Theorectical study of heats of formation using CR-CCL method.

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Introdução

The prediction of thermodynamic properties of molecular systems is a central objective of many recent electronic structure calculations. One of these properties, the standard heat of formation $\Delta_f H^o_{gas}$ which measures the thermodynamic stability, is useful in the interpretation of the mechanisms of chemical reactions[1]. Theoretical calculations represent one attempt to study absolute values of heats of formation, electron (EA) or proton affinities (PA), and other thermo chemical properties. However, accurate calculations of these properties require sophisticated and high level methods, and great amount of computational resources. This is particularly true for atoms of the 2nd or 3rd periods and for calculating properties like the heats of formation. In this work the CR-CCL energies were calculated. The CR-CCL energy is size-extensive left eigenstate completely renormalized (CR) coupled-cluster (CC) singles (S), doubles (D), and noniterative triples (T) approach abbreviated as CCL. The valence basis sets aug-CCpVnZ (n = 2, 3, and 4) were adapted to pseudopotential (ECP) using the Generator Coordinate Method (GCM)[2]. These basis sets are identified by ECP+ACCpVnZm (m = modified). The energies are obtained at the CBS limit, which is obtained by using extrapolation methods considering the three (n = 2, 3, and 4) different basis sets (ECP+ACCpVnZm).

Resultados e Discussão

The molecular calculations consist of the following steps: a) optimization of the molecular geometries and vibrational analysis are carried out at HF/ECP+ACC2Zm level. The harmonic frequencies confirm that the stationary points correspond to minima and are used to compute the zero-point energies; b) further optimization is carried out at MP2/ECP+ACC2Zm level; c) at the MP2 equilibrium geometry corrections to the total energies are performed at higher level of theory. First, at CR-CCL/ECP+ACC2Zm level, and later by addition of extra functions (s,p,d, and f) at MP2/ECP+ACC3Zm and MP2/ECP+ACC4Zm levels. Finally, the results are coupled through additive approximations, and the energy corresponds to an effective calculation at a high level of theory:

$$\mathbf{E[CR\text{-}CCL/ECP + ACC5Zm] = E[CR\text{-}CCL/ECP + ACC2Zm] + E[MP2/ECP + ACC5Zm] - E[MP2/ECP + ACC2Zm]- ZPE[HF/ECP + ACC2Zm]*scal + E(HLC)} \quad (1)$$

where *scal* (1.021) is the scaling factor on the vibrational frequencies and HLC an empirical higher-level correction term. All of these calculations were performed using the Gamess2009.

Table 1. Heats of formation (in kJ.mol^{-1}) with the method given in Eq. (1), and comparison with experimental values.

System	$\Delta_f H^o_{gas}$ (calc)	$\Delta_f H^o_{gas}$ (exp)[3]
OF	110.99	108.78
OF_2	42.58	24.52
OCl	103.48	101.22
OCl_2	92.34	87.86
SF	4.66	12.97
SF_2	-280.57	-296.65
SF_3	-462.61	-503.03
SF_4	-775.36	-763.16
SF_5	-887.77	-908.45
SF_6	-1248.99	-1220.47

The use of pseudopotential is competitive, mainly in systems containing S and Cl atoms. In calculations involving all electrons the computational performance is totally different and increases with the number of electrons. The CR-CCSD[T]/ECP computational demand is decreased by 10% when compared with all-electron calculations using the G2 and G3 procedures. For molecules containing Cl, Br or I atom the time will be drastically decreased.

Conclusões

The heats of formation of some simple systems containing atoms of the 2nd and 3rd periods obtained by the procedure outlined in this paper, are in very good agreement with experimental values. The CR-CCL/ECP+ACC5Zm method have been shown to be powerful, and of affordable computational cost for the systems addressed in this work.

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[3] http://webbook.nist.gov/chemistry/.