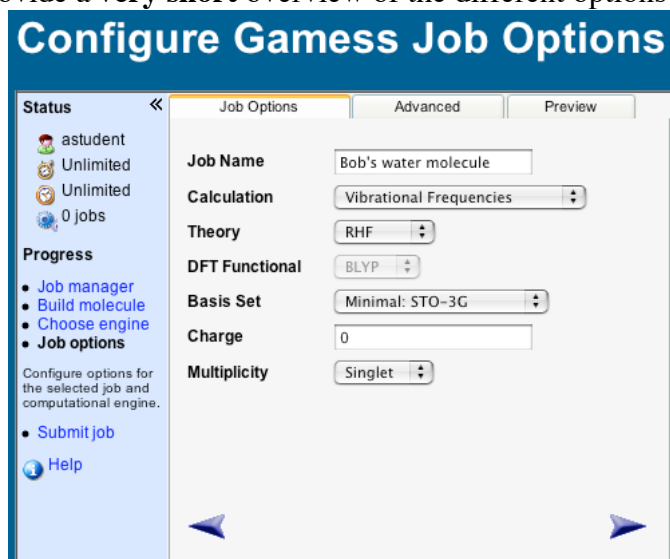


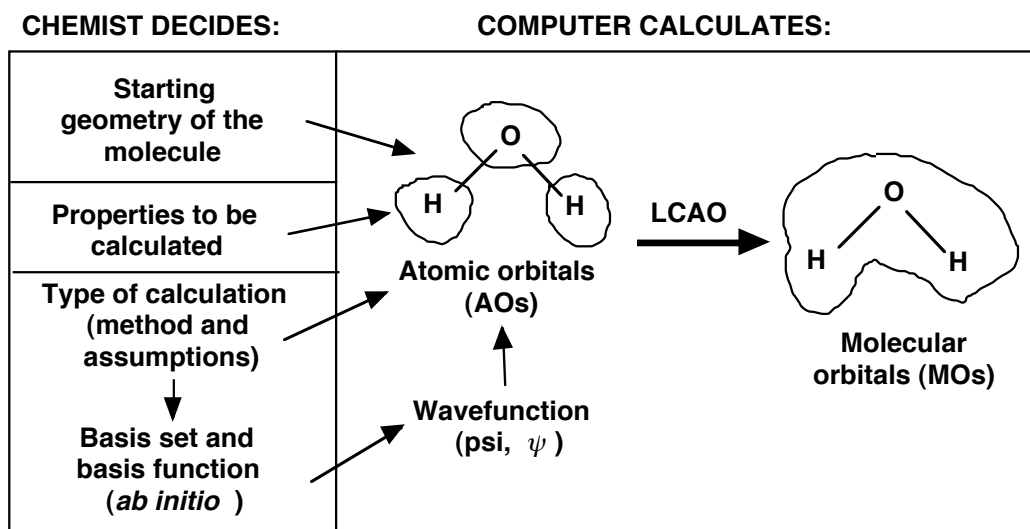
A quick guide to understanding the Configuration window in WebMO

The purpose of this document is to provide a **very short** overview of the different options that are presented in the “Configure” window of WebMO.

The knowledgeable computational chemistry teacher or computational chemistry student needs to understand these concepts in much greater detail than is presented in this reading, but this document should serve as a “quick start” to the items that appear in this window. Understanding computational chemistry requires being able to understand and communicate the various items that are described briefly in this document.



The diagram below provides a snapshot of what happens in a computational chemistry calculation. Again, this diagram leaves out a tremendous amount of detail, but should serve as a roadmap to computational chemical calculations.



The primary goal of computational chemical calculations is to determine the molecular orbitals (MOs) for a given molecule. Assuming we can do this, and we can, the

determination of the MOs provides us with a wealth of information about the properties and behavior of the molecule. Knowing the MOs is a good thing!

Unfortunately, it's a little difficult to calculate MOs for a given molecule. For a variety of reasons, however, it's not too hard to calculate the orbitals for single atoms, even those found in a molecule. These orbitals are called – wait for it – “atomic orbitals”, or AOs. Once we calculate the AOs, we use a method called “linear combination of atomic orbitals (LCAO)” to calculate the MOs. LCAO is a fancy term for “we add up all of the AOs, with a few fudge factors”. So, $MO = AO_1 + AO_2 + AO_3$, and so on. Linear (in a line) combination (add them up)!

The question you should be asking is, OK then, how does one calculate an AO? Unlike what you were taught in chemistry, or what you teach in chemistry, electrons don't revolve around the nucleus of an atom in the same way that planets revolve around the Sun. Electrons move around in a random pattern, somewhere near the nucleus. A better analogy is that there is a cloud – an electron cloud – surrounding the nucleus, and the electron is in that cloud. Because electrons behave both as particles and as waves, the mathematicians call the mathematical shape of the cloud a “wavefunction”. The wavefunction is what we're trying to calculate. The wavefunction, represented by the Greek letter psi, is determined by Schrödinger's equation, the fundamental mathematical algorithm that forms the foundation of computational chemistry.

OK, so the goal is to calculate the wavefunctions for the individual atoms, which produce the AOs, which we then add up using LCAO methods to produce MOs, and, voila, we're done. That's pretty close, leaving out a lot of details about how all of that happens. So what does that mean for me as the chemist trying to calculate a molecule? What's my responsibility? Doesn't the computer do all of this calculation stuff?

Yes and no. Obviously, you have to tell the computer a number of things. And what does all this have to do with the Configure window? We're getting to that! As the chemist, you have to tell the computer a variety of things:

1. Starting geometry of the molecule: basically, you have to tell it that, if you are doing water, that there are two hydrogens and an oxygen, all connected by single bonds. Most molecular editors, including WebMO, have a pretty good idea of the bond lengths and bond angles for molecules, so when you build a molecule, the software does a pretty good job of figuring out those things. They're not exactly right, but that's a discussion for another time! But it's your job to draw the molecule using the editor, and that's your starting geometry!
2. Properties to be calculated: you have to tell the computer that you want it to calculate an energy, or vibrational frequencies, or a transition state, or any number of properties. Most modern software packages give you a lot of data, so if you ask for a molecular energy calculation, you typically get that and lots more. Regardless, you have to know what it is you want to know about the molecule!
3. Type of calculation: this is where life gets complicated quickly! There are a wide variety of methods that one can use to perform the calculation. These have unfamiliar names (and abbreviations) such as RHF (Restricted Hartree-Fock),

- DFT (density functional theory), and others. Each of these methods, or theories, has advantages and disadvantages. Like the battle between proponents of Windows-based PCs and Macintosh computers, each of these theories has its fan club and equally vocal detractors. Regardless, if you are going to use computational chemistry as a researcher or as a teacher, getting to know these methods is an important goal.
4. **Basis set:** many theories require that you also make a decision about a “basis set”. A basis set is a set of numbers that serve to “prime the pump”, or kick-start, the calculation of the wavefunction. Like theory names, these basis sets have esoteric names such as STO-3G, 3-21G, etc. Like theories, different basis sets have advantages and disadvantages, supporters and detractors. Like theories, learning the basics of basis sets is a worthy goal!

Once you tell the computer the starting geometry, the property you want calculated, the theory you want it to use, and the basis set, the computer is ready to do the rest of the work. Let’s relate all that back to the “Configure Job” window in WebMO.

Here are the options presented in this window:

1. **Job name:** this is self-explanatory; it’s simply the title that you want to give to your calculation. If you are calculating something like the vibrational frequencies of water, you might call it “Water vibrational frequencies”. If you want to call it “Bob” you can do that as well!
2. **Calculation:** this is where you tell the computer what property you want calculated, such as molecular energy, vibrational frequencies, or the creation of UV-VIS spectra. WebMO gives you a fairly thorough list. As you become more knowledgeable, you can add more properties by modifying the input file in the “Advanced” mode.
3. **Theory:** this is where you choose the theory you wish to use for your run. The default theory is RHF, which stands for Restricted Hartree-Fock. This theory assumes that all of the electrons are paired, and it’s one of the more basic theories. It does a pretty good job for most molecules, and does the calculations fairly quickly. For original chemical research, you would need to consider using a more powerful theory. For classroom applications, it should be more than adequate!
4. **DFT Functional:** if you choose DFT (density functional theory) as your theory, the computer asks you for some variations on a theme. DFT is a new theoretical method, and it has become very popular in the research world. One of its creators is Dr. Bob Parr, currently on faculty at the University of North Carolina at Chapel Hill. For classroom purposes, you probably don’t need to use DFT; it takes longer to perform the calculations! You should know, however, that DFT is method that you will see most often in the computational literature. Dr. Parr’s paper on DFT is the second most quoted publication in all of chemistry. He’s also a really nice guy!
5. **Basis Set:** as described above, you now have a choice of basis sets. WebMO does a nice job of simplifying your choices! Instead of just giving you the esoteric names (STO-3G, etc.), it says “Minimal, Basic, Routine, Accurate”, etc. The more accurate the basis set, the longer the calculation time. For beginning

chemists, using “Minimal” or “Basic” are good choices. More accurate basis sets will consume more of the CPU resources!

6. Charge: charge is fairly self-explanatory. Most of the molecules you’ll be studying will be those with no charge, i.e., not ions. As such, charge can remain at 0. If you know you have an ion, set the charge appropriately!
7. Multiplicity: Multiplicity is a measure of how the electrons are spinning. In most molecules, for every electron spinning “up”, there is an electron spinning “down”. An electron spinning up cancels out an electron spinning down, so the value of “S”, or total spin, is zero (0). The multiplicity rule is “ $2*S+1$ ”, so in this case $S=0$, so multiplicity = $2*0+1 = 1$, or a singlet condition. Your pull-down should be set at singlet!

As you continue your study of the technologies, techniques, and tools of computational chemistry, the concepts briefly described in this reading will become more familiar!