MP2, RPA and GW within the Gaussian and Plane Waves Method

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Outline

- Goals and Requirements
  - Enhanced accuracy for solutions and interfaces
  - System size and sampling requirements
- MP2/RPA with Gaussian and Plane Waves
  - Resolution-of-identity (RI) in GPW
  - Applications to liquids and solutions
- Recent Developments
  - MP2 forces and stress tensor
  - Periodic G0W0 Method
  - Cubic scaling RPA/G0W0
- Outlook and Challenges
  - Basis set convergence
  - Properties (derivatives)
  - Sustainable code development

Acknowledgment

- Joost VandeVondele (CSCS) HFX, ADMM, MP2, RPA
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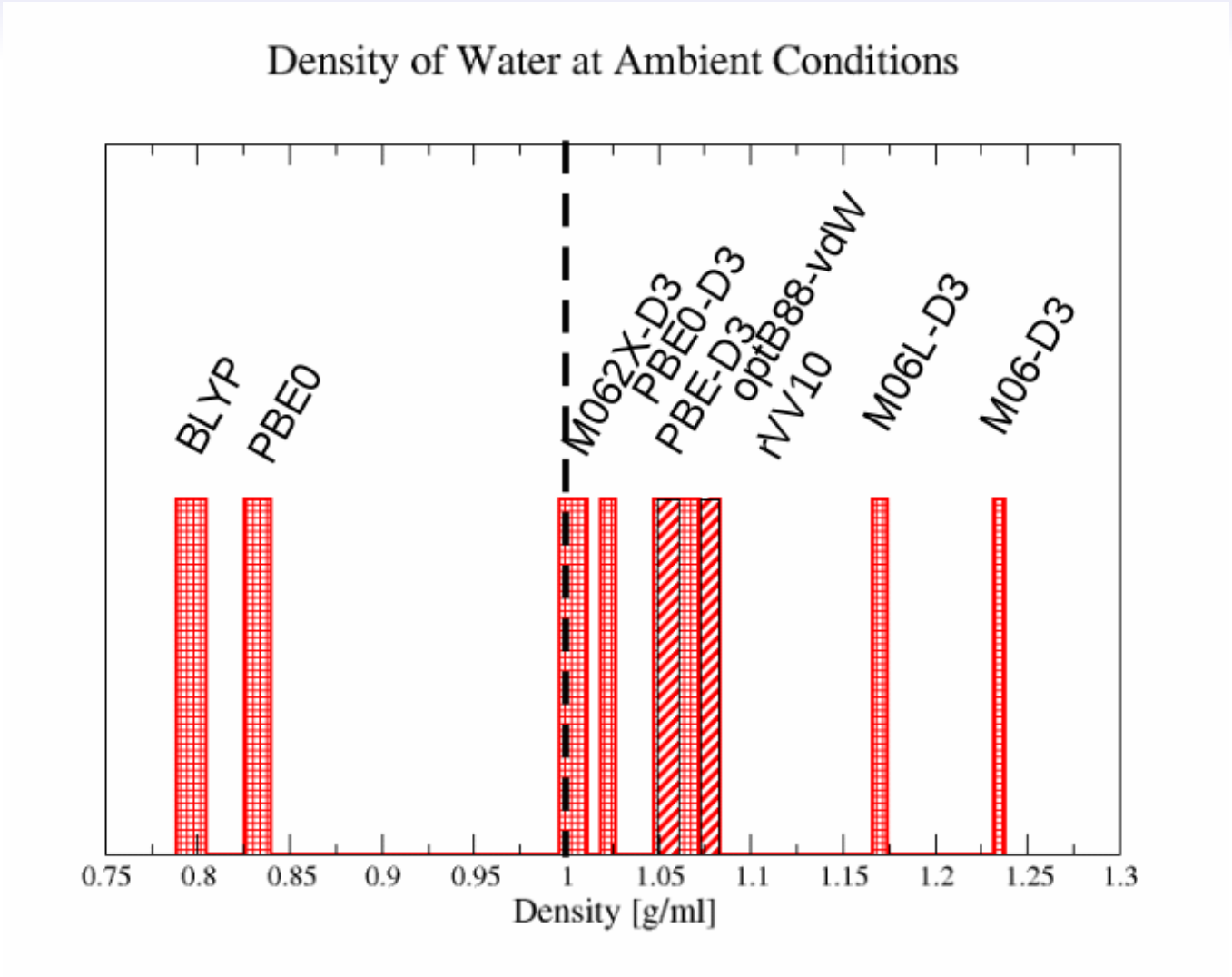
- Vladimir Rybkin (UZH) UMP2 gradients, WF embedding
- Dorothea Golze (Aalto) Integrals, LRIGPW
- Patrick Sewald (UZH) Ewald Integrals, Tensor library

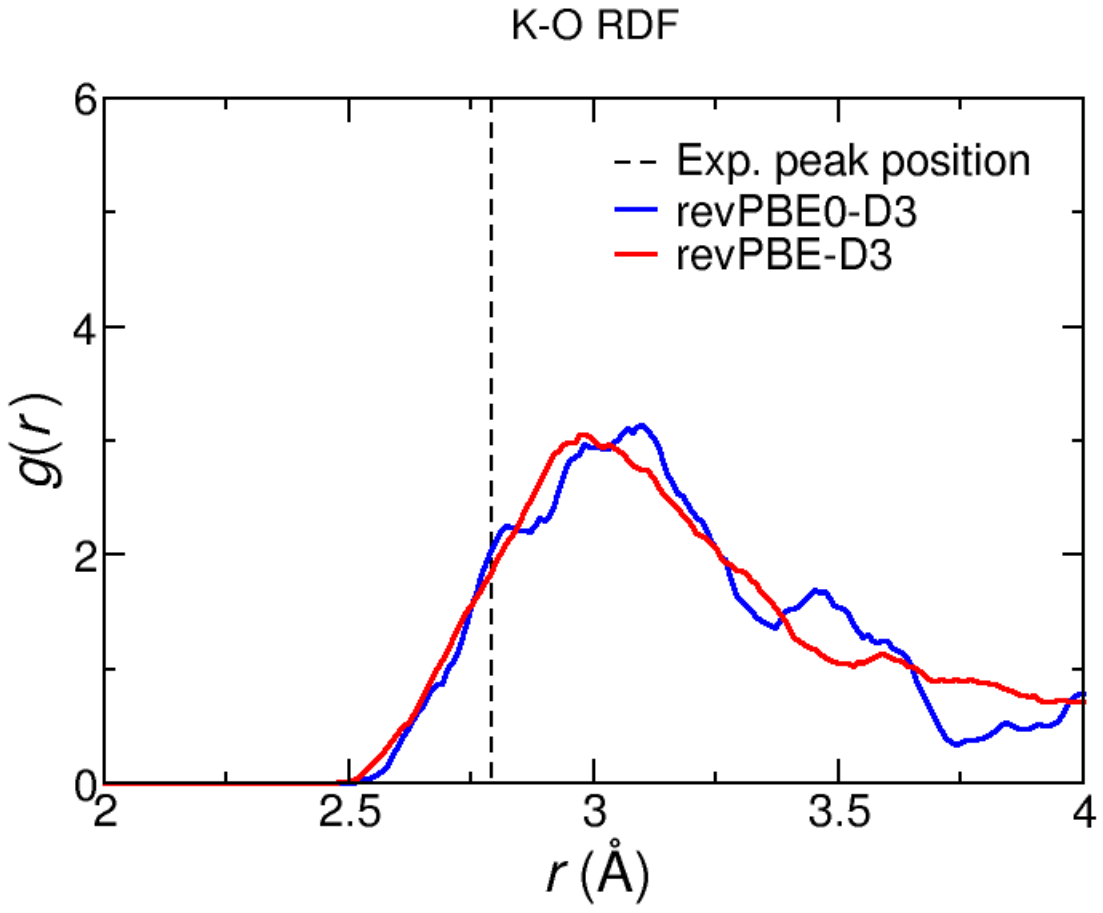
Liquids and Solutions: Shortcommings of GGA DFT

- Density of Water: Balanced description of hydrogen bonding and van der Waals interactions
- Structure of solvation shell of ions in water: Polarization and charge transfer
- Level alignment: Ions in solution and at liquid/solid interfaces



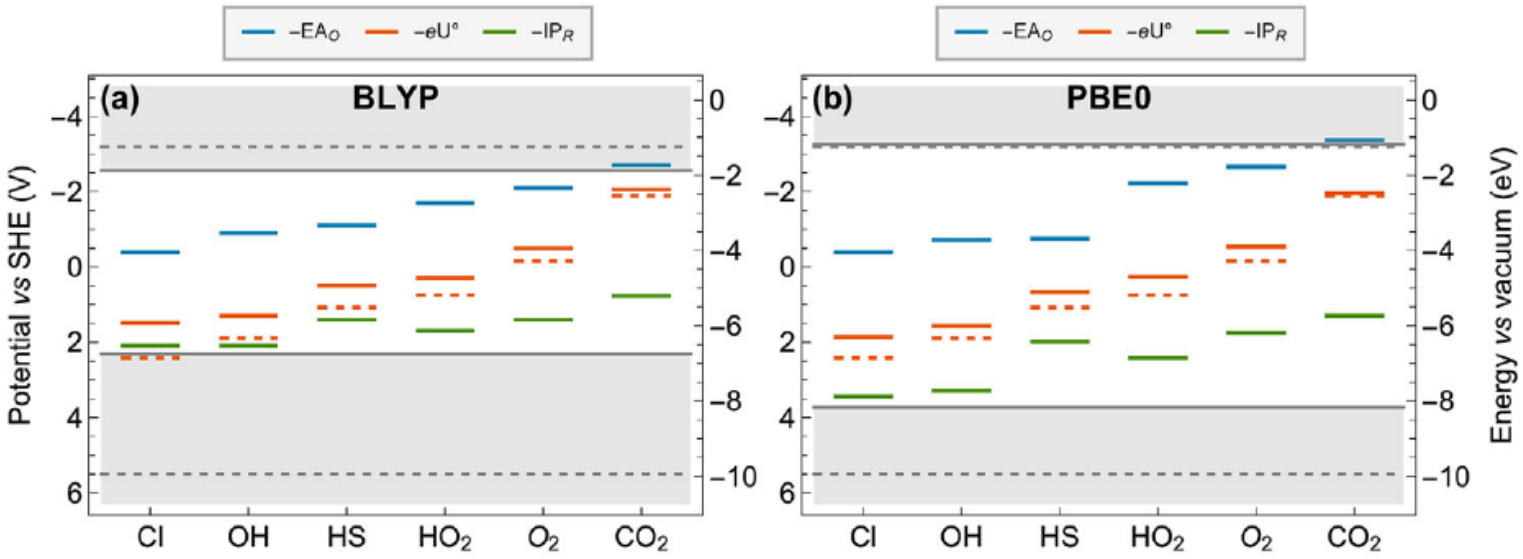
M. Del Ben et al., JCP 143 054506 (2015)

K^+ in Liquid Water



T. Duignan et al., unpublished

Energy Levels in Liquid Water



Jun Cheng and J. VandeVondele, PRL 116 086402 (2016)

Requirements: System and Method

- Electronic Structure Theory: nonlocal correlation

  MP2, SOS-MP2, dRPA, double-hybrid functionals

- System sizes

  200+ atoms, 500 correlated electrons,

  4000+ basis functions

- Periodic Boundary Conditions

  Γ-point approximation

Requirements: Sampling

- Molecular Dynamics: multiple time step schemes

  Monte Carlo: Accurate bias potentials

- Smooth energy surface and accurate analytic forces

- Sampling: 20'000+ energy or energy/force calculations

- CPU-Budget: 1 Mio node-hours, 3 months time to solution

  512 node runs, 6 min / energy calculation

Resolution of Identity Approach in CP2K

Gaussian Auxiliary Basis
Coulomb Metric (Ewald Summation)
Γ-Point approximation, all functions are periodic

$$(ia \mid jb) = \sum_{PQ} (ia \mid P) \underbrace{(P \mid Q)}_{\text{GPW Integral}}^{-1} (Q \mid jb)$$

$$= \sum_{S} (ia \mid S)(S \mid jb) = \sum_{S} B^S_{ia} B^S_{jb}$$

$$B^S_{ia} = \sum_{P} (ia \mid P)(P \mid S)^{-1/2} = \sum_{\mu} C_{\mu i} \sum_{\nu} C_{\nu a} \underbrace{(\mu\nu \mid S)}_{\text{GPW Integral}}$$

J.L. Whitten, JCP 58, 4496 (1973), O. Vahtras, J. Almlöf, M. Feyereisen, CPL 213 514 (1993)

GPW RI Integrals

$$B^S_{\mu\nu} = (\mu\nu \mid S)$$

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

$\Downarrow$ FFT

Multiply with operator to get potential

$$V_S(\mathbf{G}) = \chi_S(\mathbf{G}) \cdot \mathcal{O}(\mathbf{G})$$

$\Downarrow$ FFT

Integrate $\quad (\mu\nu| \quad$ on grid with $\quad V_S(\mathbf{R})$

$$B^S_{\mu\nu} = \sum_{\mathbf{R}} \Phi_{\mu\nu}(\mathbf{R}) \cdot V_S(\mathbf{R})$$

M. DelBen et al., JCTC 8 4177 (2012); JCTC 9 2654 (2013)

RI-MP2, RI-dRPA

$$E^{(2)} = -\sum_{i \leq j}^{o} (2 - \delta_{ij}) \sum_{ab}^{v} \frac{(ia \mid jb)[2(ia \mid jb) - (ib \mid ja)]}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j}$$

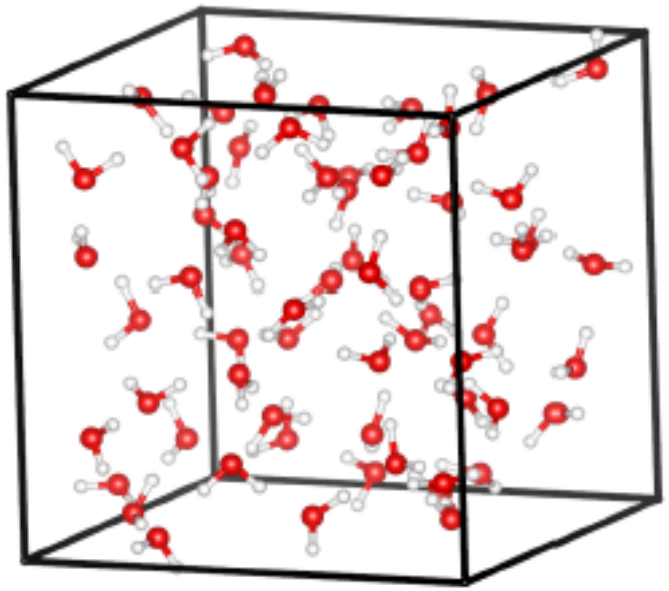
$$E_c^{\mathrm{RI-dRPA}} = \frac{1}{2} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \mathrm{Tr} \left(\ln \left(1 + Q(\omega) \right) - Q(\omega) \right)$$

$$Q(\omega) = 2B^T G(\omega) B$$

$$G(\omega)_{ia,jb} = \frac{\varepsilon_a - \varepsilon_i}{(\varepsilon_a - \varepsilon_i)^2 + \omega^2} \, \delta_{ij} \delta_{ab}$$

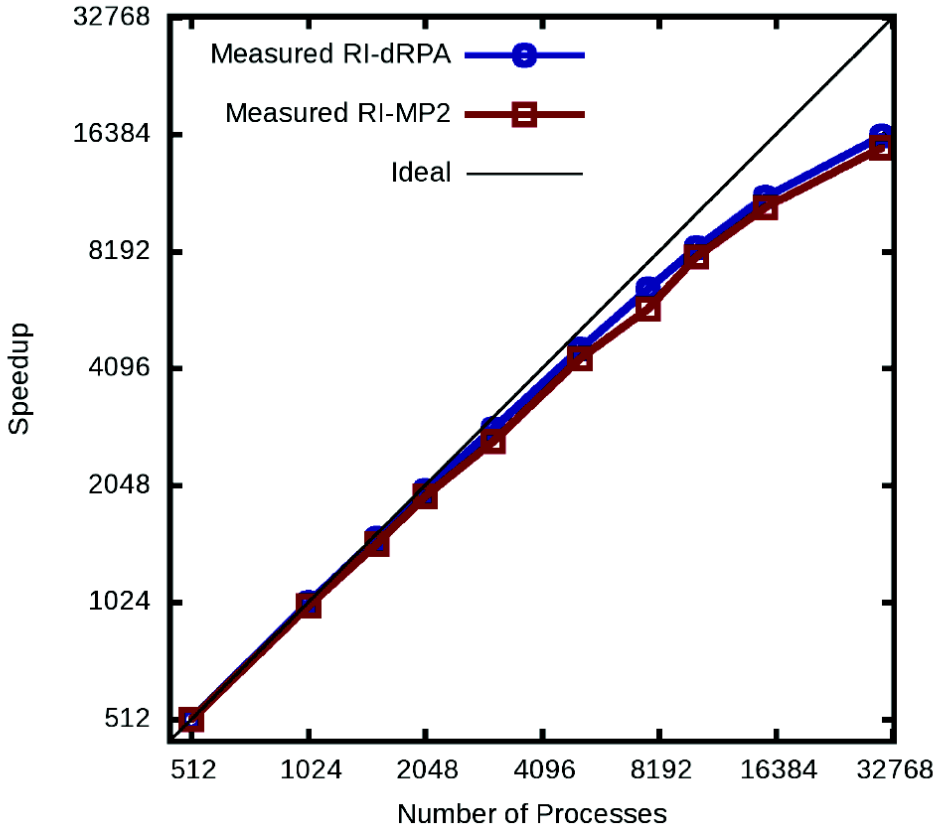
Isobaric–Isothermal Monte Carlo

Simulation of Liquid Water



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

Scaling: dRPA and MP2



64 water molecules, cc-TZVP Basis; 256 occupied orbitals,

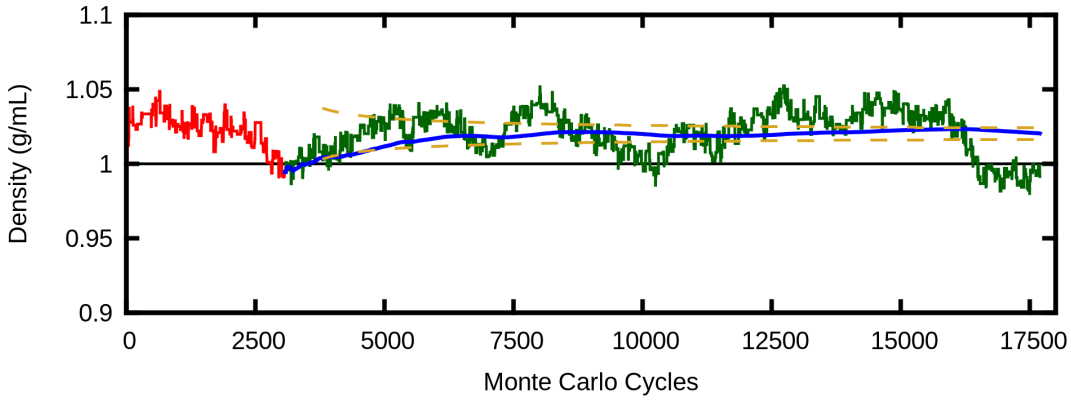
3648 basis function, 8704 RI basis functions

CPU Timings

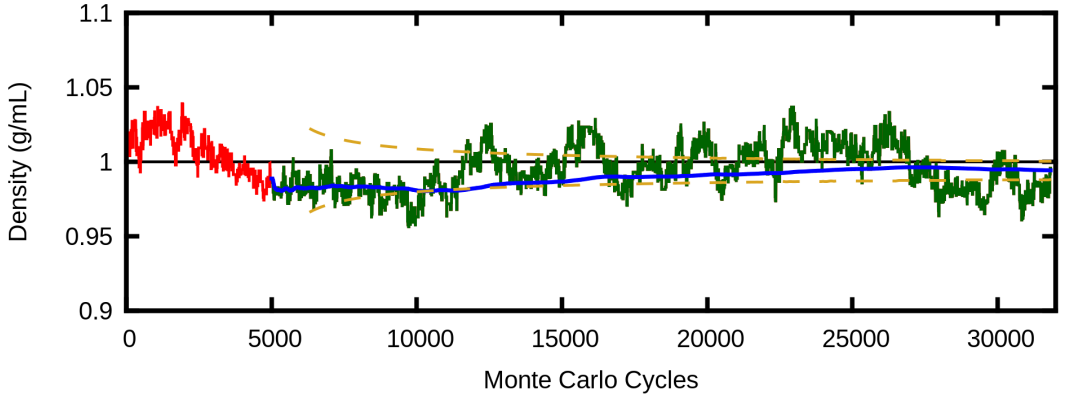
	Num. Cores	Time/MC cycle [s]	Total MC time [million Coreh]
PBE/BLYP	512	17.3	0.1
PBE0-ADMM	768	34.3	0.3
PBE0	2400	65.4	2.0
RI-dRPA	6400	275.2	7.2
RI-MP2	12800	218.1	12.2

Density of Liquid Water

MP2: 1.002 g/ml



RPA: 0.994 g/ml



M. Del Ben et al., JCP 143 054506 (2015)

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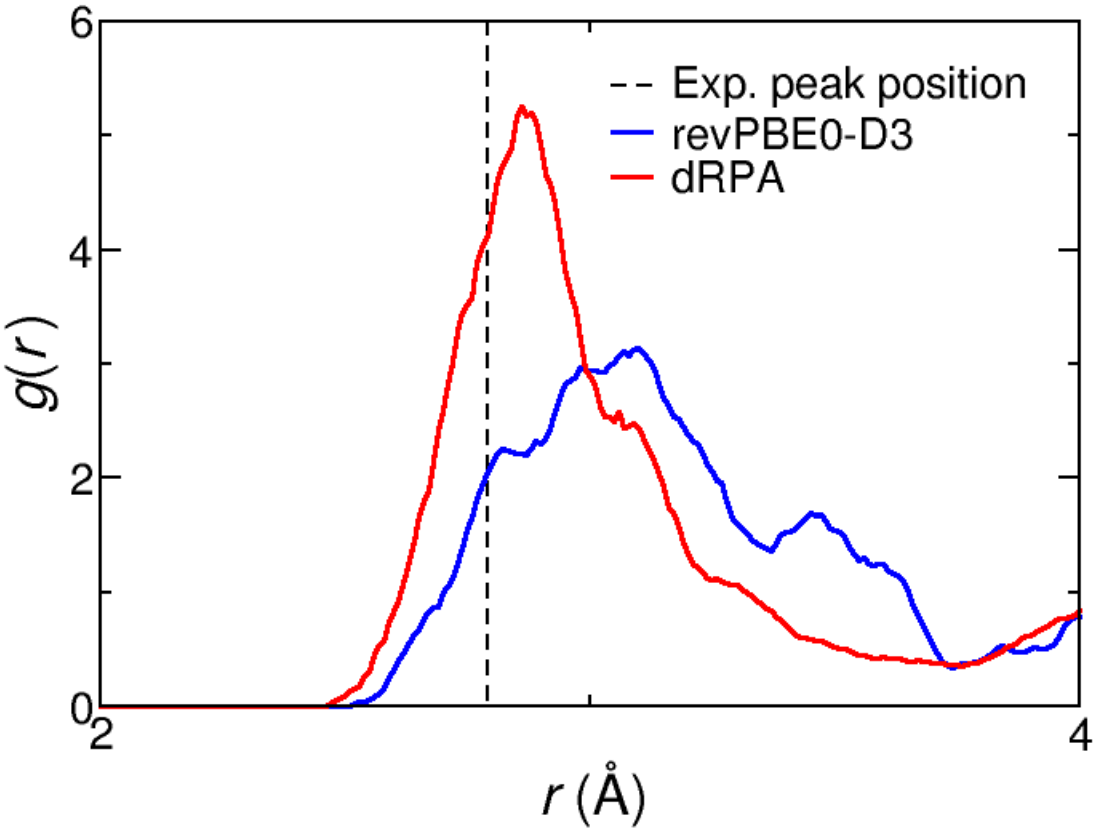

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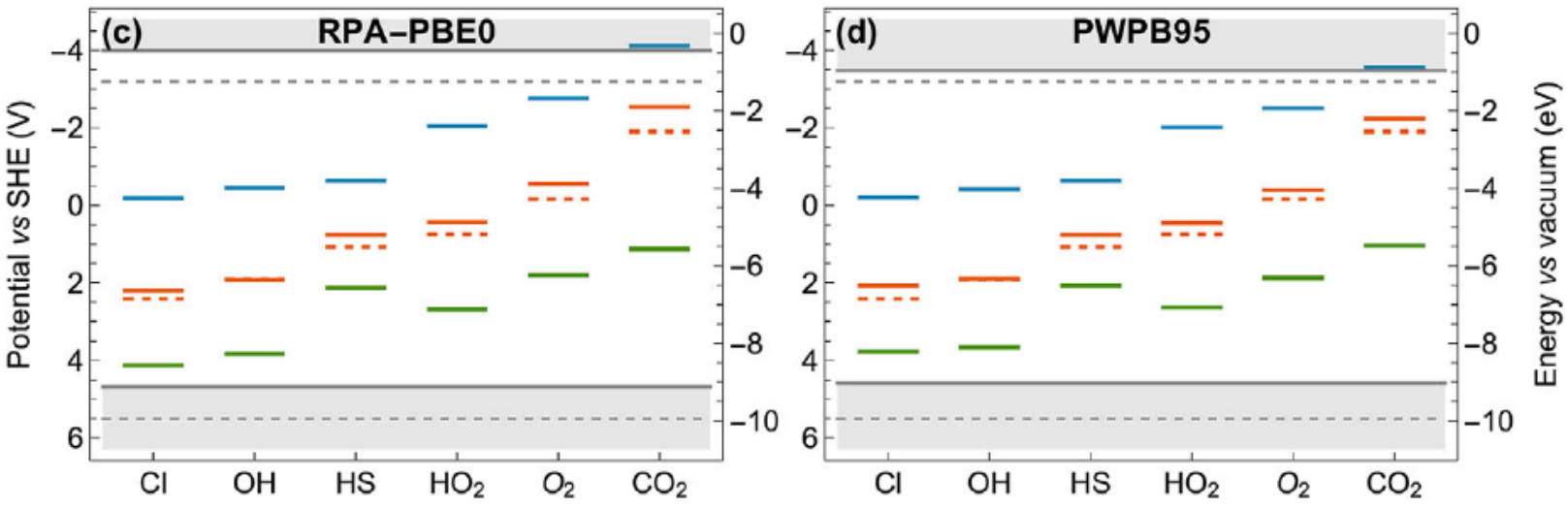
Energy Levels in Liquid Water



Jun Cheng and J. VandeVondele, PRL 116 086402 (2016)

Recent Developments

- MP2 forces and stress tensor

  M. Del Ben et al., JCP 143 102803 (2015)
  V. Rybkin, J. VandeVondele, JCTC 12 2214-2223 (2016)

- Periodic G0W0 Method

  J. Wilhelm et al. JCTC 12 3623-3635 (2016)
  J. Wilhelm, JH, PRB 95 235123 (2017)

- Cubic scaling RPA/G0W0

  J. Wilhelm et al. JCTC 12 5851-5859 (2016)
  J. Wilhelm et al. JPCL ASAP

MP2 Forces and Stress Tensor

- Restricted MP2

  M. Del Ben et al., JCP 143 102803 (2015)

- Unrestricted MP2

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

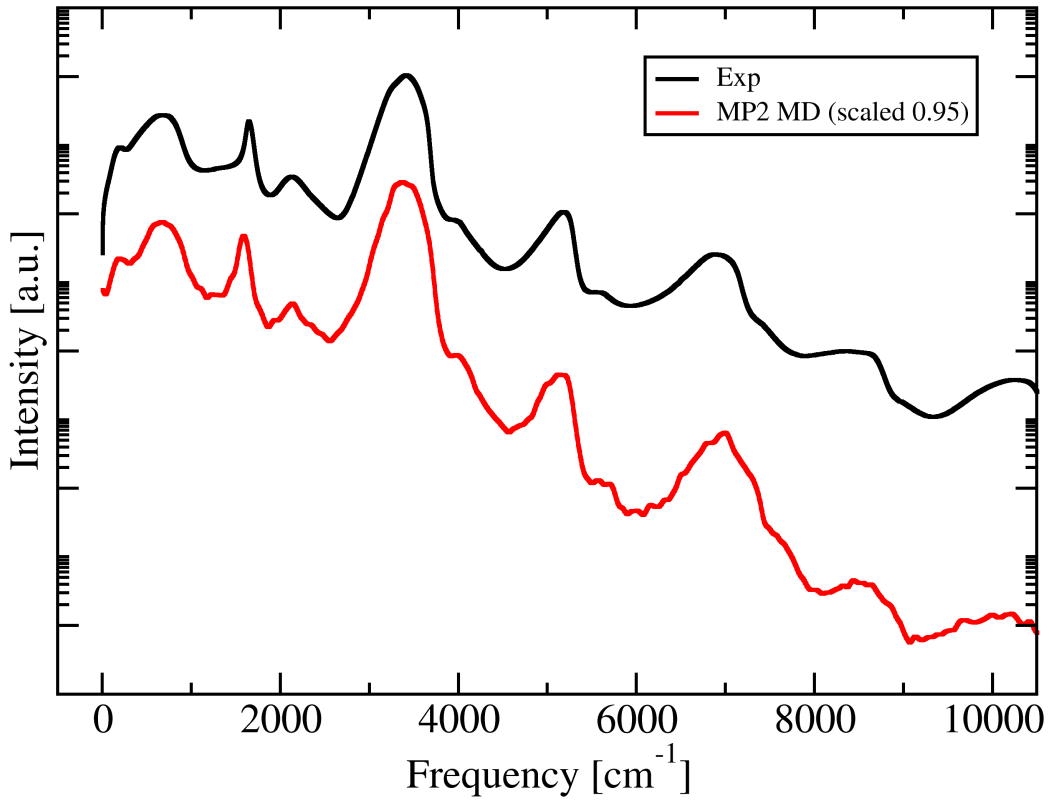
- Performance

  Forces(Stress) MP2/ Energy MP2 ≈ 4

  MP2 energy/ UMP2 energy ≈ 3

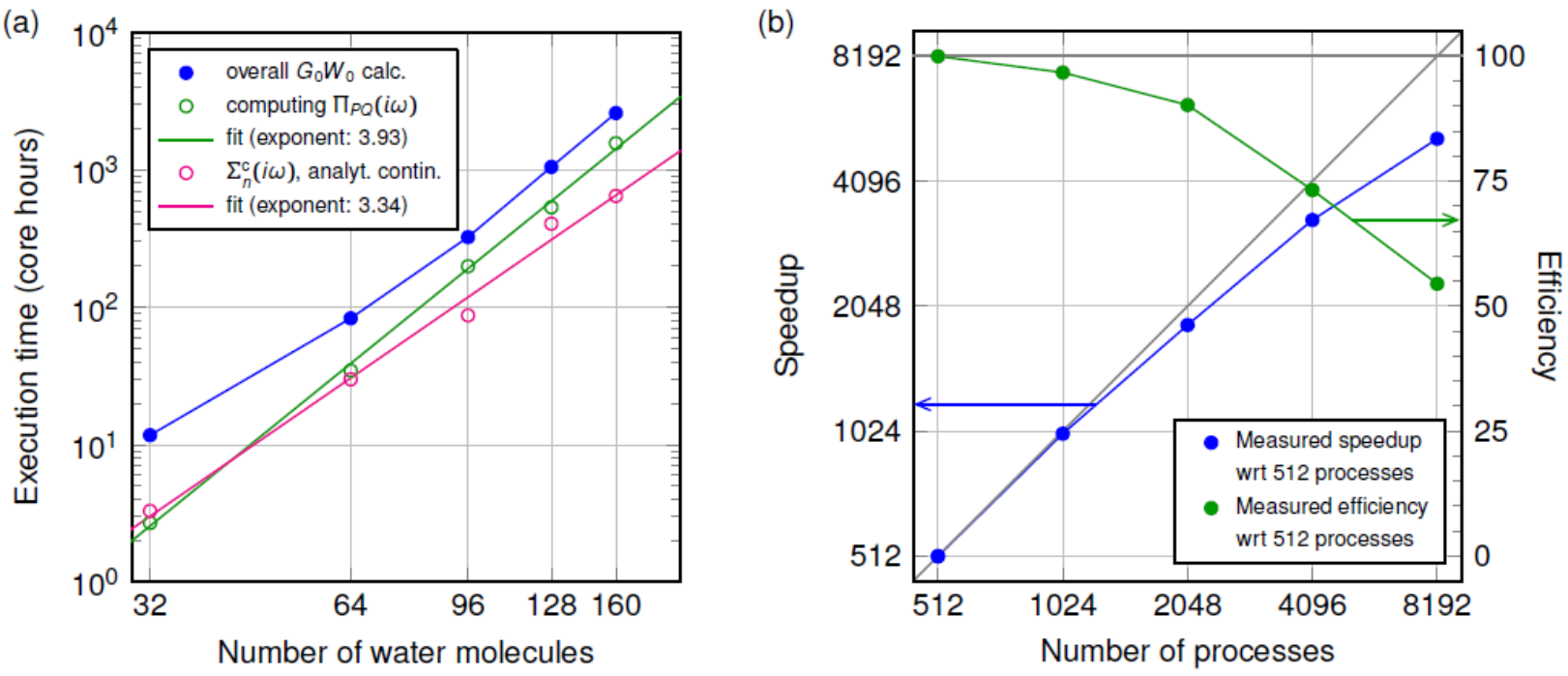
  Forces(Stress) UMP2/ Forces(Stress) MP2 ≈ 4

Applications: IR spectra from MP2 MD



M. Del Ben et al., JCP 143 102803 (2015)

Periodic G0W0 Method



Execution time and speedup for G0W0 calculations of water systems (cc-TZVP basis). Calculation of 20 quasi-particle energies. Numerical integration using 60 points.

J. Wilhelm et al. JCTC 12 3623-3635 (2016); J. Wilhelm, JH, PRB 95 235123 (2017)

Cubic Scaling RPA/GW

RI with Overlap Metric

$$(\alpha\beta \mid \gamma\delta) = \sum_{PQRS} (\alpha\beta P)\,(PQ)^{-1}\,(Q \mid R)\,(RS)^{-1}\,(S\gamma\delta)$$

$(\alpha\beta P)$	analytic 3-center overlap
(PQ)	analytic 2-center overlap
$(Q \mid R)$	semi-analytic 2-center Ewald integrals

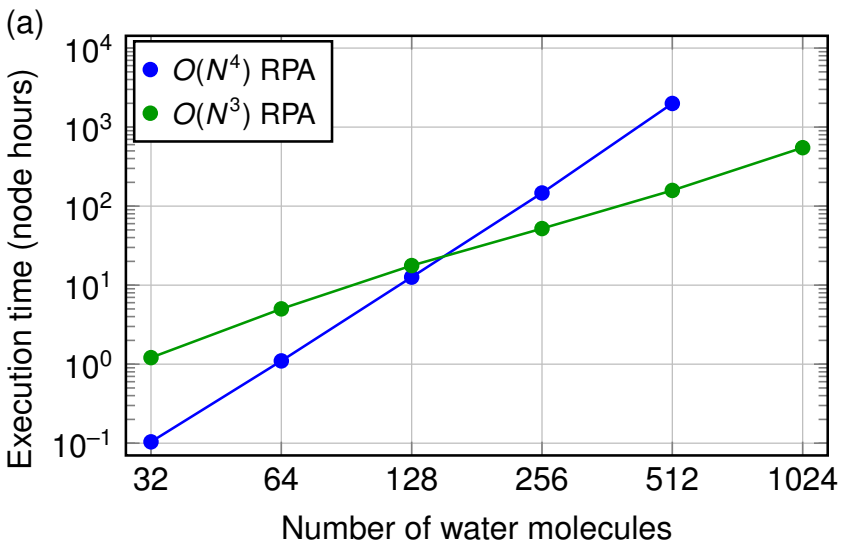
Make use of sparsity of 3-center overlap integrals

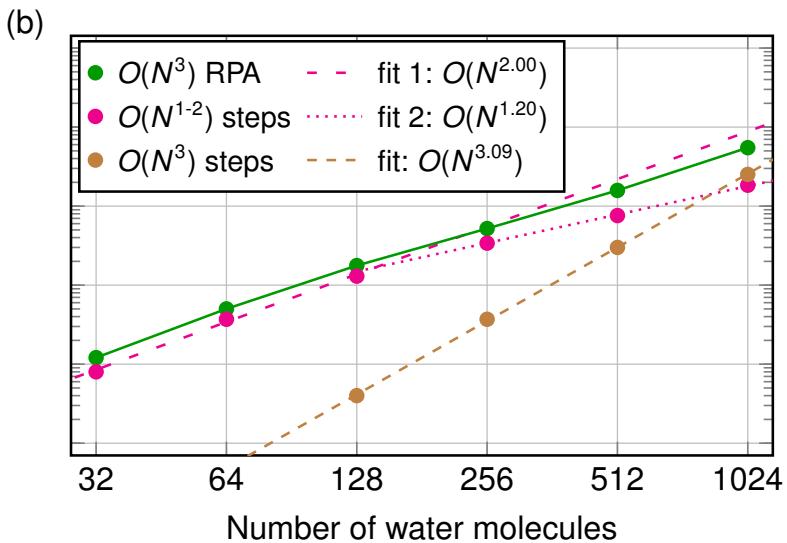
Reduced Scaling Methods (dRPA)

$$D^{\mathrm{occ}}_{\mu\lambda}(\tau) = \sum_{i}^{\mathrm{occ}} C_{\mu i} C_{\lambda i} e^{-|(\varepsilon_i - \varepsilon_F)\tau|} \qquad D^{\mathrm{virt}}_{\nu\sigma}(\tau) = \sum_{a}^{\mathrm{virt}} C_{\nu a} C_{\sigma a} e^{-|(\varepsilon_a - \varepsilon_F)\tau|}$$

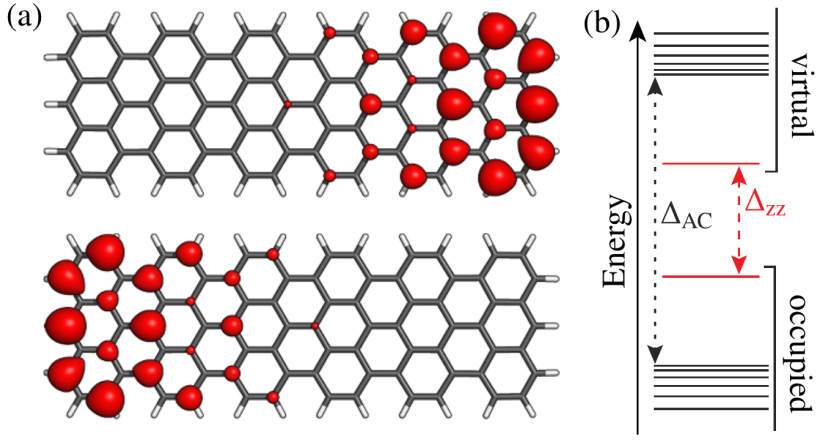
$$Q_{PQ}(\tau) = \sum_{R} K_{RP} \sum_{T} K_{TQ} \sum_{\mu\sigma} \sum_{\lambda} (\lambda\sigma R) D^{\mathrm{occ}}_{\mu\lambda}(\tau) \sum_{\nu} (\mu\nu T) D^{\mathrm{virt}}_{\nu\sigma}(\tau)$$

$$K_{RP} = \sum_{Q} (RQ)^{-1} (Q \mid P)^{1/2}$$

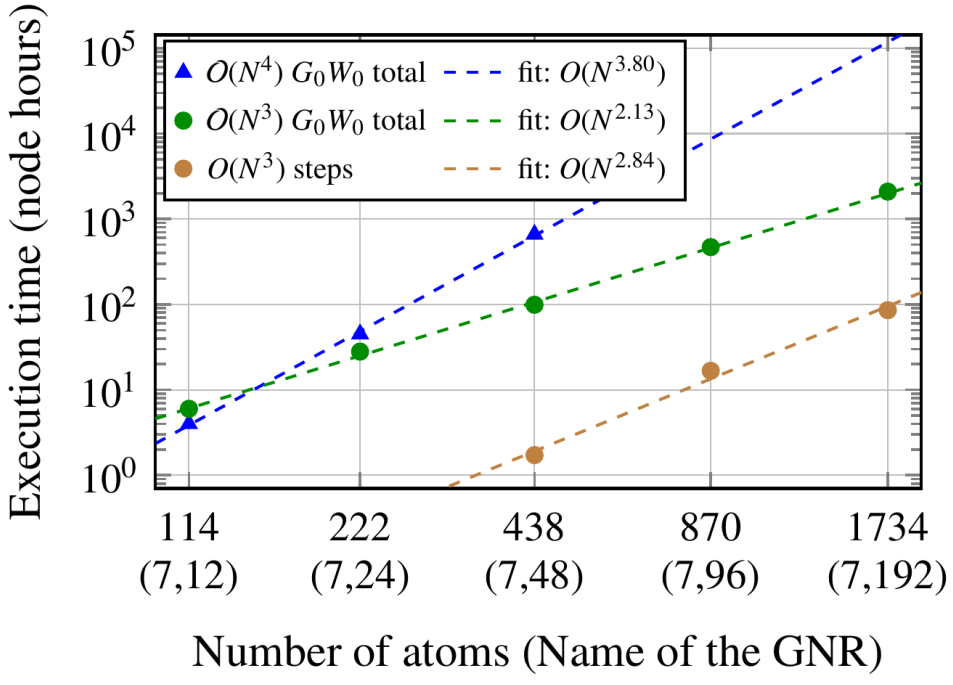




Reduced Scaling Methods (G0W0)



G0W0 calculation of the bandgap in Graphene nanoribbons



Outlook and Challenges

- Basis set convergence
- Properties (derivatives)
- Sustainable code development

Basis Sets Convergence

Table 5. All-Electron Pseudopotential HF@PBE, RI-dRPA@PBE, and RI-MP2 Contributions to the Counterpoise Corrected Cohesive Energies in mE_h of LiH at the Experimental Geometry (a = 4.084 Å) for Various Basis Set and Cell Sizes[a]

	2 × 2 × 2	3 × 3 × 3	4 × 4 × 4	extr. ($E_X^{n\to\infty}$)
		HF@PBE		
cc-DZVP	−131.91	−134.80	−135.00	
cc-TZVP	−124.84	−128.07	−128.31	
cc-QZVP	−124.41	−127.63	−127.88	
		RI-dRPA@PBE		
cc-DZVP	−27.05	−28.53	−28.95	*−29.19*
cc-TZVP	−38.42	−40.11	−40.62	*−40.89*
cc-QZVP	−41.86	−43.73	*−44.28*	*−44.59*
extr. ($E_{X\to\infty}^{n\to\infty}$)				*−46.42*
		RI-MP2		
cc-DZVP	−29.25	−30.30	−30.57	*−30.75*
cc-TZVP	−38.00	−39.33	−39.68	*−39.91*
cc-QZVP	−40.57	−41.99	*−42.36*	*−42.60*
extr. ($E_{X\to\infty}^{n\to\infty}$)				*−44.10*

[a]The text discusses how the extrapolated numbers (italic type) have been obtained.

Basis Sets Convergence

- F12 methods 'solve' basis set problem

  F12 algorithms for (low scaling) RPA and GW ?

- Double-hybrids with long-range wavefunction correlation

  No $1/r$ cusp in wavefunction

- RI basis sets: optimized minimal vs. automatic/general

  2x size of RI basis, also global vs. local RI

Properties

- Only a limited number of properties is accessible by energy calculations alone.
- 1-particle properties are accessible using the one-particle density matrix
  requires massive programming efforts for non-variational methods
- Many properties are accessible through (higher) derivatives
- Increased complexity through PBC (MP2 dipole in PBC?)

Sustainable Code Development

- More sophisticated electronic structure methods

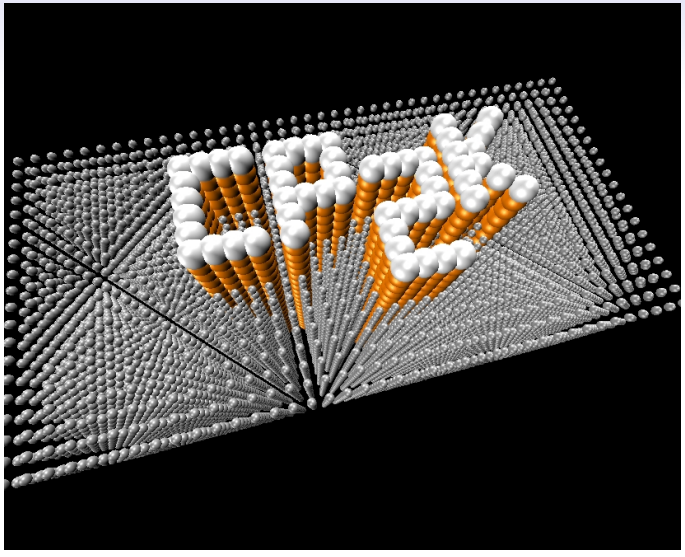
  $\longrightarrow$ increased code complexity

- Reduced scaling algorithms

  $\longrightarrow$ increased code complexity

- Hardware/Software development massive parallelism, memory hierarchy, GPU, CUDA

  $\longrightarrow$ increased code complexity



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