Supplemental Information for The Role of High-Order Electron Correlation Effects in a Model System for Non-valence Correlation-bound Anions

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Contents

1 Geometries

The geometries are given in xyz format for the $(H_2O)_4$ structures in Angstroms.

1.a Geometry at $R = 4\,\text{Å}$

```
13
WATER 4 SYSTEM 4.0 Angstroms
X   0.000000   0.000000   0.000000
O   0.000000   1.730527   2.893437
H   0.000000   1.387569   2.000001
H   0.000000   2.681413   2.785434
O   0.000000  -1.730527   2.893437
H   0.000000  -1.387569   2.000001
H   0.000000  -2.681413   2.785434
O   0.000000   1.730527  -2.893437
H   0.000000   1.387569  -2.000001
H   0.000000   2.681413  -2.785434
O   0.000000  -1.730527  -2.893437
H   0.000000  -1.387569  -2.000001
H   0.000000  -2.681413  -2.785434
```

1.b Geometry at $R = 7\,\text{Å}$

```
13
WATER 4 SYSTEM 7.0 Angstroms
X   0.000000   0.000000   0.000000
O   0.000000   1.730527   4.393437
H   0.000000   1.387569   3.500001
```

```
H   0.000000   2.681413   4.285434
O   0.000000  -1.730527   4.393437
H   0.000000  -1.387569   3.500001
H   0.000000  -2.681413   4.285434
O   0.000000   1.730527  -4.393437
H   0.000000   1.387569  -3.500001
H   0.000000   2.681413  -4.285434
O   0.000000  -1.730527  -4.393437
H   0.000000  -1.387569  -3.500001
H   0.000000  -2.681413  -4.285434
```

2 Supplemental Basis Functions

The exponents for the 7s7p and 3s1p diffuse Gaussian type orbitals are given below in the GAMESS format.

2.a 7s7p

```
S   1
  1   0.02362232    1.0
S   1
  1   0.00738198    1.0
S   1
  1   0.00230687    1.0
S   1
  1   0.00072090    1.0
S   1
  1   0.00022528    1.0
S   1
  1   0.00007040    1.0
S   1
  1   0.00002200    1.0
P   1
  1   0.02362232    1.0
P   1
  1   0.00738198    1.0
P   1
  1   0.00230687    1.0
P   1
```

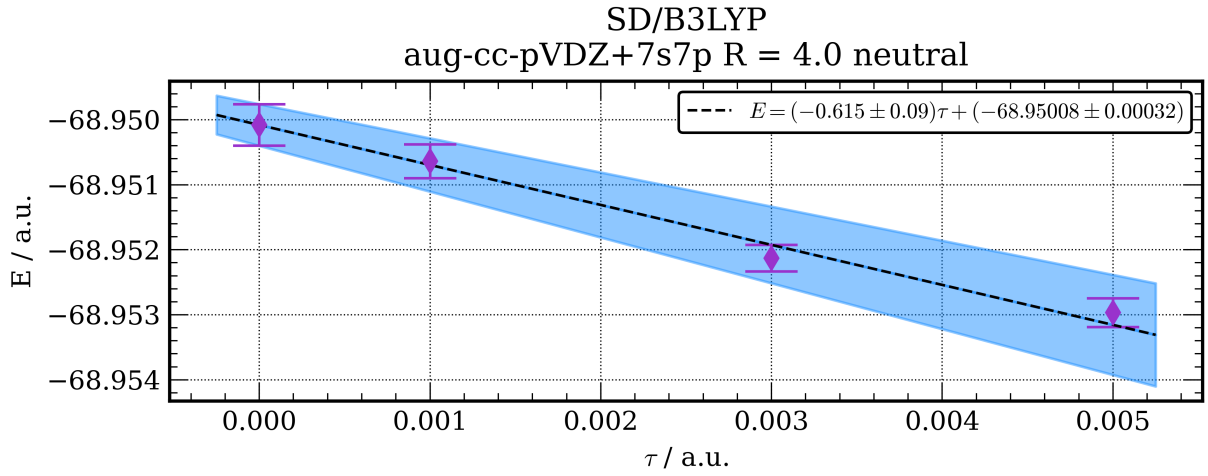
```
  1    0.00072090     1.0
P   1
  1    0.00022528     1.0
P   1
  1    0.00007040     1.0
P   1
  1    0.00002200     1.0
```

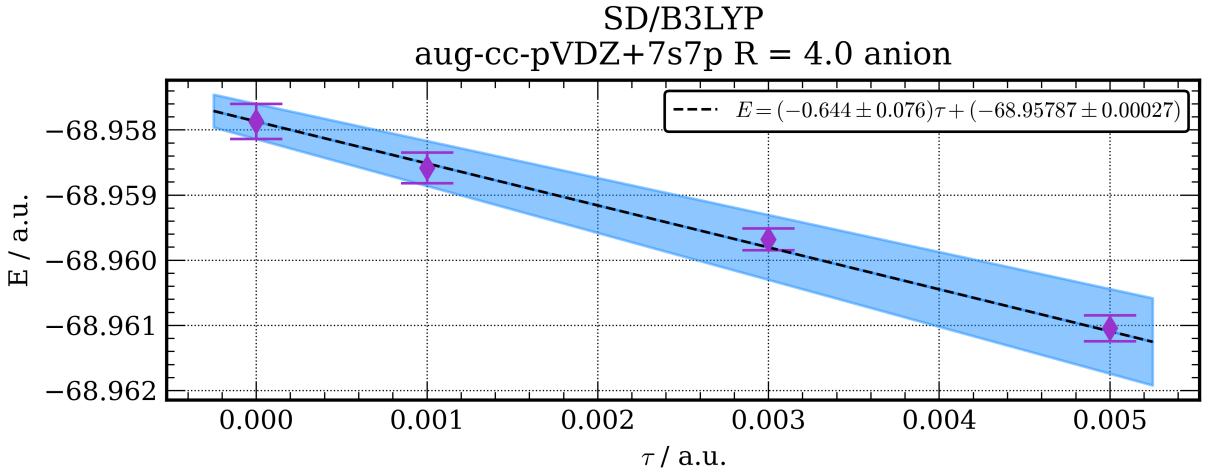
2.b 3s1p

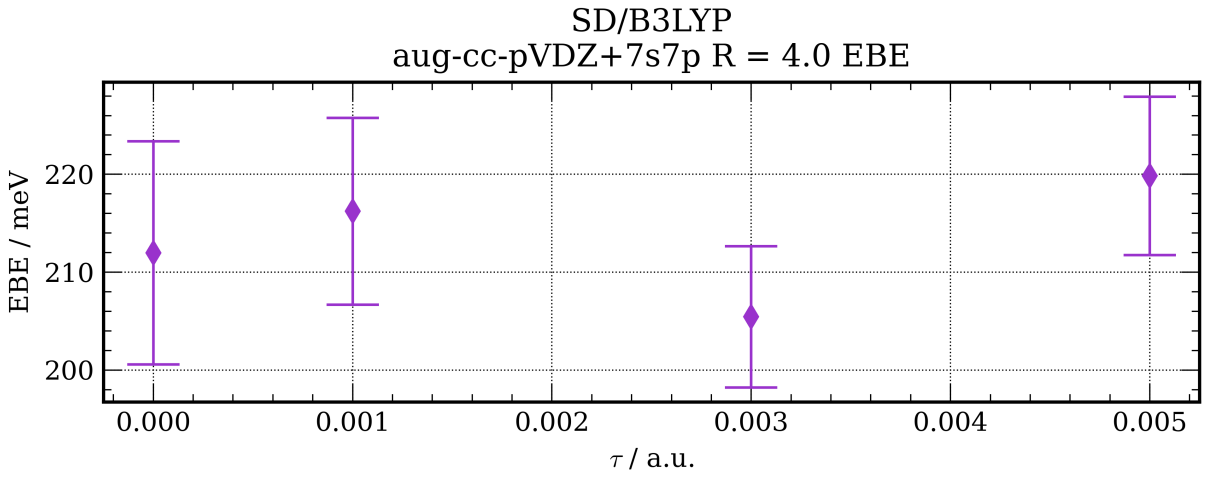
```
S   1
  1    0.02362232     1.0
S   1
  1    0.00738198     1.0
S   1
  1    0.00230687     1.0
P   1
  1    0.02362232     1.0
```

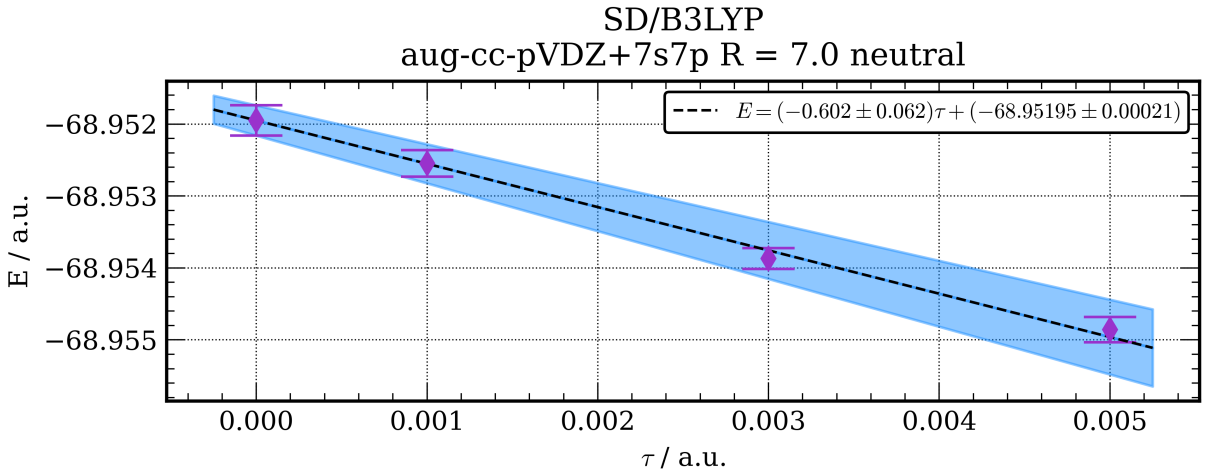
3 DMC extrapolation

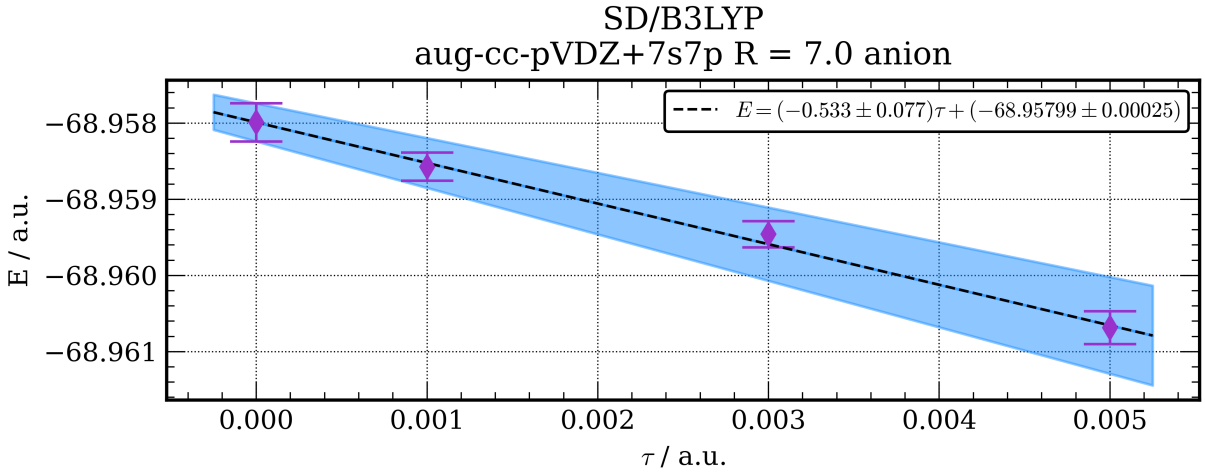
Summaries of the zero time step linear extrapolation are plotted below. The blue shaded region corresponds to the error in the fit of the DMC energies at the three timesteps (0.001, 0.003, 0.005).

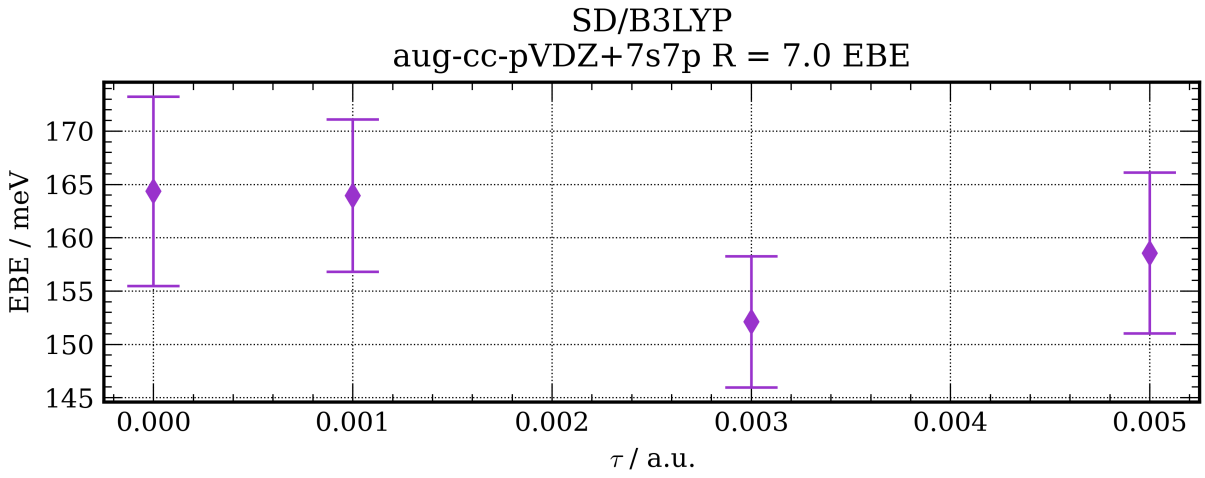

SD/B3LYP
aug-cc-pVDZ+7s7p R = 4.0 neutral
$E = (-0.615 \pm 0.09)\tau + (-68.95008 \pm 0.00032)$
E / a.u.
−68.950
−68.951
−68.952
−68.953
−68.954
0.000
0.001
0.002
0.003
0.004
0.005
τ / a.u.

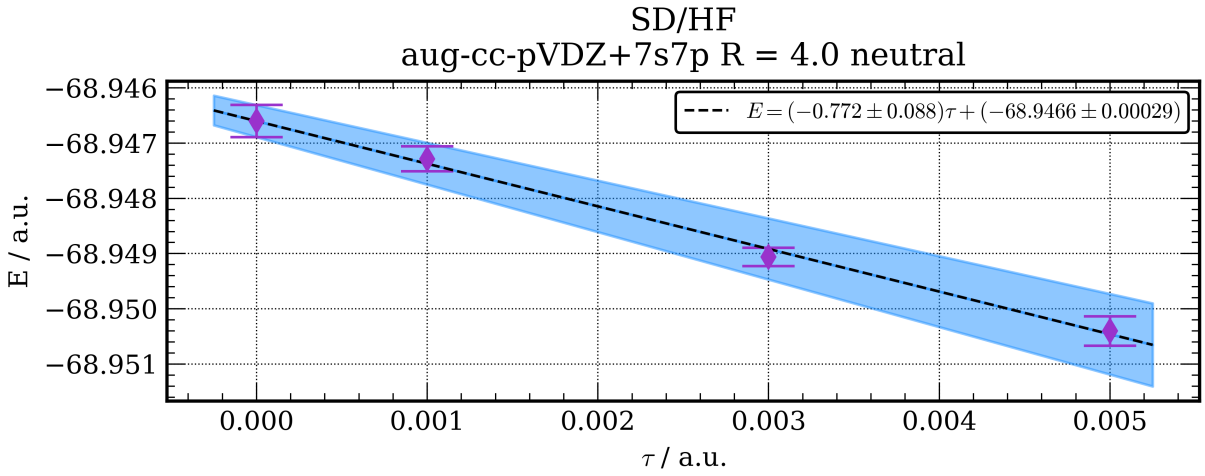

SD/B3LYP
aug-cc-pVDZ+7s7p R = 4.0 anion
$E = (-0.644 \pm 0.076)\tau + (-68.95787 \pm 0.00027)$
E / a.u.
−68.958
−68.959
−68.960
−68.961
−68.962
0.000
0.001
0.002
0.003
0.004
0.005
τ / a.u.

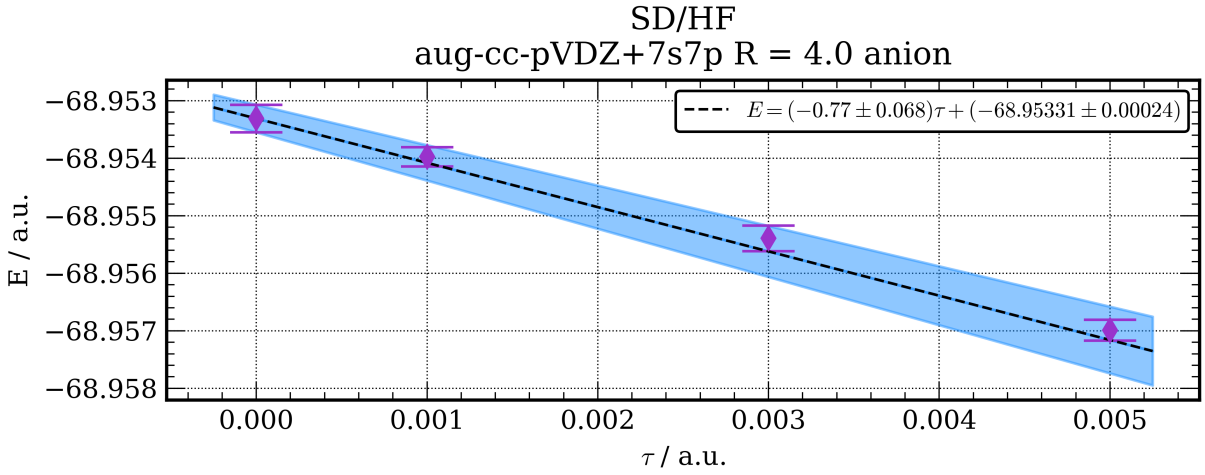

SD/B3LYP
aug-cc-pVDZ+7s7p R = 4.0 EBE
EBE / meV
220
210
200
0.000
0.001
0.002
0.003
0.004
0.005
τ / a.u.

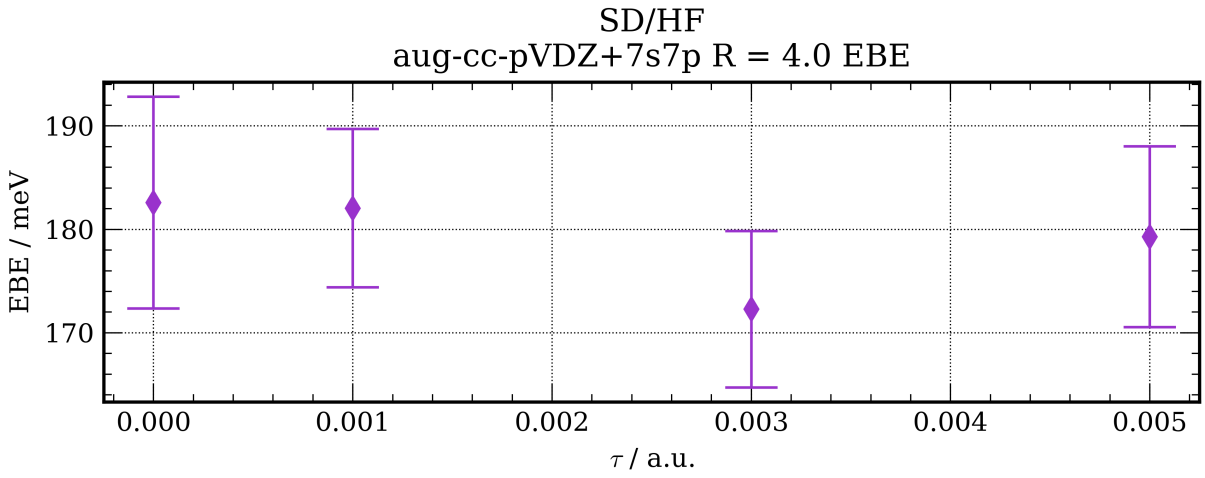

SD/B3LYP
aug-cc-pVDZ+7s7p R = 7.0 neutral
$E = (-0.602 \pm 0.062)\tau + (-68.95195 \pm 0.00021)$
E / a.u.
−68.952
−68.953
−68.954
−68.955
0.000
0.001
0.002
0.003
0.004
0.005
τ / a.u.

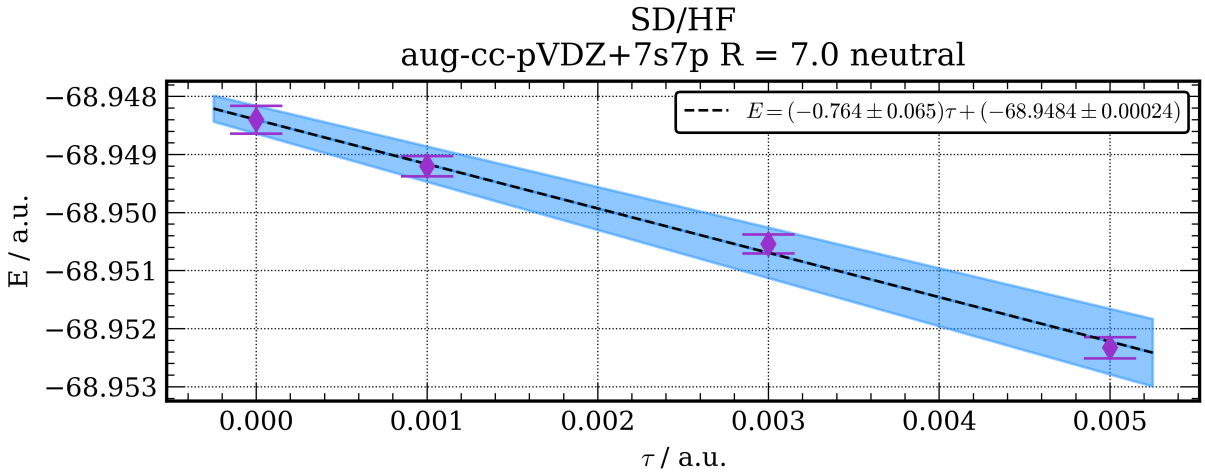

SD/B3LYP
aug-cc-pVDZ+7s7p R = 7.0 anion
$E = (-0.533 \pm 0.077)\tau + (-68.95799 \pm 0.00025)$
E / a.u.
−68.958
−68.959
−68.960
−68.961
0.000
0.001
0.002
0.003
0.004
0.005
τ / a.u.

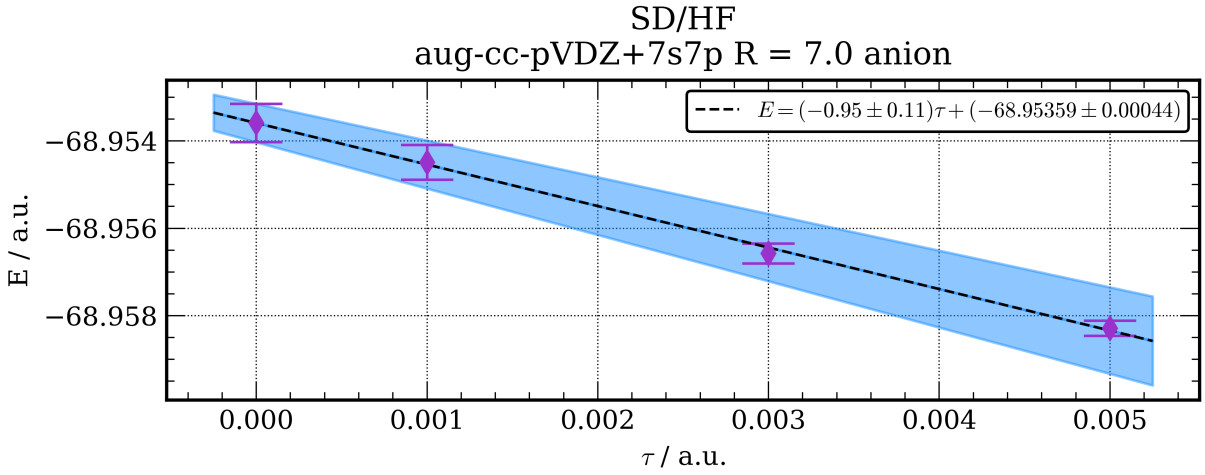

SD/B3LYP
aug-cc-pVDZ+7s7p R = 7.0 EBE
EBE / meV
170
165
160
155
150
145
0.000
0.001
0.002
0.003
0.004
0.005
τ / a.u.

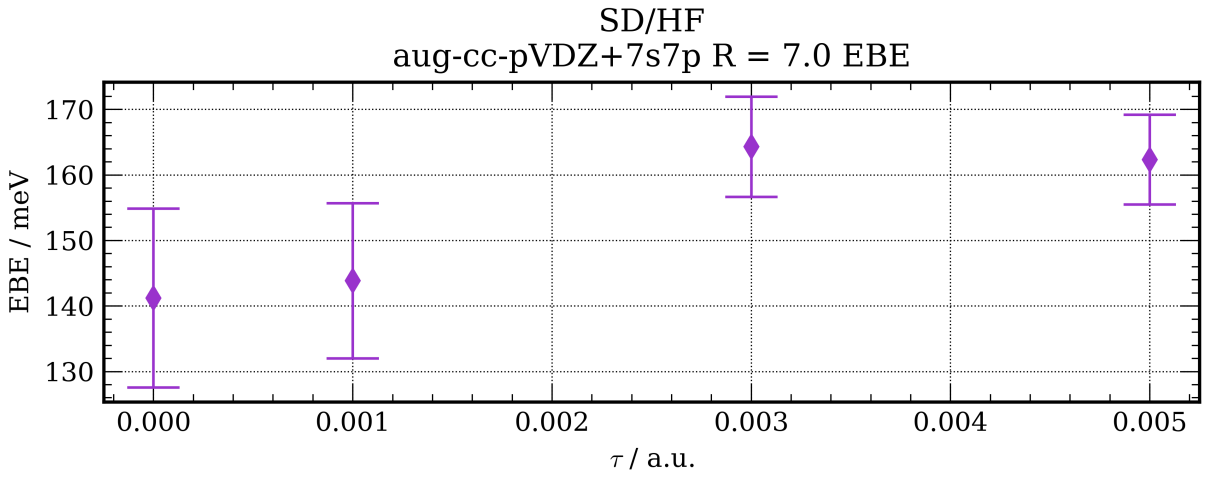

SD/HF
aug-cc-pVDZ+7s7p R = 4.0 neutral
$E = (-0.772 \pm 0.088)\tau + (-68.9466 \pm 0.00029)$
E / a.u.
−68.946
−68.947
−68.948
−68.949
−68.950
−68.951
0.000
0.001
0.002
0.003
0.004
0.005
τ / a.u.

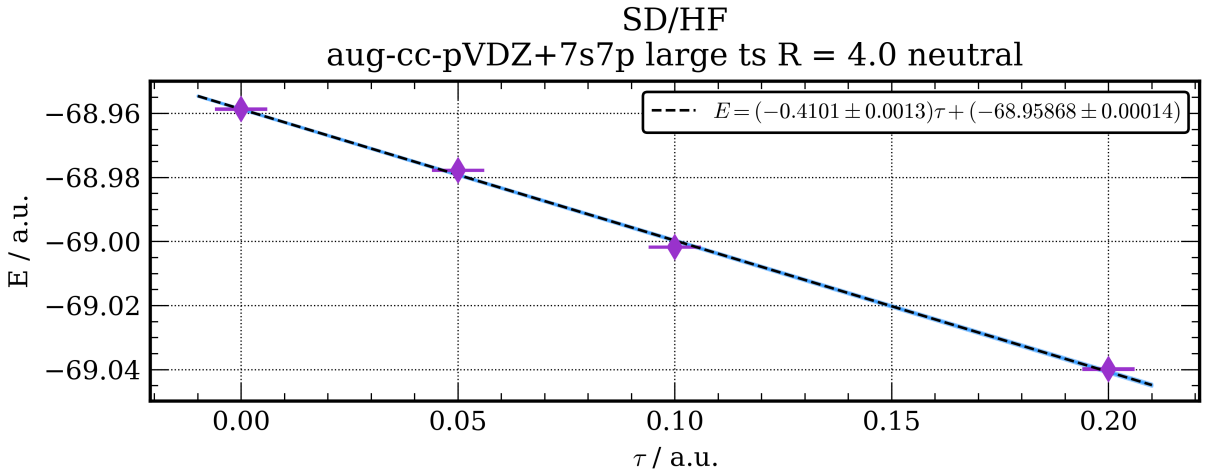

SD/HF
aug-cc-pVDZ+7s7p R = 4.0 anion
$E = (-0.77 \pm 0.068)\tau + (-68.95331 \pm 0.00024)$
E / a.u.
−68.953
−68.954
−68.955
−68.956
−68.957
−68.958
0.000
0.001
0.002
0.003
0.004
0.005
τ / a.u.

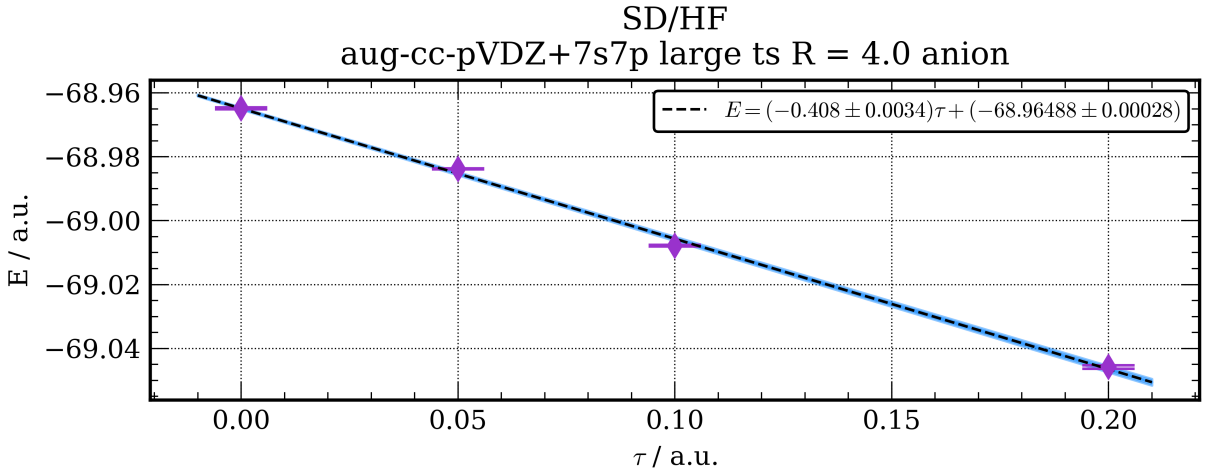

SD/HF
aug-cc-pVDZ+7s7p R = 4.0 EBE
EBE / meV
190
180
170
0.000
0.001
0.002
0.003
0.004
0.005
τ / a.u.

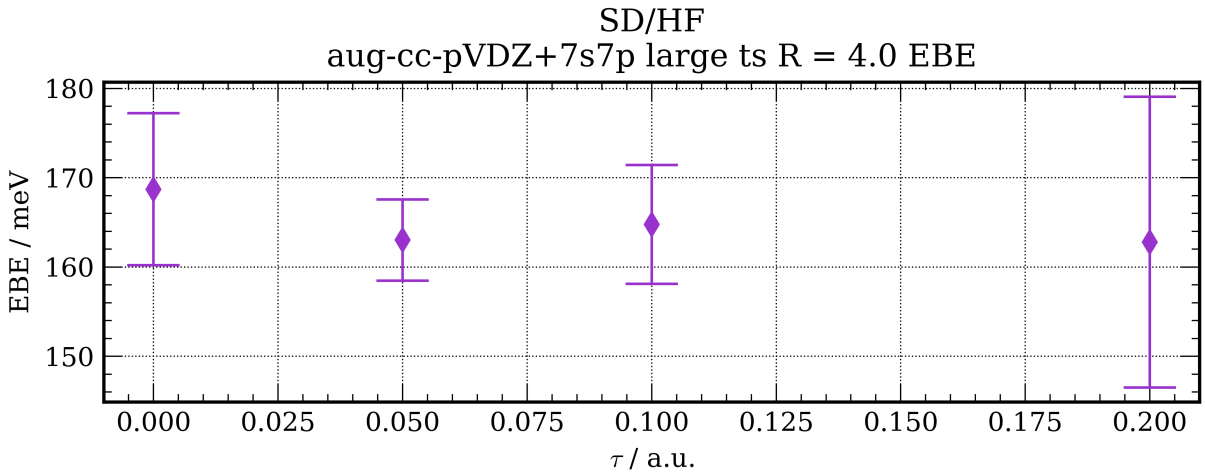

SD/HF
aug-cc-pVDZ+7s7p R = 7.0 neutral
$E = (-0.764 \pm 0.065)\tau + (-68.9484 \pm 0.00024)$
E / a.u.
−68.948
−68.949
−68.950
−68.951
−68.952
−68.953
0.000
0.001
0.002
0.003
0.004
0.005
τ / a.u.

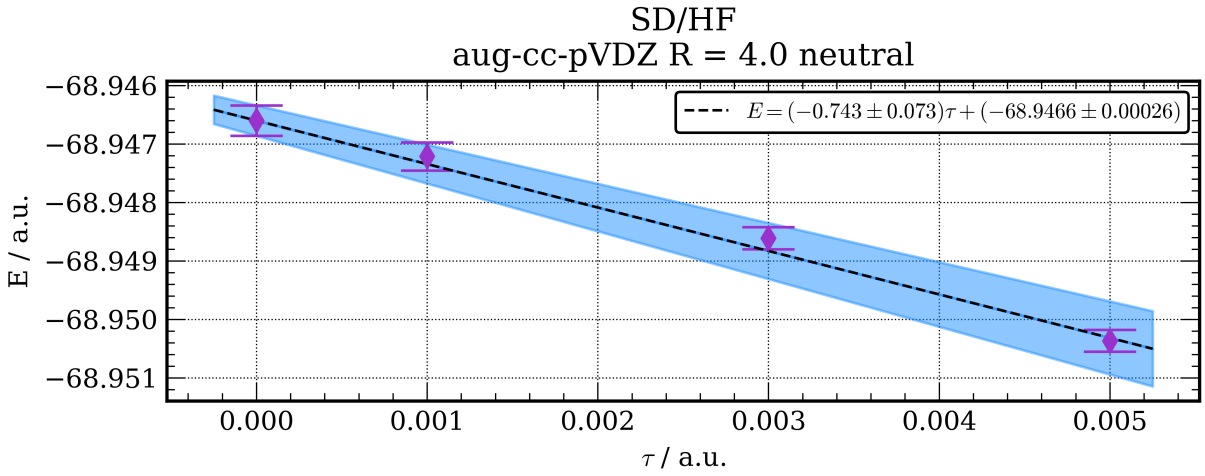

SD/HF
aug-cc-pVDZ+7s7p R = 7.0 anion
$E = (-0.95 \pm 0.11)\tau + (-68.95359 \pm 0.00044)$
E / a.u.
−68.954
−68.956
−68.958
0.000
0.001
0.002
0.003
0.004
0.005
τ / a.u.

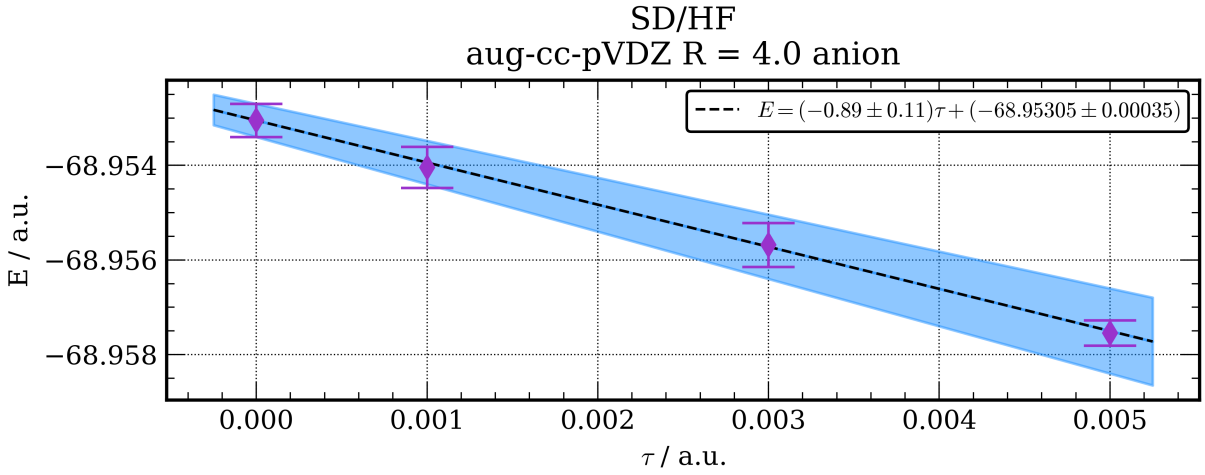

SD/HF
aug-cc-pVDZ+7s7p R = 7.0 EBE
EBE / meV
170
160
150
140
130
0.000
0.001
0.002
0.003
0.004
0.005
τ / a.u.

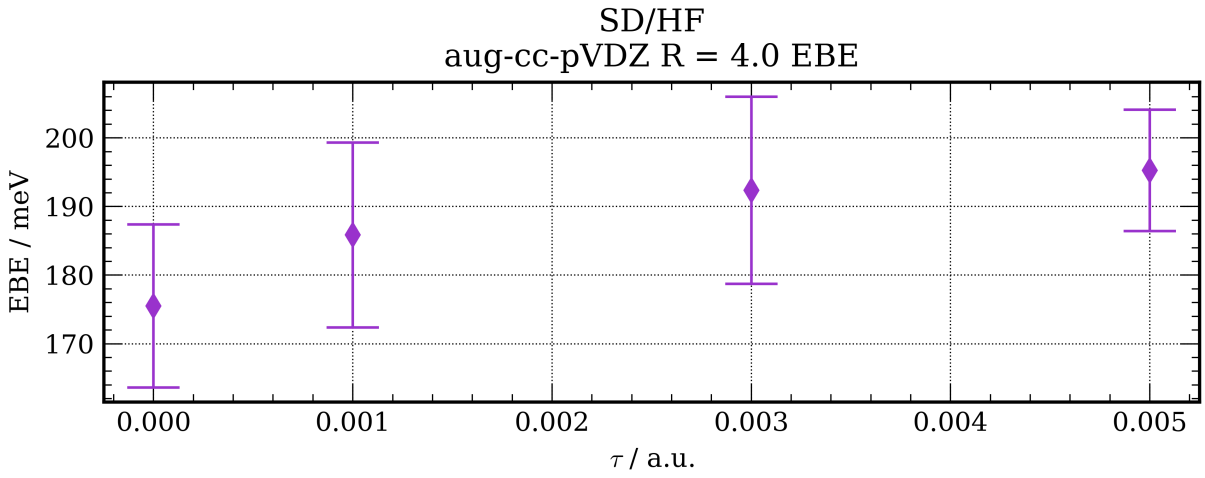

SD/HF
aug-cc-pVDZ+7s7p large ts R = 4.0 neutral
$E = (-0.4101 \pm 0.0013)\tau + (-68.95868 \pm 0.00014)$
E / a.u.
−68.96
−68.98
−69.00
−69.02
−69.04
0.00
0.05
0.10
0.15
0.20
τ / a.u.

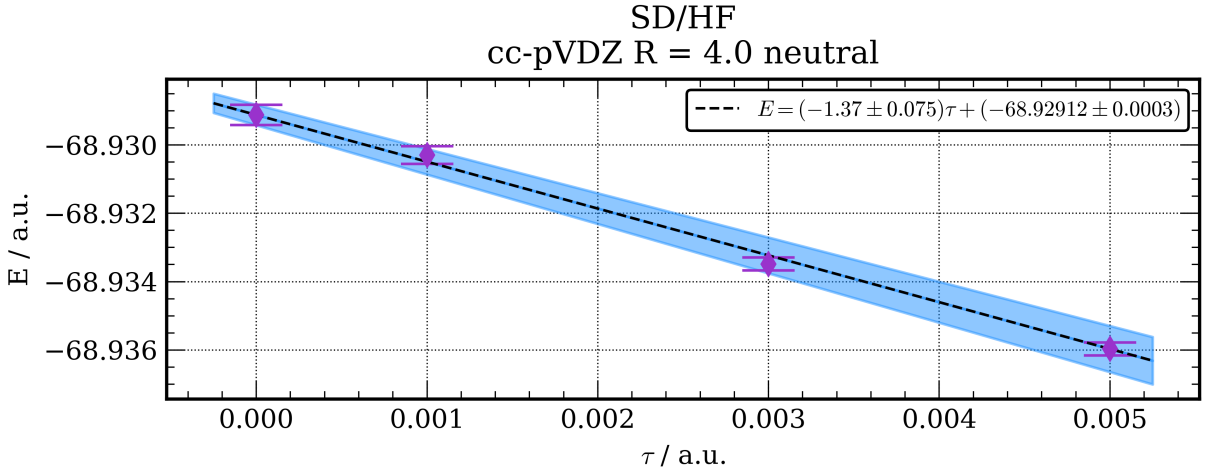

SD/HF
aug-cc-pVDZ+7s7p large ts R = 4.0 anion
$E = (-0.408 \pm 0.0034)\tau + (-68.96488 \pm 0.00028)$
E / a.u.
−68.96
−68.98
−69.00
−69.02
−69.04
0.00
0.05
0.10
0.15
0.20
τ / a.u.

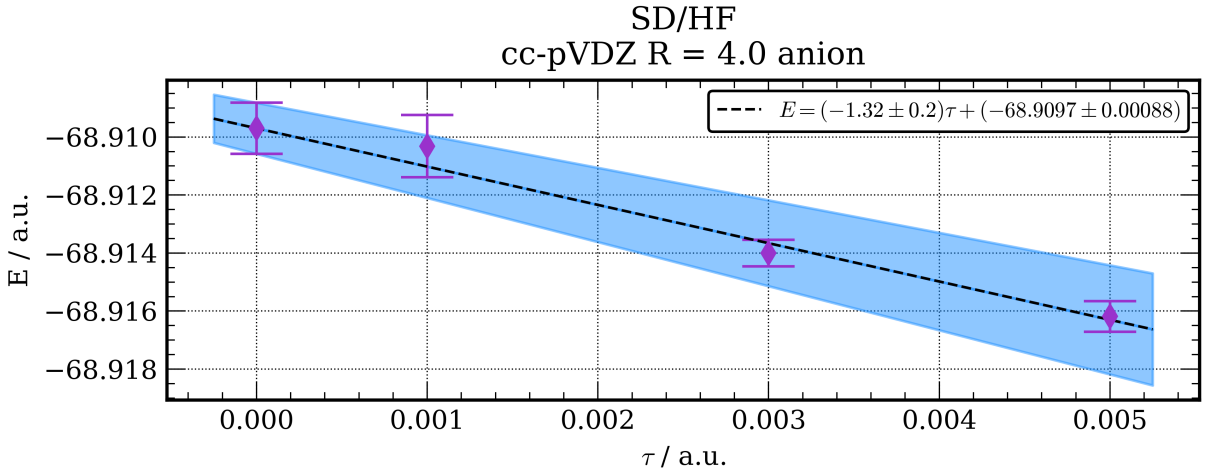

SD/HF
aug-cc-pVDZ+7s7p large ts R = 4.0 EBE
EBE / meV
180
170
160
150
0.000
0.025
0.050
0.075
0.100
0.125
0.150
0.175
0.200
τ / a.u.

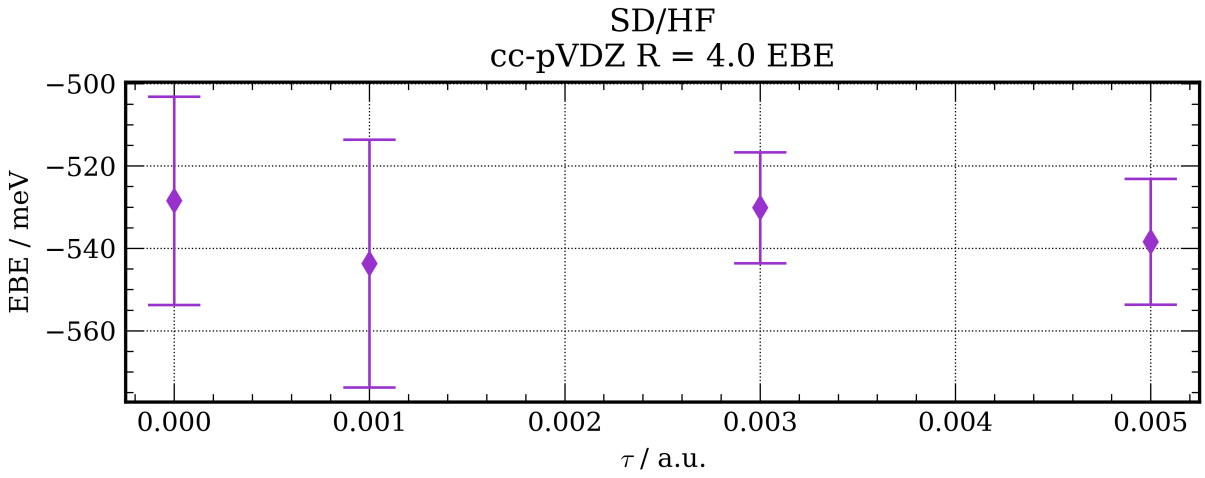

SD/HF
aug-cc-pVDZ R = 4.0 neutral
$E = (-0.743 \pm 0.073)\tau + (-68.9466 \pm 0.00026)$
E / a.u.
−68.946
−68.947
−68.948
−68.949
−68.950
−68.951
0.000
0.001
0.002
0.003
0.004
0.005
τ / a.u.

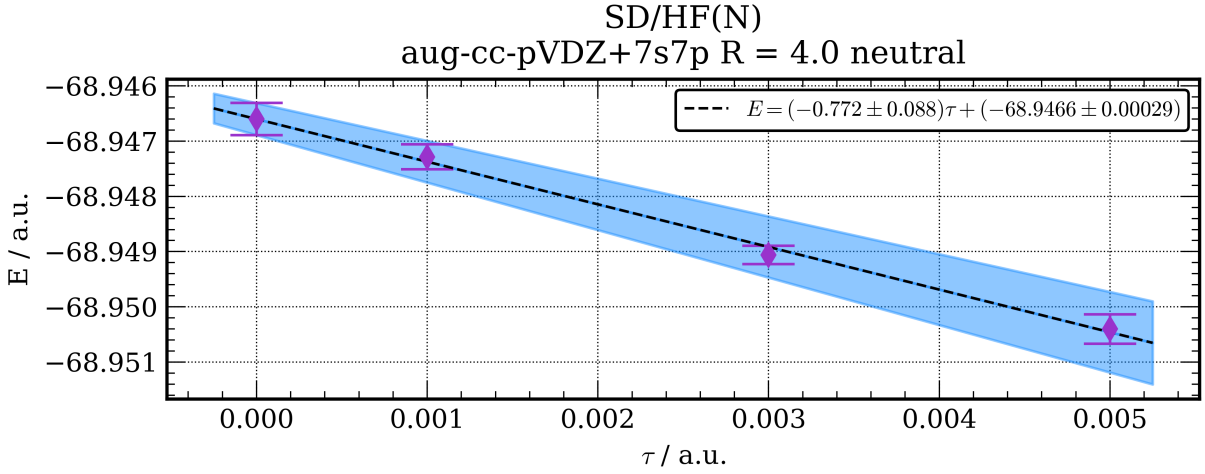

SD/HF
aug-cc-pVDZ R = 4.0 anion
$E = (-0.89 \pm 0.11)\tau + (-68.95305 \pm 0.00035)$
E / a.u.
−68.954
−68.956
−68.958
0.000
0.001
0.002
0.003
0.004
0.005
τ / a.u.

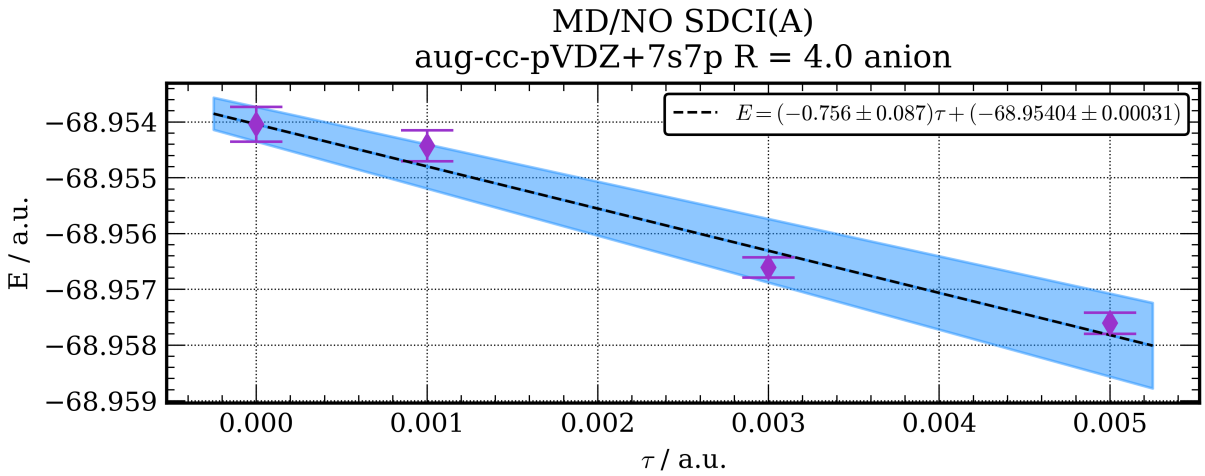

SD/HF
aug-cc-pVDZ R = 4.0 EBE
EBE / meV
200
190
180
170
0.000
0.001
0.002
0.003
0.004
0.005
τ / a.u.

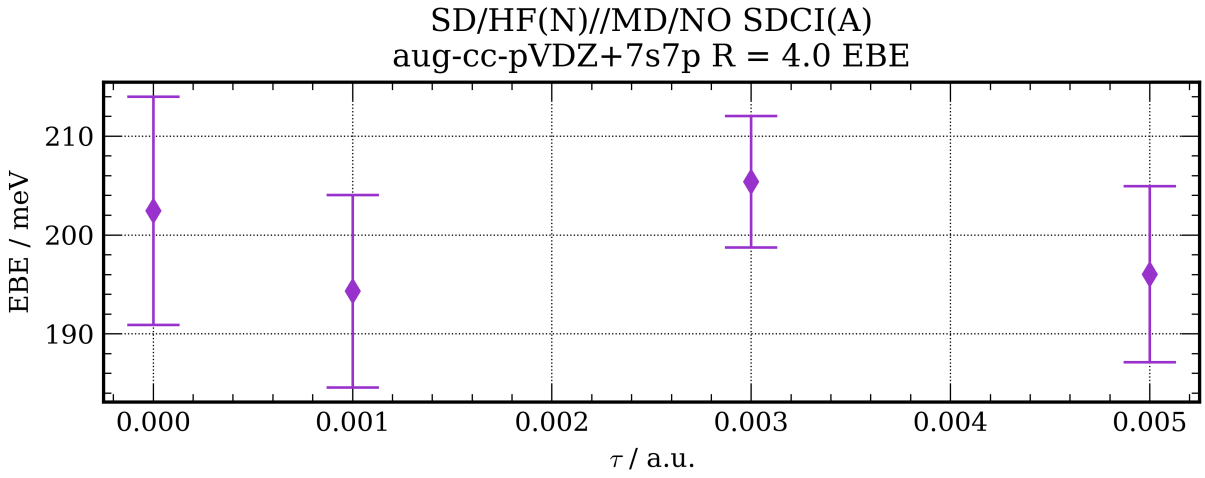

SD/HF
cc-pVDZ R = 4.0 neutral
$E = (-1.37 \pm 0.075)\tau + (-68.92912 \pm 0.0003)$
E / a.u.
−68.930
−68.932
−68.934
−68.936
0.000
0.001
0.002
0.003
0.004
0.005
τ / a.u.

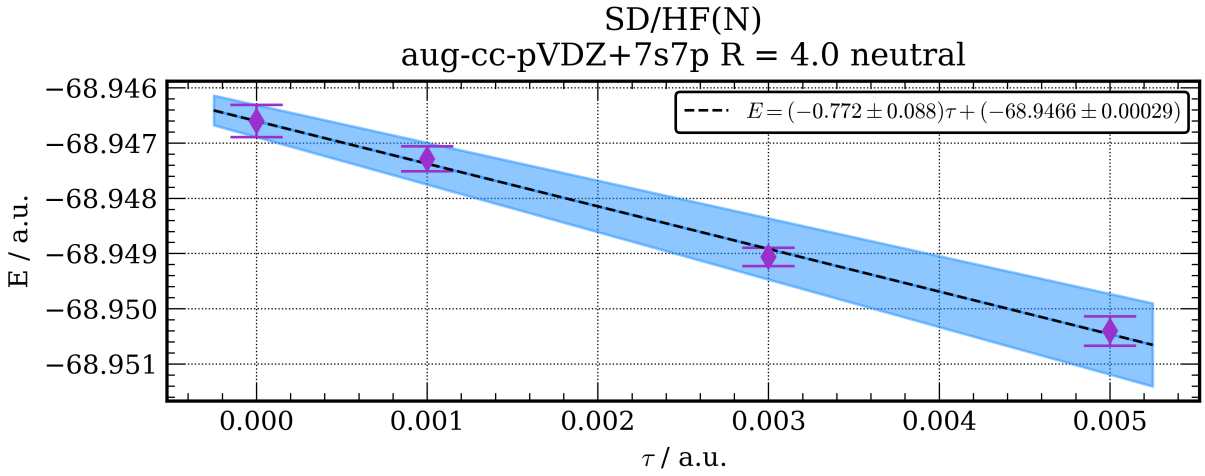

SD/HF
cc-pVDZ R = 4.0 anion
$E = (-1.32 \pm 0.2)\tau + (-68.9097 \pm 0.00088)$
E / a.u.
−68.910
−68.912
−68.914
−68.916
−68.918
0.000
0.001
0.002
0.003
0.004
0.005
τ / a.u.

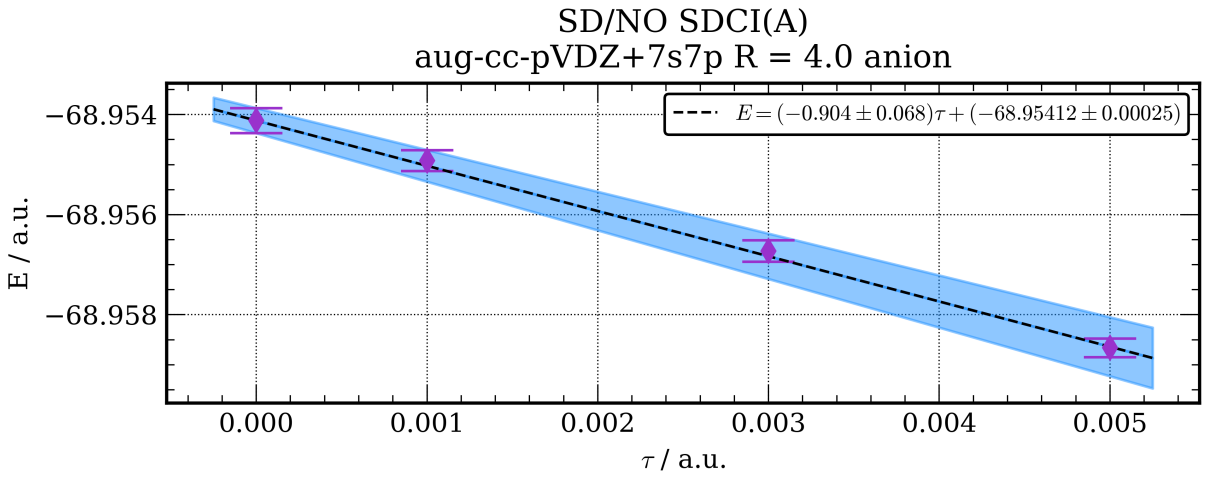

SD/HF
cc-pVDZ R = 4.0 EBE
EBE / meV
−500
−520
−540
−560
0.000
0.001
0.002
0.003
0.004
0.005
τ / a.u.

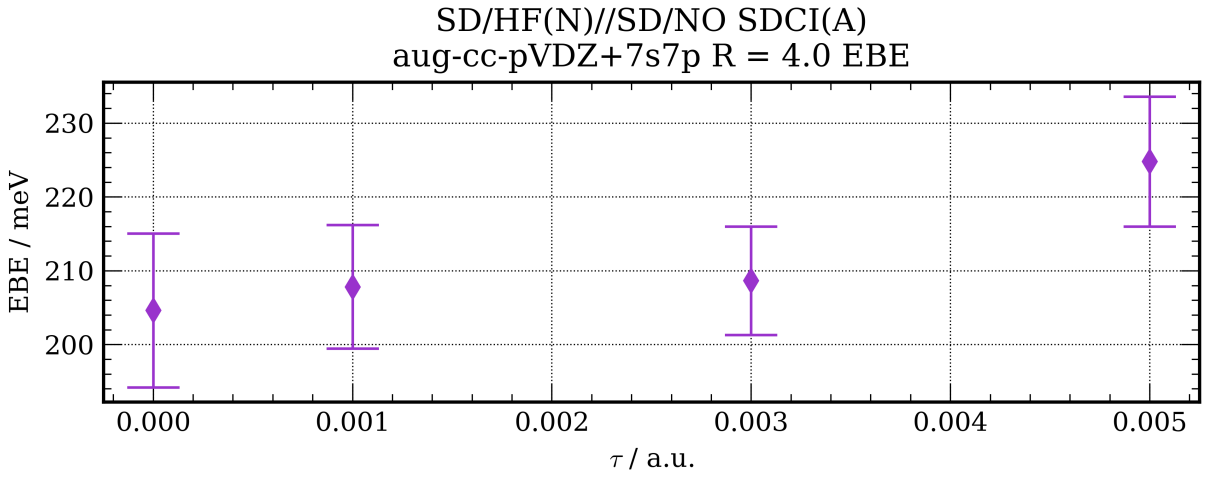

SD/HF(N)
aug-cc-pVDZ+7s7p R = 4.0 neutral
$E = (-0.772 \pm 0.088)\tau + (-68.9466 \pm 0.00029)$
E / a.u.
−68.946
−68.947
−68.948
−68.949
−68.950
−68.951
0.000
0.001
0.002
0.003
0.004
0.005
τ / a.u.

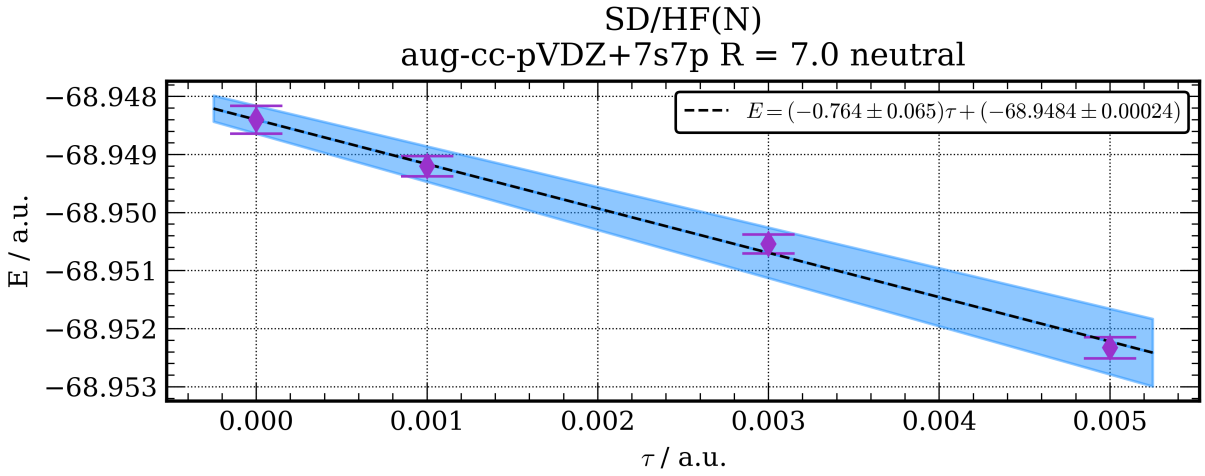

MD/NO SDCI(A)
aug-cc-pVDZ+7s7p R = 4.0 anion
$E = (-0.756 \pm 0.087)\tau + (-68.95404 \pm 0.00031)$
E / a.u.
−68.954
−68.955
−68.956
−68.957
−68.958
−68.959
0.000
0.001
0.002
0.003
0.004
0.005
τ / a.u.

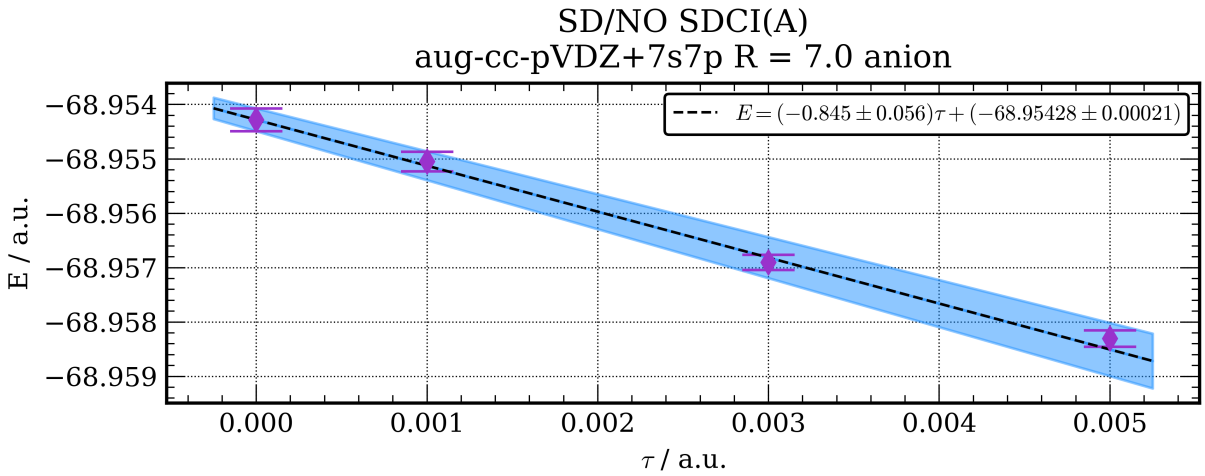

SD/HF(N)//MD/NO SDCI(A)
aug-cc-pVDZ+7s7p R = 4.0 EBE
EBE / meV
210
200
190
0.000
0.001
0.002
0.003
0.004
0.005
τ / a.u.

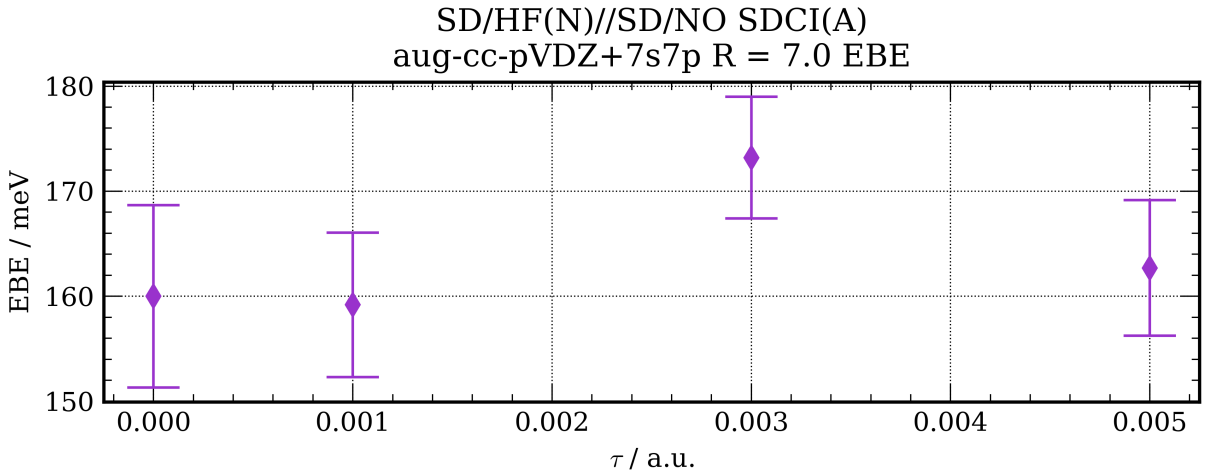

SD/HF(N)
aug-cc-pVDZ+7s7p R = 4.0 neutral
$E = (-0.772 \pm 0.088)\tau + (-68.9466 \pm 0.00029)$
E / a.u.
−68.946
−68.947
−68.948
−68.949
−68.950
−68.951
0.000
0.001
0.002
0.003
0.004
0.005
τ / a.u.


SD/NO SDCI(A)
aug-cc-pVDZ+7s7p R = 4.0 anion
$E = (-0.904 \pm 0.068)\tau + (-68.95412 \pm 0.00025)$
E / a.u.
−68.954
−68.956
−68.958
0.000
0.001
0.002
0.003
0.004
0.005
τ / a.u.


SD/HF(N)//SD/NO SDCI(A)
aug-cc-pVDZ+7s7p R = 4.0 EBE
EBE / meV
230
220
210
200
0.000
0.001
0.002
0.003
0.004
0.005
τ / a.u.


SD/HF(N)
aug-cc-pVDZ+7s7p R = 7.0 neutral
$E = (-0.764 \pm 0.065)\tau + (-68.9484 \pm 0.00024)$
E / a.u.
−68.948
−68.949
−68.950
−68.951
−68.952
−68.953
0.000
0.001
0.002
0.003
0.004
0.005
τ / a.u.


SD/NO SDCI(A)
aug-cc-pVDZ+7s7p R = 7.0 anion
$E = (-0.845 \pm 0.056)\tau + (-68.95428 \pm 0.00021)$
E / a.u.
−68.954
−68.955
−68.956
−68.957
−68.958
−68.959
0.000
0.001
0.002
0.003
0.004
0.005
τ / a.u.


SD/HF(N)//SD/NO SDCI(A)
aug-cc-pVDZ+7s7p R = 7.0 EBE
EBE / meV
180
170
160
150
0.000
0.001
0.002
0.003
0.004
0.005
τ / a.u.

4 Radial orbital density plots

The radial orbital density, $\psi^2(r)$, plots are created by integrating over angular portion of the norm of the single particle wave function.

$$\psi^2(r) = \int_0^{2\pi} \int_0^{\pi} \psi^2(r, \theta, \phi) r^2 \sin(\theta) dr d\theta d\phi \tag{1}$$

Discretizing this expression using a uniform radial grid and a Lebedev-Laikov quadrature for the angular components, yields a form that can be readily evaluated.

$$\psi^2(r_i) = 4\pi r_i^2 \sum_j^{N^{ang}} w_j^{ang} \psi^2(r_i, \theta_j, \phi_j) \tag{2}$$

The function $\psi^2(r_i)$ from Equation 2 can be plotted with the points r_i serving as the abscissa. Since the singly occupied orbitals are normalized, the proximity of the sum of the radial quadrature to unity is used as a check.

$$\sum_i^{N^{rad}} \psi^2(r_i) w_i^{rad} = \sum_i^{N^{rad}} \psi^2(r_i) \Delta r \approx 1 \tag{3}$$

4.a Required software versions

Required software	version
`numpy`	1.18.4
`quadpy`	0.16.2
`pyscf`	1.7.0
`cclib`	1.6.3

4.b Step 1: Generating a Molden file

Molden files were generated using `cclib`, with the exception of the natural orbital from the CIPSI calculations. Since QuantumPackage is not supported by `cclib`, Molden files were created using the native utility in QuantumPackage 2.0. For the Molden files generated

with cclib, the `-g/--ghost` flag indicates the presence of a ghost atom. By default the only molecular orbitals can be written to a Molden file, therefore the `-n/--naturalorbtials` flag was created to allow natural orbitals to be written in place of molecular orbitals. This flag is not yet available in the official distribution, but a request to incorporate it in the official distribution has been opened (`https://github.com/cclib/cclib/pull/948`).

```
$ ccwrite molden -g "X" -n QUANTUM_CHEMISTRY_OUTPUT_FILE
```

4.c Step 2: Integrating over the angular components of the singly occupied orbital

`quadpy` was used to generate the Lebedev-Laikov integration weights and points. The singly occupied molecular/natural orbital was evaluated at these points using `PySCF`.

```
import numpy
import quadpy
import pyscf
import pyscf.tools

filename = "FILENAME.molden"
r_max = 100
num_radial_pts = 1000
mo_idx = 20
# use pyscf to load the molden
mol, mo_energy, mo_coeff, mo_occ, irrep_labels, spins = pyscf.tools.molden.load(
    filename
)
# extract the singly occupied orbital coefficients
singly_occ_orb = mo_coeff[:, mo_idx]
# generate the angular points and weights using quadpy
```

```
lebedev_laikov = quadpy.u3.schemes["lebedev_131"]()
angular_pts = lebedev_laikov.theta_phi
angular_weights = lebedev_laikov.weights
num_angular_pts = len(angular_pts[0])
# generate the radial points and weights using numpy
radial_pts = numpy.linspace(r_max, 0, num_radial_pts, endpoint=False)[::-1]
radial_weights = numpy.ones_like(radial_pts) * (radial_pts[1] - radial_pts[0])
# a helper function to convert radial and angular points to cartesian
def sph2cart(r, theta_phi):
    theta = theta_phi[0]
    phi = theta_phi[1]
    x = r * numpy.cos(theta) * numpy.sin(phi)
    y = r * numpy.sin(theta) * numpy.sin(phi)
    z = r * numpy.cos(phi)
    return numpy.vstack((x, y, z)).T
# integrate over the angular points for each radial point
values = []
for r in radial_pts:
    r_pts = r * numpy.ones(num_angular_pts)
    coords = sph2cart(r_pts, angular_pts)
    ao = mol.eval_gto("GTOval_cart", coords)
    value = angular_weights @ ao @ singly_occ_orb
    values.append(4 * numpy.pi * r * r * value ** 2)
# output the values
values = numpy.array(values)
numpy.savetxt("{}_values.txt".format(filename), values)
numpy.savetxt("{}_r.txt".format(filename), radial_pts)
```

```
# check the norm of the orbital
print(radial_weights @ values)
```