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The optimal tunneling path for the proton transfer in malonaldehyde

Christofer S. Tautermann, Andreas F. Voegele, Thomas Loerting,
and Klaus R. Liedl[a)]
*Institute of General, Inorganic and Theoretical Chemistry, University of Innsbruck, Innrain 52a,
A-6020 Innsbruck, Austria*

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The proton tunneling reaction in malonaldehyde at low temperatures is investigated. The principal aim of this study is to find the optimal tunneling path at 0 K in the framework of the semiclassical theory with a global optimization method. An amount of 11366 *ab inito* points was determined in the reaction swath (i.e., the conformational space enclosed by the minima and the transition state) of malonaldehyde. With a simulated annealing approach, the path with the smallest integral of the imaginary action through the swath from minimum to minimum was determined. Surprisingly the optimal tunneling path was found to be quite far off the large curvature tunneling path [i.e., the straight connection of the two minima large-current tunneling (LCT path)]. At the beginning, it is following the minimum energy path (MEP) (i.e. the path with the lowest energy connecting the two minima and passing through the transition state), and then it is describing a curved path through the reaction swath. This curve was determined several times with different annealing schemes, which ended up with the same result—the tunneling path is proceeding close to the MEP rather than to the LCT path. Along the optimal tunneling path, the ground-state tunneling splitting was calculated with a new semiclassical method introduced in an accompanying study [C. S. Tautermann, A. F. Voegele, T. Loerting, and K. R. Liedl, J. Chem. Phys. **117**, 1967 (2002), following paper]. Another focus of investigation was the influence of deformation of the tunneling paths and a general scheme of determining an approximated optimal tunneling path at 0 K is introduced. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1488924]

I. INTRODUCTION

The nonclassical crossing of energy barriers is a subject which has been investigated since the quantum theory arose. Several different tunneling corrections beginning with the crude Wigner correction[1] are added to Eyrings theory of the activated complex[2] to reproduce accurate reaction dynamics of molecular systems. Wigner's correction just depends on the imaginary frequency at the transition state of the reaction, but in the meantime, there has evolved a vast number of different methods which aim to describe the tunneling correction accurately.[3,4] The most prominent methods make use of the reaction path Hamiltonian[5] and apply different tunneling schemes in this framework with further generalizations by additionally taking into account the regions where the reaction path Hamiltonian is not valid. Nonclassical behavior as quantum-chemical tunneling is considered in this theory by semiclassical methods,[6] thus yielding the so called ‘‘variational transition state theory with semiclassical tunneling.’’[7–11] A different approach is the instanton theory,[12–16] where the system is assumed to tunnel along the path of maximal tunneling probability (the so called ‘‘instanton’’) or very close to it. Unfortunately, the instanton is normally not calculated explicitly. Both aforementioned approaches were shown to yield comparable results in some cases.[17]

Within both theories, the tunneling path through the barrier is one central point to be considered. Actually one has to bear in mind that the tunneling path crosses a high dimensional space, as the dimension of a nonlinear molecular system with N atoms is $3N$-6. Therefore, the determination of the tunneling path is a nontrivial task. Normally, the space enclosed by the three stationary points of a reaction (i.e., the minima and the transition state), the so-called reaction swath is considered for tunneling. As the instanton is considered to be the path with the highest tunneling probability through a reaction swath, it would be necessary to determine it at each point along the minimum energy path (MEP) to yield accurate dynamics. In the framework of the applied instanton theory the instanton path is normally not computed explicitly but only information about the potential energy surface (PES) at the stationary points is used to calculate the transmission probability.[15,17–20] When describing the molecular system with the reaction path Hamiltonian, normally a grid of tunneling paths is determined, but their shape is predetermined: either the the tunneling occurs via a straight line through the swath[8] [i.e., the large-curvature tunneling (LCT) approach] or the tunneling occurs along paths closely related to the MEP (i.e., the small-curvature and zero-curvature tunneling approaches).[21,22] There are also attempts to determine tunneling paths with the least action,[7] composed piecewise of the small curvature tunneling and LCT paths.

When calculating the ground-state tunneling splitting in the framework of the semiclassical theory, the tunneling probability (P_0) at 0 K has to be known as it is directly related to the tunneling splitting:[23]

[a)] Electronic mail: klaus.liedl@uibk.ac.at

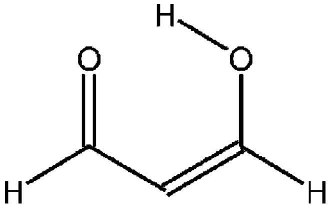

FIG. 1. The structure of malonaldehyde.

$$\Delta = \frac{\omega}{\pi}\sqrt{P_0}, \tag{1}$$

with ω being the impinging frequency. There are plenty of methods to calculate the tunneling splitting in molecular systems, most of them being within the framework of the semiclassical theory.[6,24,25] Malonaldehyde (see Fig. 1) is a system which has been investigated thoroughly, both experimentally[26,27] and theoretically.[18,28–30] Therefore, we chose this system for our benchmarks to determine the most probable tunneling path in all dimensions. The need for the explicit calculation of the path emerges from the current use of the instanton theory: The barrier for the proton transfer in malonaldehyde was assumed to be higher than 10 kcal/mol and the calculated tunneling splitting met the experimental values very well.[18] One year later, the barrier in malonaldehyde was shown to be 4–5 kcal/mol, when applying various high-level quantum chemical methods.[30] Therefore, we assume that a strong cancellation of errors must have occurred and the implementation of the instanton theory still suffers from the lack of explicitly computing the tunneling path.

Now, we calculated more than 10^4 points in the swath of malonaldehyde quantum chemically to determine the path along which the tunneling probability is a maximum with a global optimization scheme.

II. METHODS

A. Determination of the swath

The general procedure was to determine a vast amount of points in the swath with hybrid-density-functional theory (DFT) and a moderate basis and then mapping these points onto some high-level points.

First, the MEP was determined at the $B3LYP/6\text{-}31+G(d)$ level of theory with the Page–McIver algorithm[31] as implemented in POLYRATE[32] and GAUSSRATE.[33] The stepsize in mass scaled coordinates (scaled to 1 amu) was set to 0.01 a.u. and the second derivatives of the potential energy in respect to the coordinates were calculated every third step. In the spatial region enclosed by the MEP and the straight connection of the minima, 11 366 points were determined in that way, so that the neighbored points lie within a distance of 0.025 a.u., which is close enough for a good interpolation. As the DFT is known to reproduce the results of high-level methods quite well,[34] the points yield a qualitative correct description of the reaction swath. All energies were determined with the GAUSSIAN 98 program package[35] at an 8-CPU SGI Origin 2000.

With an interpolation scheme, the PES generated by DFT methods is mapped onto high-level quantum chemical points. For this, the stationary points and one additional point on the ridge of the reaction swath were determined by coupled cluster theory. As fourth geometry, the structure on half way on the straight line connecting the minima was chosen, for being the highest point on the ridge of the reaction swath (see Fig. 2). This structure differs from the transition state in that way, that the oxygen atoms have not come closer with respect to the minima. Therefore, the distance between the moving hydrogen atom and the oxygens is about 0.14 Å elongated at the highest point on the ridge of the reaction swath with respect to the transition state.

The barriers from the high-level method coupled-cluster singles and doubles with perturbative triples with Dunnings

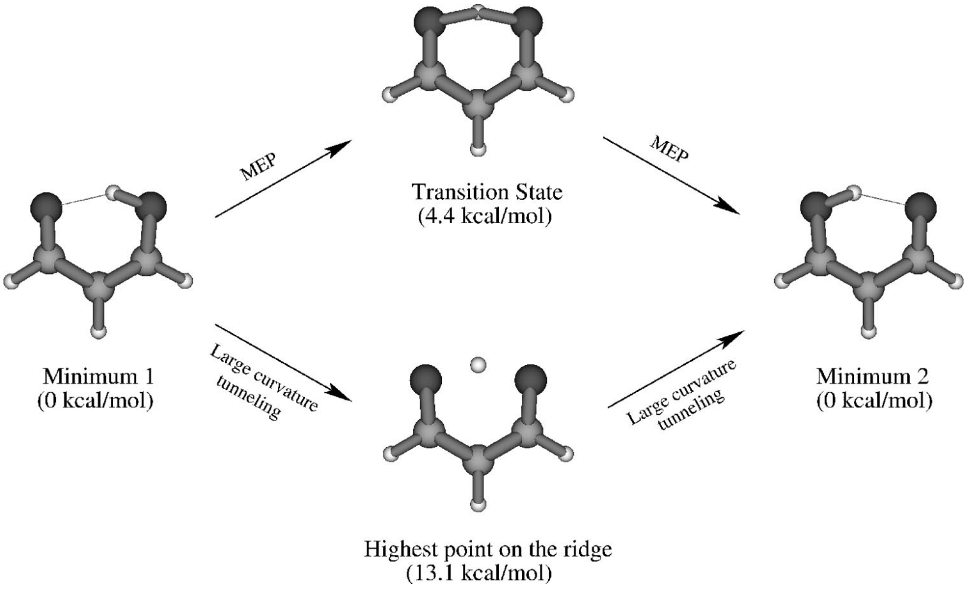

FIG. 2. The stationary points of malonaldehyde on the MEP and the highest point of the ridge of the reaction swath on the LCT path are depicted.

TABLE I. Comparison between DFT and high-level energies for the proton transfer in malonaldehyde.

Method	Reaction barrier	ΔE between minima and highest point of the ridge
$B3LYP/6\text{-}31+G(d)$	3.8 kcal/mol	11.2 kcal/mol
CCSD(T)/aug-cc-pVDZ	4.4 kcal/mol	13.1 kcal/mol
Barone *et al.*[a]	4.3 kcal/mol	

[a] See Ref. 30.

augmented correlation-consistent double zeta basis set based on the geometries obtained by Møller–Plesset perturbation theory (CCSD(T)/aug-cc-pVDZ//MP2/aug-cc-pVDZ) correspond quite well to the low level data (see Table I).

Interestingly, the deviation between the low-level and high-level data is for both energy differences about 16%. Therefore, we used the straightforward interpolation scheme, just to scale all energy differences of the low-level swath with the scaling factor 1.16 to gain an interpolated high-level swath for the electronic energies.

Another correction which has to be done due to the zero-point motion of atoms also at 0 K is the zero-point correction. The second derivatives of the energy in respect to the coordinates have to be determined along the ridge of the reaction swath and the gradient was projected out of the second derivative matrix.[5,36] The sum of the eigenvalues of the projected second derivative matrix yields the zero-point correction and this is implemented with a more subtle interpolation procedure,[37] which has already been successfully applied to many other molecular systems.[38–40]

B. Determination of the tunneling splitting

The newly introduced method is presented in an accompanying study[41] and is reviewed briefly. A reformulation of the semiclassical formula for the tunneling splitting by Garg[42] led to a new method of computation. The splitting Δ is transformed to

$$\Delta = 2\hbar\omega\sqrt{\frac{m\omega a^2}{\pi\hbar}}e^{-S_0/\hbar}e^{A}, \tag{2}$$

where the limits of the action integral S_0 are the minima $(\pm a)$ of the double well, $V(x)$ is the potential energy along the path, and ω is the so-called impinging frequency. A is a correction factor with

$$A = \int_0^a \left[\frac{m\omega}{\sqrt{2mV(x)}} - \frac{1}{a-x}\right]dx. \tag{3}$$

The action integral is computed via

$$S_0 = \int_{-a}^{a}\sqrt{(2mV(x))}dx. \tag{4}$$

The advantages of calculating the ground state tunneling splitting with Eq. (2) over other methods is discussed elsewhere.[41] The factors which are directly influenced by the choice of the tunneling path are the integration limits $\pm a$ and the potential energy $V(x)$ along the tunneling path. One very obvious fact, seen from Eq. (2) is that the splitting is very strongly influenced by S_0, which is directly related to the tunneling probability[13] via Eq. (1). Therefore, one has to find the optimal tunneling path in a way that the action integral is minimized. Thus, we have the problem of the determination of the tunneling splitting reformulated into a minimization problem, which may be solved by various minimization techniques. In the following section, the optimal tunneling path is computed with a simulated annealing approach.

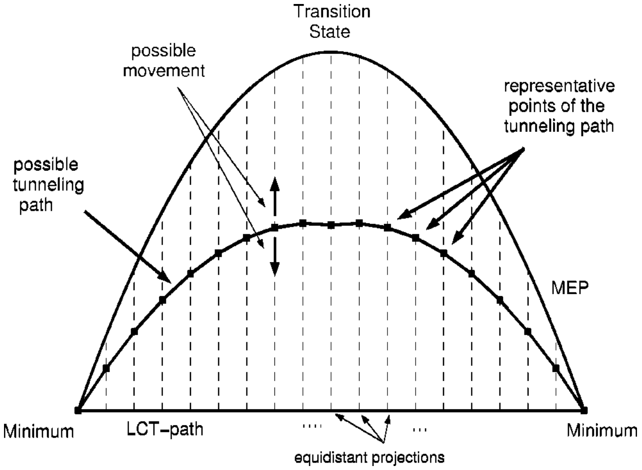

FIG. 3. Schematic two-dimensional representation of the minimization procedure for the determination of the most probable tunneling path. The path is represented by 19 equidistant points in the swath, which are allowed to move on the projection hyperplane randomly.

C. Search for the optimal tunneling path

The quest for the optimal tunneling path is a difficult task as the optimization is high dimensional. In addition to that, one is interested in finding the global minimum rather than local ones. Thus, we have applied a simulated annealing approach[43–45] with an exponential schedule to gain the most probable path. The path was described by a set of 19 points with the premise that their projections onto the LCT path is equidistant. In each annealing step, the position of one of these points was changed randomly in the swath (along the projection hyperplane, see Fig. 3) and with the Metropolis algorithm it was decided whether the step was accepted or not. As starting points, two different conformations (MEP and LCT path) were chosen for different optimization runs to be sure that the global minimum was reached. The tunneling path was assumed to be symmetric as the whole reaction swath is symmetric.

One simplification we had to take into account was the minimization of the action integral of Eq. (4) rather than the whole term with the correction factor A from Eq. (3). But, it was seen that the correction factor is very small in comparison to S_0, and therefore, we decided to concentrate on the optimization of the main contribution as the correction factor will not change the choice of the tunneling path considerably.

Thus, the goal of the optimization was to find a path with the line integral along a given function $\sqrt{V(x)}$ in mass scaled coordinates. The values for $V(x)$ at any arbitrary conformation were taken as interpolated values of the next neighbors

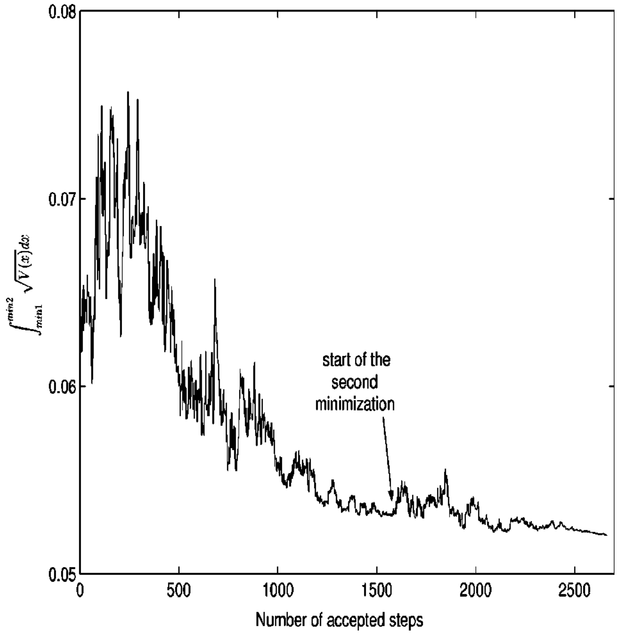

FIG. 4. Accepted steps in the minimization of $\int_{\mathrm{min1}}^{\mathrm{min2}}\sqrt{V(x)}dx$ with simulated annealing. The first minimization lasts 1600 steps with a starting temperature of 0.006 and a temperature reduction of 10% for each of the 50 steps. The second minimization started at $T=0.0003$ and the temperature is lowered every 100th step for 10%.

and the integration was numerically performed by Gauss quadrature as it is implemented in MATLAB.[46] Different annealing schedules were used, first for preoptimization, the temperature parameter T beginning with $T=0.15$ was reduced for 15% for each of 30 steps at the same temperature. Then, the annealing was slowed down as described in Fig. 4, which shows the combination of two consecutive annealing runs.

D. The optimal tunneling path

Altogether, eight different annealing schemes have been applied and all ended up with the same result for S_0. Therefore, we believe to have reached the global minimum with $\int_{\mathrm{min1}}^{\mathrm{min2}}\sqrt{V(x)}dx=0.52\sqrt{\mathrm{Hartree}}$ a.u. which leads to a tunneling splitting[41] of $7.4\times 10^{11}\ \mathrm{s}^{-1}$, which is in very good accordance with the experimental value[27] of $6.5\times 10^{11}\ \mathrm{s}^{-1}$.

The optimal tunneling path follows the MEP in the very beginning and then it crosses the swath in a curve, which lies closer to the MEP than to the LCT path. As the proton transfer in malonaldehyde is a typical case for LCT[9,47] (as a very light atom moves between two heavy ones), one would have expected a path, which lies much closer to the straight connection between the two minima. Figure 5 shows the hypothetic progression of the optimal tunneling path if the MEP was assumed to be of parabolic shape. This clearly shows the strong deviation from the LCT path and the strong curvature in the center of the tunneling region. This is a difference from other methods, which take the tunneling path to be straight in the middle part.[8]

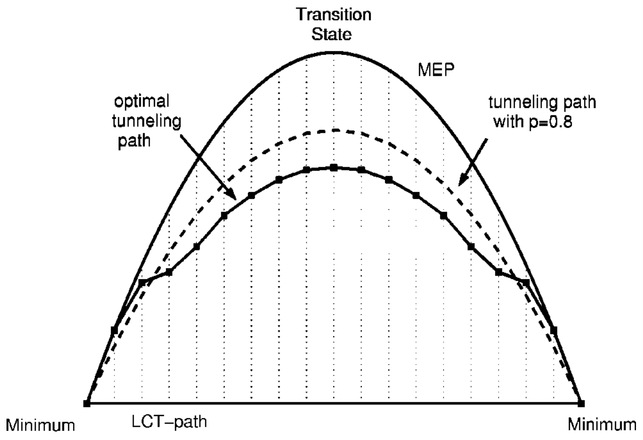

FIG. 5. The optimal tunneling path if the MEP was assumed to be parabolic. The dashed path shows a possibility to approximate the optimal tunneling path to evaluate the tunneling splitting in a more economic way.

E. Approximation of the optimal tunneling path

This method of determining the optimal tunneling path by describing the swath correctly with a vast amount of energy points is only feasible for small systems as malonaldehyde. This study should be seen as a benchmark for molecular systems which involve symmetrical proton transfers, as tropolone, the benzoic acid dimer, and many more. As one clearly sees from Fig. 5, the tunneling path is curved also in the regions of higher energy, i.e., under the ridge of the reaction swath. Thus, we tried to approximate the path with a intuitive straightforward method: It was described as a linear combination of the MEP and the LCT path with a fixed parameter p, which may be seen as the "mixing ratio" of the two paths (i.e., $p=0$ means that tunneling occurs along the LCT path and $p=1$ means that the system is tunneling along the MEP). The path with $p=0.8$ is depicted in Fig. 5.

By calculating the tunneling splitting along these very simple paths, one sees that the splitting approaches a maximum at $p=0.8$ (for details see the accompanying study)[41] and this splitting equals the splitting evaluated with the optimized tunneling path. So, we can conclude that along the tunneling path with $p=0.8$ the integral of the square root of the potential is very similar to the globally optimized one. This may sound very surprising, but if one looks at the two paths in Fig. 5, one may realize, that the paths do not differ greatly. At the beginning, the simple path takes a somewhat shorter way, but in the middle, it lies closer to the MEP. One feature, which both paths have in common is to avoid the high-energy region near the LCT path. In addition to that, is was observed in the various annealing approaches that the global minimum is very shallow, therefore, a small variation of the location of the path did not change the transmission probability very much—as far as the path did not come too close to the high-energy region around the LCT path.

So, we have found a possibility to calculate the tunneling splitting accurately along these very easily generated paths. Thus, one has to determine these paths for some values of p and then the ground-state tunneling splitting for the molecular system can be determined by interpolating and taking the maximum. This method works very well *in praxi*.[41]

III. CONCLUSIONS

The optimal tunneling path in malonaldehyde at 0 K was determined with a global optimization procedure, namely simulated annealing with an exponential annealing schedule. The reaction swath was described by 11 366 energy points, which were mapped onto high-level and zero-point corrected data, due to retrieve a zero-point corrected high-level representation of the swath. The optimized path was shown to lie far off the LCT path and surprisingly close to the MEP, a behavior, which was not expected for a system, where a proton tunnels between two heavy atoms. Along this optimized path, the tunneling splitting was determined with a newly developed method[41] and it met the experimental value very well.

Some efforts were made to find a feasible approximation for the optimized path. It was shown that a linear combination of the MEP and the LCT path sufficiently describes the path to yield an accurate tunneling splitting. This kind of approximated paths can also be used for larger systems as tropolone—it is shown in an accompanying article that the corresponding tunneling splitting meets the experiment very well again.[41] Thus, the present study legitimates the approximation of the tunneling path for the determination of the ground-state tunneling splitting by the scheme introduced herein.

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