A 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 lead 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 low energy trajectories one needs to visit a smaller number of distinguishable local minima before finding the global minimum than when using high energy trajectories.

The Bell-Evans-Polanyi (BEP) principle [1, 2] is an important fundamental principle in chemistry. It gives a relation between the free energy $\Delta G$ released in a chemical reaction and the activation free energy $\epsilon_a$ for the reaction. 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 [1, 4] who approximated the potential energy surface by straight lines. This approximation leads to a linear relation between the activation energy $\epsilon_a$ and the free energy of the reaction $\Delta G$:

$$\epsilon_a = k_1 + k_2 \Delta G$$,

where $k_1$ and $k_2$ are constants that depend on the slopes of the lines. A more accurate approach by Marcus [2, 5] approximates the potential energy surface by two parabolas centered at the two local minima of the energy. The potential energy surface in this approximation is everywhere a quadratic form with the exception of the intersection point of the two parabolas where it has a discontinuity in its derivative. From Fig.1 it is easily visible that the barrier for the reaction $A \rightarrow B$ is lowered if the parabola centered in the minimum B is shifted downward. The resulting quantitative relation [2] is given by

$$\epsilon_a = k + \frac{\Delta G}{2} + \frac{\Delta G^2}{16k}$$,

where $k$ is proportional to the curvature of the two parabolas.

In a chemical reaction the reaction coordinate connects the educt A with the product B. Hence the intersection of the two parabolas is the transition state. In this article 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 [8], [9] containing 55 atoms for which stationary points can be calculated rapidly. The parameters entering in the Lennard Jones potential were selected such that it models Argon clusters, namely $\epsilon=0.998$ kJ/Mole, $\sigma=3.4\text{Å}$ and $M=39.948$amu [9]. The free energies were calculated within the harmonic approximation as the vibrational free energy. The tem-
temperature at which the free energies were calculated is 30 K which is below the melting point (50 K) of this weakly bound system (Lennard Jones cluster). Initially we have searched for more than 130000 first order saddle points $G^s_i$ on the potential energy surface connecting energetically low local minima. Subsequently we have moved the system to the left and to the right along the direction where the curvature is negative. These two points served as the starting points for a local geometry optimization that led us in the two closest local minima. In this way we have generated pairs of local minima together with the saddle points that connect them. Fig. 3 and Fig. 2 show scatter plots of $\Delta G = G^s_i - G^a_i$ versus the activation energy $\epsilon_a = G^s_i - G^a_i$ with and without the entropy contributions respectively and Fig. 4 shows a histogram with averages of the $G^s_i - G^a_i$. 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 two scatter plots in Fig. 2 and Fig. 3 show that there is no strict linear correlation between the barrier height $\epsilon_a$ and the energy difference $\Delta G$ between the two minima. For small barrier heights one can find both high energy and low energy minima behind the 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 $\Delta G$ can not become larger than $\epsilon_a$. On the other hand, Fig. 3 shows that there is a good linear relation if one averages over $\Delta G$. Good linear Bell-Evans-Polanyi relations have been found in calculations of dissociative chemisorption of various molecules [13, 14, 15, 16].

**FIG. 2:** The relation between the activation energy $G^s - G^a$ and the reaction energy $G^a_i - G^a_i$ for more than 130000 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

**FIG. 3:** The relation between the activation energy $G^s - G^a$ and the reaction energy $G^a_i - G^a_i$ for more than 130000 saddle points at $T = 30$ K.

**FIG. 4:** The same data as in Fig. 2 and Fig. 3 but averaged within 25 bins along the x axis.

Kinetic rate theory gives the rate constant for a reaction as

$$k = \frac{k_B T}{h} \exp(-\beta \epsilon_a) = \frac{k_B T}{h} \frac{Q_s}{Q_a} \exp(\beta(E^a - E^s)),$$

where $E_a$ and $E_b$ are the energies of the two minima. $Q_s$ is the partition function for the transition state and gives in a certain sense the size of the barrier region. The importance of entropy terms can easily be seen in the classical limit. By making the same approximation as was done originally by Marcus in the derivation of the BEP principle, namely that the potential energy surface is the union of parabolas, but by considering 2-dimensional parabolas instead of 1-dimensional parabolas, one can easily see in Fig. 5 that the size of the crossing surface that can be surmounted by a MD path of limited energy is increasing strongly when the MD path goes into an energetically low basin. We expect therefore that for a fixed energy crossings into low energy minima are more
probable than crossings into high energy local minima.

Fig. 5 shows the results of a numerical experiment. For MD trajectories that start with random directions but fixed kinetic energy $E_{\text{kin}}$ 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 steps. In Fig. 5 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 in high energy basins. 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. This implies that we have replaced of property of the potential energy surface by a property of the MD trajectory exploring this surface.

As can be seen from Fig. 2, Fig. 3 and Fig. 6 both the traditional BEP principle and our MDBEP principle are only valid in an average sense. Such a validity on the average is sufficient in the context of global optimization using the minima hopping method (MHM) [6, 7]. In MHM the system moves from one local minimum to another by a combination of MD followed by a local geometry optimization. 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. In the original publication [6] it was already pointed out that the BEP principle is at least partly responsible for the success of the minima hopping method. If the MD trajectory has a small kinetic energy $E_{\text{kin}}$, it can not go over very high barriers and it is thus more likely to reach the basins of attraction of low lying minima. It was shown that the number of local minima that was visited before the global minimum was found decreases when the kinetic energy $E_{\text{kin}}$ of the trajectory is reduced. Fig. 7 demonstrates the MDBEP principle for the Lennard-Jones cluster consisting of 55 atoms. There is 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 Fig. 7 and the following similar figure were obtained by performing MHM runs that are stopped once the global minimum is found for different but fixed kinetic energies $E_{\text{kin}}$ (i.e. $\beta_1 = \beta_2 = \beta_3 = 1$ using the notation of ref. [6]) in a reasonably chosen energy interval. Subsequently we plot the values of $E_{\text{kin}}$ 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 can not cross barriers higher than $E_{\text{kin}}$ relative the starting minimum. Only new and accepted local minima are counted. In order to achieve better statistics we perform for each fixed $E_{\text{kin}}$ 100 MHM runs (for Fig. 7 the average is taken over 1000 runs), and take for the plots the averaged number of visited local minima.

Since the Lennard Jones potential is a drastic simplification of the true inter-atomic interactions in solid state systems one might wonder whether the MDBEP principle
also holds true for more realistic interactions. Using the MHM, we will therefore examine in the following the validity of the MDBEP principle for other systems, namely Morse clusters and silicon clusters described both by a force field and a tight binding scheme.

Fig. 7 and Fig. 8 present our results for the Morse clusters of 38 atoms with $\rho = 6.0$ and $\rho = 10.0$. Large values of $\rho$ 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 [9]. As a consequence considerably more minima are visited before the global minimum is found. The MDBEP principle is however well observed in both cases.

FIG. 7: The MDBEP principle for the Lennard-Jones cluster of 55 atoms.

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 many attempts before succeeding to escape from

actions that depend not only on the distance between atoms but also on things 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 a very good agreement with the DFT energies [7] and can be considered as a reliable approximation to a precise density functional treatment of silicon clusters. The MDBEP principle is valid in both cases which demonstrates that the MDBEP principle is also valid for realistic interactions and in particular for quantum mechanical interactions.

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

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.

Fig. 10 and Fig. 11 present our results for the Si$_{20}$ cluster within the Lenosky tight binding scheme [10] and for the Si$_{33}$ cluster within the Lenosky force field [11]. In contrast to the Lennard Jones and Morse potentials the silicon force field has much more complicated inter-
The number of visited local minima

FIG. 11: The MDBEP principle for the Lenosky force field cluster of 33 atoms.

the basin of attraction of the current minimum and this
will actually lead to an increase in the computer time.

In practice, the shortest computation time can be ob-
tained by giving the MD trajectories initial velocities
that have large components in the subspace of low cur-
vature of the Hessian matrix. Due to the fact that low
energy saddle points often lie at the end of low-curva-
ture modes [17, 18, 19] one can in this way even with low
energy trajectories rapidly escape from the present min-
imum.

In summary, we have shown that the BEP principle
can be extended to MD trajectories. We call this ex-
tended principle MDBEP principle and it says that MD
trajectories with low energy are more likely to lead into
basins of attraction of low energy configurations. Having
verified this principle numerically for several systems we
believe that it is valid for any solid state system.

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