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How should we calculate multi-dimensional potential energy surfaces for an accurate reproduction of partition functions?

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Abstract

The potential energy of *n*-hexane is studied since it constitutes a typical example of a single chain molecule in which various internal rotations are present and a large number of conformations are existing, which cannot be reached by using one-dimensional rotational energy profiles. For an accurate reproduction of the global partition function and all derived thermodynamic properties an adequate description of all possible conformers is necessary. The full three-dimensional potential energy surface of the internal rotations in *n*-hexane (3D-PES) is calculated at an ab initio level and compared with one-dimensional schemes to reproduce the energy. Due to the higher dimensionality of the relevant potential energy surface, the computational cost is very high. A new approximate scheme based on two-dimensional cuts is proposed that gives good accuracy for the relative conformational energies and kinetic energies at a reasonable computational cost. This scheme is of general use for any long chain molecule.

Keywords: PES; Thermodynamic properties; Conformers; *n*-hexane; Hindered rotor

1. Introduction

n-Alkanes constitute a class of very simple molecules where the all-*trans* conformation is the energetically most stable form. The one-dimensional internal rotation about a single CC bond (apart from methyl tops) gives rise to a typical potential energy curve which is shown in Fig. 1. Besides the *trans* conformation, corresponding to the absolute minimum, the CCCC torsional angle can reside in two possible gauche orientations corresponding to local minima, and usually referred to as g_+ and g_-. For a series of m subsequent rotations about single CC bonds, one expects to find 3^m minima. However, 3^m appears to be only a lower limit as pointed out by Tsuzuki et al. [1] and Tasi et al. [2].

The occurrence of a multitude of possible conformers – all but a few kJ/mol higher in energy than the all-*trans* conformation – will have a serious impact on the partition function, from which all thermodynamic properties can be derived. An accurate identification and description of these local minima in the potential energy surface (PES) is therefore decisive for the accuracy of the calculated partition function.

In this respect, the harmonic oscillator (HO) approximation is completely inadequate as it accounts for only one minimum as illustrated in Fig. 1. To include all rotational minima into the calculations, one must treat the internal rotations with an appropriate hindered rotor (HR) scheme that is capable of treating molecules with a number of asymmetric tops [3]. This scheme depends on the availability of the PES as a function of the various torsional angles. Unfortunately, due to the substantial computational cost, most literature works are restricted to a one-dimensional approximation of this

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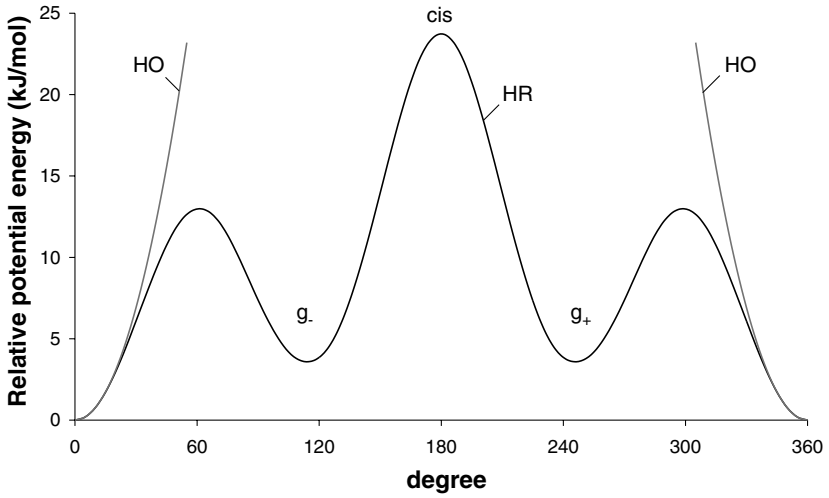

Fig. 1. Potential energy relative to the all-*trans* conformer for the one-dimensional ethyl rotation in *n*-hexane. The two gauche states are labelled.

PES: for each internal rotation a one-dimensional potential energy curve (1D-PES) is calculated, and the total multi-dimensional potential energy surface (mD-PES) is assumed to be the sum of these one-dimensional contributions:

$$V^{\mathrm{mD}}(\phi_1,\ldots,\phi_m) \approx \sum_{i=1}^{m} V_i^{\mathrm{1D}}(\phi_i). \tag{1}$$

In this approximation, the interaction between the different internal rotations is completely ignored: the rotations are not coupled to each other, and hence the potential energy curve of one rotation is not influenced by any other rotation.

General improvements of this description can be suggested. The most accurate scheme is to determine the fully coupled mD-PES, but this is computationally not feasible for most systems at an ab initio level. We present an alternative scheme that goes beyond the one-dimensional approximation, but still is feasible and practical.

In this paper, we will concentrate on the three internal rotations in *n*-hexane: two ethyl rotations and one propyl rotation ($m = 3$). For this molecule, the validity of the one-dimensional approximation (Eq. (1)) will be evaluated by a comparative study with the completely determined 3D-PES, and by the accuracy of the relative energies of the different conformers resulting from the uncoupled scheme. Based on this analysis, we suggest an approximative scheme that relies on two-dimensional surfaces, and which gives far more accurate results than the one-dimensional approach. Simultaneously, a similar study is performed for the construction of the kinetic energy. When the 3D-PES is not fully calculated, the kinetic energy matrix cannot be constructed exactly since the optimized geometries at each point of the 3D-PES are not known. The approximation scheme introduced for the potential energy enables us to construct also the kinetic energy matrix quite accurate and without additional computational cost.

2. Methodology and computational details

All ab initio calculations were performed using the Gaussian03 software package [4] in a density functional theory (DFT) [5] framework, with Becke's three-parameter B3LYP functional [6]. The molecular orbitals were expanded in a triple-ζ 6-311G basis augmented with single first d and p polarization functions [7]. This functional is known to give a reliable and quantitatively acceptable description of geometries, frequencies, and potentials [8,9,10] for a reasonable computation time. In particular, a profound quantum chemical study of conformational energies and rotational energy barriers in *n*-alkanes has been performed by Smith and Jaffe using high-level ab initio methods [11]. As already discussed in [12] the relative energies of the gauche conformers on this level of theory correspond very well with the results found with high level post-HF methods.

The 3D-PES was constructed using constrained geometry optimizations: all variables were allowed to relax to the minimal energy geometry, except for the three dihedral angles of the internal rotations under investigation. These three variables were fixed on values of the grid ($k \cdot 10°$, $l \cdot 10°$, $m \cdot 10°$), with k, l and m integer numbers going from 0 to 35. The potential energy profile is constructed using periodic cubic spline interpolation on the energy values of the 36^3 (46656) grid points.

The conformers that were identified on this 3D-PES were then optimized without constraints in separate optimization runs.

The 1D potential energy contributions $V^{\mathrm{1D}}(\phi_i)$ are also calculated using constrained geometry optimizations, with all variables allowed to relax, except for the

considered ϕ_i dihedral angle. The 1D grid constitutes of 72 evenly distributed points: $k \cdot 5°$.

The 2D-PES $V_{12}^{2D}(\phi_1, \phi_2)$ is obtained by varying the (ϕ_1, ϕ_2) angles on the grid ($k \cdot 10°$, $l \cdot 10°$) with ϕ_3 fixed in *trans* (see Fig. 2 for the numbering of the angles). All other variables are allowed to relax. Due to symmetry considerations the 2D-PES $V_{23}^{2D}(\phi_2, \phi_3)$ coincides with $V_{12}^{2D}(\phi_1, \phi_2)$.

3. Analysis of the multi-dimensional potential energy surface

In an attempt to visualize the features of the 3D-PES, two-dimensional cuts of this hypersurface are given in Figs. 2 and 3. The obvious choices for such cuts, giving information on the ethyl–propyl and the ethyl–ethyl interaction, are those in which the third

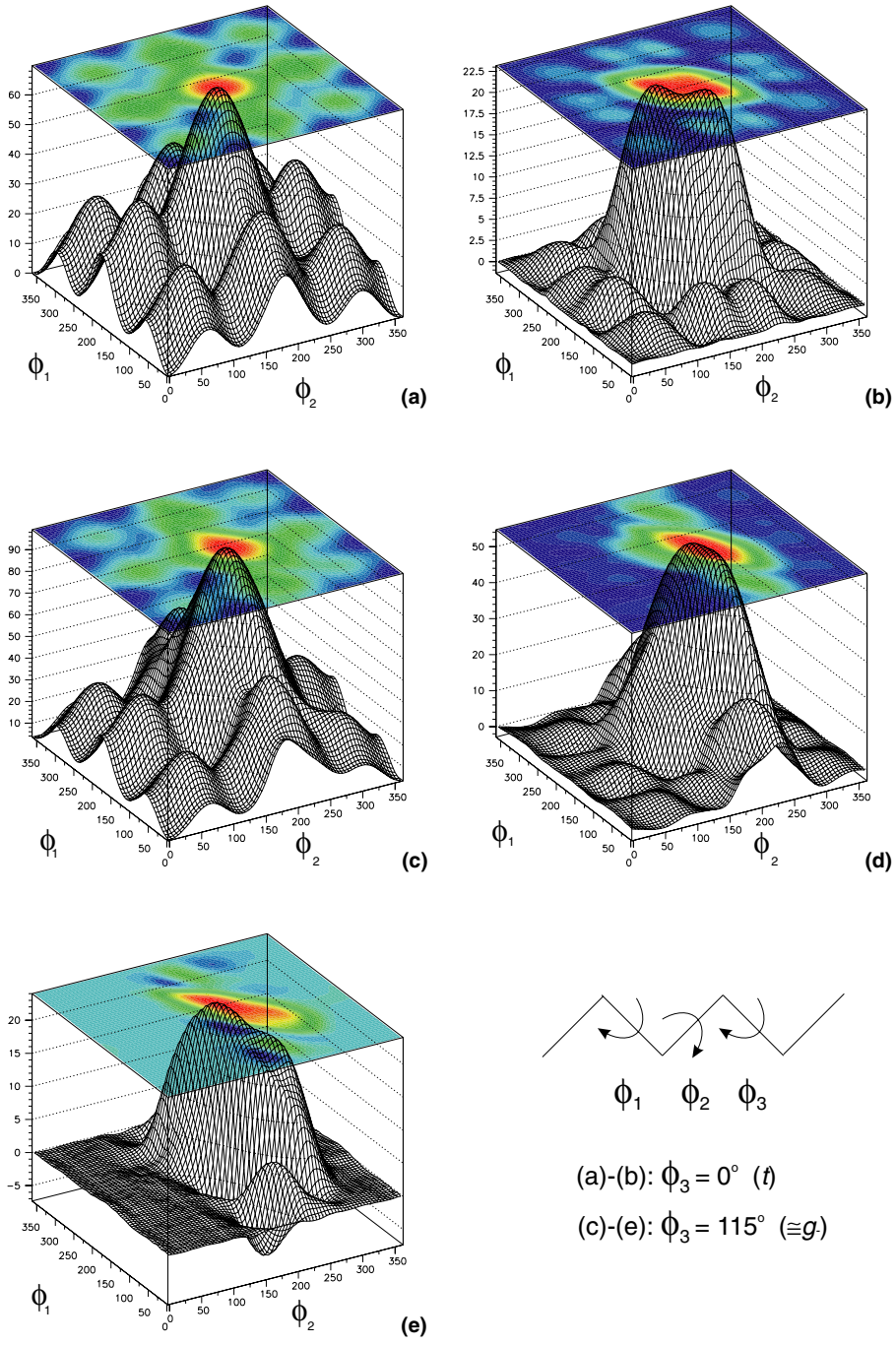

Fig. 2. Potential energy of the ethyl–propyl interaction (relative to the all-*trans* conformer) in *n*-hexane: (a) second ethyl torsion in *trans*: $\Phi_3 = 0°$; (b) difference of the 1D-approximation with (a); (c) second ethyl torsion at approximately g_-: $\Phi_3 = 115° \approx g_-$; (d) difference of the 1D-approximation with (c); (e) difference of the 2D-approximation with (c).

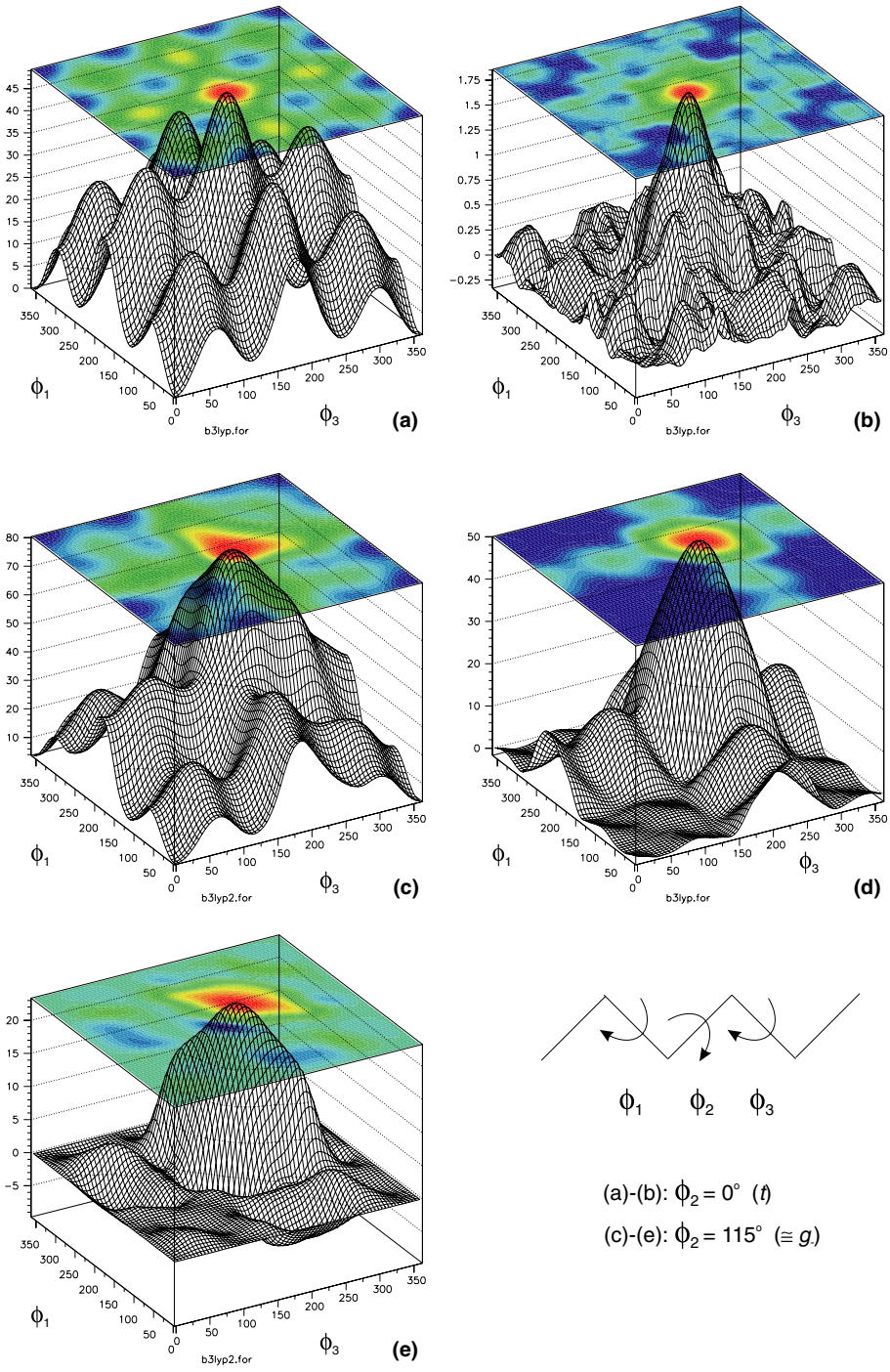

Fig. 3. Potential energy of the ethyl–ethyl interaction (relative to the all-*trans* conformer) in *n*-hexane: (a) propyl torsion in *trans*: $\Phi_2 = 0°$; (b) difference of the 1D-approximation with (a); (c) propyl torsion at approximately g_-: $\Phi_2 = 115° \approx g_-$; (d) difference of the 1D-approximation with (c); (e) difference of the 2D-approximation with (c).

torsion is kept either at the *trans* position or at the gauche standing.[1] Hence two plots are presented for the ethyl–propyl interaction: Fig. 2(a) represents the 2D-PES where the second ethyl torsion is kept in *trans*, while Fig. 2(c) gives the ethyl–propyl 2D-PES with the second ethyl rotation at approximately the gauche standing (115° from *trans*). For the ethyl–ethyl interaction a similar procedure was followed, resulting in two energy cuts where the propyl rotation was either fixed at its *trans* (Fig. 3(a)) or gauche position (Fig. 3(c)).

[1] This is only approximate: the specific dihedral is kept at 115° relative to the *trans* dihedral (≈g_-).

The first PES of Fig. 2(a) is very similar to the ethyl–ethyl surface of pentane, reported earlier in [3]. In principle, if we consider all possible combinations 0° (*trans*, *t*), 115° (gauche, g_-), and 245° (gauche, g_+), nine local minima should be present on the two-dimensional surface. The conformers of two adjacent gauche bonds with opposite sign (g_-g_+ or g_+g_-) are however characterized by severe steric interactions [1]. Without further relaxation these points are first order saddle points, but when these strains relax through a strongly asymmetric torsion of the carbon backbone, each of these saddle points give rise to two distorted gauche positions, located at about 90° from *trans*. These distorted gauche positions will be referred to as x_- (90°) and x_+ (270°), conform previous literature on this subject [2].

The ethyl–propyl interaction is further visualized in Fig. 2(c) with the second ethyl in the g_- position. This surface clearly shows different features than Fig. 2(a), where the second ethyl was at the *trans* position. The local minimum at $g_-g_+g_-$, which we would expect from combining one-dimensional potentials, disappears due to the presence of an extra barrier in this region of the surface. Again distorted gauche positions come into play leading to a $x_-g_+x_-$ conformer.

The 1D-approximation fails to reproduce the correct features of the ethyl–propyl interaction in the sense that it does not reproduce the exact number of conformers, and also the central peaks are not correctly described. This can be deduced from Fig. 2(b) and (d) which visualize the difference between the 3D-PES and the sum of one-dimensional potentials. The differences can amount to 50 kJ/mol for the energy maxima.

A similar analysis of the ethyl–ethyl coupling is presented in Fig. 3. For the propyl rotation in the *trans* geometry, the resulting 2D energy cut (Fig. 3(a)) is merely a summation of the 1D potentials. The difference of the exact with the 1D approximated values is plotted in Fig. 3(b), and reveals only small fluctuations. Maximal deviation is noticed at the *cis–cis* position and is still limited to only 1.75 kJ/mol. This fair correspondence was to be expected since both ethyl tops are far apart when the propyl torsion is in *trans*, and their mutual interaction is therefore almost non-existent.

For a gauche orientation of the propyl top on the other hand, the two ethyl tops are closer to each other, and both rotations are expected to largely affect each other. This should result in large coupling effects. The g_-g_+-effect gives rise to the conformers $x_+g_-g_-$, $x_+g_-x_+$ and $g_-g_-x_+$ in which distorted gauche positions occur due to the relaxation of the carbon backbone to release steric hindrance. The 1D-approximation fails again in reproducing the correct number of conformers and in predicting the correct barriers. Differences up to 50 kJ/mol are noticed in Fig. 3(d).

4. Analysis of conformers

In this paragraph, we will focus on the different conformers found in *n*-hexane, and assess the accuracy of the 1D-approximation for the reproduction of these stationary points.

In principle, if we consider all possible combinations of *t*, g_- and g_+ for the three internal rotations in hexane, this would result in a total of $3^3 = 27$ conformers. The coupling between two adjacent gauche states of the type g_+g_- gives rise to additional distorted gauche positions designated as x_- or x_+. The same exercise learns that all combinations of *t*, g_-, g_+, x_- and x_+ may construct a maximum of $5^3 = 125$ conformers. In reality

Table 1
List of stable conformers found in *n*-hexane

conformer	ΔE	ΔE^{1D}	ΔE^{2D}	f_A	f_A^{1D}	f_A^{2D}
ttt	0.00	**0.00**	**0.00**	1.00	**1.00**	**1.00**
g_+tt, g_-tt, ttg_+, ttg_-	3.54	**3.54**	**3.54**	1.71	**1.71**	**1.71**
tg_+t, tg_-t	3.63	**3.63**	**3.63**	2.13	**2.13**	**2.13**
gtg (4x)		7.08	7.08		2.92	2.92
$\rightarrow g_+tg_+$, g_-tg_-	7.02			2.64		
$\rightarrow g_-tg_+$, g_+tg_-	7.36			2.60		
ggt (8x)		7.17			3.64	
$\rightarrow g_+g_+t$, g_-g_-t, tg_+g_+, tg_-g_-	6.96		**6.96**	2.52		**2.52**
$\rightarrow g_-x_+t$, g_+x_-t, tx_+g_-, tx_-g_+	13.76		**13.76**	2.95		**2.95**
$\rightarrow x_-g_+t$, x_+g_-t, tg_+x_-, tg_-x_+	13.94		**13.94**	2.89		**2.89**
ggg (8x)		10.71			6.22	
$\rightarrow g_+g_+g_+$, $g_-g_-g_-$	10.18		10.29	2.89		2.98
$\rightarrow g_-x_+g_+$, $g_+x_-g_-$, $g_+x_+g_-$, $g_-x_-g_+$	17.41		17.09	3.72		3.49
$\rightarrow x_-g_+g_+$, $x_+g_-g_-$, $g_+g_+x_-$, $g_-g_-x_+$	17.54		17.27	3.49		3.42
$\rightarrow x_+g_-x_+$, $x_-g_+x_-$	25.26		24.25	4.00		3.91

ΔE is the relative potential energy difference between the fully optimized conformer and the all-*trans* conformer which is taken as reference conformer. The column labelled f_A is the correlation function of the fully optimized conformer. Columns (ΔE^{1D}, f_A^{1D}) and (ΔE^{2D}, f_A^{2D}) give estimated values based on the 1D respectively 2D method. All energy values are in kJ/mol.

35 conformers are found on the 3D-PES, in accordance with the study of Tasi et al. [2] where some selection rules to eliminate possible conformers were presented. In *n*-hexane – and all other normal alkanes – two symmetry operations are applicable in the reference all-*trans* geometry: a two-fold rotation axis (C_2), and a mirroring surface (σ_h) containing all carbon atoms. Due to these symmetry operations some of the conformers are energetically equivalent, for example, ttg_- is equivalent with ttg_+ due to the σ_h symmetry, and because of the C_2 axis they are also equivalent to g_-tt and g_+tt.

In Table 1 all conformers are listed together with the electronic energy of the fully optimized geometries relative to the energy of the all-*trans* conformer (ΔE column). Also the energies of the conformers constructed in this uncoupled scheme are also given (reported as ΔE^{1D}).

Within the one-dimensional scheme only 27 conformers are found due to the ignorance of coupling between adjacent gauche standings of opposite sign. In this approach, three energy values turn out to coincide with the 3D predictions. This is not surprising since these *ttt*, *gtt* and *tgt* classes of conformers can be reached by a single internal rotation in the reference conformer. The energy values that are exactly reproduced are given in bold. For the other conformers, no distinction can be made between gauche states of different orientation, or between distorted and normal gauche geometries. These limitations lead to three additional different energy values for *gtg*, *ggt* and *ggg* geometries, independent of the orientations of the gauche geometries. Table 1 reveals that these values are very close to the 3D conformer energy differences where subsequent gauche standings have the same orientation (g_+g_+t, $g_+g_+g_+$). On the other hand, in the cases where the orientations are different, the correspondence 1D–3D is no longer valid, and discrepancies of the order of 6.5 kJ/mol are noticed.

5. Approximation schemes for the PES and kinetic energy

One of the main goals of this paper is to present a method for reproducing accurate partition functions belonging to the multiple internal rotations figuring in long chain molecules, and which is computationally feasible. As outlined in previous section, the 1D approximation

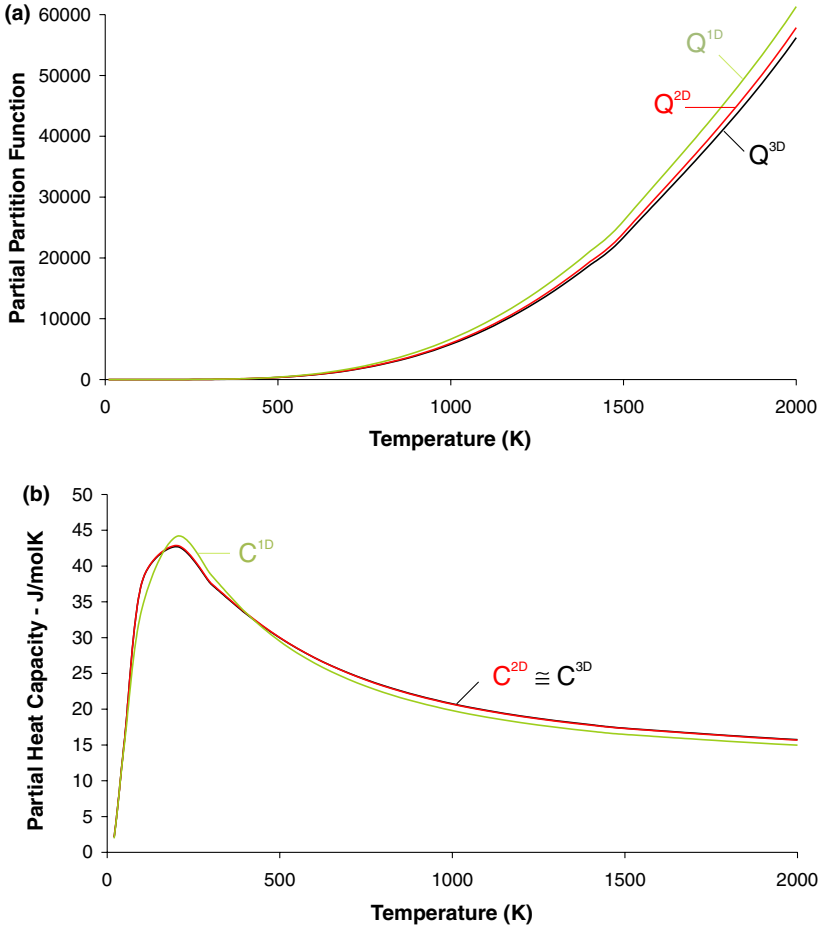

Fig. 4. Partition function (a) and heat capacity (b) of the three investigated internal rotations calculated with the exact model (Q^{3D}, C^{3D}), with the 2D-approximation (Q^{2D}, C^{2D}), and the 1D-scheme (Q^{1D}, C^{1D}).

is inadequate to describe the correct features of the multi-dimensional PES. In the following, we will investigate how large the discrepancies of the partition function are in this 1D approach, compared with the coupled 3D result.

In its simplest form the classical partition function Q_{cl} of the internal rotations and the global rotation is defined as [13]:

$$Q_{\mathrm{cl}} \sim \int \sqrt{\det A}\, \mathrm{e}^{-\frac{V(\phi_1,\ldots,\phi_m)}{k_{\mathrm{B}}T}} \mathrm{d}^m \Phi, \tag{2}$$

where k_{B} is the Boltzmann factor, T is the temperature, and V is the potential energy in function of the torsional angles. A represents the kinetic energy matrix, and incorporates the moments of inertia of the internal rotations. In Fig. 4(a), the rotational partition function is shown in terms of temperature for hexane. The 1D result overestimates the coupled partition function generated from the 3D-PES. The 1D approximation scheme affects both the potential and kinetic energy. The underestimation of the central peaks and nonexistence of some conformers on the approximate three-dimensional PES constructed with 1D contributions, as defined in Eq. (1), do shift the rotational energy states to lower energies and will enhance the partition function.

Most one-dimensional HR approaches found in literature combine a potential energy constructed along the lines of Eq. (1) with constant moments of inertia. These reduced moments are evaluated in the reference conformer geometry and hence are independent of the torsional angles. This 1D-HR approach does not include kinetic coupling between the various rotations and underestimates the kinetic energy contribution to the partition function [3]. We refer to this method as Q^{1D} shown in Fig. 4(a).

Summarizing, the 1D-HR scheme overestimates the true partition function. As both potential and kinetic energy contributions tend to cancel each other, the final result is subject of large cancellation errors. By coincidence this 1D approach turned out to give excellent agreement with experiment in reproducing thermodynamic properties in *n*-alkanes [3,12] which are evaluated from the global partition functions.

It is instructive to find a procedure which is computational feasible and which is able to reproduce partition functions close to those predicted by the 'exact', computationally intensive, 3D model. This is offered by an adapted 2D approximation. The multi-dimensional PES is approximated as follows:

$$V^{\mathrm{mD}}(\phi_1,\ldots,\phi_m) \approx \sum_{i=1}^{m} V^{\mathrm{2D}}_{i(i+1)}(\phi_i,\phi_{i+1}) - \sum_{i=2}^{m-1} V^{\mathrm{1D}}_{i}(\phi_i). \tag{3}$$

For the present case of *n*-hexane, the two 2D-PES (V^{2D}_{12} and V^{2D}_{23}) are identical due to symmetry, and correspond to the surface shown in Fig. 2(a).

In this expression the coupling between consecutive internal rotations is taken into account whereas coupling between non-adjacent internal rotations is ignored. To prevent double counting the one-dimensional potentials are subtracted.

It turns out that the 2D approximated PES, as constructed along Eq. (3), is able to reproduce the correct number of minima. The relative energies of the various conformers are given in Table 1 under ΔE^{2D}, referred to the all *trans* conformation energy. All conformers where coupling between adjacent rotors comes into play are exactly reproduced. Thus the minima of the *ggt* class are exactly described, including the distorted gauche standings. The stationary points belonging to the *gtg* and *ggg* subclasses still suffer from some deviations from the exact energies but these are limited to less than 1 kJ/mol. Some peaks on the PES are still underestimated, e.g. the peak in Fig. 2(c), but the discrepancies are reduced from 50 kJ/mol in the one-dimensional scheme to 20 kJ/mol. The plots given in Figs. 2 and 3(e) visualize the differences of the 2D-approximation with the fully calculated 3D-PES for the ethyl–propyl surface (with the second ethyl torsion near g_-), respectively for the ethyl–ethyl coupling (where the propyl rotation resides in g_-). Another striking aspect is that the fluctuations of the surface of Figs. 2 and 3(d), apart from the central bump, disappear in the proposed 2D scheme, in contrast to the 1D approximation.

Summarizing, the approximate 3D-PES, constructed with two 2D PESs along the lines of Eq. (3), closely resembles the true 3D surface: the number of conformers is exactly reproduced, the conformational energies are predicted within a maximum error of 1 kJ/mol, the central bumps are substantially better described, and the energy increase of the g_-g_+ effect is also taken into account.

The accuracy in which the PES is determined has its implications on the method for constructing the kinetic energy matrix. A fully constructed multi-dimensional PES requires a geometry optimization at each point of the grid in terms of the various torsional angles, and thus it obviously offers all necessary ingredients for constructing the exact kinetic energy matrix and its variation in function of the torsional angles. As already proposed in [3], it is convenient to factorize the determinant of the kinetic energy matrix into:

$$\det A(\phi_1,\ldots,\phi_m) = \det A_0 \cdot f_A^{\mathrm{mD}}(\phi_1,\ldots,\phi_m), \tag{4}$$

with f_A^{mD} the multi-dimensional correlation function and A_0 the kinetic energy matrix corresponding with the reference conformer which does not depend on the torsional angles. The correlation function thus gives an indication of the fluctuation of the moments of inertia in terms of the rotational angles. In the 1D scheme this function can be approximated as

$$f_A^{\mathrm{mD}}(\phi_1,\ldots,\phi_m) \approx \prod_{i=1}^{m} f_{A,i}^{\mathrm{1D}}(\phi_i). \tag{5}$$

In the literature, the 1D scheme often uses a variant to this description. The determinant is then approximated as a product of all (constant) reduced moments of inertia (I^{red}) of the different internal rotations and the (constant) principal moments of inertia ($I_xI_yI_z$) of the molecule:

$$\det\, A(\phi_1,\ldots,\phi_m) \approx I_xI_yI_z \prod_{i=1}^{m} I_i^{\mathrm{red}}. \tag{6}$$

These principle and reduced moments are calculated using the geometry of the reference conformer.

In a 2D-scheme, where coupling between adjacent rotors is taken into account, the correlation function may be approximated according to:

$$f_A^{\mathrm{mD}}(\phi_1,\ldots,\phi_m) \approx \frac{\prod_{i=1}^{m-1} f_{A,i(i+1)}^{\mathrm{2D}}(\phi_i,\phi_{i+1})}{\prod_{i=2}^{m-1} f_{A,i}^{\mathrm{1D}}(\phi_i)}. \tag{7}$$

The construction of the correlation function according to Eq. (7) is based on similar grounds as what has been proposed in Eq. (3). The nominator in Eq. (7) is required to prevent double counting.

In Table 1, the correlation functions are given for the conformers in the exact 3D scheme and approximate 1D and 2D schemes. The 2D approximation performs quite well, while the 1D scheme causes a serious overestimation of the correlation function.

The accuracy of the various schemes can further be tested by evaluating the partition function. Fig. 4(a) shows the rotational partition function in the 2D scheme. The partition function Q^{1D} (with constant reduced moments of inertia) lies rather close to the partition function Q^{3D} generated by the 3D-PES. At low temperature (≈300 K) Q^{1D} overestimates Q^{3D} by 18%, whereas at higher temperatures (≈2000 K) the overrating reduces to about 9%. The 2D based partition function Q^{2D} almost coincides with Q^{3D}, and its overestimation of the reference Q^{3D} remains lower than 3% over the full temperature range. As a consequence, also the derivatives of the 2D partition function with respect to temperature – needed for the calculation of derived thermodynamic quantities – will be very close to the 3D derivatives. On the other hand, the derivatives of Q^{1D} will show larger deviations.

As a result, the thermodynamic properties derived from Q^{2D} will be extremely close to the 3D based properties. In Fig. 4(b), we show the (partial) heat capacity of the three investigated internal rotations. The values of the 2D-scheme coincide with those of the exact 3D-scheme (C^{3D}). This is remarkable because calculation of the heat capacity involves second derivatives of the partition function, making the results relatively sensitive to subtle differences between these functions.

The 1D results C^{1D}, although very close to the reference values, show a distinct behavior compared with C^{3D}.

6. Conclusions

In this paper, we studied *n*-hexane as a typical example in which various consecutive internal rotations about single bonds are present and where effects of coupling on the potential energy and kinetic energy surfaces are important. The exact PES in these dimensions was determined from ab initio calculations at the B3LYP/6-311g** level. The 1D approximation fails in reproducing the correct features of this surface. An adopted 2D approach has been presented which succeeds in reproducing the most important characteristics of the exact PES, such as the correct number of conformers, incorporation of the g_-g_+ effect, and good estimates for the various energy peaks of the surface. Also the kinetic energy part of this 2D scheme reproduces the variation of the kinetic correlation function in a very satisfying way. The partition function calculated within this 2D scheme almost coincides with the exact 3D based partition function. All thermodynamic features which are expressed in terms of the global partition function have the same kind of accuracy.

With current computer capabilities, the proposed 2D approximation is certainly feasible, and justifies the restriction of the number of coupled internal rotations to two in all long chain molecules with multiple successive single bonds, without loosing accuracy in the ab initio evaluation of thermodynamic properties.

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