

Delocalisation Error in action: Self-consistent field convergence failure and how to fix it.

Stephen G. Dale

Queensland Micro- and Nano Technology Centre, Griffith University,
West Creek Rd, 4111 Nathan, QLD, Australia



Delocalisation Error

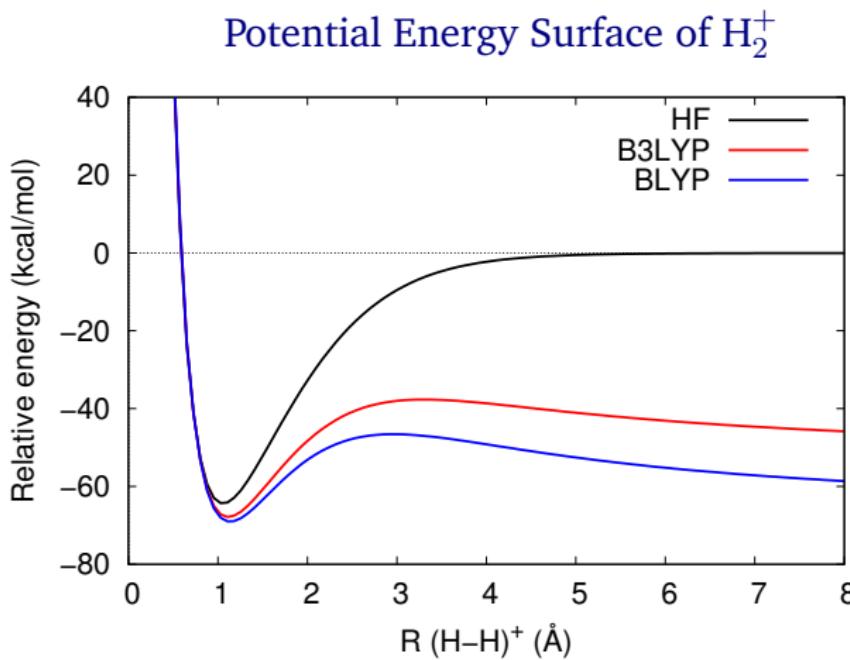
Source of the ‘band gap problem’

Approximation to the exact density functional overstabilize fractional charge.

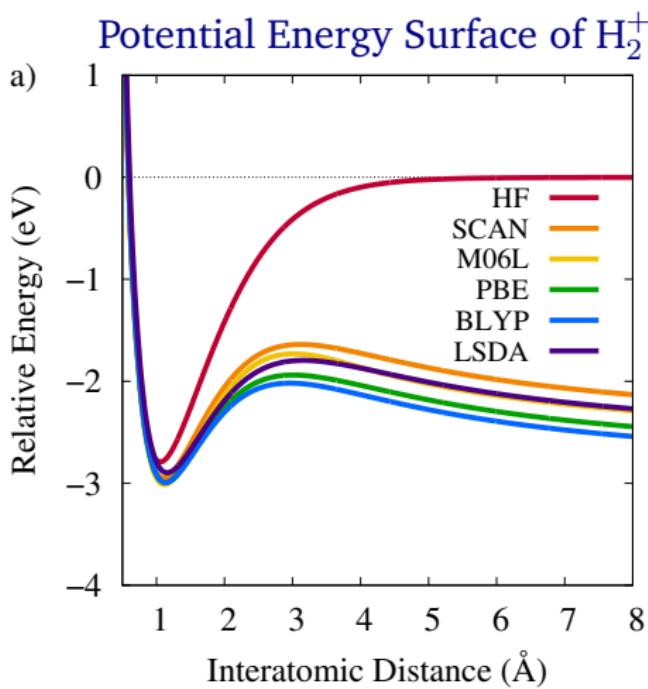
This phenomenon is known as:

- Self-interaction Error
- Delocalisation Error
- Charge-transfer Error

Classic Example



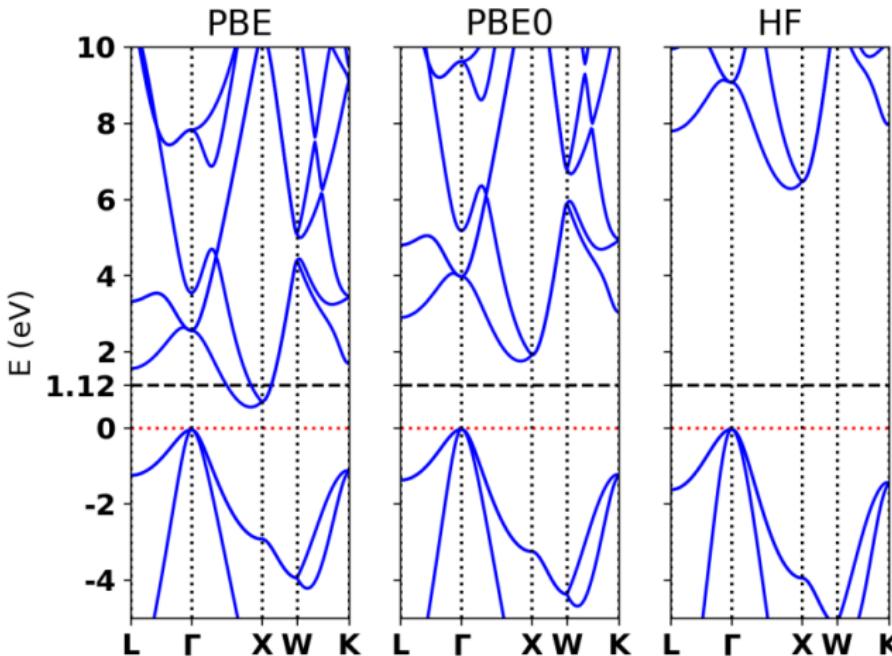
Bonus Slide: Classic Example



K. R. Bryenton, A. A. Adeleke, S. G. Dale, E. R. Johnson. WIRES (2022)

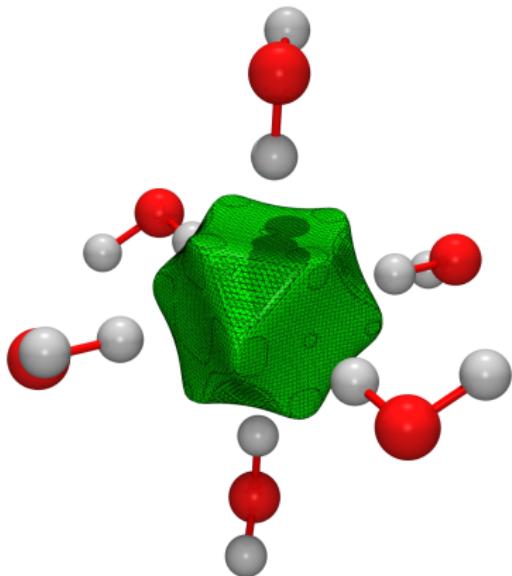
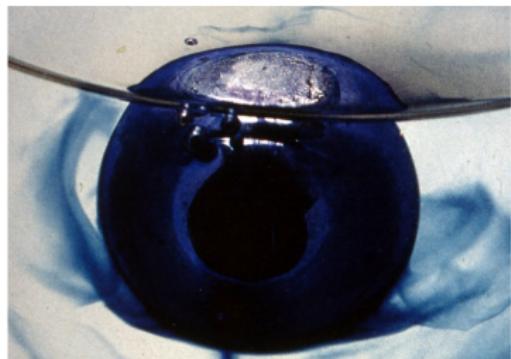
Band Gap Problem

Band structure of Si crystal according to:

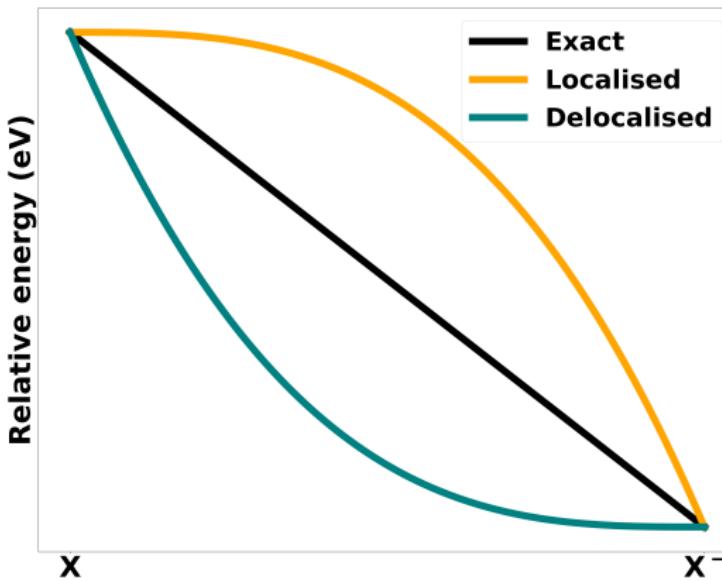


K. R. Bryenton, A. A. Adeleke, S. G. Dale, E. R. Johnson. WIRES (2022)

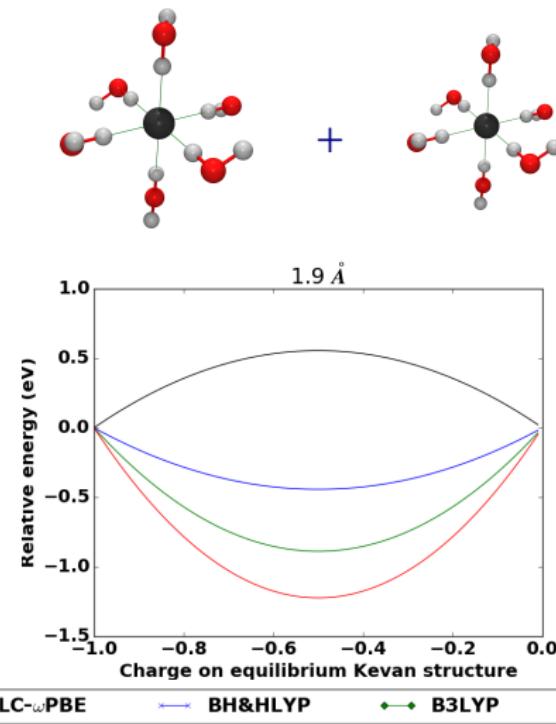
Delocalisation Error and the Solvated Electron



Typical Behaviour

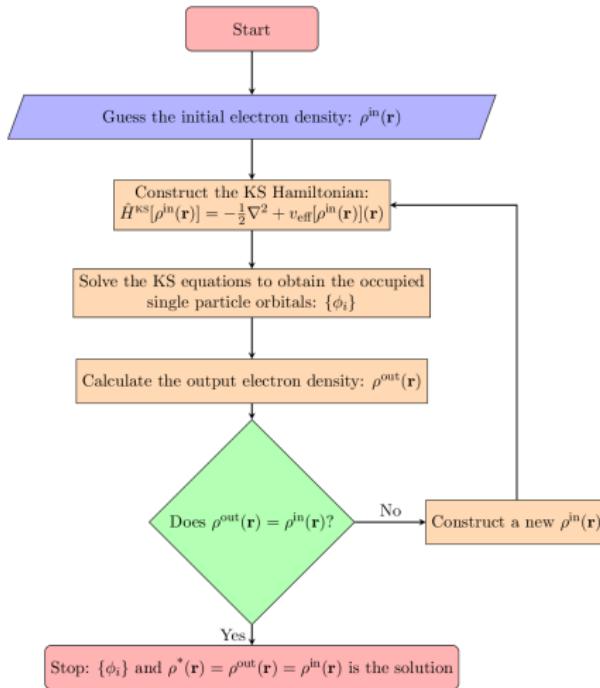


Example of Typical Behaviour

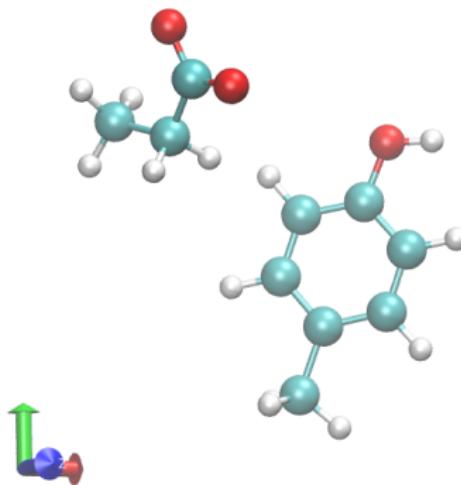


E. R. Johnson, A. Otero-de-la-Roza, S. G. Dale. J. Chem. Phys. (2013)

Self Consistent Field - SCF



Simplified Tyrosine-Aspartate pair



Basic input

```
② Select stephen@DESKTOP-FGN8SIS: ~/calc/Workshop/tailed_comf
import psi4

n = "SSI-084TYR-089ASP-1-dimer"
Basis = "def2-msvp"

psi4.set_options({"basis": Basis,
                  "reference": "uks"})
# psi4.set_output_file(f"{n}.out")
xyz = "".join(open(f'./{n}.xyz', 'r').readlines()[1:])
xyz = psi4.geometry(xyz)
e, wfn = psi4.energy('pbe', molecule=xyz, return_wfn=True)

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```

Start of convergence

	Total Energy	Delta E	RMS [F,P]
@DF-UKS iter SAD:	-612.92724315251030	-6.12927e+02	0.00000e+00
@DF-UKS iter 1:	-612.48389267056882	4.43350e-01	7.20414e-03 DIIS
@DF-UKS iter 2:	-602.22880421060404	1.02551e+01	1.34159e-02 DIIS
@DF-UKS iter 3:	-605.33900628080028	-3.11020e+00	1.30322e-02 DIIS
@DF-UKS iter 4:	-611.33264791484225	-5.99364e+00	6.51709e-03 DIIS
@DF-UKS iter 5:	-613.58756208384693	-2.25491e+00	2.88256e-03 DIIS
@DF-UKS iter 6:	-613.67607872116673	-8.85166e-02	2.06501e-03 DIIS
@DF-UKS iter 7:	-613.74172378003550	-6.56451e-02	1.21213e-03 DIIS
@DF-UKS iter 8:	-613.76092654766921	-1.92028e-02	9.10761e-04 DIIS
@DF-UKS iter 9:	-613.77706692805441	-1.61404e-02	4.70644e-04 DIIS
@DF-UKS iter 10:	-612.72321115862405	1.05386e+00	3.90027e-03 DIIS
@DF-UKS iter 11:	-613.78135802452948	-1.05815e+00	2.81782e-04 DIIS
@DF-UKS iter 12:	-612.66935482976396	1.11200e+00	3.94041e-03 DIIS
@DF-UKS iter 13:	-612.67711837765137	-7.76355e-03	3.90425e-03 DIIS
@DF-UKS iter 14:	-612.67793575083806	-8.17373e-04	3.89993e-03 DIIS
@DF-UKS iter 15:	-612.67192415525233	6.01160e-03	3.92523e-03 DIIS
@DF-UKS iter 16:	-612.67683648347975	-4.91233e-03	3.90375e-03 DIIS

Failed to converge

```
stephen@DESKTOP-FGNB3BS:~/calc/workshop/failed_conv
@DF-UKS iter 84: -612.67577837163208 4.49331e-04 3.90632e-03 DIIS
@DF-UKS iter 85: -612.67583663911864 -5.82675e-05 3.90599e-03 DIIS
@DF-UKS iter 86: -612.67572738321360 1.09256e-04 3.90630e-03 DIIS
@DF-UKS iter 87: -612.67562590472153 1.01478e-04 3.90663e-03 DIIS
@DF-UKS iter 88: -612.67552551962945 1.00385e-04 3.90717e-03 DIIS
@DF-UKS iter 89: -612.67551086360800 1.46560e-05 3.90805e-03 DIIS
@DF-UKS iter 90: -612.67584031749857 -3.29454e-04 3.90859e-03 DIIS
@DF-UKS iter 91: -612.67575775509022 8.25624e-05 3.90800e-03 DIIS
@DF-UKS iter 92: -612.67622127929053 -4.63524e-04 3.90695e-03 DIIS
@DF-UKS iter 93: -612.67500370808648 1.21757e-03 3.91018e-03 DIIS
@DF-UKS iter 94: -612.67631440140622 -1.31069e-03 3.90479e-03 DIIS
@DF-UKS iter 95: -612.67610917557386 2.05226e-04 3.90545e-03 DIIS
@DF-UKS iter 96: -612.67607734239073 3.18332e-05 3.90537e-03 DIIS
@DF-UKS iter 97: -612.67589943759776 1.77905e-04 3.90583e-03 DIIS
@DF-UKS iter 98: -612.67569545639299 2.03981e-04 3.90657e-03 DIIS
@DF-UKS iter 99: -612.67557558186218 1.19875e-04 3.90767e-03 DIIS
@DF-UKS iter 100: -612.67582000112361 -2.44419e-04 3.90857e-03 DIIS

PsiException: Could not converge SCF iterations in 100 iterations.

Failed to converge.
```

Examine SCF steps

```
stephen@DESKTOP-FGNB5BS:~/calc/workshop/failed_conv
import psi4

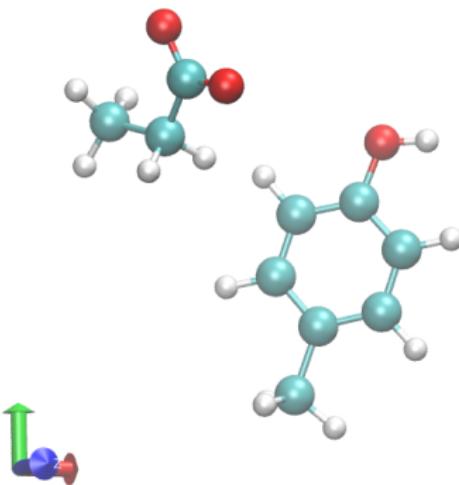
n = "SSI-084TYR-089ASP-1-dimer"
Basis = "def2-msvp"

xyz = "".join(open(f'./{n}.xyz', 'r').readlines()[1:])
xyz = psi4.geometry(xyz)
e, wfn = psi4.energy('pbe', molecule=xyz, return_wfn=True)

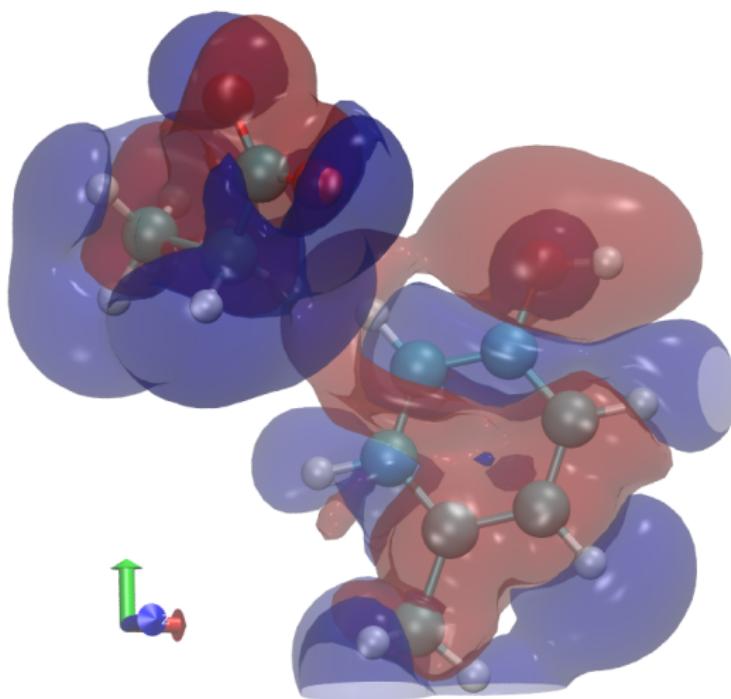
psi4.set_options({"basis": Basis,
                  "reference":"uks",
                  "fail_on_maxiter":False,
                  "maxiter":5,
                  "guess":"sad"})
e, wfn = psi4.energy('pbe', molecule=xyz, return_wfn=True)
psi4.fchk(wfn, "5.fchk")

psi4.set_options({"basis": Basis,
                  "reference":"uks",
                  "fail_on_maxiter":False,
                  "maxiter":6,
```

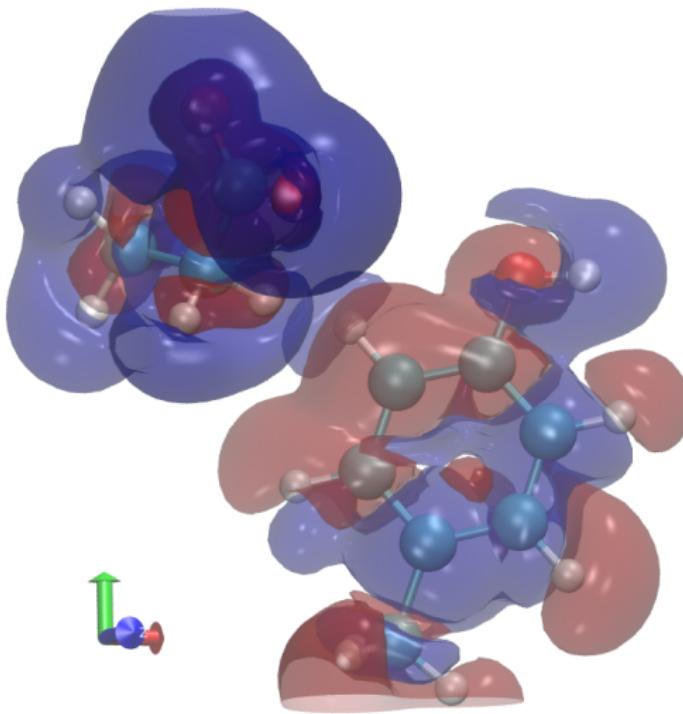
Simplified Tyrosine-Aspartate pair



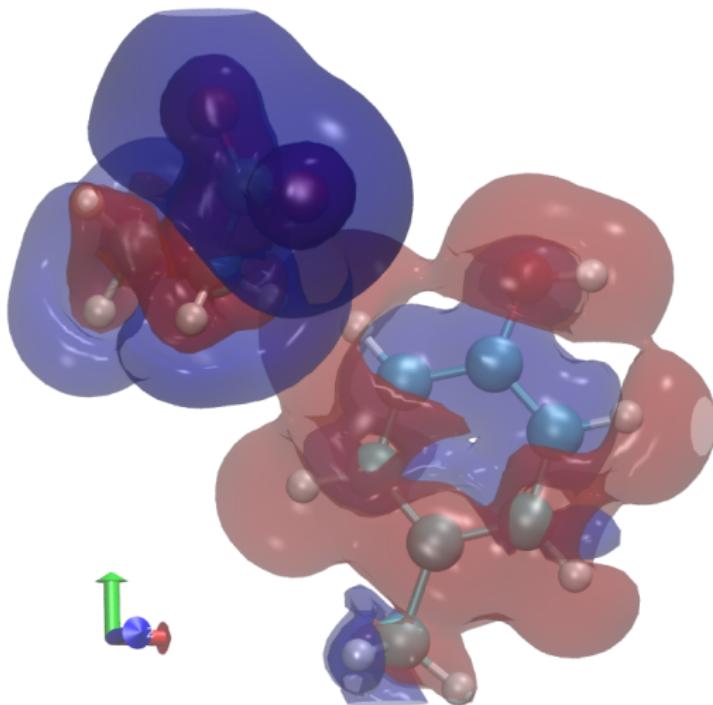
Density difference SCF step 6 vs 5



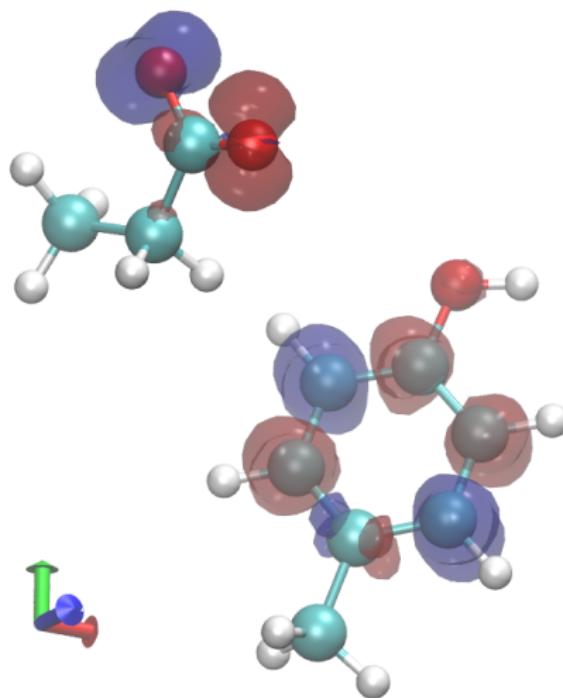
Density difference SCF step 7 vs 6



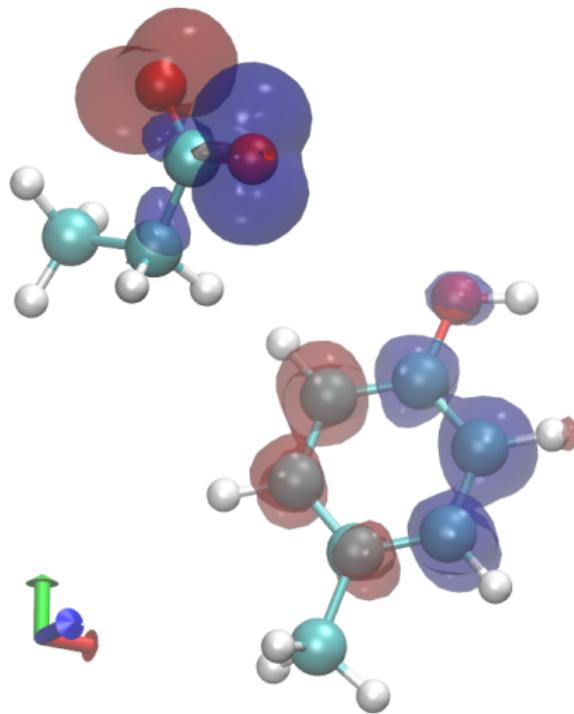
Density difference SCF step 8 vs 7



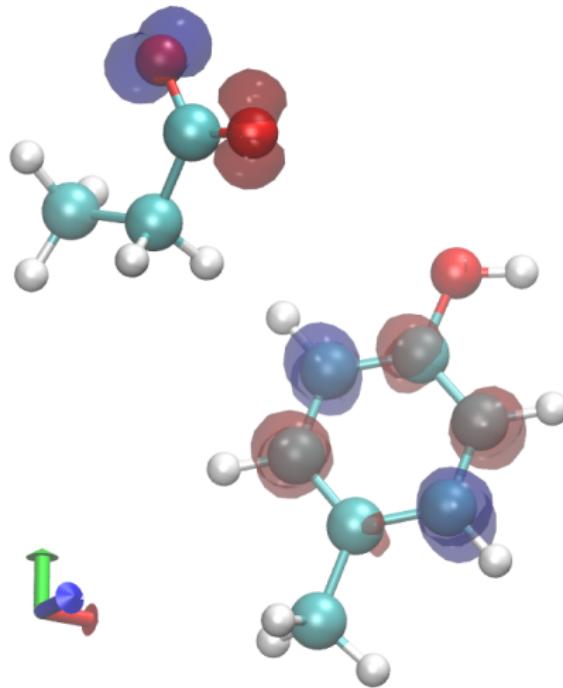
Density difference SCF step 98 vs 97



Density difference SCF step 99 vs 98



Density difference SCF step 100 vs 99



Guess SADNO

```
steven@DESKTOP-FGN85BS:~/calc/Workshop/tailed_conv
import psi4

n = "SSI-084TYR-089ASP-1-dimer"
Basis = "def2-msvp"

psi4.set_options({"basis": Basis,
                  "reference":"uks",
                  "guess":"sadno"})
# psi4.set_output_file(f"{n}.out")
xyz = "".join(open(f'./{n}.xyz', 'r').readlines()[1:])
xyz = psi4.geometry(xyz)
e, wfn = psi4.energy('pbe', molecule=xyz, return_wfn=True)

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```

Guess Core

```
steven@DESKTOP-FGN9SBS:~/calc/Workshop/failed_conv
import psi4

n = "SSI-084TYR-089ASP-1-dimer"
Basis = "def2-msvp"

psi4.set_options({"basis": Basis,
                  "reference":"uks",
                  "guess":"core"})
# psi4.set_output_file(f"{n}.out")
xyz = "".join(open(f'./{n}.xyz', 'r').readlines()[1:])
xyz = psi4.geometry(xyz)
e, wfn = psi4.energy('pbe', molecule=xyz, return_wfn=True)

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```

Damping SCF steps

```
stephen@DESKTOP-FGNB5BS:~/calc/workshop/failed_conv
import psi4

n = "SSI-084TYR-089ASP-1-dimer"
Basis = "def2-msvp"

psi4.set_options({"basis": Basis,
                  "reference": "uks",
                  "damping_percentage": 50})
xyz = "".join(open(f'./{n}.xyz', 'r').readlines()[1:])
xyz = psi4.geometry(xyz)
e, wfn = psi4.energy('pbe', molecule=xyz, return_wfn=True)

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```

Second Order SCF convergence

```
steven@DESKTOP-FGN9SBS:~/calc/Workshop/Tailed_conv
import psi4

n = "SSI-084TYR-089ASP-1-dimer"
Basis = "def2-msvp"

psi4.set_options({"basis": Basis,
                  "reference":"uks",
                  "soscf":True})
# psi4.set_output_file(f"{n}.out")
xyz = "".join(open(f'./{n}.xyz', 'r').readlines()[1:])
xyz = psi4.geometry(xyz)
e, wfn = psi4.energy('pbe', molecule=xyz, return_wfn=True)

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```

Successful convergence!

```
stephen@DESKTOP-FGNB5B:~/calc/workshop/failed_conv

      Total Energy        Delta E    RMS |[F,P]|

@DF-UKS iter SAD: -612.92724315251030 -6.12927e+02 0.00000e+00
@DF-UKS iter  1: -612.48389267056996  4.43350e-01 7.20414e-03 DIIS
@DF-UKS iter  2: -602.22880421060427  1.02551e+01 1.34159e-02 DIIS
@DF-UKS iter  3: -605.33900628080255 -3.11020e+00 1.30322e-02 DIIS
@DF-UKS iter  4: -611.33264791484362 -5.99364e+00 6.51709e-03 DIIS
@DF-UKS iter  5: -613.58756208384762 -2.25491e+00 2.88256e-03 SOKS, nmicro=5
@DF-UKS iter  6: -613.63358425177239 -4.60222e-02 1.56521e-03 SOKS, nmicro=5
@DF-UKS iter  7: -613.76877315500997 -1.35189e-01 3.68070e-04 SOKS, nmicro=5
@DF-UKS iter  8: -613.78219083851309 -1.34177e-02 1.13402e-04 SOKS, nmicro=5
@DF-UKS iter  9: -613.78333182593110 -1.14099e-03 3.88645e-05 SOKS, nmicro=5
@DF-UKS iter 10: -613.76712740007702  1.62044e-02 5.88150e-04 SOKS, nmicro=5
@DF-UKS iter 11: -613.78214377745303 -1.50164e-02 9.29611e-05 SOKS, nmicro=5
@DF-UKS iter 12: -613.78380601533854 -1.66224e-03 3.74660e-05 SOKS, nmicro=5
@DF-UKS iter 13: -613.78400412363749 -1.98108e-04 8.23983e-06 SOKS, nmicro=5
@DF-UKS iter 14: -613.78401355711094 -9.43347e-06 3.53712e-06 SOKS, nmicro=5
@DF-UKS iter 15: -613.78401442759059 -8.70480e-07 1.88187e-06 SOKS, nmicro=5
@DF-UKS iter 16: -613.78401464741160 -2.19821e-07 8.89503e-07 SOKS, nmicro=conv

Energy and wave function converged.
```

HF guess, with no PBE convergence

```
① stephen@DESKTOP-FGNB5BS:~/calc/workshop/failed_conv
import psi4

n = "SSI-084TYR-089ASP-1-dimer"
Basis = "def2-msvp"

psi4.set_options({"basis": Basis,
                  "reference":"uks"})
# psi4.set_output_file(f"{n}.out")
xyz = "".join(open(f'./{n}.xyz', 'r').readlines()[1:])
xyz = psi4.geometry(xyz)
e, wfn = psi4.energy('hf', molecule=xyz, return_wfn=True)
psi4.set_options({"basis": Basis,
                  "reference":"uks",
                  "fail_on_maxiter":False,
                  "maxiter":0,
                  "guess":"read"})
e, wfn = psi4.energy('pbe', molecule=xyz, return_wfn=True)
~
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~
```

HF SCF convergence

```
stephen@DESKTOP-FGNB5BS:~/calc/workshop/failed_conv
      Total    221    221
      -----
      ==> Iterations <==

      Total Energy        Delta E      RMS |[F,P]|
      @DF-UKS iter SAD: -609.18268432492027   -6.09183e+02  0.00000e+00
      @DF-UKS iter  1: -610.43754969477777   -1.25487e+00  3.82815e-03 DIIS
      @DF-UKS iter  2: -610.73596376861497   -2.98414e-01  1.99585e-03 DIIS
      @DF-UKS iter  3: -610.80570138837675   -6.97376e-02  3.28432e-04 DIIS
      @DF-UKS iter  4: -610.80920787906825   -3.50649e-03  1.26356e-04 DIIS
      @DF-UKS iter  5: -610.80968553913112   -4.77660e-04  2.16836e-05 DIIS
      @DF-UKS iter  6: -610.80970806540404   -2.25263e-05  7.47540e-06 DIIS
      @DF-UKS iter  7: -610.80971030496403   -2.23956e-06  2.99667e-06 DIIS
      @DF-UKS iter  8: -610.80971076038259   -4.55419e-07  1.00371e-06 DIIS
      @DF-UKS iter  9: -610.80971085403826   -9.36557e-08  4.39149e-07 DIIS
      Energy and wave function converged.

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

PBE energy on HF density

```
stephen@DESKTOP-FGNB5BS:~/calc/workshop/failed_conv
=====
      A      221      221      49      49      49      0
=====
 Total    221      221      49      49      49      0
=====

==> Iterations <==

          Total Energy          Delta E        RMS |[F,P]|
@DF-UKS iter  0: -613.69055738418319   -6.13691e+02   2.51005e-03

PsiException: Could not converge SCF iterations in 0 iterations.

Energy and/or wave function did not converge, but proceeding anyway.

==> Post-Iterations <==

Electrons on quadrature grid:
  Nalpha = 49.0000105624 ; deviation = 1.056e-05
```

PBE energy on HF density

```
hstephen@DESKTOP-FONDBE: ~\cat\workshop\failed_code
=====
      A      221      221      49      49      49      0
-----
Total    221      221      49      49      49      0
-----

==> Iterations <=

          Total Energy        Delta E      RMS |[F,P]|
@DF-UKS iter  0: -613.69055738418319  -6.13691e+02   2.51005e-03

PsiException: Could not converge SCF iterations in 0 iterations.

Energy and/or wave function did not converge, but proceeding anyway.

==> Post-Iterations <=

Electrons on quadrature grid:
  Nalpha = 49.0000105624 : deviation = 1.056e-05
```

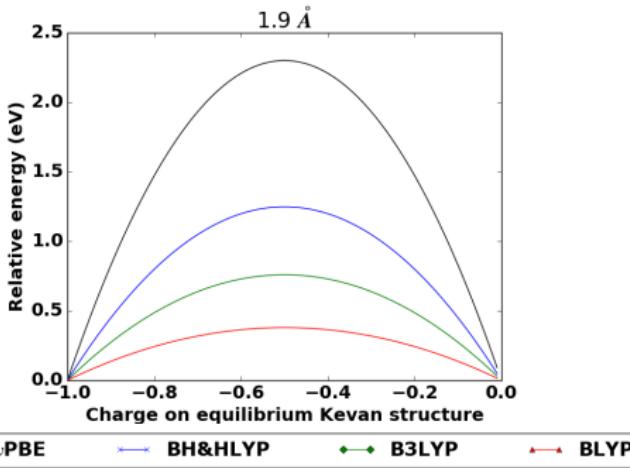
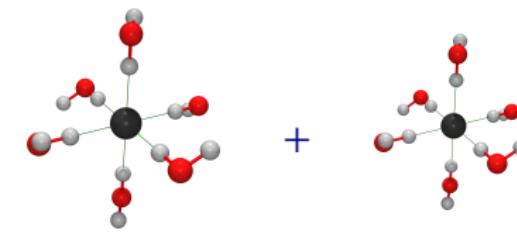


pubs.acs.org/JCTC

Density-Corrected DFT Explained: Questions and Answers

Suhwan Song, Stefan Vuckovic, Eunji Sim,* and Kieron Burke

Side Note: Localization Error using CPCM



S. G. Dale, E. R. Johnson. J. Chem. Phys. 143 18 184112 (2014)

PCM stabilised SCF

```
stephen@DESKTOP-FGNB5BS:~/calc/workshop/failed_conv
import psi4

n = "SSI-084TYR-089ASP-1-dimer"
Basis = "def2-msvp"

psi4.set_options({"basis": Basis,
                  "reference":"uks",
                  "pcm":True,
                  "pcm_scf_type":'total'})

pcm_string = '''
    Units = Angstrom
    Medium {
        SolverType = cpcm
        Solvent = Explicit
        ProbeRadius=2.0
        Green<inside> {Type=Vacuum}
        Green<outside> {Type=UniformDielectric
                         Eps=80
                         EpsDyn=2.0}
    }
'''
```

PCM stabilised SCF converged

```
stephen@DESKTOP-FGNB5BS:~/calc/workshop/failed_conv
      Total    221    221
      -----
      ==> Iterations <==

      Total Energy        Delta E      RMS |[F,P]|
      @DF-UKS iter SAD: -612.92782743992075  -6.12928e+02  0.00000e+00
      @DF-UKS iter  1: -612.66893944920457   2.58888e-01  7.07694e-03 DIIS
      @DF-UKS iter  2: -611.81673105235313   8.52208e-01  9.27816e-03 DIIS
      @DF-UKS iter  3: -613.87956680073478  -2.06284e+00  1.12801e-03 DIIS
      @DF-UKS iter  4: -613.89604398416327  -1.64772e-02  6.68267e-04 DIIS
      @DF-UKS iter  5: -613.90425882138766  -8.21484e-03  2.34244e-04 DIIS
      @DF-UKS iter  6: -613.90518014322868  -9.21322e-04  8.78316e-05 DIIS
      @DF-UKS iter  7: -613.90531707039736  -1.36927e-04  2.09915e-05 DIIS
      @DF-UKS iter  8: -613.90532724683840  -1.01764e-05  6.42227e-06 DIIS
      @DF-UKS iter  9: -613.90532807864417  -8.31806e-07  2.53475e-06 DIIS
      @DF-UKS iter 10: -613.90532823779620  -1.59152e-07  3.44895e-07 DIIS
      Energy and wave function converged.
```

Check for wavefunction stability

```
stephen@DESKTOP-FGNB5BS:~/calc/workshop/failed_conv
import psi4

n = "SSI-084TYR-089ASP-1-dimer"
Basis = "def2-msvp"

psi4.set_options({"basis": Basis,
                  "reference": "uhf",
                  "stability_analysis": 'follow'})
# psi4.set_output_file(f"{n}.out")
xyz = "".join(open(f'./{n}.xyz', 'r').readlines()[1:])
xyz = psi4.geometry(xyz)
e, wfn = psi4.energy('hf', molecule=xyz, return_wfn=True)

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```

SCF identified as unstable

```
stephen@DESKTOP-FGNB5BS:~/calc/workshop/failed_conv

==> Iterations <==

          Total Energy        Delta E      RMS |[F,P]|

@DF-UHF iter SAD: -609.18268432687023 -6.09183e+02 0.00000e+00
@DF-UHF iter  1: -610.43754969677593 -1.25487e+00 3.82815e-03 DIIS
@DF-UHF iter  2: -610.73596377061222 -2.98414e-01 1.99585e-03 DIIS
@DF-UHF iter  3: -610.80570139037081 -6.97376e-02 3.28432e-04 DIIS
@DF-UHF iter  4: -610.80920788106414 -3.50649e-03 1.26356e-04 DIIS
@DF-UHF iter  5: -610.80968554112496 -4.77660e-04 2.16836e-05 DIIS
@DF-UHF iter  6: -610.80970806739970 -2.25263e-05 7.47540e-06 DIIS
@DF-UHF iter  7: -610.80971030695878 -2.23956e-06 2.99667e-06 DIIS
@DF-UHF iter  8: -610.80971076237870 -4.55420e-07 1.00371e-06 DIIS
@DF-UHF iter  9: -610.80971085603323 -9.36545e-08 4.39149e-07 DIIS

Energy and wave function converged.

-----
UHF Stability code
Jérôme Gonthier
```

SCF re-converged to table

```
stephen@DESKTOP-FGNB5BS:~/calc/workshop/failed_conv
DLUSolver converged.

Negative totally symmetric eigenvalue detected: -0.016556
Wavefunction unstable!
Lowest UHF->UHF stability eigenvalues:
  A -0.016556

Rotating orbitals by 0.500000 * pi / 2 radians along unstable eigenvector.
Running SCF again with the rotated orbitals.

@DF-UHF iter 10: -610.79856917061602 -6.10799e+02 2.65067e-04 DIIS
@DF-UHF iter 11: -610.80417391533638 -5.60474e-03 1.34883e-04 DIIS
@DF-UHF iter 12: -610.80672224431373 -2.54833e-03 9.76061e-05 DIIS
@DF-UHF iter 13: -610.80833144179269 -1.60920e-03 7.35476e-05 DIIS
@DF-UHF iter 14: -610.81017407540412 -1.84263e-03 3.90569e-05 DIIS
@DF-UHF iter 15: -610.81078210569285 -6.08030e-04 2.14347e-05 DIIS
@DF-UHF iter 16: -610.81095105643794 -1.68951e-04 9.07607e-06 DIIS
@DF-UHF iter 17: -610.81098770438916 -3.66480e-05 3.06051e-06 DIIS
@DF-UHF iter 18: -610.81099046227018 -2.75788e-06 1.24072e-06 DIIS
@DF-UHF iter 19: -610.81099078921534 -3.26945e-07 5.48717e-07 DIIS
```

Note: Original SCF energy was -610.80971085603323.

Conclusions

Delocalisation error is a primary contributor to SCF instability. Tools for improving SCF convergence include:

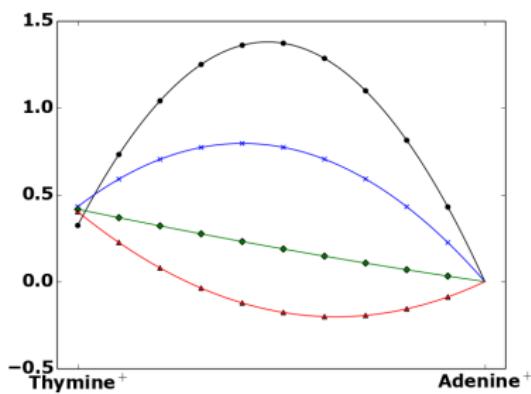
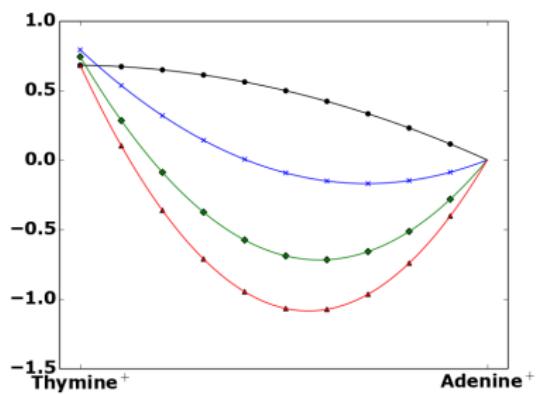
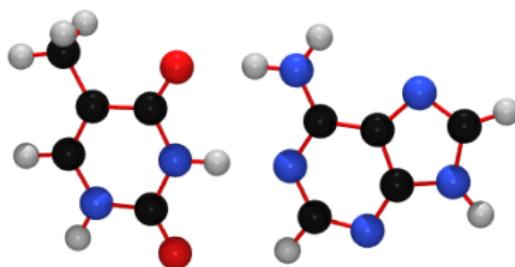
- Change initial guess
- SCF damping
- Second Order Convergence
- Convergence with a different functional
 - ▶ Density Corrected DFT
- Convergence with an applied potential (like a solvent correction)

Remember to check for SCF stability

Acknowledgements

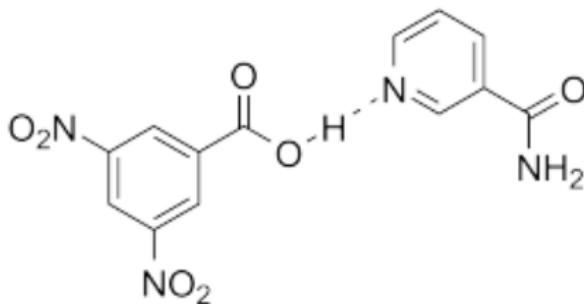


Cationic Thymine-Adenine Dimer



● ● LC- ω PBE ← → BH&HLYP ♦ ♦ B3LYP ▲ ▲ BLYP

Real Example - Erroneous Proton Transfer



Method	PBE-D3	PBE0-D3	PBEh-3c		HF-3c	
Input Structure	exp	exp	exp	PBE-D3	exp	PBE-D3
AWUDEB	salt	salt	co	salt	co	co

L. M. LeBlanc, S. G. Dale. C. R. Taylor, A. D. Becke, G. M. Day, E. R. Johnson Angew. Chemie 130 **45** 15122 (2018)

Real Example - Erroneous Proton Transfer

Method	PBE-D3	PBE0-D3	PBEh-3c		HF-3c	
Input Structure	exp	exp	exp	PBE-D3	exp	PBE-D3
AWUDEB	salt	salt	co	salt	co	co
LUNNAJ	salt	salt	co	salt	co	co
UJORAM	salt	salt	co	salt	co	co
AJAKEB	salt	salt	co	co	co	co
ULAWAF02	salt	salt	co	co	co	co
SEDJUI	salt	salt	co	co	co	co