

Correlated Wave Function Methods in CP2K: Second-Order Møller-Plesset Perturbation Theory (MP2) and Random-Phase Approximation (RPA)

A tutorial

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- 1 Beyond-Hartree-Fock methods: Definition, benefits and limitations
- 2 The resolution of the identity (RI)
- 3 RI-MP2, RI-SOS-MP2 and RI-RPA for the correlation energy
- 4 RI-MP2 analytical forces
- 5 Execution time of RI-MP2, RI-SOS-MP2 and RI-RPA
- 6 Inputs for RI-MP2, RI-SOS-MP2 and RI-RPA
- 7 Applications
- 8 Concluding remarks

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The exchange-correlation term in Beyond-Hartree-Fock methods

Total energy E_{tot} of electrons in a molecule or periodic system:

$$E_{\text{tot}} = E_{\text{kin}} + E_{\text{el-core}} + E_{\text{Hartree}} + E_{\text{exchange (x)}} + E_{\text{correlation (c)}}$$

- **DFT:** exchange and correlation is a functional of the density $n(\mathbf{r}) = \sum_{i=1}^{N_{\text{occ}}} |\psi_i(\mathbf{r})|^2$:

$$E_{\text{xc}}^{\text{DFT}} = E_{\text{xc}}^{\text{DFT}}[n] \quad (\text{cheap})$$

- **Hartree-Fock (HF):** No correlation, exchange energy only depends on occupied MOs $\psi_i(\mathbf{r})$:

$$E_{\text{xc}}^{\text{HF}} = E_{\text{x}}^{\text{HF}}[\psi_1, \dots, \psi_{N_{\text{occ}}}] \quad (\text{medium})$$

- **Beyond HF (e.g. RPA/MP2):** correlation is a functional of all MOs $\psi_n(\mathbf{r})$ and eigenvalues ε_n :

$$E_{\text{xc}}^{\text{RPA/MP2}} = E_{\text{x}}^{\text{HF}}[\psi_1, \dots, \psi_{N_{\text{occ}}}] + E_{\text{c}}^{\text{RPA/MP2}}[\psi_1, \dots, \psi_{N_{\text{occ}}}, \psi_{N_{\text{occ}}+1}, \dots] \quad (\text{expensive})$$

RPA and MP2 total energy calculations are postprocessing procedures:

- 1 Converge an SCF (for MP2 always pure HF, for RPA typically PBE):

$$\left(-\frac{\nabla^2}{2} + v_{\text{el-core}}(\mathbf{r}) + v_{\text{Hartree}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r}) \right) \psi_n(\mathbf{r}) = \varepsilon_n \psi_n(\mathbf{r})$$

- 2 Take occupied and virtual molecular orbitals $\psi_n(\mathbf{r})$ and their energies ε_n of converged SCF and calculate total energy:

$$\text{MP2: } E_{\text{tot}} = E_{\text{kin, el-core, Hartree}} + E_{\text{x}}^{\text{HF}}[\psi_1, \dots, \psi_{N_{\text{occ}}}] + E_{\text{c}}^{\text{MP2}}[\text{all } \psi_n]$$

$$\text{RPA: } E_{\text{tot}} = E_{\text{kin, el-core, Hartree}} + E_{\text{x}}^{\text{HF}}[\psi_1, \dots, \psi_{N_{\text{occ}}}] + E_{\text{c}}^{\text{RPA}}[\text{all } \psi_n]$$

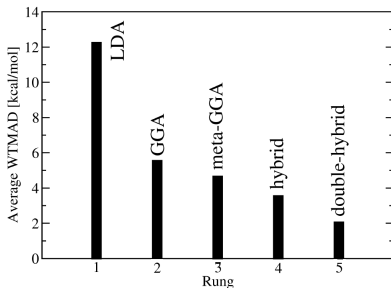
Motivation: Jacob's Ladder



Jacob's ladder of density functional approximations

Model of exchange-correlation term improved over time

- Pure DFT is not enough
- Hybrid schemes including HF improve
- Chemical accuracy (1 kcal/mol) not reached
- Go beyond DFT and hybrids with double hybrids containing MP2 and RPA



Accuracy of the density functional approximations

Mundy *et al.* SCIDAC 2010

L. Goerigk, S. Grimme, Phys. Chem. Chem. Phys. **13**, 6670 (2011)

MP2 and RPA correlation energies

- For MP2 and RPA, converge an SCF with HF/DFT to get ψ_n, ϵ_n .
- Both methods, MP2 and RPA do not give the exact correlation energy. RPA and MP2 are two different approximations to the correct correlation energy.
- Second order Møller-Plesset perturbation theory (MP2):

$$E_c^{\text{MP2}} = - \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{virt}} \frac{(ia|jb)[2(ia|jb) - (ib|ja)]}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j}$$

- Random-phase approximation (RPA):

$$E_c^{\text{RPA}} = - \frac{1}{2\pi} \int_0^\infty d\omega \text{Tr}[\ln(1 - \chi(i\omega)\mathbf{v}) + \chi(i\omega)\mathbf{v}]$$

$$\chi(\mathbf{r}_1, \mathbf{r}_2, i\omega) = 2 \sum_i^{\text{occ}} \sum_a^{\text{virt}} \psi_i(\mathbf{r}_1)\psi_a(\mathbf{r}_1)\psi_i(\mathbf{r}_2)\psi_a(\mathbf{r}_2) \frac{\epsilon_i - \epsilon_a}{(\epsilon_i - \epsilon_a)^2 + \omega^2}, \quad \mathbf{v}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

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

$$(ia|jb) = \iint \psi_i(\mathbf{r}_1)\psi_a(\mathbf{r}_1) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \psi_j(\mathbf{r}_2)\psi_b(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$$

- Rayleigh-Schrödinger perturbation theory:
- Zeroth-order Hamiltonian is the Fock operator: $\hat{H}_0 = \hat{F}$,
- Perturbation is the **fluctuation potential**: $\hat{V} = \hat{H} - \hat{F}$,
- Zeroth-order energy is the sum of orbital energies: $\sum_i \epsilon_i$
- First-order energy: HF energy (**NO MP1 EXISTS!**)
- Second-order energy: MP2 energy

$$E_c^{\text{MP2}} = - \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{virt}} \frac{(ia|jb)t_{ij}^{ab}}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j}$$

- The simplest ab initio correlated wave function method: involves multiple Slater determinants
- Also known as many-body perturbation theory (MBPT), although there are other variants of MBPT (e.g. GW)

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Gaussian Auxiliary Basis $\{P\}$; Resolution of the Identity (RI), or density fitting:

$$(ia|jb) \approx (ia|jb)_{RI} = \sum_{PQ} (ia|P) V_{PQ}^{-1} (Q|jb) = \sum_Q B_{ia}^Q B_{jb}^Q, \quad B_{ia}^Q = \sum_P (ia|P) V_{PQ}^{-1/2}$$

where

$$(ia|P) = \iint \psi_i(\mathbf{r}_1) \psi_a(\mathbf{r}_1) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \varphi_P(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$$

$$V_{PQ} = \iint \varphi_P(\mathbf{r}_1) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \varphi_Q(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$$

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

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

- Calculate Integrals using RI

$$(ia|jb) = \sum_P B_{ia}^P B_{jb}^P \quad (1)$$

- Scaling of computational effort is $\mathcal{O}(N^5)$, see Eq. (1):

occ. orbitals (i, j) each $\sim N$

virt. orbitals (a, b) each $\sim N$

auxiliary basis $(P) \sim N$

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

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

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

- Laplace-transform $1/r = \int_0^\infty e^{-rt} dt$ (I) and numerical integration (II)

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

- With RI the overall scaling is reduced to $\mathcal{O}(N^4)$ (cheaper than RI-MP2!)

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

- $N_q = 6-8$ quadrature points t_q give μH accuracy

RPA correlation energy in matrix representation:

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

where $\mathbf{Q}(\omega)$ is a matrix of size $N_{\text{RI}} \times N_{\text{RI}}$ with entries

$$Q_{PQ}(\omega) = 2 \sum_{ia} B_{ia}^P \frac{\epsilon_a - \epsilon_i}{(\epsilon_a - \epsilon_i)^2 + \omega^2} B_{ia}^Q.$$

- RI-RPA overall scaling $\mathcal{O}(N^4)$
- 10-15 quadrature points (minimax quadrature) for ω give μH accuracy
- very recently: $\mathcal{O}(N^3)$ scaling RPA with some tricks

Energy is not variational wrt. orbitals and determinant coefficients:

$$E^{(2)(x)} = 4 \sum_Q^{AUX} \sum_{\mu\nu}^{AO} \Gamma_{\mu\nu}^Q(\mu\nu|Q)^x - 2 \sum_{PQ}^{AUX} \Gamma^{PQ}(P|Q)^x + 2 \sum_{pq}^{SO} [P_{pq}^{(2)} F_{pq}^x - W_{pq}^{(2)} S_{pq}^x],$$

where μ, ν are basis functions, p, q are spin orbitals, x is a derivative and

$$\sum_p^{SO} = \sum_{p^\alpha}^{SO^\alpha} + \sum_{p^\beta}^{SO^\beta}.$$

Electron (spin) density:

$$\rho^S(\mathbf{r}) = \frac{1}{2} \sum_{p^\alpha q^\alpha} P_{p^\alpha q^\alpha} \phi_{p^\alpha}(\mathbf{r}) \phi_{q^\alpha}(\mathbf{r}) + (-) \frac{1}{2} \sum_{p^\beta q^\beta} P_{p^\beta q^\beta} \phi_{p^\beta}(\mathbf{r}) \phi_{q^\beta}(\mathbf{r}).$$

MP2 electron and spin densities are only available after a force calculation!

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- 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 [$\mathcal{O}(N^4)$ -scaling]
64 water molecules	192	3648 (8704)	22 s
512 water molecules	1536	29184 (69632)	1.7 h

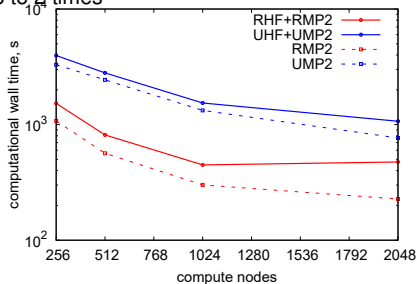
Timings on 32768 cores CRAY CX30 (= 4096 nodes on Piz Daint, 78 % of Piz Daint, worldwide 6th largest supercomputer), TZVP basis set, quadrature points: 16.

Timings for RI-MP2 gradient calculations

- On 4096 cores CRAX CX 30 with 512 GPUs (=512 nodes on Piz Daint):

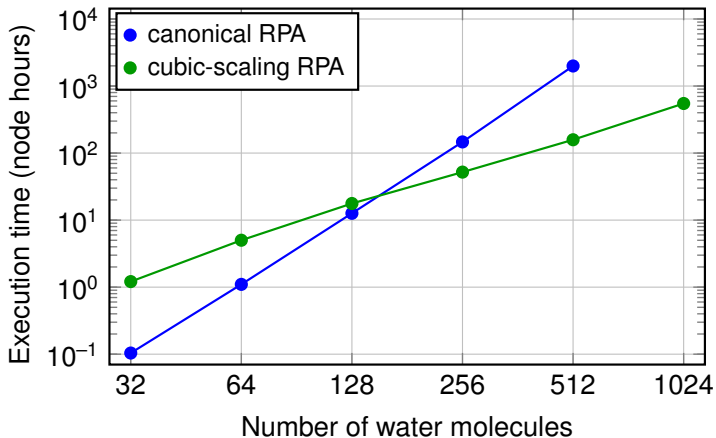
System	Atoms	Basis (RI basis)	t	t/t_E
32 CO ₂	96	2784 (7296)	4.99 min.	4.15
64 water molecules	192	3648 (8704)	9.34 min.	4.0

- GPU acceleration - up to 2 times



Spin-unrestricted (blue) and spin-restricted (red) calculations of 64 water molecules.

Scaling of $\mathcal{O}(N^4)$ (state of the art) and $\mathcal{O}(N^3)$ RPA



Scaling of quartic-scaling RPA (blue) and cubic-scaling RPA (green) with the system size, basis: cc-TZVP, CRAY XC40 machine with 36 cores per node.

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Input: Basis set and RI basis set for RI-MP2 and RI-RPA

```
&DFT
  BASIS_SET_FILE_NAME ../BASIS_RI_cc-TZ      ! RI basis sets are available for the cc-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
```

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

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

```
&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 NON
&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
```



```
&WF_CORRELATION
  METHOD RI_MP2_GPW
  &RI_MP2
    BLOCK_SIZE 1
    EPS_CANONICAL 1.0E-7
    FREE_HFX_BUFFER .FALSE. ! Memory for HFX exchange
  &END
  &CPHF ! Coupled perturbed equations
    EPS_CONV 1.0E-6
    MAX_ITER 50
  &END
  &WFC_GPW
    CUTOFF 300
    REL_CUTOFF 50
    EPS_FILTER 1.0E-12
    EPS_GRID 1.0E-10
  &END
  MEMORY 8000
  NUMBER_PROC 1
&END
```

- Coupled-perturbed equations for occupied-virtual one-particle density matrix
- Free HF exchange buffer used to solve them: saves time or memory
- Play with memory in the **HFX** and **WF CORRELATION** sections

Input non-periodic RPA on top of PBE-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
&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.
:
:
:
```

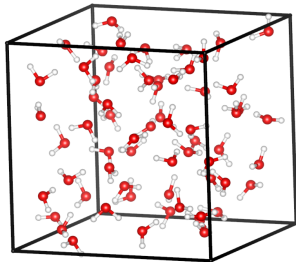
Optimize RI basis (in case you want other basis than cc-TZVP)

```
&XC                                &END DFT
&XC_FUNCTIONAL                    &SUBSYS
  &PBE
    SCALE_X 0.00
    SCALE_C 0.00
  &END
&END XC_FUNCTIONAL                &KIND H
&HF                                BASIS_SET cc-QZVP ! basis set for which
    FRACTION 1.00                    ! RI basis is optimized
  &SCREENING
    EPS_SCHWARZ 1.0E-8
    SCREEN_ON_INITIAL_P FALSE
  &END
&END                                &COORD ! optimize RI basis for H2 molecule
&WF_CORRELATION                    ! and take it for arbitrary environ-
  METHOD OPTIMIZE_RI_BASIS            ! ment of H
  &OPT_RI_BASIS
    DELTA_I_REL 5.0E-6
    DELTA_RI 5.0E-5
    EPS_DERIV 1.0E-3
    MAX_ITER 100
    H 0.0000 0.0000 0.0000
    H 0.0000 0.0000 1.42000
  &END COORD
  &END SUBSYS
! 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

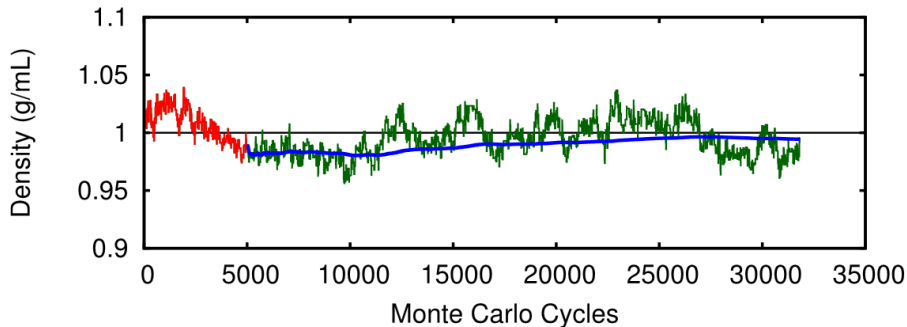
.
.
.
```

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- **Goal:** Determine **density** of liquid water at ambient conditions.
- **Method:** Isobaric–Isothermal Monte Carlo
Pre-sampling using fast methods (classical force fields, DFT with PBE)
- 64 water molecules, 192 atoms, 256 active electrons



- cc-TZVP Basis, [3s3p2d1f], [3s2p1d], 3648 basis functions, 8704 RI basis functions



- NpT simulations ($T = 295$ K and $p = 1$ bar)

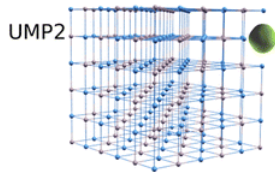
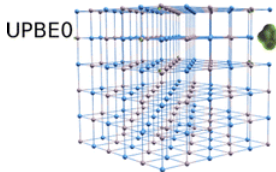
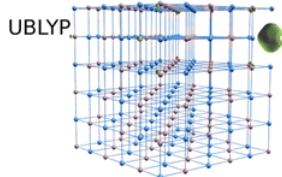
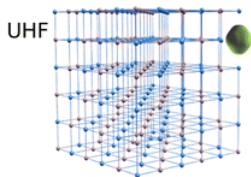
[M. Del Ben, J. Hutter, and J. VandeVondele: Probing the structural and dynamical properties of liquid water with models including non-local electron correlation, J. Chem. Phys. **143**, 054506 (2015)]

	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	

[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)]

F-center in lithium fluoride

- $3 \times 3 \times 3$ supercell, $\text{Li}_{108}\text{F}_{107}$
- 10 hours for energy and gradient on 2048 Piz Daint nodes
- Spin-density distributions: MP2 is free of delocalization error present in DFT



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MP2 and RPA implemented by Mauro Del Ben:

- **MP2**: M. Del Ben, J. Hutter, and J. VandeVondele, JCTC **8**, 4177-4188 (2012).
- **RI-MP2, RI-RPA**: M. Del Ben, J. Hutter, and J. VandeVondele, JCTC **9**, 2654-2671 (2013).
- **More efficient and massively parallel RI-RPA with GPUs**: M. Del Ben, O. Schütt, T. Wentz, P. Messmer, J. Hutter, and J. VandeVondele, Comp. Phys. Comm. **187**, 120-129 (2015).
- **RI-MP2 forces**: M. Del Ben, J. Hutter, and J. VandeVondele, JCP **143**, 102803 (2015).

Open-shell MP2 forces implemented by Vladimir Rybkin:

- V. V. Rybkin, and J. VandeVondele, JCTC **12**, 2214-2223 (2016).

Cubic-scaling RPA by Jan Wilhelm

- **Cubic-scaling RI-RPA**: J. Wilhelm, P. Seewald, M. Del Ben, and J. Hutter, submitted.

- 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 choice (for RPA), then calculate total energy with MP2, RPA
 - accurate total energies, e. g. for MD to determine density of water
- High cost: MP2: $\mathcal{O}(N^5)$, SOS-MP2, RPA: $\mathcal{O}(N^4)$, RPA also $\mathcal{O}(N^3)$
 - RPA for 64 water molecules on 64 CRAY CX30 cores: 48 min
 - largest RPA calculation so far: 1024 water molecules
- Functionality:
 - Energies: MP2, RI-MP2, SOS-MP2, RPA ($\mathcal{O}(N^4)$), RPA ($\mathcal{O}(N^3)$)
 - Forces, stress, electron and spin densities: RI-MP2

- 1 Accurate correlation energy needed. Then use double hybrid functionals containing MP2 and RPA
- 2 Systems where van-der-Waals interaction is important and dispersion-corrected density functionals do not give accurate results. Maybe pure MP2 or pure RPA give more accurate results
- 3 DFT suffers from delocalization error, e.g. for radicals and electron transfer
- 4 Not for strong/static correlation and bond breaking