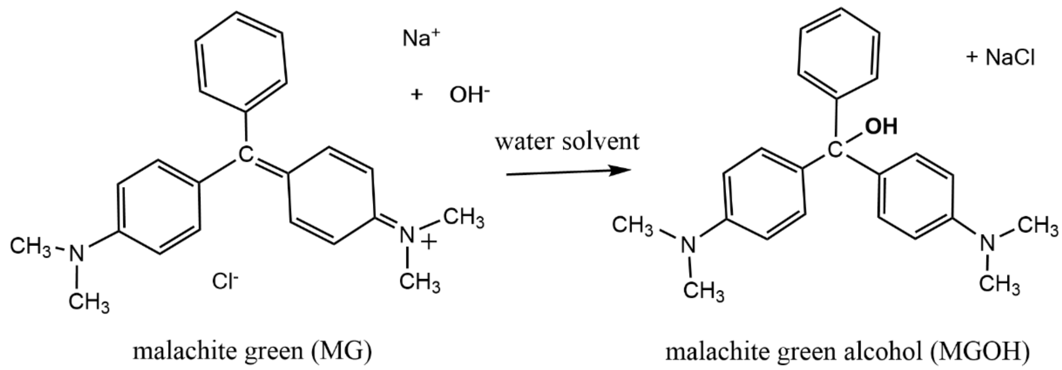
11-15-2024 ORCA version John Keller

Chem 106

Malachite Green and Quantum Theory

Introduction Malachite green (MG) is a dye used in the manufacture of paper and cloth. It is also used as an antimicrobial in fish culture. MG is one of a family of triarylmethane dyes, which contain various aromatic rings attached to the central carbon atom. Some of these are crystal violet, brilliant green, and victoria blue.



Under alkaline conditions (high pH), malachite green's color slowly fades as hydroxide ion adds to the central carbon, converting MG to the colorless malachite green alcohol (MGOH). In a previous lab we measured the rate of disappearance of MG by monitoring the decrease in its absorbance at 618 nm.

In this lab we will use quantum theory in the **ORCA program** to study the molecular details of the bleaching reaction and, in the last part, see how MG's color arises from its extensive π-bonds. In these studies we will use density functional theory (DFT), which is the main tool of computational quantum chemistry. DFT is a fast, yet accurate, method for calculating a molecule's electron distribution and energy content.

Two questions are addressed here**:**

(1) How do the **molecular orbitals** of MG control its **chemical reactivity** and **color**? As we will see, one orbital in particular, the lowest energy anti-bonding orbital (or lowest unoccupied molecular orbital LUMO), plays an important role in both.

(2) In water, hydroxide ion is surrounded by strong **hydrogen bonds**. How do these affect the MG + OH^- reaction?

This exercise has three parts:

(A) Study the distribution of partial charges within the MG cation.

(B) Calculate reaction energies and assess bonding changes during the reaction.

(C) Uncover the molecular basis for MG's color.

The **general procedure** is to (1) view interactive 3D models at the [informational website](); (2) obtain structure files from those pages; and (3) import each structure into WebMO (a graphical interface for the ORCA computational program) and carry out a short calculation.

The **worksheet** gives additional background information, explains issues raised by the calculations, provides space to record your results, and asks questions about the results. Fill in the worksheet as you do the quantum calculations. If you wish to complete the worksheet sometime later, the calculation jobs can be opened at any time by logging back into WebMO.

This handout provides background theory and describes how to use WebMO, ORCA, and the supplemental web pages. The **appendix** on p. 7 has more information on the following topics:

- Using WebMO
- Quantum chemistry background
- What is a "Molecular Energy" calculation?
- What is ORCA?
- Practical uses of molecular quantum theory
- How does WebMO work?

A. Partial charges

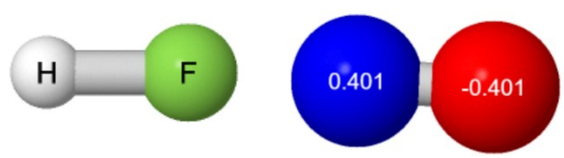
Background:

Before we delve into the distribution of charge within the MG cation we should review a few basic facts about partial charges.

In molecules containing atoms with different electronegativities, bond electrons are shared unequally, being pulled **toward** the more-electronegative atom and **away from** the less-electronegative atom. This creates a partial negative charge on the former, and a partial positive charge on the latter, and formation of a dipole moment. These charges always add up to the total charge on the molecule or ion. The partial charges calculated by ORCA are displayed in WebMO's View Job page under Calculated Quantities, Partial Charges. Four examples are discussed below.

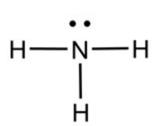
HF. In hydrogen fluoride, the partial charge on fluorine is -0.401. This indicates that on average 0.401 electrons – of the 2 that inhabit the H-F bond - shift away from H and toward F. (Sect. 6.2 in your text also discusses HF.)

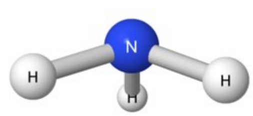
Clicking the blue icon in the Partial Charges table in WebMO displays spheres whose diameters are proportional to the partial charge value.

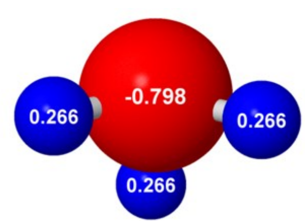


Theory: B3LYP/6-31G(d,p)/SMD

NH_3. In ammonia, the calculated partial charge on nitrogen is -0.798. Thus, in each of the bonds, 0.266 electrons (0.798 ÷ 3) shift away from H and toward N.

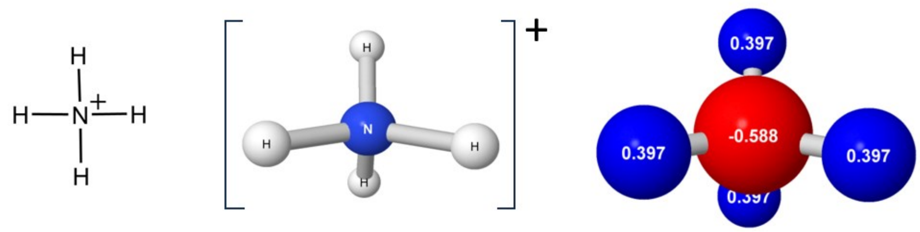




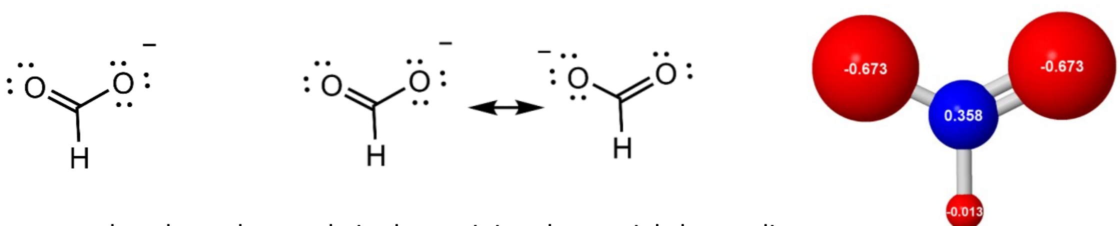


NH_4^+ In ammonium ion, the calculated partial charge on nitrogen is -0.588. It is negative despite the "+1" formal charge that appears in the Lewis formula! In each of the four bonds, 0.147 electrons (0.588 ÷ 4) must shift toward N. The N atom is still more electonegative than H, however its negative charge is less than in NH_3. The + charge is spread out among the H atoms: 0.250 units per H.

The N atom in NH_4^+ is somewhat analogous to the N's in the MG cation. That is, they are positive in the Lewis formula but have a negative calculated partial charge.



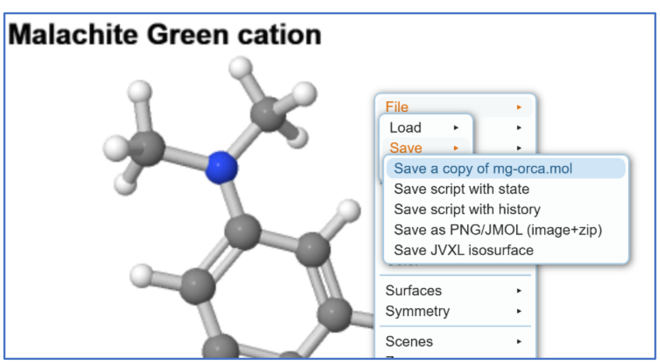
Formate ion (HCO_2^-) Another factor that can influence the partial charges within a molecule is **resonance**. For example, the Lewis formula of formate ion is sometimes written with a "-1" formal charge on one O (*left*). However, the complete formula shows that it is a **resonance hybrid** with the negative charge **shared** between two oxygens (*center*).



In MG, **resonance** also plays a large role in determining the partial charge distribution.

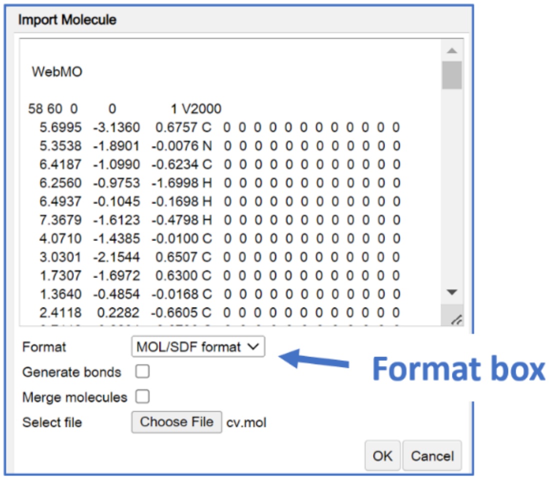
To do:

1. First, view a 3D model of MG. With Chrome, Firefox or other browser, open the informational website https://chem4.cns.uaf.edu/mg-expt/index-orca.html . Follow the link to malachite green cation. Right-click the webpage. In the pop-up window, select "Save a copy of mg-orca.mol". This file contains the xyz coordinates of the MG cation. Note the file location on your local computer, which in most cases is your Downloads folder.



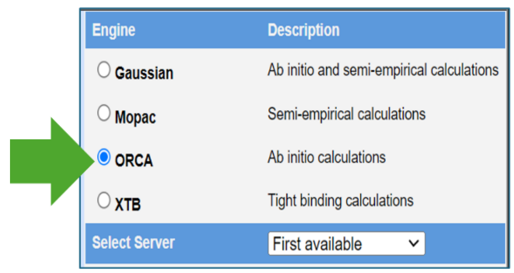
A 4-min YouTube video (https://youtu.be/oz7hsfCUX0I) shows how to save a .mol file, import it into WebMO, and do an energy calculation with ORCA. The trinitrotoluene molecule (TNT) is used as an example.

2. Log into WebMO. Select the **New Job** menu item. Click **Create New Job**. Then **File, Import Molecule**. Verify that the Format box says "MOL/SDF format." Using the Choose File button, navigate to the folder where you saved mg-orca.mol. Click the OK button at the bottom right. The MG ion should appear in the editor window.




Now, using the **Rotate tool** (3rd from the top on the toolbar), left-click-and-drag to rotate the molecule – just to get a clear view of this non-planar ion.


3. Click the Continue arrow at the bottom right corner of the workspace. Respond "OK" to "Continue without symmetrization?".

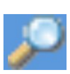



On the Choose Computational Engine page, select "ORCA" and the "First Available" server.
Click the Continue arrow.
On the Configure ORCA Job Options page, fill in the boxes:

Job Name -- (enter any informative job name)
For the following boxes, the correct default settings are inserted automatically. Do not change them:
Calculation - Molecular Energy - 106
Theory -- B3LYP
Basis Set -- Standard: 6-31G(d,p)
Charge -- 1
Multiplicity - Singlet


Click the Continue arrow to go back to the WebMO Job Manager.

4. The calculation should take 1-2 minutes. When the job is complete, click the job name.


Now scroll down to the Partial Charges table. **Record partial charges** for the atoms indicated in the worksheet. These can be read from the table values, or by clicking the blue magnifying glass icon (next to the word Charge). This places a sphere on each atom with a label showing the partial charge value.

Answer questions on the worksheet regarding the Lewis formula of MG and the nature of the central carbon atom.

B. Energy changes during the MG^{+}-OH^{-} reaction

Background:

With few exceptions, all chemical reactions require the reactants to surmount an energy barrier, or activation barrier, on the way to the product. For this to happen, individual reactant molecules must gain extra kinetic energy from thermal motions within the solution or gas phase. This is the reason that reactions speed up at higher temperatures. At higher temperatures, molecules move faster, and therefore a higher proportion can gain enough energy to overcome the reaction barrier.

What is the barrier for the reaction of MG with OH^{-}? If you take the saying that “opposites attract” literally, it is surprising that there is *any* barrier for combination of a cation and an anion. However, in water the reaction is slow, therefore the reactants must be encountering a substantial energy barrier. It turns out this is due to OH^{-} ion being hydrogen-bonded to surrounding water molecules. A certain amount of energy is required to “free up” OH^{-} from the solvent before (or as) it bonds to MG. In water, OH^{-} accepts 3 to 4 H-bonds on average (Fig. 1). When OH^{-} reacts with MG, some of these must be loosened or broken. The O atom in MGOH has a much-reduced negative charge compared to OH^{-}, which weakens the remaining H-bonds.

Fig. 2 shows the energy changes for this chemical reaction. Initially, the energy goes up as H-bonds are weakened or broken. The energy of the system reaches a maximum at the transition state, then decreases as the C-O bond forms in the stable product.

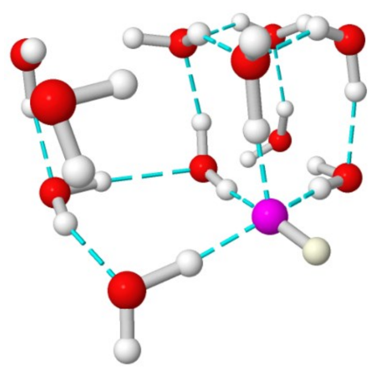


Figure 1. Computer model of an 11-water– OH^{-} ion cluster. OH- is colored fuchsia. Hydrogen bonds are cyan.

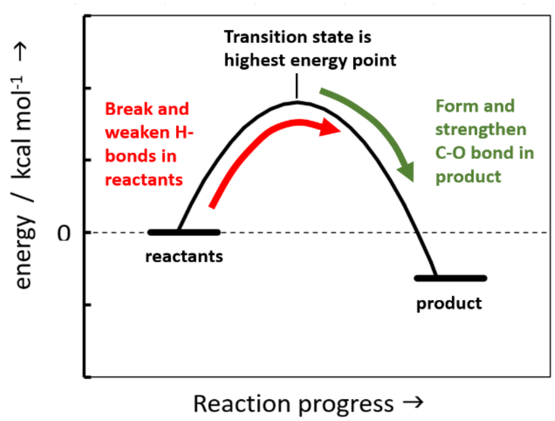


Figure 2. Energy changes during MG + $H0^{-}$ reaction.

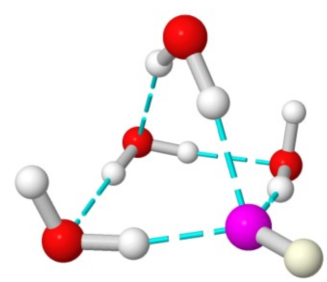
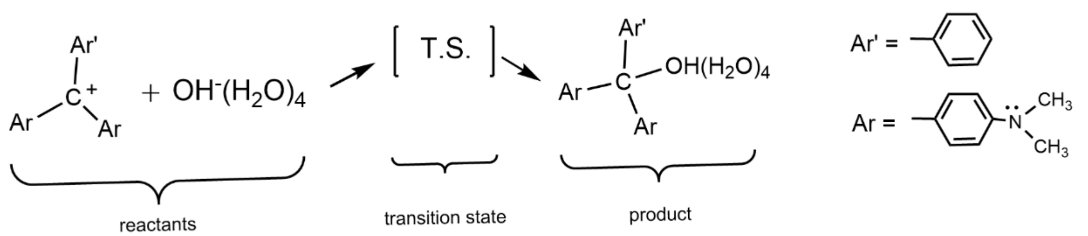


Figure 3. Computer model of a 4-water– OH^{-} ion cluster.

What are the reactants? Clearly, **MG** is one. The other reactant must be **OH^{-} surrounded by a water cluster**. The cluster in Fig. 1 is too large for a detailed quantum calculation, so we will use a 4-water-OH^{-} cluster as a model (Fig. 3). When the multiple H-bonds in this model are weakened in the transition state, a realistic reaction barrier is created.



- Malachite green cation MG
- Malachite green alcohol MGOH
- OH- ion solvated by 4 waters OH-..4waters
- Malachite green alcohol solvated by 4 waters MGOH...4waters
- Malachite green - OH transition state solvated by 4 waters MG..OH...4waters

To do:

5. Browse to the informational website again. Download the **oh-4wat.mol, mgoh-4wat.mol**, and **mg-oh-ts-4wat.mol** files. Log into WebMO. For each .mol file, import it into WebMO and use ORCA to carry out a "Molecular Energy -106" calculation. As before, enter an informative job title, accept the other default settings, then hit Continue.

When each calculation is **complete**, open the job. On the View Job page scroll down to the Overview box and record the Final Single Point Energy in the worksheet. The energy units are Hartrees, where 1 Hartree = 627.5095 kcal/mol. Also record and analyze several H-bond distances as indicated in the worksheet.

C. The color of malachite green

Background:

In Chapter 3 of your text, and in the Chem 105 spectroscopy lab last semester, you learned that in atoms, electrons inhabit atomic orbitals (AOs), which have defined energies and shapes. If extra energy is added to the atom, say by heating, electrons jump up from lower energy, occupied orbitals into higher-energy, unoccupied orbitals. When they fall back down, they emit photons, creating an emission spectrum. The frequency of an emitted photon ν is related to the energy difference between the upper and lower orbitals by $\Delta E = h\nu$. Similarly, atoms can absorb photons of those same frequencies from a light beam to create an absorption spectrum.

The same principle applies to molecules, but in this case electrons inhabit molecular orbitals (MOs) rather than AOs. Electrons occupy the lowest energy MOs - the bonding MOs - leaving a set of unoccupied MOs at higher energy, which are the anti-bonding MOs. Unoccupied MOs, especially the lowest energy one, can accept electrons jumping up from below. The **lowest energy anti-bonding MO** is called the **LUMO**, or lowest unoccupied molecular orbital.

The **highest energy bonding MO** is called the **HOMO**, or highest occupied molecular orbital. The energy gap ΔE between LUMO and HOMO determines the color of a molecule or ion. If the gap is narrow, a photon in the **visible** wavelength range can push an electron from HOMO to LUMO. If the gap is wide, a higher energy photon in the **ultraviolet** wavelength range is required. Fig. 4 shows these two scenarios, where the blue arrow identifies the HOMO-LUMO gap.

Molecules like MG with many alternating double bonds typically have narrow HOMO-LUMO gaps. Molecules with fewer (or no) alternating double bonds have wide gaps and are colorless (octane, ethanol, N_2, etc.). Most of the colors we see in the world around us are due to the absorption of visible photons by plant pigments or commercial dyes. Coloration is thus a subtractive process where our eyes are detecting the photons that pass through or bounce off.

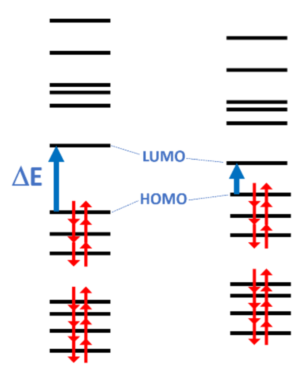


Figure 4. MO diagrams for an **ultraviolet**-absorbing molecule (left), and a **visible**-absorbing molecule (right). Each black line denotes the energy level of a molecular orbital. Red arrows represent electrons inhabiting each MO.

Fig. 5 shows the absorption spectrum of a solution of malachite green analyzed in a spectrophotometer. Malachite green **absorbs** photons of yellow and orange light, but **transmits** photons of violet, green and dark red light. The result we see is green. The maximum absorption (λ_{max}) is at 618 nm.

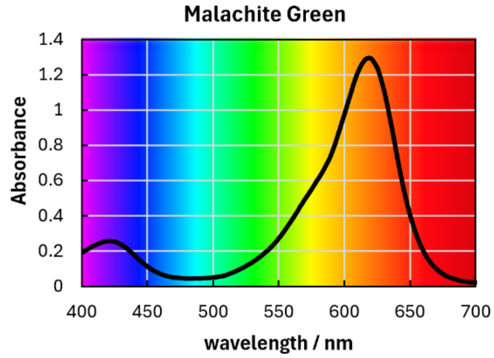


Figure 5. Absorption spectrum of malachite green (black line). The background illustrates the color of light at the indicated wavelengths.

To do:

6. For MG, open the "Molecular Energy – 106" job you did previously. Now go down to the Molecular Orbitals table near the bottom of the View Job page. Notice that the table lists 88 filled orbitals in order of increasing energy, with each orbital containing 2 electrons, plus a bunch of unfilled MOs of higher energy. (MG contains 176 electrons, which is apparent from the molecular formula $C_{23}H_{25}N_2^+$.) Visualize the HOMO (#88) by clicking the blue magnifying glass icon. This is a π orbital. Like an atomic p-orbital, it has lobes above and below the plane of the atoms.


Preferences tool

If the MO lobes appear tiny, or huge, adjust their size by clicking the Preferences tool in the left margin. On the Isosurfaces tab, set "MO isosurface value" = 0.035.

Now visualize the LUMO (#89), which is a π* orbital. Use the Molecular Orbitals table as above or the Orbitals applet that now appears on the left side of the workspace. WebMO uses a green-yellow color scheme to represent unfilled MOs (and red-blue for filled MOs). The MO display colors are arbitrary and have no physical reality.

Record the energies of both MOs (in Hartrees) on the worksheet.

7. For MGOH, go back to the informational website and download the mgoh-orc.mol file. Log into WebMO and import the mgoh-orc.mol file. Using ORCA, carry out a "Molecular Energy -106" calculation. Analyze the HOMO and LUMO as you did for MG. For MGOH, the HOMO is #93 and the LUMO is #94. Answer the questions and do the calculation on the worksheet.

Appendix

Using WebMO. First, obtain the password for the Chem106 WebMO group from your TA or instructor. The WebMO login page is at https://antec12.cns.uaf.edu/~frank/cgi-bin/webmo/login.cgi. Enter your UA username and password. Choose the Chem106 Group and enter the group password in the box. Click Login. This procedure is required only for the **first login**; subsequent logins take you directly into WebMO after you enter your UA username and password.

See a YouTube video showing how to log into a WebMO group https://youtu.be/oz7hsfCUX0I. For more help, click Help at the bottom of the blue left-hand panel in WebMO. The help page has links to Overview and QuickStart Tutorial pages.

Quantum chemistry background. Quantum chemistry programs like ORCA calculate the energy of a molecule using a combination of **theory** and **basis set**. **Theory** refers to how, mathematically, an approximate solution is obtained for the Schrödinger Equation $H\Psi=E\Psi$. B3LYP is one of several density functional theory (DFT) methods developed in the last 20 years. The letters stand for Becke, Lee, Yang, and Parr, the developers of the method. All DFT methods use the basic principle of molecular orbital (MO) theory, namely that pairs of electrons inhabit regions of space around the nuclei (the Ψ MOs), each having a characteristic energy (E).

Molecular orbitals are constructed by combining atomic orbital functions (AOs) from all the atoms in the molecule. This is the same basic process as described for the diatomic molecules in section 7.7 of your textbook. The set of AOs is called the **basis set**. The basis set used in this experiment, 6-31G(d,p), tells what kind (s, p, or d), and how many, AOs are used on each type of atom (C, N, O, or H). For malachite green cation MG, there are a total of 475 functions in the 6-31G(d,p) basis set.

What is a "Molecular Energy - 106" calculation? For a B3LYP/6-31G(d,p) calculation, ORCA assigns atomic orbitals to each atom for a total of 475; constructs an equal number of molecular orbitals (MOs) by linear combination of atomic orbitals; and adds electrons (2 per MO = 176 electrons) to the 88 lowest-energy MOs. It then calculates several properties including the total energy, the partial charge on each atom, and the dipole moment. The "106" refers to a format customized for Chem 106.

ORCA also displays a Molecular Orbitals table near the bottom of the View Job page. ORCA saves the coefficients that describe the MOs, and these are used by WebMO to print this table and display MO 3D shapes.

What is ORCA? ORCA is a powerful and versatile quantum chemistry software package, primarily developed by the group of Prof. Frank Neese of the Max Planck Institute for Coal Research in Germany. It is free for academic use. The program runs on Windows, Macs and Linux; the download is about 650 MB. By itself, the program is command line driven, however the free version of WebMO can be used as a GUI.

Of what practical use are molecular orbitals and molecular quantum theory? These methods are widely used in materials science, atmospheric science, molecular biology, chemistry research, and others. To get a sense of this trend, google "dft", plus "battery design", "tropospheric chemistry", "covid enzyme", or "green chemistry". The top hits mainly are technical research articles; however, the introductory paragraphs of these papers are worth reading because they often explain the background science in terms that general chemistry students can relate to.

How does WebMO work? WebMO provides a web page that is a graphical interface for ORCA; it uses the graphic functions in the Chrome or Firefox browser to display molecules. The WebMO server (antec12 at UAF) runs ORCA and stores user calculations in a database. ORCA calculations can also be assigned to networked server computers (merlin and trx40 at UAF). Calculations on the latter go faster than on antec12.

The WebMO – ORCA system runs 24x7 all year. Any UA student, faculty or staff with a UA username and password can log in at any time and use WebMO and ORCA (or other programs).