

Calculating electronic excitation energies and ionization potentials in Gaussian.

Besides the ground state the electronic Schrödinger equation has excited state solutions, which can be of interest in chemistry. Calculations on excited states are immediately useful when trying to interpret results in electronic spectroscopy, or, put even stronger, calculations are an integral part of spectroscopic measurements in order to assign spectra. Other types of spectroscopy implicitly probe excited states, e.g. resonance Raman and circular dichroism spectroscopy. Another use of excited state calculations occurs in understanding photochemical processes.

At present the calculations of excited states are more cumbersome than ground state calculations. The reason is that excited states can typically not be described qualitatively by a single determinant: configuration interaction is vital. Even a simple $\pi \rightarrow \pi^*$ excitation has two contributions in the singlet state:

$$|\Psi_{\text{singlet}}\rangle = \frac{1}{\sqrt{2}}(|\pi_{\alpha}\pi_{\beta}^*\dots\rangle - |\pi_{\beta}\pi_{\alpha}^*\dots\rangle), \text{ where } \alpha, \beta \text{ indicate the spin of the orbitals.}$$

This means that all excited state theories have to be to some extent “multiconfigurational”. The situation is different for the (high spin) triplet state

$$|\Psi_{\text{triplet}}\rangle = |\pi_{\alpha}\pi_{\alpha}^*\dots\rangle.$$

These states can be described both by “ground state” methods, and alternatively by excited state methods. We will gauge the accuracy of excited state methods by comparing to ground state methods applied to triplet states. We will also explore some geometry optimizations in excited states. Also this is much harder than for the ground state, and such calculations have been available only for the past decade. Frequency calculations for excited states are not possible even today in Gaussian at a reliable level. In fact Gaussian is not the most suitable software to calculate excited states at present. If you are in need of excited state calculations in your research, other packages like ACES2 (Advanced Concepts in Electronic Structure), NWChem (Northwest Chemistry, developed at PNNL), and MOLPRO are more suitable. Here we will use Gaussian as we can address the main points in excited state calculations, and it is of course convenient to use a familiar program. In subsequent labs we will explore also the MOLPRO and ACES2 programs.

A. Vertical excitation energies of Ethylene.

Symmetry is very important in calculations of excited states as the symmetry labels serve as the “names” of the states, and we have to be more strict than usual to enforce symmetry. We will start with a geometry optimization of the ground state at the B3LYP/cc-PVTZ level. Upon creating the molecule we want the geometry file to reflect the D2h symmetry of ethylene. To this end open the `connection editor` and under `ZMAT Tools` select `Sort H`. This puts the Hydrogen atoms at the end of the list. Next select the `Point Group` menu under `Edit`, and impose D2h symmetry on the molecule. Now we select the method and submit the ground state optimization. If you look at the input file, you can see that the Z-matrix is constructed to reflect the symmetry

of ethylene: all angles and bond distances are explicitly symmetric. This procedure is probably not entirely general, but it works here. Once we have the geometry we are ready to do excited state calculations.

Let us first start with the simple CIS (Configuration Interaction Singles) method to calculate excited states of ethylene. The excited states are calculated variationally by optimizing the coefficients in the wave function

$$|\Psi\rangle = \sum_{\substack{i \in \text{occupied} \\ a \in \text{virtual}}} |\Phi(i \rightarrow a)\rangle c_i^a$$

This parameterization provides a qualitatively correct description of singly excited states. See if you can figure out how to run a CIS calculation. I collected results in Table 1. See also the next paragraph for more details.

The second type of calculation we will investigate is TD-SCF using the B3LYP density functional. Using the DFT formulation the method includes additional electron correlation effects. To calculate excitation spectra, diffuse functions are VERY important, but a high level of polarization functions (f,g) are not. Therefore we will use the 6-31++G(d,p) basis set. To set up the calculation select Job Type \rightarrow Energy, Method \rightarrow TD-SCF, and then DFT, B3LYP, Basis Set as usual. Doing an excited state calculation we find some additional options. Under States we select Singlet Only, while we might ask for 10 states under Solve for more states, N= . This means that the program will calculate the 10 lowest singlet states. Let us submit another calculation in which we ask for the 10 lowest triplet states, by selecting instead Triplet Only. You can also do these calculations in one stroke by selecting Singlets and Triplets. The output is a little harder to analyse then, and I think it is easier to calculate them in two separate runs. Let us pick up the lowest state (if any) in each symmetry block in Table 1 below. We will use this to compare between different methods. In Table 2 we will collect results on the triplet states.

The accuracy of B3LYP for excited states is not entirely satisfactory. Let us also run another DFT calculation, using the same procedure as above, but using the CAM-B3LYP functional rather than B3LYP. I collected the results again in Tables 1 and 2. There is an emerging consensus in the literature that CAM-B3LYP are fairly accurate, in particular for Rydberg states and for so-call charge transfer states. B3LYP encounters problems for both. A charge transfer excitation is often accompanied by a large change in dipole moment, as the electron is excited from one part to another part of the molecule. They have interesting properties and were very hard to calculate. CAM-B3LYP solves the problem.

A completely different, and more accurate and reliable method is the SAC-CI approach, developed by Hiroshi Nakatsuji from the University of Kyoto. SAC-CI is closely related to Equation-of-Motion Coupled Cluster and Coupled Cluster Linear Response Theory, which are considered the most accurate approaches to calculate excited states, provided they are applicable. The latter caveat means that the ground state has to be qualitatively well described by a single determinant, the same requirement as for ground state coupled cluster and also for MP2 calculations (recall the on electron correlation for the H₂

molecule). If this is the case the EOMCC and CCLRT approaches will work well for *singly excited states*. In SAC-CI some additional algorithmic approximations are made that make the method faster. This makes it a little harder to fully gauge the accuracy of the method. It is certainly the most accurate approach available in Gaussian03.

Let us calculate both the singlet states and triplet states using SAC-CI with the 6-31++G(d,p) basis set. To run the calculation select SAC-CI and type the following command on the key-word line:

```
sac-ci=(singlet=(nstate=1,density),
        triplet=(nstate=2,density))
```

This input does not quite work yet. We need to open the input file explicitly and get rid of the first sac-ci keyword, such that we only keep the keyword sequence we put in ourselves on the key-word line. The `Nstate=1` indicates we calculate one state in every symmetry block (the lowest). The `density` specification indicates we calculate properties of excited states also. This is useful to characterize the excited states. The SAC-CI calculation proceeds by first doing an approximate Coupled Cluster (i.e. SAC) calculation of the ground state, and then it does an approximate variational calculation using basis functions that are constructed from single and double excitations out of the *correlated ground state*:

$$|\Psi\rangle = \sum_{\lambda} c_{\lambda} |\Phi_{\lambda}\rangle$$

$$|\Phi_{\lambda}\rangle = \hat{\Omega}_{\lambda} |\Psi_0^{SAC/CC}\rangle$$

In the simpler CISD approach the excitations would be defined with respect to the Hartree-Fock ground state determinant. The accuracy in SAC-CI/EOMCC obtains because the dynamical correlation effects are similar in ground and excited states and this similarity is built into the parameterization of the excited state wave function. We will discuss this further in the lectures.

Let us analyse the output of the calculation. Going through the outputs you can fill in Tables 1 and 2 below, as I did. The excitation energies at B3LYP are consistently lower than in CAM-B3LYP, and these are still lower than the SAC-CI results (which are most accurate, in general, provided the basis set is adequate. Here the basis set is somewhat small). The ordering of the states and the relative energies are fairly well reproduced between the various calculations. This means that these approaches might do a reasonable job calculating a spectrum, except for an overall shift of the spectrum. Absolute excitation energies are harder to calculate.

It is interesting to compare the singlet and triplet states of the same symmetry. If the energies between singlet and triplet agree to within about 0.3-0.4 eV, the states are likely to be Rydberg excitations, meaning that an occupied orbital is excited into a diffuse virtual orbital. In this case the so-called exchange integral

$$\langle ia | ai \rangle = \int \varphi_i(r_1) \varphi_a(r_2) \frac{1}{r_{12}} \varphi_a(r_1) \varphi_i(r_2)$$

is small because the occupied orbital i , and virtual orbital a occupy different regions in space. This integral is to good approximation a measure for the difference in energy between corresponding singlet and triplet excited states. If the virtual orbital is only

somewhat diffuse the singlet-triplet splitting will be larger. This information can be confirmed by examining the properties of the excited states in the SAC-CI calculation. For every state the so-called `Second moments` of the charge distribution are printed. Comparing the `XX`, `YY` and `ZZ` components for the excited state with that of the ground state provides a good idea of the diffuseness of the excited state, and this will corroborate the comparison based on the singlet-triplet splitting.

Table 1: Singlet excited states for ethylene in 6-31++G(d,p) basis.
Vertical excitation energies in eV

Symmetry	CIS	TD-SCF B3LYP	TD-SCF CAM-B3LYP	SAC-CI	EOM-CCSD
Ag	9.0537 (5)	8.6416 (7)	8.8662 (7)	9.21028	
B1g	7.8489 (2)	7.2513 (2)	7.5822 (2)	8.04062	
B2g	8.0346 (4)	7.2536 (3)	7.6644 (4)	8.07014	
B3g	10.500 (10)	8.8567 (9)	9.1915 (9)	9.84153	
Au	9.1720 (6)	8.3606 (6)	8.8357 (6)	9.27727	
B1u	7.8789 (3)	7.5004 (4)	7.5917 (3)	8.31907	
B2u	--	9.4568 (10)	--	10.54286	
B3u	7.2237 (1)	6.6582 (1)	6.9514 (1)	7.35091	

It is seen that the 6-31++G(d,p) basis set is too poor for higher excitations, but is quite reasonable for the first 4 states. The valence state in the SAC-CI approach is calculated at a too high energy, and this behaviour is well understood for the case of EOM-CCSD.

*Gaussian09 gives an option for EOM-CCSD excited state calculations. However, it seems that it has some problems for molecule with higher symmetry (Excited state calculations with ethylene, which is D_{2h} , did not succeed while it worked for water and ammonia). You may play around with options to see if we can get it to work.

Table 2: Triplet excited states for ethylene in 6-31++G(d,p) basis.
Vertical excitation energies in eV

Symmetry	CIS	TD-SCF B3LYP	TD-SCF CAM-B3LYP	SAC-CI	EOM-CCSD
Ag	8.2817 (5)	8.2208 (6)	8.4361 (6)	8.76806	
B1g	7.7452 (3)	7.1992 (4)	7.5040 (3)	8.01077	
B2g	7.8922 (4)	7.1730 (3)	7.5725 (4)	7.99339	
B3g	10.004 (10)	8.6786 (8)	9.0834 (9)	9.58475	
Au	9.1438 (7)	8.3565 (7)	8.8290 (7)	9.26357	
B1u	3.6845 (1)	4.1697 (1)	4.0141 (1)	4.60347	
B2u	--	--	--	10.24555	
B3u	7.0101 (2)	6.5754 (2)	6.8533 (2)	7.21984	

B. Vertical Ionization Energies of ethylene.

The SAC-CI approach can be used in a similar fashion to calculate ionized states that have one less electron than the ground state. We can calculate ionization potentials for ethylene by specifying

```
sac-ci=(cationdoublet=(nstate=1),density)
```

On the keyword line. Again we have to get rid of the parent sac-ci keyword that is put in by Gaussview. This calculation will find one ionized state for each symmetry block. We can simply use the 6-31G(d,p) basis set, as diffuse functions are unimportant for cations. The results of the ionization energies can be compared to the negative of the orbital energies (converted from a.u. to eV, 1 a.u = 27.2114 eV). You will see that Koopmans' theorem is fairly accurate (errors of about 1 eV) and gets the ordering of the orbitals correct for ethylene. I collected the results in Table 3. To get the SCF orbital energies we need to run a single point Hartree-Fock calculation and convert the orbital energies to eV.

Table 3: Vertical ionization energies for ethylene in eV (6-31G(d,p) basis set.

Symmetry	SAC-CI	Koopmans
Ag	14.89	15.57
B3g	13.03	13.93
B1u	19.57	21.54
B2u	16.26	17.49
B3u	10.57	9.92

C. Geometry optimization of ionized and excited states.

Let us first consider geometry optimizations of ionized states. For ethylene the symmetries (irreducible representations) are ordered Ag, B1g, B2g, B3g, Au, B1u, B2u, B3u. We can optimize each of the ionized states separately. The input to optimize the state of B3g symmetry (the lowest state in symmetry block 4) reads:

```
sac-ci=( full,cationdoublet=nstate=(0,0,0,1,0,0,0,0),  
Targetstate=(spinstate=doublet,symmetry=4,root=1) )
```

The input for states of other symmetry is analogous. It is easiest to create the various input files in a text editor and then run them individually. In this fashion we can optimize the geometries of all five states. In the Friezen lab this takes some time because you can only run one job at a time. The optimization is such that it preserves the D2h symmetry of ethylene, and this is not necessarily correct for the ionized state. Most often the symmetry is equal or lower in ionized or excited states. We can predict what one would expect to happen to bond lengths and bond angles by examining the molecular orbitals. The notion of ionized state means that an electron is removed from a particular molecular orbital, and that electron correlation effects are accounted for. If the orbital is bonding between

the carbons, the CC bond length should increase upon ionization. If the orbital is bonding between two CH atoms, the CH bond length would increase and the angle would be expected to increase. In D_{2h} symmetry we can characterize the geometry of ethylene by R(CC), R(CH) and A(CCH). In table 4 below we indicate the optimized geometry for each ionized state. For the ground state of the cation, corresponding to ionization from the HOMO, the B_{3u} orbital, we can easily optimize the geometry using the MP2 method, and calculate the frequencies. This geometry is also included in Table 4.

Table 4: Optimized Geometries for cationic states of ethylene, using SAC-CI/6-31G(d,p) method, and comparison to UMP2/6-31G(d,p).

State/Symmetry	R(CC)	R(CH)	A(CCH)
Neutral ground	1.324	1.083	121.74
A _g	1.416	1.089	111.32
B _{3g}	1.283	1.119	128.4
B _{1u}	--	--	--
B _{2u}	1.373	1.121	129.1
B _{3u}	1.404	1.079	120.7
B _{3u} / MP2	1.459	1.118	120.39

Examining the frequencies at the MP2 level, we notice that all frequencies are real. This is actually not quite correct. At the SAC-CI level the molecule will break symmetry. We can redo the optimization at the SAC-CI level, reducing the symmetry of ethylene to C₁. Then we can optimize the first root in symmetry-block 1, doing a SAC-CI calculation. At the SAC-CI level we find a dihedral angle of 9.45 degrees. All the CH distances are 1.081, the CC distance is 1.404, and the HCC angles are 120.78. So the only substantial change is breaking the plane of symmetry, leading to a small, but nonzero, dihedral angle. It appears not to be possible to optimize higher excited states in C₁ symmetry using the SAC-CI method (I tried). In practice we can only optimize the lowest state in each symmetry block for sure, but need some luck for higher states.

In a similar fashion we can optimize geometries for excited states. The valence states of ethylene are most interesting. We can optimize both the singlet and triplet state of B_{1u} symmetry, preserving D_{2h} symmetry. The lowest triplet state can also be optimized at the MP2/6-31++G(d,p) level, and we can compare the SAC-CI and MP2 results. Now the frequencies for the triplet state show imaginary (or negative) numbers. Let us reduce the symmetry to C₁ and redo the optimizations of the triplet state at both the SAC-CI and MP2 level. It is interesting to look at the geometries in Gaussview! We are running into yet another limitation of the electronic structure methods for excited states. I mentioned before that the ground state has to be well described by a single Hartree-Fock configuration. This is not the case for the singlet ground state, at the twisted geometry of the triplet. Hence the SAC-CI method becomes unreliable. Often there are no easy answers for excited states, in particular if optimized geometries and vibrational frequencies are investigated. We will consider other approaches using the ACES2 package.