Extended Second-Order Møller-Plesset Perturbation Theory

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Introduction

An efficient yet accurate treatment of both dynamical and static electron correlation effects has been elusive in electronic structure theory. Single reference methods such as second-order Møller-Plesset perturbation theory (MP2) and coupled-cluster singles and doubles have enjoyed their high accuracy in computed observables for non-degenerate systems, but it is well known that they cannot describe static correlation in degenerate systems. This failure is undoubtedly attributed by the reference wave function: Hartree-Fock (HF). A HF reference is qualitatively inadequate for (nearly-) degenerate systems where the true wave function is multi-determinantal in nature. Complete active space self-consistent field resolves this problem by treating all the configurations in an active space yielding a multi-reference state, and usually represents a good starting point when an appropriate active space is chosen. When the residual dynamical correlation is included through a perturbative correction (CASPT2) or configuration interaction (CI), it can achieve very accurate results both for the ground state and excited states. However, none of these are a black-box treatment, and their computational costs are very expensive. Especially, CASPT2 notoriously suffers from the intruder-state problem.

To tackle the aforementioned problem, spin-projected HF (PHF) has been recently revived by Scuseria as an alternative candidate for describing degenerate systems.[1] It handles the essential static correlation in a *black-box* manner. It was however shown to vastly underestimate dynamical correlation, which is necessary for quantitative accuracy. To capture the "residual" dynamical correlation in PHF, there has been extensive research along this line; among them are the non-orthogonal CI approach [2] and inclusion of DFT correlation.[3] In this talk, we will adopt MP2 to PHF in order to achieve a balanced description of both dynamical and static correlation effects. We will show that, with an appropriate perturbative correction, molecular potential energy curves and singlet-triplet splitting energies can be drastically improved over PHF.

Theory

In PHF, one uses a projected determinant as an ansatz, $\hat{P}|\Phi\rangle$, and finds a suitable set of orbitals, $\{\phi_i\}$, by minimizing the PHF energy:

$$E_{\mathrm{PHF}} = \frac{\langle\Phi|\hat{P}^\dagger\hat{H}\hat{P}|\Phi\rangle}{\langle\Phi|\hat{P}^\dagger\hat{P}|\Phi\rangle} = \frac{\langle\Phi|\hat{H}\hat{P}|\Phi\rangle}{\langle\Phi|\hat{P}|\Phi\rangle}.$$

Expanding the projected Schrödinger equation,

$$\hat{H}\hat{P}|\Psi\rangle = E\hat{P}|\Psi\rangle,$$

around the PHF wave function, we find the second order energy of extended MP2 (EMP2),

$$E_2 = \frac{1}{4} \sum_{ijab} t_{ij}^{ab} \frac{\langle \Phi |(\hat{H} - E_{\text{PHF}})\hat{P}|\Phi_{ij}^{ab}\rangle}{\langle \Phi |\hat{P}|\Phi\rangle}.$$

Each term could be straightforwardly evaluated by using generalized Wick's theorem but with an intractable computational scaling of $O(N^8)$. In the talk, we will a show how this can be scaled down to $O(N^5)$.

Results

We have implemented PHF and EMP2 in our in-house quantum chemistry program package. EMP2 is tested against full-CI for the dissociation curves of the H_2 and FH molecules (Figures) as well as the singlet-triplet splitting energies (Tables), showing a promising performance compared to the conventional methods. We will also report the results on excited states.
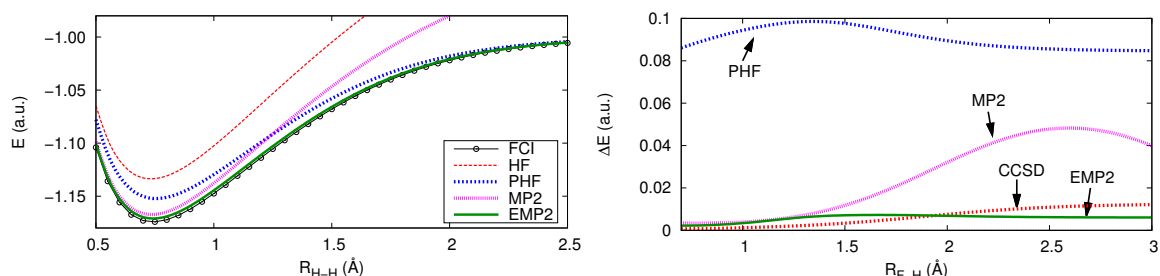

Figure: (*Left*) Potential energy curves of H_2 with cc-pV5Z. (*Right*) Energy errors from FCI for FH with 6-31G.

	PHF	EMP2	PHF+E_c^{DFT}[3]	MP2	CCSD	Expl.
C	23.1	30.1	31.1	44.8	35.7	29.0
O	39.2	46.3	41.0	66.6	55.9	45.3
Si	9.2	17.9	21.9	29.9	22.7	17.3
MAE	**6.7**	**0.9**	**3.7**	**16.6**	**7.6**	

	PHF	EMP2	MP2	CCSD	FCI
NH	49.6	45.5	58.1	50.9	45.5
OH$^-$	62.6	58.1	74.8	64.5	58.3
O$_2$	36.0	28.8	30.8	32.7	25.5
NF	47.9	40.2	50.7	48.5	40.9
MAE	**6.4**	**1.1**	**11.0**	**6.6**	

Table: (*Top*) Singlet-triplet splitting energies for atoms with cc-pVTZ (kcal/mol). (*Bottom*) Diatomic molecules with 6-31G (kcal/mol).

Acknowledgments

[1] C. A. Jiménez-Hoyoz, T. M. Henderson, T. Tsuchimochi, and G. E. Scuseria, *J. Chem. Phys.* **136**, 164109 (2012).
[2] R. Rodríguez-Guzmán, C. A. Jiménez-Hoyoz, R. Schutski, and G. E. Scuseria, *Phys. Rev. B* **87**, 235129 (2013).
[3] A. J. Garza, C. A. Jiménez-Hoyoz, and G. E. Scuseria, *J. Chem. Phys.* **138**, 134102 (2013); A. J. Garza, C. A. Jiménez-Hoyos, and G. E. Scuseria, *J. Chem. Phys.* **140**, 244102 (2014).