

# An accurate semiclassical method to predict ground-state tunneling splittings

Christofer S. Tautermann, Andreas F. Voegelé, Thomas Loerting  
and Klaus R. Liedl<sup>a)</sup>

*Institute of General, Inorganic and Theoretical Chemistry, University of Innsbruck, Innrain 52a,  
A-6020 Innsbruck, Austria*

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A new method for calculating the ground-state tunneling splitting is presented. It is based on the semiclassical theory including recently derived corrections and it is the first method, which explicitly takes into account the whole conformational space between the minima and the transition state. The density-functional theory is used to determine the qualitative shape of the potential energy surface (PES) and high level *ab initio* calculations provide information about the stationary points. With a dual level scheme, the low-level energy surface is mapped onto the high-level points to get a good quantitative description of the high-level PES. Therefore, the new method requires no adjustment of additional parameters like scaling of the energy barrier as is necessary in other methods. Once the high-level PES is calculated, the most probable tunneling paths are determined with a global optimization procedure. Along this representative tunneling path, the tunneling splitting is calculated with additional consideration of zero-point vibrational effects. The method is applied to three molecular systems, namely hydrofluoric acid dimer, malonaldehyde, and tropolone. These systems were chosen because their energy barriers differ strongly (1 kcal/mol–7 kcal/mol). The predicted tunneling splittings agree very well with the experimental ones, therefore, we expect our method to be generally applicable, independent of the magnitude of the energy barrier. © 2002 American Institute of Physics. [DOI: 10.1063/1.1488925]

## I. INTRODUCTION

The occurrence of ground-state tunneling splittings is a fundamental property of symmetric molecules and systems (i.e., chemical systems undergoing symmetric conversions with symmetric energy barriers) and has been investigated both theoretically<sup>1–20</sup> and experimentally.<sup>21–33</sup> This splitting emerges in symmetric potential double wells from a small energetic difference of the lowest symmetric and antisymmetric wave function due to coherent quantum tunneling (Fig. 1). In the case of a slightly disturbed potential, the tunneling mechanism changes into an incoherent tunneling mechanism.<sup>34–36</sup> As the splitting crucially depends on the reduced mass along the tunneling path and the reaction barrier, it is often observed in hydrogen transfer reactions due to the small mass of a proton. Therefore, the understanding of the underlying mechanism is important for a thorough investigation of the impact of tunneling on hydrogen transfer reactions. As these reactions are ubiquitous in the chemistry of biological systems,<sup>37</sup> there are great efforts toward elucidating these tunneling processes,<sup>38</sup> as even at room temperature, tunneling effects are shown to be important in enzymatic catalysis.<sup>39–42</sup> A new approach to determine the tunneling splittings gives better insights in tunneling mechanisms and describes the mechanisms in the low-temperature limit of chemical reactions.

Most of the generally used methods to predict the ground-state tunneling splitting take into account the three

stationary points of the considered reaction (i.e., the minima and the transition state) including the vibrational analysis at these points.<sup>9,10,15,20,43</sup> The most probable tunneling path on its own (in the framework of the semiclassical theory called “instanton”) is not calculated explicitly, but the tunneling features are expressed in terms of normal frequencies and energy differences.<sup>7</sup> Other methods take into account the minimum energy path (MEP), i.e., the path of lowest potential energy connecting the two minima.<sup>3</sup>

However, both methods suffer from the neglect of the conformational space enclosed by the MEP, the so-called reaction swath. This region is essential for tunneling at low-temperatures, where the reaction does not follow the MEP but tunnels through the swath far away from the transition state.<sup>6,44</sup>

There is strong evidence that the so called “instanton method” works due to error compensation: The tunneling splitting of malonaldehyde was calculated with instanton theory<sup>10</sup> and although the reaction barrier was extremely overestimated (larger than 10 kcal/mol instead of 4.1–4.4 kcal/mol)<sup>45</sup> the result was in excellent agreement with the experiment. As the tunneling behavior depends strongly on the energy barrier, we think that a cancellation of errors must have occurred. In other studies, the reaction barrier was even scaled down to a specific value to yield the correct tunneling splitting.<sup>15</sup>

Here, we propose a new semiclassical method, which overcomes the aforementioned deficiencies. On the one hand, we take into account the whole reaction swath (and therefore, all degrees of freedom relevant for the reaction)

<sup>a)</sup>Electronic mail: klaus.liedl@uibk.ac.at

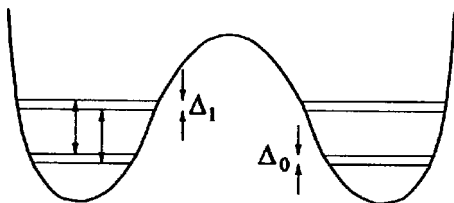


FIG. 1. Symmetric double well potential with ground-state splitting  $\Delta_0$  and splitting of the first-excited state ( $\Delta_1$ ).

and on the other hand, we use high-level quantum-chemical calculations to determine the reaction energetics. First, we search for an optimal tunneling path through the reaction swath connecting the two minima and then the tunneling splitting is calculated along this path with improved methods.

In the results section, the calculated splittings are compared to experimental values of several molecular systems, namely the hydrofluoric acid dimer, malonaldehyde, and tropolone. These systems possessing barrier heights from 1 kcal/mol to more than 7 kcal/mol were chosen to prove the reliability of the developed method in different situations. Very good accordance between the calculated splittings and the experimental values was found, and in all calculations no empirical parameters had to be adjusted, which gives confidence in this newly developed method.

## II. METHODS

In the following the term “tunneling splitting” is a synonym for “ground-state tunneling splitting” as this article is only concerned with the splitting of the ground state of the wave function in symmetric molecular systems.

### A. Improved procedure for the semiclassical calculation of the tunneling splitting

In a recent study of Garg<sup>46</sup> a correction of the well known Wentzel–Kramers–Brillouin (WKB) formula for the semiclassical ground-state tunneling splitting is introduced. Moreover, Garg gives new access to the evaluation of the imaginary action integral, where the integration does not start at the classical turning points of vibration but at the minima of the symmetric double well. This has the advantage that the integrand, which is close to a singularity, becomes well behaved. Thus the WKB formula for the ground-state tunneling splitting becomes reshaped:

$$\Delta = 2\hbar\omega \sqrt{\frac{m\omega a^2}{\pi\hbar}} e^{-S_0/\hbar} e^A, \quad (1)$$

where the limits of the action integral  $S_0$  are the minima ( $\pm a$ ) of the double well and  $A$  is the correction factor due to the changing of the integration limits

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

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

$V(x)$  is the potential energy,  $m$  is the mass of the particle, and  $\omega$  is the so-called impinging frequency.

The advantage of Eq. (1) is the improvement of the numerical stability for evaluating  $\Delta$ . To apply the WKB formula, one has to fit an analytical potential, the numerical values from the experiment to perform the integration. Now, the central part—namely  $S_0$ , can be calculated by numerical integration (Gauss quadrature was used) and just the correction factor  $A$  needs a mapping of an analytic potential onto the experimental values. Therefore, the errors caused by the mapping procedure are minimized as they only affect the correction factor, which on its own is very small in comparison to  $S_0/\hbar$ .

### 1. Computation of $S_0$ and $A$

To determine  $S_0$ , a sufficient number of potential energy values along the tunneling path and their distances have to be known. Experience has shown that 15–20 points along a tunneling path are normally sufficient to give quite accurate results. The distance between the geometries along the tunneling path is calculated in mass scaled coordinates and with a procedure developed by Chen.<sup>47</sup> The choice of the tunneling path, which is crucial for reliable description of tunneling effects is discussed in Sec. IIB and an accompanying paper.<sup>48</sup> When the energy on several sampling points is determined, one can choose different quadrature procedures as implemented, e.g. in MATLAB<sup>49</sup> and therefore the calculation of  $S_0$  is straightforward.

The determination of the correction factor  $A$  turns out to be a bit more sophisticated as a singularity appears in the integral. Numerically, it is a big problem to evaluate a singular integral. Therefore, we decided to map the potential energy of the tunneling path onto an analytical potential. As there are three crucial parameters of a double well, i.e., the height ( $V_0$ ), the distance of the minima ( $2a$ ), and the curvature at the minima ( $\kappa$ ), we chose a polynomial of the sixth degree as the analytical potential of the following shape:

$$V_a(x) = \frac{1}{8a^6} (x-a)^2 (x+a)^2 (-8x^2 + x^2\kappa a^2 + 8a^2V_0). \quad (2)$$

All variables are in atomic units and  $\kappa$  is calculated from the impinging frequency according to the relation  $\kappa = \omega^2 m$ .<sup>15</sup> With this convention, it is possible to evaluate  $A$  analytically, the lengthy formula is given in Appendix A. We expect the error due to approximation to be very small as already a polynomial of the order of 4 gives satisfying results if it is used as analytical surface for double wells.<sup>8,50</sup>

Now, both important values from Eq. (1) are theoretically derived, the last, but very important question is the determination of the tunneling path. The practical implementation, especially the computational details, including the discussion about the zero-point vibrations will be discussed next.

### B. Choice of the tunneling path

The shape of the tunneling path is one of the most important but difficult questions when dealing with tunneling

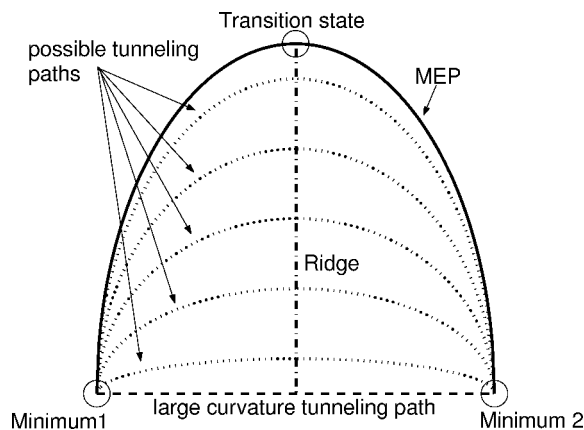


FIG. 2. Scheme of combining the MEP and the LCT path to gain the tunneling paths.

phenomena. There are various approaches, like the zero-, small-, and the large-curvature tunneling (LCT) theories,<sup>44,51–54</sup> which try to describe the tunneling behavior in chemical reactions. These theories are applied successfully to various systems to determine kinetical features of chemical reactions.<sup>18,19,55–59</sup> Although one can achieve excellent agreement between theory and experiment at temperatures above about 100 K, these tunneling theories fail if the temperature is too low. The LCT path cuts through the reaction swath in a straight line, connecting the branches of the MEP. If the temperature is too low, i.e., the system has very low thermal energy and it is not able to climb far up along the MEP branches, it has to tunnel through regions of very high potential energy, which is unfavorable. On the other hand, if no corner cutting is allowed (i.e., zero-curvature tunneling), the tunneling path is very long, and therefore, the tunneling probability will drop.

Our aim now, related to the aim of the instanton theory,<sup>60</sup> is to find the tunneling path with the highest tunneling probability (the so-called instanton) from one to the other minimum. As the tunneling splitting is directly related to the tunneling probability at 0 K, this path also yields the desired tunneling splitting. In an accompanying paper, we investigated the reaction swath of malonaldehyde and searched for the optimal tunneling path with a global optimization procedure. It is shown that the optimal tunneling path follows the MEP for the first few percent of the distance and then the optimal tunneling path may be described by a linear combination of the MEP and the LCT path. One has to be aware that due to the curvature of the MEP in many dimensions, the linear combination does not yield a two-dimensional subspace, but a manifold covering the whole reaction swath. Figure 2 provides the idea of the tunneling paths gained by the linear combining the LCT path and the MEP. A parameter  $p$  is introduced to describe the tunneling paths in terms of parts of the LCT path and the MEP (i.e., if  $p = 1$ , the tunneling path follows the MEP, if  $p = 0$  the tunneling path follows the LCT path).<sup>61</sup> Along these paths the energy profiles are calculated in dependence of  $p$  by quantum chemical means (see Fig. 3) and the corresponding tunneling splitting is determined. The path belonging to the largest splitting is chosen as the representative tunneling trajectory.

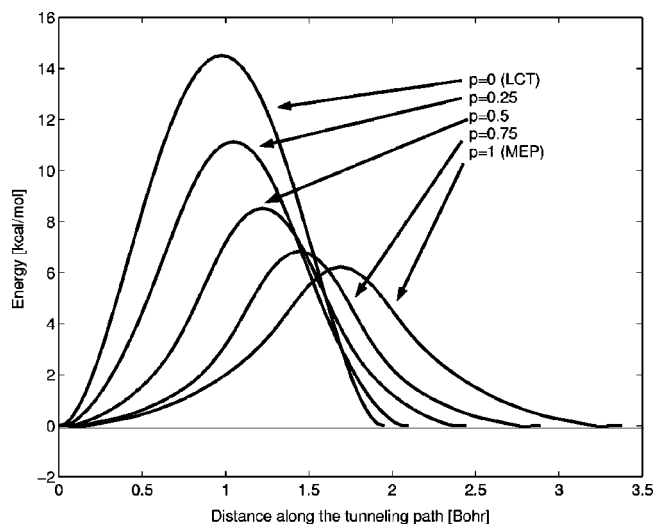


FIG. 3. Energy profiles at the  $B3LYP/6-31+G(d)$  level of the tunneling paths in tropolone in dependence of the parameter  $p$ . If  $p = 1$ , the tunneling path is equivalent to the MEP, if  $p = 0$ , the tunneling occurs along the LCT path.

### C. Mapping procedures onto high level energy data

Although the density-functional theory has been shown to yield a reliable and quite accurate description of the potential energy surface (PES), we map the PES onto some energy points, calculated by high-level methods (e.g., coupled cluster).<sup>62</sup> By comparing the two barriers (low level with high level), we get hold of a scaling factor which is used for scaling all other energy points as well. As a verification, a fourth high-level energy point at the highest point of the ridge of the reaction swath is determined and again compared to the low-level value. In all investigated systems, the difference of the two scaling factors is negligible. Therefore, the scaling of the low-level energy points to the high-level data and proceeds with the same scaling factor for the whole PES.

To get the zero-point corrected energy surface, the zero-point corrections are calculated at various points of the reaction swath. If the vibrational frequencies are determined at nonstationary points, i.e., the gradient is not equal to zero, the gradient has to be projected out of the Hess matrix prior to diagonalization.<sup>63,64</sup> (One has to bear in mind that there is no rigorous criterion for the choice of the direction to project out of the Hess matrix. We chose the gradient direction, but one may also use the direction of the tunneling path.)<sup>65</sup> These zero-point corrections are best determined at some points at the ridge of the reaction swath, where the various trial tunneling paths are highest in energy.

With this knowledge, we apply a more sophisticated interpolation procedure to take into account the zero-point correction along the tunneling paths, which we assume to stay vibrationally adiabatic over the whole tunneling range. (For some reactions and tunneling paths, this assumption may not be valid.)<sup>66</sup> We make use of the procedure developed by Truhlar *et al.*,<sup>67</sup> which was shown to give very reliable results. Therefore, the energy of the tunneling paths is interpolated twice; first, the whole PES is mapped onto three to four stationary points, then, the energy is zero-point corrected

along the various tunneling paths. From this procedure, we expect to yield very accurate energies along the various paths, and therefore, accurate values for the transmission probability.

#### D. Quantum chemical methods

In using the low-level method, we applied the density-functional method *B3LYP* with the moderate basis set  $6-31+G(d)$ . In our experience, this method yields energy barriers quite similar to ones gained by high-level methods.<sup>18,58,59,68</sup> Also, the MEP is determined at this level of theory with the algorithm developed by Page and McIver.<sup>69</sup> The stepsize was adjusted for the various systems: 0.025 a.u. for the  $(\text{HF})_2$  system, 0.01 a.u. for malonaldehyde, and 0.05 a.u. for tropolone. The second derivatives were calculated each third step for malonaldehyde and tropolone and each step for  $(\text{HF})_2$ . The computations of the MEP were performed with the POLYRATE program package,<sup>70,71</sup> which uses GAUSSIAN 98<sup>72</sup> for the quantum-chemical calculations.

The high-level methods depended on the size of the system—mostly, they are well known in literature—but at least  $G3(\text{MP2})$ <sup>73</sup> was applied to our systems. All high-level quantum-chemical calculations were performed with GAUSSIAN 98.<sup>72</sup>

### III. COMPUTATIONAL IMPLEMENTATION

We have presented all tools to determine the tunneling splitting, now we give the procedure for a computational implementation:

- (1) Computation of the stationary points, also at high-level of theory;
- (2) Determination of the MEP;
- (3) Calculation of the zero-point correction at some chosen points on the ridge of the reaction swath and the stationary points;
- (4) Mapping the low-level surface onto the high-level data; and
- (5) Search for the optimal zero-point corrected tunneling path and determination of the tunneling splitting.

### IV. RESULTS

#### A. Selection of molecules

To test the quality of our newly developed method, we chose three different systems with energy barriers in a wide range. The system with the smallest barrier is the rearrangement of the hydrofluoric acid dimer [see Fig. 4(a)] with

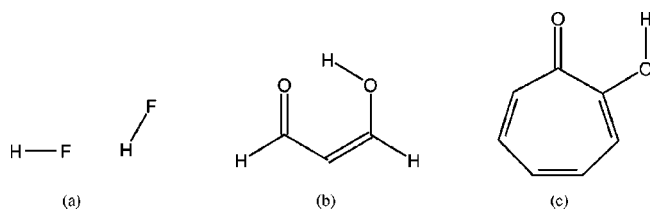


FIG. 4. Chosen molecular systems: (a) hydrofluoric acid dimer, (b) malonaldehyde, and (c) tropolone.

TABLE I. Energy barriers of the various systems. Comparison between *B3LYP/6-31+G(d)* and high-level methods. For the CCSD(T)<sup>a</sup> method, the aug-cc-pVDZ<sup>b</sup> basis was applied.

	<i>B3LYP/6-31+G(d)</i>	High level
HF dimer	1.42 kcal/mol	1.01 kcal/mol <sup>83</sup>
Malonaldehyde	3.84 kcal/mol	4.4 kcal/mol (CCSD(T)//MP2) <sup>c</sup>
Tropolone	6.25 kcal/mol	7.2 kcal/mol (G3(MP2))

<sup>a</sup>CCSD(T) indicates coupled-cluster singles and doubles with perturbative triples.

<sup>b</sup>aug-cc-pVDZ indicates Dunning's augmented correlation-consistent double zeta basis set.

<sup>c</sup>MP2 indicates Møller–Plesset perturbation theory of second order.

about 1 kcal/mol, followed by the proton hopping reaction in malonaldehyde [see Fig. 4(b)] with about 4 kcal/mol and as the system with the highest barrier, we investigated the hydrogen exchange in tropolone [see Fig. 4(c)] with a barrier of more than 7 kcal/mol.

#### B. Energetics of the stationary points

Table I shows the energy barriers of the various reactions. It is clearly shown that the density-functional values are always close to the high-level points, and therefore, we expect the PES already being described quite well by the low-level method. The energy profiles along the MEP are depicted in Fig. 5. All considered reactions show a symmetric double well, which is necessary for the appearance of a coherent ground-state tunneling splitting.

#### C. Tunneling splittings

In this section, we present the results of our calculations and give a comparison to the experiments. The newly developed method is applied to each system with path parameters  $p=0,0.25,0.5,0.75$ , and 1 and in the region, where the maximum of the tunneling splitting is expected, additional paths

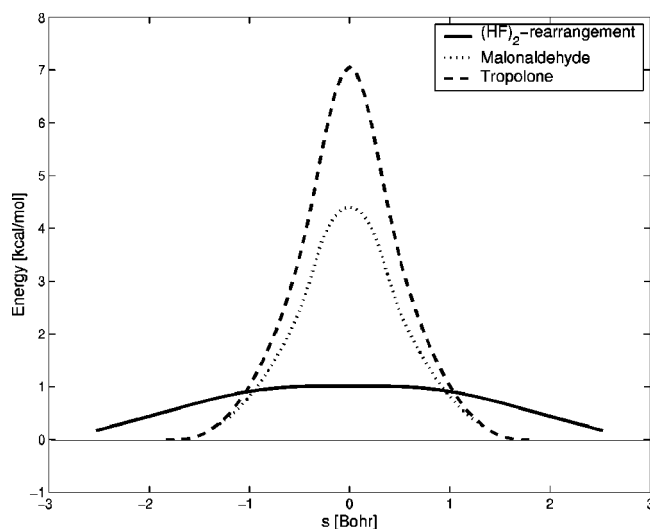
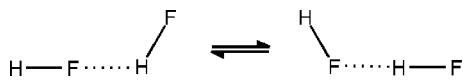


FIG. 5. Potential energy curves of the three considered reactions. Due to evaluate the general applicability of the method, systems with different barrier heights were chosen.



FIG. 6. Symmetric  $(\text{HF})_2$  rearrangement.

with other  $p$  values are computed. For each system, a detailed discussion will be presented concerning the choice of the tunneling path.

### 1. $(\text{HF})_2$ rearrangement

The rearrangement within the hydrofluoric acid dimer is depicted in Fig. 6. The energetics of the reaction is described by a symmetric double well with a barrier of 1.01 kcal/mol (see Table I and Fig. 5). The tunneling splitting in dependence of  $p$  is shown in Fig. 7. It is clearly seen, that the choice of the tunneling path influences the tunneling splitting tremendously. The splitting along the LCT path reveals to be 40 orders in magnitude smaller than the splitting along the path with  $p=0.85$ . This shows that the real tunneling path in the low-temperature limit is surprisingly close to the MEP. The tunneling splitting of this reaction was subject of investigations by Hancock *et al.*,<sup>74</sup> who also found quite reasonable tunneling splittings with a tunneling path near the MEP [in the framework of the small curvature approximation].<sup>75</sup> As is seen from Fig. 7, the two corrections of the PES, namely the high-level and zero-point correction, are extremely important as the tunneling splitting is strongly underestimated with the uncorrected PES. The calculated tunneling splitting meets the experimental values of Quack and Suhm<sup>76</sup> well.

### 2. Proton tunneling in malonaldehyde

The considered reaction is depicted in Fig. 8. The barrier within this reaction amounts to 4.4 kcal/mol, which is more than four times larger than in the  $(\text{HF})_2$  system. Again, the most probable tunneling path lies with  $p=0.8$  close to the

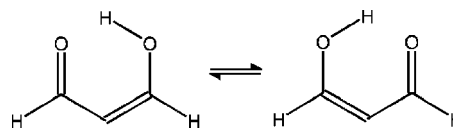


FIG. 8. Proton tunneling in malonaldehyde.

MEP and even at these very low-temperatures, LCT is not the preferred mechanism. Details about the tunneling path can be found in an accompanying article.<sup>48</sup> The determined tunneling splitting agrees very well with the experimental results<sup>22,27</sup> (see Fig. 9) and the importance of high-level data is again emphasized: The uncorrected curve overestimates the tunneling splitting because  $B3LYP$  underestimates the barrier height (see Table I).

### 3. Proton tunneling in tropolone

The reaction (see Fig. 10) is somehow similar to the proton tunneling in malonaldehyde as the proton hops between two carbon bound oxygens. The higher barrier of 7.2 kcal/mol at the  $G3(\text{MP}2)$  level of theory may be explained by a strained transition state as it consists of a five-membered ring. In comparison, the transition state of malonaldehyde contains a six-membered ring which is more relieved from strain. Also with another high-level method, namely the multicoefficient correlation method based on quadratic configuration interaction with single and double excitations<sup>77</sup> a similar high barrier (7.7 kcal/mol) was obtained. The good agreement between the two methods ensures the use of accurate barrier heights. The optimal tunneling path is again very close to the MEP. Although a proton moves between two much heavier atoms, one can therefore not conclude a LCT behavior. Again, the experimental value<sup>31</sup> is met very well by the calculations with the high-level PES and the zero-point corrections (see Fig. 11).

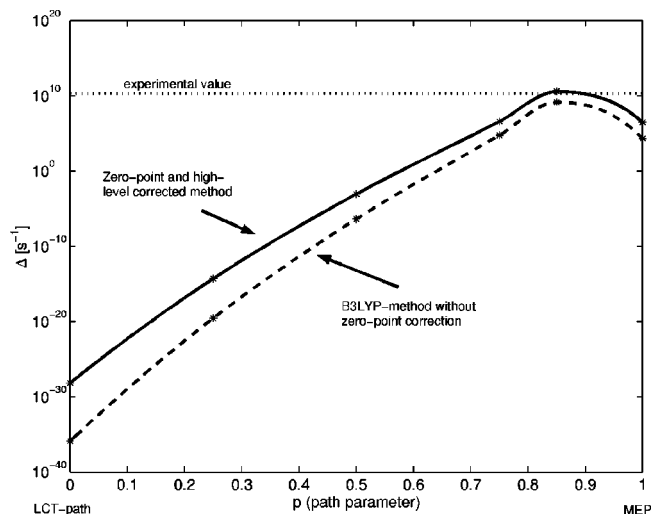


FIG. 7. The calculated tunneling splitting in the hydrofluoric acid dimer is strongly dependent on the choice of the tunneling path. In addition, there is a strong influence on the splitting of high-level corrections. The optimal tunneling path was found at about  $p=0.85$  and the determined tunneling splitting agrees very well with experimental values (see Ref. 76).

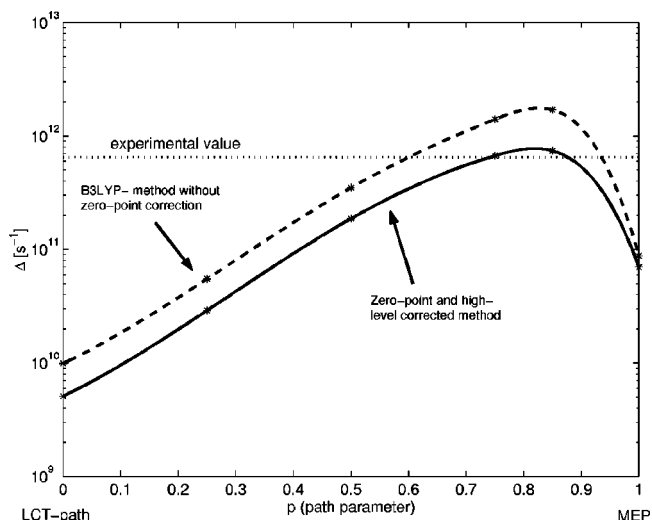


FIG. 9. Tunneling splitting in malonaldehyde. The splitting is strongly dependent on the choice of the tunneling path. The optimal path was found at a  $p$  value of about 0.8. Again a good agreement with the experiment<sup>22,27</sup> was found.

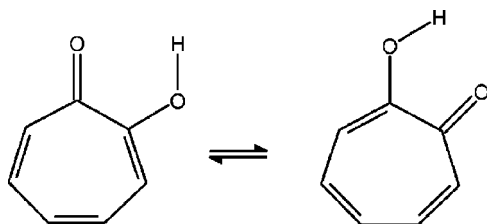


FIG. 10. Proton tunneling in tropolone.

## V. DISCUSSION

In all three cases, the calculations are very well confirmed by the experiments. As we chose three molecular systems with rather different barriers, we expect our method to yield reliable results for a wide range of symmetrical systems. One feature which has to be pointed out is that there is no empirical parameter to be set or any vibration to be chosen as it has to be done in the conventional instanton theory. The newly developed method relies only on *ab initio* energy values and second derivatives. Therefore, there is no possibility for arbitrary changes to fit the computational results better to the experimental ones. This leads to the disadvantage that the PES has to be known at a reliable level of theory. Even small errors in the reaction barrier may have strong effects on the computed tunneling splitting. This is the only limit for the application of the method, as one crucial point is the determination of the stationary points at high-level of theory. One desires at least to compute the barrier at a *CBS*<sup>78</sup> or *G3(MP2)*<sup>73</sup> level and this may just be affordable for molecular systems with 10–20 heavy atoms. From the other point of view, the experimental determination of the tunneling splitting is sometimes a very difficult task and so there are just a handful of molecular systems for which the splitting is well known.<sup>22,24,26–28,31,33,76,79,80</sup> Recently, the tunneling splitting for calix[4]arene was determined experimentally,<sup>33</sup> but this system is still too big to derive the reaction barrier at a high level of theory. Nevertheless, the

tunneling splitting of the calix[4]arene was investigated theoretically with the instanton method.<sup>81</sup> The barrier was determined at the *B3LYP* level of theory, which is in our opinion not sufficiently accurate, therefore, we assume that the result of Fernández-Ramos *et al.*<sup>81</sup> which is close to experiment suffers from an error compensation.

## VI. CONCLUSIONS

We have developed a new semiclassical method to predict the ground-state tunneling splitting of molecular systems. In the framework of the semiclassical theory, the tunneling splitting is directly related to the transmission probability at 0 K. Therefore, we have searched for the most probable tunneling path from minimum to minimum in each system on a PES which is interpolated to high-level data and zero-point corrected. These paths have been found to lie surprisingly close to the MEP for all systems investigated [i.e.,  $(\text{HF})_2$ , malonaldehyde, and tropolone], although at least for tropolone and malonaldehyde, a strong contribution of LCT was expected as a proton tunnels between two (much heavier) oxygen atoms. The systems were chosen due to significantly different barriers to prove that the method works for all different barrier heights.

For the evaluation of the tunneling splitting, we have employed a newly derived formula by Garg,<sup>46</sup> which circumvents the problems of the singularities in the semiclassical wave function if the momentum approaches zero. In addition, a small correction factor appears, which can be handled by an approximation of the potential with a polynomial of sixth order. The calculated tunneling splittings agreed very well with the experiment for all three systems.

All in all, our new method proved to be a valuable mean to predict ground-state tunneling splittings without adjusting any parameters empirically. Therefore, it may be seen as an *ab initio* method which derives low-temperature properties very accurately. The limiting factor is the determination of the barrier height at high-level of theory, as these methods usually cannot handle more than 10–20 heavy atoms by now.

## ACKNOWLEDGMENTS

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## APPENDIX: ANALYTICAL DETERMINATION OF THE CORRECTION FACTOR A

In the article by Garg,<sup>46</sup>  $A$  is defined as

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

As  $V$  is not known analytically, it is not possible to derive the upper integral exactly as a singularity arises. Therefore, we decided to approximate the potential double well with a polynomial of order 6, due to taking into account the accurate barrier height ( $V_0$ ), the accurate distance of the minima ( $2a$ ), and the accurate curvature in the minima in direction

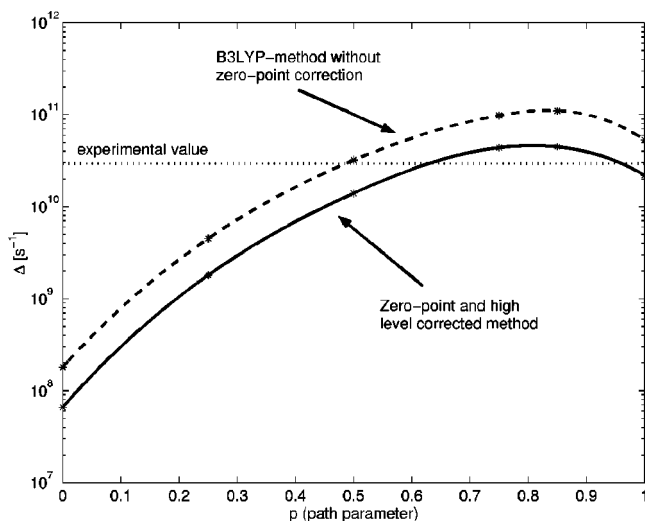


FIG. 11. Tunneling splitting in tropolone. The optimal path was found at  $p=0.8$ . The experimental value<sup>31</sup> ( $3 \times 10^{10} \text{ s}^{-1}$ ) was met very well ( $4 \times 10^{10} \text{ s}^{-1}$ ).

of the tunneling path ( $\kappa$ ), where accurate refers to the *ab initio* values. The polynomial which fits the aforementioned parameters is

$$V_a(x) = \frac{1}{8a^6}(x-a)^2(x+a)^2(-8x^2+x^2\kappa a^2+8a^2V_0).$$

Therefore, the main contribution to the tunneling splitting, i.e.,  $S_0$  is calculated with the nonapproximated energy curve and the approximation just affects the correction factor  $A$ , which has revealed to be small in comparison to  $S_0/\hbar$ .

Now,  $A$  can be computed analytically with the help of the symbolic mathematics package MAPLE<sup>82</sup> as the integration is a nontrivial task

$$A = \frac{\left( \sqrt{\frac{V_0}{a^4}} \sqrt{\kappa} \ln \left( \frac{4V_0 + \sqrt{\frac{\kappa}{a^2}} \sqrt{2} \sqrt{\frac{V_0}{a^4}} a^4}{a^5} \right) - \sqrt{\frac{V_0}{a^4}} \sqrt{\kappa} \ln \left( -\frac{4V_0 + \sqrt{\frac{\kappa}{a^2}} \sqrt{2} \sqrt{\frac{V_0}{a^4}} a^4}{a^5} \right) \right) a}{\sqrt{V_0} \sqrt{\frac{\kappa}{a^2}}} + \frac{-2 \ln(2) \sqrt{V_0} \sqrt{\frac{\kappa}{a^2}} - \ln\left(\frac{V_0}{a^5}\right) \sqrt{V_0} \sqrt{\frac{\kappa}{a^2}} + \ln\left(-\frac{\kappa}{a^2}\right) \sqrt{V_0} \sqrt{\frac{\kappa}{a^2}} - \ln(a) \sqrt{V_0} \sqrt{\frac{\kappa}{a^2}}}{\sqrt{V_0} \sqrt{\frac{\kappa}{a^2}}}.$$

With this analytical expression, we are able to compute  $A$  despite the problems with the singularities.

- <sup>1</sup> L. D. Landau and E. M. Lifschitz, *Quantenmechanik* (Academic, Berlin, 1979).
- <sup>2</sup> W. H. Miller, J. Phys. Chem. **83**, 960 (1979).
- <sup>3</sup> F. B. Brown, S. C. Tucker, and D. G. Truhlar, J. Chem. Phys. **83**, 4451 (1985).
- <sup>4</sup> W. H. Miller, Science **233**, 171 (1986).
- <sup>5</sup> N. Makri and W. H. Miller, J. Chem. Phys. **91**, 4026 (1989).
- <sup>6</sup> N. Shida, P. F. Barbara, and J. Almlöf, J. Chem. Phys. **94**, 3633 (1991).
- <sup>7</sup> V. A. Benderskii, D. E. Makarov, and C. A. Wight, *Chemical Dynamics at Low Temperatures*, Advances in Chemical Physics Vol. LXXXVIII (Wiley, New York, 1994).
- <sup>8</sup> J. J. Paz, M. Moreno, and J. M. Lluch, J. Chem. Phys. **103**, 353 (1995).
- <sup>9</sup> Z. Smedarchina, W. Siebrand, M. Z. Zgierski, and F. Zerbetto, J. Chem. Phys. **102**, 7024 (1995).
- <sup>10</sup> Z. Smedarchina, W. Siebrand, and M. Z. Zgierski, J. Chem. Phys. **103**, 5326 (1995).
- <sup>11</sup> M. Quack and M. A. Suhm, Chem. Phys. Lett. **234**, 71 (1995).
- <sup>12</sup> V. P. Sakun, W. V. Vener, and N. D. Sokolov, J. Chem. Phys. **105**, 379 (1996).
- <sup>13</sup> V. A. Benderskii, E. V. Vetoshkin, S. Y. Grebenshchikov, L. v. Laue, and H. P. Trommsdorff, Chem. Phys. **219**, 119 (1996).
- <sup>14</sup> Z. Smedarchina, A. Fernández-Ramos, and M. A. Rios, J. Chem. Phys. **106**, 3956 (1997).
- <sup>15</sup> A. Fernández-Ramos, Z. Smedarchina, M. Z. Zgierski, and W. Siebrand, J. Chem. Phys. **109**, 1004 (1998).
- <sup>16</sup> S. Miura, M. E. Tuckerman, and M. L. Klein, J. Chem. Phys. **109**, 5290 (1998).
- <sup>17</sup> T. Loerting, K. R. Liedl, and B. M. Rode, J. Chem. Phys. **109**, 2672 (1998).
- <sup>18</sup> T. Loerting and K. R. Liedl, J. Am. Chem. Soc. **120**, 12595 (1998).
- <sup>19</sup> T. Loerting, K. R. Liedl, and B. M. Rode, J. Am. Chem. Soc. **120**, 404 (1998).
- <sup>20</sup> A. Fernández-Ramos, Z. Smedarchina, and J. Rodríguez-Otero, J. Chem. Phys. **114**, 1567 (2001).
- <sup>21</sup> S. Nagaoka, T. Terao, F. Imashiro, N. Hirota, and S. Hayashi, J. Chem. Phys. **79**, 4694 (1983).
- <sup>22</sup> P. Turner, S. L. Baughcum, S. L. Coy, and Z. Smith, J. Am. Chem. Soc. **106**, 2265 (1984).
- <sup>23</sup> A. Oppenländer, C. Rambaud, H. P. Trommsdorff, and J.-C. Vial, Phys. Rev. Lett. **63**, 1432 (1989).
- <sup>24</sup> J. D. Cruzan, L. B. Braly, K. Liu, M. G. Brown, J. G. Loeser, and R. J. Saykally, Science **271**, 59 (1996).
- <sup>25</sup> D. F. Brougham, A. J. Horsewill, and R. I. Jenkinson, Chem. Phys. Lett. **272**, 69 (1997).
- <sup>26</sup> M. Araki, H. Ozeki, and S. Saito, J. Chem. Phys. **109**, 5707 (1998).
- <sup>27</sup> T. Baba, T. Tanaka, I. Morino, K. M. T. Yamada, and K. Tanaka, J. Chem. Phys. **110**, 4131 (1999).
- <sup>28</sup> D. F. Brougham, A. J. Horsewill, and H. P. Trommsdorff, Chem. Phys. **243**, 189 (1999).
- <sup>29</sup> D. F. Brougham, R. Caciuffo, and A. J. Horsewill, Nature (London) **397**, 241 (1999).
- <sup>30</sup> C. Rambaud and H. P. Trommsdorff, Chem. Phys. Lett. **306**, 124 (1999).
- <sup>31</sup> K. Tanaka, H. Honjo, T. Tanaka, H. Kohguchi, Y. Ohshima, and Y. Endo, J. Chem. Phys. **110**, 1969 (1999).
- <sup>32</sup> K. Remmers and W. L. Meerts, J. Chem. Phys. **112**, 10890 (2000).
- <sup>33</sup> A. J. Horsewill, N. H. Jones, and R. Caciuffo, Science **291**, 100 (2001).
- <sup>34</sup> V. A. Benderskii, E. V. Vetoshkin, and H. P. Trommsdorff, Chem. Phys. **244**, 299 (1999).
- <sup>35</sup> C. S. Park, S.-Y. Lee, J.-R. Kahng, S.-K. Yoo, D. K. Park, C. H. Lee, and E.-S. Yim, J. Korean Phys. Soc. **30**, 637 (1997).
- <sup>36</sup> J. L. Bjorkstam, Solid State Ionics **125**, 13 (1999).
- <sup>37</sup> H. H. Limbach and J. Manz, Ber. Bunsenges. Phys. Chem. **102**, 289 (1998).
- <sup>38</sup> P. Schuster and P. Wolschann, Monatsch. Chem. **130**, 947 (1999).
- <sup>39</sup> J. K. Hwang and A. Warshel, J. Am. Chem. Soc. **118**, 11745 (1996).
- <sup>40</sup> C. Alhambra, J. Gao, J. C. Corchado, J. Villà, and D. G. Truhlar, J. Am. Chem. Soc. **121**, 2253 (1999).
- <sup>41</sup> A. Kohen and J. P. Klinman, Acc. Chem. Res. **31**, 397 (1998).
- <sup>42</sup> A. Kohen, R. Cannio, S. Bartolucci, and J. P. Klinman, Nature (London) **399**, 496 (1999).
- <sup>43</sup> S. Chapman, B. C. Garrett, and W. H. Miller, J. Chem. Phys. **63**, 2710 (1975).
- <sup>44</sup> A. Fernandez-Ramos and D. G. Truhlar, J. Chem. Phys. **114**, 1491 (2001).
- <sup>45</sup> V. Barone and C. Adamo, J. Chem. Phys. **105**, 11007 (1996).
- <sup>46</sup> A. Garg, Am. J. Phys. **68**, 430 (2000).
- <sup>47</sup> Z. Chen, Theor. Chim. Acta **75**, 481 (1989).

- <sup>48</sup>C. S. Tautermann, A. F. Voegelé, T. Loerting, and K. R. Liedl, *J. Chem. Phys.* **117**, 1962 (2002), preceding paper.
- <sup>49</sup>MATLAB, *High Performance Numeric Computation and Visualization Software*, 5.3.1.29215a ed., The MathWorks, Inc., Natick, MA 01760-1500, 1999.
- <sup>50</sup>E. Bosch, M. Moreno, and J. M. Lluch, *J. Am. Chem. Soc.* **114**, 2072 (1992).
- <sup>51</sup>R. A. Marcus and E. Coltrin, *J. Chem. Phys.* **67**, 2609 (1977).
- <sup>52</sup>R. T. Skodje, D. G. Truhlar, and B. C. Garrett, *J. Phys. Chem.* **85**, 3019 (1981).
- <sup>53</sup>D. G. Truhlar, A. D. Isaacson, and B. C. Garrett, *Theory of Chemical Reaction Dynamics* (CRC, Boca Raton, FL, 1985), pp. 65–137.
- <sup>54</sup>D. G. Truhlar and M. S. Gordon, *Science* **249**, 491 (1990).
- <sup>55</sup>Y.-Y. Chuang and D. G. Truhlar, *J. Phys. Chem. A* **101**, 3808 (1997).
- <sup>56</sup>B. C. Garrett, T. Joseph, T. N. Truong, and D. G. Truhlar, *Chem. Phys.* **136**, 271 (1989).
- <sup>57</sup>W. P. Hu, Y. P. Liu, and D. G. Truhlar, *J. Chem. Soc., Faraday Trans.* **90**, 1715 (1994).
- <sup>58</sup>T. Loerting and K. Liedl, *J. Phys. Chem. A* **103**, 9022 (1999).
- <sup>59</sup>T. Loerting, C. Tautermann, R. T. Kroemer, I. Kohl, A. Hallbrucker, E. Mayer, and K. R. Liedl, *Angew. Chem. Int. Ed. Engl.* **39**, 891 (2000).
- <sup>60</sup>S. Coleman, in *The Whys of Subnuclear Physics*, edited by Antonino Zichichi (Plenum, New York, 1979), pp. 805–916.
- <sup>61</sup>B. C. Garrett and D. G. Truhlar, *J. Chem. Phys.* **79**, 4931 (1983).
- <sup>62</sup>R. J. Bartlett, in *Modern Electronic Structure Theory*, edited by David R. Yarkony (World Scientific, Singapore, 1995), pp. 1047–1131.
- <sup>63</sup>W. H. Miller, N. C. Handy, and J. E. Adams, *J. Chem. Phys.* **72**, 99 (1980).
- <sup>64</sup>A. G. Baboul and H. B. Schlegel, *J. Chem. Phys.* **107**, 9413 (1997).
- <sup>65</sup>P. L. Fast and D. G. Truhlar, *J. Chem. Phys.* **109**, 3721 (1998).
- <sup>66</sup>B. C. Garrett, D. G. Truhlar, A. F. Wagner, and T. H. Dunning, Jr., *J. Chem. Phys.* **78**, 4400 (1983).
- <sup>67</sup>W.-P. Hu, Y.-P. Liu, and D. G. Truhlar, *J. Chem. Soc., Faraday Trans.* **90**, 1715 (1994).
- <sup>68</sup>T. Loerting and K. R. Liedl, *Proc. Natl. Acad. Sci. U.S.A.* **97**, 8874 (2000).
- <sup>69</sup>M. Page and J. W. McIver, *J. Chem. Phys.* **88**, 922 (1988).
- <sup>70</sup>Y.-Y. Chuang, J. C. Corchado, P. L. Fast *et al.*, POLYRATE, version 8.5, University of Minnesota, Minneapolis, 2000.
- <sup>71</sup>J. C. Corchado, E. L. Coitiño, Y.-Y. Chuang, and D. G. Truhlar, GAUSSRATE 8.5, University of Minnesota, Minneapolis, 2000.
- <sup>72</sup>M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 98, Revision A.7, Gaussian, Inc., Pittsburgh PA, 1998.
- <sup>73</sup>L. A. Curtiss, K. Raghavachari, P. C. Redfern, V. Rassolov, and J. A. Pople, *J. Chem. Phys.* **110**, 4703 (1999).
- <sup>74</sup>G. C. Hancock and D. G. Truhlar, *J. Chem. Phys.* **90**, 3498 (1989).
- <sup>75</sup>R. T. Skodje and D. Truhlar, *J. Chem. Phys.* **77**, 5955 (1982).
- <sup>76</sup>M. Quack and M. A. Suhm, *Chem. Phys. Lett.* **171**, 517 (1990).
- <sup>77</sup>P. L. Fast and D. G. Truhlar, *J. Phys. Chem. A* **104**, 6111 (2000).
- <sup>78</sup>J. W. Ochterski, G. A. Petersson, and J. A. Montgomery, Jr., *J. Chem. Phys.* **104**, 2598 (1996).
- <sup>79</sup>J. D. Cruzan, M. G. Brown, K. Liu, L. B. Braly, and R. J. Saykally, *J. Chem. Phys.* **105**, 6634 (1996).
- <sup>80</sup>J. D. Cruzan, M. R. Viant, M. G. Brown, and R. J. Saykally, *J. Phys. Chem. A* **101**, 9022 (1997).
- <sup>81</sup>A. Fernández-Ramos, Z. Smedarchina, and F. P. Rib, *Chem. Phys. Lett.* **343**, 627 (2001).
- <sup>82</sup>MAPLE, 7 ed., Waterloo Maple Inc., Waterloo ON2L6C2, Canada, 2001.
- <sup>83</sup>M. P. Hodges, A. J. Stone, and E. C. Lago, *J. Phys. Chem. A* **102**, 2455 (1998).