

CP2K/QUICKSTEP: Accuracy and Efficiency

Basis sets and Pseudopotentials

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1st CP2K tutorial: enabling the power of imagination in MD simulations

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Goedecker-Teter-Hutter (GTH) pseudopotentials

Local part:

$$V_{\text{loc}}^{\text{PP}}(r) = -\frac{Z_{\text{ion}}}{r} \text{erf}(\alpha^{\text{PP}} r) + \sum_{i=1}^4 C_i^{\text{PP}} \left(\sqrt{2} \alpha^{\text{PP}} r\right)^{2i-2} \exp\left[-\left(\alpha^{\text{PP}} r\right)^2\right]$$

$$\text{with } \alpha^{\text{PP}} = \frac{1}{\sqrt{2} r_{\text{loc}}^{\text{PP}}}$$

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Non-local part:

$$V_{\text{nl}}^{\text{PP}}(\mathbf{r}, \mathbf{r}') = \sum_{lm} \sum_{ij} \langle \mathbf{r} | p_i^{lm} \rangle h_{ij}^l \langle p_j^{lm} | \mathbf{r}' \rangle$$

with the Gaussian-type projectors

$$\langle \mathbf{r} | p_i^{lm} \rangle = N_i^l Y^{lm}(\hat{r}) r^{l+2i-2} \exp \left[-\frac{1}{2} \left(\frac{r}{r_l} \right)^2 \right]$$

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GTH pseudopotential parameters

Element

Z_{eff}

r_{loc}

r_0

C_1

$h_{1,1}^0$

C_2

$h_{1,2}^0$
 $h_{2,2}^0$

C_3

$h_{1,3}^0$
 $h_{2,3}^0$
 $h_{3,3}^0$
 $h_{1,3}^1$
 $h_{2,3}^1$
 $h_{3,3}^1$
 $h_{1,3}^2$
 $h_{2,3}^2$
 $h_{3,3}^2$

C_4

r_1

$h_{1,1}^1$

$h_{1,2}^1$
 $h_{2,2}^1$

r_2

$h_{1,1}^2$

$h_{1,2}^2$
 $h_{2,2}^2$

GTH pseudopotential database

- LDA (PADE): H–Rn
- PBE: H–Rn (except Lanthanides and Actinides)
- BLYP: H–Kr plus a few selected
- BP: H–Kr
- HCTH/n: only for a few first-row elements

GTH pseudopotential generation protocol

- Checkout pseudopotential database: `cvs co potentials`
- Read `potentials/Goedecker/atom/README`
- Compile all-electron atom code:
 - `cd potentials/Goedecker/atom`
 - `g95 -O2 atom.f hcth.f90 -o atom.x`
- Generate atomic all-electron reference wavefunctions: `atom.x`
- Read `potentials/Goedecker/pseudo/v2.2/README`
- Compile GTH pseudopotential fitting code:
 - `cd /potentials/Goedecker/pseudo/v2.2`
 - `make`
- Perform pseudopotential fit: `pseudo.x -orth -c100 -n600`
- Check pseudopotential fit: `gnuplot pswf.gnu`

Generate atomic all-electron reference

Example: atom.dat input file for Oxygen

```
O
PBE
relativistic
      20.00      10.00      100.00      rmax,aa,bb
              1.38      2.75      rcov,rprb
1         9
2         0      2.00      0.00      core,valence orb.
3         0      0.00      0.00
4         0      0.00      0.00
2         1      4.00      0.00
3         1      0.00      0.00
4         1      0.00      0.00
3         2      0.00      0.00
4         2      0.00      0.00
4         3      0.00      0.00
```

- Copy atom.ae to ../psp_pbe/

Perform pseudopotential fitting w.r.t. AE reference

- Select fitting parameters in the file FITPAR:

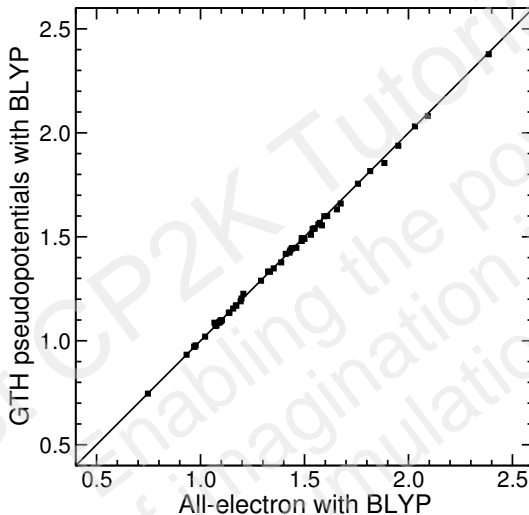
Fit	Parameter
t t t f f	rloc, gpot (1, ..., 4)
1	lmax
t t f f f f f	rl (1), h11, h12, h22, h13, h23, h33 (l=0)
t t f f f f f	rl (2), h11, h12, h22, h13, h23, h33 (l=1)
f f f f f f f	rl (3), h11, h12, h22, h13, h23, h33 (l=2)
f f f f f f f	rl (4), h11, h12, h22, h13, h23, h33 (l=3)

- Define weights in the file weights.par:

Initial weight-guess from atomic-program

```
-----
      .1E+03      weight_psr0
n l      so      eigval      chrg      dchrg      ddchrg      res      rnode
2 0 0.50      1.0e2      1.0e2      0.0e0      0.0e0      1.0e0      1.0e0
3 0 0.50      1.0e0      1.0e0      0.0e0      0.0e0      0.0e0      0.0e0
4 0 0.50      0.0e0      0.0e0      0.0e0      0.0e0      0.0e0      0.0e0
2 1 0.50      1.0e1      1.0e1      0.0e0      0.0e0      1.0e0      1.0e0
2 1 0.50      1.0e1      1.0e0      0.0e0      0.0e0      1.0e0      1.0e0
...
```

Comparison of GTH pseudopotentials with all-electron



All-electron: 6-311++G(3df,3pd) basis set

Gaussian basis sets

QUICKSTEP	Pople notation	all-electron (Gaussian 03)
SZV	4G	STO-3G
DZV	41G	6-31G
DZVP	41G*	6-31G*
TZVP	511G*	6-311G*
TZV2P	511G(2d,2p)	6-311G(2df,2pd)
QZV3P	6111G(3d,3p)	6-311G(3df,2pd)

QUICKSTEP can handle efficiently

- Large Gaussian basis sets
- High angular momentum quantum numbers

Gaussian basis sets

Nomenclature

- SZV: single-zeta valence, i.e. 1 contracted function per orbital
- DZV: double-zeta valence, i.e. 2 contracted functions per orbital
- DZVP: double-zeta valence, i.e. 2 contracted functions per orbital plus 1 set of polarization functions with $l = l_{\max} + 1$
- TZV2P: triple-zeta valence, i.e. 3 contracted functions per orbital plus 2 sets of polarization functions with $l > l_{\max}$
- QZV3P: quadruple-zeta valence, i.e. 4 contracted functions per orbital plus 3 sets of polarization functions with $l > l_{\max}$

Accuracy of QUICKSTEP

Structure optimization of small molecules

Functional: Local density approximation (LDA)

Pseudopotentials: Goedecker, Teter, and Hutter (GTH)

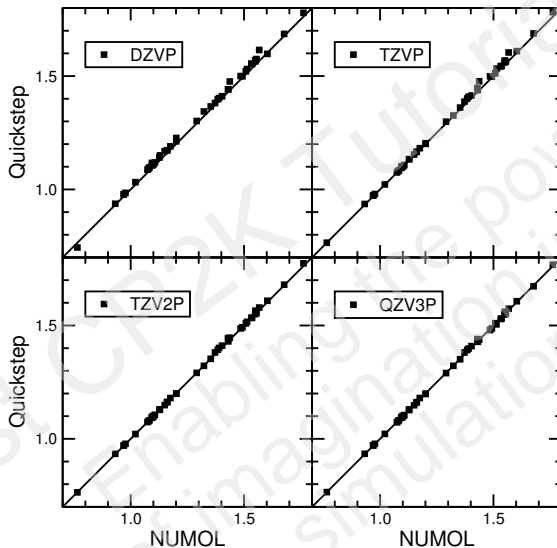
- Test set of 39 molecules:

H₂, Li₂, LiH, BH₃, CH₄, C₂H₂, C₂H₄, C₂H₆, N₂, NH₃, HCN, H₂O, H₂O₂, CO, CO₂, CH₃OH, N₂O, F₂, HF, LiF, CH₃F, OF₂, AlH, SiH₄, SiO, P₂, PH₃, HCP, PN, S₃, H₂S, CS, CS₂, SO₂, COS, SF₆, HCl, CH₃Cl, LiCl

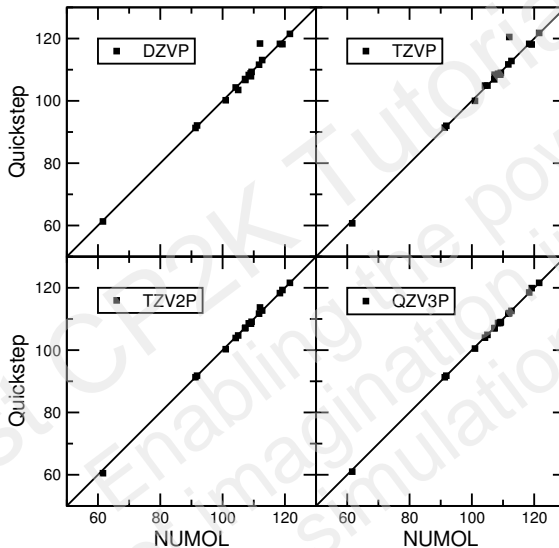
- 52 bond distances
- 18 bond angles
- compared to NUMOL* (basis set free LDA results)

*NUMOL: R. M. Dickson and A. Becke, J. Chem. Phys. **99**, 3898 (1993)

Bond distances



Bond angles



Comparison with NUMOL

Δ_{\max} : Maximum deviation

σ : Standard deviation

Basis set	Distances [Å]		Angles [°]	
	Δ_{\max}	σ	Δ_{\max}	σ
DZVP	0.107	0.027	6.4	1.6
TZVP	0.040	0.013	8.5	2.1
TZV2P	0.015	0.006	1.7	0.6
QZV3P	0.011	0.004	0.7	0.3

- Different LDA implementation
- Treatment of the core electrons

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- Different LDA implementation
- Treatment of the core electrons

Generate QS optimised Gaussian basis sets

- Checkout basis set database: `cvs co basis_sets`
- Compile optimiser code:
 - `cd basis_sets/source`
 - `make`
- Run `optbas 0-q6` in working directory

Basis set optimization

Sample input file for oxygen

```
&ATOM
  # Optimisation parameters
&END

&BASIS
  # PGF exponents for each angular momentum number l
&END

&POTENTIAL
  # GTH pseudopotential in CPMD format
&END
```

Basis set optimization

Sample input file for oxygen

```
RCOV 1.379
&ATOM
NAME O
RPRB 2.759
PPOT
OPTI 1.0D-9
ZVAL 8
ZEFF 6
LMAX 1
OCCU
1 2
1 4
MIXI 0.2
CONV 1.0D-14
ITER 200
IPPN 100
XCFN PADE
&END
```

Basis set optimization

Sample input file for oxygen

```
&BASIS
GAUS
4
  8.4855854223  2.5642200801  0.8065658147  0.2368483892
1  2  3  4
4
  8.4855854223  2.5642200801  0.8065658147  0.2368483892
1  2  3  4
&END

&POTENTIAL
# GTH pseudopotentials in CPMD format
&END
```

Oxygen basis set

O DZVP-GTH-q6 DZVP-GTH

2

2 0 1 4 2 2

8.304386 0.151017 0.000000 -0.099568 0.000000

2.457948 -0.039320 0.000000 -0.301142 0.000000

0.759737 -0.697172 0.000000 -0.475086 0.000000

0.213639 -0.384113 1.000000 -0.379878 1.000000

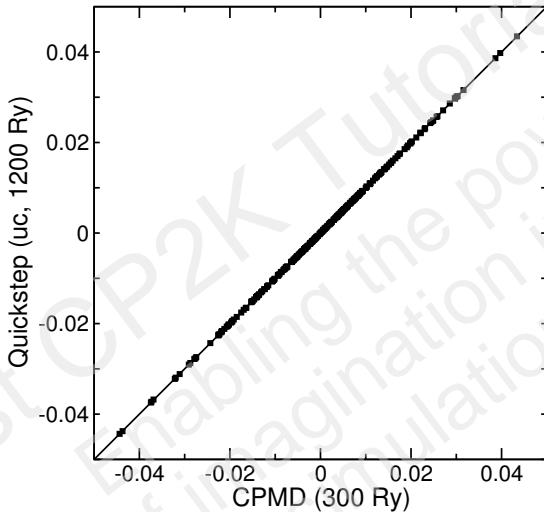
3 2 2 1 1

1.185000 1.000000

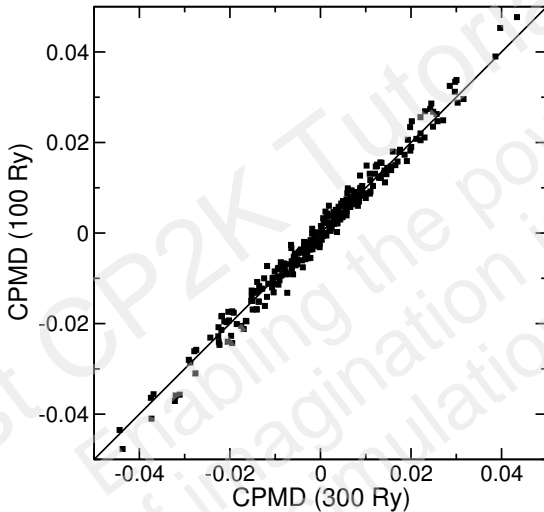
MOLOPT basis sets

- Compact accurate basis sets
- Include smooth primitive Gaussian functions → reduces BSSE
- Polarisation functions are also optimised
- Especially suited for condensed phase systems or surfaces
- Suggestion: Try also MOLOPT basis sets
- Optimisation procedure is difficult and computationally expensive

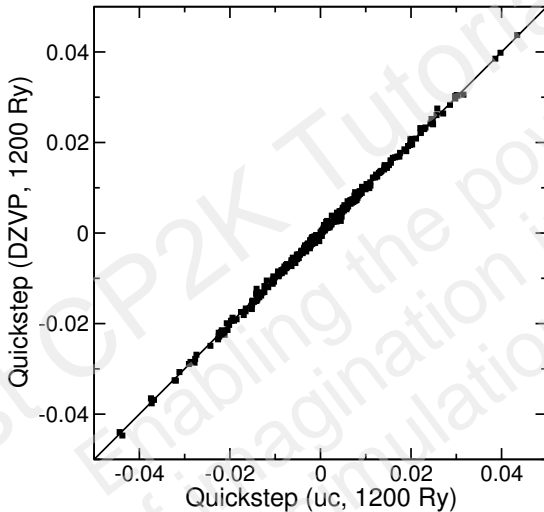
Forces (liquid water, 32 H₂O)



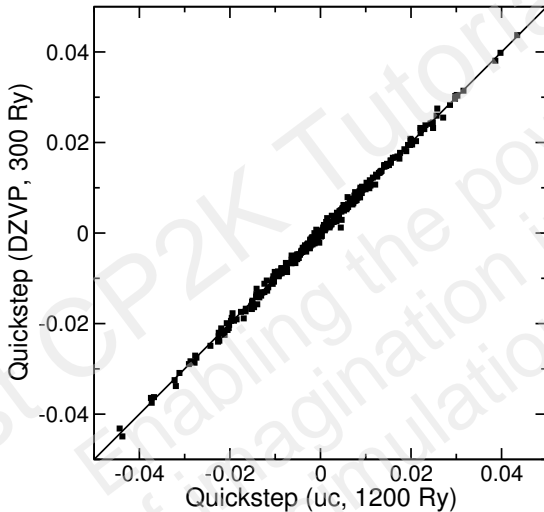
Forces (liquid water, 32 H₂O)



Forces (liquid water, 32 H₂O)



Forces (liquid water, 32 H₂O)



Efficiency and scalability of QUICKSTEP

Benchmark systems

Functional: Local density approximation (LDA)

Pseudopotentials: Goedecker, Teter, and Hutter (GTH)

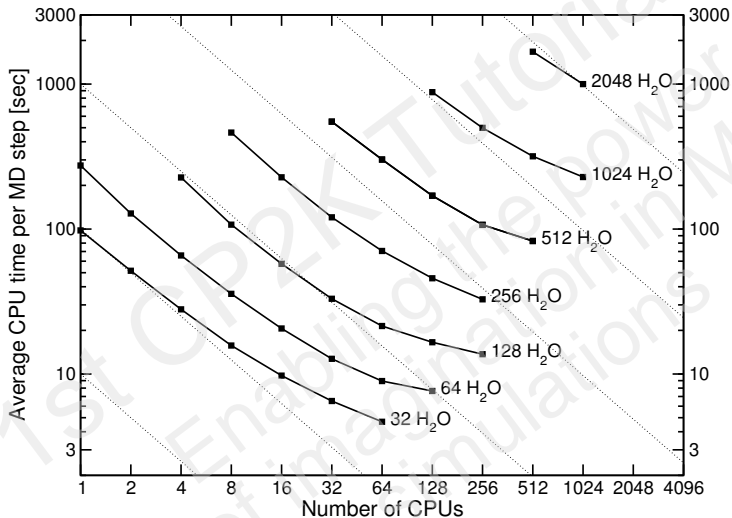
Basis set: TZV2P (40 basis function per water molecule)

Density cutoff: 280 Rydberg

System	Cell	Atoms	Orbitals	Plane waves (10^6)
32 H ₂ O	9.9 Å	96	1280	1.3
64 H ₂ O	12.4 Å	192	2560	2.0
128 H ₂ O	15.6 Å	384	5120	4.1
256 H ₂ O	19.7 Å	768	10240	9.3
512 H ₂ O	24.9 Å	1536	20480	16.0
1024 H ₂ O	31.3 Å	3072	40960	32.8
2048 H ₂ O	39.5 Å	6144	81920	64.0

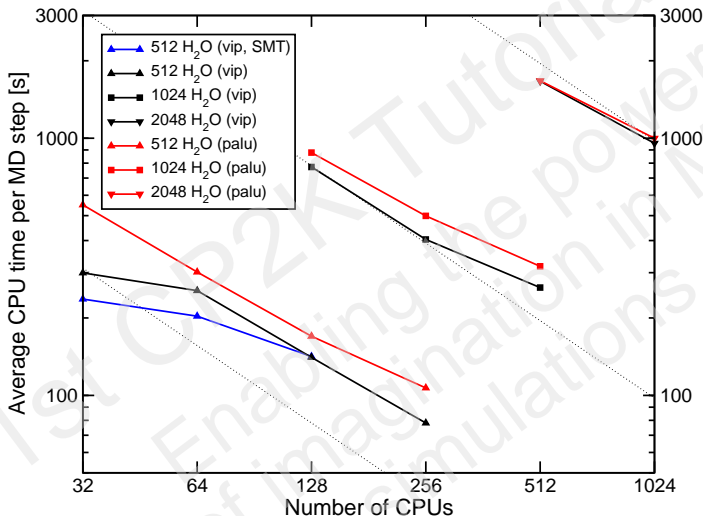
Efficiency of scalability of QUICKSTEP

Cray XT3 (palu, CSCS)



Efficiency of scalability of QUICKSTEP

IBM Power6 (vip, RZG) versus Cray XT3 (palu, CSCS)



!!! Thanks for attention !!!



??? Questions ???