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# Global materials structure search with chemically-motivated coordinates

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## Abstract

Identification of relevant reaction pathways in ever more complex composite materials and nanostructures poses a central challenge to computational materials discovery. Efficient global structure search, tailored to identify chemically-relevant intermediates, could provide the necessary first-principles atomistic insight to enable a rational process design. In this work we modify a common feature of global geometry optimization schemes by employing automatically-generated collective curvilinear coordinates. The similarity of these coordinates to molecular vibrations enhances the generation of chemically meaningful trial structures for covalently bound systems. In the application to

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hydrogenated Si clusters we concomitantly observe a significantly increased efficiency in identifying low-energy structures and exploit it for an extensive sampling of potential products of silicon-cluster soft landing on Si(001) surfaces.

## Keywords

basin hopping, global optimization, curvilinear coordinates, delocalized internals, adsorbate structure search

One of the biggest problems faced in the synthesis of nanostructured materials<sup>1</sup> and functionalized surfaces<sup>2</sup> is the identification of clear design routes starting from simple building blocks. In the surface deposition of nanoclusters one would, for instance, like to know the exact reaction conditions and prerequisites that enable a homogeneous alignment of intact clusters instead of cluster condensation, fragmentation or dissolution. From a computational point of view, this problem corresponds to finding the relevant chemical pathways and their reaction conditions from a plethora of potential reaction outcomes. Determination of the thermodynamic driving force associated with such pathways is an important first step towards a comprehensive knowledge of the full reaction kinetics. Global geometry optimization approaches are in principle the method of choice for this task. However, corresponding algorithms like basin hopping<sup>3</sup> (BH) or genetic algorithms<sup>4</sup> (GA) are generally designed to yield an unbiased determination of the energetically lowest-lying geometries. This quickly leads to unfeasible computational costs with increasing system complexity and therewith increasing number of possible configurations.<sup>5</sup>

Notwithstanding, the largest number of these configurations is chemically irrelevant or does not even remotely meet the design objectives pursued in this study. Ideally, one would thus like to focus the structural search on sub-spaces, e.g. on energetically low-lying structures in the direct conformational vicinity of the educt. This would not only bias the simulation towards the truly targeted structures, but also allow for an efficient sampling of system sizes and complexities that are otherwise not tractable. An incorporation of corresponding

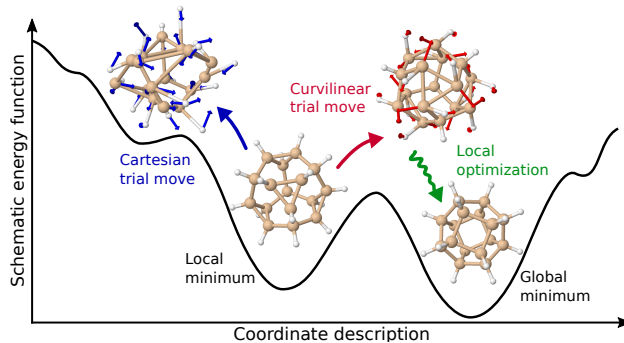


Figure 1: Illustration of the application of curvilinear coordinates in a global geometry optimization context. Stochastic global coordinate displacements followed by a local structure optimization (green arrow) enable sampling of different basins of attraction on the potential energy surface. Trial moves in delocalized internal coordinates (whose Cartesian representation is depicted by red arrows) displace atoms in a way that more closely resembles actual vibrations. This facilitates implementation of a focus on chemically motivated sub-spaces in comparison to unphysical Cartesian trial moves (blue arrows). This is shown schematically for a  $\text{Si}_{16}\text{H}_{16}$  cluster displaced from a local minimum into its global minimum.

chemically-motivated constraints or bias into structural search algorithms is generally not an easy task. One central motif characteristic for many such algorithms is the generation of new trial structures. In stochastic algorithms like BH or GA, this generation is typically achieved by displacing one or more atoms in Cartesian coordinates (CC) as illustrated in Fig. 1. Since these coordinates are of an unphysical nature, it is cumbersome to impossible to keep the resulting displacements within chemically-motivated sub-spaces. Within the example of nanoclusters and their surface deposition a large number of dissociated, fragmented or dissolved structures are the result.

The crucial relevance of the trial structure generation step has already been emphasized in earlier, system-specific work,<sup>6,7</sup> where for example simple group rotations within proteins<sup>8</sup> or clusters<sup>3</sup> already led to significant gains in sampling efficiency. Additionally, internal coordinates have shown to be beneficial for structures connected by double-ended pathways.<sup>9</sup> Furthermore, a number of more computationally demanding schemes to produce elementary moves were suggested based on short high-temperature molecular dynamics runs,<sup>10,11</sup> which in several cases have proven to be much more effective, allowing to optimize large clusters within atomistic models.<sup>12,13</sup> Here, we address this problem with a general and numerically

undemanding recipe to perform displacements in automatically generated curvilinear coordinates. The corresponding set of delocalized internal coordinates (DICs) largely resembles vibrational modes. This naturally suggests DICs as a suitable basis to impose chemically-motivated search boundaries. In the cluster context, restricting the absolute displacements along such coordinates e.g. preferentially explores intact structures. We demonstrate this in the application to hydrogenated silicon clusters, both isolated and soft-landed on a Si(001) surface. Employing DICs instead of CCs in density-functional tight-binding (DFTB) based BH searches we indeed find a significant increase in optimization efficiency.

Chemically most intuitive sets of curvilinear coordinates are natural internal coordinates (ICs), namely bond stretches, angle bends, dihedral torsions, and out-of-plane angles. The potential benefits of such coordinates was already noted in the seminal work on BH of Wales and Doye,<sup>3</sup> with several subsequent works demonstrating their usefulness when tailored to specific systems.<sup>14,15</sup> Contrary to simple ICs, so-called delocalized internal coordinates, *i.e.* orthogonal linear combinations of ICs, possess desirable properties with respect to generality and facility of construction. They have already been extensively used for efficient *local* structure optimization of covalent molecules<sup>16-18</sup> or as a basis for anharmonic vibrational calculations.<sup>19,20</sup>

Aiming for an automatized protocol to construct general curvilinear coordinates for global geometry optimization, we start by defining a set of ICs in a body-fixed frame.<sup>21</sup> Displacements  $\mathbf{x}$  from a given point  $\mathbf{x}_0$  in Cartesian space can then be transformed into a set of internal displacements  $\mathbf{q}$  by the following transformation:

$$\mathbf{q} = B\mathbf{x}; \quad B = \frac{d\mathbf{q}}{d\mathbf{x}} \quad . \quad (1)$$

The set of coordinates in  $\mathbf{q}$ -space can be chosen non-orthogonal and complete (*e.g.* via a Z-matrix). However, this is often cumbersome and not system-independent. A widely employed alternative is the automatic construction of a redundant set of  $M > (3N - 6)$

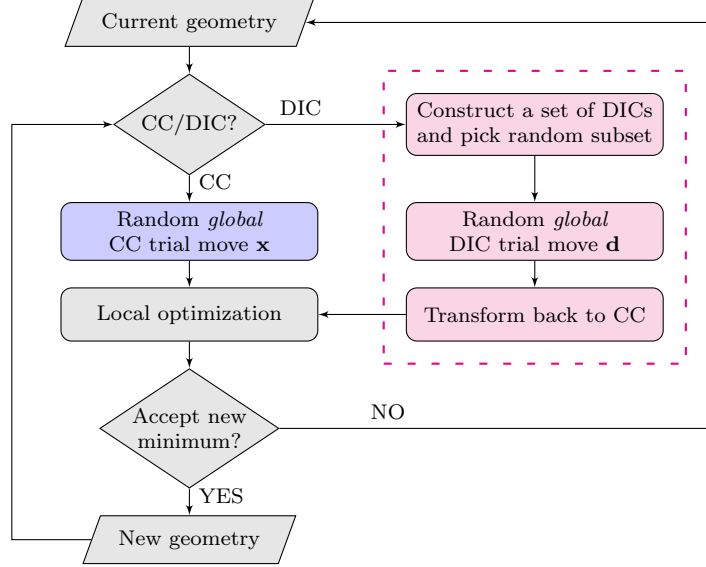


Figure 2: Flowchart representing a generic basin hopping procedure as well as the proposed modification. A starting geometry is displaced with a random global move, followed by local optimization. The new minimum is accepted with a probability dependent on an effective temperature. The accepted structure is placed as a new starting point and the procedure is repeated for a pre-fixed number of steps. Pink boxes correspond to the additional steps performed when using DIC trial moves.

internal coordinates, with  $N$  being the number of atoms.<sup>22</sup> As already shown in literature, most prominently by the works of Pulay, Fogarasi, and Baker,<sup>17,18,22,23</sup> one can construct a set of fully orthogonal coordinates by linear combination of internals. Following the spectral theorem, a matrix  $G = B^\dagger B$  then exists that is positive semi-definite and Hermitian such that:

$$B^\dagger B = U \begin{bmatrix} \Lambda & 0 \\ 0 & 0 \end{bmatrix} U^\dagger, \quad (2)$$

where  $U$  is the matrix of eigenvectors corresponding to  $3N - 6$  linearly independent coordinates and  $M - (3N - 6)$  vectors with eigenvalue zero. The subset of  $U$  that corresponds to the non-zero eigenvalues  $\Lambda$  defines a complete orthogonal coordinate system  $\{\mathbf{d}\}$  by linear combination of the primitive internal coordinates defined in Eq. (1). These coordinates are commonly referred to as DICs<sup>18</sup> or curvilinear normal modes.

We illustrate the use of DICs in the structural search context by introducing them into a generic BH scheme. BH algorithms enjoy wide-spread success thanks to their unbiased character, simplicity, and the involvement of only few technical parameters. BH samples the configurational space through consecutive jumps from one local minimum of the potential energy surface (PES) to another as illustrated in Fig. 1. The jumps, or trial moves, are thereby achieved by randomly moving one or all atoms in the system to new Cartesian positions. Each move is followed by a local geometry optimization. Acceptance or rejection of the thus created structure proceeds finally e.g. on the basis of a Metropolis criterion.<sup>24</sup> With multiple ramifications existing, already this “standard” BH approach has proven highly reliable for the optimization of clusters and biomolecules.<sup>25</sup> As depicted in Fig. 2 using DICs instead of prevalent CCs to describe the atomic displacement vectors in the trial moves implies only minimal modifications. The DICs are only constructed once every global optimization step. In the case of a  $\text{Si}_{16}\text{H}_{16}$  cluster adsorbed on Si(001) the necessary computations take about 300 ms on a single Intel core i5 with 3.50GHz. The computational overhead of constructing the coordinates becomes negligible due to the DIC trial structures being less strained than CC trial structures, effectively reducing the amount of local optimization steps by 30% on average.

In contrast to the choice of CC coordinates, which allow to selectively displace single or multiple atoms, a displacement along any individual DIC generally affects all positions of atoms involved in the construction of the DIC coordinate set, although coordinate constraints can easily be applied.<sup>26</sup> With DIC moves thus necessarily collective, one still has the choice to perform displacements along randomly picked individual DICs or superpositions of DIC vectors. In any case, any choice of CC or DIC move only defines the direction of the displacement  $\mathbf{d}/\|\mathbf{d}\|$ . In order to fully specify a trial move this normalized displacement vector thus has to be multiplied by a factor  $dr$ , referred to as the step size. This step size must be large enough to allow efficient escape from the current PES basin of attraction. It is a technical parameter to be optimized in the application to target systems, regardless of

the coordinate choice.

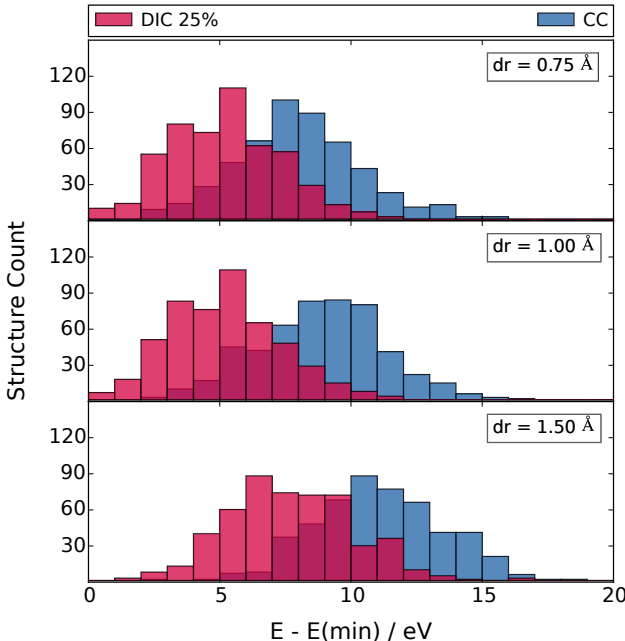


Figure 3: Comparison of the energy distribution of 500 cluster geometries of  $\text{Si}_{16}\text{H}_{16}$  found with basin hopping using CC (blue) and DIC (magenta) trial moves. The different panels correspond to different step sizes  $dr$  as indicated. Results shown are for collective CC moves involving all atoms and DIC moves consisting of random superpositions of 25% of all DICs. Equivalent superior performance of DIC moves is found for other settings (see text). Relative energies are referenced to the known global minimum.<sup>27</sup>

We evaluate the efficiency of DIC trial moves in the BH global optimization of a hydrogenated  $\text{Si}_{16}\text{H}_{16}$  cluster. The choice of this benchmark system is motivated by three main factors: Si clusters represent a class of compounds of particular interest from a nanotechnology perspective;<sup>28</sup> their covalent character confers them a certain degree of chemical complexity while at the same time their limited size enables a thorough investigation; finally, the global minimum is known<sup>27</sup> thus providing a suitable reference for the performance evaluation. Describing the PES at the DFTB-level (*cf.* Computational Details), we always execute 500 BH steps using either CC or DIC trial moves and keeping all other technical parameters like step size or temperature identical. Figure 3 compares the energy distributions of the thus identified 500 cluster geometries, suitably binned into 1.0 eV energy bins and not filtering out revisits of the same geometry. Testing a range of step sizes, the DIC distribution



is each time invariably centered at lower energies as compared to the CC distribution. DICs thus lead consistently to a preferential sampling of lower-energy structures. Furthermore and in contrast to CC moves, the known global minimum used as zero energy reference is found with DIC moves for every employed step size. The results shown in Fig. 3 specifically compare CC moves collectively displacing all atoms with DIC moves along a linear superposition of a randomly picked subset of 25% of all DICs. An improved performance of DICs over CCs was equally obtained for other DIC subsets, *cf.* Sec. SII in the Supplemental Material. However, a subset of 25% seems to represent an optimal tradeoff between sampling efficiency and revisits for this system.

An analysis of the identified cluster structures largely rationalizes the superior performance of DICs over CCs with a significantly reduced number of dissociated or fragmented structures generated. At the settings of Fig. 3 and a step size of 1 Å this amounts e.g. to 12% dissociated structures with DICs compared to 48% dissociated structures with CCs. This ensures that, for most parameter settings, *cf.* Table S1 in the Supplemental Material, DIC moves lead to a larger number of new *and* intact identified structures despite being more prone than CC to revisits of the same basin. Overall, DICs thus offer an increased sampling efficiency at constant or reduced simulation length. Nevertheless, one might argue that the suppressed sampling of high-energy dissociated structures might come at the price of an unnecessary bias or even a constraint on a subset of configurations. Considering that DICs define a complete orthogonal coordinate system it is generally not obvious why this should apply more to a finite number of trial moves performed in DICs than to a finite number of trial moves performed in CCs though. In practice, extending the CC-based BH runs from 500 to 5000 trial moves still does neither identify the known global minimum nor a significant portion of the low-lying minima found already with 500 DIC moves, *cf.* Sec. SIV of the Supplemental Material. In contrast, increasing the number of DIC moves sequentially identifies more and more of the same higher-lying isomers that were found with the CC moves.

The preferential sampling of low-energy structures results ultimately from the more chemical nature of DIC displacements that facilitates the formulation of chemical search boundaries. CC displacements correspond to fully random movements of independent atoms in space, each disregarding the positions of other atoms. In contrast, DICs consider by construction the positions of all atoms. Specifically for systems experiencing predominantly covalent, directional interactions, they form a complete basis to describe the fundamental collective vibrations.<sup>19</sup> Individual or superposed displacements in terms of these coordinates will modify the cluster almost as actual physical vibrational motion would. This understanding is supported by the analysis of the DIC modes in terms of symmetry. The set of DICs for the  $\text{Si}_{16}\text{H}_{16}$  cluster can be clearly partitioned into modes dominantly containing Si–H or Si–Si stretches, or large-scale collective subsystem-torsions (*cf.* Sec. SVI of the Supplemental Material for details; interactive animations can be accessed via [testpresentation.damaurer.at](mailto:testpresentation.damaurer.at)). The more closely the set of DICs represents the vibrational spectrum of a system, the easier it is to suppress the generation of dissociated trial structures with an appropriately set step size. Such a straightforward implementation of a chemically-motivated bias towards intact structures into the structural search procedure is not possible in the unphysical CC moves. Intriguingly, DICs hereby generate an advantage, even in systems where CC displacements perform sufficiently well, such as in predominantly metallic, isotropic clusters that exhibit soft vibrational modes. In fact, we obtain a much more similar sampling performance of DIC and CC moves in the BH geometry optimization of a pure  $\text{Fe}_{13}$  metal cluster, i.e. in the case where all vibrational modes are similarly soft also DIC moves increasingly generate dissociated structures, *cf.* Section SV of the Supplemental Material. These structures can readily be filtered out though, as for them the iterative backtransformation to CCs fails and no new set of DICs can be constructed for the next trial move. As this can be tested prior to the computationally demanding local optimization, a significant computational gain is still achieved.

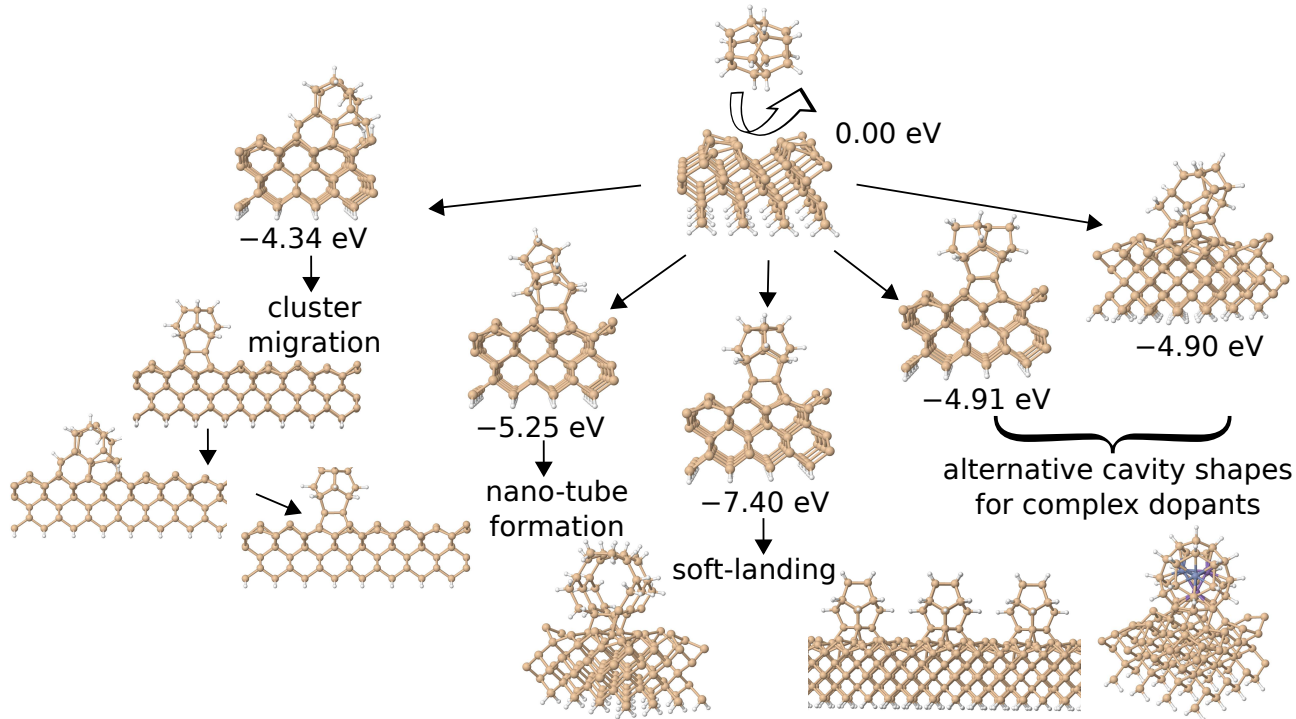


Figure 4: Selected low-energy structures of  $\text{Si}_{16}\text{H}_{16}$  at a  $\text{Si}(001)$  surface, and their perspective role as precursors in different surface reactions (bottom row). Global optimization runs were started from an initial configuration comprising the relaxed  $\text{Si}(001)$  surface and the gas-phase cluster in its global minimum structure; the relative energies of the identified structures are given with respect to this starting configuration.

The full advantage of chemically-motivated trial moves becomes evident in the case of composite materials, such as adsorbates on surfaces, where DICs can be constructed for substructures. For the  $\text{Si}_{16}\text{H}_{16}$  cluster adsorbed on a  $\text{Si}(001)$  surface, the lowest identified structure in a number of global BH searches with a total of 3000 steps and different parameters corresponds to the soft-landed intact cluster with a binding energy of  $-7.40$  eV with respect to the ground-state gas-phase cluster and the clean surface. From this starting point, a plethora of reaction paths might potentially be of relevance for nanotechnological applications and surface reactions. Using DIC trial moves focused on the cluster we readily find a range of chemically sensible, energetically low-lying isomers, the most representative of which are summarized in Fig. 4. All shown configurations are significantly more stable than the desorbed reference structure. The high thermodynamic stability of the obtained aggre-

gates is crucial for developing synthetic routes from individual clusters to complex surface structures. The identified isomers in Fig. 4 range from possible intermediates of on-surface cluster migration to precursors of nanotube formation, all of which preserve a structured pattern rather than exhibiting Si atoms spread over the surface. Further routes to be explored may include dimerization of clusters as well as heterodimerization with other structures as was recently shown for  $\text{Si}_{16}$  clusters and  $\text{C}_{60}$ .<sup>29</sup>

To summarize, we have presented a modification of current global optimization frameworks by using automatically generated curvilinear coordinate trial moves that better reflect chemical transformations. While taking the basin hopping scheme as an example, we emphasize the extensibility of this approach to other sampling schemes, such as genetic algorithms. For systems dominated by covalent interactions and stiff binding modes the similarity of the curvilinear coordinates to fundamental vibrational modes facilitates the implementation of chemically-motivated boundaries into the materials search procedure. The here presented scheme can furthermore be extended to account for subsystem translations, rotations, lattice deformations and even molecule or atom insertion. The hereby gained sampling efficiency will help to extend global optimization into the realms of molecular adsorbates on surfaces, self-assembly of dense molecular overlayers, molecular crystals, and interface reconstructions. In all these areas a rich phase behavior necessitates global optimization and interest is particularly geared towards specific chemically relevant sub-spaces that preserve certain bonding patterns.

## Computational details

The automatic DIC coordinate construction and BH global optimization runs were performed with a self-written code that was interfaced with the ASE package.<sup>30</sup> This code is available from the authors upon request. The DFTB energetics is calculated with the DFTB+ V1.1. code<sup>31,32</sup> employing standard parameter sets.<sup>33</sup> BH sampling was run with a local optimiza-

tion force threshold of 0.01 eV/Å and an effective acceptance temperature of 300 K. The initial structural guess of the isolated Si<sub>16</sub>H<sub>16</sub> cluster was always chosen as a spherical arrangement, with 16 silicon atoms placed randomly on the surface of a sphere of appropriate radius and externally saturated with hydrogen. Further computational details can be found in the Supplemental Material (Sec. SI).

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## Supporting Information Available

See Supplemental Material for computational details, energy distributions of Si<sub>16</sub>H<sub>16</sub> local minima obtained with different percentages of DIC, further details on the performance of DIC with respect to dissociations and non-equivalent minima, as well as an analysis of the DIC displacement modes. For a web-enhanced object containing an interactive visualization of the DIC modes, go to <http://pubs.acs.org/page/4authors/submission/weo.html>. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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# Graphical TOC Entry

