

15/09/2020

# SEMIEMP

-Open source code for semiempirical quantum chemistry calculation

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Please cite our original publications when you use Semiemp-

Soumen Ghosh, Jason C. Asher, Laura Gagliardi, Christopher J. Cramer, Nirranjan Govind. A Semiempirical Effective Hamiltonian Based Approach for Analyzing Excited State Wave Functions and Computing Excited State Absorption Spectra Using Real-Time Dynamics. J. Chem. Phys. 2019, 150, 104103.

Soumen Ghosh, Amity Andersen, Laura Gagliardi, Christopher J. Cramer and Nirranjan Govind. Modeling Optical Spectra of Large Organic Systems using Real-Time Propagation of Semiempirical Effective Hamiltonians. J. Chem. Theory Comput. 2017, 13, 4410–4420.

If you have any questions or suggestions, please contact me at [chemsgghosh\(at\)gmail.com](mailto:chemsgghosh@gmail.com).

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**Setting up the code-** SEMIEMP can be interfaced with NWChem. Few steps has to be followed to set up the code-

1. Download the code –

```
git clone https://github.com/SoumenChem/semiemp.git
```

2. Move "semiemp" folder to "nwchem/src/".

3. Copy task.F, task\_input.F, task\_energy, task\_gradient.F files from "nwchem/src/semiemp/setup" folder to "nwchem/src/task/" folder.

4. Copy input\_parse.F file from "nwchem/src/semiemp/setup" folder to "nwchem/src/input/" folder.

5. Copy make\_nwchem\_config from "nwchem/src/semiemp/setup" folder to "nwchem/src/config" folder.

6. Copy util\_module\_avail.F from "nwchem/src/semiemp/setup" folder to "nwchem/src/util" folder.

7. Compile nwchem. (It might be necessary to run "make realclean" before compiling the code.

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## Single point calculation

Below is a sample input for a single point calculation for INDO Hamiltonian:

```
start benzene_scf

charge 0
geometry noautosym noautoz
C      -0.804616000    0.000000000   -2.637508000
C      -1.968653000   -0.357135000   -1.934532000
C       0.359421000    0.357135000   -1.934532000
H      -2.876005000   -0.635517000   -2.482493000
H       1.266773000    0.635517000   -2.482493000
C      -1.968653000   -0.357135000   -0.528579000
C       0.359421000    0.357135000   -0.528579000
H      -2.876005000   -0.635517000    0.019382000
H       1.266773000    0.635517000    0.019382000
C      -0.804616000    0.000000000    0.174397000
H      -0.804616000    0.000000000    1.270320000
H      -0.804616000    0.000000000   -3.733431000
end

semiemp
mult 1
apx INDO/1
scftype rhf
maxiter 50
end

task semiemp energy
```

**No basis set is needed.**

### MULT- MULTIPLICITY

Multiplicity of the system can be defined here.

### APX-Approximate Hamiltonian

Currently available methods are CNDO/1, CNDO/2, INDO/1 and INDO/2. (1 and 2 indicates two different parametrization for one centre core integrals).

### SCFTYPE-Wave function type

Currently only RHF and UHF is available.

### MAXITER-Iteration limit.

This keyword indicate maximum allowed iterations. Default is 50.

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## SCFTOL-Convergence criteria for density.

Default value is  $10^{-7}$ .

## INTTYP- Integral type

0 (default) for ground state calculations

1 for spectroscopic calculations (INDO/S etc)

## INTPOL-Control for interpolation step in SCF

Default is FAST.

If SCF iteration shows instability, INTPOL should be set to SLOW. It might help with the convergence.

## RT-INDO/S

### Input for RT-INDO/S

start benzene\_y

charge 0

geometry noautosym noautoz

C	-0.804616000	0.000000000	-2.637508000
C	-1.968653000	-0.357135000	-1.934532000
C	0.359421000	0.357135000	-1.934532000
H	-2.876005000	-0.635517000	-2.482493000
H	1.266773000	0.635517000	-2.482493000
C	-1.968653000	-0.357135000	-0.528579000
C	0.359421000	0.357135000	-0.528579000
H	-2.876005000	-0.635517000	0.019382000
H	1.266773000	0.635517000	0.019382000
C	-0.804616000	0.000000000	0.174397000
H	-0.804616000	0.000000000	1.270320000
H	-0.804616000	0.000000000	-3.733431000

end

semiemp

mult 1.0

apx INDO/1

scftype rhf

maxiter 100

inttyp 1

end

rt\_semiemp

nrestarts 100

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```
tmax 1000
dt 0.1
tag "kick_y"
field_type delta
field_max 0.0001
polarization y
print dipole
end
```

```
task semiemp rt_semiemp
```

**RT-INDO/S is currently available only for RHF wave functions.**

## **NRESTARTS**

This sets the number of run-time check points where the time-dependent complex density matrix is saved to file, allowing the simulation to be restarted from that point.

## **PROPAGATOR**

If nothing is mentioned modified Chebyshev propagator will be used. Only other option available for now is conventional Chebyshev propagator. The keyword “Propagator Chebyshev” will activate the conventional Chebyshev propagator. For understanding the difference between two propagators please check our original paper (J. Chem. Phys. 2019, 150, 104103).

## **TMAX**

This option specifies the maximum time (in au) to run the simulation before stopping, which must be a positive real number.

## **DT**

This specifies the electronic time step for time integration.

## **TAG -- Output label**

This option sets a label for the output for convenient parsing (e.g., with "grep").

Tag “kick\_y”

It appears in the output as:

```
Kick_ytotal 0.1 2.20000 -7.589146713114E+001 -7.589146713114E+001 -7.589146713114E+001 #Dipole moment [system]
```

## **FIELD\_TYPE**

This option sets type of external electric field. Two options currently available are “delta” and “Gaussian”.

Gaussian field (only works with “propagator Chebyshev” keyword) has some other options-

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FREQUENCY 0.12 au #frequency of laser in au (e.g., 0.12 au = 3.27 eV)

CENTER 200.0 #center of Gaussian envelop (in au time)

WIDTH 50.0 #width of Gaussian pulse (in au time)

## **FIELD\_MAX**

This option sets the maximum value of the electric field

## **SPIN**

SPIN TOTAL has to be used for UHF wave function.

## **Polarization**

This option sets the polarization direction. It can be x, y or z.

## **PRINT**

This option sets the different time-dependent properties to be computed and printed at each time step.

Dipole: Dipole moment

## **ORBSPACE**

This option activates MO pair decomposition of the dipole moment. To reduce the amount data printed, a user defined orbital space is used. Only MO decomposed dipole moment information within that orbital space is printed. To print all the MO pair contribution full MO space can be specified. This keyword works with all propagator but **only** available for **RHF** wave functions. The key word format is-

ORBSPACE [lowest occupied MO number] [highest occupied MO number]