Calculation of optical properties.

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1. Molecular Properties

In general, a molecular property is the electronic 'response' of the molecule to an 'external perturbation'. Examples for perturbations are applied static electric fields, static magnetic fields, changes of nuclear magnetic moments, changes of nuclear spins, and incoming time-dependent electromagnetic waves. In the case of a weak perturbation ξ (e.g., weak fields), the electronic response of a molecule in the ground

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state (i.e., the perturbed ground state) may be described by a Taylor series of the energy $E(\xi)$ with respect to the unperturbed ground state energy $E(0)$,

$$E(\xi) = E(0) + \frac{dE}{d\xi}\bigg|_{\xi=0} \xi + \frac{1}{2}\frac{d^2E}{d\xi^2}\bigg|_{\xi=0} \xi^2 + \dots \tag{1}$$

The first-order derivative $dE/d\xi|_{\xi=0}$ is called 'first-order molecular property'. The second-order derivative is called 'second-order molecular property' and so on. Different perturbations *at once* lead to multivariate Taylor expansions and mixed-variable derivatives beyond the first order and thus lead to a zoo of molecular properties that may be experimentally measured (e.g., confer *Introduction to Computational Chemistry*, Frank Jensen, chapter 10, Molecular Properties). Perturbations can be *static* or *time-dependent* resulting in molecular properties, which are called *static* and *dynamic*, respectively. Time-dependent perturbations can be periodic in time (but this is not required) and may be described by linear combination of harmonic oscillations $e^{\pm i\omega t}$ with angular frequency ω. In addition to the energy E in eqn 1, other physical observables may be used to represent the electronic response of the molecule, e.g., the electric charge distribution (*electron density*) $\rho(\mathbf{r})$ over the points $\mathbf{r}$ in space and the electric current density vector $\mathbf{j}(\mathbf{r})$. ρ and $\mathbf{j}$ play important roles in electronic structure theories such as density functional theory (DFT) and time-dependent current density functional theory (TDCDFT); the latter may be simplified to time-dependent DFT (TDDFT) in the absence of magnetic fields. Nowadays, DFT and TDDFT based methods are standard tools to calculate ground state and excited state energies, electron densities and molecular properties.

2. Dipole Moments

The general definition of molecular properties is now set, and it is time to start with a simple example of such properties. If ξ of eqn 1 is a *static* electric field component $\mathcal{E}_z$, then the first-order molecular property is the *static* electric dipole moment component (where the minus sign is conventional)
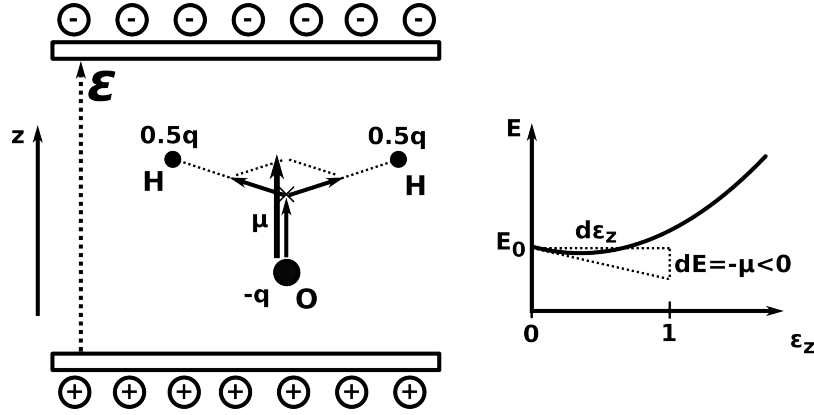
$$\mu_z = -\frac{dE}{d\mathcal{E}_z}\bigg|_{\boldsymbol{\mathcal{E}}=\mathbf{0}} \tag{2}$$

along the z axis at zero electric field $\boldsymbol{\mathcal{E}} = (\mathcal{E}_x, \mathcal{E}_y, \mathcal{E}_z)$. Figure 1 explains this definition for a water molecule in the static electric field of a capacitor.

The electronic dipole moment $\boldsymbol{\mu} = (\mu_x, \mu_y, \mu_z)$ can be obtained from the wave function Ψ,

$$\boldsymbol{\mu} \equiv \langle \boldsymbol{\mu} \rangle = \langle \Psi | \hat{\boldsymbol{\mu}} | \Psi \rangle = \langle \Psi | - \sum_{i=1}^{N} \mathbf{r}_i | \Psi \rangle = - \int d^3r \rho(\mathbf{r})\mathbf{r} \, . \tag{3}$$

2

minus sign

Figure 1: Dipole moment vector $\boldsymbol{\mu}$ of the water molecule oriented parallel to the z direction. The dipole moment vector may be obtained with partial charges q_i using the equation $\boldsymbol{\mu} = \sum_i q_i \mathbf{R}_i$ and atomic positions $\mathbf{R}_i$. Application of an electric field pointing into the positive z direction leads to the schematic change in energy shown on the right. The slope of the energy curve at $\mathscr{E}_z = 0$ represents the negative dipole component along z. On the left, the illustrated charged capacitor plates generate the $\mathscr{E}$ field in positive z direction. This makes clear why the energy of the given molecular orientation lowers for small $\mathscr{E}_z$.

In Hartree–Fock and DFT methods, the density ρ is often represented with atomic (Gaussian-type) basis functions $\eta(\mathbf{r})$,

$$\rho(\mathbf{r}) = \sum_{\mu\nu} D_{\mu\nu} \eta_\mu(\mathbf{r}) \eta_\nu(\mathbf{r}) . \tag{4}$$

Using this representation for the dipole moment, eqn 3 leads to

$$\boldsymbol{\mu} = -\int d^3r \sum_{\mu\nu} D_{\mu\nu} \eta_\mu(\mathbf{r}) \eta_\nu(\mathbf{r}) \mathbf{r} = -\sum_{\mu\nu} D_{\mu\nu} \int d^3 \eta_\mu(\mathbf{r}) \mathbf{r} \eta_\nu(\mathbf{r}) = \text{tr}(\mathbf{D}\hat{\boldsymbol{\mu}}_{\text{AO}}) , \tag{5}$$

where the tr operation means 'trace'. Within Hartree–Fock and DFT calculations, this trace is computed using the density matrix $\mathbf{D}$ obtained from the SCF procedure and is thus printed in the end of the DFT output.

3. Electronic Response

If a molecule is exposed to a 'weak' electromagnetic wave in the UV/VIS range of the spectrum, then the electrons and thus the electronic dipole moment $\boldsymbol{\mu}(t)$ start to oscillate. This happens because the electromagnetic wave introduces a time-dependent perturbation into the Hamilton operator. The time-dependent perturbation contains the electric and magnetic field, $\mathscr{E}(t)$ and $\mathscr{B}(t)$. In the limit of long

wavelengths, the electric and magnetic fields are homogeneous, i.e., constant vectors throughout the molecule at a given time. This is also called *dipole approximation*, which is always implied in the following discussion. The total response of the time-dependent dipole moment,

$$\Delta \boldsymbol{\mu}(t) = \boldsymbol{\mu}(t) - \boldsymbol{\mu}_0 , \tag{6}$$

where $\boldsymbol{\mu}_0$ is the unperturbed dipole moment, may be transformed into the angular frequency domain (ω) by a Fourier transformation,

$$\Delta \boldsymbol{\mu}(\omega) = \int_{-\infty}^{\infty} dt \Delta \boldsymbol{\mu}(t) e^{i\omega t} . \tag{7}$$

The ω-dependent response may be expanded as a series in orders of the electric and magnetic field; truncation of this series after the first order yields the *linear response* of the dipole moment, $\Delta \boldsymbol{\mu}^{(1)}$, whose components are defined by

$$\Delta \mu_j^{(1)}(\omega) = \sum_k \alpha_{jk}(\omega) \mathscr{E}_k(\omega) + \frac{i\omega}{c} \sum_k G_{jk}(\omega) \mathscr{B}_k(\omega) \quad \text{with } j,k \in \{x,y,z\}, \tag{8}$$

where α_{jk} is the linear electric dipole-electric dipole polarizability and G_{jk} is the linear electric dipole-magnetic dipole polarizability. α_{jk} is the central quantity in *UV/VIS Absorption Spectroscopy (of linearly polarized and unpolarized light)*, while G_{jk} is the central quantity in *Electronic Circular Dichroism (ECD) spectroscopy*.

4. Polarized Electromagnetic Waves, Absorption and Optical Rotation

Descriptions of light properties can be found in textbooks of classical and quantum electrodynamics and Wikipedia.org; here, some aspects are summarized. The electromagnetic wave equation has the plane wave solution for electric and magnetic fields

$$\boldsymbol{\mathscr{E}}(\mathbf{r},t) = |\boldsymbol{\mathscr{E}}| \cdot \Re[|\psi\rangle e^{i(kz - \omega t)}] \tag{9}$$

$$\boldsymbol{\mathscr{B}}(\mathbf{r},t) = \mathbf{e}_z \times \boldsymbol{\mathscr{E}}(\mathbf{r},t)/c \tag{10}$$

at position $\mathbf{r} = (x,y,z)$ and time t for a light ray propagating along the unit vector $\mathbf{e}_z$, which points into the positive direction of the z axis. Further, there are the real part $\Re$, the imaginary unit i, the z component k of the wavevector $\mathbf{k} = 2\pi/\lambda \mathbf{e}_z$, the angular frequency ω, and the speed of light c (see also Figure 2). The
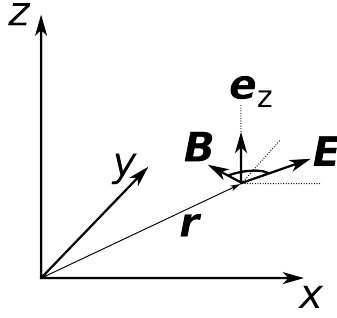
Figure 2: Alignment of $\mathcal{E}$ and $\mathcal{B}$ fields in the coordinate system.

Jones vector

$$|\psi\rangle = \begin{pmatrix} \cos\theta\, e^{i\alpha_x} \\ \sin\theta\, e^{i\alpha_y} \\ 0 \end{pmatrix} \qquad (11)$$

defines the direction of $\mathcal{E}$ in the xy plane and contains the parameters θ, α_x, and α_y as degrees of freedom, which may be freely set in the beginning of the experiment. Setting $\alpha_x = \alpha_y$ will result in *linearly polarized light*. Setting $\alpha_y = \alpha_x \pm \pi/2$ yields *right- and left-handed polarized light*. The superposition of right- and left-handed polarized light of the same magnitude $|\mathcal{E}|$ yields linearly polarized light. If light contains all directions of linearly polarized light, it is called unpolarized. Within the dipole approximation and the linear response regime, UV/VIS absorption spectra of unpolarized and linearly polarized light always depend only on the electric dipole-electric dipole polarizability α_{jk} of eqn 8, whereas circularly polarized light leads to absorption spectra which depend on both α_{jk} and the electric dipole-magnetic dipole polarizability G_{jk}. The dependence on G_{jk} may differ for left- and right-handed polarized light in case of an optically active medium yielding thus different absorption spectra; this effect is called *Electronic Circular Dichroism* (ECD). The resulting difference absorption spectrum between left- and right-handed polarized light is called *ECD Spectrum*. UV/VIS spectra may be measured in terms of the *molar absorption coefficient* ε vs wavelength, hence ECD spectra may show $\Delta\varepsilon$ vs wavelength.

In addition, the effect of *optical rotation* (see setup in Figure 3) may be understood in terms of circular polarization. Linearly polarized light with an $\mathcal{E}$ field oscillating along the y axis may be decomposed into left- and right-handed polarized waves of the same frequency. If they enter an optically active medium, left- and right-handed polarized light may propagate with different velocities (where the difference solely depends on G_{jk}). This difference in speed between left- and right-handed polarized light leads to different wavelengths in the medium. One can show that this difference in the wavelengths keeps the light linearly polarized within the medium but changes the direction of linear polarization within the xy plane at each point z along the propagation path of the ray. The directions of linear polarization of $\mathcal{E}$ along z form
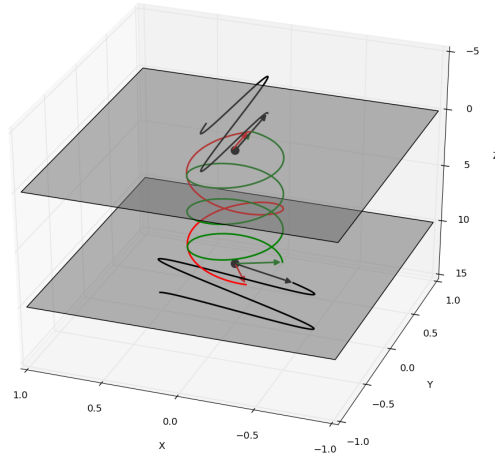
Figure 3: Optical rotation explained by decomposition of linearly polarized monochromatic light (black) into right- (green) and left-handed (red) polarized (rhp and lhp) light. For each wave, the lines show the end points of the $\mathcal{E}$ field vectors within each *xy* parallel plane. The grey colored planes show the surfaces of the optically active medium. Within the medium rhp and lhp light have different wavelengths. Arrows show $\mathcal{E}$ field vectors in the surface of the medium and make clear that the linear polarization is rotated by the medium. This illustration is a snapshot in time; the waves propagate and the lines change in time; however, the angle of rotation remains constant and depends only on the medium, the medium thickness, and the frequency of the light.

a helix in the optically active medium. When the light exits the medium, the left- and right-handed polarized light have the same speed again and the direction of the linearly polarized light keeps constant along *z*. This effect is called *optical rotation*.

5. Calculation of UV/VIS Absorption Spectra

The molar absorption coefficient $\varepsilon(\omega)$ of a molecule used in the Lambert Beer law is proportional to the isotropic photoabsorption cross section $\bar{\sigma}(\omega)$,

$$\varepsilon(\omega) = \frac{N_A}{1000 \cdot \ln 10} \bar{\sigma}(\omega) \,, \tag{12}$$

where N_A is the Avogadro number, ε is given in $\mathrm{L}/(\mathrm{mol} \cdot \mathrm{cm})$ and $\bar{\sigma}$ in cm^2. The remaining equations in this chapter are given, as usual, in atomic units. 'Isotropic' means that the photoabsorption is computed for the average of all spatial orientations between the molecule and the incoming electromagnetic wave.

As a result of *Fermi's Golden Rule*, the photoabsorption cross section may be computed as

$$\bar{\sigma}(\omega) = \frac{4\pi\omega}{c}\Im(\bar{\alpha}(\omega)) \tag{13}$$

from the trace of the electric dipole-electric dipole polarizability tensor,

$$\bar{\alpha} = \frac{1}{3}\sum_j \alpha_{jj} = \lim_{\eta\to 0^+}\sum_{n=1}^{\infty}\frac{f_n}{\omega^2 - \Omega_n^2}\,, \tag{14}$$

with oscillator strengths f_n and electronic excitation energies Ω_n from the ground state $|0\rangle$ to excited states $|n\rangle$. The frequency $\omega = w + i\eta$ is complex, where the imaginary frequency η approaches zero from the positive. The oscillator strengths may be defined as

$$f_n = \frac{2}{3}\Omega_n \sum_j^{x,y,z} |\mu_{0n,j}|^2 \tag{15}$$

with components of the electric transition dipole moment $\boldsymbol{\mu}_{0n}$, which is commonly represented in the dipole–length representation

$$\boldsymbol{\mu}_{0n} = -\langle n|\hat{\mathbf{r}}|0\rangle = \langle n|\hat{\boldsymbol{\mu}}|0\rangle \tag{16}$$

or in the equivalent dipole–velocity representation

$$\boldsymbol{\mu}_{0n} = -\frac{1}{i\Omega_n}\langle n|\hat{\mathbf{p}}|0\rangle\,. \tag{17}$$

$\hat{\mathbf{p}} = -i\sum_{k=1}^N(\partial/\partial x_k, \partial/\partial y_k, \partial/\partial z_k)$ is the linear momentum operator, and $\hat{\mathbf{r}} = \sum_{k=1}^N \mathbf{r}_k$ is the position operator formed by all spatial electron coordinates $\mathbf{r}_k = (x_k, y_k, z_k)$. Differences between results obtained from both representations appear due to approximations, such as using finite atomic basis sets to expand molecular orbitals or solving the linear response problem approximately. Agreement between oscillator strengths in length and velocity representations indicate consistent (and perhaps reliable) oscillator strengths obtained for the selected electronic structure approach. In this course, the time-dependent (TD) DFT methods are used to compute oscillator strengths f_n and excitation energies Ω_n. These methods compute the transition moments, e.g. $\langle 0|\hat{\mathbf{r}}|n\rangle$, and excitation energies Ω_n directly and *do not* compute stationary excited states $|n\rangle$. The TD-HF and TD-DFT approaches are implemented in many quantum chemistry software packages and provide oscillator strengths and excitation energies of the interacting electron system on output and you will use them in the exercices out of the box. The input for such calculations requires a well-converged SCF calculation (HF or DFT) and a selected number of lowest excitations, which will be solved in the response problem. The textbook "Time-Dependent Density-

Functional Theory" (Oxford University Press, 2012) from Carsten A. Ullrich provides an up to date overview and explanation of TD-DFT.

6. Calculation of Circular Dichroism Spectra

ECD spectra show $\Delta\varepsilon$ vs. ω, allow to distinguish diastereomers, and are very sensitive to conformational and electronic changes in the molecules. The difference absorption coefficient is determined as

$$\Delta\varepsilon(\omega) = \frac{N_A}{\ln 10} 16\pi\omega^2 \Im(\bar{G}(\omega)) . \tag{18}$$

where $\bar{G}$ is the trace of the electric dipole-magnetic dipole polarizability tensor at real angular frequencies ω,

$$\Im(\bar{G}(\omega)) = \frac{c\pi}{3} \sum_n \frac{1}{\Omega_n} \times (R_n \delta(\omega - \Omega_n) - R_n \delta(\omega + \Omega_n)) \tag{19}$$

with rotatory strengths

$$R_n = \Im(\boldsymbol{\mu}_{0n} \cdot \mathbf{m}_{0n}) \tag{20}$$

using the electric transition dipole moment $\boldsymbol{\mu}_{0n}$ from eqn (16) or (17) and the magnetic transition dipole moment

$$\mathbf{m}_{0n} = -\frac{1}{2c} \langle n|\hat{L}|0 \rangle \tag{21}$$

with angular momentum operator $\hat{L}$. In this class, the rotatory strengths are computed by using TD-DFT. Again, well-converged SCF input and the number of treated excitations must be provided. An excellent introduction to ECD is found in the review article "Circular dichroism: electronic" of Ingolf Warnke and Filipp Furche published in WIREs Comput Mol Sci, 2012, page 150.

7. Preparational exercises discussed in the seminar

All computations are performed with Gaussian09.

Exercise 1 Dipole moments
a) Classify the following methods into different levels of electronic structure theory: Hartree–Fock (HF), Perdew-Burke-Ernzerhof (PBE), PBE0, Becke-3-Lee-Yang-Parr (B3LYP), CCSD, and CCSD(T). Which methods are size-consistent and which are variational?

b) What is the difference between basis sets such as 6-31G+**, cc-pVTZ, cc-pVQZ, aug-cc-pVQZ.

What do the abbreviations mean? Explain briefly the main differences between Slater- and Gaussian-type atomic orbital (AO) basis functions. Give an example for frequently used non-AO-type basis sets. How to improve basis sets? What's the difficulties when improving AO-type basis sets?

c) The experimental bond length of the CO molecule is 1.128Å and the experimental electric dipole moment is 0.112 debye pointing from C atom to O atom. What does this mean for the partial charges on the C and O atom? Compute these partial charges. Lets optimize the CO bond length and compute its electric dipole moment with the methods and basis sets given in Tab. I. Compute the partial charges $\delta_C(\mu)$ and $\delta_O(\mu)$ from the dipole moment (take care about its sign with respect to the orientation of CO on output) and equilibrium bond length and compare these with the Mulliken charges, q_C and q_O

Technical details: Invoke tight convergence criteria using the keywords scf=tight and opt=tight. If necessary, you may use the '%nprocshared' and '%mem' flags, e.g., for CCSD(T) with aug basis sets to increase use of computational ressources, see Supporting Information section A. You will need following electronic structure method keywords: `hf`, `pbepbe`, `pbe1pbe`, `b3lyp`, `mp2`, `ccsd`, and `ccsd(t)`; basis set keywords are `6-31+g(d,p)`, `cc-pvtz`, `cc-pvqz`, `aug-cc-pvqz`. For post-SCF methods, the additional keyword `density` is required to have the population analysis and dipole moments at post-SCF level in the output. You should doublecheck the level of the population analysis printed in the corresponding headline. To avoid computation of dipole moments in every geometry optimization step, it may be useful for post-SCF methods to run the optimization first and then perform a single SCF + post-SCF calculation including the density keyword, see Supporting Information section A.

In addition, CCSD(T) dipole moments are not implemented analytically and population analysis is not available for this level. Calculate CCSD(T) dipole moments by forming the difference quotient from the two CCSD(T) energies obtained by an external positive and a negative (small!) finite electric dipole field along the CO axis (check Gaussian standard orientation of CO in the calculation to provide the correct field direction and be aware that Gaussian input of a positive E-field is indeed used like a negative E-field for the energy result). Explain graphically why positive AND negative field distortions should be used together, though the difference quotient simply represents an approximation of equation 2. Please consult Supporting Information section A for further specifications.

Exercise 2 UV/Vis absorption
a) Build the structure model of an ethylene molecule and optimize it with B3-LYP/aug-cc-pVTZ; check the dipole moment of the relaxed structure. Then perform a TDDFT calculation at the B3-LYP/aug-cc-pVTZ level including the 10 lowest singlet and triplet excitations, respectively, see Supporting Information section B for details. Assign calculated states to experimental states in Tab. II (by spin and irrep)

Table I: Methods for the computation of dipole moments and optimization of the CO structure.

basis	method	$R_{\text{opt}}/\text{Å}$	$\mu(R_{\text{opt}})/\text{debye}$	$\delta_{\text{C}}(\mu)/\text{a.u.}$	$\delta_{\text{O}}(\mu)/\text{a.u.}$	$q_{\text{C}}/\text{a.u.}$	$q_{\text{O}}/\text{a.u.}$
6-31G+**	HF						
	PBE						
	PBE0						
	B3-LYP						
	MP2						
	CCSD						
	CCSD(T)						
cc-pVTZ	HF						
	PBE						
	PBE0						
	B3-LYP						
	MP2						
	CCSD						
	CCSD(T)						
cc-pVQZ	MP2						
	CCSD						
	CCSD(T)						
aug-cc-pVQZ	MP2						
	CCSD						
	CCSD(T)						

and compare their excitation energies ... compute the mean absolute error of calculated excitation energies. Which excitations usually do not contribute to an optical absorption spectrum in terms of spin and transition dipole moments? The transition moments can be used to compute the actual measure for the peak intensity in the spectrum, how is this measure called? Extract the values of this intensity measure from the Gaussian outputs and check, which of the peaks should be visible in the spectrum.

Table II: Low-lying excitation energies, Ω, (in eV) of ethylene from experiment taken from J. B. Foresman, M. Head–Gordan, and J. A. Pople, J. Phys. Chem. 96, 135 1992.

State	Ω
$^3B_{1u}$	4.36
$^3B_{3u}$	6.98
$^1B_{3u}$	7.15
$^1B_{1u}$	7.66
$^3B_{1g}$	7.79
$^3B_{2g}$	7.79
$^1B_{1g}$	7.83
$^1B_{2g}$	8.00
^3A_g	8.15
^1A_g	8.29

b) Provide at least two straight reasons why electric-dipole forbidden transitions can appear as small peaks in experiments. [hint: Think about the approximations on structure and field in our calculations.]

c) Typically a peak for a single electronic transition exhibits a 'pattern' in a measured vapor absorption spectrum. What is the usual origin of such additional pattern in the electronic peak? Discuss if the effect for this pattern can blue or redshift the patterned peak from the peak of pure electronic transition.

Exercise 3 ECD spectra
a) Calculate the relaxed structure of R-methyl oxirane, see Fig. 4, using the B3LYP/tzvp method. Then conduct a TDDFT calculation including the 40 lowest states relevant for optical excitations. For input commands and post-modifications in the output (to make the ECD spectrum visible with GaussView) see Supporting Information section C. Open the output with GaussView and look at the absorption and ECD spectra; in which energy range (ev) these spectra are physically meaningful for the present calculation? Compare your spectra with the experimental ones, see Fig. 3 in Varsano, *PCCP* **11**, p. 4481.
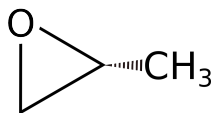
Figure 4: *R*-methyl oxirane structure model.

8. Supporting Information

A. CCSD(T)/aug-ccpVQZ optimization of CO

Input file for Gaussian optimization at CCSD/cc-pVQZ with a subsequent SCF + post-SCF step for molecular properties at the CCSD level. The 'density' keyword is necessary for all post-SCF methods. For SCF methods, simple optimization is sufficient. For CCSD(T), see below.

```
%nprocshared=4
%mem=3GB
%chk=tmp.chk
# ccsd/cc-pvqz scf=tight opt=tight

CO CCSD TZ

0 1
 O                  1.12800000    0.00000000    0.00000000
 C                  0.00000000    0.00000000    0.00000000

--Link1--
%nprocshared=4
%mem=3GB
%chk=tmp.chk
# ccsd/cc-pvqz scf=tight geom=allcheck density

#end of file
```

For CCSD(T), perform first a field-free optimization. Then use the optimized bond length in a subsequent single SCF+post-SCF step with an external electric field switched on. Warning (as figured out with careful testing among different QC programs): Z+10 means an $\mathscr{E}$-field pointing into negative z direction of magnitude 0.001 a.u., e.g.,

```
%mem=3072MB
%nprocshared=4
# ccsd(t)/cc-pvtz scf=tight Field=Z+10

 CO

0 1
 C
```

```
 O 1 r

r 1.1357

#end of file
```

B. Electronic absorption spectrum of ethylene

Build the Z-matrix of the D_{2h}-symmetric ethylene molecule and optimize the structure with
`b3lyp/aug-cc-pvtz scf=tight opt=tight`.
Then perform a TD-DFT calculation once for singlet and once for triplet excited states, e.g.,

```
%nprocshared=4
%mem=4GB
%chk=tmp.chk
# b3lyp/aug-cc-pvtz td=(triplets,nstates=10) scf=tight geom=allcheck
```

C. Electronic circular dichroism spectrum of R-methyl oxirane

The input below loads the geometry from the checkpoint file (created in a previous structure optimization)
and runs a SCF calculation followed by the TD-DFT calculation including the lowest 40 singlet states.
the calculation returns all quantities for electronic absorption and CD spectra.

```
%nprocshared=4
%mem=4GB
%chk=tmp.chk
#p b3lyp/aug-cc-pVTZ scf=tight geom=allcheck td=(singlets,nstates=40)

R-Me-Oxirane B3LYP aug-cc-pVTZ

0 1
```

In the output, you will find excitation energies, oscillator strengths, and rotatory strengths. The Gaussian09 output format seems not compatible to any running Gaussview version installed on the CIP cluster. Therefore, some minor editing in the output file is necessary to visualize the ECD spectrum in Gaussview (tested with the `gv4` binary). Here is a part from the Gaussian09 output (obtained for a TDDFT caluclation) including the rotatory strengths:

```
[...]
 Ground to excited state transition magnetic dipole moments (Au):
      state          X            Y            Z
        1        -0.3431       0.0646      -0.3664
        2         0.1142      -0.2162      -0.0592
        3         0.1583       0.2021       0.0578
        4         0.0916      -0.0214       0.1859
        5         0.0837      -0.5384      -0.1022
        6         0.0134       0.0288       0.0155
        7        -0.2073      -0.1762       0.1293
        8        -0.1180      -0.0702      -0.1138
        9         0.4335       0.2171       0.0371
```

13

```
    10         0.0542      -0.0872       0.5373
    11        -0.1747       0.0707       0.1568
    12         0.1035      -0.0105       0.1158
    13        -0.2152       0.0295       0.2525
    14        -0.0193       0.1113      -0.3805
    15         0.1294       0.1941      -0.5348
    16         0.3292      -0.1203       0.0971
    17         0.0725       0.3117       0.7485
    18         0.0494      -0.4307      -0.0860
    19         0.0583       0.1306      -0.0998
    20        -0.1377      -0.2271      -0.0838
<0|del|b> * <b|rxdel|0> + <0|del|b> * <b|delr+rdel|0>
Rotatory Strengths (R) in cgs (10**-40 erg-esu-cm/Gauss)
     state          XX          YY          ZZ    R(velocity)
      1         -2.8081     -31.3244     -10.7156     -14.9493
Total R(velocity) tensor for State=          1
               1             2             3
   1   -0.280807D+01 -0.659901D+01  0.166155D+02
   2   -0.295866D+02 -0.313244D+02 -0.146184D+02
   3    0.144455D+02  0.188898D+02 -0.107156D+02
R(velocity) tensor in inp. orien. for State=          1
               1             2             3
   1   -0.134775D+02 -0.140821D+01  0.124910D+02
   2   -0.122323D+02 -0.751363D+00  0.106443D+02
   3   -0.186600D+02  0.344853D+02 -0.306191D+02
[...]
     20         19.6091      -0.1645      -2.0253       5.8064
Total R(velocity) tensor for State=         20
               1             2             3
   1    0.196091D+02 -0.175738D+01 -0.242489D+02
   2   -0.103101D+02 -0.164463D+00  0.710873D+01
   3   -0.788401D+01 -0.156548D+01 -0.202530D+01
R(velocity) tensor in inp. orien. for State=         20
               1             2             3
   1    0.370287D+01  0.126656D+02 -0.254861D+01
   2    0.249044D+02  0.159978D+02 -0.725830D+01
   3    0.731237D+01  0.574837D+01 -0.228131D+01
1/2[<0|r|b>*<b|rxdel|0> + (<0|rxdel|b>*<b|r|0>)*]
Rotatory Strengths (R) in cgs (10**-40 erg-esu-cm/Gauss)
     state          XX          YY          ZZ    R(length)     R(au)
      1        -41.2426      -7.1786       2.3686     -15.3509    -0.0326
[...]
```

This output must be modified to (the best is you make a copy before!):

```
[..]
Ground to excited state transition magnetic dipole moments (Au):
     state          X            Y            Z
       1         -0.3431       0.0646      -0.3664
       2          0.1142      -0.2162      -0.0592
       3          0.1583       0.2021       0.0578
       4          0.0916      -0.0214       0.1859
       5          0.0837      -0.5384      -0.1022
       6          0.0134       0.0288       0.0155
```

```
    7        -0.2073     -0.1762      0.1293
    8        -0.1180     -0.0702     -0.1138
    9         0.4335      0.2171      0.0371
   10         0.0542     -0.0872      0.5373
   11        -0.1747      0.0707      0.1568
   12         0.1035     -0.0105      0.1158
   13        -0.2152      0.0295      0.2525
   14        -0.0193      0.1113     -0.3805
   15         0.1294      0.1941     -0.5348
   16         0.3292     -0.1203      0.0971
   17         0.0725      0.3117      0.7485
   18         0.0494     -0.4307     -0.0860
   19         0.0583      0.1306     -0.0998
   20        -0.1377     -0.2271     -0.0838
<0|del|b> * <b|rxdel|0>  (Au), Rotatory Strengths (R) in
cgs (10**-40 erg-esu-cm/Gauss)
     state        XX          YY          ZZ    R(velocity)
      1        -2.8081    -31.3244    -10.7156    -14.9493
      2         4.3182     -0.7277      5.0491      2.8799
      3        -1.8631     -8.0359      3.6278     -2.0904
[...]
     20        19.6091     -0.1645     -2.0253      5.8064
1/2[<0|r|b>*<b|rxdel|0> + (<0|rxdel|b>*<b|r|0>)*]
Rotatory Strengths (R) in cgs (10**-40 erg-esu-cm/Gauss)
     state        XX          YY          ZZ    R(length)     R(au)
      1        -41.2426     -7.1786      2.3686    -15.3509    -0.0326
[...]
```

Keep special attention for line `<0|del|b> * <b|rxdel|0>  (Au), Rotatory Strengths (R) in`, as there are TWO SPACES between `<b|rxdel|0>` and `(Au)`! Once you have made these changes, start Gaussview

`gv4 &`

and load your TDDFT output file with `File→Open` selecting `Gaussian Ouput Files` under `File Type`. Open your modified output file; a new molecule viewer window appears containing the molecular structure. In the Gaussview main window, go to `Results→UV-VIS` (see Fig. 5). A window appears containing the UV-VIS and ECD spectra (you may scroll down to see the ECD spectrum and you should save the spectra as images by a right click on each spectrum and selecting `Export`). For convenience, change energy axis to eV and reduce the peak broadening to 0.1 eV.
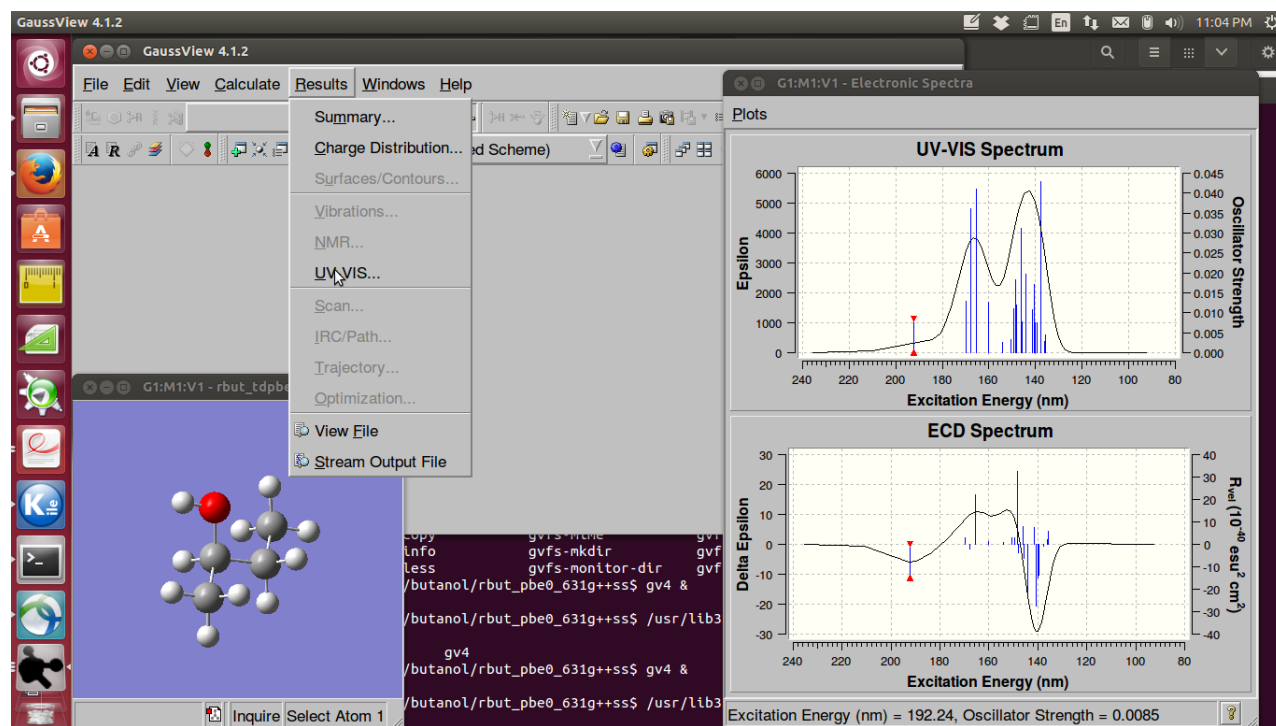
Figure 5: Screenshot from Gaussview. The structure and spectra windows are shown. The mouse pointer shows how to open the spectra.