

# s T D A

A Program Package for computing excited states  
and response functions via simplified TD-DFT  
methods (sTDA, sTD-DFT, and SF-sTD-DFT)

Version 1.6.1

## User Manual

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## General Features and Requirements

- Extremely fast calculation of excited states and spectra via sTDA and sTD-DFT
- Ground state Kohn-Sham determinant from a hybrid DFT calculation is required
- Molden file serves as input (e.g. from TURBOMOLE, MOLPRO, TERACHEM)
  - `g2molden` tool available to interface with GAUSSIAN (see Sec. 5)
  - `qc2molden.sh` script available to interface with Q-CHEM (see Sec. 6)
- Ultrafast excited states in combination with extended tight-binding ground state procedure (sTDA-xTB)
- Linear and quadratic responses to compute dynamic (hyper)polarizabilities, two-photon absorption cross-sections, and excited-state absorption spectra in an ultrafast way
- Spin-flip version
- Natural transition orbitals

## 1 About the Program

The sTDA program can calculate excited states by the simplified time-dependent density functional theory (sTD-DFT)<sup>[1]</sup> as well as the simplified Tamm-Dancoff approximation to TD-DFT (sTDA)<sup>[2]</sup>. Originally, it has been developed as an add-on for the TURBOMOLE suite of programs<sup>[3,4]</sup>.

Since version 1.2, the program uses a Molden<sup>[5]</sup> input file that contains the Cartesian GTO basis as well as the molecular orbital coefficients. Molden files generated by TURBOMOLE, MOLPRO<sup>[6]</sup> and TERACHEM<sup>[7]</sup> can be processed. GAUSSIAN<sup>[8]</sup> can be used via the interfacing tool `g2molden` (see Sec. 5) and Q-CHEM<sup>[9]</sup> via `qc2molden.sh` (see Sec. 6).

We are interested in making the program compatible with different quantum chemistry program packages and are open for suggestions. However, in the present version the sTDA code can work with Cartesian GTO basis functions only and the quantum chemistry software must provide Cartesian basis functions.

Spectra may be computed with the SpecDis<sup>[10,11]</sup> program<sup>1</sup>. Alternatively, the provided plotting tool (`g_spec`, see below) may be used.

Since version 1.5, A+B/2-corrected<sup>[12]</sup> dipole velocity rotatory strengths are computed by default in sTDA calculations. Large parts of the code make use of OpenMP parallelization and the Intel MKL, thus setting the environmental variables `OMP_NUM_THREADS` and `MKL_NUM_THREADS` to the number of available CPUs may accelerate the calculations.

---

<sup>1</sup>We thank Dr. Torsten Bruhn for the interfacing.

With version 1.6, the sTDA program is now able to compute linear and quadratic response functions<sup>[13]</sup> to evaluate dynamic (hyper)polarizabilities, two-photon absorption cross-sections, and excited-state absorption spectra<sup>[14]</sup>.

Since version 1.6.1, a spin-flip version of the sTD-DFT method is implemented<sup>[15]</sup> as well as the natural transition orbital analysis<sup>[16]</sup>.

In the following, a short outline of the theory will be given followed by a documentation on the program.

## 2 Theoretical background

To compute excited states via sTDA (Sec. 2.1) or sTD-DFT (Sec. 2.2), a ground state Kohn-Sham (or Hartree-Fock) calculation needs to be carried out with one of the programs mentioned above. The orbitals obtained from this calculation are then used in the sTDA/sTD-DFT procedure. Instead of a Kohn-Sham reference, the orbitals may be obtained via the semi-empirical extended tight-binding (xTB) scheme (see Sec. 7).

### 2.1 Simplified Tamm-Dancoff approximation to TD-DFT

The time-dependent density functional theory (TD-DFT) response problem can be expressed as the following non-Hermitian eigenvalue problem<sup>[17]</sup>.

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \begin{pmatrix} \omega & 0 \\ 0 & -\omega \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} \quad (1)$$

In the Tamm-Dancoff approximation (TDA), the matrix  $\mathbf{B}$  is neglected<sup>[18]</sup> which leads to:

$$\mathbf{A}\mathbf{X}_{TDA} = \omega_{TDA}\mathbf{X}_{TDA} \quad (2)$$

Three simplifications then yield the simplified Tamm-Dancoff approach (sTDA)<sup>[2]</sup>:

1. Neglect the response of exchange-correlation functional
2. Evaluate the two-electron integrals as damped Coulomb interactions between transition/charge density monopoles
3. Restrict the configuration space to a user-specified energy range of excitations

In the following notation, the indices  $ijk$  refer to occupied,  $abc$  to virtual orbitals and  $pq$  to general orbitals (either occupied or virtual). The elements of the simplified matrix  $\mathbf{A}'$  are then given as:

$$A'_{ia,jb} = \delta_{ij}\delta_{ab}(\epsilon_a - \epsilon_i) + \sum_{A,B}^{N_{atoms}} (s_k q_{ia}^A \gamma_{AB}^K q_{jb}^B - q_{ij}^A \gamma_{AB}^J q_{ab}^B) \quad (3)$$

$q_{pq}^A$  and  $q_{pq}^B$  are the transition/charge density monopoles located on atom  $A$  and  $B$ , respectively. These are obtained from Löwdin population analysis<sup>[19]</sup>.  $\epsilon_p$  is the Kohn-Sham orbital energy of orbital  $p$ . In the spin-restricted case,  $s_k = 2$  for singlet-singlet and  $s_k = 0$  for singlet-triplet excitations.  $\gamma_{AB}^K$  and  $\gamma_{AB}^J$  are the Mataga-Nishimoto-Ohno-Klopman damped Coulomb operators for exchange-type ( $K$ ) and Coulomb-type ( $J$ ) integrals, respectively<sup>[20,21,22]</sup>.

$$\gamma_{AB}^J = \left( \frac{1}{(R_{AB})^\beta + (a_x \eta)^{-\beta}} \right)^{\frac{1}{\beta}} \quad (4)$$

$$\gamma_{AB}^K = \left( \frac{1}{(R_{AB})^\alpha + \eta^{-\alpha}} \right)^{\frac{1}{\alpha}} \quad (5)$$

Here,  $\eta$  is the arithmetic mean of the chemical hardness of atom  $A$  and  $B$ .  $\alpha$  and  $\beta$  are the global fit parameters of the method and are dependent on the amount of non-local Fock exchange  $a_x$  in the functional (see Ref. 2 for more details).

The matrix  $\mathbf{A}'$  includes all excitations up to a user-specified energy threshold (see Sec. 3). In order not to miss important configurations beyond this threshold, such configurations will be selected perturbatively:

$$E_{thr}^{(2)} \stackrel{!}{<} \sum_{ia} \frac{|A'_{ia,kc}|^2}{A'_{kc,kc} - A'_{ia,ia}} \quad (6)$$

For each excited configuration  $kc$ , the summed coupling to all excited configurations  $ia$  is evaluated (according to Eq. 6). The configuration  $kc$  refers to an excitation of an electron from the occupied orbital  $k$  to the virtual orbital  $c$  with a diagonal element  $A'_{kc,kc}$  larger than the energy threshold. On the other hand, the configurations  $ia$  have diagonal elements  $A'_{ia,ia}$  smaller than the threshold and are therefore included in the matrix  $\mathbf{A}'$  from the very beginning.

If the summed coupling of configuration  $kc$  with all configurations  $ia$  is larger than  $E_{thr}^{(2)}$ , the configuration  $kc$  will be included (default:  $E_{thr}^{(2)} = 10^{-4} E_h$ ).

## 2.2 Simplified Time-Dependent-Density Functional Theory

In the same simplified manner, the full TD-DFT problem (Eq. 1) can be solved<sup>[1]</sup>. The elements of the simplified matrix  $\mathbf{B}'$  are given as:

$$B'_{ia,jb} = \sum_{A,B}^{N_{atoms}} (s_k q_{ia}^A \gamma_{AB}^K q_{bj}^B - a_x q_{ib}^A \gamma_{AB}^K q_{aj}^B) \quad (7)$$

$a_x$  is the amount of non-local Fock exchange in the density functional (e.g. 0.2 for B3LYP). This approach has proven to yield more reliable transition moments and therefore better UV/VIS and ECD spectra than sTDA (see Ref. 1 for more information).

The  $\alpha$  and  $\beta$  parameters (see Eqs. 4 and 5) are identical in sTDA and sTD-DFT. Thus,  $\gamma_{AB}^J$  and  $\gamma_{AB}^K$  are the same in both approaches. The same is true for the dimension of the matrices  $\mathbf{A}'$  and  $\mathbf{B}'$ , i.e. the same configuration selection as in sTDA is performed.

### 2.3 Simplified Linear and Quadratic Response Theory

The linear-response matrix equation is similar to equation 1 when the perturbation is turned on by taking its first derivative with respect to the external applied electric field ( $\frac{\partial}{\partial F_\zeta}|_{\vec{F}=0}$ ):

$$\left[ \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix} - \omega \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \right] \begin{pmatrix} \mathbf{X}_\zeta(\omega) \\ \mathbf{Y}_\zeta(\omega) \end{pmatrix} = - \begin{pmatrix} \mu_\zeta \\ \mu_\zeta \end{pmatrix}, \quad (8)$$

where the derivative of the first-order perturbation of the density matrix defines the frequency-dependent response vectors  $\frac{\partial D_{ai}^{(1)}(\omega)}{\partial F_\zeta}|_{\vec{F}=0} = X_{\zeta,ai}(\omega) + Y_{\zeta,ai}(\omega)$  and where  $\mu_{\zeta,ai} = \langle \phi_a | \hat{\mu}_\zeta | \phi_i \rangle$ . In the sTD-DFT framework, the linear-response vectors<sup>[13]</sup> used to compute the polarizability and the first hyperpolarizability are obtained by solving equation 8:

$$\mathbf{X}'_\zeta(\omega) + \mathbf{Y}'_\zeta(\omega) = \frac{-2\mu_\zeta}{(\mathbf{A}' + \mathbf{B}') - \omega^2(\mathbf{A}' - \mathbf{B}')^{-1}}. \quad (9)$$

The polarizability is then determined by

$$\alpha'_{\zeta\eta}(-\omega; \omega) = -2 \sum_{ai} \mu_{\zeta,ai} (X'_{\eta,ai}(\omega) + Y'_{\eta,ai}(\omega)), \quad (10)$$

and the second-harmonic generation first hyperpolarizability in the sTD-DFT approximations reads

$$\beta'_{\xi\zeta\eta}(-2\omega; \omega, \omega) = A' - B', \quad (11)$$

$$A' = \sum_{perm.\xi,\zeta,\eta} \left\{ \sum_{aij} X'_{\xi,ai}(-2\omega) [-\mu_{\zeta,ij}] Y'_{\eta,aj}(\omega) \right\}, \quad (12)$$

$$B' = \sum_{perm.\xi,\zeta,\eta} \left\{ \sum_{iab} X'_{\xi,ai}(-2\omega) [-\mu_{\zeta,ab}] Y'_{\eta,bi}(\omega) \right\}, \quad (13)$$

where linear response vectors are determined for  $\omega$  and  $-2\omega$ . Two-photon absorption cross-sections are obtained by the single residue of the first hyperpolarizability and the state-to-state unrelaxed dipole moments by the double residue.

### 2.4 Simplified Spin-Flip TD-DFT

In the spin-flip formalism, only single excitations from the  $\alpha$  space to the  $\beta$  space are considered. For collinear functionals, exclusively the  $(i_\alpha j_\alpha | a_\beta b_\beta)$  two-electron integrals remain and the SF-sTD-DFT<sup>[15]</sup> eigenvalue equation becomes:

$$\mathbf{A}'^{\alpha \rightarrow \beta} \mathbf{X}^{\text{SF}} = \omega \mathbf{X}^{\text{SF}}, \quad (14)$$

were

$$A'_{i_\alpha a_\beta, j_\alpha b_\beta}{}^{\alpha \rightarrow \beta} = \delta_{i_\alpha j_\alpha} \delta_{a_\beta b_\beta} (\epsilon_{a_\beta} - \epsilon_{i_\alpha}) - (i_\alpha j_\alpha | a_\beta b_\beta )'_{\alpha \rightarrow \beta}. \quad (15)$$

For simplified spin-flip two-electron integrals, the damped Coulomb operator takes the form:

$$\Gamma_{AB}^{\alpha \rightarrow \beta} = \left( \frac{1}{(R_{AB})^{y_{\alpha \rightarrow \beta}} + (1.4 \times a_x \eta)^{-y_{\alpha \rightarrow \beta}}} \right)^{\frac{1}{y_{\alpha \rightarrow \beta}}}, \quad (16)$$

where

$$y_{\alpha \rightarrow \beta} = a_x + 0.3. \quad (17)$$

From the sTD-DFT state-to-state transition dipole moment expression<sup>[14]</sup>, its spin-flip analogue reads

$$\langle m | \mu_\xi - \langle 0 | \mu_\xi | 0 \rangle | n \rangle_{SF} = \frac{\sqrt{2}}{2} \left\{ \sum_{a_\beta i_\alpha j_\alpha} \left[ X_{i_\alpha a_\beta}^n \mu_{i_\alpha j_\alpha, \xi} X_{j_\alpha a_\beta}^m \right] - \sum_{a_\beta b_\beta i_\alpha} \left[ X_{i_\alpha a_\beta}^n \mu_{a_\beta b_\beta, \xi} X_{b_\beta i_\alpha}^m \right] \right\}. \quad (18)$$

Additionally, a spin-flip version of the tight-binding sTD-DFT-xTB method<sup>[12]</sup> has been implemented. Here, the effective Fock exchange parameter in the sTDA part is changed to  $a_x = 0.36$ , whereas  $y_{\alpha \rightarrow \beta} = 3.0$ . For clarity, it is noted that the monopole correction  $\Delta_K$  for the “exchange-type” (Coulomb response) integrals is zero in SF-sTD-DFT-xTB. The vTB and xTB parts remain unchanged compared to the original formulation for open shell systems.<sup>[12]</sup>

## 3 Program Options

### 3.1 Mandatory Input Features

`-f <molden.input>`

Chooses a Molden input file that provides the GTO and MO data. In the case of TURBOMOLE, this file is created by the conversion tool `tm2molden`. Since there is no unique way to specify the GTO and MO data (i.e. the format depends on the program which generates the input), an input check is performed. Molden files generated from TURBOMOLE, MOLPRO, TERACHEM, GAUSSIAN (via `g2molden`, see below) or Q-CHEM (via `qc2molden.sh`, see below) can be processed.

Before starting an actual calculation, it is important to check whether the program correctly reads in your Molden file. Do this by executing it as:

`stda -f <molden.input> -chk`

This will perform a check of input read in (by means of a Mulliken population analysis) and print out the `-sty` flag to be used in the actual calculation. By default, `-sty 1` is used which is compatible with TURBOMOLE. From our experience the flag `-sty 2` works for MOLPRO inputs, while `-sty 3` works for both TERACHEM, GAUSSIAN (via `g2molden`, see below) or Q-CHEM (via `qc2molden.sh`, see below) input files.

After you ran the check, you can run the actual calculation by running the program without the `-chk` flag, but using the respective `-sty` flag as well as the options presented below.

`-ax <amount of Fock exchange>`

Specifies the amount of Fock exchange in the density functional (e.g. `-ax 0.25` for PBE0).

`-e <Ethr>`

This specifies the energy threshold (in eV) for configurations to be considered in the sTDA or sTD-DFT procedure. Important configurations beyond the threshold are selected by perturbation theory and added to the configuration space (see Ref. 2 for details). The default value is 7 eV and it is recommended to adjust this threshold depending on the energy range of interest.

## 3.2 Optional Features

`-p <Pthr>`

Defines the selection criterion used to select important configurations beyond the energy threshold `<Ethr>`. E.g. a an input of `-p 5` corresponds to  $E_{thr}^{(2)} = 10^{-5} E_h$  (see Eq. 6).

`-lpt <PTmax>`

For very large systems, it might be useful to restrict the space that is scanned to select important configurations. The flag above specifies the energy threshold (in eV) for configurations to be considered. Obviously, it must always be larger than `<Ethr>`. By default, all excitations are considered, but this may be adjusted to e.g., `<PTmax> = 3 · <Ethr>` in case it is necessary.

`-al <alpha> -be <beta>`

This provides user-defined parameters for  $\alpha$  and  $\beta$  which are used in the calculation of  $\gamma_{AB}^K$  and  $\gamma_{AB}^J$ , respectively. By default, they are calculated from the amount of Fock exchange and the standard parameters for global hybrid functionals<sup>[2]</sup>. It is wise to change these parameters for range-separated hybrid functionals. Parameters for five widely available range-separated hybrid functionals can be found in Ref. 23 (see also Sec. 3.3.2).

`-t`



Calculate singlet-triplet excitations (using a spin-restricted ground state).

**-rpa**

This invokes the sTD-DFT procedure instead of the default sTDA<sup>[1]</sup>.

It is possible to get the eigenvectors printed out (in TURBOMOLE format). This is achieved by:

**-vectm <#vec>**

Depending on the method (sTDA or sTD-DFT), this creates the files `ciss.a`, `cist.a`, `sing.a` or `trip.a` and prints out the lowest eigenvectors up to `<#vec>` (i.e., `-vectm 5` will print out the five lowest eigenvectors). If no number is specified, all eigenvectors that were determined are printed, but one should keep in mind that this can lead to very huge files!

**-xtb**

Invoke sTDA-xTB calculation scheme (see Sec. 7). In this case, the `xtb4stda` binary wavefunction file (`wfn.xtb`) is read instead of a Molden input file. The respective parameters  $\alpha$ ,  $\beta$ , and  $a_x$  are set automatically.

**-oldtda**

In the case of sTDA calculations (i.e., `-rpa` is NOT set), this keyword requests to compute the dipole velocity rotatory strengths from sTDA in the “traditional” fashion, i.e., simply from the  $\mathbf{X}_{TDA}$  eigenvector. Since version 1.5, by default the A+B/2 corrected vector is used instead (for details, see Ref.<sup>[12]</sup>), which allows to reliably compute electronic circular dichroism spectra even for systems that are otherwise problematic for Tamm-Dancoff approximated methods<sup>[24]</sup>.

**-resp <#wav>**

To compute sTD-DFT frequency-dependent polarizabilities and second-harmonic generation first hyperpolarizabilities, you need a file called `wavelength` in your directory with desired wavelengths. Specify the number of wavelengths after the `-resp` argument. The `-resp` argument implies the `-rpa` argument. Use a slightly larger energy window than for excited states (above 10 eV, 15 eV seems doing great).

**-aresp <#wav>**

The same as the previous argument but to compute sTD-DFT frequency-dependent

polarizabilities only.

`-2PA <#exc>`

To compute sTD-DFT two-photon absorption cross-sections, just specify the number of states you want after the `-2PA` argument. Note that you need to use a larger energy window than for excited states calculation since the quality of the response vectors are dependent of the truncation of (A+B) and (A-B) matrices. This option is still for testing purpose only since the two-photon induced transitions are not so well described by the monopole approximation. Improvements are under investigation.

`-s2s <#state>`

To compute an excited-state absorption spectrum using unrelaxed state-to-state transition dipole moments, use the `-s2s` argument followed by the reference state number.

`-sf`

To use the SF-sTD-DFT method<sup>[15]</sup> with a high-spin reference. First-SF-state-to-SF-state transitions are computed as well.

`-nto <#state>`

To compute natural transition orbitals for the `#state` first states. All NTOs are computed in molden files where the orbital energy parameter is in fact the weight of this pair of NTOs. A `jmol.spt` script file may be used with `jmol` to generate all NTOs pictures. Then, one can easily visualize them by opening the `NTOs.html` file.

`-rw`

Saving some memory by writing on the disc large temporary files when running a restricted calculation.

### 3.3 Exemplary Procedure

#### 3.3.1 Using a global hybrid functional

Perform a Kohn-Sham DFT ground state calculation with a hybrid density functional. In this example, we assume a PBE0 calculation was performed with TURBOMOLE. Then run

`tm2molden`

and make sure that the GTO/MO data is written into the Molden input file (here:

pbe0.molden.inp). Let us assume that we are interested in all excitations up to 6 eV. The sTDA program is called by:

```
stda -f pbe0.molden.inp -ax 0.25 -e 6 > output
```

We pipe the standard output into the file `output`. The program also writes the file `tda.dat` which contains for each state the transition energy and the length and velocity representations of the oscillator and rotatory strengths (in  $10^{40}$  erg · cm<sup>3</sup>), respectively.

### 3.3.2 Using a range-separated hybrid functional

If we have Molden input file from e.g. an  $\omega$ B97X single-point calculation (here: `wb97x.molden.inp`), the respective sTDA calculation can be performed as:

```
stda -f wb97x.molden.inp -ax 0.56 -be 8.00 -al 4.58 -e 10 > output
```

The sTDA parameters ( $\alpha$ ,  $\beta$ , and  $a_x$ ) for this range-separated hybrid functional are taken from Tab. 1 in Ref. 23.

Note that  $\alpha^{(1)}$  given therein corresponds to  $\beta$  and  $\beta^{(1)}$  to  $\alpha$  (according to Eqs. 4 and 5). Thus for  $\omega$ B97X, the parameter used to calculate  $\gamma_{AB}^J$  is  $\beta = 8.00$ .

To perform a sTD-DFT calculation with the same set-up, just add the `-rpa` flag:

```
stda -f wb97x.molden.inp -ax 0.56 -be 8.00 -al 4.58 -e 10 -rpa > output
```

So far, five range-separated hybrid functionals were parametrized. The parameters are given below:

| functional       | $a_x$ | $\alpha$ | $\beta$ |
|------------------|-------|----------|---------|
| CAM-B3LYP        | 0.38  | 0.90     | 1.86    |
| LC-BLYP          | 0.53  | 4.50     | 8.00    |
| $\omega$ B97     | 0.61  | 4.41     | 8.00    |
| $\omega$ B97X    | 0.56  | 4.58     | 8.00    |
| $\omega$ B97X-D3 | 0.51  | 4.51     | 8.00    |

## 4 The Spectrum Plotting Tool

Spectra may be plotted and visualized with the SpecDis program. Alternatively, we provide a processing tool called `g_spec`. It uses the file `tda.dat` (written by the sTDA program) as input. Run the tool as:

```
g_spec < tda.dat
```

It will generate two files, `spec.dat` and `rots.dat`. The first file contains the spectrum broadened by Gaussian curves, the latter one contains the pure oscillator/rotatory

strengths that can be used to plot a stick spectrum.

The header of the `tda.dat` defines the options for `g.spec`. Important features are:

|         |   |
|---------|---|
| UV      | Calculate absorption spectra (if not specified, CD is calculated)                 |
| VELO    | Use the velocity representations of R and f (the latter if UV is also specified). |
| NM      | Plot spectrum in nanometer scale instead of eV.                                   |
| WIDTH   | Half width at 1/e maximum of Gaussian curve (in eV).                              |
| SHIFT   | Energy shift applied to whole spectrum (in eV).                                   |
| LFAKTOR | Scaling factor for the stick spectrum printed to <code>rots.dat</code> .          |
| RFAKTOR | Scaling factor for the broadened spectrum printed to <code>spec.dat</code> .      |

The Gaussian broadened spectrum (`spec.dat`) contains the molar extinction coefficient (for absorption) or molar circular dichroism (for CD) spectra, both given in units of  $\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ . The individual transition strengths are given in the same units in `rots.dat`. Note that by default LFAKTOR is set to 0.5, i.e., these are scaled down to allow easy plotting of broadened spectra with individual transition strengths.

## 5 Usage with GAUSSIAN 09

From version 1.3 on, the sTDA program can be interfaced with the GAUSSIAN 09 program<sup>[8]</sup> via the tool `g2molden`. This converts a GAUSSIAN 09 output file into a Molden<sup>[5]</sup> input file which is processible by the sTDA program. Make sure that the following keywords in your GAUSSIAN 09 input file are set:

|                        |   |
|------------------------|---|
| #P                     | Additional printout (necessary for <code>g2molden</code> ). |
| ginput                 | Print out basis set information.                            |
| pop=full or I0p(6/7=3) | Print out LCAO-MO coefficients.                             |
| 6D 10F                 | Use Cartesian basis to generate orbitals.                   |

The last point is necessary since the sTDA program can only handle Cartesian atomic orbitals. An exemplary input for the calculation with GAUSSIAN (on a water molecule) may look like this:

```
#P B3LYP/TZVP pop=full ginput 6D 10F
```

```
water singlepoint
```

```
O 1 xyz
H 0.000000 0.776483 -0.472981
H 0.000000 -0.776483 -0.472981
O 0.000000 0.000000 0.118245
```

After running the ground-state calculation with GAUSSIAN 09, you may convert the output file (termed `g09.log` here) into a Molden input file by:

```
g2molden g09.log > molden.input
```

The `molden.input` file may be used as an input file for the `sTDA` program as described above (using `-sty 3`, see Sec. 3). If you encounter problems with the `g2molden` tool or the `sTDA` program, feel free to contact us. However, we cannot give any support for problems related to GAUSSIAN itself.

## 6 Usage with Q-CHEM 5.1

A molden file can be automatically generated by Q-CHEM using the following arguments in the `$rem` section of your input file:

```
PRINT_ORBITALS = 2000000
MOLDEN_FORMAT = true
PURECART = 2222
```

`PRINT_ORBITALS` is the maximum number of orbitals printed, it needs to be very large to have all orbitals printed. `PURECART = 2222` specified that a Cartesian orbital basis set is used in the calculation. The molden file generated by Q-CHEM cannot be directly read by `sTDA`. The `qc2molden.sh` script extracts and converts the molden file. Just run `qc2molden.sh your_qchem_output` and a `molden.input` file is generated. The `-sty 3` argument needs to be used when running `sTDA`.

## 7 sTDA-xTB Procedure

The `sTDA` approach has recently been combined with a semi-empirical extended tight-binding (xTB) procedure for the ground state (for details see Ref. 12). The xTB calculation can be carried out with the standalone `xtb4stda` which can be obtained along with the necessary parameter files from our GitHub page.<sup>[25]</sup>

### 7.1 xTB Options

The `xtb4stda` program then requires a geometry file (Xmol or TURBOMOLE coord) as input.

```
xtb <coord>
```

The program will then write a binary file `wfn.xtb` which can be read from the `stda` program no additional input is required. For charged systems, a `.CHRG` file containing the molecular charge in the first line need to be present in the local directory. Similarly for open-shell systems, the number of unpaired electrons can be specified in the `.UHF` file. For additional options, run the `xtb` program with the `-h` flag.

## 7.2 sTDA based on xTB

After running the ground state calculation with xTB, the `stda` program can be used to compute the excited states via:

```
stda -xtb -e 10
```

This will read the `wfn.xtb` file in the working directory and compute all excited states up to 10 eV. The method-specific parameters  $\alpha$ ,  $\beta$ , and  $a_x$  are set automatically. Due to computational efficiency, we recommend to use the Tamm-Dancoff approximated variant (i.e., sTDA-xTB) although the full linear response (i.e., sTD-xTB) treatment may be invoked with the `-rpa` flag. Due to the  $A+B/2$  correction,<sup>[12]</sup> which is invoked by default in sTDA, even electronic circular dichroism spectra in the origin independent dipole velocity formalism may be computed reasonably well with sTDA-xTB.

## References

- [1] C. Bannwarth, S. Grimme, A simplified time-dependent density functional theory approach for electronic ultraviolet and circular dichroism spectra of very large molecules, *Comput. Theor. Chem.* 1040 – 1041 (2014) 45 – 53.
- [2] S. Grimme, A simplified Tamm–Dancoff density functional approach for the electronic excitation spectra of very large molecules, *J. Chem. Phys.* 138 (2013) 244104.
- [3] R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, Electronic structure calculations on workstation computers: The program system turbomole, *Chem. Phys. Lett.* 162 (1989) 165–169.
- [4] TURBOMOLE V6.5 2013, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989–2007, TURBOMOLE GmbH, since 2007; available from <http://www.turbomole.com>.
- [5] G. Schaftenaar, J. H. Noordik, Molden: a pre- and post-processing program for molecular and electronic structures, *J. Comput.-Aided Mol. Design* 14 (2000) 123–134, see <http://www.cmbi.ru.nl/molden>.
- [6] H.-J. Werner, P. J. Knowles, R. Lindh, F. R. Manby, M. Schütz, P. Celani, T. Korona, G. Rauhut, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, C. Hampel, G. Hetzer, A. W. Lloyd, S. J. McNicholas, W. Meyer, M. E. Mura, A. Nicklass, P. Palmieri, R. Pitzer, U. Schumann, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson, Molpro, version 2006.1, a package of ab initio programs, see <http://www.molpro.net>.
- [7] PetaChem. [www.petachem.com](http://www.petachem.com) (accessed on 28.10.14).
- [8] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji,

M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09 Revision D.01, Gaussian Inc. Wallingford CT 2009.

- [9] Y. Shao, Z. Gan, E. Epifanovsky, A. T. Gilbert, M. Wormit, J. Kussmann, A. W. Lange, A. Behn, J. Deng, X. Feng, D. Ghosh, M. Goldey, P. R. Horn, L. D. Jacobson, I. Kaliman, R. Z. Khaliullin, T. Kuś, A. Landau, J. Liu, E. I. Proynov, Y. M. Rhee, R. M. Richard, M. A. Rohrdanz, R. P. Steele, E. J. Sundstrom, H. L. W. III, P. M. Zimmerman, D. Zuev, B. Albrecht, E. Alguire, B. Austin, G. J. O. Beran, Y. A. Bernard, E. Berquist, K. Brandhorst, K. B. Bravaya, S. T. Brown, D. Casanova, C.-M. Chang, Y. Chen, S. H. Chien, K. D. Closser, D. L. Crittenden, M. Diedenhofen, R. A. D. Jr., H. Do, A. D. Dutoi, R. G. Edgar, S. Fatehi, L. Fusti-Molnar, A. Ghysels, A. Golubeva-Zadorozhnaya, J. Gomes, M. W. Hanson-Heine, P. H. Harbach, A. W. Hauser, E. G. Hohenstein, Z. C. Holden, T.-C. Jagau, H. Ji, B. Kaduk, K. Khistyayev, J. Kim, J. Kim, R. A. King, P. Klunzinger, D. Kosenkov, T. Kowalczyk, C. M. Krauter, K. U. Lao, A. D. Laurent, K. V. Lawler, S. V. Levchenko, C. Y. Lin, F. Liu, E. Livshits, R. C. Lochan, A. Luenser, P. Manohar, S. F. Manzer, S.-P. Mao, N. Mardirossian, A. V. Marenich, S. A. Maurer, N. J. Mayhall, E. Neuscamman, C. M. Oana, R. Olivares-Amaya, D. P. O'Neill, J. A. Parkhill, T. M. Perrine, R. Peverati, A. Prociuk, D. R. Rehn, E. Rosta, N. J. Russ, S. M. Sharada, S. Sharma, D. W. Small, A. Sodt, T. Stein, D. Stück, Y.-C. Su, A. J. Thom, T. Tsuchimochi, V. Vanovschi, L. Vogt, O. Vydrov, T. Wang, M. A. Watson, J. Wenzel, A. White, C. F. Williams, J. Yang, S. Yeganeh, S. R. Yost, Z.-Q. You, I. Y. Zhang, X. Zhang, Y. Zhao, B. R. Brooks, G. K. Chan, D. M. Chipman, C. J. Cramer, W. A. G. III, M. S. Gordon, W. J. Hehre, A. Klamt, H. F. S. III, M. W. Schmidt, C. D. Sherrill, D. G. Truhlar, A. Warshel, X. Xu, A. Aspuru-Guzik, R. Baer, A. T. Bell, N. A. Besley, J.-D. Chai, A. Dreuw, B. D. Dunietz, T. R. Furlani, S. R. Gwaltney, C.-P. Hsu, Y. Jung, J. Kong, D. S. Lambrecht, W. Liang, C. Ochsenfeld, V. A. Rassolov, L. V. Slipchenko, J. E. Subotnik, T. V. Voorhis, J. M. Herbert, A. I. Krylov, P. M. Gill, M. Head-Gordon, *Advances in molecular quantum chemistry contained in the q-chem 4 program package*, *Molecular Physics* 113 (2) (2015) 184–215.
- [10] T. Bruhn, A. Schaumlöffel, Y. Hemberger, G. Bringmann, *SpecDis: Quantifying the Comparison of Calculated and Experimental Electronic Circular Dichroism Spectra*, *Chirality* 25 (2013) 243–249.

- [11] [http://www-organik.chemie.uni-wuerzburg.de/en/research\\_groups/bringmann/specdis](http://www-organik.chemie.uni-wuerzburg.de/en/research_groups/bringmann/specdis).
- [12] S. Grimme, C. Bannwarth, Ultra-fast computation of electronic spectra for large systems by tight-binding based simplified Tamm-Dancoff approximation (sTDA-xTB), *J. Chem. Phys.* 145 (2016) 054103.
- [13] M. de Wergifosse, S. Grimme, Nonlinear-response properties in a simplified time-dependent density functional theory (std-dft) framework: Evaluation of the first hyperpolarizability, *J. Chem. Phys.* 149 (2) (2018) 024108.
- [14] M. de Wergifosse, S. Grimme, Nonlinear-response properties in a simplified time-dependent density functional theory (std-dft) framework: Evaluation of excited-state absorption spectra, *J. Chem. Phys.* 150 (2019) 094112.
- [15] M. de Wergifosse, C. Bannwarth, S. Grimme, A simplified spin-flip time-dependent density functional theory (sf-std-dft) approach for the electronic excitation spectra of very large diradicals, *J. Phys. Chem. A* 123 (27) (2019) 815–5825.
- [16] M. de Wergifosse, J. Seibert, B. Champagne, S. Grimme, Are fully conjugated expanded indenofluorenes analogues and diindeno[n]thiophene derivatives diradicals? a simplified (spin-flip) time-dependent density functional theory [(sf)-std-dft] study, *J. Phys. Chem. A* 123 (45) (2019) 9828–9839.
- [17] M. E. Casida, Time-dependent density functional response theory for molecules, in: D. P. Chong (Ed.), *Recent Advances in Density Functional Methods*, Vol. 1, World Scientific, Singapore, 1995, pp. 155–192.
- [18] S. Hirata, M. Head-Gordon, Time-Dependent Density Functional Theory within the Tamm-Dancoff Approximation, *Chem. Phys. Lett.* 314 (1999) 291–299.
- [19] P.-O. Löwdin, On the Non-Orthogonality Problem Connected with the Use of Atomic Wave Functions in the Theory of Molecules and Crystals, *J. Chem. Phys.* 18 (1950) 365–375.
- [20] K. Nishimoto, N. Mataga, Electronic Structure and Spectra of Some Nitrogen Heterocycles, *Z. Phys. Chem.* 12 (1957) 335–338.
- [21] K. Ohno, Some Remarks on the Pariser-Parr-Pople Method, *Theor. Chim. Acta* 2 (1964) 219–227.
- [22] G. Klopman, A Semiempirical Treatment of molecular Structures. II. Molecular Terms and Application to diatomic Molecules, *J. Am. Chem. Soc.* 86 (1964) 4550–4557.
- [23] T. Risthaus, A. Hansen, S. Grimme, Excited States using the simplified Tamm-Dancoff-Approach for Range-Separated Hybrid Density Functionals: Development and Application, *Phys. Chem. Chem. Phys.* 16 (2014) 14408–14419.



- [24] C. Bannwarth, S. Grimme, Electronic Circular Dichroism of Highly Conjugated  $\pi$ -Systems: Breakdown of the Tamm–Dancoff/Configuration Interaction Singles Approximation, *J. Phys. Chem. A* 119 (2015) 3653–3662.
- [25] <https://github.com/grimme-lab/xtb4stda>.