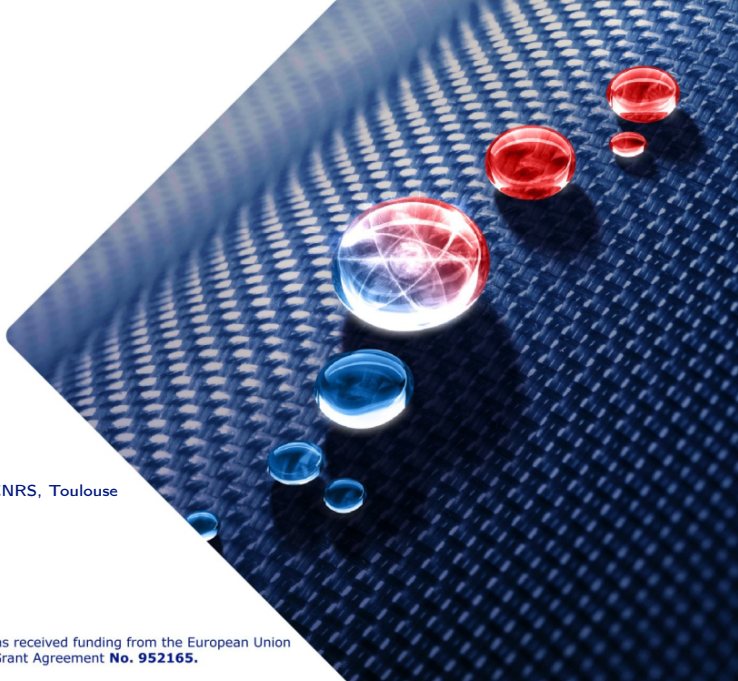


# TREXIO in QP and QMC=Chem

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## Quantum Package (QP)

Water molecule, BFD pseudopotentials, cc-pVDZ basis set

- Create EZFIO<sup>1</sup> directory:

---

```
$ qp create_ezfio --pseudo=bfd --basis=cc-pvdz_ecp_bfd h2o.xyz --output=h2o
$ ls
h2o/ h2o.xyz
```

---

h2o/ contains all input data: geometry, basis, pseudo, default control parameters of the program

- Display/modify content of EZFIO directory with `qp edit`

---

<sup>1</sup>Easy Fortran Input/Output: <https://gitlab.com/scemama/ezfio>

- Run the Hartree-Fock calculation

---

```
$ qp run scf > h2o.scf.out
```

---

Now, the h2o/ directory contains the Hartree-Fock MO coefficients, and the energy.

---

```
$ qp get hartree_fock energy
-16.9480400408233
```

---

- Quantum package has a system of *plugins*.
- Advantage: Users are responsible for distributing and maintaining their plugins.
- When a plugin is of general use, it can be moved into the main distribution.

---

```
$ qp plugins download https://gitlab.com/scemama/qp_plugins_scemama
$ qp plugins install trexio
$ cd $QP_ROOT/src/trexio
$ ninja
```

---

*# compile QP with the plugin*

---

The plugin adds a few options in the EZFIO directory:

---

Back-end used in TREXIO. 0: HDF5, 1:Text ::

```
backend = 0
```

Name of the exported TREXIO file ::

```
trexio_file = None
```

If True, export two-body reduced density matrix ::

```
export_rdm = false
```

If True, export two-electron integrals in AO basis ::

```
export_ao_ints = false
```

If True, export two-electron integrals in MO basis ::

```
export_mo_ints = true
```

---

- Nuclei: coordinates, charges, labels, nuclear repulsion energy
- Electrons: Number of  $\uparrow$  and  $\downarrow$  electrons
- AO basis (Cartesian)
- ECP
- MOs: coefficients, type
- One-e integrals in AO basis : overlap, kinetic, potential, ECP
- One-e integrals in MO basis : kinetic, potential, ECP
- Two-e integrals in AO basis :  $1/r_{12}$
- Two-e integrals in MO basis :  $1/r_{12}$
- One-electron reduced density matrix in MO basis
- Two-electron reduced density matrix in MO basis

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- Two-e integrals in MO basis :  $1/r_{12}$



- Export to TRESPLO, re-import from TRESPLO, check energy
- Convert GAMESS to TRESPLO, import from TRESPLO, check energy
- Convert Gaussian to TRESPLO, import from TRESPLO, check energy
- Export integrals and RDMs to TRESPLO, write a simple code which computes the energy

QMC=Chem

Use the qmcchem quantum package plugin to prepare the EZFIO directory (pseudopotential grids, sorting determinants, etc):

---

```
$ qp run qmcchem
```

---

QMC=Chem is very easy to use: all parameters of the sampling can be set with the command line:

---

```
$ qmcchem edit --time-step=0.15 --jastrow=Simple --method=VMC --stop-time=290
$ qmcchem run h2o
$ qmcchem result h2o
      Cpu : 10:02:36
      E_loc : -17.1582441499 +/-      0.0001176055
E_loc_qmcvar : 0.5069435505 +/-      0.0007318594
      Wall : 0:04:52
      Accep : 0.9771475222
      Speedup : 123.47 x
```

---



- A new repository was created for QMC=Chem v2.0
- In this version, the wave function will be completely read from TREXIO
- Objective: The preliminary Quantum package run will not be required

### Good feedback

- Very easy to use
- Very fast
- Done now: nuclear coordinates, charge, electrons, MO coefficients
- QMCKI is also introduced in QMC=Chem, so TREXIO comes naturally

### Difficulties

- Conventions for basis set and pseudo are different  $\implies$  Needs some work
- QMC=Chem uses pseudopotentials on a grid generated by QP  $\implies$  whether store the grids in TREXIO if it can be useful to others, or make QMC=Chem pre-compute the grids

Ideas for the future



## Make our codes independent of external codes

- Use `libint` or `libcint` library or to write AO integrals in a TRESPIO file (C++)
- Write a Hartree-Fock code using TRESPIO integrals
- Write a fast 4-index transformation code for integrals

## Evaluating two-electron-repulsion integrals over arbitrary orbitals using Zero Variance Monte Carlo: Application to Full Configuration Interaction calculations with Slater-type orbitals

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A Monte Carlo method for evaluating multi-center two-electron-repulsion integrals over any type of orbitals (Slater, Sturmian, finite-range, numerical, etc.) is presented. The approach is based on a simple and universal (orbital-independent) gaussian sampling of the two-electron configuration space and on the use of efficient zero-variance Monte Carlo estimators. Quite remarkably, it is shown that the high level of accuracy required on two-electron integrals to make Hartree-Fock (HF) and configuration interaction (CI) calculations feasible can be achieved. A first zero-variance estimator is built by introducing a gaussian approximation of the orbitals and by evaluating the two-electron integrals using a correlated sampling scheme for the difference between exact and approximate orbitals. A second one is based on the introduction of a general coordinate transformation. The price to pay for this simple and general Monte Carlo scheme is the high computational cost required. However, we argue that the great simplicity of the algorithm, its embarrassingly parallel nature, its ideal adaptation to modern computational platforms and, most importantly, the possibility of using more compact and physically meaningful basis sets make nevertheless the method attractive. HF and near full CI (FCI) calculations using Slater-type orbitals (STO) are reported for Be, CH<sub>4</sub> and [H<sub>2</sub>N(CH)NH<sub>2</sub>]<sup>+</sup> (a simple model of cyanine). To the best of our knowledge, our largest FCI calculation involving 18 active electrons distributed among 90 orbitals for the cyanine molecule, is the most extensive molecular calculation performed so far using pure STO orbitals (no gaussian approximation, even for the challenging four-center two-electron integrals).

- Trial wave functions for QMC using STO
- All methods of Quantum Package with STO:
  - Hartree-Fock
  - CI, CAS-SCF
  - CIPSI
  - Localized MOs
- FCIQMC with STO
- SAPT with CI expansions in STO, ...