

FCclasses

A Program for the calculation of vibrationally resolved
electronic absorption, emission and circular dichroism
spectra in harmonic approximation,
including Duschinsky, Herzberg-Teller and temperature effects

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The code implements the method published in the following references

- F. Santoro, R. Improta, A. Lami, J. Bloino, V.Barone,
Effective method to compute Franck-Condon integrals for optical spectra of large molecules in solution”
J. Chem. Phys. **126**, 084509-(1-13) (2007).
- F. Santoro, R. Improta, A. Lami, V.Barone,
An effective method to compute vibrationally resolved optical spectra of large molecules at finite temperature in the gas-phase and in solution
J. Chem Phys, **126**, 184102 (2007)
- F. Santoro, R. Improta, A. Lami, J. Bloino, V.Barone,
Effective method for the computation of optical spectra of large molecules at finite temperature including the Duschinsky and Herzberg-Teller effect. The Qx band of porphyrin as a case study
J. Chem. Phys. **128**, 224311 (2008)

- F. Santoro, V. Barone,
Computational approach to the study of the lineshape of absorption
and electronic circular dichroism spectra
Int. J. Quantum. Chem, DOI:10.1002/qua.22197 (2009)

These references should be cited in any article whose results are obtained, also partially, by using *FCclasses*. Please also cite the following reference to the code

- F. Santoro, "*FCclasses*, a Fortran 77 code": visit
<http://village.ipcf.cnr.it>

1 Short notes

FCclasses is free software in Fortran 77. It is distributed because it is supposed it can be of some help for people interested in calculating vibrationally resolved electronic spectra, especially when large molecules are considered. It has been written during several years, and continuously modified for personal usage only. As a consequence it is neither optimized nor elegant as far as the programming style is concerned. Nonetheless it is usually quite efficient in obtaining converged spectra with a moderate computational time.

Because of its story the code might result not very friendly to be read or modified. Compatibly with time the author tries to help users which want to modify it, and he is glad to open new collaborations, but users are free to work on the code independently of him.

It is not guaranteed that *FCclasses* is free of bugs. Please report any comments or bugs to f.santoro@ipcf.cnr.it.

2 Introduction

In this Introduction we give a very concise explanation of the method and we define the necessary symbols. *FCclasses* implements a time-independent method for computing spectra between electronic states with negligible non-adiabatic couplings. It is suitable for semirigid molecules for which harmonic approximation is reliable.

To fix the ideas, consider the radiative transition $|e1\rangle \rightarrow |e2\rangle$ from the initial vibrational state $|\mathbf{w1}\rangle$; we collect the manifold of vibrational states $|\mathbf{w2}\rangle$ of the final state $|e2\rangle$ (and of the corresponding transitions) in different classes C_n , depending on the number n of oscillators whose quantum num-

ber is different from zero. For instance $\langle \mathbf{w1}|3, 0, \dots\rangle$ is a C_1 transition, and $\langle \mathbf{w1}|0, 3, 0, 5, 4, 0, \dots\rangle$ is a C_3 transition. For each C_n , a maximum-allowed excitation vector \mathbf{W}_n^{\max} is defined so that all the integrals $\langle \mathbf{w1}|\mathbf{w2}\rangle$ to states $|\mathbf{w2}\rangle$ involving larger quantum numbers can be considered negligibly small. The determination of \mathbf{W}_n^{\max} is based only on the analysis of the computationally cheap C_1 and C_2 transitions.[4]

For steady-state spectroscopy, at finite temperature a Boltzmann distribution of the vibrational states of the initial electronic state must be taken into account in the computation of the spectra. In ref. [5] we presented a generalization of our method illustrated in ref. [4] to deal with finite temperature spectra, proposing a general scheme for selecting the relevant transitions for each vibrationally excited state. It is convenient to collect the initial states populated by temperature into "mother states", since the computation of the contribution to the spectrum of one of these states also provides the necessary information for the calculation of the contributions of all the states which have equal or lower quantum numbers for each normal mode. For a detailed explanation the reader is referred to the original paper.[5]

In ref. [6] the method, initially focussed on Franck-Condon (FC) spectra, has been further generalized to face with spectra where Herzberg-Teller (HT) effects must be taken into account. The new version 2.1 of the code implements also the possibility to compute electronic circular dichroism spectra (at FC and HT level) along the lines reported in ref. [9]. *FCclasses* has been utilized to compute ECD spectra in ref. [9–12]. Development version of the codes also exist for computing FC and HT two-photon absorption and circular dichroism spectra (see ref. [12]).

The variables utilized by the code are labeled with "1" or "2" to specify which electronic state they are referred to. State 1 is the initial state and

State 2 is the final state of the transition.

The code works in harmonic approximation and calls **Q1** and **Q2** the N normal coordinates of the two electronic states $|e1\rangle$ and $|e2\rangle$, respectively. The vibrational states are direct products of 1D states $|w_k\rangle$ for each mode k , $|\mathbf{w}\rangle = |w_1\rangle \otimes |w_2\rangle \dots \otimes |w_N\rangle$, where w_k is the quantum number of $|w_k\rangle$ and the vector $\mathbf{w} = (w_1, w_2, \dots, w_k, \dots, w_N)$. The sets of normal coordinates **Q1** and **Q2** are related by the linear transformation

$$\mathbf{Q1} = \mathbf{JQ2} + \mathbf{K} \quad (1)$$

where **J** is the Duschinsky matrix.

For Herzberg-Teller absorption or emission spectra, the transition electric dipole moment integrated on electronic coordinates $\boldsymbol{\mu}_{e',e}$ is expanded on the normal coordinates of the final state

$$\boldsymbol{\mu}_{e1,e2} \simeq \boldsymbol{\mu}_0(2) + \sum_k \boldsymbol{\mu}_k Q_{2k} \quad (2)$$

For electronic circular dichroism (ECD) spectra also the transition magnetic dipole moment integrated on electronic coordinates $\mathbf{m}_{e1,e2}$ is needed, and for HT spectra it is written as

$$\mathbf{m}_{e1,e2} \simeq \mathbf{m}_0(2) + \sum_k \mathbf{m}_k Q_{2k} \quad (3)$$

Notice that $\boldsymbol{\mu}_0(2)$ and $\mathbf{m}_0(2)$ are taken at the equilibrium geometry of the final state. In principle these values are different from those taken at the equilibrium geometry of the initial state $\boldsymbol{\mu}_0(1)$ and $\mathbf{m}_0(1)$. Eq. 2 and 3 allow to get estimates for these values

$$\bar{\boldsymbol{\mu}} = \boldsymbol{\mu}_0(2) + \sum_k \boldsymbol{\mu}_k K_k \quad (4)$$

$$\bar{\mathbf{m}}_0(1) = \mathbf{m}_0(2) + \sum_k \mathbf{m}_k K_k \quad (5)$$

The equalities $\bar{\boldsymbol{\mu}}_0(1) \equiv \boldsymbol{\mu}_0(1)$ and $\bar{\mathbf{m}}_0(1) \equiv \mathbf{m}_0(1)$ are never fulfilled unless the HT linear approximation is exact, which never happens in practical cases. This difference raises some problems when comparing absorption and emission spectra, or FC and HT spectra, that will be discussed in Section 7.

For a full harmonic calculation the user must supply the equilibrium geometries, frequencies and normal modes for both the initial and final electronic states. They can be computed with any suitable electronic-structure method. The code assumes they are written in the Gaussian style (see below the section Notes for the interface with GAUSSIAN). These data are supplied through formatted input files prepared by the user (files F01 and F02, see below) the data must be written in the proper way and units. A small fortran code *prep.fc.f90* is added in this new release to help preparing files F01 and F02 from GAUSSIAN outputs, see the appendix. When the full data are not disposable (typically when excited-state normal analysis is too computationally demanding) a first-estimate of the spectrum can be obtained assuming that the normal modes and frequencies of the two electronic states are the same, and only the equilibrium geometries are displaced. File F01 and F02 must be prepared consequently. This approximation is expected to perform better for low-resolution spectra, while stick spectra can differ considerably from the full harmonic ones.

3 Distribution of the code

The code is distributed as a single tar zipped file "fcclasses21.tar.bz2". To unzip launch "bunzip2 fcclasses21.tar.bz2". A tar file fcclasses.tar is obtained.

Launch the command "tar -xvf fcclasses21.tar". Directory FCCLASSES2-1/ includes the source file "fcclasses.f", the executable file "fcclasses.e" (compiled on Intel(R) Xeon(R) CPU E5440 by the Intel Compiler 10.1 "ifort") and the pdf short manual FCclasses21_man.pdf. Subdirectory PORPH/ includes the three files "state-porph-s0", "state-porph-s1-ns", "tr-dipoles-porph-ns-mod" for test calculations of the $S_1 \rightarrow S_0$ emission spectrum of free-base porphyrin. The sub-subdirectories FC-0K/, FC-TEMPERATURE/, HT-0K/, and HT-TEMPERATURE/ report different input and output files for the calculation respectively at FC level and T=0 Kelvin, at FC level and T=100 K, at HT level and T=0 K, and at HT level and T=100 K of porphyrin. Subdirectory R3MCP/ includes files for the $S_0 \rightarrow S_2$ transition of the *Ax* conformer of (R)-(+)-3-methylcyclopentanone (R3MCP). Sub-subdirectories EMI-FC-0K/, EMI-HT-0K/, ABS-FC-0K/, ABS-HT-0K/, ECD-FC-0K/ and ECD-HT-0K/ report example calculations for the emission, absorption, and ECD spectrum of R3MCP (at FC and HT level) at T=0 Kelvin. Notice that results for absorption and ECD are slightly different from those presented in refs. [11] and [12], since here we use transition dipoles and derivatives obtained at the excited-state geometry at B3LYP/aug-cc-pVDZ level, while in the cited papers we adopted transition dipoles and derivatives obtained at the ground-state geometry at B3LYP/aug-cc-pVTZ level.

4 Compiling the Code

FCclasses is distributed as a single file. It can be compiled with the Intel Fortran Compiler with the simplest option

```
ifort -o fcclasses.e fcclasses.f
```

or with `g77` compiler with the simplest option

```
g77 -o fcclasses.e fcclasses.f
```

According to some tests the executable obtained with `g77` is sensibly slower.

Finally the code can be also compiled with Portland Fortran, but the calls to routine "cpu_time" for the calculation of computational time must be skipped, commenting the relative lines of the code.

5 Running a job

A job is launched by the following command

```
fcclasses.e < fileinput > fileoutput
```

It needs four input files

- fileinput. It is the standard input
- F01. State1 data. Its name is defined in fileinput
- F02. State2 data. Its name is defined in fileinput
- F03. Transition electric dipole at the equilibrium geometries of the ground and excited states; also its derivatives are needed for HT spectra. Notice that for FC calculation these data are only needed to provide the spectrum in absolute units. One can obtain the spectral line-shape in arbitrary units by supplying any value (but the module of the vector must be not vanishing). The name of file f03 is defined in fileinput.

- F04. For absorption or emission spectra it is not read. For ECD calculation it must report the transition magnetic dipole, and if an HT calculation must be performed, also its derivatives. The name of file f04 is defined in fileinput

The code prints five output files

- fileoutput Standard output
- fort.8 Stick spectrum
- fort.9 Stick spectrum in a different format
- fort.18 Convolution spectrum. For absorption spectra the molar absorptivity $\epsilon(\omega)$ is given in $\text{dm}^3 \times \text{mol}^{-1} \times \text{cm}^{-1}$ according to the expression

$$\epsilon(\omega) = \frac{4\pi^2 N_A}{3000 \ln(10) \hbar c (4\pi \epsilon_0)} \sum_{\mathbf{w1}, \mathbf{w2}} p_{\mathbf{w1}} \omega g(\omega, \omega_{\mathbf{w2}, \mathbf{w1}}) |\langle \mathbf{w1} | \boldsymbol{\mu}_{e1, e2} | \mathbf{w2} \rangle|^2 \quad (6)$$

where N_A is the Avogadro number, c the light velocity, ϵ_0 the vacuum permittivity, $p_{\mathbf{w1}}$ the Boltzmann population of state $|\mathbf{w1}\rangle$, and $g(\omega, \omega_{\mathbf{w2}, \mathbf{w1}})$ the normalized lineshape. It is possible to choose (see below) between Gaussian (inhomogeneous) or Lorentzian (homogeneous) broadenings, according to the following expressions

$$g(\omega, \omega_{\mathbf{w2}, \mathbf{w1}}) = \frac{1}{\gamma [\pi / \ln(2)]^{1/2}} \exp[-\ln(2)(\omega - \omega_{\mathbf{w2}, \mathbf{w1}})^2 / \gamma^2] \quad (7)$$

$$g(\omega, \omega_{\mathbf{w2}, \mathbf{w1}}) = \frac{\gamma \pi^{-1}}{\gamma^2 + (\omega - \omega_{\mathbf{w2}, \mathbf{w1}})^2} \quad (8)$$

Notice that, in both the lineshapes, γ represents the half width at half maximum (HWHM).

For emission spectra the number of emitted photon per molecule and per nanosecond is given ($\text{molecules}^{-1} \times \text{ns}^{-1}$), according to the expression

$$N(\omega) = \frac{4}{3\hbar c^3} \sum_{\mathbf{w1}, \mathbf{w2}} p_{\mathbf{w1}} \omega^3 g(\omega, \omega_{\mathbf{w2}, \mathbf{w1}}) |\langle \mathbf{w1} | \boldsymbol{\mu}_{e1, e2} | \mathbf{w2} \rangle|^2 \quad (9)$$

Finally, for ECD spectra the anisotropy of the molar absorptivity $\Delta\epsilon(\omega) = \epsilon_L(\omega) - \epsilon_R(\omega)$ is given in $\text{dm}^3 \times \text{mol}^{-1} \times \text{cm}^{-1}$, according to the following expression

$$\Delta\epsilon(\omega) = \frac{16\pi^2 N_A}{3000 \ln(10) \hbar c^2 (4\pi\epsilon_0)} \sum_{\mathbf{w1}, \mathbf{w2}} p_{\mathbf{w1}} \omega g(\omega, \omega_{\mathbf{w2}, \mathbf{w1}}) R^{e1, \mathbf{w1}, e2, \mathbf{w2}} \quad (10)$$

where the rotatory strength is $R^{e1, \mathbf{w1}, e2, \mathbf{w2}}$

$$R^{e1, \mathbf{w1}, e2, \mathbf{w2}} = \text{Im}[\langle \mathbf{w1} | \boldsymbol{\mu}_{e1, e2} | \mathbf{w2} \rangle \langle \mathbf{w2} | \mathbf{m}_{e2, e1} | \mathbf{w1} \rangle] \quad (11)$$

- fort.21 stick bands assignments

6 Input Description

6.1 Standard Input

Table 1: Standard input (fileinput)

Line	Variable	Type	Explanation
Line 1	N	Integer	Number of atoms
Line 2	N36	Integer	Number of normal modes
Line 3,..3+N-1	Real	PM(i) i=1,N	Atomic masses in amu
Line 3+N	DE	Real	Adiabatic energy difference between the two states $ E_2 - E_1 $ in eV. Notice that the zero-point-energy must not be included
Line 4+N	optrans, optrans1, opdip	Character	optrans='abs' sets an absorption calculation; optrans='emi' sets an emission calculation. optrans1='ECDYES' sets a ECD calc. Choose optrans1='ECDNO ' for a simple absorption calculation. opdip='FC' sets a Franck-Condon calculation, while opdip='HT' set an Herzberg-Teller calculation. In the latter case both the zero-order and the first order terms in eq. 2 are considered (sometimes called FCHT spectrum.) When a pure HT calculation is desired, the transition dipole moments in file F03 (see below) must be set to zero.
Line 5+N	Tem, pestem	Real	Temperature in Kelvin and minimum weight taken into account in the Boltzmann distribution. The weights is expressed as a fraction of the weight of the ground vibrational state (set to 1)
Line 6+N	F01	Character	File input for state1. See below for details
Line 7+N	F02	Character	File input for state2. See below for details

Line	Variable	Type	Explanation
Line 8+N	f03	Character	File input for transition electric dipole moment and its derivatives (in atomic units). Derivatives are read and used only if an HT calculation is requested. See below for details.
Line 9+N	f04	Character	It is only used only for ECD calculation. File input for transition magnetic dipole moment and its derivatives (in atomic units). Derivatives are read and used only if an HT calculation is requested. See below for details.
Line 10+N	iopeu	Integer	Option for rotating the coordinates of State1, looking for a rotation that minimizes the RSMD with the equilibrium geometry of State2. It is activated by iopeu=1, and switched off by iopeu=0
Line 11+N	nov	Integer	Number of states (max. quantum number=nov-1) to be considered for each oscillator in the computation of C_1 class transitions (Overtones). Typical values 20-25
Line 12+N	nco2	Integer	Number of states (max. quantum number=nco2-1) to be computed for each oscillator in the computation of C_2 class transitions (combinations of 2 modes). Typical values 15-20
Line 13+N	Dnfcmax	Real	Accuracy parameter. Nominal maximum number of integrals to be computed for each class Typical values : $10^6 - 10^7$ (easy cases: rigid molecules with small displacements) 10^8 (standard) $10^9 - 10^{10}$ (difficult cases: very large molecules, and/or large displacements). Choices $> 10^{10}$ usually require very long computational times
Line 14+N	opzbro, en0 enfin, nene, dga	character, real, real, integer, real	Broadening. Set opzbro='Gau' for Gaussian and opzbro='Lor' for Lorentzian. The spectrum is plotted in the energy interval (eV) (en0, enfin) with nene points. dga (eV) is the HWHM of the lineshape

6.2 Auxiliary Formatted Input files

- F01 and F02.

F01 contains information on State1 and F02 on State2. If an absorption calculation is requested, State1 must be the lower-energy state and State2 the higher-energy state. The opposite is true if an emission calculation is desired.

In each of the two files, the code reads a large column vector reporting, in order of appearance (in the code all the variables are labeled with a suffix "1" or "2" to indicate the state):

GEO(I), I=1,3N cartesian equilibrium coordinates in angstrom

T(I,J), J=1,N36, I=1,N3 normal modes matrix in cartesian coordinates \mathbf{x} (not mass-weighted) $\mathbf{x} = \mathbf{T}\mathbf{Q}$ (in literature T is usually named L). Notice that j is the faster index (reading row by row).

G(I), I=1,3N-6 frequencies in cm^{-1}

- F03 (transition electric dipole).

It is always opened. If a FC calculation is requested the code reads a matrix (2,3) reporting in order of appearance

$-\boldsymbol{\mu}_0(1)$ the transition electric dipole moment integrated on the electronic coordinates at the equilibrium geometry of the lower-energy electronic state as a 3D vector $(\mu_0^x(1), \mu_0^y(1), \mu_0^z(1))$

$-\boldsymbol{\mu}_0(2)$ the transition electric dipole moment integrated on the electronic coordinates at the equilibrium geometry of the lower-energy electronic state as a 3D vector $(\mu_0^x(2), \mu_0^y(2), \mu_0^z(2))$. Notice that the order in which the transition dipole moment at the two different geometries must be supplied is always the same "lower-energy", "higher-energy"

independently of the type of calculation required (i.e. either absorption or emission).

If a HT calculation is requested the code also reads just after the first (2,3) matrix an additional matrix (3N,3) reporting the transition dipole derivatives. Specifically

-In $3 \times N$ lines $i = 1, 3 \times N$: $\frac{\partial \boldsymbol{\mu}}{\partial q_i}$ as a 3S vector $\left(\frac{\partial \mu^x}{\partial q_i}, \frac{\partial \mu^y}{\partial q_i}, \frac{\partial \mu^z}{\partial q_i}\right)$, where $q_1 = x_1, q_2 = y_1, q_3 = z_1, q_4 = x_2, \dots$ etc.

- F04 (transition magnetic dipole).

It is opened only if an ECD calculation is requested. In that case if a FC calculation is requested the code reads a matrix (2,3) reporting in order of appearance

- $\mathbf{m}_0(1)$ the transition magnetic dipole moment integrated on the electronic coordinates at the equilibrium geometry of the lower-energy electronic state as a 3D vector $(m_0^x(1), m_0^y(1), m_0^z(1))$

- $\mathbf{m}_0(2)$ the transition magnetic dipole moment integrated on the electronic coordinates at the equilibrium geometry of the excited-energy electronic state as a 3D vector $(m_0^x(2), m_0^y(2), m_0^z(2))$. Notice that the order in which the transition dipole moment at the two different geometries must be supplied is always the same: "lower-energy", "higher-energy" independently of the type of calculation required (i.e. either absorption or emission)

If a HT calculation is requested the code also reads just after the first (2,3) matrix an additional matrix (3N,3) reporting the transition dipole derivatives. Specifically

-In $3 \times N$ lines $i = 1, 3 \times N$: $\frac{\mathbf{m}}{\partial q_i}$ as a 3S vector $\left(\frac{\partial m^x}{\partial q_i}, \frac{\partial m^y}{\partial q_i}, \frac{\partial m^z}{\partial q_i}\right)$, where $q_1 = x_1, q_2 = y_1, q_3 = z_1, q_4 = x_2, \dots$ etc.

7 Conventional choices for absorption and emission FC and HT spectra

As reported in section 2 the code treats the transition dipoles as a linear expansion of the final state normal coordinates expanded around the final-state equilibrium geometry (where they have the values $\boldsymbol{\mu}_0(2)$ and $\mathbf{m}_0(2)$, respectively). In principle these values are different from those taken at the equilibrium geometry of the initial state $\boldsymbol{\mu}_0(1)$ and $\mathbf{m}_0(1)$. Eq. 2 and 3 allow to get estimates for these values

$$\bar{\boldsymbol{\mu}}_0(1) = \boldsymbol{\mu}_0(2) + \sum_k m_k K_k \quad (12)$$

$$\bar{\mathbf{m}}_0(1) = \mathbf{m}_0(2) + \sum_k m_k K_k \quad (13)$$

The equalities $\bar{\boldsymbol{\mu}}_0(1) \equiv \boldsymbol{\mu}_0(1)$ and $\bar{\mathbf{m}}_0(1) \equiv \mathbf{m}_0(1)$ are never fulfilled unless the HT linear approximation is exact, which never happens in practical cases. This is the reason why both the sets of values $\boldsymbol{\mu}_0(1)$ and $\boldsymbol{\mu}_0(2)$, and $\mathbf{m}_0(1)$ and $\mathbf{m}_0(2)$ are requested in files F03 and F04, respectively. As already stressed, in files F03 and F04 the code reads first the transition dipole moments' values at the equilibrium geometry of the ground state and, after, those at the equilibrium geometry of the excited state. Notice that here the convention is different and we do not speak of "initial" and "final" states, but of "ground" and "excited" states. For an absorption calculation the initial state is the ground state, while the final state is the excited one, but the opposite is true for an emission calculation. Notice that, for the actual calculation of HT spectra, the code considers that the derivatives in input are independent on the geometry (linear-approximation is considered exact). Concerning the reference geometry for the transition dipole values always the final-state values are chosen (notice this is unconventional with respect

to traditional HT theory, but is perfectly equivalent if the linear approximation is exact; see below how to obtain conventional results, for other cases). When comparing absorption and emission calculations, the limits of the linear approximation must be taken in mind. The code writes in standard output the values $\bar{\boldsymbol{\mu}}_0(1)$ and $\bar{\mathbf{m}}_0(1)$ and compare them with $\boldsymbol{\mu}_0(1)$ and $\mathbf{m}_0(1)$. If the differences are too large, it must be considered that the HT approximation is probably not good enough and one should also include higher-order terms in the expansion. Taken this well in mind, let us see the convention adopted in the code

- For FC calculations the code uses the values of the transition dipole moments obtained at the ground state equilibrium geometry for absorption and at the excited-state equilibrium geometry, for emission. This is in line with the traditional FC and HT theories.
- for HT calculations the code uses the derivatives obtained at the excited equilibrium geometry and the transition dipole moment at the final-state equilibrium geometry. The reason for that is that method was conceived in order to be effective for large molecules, and its characteristics reflect this choice. In fact considering large systems, at the state of the art TD-DFT method allow the best compromise between accuracy and computational time, and for this reason the method has been implemented having in mind TD-DFT input data, even if is fully usable also with data obtained with different methods. Since in TD-DFT calculations excited-state frequencies are computed by numerical derivatives of the energy gradients at the excited-state equilibrium geometry, this calculation provides with no additional cost also the derivatives of the transition dipole moment at this geometry. This explains

the adopted convention. Notice however, that transition derivatives are read in cartesian coordinates, and then transformed to normal coordinates of the final state. As remembered, if the user uses TD-DFT calculation, she/he will probably prefer to supply derivatives computed at the excited-state equilibrium geometry. Nonetheless it is worthy to stress that if the user prefers to use, for absorption calculations, derivatives computed at the ground-state equilibrium geometry, this can be done without no problem, the code will express them in the normal coordinates of the excited state, but this is only a technicality and no error is introduced. (*Why a user should do that? Because the traditional HT theory is written according to an expansion around the equilibrium geometry of the initial state. On the other hand, while this is certainly true, the user should always remember that, if the two choices lead to significant different results, this means that HT approximation is not adequate, no matter what choice is performed*).

Some practical suggestions can be helpful (in the following ECD spectra are not explicitly named, they are a special case of "absorption" spectra, and therefore whatever is written for the latter applies also to the former). They are always based on the use of the estimated values $\bar{\mu}_0(1)$ and $\bar{\mathbf{m}}_0(1)$, which can be determined by the user, or through preliminary calculation with *FCclasses*, in the following we assume the user wants to use *FCclasses* to get $\bar{\mu}_0(1)$ and $\bar{\mathbf{m}}_0(1)$ (they can be retrieved in the standard-output file, where they are explicitly indicated like the ones to be used for HT theory based on initial-state geometry reference):

How to obtain fully coherent results for FC and HT absorption calculations. The user should preliminarily run an "emis-

sion" calculation. Just after starting, the code finds n estimated values of the transition dipole moments at the "initial" geometry through interpolation starting from the final geometry. Therefore it finds "excited-state geometry" values that are coherent (within the linear HT approximation) with the "ground-state geometry" values. The user can then use these new values at the "excited-state geometry" in the F03 and F04 files and run the "absorption" calculation. In this case the code will use values fully coherent with the traditional HT theory, where the FC contribution is exactly what the code computes in the "FC absorption" calculation.

How to obtain fully coherent results for FC and HT emission calculations. In a completely equivalent way, with respect to the previous point, the user should preliminarily run an "absorption" calculation. Just after starting, the code finds estimated values of the transition dipole moments at "initial" geometry starting from the final geometry. Therefore it finds the "ground-state geometry" values coherent (within the linear HT approximation) with the "excited-state geometry" values. The user can then use this new value at the "ground-state geometry" in the F03 and F04 files and run the "emission" calculation. In this case the code will use values fully coherent with the traditional HT theory, where the FC contribution is exactly what the code computes in the "FC emission" calculation.

How to obtain fully coherent absorption and emission HT results. Fully coherent absorption and emission spectra can only be computed adopting a single reference geometry. The user should choose one (between the two possible choice) reference geometry for the transition dipole moment and run a preliminary "emission"/"absorption"

calculation if one chooses the ground-state/excited-state geometry, and find coherent values for the transition dipole at the other reference excited-state/ground-state geometry. Then the user can use these sets of data (the ones at the chosen reference geometry and those interpolated at the other geometry) to run the desired calculations.

How to obtain the separated FC and "pure HT" spectra.

FC spectra are computed with the "FC" option. The code gives by default intensities with respect to the transition dipole moment computed at the initial state equilibrium geometry (in line with HT theory). Nonetheless FC lineshape is fully independent from the transition dipole moment values, since they simply give a scaling, pre-factor (see ref. [6]). The user can therefore obtain the FC contribution, according to any "convention" simply rescaling the spectrum.

A "pure HT" is defined like the HT spectrum where the FC contribution is set to zero. Two choices are possible. To obtain a "pure HT" spectrum where the transition dipole moments at the final equilibrium geometry is zero, simply set "0.0 0.0 0.0" in the first two lines of files F03 and F04 (notice that this choice is not the conventional HT one). If one wants to obtain a conventional "pure HT" spectrum it is the transition dipole moments at the initial equilibrium geometry that must be set to zero. To get this result in a absorption/emission calculation, the user should run a preliminary emission/absorption calculation setting the first/second line in file F03 and F04 "0.0 0.0 0.0", obtain by interpolation coherent values of the transition dipole at the excited-state equilibrium/ground-state equilibrium geometry and the use these value in files F03 and F04 and run a normal "HT" absorption/emission calculation.

8 Output

8.1 Standard Output

Standard output is very verbose and hopefully it is self explanatory. Here a very concise description is given.

- Data read from standard input and geometries read from input files F01 and F02 are printed out. Center of mass and principal axes of inertia are computed for each of the equilibrium structures of the two electronic states. If the center of mass does not coincide with the origin, the molecule is translated so to fulfill this condition. Displacements (named shifts in the output) are computed and printed out.
- Frequencies and normal modes from files F01 and F02 are printed out. Normal modes are printed both in cartesian and in mass-weighted cartesian coordinates (it is assumed that the normal modes are read according to Gaussian format see "Notes for the interface with GAUSSIAN"). Afterward some analysis is performed and reduced masses are printed for the two sets of normal coordinates.
- if an Herzberg-Teller (HT) calculation is requested, transition dipole moments and their derivatives are read from file F03 and printed out.
- Normal modes matrices T1 and T2 are re-orthogonalized according to Löwdin and then printed out.
- Duschinsky transformation matrix \mathbf{J} (GM in the code) and $\mathbf{J}^T\mathbf{J}$ are printed out.
- A long analysis of the normal modes follows. Modes of State 1 Q1 are

analyzed by projection on modes **Q2** and viceversa. A mode is labeled as

-”P” =pure if it is projected on a single mode of the other state by more than 0.90

-”M2” if it is projected on two modes of the other state by more than 0.90

-”M3” if it is projected on three modes of the other state by more than 0.90

-”M>3” if more than three modes of the other electronic state are needed to get a projection larger than 0.90

I_{xy} and C_{xy} with $x=1$ or 2 depending on the analyzed state ”2” or ”1” and $y=1,2,3$ report a further analysis of the Duschinsky mixing. To fix the ideas consider the normal modes **Q1** and project them onto **Q2**. Each line of the analysis refers to a mode $Q1_i$ of the set **Q1**. The three modes of the set **Q2** on which it is mainly projected are I21, I22, I23. The corresponding squared scalar products are C21, C22 and C23 respectively.

$DFR - I21$ is the frequency difference of $Q1_i$ and $Q2_{i21}$.

For each mode $Q1_i$ the columns $I90$, $I95$ and $I99$ indicate the number of **Q2** modes needed to get a projection of $Q1_i$ larger than 0.90, 0.95 and 0.99, respectively.

- Dimensionless displacements (or shifts) are printed out for the modes of both states and modes are sorted (only for analysis) in order of decreasing dimensionless displacements
- Only for analysis, modes are sorted in order of decreasing frequency coupling which is estimated by the inverse of the unidimensional (1D)

0-0 integral, supposing a "pure" mode with no displacement

- Transition dipole moment derivatives in normal coordinates with respect to **Q2** are reported. They are set to zero if a Franck-Condon (FC) calculation is requested. In that case the transition dipole moment is conventionally set to (1,0,0).
- Total intensity is computed according to the analytical sum rules derived in [6] for subsequent checks of the spectrum calculation convergence. Some checks are performed.
- 0-0 (C_0 class) Franck-Condon integral is printed out
- SUM FC reports the sum of the FC factors computed up to the current step of the calculation
- Vectors and matrices needed in recursion formulae for computation of excited states FC overlaps
- The analysis is reported for the determination of the needed mother states to take into account temperature effects
- For each mother state:
 - definition of the Core of **Q2** modes to project by more than 90 % the thermally excited **Q1** modes
 - if an excited mother state is considered, integrals $\langle \mathbf{w}' | \mathbf{0} \rangle$ are printed out
 - step for C_1 transitions (the absolute values of the FC overlaps are reported for each mode).
 - step for C_2 transitions

-steps for C_3 - C_7 transitions. For each class the analysis is reported for the determination of the vector of the maximum number of allowed quantum numbers for each mode of state 2 (\mathbf{W}_n^{\max} , here named "ennupla"). When an acceptable "ennupla" is obtained, the number of modes to be actually excited is reported. Afterward, the calculation is monitored printing out step-by-step the increase of the slowest index of the nested loops (referring to the considered modes of states 2). Also the number of computed integrals is printed out

For each class the sum of the FC factors, its analysis in energy, the sum of the FC factors up to the considered class, and the sum of the intensities (for HT calculations) are reported.

- Recovered fraction of the FC spectrum and, if an HT calculation is requested, also the FULL (FC+HT) spectrum. Notice that for full convergence these variables must be 1. Usually for values > 0.9 the shape of the convoluted spectrum is already fully converged and no relevant stick intensity is missing.

8.2 Auxiliary Output Files

- File Fort.8 **Stick Spectrum**

Transition energies and stick intensities are given in two columns (e_i, I_i) divided in sections: 0-0 (C_0) transition, C_1 transitions,... C_7 transitions. Transition energies $\omega_{\mathbf{w}2,\mathbf{w}1}$ are given in eV. Printed intensities are $p_{\mathbf{w}1}\omega_{\mathbf{w}2,\mathbf{w}1}|\langle\mathbf{w}1|\boldsymbol{\mu}_{e1,e2}|\mathbf{w}2\rangle|^2$ (absorption), $p_{\mathbf{w}1}\omega_{\mathbf{w}2,\mathbf{w}1}^3|\langle\mathbf{w}1|\boldsymbol{\mu}_{e1,e2}|\mathbf{w}2\rangle|^2$ (emission), $p_{\mathbf{w}1}\omega_{\mathbf{w}2,\mathbf{w}1}R^{e1,\mathbf{w}1,e2,\mathbf{w}2}$ (ECD), where frequencies are in eV, dipoles are in atomic units and Boltzmann weights are numbers. Only intensities above a given threshold (defined in routine "ennemme") are

reported. On the contrary, all computed intensities are utilized to evaluate the convoluted spectrum printed in file Fort.18.

- File Fort.9 **Stick Spectrum**

The same data reported in file Fort.8, but each single line (e_i, I_i) is preceded and followed by a line $(e_i, 0.0)$. It is useful for plotting stick intensities as bars with some Plot packages.

- File Fort.18 **Convoluted Spectrum**

For each mother state utilized in the computation of the spectrum (1 at $T=0$ K, > 1 when temperatures effect is included, see [5] for details) two columns are printed, respectively the transition energies (on the energy grid decided by input) and the convoluted spectrum. As reported in Section 5, the latter is obtained convoluting the stick intensities with a Gaussian or a Lorentzian (whose HWHM γ is given in input). For each mother state *FCclasses* prints the convoluted spectrum relative to: 0-0 (C_0) transition, C_1 transitions,.... C_7 transitions, and afterward it prints the total spectrum $C_0 + C_1 + C_2 + \dots C_7$. The last set of data is the total spectrum obtained by summing with Boltzmann weights the total spectrum for each mother state. More details on the adopted working expressions have been given in Section 5.

- File Fort.21 **Assignments**

In this file the most intense stick transitions (reported in file Fort.8) are assigned in terms of the number of quanta of the final state. The transitions are collected with respect to the classes they belong to.

9 Hints and Suggestions

- **When an HT calculation is needed?.** This is something one has to learn by experience. For absorption/emission, when the oscillator strength is small (say < 0.1) one should be cautious in using only FC, most of all if there are other states lying close in energy with larger oscillator strengths. Another thing to check is the variation of the oscillator strength divided by the excitation energy (or for ECD calculation simply of the rotatory strength) at the equilibrium geometry of the initial and final state. Sensible changes, let us say $> 10\text{-}20\%$ suggest to investigate possible HT effects.
- **Reliability of the results.** Always check the 0-0 FC overlap and determinant of the transformation matrix J in the standard-output file. If the former is very small $< 10^{-4}$ and the latter is far from 1, very probably something is wrong. In this case be sure that the rotation of the data of STATE1 is enabled (iopeu=1 in input). If the problem persists, check carefully that the order of the atoms in the two structures is the same. Notice that if large displacements exist between the two structures (example large amplitude motions) the problem can hardly be treated in cartesian coordinates.
- **Reduction of the symmetry in one of the two electronic states.** It can often happen that the symmetry in one of the two electronic states is higher than in the other. A typical example is a π molecule that is planar in the ground state and not planar anymore in the excited-state. These problems are intrinsically anharmonic since reduction of the symmetry can occur along a non-total symmetric mode, and equivalently for positive and negative displacements. This means that the

energy profile of the lower-symmetry (*ls*) electronic state along such a mode is a double-well with the barrier occurring at the higher-symmetry equilibrium structure of the other higher-symmetry *hs* electronic state. Brute force treatments, describing each state in its minimum, very often lead to poor convergence and/or unphysical results. One way to solve the problem is to follow Noojien [13] and/or resort to the use of internal coordinates [14]. This method is not yet implemented in *FCclasses*. The most crude way to face with these cases is to perform a constrained optimization of the *ls* state imposing the same symmetry of the *hs* state. The former will have negative frequencies. A rough idea of the spectrum shape can be obtained turning the negative frequencies into positive ones and checking that, hopefully, the spectral shape is not very dependent on the chosen values for these frequencies. However, please notice that in a time-dependent perspective, such a choice is better justified for slow low-frequency modes than for fast high-frequency ones.

- . **For Gaussian users:** set the freq=HPModes keyword.

10 Appendix: preparing input files from Gaussian outputs

10.1 Files F01 and F02

In this new release 2.1 of *FCclasses* we also distribute a small Fortran90 code that helps to prepare the F01 and F02 files starting from Gaussian outputs. Specifically, prep.fc.f90 is a small code that reads a modified output Gaussian file with a freq=HPmodes calculation for the ground/excited electronic state

and produces the file "F01" (or "F02") for *Fcclasses.f*. In the following the F01 or F02 file is simply named "state". Please notice that the user does not need to use this code and she/he can prepare the input files for *Fcclasses.f* according to her/his own convenience. The code, and an example of an input and output files are given in the directory "PREPFC"

`prep.fc.f90` can be compiled with any fortran compiler without any particular option

for fortran intel simply writes

```
ifort -o pre.fc.e prep.fc.f90
```

This creates an executable file `prep.fc.e`

It can be simply executed with the command

```
prep.fc.e < output-gaussian > state
```

(please notice that the names of output-files and state can be freely chosen)

In the present example the input file obtained cutting the Gaussian output file, and the "state" file are respectively

- output-s1
- state-porph-s1-ns-test

Running `prep.fc.e<output-s1>state` one should obtain a file identical to "state-porph-s1-ns-test". This latter is exactly the file "state-porph-s1-ns" given in the *FCclasses* directory of the distributed "fcclasses21.tar.bz2" file.

`prep.fc.e` also produces a file "masses" where the atoms' masses in amu are already written in the right order to be pasted in the *FCclasses* input file.

Notice that this only works for the most common atoms, reading the source file it is apparent how new atoms' data can be introduced. Of course the user can write down by her/himself these data without using the "masses" file.

The file output-gaussian can be easily generated cutting a Gaussian output file. In the example the file "output-gaussian" corresponding to the s1 excited state of porphyrin (adopted as a test example for *FCclasses*) has been given

First three line of "output-gaussian" must be written by the user. They report:

- First line: the number of atoms NA
- Second line: a scaling factor for frequencies: set 1.d0 to have no scaling
- Third line: an option "yes" or "no" to sort the atoms list according to a different order. The two "state" files for the initial and final states of the electronic transition must clearly consider the same order for the atom list. If this is not the case (Gaussian outputs generated without any precaution) this option allow to sort the atoms for one state , say STATE2 in order they have the same order they have in STATE1. If the user sets "no" no other data need to be specified (the case in the example). If the user sets "yes" he has to write a column of NA lines (from line 4 to line NA+3), each line reporting a single integer number "position(i)". At line "i" one should specify the new position in the new list "position(i)" of the atom that is number "i" in the old list.

After that, from line 4 to line NA+3 the user must report the molecular geometry taken from the Gaussian Output (The user must be careful to copy

the right "optimized geometry". It is the last printed one if an optimization is required. Moreover if "nosymm" is required in the Gaussian calculation, the geometry specified as "Input orientation" must be considered, otherwise the geometry specified as "Standard orientation" must be taken. In the following lines the part of the Gaussian output file reporting the normal coordinates (printed with the Freq=HPmodes keyword) must be pasted

Note for the preparation of the input file for \mathcal{FC} classes.

If the geometries of the two states are very similar (for example if one has been generated from the other with an "opt" calculation with the keyword "nosymm"), usually in \mathcal{FC} classes input file the "option for rotation" can be set to "0" (no rotation). Otherwise the user is advised to set it to "1". When the user finds a very small 0-0 FC integral (say $< 10^{-4}$) it is always the case to check the relative orientation of the two molecular structures

10.2 Files F03 and F04

File F03 contains the transition electric dipole at the ground-state and excited-state equilibrium geometry and its derivatives with respect to the cartesian coordinates (used only for HT calculations). Files F04 (used only for ECD calculations) contains the transition magnetic dipole at the ground-state and excited-state equilibrium geometry and its derivatives. The values of the transition dipoles can be simply retrieved by the Gaussian output. Derivatives can be obtained numerically by a proper sequence of Gaussian calculations. If the user is adopting TD-DFT, an excited-state frequency calculation is executed by computing numerical derivatives of the energy gradients. Such a calculation provides all the information for computing the transition dipoles derivatives at the excited-state geometry. Here we assume

that the user has run a Gaussian calculation for excited-state frequency on a optimized geometry (optimization has been run in previous calculation) and the output file is "Gaussian-output". To compute the derivatives of the electric transition dipole, execute the following Linux commands (enclosed by the parentheses [and])

- [grep -An "electric dipole" Gaussian-output > temp] (where the state of interest is n-1, i.e. for first excited state "-A2")
- [grep -v "electric dipole\|state\|- "- temp > el-dipoles]

If things work properly, file el-dipoles should contain $6N+1$ lines (if N is the number of atoms) each reporting the three x , y , z components of the transition electric dipole at a different geometry. The first line gives the dipole at the initial geometry reported in input (excited-state equilibrium) and the next $6N$ lines report the dipole at geometries obtained displacing sequentially a single coordinate (of the $3N$ $x_1, y_1, z_1, x_2, \dots, z_N$) by an amount $\pm\Delta = 10^{-3} \text{ \AA}$. Specifically, at line 2 x_1 is displaced to $x_1 + \Delta$, at line 3 it is $x_1 - \Delta$, at line 4 y_1 is displaced to $y_1 + \Delta$, and so on till at the last line $6N+1$ where z_n is displaced to $z_n - \Delta$. From these data numerical derivatives can be obtained trivially. However, it must be taken in mind that standard Gaussian output gives the dipoles with few decimal digits (4) which can lead to sensible accuracy problems for the derivatives. The user, if possible, should compile Gaussian in order to make it provide these data with more digits.

The same procedure can be followed for the magnetic dipole, by substituting of course the word "magnetic" to "electric" when executing the "grep" command. Remember in this case that the magnetic dipole values must be

divided by a factor "- 2" to obtain values consistent with the calculation of the rotatory strength according to Eq. 11.

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