

***VEMGAUSS:***  
**A Program Incorporating the VEM and SMSSP Models  
to Calculate Vertical Electronic Excitation or Emission Energies in  
Solution from *Gaussian 09* Output**

**Users Manual**

Version 2013

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Aleksandr V. Marenich, Christopher J. Cramer, and Donald G. Truhlar

*Department of Chemistry, Chemical Theory Center, and Supercomputing Institute*

*University of Minnesota*

*Minneapolis, MN 55455-0431, U. S. A.*

Distribution site: <https://comp.chem.umn.edu/vemgauss>

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## 1. Licensing

*VEMGAUSS* - version 2013 is licensed under the [Apache License, Version 2.0](#).  
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Publications of results obtained with the *VEMGAUSS* - version 2013 software should cite the program and/or the article describing the program.

No guarantee is made that this software is bug-free or suitable for specific applications, and no liability is accepted for any limitations in the mathematical methods and algorithms used within. No consulting or maintenance services are guaranteed or implied.

The use of the *VEMGAUSS* - version 2013 implies acceptance of the terms of the licenses.

## 2. Executive summary

*VEMGAUSS* is a package containing a C Shell script and a Fortran program to carry out a calculation by the Vertical Excitation/Emission Model (VEM) [Marenich, A. V.; Cramer, C. J.; Truhlar, D. G.; Guido, C. A.; Mennucci, B.; Scalmani, G.; Frisch, M. J. *Chem. Sci.* **2011**, 2, 2143-2161]. The VEM is a model for calculating the vertical excitation (absorption) or vertical emission energy in solution according to a two-time-scale model of solvent polarization. The abbreviation VEM originally referred to the vertical excitation model [Li, J.; Cramer, C. J.; Truhlar, D. G. *Int. J. Quantum Chem.* **2000**, 77, 264-280] but with the *VEMGAUSS* program it can be used for both excitation and emission calculations in solution, and the E in VEM now stands for excitation/emission.

Optionally, *VEMGAUSS* can augment the VEM calculation of the two-time-scale bulk-electrostatic contribution to the vertical excitation or emission energy in solution by an SMSSP calculation of the solute–solvent dispersion contribution.

To run a VEM calculation, *VEMGAUSS* employs *Gaussian 09*'s output file from an excited electronic state calculation using the Polarizable Continuum Model (PCM) (either IEFPCM or CPCM) and the configuration interaction singles (CIS) method or time-dependent density functional theory (TDDFT). The TDDFFT calculations can be done using either full TDDFFT or the Tamm-Dancoff approximation to TDDFT (TDDFT-TDA). This requires the user to have a *Gaussian 09* executable (Revision A or later for CIS and full TDDFT and Revision D for TDDFT-TDA) installed. The *VEMGAUSS* program does not require *Gaussian 09* source code, nor does it make any modifications to *Gaussian 09* code. *Gaussian 09* licenses are available from Gaussian, Inc., and *VEMGAUSS* is available from the University of Minnesota: <https://comp.chem.umn.edu/vemgauss>

### 3. Theoretical details

#### 3.1. Definition of VEM

The VEM model is a self-consistent state-specific vertical excitation or emission model for electronic excitation in solution. The present implementation of VEM can also be used for either absorption energy or emission energy calculations in liquid-phase solution. The VEM model allows for a calculation of the bulk electrostatic (solvent dielectric polarization) contribution to solvatochromic shifts using either the generalized Born (GB) approximation or by solving the nonhomogeneous-dielectric Poisson equation for bulk electrostatics according to the PCM algorithm. The *VEMGAUSS* program uses the PCM version of the VEM which is denoted more explicitly as VEM(d,RD)/PCM in our 2011 VEM paper (please see this article for a full derivation):

- Marenich, A. V.; Cramer, C. J.; Truhlar, D. G.; Guido, C. A.; Mennucci, B.; Scalmani, G.; Frisch, M. J. Practical computation of electronic excitation in solution: vertical excitation model. *Chem. Sci.* **2011**, 2, 2143-2161.  
DOI: <http://dx.doi.org/10.1039/C1SC00313E>

In the case of excitation energy calculations by *VEMGAUSS*, the initial state is the ground electronic state and the final state is any excited state. In the case of emission energy calculations, the initial state is an excited electronic state and the final one is the ground electronic state. Excited states can be treated only by TDDFT, TDDFT-TDA, or CIS in the present version of the model. The excited state can be a singlet or a triplet, and the ground state should be a closed-shell singlet.

#### 3.2. Nonequilibrium solvation

The VEM model includes nonequilibrium solvation based on two-time-scale solvent response. The solvent's polarization is described in terms of the reaction field partitioned into slow and fast components, and only the fast component is self-consistently (iteratively) equilibrated with the charge density of the solute molecule in its final state. During the calculation, the slow component is kept in equilibrium with the initial state's solute charge density but not with the final state's one. We use a partition scheme denoted as Partition II in our VEM paper (*Chem. Sci.* **2011**, 2, 2143).

#### 3.3. Solvation effects beyond VEM

Excitation and emission energies in solution have other contributions beyond bulk-solvent dielectric polarization (also called bulk electrostatics), and these additional contributions are not explicitly accounted for in a VEM calculation. The other contributions may include solute–solvent dispersion interactions, exchange repulsion, solute–solvent charge transfer, the non-bulk character of solvent polarization response in the first solvent shell, and the partial covalent character of solute–solvent hydrogen bonding (the rest of hydrogen bonding may be included *implicitly* in the electrostatics). When one considers solvatochromic shifts, the main contributions beyond bulk electrostatics are solute–solvent dispersion interactions and hydrogen bonding, with the latter being most important in protic solvents.

To *explicitly* account for solute–solvent charge transfer and hydrogen bonding, the user can run a *VEMGAUSS* calculation on a supersolute that involves a solute–solvent molecular cluster with one or a few solvent molecules added explicitly to a bare solute. Details on constructing such solute–solvent clusters are beyond the scope of this document, but some examples are discussed in

- Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. Sorting out the relative contributions of electrostatic polarization, dispersion, and hydrogen bonding to solvatochromic shifts on vertical electronic excitation energies. *J. Chem. Theory Comput.* **2010**, *6*, 2829-2844. DOI: <http://dx.doi.org/10.1021/ct100267s>

The solute–solvent dispersion contribution to solvatochromic shifts can be accounted for by *VEMGAUSS* by means of the solvation model with state-specific polarizability (SMSSP). The SMSSP model is described in detail in the following paper (in particular, see equation 10 there):

- Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. Uniform treatment of solute–solvent dispersion in the ground and excited electronic states of the solute based on a solvation model with state-specific polarizability. *J. Chem. Theory Comput.* **2013**, *9*, 3649-3659. DOI: <http://dx.doi.org/10.1021/ct400329u>

## 4. Description of *VEMGAUSS*

The *VEMGAUSS* program consists of one parent C Shell script called `vemgauss` and one child Fortran binary called `vemgauss.exe`. The user provides a *Gaussian 09* input file for a single-point energy calculation in the format specified in Section 6. The *VEMGAUSS* program uses the user's provided input file to run automatically a series of *Gaussian* calculations necessary to compute the VEM excitation or emission energy in solution. The *VEMGAUSS* program creates an output file that contains results of these intermediate *Gaussian* computations as part of the *VEMGAUSS* calculation. If the *VEMGAUSS* calculation is successful, the user will find the final VEM excitation or emission energy at the end of the *VEMGAUSS* output file along with the liquid-phase energies of the initial and the final electronic state of the vertical excitation or emission process.

The user's provided input file should include the solute's Cartesian coordinates, multiplicity, and charge, and the solvent's dielectric constant and other descriptors as well as the name of basis set, density functional, and excited-state specifications (e.g., a number of TDDFT or CIS excited states) (see Section 6). In addition, certain parameters can be introduced as command line arguments to the *VEMGAUSS* program (see Section 7).

## 5. *VEMGAUSS* installation

The *VEMGAUSS* software package comes as a single tar file (`VEMGAUSS_X.tar` where the version number *X* is `v2013`, for example) that contains a directory called `VEMGAUSSdir`.

- The tar file should be placed in the user's home directory (on a computer with a Unix or Linux operating system), and then it should be untarred by executing the following command:  

```
tar xvf VEMGAUSS_X.tar
```

The extracted directory `VEMGAUSSdir` contains the following two files and directory `Tests`:

```
-rw-----. 1 user group 3059 Sep  5 13:43 vemgauss.f
-rwx-----. 1 user group 30651 Sep  5 13:43 vemgauss
drwx-----. 3 user group 4096 Sep  5 13:43 Tests
```

- The user should set the working directory to `VEMGAUSSdir` and then compile the Fortran code `vemgauss.f` by executing the following commands:  

```
gfortran -o vemgauss.exe vemgauss.f
```
- The user should define the full path to `VEMGAUSSdir` through the `$PATH` environment variable in a dot-file called `.bashrc` or in `.cshrc` (depending on which shell is used), for instance, by adding a line:  

```
export PATH=$PATH:$HOME/VEMGAUSSdir
```

or  

```
setenv PATH ${PATH}:$HOME/VEMGAUSSdir
```

Users familiar with Unix may place the code in any subdirectory instead of the home directory and modify the files `.bashrc` or `.cshrc` accordingly.

- The user should check if the *VEMGAUSS* package is properly set up by executing the following command:  

```
which vemgauss vemgauss.exe
```
- In addition, the user should set the variable `$G09PATH` in line #5 in the file `vemgauss` to the actual location of the `g09` directory containing *Gaussian 09*'s executables. For example, line #5 can read  

```
set G09PATH = "/soft/gaussian/g09.c01"
```



## 6. Input file

First of all, the user should create *Gaussian 09*'s input file (with an extension "g09") containing appropriate keywords for a *VEMGAUSS* single-point energy calculation. Here is an example of *Gaussian 09*'s input file for such a calculation (see the directory `Tests` for more examples):

```
%nproc=8
%mem=9000mb
# m06/6-311+G(2df,2p) scrf=(solvent=water) int=ultrafine td=(nstates=10,root=1) density=current

Formaldehyde in water at ground-state liquid-phase geometry (Input 1)

0 1
 8  0.0000000000  0.0000000000  0.6743110000
 6  0.0000000000  0.0000000000 -0.5278530000
 1  0.0000000000  0.9370330000 -1.1136860000
 1  0.0000000000 -0.9370330000 -1.1136860000
```

Note that the file should be ended with a blank line. This input file (Input 1) is equivalent to the following input (Input 2) (which is also acceptable for *VEMGAUSS* calculations):

```
%nproc=8
%mem=9000mb
# m06/6-311+G(2df,2p) scrf=(iefpcm,read) int=ultrafine td=(nstates=10,root=1) density=current

Formaldehyde in water at ground-state liquid-phase geometry (Input 2)

0 1
 8  0.0000000000  0.0000000000  0.6743110000
 6  0.0000000000  0.0000000000 -0.5278530000
 1  0.0000000000  0.9370330000 -1.1136860000
 1  0.0000000000 -0.9370330000 -1.1136860000

radii=smdcoulomb eps=78.3553 epsinf=1.777849 hbondacidity=0.82
```

The keywords are described in the G09 manual at [http://www.gaussian.com/g\\_tech/g\\_ur/1\\_keywords09.htm](http://www.gaussian.com/g_tech/g_ur/1_keywords09.htm).

### 6.1. Notes on SCRF specification

- The input file should contain either the `scrf=(iefpcm,read)` keyword or the `scrf=(solvent=X)` keyword where *X* is the name of any *Gaussian 09* solvent except `solvent=generic`. There is no default value for the `scrf=()` keyword.
- If the `scrf=(iefpcm,read)` keyword is employed, the user should provide a PCM read list containing a specification for Coulomb atomic radii (e.g., `radii=smdcoulomb` for the SMD radii; note that the SMD radii are the only tested type of radii for such calculations). There is no default value for `radii`.
- The PCM read list should also specify the solvent by using the appropriate static (`eps`) and optical (`epsinf`) value for dielectric constant  $\epsilon$ , and, in the case of `radii=smdcoulomb`, the appropriate value for Abraham's hydrogen bond acidity parameter ( $\alpha_{\text{H}}$ ) (`hbondacidity`). For example, one can use `eps=78.4`, `epsinf=1.8`, and `hbondacidity=0.82` for water. There is no default value for `eps`, `epsinf`, or `hbondacidity`.
- Note that the optical value of dielectric constant is usually set to  $n^2$  where  $n$  is index of refraction at optical frequencies at 293 K. See the Minnesota Solvent Descriptor Database for reference data on the values of  $n$ ,  $\epsilon_{\text{stat}}$  (`eps`), and  $\alpha_{\text{H}}$  for several dozen solvents at <http://comp.chem.umn.edu/solvation/mnsddb.pdf>.

- The PCM read list cannot contain keywords other than `radii`, `eps`, `epsinf`, and `hbondacidity`.
- The PCM read list should be terminated by a blank line.
- The optical dielectric constant (`epsinf`) cannot be larger than the static one (`eps`).
- If the `scrf=(solvent=X)` keyword is employed, no PCM read list should be provided. In this case the program will use `radii=smdcoulomb` and the G09 default values of `eps`, `epsinf`, and `hbondacidity` for the solvent *X*.

## 6.2. Notes on CIS/TDDFT specification

- The *VEMGAUSS* excited-state calculation can be performed by CIS or TDDFT using the `cis=()`, `td=()`, and `tda=()` keywords. The `cis=()` keyword is specified for the CIS method, the `td=()` keyword is specified for full (or regular) TDDFT, and the `tda=()` keyword is specified if the Tamm-Dancoff approximation to TDDFT is requested (which is available only in Revision D or later of *Gaussian 09*). The parentheses can include the following options: `nstates`, `root`, `singlets`, `triplets`, `50-50`, and `conver`. See *Gaussian 09*'s manual at [http://www.gaussian.com/g\\_tech/g\\_ur/k\\_td.htm](http://www.gaussian.com/g_tech/g_ur/k_td.htm) for the meaning of these options. For example, by using `td=(nstates=10, root=2)` the user requests a full TDDFT calculation for ten excited states (singlets) with the second state as the state of interest (it means that the VEM reaction field will be equilibrated with respect to the second excited state). There is no default value for `cis=()`, `td=()`, or `tda=()`. It is recommended that `nstates` be at least ten larger than `root`.
- Excited-state density type can be specified using the `density` keyword. The available options include `density=current` (by default) and `density=rhoci`. In the case of `density=current` the user requests a VEM(d,RD) calculation based on a *relaxed* excited-state density (RD). Such a density is calculated using the Z-vector method, and it yields multipole moments which are the correct analytical derivatives of the energy. See *Gaussian 09*'s manual at [http://www.gaussian.com/g\\_tech/g\\_ur/k\\_density.htm](http://www.gaussian.com/g_tech/g_ur/k_density.htm). In the case of `density=rhoci` the user requests a VEM(d,UD) calculation based on a *unrelaxed* excited-state density (UD). This option can be useful for debugging purposes, but it is not recommended in general.

## 6.3. Basis set specification

- The user can employ any basis sets stored internally in the *Gaussian 09* program by using an appropriate keyword [e.g., `6-31G(d)`, `6-311+G(2df,2p)`, etc.].
- The user can also employ an external basis set or effective core potential via the keywords `Gen` or `GenECP` and by using the `include(@)` function to specify the name of a user-provided file that contains the external basis set or ECP (if applicable). Here is an example of the input file to specify the `6-311+G(2df,2p)` basis stored in an external file `MG3S_HCO.dat`:

```
%nproc=8
%mem=9000mb
# m06/gen scrf=(iefpcm,read) int=ultrafine td=(nstates=10,root=1) density=current

Formaldehyde in water at ground-state liquid-phase geometry (with gen keyword)
```

```
0 1
 8 0.0000000000 0.0000000000 0.6743110000
 6 0.0000000000 0.0000000000 -0.5278530000
 1 0.0000000000 0.9370330000 -1.1136860000
 1 0.0000000000 -0.9370330000 -1.1136860000
```

```
@MG3S_HCO.dat
```

```
radii=smdcoulomb eps=78.3553 epsinf=1.777849 hbondacidity=0.82
```

## 6.4. Further notes

- The input file should not contain the keywords `chk`, `cis`, `freq`, `opt`, and `scf`.
- The input file should contain the Cartesian coordinates of the solute's ground-state equilibrium structure in solution in the case of an excitation energy calculation or the solute's excited-state equilibrium structure in solution in the case of an emission energy calculation.
- The ground electronic state should be a closed-shell spin singlet, and the excited states can only be singlets or triplets.
- The directory `Tests` contains more input file examples for which the *VEMGAUSS* program was tested successfully. The user should use these files as templates.
- If Revision A is employed, the `#P` option in the route line should always be used. See more details at [http://www.gaussian.com/g\\_tech/g\\_ur/k\\_route.htm](http://www.gaussian.com/g_tech/g_ur/k_route.htm).

## 7. *VEMGAUSS* execution

The user can run a *VEMGAUSS* calculation by executing the following command:

```
vemgauss name.g09 arguments
```

The *VEMGAUSS* program will create an output file `name.log`.

Further notes are given below.

- Replace `name.g09` with the name of your *Gaussian 09* input file constructed according to the instructions outlined in the previous section (it should have an extension "g09").
- Replace `arguments` with one or more arguments (see the text below). The arguments should be separated by a space. The order of arguments and the letter case are not important. The user can provide arguments for
  - ♦ Print level specification,
  - ♦ Spectrum type specification, and
  - ♦ *VEMGAUSS* convergence specification.

See the next section for more details.

- The *VEMGAUSS* program can run with no specified arguments (other than the input file's name) as
 

```
vemgauss name.g09
```

 In this case, the arguments' default values will be used. In particular, the command line above is equivalent to
 

```
vemgauss name.g09 terse excitation vemconv=1.0
```
- The *VEMGAUSS* program creates multiple files `pid*` and `Gau-*` that will be deleted in the end unless the program is terminated abnormally. In the case of abnormal termination these files can be used for debugging purposes and then be deleted manually.
- The *VEMGAUSS* program creates the file `name.check` to store some intermediate results that can be used for restarting the program using these data. The program will read this file upon restart unless the user deletes the file manually.

## 8. Command line arguments to the *VEMGAUSS* program

### 8.1. Print level specification

terse

The *VEMGAUSS* output file will contain intermediate and final VEM energies plus excerpts from intermediate *Gaussian 09* output files.

verbose

The *VEMGAUSS* output file will contain intermediate and final VEM energies plus the content of all intermediate *Gaussian 09* output files. This option can be useful only for debugging purposes and it is not recommended in general.

The *VEMGAUSS* default is *terse*.

### 8.2. Specification for calculating the solute–solvent dispersion contribution to the vertical excitation energy

ssp=none

No dispersion calculation is requested.

'ssp= (X1, X2)'

The user requests the SMSSP solute–solvent dispersion calculation using the user's provided state-specific polarizabilities. Replace *X1* and *X2* with the spherically averaged values of the ground-state polarizability and the excited-state polarizability of the solute molecule in the gas phase, respectively. Both the value should be expressed in Å<sup>3</sup> in the fixed-point format (note that a conversion factor from atomic units,  $a_0^3$ , to Å<sup>3</sup> is 0.148184).

The *VEMGAUSS* default is *ssp=none*.

Note that the gas-phase polarizabilities can be taken from experimental data (if available) or can be computed. Here is an example of *Gaussian 09*'s input file for ground-state and excited-state polarizability calculations for the formaldehyde molecule using the MG3 basis set [which is equivalent to 6-311++G(2df,2p) in this case] at the M06/MG3S ground-state geometry:

```
%nproc=8
%mem=9000mb
%chk=test.chk
#P m06/6-311++G(2df,2p) int=ultrafine Polar

Formaldehyde in the gas phase (ground state)

0 1
 8  0.0000000000  0.0000000000  0.6698330000
 6  0.0000000000  0.0000000000 -0.5212030000
 1  0.0000000000  0.9379150000 -1.1157240000
 1  0.0000000000 -0.9379150000 -1.1157240000

--link1--
%nproc=8
%mem=9000mb
%chk=test.chk
%nosave
# m06 chkbasis int=ultrafine guess=check geom=check td=(root=1,nstates=10) Polar=Numer

Formaldehyde in the gas phase (excited state)

0 1
```

To run this calculation, use the following command (by replacing `input` with the name of an actual input file):

```
g09 input
```

Two excerpts from the corresponding output file with computed values of the spherically averaged (labeled "isotropic" in the output) polarizabilities are given below:

```
Isotropic polarizability for W= 0.000000 16.39 Bohr**3.
Isotropic polarizability= 21.65 Bohr**3.
```

The first excerpt contains the M06/MG3 value for the polarizability of the formaldehyde molecule in the ground state, 16.39 a.u. or 2.429 Å<sup>3</sup>. The second excerpt contains the TDM06/MG3 value for the molecular polarizability of formaldehyde in the first excited state, 21.65 a.u. or 3.208 Å<sup>3</sup>.

### 8.3. Spectrum type specification

```
excitation
```

The user requests a *VEMGAUSS* excitation energy calculation for a vertical electronic transition from the ground electronic state (initial state) to the user's specified excited state (final state). The excited state of interest can be specified via the `root` option (see above).

```
emission
```

The user requests a *VEMGAUSS* emission energy calculation for a vertical electronic transition from the user's specified excited state (initial state) to the ground electronic state (final state). The excited state of interest can be specified via the `root` option (see above).

The *VEMGAUSS* default is `excitation`.

### 8.4. *VEMGAUSS* convergence specification

```
vemconv=X
```

Replace *X* with an integer (e.g., `vemconv=2`) or floating-point value in the fixed-point format (e.g., `vemconv=0.5`) expressed in cm<sup>-1</sup>. The *VEMGAUSS* calculation will be terminated normally if the difference in the VEM excitation energy between two consecutive iterations does not exceed this threshold.

The *VEMGAUSS* default is `vemconv=1.0`.

## 9. Test suite

The *VEMGAUSS* test suite (directory `Tests`) contains several tests as described below. The user is encouraged to run these tests after installing the program. The command lines with correct arguments for each test are given in the batch file `run_tests.bat` which can be simply run as `./run_tests.bat >& run_tests.out &`

To verify if the run was successful, the user can execute the Perl script `compare.pl` located in the same directory as `./compare.pl *.log`

**Test 1.** The VEM(d,RD) nonequilibrium vertical electronic excitation energy from the ground state to the first excited state of the formaldehyde molecule in water using TDM06/MG3S. Note that MG3S is equivalent to 6-311+G(2df,2p) in this case. The test demonstrates the use of input style Input 1 as described in Section 6.

Input file: `H2CO_watVEx_1.g09`

Output file: `H2CO_watVEx_1.log`

Excerpt from the output file:

```
VEM(d) excitation energy (cm-1) (iter. 3) = 32755.74
GS total energy (a.u.) (iter. 3) = -114.487252
ES total energy (a.u.) (iter. 3) = -114.338006
```

**Test 2.** The same as Test 1 except that this test also demonstrates the use of input style Input 2.

Input file: `H2CO_watVEx_2.g09`

Output file: `H2CO_watVEx_2.log`

Excerpt from the output file:

```
VEM(d) excitation energy (cm-1) (iter. 3) = 32755.74
GS total energy (a.u.) (iter. 3) = -114.487252
ES total energy (a.u.) (iter. 3) = -114.338006
```

**Test 3.** The same as Test 1 except that this test also demonstrates the use of the *VEMGAUSS* keywords `vemconv=0.01` and `'ssp=(2.429,3.208)'`.

Input file: `H2CO_watVExSSP.g09`

Output file: `H2CO_watVExSSP.log`

Excerpt from the output file:

```
VEM(d) excitation energy (cm-1) (iter. 4) = 32755.74
GS total energy (a.u.) (iter. 4) = -114.487252
ES total energy (a.u.) (iter. 4) = -114.338006
SMSSP dispersion gas-sol shift (cm-1) = 103.78
```

**Test 4.** The same as Test 2 except that Test 4 is for to the *second* excited state of the formaldehyde molecule, and this test also demonstrates the use of *Gaussian 09's* keyword `gen` with an external basis set stored in the file `MG3S_HCO.dat`.

Input file: `H2CO_watVEx_root2.g09`

Output file: `H2CO_watVEx_root2.log`

Excerpt from the output file:

```
VEM(d) excitation energy (cm-1) (iter. 4) = 50787.15
GS total energy (a.u.) (iter. 4) = -114.487252
ES total energy (a.u.) (iter. 4) = -114.255849
```

**Test 5.** The same as Test 1 except that this test demonstrates the use of TDA instead of full TDDFT.

Input file: H2CO\_watVEx\_tda.g09

Output file: H2CO\_watVEx\_tda.log

Excerpt from the output file:

```
VEM(d) excitation energy (cm-1)(iter. 3) = 33083.33
GS total energy (a.u.)(iter. 3) = -114.487252
ES total energy (a.u.)(iter. 3) = -114.336513
```

**Test 6.** The same as Test 1 except that this test demonstrates a calculation on the lowest triplet excited state.

Input file: H2CO\_watVEx\_triplet.g09

Output file: H2CO\_watVEx\_triplet.log

Excerpt from the output file:

```
VEM(d) excitation energy (cm-1)(iter. 3) = 29436.73
GS total energy (a.u.)(iter. 3) = -114.487252
ES total energy (a.u.)(iter. 3) = -114.353128
```

**Test 7.** The VEM(d,RD) nonequilibrium vertical electronic excitation energy from the ground state to the first excited state of the acetone molecule in acetonitrile using TDM06/MG3S (see Scheme 1 in the next section).

Input file: ac\_acnVEx\_1.g09

Output file: ac\_acnVEx\_1.log

Excerpt from the output file:

```
VEM(d) excitation energy (cm-1)(iter. 3) = 36810.33
GS total energy (a.u.)(iter. 3) = -193.099297
ES total energy (a.u.)(iter. 3) = -192.931577
```

**Test 8.** The VEM(d,RD) nonequilibrium vertical emission energy from the first excited state of the acetone molecule in acetonitrile to the ground state using TDM06/MG3S at the ground-state geometry in solution (see Scheme 1 in the next section). The test demonstrates the use of the keyword `emission`.

Input file: ac\_acnVEm\_1.g09

Output file: ac\_acnVEm\_1.log

Excerpt from the output file:

```
VEM(d) emission energy (cm-1) = 36019.57
GS total energy (a.u.) = -193.098319
ES total energy (a.u.) = -192.934202
```

**Test 9.** The same as Test 8 except that the excited-state geometry in solution is used.

Input file: ac\_acnVEm\_2.g09

Output file: ac\_acnVEm\_2.log

Excerpt from the output file:

```
VEM(d) emission energy (cm-1) = 30508.67
GS total energy (a.u.) = -193.085379
ES total energy (a.u.) = -192.946371
```

**Test 10.** The VEM(d,RD) nonequilibrium vertical electronic excitation energy from the ground state to one of the metal-to-ligand charge transfer excited electronic states of a carbonyl cyano rhenate(I) diimine complex  $[\text{Re}(\text{I})(\text{H}_4\text{C}_2\text{N}_2)(\text{CO})_3(\text{CN})]^0$  in ethanol (see Fig. 1). The test demonstrates the use of *Gaussian 09*'s keyword `genecp` with an external effective core



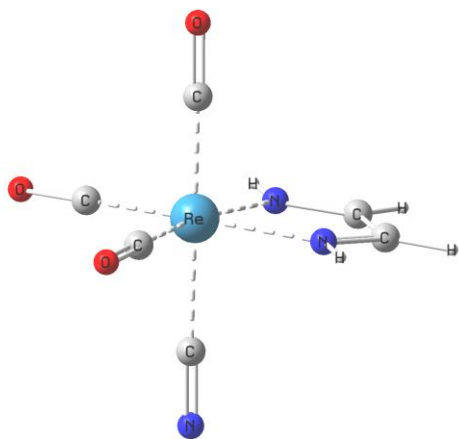
potential on Re stored in the file HCNORe\_LANL2DZ.dat, and it also demonstrates the use of a modified value of the Coulomb radius on Re through *Gaussian 09's* keyword `modifysph`.

Input file: Re\_ethVEx.g09

Output file: Re\_ethVEx.log

Excerpt from the output file:

```
VEM(d) excitation energy (cm-1) (iter. 4) = 23865.21  
GS total energy (a.u.) (iter. 4) = -699.689753  
ES total energy (a.u.) (iter. 4) = -699.581015
```



**Figure 1.** The structure of the  $[\text{Re}(\text{I})(\text{H}_4\text{C}_2\text{N}_2)(\text{CO})_3(\text{CN})]_0$  complex used in Test 10.

## 10. Interpretation of results

If the *VEMGAUSS* calculation is terminated normally, the final VEM vertical excitation energy or vertical emission energy in wavenumbers (that is,  $\text{cm}^{-1}$ ) can be found at the end of the *VEMGAUSS* output file, along with the total energies of the initial and final electronic states of the solute molecule in solution. These are the only results the user usually needs from *VEMGAUSS* computations.

For the vertical excitation energy calculation the program reports the GSRF and cGSRF excitation energies in addition to the VEM excitation energy in solution. If the `ssp` option is requested, the program also reports the SMSSP solute–solvent dispersion contribution to the gas–solvent solvatochromic shift (this contribution is not included in the VEM, GSRF, or cGSRF energies). Here is an excerpt from the VEM excitation energy calculation for formaldehyde in water:

```
Symmetry of the excited state is Singlet-A2
DATA FOR EXCITATION: GS=initial_state, ES=final_state
  GSRF excitation energy (cm-1)(iter. 4) = 33354.11
  cGSRF excitation energy (cm-1)(iter. 4) = 33043.44
    VEM(asterisk) (cm-1)(iter. 4) = 32445.05
VEM(d) excitation energy (cm-1)(iter. 4) = 32755.74
GS total energy (a.u.)(iter. 4) = -114.487252
ES total energy (a.u.)(iter. 4) = -114.338006
SMSSP dispersion gas-sol shift (cm-1) = 103.78
```

Here is an excerpt from the VEM vertical emission energy calculation for formaldehyde in water:

```
Symmetry of the excited state is Singlet-A2
DATA FOR EMISSION: ES=initial_state, GS=final_state
VEM(d) emission energy (cm-1) = 31012.46
GS total energy (a.u.) = -114.484568
ES total energy (a.u.) = -114.343265
```

The *VEMGAUSS* solvatochromic shift is calculated as  $\omega_{\text{gas}} - \omega_{\text{sol}}$  where  $\omega_{\text{gas}}$  is the gas-phase vertical excitation energy and  $\omega_{\text{sol}}$  is the vertical excitation energy in solution. The vertical excitation energy in the gas phase should be calculated at the gas-phase optimized geometry of the solute molecule in the ground electronic state. In general, the *VEMGAUSS* vertical excitation energy in solution should be calculated at the liquid-phase geometry of the solute molecule optimized in the ground state, for example, using *Gaussian 09* and the SMD implicit solvent model. Here is an input example for the SMD ground-state geometry optimization for formaldehyde ( $\text{H}_2\text{CO}$ ) in water at the M06/MG3S level of theory {the MG3S basis is described in [Lynch, B. J.; Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A.* **2003**, *107*, 1384-1388], and for H, C, and O [in fact for all elements from H to Ne], it is identical to 6-311+G(2df,2p)}:

```
%nproc=8
%mem=9000mb
# m06/6-311+G(2df,2p) opt scrf=(smd,solvent=water) int=ultrafine

GS geometry optimization of H2CO in water using SMD/M06/MG3S

0 1
8 0.0000000000 0.0000000000 0.6743110000
6 0.0000000000 0.0000000000 -0.5278530000
1 0.0000000000 0.9370330000 -1.1136860000
1 0.0000000000 -0.9370330000 -1.1136860000
```

To run an SMD ground-state geometry optimization, use the command `g09 input` (by replacing `input` with the name of an actual input file).

## 10.1. Vertical excitation energy calculation using the CIS method

We start in this section with the use of the CIS method and continue in section 10.2 with the use of full TDDFT and TDDFT-TDA.

In practice, the *VEMGAUSS* vertical excitation energy calculation in solution by the VEM method is carried out in several steps, which are done automatically without the user's intervention. In the rest of this section we describe the calculations carried out when the CIS option is chosen. First, the program runs a regular ground-state solvation calculation (using an automatically created input file `pidXGS0.g09` where *X* is some process identifier) to obtain the molecular orbitals (MOs) and orbital energies corresponding to the equilibrium ground-state reaction field at the static dielectric constant  $\epsilon_{\text{stat}}$  (Step 1) within the framework of Hartree–Fock theory. These MOs and orbital energies are respectively eigenfunctions and eigenenergies of the liquid-phase Fock operator defined as

$$F = F_0 + \Phi \quad (1)$$

where  $\Phi = \Phi(\text{GS}, \epsilon_{\text{stat}})$  is the equilibrium ground-state (GS) reaction field, and the operator  $F_0$  is expressed as

$$F_0 = h + \sum_q^{n/2} (2J_q - K_q) \quad (2)$$

where  $h$  is the one-electron operator,  $J$  and  $K$  are the Coulomb and Hartree–Fock exchange operators, respectively, and the sum over  $q$  runs over all  $n/2$  doubly occupied orbitals in the closed-shell solute ground state. The reaction field  $\Phi$  is retrieved by *VEMGAUSS* from *Gaussian 09*'s output file as a contribution to the Fock matrix labeled as "PCM contribution to FA" [IOp(5/33=4) needs to be used]. The matrix  $\mathbf{C}$  of ground-state MO coefficients in the basis of atomic orbitals and the corresponding MO energies are stored in the checkpoint file `pidXGS0.chk`. The MO energies are equal to diagonal values of the  $\mathbf{C}^T \mathbf{F} \mathbf{C}$  matrix defined as

$$\mathbf{C}^T \mathbf{F} \mathbf{C} = \mathbf{C}^T \mathbf{F}_0 \mathbf{C} + \mathbf{C}^T \Phi_1 \mathbf{C} \quad (3)$$

where  $\Phi_1$  is a contribution to the Fock matrix due to the reaction field  $\Phi(\text{GS}, \epsilon_{\text{stat}})$ , and the superscript  $\text{T}$  denotes a transpose. The  $\mathbf{C}^T \mathbf{F} \mathbf{C}$  matrix is diagonal whereas the matrices  $\mathbf{C}^T \mathbf{F}_0 \mathbf{C}$  and  $\mathbf{C}^T \Phi_1 \mathbf{C}$  need not be diagonal.

In Step 2, the *VEMGAUSS* program runs another ground-state calculation (input file `pidXGS0d.g09`) with the static dielectric constant  $\epsilon_{\text{stat}}$  replaced by the optical dielectric constant  $\epsilon_{\text{opt}}$  and by using guess MOs set to the MOs calculated in Step 1. Note that this calculation is performed with fixed MO coefficients (the matrix  $\mathbf{C}$ ), i.e., without actually solving a new SCRF problem. In this step, we solve Eq. (17) from our VEM paper (*Chem. Sci.* **2011**, *2*, 2143) and find the matrix  $\mathbf{C}^T \Phi_2 \mathbf{C}$  where  $\Phi_2$  is a contribution to the Fock matrix due to the reaction field  $\Phi(\text{GS}, \epsilon_{\text{opt}})$ . This matrix will be used later on.

In Step 3, the program runs an excited-state calculation (input file `pidXES1.g09`) on the MOs from Step 1 by diagonalizing the CIS matrix constructed using the following equation

$$H_{ia,jb} = \delta_{ij}\delta_{ab}[\varepsilon_a - \varepsilon_i] + \langle aj || ib \rangle \quad (4)$$

where the indices  $i$  and  $j$  run over all occupied MOs, the indices  $a$  and  $b$  run over all virtual MOs,  $\langle aj || ib \rangle$  is the antisymmetrized two-electron repulsion integral in the MO basis {see, for example, Eq. (5) in [Maurice, Head-Gordon, *Int. J. Quantum Chem.: Quantum Chem. Symp.* **1995**, *29*, 361-370]}, and  $\varepsilon_p$  is the energy of the molecular orbital  $\psi_p$  ( $p = a$  or  $i$ ) calculated in Step 1. This calculation gives us the CIS excitation energy and the electron density for the excited state of interest in the ground-state reaction field approximation abbreviated as GSRF in the *VEMGAUSS* output and in our VEM paper. The excited-state (ES) reaction field,  $\Phi(\text{ES}, \varepsilon_{\text{opt}})$ , corresponding to the estimated excited-state density is then evaluated by solving Eq. (19) in the VEM paper (*Chem. Sci.* **2011**, *2*, 2143). The reaction field  $\Phi(\text{ES}, \varepsilon_{\text{opt}})$  which represents the fast (dynamic) component of the total nonequilibrium reaction field is automatically saved in the checkpoint file `pidXES1.chk` for further use.

In Step 4, the program runs a ground-state calculation (input file `pidXGS1d.g09`) at the fixed MO coefficients (the matrix  $\mathbf{C}$ ) obtained in Step 1 and at the reaction field fixed at  $\Phi(\text{ES}, \varepsilon_{\text{opt}})$  from Step 3. As in Step 2, this calculation does not solve a new SCRF problem, and its only purpose is to obtain the  $\mathbf{C}^T \mathbf{\Phi}_3 \mathbf{C}$  matrix where  $\mathbf{\Phi}_3$  is a contribution to the Fock matrix due to the reaction field  $\Phi(\text{ES}, \varepsilon_{\text{opt}})$  from Step 3.

In Step 5, we repeat the excited state calculation using a new CIS matrix constructed as

$$H_{ia,jb} = \delta_{ij}\delta_{ab}[\varepsilon'_a - \varepsilon'_i] + \langle aj || ib \rangle \quad (5)$$

where the energies  $\varepsilon'_p$  ( $p = a$  or  $i$ ) are expressed as

$$\varepsilon'_p = \varepsilon_p + \langle \psi_p | \Delta \Phi | \psi_p \rangle \quad (6)$$

where  $\varepsilon_p$  is the energy of the molecular orbital  $\psi_p$  obtained in Step 1. The second term of Eq. (6) is equal to the corresponding diagonal element of the following matrix

$$\mathbf{C}^T \Delta \Phi \mathbf{C} = \mathbf{C}^T \mathbf{\Phi}_3 \mathbf{C} - \mathbf{C}^T \mathbf{\Phi}_2 \mathbf{C} \quad (7)$$

where  $\mathbf{\Phi}_3$  is a Fock matrix contribution due to the reaction field  $\Phi(\text{ES}, \varepsilon_{\text{opt}})$  from Step 3 and  $\mathbf{\Phi}_2$  corresponds to the reaction field  $\Phi(\text{GS}, \varepsilon_{\text{opt}})$  from Step 2. Diagonalization of the CIS matrix constructed using Eq. (5) yields the solute's excitation energy in the nonequilibrium excited-state reaction field expressed as  $\Phi(\text{GS}, \varepsilon_{\text{stat}}) + \Phi(\text{ES}, \varepsilon_{\text{opt}}) - \Phi(\text{GS}, \varepsilon_{\text{opt}})$ . The corresponding excited-state electron density is computed and used to obtain a new version of  $\Phi(\text{ES}, \varepsilon_{\text{opt}})$  while keeping  $\Phi(\text{GS}, \varepsilon_{\text{stat}})$  and  $\Phi(\text{GS}, \varepsilon_{\text{opt}})$  unchanged. The excited-state calculation of Step 5 uses the MOs fixed at the MOs obtained in Step 1 and the corresponding orbital energies  $\varepsilon_p$  replaced with the new values  $\varepsilon'_p$  by modifying the checkpoint file `pidXGS0.chk` (that comes from Step 1).

By repeating Step 4 and Step 5 we can iteratively equilibrate  $\Phi(\text{ES}, \varepsilon_{\text{opt}})$  with the excited-state electron density for the specific excited state, thereby using a state-specific self-consistent reaction field approach. The VEM excitation energy at the  $k$ th iteration (i.e., at the  $k$ th call of Step 5) is defined by

$$\omega_{\text{VEM}}^{(k)} = \omega_{\text{VEM}}^{*(k)} - \frac{1}{2} \sum_m \Delta V_m^{(k-1)} \Delta Q_m^{(k-1)} \quad (8)$$

where the first term on the right-hand side is the eigenvalue of the CIS matrix (5) [this energy is given in the output file under the label VEM(asterisk)], the second term is expressed in terms of the solute's electrostatic potential ( $V$ ) and dielectric dependent surface charges ( $Q$ ) on the discretized solute–solvent boundary representing the effect of solvent polarization, and the index  $m$  runs over all surface elements (sometimes called tesserae). In particular, we use the following relation in vector form

$$\Delta \mathbf{V}^T \Delta \mathbf{Q} = \mathbf{V}_{\text{ES}}^T \mathbf{Q}_{\text{ES,dyn}} - \mathbf{V}_{\text{GS}}^T \mathbf{Q}_{\text{ES,dyn}} - \mathbf{V}_{\text{ES}}^T \mathbf{Q}_{\text{GS,dyn}} + \mathbf{V}_{\text{GS}}^T \mathbf{Q}_{\text{GS,dyn}} \quad (9)$$

where the column vector  $\mathbf{V}_{\text{GS}}$  refers to the solute's ground-state electrostatic potential derived from the MOs obtained in Step 1,  $\mathbf{V}_{\text{ES}}$  refers to the solute's excited-state potential derived from the CIS electron density obtained at Step 5 at iteration ( $k - 1$ ) [we omit the corresponding superscript in Eq. (9) for simplicity],  $\mathbf{Q}_{\text{GS,dyn}}$  denotes a set of fast (or dynamic) polarization charges derived from the ground-state reaction field  $\Phi(\text{GS}, \epsilon_{\text{opt}})$  in Step 2, and  $\mathbf{Q}_{\text{ES,dyn}}$  denotes a set of dynamic polarization charges from the excited-state reaction field  $\Phi(\text{ES}, \epsilon_{\text{opt}})$  obtained at Step 5 at iteration ( $k - 1$ ). The terms on the right-hand side of Eq. (9) can be recovered from *Gaussian 09*'s output files `pidXGS0d.log`, `pidXGS1d.log`, and `pidXES1.log`. Note that we use the relation  $\mathbf{V}_{\text{ES}}^T \mathbf{Q}_{\text{GS,dyn}} = \mathbf{V}_{\text{GS}}^T \mathbf{Q}_{\text{ES,dyn}}$  [according to Eq. (8) in Caricato *et al.*, *J. Chem. Phys.* **2006**, *124*, 124520] to simplify a calculation by Eq. (9), which is also used in our original publication (*Chem. Sci.* **2011**, *2*, 2143).

The *VEMGAUSS* implementation of the VEM model is based on the diagonal approximation called VEM(d) (where "d" stands for diagonal) when the off-diagonal terms  $\langle \varphi_a | \Delta \Phi | \varphi_b \rangle$  and  $\langle \varphi_i | \Delta \Phi | \varphi_j \rangle$  ( $a \neq b, i \neq j$ ) in Step 5 are neglected. The difference between the VEM(d) results and the VEM(f) results (where "f" stands for full) is typically less than 0.1 eV (*Chem. Sci.* **2011**, *2*, 2143).

## 10.2. Vertical excitation energy calculation using TDDFT and TDDFT-TDA

*VEMGAUSS* vertical excitation energies in solution are calculated using TDDFT and TDDFT-TDA in the same way as in the CIS case (i.e., through Steps 1–5 as described in the previous section), with two exceptions described next.

First, within the DFT framework, the Fock operator  $F_0$  used in Eq. (1) is replaced with the molecular Kohn-Sham (KS) operator, which can involve the one-electron Hamiltonian  $h$ , the Coulomb and scaled Hartree–Fock exchange term, and the exchange–correlation potential. The MOs obtained in Step 1 are now KS MOs.

Second, TDDFT excitation energies are determined as solutions of non-Hermitian eigensystem composed of the two matrices **A** and **B**. The matrices **A** and **B** are constructed according to [Casida, *M. J. Mol. Struct. Theochem* **2009**, *914*, 3-18] as

$$A_{ia,jb} = \delta_{ij} \delta_{ab} [\epsilon_a - \epsilon_i] + K_{ia,jb} \quad (10)$$

$$B_{ia,jb} = K_{ia,bj} \quad (11)$$

where the quantities  $K_{ia,jb}$  involve the matrix elements of the Hartree kernel and the exchange–correlation kernel that depend on the KS MOs obtained in Step 1, and they do not include any PCM terms. In Step 3, the matrix  $\mathbf{A}$  is based on the KS orbital energies  $\varepsilon_p$  ( $p = a$  or  $i$ ) calculated in Step 1, but in Step 5 we replace  $\varepsilon_p$  with  $\varepsilon'_p$  computed according to Eq. (6).

In the case of TDDFT-TDA, the KS operator and the matrix  $\mathbf{A}$  are constructed in the same way as in the full TDDFT calculation but the matrix  $\mathbf{B}$  is set to zero. The TD Hartree–Fock TDA calculation is completely equivalent to the CIS calculation.

### 10.3. Note on the calculation of the relaxed density matrix

Results obtained using the current implementation of the VEM(d) method may differ slightly from the VEM(d,RD)/PCM results cited in our original publication (*Chem. Sci.* **2011**, 2, 2143) because of an additional simplification in the case when the excited-state density is computed using the  $Z$ -vector method which is *Gaussian's* default for TDDFT or CIS excited-state density calculations (see [http://www.gaussian.com/g\\_tech/g\\_ur/k\\_density.htm](http://www.gaussian.com/g_tech/g_ur/k_density.htm)). In particular, the relaxed (rel) one-particle excited-state density in solution (sol) is approximated as

$$\mathbf{P}_{\text{sol}}^{\text{rel}} = \mathbf{P}_{\text{sol}}^{\text{unr}} + \Delta\mathbf{P}_{\text{GS(gas)} \rightarrow \text{ES(gas)}} \quad (12)$$

where the first term on the right-hand side is the *unrelaxed* excited-state density matrix (obtained via *Gaussian 09's* keyword `density=RhoCI`), and the second term accounts for orbital relaxation effects due to the electronic excitation by solving the gas-phase  $Z$ -vector equation that does not include any explicit reaction-field contributions such as the PCM term included in the  $\mathbf{G}^+$  matrix used in Eq. (15) by Scalmani *et al.*, *J. Chem. Phys.* **2006**, 124, 094107. Such contributions were included in the original VEM/PCM formulation. However, in the current implementation of VEM/PCM the solvation effects are still included *implicitly* in relaxed excited-state density calculations because the TDDFT or CIS matrices are constructed using solvated MOs from Step 1 and the second term of Eq. (6) from Step 5.

For background, we note that the relaxed density is explained in [Rendell, A. P. L.; Bacskay, G. B.; Hush, N. S.; Handy, N. C. *J. Chem. Phys.* **1987**, 87, 5976-5986].

### 10.4. Vertical emission energy calculation

The *VEMGAUSS* vertical emission energy calculation should be done in general using the molecular geometry of the solute optimized for an excited electronic state of interest in solution. The excited-state molecular geometry in solution can be optimized by *Gaussian 09* using linear response TDDFT calculations. Here is an example of the input file for such an optimization.

```
%nproc=8
%mem=9000mb
# m06/6-311+G(2df,2p) opt scrf=(smd,solvent=water) int=ultrafine td=(nstates=10,root=1)

ES geometry optimization of H2CO in water using SMD/TDM06/MG3S

0 1
8 0.0000000000 0.0000000000 0.6743110000
6 0.0000000000 0.0000000000 -0.5278530000
1 0.0000000000 0.9370330000 -1.1136860000
1 0.0000000000 -0.9370330000 -1.1136860000
```

To run the excited-state geometry optimization in solution, use the following command:  
`g09 input`

The *VEMGAUSS* vertical emission energy calculation requires the same input file as for the *VEMGAUSS* vertical excitation energy calculation (except that the geometry may be different).

In the following, "em" denotes emission.

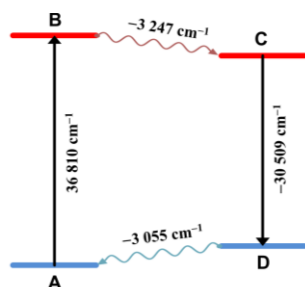
In practice, the *VEMGAUSS* vertical emission energy calculation is carried out in three steps that do not require the user's intervention. In Step 1(em), the program runs a state-specific self-consistent vertical *excitation* energy calculation as described in the previous paragraph, Step 1 through 5. Such a calculation is carried out in the equilibrium approximation by equating  $\epsilon_{\text{opt}}$  to  $\epsilon_{\text{stat}}$ . The resulting excited-state reaction field,  $\Phi(\text{ES}, \epsilon_{\text{stat}})$ , is fully equilibrated with the electron density for the excited state of interest.

In Step 2(em) (input file `pidXES1em.g09`), the converged reaction field  $\Phi(\text{ES}, \epsilon_{\text{stat}})$  is recalculated and then partitioned using the original values of  $\epsilon_{\text{opt}}$  and  $\epsilon_{\text{stat}}$ . By treating the excited state as an initial state and the ground state as a final state, the slow portion of  $\Phi(\text{ES}, \epsilon_{\text{stat}})$  with respect to the final state is saved in a checkpoint file.

In Step 3(em), the program runs a nonequilibrium ground-state calculation (input file `pidXGS0em.g09`) using the slow portion of the reaction field saved in Step 2(em).

## 10.5. Numerical examples

Scheme 1 shows results of the VEM(d,RD)/TDM06/MG3S calculations of vertical excitation and emission energies of the acetone molecule in acetonitrile.



**Scheme 1.** Excitation and emission energies of the acetone molecule in acetonitrile.

State A is the equilibrium ground electronic state of the solute (acetone) molecule in solution (from Test 7 in Section 9). State B is the first excited electronic state of the solute molecule calculated using *nonequilibrium* solvation at the *ground*-state geometry (Test 7) when only the fast component of the total reaction field is equilibrated with the excited-state electron density of the solute molecule. State C is the first excited electronic state of the solute molecule calculated using *equilibrium* solvation at the *excited*-state geometry in solution (Test 9). The B→C relaxation step includes the full equilibration of the fast and slow degrees of freedom of the solute–solvent system with the excited-state electron density of the solute molecule including the solute's excited-state geometry relaxation. State D is the ground electronic state of the solute molecule in solution calculated using *nonequilibrium* solvation at the solute's *excited*-state geometry in solution (Test 9) when only the fast component of the total reaction field is

equilibrated with the solute's ground-state density. The relaxation step D→A includes the full equilibration of the fast and slow degrees of freedom of the solute–solvent system with the ground-state electron density of the solute molecule including the solute's ground-state geometry relaxation.

Note that if we neglect the excited-state geometry relaxation in the step B→C by performing the calculations of C and D at the ground-state equilibrium geometry (see Test 8), the B→C relaxation energy will change from 3,247 to 576  $\text{cm}^{-1}$ , the C→D vertical emission energy will change from 30,509 to 36,020  $\text{cm}^{-1}$ , and the D→A relaxation energy will change from 3,055 to 215  $\text{cm}^{-1}$ .



## 11. Citation of the methods used by *VEMGAUSS*

Publications including work performed with *VEMGAUSS* should cite the following:

- Marenich, A. V.; Cramer, C. J.; Truhlar, D. G.; Guido, C. A.; Mennucci, B.; Scalmani, G.; Frisch, M. J. Practical computation of electronic excitation in solution: vertical excitation model. *Chem. Sci.* **2011**, *2*, 2143-2161.  
DOI: <http://dx.doi.org/10.1039/C1SC00313E>
- Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *VEMGAUSS*–version 2013, University of Minnesota, Minneapolis, 2013. <http://comp.chem.umn.edu/vemgauss>

If the SSP option is used to include the dispersion contribution to the solvatochromic shift, the publication should also cite

- Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. Uniform treatment of solute–solvent dispersion in the ground and excited electronic states of the solute based on a solvation model with state-specific polarizability. *J. Chem. Theory Comput.* **2013**, *9*, 3649-3659.  
DOI: <http://dx.doi.org/10.1021/ct400329u>

Users of the *Gaussian 09* code should follow the instructions in their *Gaussian 09* license for citing the *Gaussian 09* code.

## 12. Computers and operating systems on which *VEMGAUSS* has been tested

The *VEMGAUSS* program has been tested using the following specifications:

- HP Linux cluster with 1,091 HP ProLiant BL280c G6 blade servers, each with two-socket, quad-core 2.8 GHz Intel "Nehalem" processors; with gfortran gcc version gcc-4.4.7 [CentOS release 6.4 (Final)]
- SGI Altix XE 1300 Linux cluster with 180 SGI Altix XE 300 compute nodes, each containing two quad-core 2.66 GHz Intel Xeon "Clovertown"-class processors; with gfortran gcc version gcc-4.4.6 [CentOS release 6.3 (Final)]
- SGI Altix UV 1000 Linux cluster with 1,140 compute cores (190 6-core Intel Xeon X7542 "Westmere" processors at 2.66 GHz); with gfortran gcc version gcc-4.4.3 [SUSE Linux Enterprise Server 11 SP2 (x86\_64)]

## **13. Revision history**

### **Version 2013**

Version 2013 is the first distributed version.