FITTING POTENTIAL ENERGY SURFACE OF REACTIVE SYSTEM VIA GENETIC ALGORITHM

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In this work, we present a new fitting of the Na + HF potential energy surface (PES) utilizing a new optimization method based in Genetic Algorithm. Topology studies, such as isoenergetic contours and Minimum Energy Path (MEP), show that the quality of this new PES is comparable to the best PES of literature. These facts, suggests that this new approach can be utilized as new tool to fit PES of reactive systems.

I. INTRODUCTION

Genetic algorithms [1, 2, 3, 4, 5, 6] have been applied successfully in the description of a variety of global minimization problems. It have as well attracted significant attention due to their suitability for large-scale optimization problems, specially for those in which a desired global minimum is hidden among many local minima.

The main object of this paper is to propose a genetic algorithm optimization technique(GAOT) for fitting the PES through electronic energies obtained by ab initio calculations. In order to present and to test the method, we reproduce the PES of the reaction involving HF and an alkali metal, namely

Na(3^2S_{1/2}) + HF(X^1Σ^+) → NaF(X^1Σ^+) + H(2^3S_{1/2}),

utilizing as a trial function a Bond Order (BO) polynomial expansion [7] as well as ab initio calculations published by Laganà et al [8]. The motivation behind the choice of this reaction is its high endoergicity and its bent transition state [13]. Furthermore, this reactive process has been experimentally [9, 12], theoretically [14, 16] and computational investigated [17].

This paper is organized as follows. In Section 2, we present the main characteristics of the GAOT. The details of the GAOT fitting and its comparison with other SEPs are shown in the Section 3. Our conclusions are contained in the Section 4.

II. MODEL

A. The Problem

In order to fit a given functional form $V([a], \vec{r})$ in some set of $n_p$ points $(r^p_p, e_p)$, we want that the GAOT finds a set of parameters $[a] = [a_1, a_2, ..., a_m]$ that minimize the mean square deviation

$$ S = \sum_{p}^{n_p} \delta^2_p = \sum_{p}^{n_p} (e_p - \bar{e}_p)^2 $$

where $\bar{e}_p = V([a], r^p_p)$.

B. Codification

In our genetic algorithm the population is coded in a binary discrete cube named $A$, with $l \times m \times n$ bits. The elements of $A$, $a_{ijk}$, are either 0 or 1, with $i, j, k$ integers numbers $1 \leq i \leq n$, $1 \leq j \leq m$, $1 \leq k \leq n$. The label $i$ refers to the component $i$ of the gene $j$ of the individual $k$. Therefore, $A$ represents a population of $n$ individuals, each one of them have a genetic code with $m$ genes. Each gene is a binary string with $l$ bits.

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The genetic code of the individual $k$ is given by

$$\overline{a}_k = [a_{1k}, a_{2k}, ..., a_{mk}],$$

were

$$\overline{a}_{jk} = \sum_{i=1}^{l} 2^{i-1} a_{ijk} \quad (3)$$

is a integer number composed with the binary string $a_{1jk} a_{2jk} ... a_{ijk}$. It is defined on the interval $[0, 2^l - 1]$. To define the real search space for each parameter, we transform

$$a_{jk} \rightarrow a_{jk} = \frac{(a_{j}^{\text{max}} - a_{j}^{\text{min}})}{2^l - 1} \overline{a}_{jk} + a_{j}^{\text{min}} \quad (4)$$

were $a_{jk}$ is a real number defined on the interval $\delta_j = [a_{j}^{\text{min}}, a_{j}^{\text{max}}]$. 

Now we define the phenotype of the individual $k$, $V_k \equiv V(\overline{a}_k, \vec{r})$ where

$$[\overline{a}_k] = [a_{1k}, a_{2k}, ..., a_{jk}, ..., a_{mk}] \quad (5)$$

is a set of coefficients that characterize the individual $k$. With this we define the fitness of a phenotype $k$

$$F_k = S^{\text{max}} - S_k$$

where

$$S_k = \sum_{p}^{n_p} (\delta_{kp})^2 = \sum_{p}^{n_p} (e_p - V_{kp})^2 \quad (6)$$

and $S^{\text{max}}$ is worst individual in the population. $V_{kp} \equiv V([\overline{a}_k], \vec{r}_p)$ and $\delta_{kp}$ is the difference among the ab initio energy $e_p$ and the fit of the individual $k$ in the configuration $\vec{r} = \vec{r}_p$.

### C. Operators

We use the most common operators: selection, recombination and mutation. The selection operator normalize the vector $S_k$

$$P_k = \frac{S_k}{\sum S_k} \quad (7)$$

that represents the probability of each individual been selected for a recombination through a roulette spinning. For the purpose of this work we selected $n/2$ individuals (parents) that will generate, through the recombination operator, $n/2$ new individuals (offsprings). So, to make a new generation we joint the $n/2$ old strings (parents) with a $n/2$ new strings (offsprings) in order to maintain a population with fixed number $n$. The recombination operator is a cross-over operator that recombine the binary string of each gene $j$ of two random selected individuals to form two new individuals. In this work we use a two random point cross-over.

The mutation operator flip $N_{\text{mut}}$ random selected bits in a population. We choose $N_{\text{mut}}$ to make the probability of change of a given bit equal to 0.01 per cent. So, in a population of $l \times m \times n$ bits, we make

$$q = \frac{N_{\text{mut}}}{l \times m \times n} \quad (8)$$

where $q$ is the probability of change in one bit.

The elitist strategy consists of copying an arbitrary number $N_{\text{el}}$ of the best individual on the population in the next generation. It warrants that this individual will not be extinguished.
III. FITTING THE AB INITIO PES

Laganà et al. construed the BO5 PES of the Na+HF reaction considering a total of the 425 ab initio values, being 42 values (Table 2 of the Ref.[8]) calculated in the region that better characterize the collinear Na-HF and F-NaH geometries (insertion). All these 425 energy values cover a relevant portion of the surface at \( \theta = 0^\circ\), 45\(^\circ\), 60\(^\circ\), 75\(^\circ\), 90\(^\circ\), 120\(^\circ\), and 180\(^\circ\). Analytical representations of the BO5 PES were obtained using a BO polynomial expansion for both two- and three-body terms, following the standard many-body form. Each two-body term was construed fitting a polynomial of the fourth order in the related BO variables. The three-body term was fitted using the BO polynomial expansion given by

\[
V(R_{NaF}, R_{HF}, R_{NaH}) = \sum_{x=0}^{5} \sum_{y=0}^{5} \sum_{z=0}^{5} a_{xyz} \eta_{NaF}^x \eta_{HF}^y \eta_{NaH}^z
\]

with \( x + y + z \leq 6 \) and at least two indices differing from zero. The quantities \( \eta_m \) are defined as

\[
\eta_m = e^{-\beta M(R_e - R_{eM})}
\]

with \( M = \text{NaF}, \text{HF and NaH} \), where the parameters values of the Na+HF reactive process are \( R_{eNaF} = 1.92595 \) Å, \( R_{eHF} = 0.91681 \) Å, \( R_{eNaH} = 1.88740 \) Å, \( \beta_{NaF} = 0.88260 \) Å\(^{-1}\), \( \beta_{HF} = 2.19406 \) Å\(^{-1}\) and \( \beta_{NaH} = 1.19798 \) Å\(^{-1}\).

In order to use the GAOT method to reproduce the Na+HF PES, we used only the BO polynomial expansion for three-body term given by Eq. (10), with the same powers utilized to fit the BO5 PES. It should be pointed that we used only 243 of a total of the 425 ab initio values used to produce the BO5 PES. This number was the same used in the GSA PES fitting (see table 1 of the Ref.[8]).

Using the notation of Section II and Eq. (10) we define the phenotype of the individual \( k \)

\[
V_k \equiv V([a]_k, R_{NaF}, R_{HF}, R_{NaH}) = \sum_{j=1}^{m} a_{jk} \eta_{NaF}^{x_j} \eta_{HF}^{y_j} \eta_{NaH}^{z_j}
\]

where \( m \) is the number of coefficients that we use in the expansion. Each coefficient \( a_{jk} \) had a specific fixed combination of powers \( (x_j, y_j, z_j) \). In this way, we guarantee that the fittest individual in the population had a set of coefficients \( [a]_k \) that better fit the Eq. (10).

In this work, we define as an acceptable solution the set of 77 coefficients \( [a]_k \) that fit the expansion 10 to 243 ab initio points in a way that the root mean square deviation \( \sigma \) be less than 1.0 Kcal/mol. In fact, we can find a large number of acceptable solutions. The set of all solutions is the definition of search space \( \Gamma \). The length of \( \Gamma \) is defined by the number \( m \) of coefficients and the length \( l \) of the binary codification. Each one of the 77 coefficients, that define the individual \( k \), can assume \( 2^l \) distinct values. So, an individual in the population is only one possibility among \( 2^{l \times m} \). This value defines the length of \( \Gamma \). The precision of \( \Gamma \) describes the number of digits that are used to express a real value \( a_{jk} \) and shows the minimal difference between two possible values of \( a_{jk} \). Being each coefficient defined on an arbitrary interval \( \delta_j \) [5], the precision of the coefficient \( a_{jk} \) is

\[
\frac{a_{jk}^{\text{max}} - a_{jk}^{\text{min}}}{2^l}
\]

If we do not have any information about the order of magnitude of the \( a_{jk} \) values, we must choose the intervals \( \delta_j \)'s such that they cover the greatest number of values. However, after some generations, we obtained more precise information about the order of magnitude of each coefficient \( a_{jk} \). In order to improve the performance of the standard GAOT, we include in our technique the concept of dynamic search space. It consist in the use of information of past generations to determine the length and precision of the search space for the next generations. For the first generations, when we have few information about the order of magnitude of the coefficients, we do not need many digits to represent a real number \( a_{jk} \), that is, we use a low precision codification given by a low value of \( l \). In this way, we make \( \Gamma \) a "small" search space and the GAOT can find the regions of acceptable solutions faster. Once found some of these regions we can redefine the intervals \( \delta_j \)'s and rise the precision raising the length of binary codification \( l \). After extensive trials of the parameters values we take \( m = 77 \), \( n = 100 \), \( q = 0.01 \) and \( N_{el} = 10 \). Beside that, we always start the GAOT with a random population defined in the initial intervals \( \delta_j = [a_{jk}^{\text{min}}, a_{jk}^{\text{max}}] = [-10^5, 10^5] \) and set the initial value for the length of the binary codification \( l = 12 \). In this way we had a search space of length \( 2^{l \times m} = 2^{12 \times 77} = 2^{9224} \) and the minimal difference of two possible values of \( a_{jk} \) is \( 10^6 \) \( \frac{1}{2^{12}} \approx 49 \). After 1000 generations we
redefine \( l = l + 4 \) and \( \delta_j = [a^\text{min}_j, a^\text{max}_j] \) where \( a^\text{min}_j = a^\text{best}_j + a^\text{min}_j \times 10^{-1} \), \( a^\text{max}_j = a^\text{best}_j + a^\text{max}_j \times 10^{-1} \) and \( a^\text{best}_j \) is the fittest individual in the population found along the last 1000 generations. We set 10000 generations for each run of the GAOT. It should be pointed out that the algorithm is very robust and works properly with a wide range of these parameters.

Coefficients and powers of the polynomial given by Eq. (11) for the GAOT PES are showed in the table II. We plot in the figure IV the GAOT PES, considering \( \theta = 30.0^\circ \) (a), \( \theta = 180.0^\circ \) (b) and \( \theta = 77.2^\circ \) (c), with the respective isoenergetic contours. The dashed contours are taken between -160 and -40 kcal/mol and they are spaced each other by 5 kcal/mol. One can see that the global shape of the GAOT PES is closed similar to both GSA and BO5 PES.

To better test the new PES, we plot in figure V the GAOT fixed angle minimum energy paths (GAOT MEP) of the Na+HF reaction considering \( \theta = 30.0^\circ \) (a), \( \theta = 180.0^\circ \) (b) and \( \theta = 77.2^\circ \) (c), respectively. In these figures are also shown both GSA and BO5 MEPs. In all these MEPs the zero energy was set at the BO5 Na+HF asymptote. All these figures show that overall shape of the GAOT, BO5 and GSA MEP are very similar. At \( \theta = 77.2^\circ \) the barrier of the BO5 reaction is minimum and increases when moving towards collinear or towards more bent geometries. The same value was found for GAOT PES. In the table II are represented the values of the reactant energy, product energy, barrier height and well depth of the BO5-GAOT and GSA-GAOT MEP, for all values of the \( \theta \). These differences are about 0.02 kcal/mol and 0.73 kcal/mol, respectively. However, in the NaF+H product region these differences are about 1.4 and 1.48 kcal/mol, respectively. In the well region, the maximum differences of the energies between BO5-GAOT and GSA-GAOT are about 0.26 and 0.52 kcal/mol, respectively. The maximum values of these differences in the barrier region are about 0.5 and 1.2 kcal/mol, respectively.

IV. CONCLUSIONS

In this work, we have presented the GAOT method as a new option to fit PES for reactive system. Plots of the GAOT PES and BO5, GSA and GAOT MEP of the Na+HF system were made considering different values of the Na\( \hat{F} \)H angle. From comparison among these plots, we concluded that these PES have the same global shape. The values of the reactant energy, product energy, barrier height and well depth of these MEP at the principal \( \hat{NaF} \)H angle considered were very small, within of the error acceptable to reactive process. This ample topologies studies reveals that quality of the GAOT PES is comparable the with the best PES find for Na+HF reaction, i.e, BO5 and GSA PES.

In a future work, we will present a complete study of the dynamics properties of the Na+HF reaction utilizing the GAOT PES. These properties will be compared with the dynamics properties determined with the both BO5 GSA PES.

V. ACKNOWLEDGMENTS

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| $a_{xyz}$ | $x$ | $y$ | $z$ | $a_{xyz}$ | $x$ | $y$ | $z$ |
|---------|-----|-----|-----|---------|-----|-----|-----|
| $-306652213 \times 10^3$ | 1 | 0 | 0 | $.154007168 \times 10^2$ | 1 | 2 | 2 |
| $.340192379 \times 10^3$ | 2 | 0 | 0 | $-373620122 \times 10^4$ | 1 | 2 | 3 |
| $-255207454 \times 10^3$ | 3 | 0 | 0 | $-228197478 \times 10^2$ | 1 | 3 | 0 |
| $.982450848 \times 10^2$ | 4 | 0 | 0 | $-747920955 \times 10^2$ | 1 | 3 | 1 |
| $-203524473 \times 10^3$ | 0 | 1 | 0 | $.145451925 \times 10^2$ | 1 | 2 | 3 |
| $.177532304 \times 10^3$ | 0 | 2 | 0 | $.267614848 \times 10^2$ | 1 | 4 | 0 |
| $-393247020 \times 10^2$ | 0 | 3 | 0 | $.163502219 \times 10^2$ | 1 | 4 | 1 |
| $.141315171 \times 10^2$ | 0 | 4 | 0 | $-722678436 \times 10^2$ | 1 | 5 | 0 |
| $-98906904 \times 10^2$ | 0 | 0 | 0 | $.781884174 \times 10^2$ | 2 | 0 | 1 |
| $.656452121 \times 10^2$ | 0 | 0 | 2 | $.280647062 \times 10^2$ | 2 | 0 | 2 |
| $-148175260 \times 10^2$ | 0 | 0 | 3 | $.571812073 \times 10^2$ | 2 | 0 | 3 |
| $.302807924 \times 10^2$ | 0 | 0 | 4 | $-4.43796038 \times 10^2$ | 2 | 0 | 4 |
| $.141262929 \times 10^2$ | 0 | 1 | 1 | $-1.03732088 \times 10^4$ | 2 | 1 | 0 |
| $-907353392 \times 10^2$ | 0 | 1 | 2 | $.290375682 \times 10^2$ | 2 | 1 | 1 |
| $.618984796 \times 10^2$ | 0 | 1 | 3 | $-964447908 \times 10^2$ | 2 | 1 | 2 |
| $-118497362 \times 10^2$ | 0 | 1 | 4 | $.743005471 \times 10^2$ | 2 | 1 | 3 |
| $.707766194 \times 10^2$ | 0 | 1 | 5 | $1.05653468 \times 10^2$ | 2 | 2 | 0 |
| $.692426579 \times 10^2$ | 0 | 2 | 1 | $.391133693 \times 10^2$ | 2 | 2 | 1 |
| $-125347613 \times 10^2$ | 0 | 2 | 2 | $.796425832 \times 10^2$ | 2 | 2 | 2 |
| $-152740958 \times 10^2$ | 0 | 2 | 3 | $-4.16672911 \times 10^2$ | 2 | 3 | 0 |
| $.86466874 \times 10^1$ | 0 | 2 | 4 | $.222050269 \times 10^2$ | 2 | 3 | 1 |
| $.607286269 \times 10^2$ | 0 | 3 | 1 | $.580961193 \times 10^2$ | 2 | 4 | 0 |
| $.773420902 \times 10^2$ | 0 | 3 | 2 | $.612684773 \times 10^2$ | 3 | 0 | 1 |
| $.100454752 \times 10^2$ | 0 | 3 | 3 | $.24570625 \times 10^3$ | 3 | 0 | 2 |
| $.84822048 \times 10^2$ | 0 | 4 | 1 | $.537198805 \times 10^2$ | 3 | 0 | 3 |
| $.107320707 \times 10^2$ | 0 | 4 | 2 | $.520636389 \times 10^2$ | 3 | 1 | 0 |
| $.199301048 \times 10^2$ | 0 | 5 | 1 | $-1.1485817 \times 10^2$ | 3 | 1 | 1 |
| $.43595539 \times 10^3$ | 1 | 0 | 1 | $.378941105 \times 10^3$ | 3 | 1 | 2 |
| $.153727626 \times 10^3$ | 1 | 0 | 2 | $-3.12500339 \times 10^3$ | 3 | 2 | 0 |
| $.254081744 \times 10^2$ | 1 | 0 | 3 | $.293249874 \times 10^2$ | 3 | 2 | 1 |
| $.493407059 \times 10^1$ | 1 | 0 | 4 | $.633689268 \times 10^2$ | 3 | 3 | 0 |
| $.992614849 \times 10^1$ | 1 | 0 | 5 | $-1.87852456 \times 10^3$ | 4 | 0 | 1 |
| $.983517263 \times 10^3$ | 1 | 1 | 0 | $.171140643 \times 10^2$ | 4 | 0 | 2 |
| $.346826236 \times 10^1$ | 1 | 1 | 1 | $-1.5087795 \times 10^1$ | 4 | 1 | 0 |
| $.972616646 \times 10^2$ | 1 | 1 | 2 | $.479562662 \times 10^2$ | 4 | 1 | 1 |
| $.250389966 \times 10^2$ | 1 | 1 | 3 | $.23152882 \times 10^2$ | 4 | 2 | 0 |
| $.246833760 \times 10^2$ | 1 | 1 | 4 | $.27726868 \times 10^2$ | 5 | 0 | 1 |
| $.861838273 \times 10^1$ | 1 | 2 | 0 | $.126767492 \times 10^2$ | 5 | 1 | 0 |
| $.171256749 \times 10^2$ | 1 | 2 | 1 |

**TABLE I:**
| $\Theta$ | MEP  | Reactant | Product | Barrier | Well  |
|---------|------|----------|---------|---------|-------|
| 30°     | BO5  | -0.2303  | 17.6297 | 77.6465 | -1.7699 |
|         | GSA  | -0.9266  | 17.9334 | 78.7675 | -2.0017 |
|         | GAOT | -0.2144  | 17.4871 | 77.5946 | -1.7776 |
| 60°     | BO5  | -0.1978  | 17.5697 | 23.2639 | -3.1729 |
|         | GSA  | -0.9001  | 17.8983 | 23.3119 | -3.0291 |
|         | GAOT | -0.1819  | 17.4256 | 23.0681 | -3.3211 |
| 77.20°  | BO5  | -0.1817  | 17.5518 | 18.6754 | -6.1842 |
|         | GSA  | -0.8869  | 17.8874 | 18.5825 | -5.9927 |
|         | GAOT | -0.1659  | 17.4072 | 18.5229 | -6.3219 |
| 90°     | BO5  | -0.1724  | 17.5444 | 18.9925 | -7.3662 |
|         | GSA  | -0.8793  | 17.8829 | 19.4903 | -7.1637 |
|         | GAOT | -0.1565  | 17.3996 | 19.4439 | -7.4910 |
| 120°    | BO5  | -0.1586  | 17.5371 | 22.7954 | -8.3329 |
|         | GSA  | -0.8681  | 17.8784 | 22.7551 | -8.1231 |
|         | GAOT | -0.1427  | 17.3996 | 22.6442 | -8.4518 |
| 150°    | BO5  | -0.1525  | 17.5351 | 24.3159 | -8.7335 |
|         | GSA  | -0.8631  | 17.8772 | 24.3115 | -8.4731 |
|         | GAOT | -0.1366  | 17.3889 | 24.5618 | -8.9936 |
| 180°    | BO5  | -0.1508  | 17.5347 | 24.7239 | -8.8681 |
|         | GSA  | -0.8617  | 17.8769 | 24.7062 | -8.6105 |
|         | GAOT | -0.1349  | 17.3884 | 24.5618 | -8.9936 |

**TABLE II:**
FIG. 1: The figure shows the isoenergetic contours of the GAOT PES, at $\theta=30.0^\circ$ (a), $\theta=180.0^\circ$ (b) and $\theta=77.2^\circ$ (c). The zero energy was set at the Na+HF asymptote. The dashed contours are taken between -160 and -40 kcal/mol and them are spaced each other by 5 kcal/mol.
FIG. 2: The figure shows the plots of the BO5, GSA and GAOT MEP for the Na+HF reaction calculated at $\theta = 30.0^\circ$ (a), $\theta = 180.0^\circ$ (b) and $\theta = 77.2^\circ$ (c). The $\Phi$ angle is associated with the definition of the MEP (see text for discussion).