Maple Quantum Chemistry Toolbox

The Maple Quantum Chemistry Toolbox from RDMChem, a separate add-on product to Maple, is a powerful environment for the computation and visualization of the electronic structure of molecules. In Maple 2022, this toolbox has significant new features and enhancements: (1) a new option for solvents in Density Functional Theory as well as a new extendable database of solvents and their dielectric constants, (2) a new option for ghost atoms to correct basis set superposition errors, (3) new commands for computing and visualizing exciton populations in molecules, (4) a new option for exporting skeletal structures to a graphics file including jpg, png, tif, and bmp formats, (5) a new addition to the 30 builtin lessons for classroom learning in undergraduate-to-graduate chemistry and physics, and (6) additional enhancements throughout the package.

Note that the Maple Quantum Chemistry Toolbox (QCT) is required in order to execute the examples in this worksheet.

Continuum Solvents

QCT 2022 adds support for continuum solvents in Density Functional Theory (DFT). Before we begin we load the *QuantumChemistry* package,

```
> with(QuantumChemistry);
```

```
[AOLabels, ActiveSpaceCI, ActiveSpaceSCF, AtomicData, BondAngles, BondDistances, Charges,
  ChargesPlot, ContractedSchrodinger, CorrelationEnergy, CoupledCluster, DensityFunctional,
  DensityPlot3D, Dipole, DipolePlot, Energy, ExcitationEnergies, ExcitationSpectra,
  ExcitationSpectraPlot, ExcitedStateEnergies, ExcitedStateSpins, ExcitonDensityPlot,
  ExcitonPopulations, ExcitonPopulationsPlot, FullCI, GeometryOptimization, HartreeFock, Interactive,
  Isotopes, MOCoefficients, MODiagram, MOEnergies, MOIntegrals, MOOccupations,
  MOOccupationsPlot, MOSymmetries, MP2, MolecularData, MolecularDictionary,
  MolecularGeometry, NuclearEnergy, NuclearGradient, OscillatorStrengths, Parametric2RDM,
  PlotMolecule, Populations, Purify2RDM, RDM1, RDM2, RTM1, ReadXYZ, Restore, Save, SaveXYZ,
  SearchBasisSets, SearchFunctionals, SkeletalStructure, SolventDatabase, Thermodynamics,
  TransitionDipolePlot, TransitionDipoles, TransitionOrbitalPlot, TransitionOrbitals,
  Variational2RDM, VibrationalModeAnimation, VibrationalModes, Video]
```

The new command *SolventDatabase* accepts a name or part of a name and returns all matching solvents and their dielectric constants. Using *SolventDatabase*, we search for solvents containing "Toluene"

```
> SolventDatabase("Toluene");
```

```
[["p-IsoPropylToluene", 2.23220000], ["Toluene", 2.37410000], ["o-ChloroToluene", 4.63310000],
  ["a-ChloroToluene", 6.71750000], ["o-NitroToluene", 25.66900000]]
```

Next we can perform a DFT calculation for a water molecule in the one of these solvents, i. e. "Toluene". After we import the geometry of water with the *MolecularGeometry* command

```
> water := MolecularGeometry("water");
```

$$water := [["O", 0, 0, 0], ["H", 0.27740000, 0.89290000, 0.25440000], ["H", 0.60680000, -0.23830000, -0.71690000]]$$

we use the *DensityFunctional* command to perform the DFT calculation

```
> data := DensityFunctional(water, basis = "cc-pvdz", "solvent="Toluene");
```

$$data := \text{table}\left(\left[\begin{array}{l} e\_tot = -76.38344245,\ aolabels = \underset{\text{24 element Vector[column]}}{\begin{bmatrix} \text{"0 O 1s"} \\ \text{"0 O 2s"} \\ \text{"0 O 3s"} \\ \text{"0 O 2px"} \\ \text{"0 O 2py"} \\ \text{"0 O 2pz"} \\ \vdots \end{bmatrix}},\ charges = \begin{bmatrix} -0.26528412 \\ 0.13264195 \\ 0.13264217 \end{bmatrix}, \\ converged = 1,\ group = \text{"C1"},\ mo\_coeff = [[[\ 1.00312141,\ -0.00603245, \\ -5.30776238 \times 10^{-8},\ 0.00746752,\ -1.20730690 \times 10^{-8},\ -0.03080595,\ \ldots\ ], \\ [\ 0.00756206,\ 0.44287033,\ -3.91192518 \times 10^{-8},\ -0.16555268,\ -1.57285449 \times 10^{-8}, \\ 0.12750733,\ \ldots\ ], \\ [\ -0.00692984,\ 0.35469464,\ 5.21929912 \times 10^{-7},\ -0.37827410,\ 8.06679786 \times 10^{-8},\ 0.89663401, \\ \ldots\ ], \\ [\ 0.00144541,\ 0.08431287,\ -0.10846229,\ 0.40395131,\ 0.40489506,\ 0.18449760,\ \ldots\ ], \\ [\ 0.00107008,\ 0.06241911,\ 0.37247229,\ 0.29905675,\ -0.24680815,\ 0.13658958,\ \ldots\ ], \\ [\ -0.00075606,\ -0.04410181,\ 0.31982206,\ -0.21129581,\ 0.42475185,\ -0.09650522,\ \ldots\ ], \\ [\ :,\ :,\ :,\ :,\ :,\ :,\ :,\ ]]], \end{array}\right.$$

$$\left[\begin{array}{l} \text{24 × 24 Matrix} \end{array}\right], mo\_occ = \underset{\text{24 element Vector[column]}}{\begin{bmatrix} 2.00000000 \\ 2.00000000 \\ 2.00000000 \\ 2.00000000 \\ 2.00000000 \\ 0. \\ \vdots \end{bmatrix}}, mo\_symmetry = \underset{\text{24 element Vector[column]}}{\begin{bmatrix} \text{"A"} \\ \text{"A"} \\ \text{"A"} \\ \text{"A"} \\ \text{"A"} \\ \text{"A"} \\ \vdots \end{bmatrix}}, dipole$$

$$= \begin{bmatrix} 1.42306177 \\ 1.05353446 \\ -0.74436405 \end{bmatrix}, rdm1$$

$=$

$$[[[2.01268945, 0.00735560, -0.02383183, 0.00791565, 0.00586015, -0.00414050, \ldots],$$
$$[0.00735560, 0.44719800, 0.43931124, -0.05904925, -0.04371599, 0.03088693, \ldots],$$
$$[-0.02383183, 0.43931124, 0.53789521, -0.24581807, -0.18198588, 0.12858099, \ldots],$$
$$[0.00791565, -0.05904925, -0.24581807, 0.69198298, -0.02852391, 0.09643726, \ldots],$$
$$[0.00586015, -0.04371599, -0.18198588, -0.02852391, 0.58596420, -0.10330082, \ldots],$$
$$[-0.00414050, 0.03088693, 0.12858099, 0.09643726, -0.10330082, 0.65858348, \ldots],$$
$$[\vdots, \vdots, \vdots, \vdots, \vdots, \vdots,]]],$$

$$\begin{bmatrix} \\ 24 \times 24 \text{ Matrix} \\ \\ \end{bmatrix}, populations = \underset{24 \text{ element Vector[column]}}{\begin{bmatrix} 2.00621803 \\ 0.84110733 \\ 0.81657149 \\ 1.00740790 \\ 0.88433851 \\ 0.96606128 \\ \vdots \end{bmatrix}}, mo\_energy = \underset{24 \text{ element Vector[column]}}{\begin{bmatrix} -19.12050478 \\ -0.98721541 \\ -0.50535422 \\ -0.36137824 \\ -0.28382642 \\ 0.05236958 \\ \vdots \end{bmatrix}} \end{bmatrix}\Bigg)$$

The new *solvent* keyword implements a domain-decomposition COnductor-like Screening MOdel (ddCOSMO) for solvation, which accounts implicitly for the interactions between the specified molecule (solute) and solvent.

Ghost Atoms

When modeling intermolecular interactions, it is often necessary to correct for basis set superposition error (BSSE). In BSSE the intermolecular interaction is overestimated due to the incompleteness of the basis set. A common approach to correcting BSSE is the counterpoise correction. The counterpoise correction estimates the basis-set incompleteness by performing a series of calculations with ghost atoms. Ghost atoms are ethereal in that they only contribute basis functions of the specified atom without adding a nucleus or any additional electrons. QCT 2022 adds support for ghost atoms to all methods through the new keyword *ghost*. For example, we can perform a *Parametric2RDM* calculation of neon with a neon ghost atom.

```
> data := Parametric2RDM([["Ne", 0, 0, 0]], basis = "cc-pvdz", ghost = [["Ne", 0, 0, 1.0]]);
```

$$data := \text{table}\left(\begin{bmatrix} e\_tot = -128.68548282,\ aolabels = \begin{bmatrix} \text{"0 Ne 1s"} \\ \text{"0 Ne 2s"} \\ \text{"0 Ne 3s"} \\ \text{"0 Ne 2px"} \\ \text{"0 Ne 2py"} \\ \text{"0 Ne 2pz"} \\ \vdots \end{bmatrix} \\ \text{28 element Vector[column]} \end{bmatrix}, charges = \begin{bmatrix} -0.00184245 \\ 0.00184245 \end{bmatrix},\right.$$

$$\left. active\_orbitals = [1..28], group = \text{"C1"}, mo\_coeff \right)$$

$$=$$

$$\left[\left[\begin{array}{cccccc} 1.00057892 & -0.01398654 & 0. & 0. & 0.00139986 & -0.00906630 & \dots \\ -0.00686084 & -0.51618079 & 0. & 0. & -0.00332241 & -0.02024781 & \dots \\ -0.01161852 & -0.56395289 & 0. & 0. & -0.02691747 & 0.05108698 & \dots \\ 0. & 0. & 0.46318610 & 0.51743756 & 0. & 0. & \dots \\ 0. & 0. & 0.51743756 & -0.46318610 & 0. & 0. & \dots \\ 0.00004471 & 0.00840623 & 0. & 0. & -0.69257355 & -0.91611571 & \dots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \end{array}\right]\right.$$

$$\left.\right],$$

$$\left[\begin{array}{c} 28 \times 28 \text{ Matrix} \end{array}\right], mo\_occ = \underset{28 \text{ element Vector[column]}}{\left[\begin{array}{c} 1.99995066 \\ 1.99229725 \\ 1.98397369 \\ 1.98397369 \\ 1.98334653 \\ 0.01179293 \\ \vdots \end{array}\right]}, e\_corr = -0.19560646, dipole = \left[\begin{array}{c} 0. \\ 0. \\ -0.05011035 \end{array}\right], rdm1$$

$$= \left[\left[\left[1.99994907,\ -0.00010947,\ 0.,\ 0.,\ -2.77800924 \times 10^{-6},\ -0.00002971,\ \dots \right], \right.\right.$$

$$\left[-0.00010947,\ 1.99227236,\ 0.,\ 0.,\ -0.00013600,\ 0.00412310,\ \dots \right],$$

$$\left[0.,\ 0.,\ 1.98394165,\ 0.,\ 0.,\ 0.,\ \dots \right],$$

$$\left[0.,\ 0.,\ 0.,\ 1.98394165,\ 0.,\ 0.,\ \dots \right],$$

$$\left[-2.77800924 \times 10^{-6},\ -0.00013600,\ 0.,\ 0.,\ 1.98323965,\ 0.01395312,\ \dots \right],$$

$$\left[-0.00002971,\ 0.00412310,\ 0.,\ 0.,\ 0.01395312,\ 0.00286435,\ \dots \right],$$

$$\left.\left[:,\ :,\ :,\ :,\ :,\ :,\ \right]\right],$$

$$\left[\begin{array}{c}\text{28 × 28 Matrix}\end{array}\right], populations = \left[\begin{array}{c}2.00129196\\0.94473303\\1.04823226\\1.26614566\\1.26614566\\1.26051998\\\vdots\\\text{28 element Vector[column]}\end{array}\right]\Bigg)\Bigg)$$

The additional basis functions on the neon ghost atom lower the total energy from -128.679 hartrees (without the ghost atom) to -128.685 hartrees.

Exciton Populations

QCT2022 can compute the exciton populations of a molecule. Excitons are quasi-particles that consist of an electron and a hole (the absence of an electron). These particles are important because they can absorb, transport, and emit energy. Consider the benzene molecule

```
> benzene := MolecularGeometry("benzene");
```

$$benzene := [["C", -1.21310000, -0.68840000, 0], ["C", -1.20280000, 0.70640000, 0.00010000], ["C", -0.01030000, -1.39480000, 0], ["C", 0.01040000, 1.39480000, -0.00010000], ["C", 1.20280000, -0.70630000, 0], ["C", 1.21310000, 0.68840000, 0], ["H", -2.15770000, -1.22440000, 0], ["H", -2.13930000, 1.25640000, 0.00010000], ["H", -0.01840000, -2.48090000, -0.00010000], ["H", 0.01840000, 2.48080000, 0], ["H", 2.13940000, -1.25630000, 0.00010000], ["H", 2.15770000, 1.22450000, 0]]$$

We perform a variational 2-RDM calculation with a 6-electrons-in-6-orbitals [6,6] active space

```
> data := Variational2RDM(benzene, active = [6, 6], return_rdm = "rdm1_and_rdm2");
```

$$data := \text{table}\left(\left[\begin{array}{l}e\_tot = -227.95444685, mo\_coeff\_canonical\end{array}\right]\right)$$

=

[[[−0.17009035, 0.53184999, 0.42048984, −0.12113394, 0.56067469, −0.40839320, …
],
[−0.00534589, 0.01550896, 0.00962921, −0.00522920, 0.02437501, −0.02107402, …],
[−0.00169716, −0.00117440, −0.00111974, 0.00153726, 0.00206940, −0.00210823, …],
[0.00300187, 0.00101462, −0.00116050, −0.00350446, 0.00016799, −0.00128489, …],
[0., 0., 0., 0., 0., 0., …],
[−0.51188917, 0.08029166, 0.47308245, 0.54103986, −0.16599067, 0.41456010, …],
[⋮, ⋮, ⋮, ⋮, ⋮, ⋮,]]],

$$\begin{bmatrix} \text{36 × 36 Matrix} \end{bmatrix}, \; aolabels = \underbrace{\begin{bmatrix} \text{"0 C 1s"} \\ \text{"0 C 2s"} \\ \text{"0 C 2px"} \\ \text{"0 C 2py"} \\ \text{"0 C 2pz"} \\ \text{"1 C 1s"} \\ \vdots \end{bmatrix}}_{\text{36 element Vector[column]}}, \; charges = \underbrace{\begin{bmatrix} -0.06220440 \\ -0.06225210 \\ -0.06224581 \\ -0.06226661 \\ -0.06224119 \\ -0.06220159 \\ \vdots \end{bmatrix}}_{\text{12 element Vector[column]}}, \; converged = 1,$$

$active\_orbitals = [\,19 \,..24\,], \; group = \text{"C1"}, \; mo\_coeff$

=

[[[−0.00892741, −0.10627428, 0.04211509, −0.06701835, −0.13027557,
−0.10467581, …],
[0.03644646, 0.31318600, −0.12410580, 0.18086649, 0.35157420, 0.26484248, …],
[−0.20379512, −0.02592619, 0.13297960, 0.06827088, −0.00798270, 0.05386142, …],
[−0.11566987, −0.11262086, −0.17156676, −0.09457665, 0.06407487, 0.03057589, …],
[0., 0., −0.00001147, 0., 0., 0., …],
[−0.00891819, 0.08961578, 0.07097658, 0.07929337, −0.12318611, −0.10467801, …],
[⋮, ⋮, ⋮, ⋮, ⋮, ⋮,]]],

$$\begin{bmatrix} \text{36 × 36 Matrix} \end{bmatrix}, \; mo\_occ = \underbrace{\begin{bmatrix} 2.00000000 \\ 2.00000000 \\ 2.00000000 \\ 2.00000000 \\ 2.00000000 \\ 2.00000000 \\ \vdots \end{bmatrix}}_{\text{36 element Vector[column]}}, \; e\_corr = -0.06361461, \; rdm2$$

$$= \begin{bmatrix} 1.99938995 & 0. & 0. & 0. & 0. & 0. \\ 0. & 3.80057155 & -0.00012216 & 0. & 0. & 0.00019356 \\ 0. & -0.00012216 & 3.80095776 & 0. & 0. & 0.00015167 \\ 0. & 0. & 0. & 0.18448784 & 0.00003398 & 0. \\ 0. & 0. & 0. & 0.00003398 & 0.18422742 & -0.00001021 \\ 0. & 0.00019356 & 0.00015167 & 0. & -0.00001021 & 0.02728402 \end{bmatrix},$$

slice of 6 × 6 × 6 × 6 Array

$$dipole = \begin{bmatrix} -0.00005362 \\ -0.00003057 \\ 0.00003380 \end{bmatrix}, rdm1$$

$$= \begin{bmatrix} 1.99938371 & 0. & 0. & 0. & 0. & 0. \\ 0. & 1.90061899 & -0.00002346 & 0. & 0. & 0.00006981 \\ 0. & -0.00002346 & 1.90068179 & 0. & 0. & 0.00004763 \\ 0. & 0. & 0. & 0.09251396 & -0.00001176 & 0. \\ 0. & 0. & 0. & -0.00001176 & 0.09254601 & 0. \\ 0. & 0.00006981 & 0.00004763 & 0. & 0. & 0.01425553 \end{bmatrix},$$

$$populations = \begin{bmatrix} 1.99277191 \\ 1.13643038 \\ 0.97288746 \\ 0.96006097 \\ 1.00005368 \\ 1.99277190 \\ \vdots \end{bmatrix}$$

36 element Vector[column]

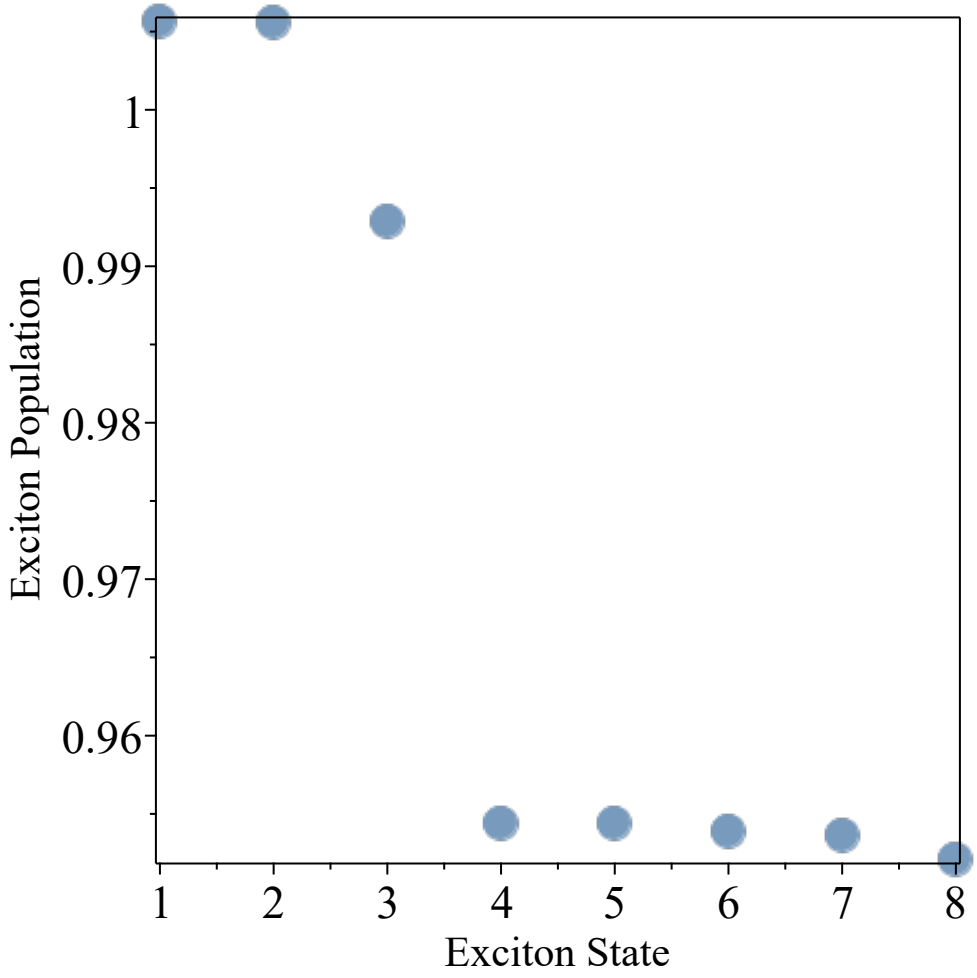
After the calculation we use the new command *ExcitonPopulations* to compute the exciton populations, the number of excitons in a given exciton (particle-hole) state

> $pops := ExcitonPopulations(benzene, data, nexcitons = 8, showtable = true)$:

Exciton State	Exciton Population
1	1.00564746
2	1.00559656
3	0.99287953
4	0.95440962
5	0.95438150
6	0.95385219
7	0.95361623
8	0.95208483

The populations can be plotted with the new command *ExcitonPopulationsPlot*

```
> ExcitonPopulationsPlot(pops, color = "Nautical Light Blue");
```



The particle and hole relationship of each exciton can be visualized with the new command *ExcitonDensityPlot*. Figure 1, for example, shows the particle and hole densities for the first exciton state in the table and figure above.

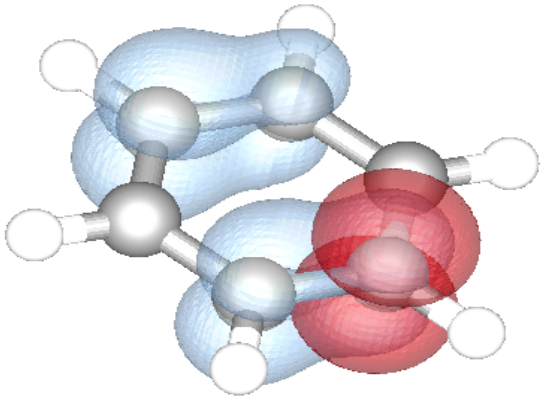


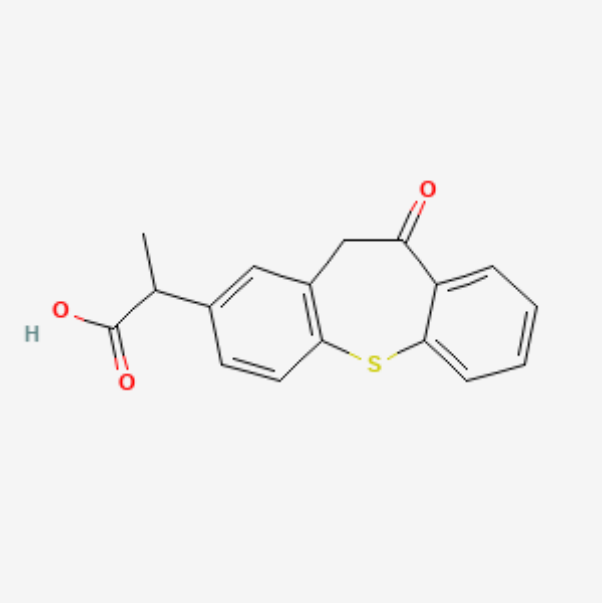
Figure 1: Output from *ExcitonDensityPlot*

For a particle placed in the $2p_z$ orbital of one of the carbon atoms, whose density is shown in nautical red, the density of the hole is shown in light nautical blue.

Exporting Skeletal Structures

A new keyword option to the command *SkeletalStructure* allows us to write skeletal structures to a jpg, png, tif, or bmp graphics file. The file type is determined from the extension given to the file name. For example, let's retrieve the skeletal structure of the non-steroidal anti-inflammatory drug (NSAID) Zaltoprofen.

```
> SkeletalStructure("Zaltoprofen");
```



In QCT2022 we can export the skeletal structure to a file with the keyword *file*.

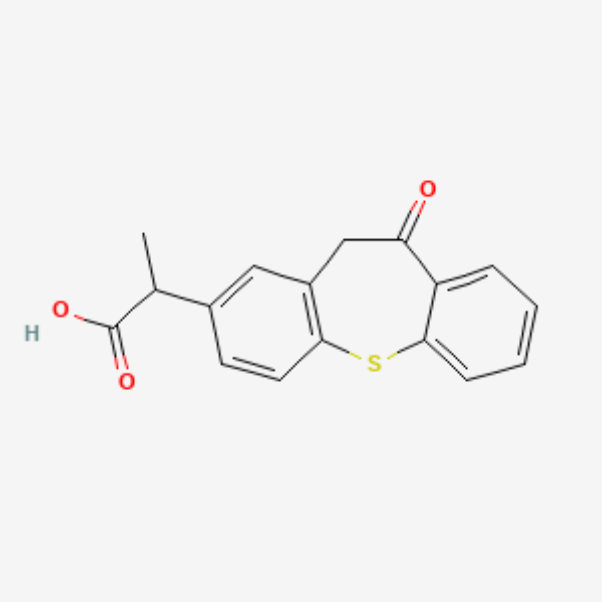
```
> dir := kernelopts(homedir);
```

$$dir := \text{"C:\Users\david"}$$

```
> filename := cat(dir, "\\Zaltoprofen.png");
```

$$filename := \text{"C:\Users\david\Zaltoprofen.png"}$$

> *SkeletalStructure*("Zaltoprofen", *file* = *filename*);



In addition to printing the skeletal structure, the command with *file* writes a png file to the filename. Note that we must use a directory with write permissions.

Using the Package in the Classroom

The Maple Quantum Chemistry Toolbox includes approximately 30 lessons that can be used in chemistry and physics courses from advanced high school courses through the graduate level. These lessons and associated curricula provide instructors and students with real-time quantum chemistry computations and visualizations that quickly deepen understanding of molecular concepts. Detailed lesson plans and curricula are provided for Introductory (General) Chemistry, Physical Chemistry (Quantum Mechanics and Thermodynamics), Thermodynamics (Physics), Quantum Mechanics (Physics), Computational Chemistry, and Quantum Chemistry as well as Advanced Placement (AP) and International Baccalaureate (IB) chemistry courses. Topics include atomic structure, chemical bonding, the Maxwell-Boltzmann distribution, heat capacity, enthalpy, entropy, free energy, particle-in-a-box, vibrational normal modes, infrared spectroscopy, as well as advanced electronic structure methods. Use of the QCT in the classroom is described in a recent paper in J. Chem. Ed. QCT 2022 includes a new lesson for Physical Chemistry and Undergraduate Quantum Mechanics on Huckel Theory and Conjugated Molecules. Within the lesson we compare the molecular orbitals predicted from Huckel Theory with those predicted from *ab initio* electronic structure calculations using the *Variational2RDM* method. The Maple environment allows us to seamlessly combine analytical work using the *LinearAlgebra* package with electronic structure calculations and visualizations from the QCT.