

Efficient corrections to strongly orthogonal geminals derived from the extended random phase approximation

Katarzyna Pernal¹

¹ Institute of Physics, Lodz University of Technology,
ul. Wolczanska 219, 90-924 Lodz, Poland

Predicting electronic structure of ground-state molecules is one of the main goals of quantum chemistry. Methods that are widely used are either limited by high computational costs and are applicable to relatively small systems or, like density functional approximations, they are efficient but suffer from generic problems. For example, most widely used density functionals are notorious for providing incorrect description of systems when static electron correlation or long-range dynamic correlation plays a role. Consequently, molecules with stretched bonds or van der Waals complexes are problematic for most density functionals.

Antisymmetrized product of strongly orthogonal geminal (APSG) theory has been proposed as computationally efficient method that allows one to take into account electron correlation and keep a clear chemical picture of bonds in molecules. It turns out, however, that APSG includes static correlation but it is deficient in capturing dynamic correlation. One of the consequences is that APSG fails for noncovalently bonded systems.

We propose a set of corrections to APSG that results in a size-extensive method that is computationally efficient and includes short- and long-range correlation effects. The corrections are derived from the recently proposed extended random phase approximation [1,2] and application of the fluctuation-dissipation theorem. The new method is applied to obtaining dissociation curves of molecules and to describing weakly interacting complexes. It improves greatly upon APSG and, unlike the latter, yields bonded van der Waals complexes.

[1] K. Chatterjee and K. Pernal, *J. Chem. Phys.* **137**, 204109 (2012).

[2] K. Pernal, K. Chatterjee and P. H. Kowalski, *J. Chem. Phys.* **140**, 014101 (2014).