

Assessing the quality of new quantum chemical methods by comparison with Full CI exchange-correlation holes

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Although the electron density is a deceptively simple expectation value of the wave function, namely an expectation value over a Dirac delta function type operator, the catch lies in the wave function. Over roughly 100 years, people have been developing quantum chemical roads towards the wave function. More recently, other methods have become popular, including density functional theory (DFT) which avoids the wave function altogether as too complicated an object. However, the exact functional is not known and hence one has to use one of many Density Functional Approximations (DFA). Likewise, because the exact wave function is not (always) computationally tractable, density matrix functionals and direct density matrix optimization approaches continue to be developed.

When developing such new methods, it is very important to be able to examine their quality. This is often done using different observables, such as thermochemical data, but this is not always the optimal way. For instance, despite giving fairly good energies, variational optimization of the second order density matrix has been shown to be flawed when using the most common N-representability constraints [1].

I will present results on an original way to assess the quality of new quantum chemical methods by studying the exchange-correlation holes resulting from these methods versus that obtained using Full CI quality data for a set of atomic and diatomic systems [2]. It will be shown how this allows us to critically assess the quality of the method and thus the reliability. Moreover, exchange correlation holes are directly related to chemical bonding as its double integration is none other than the bond order between atoms [3].

1. Van Aggelen, H.; Bultinck, P.; Verstichel, B.; Van Neck, D.; Ayers, P. W., *Phys. Chem. Chem. Phys.*, 2009, 11, 5558 - 5560.
2. Van Aggelen, H.; Acke, G.; Ayers, P.W.; Bultinck, P.; Cardenas, C., in preparation.
3. Bultinck, P.; Cooper, D.L.; Ponec, R., *J. Phys. Chem. A*, 2010, 114, 8754 - 8763.