CP2K: Selected Developments

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Outline

- Introduction
  - History and Performance
  - Current and Future Developments
- Post-Hartree-Fock Methods
  - GW Methods
  - RPA and MP2
  - Future Developments
- Wavefunction Analysis in CP2K
  - Hirshfeld Charges
  - RESP Charges
  - MAO Analysis

25. June 2001

CP2K source repository goes online on berlios.de

Now on sourceforge.net

15 years of open development

Origins

- Quickstep DFT Code, Max-Planck-Institute, Stuttgart

  Gerald Lippert, Matthias Krack, JH

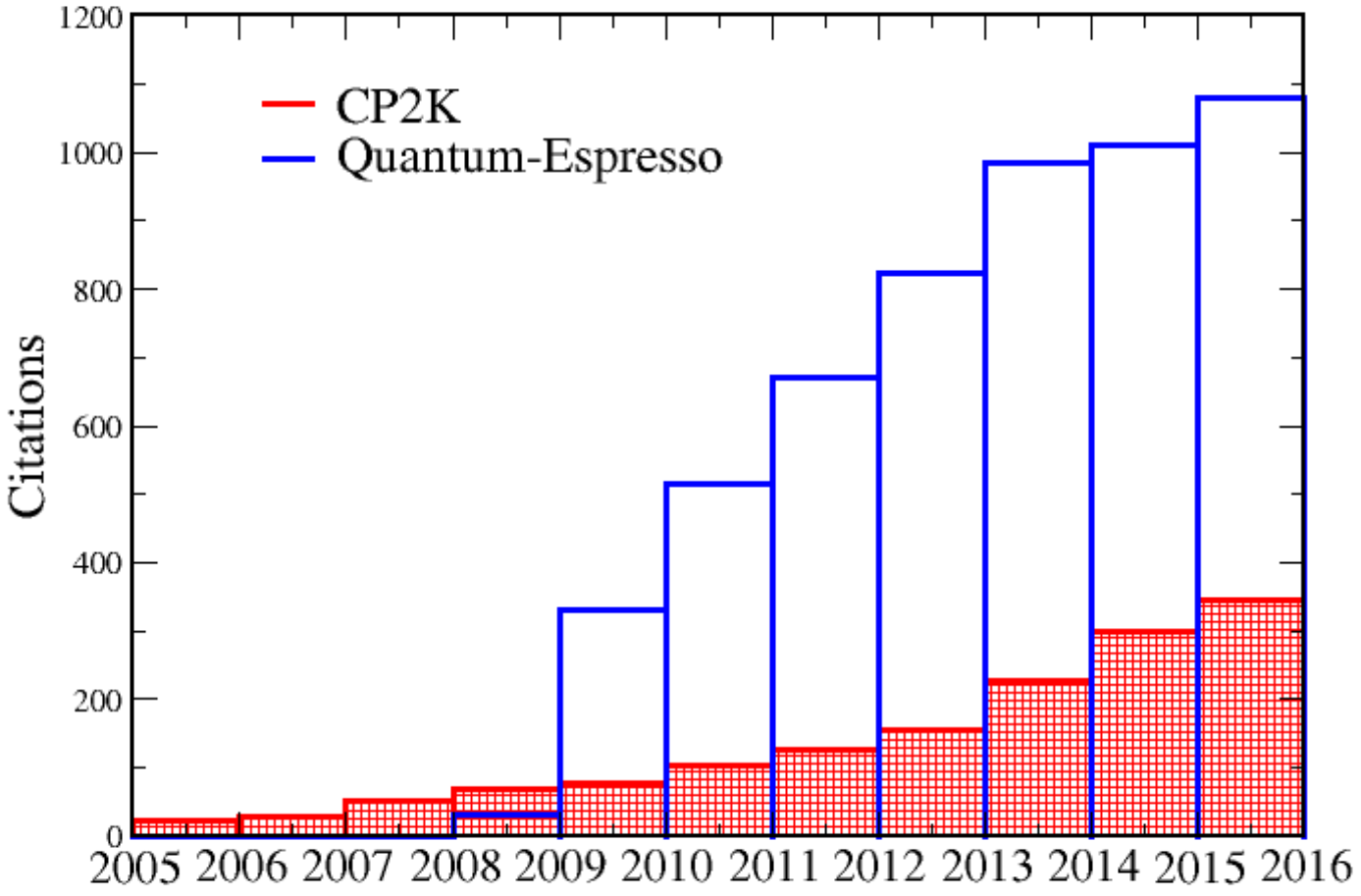
- Fist MD Code, UPenn, Philadelphia

  Chris Mundy, S. Balasubramanian, Ken Bagchi

Released Versions

Date	Version	Source lines	Commit
10.2011	2.2	891’928	11883
09.2012	2.3	919’583	12358
06.2013	2.4	968’038	12977
02.2014	2.5	947’762	13637
12.2014	2.6	990’282	14881
12.2015	3.0	937’330	16458
10.2016	4.1	980’804	17462

CP2K: Impact on Science



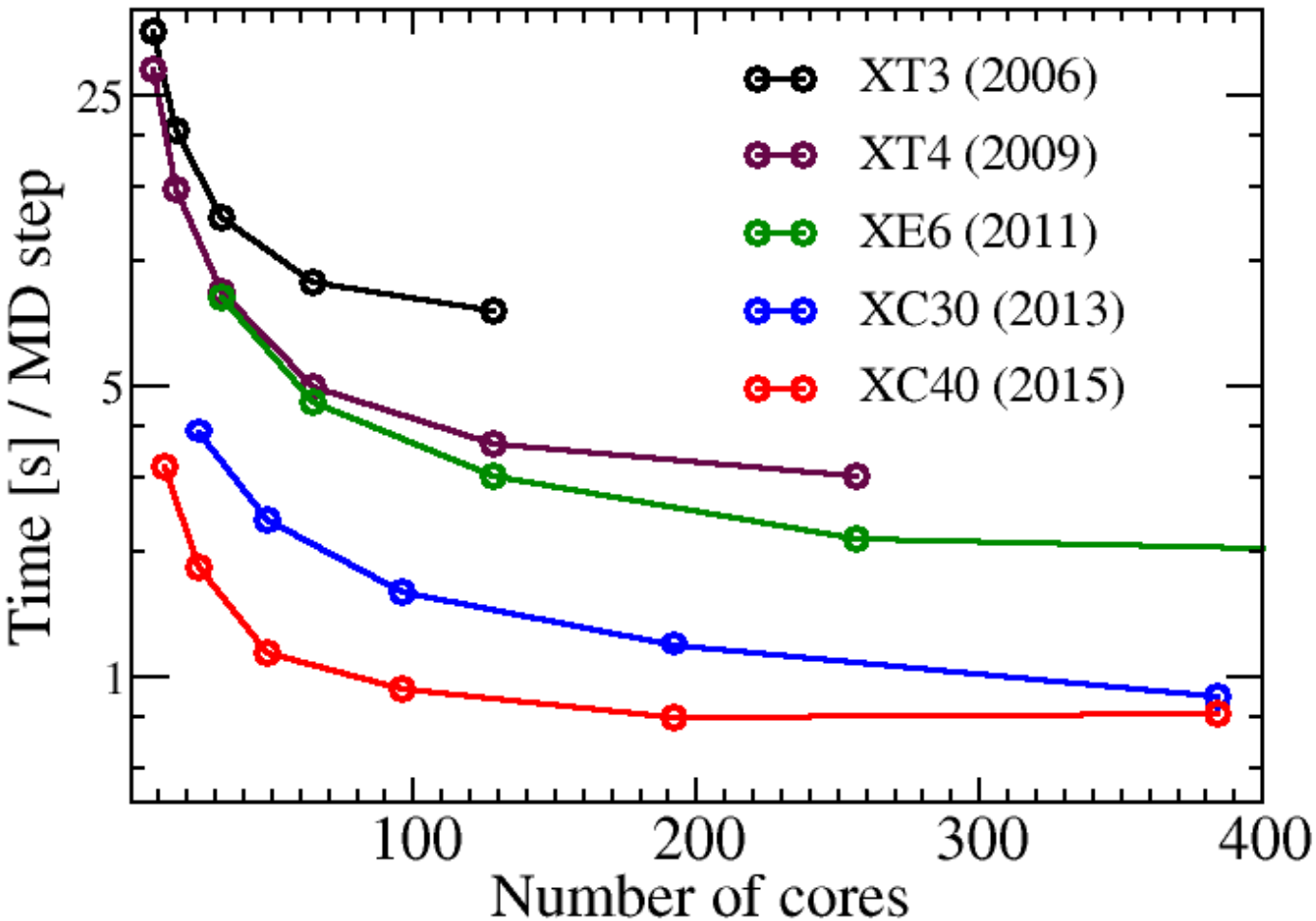
CP2K: Application Fields[1]

	Chemistry	Materials Science	Physics
CP2K	$> 70\%$	$\approx 40\%$	$\approx 40\%$
Quantum-Espresso	35%	57%	69%
VASP	36%	50%	65%

[1] scopus.com

Quickstep DFT Code Performance

64 Water, Time/MD step



k-points

- Status of Implementation
  - Energy (Forces, Stress) for GPW, GAPW, DFTB
  - Band structure along special k-point lines
    also available as post-Gamma point calculation
- Not working
  - Symmetry reduction of k-points
  - Hybrid Functionals (HFX)
  - Interface to wannier90 code (www.wannier90.org)
- Parallelization issues
  - Use "`PARALLEL_GROUP_SIZE -1`" if possible
  - Minimize communication of matrices at k-point
- Delta Test in preparation (Tiziano Müller

vdW Functionals/Potentials

- Grimme D3
  - *C*9 terms: full vs. reference coordination numbers

	C6 only	C9(R)	C9
Energy	0.03	15.84	15.98
Force	0.10	17.14	34.37

- nl-vdW DFT
  - Use reduced CUTOFF feature of CP2K

Cutoff	Time	Energy
400	3.62	4.277273
300	3.96	4.283564
200	1.77	4.315681
100	1.23	4.331886

Continuum Solvation Models

- SCCS (M. Krack)

  Andreussi, O; Dabo, I; Marzari, N. J. Chem. Phys., 136 (6), 064102 (2012).

  Revised self-consistent continuum solvation in electronic-structure calculations

  `DFT/SCCS`

- Generalized Possion Solver (J. VandeVondele)

  Bani-Hashemian, M.H.; Brück S.; Luisier, M.; VandeVondele, J J. Chem. Phys., 144, 044113 (2016).

  A generalized Poisson solver for first-principles device simulations

  `DFT/POISSON/IMPLICIT`

- psolver Library (BigDFT)

  Fisicaro, G.; Genovese, L.; Andreussi, O.; Marzari, N.; Goedecker, S J. Chem. Phys., 144, 014103 (2016).

  A generalized Poisson and Poisson-Boltzmann solver for electrostatic environments

Post-Hartree-Fock Methods

- Based on Gaussian and plane waves (GPW) method
- Resolution of Identity (RI) approach to integrals
- Periodic, but Γ-Point only
- RPA and MP2 (Laplace-SOS-MP2)

  M. DelBen et al. JCTC 9, 2654-2671 (2013)
- G0W0

  J. Wilhelm et al. JCTC 12 3623-3635 (2016)
- Cubic scaling RPA

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

Resolution of Identity Approach

Gaussian Auxiliary Basis
Coulomb Metric (Ewald Summation)

$$(ia \mid jb) = \sum_{PQ} (ia \mid P)\,(P \mid Q)^{-1}\,(Q \mid jb)$$

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

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

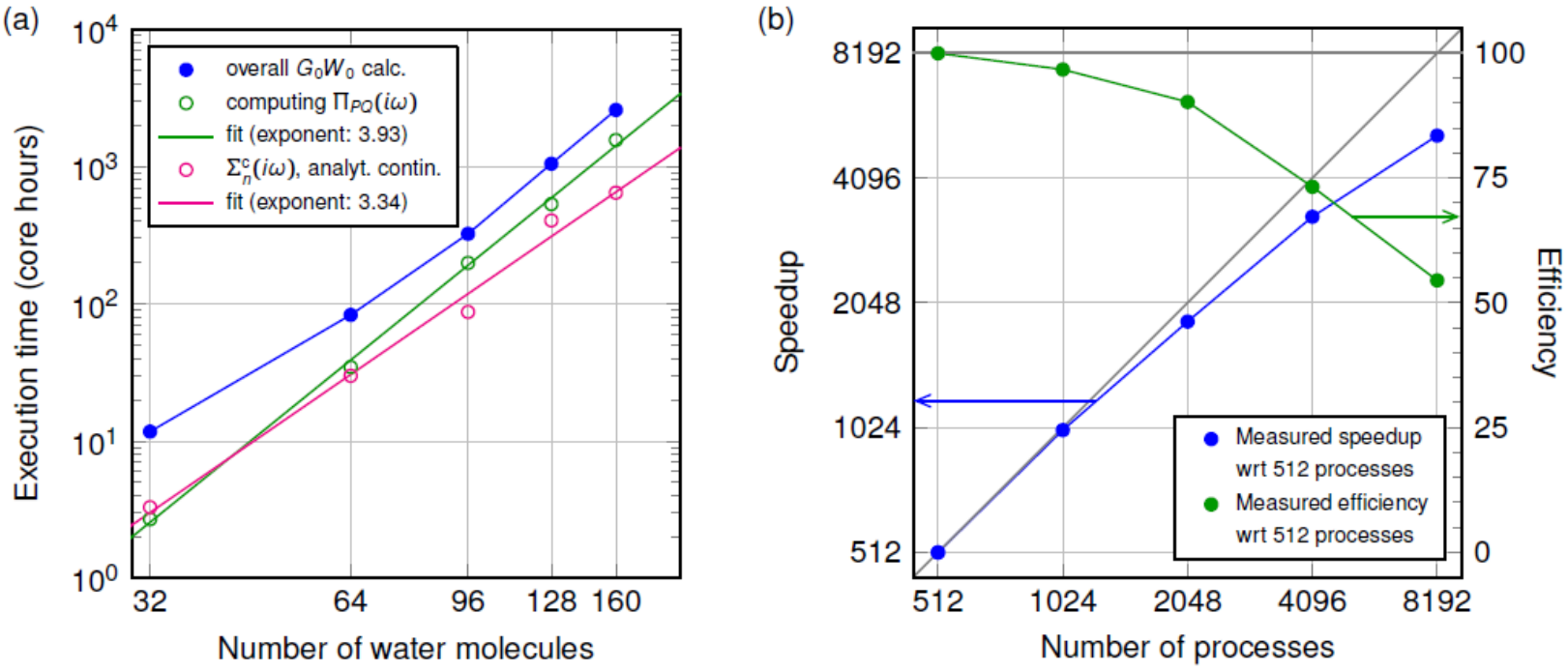
J.L. Whitten, JCP 58, 4496 (1973), O. Vahtras, J. Almlöf, M. Feyereisen, CPL 213 514 (1993)

Performance: RPA and MP2

System	Atoms	Basis	MP2	OS-MP2	RPA
Urea	128	2752 (6784)	144(12.9)	78	150
Benzene	192	4128 (10176)	624(12.7)	252	528
Water	192	3648 (8704)	450(17.3)	204	384

Timings in seconds on 3200 cores Cray-XK6,
Quadrature points: RPA 40, OS-MP2 10.

Performance: G0W0



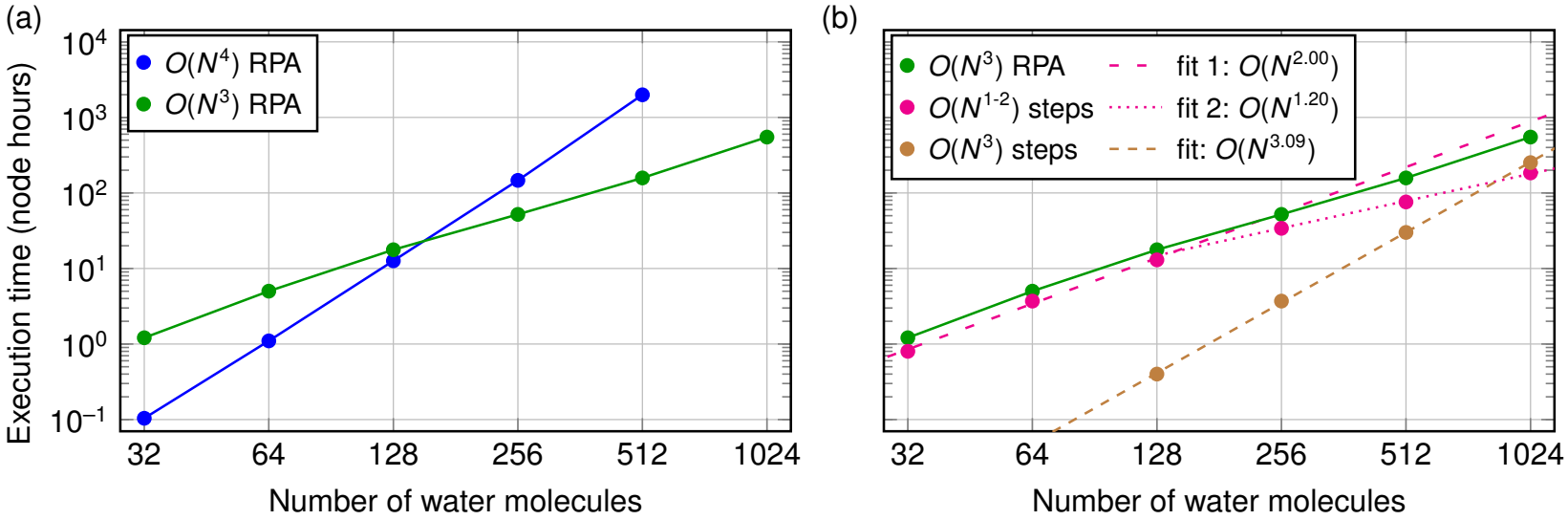
Execution time and speedup for G0W0 calculations of water systems (cc-TZVP basis). Calculation of 20 quasi-particle energies. Numerical integration using 60 points.

Reduced Scaling Methods

RI with Overlap Metric

$$(ia \mid jb) = \sum_{PQRS} (ia \mid P)\,(PQ)^{-1}\,(Q \mid R)\,(RS)^{-1}\,(S \mid jb)$$

Can make use of sparsity of 3-center overlap integrals



Sparse Tensor Linear Algebra (Partick Seewald)

- General library for sparse tensors of rank n
- Tensor contractions make use of DBCSR library

$$[ijA] = \sum_k [ijk][kA]$$

$$[(ij), A] = \mathrm{MATMUL}([(ij), k], [k, A])$$

- Simplified implementation for new algorithms
  - Post-Hartree-Fock methods
  - RI Hartree-Fock exchange
  - RI Hartree-Fock exchange for k-points

Wavefunction Analysis

- Hirshfeld charges

  F. L. Hirshfeld, Theor. Chim. Acta 44 129 (1977)

  P. Bultink et al, J. Chem. Phys. 126 144111 (2007)

- RESP charges

  C. Campana et al J. Chem. Theory Comput., 2009 2866 (2009)

  D. Golze et al, PCCP 17 14307 (2015)

- MAO analysis

  C. Ehrhardt and R. Ahlrichs, Theor. Chim. Acta 68 231 (1985)

- Minimal localized basis analysis

  W. C. Lu et al, JCP 120 2629 (2004)

Hirshfeld AIM Charges

Definition of AIM charge distribution

$$\rho_A(r) = \frac{\rho_A^0(r)}{\rho_{tot}^0}\,\rho_{tot}(r)$$

Atomic charges

$$q_A = Z_A - \int \rho_A(r)\,dr$$

Charges depend on $\rho_A^0(r)$, often very small charges

Hirshfeld-I charges (Reference density depends on final charge)

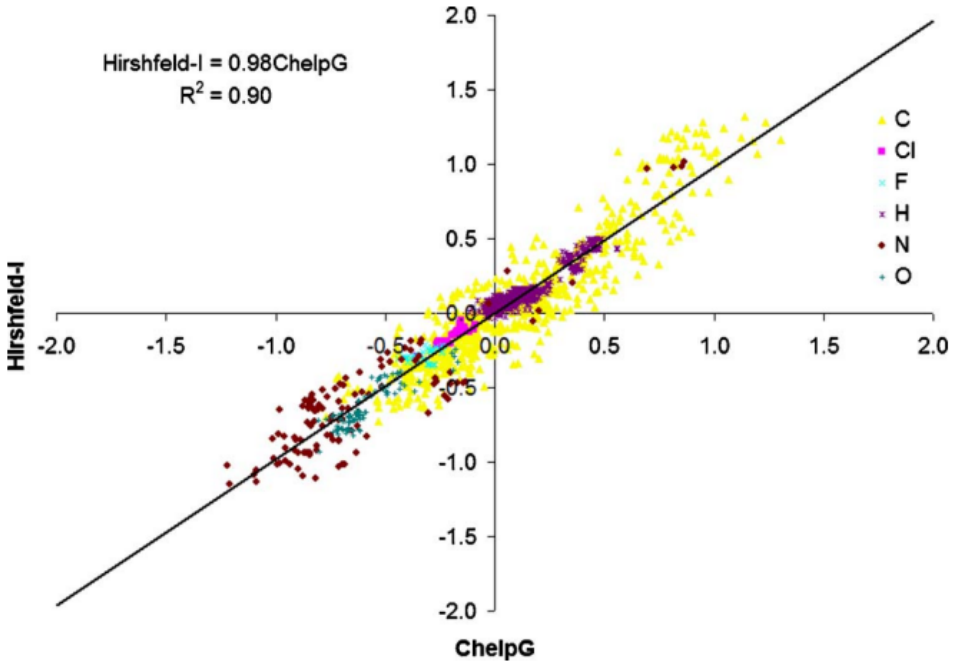
$$\rho_A(r) = \frac{\rho_A^0[q_A]}{\rho_{tot}^0}\,\rho_{tot}(r)$$

Hirshfeld-I Charges

Example: LiNH3

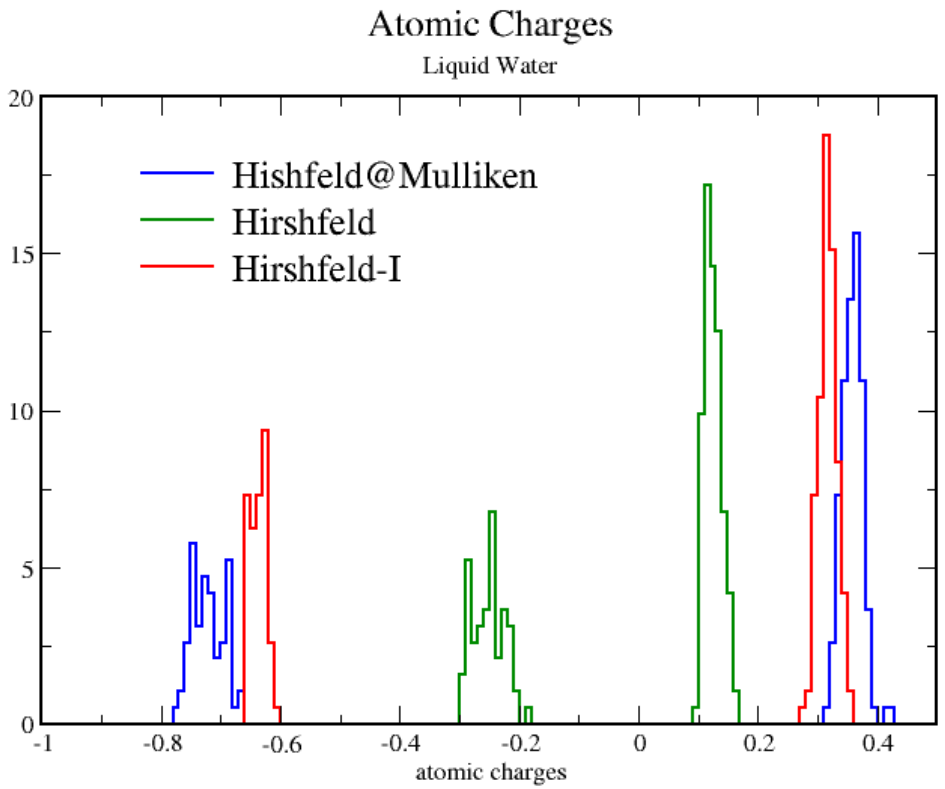
	Hirshfeld	Hirshfeld-I	CHELPG
Li	0.751	1.009	0.939
N	-0.203	-1.278	-1.278
H	0.151	0.423	0.446

Correlation between Hirshfeld-I and CHELPG charges.



Implementation in CP2K

- Atomic reference charges can be scaled
- Self-consistent scaling of charges
- Mulliken scaling of charges



RESP Charges

Restraint Electrostatic Potential Charges

$$V_{ESP}[\rho](r) \approx \sum_A q_A \int \frac{g_A(r')}{|r - r'|}\, dr'$$

- Definition of sampling points
- Definition of restraints (target charges)
- Definition of constraints (total charge, atom types)
- Definition of Gaussian function $g_A(r)$

RESP Charges at Surfaces

D. Golze et al, PCCP 17 14307 (2015)

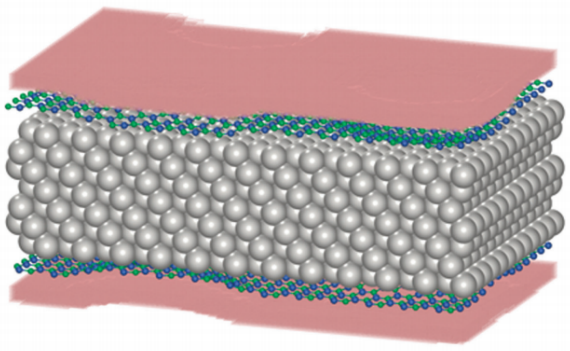
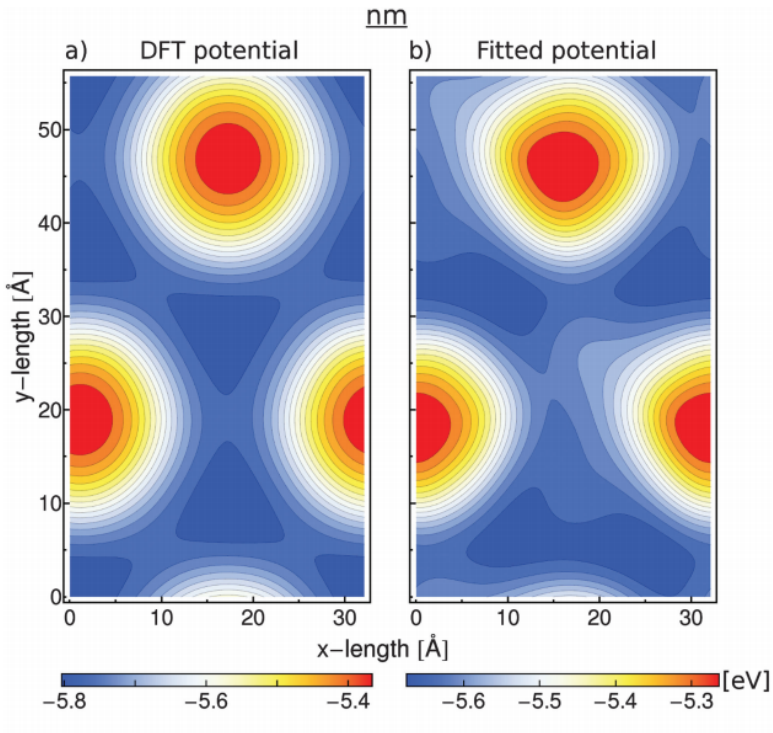
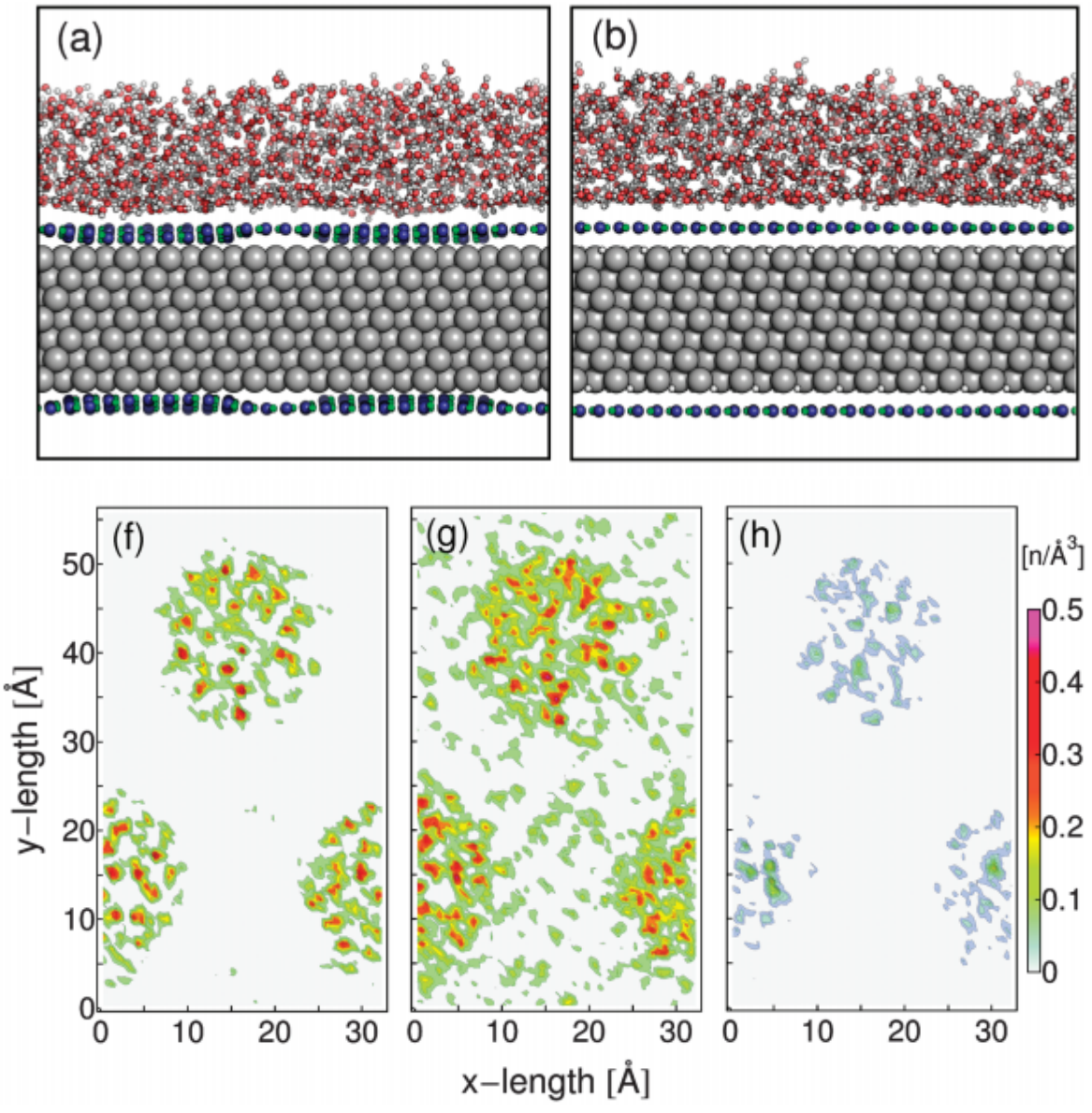


Fig. 2 Grid points sampled in the range of 2–4 Å above the surface for the symmetric corrugated h-BN/Rh(111) slab. Color code: B green, N blue, Rh gray, grid points pink.



Wetting of h-BN on Metal Surface



Modified Atomic Orbital Analysis

C. Ehrhardt and R. Ahlrichs, Theor. Chim. Acta 68 231 (1985)

- MAOs are linear combination of functions centered on ONE atom
- Number of MAOs per atom is given in the input
- MAOs are determined by projection (= diagonalization of atomic density matrix block) or by minimization of total charge deficiency ($N - Tr(DS)$), where D and S are the density and overlap matrices in the MAO basis.

Subspace Projections

Projection on a atomic subspace [XYZ...]

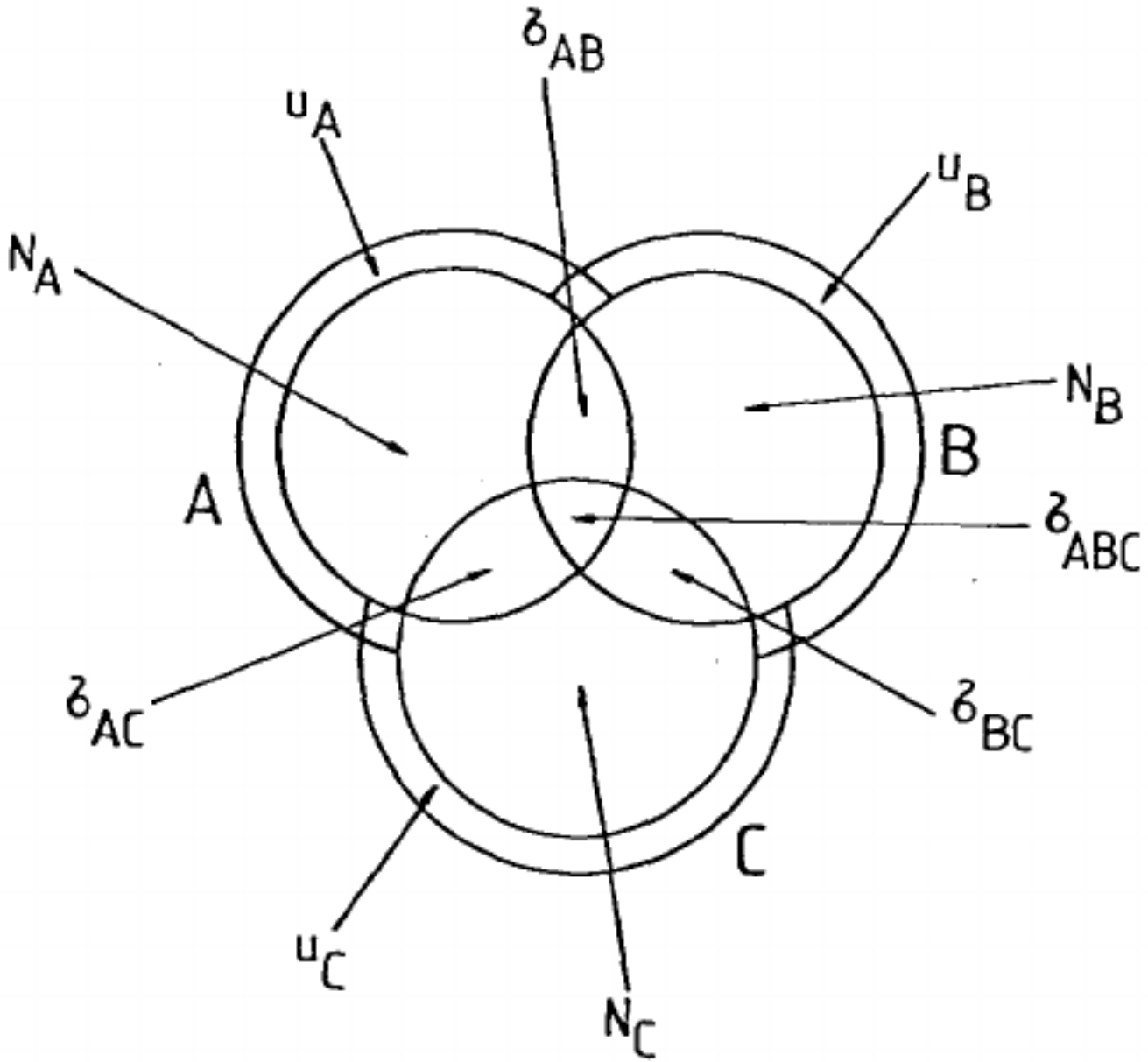
$$P_{XY\ldots} = \sum_{\mu} \sum_{\nu} |\mu\rangle \left(S^{-1}\right)_{\mu\nu} \langle\nu|$$

where μ, ν are MAO functions on all atoms X, Y, ...
Definition of subspace electron counts:

$$N_{XY\ldots} = \mathrm{Tr} D P_{XY\ldots}$$

This gives us atomic subspace charges N_A, N_{AB}, N_{ABC}, ...

Interpretation of Atomic Occupations



Shared Electron Numbers

$$\sigma_{AB} = N_A + N_B - N_{AB}$$

$$\sigma_{ABC} = N_A + N_B + N_C - N_{AB} - N_{AC} - N_{BC} + N_{ABC}$$

Atomic Charge

$$q_A = Z_A - R_A$$

$$R_A = N_A - \frac{1}{2}\sum_{B \neq A} \sigma_{AB} + \frac{1}{3}\sum_{B > C \neq A} \sigma_{ABC} + \cdots$$

MAO: Water

	ATOM	MAO	S	P	D	F
1	O	1	0.7596	0.2400	0.0004	0.0000
		2	0.0464	0.9530	0.0006	0.0000
		3	0.1887	0.8028	0.0086	0.0000
		4	0.0028	0.9773	0.0200	0.0000
2	H	1	0.9056	0.0944	0.0000	0.0000
3	H	1	0.8966	0.1034	0.0000	0.0000

Shared electron numbers

Atom	Atom	σ_{AB}
35 O	76 H	0.013222
35 O	133 H	1.567220
35 O	134 H	1.561719
35 O	164 H	0.013577

How to you contribute?

- Do good science using CP2K.

  10% of papers citing CP2K are in high-impact journals.

- Contribute to the CP2K mailing list

  Google Groups CP2K

- Contribute to the CP2K Wiki and the manual

  e.g. additional material from courses or papers

  Edit button in online manual.

- Contribute bug fixes or new features to the code

Acknowledgment

CP2K Community