Extension of frozen natural orbital approximation to open-shell references: Theory, implementation, and application to single-molecule magnets

Pavel Pokhilko[a], Daniil Izmodenov[a,b], and Anna I. Krylov[a]

[a] Department of Chemistry, University of Southern California, Los Angeles, California 90089-0482

[b] Department of Chemistry, Lomonosov Moscow State University, Moscow 119991, Russia

December 16, 2019

1 Additional FNO and OSFNO results

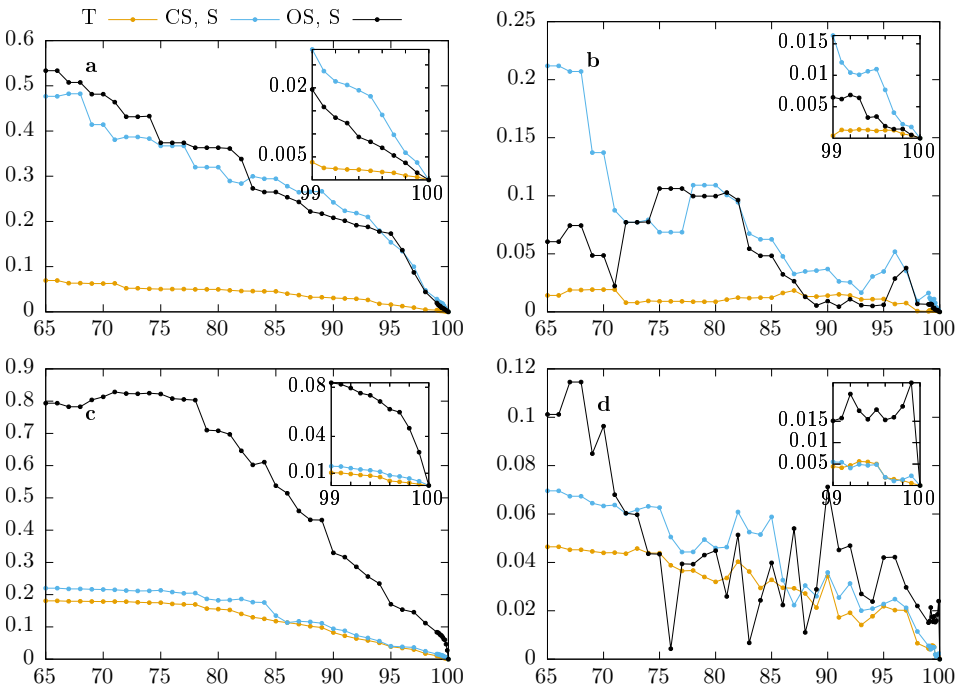

Figure S1: Statistical characteristics of the OSFNO approximation for EOM-SF-CCSD. The shown values are the errors in energy gaps (eV) between the reference CCSD state and the three target EOM-SF states ($M_S = 0$): triplet (T), closed-shell singlet (CS, S) and open-shell singlet (OS, S) with the cc-pVTZ basis set. Panels (a) and (b) show mean values and standard deviations for CH_2, SiH_2, NH_2^+, and PH_2^+. Panels (c) and (d) show the results for *ortho*-, *meta*-, and *para*-benzynes.

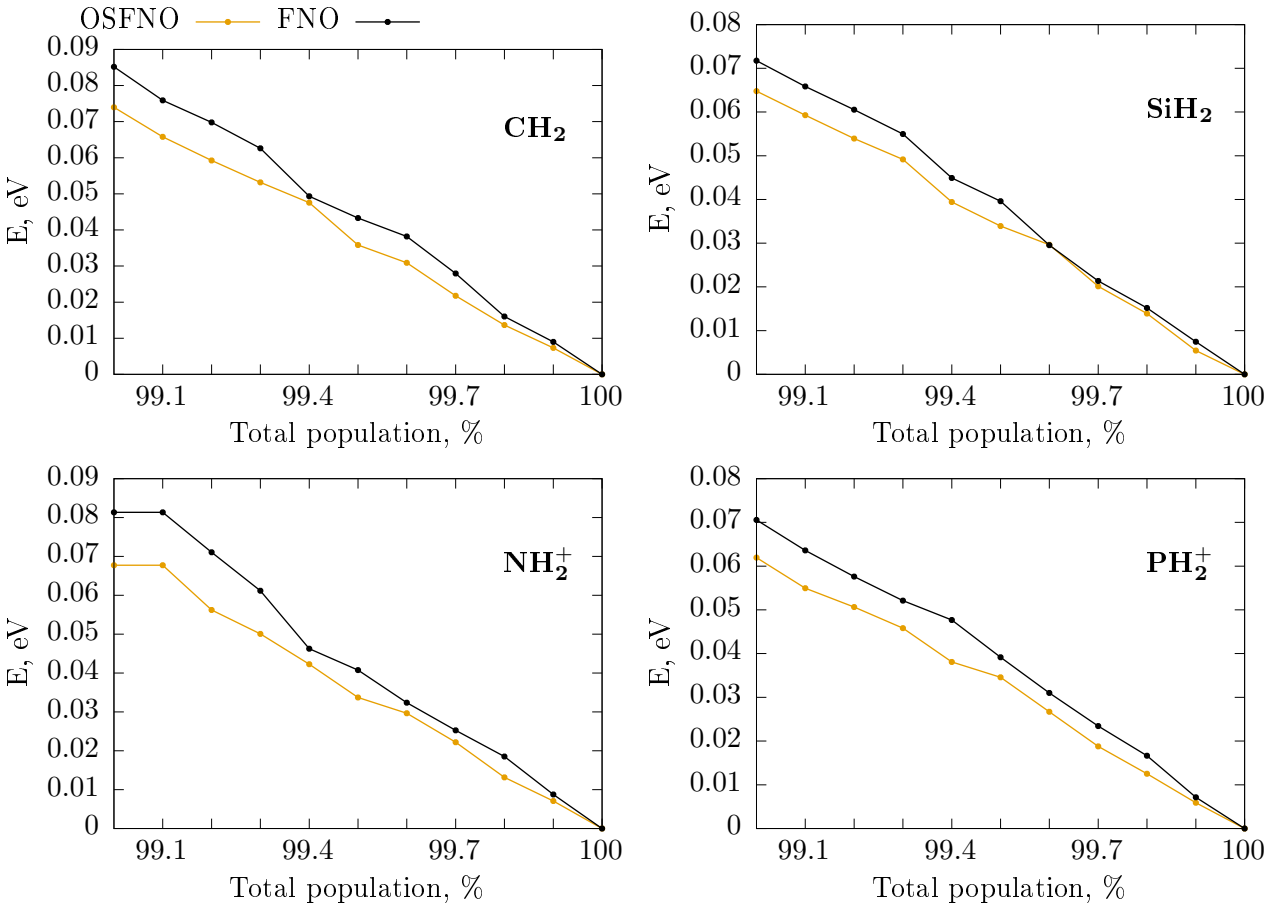

Figure S2: Errors in total energies of the high-spin reference state calculated using the original FNO and OSFNO schemes for CH_2, SiH_2, NH_2^+, and PH_2^+ with CCSD/cc-pVTZ.

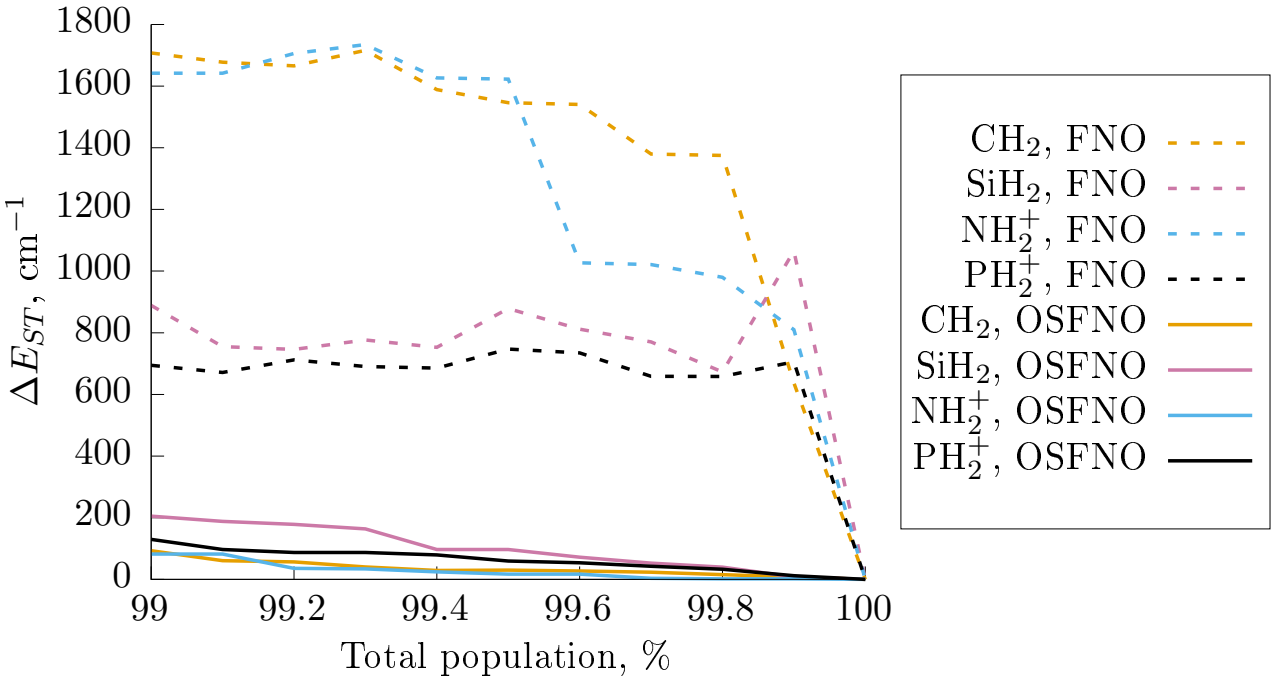

Figure S3: Errors in the energy gap between open-shell singlet and triplet states calculated using the original FNO and OSFNO schemes with EOM-SF-CCSD/cc-pVTZ.

2 Relevant Cartesian geometries

```
$comment
2-DMX
The quartet state is optimized with CCSD/cc-pVDZ
Nuclear Repulsion Energy = 306.66084559 hartrees
$end

$molecule
0 4
  H          2.1779993229    1.6126219346    0.0220094335
  C          1.2316383235    1.0591102020    0.0170509023
  C          0.0067407068    1.7449750260    0.0232715697
  C         -1.2218068005    1.0657498072    0.0172414394
  H         -2.1651940217    1.6243154403    0.0223406129
  C         -1.2697547499   -0.3837381005    0.0041875309
  C         -0.0007117314   -1.0178133387   -0.0015490490
  C          1.2717398995   -0.3905766458    0.0039764389
  C          2.4834586177   -1.1052465217   -0.0026169423
  C         -2.4853377419   -1.0917894515   -0.0022303563
  H          2.4896680064   -2.1991429278   -0.0125192653
  H          3.4421181549   -0.5764388687    0.0020686734
  H         -2.4975169877   -2.1856368798   -0.0121519881
  H         -3.4411032659   -0.5577713316    0.0025807846
```

```
  H          0.0097060682    2.8409134546    0.0330871775
$end

$comment
5-DMX
The quartet state is optimized with CCSD/cc-pVDZ
Nuclear Repulsion Energy = 308.26134251 hartrees
$end

$molecule
0 4
 H          2.1787597750    1.7307689406    0.0023968634
 C          1.2380017709    1.1699498565    0.0019847041
 C          0.0000546892    1.7926615226    0.0038293650
 C         -1.2379475829    1.1700256439    0.0033293323
 H         -2.1786628337    1.7309114321    0.0048874326
 C         -1.2551488653   -0.2801695418    0.0006282192
 C         -0.0000414472   -0.9630803594   -0.0012762989
 H         -0.0000720323   -2.0597600167   -0.0033445618
 C          1.2551272622   -0.2802577900   -0.0005802981
 C          2.4763594548   -0.9889377656   -0.0022116137
 C         -2.4764396979   -0.9887718906   -0.0001269957
 H          2.4898330646   -2.0837945681   -0.0041277531
 H          3.4345798928   -0.4596458546   -0.0016942084
 H         -3.4346164231   -0.4594059385    0.0014919777
 H         -2.4899798840   -2.0836264692   -0.0023117943
$end

$comment
CUAQAC02
The triplet state is optimized with wB97X-D/cc-pVTZ
Nuclear Repulsion Energy = 3174.87801338 hartrees
$end

$molecule
0 3
 Cu        -0.4475643610   -0.0120963053   -1.2187131839
 C         -1.5516738597   -1.9174459710    0.6216855123
 C         -2.4404422951   -3.0767823055    0.9891436674
 C          1.7884683766   -1.6766996168   -0.6862923408
 C          2.8741200254   -2.6422066929   -1.0840583784
 H         -1.8293382510   -3.9790509196    1.0248530293
 H         -3.2258364073   -3.2142752931    0.2520287447
 H         -2.8627428887   -2.9234745771    1.9793067222
 H          2.9887046283   -3.4087941897   -0.3208559893
 H          2.6596867698   -3.0896360878   -2.0494344473
 H          3.8148426588   -2.0943168142   -1.1445126369
```

```
 H        -2.3601778555    0.6855733244   -2.7932158752
 H        -2.2881709015   -0.8355308500   -2.8370271162
 O        -1.6039546736   -1.4940498512   -0.5633853188
 O         0.8033864073    1.4688139814   -1.5261581319
 O         0.9814838837   -1.3115042001   -1.5765454220
 O        -1.7814477378    1.2892257086   -0.5128288755
 O        -1.7940678183   -0.0428536234   -3.0630837058
 Cu        0.4475643610    0.0120963053    1.2187131839
 O        -0.8033864073   -1.4688139814    1.5261581319
 C         1.5516738597    1.9174459710   -0.6216855123
 O         1.7814477378   -1.2892257086    0.5128288755
 C        -1.7884683766    1.6766996168    0.6862923408
 O         1.6039546736    1.4940498512    0.5633853188
 O        -0.9814838837    1.3115042001    1.5765454220
 O         1.7940678183    0.0428536234    3.0630837058
 C         2.4404422951    3.0767823055   -0.9891436674
 C        -2.8741200254    2.6422066929    1.0840583784
 H         2.3601778555   -0.6855733244    2.7932158752
 H         2.2881709015    0.8355308500    2.8370271162
 H         1.8293382510    3.9790509196   -1.0248530293
 H         3.2258364073    3.2142752931   -0.2520287447
 H         2.8627428887    2.9234745771   -1.9793067222
 H        -2.9887046283    3.4087941897    0.3208559893
 H        -2.6596867698    3.0896360878    2.0494344473
 H        -3.8148426588    2.0943168142    1.1445126369
$end

$comment
Ground-state formaldehyde geometry,
optimized with CCSD/cc-pVDZ
Nuclear Repulsion Energy = 31.09707922 hartrees
$end

$molecule
0 1
  C         0.0000000000    0.0000000000    0.5115557582
  O         0.0000000000    0.0000000000   -0.6987691962
  H         0.9441753015    0.0000000000    1.1099901293
  H        -0.9441753015    0.0000000000    1.1099901293
$end
```