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The generator coordinate Hartree–Fock method as strategy for building Gaussian basis sets to ab initio study of the process of adsorption of sulfur on platinum (200) surface

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Abstract

The scheme named generator coordinate Hartree–Fock method (GCHF) is used to build (22s14p) and (33s22p16d9f) gaussian basis sets to S (^{3}P) and Pt (^{3}D) atoms, respectively. Theses basis sets are contracted to [13s10p] and [19s13p9d5f] through of Dunning's segmented contraction scheme and are enriched with *d* and *g* polarization functions, [13s10p1d] and [19s13p9d5f1g]. Finally, the [19s13p9d5f1g] basis set to Pt (^{3}D) was supplemented with *s* and *d* diffuse functions, [20s13p10d5f1g], and used in combination with [13s10p1d] to study the effects of adsorption of S (^{3}P) atom on a Pt (^{3}D) atom belonged to infinite Pt (200) surface. Atom–atom overlap population, bond order, and infrared spectrum of $[Pt–S]^{2-}$ were calculated properties and were carried out at Hartree–Fock–Roothaan level. The results indicate that the process of adsorption of S (^{3}P) on Pt (^{3}D) in the infinite Pt (200) surface is mainly caused by a strong contribution of σ between the 3p$_z$ orbital of S (^{3}P) and the 6s orbital of Pt (^{3}D).

Keywords: Gaussian basis sets; Contracted basis sets; GCHF method; Adsorption of sulfur on platinum; Surface process

1. Introduction

In previous article, we used the generator coordinate Hartree–Fock (GCHF) method in the design of gaussian basis sets to the theoretical study of piezoelectric effect of perovskite ($BaTiO_3$) [1]. The GCHF method was inserted in literature in 1986 by Mohallem and co-workers [2] as a new technique for basis sets development. Today, 18 years later, innumerable basis sets obtained from the method's strategy have been reported in literature. Mohallem and co-workers [3] and da Costa and co-workers [4] used the method in the design of the gaussian-type orbital (GTO) and Slater-type orbital (STO), respectively. Da Silva and Trsic presented STO and GTO universal basis sets for H–Xe atoms [5]. Also, the GCHF method was tested successfully by Pinheiro and co-workers as a tool for choosing polarization functions to be used in GTF basis sets for first- [6] and second-row [7] atoms. In the posterior years some approaches deviated from the GCHF method also were reported in literature [8–11]. Besides, the GCHF method was exploited by da Costa and co-workers with large polarized basis sets yielding HF limit [12,13]. In recent years some applications of the basis sets designed with the GCHF method have been available to ab initio studies of atoms and poliatomic molecules. Treu Filho and co-workers studied the electronic properties in IR-spectrum of high trydimite [14]. Savedra and co-workers calculated the electronic affinities of some enolates [15] and theoretically studied the IR-spectrum of hexaoxochromium (III) ion, tetraoxo chromium (IV) ion, and tetraoxochromium (VI) ion [16]. Also, Treu Filho and co-workers theoretically studied the Raman spectrum and vibrational structure of hexaaquachromium (III) ion [17,18]. Indeed, applications of GCHF method basis sets in

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calculations of electronic structure of perovskites have been realized by Treu Filho and co-workers [19–21].

Even being a powerful technique in generation of basis sets in atomic and molecular environments, the GCHF method and mainly the use of basis sets, built according with its strategy, in molecular studies is still very timid.

In this article, with the aid of the GCHF method, we build (22s14p) and (33s22p16d9f) Gaussian basis sets to S (^{3}P) and Pt (^{3}D) atoms, respectively. Then, these basis sets are contracted to [13s10p] and [19s13p9d5f] and enriched with *d* and *g* polarization functions, [13s10p1d] and [19s13p9d5f1g]. Finally, the [19s13p9d5f1g] basis set to Pt (^{3}D) was supplemented with *s* and *d* diffuse functions, [20s13p10d5f1g], and used in combination with [13s10p1d] to study the effects of adsorption of S (^{3}P) atom on a Pt (^{3}D) atom belonged to infinite Pt (200) surface.

2. Methodology

2.1. Computational

In this section we will make a brief presentation of the GCHF method as strategy for building the Gaussian basis sets as well a short description of the contraction of the primitives (22s14p) and (33s22p16d9f) basis sets and the choice of diffuse and polarization functions used in contracted [13s10p] and [19s13p9d5f] basis sets. A deeper and detailed description of these matters can be found elsewhere [2,15].

2.1.1. The GCHF method

The GCHF method is a result of choosing the one-electron functions as integral transforms

$$\Phi_i(1) = \int \phi_i(1,\alpha) f_i(\alpha)\,\mathrm{d}\alpha \quad i = 1,2,\ldots,n \tag{1}$$

where the ϕ_i are the generator functions (GTF in this report), f_i are the weight functions, and α is the generator coordinate.

The Φ_i are then employed to built a Slater determinant and the mean value of the total energy, $<E>$. With the variation of $<E>$ with respect to f_i, one can obtain the Griffin–Wheeler–HF (GWHF) equations

$$\int [F(\alpha,\beta) - \varepsilon_i S(\alpha,\beta)] f_i(\beta)\,\mathrm{d}\beta = 0 \quad i = 1,2,\ldots,n \tag{2}$$

where ε_i are the HF eigenvalues, and $F(\alpha,\beta)$ and $S(\alpha,\beta)$ are the Fock and overlap kernels, respectively. The Fock and overlap kernels are defined explicitly in Ref. [2].

The GWHF Eq. (2) are solved numerically through discretization with a technique that preserves the integral character of the GCHF method, i.e. the integral discretization (ID) technique [22]. The ID technique is implemented through a relabeling of the generator coordinate space α, viz.

$$\Omega = \ln \alpha / A \quad A > 1 \tag{3}$$

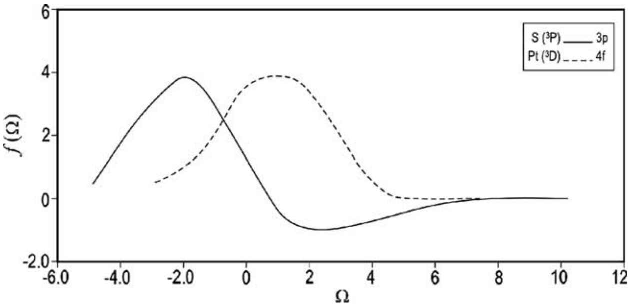

Fig. 1. The 3p and 4f weight functions for S (^{3}P) and La (^{3}D) atoms obtained with(22s14p) and (33s22p16d9f) Gaussian basis sets, respectively.

The new generator coordinate space Ω is discretized for each *s*, *p*, *d*, and *f* symmetries in a equally spaced mesh $\{\Omega\}$ so that

$$\Omega_\mathrm{k} = \Omega_\mathrm{min} + (t-1)\Delta\Omega \quad t = 1,2,\ldots,N \tag{4}$$

In Eq. (4), the set $\{\Omega\}$ is characterized by an initial point Ω_min, an increment $\Delta\Omega$, and N (discretization point number), where the discretization point number defines the Gaussian basis set size. The values of Ω_min (lowest value) and highest value $\Omega_\mathrm{max}[\Omega_\mathrm{max} = \Omega_\mathrm{min} + (t-1)\Delta\Omega]$ are chosen so as to adequately encompass the integration range for the *s*, *p*, *d*, and *f* weight functions for S (^{3}P) and Pt (^{3}D) atoms, $f(\Omega)$. This is visualized by drawing the weight functions from preliminary calculations with arbitrary discretization parameters. Fig. 1 shows this situation and shows and weight functions for S (^{3}P) and Pt (^{3}D) atoms, respectively.

In the solution of the discretizatized form of Eq. (2), the (22s14p) and (33s22p16d9f) Gaussian basis sets were used as defined by the mesh of Eq. (3). The values of Ω_min and Ω_max were selected in order to satisfy the relevant integration range of each atom $f(\Omega)$. In Table 1, the discretization parameters (basis set exponents) for the built basis sets are shown.

The (22s14p) and (33s22p16d9f) Gaussian basis sets used in this report were developed by employing Eqs. (3) and (4) and were designed taking into account the ground electronic state of the S (^{3}P) and Pt (^{3}D) atoms.

Table 1
Discretization parameters (basis set exponents) for S (^{3}P) and Pt (^{3}D) atoms in this work[a]

Symmetry	S			Pt		
	Ω_min	$\Delta\Omega$	N	Ω_min	$\Delta\Omega$	N
s	−0.360	0.120	22	−0.581	0.112	33
p	−0.487	0.116	14	−0.430	0.111	22
d	–	–	–	−0.294	0.112	16
f	–	–	–	−0.290	0.129	9

[a] The discretization parameters for all atoms is 6.0.