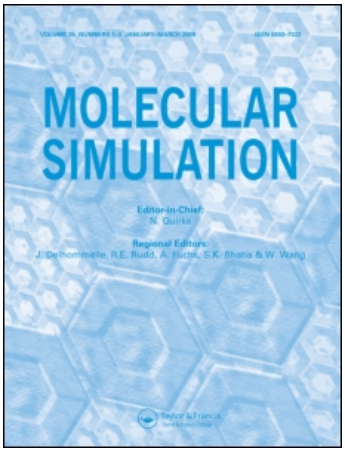

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M. Sánchez[a]; L. S. Rodríguez[b]; G. Larrazabal[c]; L. Galean[c]; N. Bello[c]; F. Ruette[b]
[a] Departamento de Química, IUT Federico Rivero-Palacio, Caracas, Venezuela [b] Laboratorio de Química Computacional, Centro de Química, Instituto Venezolano de Investigaciones Científicas, Caracas, Venezuela [c] Escuela de Computación, FACYT, Universidad de Carabobo, Valencia, Venezuela

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Molecular parameter optimization using simulated annealing and evolutionary algorithm techniques in a quantum parametric method (CATIVIC)

M. SÁNCHEZ†*, L. S. RODRÍGUEZ‡, G. LARRAZABAL¶, L. GALEAN¶, N. BELLO¶ and F. RUETTE‡

†Departamento de Química, IUT Federico Rivero-Palacio, Apartado 40347, Caracas, Venezuela
‡Laboratorio de Química Computacional, Centro de Química, Instituto Venezolano de Investigaciones Científicas, Apartado 21827, Caracas 1020-A, Venezuela
¶Escuela de Computación, FACYT, Universidad de Carabobo, Valencia, Venezuela

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Application of simulated annealing (SA) and evolutionary algorithm (EA) techniques for optimization of parameters in the parametric quantum chemistry method (CATIVIC) was performed. A set of organic molecules and gold clusters were selected for test these techniques. Comparison was performed with respect to experimental values and DFT calculated equilibrium bond distances (EBD) and bond angles (BA). Results show that EA is more efficient than SA with respect to computer time. Accuracy is similar in both methods; however, there are important differences in the set of parameters.

Keywords: Parametric methods; Simulated annealing; Evolutionary algorithm; Global minimum; Parameterization

1. Introduction

Molecular calculations using *ab initio* methods remain prohibitively expensive for large amorphous systems. However, qualitative information obtained from parametric quantum methods (PQM) expends three or four orders of magnitude less in computer time than *ab initio* ones. This is very encouraging because the PQMs have been successfully applied to predict chemical properties of complex systems [1]. Therefore, development of efficient techniques to compute molecular parameters, required in PQM approaches, is of paramount importance. It is well known that parameter calculation is a troublesome task for improving the accuracy of these methods. So, the development of optimization tools to obtain atomic and molecular parameters and the corresponding functionals is a priority for the future of molecular modelling of multifaceted systems, in order to reproduce experimental properties of realistic molecular models.

Previous applications of simulated annealing (SA) and the SIMPLEX method [2] have been efficiently used to calculate optimal atomic parameters in CATIVIC method [3] by comparing with electronic atomic spectra [4]. A test of SA has been recently also carried for molecular parameters [5] with the CATIVIC program. On the other hand, Cundari *et al.* [6] have been successfully applied genetic algorithms to parameterize PM3(tm) for technetium complexes.

In this work, molecular parameters used in functionals of CATIVIC [7–10] were optimized using SA and evolutionary algorithms (EA) techniques by minimizing the differences between theoretical and experimental data. A set of simple molecules was selected for parameterization with respect to experimental structural properties. It was found that an adequate selection of the starting point, general energy functionals and constrains for diatomic molecules (DM) allow to obtain a set of parameters that reasonably reproduces experimental molecular properties.

Very few applications of non-linear optimization techniques to find optimal parameters in PQM methods have been reported in the literature. The potentiality of PQM methods depends on the feasibility of find well-defined parametric functionals and their corresponding parameters. Here, we present the first application of SA and EA techniques to a new PQM method (CATIVIC) to obtain molecular parameters. In order to have a complete range of applications to molecular parameters, two different set of molecular systems were selected one

*Corresponding author.

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with bonds of very light atoms (H–H, C–H and C–C) and other with very heavy ones (Au–Au).

This work is organized in the following way. Theoretical background of parametric methods and SA and EA techniques are presented in Section 2. There, it is included: simulation equations; parametric functionals; characteristics; and schemes of each technique with their corresponding conditions and constrains. Results and discussions for applications of SA and EA to a set of organic molecules and gold clusters are discussed in Section 3. Finally, conclusions and comments are presented in Section 4.

2. Theoretical background

2.1 Parametric methods

The development of parametric methods based on simulation techniques [7,8] requires molecular data for DM ($X - 5Y$) in order to adjust molecular parameters that simulate $X - Y$ potential energy curve. The philosophy of a new parametric method proposed elsewhere [3] is based on a correct representation of the most elementary molecule (DM) and then the extension to more complex systems. Hitherto, the transferability to polyatomic molecules does not consider explicitly because, it depends on a correct representation of parametric functionals to simulate the optimal analytical functionals.

Parametric methods in quantum chemistry are based on parametric bond energy functionals (BE_{pa}) that are defined in terms of simulation techniques, such as,

$$\min\left(\sum_{I}\left|BE_{exa}^{(X-Y)_I} - BE_{pa}^{(X-Y)_I}\right|^2\right)^{1/2} \quad (1)$$

where $BE_{exa}^{(X-Y)_I}$ and $BE_{pa}^{(X-Y)_I}$ are the bonding energies of the $X - Y$ molecule in the Ith molecular electronic state, obtained experimentally or theoretically evaluated as good as possible and calculated from the parametric functionals, respectively.

$$BE_t^{X-Y} = E^{X-Y} - E^X - E^Y \quad (2)$$

where $t =$ exa, pa. The total energy for a molecular system is divided in diatomic and monoatomic energy terms

$$E = \sum_X E_X + \sum_{X>Y} E_{XY} \quad (3)$$

where the diatomic term is expressed in terms of fundamental parametric functionals such as,

$$E_{XY} = f\left(\left\{h_{X\mu Y\nu}\right\}, \left\{\gamma_{X\mu Y\nu}\right\}, \left\{V_{XY\nu}\right\}, \left\{E_{XY}^C\right\}\right), \quad (4)$$

and where $h_{X\mu Y\nu}$, $\gamma_{X\mu Y\nu}$, $V_{XY\nu}$ and E_{XY}^C correspond to resonance, electron–electron repulsion, electron–nucleus attraction and core–core repulsion functionals, respectively. Labels μ and ν represent orbital basis ($\mu \in X$; $\nu \in Y$) for elementary electronic interactions. Different E_{XY} functionals have been tested, in particular, we select a different core–core energy term (E_{XY}^C) and left standard functionals for the rest [7]:

$$E_{XY}^C = Z_X Z_Y\left(RCP_{XY}\gamma_{XY}^P(R,D) + \alpha_{XY}\left(\left(\frac{1}{R_{XY}}e^{-REP_{XY}R_{XY}}\right) - RCC_{XY} * \gamma_{XY}^C(R,D')e^{-REC_{XY}R_{XY}}\right)\right) \quad (5)$$

where RCP_{XY}, D, D', α_{XY}, REP_{XY}, RCC_{XY} and REC_{XY}, are parameters to be adjusted for each pair of XY atoms to find the minimum in equation (1). $\gamma_{XY}^P(R,D)$ and $\gamma_{XY}^C(R,D')$ are pseudo-potential and electronic average correlation functionals [7], respectively. Z_X and Z_Y are constant values that correspond to core nuclear charges for atoms X and Y, respectively.

The simulation proposed in equation (1) corresponds to a minimization of the difference between two sets of functionals: one that represent the exact binding energy (BE) from accurate solution of the Schrödinger's equation or experimental data and other that is obtained from functionals based on parameters. For practical reasons, ground states of neutral molecules are, in general, mainly considered here.

2.2 Simulated annealing

A procedure for the calculation of parameters is based on the SA algorithm developed by González, as presented in reference [2]. The SA is a method to locate global minima in complicated multivariable functions. Starting with an initial set of parameters, the calculation of a set of molecules, for example those that contain C–H, H–H and C–C bonds, is performed. Then, the geometry difference between several calculated bond distances R_i^{cal}(in Å) and angles θ_j^{cal}(in radians) of different molecules is compared with the experimental values (R_i^{exp} and θ_j^{exp}) taken from refs. [11–13]. The change in the cost function (ΔC) depends on the difference between the geometries (internuclear distances and angles) calculated and the experimental ones in two successive moves for Nm molecules, each one with Nr_k distances and Na_k angles of interest. The expression of cost function for the move n is defined as,

$$C_n = \frac{\left(\sum_k^{Nm}\left(\sum_{i=1}^{Nr_k}\frac{1}{Nr_k}\left(R_i^{cal_n} - R_i^{exp}\right)^2 + \sum_{i=1}^{Na_k}\frac{1}{Na_k}\left(\theta_j^{cal_n} - \theta_j^{exp}\right)^2\right)\right)^{1/2}}{Nm} \quad (6)$$

A variation in the parameters is made and the results compared. The probability P of accepting a change in the parameters or a move is given by the Metropolis criterion [14]:

$$P(\Delta C) = 1 \quad \Delta C < 0 \tag{7}$$

$$P(\Delta C) = \exp\left(\frac{-\Delta C}{kT}\right) \quad \Delta C > 0 \tag{8}$$

where $\Delta C = C_n - C_{\mathrm{ns}}$ and ns is the previous selected move. The variable k is the Boltzmann constant and T the temperature.

The probability of accepting a move for $\Delta C > 0$ is compared with a random number in the interval [0–1], if it is smaller than or equal to P, the configuration is accepted. This criterion permits a non-zero probability of moving to a configuration with a cost function higher than the last configuration and at high temperatures the algorithm can easily jump from one local minimum to another.

All calculations were performed in the temperature range of 5000–0.5 K using a quenching rate of 0.99. T is updated according to the geometric temperature quenching introduced by Kirkpatrick [15]:

$$T_{i+1} = \beta T_i \tag{9}$$

with $0 < \beta < 1$.

A simplified scheme of the procedure for SA method is depicted in figure 1. Here, we include parameter constrains to reproduce experimental BE and EBD of $X - Y$ DM. Experimental or well-calculated DM properties for the first to third row elements were taken from data base included in CATIVIC and given in reference [16]. The termination condition is reached when no movement in the space of configurations is obtained after four different temperatures or when the minimum temperature is attained.

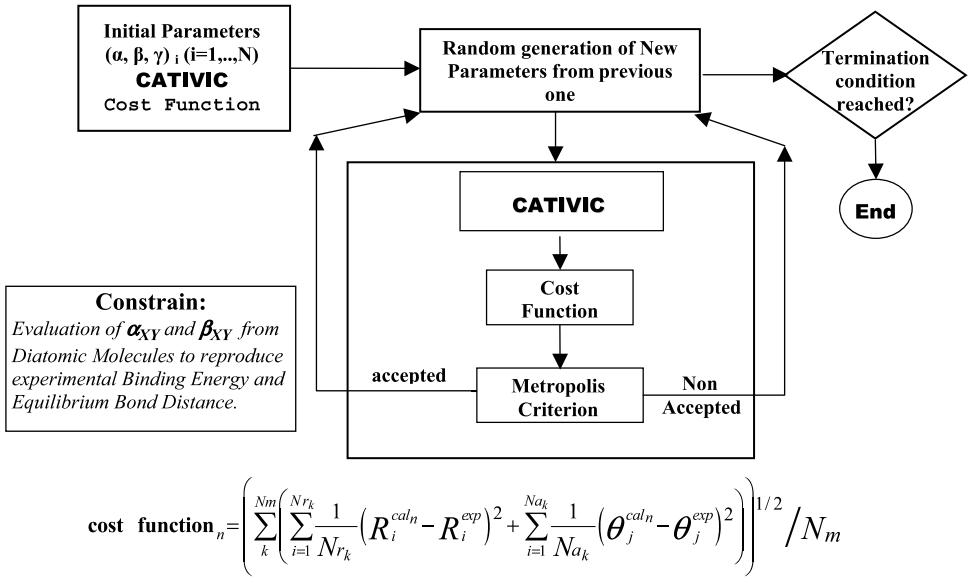
2.3 Evolutionary algorithms

EAs are very efficient for fast finding of the approximate global minimum or maximum value by searching the domain space with mutation and taking advantage of good results with selection and crossover.

A population is decoded and evaluated according to some predefined quality criterion, referred to as the fitness. The initial population of individuals is generated at random or heuristically. For each evolutionary step or generation, individuals are selected consistent with their fitness according to several procedure assortments. Thus, emulating natural evolution, high-fitness implies better adapted individuals and a better chance of reproducing, while low-fitness ones are more likely to disappear.

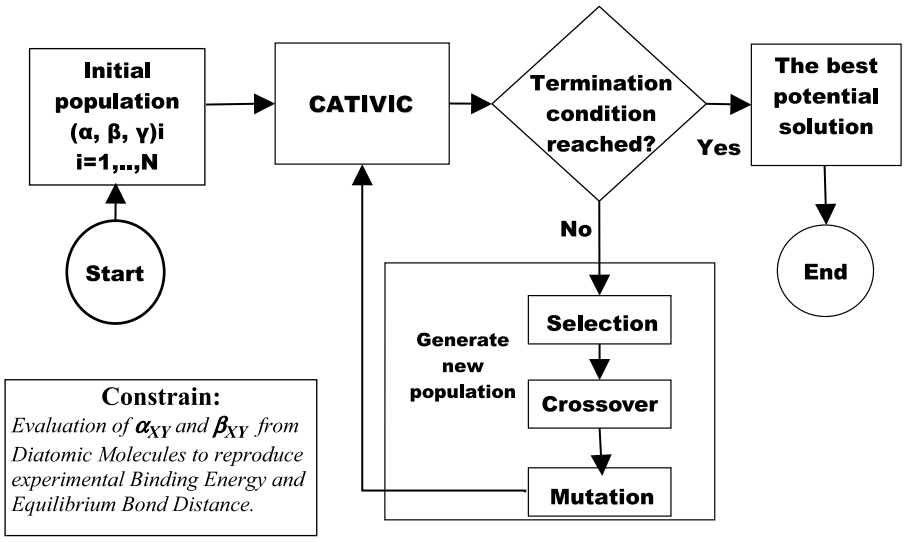
In order to introduce new individuals or chromosome into the population, operators of crossover and mutation are employed. Crossover is performed between two selected individuals (parents) by exchanging their genes (21 genes in this work) to generate two new individuals (offspring), after a randomly selected crossover operation. Mutation is introduced to prevent convergence to local minimum by randomly sampling new points in the search space. EAs are techniques based on stochastic iterative processes that are not guaranteed to converge. For this reason in this work, SA and EA are compared, in order to investigate the effectiveness of these methods to find optimal parameters from PQM.

The major problem with genetic algorithms is creating an effective evaluation function (EF) or fitness. In this case, we use the equation (6), see expression shown in figure 2. The implementation of an EA is quite costly in many cases, since populations of solutions are involved possibly coupled with computation-intensive fitness evaluations, which is the case for the calculation of a series of molecules. One possible solution is to parallelize the process, an idea which has been explored to some



$$\text{cost function}_n = \left(\sum_k^{Nm} \left(\sum_{i=1}^{Nr_k} \frac{1}{Nr_k} \left(R_i^{cal_n} - R_i^{exp} \right)^2 + \sum_{i=1}^{Na_k} \frac{1}{Na_k} \left(\theta_j^{cal_n} - \theta_j^{exp} \right)^2 \right) \right)^{1/2} \Big/ Nm$$

Figure 1. Scheme of SA procedure for parameter optimization in parametric methods.



$$\text{Fitness}_n = \left(\sum_{k}^{Nm} \left(\sum_{i=1}^{Nr_k} \frac{1}{Nr_k} \left(R_i^{cal_n} - R_i^{exp} \right)^2 + \sum_{i=1}^{Na_k} \frac{1}{Na_k} \left(\theta_j^{cal_n} - \theta_j^{exp} \right)^2 \right) \right)^{1/2} \Big/ N_m$$

Figure 2. Scheme of EA procedure for parameter optimization in parametric methods.

extent in recent years [17–19]. This may requires judicious modifications of existing algorithms or the introduction of new ones, in order to meet the constraints of a given parallel machine.

The scheme of EA process is displayed in figure 2. Here, the same constrain imposed to SA is considered and the fitness calculation is based on the cost function in equation (6). The termination condition is achieved after all generations have been evaluated. The optimal conditions for EA: population size; number of generations; crossover; mutation; and substitution probabilities are presented in table 1. The analysis of convergence with the number of generations is presented in figure 3. Results indicate that about 100 generation is sufficient for obtaining a fitness or EF value similar to that of the maximum number of generations (1000). The operator weight is changed according to Davis' procedure [20] of adaptable technique in order to obtain optimal trajectories. The roulette wheel criterion was used to modify operator weights.

3. Results and discussion

In order to compare the performance of SA and EA methods, calculations for a small set of molecules were carried out with both techniques. Atomic parameters for H and C were previously evaluated using the methodology shown in ref. [2]. The optimization of 18 molecular parameters (RCP_{XY}, REC_{XY}, RCC_{XY}, REP_{XY}, D and D' for core–core functional, see equation (5), for each different XY pair of atoms (XY corresponds to CC, CH and HH)) was carried out. In addition, three atomic orbitals exponents (ξ_{Cs}, ξ_{Cp} and ξ_{Hs}), used to evaluate the resonance functional, were also optimized. Parameters α_{XY} from the core–core functional and β_{XY} from the resonance functional were obtained in order to fit experimental BE and EBD of $X - Y$ DM, using an iterative procedure. The performance of both methods is presented in table 2, considering the average errors of optimized EBD ($\overline{\Delta R}$)and bond angles (BA) ($\overline{\Delta\theta}$). Results show very similar accuracy in SA and EA methods, however, EA is ten time faster than SA.

Table 1. Conditions used in EA.

Population size	100
Number of generations	1000
Crossover probability (maximum)	100%
Crossover probability (minimum)	50%
Mutation probability (maximum)	15%
Mutation probability (minimum)	1%
Substitution probability	20%

In order to include different types of bond interactions (single, double, triple and aromatic bonds), a set of 18 molecules with C–H, C–C and H–H interactions was selected as shown in table 3. Maxima average errors, respect to selected experimental EBD and BA data, are about 0.03 Å and 9° for EBD and BA, respectively. Although, there is not a big difference in errors between both methods, the computer time employed in EA is consistently lower than in SA technique. Similar trend is reported by Zacharias *et al.* [19]. On the other hand, results indicate some important differences between parameters obtained with these two methods. This is an indication that is important to combine both techniques in order to improve the accuracy and performance of parameter's finding.

A similar process was performed for gold clusters (Au_n, $n = 1–5$) with different geometries and

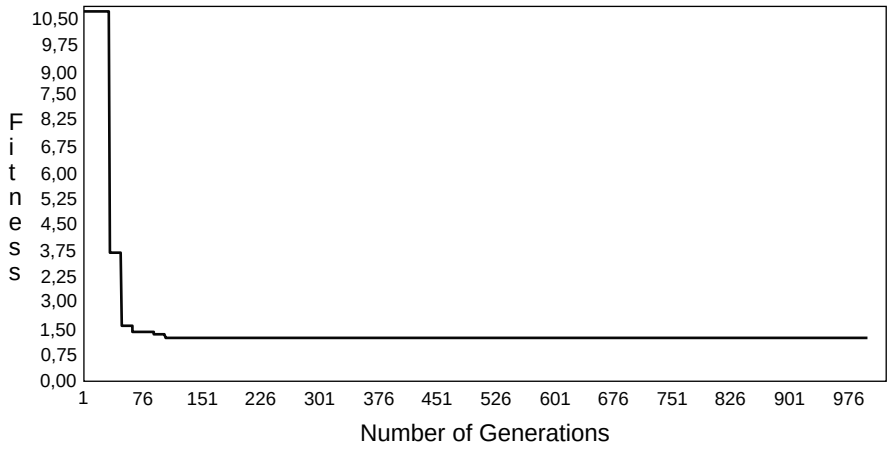


Figure 3. Variation of fitness with the number of generations.

coordinations. Atomic parameters were previously obtained using SA method [2] adjusting with experimental energies of different gold electronic atomic states with respect to its ground state. In order to optimize Au–Au molecular parameters, clusters results were compared with DFT calculation of Sierralta [19]. Values of average bond distances and angles errors are shown in table 4. Results indicate reasonable and similar errors using both techniques (maxima errors of $\overline{\Delta R} = 0.12$ Å and $\overline{\Delta\theta} \approx 5°$); however as in the case hydrocarbon molecules, again there are important differences in the obtained parameters.

4. Conclusions and comments

The future of PQMs depends on the possibility to get in an easy way parametric functionals and their corresponding parameters. Non-linear optimization techniques to obtain optimal parameters in PQM are scarce reported in the literature [2,5,6,21]. In this work, parameters for molecular systems of different levels of complexity have been found by the use of two non-linear optimization techniques (SA and EA). Results show that these techniques can be successfully employed to find satisfactory molecular parameters for the CATIVIC method. The following conclusions and recommendations are presented as follows:

(a) EA is faster than SA for obtaining parameters. Convergence of the fitness (EF) with number of generation is reached at about 100 generations, using adaptable EA technique.
(b) The accuracy of both methods (error) is similar with respect to the experimental values or higher level of calculations; however, the set of parameters have important differences. A combination of both methods would be convenient in order to have more security to reach the global minimum.
(c) Constrains imposed to these techniques may have influence in obtaining of the optimal parameters and reach the global minimum. Here, in each iteration cycle (move or individual), new α_{XY} and β_{XY} parameters are evaluated in order to obtain experimental or well-calculated EBDs and BEs of

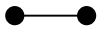
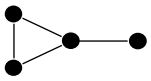
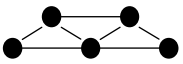
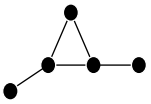
Table 2. Performance of SA vs. EA. $\overline{\Delta R}$ and ($\overline{\Delta\theta}$) are average internuclear distances and angles in Å and degrees, respectively.

Molecules	*SA*		*EA*	
	$\overline{\Delta R}$	$\overline{\Delta\theta}$	$\overline{\Delta R}$	$\overline{\Delta\theta}$
CH	0.000	0.000	0.000	0.000
CH_2 singlet	0.002	0.107	0.002	0.179
CH_2 triplet	0.007	0.801	0.008	0.820
CH_3	0.003	0.000	0.003	0.000
C_3H_4	0.011	0.860	0.013	0.869
C_3H_8	0.015	6.756	0.012	6.246
Time (h)	87.32		8.92	

Table 3. Errors of average internuclear distances ($\overline{\Delta R}$) and angles ($\overline{\Delta\theta}$) in Å and degrees, respectively, for organic molecules using EA and SA techniques.

Method / *Molecule*	*EA*		*SA*	
	$\overline{\Delta R}$	$\overline{\Delta\theta}$	$\overline{\Delta R}$	$\overline{\Delta\theta}$
H_2	0.000	0.000	0.000	0.000
CH	0.000	0.000	0.000	0.000
C_2	0.000	0.000	0.000	0.000
$1CH_2$	0.007	1.808	0.001	0.030
CH_3	0.002	0.000	0.014	0.000
CH_4	0.002	0.001	0.016	0.000
C_2H_2	0.016	0.000	0.013	0.000
C_2H_4	0.011	1.452	0.013	1.343
C_2H_6	0.006	4.073	0.011	1.390
Alene	0.016	8.959	0.015	5.778
C_3H_4	0.009	2.416	0.006	0.143
Ciclopropene	0.018	4.316	0.033	2.151
C_3H_6	0.008	3.502	0.010	3.763
C_3H_8	0.004	1.583	0.002	4.519
HCCCCH	0.023	2.147	0.019	0.000
C_4H_{10}	0.009	2.991	0.010	5.325
C_6H_6	0.008	0.174	0.0071	0.577
$CH_3C_6H_6$	0.007	2.74	0.013	3.249

Table 4. Errors of average internuclear distances ($\overline{\Delta R}$) and angles ($\overline{\Delta\theta}$) in Å and degrees, respectively, for gold clusters.

Method / *Cluster*		*EA*		*SA*	
		$\overline{\Delta R}$	$\overline{\Delta\theta}$	$\overline{\Delta R}$	$\overline{\Delta\theta}$
Au_2		0.00	0.00	0.00	0.00
Au_3		0.01	0.05	0.01	0.45
Au_3		0.01	0.02	0.07	5.28
Au_3		0.01	0.00	0.12	0.07
Au_4		0.02	5.17	0.05	4.12
Au_4		0.08	3.52	0.01	2.32
Au_5		0.00	0.68	0.00	0.68
Au_5		0.01	0.03	0.01	0.03

the correspondent ground state of DM (for example, H_2, C_2, CH and Au_2).

(d) It is important to note that not only parameters have to be optimized but also the parametric functionals. Therefore, the quality of the analytical expression of the functional is very important to reproduce experimental values. Several types of functionals: resonance, electron–electron repulsion, core–core repulsion and electron–nucleus attraction have to be explored in future works in order to get a better correlation theory-experiment.

(e) Adaptable techniques can be implemented to SA to obtain the best relative weight for changing of parameters. In this way, SA should be more efficient. A combination of both techniques is suggested, because EAs have faster convergence with respect to SA. Then, as mention Zacharias *et al.* [19], SA is not efficient at the beginning of the search procedure; on the other hand, SA is more accurate and can be used at the end of the configurational search. In addition, SIMPLEX method can be implemented for improving the location of the global minimum, as was done in atomic parameters [2].

(f) The energetic part (heats of formation) must be considered for future parameterizations, as shown in reference [5].

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