A Molecule-independent and dynamics-friendly methodology to build continuous potential energy surfaces in high dimensions for molecule-surface interactions: N_2O/Cu

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We build continuous potential energy surfaces (PES) for the interaction of a polyatomic molecule with a surface, N_2O with Cu in this case.

Even under the frozen surface approximation, a triatomic molecule over a solid surface has nine degrees of freedom (DOF), which has so far dissuaded researchers from building continuous PESs for such systems, most potential fitting methods not being suited for dimensionalities and the low density of *ab initio* data encountered in systems with more than about six dimensions[1]. Such systems have therefore been studied with *ab initio* methods.

This is unfortunate, as specifically in high dimensionality, in view of the high computational cost of electronic structure calculations, a good case can be made for the use of continuous PESs, in particular:

1. In direct dynamics, the information generated during propagation is thrown away after. When producing (fitting) a continuous PES, all *ab initio* data contribute to the shape of the potential function.
2. A PES, once produced, can be used for calculations with different methods, by different research groups, and unlimited number of times.
3. Some calculations (e.g. modeling of rare events, or quadrature grids) would incur a prohibitive computational cost with direct methods, whereas a PES, once produced, is cheap to recall at any point in the configuration space it covers.

The absence of potential functions for systems with DOF>>6 is due to the fact that the curse of dimensionality plagues of course not only the electronic structure methods but also potential fitting methods. A method is needed to produce a well-behaved surface from very sparse data in a back-box way (as it is increasingly more difficult to intuit the right functional form). We test such a method here[2].

Prediction of reactivity of polyatomic molecules with surfaces has acquired a great technological, economical, and ecological significance. We believe the production of continuous PESs in a black-box, molecule independent way will facilitate the modelling of reactivity of such systems. We apply here the High dimensional model representation + Neural networks method (described below) to fit the nine-dimensional PES of N_2O on Cu(100) in the frozen surface approximation but with all DOFs of the molecule explicitly considered. Reactions of N_2O with surfaces are important to several directions of modern chemistry: search for cheap catalytic materials, removal of greenhouse gases, technological processes[3]. Here we present a step towards modelling the reactivity with a continuous PES: the building of the PES.

A 4-layer, 16 Cu atom slab calculation using SIESTA DFT code shows a favoured chemisorption of N_2O on a hollow site and dissociation of N_2O into N_2+O. The PES was then sampled with Metropolis-type random walks around a minimum energy path in the range of

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[2] J. Chem. Phys. **127**, 014103 (2207)
[3] Surf. Sci. 600, 386 (2005); Surf. Sci. **601**, 3996 (2007); Appl. Surf. Sci. 253, 7501 (2007); Phys. Chem. Chem. Phys. **10**, 1640 (2008)

50,000 cm^{-1} and fitted to chemical accuracy using a small number of low-dimensional functions.

PES fitting method. We alleviate the problem of dimensionality scaling in producing the PES by using representations *via* lower-dimensional functions which are based on a variant of High-dimensional Model Representations[4] (HDMR) and Neural Networks (NN). A PES can be written as a hierarchy of orders of coupling (a sum of terms each of which depends on a subset of the coordinates). This form facilitates quantum dynamics calculations in which the function is used, and in this, it is similar to MULTIMODE[5]:

$$f^{HDMR}\left(x_1, x_2, ...x_D\right) = f_0 + \sum_{i=1}^{N_1} f_i\left(x_i\right) + \sum_{i<j=1}^{N_2} f_{ij}\left(x_i, x_j\right) + ... + f_{12...D}\left(x_1, x_2, ..., x_D\right) \qquad (1)$$

This form is desirable when modeling higher dimensional systems when the density of sampling of f (with *ab initio* data) is very low and only low-order coordinate coupling can in principle be recovered[6]. However, at high D, this representation suffers from several severe drawbacks that we have addressed:

a) The number of component functions N_i scales combinatorially with the dimensionality D of f as well as with the order of expansion i.

b) The widely accepted MULTIMODE minimizes the representation error only on low, 2-, 3-dimensional, hypersurfaces in the configuration space. Not only does this result in non-optimal error optimization, it also requires a separate sample of f for each of the functions $f_{j_1,...,j_d}$ in (1), i. e. hundreds or thousands of data sets and functions for $i>2$ in 6- or more atomic systems. The information contained in other dimensions of these samples is wasted.

c) It is possible to determine all component functions of (1) from *one* set of randomly distributed samples of the function by using the so-called Random Sampling (RS) HDMR[4], but the calculations involve quadratures of dimensions up to D and are shunned by researchers[7].

The above makes a straightforward application of (1) prohibitively costly. We resolve (a-c) while retaining the advantages of the orders-of-coupling expansion (1) by

i. Using Neural Networks to fit the component functions of (1). This dispenses with costly integrals of RS-HDMR and makes for a black-box, molecule-independent method.

ii. Optimizing the coordinates on which $f_{j_1,...,j_d}$ depend. We can prove that there exists a linear transformation to new (redundant) coordinates in which the HDMR expansion (1) can be made arbitrarily precise at any order of coupling i. We show that the quadrature-friendly nature of (1) can be preserved in the new coordinates.

The result is an expansion

$$f\left(x_1, x_2, ...x_D\right) \approx \sum_{j=1}^{N} f_j^{NN}\left(y_1^j, y_2^j, ..., y_{d<D}^j\right), \quad \vec{y} = \hat{A}\vec{x}$$

with arbitrary N. This allows both to obtain a required fit accuracy with functions of arbitrarily low dimensionality and to avoid the combinatorial explosion of the number of terms in HDMR / MULTIMODE type expansions. It yields a general, molecule-independent method to represent multivariate functions arising in different research areas, which we here apply to the potential surface of the interaction of N_2O with Cu(100).

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[4]   J. Math. Chem. **25**, 197 (1999)
[5]   Int. Rev. Phys. Chem. **22**, 533 (2003)
[6]   J. Chem. Phys. **125**, 084109 (2006)
[7]   J. Chem. Phys. **127**, 184302 (2007)