Bell-Evans-Polanyi principle for molecular dynamics trajectories and its implications for global optimization

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The Bell-Evans-Polanyi principle that is valid for a chemical reaction that proceeds along the reaction coordinate over the transition state is extended to molecular dynamics trajectories that in general do not cross the dividing surface between the initial and the final local minima at the exact transition state. Our molecular dynamics Bell-Evans-Polanyi principle states that low energy molecular dynamics trajectories are more likely to cross into the basin of attraction of a low energy local minimum than high energy trajectories. In the context of global optimization schemes based on molecular dynamics our molecular dynamics Bell-Evans-Polanyi principle implies that using trajectories that have an energy that is only somewhat higher than the energy necessary to overcome the barriers lead fastest to the global minimum of funnellike energy landscapes.

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The Bell-Evans-Polanyi (BEP) principle is a conceptual tool in chemistry that is introduced in standard textbooks on physical chemistry [1,2]. It gives a relation between the free energy ΔG released in a chemical reaction and the activation free energy ϵ_a for the reaction. It is generally assumed to be well obeyed for chemically similar reactions. It was qualitatively first put forward by Brønsted [3] who observed that strongly exothermic reactions have a low activation energy. A more quantitative relation was then derived by Polanyi *et al.* [4,1] who approximated the potential energy surface by straight lines. This approximation leads to a linear relation between the activation energy ϵ_a and the free energy of the reaction ΔG as follows:

$$\epsilon_a = k_1 + k_2 \Delta G, \tag{1}$$

where k_1 and $k_2 > 0$ are constants that depend on the slopes of the lines. A more accurate approach by Marcus [5,2] approximates the potential energy surface by two parabolas centered at the two local minima of the energy, which leads to an additional quadratic term in Eq. (1).

In a chemical reaction, the reaction coordinate connects the educt A with the product B. In this paper we will study the BEP principle not for this hypothetical path along the reaction coordinate but for molecular dynamics (MD) trajectories that cross the dividing hypersurface between the two basins of attraction of two local minima on the potential energy surface. The notions of educt and product are replaced by the notions of initial and final local minima in this context. We will show that the BEP principle is also valid in the context of MD. Since our study requires the calculation and statistical evaluation of a very large number of local minima and saddle points, we will initially base our study on a Lennard-Jones cluster containing 55 atoms [6] for which stationary points can be calculated rapidly.

We will first investigate how well the traditional BEP principle is satisfied for these Lennard-Jones clusters. To do so we have searched for more than 130 000 first order saddle points G_i^s on the potential energy surface connecting energetically low local minima. Subsequently, we have moved the system by a small amount away from the saddle point along the two directions where the curvature is negative, i.e., we moved the system in the direction of the eigenvector associated with the negative eigenvalue of the Hessian matrix and in the negative direction of this eigenvector. These two points served as the starting points for a local geometry optimization that led us in the two closest local minima with energies E^a and E^b. In this way we have generated a set of pairs of local minima together with the saddle points that connect them. Figures 1 and 2 show a scatter plot of $\Delta G = G_i^b - G_i^a$ versus the activation energy $\epsilon_a = G_i^s - G_i^a$ and the red line in the same figure shows a histogram with averages of the $G_i^s - G_i^a$. Each pair of local minima contributed two data points to these plots since one can surmount the barrier by going from the minimum A to minimum B as well as by going from minimum B to minimum A. The scatter plots in Figs. 1 and 2 show that there is no strict linear correlation between the barrier height ϵ_a and the energy difference ΔG between the two minima. For small barrier heights one can find both high energy and low energy minima behind the

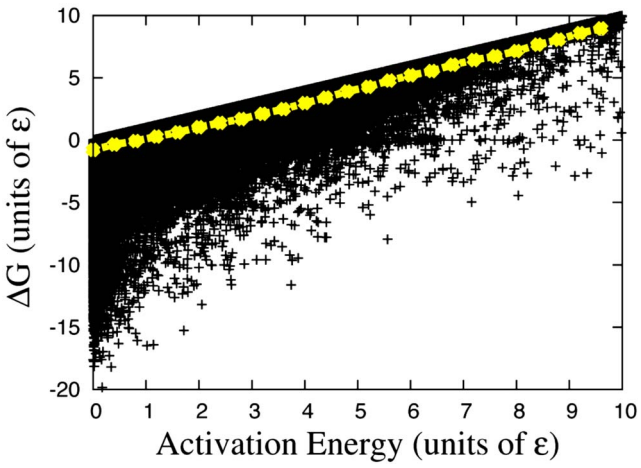

FIG. 1. (Color online) The relation between the activation energy $G^s - G^a$ and the reaction energy $G_i^b - G_i^a$ for more than 130 000 saddle points in a Lennard-Jones cluster of 55 atoms. All the energies plotted here are free energies at $T=0$, i.e., just energies. The red line is the same data but averaged within 25 bins along the x axis.

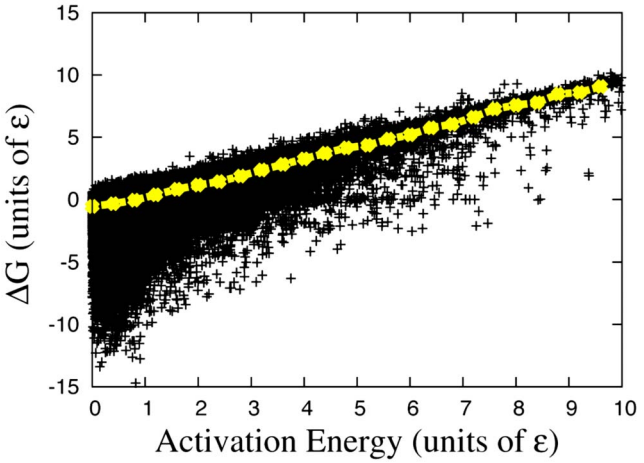

FIG. 2. (Color online) Same as Fig. 1,however, at a temperature (T=30 K), which is below the melting point (50 K) of this weakly bound system [14]. The entropy contribution was calculated in the harmonic approximation from the vibrational frequencies [2]. The figure shows that the free energy has essentially the same behavior as the energy. The fact that some points are above the diagonal shows that some shallow minima of the potential energy surface are not any more minima of the free energy surface. In principle, these points should be eliminated, but we left them in the figure since they indicate the size of the entropic corrections.

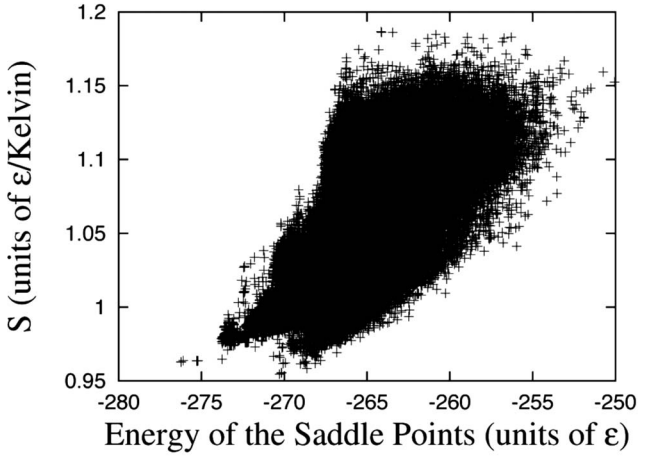

FIG. 3. Entropy vs height of the saddle point (in energy unit, ϵ). As in Fig. 2 the entropy was calculated in the harmonic approximation.

barrier. However, the BEP principle holds as a negation. If one goes over high barriers it is extremely unlikely that one will end up in a low energy minimum. The better correlation for large activation energies is simply due to the fact that ΔG cannot become larger than ϵ_a. On the other hand, the red line in Figs. 1 and 2 shows that there is a good linear relation if one averages over ΔG. Good linear Bell-Evans-Polanyi relations have been found in calculations of dissociative chemisorption of various molecules [7].

Kinetic rate theory gives the rate constant for a reaction as

$$k = \frac{k_B T}{h} \exp[-\epsilon_a/(k_B T)] = \frac{k_B T}{h} \frac{Q_s}{Q_a} \exp[-(E^s - E^a)/(k_B T)], \tag{2}$$

where E_a and E_s are the energies of the initial minimum and of the saddle point and Q_s and Q_a are the partition functions corresponding to the saddle point and the initial minimum, respectively. Combining this formula with the linear BEP relationship of Eq. (1) gives a formula where the speed of the reaction depends only on the energy of the final minimum E^b relative to the initial minimum E^a

$$k = \frac{k_B T}{h} \frac{Q_s}{Q_a} \exp\{-[k_1 + k_2(E^b - E^a)]/(k_B T)\}. \tag{3}$$

On the macroscopic level a chemical reaction proceeds along a molecular dynamics trajectory. Its energy is determined by the temperature T. The above formula reflects therefore our MDBEP principle. At low temperature one will rarely find MD trajectories that cross into high energy local minima E^b. This statement may sound similar to the well known fact that an ergodic system obeys the Boltzmann distribution and will therefore be preferentially found in low energy regions. Our statement is, however, not on thermodynamic equilibrium distributions but on the dynamics of the system. The derivation of the above formula [Eq. (3)] has several weak points. As we have seen before, the BEP principle for the energies (Fig. 1) holds only on average for similar processes. The rate equation [Eq. (2)] is itself derived using several approximations. In particular, it only holds for trajectories which cross the dividing surface close to the transition state and it is thus not valid for very high energy MD trajectories. Up to now we have also neglected the dependence of the partition function Q_s at the saddle point on the temperature. Q_s is a measure of the size of the dividing surface that is accessible at a certain temperature. The area of this surface increases as the energy of the MD trajectory relative to the saddle point increases. Hence the crossing area is larger for energetically lower saddle points and this effect increases thus the preference of MD trajectories for crossings into the basins of attraction of low energy minima. In addition to this dependence of Q_s on the kinetic energy of the MD trajectory, i.e., on the temperature, we have also empirically found a dependence of Q_s on the height of the saddle point. The positive curvatures of the potential energy surface near low energy saddle points is typically larger and so their entropy associated to Q_s becomes smaller (Fig. 3). This decreases the preference of MD trajectories for crossings into low energy basins.

Because of all the uncertainties listed above, we will now present numerical experiments to verify the MDBEP principle. In all these experiments the kinetic energy of the MD trajectories was considerably larger than the minimum energy required to be able to overcome the transition states. Figure 4 shows the results of the first numerical experiment. For a large number of MD trajectories that start with random directions but fixed kinetic energy E_{kin} from a certain minimum with energy E_a we have recorded how many times this trajectory reaches the basin of attraction of neighboring minima with energy E_b. To check whether the MD trajectory has crossed into another basin of attraction steepest descent geometry optimizations were started after every 20 MD

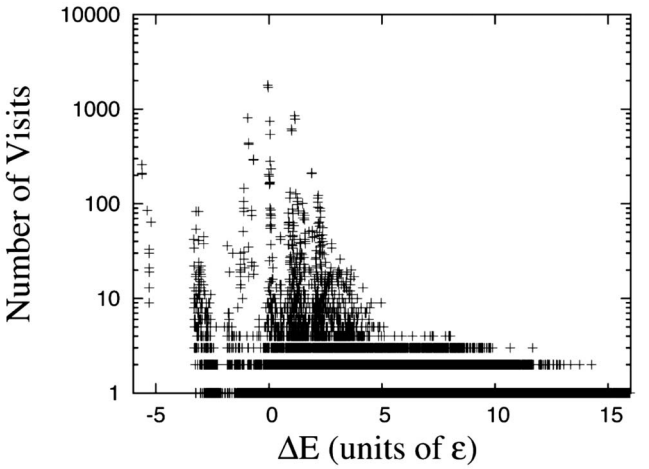

FIG. 4. The number of visits as a function of $E_b - E_a$ for a MD trajectory with a kinetic energy of 4.0ϵ per atom.

steps. Once the crossing occurred the MD run was stopped. In Fig. 4 we then plot the number of visits as a function of $E_b - E_a$. We see that it is orders of magnitude more likely that the MD trajectory crosses into low energy basins than into high energy basins. By varying the kinetic energy of the trajectory we can tune the strength of the preference for low energy minima. Low energy trajectories have a much stronger preference for low energy minima than high energy trajectories as shown in Fig. 5. We will denote this correlation as the MDBEP principle: low energy MD trajectories are more likely to lead into the basin of attraction of a low energy local minimum than high energy trajectories. The activation energy of the original BEP principle has thus been replaced by the energy of the trajectory. As can be seen from Figs. 1 and 4, both the traditional BEP principle and our MDBEP principle are only valid in an average sense. As we will see, this validity in the average sense is sufficient in the context of global optimization.

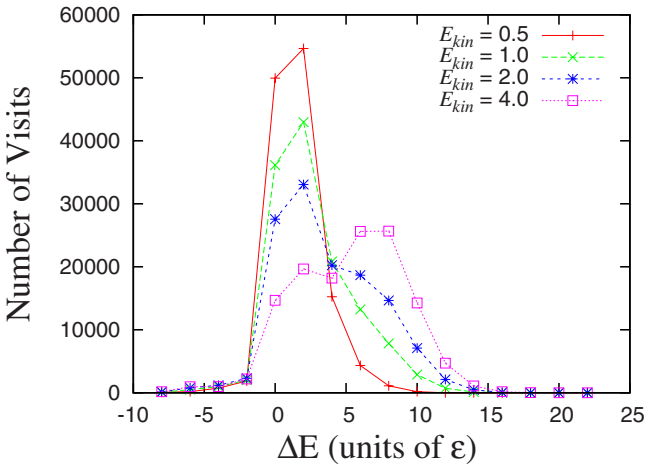

FIG. 5. (Color online) The number of visits as a function of $E_b - E_a$ summed over energy bins of length 2 for 4 MD trajectories with different kinetic energies. The curve for an energy of 4.0ϵ represents the same data as the scatter plot in Fig. 4.

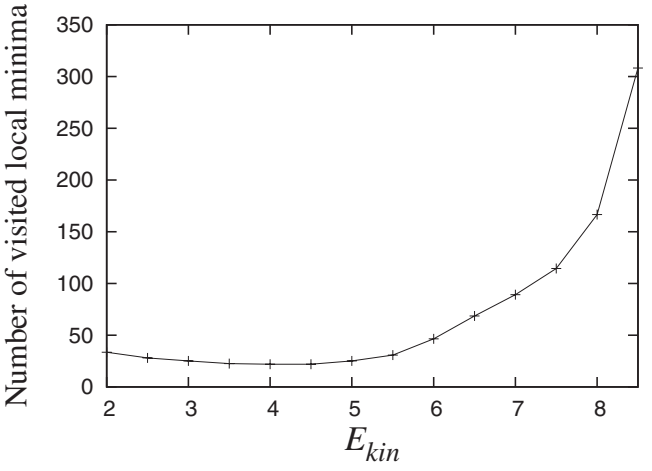

FIG. 6. The MDBEP principle for the Lennard-Jones cluster of 55 atoms.

Methods for global geometry optimization are an active area of research, as can be decided from the large number of publications in this field. A basic problem in this context is to construct moves that on the one hand rapidly lead downward in energy and on the other hand, avoid trapping [12,13,15] in a local minimum that is not the global minimum. We will exemplify this issue in the context of the minima hopping method (MHM) [8,9]. In the MHM the system moves from one local minimum to another by a combination of MD and local geometry optimizations. With the MD part one jumps from one minimum into the basin of attraction of another minimum. The subsequent local geometry optimization part brings us then into the local minimum of this basin of attraction. From the MDBEP principle we expect that low energy MD trajectories are the most efficient for global optimization. Figures 6 and 7 show that there is indeed a very strong correlation between the energy of the MD trajectory and the number of minima that are visited before the global minimum is found. The data for Figs. 6–10 were obtained by performing MHM runs that are stopped once the global minimum is found for different but fixed kinetic energies E_{kin} (i.e., $\beta_1 = \beta_2 = \beta_3 = 1$ using the notation of Ref. [8]) in a rea-

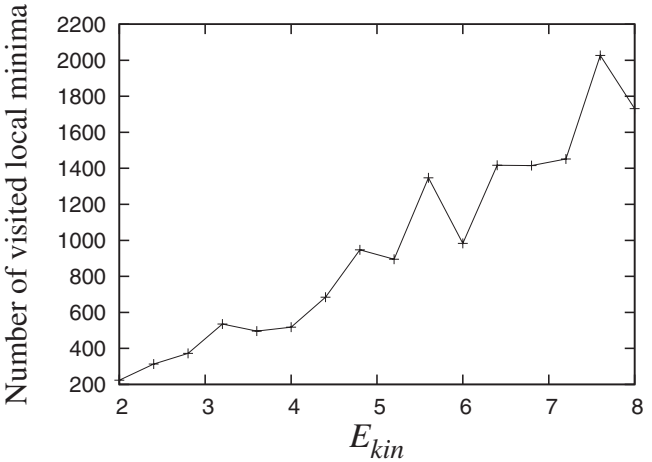

FIG. 7. The MDBEP principle for the Lennard-Jones cluster of 38 atoms.

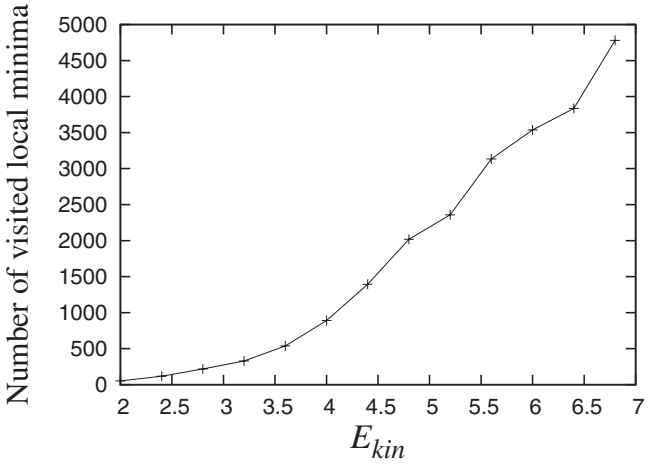

FIG. 8. The MDBEP principle for the Morse cluster of 38 atoms with $\rho=6.0$.

sonably chosen energy interval. Subsequently, we plot the values of E_{kin} versus the number of local minima that were visited before the global minimum was found. The potential energy of the local minimum from which the MD trajectory starts is set to zero. In this way the kinetic energy is the total energy of the MD trajectory and by energetic reasons it cannot cross barriers higher than E_{kin} relative to the starting minimum. Only new and accepted local minima are counted. In order to achieve better statistics we perform for each fixed E_{kin} 100 MHM runs (for Fig. 6 the average is taken over 1000 runs), and we take for the plots the averaged number of visited local minima. The Lennard-Jones 55 cluster whose behavior is shown in Fig. 6 is a system for which it is very easy to find the global minimum since it has a one funnel structure. Other Lennard-Jones clusters such as the 38 atom cluster whose behavior is shown in Fig. 7 have two or more funnels [14]. In this case low kinetic energy MD trajectories will rapidly lead into a funnel which is not necessarily the funnel containing the global minimum. Once the system is trapped in a wrong funnel a sufficiently large kinetic energy is evidently required to escape from it. Figure 7, however, shows that also in this case the efficiency of the global optimization is mainly determined by how rapidly the bottom of a funnel is reached and high energy trajectories are thus less efficient than low energy trajectories even though they can more easily escape from any wrong funnel.

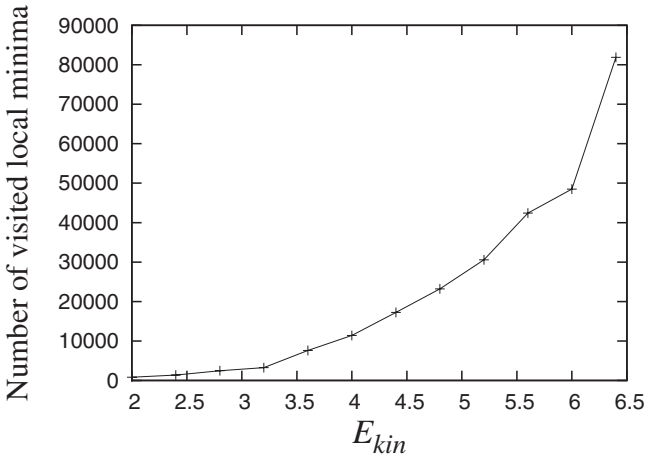

FIG. 9. The MDBEP principle for the Morse cluster of 38 atoms with $\rho=10.0$.

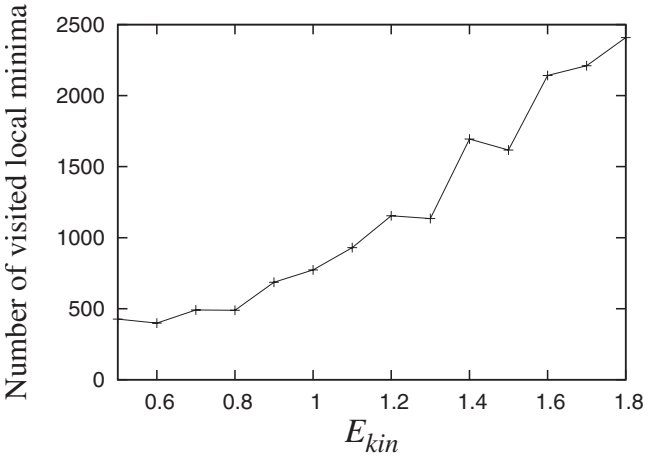

FIG. 10. The MDBEP principle for the Lenosky tight-binding cluster of 20 atoms.

Even for one funnel structures there is, of course, a lower limit to the kinetic energy. Once it is too low no barriers can any more be overcome and the system gets trapped. One has thus to reconcile two opposite requirements on the kinetic energy of the MD trajectories. This is done in a very efficient way in the minima hopping method. If the system goes down in one funnel it explores new local minima and the kinetic energy of the trajectories used to hop from one minimum to another one is reduced. Once the system gets trapped the kinetic energy is increased through a feedback mechanism and the system can escape from any funnel. Minima hopping keeps a history list of all the minima that were previously visited and the feedback is activated if old minima are revisited. Since escapes from a funnel seldom occur, one can achieve in the minima hopping method very low average energies for the MD trajectories without being trapped.

Figures 8 and 9 present our results for Morse clusters of 38 atoms with $\rho=6.0$ and $\rho=10.0$. Large values of ρ lead to an interaction that varies over shorter length scales. As a consequence, the potential energy surface becomes more rugged and has significantly more local minima. As a consequence, considerably more minima are visited before the global minimum is found. The global optimization is, however, also in this case more efficient for low energy trajectories which implies that the MDBEP principle is well observed for very rugged potential energy surfaces.

Figure 10 presents our results for the Si_{20} cluster [10] within the Lenosky tight-binding scheme [11]. In contrast to the Lennard-Jones and Morse potentials the silicon tight-binding scheme has much more complicated interactions that depend not only on the distance between atoms but also on the quantities like the bond angles. Tight-binding schemes are the simplest way to treat solid state systems at a quantum mechanical level. The Lenosky tight-binding scheme gave very good agreement with the DFT energies [9] and can be considered as a reliable approximation to a precise density functional treatment of silicon clusters. The fact that low

energy trajectories again lead faster into the global minimum indicates that the MDBEP principle is also valid for realistic interactions and, in particular, for quantum mechanical interactions.

The fact that for small values of E_{kin} the global minimum is found after having visited only a small number of local minima does not imply that the computational time in the MHM is continuously decreasing with smaller values of E_{kin}. If E_{kin} is getting too small the system has to make a huge number of attempts before succeeding to escape from the basin of attraction of the current minimum and this will actually lead to an increase in the computer time (Fig. 11). For this reason it is also in practice virtually impossible to explore the behavior of trajectories with lower energy than those shown in Figs. 6–10. Figure 6 shows, however, that the minimum of the CPU time is reached when the number of minima visited becomes small. The BEP principle is thus not only of conceptual interest but can in practice also help to save CPU time. In practice, the short computation time can be obtained by giving the MD trajectories initial velocities that have large components in the subspace of low curvature of the Hessian matrix. Due to the fact that low energy saddle points often lie at the end of low-curvature modes [16–18] one can in this way even with low energy trajectories very rapidly escape from the present minimum. A similar gain in efficiency was found in the context of global optimization using random moves if those moves were biased in the direction of the low-curvature modes [19]. In summary, we have shown that the BEP principle can be extended to MD trajectories with high energies which cross from one basin of attraction into another one far from the transition state. We call this extended principle MDBEP principle. It says that MD trajectories with lower energy are more likely to lead into basins of attraction of low energy configurations than very high energy trajectories. In the context of global optimization this principle can be used to improve the efficiency of existing MD based methods by tuning the energy of the MD trajectories.

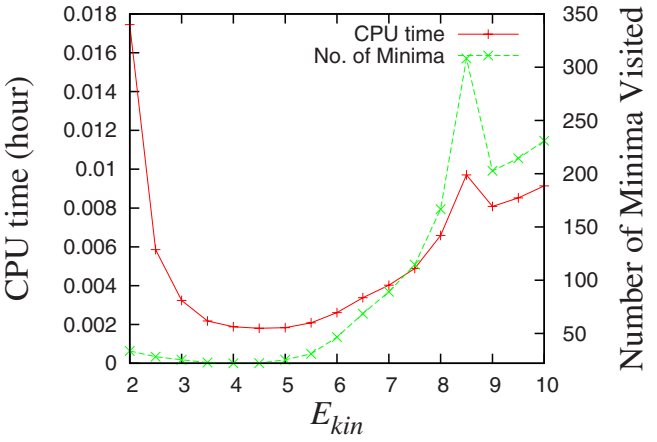

FIG. 11. (Color online) The average CPU time (left Y axis) along with the average number of distinct local minima visited (right Y axis) before reaching the global minimum for the Lennard-Jones cluster of 55 atoms are plotted against the Kinetic energy of the MD trajectory per atom (E_{kin}).

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