

CBS-QB3 Composite Method Along with Pseudopotential for the Calculation of Standard Enthalpy of Formation

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Abstract: Composite methods currently represent the one of the best choices for the calculation of electronic and thermochemical properties due to the reasonable computational cost and applicability to chemical systems with up to 100 electrons. One of the best alternative of this class of methods was introduced by Petersson et al. [1] known as CBS (Complete Basis Set). These methods incorporate additive corrections to the order of electronic correlation and considers extrapolation techniques to a complete basis set. CBS presents similar accuracy with the Gn methods [2]. However, they can seldom be applied to systems containing many electrons due to the high number of integrals appearing in CCSD(T) and QCISD(T). In this sense, the use of pseudopotential reduces the computational cost and extends the applicability of the method to larger systems preserving its accuracy. In the present paper the authors report the development of a composite method based on the implementation of pseudopotential in the CBS-QB3 (Eq.1) methodology [3]. The calculation of the electronic energy of a hypothetical system according to the CBS-QB3 method is described as follows:

$$\begin{split} E_e &= E(MP2) + \Delta E(MP4(SDQ)) + \Delta E(CCSD(T)) + \Delta E(CBS) + \Delta E(NaCorr) + \\ &+ \Delta E(emp) + \Delta E(Spin) + \Delta E(SO) \end{split}$$

The method, referred to as CBS-QB3//CEP-31G(d)/CEP, uses calculations at MP2(fc)/CEP-CBSB3 as reference energy. The basis set was optimized according to the variational principle within the boundary conditions of the reference energy. The cutoff of the basis set (6-311G(2df,2p) H-Ne and 6-311G(3d2f) for Na-Ar) to be used with the pseudopotential was defined from the Hartree-Fock density matrix maps [4]. For the optimization of the equilibrium structure, frequency calculation (ZPE correction) and $\Delta E(CCSD(T))$ (E(CCSD(T)) - E(MP4(SDQ))) the CEP-31G(d) basis set was used. The MP4 calculation and $\Delta E(NaCorr)$ were discarded. The latter correction was used only for species containing sodium atoms. The other steps were maintained, whereas the parameters for empirical correction and $\Delta E(Spin)$, due to spin contamination, were adapted to the set of 234 enthalpies of formation. The expression for CBS-QB3//CEP-31G(d)/CEP is then defined as follows:



 $+ \Delta E(emp) + \Delta E(Spin) + \Delta E(SO)$

This method was applied to the calculation of 234 standard enthalpies of formation taken from the G3/05 test set for validation. **Figure 1** shows the histogram containing the error between theoretical enthalpy (CBS-QB3//CEP-31G(d)/CEP) with respect to the experimental data and comparison of mean absolute error of the proposed method with other methods [5-6].



Figure1. (a) Histogram for 234 $\Delta_f H^0_{Theo.}$ - $\overline{\Delta_f H^0}_{Exp.}$ calculated with CBS-QB3 (red bar) and Gaussian Fit. (b) Bar chart containing the comparison between the mean absolute error of various methods [5-6].

When compared to other composite methods, a mean absolute error of 2.1 kcalmol-1 is achieved against 2.0 kcalmol⁻¹ for G3 and 2.6 kcalmol⁻¹ for G3X (for a set of 19 nonhydrogenic molecules) and 1.0 kcalmol⁻¹ (our method) against 1.5 kcalmol⁻¹ CBS-QB3 (original) 1.2 kcalmol⁻¹ CBS-APNO; 0.7 kcalmol⁻¹ G3; 0.8 kcalmol⁻¹ G4; 0.9 kcalmol⁻¹ W1BD and 0.2 kcalmol⁻¹ ATcT for a set of 20 organic molecules [5-6]. With these previous results, it is notable that the implementation of pseudopotential in CBS-QB3 shows to be an efficient strategy for the calculation of enthalpy of formation.

Key-words: Pseudopotential, Composite Methods, Complete Basis Set.

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