DFT grid options in PSI4

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Why change grid defaults?

- exceptional accuracy, e.g. benchmarking, highly accurate functionals.
  (typically basis and functional error > grid error)

- wobbles and bumps in potential curves scans

- unstable SCF

- boss wants results this afternoon! (speed-accuracy tradeoff)

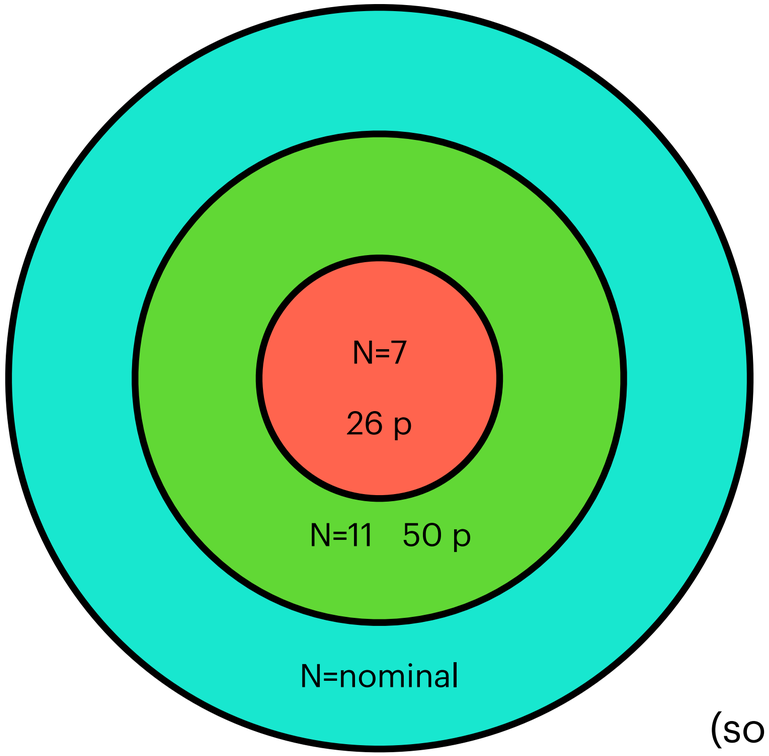
new grid options in v1.4 - pruning

grid weights screening: `set DFT_WEIGHTS_TOLERANCE 1e-15 (default)`
PR #1581

grid pruning:
PR #1591

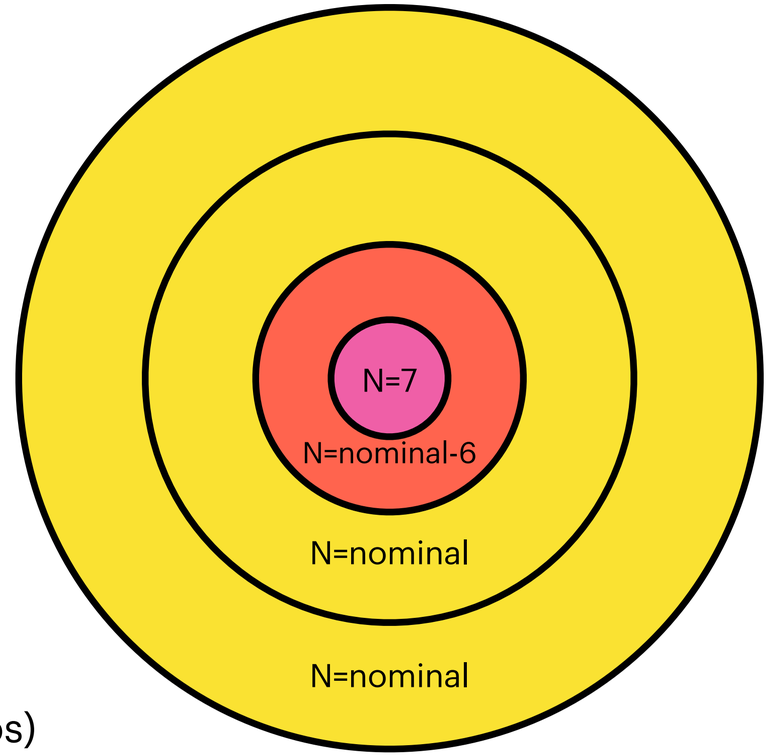
```
set DFT_PRUNING_SCHEME ROBUST (default)
set DFT_PRUNING_SCHEME TREUTLER ( used in turbomole)
```

TREUTLER = sphere into thirds



Bragg-Slater radius
(updated in 1.4)

ROBUST = sphere into quarters



(sorry for the imperfect ratios)

weights screening errors

```
set DFT_PRUNING_SCHEME NONE
set DFT_WEIGHTS_TOLERANCE N
```

water dimer

PBE/aug-cc-pVTZ (590/99)

tolerance	abs. e. error	#points
off	0.0	350460
1E-30	1.36E-12	349417
1E-25	1.65E-12	348670
1E-20	1.65E-12	346918
1E-18	1.68E-12	345747
1E-16	1.63E-11	340646
1E-15	2.74E-11	339647
1E-14	5.73E-09	335089
1E-13	3.65E-08	331285
1E-12	3.18E-07	326462

C60 (C2 sum)

PBE/aug-cc-pVDZ (590/99)

tolerance	abs. e. error	#points
off	0.0	1359000
1E-30	3.17E-10	1229846
1E-25	-5.34E-10	1209622
1E-20	5.94E-10	1183674
1E-18	5.41E-10	1171102
1E-16	-6.25E-10	1156776
1E-15	2.48E-09	1131228
1E-14	3.54E-09	1123018
1E-13	1.25E-07	1110668
1E-12	1.07E-06	1085824

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grid pruning errors

S22: non-covalent interaction of 22 bio-dimers (psi4's db command)

M06-2X/def2-TZVP

590/99 'ultrafine' grid

'grid sensitive functional'

100% gau2grid cache

Psi4 1.4a3.dev1 (conda)

S22 time without pruning: 18 min

(16 threads @ 3.20GHz E5-2667v4)

```
set DFT_PRUNING_SCHEME ROBUST
```

grid point reduction [%] and errors [kcal/mol]

weights screening	reduction [%]	speed-up	error E int	error E abs
none	30.1	27.5	0.0	2.8E-07
1E-15	35.0	31.6	0.0	2.8E-07
1E-14	35.4	31.5	0.0	2.8E-07

```
set DFT_PRUNING_SCHEME TREUTLER
```

weights screening	reduction [%]	speed-up	error E int	error E abs
none	47.0	43.8	0.214	4.1E-04
1E-15	51.9	47.4	0.214	4.1E-04
1E-14	52.3	47.6	0.214	4.1E-04

new grid options in v1.4 - density screening

density screening:
PR #1860

```
set DFT_DENSITY_TOLERANCE -1.0 (default=off, typical value 1e-10)
```

Overwrites density thresholds defaults in LibXC
(LibXC has own defaults)

new output:

```
=> LibXC Density Thresholds  <==

 XC_MGGA_C_M06_2X:  1.00E-23
 XC_HYB_MGGA_X_M06_2X:  1.00E-20
```

not a 'speed' option!

'Tough' case

```
molecule hatom {
0 2
H 0.0 0.0 0.0
}

set {
reference uks
DFT_DENSITY_TOLERANCE 1e-10
}

energy('tpss/sto-3g')
```

new grid options in v1.4 - new nuclear scheme

`set DFT_NUCLEAR_SCHEME SBECKE (smooth Becke)`

PR #1591

An improved molecular partitioning scheme for numerical quadratures in density functional theory

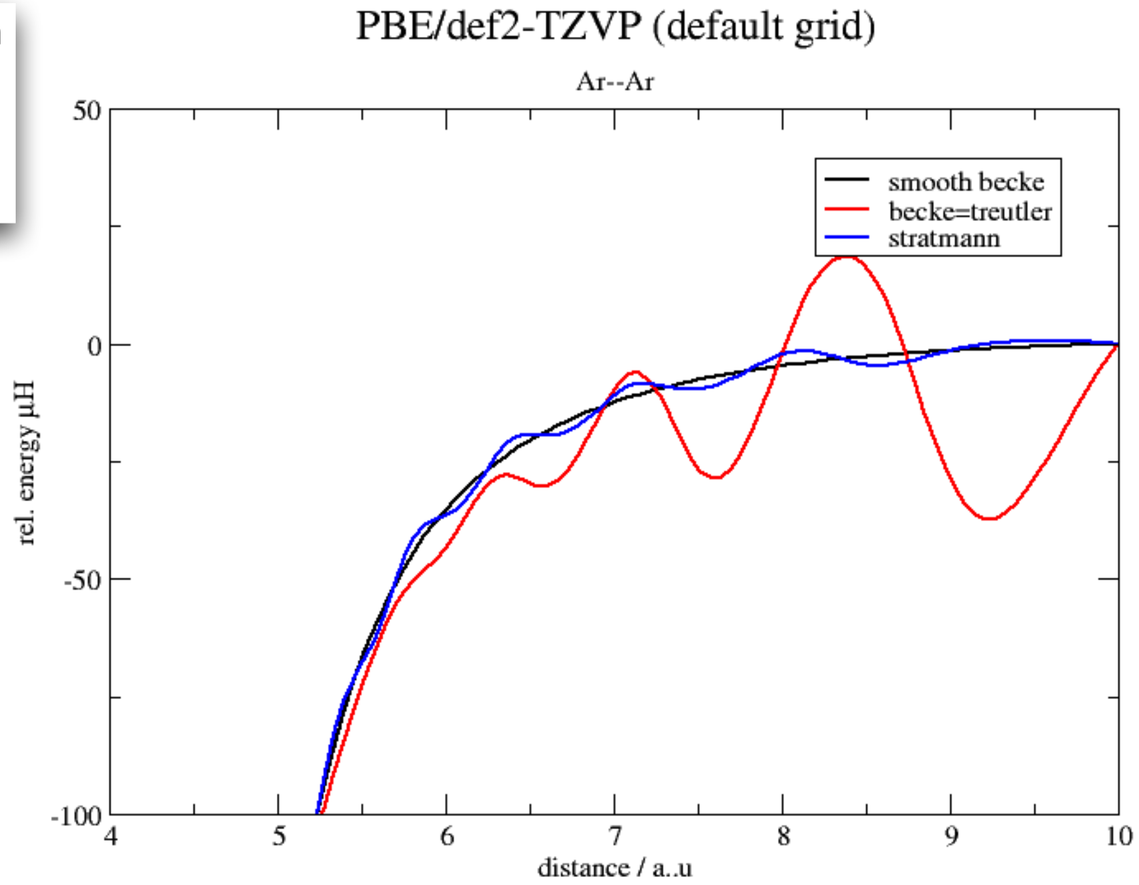
J. Chem. Phys. 149, 204111 (2018); https://doi.org/10.1063/1.5049435

Henryk Laqua, Jörg Kussmann, *and* Christian Ochsenfeld[a)]

```
302/75 grid; unpruned
set DFT_NUCLEAR_SCHEME SBECKE
set DFT_NUCLEAR_SCHEME STRATMANN
set DFT_NUCLEAR_SCHEME BECKE
set DFT_NUCLEAR_SCHEME TREUTLER
```

good for long-range interactions
(i.e. including big systems)

Ar dimer dissociation



new grid options in v1.4 - overview

grid weights screening: `set DFT_WEIGHTS_TOLERANCE 1e-15 (default)`

grid pruning:

`set DFT_PRUNING_SCHEME ROBUST (default)`

`set DFT_PRUNING_SCHEME TREUTLER`

additional nuclear scheme:

`set DFT_NUCLEAR_SCHEME SBECKE (smooth Becke, default is TREUTLER)`

density screening:

An improved molecular partitioning scheme for numerical quadratures in density functional theory

J. Chem. Phys. **149**, 204111 (2018); https://doi.org/10.1063/1.5049435

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`set DFT_DENSITY_TOLERANCE -1.0 (default=off, typical value 1e-10)`

(LibXC has own defaults for screening small densities)

good-to-know grid options

grid construction:

```
set DFT_SPHERICAL_POINTS 302 (default, Lebedev points)

set DFT_RADIAL_POINTS    75  (default)
```

dealing with issues:

```
set DFT_NUCLEAR_SCHEME SBECKE (wobbles in PES, weak interactions)

set DFT_DENSITY_TOLERANCE 1e-10 (if functional is unstable)

set DFT_BS_RADIUS_ALPHA  1.1 (default 1.0, scales BS radii,
                      e.g. for very diffuse basis sets.
                      indicator is slow density convergence.
```

```
==> Post-Iterations <==

 Electrons on quadrature grid:
    Ntotal   =   49.9999869979 ; deviation = -1.300e-05

  Orbital Energies [Eh]
  ---------------------
```

last slide

- standard DFT application (some hybrid + TZ basis):
  - basis and functional error > grid error !
- PSI4 has very conservative cutoffs compared to other programs.
- Don't be afraid to tune cutoffs for low-accuracy high-throughput work.
- future idea and wish: "PSI4 grids"
  - period specific radial grids (light vs heavy elements)
  - cutoffs adapted to overall accuracy
  - ...