Formulation of partial triples to the electronic transition dipole moments within Fock-space multi-reference coupled cluster framework

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Abstract

Fock-space multi-reference coupled cluster method is well established to describe excited state molecular properties. In this framework, we have evaluated the electronic transition dipole moments, which depend on matrix elements between two different wave functions (e.g. ground to the excited states). We present two different ways to evaluate the transition moments. In one method, we have constructed the ground and excited state wave functions with the exponential ansatz of Fock-space coupled cluster theory. This is given by the following equation [1],

$$d_{pq} = \left[\langle \psi_{HF} | \Omega_{gr}^{\dagger} \hat{O} \left(\Omega_{ex} C_{\mu}^{(1,1)} \right) | \Phi^{(1,1)} \rangle \langle \Phi^{(1,1)} | \left(\tilde{C}_{\mu}^{(1,1)} \Omega_{ex}^{\dagger} \right) \hat{O} \Omega_{gr} | \psi_{HF} \rangle \right]^{1/2}$$

Computation of the relevant off-diagonal matrix elements from the above equation gives us the transition moment. In the second approach, we have linearized the exponential form of the wave operator by using Lagrange formulation. This gives us a linear left vector and an exponential right vector.

$$d_{pq} = \left[\langle \psi_{HF} | (1+\Lambda) \Omega_{gr}^{-1} \hat{O} \left(\Omega_{ex} C_{\mu}^{(1,1)} \right) | \Phi^{(1,1)} \rangle \langle \Phi^{(1,1)} | \tilde{C}_{\mu}^{(1,1)} \left(1+\tilde{\Lambda} \right) \Omega_{ex}^{-1} \hat{O} \Omega_{gr} | \psi_{HF} \rangle \right]^{1/2}$$

Where, $\tilde{\Lambda}$ contains the linearized left vectors of all the valence sectors [1]. The entire implementation has been done under the CCSD approximation. Transition moments and oscillator strengths of a few molecules are presented and compared with other available theoretical methods. We will be adding partial triples correction (corrected up to third order) to the above formulated transition dipole equations.

References:

[1] Bhattacharya, D., Vaval, N., Pal, S. *J. Chem. Phys.,* 138: 094108 (1-9), 2013