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A scaled hypersphere search method for the topography of reaction pathways on the potential energy surface

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Abstract

An algorithm for finding pathways to transition states (TS) or dissociation channels (DC) from equilibrium structures (EQ) on the potential energy surface (PES) is presented. The pathways around an EQ can be discovered at minima on the scaled hypersphere which would have a constant energy when the potentials are harmonic. Topographic maps including all TS, DC, and EQ were obtained for ab initio PES of H₂O and HCHO in the MP2/3-21G level. The present scaled hypersphere search technique in combination with a downhill-walk algorithm enables us to make a topographic analysis of the PES for a given chemical composition.

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1. Introduction

In both reaction dynamics and kinetics, reaction paths play most important roles [1]. However, complete maps for reaction paths on potential energy surfaces (PES) have not yet been elucidated except for very simple cases, such as three atomic systems. A systematic search for all reaction paths starting from an equilibrium structure is a challenging problem. Important stationary points on PES are equilibrium structures (EQ) and transition states (TS). A reaction path is defined as the steepest descent path connecting the reactant and the product on the PES. When mass-weighted coordinates are used, such a path is the intrinsic reaction coordinate (IRC) [1].

Although recent developments of geometry optimization techniques have made it rather easy to obtain EQ, finding all EQ for a given set of chemical components is still very difficult, especially for floppy molecules or clusters. The situation is much worse for finding out all TS, since uphill walking is in general much more troublesome in comparison with downhill walking. A pio-

neering work by Cerjan and Miller [2] gave an algorithm to reach a TS from an EQ, and subsequent studies [3,4] confirmed that this technique called the eigen-vector following (EVF) is an excellent method for finding a TS. The geometry direct inversion in the iterative subspace (GDIIS) approach by Csaszar and Pulay [5] provided an alternative method finding a TS with a suitable initial guess not far from the TS. Although both of the EVF and GDIIS methods are available in a conventional program package [6], it is very difficult to find out all TS. The gradient extremal following (GEF) algorithm developed by Sun and Ruedenberg [7] has been used to find many TS on the PES of a HCHO molecule [8]. Although the GEF algorithm has an excellent feature, its computational demand is very heavy because of the use of the third order derivatives in addition to the second order derivatives (Hessian). Since a GEF path is not always an IRC path and sometimes far away from the IRC [7], GEF walking cannot avoid to wander around useless parts on PES. Complete connections among all TS and all EQ cannot be guaranteed in the GEF approach. Floudas and coworkers proposed the α BB global optimization algorithm to search all stationary points [9,10]. Although the α BB method is deterministic within a subdivision of the total coordinate

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space in principle, the application of the α BB method to full dimensional analyses has been limited to three atomic systems to which other brute-force methods may be applicable.

Since it is a simple matter to descend from a TS to an EQ, all TS and all EQ for a given chemical composition can be traced, if a general method to ascend from an EQ to all neighboring TS is established. The obstacle for uphill walks from EQ is to find out initial parts of the pathways. A try and error approach to find right paths is prohibited, because of too heavy computational demands for a multidimensional PES.

It should be noted that all reaction paths always change their curvatures from a concave to a convex on going to TS or dissociation limits. This indicates that slopes should always decline their inclinations because of energy-lowering interactions leading to TS or dissociation. When one starts from a minimum of the PES, an indication of a reaction path will appear as an energy lowering with respect to its neighbors. Thus, one may expect that reaction pathways can be found as downward distortion on the potential surface. An efficient algorithm finding out downward distortion around an EQ can be obtained by comparison of real potential energies with reference harmonic values.

In the present paper, we report a very efficient algorithm finding out pathways leading to TS and dissociation channels (DC) around an equilibrium structure, which may lead to a complete topographic search of PES for a given chemical composition to discover all TS and all EQ together with their relationships in addition to all DC.

2. Method and calculations

2.1. Uphill walks to TS and DC by scaled hypersphere search algorithm

At an equilibrium structure EQ for a given chemical composition, normal coordinates should be determined at first. Around the EQ, PES can be expanded in terms of normal coordinates Q_i with respective eigenvalues λ_i . For systematic treatments, scaled normal coordinates defined by $q_i = \lambda_i^{1/2} Q_i$ are suitable, since this representation transforms a reference hypersurface into a hypersphere surface on which every point should have the same energy when the potentials are harmonic. This scaled hypersphere representation makes it very simple to find out reaction pathways. It should be noted that subtle downward deformations of PES can be detected very efficiently as minima on the scaled hypersphere with a center at the EQ. The use of the hypersphere has another advantage that all directions can be treated equivalently. The treatment with the hypersphere is very important, since reaction paths are not always along

particular normal coordinates but possibly along oblique directions corresponding to mixtures of several coordinates.

An energy minimum on the hypersphere indicates a distinct downward distortion of the potential. Hence, pathways to TS and DC around the equilibrium structure EQ may be traced via energy minima on the scaled hypersphere surface. Using several sizes of hypersphere, we can obtain series of points for the pathways around the EQ. These paths can be denoted as scaled hypersphere search (SHS) paths. If the magnitude of the gradient at each minimum on the hypersphere becomes smaller than a threshold value, further tests are made to confirm the type of the stationary point. An indication of a TS region can be obtained from first and second order derivatives on the SHS path point. Location of each TS can be determined precisely by an application of a conventional technique in the TS region [4,5]. Asymptotic behavior separating a fragment from the remaining part indicates a DC.

The present SHS algorithm is different from the sphere optimization technique (SOT) proposed by Abashkin and Russo [11]. Minima on the hypersphere in SOT are always located around the softest modes with the lowest vibrational frequencies at around the initial parts from the equilibrium structure. Since a true reaction path (IRC) should not necessarily follow the softest mode, the SOT algorithm often gives wrong paths far from the IRC paths, as shown below with some examples. Similar tendencies following the softest mode have also been found for the EVF method [4]. On the other hand, the present SHS technique does not suffer from such a biased propensity on account of the scaled coordinate system.

In practical applications of the present SHS algorithm for finding out all reaction pathways around an EQ, an efficient algorithm finding out all minima on the hypersphere surface is required. In connection with this problem, we have developed a scaled hypersphere interpolation (SHI) technique based on a successive application of one-variable cubic spline procedures to polar coordinates in order to construct *ab initio* PES around an equilibrium structure efficiently and accurately [12]. All minima can be determined easily from the obtained cubic spline data. Computational details finding minima on the hypersphere will be reported separately [13].

2.2. Downhill walks from a TS

Once a TS is discovered, the remaining algorithms are straightforward. As for downhill walks on PES, there are many algorithms using predictor–corrector methods [14,15]. More correct curvature for reaction paths can be obtained by the second order approach [16]. A technique using a relatively large circle [17,18] can be used

alternatively. With these techniques, an IRC from the TS can be determined precisely.

2.3. Model potential calculations and *ab initio* PES calculations

Test calculations were made for the following benchmark model potentials. The symmetric two-dimensional model potential

$$V(x, y) = (a - by^2)x^2e^{-x^2} + (c/2)y^2 \quad (1)$$

proposed by Cerjan and Miller [2] was used as an example with $a = b = c = 1$.

The anisotropic two-dimensional model potential

$$V(x, y) = \sum_i A_i \exp[a_i(x - x_{0i})^2 + b_i(x - x_{0i})(y - y_{0i}) + c_i(y - y_{0i})^2] \quad (2)$$

devised by Müller and Brown [15] was used as another example with the standard parameter values for A_i , a_i , b_i , x_{0i} , and y_{0i} .

Applications of the present method finding out reaction pathways to *ab initio* PES were made for H₂O and HCHO molecules in the MP2/3-21G level by using GAUSSIAN 94 [6].

3. Result and discussion

3.1. Applications to model potentials

Fig. 1 shows uphill walks on the Cerjan–Miller potential from the minimum at (0,0) toward TS at ($\pm 1, 0$).

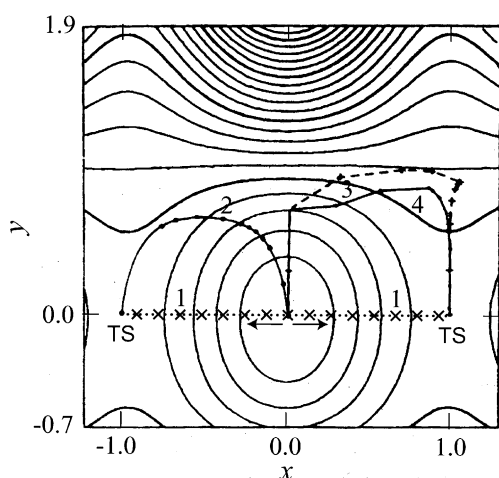


Fig. 1. Uphill-walks on Cerjan–Miller potential surface from the minimum at (0,0) toward two transition states (TS) at ($\pm 1, 0$). (1) The present scaled hypersphere search (SHS) algorithm specified by crosses (x) perfectly follows the correct IRC paths shown by dotted lines directly going up to the TS. (2) Sphere optimization technique (SOT) walk from [9] and (3,4) eigen vector following (EVF) walks from [4] with different choices of steps are diverted far away from the IRC.

Curve 1 indicated by crosses (x) shows the present result which directly goes up to two TS following the IRC paths shown by dotted lines. Other curves 2–4 were taken from a figure reported by Abashkin and Russo [11]. Curve 2 obtained by the SOT [11] also reaches the TS, but the route is extremely deviated far away from the IRC. Although minima are searched on the hypersphere in the SOT approach, the initial part for going to the TS becomes to be in the wrong direction, because the smallest curvature along the softest mode is preferentially traced in the coordinates without scaling. Curves 3 and 4 are analytical Hessian paths [4] with different choice of the steps based on the EVF algorithm [2]. The EVF algorithm also follows the softest mode in the wrong directions far apart from the IRC, though they finally reach the TS.

Fig. 2 shows uphill walks on the Müller–Brown potential from three minima, M_1 , M_2 , and M_3 as well as the IRC paths shown in dotted curves, which were separately obtained by downhill algorithms. As can be seen in Fig. 2, the IRC curves connect (1) M_1 and T_1 , (2) T_1 and M_2 , (3) M_2 and T_2 , and (4) T_2 and M_3 . No other IRC exists in the Müller–Brown potential. In Fig. 2a, the SOT [11] algorithm gave a wrong path from M_1 , as shown by a dashed curve, because the SOT path follows the softest part. While for the present SHS algorithm, the SHS paths shown with crosses (x) in Fig. 2a follow the right connections around the IRC paths from M_1 to T_1 , M_2 to T_1 and T_2 , and M_3 to T_2 . In order to finding out TS on PES, connected routes between EQ and TS are of great significance, even though they are approximate. In Fig. 2b GEF paths on the Müller–Brown potential are shown in solid curves. GEF paths starting from the minima include several other paths not connected with the transition states, and especially the GEF paths do not connect M_1 and T_1 [7]. This behavior of the GEF algorithm is serious, because M_1 is isolated from other minima, M_2 and M_3 .

Since the present SHS algorithm gives all TS with right connections, one can perform a complete search starting from an arbitrary minimum, using a suitable downhill algorithm from TS points after they are found. The present SHS uphill-walk algorithm in combination with well known downhill-walk techniques directly connects all stationary points, M_1 – T_1 – M_2 – T_2 – M_3 , even if we starts from any one of the three minima and two saddle points. The results in Fig. 2 demonstrate that the present SHS algorithm provides a practical method for a complete search of all TS and all EQ via all IRC connected with an arbitrary EQ.

3.2. Applications to *ab initio* PES of H₂O and HCHO

Figs. 3 and 4 show reaction route maps obtained in the MP2/3-21G level of calculations by the present SHS algorithm for H₂O and HCHO. TS, EQ, and DC are

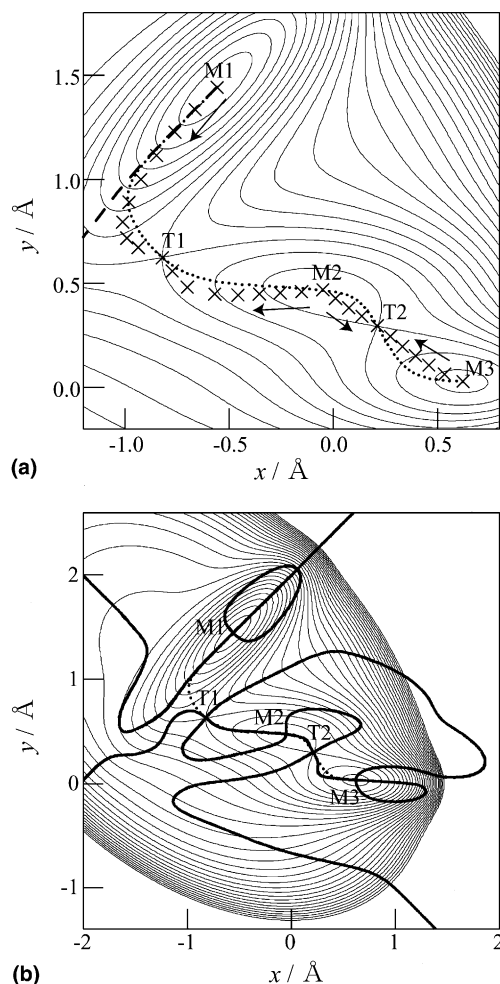


Fig. 2. Walks on Müller–Brown potential surface with three minima (M1, M2, and M3) and two saddle points (transition states: T1 and T2). (a) The dashed curve from M1 is obtained by the sphere optimization technique (SOT), which extremely deviates from the IRC path. The present scaled hypersphere search (SHS) algorithm specified by crosses (×) gives direct uphill-walk paths from M1 to T1, from M2 to T1 and T2, and from M3 to T2, which can be compared with the correct IRC paths of dotted curves obtained separately by downhill walk techniques. (b) Uphill walks on Müller–Brown potential surface by the gradient extremal following (GEF) algorithm from [7] are shown in solid curves. The GEF algorithm does not give a direct connection between M1 and T1. The GEF method makes unnecessary detours, though connections among T1, M2, T2, and M3 are given.

shown with geometrical parameters and relative energies from the initial structure EQ₀ (H₂O or HCHO). Connections via TS were confirmed by downhill walks. Further decomposition routes of fragments were not included in the Figures. Very shallow wells smaller than ca. 1 kcal mol^{−1} were disregarded in Fig. 4, in view of the accuracy of the MP2/3-21G calculations,

In the case of H₂O, three reaction paths were found from EQ₀. Among them, a path (Path 1) is along an inversion of angle bending motion leading to EQ₁ equivalent to EQ₀, and this path has a TS point (TS₁) at the linear structure. The other two are DC leading to

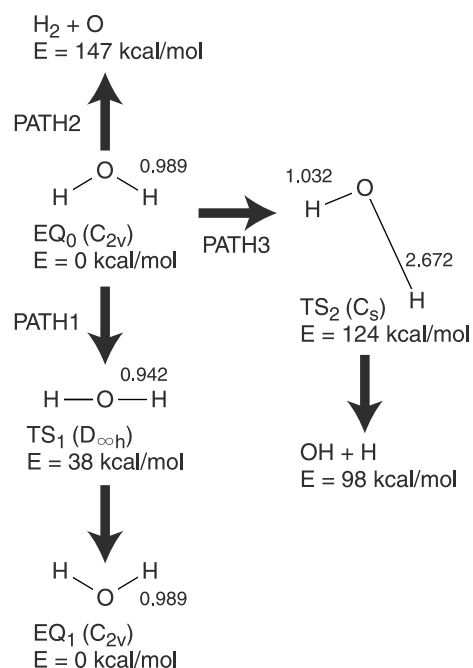


Fig. 3. The reaction route map for H₂O obtained in the MP2/3-21G level of calculations by the present SHS method. Optimized interatomic distances are given in Å. Relative energies are shown with respect to the energy of H₂O at the started geometry EQ₀.

H₂ + O (Path 2) and OH + H (Path 3). As for dissociation into two singlet species (H₂ + O), there is no TS, and the bond dissociation curve is simply going down the repulsive slope. On the other hand for dissociation into two doublet species (OH + H), a TS (TS₂) was found. It is well known that insufficient levels of calculations often show an incorrect bump in the bond dissociation curve [19]. The TS₂ for H₂O in Fig. 3 does not exist in higher levels of calculations, such as CASSCF.

In HCHO the present SHS method gave four independent reaction paths starting from EQ₀. Path 1 is largely a C=O stretching motion leading directly to dissociation into CH₂ + O. Path 2 is a combination of symmetric and antisymmetric CH stretching modes, which leads to dissociation into HCO + H. Path 3 is a strongly coupled motion of CO stretching and CH₂ rocking motion leading to CO + H₂ via a TS₁(C_s). In the GEF algorithm [8], a path starting from TS₁ is not connected directly with the EQ₀ of HCHO, and they are only indirectly connected via a very long detour including some other TS. Path 4 is a motion of a hydrogen atom leading to a *trans*-HCOH structure (EQ₁: C_s) via a TS₂(C_s) with a triangle HCO. The present SHS method gives the Path 4 leading to TS₂ for HCHO directly without detour, though the GEF method [8] gave a long detour via seven branching points together with three turning points. Subsequent traces by the SHS algorithm revealed as a whole TS₁–TS₇ and twelve DC including the *cis* isomer of HCOH (EQ₂: C_s) and a complex (EQ₃:

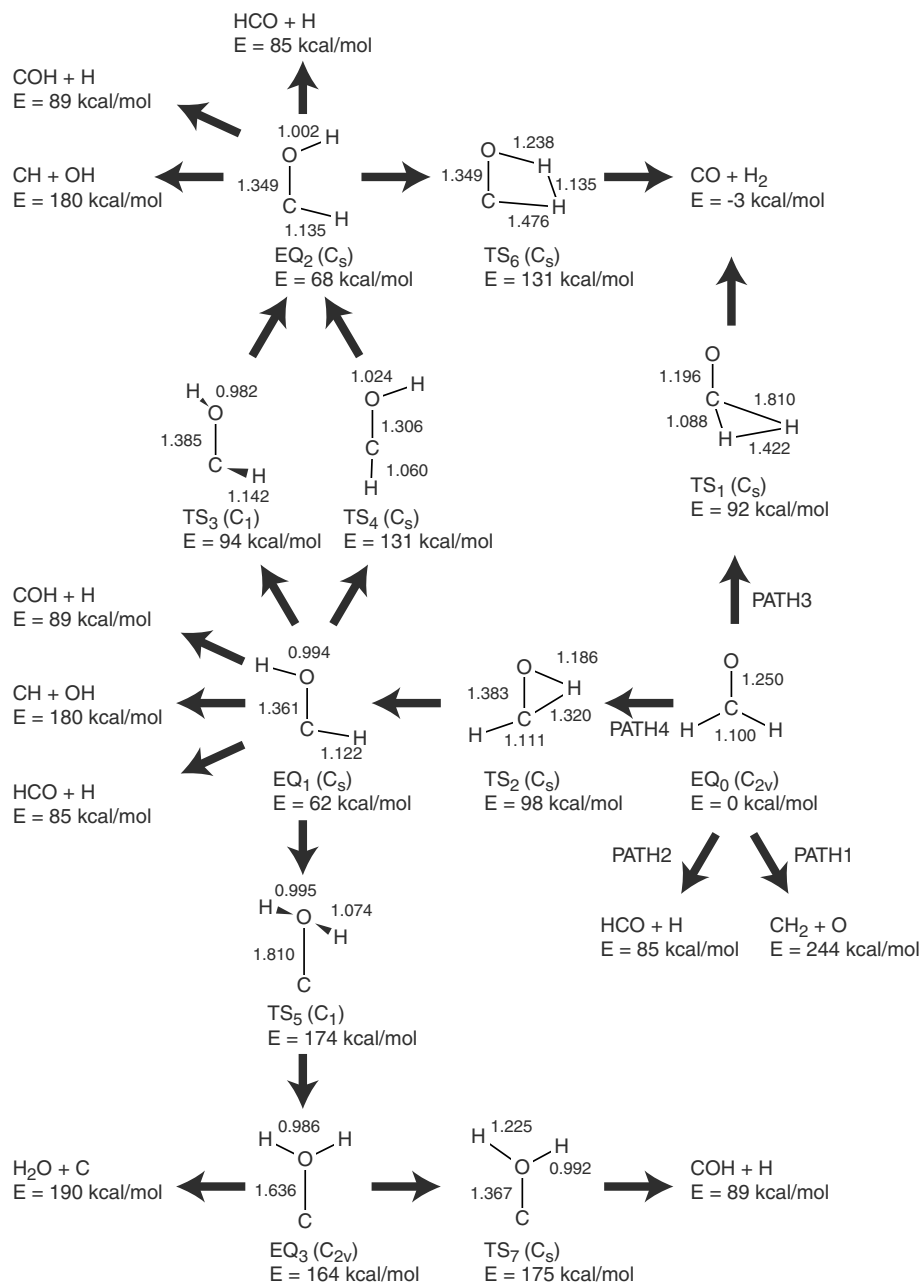


Fig. 4. The reaction route map for HCHO obtained in the MP2/3-21G level of calculations by the present SHS method. Optimized interatomic distances are given in Å. Relative energies are shown with respect to the energy of HCHO at the started geometry EQ₀.

C_{2v}) of H₂O with a C atom. In view of the present level of calculations, TS on the DC routes into two singlet species were disregarded from the reason as mentioned for H + OH. The present SHS MP2/3-21G calculations gave almost the same TS and EQ as those in the GEF result in HF/STO-3G calculations by Bondensgård and Jensen [8] except for a few differences. Our MP2 results showed only one TS from *cis*-HCOH to CO + H₂, though two TS structures were found by the HF/STO-3G calculation. The present MP2/3-21G calculation gave a C_{2v} structure for EQ₃, while the HF/STO-3G

calculation gave a C_s structure. These differences are due to the levels of calculations. Since MP2 calculations may have some inaccuracies especially along dissociation channels, further studies by more sophisticated calculations such as CASSCF calculations will be reported in the subsequent paper [13].

The present results for a HCHO molecule demonstrate that the SHS algorithm makes it possible to search directly all TS starting from an EQ. This has a great significance, since in many cases only limited TS and EQ have been looked for with some initial guess or intuition.

It should also be noted that the present algorithm yields reaction paths leading to dissociation directly, which is very important in connection with reactive scattering, production of fragmented species, and synthesis of the parent molecule from the fragments.

3.3. Characteristic remarks on the SHS algorithm

Uphill walk pathways to TS and DC from an EQ can be found by the present SHS algorithm. For each TS a downhill walk leading to EQ or DC can easily be traced by a conventional descending algorithm. If a new EQ is found, then SHS uphill walks should be repeated followed by a downhill walk from each new TS. These procedures should be continued until no new EQ is found. It is of note that the above procedures can be accomplished after a finite number of processes from the initial EQ. Thus, a topographic map including EQ, TS, DC, and their connections can be obtained for the PES of a given chemical composition.

The present SHS algorithm is based on a simple intuition that the potential surface should be distorted downward because of some energy-lowering interactions on going towards TS or DC. Although the SHS algorithm worked well for the model potentials and *ab initio* PES for H₂O and HCHO, energy-lowering effects of neighboring pathways may interfere on a hypersphere with a small radius, when there are several pathways around the EQ. Since distortion from the harmonic potential is rather larger for a DC than for a TS, the pathway for a TS may be obscured by the more distinct pathway for a DC, when they are in a proximity. Even in this case, the larger hypersphere gives a SHS path for the TS. Alternatively, deconvolution of downward dents or analyses of gradient extremals can be used to discover a hidden pathway. When the pathway is rounding from the radial direction to the tangential direction, the SHS path will become unable to be traced. This is unlikely, provided that the energy-lowering interactions are strong enough. It is well known that the potential energy curve around the transition state is in most cases simply related to the potentials around the reactant or the product. Such a tendency has been used in Bell, Evans, and Polanyi principle [20,21], the Hammond postulate [22], and frontier molecular orbital theory [23,24]. The Marcus equation [25] also assumes that potentials of the reactant and the product are closely related with the activation energy and the location of the TS. Thus, the present SHS algorithm is appropriate for systems in which the relationship between EQ and TS are straightforward, as in many other studies.

Although IRC paths do not branch or merge in rigorous conditions except for stationary points, numerically obtained reaction paths may branch or merge

because of numerical errors. Even in such situations the SHS algorithm may handle a branching or a merging from changes of the numbers of SHS minima on different sizes of hypersphere.

4. Conclusion

An efficient method producing the topographic map of the potential energy surface (PES) for a given chemical composition was proposed and applied to H₂O and HCHO. The present scaled hypersphere search (SHS) algorithm can be used to discover dissociation channels (DC) and transition states (TS), which are connected with an equilibrium structure (EQ). Starting from a TS and using conventional downhill-walk techniques, other EQ and DC may also be found. After having found other EQ, the present SHS method can also be used to find out reaction pathways around the new EQ. In this manner, the topographic map of the PES can be obtained. Such procedures may be used to disclose all reaction pathways to chemical products starting from a given chemical composition.

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