5.6.8 Simplified TDA and TD-DFT

ORCA also supports calculations of excited states using the simplified Tamm-Dancoff approach (sTDA) by S. Grimme[633]. The sTDA is particularly suited to calculate absorption spectra of very large systems. sTDA as well as the simplified time-dependent density functional theory (sTD-DFT)[634] approach require a (hybrid) DFT ground state calculation. For large systems, using range-separated hybrid functionals (e.g. ωB97X) is recommended.[635] The sTD-DFT approach in particular yields much better electronic circular dichroism (ECD) spectra and should be used for this purpose.

Theoretical Background

A brief outline of the theory will be given in the following. For more details, please refer to the original papers[633, 634]. In the sTDA, the TDA eigenvalue problem from eq. (5.67) is solved using a truncated and semi-empirically simplified A' matrix. The trunctation negelects all excitations that are beyond the energy range of interest, except a few strongly coupled ones. The matrix elements from eq. (5.68) are simplified by neglecting the response of the density functional and by approximating the remaining two-electron integrals as damped Coulomb interactions between transition/charge density monopoles. In the following, the indices i, j denote occupied, a, b virtual and p, q either kind of orbitals.

$$A'_{ia,jb} = \delta_{ij}\delta_{ab}(\epsilon_a - \epsilon_i) + \sum_{A,B}^{N_{\text{atoms}}} (2q_{ia}^A \gamma_{AB}^K q_{jb}^B - q_{ij}^A \gamma_{AB}^J q_{ab}^B) \tag{5.73}$$

q_{pq}^A and q_{pq}^B are the transition/charge density monopoles located on atom A and B, respectively. These are obtained from Löwdin population analysis (see Sec. *Löwdin Population Analysis*). ϵ_p is the Kohn-Sham orbital energy of orbital p. γ_{AB}^K and γ_{AB}^J are the Mataga-Nishimoto-Ohno-Klopman damped Coulomb operators for exchange-type (K) and Coulomb-type (J) integrals, respectively.

$$\gamma_{AB}^J = \left(\frac{1}{(R_{AB})^\beta + (a_X\eta)^{-\beta}} \right)^{\frac{1}{\beta}} \tag{5.74}$$

$$\gamma_{AB}^K = \left(\frac{1}{(R_{AB})^\alpha + \eta^{-\alpha}} \right)^{\frac{1}{\alpha}} \tag{5.75}$$

Here, η is the arithmetic mean of the chemical hardness of atom A and B. α and β are the parameters of the method and are given by:

$$\alpha = \alpha_1 + a_x\alpha_2 \tag{5.76}$$

$$\beta = \beta_1 + a_x\beta_2 \tag{5.77}$$

For any global hybrid functional, α_1, α_2, β_1 and β_2 are identical. α and β then depend on the amount of Fock exchange (a_X) only. This is different for range-separated hybrid functionals where α_2 and β_2 are set to zero. α_1 and β_1 along with a value a_x for the sTDA treatment are individually fitted for each range-separated hybrid functional.[635] It can bee seen from eq. (5.73) that the method is asymptotically correct which is crucial for excitations of charge transfer type.

In sTD-DFT, eq. (5.66) is solved using the simplified matrices A' (see above) and B'.

$$B'_{ia,jb} = \sum_{A,B}^{N_{\text{atoms}}} (2q_{ia}^A \gamma_{AB}^K q_{bj}^B - a_X q_{ib}^A \gamma_{AB}^K q_{aj}^B) \tag{5.78}$$

This approach yields better transition dipole moments and therefore spectra but the method is more costly than sTDA (a factor of 2–5 for typical systems). The parameters used in sTDA and sTD-DFT are identical. There are **no** additional parameters fitted for this method.

Calculation Set-up

sTDA and sTD-DFT can be combined with any (restricted or unrestricted) hybrid DFT singlepoint calculation. Gradients and frequencies are **not** implemented! The methods can be invoked via the `%tddft` block. Table *Keyword list for sTDA and sTD-DFT.* gives a list of the possible keywords.

Table 5.6: Keyword list for sTDA and sTD-DFT.

Mode sTDA	Invokes a sTDA calculation
Mode sTDDFT	Invokes a sTD-DFT calculation
EThresh *value*	Energy threshold up to which CSFs are included (in eV)
PTLimit *value*	Energy threshold up to which CSFs beyond EThresh may be selected (in eV)
PThresh *value*	Selection criterion to include CSF beyond EThresh (in Eh)
axstda *value*	Fock exchange parameter used in sTDA/sTD-DFT calculation (for range-separated hybrids)
beta1 *value*	Constant part of J integral parameter β
beta2 *value*	a_X scaled part of J integral parameter β
alpha1 *value*	Constant part of K integral parameter α
alpha2 *value*	a_X scaled part of K integral parameter α
triplets true	Calculate singlet-triplet excitations (default: singlet-singlet)

The following example shows how to run such a sTDA calculation using the BHLYP functional if one is interested in all excitations up to 10 eV.

```
! bhlyp def2-SVP tightscf smallprint printgap nopop

%tddft
 Mode sTDA
 Ethresh 10.0
end

*xyz 0 1
  N     -1.726176    0.687742   -0.007335
  N      1.213763    0.735949   -0.027163
  N     -1.545188   -2.243058   -0.016803
  N      1.395005   -2.195166   -0.036972
  C      2.736733   -1.895646   -0.045209
  C      3.277248   -0.608637   -0.045175
  C      2.575908    0.605756   -0.036945
  C      0.977551    2.083559   -0.021690
  C     -0.288108    2.687287   -0.011220
  C     -1.529488    2.048274   -0.004419
  C     -3.067756    0.388045    0.001354
  H     -0.976948   -0.007843   -0.015911
  C     -3.608477   -0.899096    0.001258
  C     -2.907149   -2.113434   -0.007085
  C     -1.308388   -3.590806   -0.022331
  C     -0.042695   -4.194596   -0.032673
  C      1.198590   -3.555847   -0.039419
  H      0.645751   -1.499625   -0.028098
  C     -3.768181    1.641701    0.010433
  C     -2.832985    2.651061    0.006924
  C      2.228928    2.835679   -0.028158
  C      3.228183    1.912006   -0.037679
  C      3.437220   -3.149227   -0.053963
  C      2.502048   -4.158627   -0.050442
  C     -3.558669   -3.420017   -0.006390
  C     -2.559381   -4.343652   -0.015901
  H     -4.633051   -3.589818    0.000518
```

(continues on next page)

```
  H     -2.644718    -5.427990    -0.018393
  H     -0.016400    -5.285446    -0.035842
  H      2.681678    -5.229875    -0.055110
  H      4.519010    -3.247119    -0.061999
  H      4.366739    -0.548807    -0.052422
  H      2.314239     3.920088    -0.025633
  H      4.302487     2.081864    -0.044563
  H     -0.315062     3.778120    -0.007889
  H     -3.013895     3.722099     0.011827
  H     -4.849852     1.740964     0.018679
  H     -4.697992    -0.958441     0.008649
end
```

Replacing `Mode sTDA` by `Mode sTDDFT` will invoke a sTD-DFT calculation instead. This is shown in the next example in combination with the ωB97X functional and user specified parameters:

```
! wb97x def2-SVP tightscf smallprint printgap nopop

%tddft
 Mode sTDDFT
 Ethresh 10.0
 axstda  0.56
 beta1  8.00
 beta2  0.00
 alpha1 4.58
 alpha2 0.00
end

*xyz 0 1
  N     -1.726176     0.687742    -0.007335
  N      1.213763     0.735949    -0.027163
  N     -1.545188    -2.243058    -0.016803
  N      1.395005    -2.195166    -0.036972
  C      2.736733    -1.895646    -0.045209
  C      3.277248    -0.608637    -0.045175
  C      2.575908     0.605756    -0.036945
  C      0.977551     2.083559    -0.021690
  C     -0.288108     2.687287    -0.011220
  C     -1.529488     2.048274    -0.004419
  C     -3.067756     0.388045     0.001354
  H     -0.976948    -0.007843    -0.015911
  C     -3.608477    -0.899096     0.001258
  C     -2.907149    -2.113434    -0.007085
  C     -1.308388    -3.590806    -0.022331
  C     -0.042695    -4.194596    -0.032673
  C      1.198590    -3.555847    -0.039419
  H      0.645751    -1.499625    -0.028098
  C     -3.768181     1.641701     0.010433
  C     -2.832985     2.651061     0.006924
  C      2.228928     2.835679    -0.028158
  C      3.228183     1.912006    -0.037679
  C      3.437220    -3.149227    -0.053963
  C      2.502048    -4.158627    -0.050442
  C     -3.558669    -3.420017    -0.006390
  C     -2.559381    -4.343652    -0.015901
  H     -4.633051    -3.589818     0.000518
  H     -2.644718    -5.427990    -0.018393
  H     -0.016400    -5.285446    -0.035842
  H      2.681678    -5.229875    -0.055110
  H      4.519010    -3.247119    -0.061999
  H      4.366739    -0.548807    -0.052422
```

5.6. Excited States via RPA, CIS, TD-DFT and SF-TDA   **825**

```
  H      2.314239    3.920088   -0.025633
  H      4.302487    2.081864   -0.044563
  H     -0.315062    3.778120   -0.007889
  H     -3.013895    3.722099    0.011827
  H     -4.849852    1.740964    0.018679
  H     -4.697992   -0.958441    0.008649
end
```

For the range-separated hybrid functionals LC-BLYP, CAM-B3LYP, ωB97, ωB97X, ωB97X-D3 and ωB97X-D3BJ, parameters are available and will be used by default if one of these functionals is used. The way of specifying parameters as shown above is useful if there is a range-separated hybrid functional that has not been parametrized for sTDA yet. For very large systems (e.g. > 500 atoms), it may be useful to define an upper boundary PTLimit for the selection of configurations that are beyond EThresh (otherwise the whole configuration space will be scanned). This can be done as shown below:

```
! cam-b3lyp def2-SVP tightscf smallprint printgap nopop

%tddft
 Mode sTDDFT
 Ethresh 10.0
 PThresh 1e-4
 PTLimit 30
end

*xyz 0 1
  N     -1.726176    0.687742   -0.007335
  N      1.213763    0.735949   -0.027163
  N     -1.545188   -2.243058   -0.016803
  N      1.395005   -2.195166   -0.036972
  C      2.736733   -1.895646   -0.045209
  C      3.277248   -0.608637   -0.045175
  C      2.575908    0.605756   -0.036945
  C      0.977551    2.083559   -0.021690
  C     -0.288108    2.687287   -0.011220
  C     -1.529488    2.048274   -0.004419
  C     -3.067756    0.388045    0.001354
  H     -0.976948   -0.007843   -0.015911
  C     -3.608477   -0.899096    0.001258
  C     -2.907149   -2.113434   -0.007085
  C     -1.308388   -3.590806   -0.022331
  C     -0.042695   -4.194596   -0.032673
  C      1.198590   -3.555847   -0.039419
  H      0.645751   -1.499625   -0.028098
  C     -3.768181    1.641701    0.010433
  C     -2.832985    2.651061    0.006924
  C      2.228928    2.835679   -0.028158
  C      3.228183    1.912006   -0.037679
  C      3.437220   -3.149227   -0.053963
  C      2.502048   -4.158627   -0.050442
  C     -3.558669   -3.420017   -0.006390
  C     -2.559381   -4.343652   -0.015901
  H     -4.633051   -3.589818    0.000518
  H     -2.644718   -5.427990   -0.018393
  H     -0.016400   -5.285446   -0.035842
  H      2.681678   -5.229875   -0.055110
  H      4.519010   -3.247119   -0.061999
  H      4.366739   -0.548807   -0.052422
  H      2.314239    3.920088   -0.025633
  H      4.302487    2.081864   -0.044563
  H     -0.315062    3.778120   -0.007889
  H     -3.013895    3.722099    0.011827
```

```
  H     -4.849852    1.740964    0.018679
  H     -4.697992   -0.958441    0.008649
end
```

In this case, all excitations up to 10 eV are considered from the very beginning. Configurations between 10 and 30 eV are included if their coupling to the configurations below 10 eV is strong enough (in total larger than `PThresh`). All configurations beyond 14 eV are neglected. Note furthermore that for very large systems, using a functional with the correct asymptotic behaviour is very important (due to the fixed amount of GGA exchange, CAM-B3LYP does **not** provide this property).

The ORCA output will summarize the important properties of your calculation which allows you to check your input:

```
-------------------------------------------------------------------------------

                       ORCA sTD-DFT CALCULATION


                       please cite in your paper
 orginal sTDA method: S. Grimme, J. Chem. Phys. 138, 244104 (2013)
 range-separated sTDA: T. Risthaus, A. Hansen, S. Grimme, Phys. Chem. Chem. Phys.
                       16, 14408-14419 (2014)
 sTD-DFT approach:     C. Bannwarth, S. Grimme, Comp. Theor. Chem.
                       1040-1041, 45-53 (2014)


-------------------------------------------------------------------------------


spectral range up to (eV)       ...    10.000000
occ. MO cut-off (eV)            ...    -27.751992
virt. MO cut-off (eV)           ...    19.711835
perturbation threshold          ...    1.000e-04
CSF selection range up to (eV) ...    30.000000
MOs in sTD-DFT                   ...          150
occ. MOs in sTD-DFT             ...           55
virt. in sTD-DFT                 ...           95
calculate triplets         ...    no

Transforming dipole length integrals    ... (read-ok)(trafo-ok)
Transforming dipole velocity integrals ... (read-ok)(trafo-ok)
Transforming ang. momentum integrals    ... (read-ok)(trafo-ok)

SCF atom population (using active MOs):

   4.196    5.171    5.171    4.196    3.616    3.996    3.991    3.991    3.996    3.616
   3.616    0.796    3.996    3.991    3.991    3.996    3.616    0.796    3.893    3.893
   4.040    4.040    3.893    3.893    4.040    4.040    0.971    0.971    0.956    0.957
   0.957    0.956    0.971    0.971    0.956    0.957    0.957    0.956

Number of electrons in sTDA:  110.000

ax(DF)  :  0.3800
s^k     :  2.0000
beta  (J):  1.8600
alpha (K):  0.9000
```

The spectroscopic data is also printed out after the calculation has finished:

```
-------------------------------------------------------------------------------
        ABSORPTION SPECTRUM VIA TRANSITION ELECTRIC DIPOLE MOMENTS
-------------------------------------------------------------------------------
State   Energy  Wavelength  fosc        T2        TX        TY        TZ
        (cm-1)    (nm)                 (au**2)    (au)      (au)      (au)
```

```
------------------------------------------------------------------------------
    0    16964.7     589.5    0.000083715    0.00162     0.02872   -0.02828   -0.00022
    1    19477.4     513.4    0.001269789    0.02146    -0.09723   -0.10958    0.00035
    2    25753.4     388.3    1.245683315   15.92387     2.92682   -2.71234   -0.02807
    3    26309.7     380.1    1.402883697   17.55424     2.84893    3.07209   -0.01073
    4    30311.6     329.9    0.000000355    0.00000    -0.00146   -0.00131    0.00001
    5    32710.4     305.7    0.000000640    0.00001     0.00178   -0.00181    0.00000
    6    33285.3     300.4    0.349285082    3.45464     1.37427   -1.25134   -0.01315
    7    33622.4     297.4    0.097718276    0.95680     0.64724    0.73340   -0.00233
    8    34974.4     285.9    0.000000018    0.00000    -0.00024    0.00024    0.00024
    9    34994.6     285.8    0.000000073    0.00000    -0.00005   -0.00002    0.00082
   10    35723.1     279.9    0.000000022    0.00000    -0.00021   -0.00022   -0.00033
   11    35826.4     279.1    0.008160622    0.07499     0.00215   -0.00104    0.27383
   12    36282.4     275.6    0.000000000    0.00000    -0.00004    0.00000    0.00000
   13    37373.0     267.6    0.000000104    0.00000    -0.00067    0.00067   -0.00012
   14    37439.7     267.1    0.000000030    0.00000     0.00036    0.00037    0.00000
   15    38835.7     257.5    0.101992631    0.86460     0.63387    0.68029   -0.00240
   16    40111.9     249.3    0.000001866    0.00002    -0.00286    0.00267    0.00010
   17    40376.1     247.7    0.119778731    0.97663     0.72310   -0.67358   -0.00678
   18    41527.5     240.8    0.000000020    0.00000     0.00024    0.00031   -0.00000
   19    43202.8     231.5    0.000000006    0.00000     0.00015   -0.00014   -0.00008
   20    45265.3     220.9    0.000000008    0.00000     0.00013   -0.00014    0.00014
   21    46775.7     213.8    0.000000000    0.00000     0.00002    0.00003    0.00001
   22    49449.3     202.2    0.151078886    1.00582     0.73590   -0.68133   -0.00709
   23    51144.8     195.5    0.000000001    0.00000     0.00005   -0.00007    0.00003
   24    51371.9     194.7    0.000000069    0.00000    -0.00047   -0.00047   -0.00000
   25    53195.6     188.0    0.002581321    0.01598     0.00537   -0.00532   -0.12617
   26    53198.4     188.0    0.000000045    0.00000    -0.00031   -0.00038   -0.00020
   27    53341.2     187.5    0.065343188    0.40329     0.46944   -0.42767   -0.00298
   28    54136.6     184.7    0.006562015    0.03990     0.13280    0.14923   -0.00049
   29    54279.9     184.2    0.086565034    0.52502     0.49226    0.53170   -0.00183
   30    54285.4     184.2    0.078803195    0.47790    -0.46967   -0.50725    0.00179
   31    54351.4     184.0    0.000000001    0.00000     0.00005    0.00004   -0.00006
   32    54428.8     183.7    0.000000565    0.00000     0.00124    0.00137   -0.00011
   33    55214.4     181.1    0.130630885    0.77888     0.64617   -0.60109   -0.00629
   34    55671.1     179.6    0.000000219    0.00000     0.00083   -0.00077    0.00011
   35    56264.4     177.7    0.000000097    0.00000     0.00051    0.00055   -0.00000
   36    56499.9     177.0    0.013901825    0.08100    -0.19211   -0.20999    0.00072
   37    56694.8     176.4    0.000000005    0.00000    -0.00012   -0.00011    0.00000
   38    56885.1     175.8    0.000000018    0.00000    -0.00022   -0.00024   -0.00001
   39    57366.4     174.3    0.000144667    0.00083     0.01438    0.02497   -0.00003
   40    57498.6     173.9    0.000000213    0.00000    -0.00082    0.00074   -0.00002
  ...
```

5.6.9 Double-hybrid functionals and Doubles Correction

The program can compute a doubles correction to the CIS excitation energies. The theory is due to Head-Gordon and co-workers.[636] The basic idea is to compute a perturbative estimate (inspired by EOM-CCSD theory) to the CIS excited states that is compatible with the MP2 ground state energy. In many cases this is a significant improvement over CIS itself and comes at a reasonable cost since the correction is computed *a posteriori*. Of course, if the CIS prediction of the excited state is poor, the (D) correction – being perturbative in nature – cannot compensate for qualitatively wrong excited state wavefunctions.

In addition – and perhaps more importantly – the (D) correction is compatible with the philosophy of the double-hybrid functionals and should be used if excited states are to be computed with these functionals. The results are usually much better than those from TD-DFT since due to the large fraction HF exchange, the self-interaction error is much smaller than for other functionals and after the (D) correction the results do not suffer from the overestimation of transition energies that usually comes with increased amounts of HF exchange in TD-DFT calculations.

Since the calculations would require a fairly substantial integral transformation that would limit it to fairly small

molecules if no approximation are introduced we have decided to only implement a RI version of it. With this approximation systems with more than 1000 basis functions are readily within the reach of the implementation.

Since one always has a triad of computational steps: MP2-CIS solution-(D) correction, we have implemented several algorithms that may each become the method of choice under certain circumstances. The choice depends on the size of the system, the number of roots, the available main memory and the available disk space together with the I/O rate of the system. The formal cost of the (D) correction is $O(N^5)$ and its prefactor is higher than that of RI-MP2. In the best case scenario, the rate limiting step would be the calculation of the pair-contribution in the "U-term" which requires (for a closed-shell system) twice the effort of a RI-MP2 calculation *per state*.

The use of the (D)-correction is simple. Simply write:

```
! HF DEF2-SVP DEF2-SVP/C TightSCF
%cis dcorr n # n=1-4. The meaning of the four algorithms is
             # explained below.
   # algorithm 1 Is perhaps the best for small systems. May use a
   #             lot of disk space
   # algorithm 2 Stores less integrals
   # algorithm 3 Is good if the system is large and only a few
   #             states are calculated. Saves disk and main
   #             memory.
   # algorithm 4 Uses only transformed RI integrals. May be the
   #             fastest for large systems and a larger number
   #             of states
end
```

Table 5.7: Integral handling in various implementations of the (D) correction (i,j=occupied MOs, a,b=virtual MOs, Q=aux function; NumInt=numerical integration).

DCORR =	1	2	3	4
(ia|jb) integrals	Stored	Stored	Not stored	Not stored
(ij|ab) integrals	Stored	Not made	Not made	Not made
(ab|Q) integrals	Stored	Not made	Not made	Stored
(ij|Q) integrals	Stored	Stored	Stored	Stored
(ia|Q) integrals	Stored	Stored	Stored	Stored
Coulomb CIS	From (ia|jb)	From (ia|jb)	From (ia|Q)	From (ia|Q)
Exchange CIS	From (ij|ab)	RI-AO-direct	RI-AO-direct	From (ab|Q)
XC-CIS	Num. Int.	Num. Int.	Num. Int.	Num. Int.
V-term in (D)	From (ia|jb)	From (ia|jb)	From (ia|Q)	From (ia|Q)
U-term in (D)	From (ab|Q)	RI-AO-direct	RI-AO-direct	From (ab|Q)

Spin-component scaling versions of CIS(D) can be evoked in the %cis block by setting DOSCS TRUE and the four scaling parameters, as defined by Head-Gordon and co-workers [637], in the following order: same-spin indirect term (CTss), opposite-spin indirect term(CTos), same-spin direct term(CUss), and opposite-spin direct term(CUos). Note that this implementation only works for the version with the parameter $\lambda = 1$ as defined in Ref. [637]. The example below shows how to apply the SCS-CIS(D) version with $\lambda = 1$ whose usage has been advocated in Ref. [638]. The user is able to specify other scaling parameters.

```
%cis
dcorr      # n=1,2,3,4
doscs      true                      # set SCS-CIS(D) to true (default: false)
scspar     0.333, 1.2, 0.43, 1.24  #SCS-CIS(D) scaling parameters in this order
                                     CTss, CTos, CUss, CUos
end
```

Note the use of commas to separate the parameters. These parameters do not communicate with the SCS/SOS parameters set for ground-state SCS/SOS-MP2 in the %mp2 block.

> **ℹ Note**
>
> - CIS(D) is often a quite big improvement over CIS.
>
> - In all three involved code sections (MP2, CIS, (D)) the storage format FLOAT is respected. It cuts down use of disk and main memory by a factor of two compared the default double precision version. The loss of accuracy should be negligible; however it is – as always in science – better to double check.
>
> - The (ab|Q) list of integrals may be the largest for many systems and easily occupies several GB of disk space (hence algorithms 2 and 3). However, that disk-space is often well invested unless you run into I/O bottlenecks.
>
> - The (ia|jb) and (ij|ab) lists of integrals is also quite large but is relatively efficiently handled. Nevertheless, I/O may be a problem.
>
> - The cost of the (D) correction is $O(N^5)$ and therefore comparable to RI-MP2. Since there are quite a few things more to be done for (D) compared to RI-MP2, expect the calculations to take longer. In the most elementary implementation the cost is about two times the time for RI-MP2 for each root.
>
> - The (D) correction is compatible with the philosophy of the double-hybrid density functionals and should be used if these functionals are combined with TD-DFT. The program takes this as the default but will not enforce it. The (D) correction can be used both in a TD-DFT and TDA-DFT context.
>
> - In our implementation it is only implemented together with the RI approximation and therefore you need to supply an appropriate ("/C") fitting basis.
>
> - The program will automatically put the RI-MP2 module into operation together with the (D) correction. This will result in the necessary integrals becoming available to the CIS module.
>
> - Making the exchange contribution to the CIS residual vector in an RI-AO direct fashion becomes quite expensive for a larger number of states. It may be a good choice if only one or two excited states are to be calculated for a larger system.
>
> - Singlet-triplet excitations can be calculated by setting TRIPLETS TRUE in the %cis or %tddft blocks, respectively. The implementation has been tested for double hybrids in Ref. [639].
>
> - For spin-adapted triplets (TRIPLETS TRUE), the only option available currently is DCORR 1.
>
> - Spin-component and spin-opposite scaling techniques for double-hybrids within the TD- and TDA-DFT frameworks, as defined by Schwabe and Goerigk [640], can be evoked in the same way in the %tddft block as described for SCS-CIS(D) above. While user-defined parameters can be entered in such a way, a series of new functionals are available through normal keywords, which use the herein presented SCS/SOS-CIS(D) implementation. [266] See Sec. *Basic Usage* for a list of those functionals.
>
> - Usage of time-dependent double-hybrids should be cited as follows: For TD or TDA with any double hybrid,[641] TD-B2GPLYP,[642] TDA-PBE0-DH or TDA-PBE0-2,[643] TD-PBE0-DH, TD-PBE0-2, or TDA-B2GP-PLYP [640], TD-ωB2PLYP or TD-ωB2GPPLYP [270], TDA-ωB2PLYP or TDA-ωB2GPPLYP [639], TD(A)-RSX-QIDH or TD(A)-RSX-0DH [639], TDA-PBE-QIDH [268], TD-PBE-QIDH [644], TD(A)-DSD-BLYP or TD(A)-DSD-PBEP86 or many other spin-component-scaled double-hybrid functionals with TD(A)-DFT from 2017 [640], TD(A) ωB88PP86 or TD(A) ωPBEPP86 or many other spin-component and opposite scaled double hybrids with TD(A)-DFT from 2021 [266].
>
> - Note that SCS/SOS-CIS(D) is only automatically used when a TD(A)-DFT calculation is requested for the functionals from 2021 by Casanova-Páez and Goerigk. [266] In those instances, "doscs" has not to be set. SCS/SOS-CIS(D) is not automatically used for PWPB95, ωwB97X-2, or the DSD functionals.

5.6.10 Spin-orbit coupling

It also possible to include spin-orbit coupling between singlets and triplets calculated from TD-DFT by using quasi-degenerate perturbation theory (please refer to the relevant publication [601]), similarly to what is done in ROCIS. In order to do that, the flag DOSOC must be set to TRUE. The reduced matrix elements are printed and the new transition dipoles between all SOC coupled states are also printed after the regular ones. This option is currently still not compatible with double hybrids, but works for all other cases including CPCM. All the options regarding the SOC integrals can be altered in the %rel block, as usual.

```
%CIS DOSOC   TRUE END
```

Please have in mind that, as it is, you can only calculate the SOC between excited singlets and the spin-adapted triplets. There is no SOC starting from a UHF/UKS wavefunction. If you want more information printed such as the full SOC matrix or triplet-triplet couplings, please set a higher PRINTLEVEL.

SOC and ECPs

ORCA currently does not have SOC integrals for ECPs, and these are by default ignored in the SOC module. If you try to use ORCA together with ECPs, an abort message will be printed. If you absolutely need to use ECPs, for instance for embedded potentials, please use:

```
%TDDFT FORCEECP TRUE END
```

OBS.: Do not use ECPs in atoms where SOC might be important. In that case, always use all-electron basis functions or the results will not make sense.

5.6.11 Natural Transition Orbitals

Results of TD-DFT or CIS calculations can be tedious to interprete as many individual MO pairs may contribute to a given excited state. In order to facilitate the analysis while keeping the familiar picture of an excited state originating from essentially an electron being promoted from a donor orbital to an acceptor orbital, the concept of "natural transition orbitals" can be used.

The procedure is quite straightforward. For example, consider the following job on the pyridine molecule:

```
! PBE def2-SVP tightscf

%tddft
 nroots 5
 DoNTO   true       # flag to turn on generation of natural transition orbitals
 NTOStates 1,2,3  # States to consider for NTO analysis;
                   # if empty all will be done
 NTOThresh 1e-4   # threshold for printing occupation numbers
end

* xyz 0 1
  N      0.000000    0.000000    1.401146
  C      0.000000    1.146916    0.702130
  C      0.000000   -1.146916    0.702130
  C     -0.000000    1.205574   -0.702848
  C     -0.000000   -1.205574   -0.702848
  C      0.000000   -0.000000   -1.421344
  H     -0.000000    2.079900    1.297897
  H     -0.000000   -2.079900    1.297897
  H     -0.000000    2.179600   -1.219940
  H     -0.000000   -2.179600   -1.219940
  H      0.000000    0.000000   -2.525017
*
```

which results in:

```
-------------------------------------------
NATURAL TRANSITION ORBITALS FOR STATE    1
-------------------------------------------

Making the (pseudo)densities                        ... done
Solving eigenvalue problem for the occupied space  ... done
Solving eigenvalue problem for the virtual space   ... done
Natural Transition Orbitals were saved in example10.s1.nto
Threshold for printing occupation numbers 0.000100

 E=   0.157831 au      4.295 eV    34639.9 cm**-1
    20a -> 21a  : n=  0.99945993
    19a -> 22a  : n=  0.00018772
    18a -> 23a  : n=  0.00018562


-------------------------------------------
NATURAL TRANSITION ORBITALS FOR STATE    2
-------------------------------------------

Making the (pseudo)densities                        ... done
Solving eigenvalue problem for the occupied space  ... done
Solving eigenvalue problem for the virtual space   ... done
Natural Transition Orbitals were saved in example10.s2.nto
Threshold for printing occupation numbers 0.000100

 E=   0.158973 au      4.326 eV    34890.5 cm**-1
    20a -> 21a  : n=  0.99857289
    19a -> 22a  : n=  0.00054014
    18a -> 23a  : n=  0.00039643
    17a -> 24a  : n=  0.00029339


-------------------------------------------
NATURAL TRANSITION ORBITALS FOR STATE    3
-------------------------------------------

Making the (pseudo)densities                        ... done
Solving eigenvalue problem for the occupied space  ... done
Solving eigenvalue problem for the virtual space   ... done
Natural Transition Orbitals were saved in example10.s3.nto
Threshold for printing occupation numbers 0.000100

 E=   0.200016 au      5.443 eV    43898.4 cm**-1
    20a -> 21a  : n=  0.63243468
    19a -> 22a  : n=  0.36314467
    18a -> 23a  : n=  0.00120185
    17a -> 24a  : n=  0.00103035
    16a -> 25a  : n=  0.00063379
    15a -> 26a  : n=  0.00051555
    14a -> 27a  : n=  0.00040257
    13a -> 28a  : n=  0.00020605
    12a -> 29a  : n=  0.00013070
    11a -> 30a  : n=  0.00010297


----------------------------
TD-DFT/TDA-EXCITATION SPECTRA
----------------------------

Center of mass = (  0.0000,  0.0000,  0.0036)
Generating CIS transition densities                 ... done
```

```
--------------------------------------------------------------------------------
↪----------------
                  ABSORPTION SPECTRUM VIA TRANSITION ELECTRIC DIPOLE MOMENTS
--------------------------------------------------------------------------------
↪----------------
    Transition     Energy    Energy  Wavelength fosc(D2)      D2        DX       ␣
↪  DY        DZ
                   (eV)      (cm-1)    (nm)                 (au**2)    (au)      ␣
↪ (au)      (au)
--------------------------------------------------------------------------------
↪----------------
  0-1A  ->  1-1A   4.294795  34639.9   288.7   0.000000000  0.00000   0.00000   -
↪0.00000  -0.00000
  0-1A  ->  2-1A   4.325874  34890.5   286.6   0.003830922  0.03615   0.19012   ␣
↪0.00000   0.00000
  0-1A  ->  3-1A   5.442702  43898.4   227.8   0.019114326  0.14335   0.00000   -
↪0.37861   0.00000
  0-1A  ->  4-1A   6.579556  53067.7   188.4   0.017637721  0.10942   0.00000   ␣
↪0.00000   0.33078
  0-1A  ->  5-1A   6.739163  54355.0   184.0   0.007560799  0.04579  -0.00000   -
↪0.00000   0.21399
```

We see that there is a weakly allowed transition (STATE 2) that is essentially totally composed of a single NTO pair (20a→21a : n= 0.99857289), while the third excited state (S3) is strongly allowed and requires two NTO pairs for its description (20a→21a : n= 0.63243468 and 19a→22a : n= 0.36314467).

These orbitals are shown below. It is evident that the state 2 donor orbital (NTO20) is a nitrogen lone pair and the acceptor orbital is a $\pi*$ orbital of the ring. For the state 3 the two NTO donor orbitals are comprised of a nearly degenerate set of π orbitals (they would be degenerate in the parent benzene) and the acceptor orbitals are a pair of nearly degenerate $\pi*$ orbitals. It is evident from this example that by looking at the NTOs one can obtain a nicely pictorial view of the transition process, even if many orbital pairs contribute to a given excited state in the canonical basis.
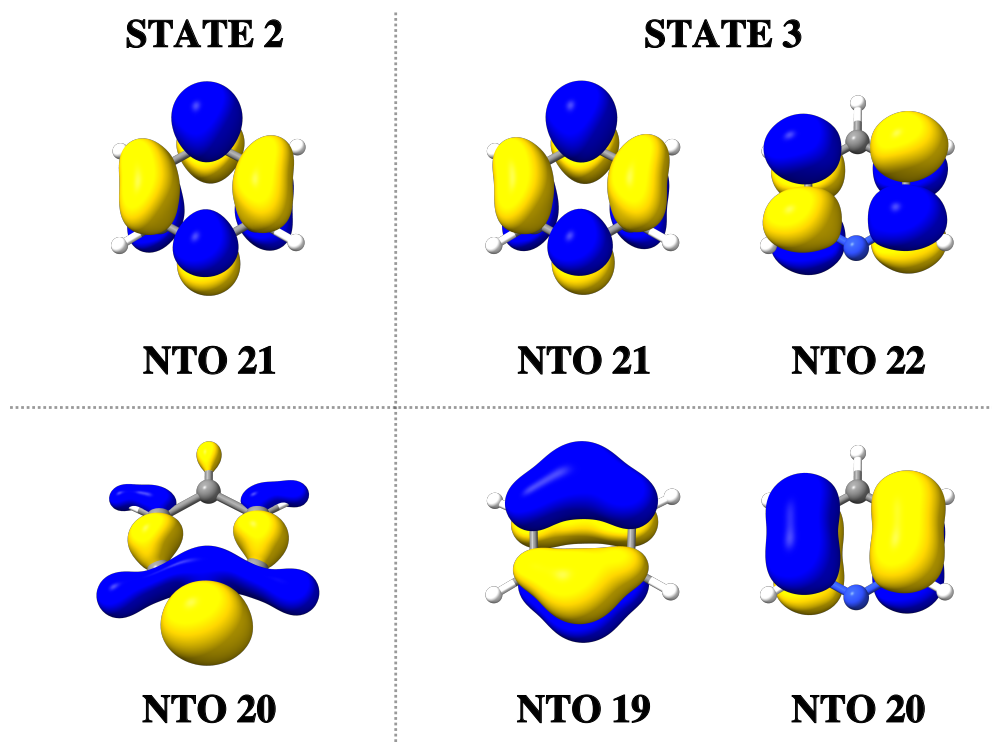

Fig. 5.22: Natural transition orbitals for the pyridine molecule in state 2 and state 3.

Similar analysis can be performed in the case of ROCIS and DFT/ROCIS calculations as it will be described in section *Natural Transition Orbitals/ Natural Difference Orbitals*.

5.6.12 Computational Aspects

RI Approximation (AO-Basis)

If the SCF calculation used the RI approximation it will also be used in the TD-DFT calculation. The RI approximation saves a large amount of time while giving close to identical results (the errors will usually be <0.1 eV) and is generally recommended. If the functional is a hybrid functional the RI-approximation will only be applied to the Coulomb term while the exchange will be treated as before. In the SCF you can use this feature with the keyword (`! RIJONX`). It will then also be used in the TD-DFT calculation. Again, the RIJCOSX approximation can be used in TD-DFT and CIS calculations and leads to very large speedups at virtually no loss in accuracy.

Integral Handling

If the SCF calculation is carried out in an integral direct fashion this will also be done in the CIS/TD-DFT calculation. Thus, no bottlenecks arising from large integral transformations or large disk space requirement arise in the calculations. An exception is the MO based RI approximations described in the previous section.

Valence versus Rydberg States

For valence excited states the usual orbital basis sets are reasonable. Thus, with polarized double-zeta basis sets sensible results are obtained. Especially DFT calculations have the nice feature of not being overly basis set dependent.

If Rydberg states are desired, you should make sure that diffuse functions are present in your basis set. You could always use the augmented-specific basis, e.g. DEF2-TZVPD, ma-DEF2-TZVP, or aug-cc-pVTZ, or add some extra diffuse basis to your regular basis. These can be added to any "normal" basis set. For example, the following example provides a rather high quality basis for excited state calculations that is based on the Ahlrichs basis set:

```
%basis
  # augment the carbon basis set by diffuse functions
  addgto 6
    s 1
      1 0.01 1.0
    p 1
      1 0.01 1.0
    d 1
      1 0.07 1.0
    end
end
```

> **Tip**
>
> If you want to augment a given basis set it is sensible to run a preliminary SCF calculation and use `%output print[p_basis] 2 end`. This will provide you with a detailed listing of basis functions and their exponents. You can then add additional s, p and perhaps d-functions with the `AddGTO` command as in the example above. It is sensible to decrease the exponent of the diffuse functions by roughly a factor of 3 from the smallest exponent in the original basis.

Restrictions for Range-Separated Density Functionals

Several restrictions apply for range-separated (hybrid as well as double-hybrid) density functionals. They are currently only implemented to work with the AO-based algorithm within the RIJONX, RIJCOSX, and NORI integral schemes. Additionally, the asymptotic correction has been disabled. However, the nuclear gradient for the excited states is now available, including for the triplets. Please no that the IROOTMULT flag must be set to TRIPLET under %CIS or %TDDFT in order to obtain that.

Printing Extra Gradients Sequentially

If you want to print extra gradients for external applications or any other reason, you can use the keywords SGRADLIST and TGRADLIST, for singlets and triplets. This will print the gradients sequentially after the CIS/TDDFT run. If you put 0 on the singlet list, the ground state gradient will also be added, always at the end.

```
%TDDFT SGRADLIST  0, 1, 2
       TGRADLIST  2, 3
END
```

In order to save this gradients in a text file, please use:

```
%METHOD STORECISGRAD TRUE END
```

5.6.13 Restarting TD-DFT Calculations

TD-DFT amplitudes are stored by default in the GBW file. This also means that TD-DFT calculations can be restarted, if a suitable GBW file is provided. The restart is relatively flexible. It allows for the geometry, basis set or density functional to change between the source and target calculation. However, the source calculation must at least have the same number of roots than the target calculation or more, fewer roots in the source is not allowed.
Here is a simple example:

```
* gzmt 0 1
  O
  H  1 1.0
  H  1 1.0 2 104.0
*

%compound
 New_Step
   ! B3LYP def2-SVP def2/J VeryTightSCF PModel
   %Base "FirstJob"
   %cis nroots   10
       triplets true
       tda      true
       end
  Step_end

  New_Step
   ! B3LYP def2-SVP def2/J VeryTightSCF
   %Base "SecondJob"
   %cis nroots   10
       triplets true
       tda      true
       Restart "FirstJob.gbw"
       end
  Step_end

endrun;
```

> **ℹ Note**
>
> - This is supposed to work for all combinations of TDA or RPA, singlets and triplets and also for spin-flip TD-DFT calculations.
>
> - We make several consistency checks but it will certainly be possible to create nonsensical inputs that will fail – please proceed with caution.

5.6.14 Use of TD-DFT for the Calculation of X-ray Absorption Spectra

In principle X-ray absorption spectra are "normal" absorption spectra that are just taken in a special high-energy wavelength range. Due to the high energy of the radiation employed (several thousand eV), core-electrons rather than valence electrons are excited. This has two consequences: a) the method becomes element specific because the core-level energies divide rather cleanly into regions that are specific for a given element. b) the wavelength of the radiation is so short that higher-order terms in the expansion of the light-matter interaction become important. Most noticeably, quadrupole intensity becomes important.

X-ray absorption spectra can be generally divided into three regions: a) the pre-edge that corresponds to transitions of core electrons into low lying virtual orbitals that lead to bound states. b) the rising edge that corresponds to excitations to high-lying states that are barely bound, and c) the extended X-ray absorption fine structure region (EXAFS) that corresponds to electrons being ejected from the absorber atom and scattered at neighbouring atoms.

With the simple TD-DFT calculations described here, one focuses the attention on the pre-edge region. Neither the rising edge nor the EXAFS region are reasonably described with standard electronic structure methods and no comparison should be attempted. In addition, these calculations are restricted to K-edges as the calculation of L-edges is much more laborious and requires a detailed treatment of the core hole spin orbit coupling.

It is clearly hopeless to try to calculate enough states to cover all transitions from the valence to the pre-edge region. Hence, instead one hand-selects the appropriate donor core orbitals and only allows excitations out of these orbitals into the entire virtual space. This approximation has been shown to be justified.[645] One should distinguish two situations: First, the core orbital in question may be well isolated and unambiguously defined. This is usually the case for metal 1s orbitals if there is only one metal of the given type in the molecule. Secondly, there may be several atoms of the same kind in the molecule and their core orbitals form the appropriate symmetry adapted linear combinations dictated by group theory. In this latter case special treatment is necessary: The sudden approximation dictates that the excitations occurs from a local core orbital. In previous versions of the program you had to manually localize the core holes. In the present version there is an automatic procedure that is described below.

A typical example is $TiCl_4$. If we want to calculate the titanium K-edge, the following input is appropriate:

```
! BP86 x2c x2c-SVPall x2c/J TightSCF

%tddft
 OrbWin[0] = 0,0,-1,-1
 NRoots 25
 DecomposeFosc true
 DoFullSemiclassical true
end

* int 0 1
 Ti 0 0 0  0 0 0
 Cl 1 2 3 2.15 0 0
 Cl 1 2 3 2.15 109.4712 0
 Cl 1 2 3 2.15 109.4712 120
 Cl 1 2 3 2.15 109.4712 240
*
```

> **ℹ Note**

- The absolute transition energies from such calculations are off by a few hundred electron volts due to the shortcomings of DFT. The shift is constant and very systematic for a given element. Hence, calibration is possible and has been done for a number of edges already. Calibration depends on the basis set!

- Electric quadrupole contributions and magnetic dipole contributions have been invoked with `DecomposeFosc true` (check section *One Photon Spectroscopy* for more information), which is essential for metal edges. For ligand edges, the contributions are much smaller.

- `OrbWin` is used to select the single donor orbital (in this case the metal 1s). The LUMO (45) and last orbital in the set (174) are selected automatically if "-1" is given. This is different from previous program versions where the numbers had to be given manually.

The output contains standard TD-DFT output:

```
--------------------------------------------------------------------------------
                 ABSORPTION SPECTRUM VIA TRANSITION ELECTRIC DIPOLE MOMENTS
--------------------------------------------------------------------------------
    Transition       Energy      Energy  Wavelength fosc(D2)      D2       DX
 DY         DZ
                      (eV)       (cm-1)    (nm)                 (au**2)   (au)
 (au)       (au)
--------------------------------------------------------------------------------
 0-1A  ->  1-1A   4864.738909 39236769.5    0.3   0.000000000   0.00000  -0.
00000   0.00000   0.00000
 0-1A  ->  2-1A   4864.738936 39236769.7    0.3   0.000000000   0.00000   0.
00000   0.00000  -0.00000
 0-1A  ->  3-1A   4865.587026 39243610.0    0.3   0.000378325   0.00000  -0.
00041   0.00173   0.00000
 0-1A  ->  4-1A   4865.587084 39243610.5    0.3   0.000378325   0.00000  -0.
00000  -0.00000   0.00178
 0-1A  ->  5-1A   4865.587090 39243610.6    0.3   0.000378325   0.00000   0.
00173   0.00041   0.00000
 0-1A  ->  6-1A   4868.943422 39270681.2    0.3   0.000000000   0.00000   0.
00000   0.00000   0.00000
 0-1A  ->  7-1A   4872.449970 39298963.4    0.3   0.000822318   0.00001   0.
00000  -0.00000  -0.00262
 0-1A  ->  8-1A   4872.450113 39298964.6    0.3   0.000822428   0.00001   0.
00168  -0.00202   0.00000
 0-1A  ->  9-1A   4872.450248 39298965.7    0.3   0.000822896   0.00001   0.
00202   0.00168  -0.00000
 0-1A  -> 10-1A   4873.185027 39304892.1    0.3   0.000000000   0.00000   0.
00000   0.00000  -0.00000
 0-1A  -> 11-1A   4873.752986 39309473.0    0.3   0.001152303   0.00001   0.
00035  -0.00309   0.00000
 0-1A  -> 12-1A   4873.753219 39309474.8    0.3   0.001152646   0.00001  -0.
00001   0.00000   0.00311
 0-1A  -> 13-1A   4873.753350 39309475.9    0.3   0.001152359   0.00001  -0.
00309  -0.00035  -0.00001
 0-1A  -> 14-1A   4873.877226 39310475.0    0.3   0.000000003   0.00000  -0.
00000   0.00000   0.00000
 0-1A  -> 15-1A   4873.877345 39310476.0    0.3   0.000000000   0.00000   0.
00000   0.00000   0.00000
 0-1A  -> 16-1A   4881.110098 39368812.1    0.3   0.000000000   0.00000  -0.
00000  -0.00000  -0.00000
 0-1A  -> 17-1A   4881.110123 39368812.3    0.3   0.000000000   0.00000  -0.
00000  -0.00000   0.00000
 0-1A  -> 18-1A   4883.621665 39389069.2    0.3   0.000014919   0.00000   0.
00021  -0.00029  -0.00000
```

```
 0-1A  -> 19-1A   4883.621737 39389069.8    0.3   0.000014917   0.00000   -0.
↪00000   0.00000  -0.00035
 0-1A  -> 20-1A   4883.621842 39389070.7    0.3   0.000014922   0.00000    0.
↪00029   0.00021  -0.00000
 0-1A  -> 21-1A   4884.177852 39393555.2    0.3   0.000158653   0.00000   -0.
↪00069   0.00092   0.00000
 0-1A  -> 22-1A   4884.178076 39393557.0    0.3   0.000158639   0.00000   -0.
↪00092  -0.00069   0.00001
 0-1A  -> 23-1A   4884.178104 39393557.2    0.3   0.000158643   0.00000   -0.
↪00001  -0.00001  -0.00115
 0-1A  -> 24-1A   4885.935396 39407730.7    0.3   0.000000000   0.00000    0.
↪00000   0.00000   0.00000
 0-1A  -> 25-1A   4885.941881 39407783.0    0.3   0.000000000   0.00000   -0.
↪00000  -0.00000   0.00000
```

One may obtain origin independent transition moments formulations which can be combined with the multipole moments up to 2nd order to regenerate the electric dipole, electric quadrupole and magnetic dipole contributions in either length or the velocity representations. This requires in addition to the electric dipole (D), electric quadrupole (Q) and magnetic dipole (m) intensities the corresponding electric dipole - magnetic quadrupole (DM) and the electric dipole - electric octupole (DO) intensities.[646][647]. See also section *Excited States with Restricted Open-shell CIS - ROCIS*.

These spectra are requested by:

```
DecomposeFosc   true
```

Check section *One Photon Spectroscopy* for more information.

Resulting in:

```
------------------------------------------------------------------------------
↪--------------------------------------------
                  ABSORPTION SPECTRUM COMBINED ELECTRIC DIPOLE + MAGNETIC␣
↪DIPOLE + ELECTRIC QUADRUPOLE SPECTRUM (Origin Independent, Length)
------------------------------------------------------------------------------
↪--------------------------------------------
   Transition      Energy    Energy  Wavelength fosc(D2)  fosc(M2)  fosc(Q2)␣
↪fosc(D2+M2+Q2+DM+DO) D2/TOT   M2/TOT   Q2/TOT
                    (eV)     (cm-1)    (nm)      (au)     (au*1e6)  (au*1e6)
------------------------------------------------------------------------------
↪--------------------------------------------
 0-1A  ->  1-1A   4864.738909 39236769.5    0.3    0.00000   0.00000   3.57414 ␣
↪ 0.00000357413611   0.00000   0.00000   1.00000
 0-1A  ->  2-1A   4864.738936 39236769.7    0.3    0.00000   0.00000   3.57419 ␣
↪ 0.00000357419113   0.00000   0.00000   1.00000
 0-1A  ->  3-1A   4865.587026 39243610.0    0.3    0.00038   0.00000   2.91269 ␣
↪ 0.00014515284191   2.60639   0.00000   0.02007
 0-1A  ->  4-1A   4865.587084 39243610.5    0.3    0.00038   0.00000   2.91280 ␣
↪ 0.00014514667816   2.60650   0.00000   0.02007
 0-1A  ->  5-1A   4865.587090 39243610.6    0.3    0.00038   0.00000   2.91281 ␣
↪ 0.00014515283005   2.60639   0.00000   0.02007
 0-1A  ->  6-1A   4868.943422 39270681.2    0.3    0.00000   0.00000   0.00000 ␣
↪ 0.00000000001034   0.12373   0.00000   0.00436
 0-1A  ->  7-1A   4872.449970 39298963.4    0.3    0.00082   0.00000  66.02903 ␣
↪ 0.00020716626448   3.96936   0.00000   0.31872
 0-1A  ->  8-1A   4872.450113 39298964.6    0.3    0.00082   0.00000  66.03525 ␣
↪ 0.00020716617979   3.96990   0.00000   0.31875
 0-1A  ->  9-1A   4872.450248 39298965.7    0.3    0.00082   0.00000  66.06697 ␣
↪ 0.00020743853075   3.96694   0.00000   0.31849
 0-1A  -> 10-1A   4873.185027 39304892.1    0.3    0.00000   0.00000   0.00000 ␣
↪ 0.00000000001255   1.59564   0.00000   0.11619
```

```
  0-1A  -> 11-1A   4873.752986 39309473.0    0.3      0.00115   0.00000   65.17922 ␣
↪ 0.00112267473065   1.02639   0.00000   0.05806
  0-1A  -> 12-1A   4873.753219 39309474.8    0.3      0.00115   0.00000   65.20318 ␣
↪ 0.00112279513057   1.02659   0.00000   0.05807
  0-1A  -> 13-1A   4873.753350 39309475.9    0.3      0.00115   0.00000   65.18429 ␣
↪ 0.00112283712761   1.02629   0.00000   0.05805
  0-1A  -> 14-1A   4873.877226 39310475.0    0.3      0.00000   0.00000   0.95985 ␣
↪ 0.00000096238863   0.00274   0.00000   0.99737
  0-1A  -> 15-1A   4873.877345 39310476.0    0.3      0.00000   0.00000   0.95957 ␣
↪ 0.00000096000219   0.00031   0.00000   0.99955
  0-1A  -> 16-1A   4881.110098 39368812.1    0.3      0.00000   0.00000   59.20440 ␣
↪ 0.00005920440172   0.00000   0.00000   1.00000
  0-1A  -> 17-1A   4881.110123 39368812.3    0.3      0.00000   0.00000   59.20493 ␣
↪ 0.00005920493511   0.00000   0.00000   1.00000
  0-1A  -> 18-1A   4883.621665 39389069.2    0.3      0.00001   0.00000   1.60824 ␣
↪-0.00004102527947  -0.36365  -0.00000  -0.03920
  0-1A  -> 19-1A   4883.621737 39389069.8    0.3      0.00001   0.00000   1.60871 ␣
↪-0.00004102945913  -0.36356  -0.00000  -0.03921
  0-1A  -> 20-1A   4883.621842 39389070.7    0.3      0.00001   0.00000   1.60930 ␣
↪-0.00004103096489  -0.36367  -0.00000  -0.03922
  0-1A  -> 21-1A   4884.177852 39393555.2    0.3      0.00016   0.00000   7.33000 ␣
↪-0.00001710675356  -9.27427  -0.00000  -0.42849
  0-1A  -> 22-1A   4884.178076 39393557.0    0.3      0.00016   0.00000   7.32938 ␣
↪-0.00001711175162  -9.27075  -0.00000  -0.42832
  0-1A  -> 23-1A   4884.178104 39393557.2    0.3      0.00016   0.00000   7.32928 ␣
↪-0.00001712730312  -9.26257  -0.00000  -0.42793
  0-1A  -> 24-1A   4885.935396 39407730.7    0.3      0.00000   0.00000   0.00000 ␣
↪-0.00000000000329  -1.98584  -0.00000  -0.11175
  0-1A  -> 25-1A   4885.941881 39407783.0    0.3      0.00000   0.00017   0.00000 ␣
↪ 0.00000000016832   0.01099   1.00335   0.00021
```

The multipole moments up to 2nd order:

- Only approximate origin independence is achieved by using the length approximation for distances from the excited atom up to about 5 Angstrom.

- Can form negative intensities which can be partly cured by using larger basis sets.

Starting from ORCA version 6.0 the full semi-classical ligth-matter interaction[647][648][649] can be computed by including the keyword:

```
DoFullSemiclassical true
```

Resulting in:

```
--------------------------------------------------------------------------
            ABSORPTION SPECTRUM VIA FULL SEMI-CLASSICAL FORMULATION
--------------------------------------------------------------------------
   Transition       Energy    Energy  Wavelength   fosc(FFMIO)
                      (eV)     (cm-1)    (nm)
--------------------------------------------------------------------------
  0-1A  ->   1-1A   4864.738909 39236769.5    0.3      0.00000225252009
  0-1A  ->   2-1A   4864.738936 39236769.7    0.3      0.00000225274848
  0-1A  ->   3-1A   4865.587026 39243610.0    0.3      0.00021278365996
  0-1A  ->   4-1A   4865.587084 39243610.5    0.3      0.00021278361154
  0-1A  ->   5-1A   4865.587090 39243610.6    0.3      0.00021278187385
  0-1A  ->   6-1A   4868.943422 39270681.2    0.3      0.00000000000237
  0-1A  ->   7-1A   4872.449970 39298963.4    0.3      0.00024200529569
  0-1A  ->   8-1A   4872.450113 39298964.6    0.3      0.00024205635341
  0-1A  ->   9-1A   4872.450248 39298965.7    0.3      0.00024227298357
  0-1A  -> 10-1A   4873.185027 39304892.1    0.3      0.00000000004292
  0-1A  -> 11-1A   4873.752986 39309473.0    0.3      0.00086416333614
```

5.6. Excited States via RPA, CIS, TD-DFT and SF-TDA

```
0-1A  -> 12-1A    4873.753219 39309474.8      0.3      0.00086431970479
0-1A  -> 13-1A    4873.753350 39309475.9      0.3      0.00086419143873
0-1A  -> 14-1A    4873.877226 39310475.0      0.3      0.00000011039866
0-1A  -> 15-1A    4873.877345 39310476.0      0.3      0.00000010856486
0-1A  -> 16-1A    4881.110098 39368812.1      0.3      0.00000159577723
0-1A  -> 17-1A    4881.110123 39368812.3      0.3      0.00000159558300
0-1A  -> 18-1A    4883.621665 39389069.2      0.3      0.00000254791052
0-1A  -> 19-1A    4883.621737 39389069.8      0.3      0.00000254735746
0-1A  -> 20-1A    4883.621842 39389070.7      0.3      0.00000254890168
0-1A  -> 21-1A    4884.177852 39393555.2      0.3      0.00008141388446
0-1A  -> 22-1A    4884.178076 39393557.0      0.3      0.00008141175909
0-1A  -> 23-1A    4884.178104 39393557.2      0.3      0.00008140437907
0-1A  -> 24-1A    4885.935396 39407730.7      0.3      0.00000000004646
0-1A  -> 25-1A    4885.941881 39407783.0      0.3      0.00000000003815
```

The full-semiclassical transition moments:

- Behave like the multipole expansion in the velocity representation.

- They are by definition origin independent they do not suffer from artificial negative values like the multipole moments beyond 1st order.

> **ⓘ Note**
>
> - For information on plotting the obtained spectra check *orca_mapspc*

Now, let us turn to the Cl K-edge. Looking at the output of the first calculation, we have:

```
---------------
ORBITAL ENERGIES
---------------

 NO   OCC         E(Eh)           E(eV)
  0   2.0000    -178.943613     -4869.3033
  1   2.0000    -101.066445     -2750.1578
  2   2.0000    -101.066399     -2750.1565
  3   2.0000    -101.066377     -2750.1559
  4   2.0000    -101.066372     -2750.1558
  5   2.0000     -19.810459      -539.0700
  6   2.0000     -16.410626      -446.5558
  7   2.0000     -16.410625      -446.5558
  8   2.0000     -16.410625      -446.5558
  9   2.0000      -9.272000      -252.3039
 10   2.0000      -9.271962      -252.3029
 11   2.0000      -9.271945      -252.3024
 12   2.0000      -9.271940      -252.3023
 ...
```

And looking at the energy range or the orbital composition, we find that orbitals 1 through 4 are Cl 1s-orbitals. They all have the same energy since they are essentially non-interacting. Hence, we can localize them without invalidating the calculation. To this end, you can invoke the automatic localization for XAS which modifies the input to:

```
! BP86 x2c x2c-SVPall x2c/J TightSCF

%tddft
 XASLoc[0] = 1,4
 OrbWin[0] = 1,1,-1,-1
 NRoots    25
 DecomposeFosc  true
 DoFullSemiclassical true
```

```
end

* int 0 1
 Ti 0 0 0  0 0 0
 Cl 1 2 3 2.15 0 0
 Cl 1 2 3 2.15 109.4712 0
 Cl 1 2 3 2.15 109.4712 120
 Cl 1 2 3 2.15 109.4712 240
*
```

> **ⓘ Note**
>
> - This localizes the orbitals 1 through 4 of operator 0 (the closed-shell) and then allows excitations (arbitrarily) from core hole 1 only. You could choose any of the three other localized 1s orbitals instead without changing the result. You could even do all four core holes simultaneously (they produce identical spectra) in which case you have the entire ligand K-edge intensity and not just the one normalized to a single chlorine (this would be achieved with `OrbWin[0] = 1,4,-1,-1`).
>
> - If you have a spin unrestricted calculation, you need to give the same `XASLoc` and `OrbWin` information for the spin-down orbitals as well.

The obtained Cl K-edge absorption is:

```
--------------------------------------------------------------------------------
→-----------------
                  ABSORPTION SPECTRUM VIA TRANSITION ELECTRIC DIPOLE MOMENTS
--------------------------------------------------------------------------------
→-----------------
   Transition      Energy    Energy  Wavelength fosc(D2)      D2        DX     ␣
→  DY        DZ
                    (eV)     (cm-1)    (nm)                 (au**2)    (au)    ␣
→ (au)     (au)
--------------------------------------------------------------------------------
→-----------------
  0-1A  ->  1-1A  2745.600263 22144761.9   0.5  0.000527911  0.00001   0.
→00000   0.00000   0.00280
  0-1A  ->  2-1A  2745.600291 22144762.1   0.5  0.000527960  0.00001  -0.
→00000  -0.00280   0.00000
  0-1A  ->  3-1A  2746.447743 22151597.3   0.5  0.000444357  0.00001   0.
→00001  -0.00257  -0.00000
  0-1A  ->  4-1A  2746.447798 22151597.7   0.5  0.000444395  0.00001   0.
→00000   0.00000  -0.00257
  0-1A  ->  5-1A  2746.458249 22151682.0   0.5  0.001391214  0.00002  -0.
→00455  -0.00000  -0.00000
  0-1A  ->  6-1A  2749.820836 22178803.1   0.5  0.000108586  0.00000  -0.
→00127   0.00000  -0.00000
  0-1A  ->  7-1A  2753.309672 22206942.5   0.5  0.000642499  0.00001  -0.
→00000  -0.00000  -0.00309
  0-1A  ->  8-1A  2753.309873 22206944.1   0.5  0.000643000  0.00001  -0.
→00004  -0.00309   0.00000
  0-1A  ->  9-1A  2753.320060 22207026.2   0.5  0.001717215  0.00003   0.
→00505  -0.00002  -0.00000
  0-1A  -> 10-1A  2753.907046 22211760.6   0.5  0.001737693  0.00003  -0.
→00507  -0.00000   0.00000
  0-1A  -> 11-1A  2754.608481 22217418.1   0.5  0.000027939  0.00000   0.
→00000   0.00064  -0.00000
  0-1A  -> 12-1A  2754.608709 22217419.9   0.5  0.000027879  0.00000  -0.
→00000   0.00000   0.00064
  0-1A  -> 13-1A  2754.709845 22218235.6   0.5  0.000149389  0.00000   0.
```

```
↪00149  -0.00001   0.00000
 0-1A  -> 14-1A   2754.736803 22218453.0    0.5   0.000681956   0.00001  -0.
↪00001  -0.00318   0.00000
 0-1A  -> 15-1A   2754.736928 22218454.0    0.5   0.000682692   0.00001  -0.
↪00000   0.00000   0.00318
 0-1A  -> 16-1A   2761.966240 22276762.4    0.4   0.000069982   0.00000   0.
↪00000  -0.00000   0.00102
 0-1A  -> 17-1A   2761.966265 22276762.6    0.4   0.000069999   0.00000   0.
↪00000   0.00102   0.00000
 0-1A  -> 18-1A   2764.478344 22297023.9    0.4   0.000309542   0.00000   0.
↪00000  -0.00214  -0.00001
 0-1A  -> 19-1A   2764.478355 22297024.0    0.4   0.000309644   0.00000   0.
↪00000  -0.00001   0.00214
 0-1A  -> 20-1A   2764.662301 22298507.6    0.4   0.000422965   0.00001  -0.
↪00250  -0.00000   0.00000
 0-1A  -> 21-1A   2765.033563 22301502.0    0.4   0.000115414   0.00000   0.
↪00000   0.00131  -0.00000
 0-1A  -> 22-1A   2765.033736 22301503.4    0.4   0.000115508   0.00000   0.
↪00000   0.00000   0.00131
 0-1A  -> 23-1A   2765.243962 22303199.0    0.4   0.000222110   0.00000  -0.
↪00181   0.00000   0.00000
 0-1A  -> 24-1A   2766.796424 22315720.5    0.4   0.000000384   0.00000   0.
↪00000  -0.00000   0.00008
 0-1A  -> 25-1A   2766.796522 22315721.3    0.4   0.000002667   0.00000   0.
↪00000   0.00020   0.00000
```

Quite nice results have been obtained for a number of systems in this way.[650]

5.6.15 Transient spectra

If one wants to compute transient spectra, or transition dipoles starting from a given excited state, the option DOTRANS must be set to TRUE and an IROOT should be given for the initial state (the default is 1). If `DOTRANS ALL` is requested instead, the transition dipoles between all states are computed. The transient transition dipoles will then be printed after the normal spectra. This option is currently only available for CIS/TDA and is done usng the expectation value formalism, as the other transition dipole moments in ORCA.

```
%cis
  DOTRANS  TRUE
          #or
  DOTRANS  ALL
end
```

5.6.16 Excited State Geometry Optimization

For RPA, CIS, TDA and TD-DFT the program can calculate analytic gradients. With the help of the `IRoot` keyword, a given state can be selected for geometry optimization. Note however, that if two states cross during the optimization it may fail to converge or fail to converge to the desired excited state (see section *Root Following Scheme for Difficult Cases* below)!

> ℹ **Note**
>
> • If you want to follow a triplet state instead of the singlet, please include `IROOTMULT TRIPLET`.

```
!def2-SVP Opt Freq
```