Applicability of the Hunjan-Ramaswamy global optimization method

Zacharias G. Fthenakis*
Institute of Electronic Structure and Laser, P.O. Box 1527, Heraklion-Crete 71110, Greece
and Department of Physics, University of Crete, Heraklion-Crete, 71110, Greece
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Hunjan and Ramaswamy presented [Int. J. Mol. Sci. **3**, 30 (2002); Phys. Rev. E **66**, 046704 (2002)] a method for global optimization, according to which the global minimum of a potential V_f can be found, if a potential V_i (with a known global minimum) is transformed adiabatically in time to V_f, with the use of a switching function of time $g(t)$, which interpolates between 0 and 1, and lies in the [0,1] interval. In the present work, the method is examined in detail. With the use of a very simple one-dimensional hypothetical potential, it is shown that the potential transformation may not always be followed by a global minimum transformation, which indicates that the method may not always be safely applied in determining the global minimum. An attempt to improve the method is made by allowing the switching function $g(t)$ to take values outside the [0,1] interval. This improved method is shown to succeed in three different realistic problems, for which the original method fails.

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I. INTRODUCTION

The determination of the lowest energy configuration of an N-atom cluster is an old but still open problem. Although several methods have been proposed for global optimization (GO) (see, for example, Refs. [1–13]), a general method unambiguously determining the global minimum (GM) is still far from reach. The only way to ensure a GM of a potential energy surface (PES) is the complete knowledge of the PES. In most cases, this implies an extensive search over all the configuration space of the cluster, which is feasible only for small clusters. However, it becomes increasingly harder for larger ones. Actually, the number of minima rises exponentialy with the number of the cluster atoms [14,15] [for example, the PES of the Lennard-Jones (LJ) 55-atom cluster, excluding permutational isomers, has at least 10^{10} minima [4]]. Thus, there is always a doubt about the GM determination of a GO method. In most cases, especially for large clusters, the lowest minimum is accepted as the GM until a lower minimum is found.

GO methods have been evolved in order to avoid this laborious extensive search, confining it to areas of the cluster configuration space where the GM is likely to be found. However, they still have the disadvantage that they could be trapped in a local minimum (LM). This is a major problem for all these methods and several techniques have been suggested to overcome the problem (see, for example, the jump-walking method [16] or the taboo search method [17] applied to improve the simulated annealing method).

GO methods can be separated into four categories: (a) gradient-based methods (Newton's method, steepest descent, conjugate gradient, etc.), (b) stochastic methods (simulated annealing [1], genetic algorithms [6–8], etc.), (c) potential deformation methods (diffusion equation method [11], distance scaling method [5], and (d) combinatorial methods (basin hopping [2–4], stochastic approximation with smoothing [12,13], Hunjan-Ramaswamy (HR) method [9,10], etc.) which combine aspects from the three former classes of methods. This paper is primarily focused on the applicability of the HR method. However, a short reference to the existing methods will follow for completeness purposes.

Given a good starting point, the gradient-based methods find the GM quite rapidly, either using molecular dynamics (Newton's method) or following the PES gradient at the starting point (steepest descent or conjugate gradient). A major disadvantage of these methods is the choice of the starting point, which may lead to a trapping of the solution in the closer LM, failing to reach the GM.

Stochastic methods (especially the simulated annealing method [1]) have the disadvantage that they often require a large amount of CPU time to obtain an acceptable degree of reliability for their results. The simulated annealing algorithm is one of the earliest proposed methods for GO and became quite popular. Nowadays it is not as popular as it was earlier due to its computational expense and inability to escape from trapping at low temperatures.

Related to the simulated annealing method, is a combinatorial method, the so-called "basin hopping" method, first introduced by Li and Scheraga [2] and further improved by Wales and Doye [3,18]. This method has gained interest due to its success in predicting the correct GM structure for nonicosahedral LJ clusters and especially the 38- and 75-atom LJ clusters. To date, basin hopping seems to be the most efficient GO method for LJ clusters containing up to 100–150 atoms. Its results are comparable only to the so-called "genetic algorithm" method. The main disadvantage of the method is that it is time consuming due to the large number of local minimizations required.

Evolutionary or genetic algorithms provide a different approach to the GO problem [6–8]. These algorithms try to mimic some aspects of biological evolution and, as mentioned earlier, their success is comparable to the basin hopping results. According to a genetic algorithm, an initial population of cluster geometries is randomly constructed.

*Electronic address: fthenak@iesl.forth.gr

From this population, the structures with low energy are selected for "reproduction." In the reproduction phase, new clusters are derived via recombination and mutation and a new cluster "generation" is produced. Repeating this iteration scheme until it converges, it derives the GM, which can be further locally optimized for a more accurate result.

Finally the category of potential deformation methods provides a different approach to the GO problem. Within these methods a transformation is applied to the PES which smooths it out, thus reducing the number of its minima and making the search for the GM easier. The GM of the deformed PES is then mapped back with the reverse transformation, in the expectation that it will lead to the GM of the original PES. Nevertheless, it is not guaranteed that the GM of the deformed PES will be mapped back to the GM of the original PES [19,20].

From the above, it becomes clear that to date no method can safely determine the GM but rather they could be used as complementary to each other. The interest in this work is focused on the HR method and its safe applicability.

The HR method [9,10] is categorized as a combinatorial method. It is a combination of a potential deformation method with molecular dynamics. The difference between the HR and the other potential deformation methods is that the PES is not smoothed to a PES with fewer minima. Instead, a PES with a known GM is mapped to the original PES.

To find the GM, Hunjan and Ramaswamy simply used molecular dynamics (MD) including damping forces acting on the atoms of the clusters; namely, they solve the following equations of motion:

$$m\ddot{\vec{r}}_i + \gamma\dot{\vec{r}}_i = -\nabla_i V, \quad i = 1,2,\ldots,N, \tag{1}$$

where m is the mass of each atom of the cluster, γ is the damping factor, $\vec{r}_i$ is the position vector for the ith atom, and V is the potential for the N-atom cluster. As V they introduce a time dependent potential which is a combination of two different potentials, having the form

$$V(t) = V_i(\vec{r})g(t) + V_f(\vec{r})[1 - g(t)], \tag{2}$$

where $g(t)$ is an adiabatically varying switching function ranging between 1 and 0 $[g(t=0)=1, g(t\to\infty)=0]$. That is, $V(t=0)=V_i$ and $V(t\to\infty)=V_f$. Hence, the PES evolves in time in such a way that the initial potential V_i is transformed adiabatically into the final potential of interest V_f. The MD simulation uses the GM configuration of the initial potential V_i and the time dependent potential already described. Under these conditions, it is expected that the cluster will follow a trajectory in the time dependent configuration space, very close to the trajectory that the GM of the time dependent potential would have followed. According to the HR method, when the time dependent potential becomes equal to the final potential (with no time dependence any more) the GM of the final potential V_f is reached.

Hunjan and Ramaswamy, in their first work [9], used this method to find the GM configuration of clusters described by the Sutton-Chen (SC) [21] potential, starting from the GM configuration of the Lennard-Jones associated clusters. In a subsequent work [10], they used their method in two similar approaches to find the GM of a number of LJ clusters. In the first one, they used a variety of switching functions $g(t)$ interpolating between 0 and 1 and as V_i they used a pairwise sum of harmonic terms $V(r_{ij})=(r_{ij}-2^{1/6}\sigma)^2/2$. In the second one, they introduced a parameter α instead of the function $g(t)$ and they employed a conjugate gradient minimization for that parameter. For that second approach V_i was taken to be $\beta\Sigma_{j=1}^{N}(\vec{r}_j-\vec{r}_j^{\,0})^2$, with $\vec{r}_j^{\,0}$ being the initial position of the jth atom.

In this work, the idea of using a time dependent potential, which switches adiabatically from the potential V_i to the potential V_f, to find the GM is examined in detail. Even though it was claimed in the two previous works that the method succeeds in predicting the GM of the investigated systems [9,10], it is clearly shown here that there are cases where the minimum found within this method is not the GM. This is because the transformation of V_i to V_f does not ensure that the GM of V_i will be transformed to the GM of V_f. An improvement of the HR method is also proposed based on a proper choice of the switching function. This improvement is applied to three different cases of realistic model potentials for which the original HR method fails.

II. APPLICATION TO A SIMPLIFIED ONE-DIMENSIONAL MODEL POTENTIAL

In this section the HR is applied to a simple one-dimensional (1D) hypothetical potential. This potential has the general form

$$V(x) = ax^4 - bx^2 + cx, \quad a > 0. \tag{3}$$

Because of its simplicity this hypothetical potential is easy to manipulate and convenient to understand how the HR method is applied to a realistic model potential.

Under certain conditions for a, b, and c, this potential exhibits two minima and a local maximum (Fig. 1). If $c=0$ and $b>0$ then $V(x)$ exhibits two minima at $x=\pm\sqrt{b/2a}$. Both of these minima are global minima and their value is $V_{\min}=V(\pm\sqrt{b/2a})=-b^2/4a$. The local maximum is located at $x=0$ and its value is $V_{l,max}=0$. If $c>0$, the negative-x minimum of $V(x)$ for $c=0$ becomes the GM and if $c<0$, the positive-x minimum of $V(x)$ for $c=0$ becomes the GM. Let us now suppose that the GM of the potential $V_i(x)=ax^4-bx^2+cx$, with $c>0$, is known and the GM of the potential $V_f(x)=ax^4-bx^2-cx$ is to be determined with the HR method. As one can see $V_i(-x)=V_f(x)$. Thus, if V_i exhibits its GM at x_2 and its LM at x_3, V_f will exhibit its GM at $-x_2$ and its LM at $-x_3$ (Fig. 1). In the same way, if V_i exhibits a local maximum at x_1, V_f will exhibit it at $-x_1$.

According to the HR method, the time dependent potential according to Eq. (2) has the form

$$V(x;t) = ax^4 - bx^2 + cx[2g(t) - 1]. \tag{4}$$

The minima and maxima are determined by setting the first derivative of the polynomial with respect to x equal to zero, i.e.,

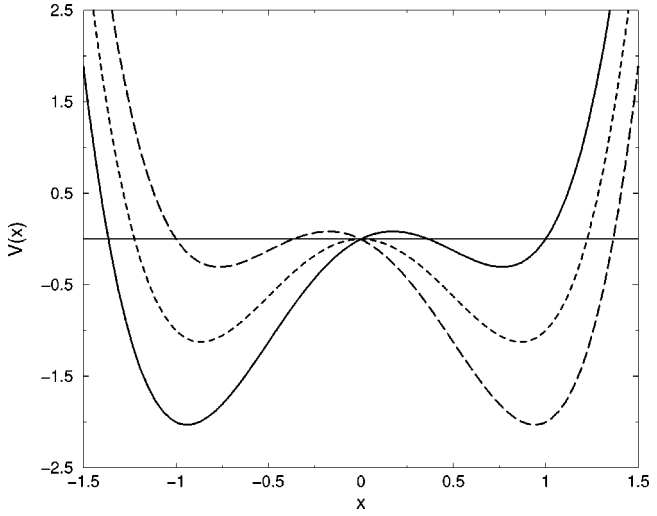

FIG. 1. Function $V(x)=ax^4-bx^2+cx$ with $a=2$, $b=3$. Solid line, $c=1$; dotted line, $c=0$; dashed line, $c=-1$. $c=1$ corresponds to the initial potential $V_i(x)$, while $c=-1$ corresponds to the final potential $V_f(x)$.

$$4ax^3 - 2bx + c(2g(t) - 1) = 0. \tag{5}$$

This is a third order polynomial equation and in case the three roots are real it can be analytically solved using the trigonometric identity

$$-4\sin^3\phi + 3\sin\phi = \sin 3\phi. \tag{6}$$

The solutions are

$$x_1 = 2\sqrt{\frac{b}{6a}}\sin\phi,$$

$$x_{2,3} = -\sqrt{\frac{b}{6a}}(\sin\phi \pm \sqrt{3}\cos\phi), \tag{7}$$

where

$$\sin 3\phi = \frac{c}{8a}\left(\frac{6a}{b}\right)^{3/2}[2g(t) - 1]. \tag{8}$$

These solutions are functions of time. For the sake of simplicity we may choose ϕ such that $x_2 < x_1 < x_3$ or $x_3 < x_1 < x_2$. This would restrict ϕ for the first case in the range of $[-\pi/6, \pi/6]$ and for the second case in the range of $[\pi - \pi/6, \pi + \pi/6]$. This restriction does not affect the generality but just sets x_1 to be the position of the local maximum of $V(x;t)$, while x_2 and x_3 are then the positions of the two corresponding minima. Thus, the functions $V_2(t)=V(x_2;t)$ and $V_3(t)=V(x_3;t)$ represent the trajectory in time of the potential minima. Accordingly, the function $V_1(t)=V(x_1;t)$ represents the trajectory of the local maximum. Their expressions are

$$V_1(t) = \frac{2b^2}{3a}\sin^2\phi\cos 2\phi,$$

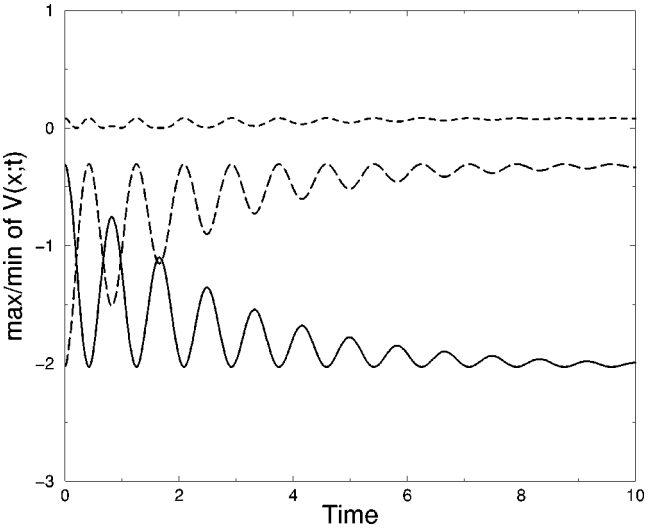

FIG. 2. The trajectories in time for the maximum (dotted line), initial GM (dashed line), and initial LM (solid line) of $V(x;t) = ax^4 - bx^2 + cx[2g(t)-1]$. $a=2$, $b=3$, $c=1$, and $g(t) = e^{-\zeta t}\cos^2(3\pi\zeta t)$ with $\zeta = 0.4$.

$$V_{2,3}(t) = -\frac{b^2}{2\sqrt{3}a}\left[2\cos\left(2\phi \mp \frac{\pi}{6}\right) - \cos\left(4\phi \pm \frac{\pi}{6}\right)\right] + V_1(t). \tag{9}$$

These three functions are plotted in Fig. 2 for the values of $a=2$, $b=3$, and $c=1$. As for $g(t)$, we used the same function as Hunjan and Ramaswamy in Ref. [9], i.e., $g(t) = e^{-\zeta t}\cos^2(3\pi\zeta t)$. Since $V(x;t=0)=V_i(x)$, the GM of $V(x;t)$ at $t=0$ is the same as the GM of $V_i(x)$. Similarly, $V(x;t\to\infty) = V_f(x)$ so the GM of $V(x;t\to\infty)$ is the same as the GM of $V_f(x)$. As can be seen from Eq. (9), the function $V_2(t)$ [which represents the GM trajectory of $V_i(x)$] evolves in time, initiating with a value equal to the value of the GM of $V_i(x)$, then oscillates due to the $\cos^2$ factor of $g(t)$, and finally, as $t \to \infty$, it reaches the value of the second (i.e., the local) minimum of $V_f(x)$ (see Fig. 2). On the other hand, the function $V_3(t)$ [which represents the LM trajectory of $V_i(x)$], also oscillates in time and starting from the LM of $V_i(x)$ it finally reaches the GM of $V_f(x)$ (see Fig. 2). Thus, through this simple example, it is clear that the final GM is reached through the time evolution of the initial LM, while at the same time the initial GM fails to reach the correct GM, after being trapped in the final LM.

It is worth noticing that the function $V_1(t)$ is always higher than the trajectories of the two minima, setting a barrier between the two minima of $V(x,t)$. This barrier does not allow the trajectories of the two minima to "communicate" with each other in time within a MD simulation. In a real adiabatic transformation of V_i to V_f (i.e., a slow evolution of V_i to V_f compared to the time scale of a MD simulation), the kinetic energy remains close to zero, so that the total energy is almost equal to the potential energy. This explains the trapping of the GM trajectory to the final LM.

However, if the transformation of V_i to V_f is not slow enough, then the kinetic energy may become large enough to

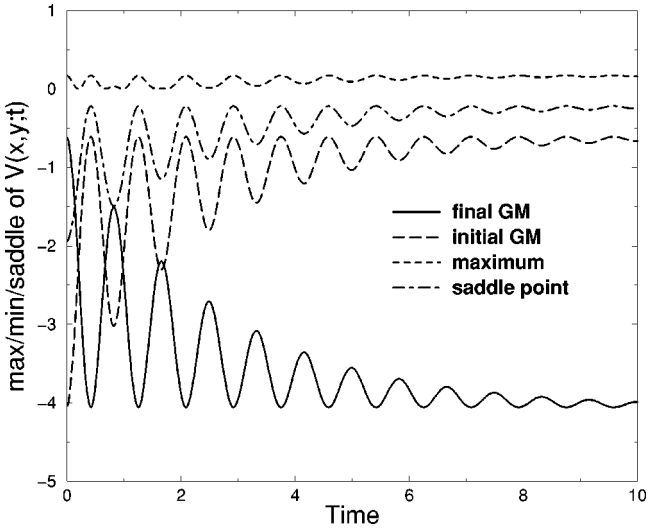

FIG. 3. Same as in Fig. 2 for the 2D case.

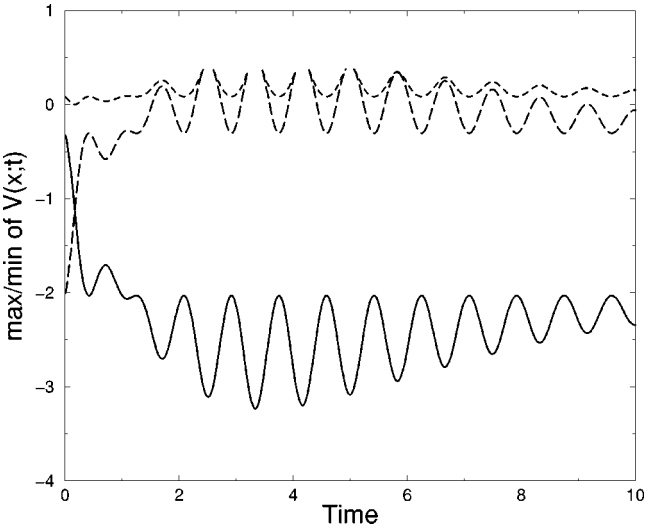

FIG. 4. Same as in Fig. 2 but for $g(t)=e^{-\zeta t}\cos^2(3\pi\zeta t)(1-t)$.

overpass the existing barrier. In that case, the cluster will jump to the trajectory of the other minimum, leading to the GM. Thus, the GM will be reached but only accidentally.

For higher dimension potentials, the same results can be obtained. As an example one can see the 2D potential

$$V(x,y) = a(x^4 + y^4) + b(x^2 + y^2) + c(x + y). \tag{10}$$

This potential is of the same type as the 1D potentials used and it is also easy to manipulate theoretically. Following the same steps as in the 1D case, it can be easily shown that there is always a barrier between the trajectories of the initial and the final GM of the time dependent potential of Eq. (2), set by the trajectory of one of the saddle points. These trajectories are presented in Fig. 3.

From the above it becomes evident that the HR method is quite safe in cases where the GMs of V_i and V_f follow the same trajectory in time. However, in cases where these trajectories split, then the final outcome is by no means safe, as it may well lead to a LM instead of the GM. Next, the latter case is examined. The proposed idea is to overcome the barrier between the two minima of $V(x;t)$, giving the possibility to a cluster to jump to the other minimum and finally reach the GM. Let us see how this works.

Let us define the quantity ΔV as the difference between the maximum and the LM of $V(x;t)$. This quantity equals the height of the barrier which needs to be overcome and reads [Eq. (9)]

$$\Delta V = V_1(t) - V_{2,3}(t) = \frac{b^2}{2\sqrt{3}a}\left[2\cos\left(2\phi \mp \frac{\pi}{6}\right) - \cos\left(4\phi \pm \frac{\pi}{6}\right)\right]. \tag{11}$$

The minimum of ΔV is obtained by setting the first derivative equal to zero, i.e.,

$$\sin\left(2\phi \mp \frac{\pi}{6}\right) = \sin\left(4\phi \pm \frac{\pi}{6}\right), \tag{12}$$

recalling that $-\pi/6 < \phi < \pi/6$ or $\pi - \pi/6 < \phi < \pi + \pi/6$. The accepted solutions are $\phi = \pm\pi/6$ or $\phi = \pi \pm \pi/6$, for which ΔV equals zero (i.e., the barrier is eliminated). Then from Eq. (8) it is seen that the condition for $\Delta V = 0$ is reached when

$$\frac{c}{8a}\left(\frac{6a}{b}\right)^{3/2}[2g(t) - 1] = \pm 1. \tag{13}$$

This is possible if either the potential parameters a, b, c permit that and/or a proper selection of the function $g(t)$ has been made. In the discussed example shown in Figs. 1 and 2, neither the potential parameters nor the function $g(t)$ satisfy Eq. (13). As one can see, for the values of $a=2$, $b=3$, and $c=1$, the quantity $(c/8a)(6a/b)^{3/2}$ equals 0.5. As the function $g(t)$ interpolates between 1 and 0 and its values lie within the interval [0,1], the left side quantity of Eq. (13) will never cross the inteval $[-0.5, 0.5]$, unless $g(t)$ is allowed to reach larger values such that $|2g(t)-1| > 2$.

With the choice of $g(t)=e^{-\zeta t}\cos^2(3\pi\zeta t)(1-t)$, $g(t)$ still interpolates between 0 and 1 but its value extends out of the interval [0,1]. Then, the existing barrier in our example is eliminated for some time intervals. For these time intervals, the minimum that corresponds to the trajectory of the initial GM [which leads to the LM of $V_f(x)$] and the local maximum are both eliminated and only the minimum that corresponds to the trajectory of the initial LM (which leads to the GM) survives. Another way to realize this is to notice that with the new choice of $g(t)$, Eq. (5) has only one real and two complex roots for some time intervals. Thus, for these time intervals, the time dependent potential $V(x)$ has only one minimum. This minimum is evolved in time and finally it reaches the GM of $V_f(x)$. The corresponding functions $V_1(t)$, $V_2(t)$, and $V_3(t)$ for the case of the new choice of $g(t)$ are shown in Fig. 4.

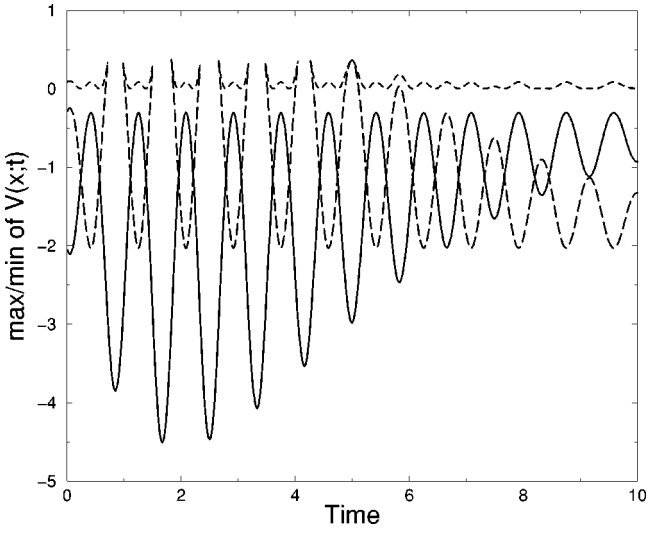

FIG. 5. Same as in Fig. 2 but for $g(t)=e^{-\zeta t}\cos^2(3\pi\zeta t)(1+2t)$.

It is important to notice that a condition like Eq. (13) is not always known for a realistic potential. Thus, it becomes rather difficult to know if a choice of a switching function is a proper one. Moreover, the rule of overpassing the interval of [0, 1] for the $g(t)$ values may serve as a guiding light, but by no means should be blindly trusted. As an example, the reader may test the switching function $g(t)=e^{-\zeta t}\cos^2(3\pi\zeta t)\times(1+2t)$. With this choice of $g(t)$, the trajectory of the GM is the one that is eliminated together with the trajectory of the local maximum. This can be seen in Fig. 5 where the corresponding functions $V_1(t)$, $V_2(t)$, and $V_3(t)$ are presented. In this case, even if the initial configuration corresponds to the LM of $V_i(x)$ [which with the first and the second choices of $g(t)$ would lead to the GM], finally the cluster will be trapped by the trajectory which leads to the LM of $V_f(x)$. Thus, with this choice of $g(t)$, the HR method cannot reach the GM with any choice of the initial configuration.

From the above, it is quite clear that the HR is not a safe method for determining the GM but it can be improved by a proper choice of the switching function $g(t)$. Actually, it seems that there is not a safe procedure for the choice of $g(t)$, but rather an inspired trial and error method. Toward the goal of a proper choice, the rule suggested in this paper of allowing the values of a switching function outside the HR proposed interval [0,1] seems to serve better. This will become evident in the next section where three realistic examples of GM determination are given.

III. APPLICATION OF THE METHOD TO MODEL POTENTIALS FOR REALISTIC PROBLEMS

Hunjan and Ramaswamy [9] have shown that their method works using as V_i the LJ potential and as V_f the SC potential, the form of which can be found in Refs [9,10,21]. According to Ref. [9], their results on the switching from the minimum of the LJ_N system to the minimum of the SC_N system of the 6-9 family agree with the results which are tabulated in the Cambridge Cluster Database [22]. Especially, the initial 15-atom LJ ground state with C_{2v} symmetry, is transformed to the SC ground state with D_{6d} symmetry. They also found that if $g(t)=0$, then the cluster reaches the nearest available minimum, which is not the SC GM.

These results were tested with the HR method but with a slightly different MD approach, in which the equations of motion do not include any damping term. Instead, the velocity is lowered by 1% at each time step, which is equal to 0.1 ns. For convenience, we shall call this lowering factor the damping factor. A fifth order Gear predictor-corrector algorithm [23] was applied to solve the Newtonian equations of motion and after some thousands of time steps the equilibrium was reached. It was found that the GM could not be reached either by using the switching function $g(t)$ or not. Both ways reached a local minimum with energy $E=-51.250\,909$ eV. Nevertheless, in the case where the damping factor was lowered to 0.1%, both ways reached the GM, with energy $E=-51.323\,094$ eV [22]. In both cases the switching function was the one proposed by Hunjan and Ramaswamy in Ref. [9].

As one can see the MD method is sensitive to the damping factor. Of course, for adiabatic switching, the damping factor should not be small, because the kinetic energy may contribute substantially to the total energy and (as already discussed in Sec. I) may overpass the barriers of the trajectory of the initial GM to reach a LM. On the other hand, if the damping factor is very low, the MD becomes very time consuming and thus inadequate for the GM search. For the following studies a damping factor 1% was found satisfactory for both the GM search and time consuming considerations.

Next, the HR method, optimized by the suggestion presented in Sec. II is applied in three different cases. In the first one, starting from the ground state of the LJ Ni_8 cluster, the ground state of the Ni_8 Morse cluster is found. In the second case, starting from the ground state of the SC [21] Ni_8 cluster, the ground state of the Uppenbrink-Wales (UW) Ni_8 cluster is found. Finally, in the third case, starting from the ground state of the Ni_{13} SC cluster, the ground state of the UW Ni_{13} cluster is found.

The form of the UW potential can be found in Ref. [24]. Uppenbrink and Wales have proposed two set of parameters for this potential. For Ni, the first set of parameters is $\epsilon=1.136$ eV, $\sigma=2.225$ Å, and $Z^\star=0.393$, and the second is $\epsilon=0.613$ eV, $\sigma=2.508$ Å, and $Z^\star=-0.059$. The first set of parameters was used for the Ni_{13} case, while the second for the case of Ni_8. Also the form of the Morse potential, fitted for Ni, can be found in Ref. [25].

The choice of these three cases was made because each pair of initial (V_i) and final (V_f) potentials exhibits different ground state geometries. In Table I is shown the point group symmetry associated with the ground state geometry of the 8- and 13-atom Ni clusters for the LJ, Morse, SC, and UW potentials. The configuration of the ground state of the Ni_{13} UW cluster is shown in Fig. 6. It is expected that due to their geometrical differences, the two minima of each case are not connected with the same trajectory. Thus, switching functions $g(t)$, like those proposed in Refs. [9,10], may not be proper for the switching, as shown in Sec. I.

TABLE I. Point group symmetries of the Ni_8 and Ni_{13} clusters for the potentials used.

	LJ	Morse	SC	UW
Ni_8	C_{2v}	D_{2d}	D_{2d}	C_{2v}
Ni_{13}			I_h	C_{2v}[a]

[a]The configuration of the ground state of the Ni_{13} UW cluster is shown in Fig. 6.

For the first two cases, if the damping factor in the MD simulation equals 0.1%, the GM is reached, independently of using or not a switching function. But if the damping factor is raised to 1% the GM is not reached. For the third case the GM is not reached even if the damping factor becomes 0.01%.

As switching functions for this investigation we used the function $g(t)=e^{-\zeta t}\cos^2(3\pi\zeta t)$ with $\zeta=0.4$, as proposed in Ref. [9], and the functions proposed in Table I of Ref. [10]; namely, $e^{-\zeta t}$, $1-\sin(\pi\zeta t/2T)$, $1-\zeta t/T$, and $[1-\tanh(\zeta t-10)]/2$. All these switching functions lie only within the [0, 1] interval. For the three cases of investigation and with a damping factor of 1%, the GM cannot be reached with the use of these switching functions, as already mentioned.

However, as will be shown below, the HR method can be optimized, leading to correct findings, if a proper choice of switching function is made. In particular, the family of functions

$$g(t) = e^{-\zeta t}\cos^2(3\pi\zeta t)(1-\lambda\zeta t), \tag{14}$$

with the free parameters ζ and λ, interpolate between 1 and 0 but their values overpass the [0, 1] interval. Using this family of functions as switching functions, for the values of $\zeta=4$, 0.4, 0.04, 0.004 and for integer values of λ, an attempt was made to find the GM of the clusters for the three cases already described. The findings are presented in Figs. 7, 8, and 9.

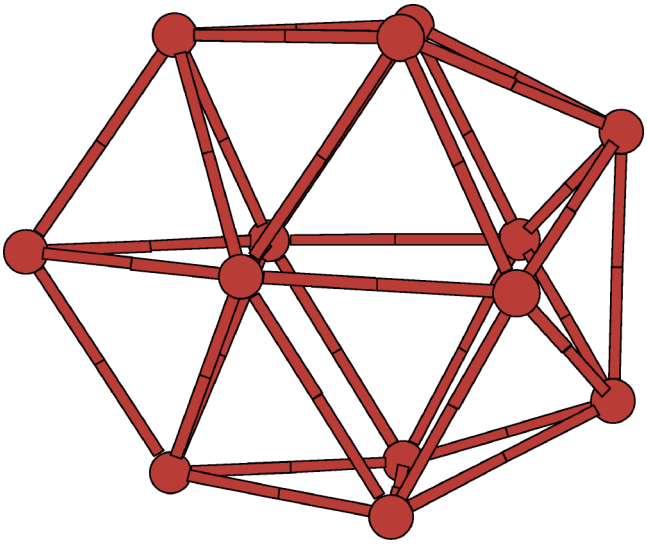

FIG. 6. The configuration of the GM for the Uppenbrink-Wales Ni_{13} cluster.

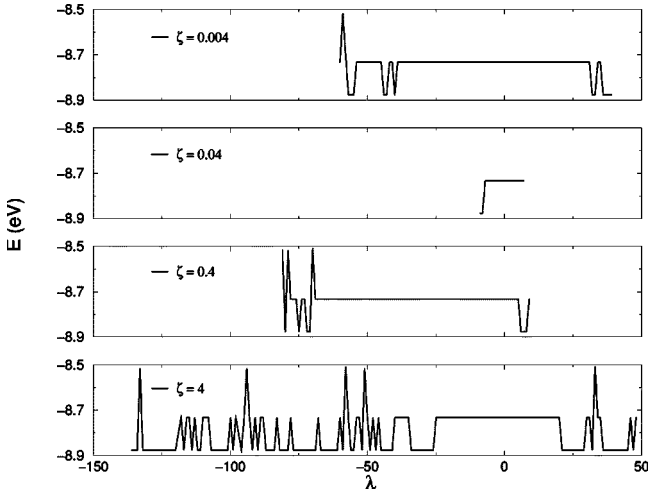

FIG. 7. The energies of the Ni_8 Morse minima found for the various values of λ switching from the LJ potential.

As one can see for the value of $\lambda=0$, which corresponds to the function $g(t)=e^{-\zeta t}\cos^2(3\pi\zeta t)$ presented by Hunjan and Ramaswamy [9], the method reaches the nearest available minimum, which is not the GM. For the first, the second, and the third cases, the minima reached had energy $E=-8.733\,04$ eV, $-12.579\,169$ eV, and $-25.186\,353$ eV, respectively, while their GMs have energy $E=-8.877\,03$ eV, $-13.192\,970$ eV, and $-25.964\,138$ eV, respectively.

The switching functions $g(t)$ with their values of λ close to 0 give the same minimum as the $\lambda=0$ switching functions. For values of λ different from these, many different minima arise from this method, which also include the GM. Thus this method is also applicable when the various local minima of a potential are studied. Especially for the third case, of Ni_{13} with $\zeta=4$, 82 different minima were found with minimum energy distance equal to 2.25×10^{-4} eV. The number of minima found as a function of their energy is presented as a histogram in Fig. 10. For λ larger or lower than certain values, a cluster fragmentation takes place. For these values there are no minima presented in Figs. 7, 8, and 9.

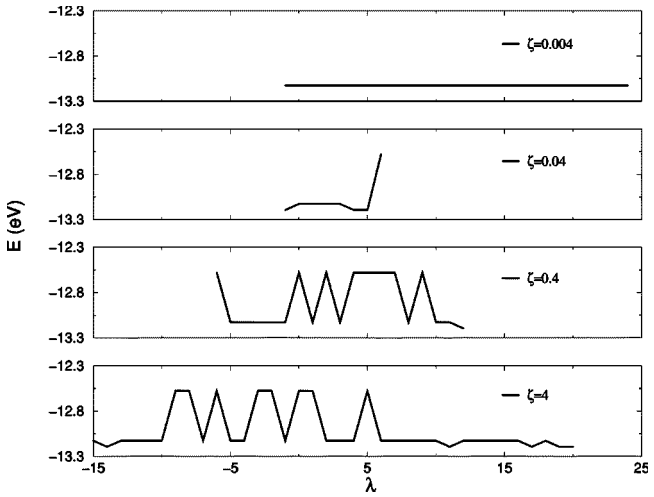

FIG. 8. The energies of the Ni_8 UW minima found for various values of λ switching from the SC potential.

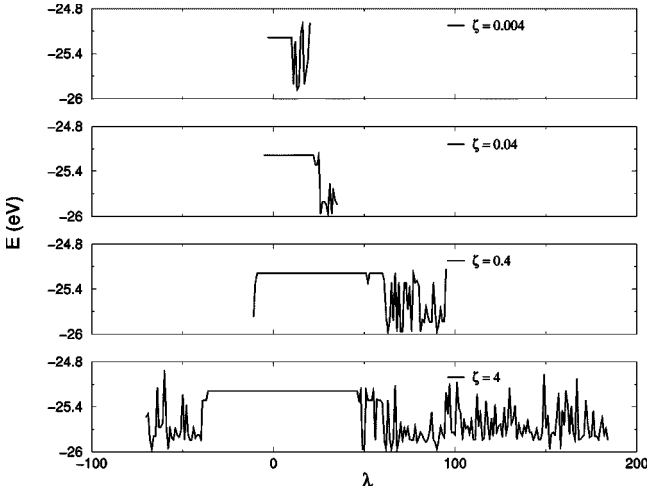

FIG. 9. The energies of the Ni_{13} UW minima found for various values of λ switching from the SC potential.

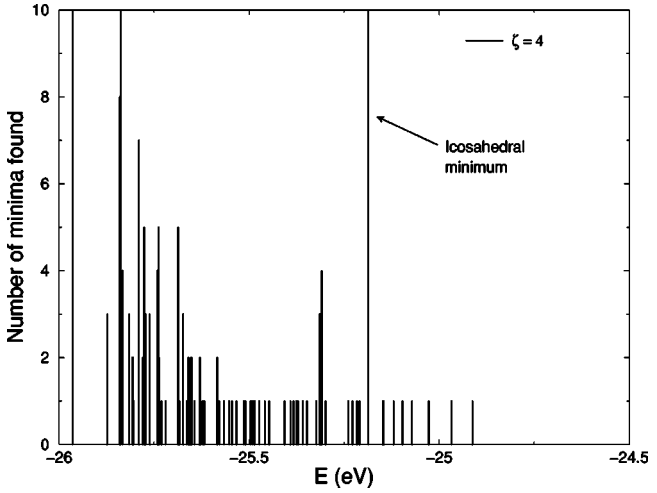

FIG. 10. The number of the Ni_{13} UW minima found with $\zeta=4$ for various values of λ switching from the SC potential.

From the above study, it becomes more than evident that the HR method, under the proposed improvement related to the choice of the switching function, may become a convenient tool in treating realistic problems in GM determination. Without this improvement it is not safe to be used.

IV. SUMMARY AND CONCLUSION

To summarize, the applicability of the HR method, in the determination of the lowest energy configuration of an *N*-atom cluster, as proposed in Refs. [9,10], was examined in detail. Using a simple 1D hypothetical potential it was shown that the HR method may well lead to incorrect results, raising questions about the safe applicability of the method in realistic problems. An improvement of the method was proposed, based on allowing the switching function in use to take values outside the [0,1] interval originally proposed by Hunjan and Ramaswamy. The success of this improvement is depicted in three different realistic examples, for which the original HR method fails. However, this improvement needs further investigation for more complicated cases, for which the choice of a proper switching function may not be an easy task.

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