

A Perturbative Approach to Multireference Equation-Of-Motion Coupled Cluster

Supplementary Material

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1 Explicit Equations for all Perturbative Amplitudes

In this section, we give explicit expressions for the amplitudes used in MR-EOMPT theory that were not fully described in the main article.

In the first similarity transformation of \hat{H} with the cluster operator \hat{T} , the t_{ab}^{ii} amplitudes are computed with the results of the EKT-IP calculation,

$$t_{ab}^{ii} = \sum_{\tilde{v}} c_{i\tilde{v}}^{\text{IP}} \frac{(\tilde{v}a | ib)}{\epsilon_{\tilde{v}}^{\text{IP}} + \epsilon_i - (\epsilon_a + \epsilon_b)}, \quad (1)$$

and the transformed integral being defined as

$$(\tilde{v}a | ib) = \sum_t c_{i\tilde{v}}^{\text{IP}} (ta | ib). \quad (2)$$

The \hat{X} and \hat{D} operators describe the spin-flip and spectator excitations, respectively. Hence, their estimates are effectively identical. They require both the EKT-EA and -IP results,

$$x_{au}^{ii} = d_{au}^{ii} = \sum_{\tilde{v}\tilde{w}} c_{i\tilde{v}}^{\text{IP}} c_{u\tilde{w}}^{\text{EA}} \frac{(\tilde{v}a | i\tilde{w})}{\epsilon_{\tilde{v}}^{\text{IP}} + \epsilon_i - (\epsilon_a + \epsilon_{\tilde{w}}^{\text{EA}})}, \quad (3)$$

And the transformed integrals are defined as

$$(\tilde{v}a | i\tilde{w}) = \sum_{tu} c_{i\tilde{v}}^{\text{IP}} c_{u\tilde{w}}^{\text{EA}} (ta | iu). \quad (4)$$

2 Total Energies for the Diatomic Systems

Table 1: Total energies for all the states of the diatomic test systems (E_h).

| | State | ICE-FCI | CASSCF | NEVPT2 | MR-EOM | |
|-----------------|-----------------|-------------|-------------|-------------|-------------|-------------|
| | | | | | -PT | -CC |
| CH | $^2\Pi$ | -38.341204 | -38.262875 | -38.324470 | -38.333238 | -38.340435 |
| | $^2\Delta$ | -38.229473 | -38.148534 | -38.213131 | -38.222298 | -38.228601 |
| | $^2\Sigma^-$ | -38.216293 | -38.141776 | -38.200474 | -38.209134 | -38.216941 |
| | $^2\Sigma^+$ | -38.188757 | -38.111817 | -38.170641 | -38.177167 | -38.182974 |
| CN | $^2\Sigma^+$ | -92.411165 | -92.256484 | -92.387161 | -92.397334 | -92.406678 |
| | $^2\Pi$ | -92.357545 | -92.199593 | -92.332711 | -92.341581 | -92.352792 |
| | $2\ ^2\Sigma^+$ | -92.299721 | -92.142378 | -92.274137 | -92.283921 | -92.294449 |
| CO | $^1\Sigma^+$ | -112.956081 | -112.757326 | -112.928519 | -112.938722 | -112.948687 |
| | $^1\Pi$ | -112.633516 | -112.417543 | -112.603116 | -112.615749 | -112.630480 |
| | $^1\Sigma^-$ | -112.577475 | -112.373032 | -112.547200 | -112.557868 | -112.570080 |
| | $^1\Delta$ | -112.573236 | -112.371343 | -112.543189 | -112.553937 | -112.566753 |
| | $^3\Pi$ | -112.723349 | -112.517232 | -112.694774 | -112.706374 | -112.718998 |
| | $^3\Sigma^+$ | -112.639166 | -112.436013 | -112.608350 | -112.616281 | -112.627272 |
| | $^3\Delta$ | -112.605164 | -112.401214 | -112.574667 | -112.583921 | -112.595651 |
| | $^3\Sigma^-$ | -112.587212 | -112.386993 | -112.556752 | -112.566144 | -112.578439 |
| CO ⁺ | $^2\Sigma^+$ | -112.457861 | -112.306248 | -112.435987 | -112.454541 | -112.454541 |
| | $^2\Pi$ | -112.326110 | -112.165787 | -112.302484 | -112.322395 | -112.322395 |
| | $2\ ^2\Sigma^+$ | -112.243498 | -112.080508 | -112.218682 | -112.239518 | -112.239518 |
| N ₂ | $^1\Sigma^+$ | -109.180593 | -108.987865 | -109.152424 | -109.164935 | -109.178091 |
| | $^1\Pi$ | -108.826143 | -108.617307 | -108.795425 | -108.808434 | -108.821585 |
| | $^1\Sigma^-$ | -108.797986 | -108.588103 | -108.766897 | -108.781815 | -108.795314 |
| | $^1\Delta$ | -108.783765 | -108.576669 | -108.752244 | -108.765952 | -108.779008 |
| | $^3\Sigma^+$ | -108.888730 | -108.690236 | -108.858394 | -108.869729 | -108.883982 |
| | $^3\Pi$ | -108.877161 | -108.666838 | -108.847484 | -108.858646 | -108.870944 |
| | $^3\Delta$ | -108.840258 | -108.635921 | -108.809593 | -108.822670 | -108.836396 |
| | $^3\Sigma^-$ | -108.811041 | -108.610542 | -108.779487 | -108.791419 | -108.804613 |
| O ₂ | $^1\Delta$ | -149.813573 | -149.540200 | -149.776548 | -149.791507 | -149.809050 |
| | $^1\Sigma^+$ | -149.789449 | -149.520996 | -149.752842 | -149.766966 | -149.785038 |
| | $^3\Sigma^+$ | -149.852988 | -149.575157 | -149.814595 | -149.829455 | -149.846299 |
| | $^3\Delta$ | -149.619889 | -149.349011 | -149.581360 | -149.596704 | -149.615225 |
| OH | $^2\Pi$ | -75.492499 | -75.344410 | -75.471198 | -75.479295 | -75.490188 |
| | $^2\Sigma^+$ | -75.334985 | -75.174579 | -75.312906 | -75.322854 | -75.335956 |

3 Summary of Active Spaces

Table 2: Summary of the active spaces (all calculations) and reference states for the MR-EOMCC and MR-EOMPT calculations. In this condensed notation, “Mult. 4,2 Roots 1,2” would be interpreted as a single quartet and two doublet roots, for example.

| System | Active El. | Active Orb. | Mult. | Roots | Project singular? | Notes |
|--|------------|-------------|-------|-------|-------------------|--|
| <i>Diatomic Systems</i> | | | | | | |
| CH | 5 | 5 | 4,2 | 1,2 | Yes | Full valence |
| CN | 9 | 8 | 2 | 1 | Yes | Full valence |
| CO | 10 | 8 | 3 | 2 | Yes | Full valence |
| CO ⁺ | 9 | 8 | 2 | 4 | Yes | Full valence |
| N ₂ | 10 | 8 | 3 | 1 | Yes | Full valence |
| O ₂ | 12 | 8 | 3 | 3 | No | Full valence |
| OH | 7 | 5 | 2 | 2 | Yes | Full valence |
| <i>Selected Systems from Thiel Benchmark</i> | | | | | | |
| Cyclopropene | 4 | 3 | 3 | 2 | No | |
| Ethene | 2 | 2 | 3,1 | 1,2 | No | pi-system |
| Butadiene | 4 | 4 | 3 | 2 | No | pi-system |
| Benzene | 6 | 6 | 3,1 | 3,2 | Yes | pi-system, Stol 8e-5 |
| Pyrrrole | 6 | 5 | 3,1 | 2,1 | Yes | pi-system, Stol 3e-5 |
| <i>Example Systems</i> | | | | | | |
| LiF | 2 | 2 | 1 | 2 | Yes | Li 2s + F p _z |
| CH ₂ S/T Splitting | 6 | 6 | 3 | 1 | Yes | SA-CASSCF not possible b/c different geometries |
| CH ₂ S/T Splitting | 6 | 6 | 1 | 1 | Yes | |
| SiH ₂ S/T Splitting | 6 | 6 | 3 | 1 | Yes | SA-CASSCF not possible b/c different geometries |
| SiH ₂ S/T Splitting | 6 | 6 | 1 | 1 | Yes | |
| Co | 9 | 6 | 4 | 14 | No | |
| Cr | 6 | 6 | 7,5 | 1,6 | Yes | 50% weight on S states, 50% weight on five roots for D state |
| <i>Comparison with LR-ic-MRCCSD</i> | | | | | | |
| CH ₂ | 6 | 6 | 1 | 7 | Yes | Full valence |
| Hexatriene | 6 | 6 | 1 | 3 | Yes | pi-system |

4 Methylene

The geometry of this test system for comparison to the LR-ic-MRCC method has already been published in Refs. [1,2]. Note that the distances are given in Bohr radii a_0 , and not in Ångstrom. The basis set is a slightly augmented variant of the cc-pVDZ [3] basis, with an *s*-function added each to carbon and hydrogen with exponents of 0.015 and 0.025, respectively. For ORCA, the input is:

```

! cc-pVDZ Bohrs [...]

%basis
AddGTO C
  s 1
  1 0.015 1.0
end
AddGTO H
  s 1
  1 0.025 1.0
end
end

[...] method settings ...

* xyz 0 1
C    0.0    0.0    0.0
H    0.0    1.644403  1.32213
H    0.0   -1.644403  1.32213
*

```

In total, this system has 8 electrons and 27 orbitals, which generally allows FCI calculations to be performed on single servers given a recent CPU and sufficient RAM.

5 References

- [1] Henrik Koch, Ove Christiansen, Poul Jørgensen, and Jeppe Olsen, *Chem. Phys. Lett.* **244** (1-2), 75 (1995).
- [2] Pradipta Kumar Samanta, Debashis Mukherjee, Matthias Hanauer, and Andreas Köhn, *J. Chem. Phys.* **140** (13), 134108 (2014).
- [3] Thom H. Dunning, *J. Chem. Phys.* **90** (2), 1007 (1989).