A many-body method without strong correlation?

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In this talk, I will revisit the orbital optimized MP2 method (OO-MP2), by introducing an energy-dependent regularization [1] that removes all strong correlation associated with small energy gaps. I will discuss the motivation, formulation, and implementation of this 1-parameter semi-empirical modification to OO-MP2. This new regularization provides some important benefits.

(i) Energy-dependent regularization restores Coulson-Fischer (CF) points that are otherwise lost in OO-MP2. The presence of a CF point is crucial so that a theory that does not accurately describe strong correlation can break symmetry when such correlations are present. Relative to Hartree-Fock (HF), conventional OO-MP2 in fact provides false symmetry restoration, as a result of strongly overestimating strong correlations with restricted orbitals.

(ii) A reasonable choice of the regularizer parameter statistically improves the accuracy of OO-MP2. This is further evidence that having no treatment of strong correlations is, in fact, preferable, to the usual situation of including a poor treatment of strong correlation. The resulting orbitals are also very useful in general: they are self-interaction free, and also free from artificial symmetry breaking. I will discuss their use to dramatically improve the accuracy of MP3 [2].

(iii) Symmetry breaking in regularized OO-MP2 is a diagnostic for the presence of strong correlations [3]. This contrasts with HF, where symmetry-breaking quite often is better classified as artificial, and associated with the neglect of all correlation, rather than the neglect of strong correlation. When using a theory that cannot describe strong correlations, the ability to have simple internal diagnostics for when they may break down is highly desirable. Beyond diagnostics, I will also discuss how biradicaloid strongly correlated electron problems can be treated by regularized OO-MP2 [4].

[1] "Regularized Orbital-Optimized Second-Order Møller-Plesset Perturbation Theory: A Reliable Fifth-Order Scaling Electron Correlation Model with Orbital Energy Dependent Regularizers", J. Lee and M. Head-Gordon, J. Chem. Theory Comput. 14, 5203-5219 (2018).

[2] "Third-Order Møller-Plesset Perturbation Theory Made Useful? Choice of Orbitals and Scaling Greatly Improves Accuracy for Thermochemistry, Kinetics and Intermolecular Interactions", L.W. Bertels, J. Lee, and M. Head-Gordon, J. Phys. Chem. Lett. 10, 4170−4176 (2019).

[3] "Distinguishing Artificial and Essential Symmetry Breaking in a Single Determinant: Approach and Application to the C60, C36, and C20 Fullerenes", J. Lee and M. Head-Gordon, Phys. Chem. Chem. Phys. 21, 4763-4778 (2019).

[4] "Two Single-Reference Approaches to Singlet Biradicaloid Problems: Complex, Restricted Orbitals and Approximate Spin-Projection Combined With Regularized Orbital-Optimized Møller-Plesset Perturbation Theory", J. Lee and M. Head-Gordon, J. Chem. Phys. 150, 244106 (2019).