Chiroptical properties of molecular excited electronic states. A Vibronic approach Short Stay at Prof. Crawford group (Virginia Tech)

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1 General overview

This short stay in the group of Prof. Daniel Crawford at Virginia Tech has introduced some state-of-the-art techniques in the fields of electronic structure theory and its application to the study of chiroptical electronic spectroscopies. The fruitful interactions with the group leader and the post-doc and graduate students within has permitted the acquisition of some new skills useful both for the development of the current project as well as my ongoing research career. Such new abilities include programing techniques (C++) to work on the *Psi4* code developed in the hosting group and the methodologies to compute, using highly theoretical structure methods implemented in that program, the rotatory strengths between any two electronic states, which are required to simulate chiral electronic spectroscopies. In the next sections, we describe more in detail the scientific outcomes from this period.

2 Introduction to ***Psi4*** code.

One of the strongest motivations for this visit was the advanced skills of the hosting group in the field of accurate electronic structure methods, as coupled clusters (CC) and its extension to excited states through the equations-of-motion (EOM) formulation. In fact, Prof. Daniel Crawford leads the development of *Psi4*,[1] an open source electronic structure code which includes efficient implementations of both CC and EOM-CC techniques and which provides not only the energetics but also other molecular properties relevant for the simulation of electronic spectroscopies. Concretely, it performs the evaluation of the transition electric and magnetic dipole moments between different electronic states (including those which only involve excited states). The latter feature allows one to simulate chiral electronic spectroscopies for transitions either from the ground to excited state or exclusively between excited states.

The characteristics of *Psi4* described above highlight the importance of mastering such a code in order to pursue the goals of this project. Regarding the interaction schemes available in the program, it is worth noticing its high flexibility, which allows not only to carry out the plethora of methods already implemented, but also to extend the program capabilities with user-code, which is easily included in the *Psi4* streamline through the so-called plugin mechanism. Such excellent feature of the *Psi4* code allows the user to access all the libraries within *Psi4* to build up its own code (e.g., the scf solvers, the molecular objects...) and then run the code within a standard *Psi4* input, where it can be mixed up with other program modules. The great freedom of that protocol, allowing customized calculations and analysis using the superb infrastructure of *Psi4*, also carries additional complexity to run the code. Concretely, the plugin mechanism expects the user-code to be written in C++ and requires of some knowledge about the inner details of *Psi4* structure (libraries, objects...), in order to exploit all its advantages. In that sense, it is very remarkable that, during this visit, we got a knowledge of the *Psi4* structure deep enough so as to allow us to build plugins and other interfaces useful to couple it with subsequent computations to provide the vibrational structure of the spectrum with a code developed in our laboratory. Concretely, in this project we propose the simulation of the whole vibrational lineshape for chiral electronic spectroscopies using information from electronic structure calculations (rotatory strengths associated with the electronic transitions and topology of the potential electronic surfaces for the involved states).

To that end, we use *$\mathcal{FC}$classes*, a code that is able to simulate different electronic spectroscopies which is developed in our laboratory at ICCOM-CNR (Pisa), and that uses the aforementioned data from a electronic structure calculation. We should note here that one of the main goals for the future enhancements of *$\mathcal{FC}$classes* is its interface with a larger range of electronic structure softwares, so as to expand its usability. In this sense, the interface with *Psi4* reveals particularly useful in order to perform simulations of spectroscopic transitions involving only excited states. Indeed, unlike other methodologies, the EOM-CCSD implemented in *Psi4* is able to provide the rotatory strengths for these type of transitions. In that context, the throughout understanding of the *Psi4* code got during this visit, made possible the refinement of our general interface tools to *$\mathcal{FC}$classes*[*], which now parse *Psi4* output files to produce the input for the spectral simulations.

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[*] Code at a public repository hosted in: `https://github.com/jcerezochem/fcc_tools`

Furthermore, we have implemented some of the features of *$\mathcal{FC}$classes* directly on *Psi4* code by means of a plugin[†], so that to allow the computation of the vibronic spectrum by means of the simplest models implemented in our code. Our plans is that this plugin will be also able to generate *$\mathcal{FC}$classes* inputs.

3 Chiroptical properties in the excited states, application to small molecules

Apart from leading the development of *Psi4*, the hosting laboratory is also recognized for its studies on chiral molecules, mainly in the study of different chiral spectroscopies, including electronic circular dichroism (ECD) and Circularly Polarized Luminescence (CPL). Such experience is of particular relevance for this project, that deals with electronic state ECD (ESECD), since their previous works on ECD and CPL set up a good starting point.

Concretely, we focus on 3-methylcyclopentanone and norbornenone (Figure 1), which were recently studied by Prof. Crawford's group using EOM-CCSD calculation to study the CPL spectra.[2] The use of the most recent version of the *Psi4* code allowed us to extend the study to ESECD by computing the electric and magnetic transition dipole moments associated to transitions between different excited states, also using EOM-CCSD. This systems were useful to get introduced into the computation of the rotatory strength and with EOM-CCSD calculations. However, the next step, which would involve the simulation of the ESECD spectra with vibrational and solvent effects turns out to be rather complicated, since the pyramidalization of the cyclic ketone prevents the straightforward application of the harmonic approximation. Such difficulty can be approached by separating the non-harmonic coordinate and solving for it the anharmonic problem with numerical methods. Though interesting, this kind of studies lye out of the scope of the current visit, and we decided to continue with other systems for which we benefit more from the knowledge of the hosting group.

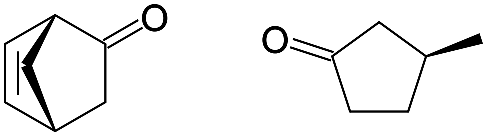

Figure 1: Structural formula of norbornenone (left) and 3-methylcyclopentanone (right).

It is worthy to note at this point that alternative to the use of EOM-CC meth-

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[†] Code available at a public repository hosted in: `https://github.com/jcerezochem/my_psi4_plugins`

ods, the rotatory strength between two excited states have also been computed using quadratic response techniques with DFT methods, which required less computational resources.[3] Such calculations were actually conducted, in part, by Dr. Antonio Rizzo, from IPCF-CNR institute in Pisa, who is also involved in the project discussed here. In order take advantage of the efficient of DFT calculations, we require a most accurate computational approach against which we could validate the DFT results. In this sense, this visit offers the possibility to use the EOM-CC data as reference to validate DFT, which could then be applied more widely. To begin with, we have taken one of the systems included in the study of Dr. Rizzo, methyloxyrane (Figure 2), and recompute the rotatory strengths obtained at DFT and EOM-CCSD levels.

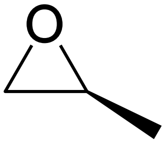

Figure 2: Structural formula of norbornenone (left) and methylciclopentatanone (right).

In Table 1 we show the results for the 8 first lying states. As indicated by these results, DFT gives a similar behavior as EOM-CCSD for the first excited state, although for hight excited states significant discrepancies are observed. This points out the importance of benchmarking the DFT results against more accurate methods prior to validate the results for the specific transition being considered. Furthermore, we have developed specific applications and *Psi4* plugins able to parse from *Psi4* outputs the required data to produce the input files to run our code $\mathcal{FC}$*classes*.

Table 1: Energy and rotatory strengths corresponding to the transition between the 8 first low lying states of MO.

Transition	CAM-B3LYP/d-aug-cc-pVQZ[3]				EOM-CCSD/aug-cc-pVDZ				EOM-CCSD/d-aug-cc-pVDZ			
	Energy (cm^{-1})	RS(l) (10^{-3} au)	RS(v) (10^{-3} au)	$\frac{\text{RS(l)}}{\text{RS(v)}}$	Energy (cm^{-1})	RS(l) (10^{-3} au)	RS(v) (10^{-3} au)	$\frac{\text{RS(l)}}{\text{RS(v)}}$	Energy (cm^{-1})	RS(l) (10^{-3} au)	RS(v) (10^{-3} au)	$\frac{\text{RS(l)}}{\text{RS(v)}}$
1 → 2	1663	63.2	63.2	1.0	2434	60.9	24.3	2.5	2015	50.0	51.4	1.0
1 → 3	3703	-72.2	-72.3	1.0	3728	-59.1	-31.4	1.9	3541	-42.5	-45.3	0.9
1 → 4	4585	-260.4	-260.7	1.0	5424	-52.3	-55.9	0.9	5144	-40.0	-40.9	1.0
1 → 5	5763	359.5	358.4	1.0	7225	81.3	77.4	1.1	7268	73.2	68.7	1.1
1 → 6	8196	34.3	34.6	1.0	10859	8.0	8.3	1.0	10158	16.3	16.7	1.0
1 → 7	8916	-28.8	-28.8	1.0	11359	-1.8	-0.5	3.6	10529	7.0	7.0	1.0
1 → 8	9481	-18.9	-18.9	1.0	11465	-4.7	-5.5	0.9	10818	-25.2	-25.1	1.0
2 → 3	2040	-27.4	-28.6	1.0	1294	33.8	295.4	0.1	1526	16.7	3.9	4.3
2 → 4	2922	-118.8	-119.6	1.0	2990	-74.7	-228.7	0.3	3129	-63.9	-69.0	0.9
2 → 5	4100	-57.3	-57.0	1.0	4791	-4.6	-6.9	0.7	5254	-7.5	-10.3	0.7
2 → 6	6533	-204.7	-205.3	1.0	8425	-172.3	-197.6	0.9	8144	-285.0	-299.0	1.0
2 → 7	7253	257.6	258.0	1.0	8925	-8.0	-8.0	1.0	8514	83.1	82.8	1.0
2 → 8	7818	88.7	88.6	1.0	9031	70.1	89.4	0.8	8804	286.7	291.4	1.0
3 → 4	882	88.7	90.3	1.0	1696	103.3	84.0	1.2	1603	55.0	91.6	0.6
3 → 5	2060	23.5	23.3	1.0	3497	0.7	0.2	3.5	3727	0.2	0.0	–
3 → 6	4493	-3.2	-3.0	1.1	7130	-26.1	-25.7	1.0	6617	48.0	49.6	1.0
3 → 7	5214	13.6	13.3	1.0	7631	64.9	60.3	1.1	6988	31.2	31.1	1.0
3 → 8	5778	-303.9	-304.7	1.0	7737	-52.1	-47.6	1.1	7277	-127.1	-128.5	1.0
4 → 5	1178	-36.7	-37.1	1.0	1801	-6.9	-10.8	0.6	2124	-7.9	-10.2	0.8
4 → 6	3611	-118.0	-117.3	1.0	5435	11.4	16.1	0.7	5014	-101.3	-101.9	1.0
4 → 7	4331	-472.4	-471.8	1.0	5935	-77.7	-64.5	1.2	5385	-118.1	-118.3	1.0
4 → 8	4896	14.0	14.0	1.0	6041	-138.8	-130.5	1.1	5674	77.3	76.6	1.0
5 → 6	2433	54.5	54.3	1.0	3634	75.0	57.2	1.3	2890	20.4	19.3	1.1
5 → 7	3153	-62.6	-62.9	1.0	4134	66.6	81.0	0.8	3260	36.4	37.6	1.0
5 → 8	3718	102.2	102.7	1.0	4240	-81.4	-65.1	1.3	3550	-17.2	-16	1.1
6 → 7	720	27.3	20.1	1.4	500	-84.5	-2.9	29.1	370	81.4	-25.4	-3.2
6 → 8	1285	71.0	80.4	0.9	607	178.2	254.8	0.7	660	-143.5	-57.5	2.5
7 → 8	565	-160. 9	-177.1	0.9	106	-60.2	44.8	-1.3	290	-132.0	-37.3	3.5

4 Perspectives

In this short stay we have exploit the EOM-CCSD code implemented in *Psi4*, including the module to compute response properties, to evaluate the rotatory strength between excited states, and compared this results with those obtained by the more computationally feasible QR-DFT.

The protocol proposed here relies on the benchmark and validation of QR-DFT simulations of the ESECD energies and intensities against EOM-CCSD calculation. Once an affordable theoretical model is selected, we can envisage its application to system of biological relevance, carrying out the simulation of the whole spectral lineshape including vibrational and environmental effects. In this respect, chromophores in proteins stands as very attractive system due to their biotechnological implications. Concretely, for the future stages, we select the chromophore of the photoactive yellow protein (PYP), a biosystem thoroughly studied by experimental techniques including ESECD.

References

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[3] Rizzo, A.; Vahtras, O. *J. Chem. Phys.* **2011**, *134*, 244109.