Beyond-Hartree-Fock methods in CP2K: MP2, RPA and *GW*
A tutorial

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Overview

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

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

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

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

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

$$E_{xc}^{HF} = E_x^{HF}[\psi_1, \ldots, \psi_{N_{occ}}] \qquad \text{(medium)}$$

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

$$E_{xc}^{RPA/MP2} = E_x^{HF}[\psi_1, \ldots, \psi_{N_{occ}}] + E_c^{RPA/MP2}[\psi_1, \ldots, \psi_{N_{occ}}, \psi_{N_{occ}+1}, \ldots] \qquad \text{(expensive)}$$

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RPA and MP2 total energy calculations are postprocessing procedures:

1. Converge an SCF (for MP2 typically 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:

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

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

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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
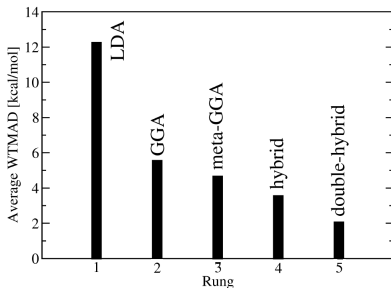
Accuracy of the density functional approximations

Mundy *et al.* SCIDAC 2010

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

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MP2 and RPA correlation energies

- For MP2 and RPA, converge an SCF with DFT or hybrid 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):

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

- Random-phase approximation (RPA):

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

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

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

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

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

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

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

- Calculate Integrals using RI

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

- 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 $(P) \sim N$

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

- 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)

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

- 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

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RPA correlation energy in matrix representation:

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

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

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

- 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

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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.

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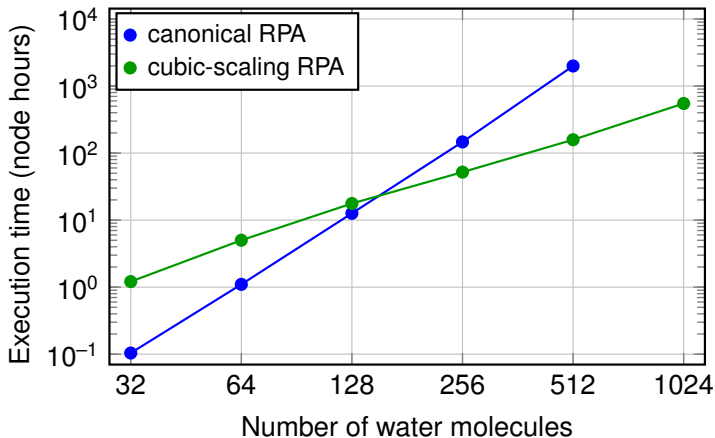
Scaling of quartic-scaling RPA (blue) and cubic-scaling RPA (green) with the system size, basis: cc-TZVP, CRAY XC40 machine with 36 cores per node.

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```
&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
```

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*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
```

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```
&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
```

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```
                                                                    .
                                                                    .
&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.

                    .
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```
&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

               .
               .
               .
```
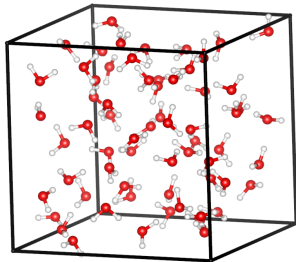
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- Goal: Determine density of liquid water at ambient conditions.
- Method: Isobaric–Isothermal Monte Carlo

  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

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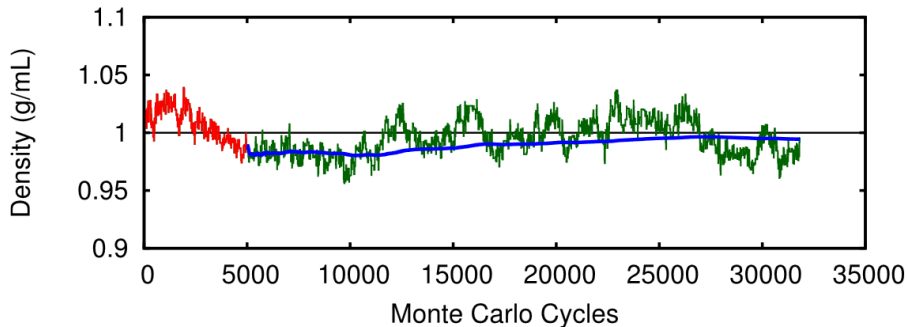
- NpT simulations ($T = 295\,\text{K}$ and $p = 1\,\text{bar}$)

[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)]

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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	

[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)]

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- In DFT and Hartree-Fock, there is no theoretical foundation that the eigenvalues ε_n from an SCF,

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

have anything to do with single-electron energies.
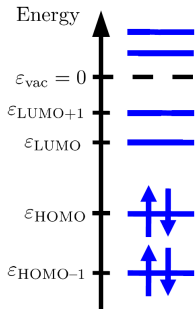
- **Theorem:**
  A self-energy $\Sigma(\mathbf{r}, \mathbf{r}', \varepsilon)$ (non-local, energy-dependent) containing exchange and correlation effects exists, such that the solution of

$$\left(\frac{-\nabla^2}{2} + v_{\text{el-core}}(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) \right) \psi_n(\mathbf{r}) + \int d\mathbf{r}' \, \Sigma(\mathbf{r}, \mathbf{r}', \varepsilon_n) \psi_n(\mathbf{r}') = \varepsilon_n \psi_n(\mathbf{r})$$

gives the correct quasiparticle energies ε_n of the interacting many-electron system.

- In the *GW* approximation, the self-energy reads

$$\Sigma^{GW}(\mathbf{r}, \mathbf{r}', \varepsilon) = \frac{i}{2\pi} \int_{-\infty}^{\infty} d\varepsilon' \, G(\mathbf{r}, \mathbf{r}', \varepsilon - \varepsilon', \{\varepsilon_n\}, \{\psi_n\}) \, W(\mathbf{r}, \mathbf{r}', \varepsilon', \{\varepsilon_n\}, \{\psi_n\})$$

Energy

$\varepsilon_{\text{vac}} = 0$
$\varepsilon_{\text{LUMO}+1}$
$\varepsilon_{\text{LUMO}}$

$\varepsilon_{\text{HOMO}}$

$\varepsilon_{\text{HOMO}-1}$

Single-electron (quasiparticle) levels
of a closed shell molecule

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Reminder: One gets the correct eigenvalues ε_n by solving

$$\left(\frac{-\nabla^2}{2} + v_{\text{el-core}}(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) \right) \psi_n(\mathbf{r}) + \int d\mathbf{r}'\, \Sigma(\mathbf{r}, \mathbf{r}', \varepsilon_n)\psi_n(\mathbf{r}') = \varepsilon_n\, \psi_n(\mathbf{r})$$

1. Practically, first converge SCF with DFT

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

2. Compute the (n, n) diagonal elements Σ_n^{GW} of the $G_0 W_0$ self-energy and the xc potential:

$$\Sigma_n^{GW} = \iint d\mathbf{r}\, d\mathbf{r}'\, \psi_n^{\text{DFT}}(\mathbf{r})\, \Sigma^{GW}(\mathbf{r}, \mathbf{r}', \varepsilon_n^{\text{DFT}})\, \psi_n^{\text{DFT}}(\mathbf{r}')$$

$$v_{\text{xc},n} = \int d\mathbf{r}\, \psi_n^{\text{DFT}}(\mathbf{r})\, v_{\text{xc}}(\mathbf{r})\, \psi_n^{\text{DFT}}(\mathbf{r})$$

3. Correct the DFT eigenvalues $\varepsilon_n^{\text{DFT}}$ by $G_0 W_0$ ($Z_n \approx 1$ typically):

$$\varepsilon_n^{G_0 W_0} = \varepsilon_n^{\text{DFT}} + Z_n \left(\Sigma_n^{GW} - v_{\text{xc},n} \right)$$

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Eigenvalue selfconsistent GW (evGW) yields best results for the HOMO-LUMO gap of molecules [Blase et al., Phys. Rev. B 83, 115103 (2011)]:

Iterate the G_0W_0 equation to self-consistency in the eigenvalues:

G_0W_0 : $\qquad \varepsilon_n^{G_0W_0} = \varepsilon_n^{\text{DFT}} + Z_n \left(\Sigma_n^{GW}(\{\varepsilon_n^{\text{DFT}}\}, \{\psi_n^{\text{DFT}}\}) - v_{\text{xc},n} \right)$

ev$GW(1)$: $\quad \varepsilon_n^{\text{ev}GW(1)} = \varepsilon_n^{G_0W_0} + Z_n \left(\Sigma_n^{GW}(\{\varepsilon_n^{G_0W_0}\}, \{\psi_n^{\text{DFT}}\}) - \Sigma_n^{GW}(\{\varepsilon_n^{\text{DFT}}\}, \{\psi_n^{\text{DFT}}\}) \right)$

ev$GW(2)$: $\quad \varepsilon_n^{\text{ev}GW(2)} = \varepsilon_n^{\text{ev}GW(1)} + Z_n \underbrace{\left(\Sigma_n^{GW}(\{\varepsilon_n^{\text{ev}GW(1)}\}, \{\psi_n^{\text{DFT}}\}) - \Sigma_n^{GW}(\{\varepsilon_n^{G_0W_0}\}, \{\psi_n^{\text{DFT}}\}) \right)}_{\to \, 0 \ \text{in case of self-consistency}}$

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```
&DFT
  BASIS_SET_FILE_NAME   ./BASIS
  POTENTIAL_FILE_NAME   ./POTENTIAL
  UKS
  MULTIPLICITY 1
  &QS
    METHOD GPW
  &END QS
  &POISSON
    PERIODIC NONE
  &END POISSON
  &XC
    &XC_FUNCTIONAL PBE
    &END XC_FUNCTIONAL
    &WF_CORRELATION
      METHOD RI_RPA_GPW
      &RI_RPA
        RPA_NUM_QUAD_POINTS  100
        SIZE_FREQ_INTEG_GROUP 512
        GW
        &HF
          FRACTION  1.0000000
          &SCREENING
            EPS_SCHWARZ    1.0E-11
            SCREEN_ON_INITIAL_P FALSE
          &END SCREENING
          &MEMORY
            MAX_MEMORY 0
          &END
        &END HF

                    .
                    .
                    .
```

```
                    .
                    .
                    .
        &RI_G0W0
          ! tell the code how many eigenvalues
          ! should be corrected by GW
          CORR_OCC 1000
          CORR_VIRT 400
          ! how many evGW iterations should be
          ! done at most
          EV_SC_ITER 10
        &END RI_G0W0
      &END RI_RPA
      NUMBER_PROC  16
    &END
  &END XC
&END DFT
```

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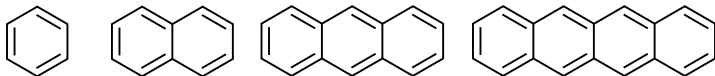
First four linear acenes.

HOMO-LUMO gaps of known acenes from DFT, G_0W_0 and evGW starting from two functionals:

N_{rings}	PBE0			tuned CAM-B3LYP			Exp.
	DFT	G_0W_0	evGW	DFT	G_0W_0	evGW	
3	3.87	6.63	6.94	6.16	6.90	6.95	6.91
4	3.03	5.54	5.83	5.30	5.81	5.84	5.91
5	2.61	4.77	5.11	4.73	5.01	5.03	5.22

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Literature

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).

GW and cubic-scaling RPA by myself:

- *GW*: J. Wilhelm, M. Del Ben, and J. Hutter, JCTC **12**, 3623-3635 (2016).
- **Cubic-scaling RI-RPA**: J. Wilhelm, P. Seewald, M. Del Ben, and J. Hutter, submitted.

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Summary

- 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

- *GW*: method to compute single-electron energies

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

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Where you may need MP2, RPA and *GW*

- MP2 and RPA:

  1. Accurate correlation energy needed. Then use double hybrid functionals containing MP2 and RPA.

  2. Systems where van-der-Waals interaction is important and disperion-corrected density functionals do not give accurate results. Maybe pure MP2 or pure RPA give more accurate results.

- *GW*: For calculating single-electron levels, e.g. the HOMO-LUMO gap (there is no foundation to use DFT to compute single-electron levels!).

Offer

In case you want to do an MP2, RPA, or *GW* calculation, you are cordially invited to write me an e-mail. I am happy to help!

University of Zurich