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Alternative Approach to Calculate Two-Center Overlap Matrix through Deformed Exponential Function

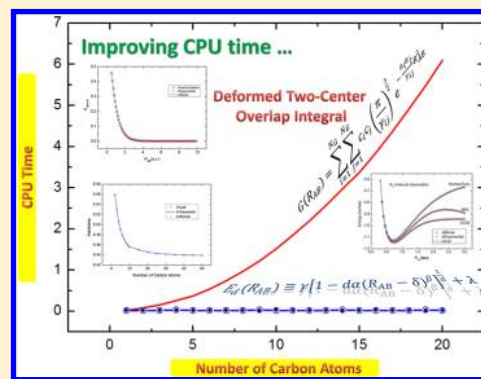
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Supporting Information

ABSTRACT: In this work, we propose an alternative approach to evaluate two-center overlap integrals. It is computationally more efficient than the standard procedure and is based on the deformed exponential function. In the new procedure, the CPU time to calculate each element of the overlap matrix ($S_{\mu,\nu}$) is constant and independent of the number of Gaussian primitives (N_G), whereas in the usual procedure this time increases, formally, with N_G^2 . To evaluate the accuracy of the proposed methodology, we computed different molecular properties such as dipole moments, hardness values, atomic charges, multicenter bond indices, group indices, and some thermodynamic properties. In this work, all calculations were performed using a minimal STO-6G basis set and WTBS and the double- ζ Pople split-valence 6-31G basis set on the Hartree–Fock (HF) and post-HF approximations. The integrals were parametrized for the atoms of the first two rows of the periodic table. All calculations were performed in the general ab initio quantum chemistry package GAMESS, where the integrals were implemented.



1. INTRODUCTION

Today's quantum chemistry, particularly ab initio molecular electronic structure theory, has well-defined scaling parameters for the computation of total molecular energies and other properties derived from these quantities. Using this theory, in principle, it is possible to characterize and describe every chemical system. In practice, however, only the simplest chemical systems can realistically be investigated using the purely quantum mechanical procedure. Thus, some approximations must be made for most practical purposes of predicting and elucidating properties of chemical systems. In these calculations, it is usually necessary to evaluate a large number of electronic integrals in which the computational time spent grows and quickly becomes prohibitive when the size of the molecule increases.

In quantum chemistry, the evaluation of two-center overlap integrals is a long-standing problem because of the large number of integrals and the difficulty of evaluating them to a level of high accuracy.¹ Different approaches have been used for the analytical development of these two-center integrals and for their accurate numerical evaluation.^{2–7} Therefore, any methodology that reduces the computer time for these tasks is very welcome.

In this context, we propose an alternative methodology to calculate electronic integrals, one that is computationally more efficient than the standard procedure. The alternative method proposed in this work is based on a deformed exponential function (see next section). To evaluate the accuracy of this

methodology in calculating overlap integrals ($S_{\mu,\nu}$), we computed different molecular properties that are sensitive to small errors in $S_{\mu,\nu}$ calculations. In this work, the calculations were performed using a minimal STO-6G basis set⁸ and a WTBS (well-tempered basis set)^{9–13} and the double- ζ Pople split-valence 6-31G basis set on the Hartree–Fock (HF)^{14–16} and post-HF^{17–22} approximations. The integrals were parametrized for the atoms of the first two rows of the periodic table. To validate the proposed methodology, calculations for organic molecules consisting of carbon, hydrogen, and oxygen were performed. In previous works, we used the generalized Morse function (d -Morse) in the HF,^{23,24} density functional theory (DFT),²⁵ second-order Møller–Plesset perturbation theory (MP2), and coupled-cluster (CC)²⁶ methodologies. The deformed exponential function has been applied successfully to a variety of problems in electronic structure.^{27–29} All calculations were performed in the general ab initio quantum chemistry package GAMESS,³⁰ where we implemented the new integrals.

This article is organized as follows: In section 2, we present the technical details of the usual method. The computational procedure performed in this work is presented in section 3. Analysis and discussion of the results are presented in section 4.

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Table 1. Overlap Matrix Elements Obtained by the Usual Procedure and by *d*-Exponential and *d*-Morse Function Adjustments

$S_{\mu,\nu}$	usual	<i>d</i> -exponential	<i>d</i> -Morse
$S_{s,s}$	$\sum_{i,j}^{N_G} c_i c_j \left(\frac{\pi}{\gamma_{ij}} \right)^{3/2} \exp \left(-\frac{\alpha_i \alpha_j}{\gamma_{ij}} R_{AB}^2 \right)$	$E_d(R_{AB})$	$M_d(R_{AB})$
S_{s,p_x}	$(x_A - x_B) \sum_{i,j}^{N_G} c_i c_j \left(\frac{\pi}{\gamma_{ij}} \right)^{3/2} \frac{\alpha_i}{\gamma_{ij}} \exp \left(-\frac{\alpha_i \alpha_j}{\gamma_{ij}} R_{AB}^2 \right)$	$(x_A - x_B) E_d(R_{AB})$	$(x_A - x_B) M_d(R_{AB})$
$S_{p_x,s}$	$-(x_A - x_B) \sum_{i,j}^{N_G} c_i c_j \left(\frac{\pi}{\gamma_{ij}} \right)^{3/2} \frac{\alpha_j}{\gamma_{ij}} \exp \left(-\frac{\alpha_i \alpha_j}{\gamma_{ij}} R_{AB}^2 \right)$	$-(x_A - x_B) E_d(R_{AB})$	$-(x_A - x_B) M_d(R_{AB})$
S_{p_x,p_y}	$(x_B - x_A)(y_A - y_B) \pi^{3/2} \sum_{i,j}^{N_G} c_i c_j \frac{\alpha_i \alpha_j}{\gamma_{ij}^{7/2}} \exp \left(-\frac{\alpha_i \alpha_j}{\gamma_{ij}} R_{AB}^2 \right)$	$(x_B - x_A)(y_A - y_B) E_d(R_{AB})$	$(x_B - x_A)(y_A - y_B) M_d(R_{AB})$
S_{p_x,p_z}	$\sum_{i,j}^{N_G} c_i c_j \left[-\pi^{3/2} \frac{\alpha_i \alpha_j}{\gamma_{ij}^{7/2}} (x_B - x_A)^2 + \frac{\pi^{3/2}}{2\gamma_{ij}^{5/2}} \right] \exp \left(-\frac{\alpha_i \alpha_j}{\gamma_{ij}} R_{AB}^2 \right)$	$(x_B - x_A)^2 E_{d_1}(R_{AB}) + E_{d_2}(R_{AB})$	$(x_B - x_A)^2 M_{d_1}(R_{AB}) + M_{d_2}(R_{AB})$

2. TECHNICAL DETAILS OF THE USUAL METHOD

In electronic structure calculations, the most common approximation is the Hartree–Fock method, which is based on a linear combination of atomic orbitals to construct molecular orbitals (LCAO-MO) in a self-consistent field procedure. The resulting equations are solved using matrix methods in terms of a basis set of so-called primitive functions, known as the matrix Hartree–Fock equations or the Hartree–Fock–Roothaan (HFR) method. That is, the MOs are defined in terms of variationally determined linear expansion coefficients of *n* contracted basis functions. Therefore, in the usual methodology, the basis set functions ϕ_μ of atomic orbitals are frequently chosen to be contracted Gaussian functions, that is, fixed linear combinations of Gaussian functions. By a proper choice of the contraction parameters, one can thus use basis functions that are approximate Hartree–Fock functions.

The primitive basis functions for polyatomic molecules are most often chosen to be Cartesian Gaussian functions $x^l y^m z^n e^{-\alpha r^2}$, where α is a constant and *x*, *y*, *z*, and *r* measure nucleus–electron distances. Contracted Gaussian-type functions (CGTFs), fixed linear combinations of primitive functions that are based on atomic wave functions, are commonly used to reduce the effective number of functions used in HF and post-HF procedures.

The procedure that has come into wide use is to fit a Slater-type orbital (STO) to a linear combination of a set of N_G primitive Gaussian functions.⁸ In this methodology, the atomic orbital function (ϕ_μ) is defined as a linear combination of Gaussian functions as follows

$$\phi_\mu(\mathbf{R}) = \sum_{i=1}^{N_G} d_{\mu,i} \chi_{\mu,i} = (x - x_A)^{l_\mu} (y - y_A)^{m_\mu} (z - z_A)^{n_\mu} \sum_{i=1}^{N_G} d_{\mu,i} \exp \{ -\alpha_i [(x - x_A)^2 + (y - y_A)^2 + (z - z_A)^2] \} \quad (1)$$

where *i* runs over all N_G primitive Gaussian functions ($\chi_{\mu,i}$) and $d_{\mu,i}$ represents the contracted expansion coefficients. $\phi_\mu(r)$ is an atomic basis function with the angular momentum index $L_\mu = l_\mu + m_\mu + n_\mu$ centered at the atom A located at

$$\mathbf{R} = \mathbf{r} - \mathbf{R}_A = (x - x_A, y - y_A, z - z_A)$$

and with orbital exponent α_i . In this case, $\phi_\mu(r)$ is called a contracted Cartesian Gaussian function. Despite the fact that the angular indices (*l*, *m*, *n*) are not proper angular momentum labels, it is common to assign the angular momentum index $l_\mu + m_\mu + n_\mu$ to each primitive function and refer to functions with $L_\mu = 0$ as s-type, $L_\mu = 1$ as p-type, and so on, in analogy with atomic orbitals. For example, one often refers to a primitive with indices $l_\mu = 1$, $m_\mu = 0$, and $n_\mu = 0$ as a p_x function.

Using eq 1, the overlap matrix, in Cartesian coordinates, is defined by the general expression

$$S_{\mu,\nu} = \int_{-\infty}^{\infty} \phi_\mu \phi_\nu d\tau = \int_{-\infty}^{\infty} \sum_{i=1}^{N_G} d_{\mu,i} \chi_{\mu,i} \sum_{j=1}^{N_G} d_{\nu,j} \chi_{\nu,j} d\tau = \sum_{i,j=1}^{N_G} d_{\mu,i} d_{\nu,j} \int_{-\infty}^{\infty} \chi_{\mu,i} \chi_{\nu,j} d\tau = \sum_{i,j=1}^{N_G} c_{\mu,i} c_{\nu,j} S_{i,j} \quad (2)$$

with

$$S_{i,j} = \exp \left(-\frac{\alpha_i \alpha_j}{\gamma_{ij}} R_{AB}^2 \right) \int_{-\infty}^{\infty} (x - x_A)^{l_A} (x - x_B)^{l_B} (y - y_A)^{m_A} (y - y_B)^{m_B} (z - z_A)^{n_A} (z - z_B)^{n_B} \exp[-\gamma_{ij}(x - x_p)^2] \exp[-\gamma_{ij}(y - y_p)^2] \exp[-\gamma_{ij}(z - z_p)^2] dx dy dz \quad (3)$$

where $\gamma_{ij} = \alpha_i + \alpha_j$ and $\mathbf{R}_{AB} = \mathbf{R}_A - \mathbf{R}_B = (x_A - x_B, y_A - y_B, z_A - z_B)$.

Using the Gaussian product theorem, which states that the product of two arbitrary Gaussian functions on centers A and B can be written as one Gaussian function centered on an intermediary point between A and B, one can easily solve the integral of eq 3. Some of these integrals are presented in Table 1.

In this article, we describe a new procedure that can be used for evaluating any kind of overlap integral over contracted Cartesian Gaussian functions, by introducing an auxiliary deformed exponential function, which enables the CPU time for $S_{\mu,\nu}$ calculations to be reduced.

3. D-OVERLAP MATRIX PROCEDURE

This article is concerned with an alternative procedure for evaluating atomic overlap integrals, reducing the CPU time in this type of calculation. In this procedure, the sum of contracted Gaussian functions is fitted by one deformed exponential function,³¹ defined as

$$f(r) = e_d^{\pm\alpha r} \equiv (1 \pm d\alpha r)^{1/d} \quad (4)$$

In the limit of $d \rightarrow 0$, this d -exponential or generalized exponential function is equal to the usual exponential function as defined by Euler, that is

$$\lim_{d \rightarrow 0} e_d^{\pm\alpha r} = e^{\pm\alpha r} \quad (5)$$

where α is a constant and d is an external adjustable parameter to fit the usual exponential function. The $f(r)$ in eq 4 is the type of d -exponential function with which we are concerned in this article to redefine the overlap integrals.

More properly, in our procedure, the radial part of the linear combination of primitive Gaussian function, namely

$$G(R_{AB}) = \sum_{i=1}^{N_G} \sum_{j=1}^{N_G} c_i c_j \left(\frac{\pi}{\gamma_{ij}} \right)^{3/2} \exp \left(-\frac{\alpha_i \alpha_j}{\gamma_{ij}} R_{AB}^2 \right) \quad (6)$$

is fitted by a d -exponential (E_d) or a d -Morse (M_d) function, defined as

$$E_d(R_{AB}) \equiv \gamma [1 - d\alpha(R_{AB} - \delta)^{\beta}]^{1/d} + \lambda \quad (7)$$

and

$$M_d(R_{AB}) \equiv E_d(E_d + \theta) \quad (8)$$

respectively, where N_G is the number of contracted primitive Gaussian functions and α , β , γ , δ , λ , θ , and d are adjustable parameters.

It is important to emphasize that, to calculate each overlap matrix element ($S_{\mu,\nu}$) in the conventional case, it is necessary to perform, formally, N_G^2 mathematical operations as represented in eq 6, whereas in the new procedure, only one mathematical operation is needed, as represented in eq 7 or 8. In the next section, we show that there is a reasonable difference in the computational efforts for rating the two-center overlap matrixes ($S_{\mu,\nu}$) between the usual and d -overlap methods. Whereas the methodology formally requires the calculation of $K^2 N_G^2$ integrals of the type S_{ij} for the d -overlap method, it is necessary to evaluate only $K^2 S_{ij}$ -type integrals. In this case, K and N_G are the number of base functions and the number of primitive contracted Gaussian functions used to expand the atomic orbital, respectively.

In the case of a WTBS, where the dimension of primitive Gaussian functions is $N_G = 20$, the number of mathematical operations as represented in eq 6 is equal to 400, whereas to perform the same operation in our methodology, it is necessary to execute just one mathematical operation as in eq 7 or 8, independently of the basis set size N_G . It is known that the accuracy of the overlap matrix increases with the number of primitive Gaussian functions. It is important to point out that, in our procedure, the CPU time to calculate each element $S_{\mu,\nu}$ is constant and independent of the number of Gaussian primitive functions (N_G), whereas in the usual procedure, this time increases with N_G^2 .

The fitting procedure of the d functions over the linear combination of Gaussian functions includes the following steps:

(1) First, select the pair of orbitals μ and ν belonging to different atoms A and B, respectively.

(2) Next, use the generalized simulated annealing (GSA) procedure^{32,33} to find the parameters α , β , γ , δ , λ , θ , and d that fit the sum of Gaussian functions, eq 6, by just one d -exponential, eq 7 or 8, for different values of interatomic distance R_{AB} .

(3) Continue the GSA procedure until a χ^2 value is reached within the desired precision. (In this work, the precision established was $\chi^2 < 10^{-8}$.) The χ^2 error is defined as the sum of the squares of the differences between the two functions for each distance R_{AB} , which is given by

$$\chi_E^2 = \frac{1}{N} \sum_{k=1}^N [G(R_k) - E_d(R_k)]^2 \quad (9)$$

for a d -exponential and

$$\chi_M^2 = \frac{1}{N} \sum_{k=1}^N [G(R_k) - M_d(R_k)]^2 \quad (10)$$

for a d -Morse function, where N is the number of interatomic distance values R_k .

In Table 1, we present the mathematical equations for the usual overlap matrix (second column) and the equivalent d -overlap matrixes (third and fourth columns). The usual overlap equations were obtained integrating eqs 2 and 3. Symbols such as $S_{\mu,\nu} = S_{p_x s}$ mean a p_x orbital belonging to atom A and an s orbital belonging to atom B.

The second column contains some elements of the overlap matrix for s and p atomic orbitals. In the third and fourth columns are the equivalent elements for the proposed d -overlap matrix. The same procedure was applied to obtain the other terms of the $S_{\mu,\nu}$ matrix; for example, S_{s,p_y} was obtained by just changing the atomic coordinates ($x_A - x_B$) to ($y_A - y_B$) in the S_{s,p_x} matrix element.

Figure 1 shows plots that represent the usual overlap matrix element $S_{p_x s}$ and its equivalent d - $S_{p_x s}$ using the STO-6G basis set and $S_{2s,2p_x}$ and its equivalent d - $S_{2s,2p_x}$ using the 6-31G basis set.

4. RESULTS AND DISCUSSION

The following section is dedicated to evaluating how the error introduced by our procedure is propagated in the calculation of different molecular properties, for example with atomic dissociation energy, thermodynamic properties, atomic charges, group indices and bond indices.^{34,35}

The calculations to compare CPU time were done by using a minimal STO-6G basis set and a WTBS. For the calculation of molecular properties the STO-6G basis set at the HF level was used, and for the dissociation energy of the hydrogen molecule, the calculations were performed using the same basis set at the HF, MP2 and CCSD levels of theory. All parameters of the two-center d -overlap integrals can be found in the Supporting Information.

4.1. Comparison of CPU Times. We compared the times required for the calculation of integrals using the usual method and the d -Morse and d -exponential functions for an increasing number (N_G) of primitive Gaussian functions. For this purpose, we used an AMD-Turion Dual-Core Mobile M500 2.2 GHz computer to obtain the elements of the overlap matrix ($S_{\mu,\nu}$). In this case, the computational time required to perform the

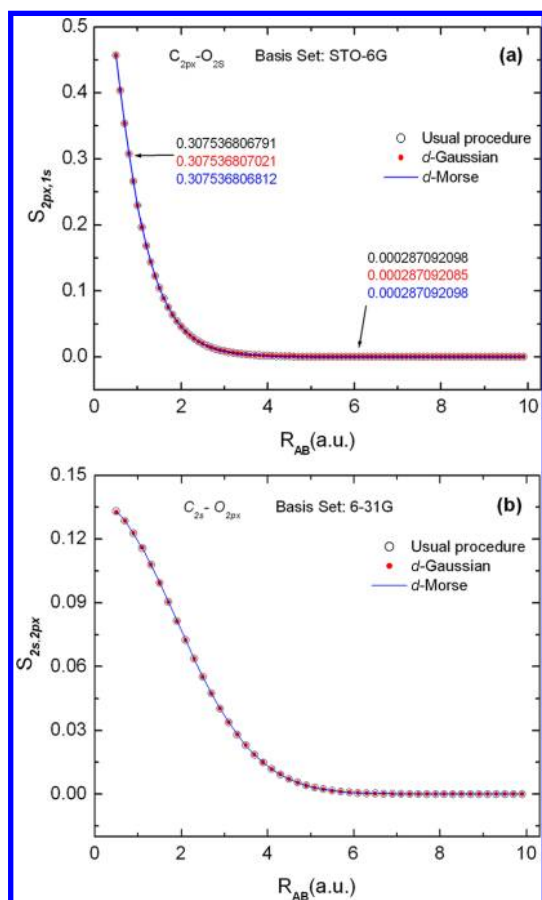


Figure 1. (a) Usual overlap matrix element $S_{p_x, s}$ and its equivalent $d-S_{p_x, s}$ where the orbitals $2p_x$ and $1s$ belong to the carbon and oxygen atoms, respectively. (b) Usual overlap matrix element $S_{s, 2p_x}$ and its equivalent $d-S_{s, 2p_x}$ where the orbitals $2s$ and $2p_x$ belong to the carbon and oxygen atoms, respectively. In cases a and b, the χ^2 errors are $\chi^2 = 1.52 \times 10^{-9}$ hartree and $\chi^2 = 2.58 \times 10^{-14}$ hartree, respectively. The calculations were performed using the (a) STO-6G and (b) 6-31G basis sets. For two specific interatomic distances, the values of the S matrix for the usual (black), d -Gaussian (red), and d -Morse (blue) procedures are included.

calculation of the matrix elements of $S_{\mu, \nu}$ grew as $O(N_G^2)$ using the usual approach, whereas with the proposed approach, the CPU time for the same calculation remained constant (6.25×10^{-8} s). We looped 10 million times over the same matrix elements to average out these tiny times.

To display the computational gain from the proposed methodology effectively, we calculated the CPU time needed to obtain the overlap integrals necessary for a cluster of carbon-atom calculations. We calculated the computational time required to obtain the overlap matrix from a system varying from 50 to 1000 carbon atoms, as can be seen in Figure 2. In this case, we used the minimal STO-6G basis set and a WTBS for the calculation of overlap integrals using the conventional method, and we performed the calculation with equivalent d -integrals (d -STO-6G) for comparison.

For a system with 500 carbon atoms, the calculations of integrals using the STO-6G basis set (WTBS) required about 13.92 s (91.53 s). However, when using the d -integral equivalent to either the STO-6G basis set or the WTBS, the CPU time was approximately 4.42 s. For a system with 1000 carbon atoms, the calculation of integrals using the STO-6G

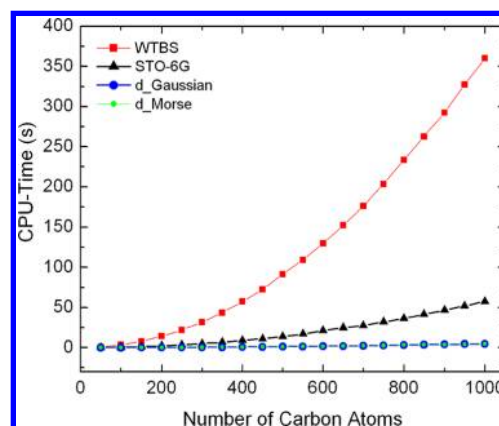


Figure 2. CPU times required to evaluate the total overlap matrices of carbon atom clusters using the usual and new approaches.

basis set (WTBS) required about 57.64 s (360.19 s). Using both d -integral equivalents to the STO-6G and WTBS functions, the CPU time was also approximately 17.34 s. For this comparison, we also used a Fortran ab initio computational code developed and optimized in our research group.

To evaluate the overlap integrals for the system containing a cluster with 1000 carbon atoms, the procedure proposed here was approximately 3 or 20 times faster than the time of calculation using the STO-6G basis set or WTBS, respectively. It is important to point out that, as the size of atomic basis increases, to better represent the atomic orbital, the CPU time also increases substantially.

We emphasize that the d -integral method is more efficient than the conventional method when the molecular system exhibits symmetries other than that of s -type orbitals, because the difficulty of calculating integrals involving orbitals of other symmetries (p , d , etc.) is greater than that of calculating integrals involving s -type orbitals.

4.2. Comparison of Electronic and Physicochemical Properties. In this subsection, we present some results from electronic and physicochemical measurements of different molecular systems using the usual methodology and the new approach proposed in this article.

The graph in Figure 3 shows the results for the molecular hardness values of hydrocarbon chains of different lengths using the usual $S_{\mu, \nu}$ and $d-S_{\mu, \nu}$ procedures. As shown in Figure 3, the hardness chemical property values obtained by the d -Gaussian

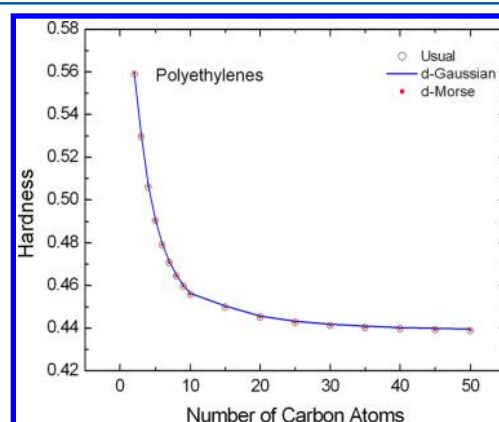


Figure 3. Hydrocarbon chain hardness as a function of number of carbon atoms.

(blue line) and *d*-Morse (red points) techniques agree well with those obtained by the usual method (black circles). The maximum error observed was about 5.0×10^{-5} . Therefore, the error is in the fifth decimal place, which indicates the accuracy of the proposed methodology for calculating this type of chemical property.

To make the method's accuracy clear, other properties were also calculated for the propane molecule and are reported in Tables 2 and 3. In Table 2, the residual atomic charges for the

Table 2. Mulliken and Löwdin Residual Atomic Charges for the Propane Molecule

atom	Mulliken			Löwdin		
	usual	<i>d</i> -Morse	<i>d</i> -Gaussian	usual	<i>d</i> -Morse	<i>d</i> -Gaussian
C ₁	−0.184	−0.184	−0.184	−0.097	−0.097	−0.097
H ₂	0.058	0.059	0.059	0.029	0.029	0.029
H ₃	0.058	0.059	0.059	0.029	0.029	0.029
H ₄	0.059	0.059	0.059	0.030	0.030	0.030
C ₅	−0.091	−0.091	−0.091	−0.029	−0.029	−0.029
H ₆	0.054	0.054	0.054	0.023	0.023	0.023
H ₇	0.054	0.054	0.054	0.023	0.023	0.023
C ₈	−0.184	−0.184	−0.184	−0.097	−0.097	−0.097
H ₉	0.058	0.059	0.059	0.029	0.029	0.029
H ₁₀	0.058	0.059	0.059	0.029	0.029	0.029
H ₁₁	0.059	0.059	0.059	0.030	0.030	0.030

propane molecule are presented. According to these data, no error was greater than 0.001 units of charge. Considering that, for the evaluation of residual atomic charges, two decimal places are not necessary, the proposed method shows excellent accuracy compared to the usual method for electronic structure calculations of molecular systems.

Other properties such as internal energy, enthalpy, Gibbs free energy, heat capacity at constant volume, heat capacity at constant pressure, and entropy were calculated and differentiated into translational, rotational, and vibrational energy levels. The results are listed in Table 3. Comparing the properties calculated using the usual method and the proposed method, we obtained identical values for the translational and rotational levels. For the last three columns, which present the sums of translational, rotational, and vibrational energy levels, the maximum error percentage obtained was 0.034% for the property entropy, considering the *d*-Gaussian method. This error is very small, so the use of this approach for the calculations will not affect the predictions of the properties calculated. With respect to the internal energy, the maximum error obtained was 0.014% ($0.011 \text{ kcal}\cdot\text{mol}^{-1}$). Considering

that $1 \text{ kcal}\cdot\text{mol}^{-1}$ is an acceptable limit for the error in energy calculations, it appears that the error obtained is well below this limit.

One of the properties that has attracted growing interest in the theoretical chemistry community is the multicenter bond index.^{36–39} These indices are important for identifying multicenter bonds in molecular systems. Another option involves the indices proposed by Mundim and co-workers.^{34,35} These indices are generalizations of the bond order, which describes the order of connection between chemical groups. The calculations of these two properties are suitable for this work, because these two indices are constructed with a larger number of terms of the density matrix than those used for typical two-center indices. This implies, therefore, a greater potential for error propagation.

According to Table 4, the errors obtained for three-center bond indices and group indices are in the fourth decimal place. It is worth mentioning here that, for a reliable assessment of these properties, no more than three decimal places are needed.

In Table 5, some results for dipole moment calculations of organic molecules are presented. Because this property is very sensitive to small errors, it is a good alternative for validating the adjustments implemented in the calculation of the overlap matrix.

By analyzing Table 5, it can be seen that the maximum error obtained was for dialcohol. For this molecule, the calculated dipole moment was 0.01627 D using the *d*-Gaussian procedure and 0.005097 D using the *d*-Morse procedure. It is known, for example, that the component of the heat of electrostatic hydration varies as μ^2 .⁴⁰ Thus, an error of 0.1 D corresponds to 0.5–0.7 $\text{kcal}\cdot\text{mol}^{-1}$ for hydration enthalpies. Therefore, the error obtained does not significantly affect the value of this property.

We also compared the potential energy curves (PECs) calculated using two different methods to evaluate the overlap integrals, the usual procedure and the proposed one. In our procedure, the overlap integrals were fitted by two different functions, which were a *d*-exponential and a *d*-Morse function. In Figure 4 is a plot of the potential energy curves of the H₂ molecular system calculated using the two procedures. To avoid the proliferation of figures, only the STO-6G PECs calculated using the HF, MP2, and CCSD approaches are included in Figure 4.

The results of the maximum(minimum) quadratic deviation and $[\chi^2]$ error between the calculation of the PECs and *d*-PECs using the STO-6G basis set and their respective *d*-Gaussian- $S_{\mu\nu}$ and *d*-Morse- $S_{\mu\nu}$ integrals are, respectively: 9.7×10^{-8} (8.3×10^{-12}) [5.3×10^{-7}] au and 3.9×10^{-8} (3.1×10^{-15}) [1.9×10^{-7}] au at the HF level; 7.8×10^{-8} (1.2×10^{-14}) [4.2×10^{-7}]

Table 3. Internal Energy *E* (kcal·mol^{−1}), Enthalpy *H* (kcal·mol^{−1}), Gibbs Free Energy *G* (kcal·mol^{−1}), Heat Capacity at Constant Volume *C_v* (cal·mol^{−1}·K), Specific Heat at Constant Pressure *C_p* (cal·mol^{−1}·K), and Entropy *S* (cal·mol^{−1}·K) for Propane

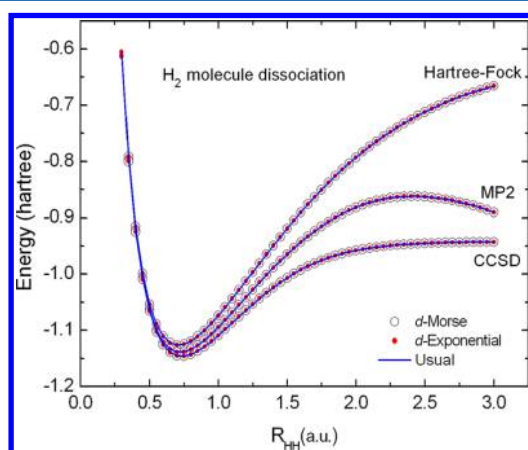
	translational			rotational			vibrational			total		
	usual	<i>d</i> -Morse	<i>d</i> -Gaussian	usual	<i>d</i> -Morse	<i>d</i> -Gaussian	usual	<i>d</i> -Morse	<i>d</i> -Gaussian	usual	<i>d</i> -Morse	<i>d</i> -Gaussian
<i>E</i>	0.889	0.889	0.889	0.889	0.889	0.889	78.849	78.842	78.838	80.626	80.620	80.615
<i>H</i>	1.481	1.481	1.481	0.889	0.889	0.889	78.849	78.842	78.838	81.219	81.212	81.208
<i>G</i>	−9.632	−9.632	−9.632	−5.874	−5.874	−5.874	77.413	77.401	77.395	61.906	61.895	61.889
<i>C_v</i>	2.981	2.981	2.981	2.981	2.981	2.981	7.027	7.031	7.033	12.988	12.992	12.995
<i>C_p</i>	4.968	4.968	4.968	2.981	2.981	2.981	7.027	7.031	7.033	14.976	14.980	14.982
<i>S</i>	37.275	37.275	37.275	22.683	22.683	22.683	4.817	4.833	4.839	64.775	64.791	64.797

Table 4. Valence Group Indices and Three-Center Bond Indices Calculated for Some Organic Molecules through the Usual Method and the *d*-Morse and *d*-Gaussian Methods

dimer	groups [G1...G2]	group index I_{G1-G2}			atoms	three-center bond index I_{ABC}		
		usual	<i>d</i> -Morse	<i>d</i> -Gaussian		usual	<i>d</i> -Morse	<i>d</i> -Gaussian
$[(H_3C)_3C]^+$	$[(H_3C)_3...C]^+$	3.522	3.522	3.522	^+CCH	0.044	0.044	0.044
benzene	$[H_5C_5...CH]$	2.878	2.878	2.878	HCC	−0.0004	−0.0004	−0.0004
diborane	$[H_2BH...HBH_2]$	1.475	1.4750	1.474	BHB	0.232	0.232	0.232
H_3NBH_3	$[H_3N...BH_3]$	0.570	0.570	0.570	HBN	−0.001	−0.001	−0.001

Table 5. Dipole Moments (in Debye) Calculated for Some Organic Molecules Using the Usual Procedure and the *d*-Gaussian and *d*-Morse Adjustments

molecule	usual	<i>d</i> -Gaussian	<i>d</i> -Morse
glycerol	2.117	2.120	2.117
H_3COH	1.557	1.559	1.559
F_2CH_2	2.070	2.085	2.074
$(CH_3)(CH_2)(CO)(CH_2)(CH_3)$	1.912	1.914	1.911
$(CH_3)(CH_2)_2(CH)(OH)_2$	2.012	1.996	2.007
$CH_3(CH_2)_3(CO)(CH_2)_3CH_3$	1.882	1.888	1.883

**Figure 4.** Potential energy curves of the H_2 molecular system obtained from the usual overlap matrix and the *d*-exponential and *d*-Morse variations using the HF, MP2, and CCSD methods.

au and 3.2×10^{-8} (9.1×10^{-16} [1.5×10^{-7}] au at the MP2 level; 6.9×10^{-8} (1.7×10^{-13} [3.5×10^{-7}] au and 2.8×10^{-8} (2.1×10^{-16}) [1.3×10^{-3}] au at the CCSD level.

Again, the *d*-Morse function reproduces better results than the *d*-Gaussian function. This can be attributed to the fact that a *d*-Morse function is a combination of *d*-exponential functions. Another important fact is the decrease in χ^2 with increased level of calculation, considering the same kind of adjustment.

5. CONCLUSIONS

In this work, we proposed an alternative methodology for evaluating overlap integrals. The results obtained clearly indicate that the *d*-overlap procedure is accurate enough to be used in any molecular quantum mechanical calculation. The main advantage of our procedure when compared with the usual one is the reduction of the CPU time required to calculate the overlap matrix.

Comparing the *d*-Gaussian and *d*-Morse methods, the results obtained by the latter were more accurate. This is because the Morse function is a combination of *d*-exponentials. In the new procedure, the CPU time required to calculate each element of the overlap matrix ($S_{\mu\nu}$) is constant and independent of the

number of primitive Gaussian functions (N_G), whereas for the usual procedure, this time increases with N_G^2 . It is important to emphasize that using the alternative approach proposed in this work still involves the computation of K^2 total elements, so this is not linear scaling of the total calculation, but rather linear scaling for each element of S . Finally, it should be noted that the procedure proposed in this work can be successfully applied to the calculation of all kinds of electronic molecular integrals involved in ab initio and DFT calculations, in particular, two-, three-, and four-center Coulomb two-electron integrals, for which the computer time is necessarily reduced even more because of the greater number of integrals than overlaps.

■ ASSOCIATED CONTENT

Supporting Information

Additional information as noted in text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Ozdogan, T.; Orbay, M.; Degirmenci, S. Evaluation of Two-Center Overlap Integrals Using Slater Type Orbitals in Terms of Bessel Type Orbitals. *J. Math. Chem.* **2005**, 37 (1), 27–35.
- (2) Mekelleche, S. M.; Baba-Ahmed, A. Calculation of the One-Electron Two-Center Integrals over Slater-Type Orbitals by Means of the Ellipsoidal Coordinates Method. *Int. J. Quantum Chem.* **1997**, 63 (4), 843–852.
- (3) Guseinov, I. I.; Öztekin, E.; Hüseyin, S. Computation of Molecular Integrals over Slater-Type Orbitals. Part VI. Calculation of Overlap Integrals with the Same Screening Parameters Using Gegenbauer Coefficients. *J. Mol. Struct. (THEOCHEM)* **2001**, 536 (1), 59–63.
- (4) Grotendorst, J.; Weniger, E. J.; Steinborn, E. O. Efficient Evaluation of Infinite-Series Representations for Overlap, Two-Center Nuclear Attraction, and Coulomb Integrals Using Nonlinear Convergence Accelerators. *Phys. Rev. A* **1986**, 33 (6), 3706–3726.
- (5) Safouhi, H. Numerical Treatment of Two-Center Overlap Integrals. *J. Mol. Model.* **2006**, 12 (2), 213–220.
- (6) Weniger, E. J.; Steinborn, E. O. Numerical Properties of the Convolution Theorems of B Functions. *Phys. Rev. A* **1983**, 28 (4), 2026–2041.

- (7) Pashaev, F. G. Use of Filter-Steinborn B and Guseinov Q_{α}^g Auxiliary Functions in Evaluation of Two-Center Overlap Integrals over Slater Type Orbitals. *J. Math. Chem.* **2009**, *45* (4), 884–890.
- (8) Hehre, W. J.; Stewart, R. F.; Pople, J. A. Self-Consistent Molecular-Orbital Methods. I. Use of Gaussian Expansions of Slater-Type Atomic Orbitals. *J. Chem. Phys.* **1969**, *51* (6), 2657–2664.
- (9) Huzinaga, S.; Klobukowski, M.; Tatewaki, H. The Well-Tempered GTF Basis Sets and Their Applications in the SCF Calculations on N_2 , CO , Na_2 , and P_2 . *Can. J. Chem.* **1985**, *63* (7), 1812–1828.
- (10) Huzinaga, S.; Klobukowski, M. Well-Tempered GTF Basis Sets for the Atoms K through Xe. *Chem. Phys. Lett.* **1985**, *120* (6), 509–512.
- (11) Huzinaga, S.; Miguel, B. A Comparison of the Geometrical Sequence Formula and the Well-Tempered Formulas for Generating GTO Basis Orbital Exponents. *Chem. Phys. Lett.* **1990**, *175* (4), 289–291.
- (12) Klobukowski, M. Systematic Sequences of Well-Balanced Gaussian Basis Sets. *Can. J. Chem.* **1994**, *72* (7), 1741–1752.
- (13) Huzinaga, S.; Klobukowski, M. Well-Tempered Gaussian Basis Sets for the Calculation of Matrix Hartree–Fock Wavefunctions. *Chem. Phys. Lett.* **1993**, *212* (3–4), 260–264.
- (14) Fock, V. Näherungsmethode zur Lösung des quantenmechanischen Mehrkörperprobleme. *Z. Phys.* **1930**, *61* (1–2), 126–148.
- (15) Hartree, D. R. The Wave Mechanics of an Atom with a Non-Coulomb Central Field. I. Theory and Methods. *Proc. Cambridge Philos. Soc.* **1928**, *24* (1), 89–110.
- (16) Slater, J. C. The Theory of Complex Spectra. *Phys. Rev.* **1929**, *34* (10), 1293–1322.
- (17) Sekino, H.; Bartlett, R. J. Spin Density of Radicals by Finite Field Many-Body Methods. *J. Chem. Phys.* **1985**, *82* (9), 4225–4229.
- (18) Carmichael, I. Ab Initio Calculation of the Hyperfine Coupling Constants in B_2 . *J. Chem. Phys.* **1989**, *91* (2), 1072–1078.
- (19) Perera, S. A.; Watts, J. D.; Bartlett, R. J. A Theoretical Study of Hyperfine Coupling Constants. *J. Chem. Phys.* **1994**, *100* (2), 1425–1434.
- (20) Feller, D.; Glendening, E. D.; McCullough, E. A.; Miller, R. J. A Comparison of Unrestricted Hartree–Fock- and Restricted Open-Shell Hartree–Fock-Based Methods for Determining the Magnetic Hyperfine Parameters of NO ($X^2\Pi$). *J. Chem. Phys.* **1993**, *99* (4), 2829–2840.
- (21) Feller, D.; Davidson, E. R. A Multireference CI Determination of the Isotropic Hyperfine Constants for First Row Atoms B–F. *J. Chem. Phys.* **1988**, *88* (12), 7580–7587.
- (22) Fernández, B.; Jørgensen, P.; McCullough, E. A.; Simons, J. Calculation of Hyperfine Coupling Constants of the Ground State $X^3\Sigma^-$ of NH and B_2 . *J. Chem. Phys.* **1993**, *99* (8), 5995–6003.
- (23) de Oliveira, H. C. B.; Esteves, C. S.; Gargano, R.; do Nascimento, M. A. C.; Malbouisson, L. A. C.; Mundim, K. C. Molecular Properties Calculations Using the q -Integral Method. *Int. J. Quantum Chem.* **2008**, *108* (13), 2540–2549.
- (24) Mundim, K. C. An Analytical Procedure to Evaluate Electronic Integrals for Molecular Quantum Mechanical Calculations. *Physica A* **2005**, *350* (2–4), 338–348.
- (25) Rangel, F. C.; de Oliveira, H. C. B.; Montel, A. L. B.; Mundim, K. C. Calculation of DFT Molecular Properties Using the q -Integral Method. *Physica A* **2010**, *389* (22), 5208–5215.
- (26) de Oliveira, H. C. B.; Rangel, F. C.; Esteves, C. S.; Vieira, F. M. C.; Mundim, K. C. Calculation of MP₂ and Coupled-Cluster Molecular Properties Using the q -Integral Method. *J. Phys. Chem. A* **2009**, *113* (52), 14691–14698.
- (27) Esteves, C. S.; de Oliveira, H. C. B.; Ribeiro, L.; Gargano, R.; Mundim, K. C. Modeling Diatomic Potential Energy Curves through the Generalized Exponential Function. *Chem. Phys. Lett.* **2006**, *427* (1–3), 10–13.
- (28) Machado, D. F. S.; Silva, V. H. C.; Esteves, C. S.; Gargano, R.; Macedo, L. G. M.; Mundim, K. C.; de Oliveira, H. C. B. Fully Relativistic Rovibrational Energies and Spectroscopic Constants of the Lowest $X:(1)0_g^+$, $A':(1)2_w$, $A:(1)1_w$, $B':(1)0_u^-$ and $B:(1)0_u^+$ States of Molecular Chlorine. *J. Mol. Model.* **2012**, *18* (9), 4343–4348.
- (29) Salviano, L. R.; Esteves, C. S.; de Oliveira, H. C. B.; Mundim, K. C.; Ribeiro, L.; Gargano, R. Use of Generalized Exponential Function to Build Three-Dimensional Reactive Surfaces. *Physica A* **2010**, *389* (17), 3604–3612.
- (30) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. General Atomic and Molecular Electronic Structure System. *J. Comput. Chem.* **1993**, *14* (11), 1347–1363.
- (31) Aquilanti, V.; Mundim, K. C.; Elango, M.; Kleijn, S.; Kasai, T. Temperature Dependence of Chemical and Biophysical Rate Processes: Phenomenological Approach to Deviations from Arrhenius Law. *Chem. Phys. Lett.* **2010**, *498* (1–3), 209–213.
- (32) Mundim, K. C.; Tsallis, C. Geometry Optimization and Conformational Analysis through Generalized Simulated Annealing. *Int. J. Quantum Chem.* **1996**, *58* (4), 373–381.
- (33) de Andrade, M. D.; Mundim, K. C.; Malbouisson, L. A. C. GSA Algorithm Applied to Electronic Structure: Hartree–Fock–GSA Method. *Int. J. Quantum Chem.* **2005**, *103* (5), 493–499.
- (34) Giambiagi, M.; Degiambiagi, M. S.; Mundim, K. C. Group–Group Bond Index for Molecular Systems. *J. Chem. Soc., Faraday Trans.* **1992**, *88* (20), 2995–2999.
- (35) Mundim, K. C.; Giambiagi, M.; Degiambiagi, M. S. Molecular Invariants: Atomic-Group Valence. *Nuovo Cimento Soc. Ital. Fis. D* **1990**, *12* (6), 765–769.
- (36) Giambiagi, M.; Giambiagi, M.; Mundim, K. Definition of a Multicenter Bond Index. *Struct. Chem.* **1990**, *1* (5), 423–427.
- (37) Mundim, K. C.; Giambiagi, M.; Degiambiagi, M. S. Multicenter Bond Index: Grassmann Algebra and N -Order Density-Functional. *J. Phys. Chem.* **1994**, *98* (24), 6118–6119.
- (38) Sannigrahi, A. B.; Kar, T. Three-Center Bond Index. *Chem. Phys. Lett.* **1990**, *173* (5–6), 569–572.
- (39) Rangel, F. C.; Montel, A. L. B.; Mundim, K. C. A Study of Dihydrogen Bond Interactions through Three-Centre Bond and Group Indices. *Mol. Simul.* **2009**, *35* (4), 342–348.
- (40) Rashin, A. A.; Young, L.; Topol, I. A. Quantitative Evaluation of Hydration Thermodynamics with a Continuum Model. *Biophys. Chem.* **1994**, *51* (2–3), 359–374.