Comparative Analysis of Simulated Annealing (SA) and Simplified Generalized SA (SGSA) for Estimation Optimal of Parametric Functionals in CATIVIC

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Abstract. Application of simulated annealing (SA) and simplified GSA (SGSA) techniques for parameter optimization of parametric quantum chemistry method (CATIVIC) was performed. A set of organic molecules were selected for test these techniques. Comparison of the algorithms was carried out for error function minimization with respect to experimental values. Results show that SGSA is more efficient than SA with respect to computer time. Accuracy is similar in both methods; however, there are important differences in the final set of parameters.

Keywords: simulated annealing, generalized, simplified, parametric functionals.
PACS: 02.70.-c

PARAMETRIC METHODS

Parametric methods, such as CATIVIC, are based on simulation techniques and parametric functionals [1]. In these methods, the total energy parametric functional (E_{pa}) is defined in terms of a set of n parameters {q_1, q_2,..... q_n} that are optimized with respect to accurate data obtained from experiment or faithful theoretical *ab initio* calculations (E_{exa}) of a set of molecules. The E_{pa} depends on atomic and molecular parameters ($E_{pa} = f$ [{atomic parameters}, {molecular parameters}]). Thefore, the key point of these methods is to find the set of parameters and functionals that minimize the following expression (error function or cost function):

$$\min_{P_{pa}^{Mp} \in \boldsymbol{P}} \left(\sum_{M=1}^{m} \sum_{p=1}^{r} \left| P_{exa}^{Mp} - P_{pa}^{Mp} \right|^2 \right) \tag{1}$$

where P corresponds to a family of parametric expressions of r properties and a selected set of m molecules to reproduce a collection of r properties, with the condition: $m.r > n$. Properties are evaluated from the solution of the Schrödinger equation to calculate the total energy of the set of molecules and their corresponding atoms. Thus, total binding energy (BE_{tJ}^{M}) of M molecule in the J state with k_M atoms is calculated, as follows,

$$BE_{tJ}^{M} \Psi = \left(H_J^M , \Psi^M \right) - \sum_{X}^{k_M} \Psi \left(H^X , \Psi^X \right) \tag{2}$$

where H^M and H^X are Hamiltonians for the M molecule and the X atom of M, respectively.

CP1148, Vol. 2, *Computational Methods in Science and Engineering, Advances in Computational Science*
edited by T. E. Simos and G. Maroulis

Parameterization requires the geometry optimization of a set of molecules in each cycle of the optimization process in order to evaluate the cost function and in this way to obtain the best parameters and functionals. This is a computational expensive process. For this reason, a very efficient algorithm to find the global minimum of Eq. (1) is required to perform in a reasonable time the optimization of different functionals, parameters and different properties. Note that, in addition to binding energies and geometry, CATIVIC could be employed to simulate other properties, such as, electronic transitions, polarizability, transition state, vibrational frequencies, mechanical properties, magnetism, optical spectra, reactivity, electric conductivity, etc.

OPTIMIZATION TECHNIQUES

Simulated Annealing (SA)

The SA method resembles the cooling process of molten metals through annealing and it was first implemented as a minimization algorithm by Kirkpatrick, Gelatt, and Vecchi [2]. At high temperature, the atoms in the metal can move freely with respect to each other, but as the temperature is reduced, their movement get restricted and then finally they form crystals (the minimum possible energy), which depends on the cooling rate. If the temperature is reduced at a very fast rate, the crystalline state may not be achieved at all and instead, the system may end up in a polycrystalline state, which may have a higher energy than the crystalline one. Therefore, in order to achieve the absolute minimum energy state, the cooling phenomenon is simulated by controlling a parameter, namely, temperature T introduced with the concept of the Boltzmann probability distribution,

$$P(\Delta E) = e^{-\frac{\Delta E}{k_b \cdot T}} \tag{3}$$

Therefore, a system in thermal equilibrium at a temperature T has its energy distributed probabilistically according to Eq. (3), where ΔE is the energy of the system and k_b is the Boltzmann constant. In problems with more complex domains, the Boltzmann-Gibbs probability distribution function is also used as a visiting function.

Given a cost function, the simulated annealing family of algorithms works as follow:

1. From an initial set of parameter values of the given cost function, generally randomly chosen, an initial "energy", E_{ref}, of the system is evaluated and an initial "artificial temperature" $T = T_0$ is selected.
2. A random perturbation is generated into the parameters ($x_{t+1} = x_t + \Delta x_t$) of the cost function using the visiting function (Δx_t), and the new "energy" of the system, E_{new}, is then calculated.
3. If $\Delta E = E_{new} - E_{ref} \leq 0$, the new point is better or at least of the same quality as the previous one. This new set of parameter values becomes the reference set.
4. If $\Delta E > 0$, the new point is worse than the reference point but still could be accepted depending on the comparison between acceptance probability function (Eq. 3) and a random number.
5. The "temperature" T is decreased, according to a temperature decaying function.
6. Steps 2 through step 5 are repeated during a giving number of steps or until some other stopping criteria become satisfied.

Generalized Simulated Annealing algorithm

The generalized simulated annealing (GSA) algorithm remains the same as that of SA except for the annealing schedule. GSA has been proposed by Stariolo and Tsallis [3] and use, instead of the Boltzmann-Gibbs statistics, the generalized statistic approach (Tsallis machine). This approach is computationally faster as compared to classical SA that usually requires a large number of function evaluations to find the optimal solution. It is necessary to search for faster algorithms to quenching the temperature in the system which is the basis of GSA[1]. Thus, the initial temperature, cooling rate, and the number of iterations performed at a particular temperature are the three important parameters which govern the successful working of GSA.

SGSA algorithm

A modification to GSA for even more efficient search of minima has been proposed by Dall'Igna at al. [4]. The SGSA algorithm uses an acceptance probability function similar to GSA in the cases where $E(x_{t+1}) > E(x_t)$, shown in the expression,

$$P_{q_A}(\Delta E) = \left\{ 1 + \left\{ 1 + (q_A - 1)\frac{\left[E(x_{t+1}) - E(x_{t+1}) \right]}{T_{qt}(t)} \right\} \frac{1}{(q_A - 1)} \right\}^{-1} \tag{4}$$

where q_A ($1.0 < q_A < 3.0$) is the acceptance parameter.

An efficient and simplified visiting function that depends on the Tsallis probability density function with dimension D = 0, is proposed by Dall'Igna at al. [4], such as,

$$\Delta x \propto g_{q_V}(r_t) = \left[\frac{1}{1 + \frac{(q_V - 1) r_i^2}{T_{q_V}^{2/(3-q_V)}}} \right]^{\frac{1}{q_V - 1} - \frac{1}{2}} \tag{5}$$

where q_V ($1.0 < q_V < 3.0$) is the visiting parameter, this simplified expression guaranteed x always inside a given domain.

The temperature decaying in Eq. (5) is, as in GSA, controlled by the following equation,

$$T_{q_T}(t) = T_{q_T}(t_0) \cdot \frac{2^{q_T - 1} - 1}{(1 + t)^{q_T - 1} - 1} \tag{6}$$

where q_T corresponds to a temperature decaying parameter that is in the same range of q_V. It allows a more independent control of T over the annealing process.

RESULTS AND CONCLUSIONS

In this work, 52 organic molecules with C-C, C-H, and H-H bonds, obtained from the MOPAC data [5], were selected as a trial set. This set includes small molecular systems, such as H_2, H_2^+, H_2^-, H_3^+, CH, C_2, and C_3 that may be very important for modeling intermediates in catalytic reactions. Calculations of this set of molecules and SGSA approach show that the accuracy obtained with a new set of functionals [6] can be better or equal to that reported by MOPAC-2007 [7].

Here, a comparison between SA and SGSA algorithms is presented in Fig. 1. These results indicate that the SGSA reduces the error function in a 68 percent in just 15 minutes, with only 33 iterations. On the other hand, the SA algorithm reduces 0.1% of error in 84 iterations, requiring more time (approx. 36 hours) to match the values obtained by the SGSA one. Note that this difference was largely due to the adjustment of q_A, q_V and q_T parameters (see Eqs. 4-5), which allowed a more efficient search of optimal values for quantum parametric functionals (molecular and atomic parameters).

The SGSA algorithm does not only allow minimizing the error function, but also it minimizes time for obtaining optimal results. Furthermore, a much better results were obtained in less time using parameter clustering tests based on the parameter sensitivity (high, medium and low) in the cost function. As a result of this

discrimination, this new strategy is an evolutionary model that allows to modify and to adjust the step and direction of parameter changes, according to the parameter sensitivity in the cost function.

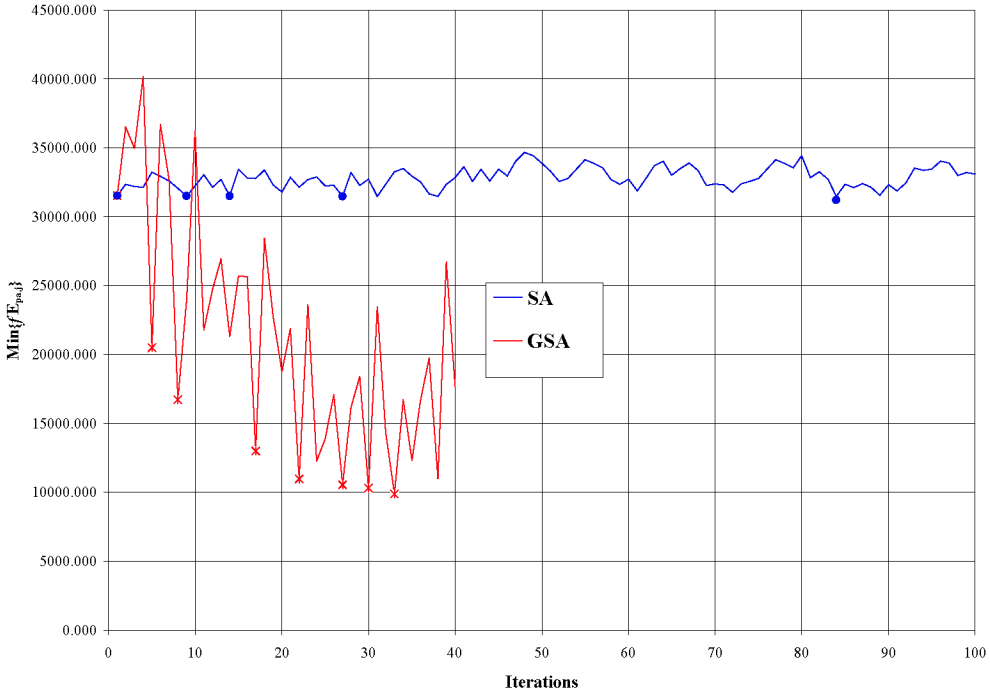

FIGURE 1. Comparison of values the error function obtained by SA and SGSA

ACKNOWLEDGMENTS

This work was supported by LOCTI Project: Development of computational programs based on parametric methods for applications to chemical industry in catalysis. IVIC, Venezuela.

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