Post Hartree-Fock: MP2 and RPA in CP2K
A tutorial

Jan Wilhelm
jan.wilhelm@chem.uzh.ch

University of Zurich

4 September 2015

Further reading

MP2 and RPA by Mauro Del Ben, Jürg Hutter, Joost VandeVondele

- Del Ben, M; Hutter, J; VandeVondele, J. JOURNAL OF CHEMICAL THEORY AND COMPUTATION **8**, 4177-4188 (2012). Second-Order Møller-Plesset Perturbation Theory in the Condensed Phase: An Efficient and Massively Parallel Gaussian and Plane Waves Approach.
  http://dx.doi.org/10.1021/ct300531w
- Del Ben, M; Hutter, J; VandeVondele, J. JOURNAL OF CHEMICAL THEORY AND COMPUTATION **9**, 2654-2671 (2013). Electron Correlation in the Condensed Phase from a Resolution of Identity Approach Based on the Gaussian and Plane Waves Scheme.
  http://dx.doi.org/10.1021/ct4002202
- Del Ben, M; Schütt, O; Wentz, T; Messmer, P; Hutter, J; VandeVondele, J. COMPUTER PHYSICS COMMUNICATIONS **187**, 120-129 (2015). Enabling simulation at the fifth rung of DFT: Large scale RPA calculations with excellent time to solution.
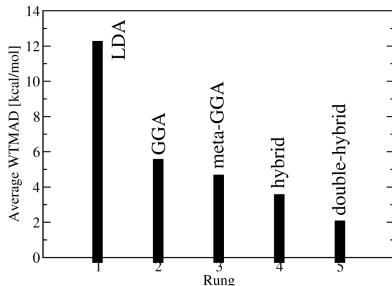 http://dx.doi.org/10.1016/j.cpc.2014.10.021

Jacob's ladder of density functional approximations

Model of exchange-correlation term improved over time

- Pure DFT is not enough
- Hybrid schemes improve
- Chemical accuracy (1 kcal/mol) not reached
- Go beyond DFT and hybrids (e. g. MP2, RPA)

Accuracy of the density functional approximations

University of Zurich

Density functional versus wavefunction methods

- Energy of Coulomb repulsion E_{Coul} of electrons:

$$E_{\text{Coul}} = E_{\text{Hartree }(H)} + E_{\text{exchange }(x)} + E_{\text{correlation }(c)}$$

- DFT: exchange and correlation are functionals of the density $n(\vec{r})$:

$$E_{xc}^{\text{DFT}} = E_{xc}^{\text{DFT}}[n]$$

- RPA/MP2: exchange and correlation are functional of all electronic wavefunctions:

$$E_{xc}^{\text{exact exchange and RPA/MP2}} = E_x^{\text{HF}}[\{\Psi_j\}] + E_c^{\text{RPA/MP2}}[\{\Psi_j, \varepsilon_j\}]$$

- RPA and MP2 total energy calculations are postprocessing procedures:
  1. converge an SCF with Hartree-Fock (for MP2) and functional of your choice for RPA (e. g. GGA or hybrid functional)
  2. take molecular orbitals and their energies $\{\Psi_j, \varepsilon_j\}$ of converged SCF and calculate $E_{xc}^{\text{EXX/RPA}}$ or $E_{xc}^{\text{EXX/MP2}}$.

- Second order Møller-Plesset perturbation theory:

$$E_c^{\mathrm{MP2}} = - \sum_{ij,ab}^{occ,vir} \frac{(ia|jb)[2(ia|jb) - (ib|ja)]}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j}$$

- Random-phase approximation (RPA)

$$E_c^{\mathrm{RPA}} = -\frac{1}{2\pi} \iint d\vec{r_1} d\vec{r_2} \int_0^\infty d\omega \ln \left(1 - \frac{\chi^0(\vec{r_1}, \vec{r_2}, i\omega)}{|\vec{r_1} - \vec{r_2}|} \right) - \frac{\chi^0(\vec{r_1}, \vec{r_2}, i\omega)}{|\vec{r_1} - \vec{r_2}|}$$

$$\chi^0(\vec{r_1}, \vec{r_2}, i\omega) = 2 \sum_{ia} \frac{\Psi_i(\vec{r_1})\Psi_a(\vec{r_1})\Psi_i(\vec{r_2})\Psi_a(\vec{r_2})}{(\varepsilon_a - \varepsilon_i)^2 + \omega^2}$$

- In both cases 4-center 2-electron repulsion integrals $(ia|jb)$ have to be computed

$$(ia|jb) = \int \int \Psi_i(\vec{r_1})\Psi_a(\vec{r_1}) \frac{1}{|\vec{r_1} - \vec{r_2}|} \Psi_j(\vec{r_2})\Psi_b(\vec{r_2}) d\vec{r_1} d\vec{r_2}$$

Resolution of Identity Approach (RI)

Gaussian Auxiliary Basis $\{P\}$ with Coulomb Metric:

$$(ia|jb) \approx (ia|jb)_{RI} = \sum_{PQ} (ia|P)(P|Q)^{-1}(Q|jb)$$
$$= \sum_{S} (ia|S)(S|jb) = \sum_{S} B_{ia}^{S} B_{jb}^{S}$$

Instead of computing 4-center 2-electron repulsion integrals $(ia|jb)$ we compute 3-center 2-electron repulsion integrals $(ia|S)$

$$B_{ia}^{S} = \sum_{P} (ia|P)(P|S)^{-1/2}$$

$$= \sum_{\mu} C_{\mu i} \sum_{\nu} C_{\nu a} \underbrace{(\mu\nu|S)}_{\text{GPW Integral}}$$

$$B_{\mu\nu}^{S} = (\mu\nu|S)$$

Calculate $|S)$ on grid $\rho_S(\mathbf{R})$

$\Downarrow$ FFT

Multiply with operator to get potential
$$V_S(\mathbf{G}) = \rho_S(\mathbf{G}) \cdot \mathcal{O}(\mathbf{G})$$

$\Downarrow$ FFT

Integrate $(\mu\nu|$ on grid with $V_S(\mathbf{R})$
$$B_{\mu\nu}^{S} = \sum_{\mathbf{R}} \Phi_{\mu\nu}(\mathbf{R}) \cdot V_S(\mathbf{R})$$

$$E_c^{\text{MP2}} = -\sum_{ij}^{o} \sum_{ab}^{v} \frac{(ia|jb)\,[2(ia|jb) - (ib|ja)]}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j}$$

Calculate Integrals using RI

$$(ia|jb) = \sum_{S} B_{ia}^{S}\, B_{jb}^{S} \tag{1}$$

- Scaling of computational effort is $\mathcal{O}(N^5)$, see Eq. (**??**):

  occ. orbitals $(i, j) \sim N$
  virt. orbitals $(a, b) \sim N$
  auxiliary basis $(S) \sim N$

- Reduction of prefactor (typically one order of magnitude) compared to non-RI MP2

University of Zurich

RI-SOS-MP2

$$E_c^{\text{MP2,OS}} = -\sum_{iajb} \frac{(ia|jb)^2}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j} = -\sum_{iajb} \frac{(ia|jb)^2}{\Delta_{ij}^{ab}}$$

- Empirical observation [Y. Jung *et al.*, J. Chem. Phys. **121**, 9793 (2004)]:

$$E_c^{\text{MP2}} \approx 1.3 \cdot E_c^{\text{MP2,OS}}$$

- Transform $1/x = \int_0^\infty e^{-xt} dt$ (I) and numerical integration (II)

$$E_c^{\text{MP2,OS}} \overset{\text{(I)}}{=} -\int_0^\infty dt \sum_{iajb} (ia|jb)^2 e^{-t\Delta_{ij}^{ab}} \overset{\text{(II)}}{\approx} -\sum_q^{N_q} w_q \sum_{iajb} (ia|jb)^2 e^{-t_q \Delta_{ij}^{ab}}$$

- With RI the overall scaling is reduced to $\mathcal{O}(N^4)$

$$\sum_{PQiajb} B_{ia}^P B_{jb}^P B_{ia}^Q B_{jb}^Q e^{-t_q \Delta_{ij}^{ab}} = \sum_{PQ} \sum_{ia} B_{ia}^P B_{ia}^Q e^{-t_q(\varepsilon_a - \varepsilon_i)} \sum_{jb} B_{jb}^P B_{jb}^Q e^{-t_q(\varepsilon_b - \varepsilon_j)}$$

- 6-8 quadrature points give µH accuracy

University of Zurich

RPA correlation energy in matrix representation:

$$E_c^{\text{RPA}} = \int_0^\infty \frac{d\omega}{2\pi} \, \text{Tr} \left(\ln \left(1 + Q(\omega) \right) - Q(\omega) \right) \tag{2}$$

where $Q(\omega)$ is a matrix of size $N_{\text{aux. bf.}} \times N_{\text{aux. bf}}$ with entries

$$Q_{PQ}(\omega) = 2 \sum_{ia} B_{ia}^P G_{ia}(\omega) B_{ia}^Q$$

and

$$G_{ia}(\omega) = \frac{\varepsilon_a - \varepsilon_i}{(\varepsilon_a - \varepsilon_i)^2 + \omega^2}$$

- RI-RPA overall scaling $\mathcal{O}(N^4)$
- 10-15 quadrature points (minimax quadrature) give µH accuracy

University of Zurich

Scaling
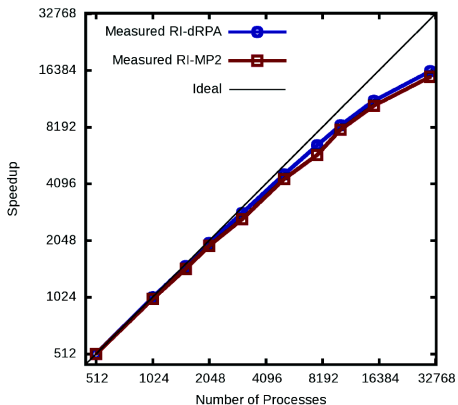
64 water molecules, cc-TZVP Basis; 256 occupied orbitals,
3648 basis function, 8704 RI basis functions

University of Zurich

- On 64 cores CRAY XC30:

System	Atoms	Basis (RI basis)	MP2	SOS-MP2	RPA
64 water molec.	192	3648 (8704)	140 min	64 min	48 min

Timings on 64 cores CRAY CX30 (= 8 nodes on Piz Daint, smallest possible number of nodes due to memory requirements), TZVP basis set, quadrature points: 16 (RPA), 10 (OS-MP2).

- On 32768 cores CRAY XC30:

System	Atoms	Basis (RI basis)	RPA
64 water molecules	192	3648 (8704)	22 s
512 water molecules	1536	29184 (69632)	1.7 h

Timings on 32768 cores CRAY CX30 (= 4096 nodes on Piz Daint, 78 % of Piz Daint, worldwide 6th largest supercomputer), TZVP basis set, quadrature points: 16.

University of Zurich

```
&DFT
  BASIS_SET_FILE_NAME ../BASIS_RI_cc-TZ        ! RI basis sets are available for TZVP basis
  POTENTIAL_FILE_NAME ../POTENTIAL

                  .
                  .
                  .
&END DFT
&SUBSYS


                  .
                  .
                  .
 &KIND H
   BASIS_SET cc-TZ
   RI_AUX_BASIS_SET RI_TZ        ! For RI calculations, we additionally need RI basis sets.
   POTENTIAL GTH-PBE-q1
 &END KIND
 &KIND O
   BASIS_SET cc-TZ
   RI_AUX_BASIS_SET RI_TZ        ! For RI calculations, we additionally need RI basis sets.
   POTENTIAL GTH-PBE-q6
 &END KIND
&END SUBSYS
```

University of Zurich

Input non-periodic* MP2 on top of Hartree-Fock-SCF

*for periodic calculations, change section PERIODIC NONE and truncate Hartree-Fock

```
&DFT
  BASIS_SET_FILE_NAME ../BASIS_RI_cc-TZ
  POTENTIAL_FILE_NAME ../POTENTIAL
  &QS
    METHOD GPW
  &END QS
  &POISSON
    PERIODIC NONE
    PSOLVER MT
  &END POISSON
  &SCF
    SCF_GUESS RESTART
  &END SCF
  &XC
    &XC_FUNCTIONAL NONE
    &END XC_FUNCTIONAL
    &HF
      FRACTION 1.00
      &SCREENING
        EPS_SCHWARZ 1.0E-8
      &END SCREENING
    &END HF
  &END XC
  &WF_CORRELATION
    METHOD  RI_MP2_GPW  ! do MP2 calculation
    NUMBER_PROC 2        ! number of processes for storing grids. In case you run out of memory when
                         ! computing integrals, increase number. Large number slows the calculation down.
    &RI_MP2
    &END RI_MP2
  &END WF_CORRELATION
&END DFT
```

Input non-periodic SOS-MP2 on top of Hartree-Fock-SCF

```
&DFT
  BASIS_SET_FILE_NAME ../BASIS_RI_cc-TZ
  POTENTIAL_FILE_NAME ../POTENTIAL
  &QS
    METHOD GPW
  &END QS
  &POISSON
    PERIODIC NONE
    PSOLVER MT
  &END POISSON
  &SCF
    SCF_GUESS RESTART
  &END SCF
  &XC
    &XC_FUNCTIONAL PBE
    &END XC_FUNCTIONAL
    &HF
      FRACTION 1.00
      &SCREENING
        EPS_SCHWARZ 1.0E-8
      &END SCREENING
    &END HF
  &END XC
  &WF_CORRELATION
    METHOD RI_SOS_LAPLACE  ! do SOS-MP2 calculation
    NUMBER_PROC 2
    SCALE_S 1.3      ! scale the OS-MP2 energy by 1.3
    &RI_LAPLACE
      QUADRATURE_POINTS 10
      SIZE_INTEG_GROUP 64 ! number of processes dealing with a single frequency grid point. Increase
                          ! this number when running out of memory during the frequency integration.
                          ! A larger number slows the calculation down.
    &END RI_LAPLACE
  &END WF_CORRELATION
&END DFT
```

University of Zurich

```
                                                        .
                                                        .
&DFT                                                    .
  BASIS_SET_FILE_NAME ../BASIS_RI_cc-TZ
  POTENTIAL_FILE_NAME ../POTENTIAL                      &HF              ! Hartree-Fock for exchange energy
  &QS                                                     FRACTION 1.00
    METHOD GPW                                            &SCREENING
  &END QS                                                   EPS_SCHWARZ 1.0E-8
  &POISSON                                                &END SCREENING
    PERIODIC NONE                                         &MEMORY
    PSOLVER MT                                              MAX_MEMORY 0  ! we need not to store
  &END POISSON                                                          ! any HF integrals because  there
  &SCF                                                                  ! are no subsequent SCF steps
    SCF_GUESS RESTART                                    &END MEMORY
  &END SCF                                             &END HF
  &XC                                                 &END RI_RPA
    &XC_FUNCTIONAL PBE                              &END WF_CORRELATION
    &END XC_FUNCTIONAL                            &END DFT
  &END XC
  &WF_CORRELATION
    METHOD RI_RPA_GPW   ! do an RPA calculation
    NUMBER_PROC 2
    &RI_RPA
      MINIMAX_QUADRATURE TRUE  ! choose Minimax quadrature grid points. Then, only few grid points are
                               ! necessary in order to converge the frequency integration in Eq. (2).
      QUADRATURE_POINTS 15     ! number of grid points for the frequency integration
      SIZE_FREQ_INTEG_GROUP 16 ! number of processes dealing with a single frequency grid point. Increase
                               ! this number when running out of memory during the frequency integration.
                               ! A larger number slows the calculation down.
              .
              .
              .
```

Optimize RI basis (in case you want other basis than cc-TZVP)

```
&XC                                          &END DFT
 &XC_FUNCTIONAL                              &SUBSYS
   &PBE
     SCALE_X 0.00                                            .
     SCALE_C 0.00                                            .
   &END                                                      .
 &END XC_FUNCTIONAL
 &HF                                           &KIND H
   FRACTION 1.00                                 BASIS_SET cc-QZVP  ! basis set for which
   &SCREENING                                                       ! RI basis is optimized
     EPS_SCHWARZ 1.0E-8                          POTENTIAL GTH-PBE-q1
     SCREEN_ON_INITIAL_P FALSE                 &END KIND
   &END                                        &COORD  ! optimize RI basis for H2 molecule
 &END                                                  ! and take it for arbitrary environ-
 &WF_CORRELATION                                       ! ment of H
   METHOD OPTIMIZE_RI_BASIS                     H  0.0000    0.0000    0.0000
   &OPT_RI_BASIS                                H  0.0000    0.0000    1.42000
     DELTA_I_REL   5.0E-6                      &END COORD
     DELTA_RI      5.0E-5                      &END SUBSYS
     EPS_DERIV     1.0E-3
     MAX_ITER      100
!     BASIS_SIZE   MEDIUM  ! in case you do not want to specify the number of auxiliary basis functions
     NUM_FUNC 4 4 3 2 1 ! specify number of basis functions in RI basis for each shell, e.g.
                        ! there are 3 d-functions and 1 g-function. Rule of thumb: maximum
                        ! l-quantum  number of RI basis exceeds the primary basis by one.
   &END
   NUMBER_PROC  1
 &END
&END XC

               .
               .
               .
```
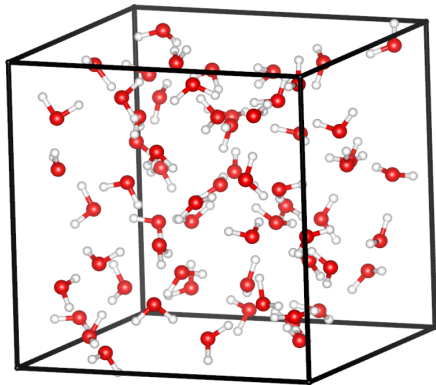
- Goal: Determine density of liquid water at ambient conditions.

- Method: Isobaric–Isothermal Monte Carlo
  Pre-sampling using fast methods
  (classical force fields, DFT with GGA functionals)

University of Zurich

Model

- 64 water molecules, 192 atoms, 256 active electrons
- cc-TZVP Basis, [3s3p2d1f], [3s2p1d], 3648 basis functions, 8704 RI basis functions

University of Zurich

RPA density of liquid water
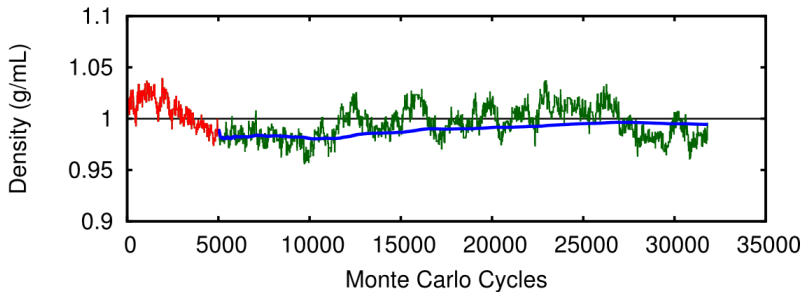
- NpT simulations ($T = 295\,\mathrm{K}$ and $p = 1\,\mathrm{bar}$)

[M. Del Ben, J. Hutter, and J. VandeVondele: Probing the structural and dynamical properties of liquid water with models including non-local electron correlation, J. Chem. Phys. **143**, 054506 (2015)]

Density of Water

	ρ[g/mL]	Error estimate Δ_ρ
BLYP	0.797	0.008
BLYP-D3	1.066	0.007
PBE-D3	1.055	0.006
M062X-D3 (ADMM)	1.004	0.008
MP2	1.020	0.004
RPA	0.994	0.006
Exp.	0.998	

University of Zurich

Very recently: MP2 gradients

- Del Ben, M; Hutter, J; VandeVondele, J. JOURNAL OF CHEMICAL PHYSICS **143**, 102803 (2015). Forces and stress in second order Møller-Plesset perturbation theory for condensed phase systems within the resolution-of-identity Gaussian and plane waves approach.
  http://dx.doi.org/10.1063/1.4919238

University of Zurich

- MP2 and RPA: two different approximate approaches for the correlation energy

  - post-SCF methods: first, converge SCF with Hartree-Fock (for MP2) or method of your choise (for RPA), then calculate total energy with MP2, RPA

  - accurate total energies, e. g. for MD to determine density of water

- High computational cost: MP2: $\mathcal{O}(N^5)$, SOS-MP2, RPA: $\mathcal{O}(N^4)$

  - RPA for 64 water molecules on 64 CRAY CX30 cores: 48 min

  - largest RPA calculation so far: 512 water molecules

University of Zurich