This is an add-on to the main deMon2k manual describing options to conduct Real-Time Time-Dependent Density Functional Theory calculation.

Link to the main deMon2k manual:

http://www.demon-software.com/public_html/support/htmlug/index.html

Any bugs with the options described in this add-on manual should be reported to :

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List of keywords :

the "modified keyword" mention indicates an already existing keyword for which new options have been added or altered with respect to the original version.

Test cases: A series of test cases are provided in the source code with a README file.

Installation: See the README file in the source code.

Original publications: The methodology implemented in the 6.1.6 local version of deMon2k has been described in the following references[1–3]:

[1]   Wu X, Teuler J-M, Cailliez F, Clavaguéra C, Salahub D R and de la Lande A 2017 Simulating Electron Dynamics in Polarizable Environments *J. Chem. Theor. Comput.* **13** 3985–4002

[2]   Alvarez-Ibarra A, Omar K A, Hasnaoui K and de la Lande A 2022 Chapter 4 Electron and Molecular Dynamics Simulations with Polarizable Embedding *Multiscale Dynamics Simulations: Nano and Nano-bio Systems in Complex Environments* (The Royal Society of Chemistry) pp 117–43

[3]   Martínez, Pablo Antonio, Vock, Theresa, Kharchi , Liliane Racha, Pedroza-Montero J N, Hasnaoui K and de la Lande, Aurélien A A Multi-GPU Implementation of Real-Time Time-Dependent Auxiliary Density Functional Theory for the Investigation of Nanosystems Irradiations *Computer Physics Communications* **under review**

[4]   Wu X 2018 *Contribution to the Development of Advanced Approaches for Electron and Molecular Dynamics Simulations in Extended Biomolecules* Theses (Université Paris Saclay (COmUE))

[5]   Blackford L S, Choi J, Cleary A J, D'Azevedo E F, Demmel J, Dhillon I S, Dongarra J, Hammarling S, -Henry G, Petitet A, Stanley K, Walker D W and Whaley R C 1997 *ScaLAPACK: A Linear Algebra Library for Message-Passing Computers*

RTDFT

The **RTDFT** keyword activates attosecond electron dynamics simulations

  STEP=<REAL>   Set propagation time step length in fs. The default is 0.001fs.

  MAX=<INTEGER>   Set maximum number of propagation cycles.

  NUEL=<INTEGER>   Set number of interpolation steps in Ehrenfest MD simulations.

  INT=<INTEGER>   Step interval to update deMon.out file. The default value is 1.

  INS=<INTEGER>   Step interval to update deMon.rstrt (restart) file. The default value is 999999.

  INA=<INTEGER>   Step interval perform on-the-fly analyses. The default value is 10.

  PART=<INTEGER>- Restrict on-the-fly analyses to steps comprised within the two values
  <INTEGER>

  RESTART   An electron dynamics simulation is restarted.

  ITP   A propagation in imaginary time is activated.

When RDFT is activated without activating the DYNAMICS keyword, pure electron dynamics simulation under the frozen nuclear position approximation is carried out. The option ITP triggers a propagation in imaginary time, which has the effect to drive the system toward the ground state. ITP can be used as an alternative to the standard SCF minimization procedure.

The STEP option defines the length of the propagation time step. As RTDFT aims at simulating the motion of light particles like electrons adequate time steps are usually much smaller than those employed in molecular dynamics simulations. Typically, STEP is set to of a few attoseconds. The chosen time step has to be small enough to resolve the physical phenomena of interest for the system under study. Values comprised between 0.5 to 5 as generally ensures stable propagations. Optimal values depend on the choice of the propagator (see PROPAGATOR keyword) and on the method followed to evaluate the exponent of the Hamiltonian matrix (see EXPOMAT keyword).

In pure RTDFT simulations the MAX option specifies how many propagation steps are to be operated.

The options INT, INA and INS determine respectively how often information should be printed in the deMon.out file, how often on-the-fly analyses of the density and of field plotting should be carried out,

and finally how often a RTDFT restart file (deMon.rstrt) should be produced. For example, INA=5 requests the program to carry out population analyses every 5 propagation steps (population analysis options must be specified by the POPULATION and TOPOLOGY keywords). By specifying INS=50 one requests a RT-TDDFT file (deMon.rstrt) to be updated every 50 steps. Note that a RTDFT restart file is produced in any case at the end of the RTDFT simulation whatever the value of INS.

The PART option permits to restrict the analyses and the plotting of molecular fields to a specific range of propagation steps. The two numbers refer to the absolute values of the propagation history. For example, if one carries out a total of 10,000 propagation steps in two runs using the RESTART option (see below), each run comprising 5,000 steps, setting PART=6000-7000 in input files will trigger analyses only in the second run.

Usually a RTDFT simulation is launched from the SCF solution. If no perturbation is applied to the system the electron density should remain steady during RTDFT simulations (see example 1 just below). This is actually a good test if the simulation parameters chosen by the user are adequate.

Example 1: stable propagation *(Propagation from SCF solution, no perturbation applied)*

```
RTOUT:    0.500     -75.901130964  0.1067533E-05  -0.1174287E-04  0.1911590E+01  0.1911590E+01  10.0000
RTOUT:    1.500     -75.901130964  0.1067533E-05  -0.1174287E-04  0.1911590E+01  0.1911590E+01  10.0000
RTOUT:    2.500     -75.901130964  0.1067533E-05  -0.1174287E-04  0.1911590E+01  0.1911590E+01  10.0000
RTOUT:    3.500     -75.901130964  0.1067533E-05  -0.1174287E-04  0.1911590E+01  0.1911590E+01  10.0000
RTOUT:    4.500     -75.901130964  0.1067533E-05  -0.1174287E-04  0.1911590E+01  0.1911590E+01  10.0000
RTOUT:    5.500     -75.901130964  0.1067533E-05  -0.1174287E-04  0.1911590E+01  0.1911590E+01  10.0000
RTOUT:    6.500     -75.901130964  0.1067533E-05  -0.1174287E-04  0.1911590E+01  0.1911590E+01  10.0000
RTOUT:    7.500     -75.901130964  0.1067533E-05  -0.1174287E-04  0.1911591E+01  0.1911591E+01  10.0000
RTOUT:    8.500     -75.901130964  0.1067533E-05  -0.1174287E-04  0.1911591E+01  0.1911591E+01  10.0000
RTOUT:    9.500     -75.901130964  0.1067533E-05  -0.1174287E-04  0.1911591E+01  0.1911591E+01  10.0000
RTOUT:   10.500     -75.901130964  0.1067533E-05  -0.1174287E-04  0.1911591E+01  0.1911591E+01  10.0000
RTOUT:   11.500     -75.901130964  0.1067533E-05  -0.1174287E-04  0.1911591E+01  0.1911591E+01  10.0000
RTOUT:   12.500     -75.901130964  0.1067533E-05  -0.1174287E-04  0.1911591E+01  0.1911591E+01  10.0000
```

Example 2: stable propagation *(Propagation from SCF solution, electric field kick at first step)*

```
RTOUT:    0.500     -75.901130766  0.2010267E-03  -0.1159036E-04  0.1911590E+01  0.1911590E+01  10.0000
RTOUT:    1.500     -75.901130176  0.5899393E-03  -0.1159036E-04  0.1911590E+01  0.1911590E+01  10.0000
RTOUT:    2.500     -75.901130177  0.9537140E-03  -0.1159036E-04  0.1911590E+01  0.1911590E+01  10.0000
RTOUT:    3.500     -75.901130177  0.1292503E-02  -0.1159036E-04  0.1911590E+01  0.1911591E+01  10.0000
RTOUT:    4.500     -75.901130177  0.1617949E-02  -0.1159036E-04  0.1911590E+01  0.1911591E+01  10.0000
RTOUT:    5.500     -75.901130177  0.1945402E-02  -0.1159036E-04  0.1911590E+01  0.1911591E+01  10.0000
RTOUT:    6.500     -75.901130177  0.2279845E-02  -0.1159036E-04  0.1911590E+01  0.1911592E+01  10.0000
RTOUT:    7.500     -75.901130177  0.2610729E-02  -0.1159036E-04  0.1911590E+01  0.1911592E+01  10.0000
RTOUT:    8.500     -75.901130177  0.2919806E-02  -0.1159036E-04  0.1911590E+01  0.1911592E+01  10.0000
RTOUT:    9.500     -75.901130177  0.3190375E-02  -0.1159036E-04  0.1911590E+01  0.1911593E+01  10.0000
RTOUT:   10.500     -75.901130177  0.3418064E-02  -0.1159036E-04  0.1911590E+01  0.1911593E+01  10.0000
RTOUT:   11.500     -75.901130177  0.3613931E-02  -0.1159036E-04  0.1911590E+01  0.1911594E+01  10.0000
RTOUT:   12.500     -75.901130177  0.3793378E-02  -0.1156495E-04  0.1911590E+01  0.1911594E+01  10.0000
```

Example 3: unstable propagation *(Propagation from SCF solution, no perturbation applied)*

```
RTOUT:    0.500     -75.901130129  0.1067533E-05  -0.1174287E-04  0.1911588E+01  0.1911588E+01  10.0000
RTOUT:    1.500     -75.900954713  0.1067533E-05  -0.1174287E-04  0.1911585E+01  0.1911585E+01  10.0000
RTOUT:    2.500     -75.900779295  0.1067533E-05  -0.1174287E-04  0.1911582E+01  0.1911582E+01  10.0000
```

```
RTOUT:   3.500    -75.900603875  0.1067533E-05  -0.1174287E-04  0.1911579E+01  0.1911579E+01  10.0000
RTOUT:   4.500    -75.900428452  0.1067533E-05  -0.1174287E-04  0.1911576E+01  0.1911576E+01  10.0000
RTOUT:   5.500    -75.900253027  0.1067533E-05  -0.1174287E-04  0.1911573E+01  0.1911573E+01   9.9999
RTOUT:   6.500    -75.900077600  0.1067533E-05  -0.1174287E-04  0.1911571E+01  0.1911571E+01   9.9999
RTOUT:   7.500    -75.899902171  0.1067533E-05  -0.1174287E-04  0.1911568E+01  0.1911568E+01   9.9999
RTOUT:   8.500    -75.899726740  0.1067533E-05  -0.1174287E-04  0.1911566E+01  0.1911566E+01   9.9999
RTOUT:   9.500    -75.899551307  0.1067533E-05  -0.1174287E-04  0.1911564E+01  0.1911564E+01   9.9999
RTOUT:  10.500    -75.899375872  0.1067533E-05  -0.1174287E-04  0.1911562E+01  0.1911562E+01   9.9999
RTOUT:  11.500    -75.899200435  0.1067533E-05  -0.1174287E-04  0.1911560E+01  0.1911560E+01   9.9999
RTOUT:  12.500    -75.899024997  0.1067533E-05  -0.1174287E-04  0.1911558E+01  0.1911558E+01   9.9999
```

Note that unstable simulations are detected when seeing rapid and/or unphysical energy fluctuations within just a few propagation steps or if the total number of electrons is not conserved (see example 3 above). This latter remark is not relevant if using complex absorbing potentials (see ABSPOT keyword). Note that in some cases instability becomes manifest only several hundreds of steps after the beginning of the simulation. To avoid instability issues the tolerance criteria chosen in SCF procedure should be tight enough. Advisable values for the TOL and CDF options of the SCFTYPE keyword are 1.0E-10 Ha and 1.0E-7 Ha. respectively even though looser convergence criteria may also work for some systems. Also, the activation of the SHIFT keyword with large values (e.g. > 0.05) is ill-advised as this tends to produce metastable electronic states that turn to be unstable in RT-TDDFT simulations.

It is also possible to start a RT-TDDFT simulation from a set of MOs generated in a separate SCF calculation and stored in the deMon.rst. The MAX option of the SCFTYPE keyword simply needs to be set to 0 in the input file of the real time TDDFT simulation. The set of MOs will be read from the deMon.rst file, and eventually undergo modifications before starting the ED simulation. For example, one can permute a pair of occupied/vacant MOs and follow the evolution of the non-stationary state produced by this permutation. MOs can be localized at this stage. Another possibility is to change the total charge of the system between the preliminary SCF calculation and the ED simulation.

RT-TDDFT simulations can be restarted with the RESTART keyword. The deMon.rstrt file produced in a previous run must be supplied. No SCF will be carried out and ED will restart where it stopped in the previous run.

Basic simulation data are printed in the deMon.out file. By default, time (in attosecond), total potential energy (in Hartrees), the x, y and z components and the norm of the molecular dipole moment, and the total number of electrons are printed. Depending on the unit selection in the GEOMETRY keyword, the electrostatic moments are printed either in esu (for ANGSTROM) or atomic units (for BOHR).

The RT option of the PRINT keyword activates supplementary printing.

More information is printed in deMon.rtp file, for example energy decomposition in case of QM/MM simulations, the results of population analyses carried out on-the-fly, of KS orbitals occupation numbers…

PROPAGATOR

The **PROPA**GATOR specifies which algorithms is to be used to propagate numerically the electron density over time. This keyword has no effect if the keyword RTDFT is not active.

EULER	The Euler propagator is selected in electron dynamics simulations
MAGNUS	The second order Magnus propagator is selected in electron dynamics simulations. This is the default.
PC	A predictor-Corrector algorithm is selected.
ITERATIVE	An iterative solver is selected for the propagation. This is the default
TOL=<REAL>	Energy tolerance criteria. The default is the TOL valued of SCFTYPE keyword
CDF=<REAL>	Density fitting energy tolerance criteria. The default is 1.0E-4.
MAX=<INTEGER>	Maximum number of cycles in iterative solver. The default is 50.

Electron dynamics simulations are based on the Liouville-Von Neuman equation in the basis of the Kohn-Sham orbitals.

$$i \frac{\partial P(t)}{\partial t} = [H(t), P(t)]$$

Three propagators are available in deMon2k to evolve the density matrix P from time t_i to $t_i + \Delta t$, knowing the KS potential H. One relies on the Euler formula:

$$P(t_i + \Delta t) = P(t_i) - i[H(t_i), P(t_i)] * \Delta t$$

This propagator requires very small time steps of a fraction of attosecond to ensure propagation stability

More stable propagators are provided by the second order Magnus formula.

$$P(t + \Delta t) = e^{-iH\left(t + \frac{\Delta t}{2}\right).\Delta t} P(t) e^{-H\left(t + \frac{\Delta t}{2}\right).\Delta t}$$

Both a predictor-corrector (PC) and an iterative algorithms are available to apply the 2nd order Magnus propagation formula (see Figures below).

① Form $H\left(t_n + \frac{\Delta t}{4}\right)$ by extrapolation from $H\left(t_{n-1} + \frac{\Delta t}{2}\right)$ and $H\left(t_{n-2} + \frac{\Delta t}{2}\right)$ — Predictor step

② Propagate $P(t_n)$ to $P\left(t_n + \frac{\Delta t}{2}\right)$ using $H\left(t_n + \frac{\Delta t}{4}\right)$ with Magnus formula

③ Build Kohn-Sham potential $H\left(t_n + \frac{\Delta t}{2}\right)$ from $P\left(t_n + \frac{\Delta t}{2}\right)$ — Corrector step

④ Propagate $P(t_n)$ to $P(t_n + \Delta t)$ using $H\left(t_n + \frac{\Delta t}{2}\right)$ with Magnus formula
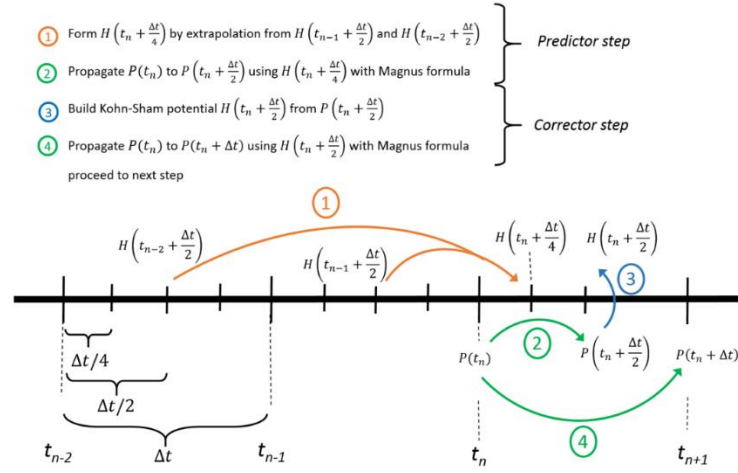
proceed to next step

Figure 1: schematic representation of the Predictor-Corrector algorithm coupled to 2nd order Magnus propagator[4].

The PC requires only one evaluation of the KS potential per propagation step and is therefore the less computationally time-consuming method. The iterative method seeks for a self-consistent KS potential at each real-time propagation step. It is the most stable propagator available in deMon2k. As for the SCF procedure two tolerance criteria are introduced to define self-consistency, one on the total energy (TOL), the other on the auxiliary density fitting energy (CDF).

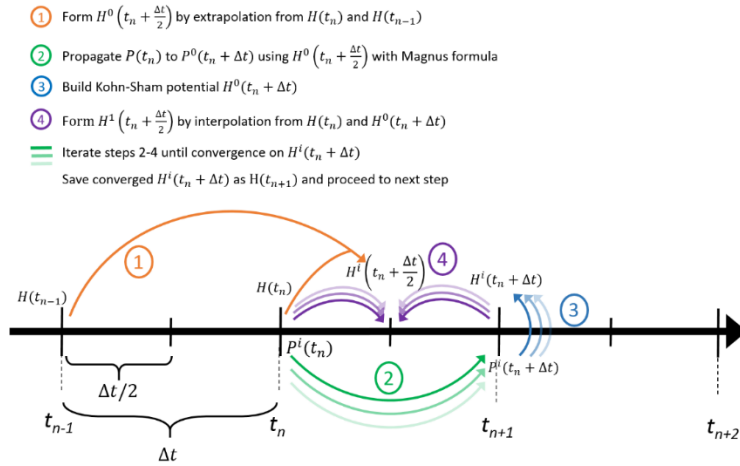The MAX option specifies the maximum number of iterations.

① Form $H^0\left(t_n + \frac{\Delta t}{2}\right)$ by extrapolation from $H(t_n)$ and $H(t_{n-1})$

② Propagate $P(t_n)$ to $P^0(t_n + \Delta t)$ using $H^0\left(t_n + \frac{\Delta t}{2}\right)$ with Magnus formula

③ Build Kohn-Sham potential $H^0(t_n + \Delta t)$

④ Form $H^1\left(t_n + \frac{\Delta t}{2}\right)$ by interpolation from $H(t_n)$ and $H^0(t_n + \Delta t)$

⸺ Iterate steps 2-4 until convergence on $H^i(t_n + \Delta t)$

Save converged $H^i(t_n + \Delta t)$ as $H(t_{n+1})$ and proceed to next step

Figure 2: schematic representation of the self-consistent algorithm coupled to 2nd order Magnus propagator[4].

EXPOMAT

This keyword defines which method has to be used to evaluate the exponential of the Hamiltonian matrix involved in Magnus propagation of the electron density. This keyword has no effect if the keyword RTDFT is not active.

DIAGONALIZATION	Diagonalization of Hamiltonian is calculated.
CHEBYSHEV	A Chebyshev expansion is used.
TAYLOR	A Taylor expansion is used.
BCH	A Baker-Campbell-Haussdorff expansion is used.
FREQ=<INTEGER>	Frequency at which electronic spectra is recomputed for CHEBY.
TOL=<REAL>	Tolerance criteria to consider expansion converged. The default is 1.0E-50
NEXP=<INTEGER>	Number of terms accumulated in expansion. The default value is 20
SCA=<REAL>	Value for scaling Hamiltonian for Chebyshev option.

Propagation of the electron density requires most of the time to evaluate a term of the form $e^{-iH.\Delta t} = e^W$ where H is a Hermitian matrix. With the DIAGO option the matrix H is first diagonalized to form the exponential of the matrix. With the options TAYLOR, BCH and CHEBY, e^W is approximated by summing a series of matrices. With TAYLOR this sum reads $e^W = \sum_{n=0}^{NEXP} \frac{1}{n!} W^n$ where NEXP is the number of terms to be included. If a tolerance criterion is supplied by the TOL option convergence of the series is considered to be achieved when the trace of the new added matrix is lower than the tolerance criteria. Note that in this case the NEXP specifies the maximum number of matrices to be summed up.

With CHEBY the sum reads, $e^W = \mathcal{N} \sum_{n=0}^{NEXP} (-i)^n (2 - \delta_{n0}) J_n(\tilde{a}) T_n(\widetilde{W})$, where J_n and T_n are Bessel functions of the first kind and Chebyshev polynomials of order n respectively.

The BCH option requests the use of Baker-Campbell-Haussdorff: $P(t + \Delta t) = P(t) + \sum_{n=1}^{\infty} \frac{1}{n!} [W, C_{n-1}]$ Note that the BCH formula is valid only real H matrices. It is therefore not compatible with hybrid XC functionals or if complex absorbing potentials are used (see CAP keyword)

CAP

Complex Absorbing Potentials (CAP) are specified by CAP keyword. This keyword has no effect if the keyword RTDFT is not active.

SPACE	The CAP is defined in real-space. This is the default.
ENERGY	The CAP is defined in energy space.
COARSE	A coarse grid is used to integrate space CAP matrix elements.
MEDIUM	A medium grid is used to integrate space CAP matrix elements.
FINE	A fine grid is used to integrate space CAP matrix elements.
REFER	A reference grid is used to integrate space CAP matrix elements.
THRES=<REAL>	Threshold distance value at which CAP becomes non-zero. The default is 10. Å
WIDTH=<REAL>	Distance width at which CAP becomes non zero. The default is 5. Å
VMAX=<REAL>	Maximum value of CAP. The default is 10 Ha.
GAM=<REAL>	Sets energy scaling for energy CAP. The default is 1.0
REFE=<REAL>	Shifts energy states according to by this value. The default in 0.0 Ha
KSI=<REAL>	Determines at which electrons are absorbed. The default is 100.0

When simulating the response of molecules to strong perturbations electrons may be emitted with certain kinetic energy. Complex Absorbing Potentials (CAP) can be introduced in the imaginary part of the Kohn-Sham potential to remove fractions of electron density. Two options are available. One is to absorb fractions of electron density that reach a threshold distance from the molecule (the QM region in case of QM/MM simulations). The other one is to absorb fractions of electron density in KS orbitals above a certain energy threshold. One or the other ways are selected by the SPATIAL and ENERGY options respectively. Addition of CAP make propagation non-unitary and should be used with extreme care.

When SPATIAL is activated, the CAP for the molecular system is defined as a superposition of atom-centered absorbing potentials (CAP_a) as:

$$CAP(R) = \min_a CAP_a(R)$$

$$CAP_a(R) = \begin{cases} 0 & for \ R < R° \\ V^{max} \sin^2\left(\dfrac{\pi}{2W}(R - R°)\right) for & R° + W < R < R° \\ V^{max} & R > R° + W \end{cases}$$

R is the distance from nucleus a, $R°$ is a threshold distance, W is distance over which the absorbing potential goes from zero to its maximum value V^{max}. The three parameters are specified by THRESH, WIDTH and VMAX respectively. The matrix elements of CAP are calculated by numerical integration on fixed Lebedev grids (see GRID or TOPOLOGY keywords). The COARSE, MEDIUM, FINE and REFERENCE options have the same meaning as for TOPOLOGY keyword.

When ENERGY option is activated the CAP is defined in matrix representation as $CAP = C(t)\Lambda C^\dagger(t)$ where C is the matrix of MO coefficients at the beginning of the RT-TDDFT simulation. The matrix Λ is a diagonal matrix the elements of are noted γ_i and computed according to:

$$\gamma_i = \begin{cases} 0 & for \ \tilde{\varepsilon}_i \leq 0 \\ \gamma_0[\exp(\xi\tilde{\varepsilon}_i) - 1] & for \ \tilde{\varepsilon}_i > 0 \end{cases}$$

Where $\tilde{\varepsilon}_i = \varepsilon_i - \varepsilon_O$ are the energies of MO *i* shifted by the value ε_O. γ_0 sets the energy scale. ξ specifies the speed at which electrons populating state *i* will be absorbed. The parameters ε_O, γ_0 and ξ are specified by the options REFE, GAM and KSI respectively.

GPU

MAGMA   Use MAGMA library for GPU parts of the simulations.

NGPU=<INTEGER>   Number of GPU per node to be used. Default is 1.

NCOR=<INTEGER>   Number of CPU available per GPU. Defaults is 1.

The GPU keyword activates the calculation of the Kohn-Sham matrix exponential involved RT-TD-DFT simulations with the MAGMA library. The latter library has to be linked when compiling the code. This option is only available for the TAYLOR option of the EXPOMAT keyword. GPU is also used for basis set transformations. All other tasks involved in RT-TD-DFT are handled by CPUs.

NGPU specifies the number of GPU available per node for the program and NCOR specifies the number of CPU available for each CPU. For example, with a GPU node equipped with 4 GPUs and 40 CPUs, one would ideally use NGPU=4 NCOR=10. More than one GPU node can be used. Matrix exponentiations are operated on multi-GPU as soon a NGPU > 1, but basis set transformations are always operated on a unique GPU as this task is usually not computationally demanding.

PROJECTILE

With the PROJECTILE option, classical projectile can be defined. This keyword has no effect if the keywords RTDFT or MD are not active.

LWP	A Liénard-Wiechert potential is used.
Q=\<REAL\>	Charge of the projectile. The default is 1.
MASS=\<REAL\>	Atomic mass of the projectile. The default is 1.
KIN=\<REAL\>	Initial kinetic energy of the projectile in MeV. The default is 1.
DIST=\<REAL\>	Distance at which the projectile is positioned at the beginning of the simulation in Å. The default is 30 Å.
FRAG=\<INTEGER\>	Use a fragment number to define collision trajectory.
SCF	Introduce the projectile field created during SCF. This is not the case by default.

deMon2k enables simulating collision of molecular systems by charged moving particles. In pure RT-TDDFT simulations, *i.e.* at fixed nuclear positions, inelastic collisions are simulated: the projectile speed and the propagation direction are kept constant throughout the simulations.

By default, the potential created by the moving point charge is calculated by a Coulomb law. For projectiles approaching the speed-of-light a relativistic Liénard-Wiechert potential is more adapted and can be selected with the LWP option. By default, the electric field created by the projectile is absent when carrying out SCF energy minimization, but it can be introduced upon activation of the SCF option.

The projectile charge, mass and kinetic energy are defined respectively by the Q, MASS and KIN options. DIST defines the distance from the van der Waals' envelope of the molecule (the QM region in case of a QM/MM simulation) at which the projectile has to be placed at the beginning of the simulation. The direction and displacement vectors (denoted as **dir** and **disp** respectively) have to be specified in two separate lines following the PROJECTILE keyword line (see Figure below). They are normalized automatically. By default, the center-of-mass of the whole molecule (the QM region in case of a QM/MM simulation) is used to determine the two vectors (sketch on the lhs). However, if molecular fragments have been defined (see FRAGMENT keyword) a specific fragment can be chosen to selectively target a well-defined fragment.
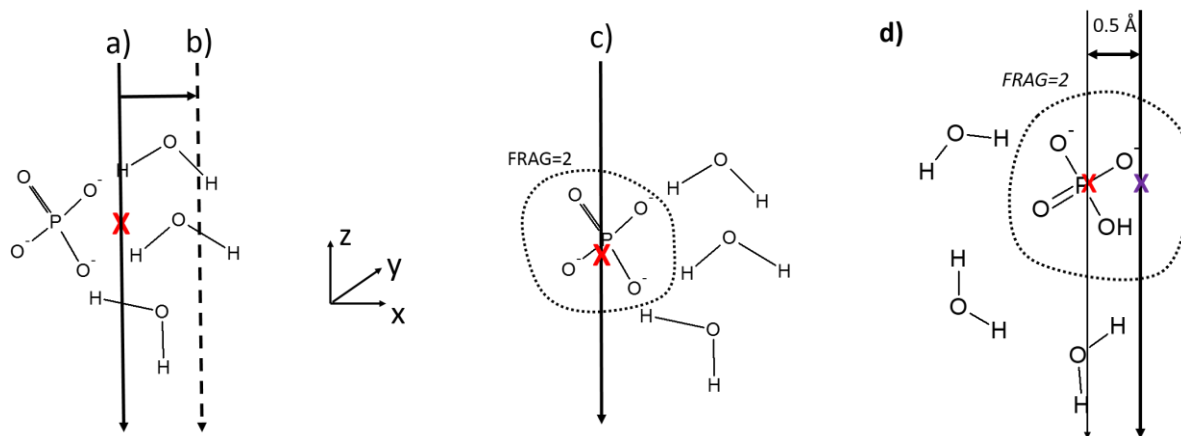
*Figure 3: The direction and displacement vectors defines the propagation of projectile. By default, the center of mass of QM region as denoted by the red mark is used. Propagation a): **dir**=(0.0, 0.0, -1.0) and **disp**=(0.0, 0.0, 0.0). Propagation b): **dir**=(0.0, 0.0, -1.0) and **disp**=(1.0, 0.0, 0.0). Propagation c): **dir**=(0.0, 0.0, -1.0) and **disp**=(0.0, 0.0, 0.0). In the middle, the phosphate group, defined in PDB file as fragment number 2 is selected by setting FRAG=2. Propagation c): **dir**=(0.0, 0.0, -1.0) and **disp**=(0.0, 0.0, 0.0). d)): **dir**=(0.0, 0.0, -1.0) and **disp**=(0.5, 0.0, 0.0)*

Examples:

1) This corresponds to case a). A 0.5 MeV proton positioned initially 50 Å away from the QM system will travel along the z-axis and will go through the QM system's center of mass.

PROJECTILE Q=1. MASS=1.0 KIN=0.5 DIST=50.
0.0 0.0 -1.0 DIR
0.0 0.0   0.0 DISP

2) This corresponds to case d). A 10 MeV alpha particle positioned initially 70 Å away from the QM system will travel along the x-axis. It will be described by a Liénard-Wiechert potential. It will go through the displaced center of mass of fragment 2 (the violet mark).

PROJECTILE LWP Q=2.0 MASS=4.0 KIN=10. FRAG=2 DIST=70.
0.0   0.0   -1.0 DIR
0.5   0.0   0.0 DISP

FRAGMENT

PDB   Read molecular fragments from a file in PDB format.

The FRAGMENT keyword enables one to define molecular "fragments", that is groups of atoms. This is currently only useful for RT-TDDFT simulations. If molecular fragments are specified, The FRAG option of the PROJECTILE option becomes available. When population analyses are activated (POPULATION keywords) the deMon.rtp file provide an analysis per fragment.

Currently fragments can only be provided via a file in the protein data bank format (PDB) which must ne name PDB as exampled below:

```
ATOM     1 N   TYR   1    -1.234  2.651 -4.919 1.00 1.00    MTNK
ATOM     2 HT1 TYR   1    -0.646  3.403 -5.331 1.00 0.00    MTNK
ATOM     3 HT2 TYR   1    -1.758  3.076 -4.128 1.00 0.00    MTNK
ATOM     5 CA  TYR   1    -0.491  1.407 -4.466 1.00 1.00    MTNK
ATOM     6 HA  TYR   1    -0.408  0.906 -5.419 1.00 1.00    MTNK
ATOM     7 CB  TYR   1     0.846  1.760 -3.761 1.00 1.00    MTNK
ATOM     8 HB1 TYR   1     0.697  2.248 -2.774 1.00 0.00    MTNK
ATOM     9 HB2 TYR   1     1.303  2.663 -4.221 1.00 0.00    MTNK
ATOM    10 CG  TYR   1     1.816  0.687 -3.711 1.00 1.00    MTNK
ATOM    11 CD1 TYR   1     2.189 -0.011 -4.841 1.00 1.00    MTNK
ATOM    12 HD1 TYR   1     1.677  0.162 -5.777 1.00 0.00    MTNK
ATOM    13 CE1 TYR   1     2.988 -1.088 -4.734 1.00 1.00    MTNK
ATOM    14 HE1 TYR   1     3.088 -1.620 -5.669 1.00 0.00    MTNK
ATOM    15 CZ  TYR   1     3.652 -1.405 -3.561 1.00 1.00    MTNK
ATOM    16 OH  TYR   1     4.580 -2.430 -3.676 1.00 1.00    MTNK
ATOM    17 HH  TYR   1     5.325 -2.299 -3.085 1.00 0.00    MTNK
ATOM    18 CD2 TYR   1     2.424  0.400 -2.472 1.00 1.00    MTNK
ATOM    19 HD2 TYR   1     2.317  0.940 -1.543 1.00 0.00    MTNK
ATOM    20 CE2 TYR   1     3.369 -0.690 -2.401 1.00 1.00    MTNK
ATOM    21 HE2 TYR   1     3.798 -1.012 -1.463 1.00 0.00    MTNK
ATOM    22 C   TYR   1    -1.325  0.338 -3.796 1.00 1.00    MTNK
ATOM    23 O   TYR   1    -2.135 -0.214 -4.523 1.00 1.00    MTNK
ATOM    24 N   GLY   2    -1.158 -0.022 -2.479 1.00 1.00    MTNK
ATOM    25 HN  GLY   2    -0.385  0.361 -1.981 1.00 0.00    MTNK
ATOM    26 CA  GLY   2    -2.010 -0.984 -1.730 1.00 1.00    MTNK
ATOM    27 HA1 GLY   2    -1.420 -1.188 -0.850 1.00 0.00    MTNK
ATOM    28 HA2 GLY   2    -2.203 -1.854 -2.341 1.00 0.00    MTNK
ATOM    29 C   GLY   2    -3.292 -0.388 -1.305 1.00 1.00    MTNK
ATOM    30 O   GLY   2    -4.373 -1.054 -1.368 1.00 1.00    MTNK
ATOM    31 N   GLY   3    -3.215  0.855 -0.888 1.00 1.00    MTNK
ATOM    32 HN  GLY   3    -2.385  1.372 -0.698 1.00 0.00    MTNK
ATOM    33 CA  GLY   3    -4.369  1.535 -0.377 1.00 1.00    MTNK
```

This PDB file defines three fragments. deMon2k reads the file atom by atom (i.e. line by line). It checks the name of the chain (11th column), and of the residue number (5th column) to which the atom pertains. A new fragment is defined if the chain name or the residue number is different from the precedent atom.

SIMULATION (Modified keyword)

Supplementary options.

    WFN   wfn files are produced during Electron Dynamics Simulations

    OCCUP   Calculate time dependent occupation number of KS orbitals

    ELKIN   Integrate electron kinetic energy over atoms and fragments.

The WFN option activates the production of ASCII files containing sets of MO coefficients in the course of electron dynamics simulations by RT-TDDFT. As MO are complex numbers, a block for the real part of the coefficients are given for all the orbitals followed by a block for the imaginary components of MO coefficient. In open-shell simulations MO coefficients for alpha electrons are given before MO coefficients for beta electrons.

Upon activation of the OCCUP option, the time-dependent occupations of the Kohn-Sham orbitals $(n_k(t))$ can been computed as $n_k(t) = \boldsymbol{C}^{k\dagger}\boldsymbol{P}(t)\boldsymbol{C}^k$ where the $\boldsymbol{C}^k$ are the eigenvectors of the Kohn-Sham potential obtained from a Self-Consistent-Field calculation and $\boldsymbol{P}$ is the time dependent density matrix in the Molecular Orbital basis. The results of the analysis are printed in the deMon.rtp file.

The electron kinetic energies integrated over atoms according to a population scheme selected by the POPULATION keyword. Following Bader and Preston the total kinetic density on each point is space $(K(\boldsymbol{r}))$ is determined by the Laplacian of the total density $(L(\boldsymbol{r}))$ and by the gradient of its components $(G(\boldsymbol{r}))$.

$$K(\boldsymbol{r}) = L(\boldsymbol{r}) + G(\boldsymbol{r})$$

$$L(\boldsymbol{r}) \equiv -\frac{1}{4}\nabla^2\rho(\boldsymbol{r})$$

$$G(\boldsymbol{r}) \equiv \frac{1}{8}\sum_{i=1,3}\frac{\nabla\rho_i(\boldsymbol{r}).\nabla\rho_i(\boldsymbol{r})}{\rho_i(\boldsymbol{r})}$$

Integration of K over the entire space leads to the total electron kinetic energies while L, which can locally takes positive or negative values globally integrates to zero. The results of the analysis are printed in the deMon.rtp file.

EFIELD (Modified keyword)

New or modified options:

SCFOFF	Deactivate electric field in all SCF calculations.
EDSOFF	Deactivate electric field in ED simulations.
KICK	A sudden electric field is applied in first propagation step of ED simulations.
GPULSE	A Gaussian shaped pulse is applied in ED simulations.
SCPULSE	A squared cosine shaped pulse is applied in ED simulations
LRAMP	A linear ramp is applied in ED simulations.
E=(<REAL>;<REAL>;<REAL>)	Vector defining components of the field.
TIMEP=<REAL>	Time parameter with meaning depending on the field shape. The default is 5 fs.
OMEGA=<REAL>	Frequency of light. The default is 0 Ha.
SIGMA=<REAL>	Standard deviation of Gaussian shaped pulses in Ha. The default is 1 fs.

With this keyword an external homogeneous electric field can be specified in SCF or RT-TDDFT simulations. By default, electric field is applied both in SCF and in EDS (Electron Dynamics Simulation) of the electron density. With the options SCFOFF and EDSOFF one can selectively turn off the application of the electric field during SCF or during RTP respectively.

In SCF the time independent electric field is applied and only the option defining the electric field components has an effect.

In RTP, the KICK option permits to apply a sudden electric field only in the very first propagation step. This has for consequence to excite the electron cloud toward all accessible excited states. Note that if restarting the simulation in a subsequent run the kick will not be applied again in the first step of the restarted ED simulation.

The general expression for time dependent fields applied in ED simulations is given by $\boldsymbol{F}(t) = . X(\text{t}) . \sin \omega t . \boldsymbol{d}_{max}$. $\boldsymbol{d}_{max}$ is a direction vector of the pulse specifying the maximum field strength in each direction. ω is the frequency of the light. It is specified by the OMEGA option in Ha. X is the envelop of the

pulse which can defined by the GPLUS, SCPUL and LRAMP options which are mutually exclusive. GPULS activates a Gaussian shaped pulse:

$$X(\text{t}) = \exp[-(t - TIMEP)^2/2.SIGMA^2].$$

SCPULS activates a squared cosine shaped pulse:

$$X(t) = \begin{cases} 0 & if\ t > 2.TIMEP \\ cos^2[\pi(t - TIMEP)/2.TIMEP] & if\ t \leq 2.TIMEP \end{cases}$$

LRAMP activates a squared cosine shaped pulse:

$$X(t) = \begin{cases} t/TIMEP & if\ t < TIMEP \\ 1 & if\ t > TIMEP \end{cases}$$

PARALLEL (Modified keyword)

New or modified options:

SCALA   Calculate matrix exponential with ScaLAPACK library.

NCOL=<INTEGER>   Number of columns in the MPI ScaLAPACK/BLACS grid.

NROW=<INTEGER>   Number of raw in the MPI ScaLAPACK/BLACS grid.

NSUB=<INTEGER>   Column Blocking factor where MSUB >=1. Default is 2.

MSUB=<INTEGER>   Row Blocking factor where NSUB >=1. Default is 2.

The SCALA option activates the calculation of the Kohn-Sham matrix exponential involved RT-TD-DFT simulations with the ScaLAPACK library[5]. The latter library has to be linked when compiling the code. This option is only available for the TAYLOR option of the EXPOMAT keyword. ScaLAPACK is also used for basis set transformations[2].

The NCOL and NROW options specify how matrices should be distributed over different tasks. They determine how to set the 2D MPI ScaLAPACK/BLACS grid, therefore how the matrix data will be distributed among MPI processes. The choice of these parameters can have huge impact on code performances. It is advised to set NCOL to the number CPU cores per nodes and NROW to the number of computer nodes used for the simulations. Typically, NCOL>NROW. NCOL*NROW is always equal to the total number of MPI processes available for a given simulation.

MSUB and NSUB are the blocking factor used to distribute respectively the rows and the columns of the array with the ScaLAPACK library. It is advice to set MSUB and NSUB equal to 64 for modern architectures.

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