continued)

- A second problem: the hydrogen-like atomic orbitals have an exponential dependence on  $r$ , the distance from the nucleus. This turns out to be computationally inefficient.
- Instead of exponentials, we use Gaussian functions, with a  $e^{-\zeta r^2}$  dependence.
- Although Gaussians are even more “wrong” than atomic orbitals, the Gaussians, in the limit that we include an infinite number of them, form a complete basis set.
- Of course, we won't use an infinite basis set.

## The variational theorem

- (Paraphrasing wildly) the **variational theorem** says that the calculated electronic energy is minimized as we approach the true solution.
- This says that if we write the orbital wavefunctions as a superposition of Gaussians, all we need to do is to minimize the energy with respect to the coefficients of the expansion.
- Using more Gaussian basis functions gives us a more accurate solution.
- The electronic energy is

$$\epsilon_{\text{elec}} = K_e + V_{ee} + V_{eN}$$

where  $K_e$  is the total kinetic energy of the electrons,  $V_{ee}$  is the electron-electron potential energy (repulsive), and  $V_{eN}$  is the electron-nuclear potential energy (attractive).

## Geometry optimization

- The potential energy experienced by the nuclei is

$$V_{\text{eff}}(\mathbf{R}) = \epsilon_{\text{elec}}(\mathbf{R}) + V_{NN}(\mathbf{R})$$

where  $\mathbf{R}$  is the vector of nuclear coordinates,  $\epsilon_{\text{elec}}(\mathbf{R})$  is the electronic energy and  $V_{NN}(\mathbf{R})$  is the nuclear-nuclear repulsion.

- Geometry optimization refers to find a local minimum in  $V_{\text{eff}}$ , an **equilibrium geometry**.
- There may be many local minima, or just one.

## Basis sets

- You (mostly) can't go wrong by using a bigger basis set **but** the computational time goes up significantly too.
- Here are a few of the recommended basis sets available in Gaussian in increasing order of size:

$$6-31G < 6-311G \approx \text{cc-pVDZ} < \text{cc-pVTZ}$$



# Basis sets

## Pople family

- These have names like 6-31G.
- The name encodes how orbitals in different shells are approximated by Gaussian functions.
- \* indicates that **polarization functions** have been added on “heavy atoms” (anything other than H), and \*\* indicates that polarization functions have been added to H as well. Polarization functions mimic the distortion of AOs towards neighboring nuclei.
- + indicates that **diffuse** functions have been added on heavy atoms, ++ on H as well. Diffuse functions extend farther into space and are useful to model intermolecular interactions.

# Basis sets

## Dunning family

- These have names like cc-pVDZ.
- Polarization functions are always included in these.
- The 'D' indicates a double-zeta basis set (two different values of  $\zeta$  in valence shell).  
    'T' is a triple-zeta basis set.
- 'aug-' indicates that diffuse functions have been added.

## Correlation and exchange effects

- **Electron correlation** refers to the fact that electrons repel and therefore tend to stay away from each other.
- Orbitals containing two electrons don't properly take electron correlation into account.
- The **exchange energy** is a quantum-mechanical effect connected to Pauli exclusion.

# Density functional theory

- Density functional theory (DFT) calculations are based on a formulation of quantum mechanics focusing on the electron density.
- Correlation and exchange are included through semi-empirical functionals.
- These methods are much faster than alternative methods for describing electron correlation.
- The catch: there are a gazillion correlation and exchange functionals.
- Recommendation: Until you have reason to do otherwise, use B3PW91. This functional does a decent job for a variety of problems.

## Restricted vs unrestricted wavefunctions

- The full theory describes the multi-electron wavefunction in terms of **spin-orbitals**.
- If we are to take the double occupancy of orbitals seriously, then spin-orbitals come in pairs with a common spatial function and different spin functions.  
The computational equivalent is called a **restricted** calculation.
- We can get a lower overall energy by allowing the spin-orbitals to have different spatial parts in an **unrestricted** calculation. The interpretation of unrestricted calculations is not trivial, and I would recommend not using this option unless you have good reason to. However, if you're having trouble with an open-shell calculation, this will sometimes help the calculation complete normally.

# Spin multiplicity

- It's a good idea to think a bit about the expected MO diagram before plunging ahead.
- In particular, you should have some idea if all the electrons are paired or not.
- The **spin multiplicity** is calculated by  $2S + 1$ , where  $S$  is the net spin.

No unpaired electrons  $\Rightarrow S = 0 \Rightarrow$  multiplicity = 1  $\Rightarrow$  singlet electronic state

One unpaired electrons  $\Rightarrow S = \frac{1}{2} \Rightarrow$  doublet

Two unpaired electrons  $\Rightarrow S = 1 \Rightarrow$  triplet

# Our first MO calculation: the OH radical

## Building the radical

- Start up GaussView.
- Click on the element fragment button ( ${}^6\text{C}$ ).
- In the periodic table, click on O, then choose the O with two separate bonds.
- Click in the blank canvas. A water molecule appears.
- Right-click on one of the hydrogen atoms, then choose `Select Atom H?`. (The question mark will be an atom number.)
- Hit the delete key on your keyboard. You now have an OH radical.

# Our first MO calculation: the OH radical

## Setting up a geometry optimization

- We want to optimize the geometry and collect some statistics.
- Click on Calculate→Gaussian Calculation Setup.
- In the Job Type tab, select Opt+Freq, which will both optimize the geometry and calculate the vibrational frequency. The defaults should be OK.
- In the Method tab, in the Method row, select Ground State, DFT, Restricted-Open, B3PW91.  
In the Basis set row, select 6-31G.  
Make sure the spin is Doublet. (Why?)



## Our first MO calculation: the OH radical

### Running the job

- Click on `Submit`.
- Save the input file to some appropriate folder with an appropriate name.
- When the job finishes, say `No` to closing the Gaussian window.

## Our first MO calculation: the OH radical

### Gaussian output

- Two output files:
  - .log file contains the Gaussian text output (which should still be on your screen)
  - .chk file contains the structure in a format that GaussView can read
- If you scroll back a little, you should see a table giving (for a diatomic) a quantity called R1 as 0.9933 Å. this is the equilibrium (minimum energy) bond length computed by Gaussian.
- Keep scrolling back. You should find a table of Q values. These are partition functions at the default temperature of 25 °C.  
Note the value of  $Q_{\text{Vib}} (V=0)$ , which is the value of the partition function if we define the ground vibrational state as being the zero of energy. What does this tell you?

## Our first MO calculation: the OH radical

### Measuring geometric parameters

- You can get geometric parameters after optimization by clicking on atoms.
- If you click on one atom and then the other in the main output window, then move the cursor away from the atoms, you will see the bond length in the bottom window frame.
- For more complex molecules, clicking on three atoms in succession gives a bond angle.
- Clicking on four atoms gives a dihedral angle.

## Scanning a coordinate

- It's going to be useful to us to scan a coordinate systematically.
- In the simplest case, this will give us a potential energy curve associated with a particular coordinate.
- Close the Gaussian window of the previous example and dismiss the pop-up that appears. Now go back to your original drawing canvas.
- Right-click on the canvas. From the pop-up menu, select View→Builder.
- In the Builder pop-up, click on Modify bond (diatomic molecule with double-ended arrow over it).
- Now select the two atoms in your OH radical by clicking on each one in turn. This will open a window that allows you to modify bond properties. Change the bond length using the slider or by typing in a value to approximately 0.6.

## Scanning a coordinate (continued)

- In the main GaussView window, click on Tools→Redundant Coordinates.
- In the window that opens up, click on Add. In the drop-down menu about half-way down the page, replace Unidentified by Bond. Then in the canvas click on each of the two atoms. The two boxes labeled Coordinate should be filled with the numbers 1 and 2 (not necessarily in this order).
- In the next drop-down, select Scan Coordinate. Take 22 steps of 0.2 Å each. Click on OK.
- Click on Calculate→Gaussian Calculation Setup.
- Job Type should be set to Scan, Relaxed (Redundant Coord).
- Replace Restricted-Open by Default Spin and add ++ to the basis set. (Why?) Click Submit. Save the job with a new file name.
- Now sit back. This will take a little bit of time.

## Scanning a coordinate (continued)

- Once the calculation finishes, close the Gaussian window and open the `.chk` file.
- Click `Results`→`Scan`. This will show a plot of  $V_{\text{eff}}$  as a function of the step.
- If you want the axis to read out in Å, click on `Plots`, then `Properties`.
  - Step 1 (the shortest bond length) is 0.6 Å, so to correct the origin of the plot we need to subtract 0.4 from the step number. Thus, set `Origin` to `-0.4`.
  - Each step was 0.2 Å long, so `Scale` by 0.2. Then click `Ok`.

## Classroom exercise

Determine the potential energy of HCN as a function of both the length of the H-C bond and the bond angle.