Sum of squares decompositions of potential energy surfaces

Martin Burke and Sophia N. Yaliraki

Department of Chemistry, Imperial College London,
South Kensington Campus, London, SW7 2AZ, United Kingdom

(Dated: March 23, 2022)

Abstract

The difficulty in exploring potential energy surfaces, which are nonconvex, stems from the presence of many local minima, typically separated by high barriers and often disconnected in configurational space. We obtain the global minimum on model potential energy surfaces without sampling any minima a priori. Instead, a different problem is derived, which is convex and hence easy to solve, but which is guaranteed to either have the same solution or to be a lower bound to the true solution. A systematic way for improving the latter solutions is also given. Because many nonconvex problems are projections of higher dimensional convex problems, Parrilo has recently showed that by obtaining a sum of squares decomposition of the original problem, which can be subsequently transformed to a semidefinite programme a large class of non-convex problems can be solved efficiently. The semidefinite duality formulation also provides a proof that the global minimum of the energy surface has either been found exactly or has been bounded from below. It additionally provides physical insight into the problem through a geometric interpretation. The sum of squares polynomial representation of the potential energy surface may further reveal information about the nature of the potential energy surface. We demonstrate the applicability of this approach to low dimensional potential energy landscapes and discuss its merits and shortcomings.
I. INTRODUCTION

The thermodynamic and kinetic properties of atomic and molecular assemblies in physics, chemistry and biology are often linked to their underlying potential energy surface (PES)\textsuperscript{3,4,5}. Even in the simplest cases, exploring potential energy surfaces or even just important regions becomes computationally demanding very rapidly. This is primarily due to the non-convexity of the underlying potential energy surface. A key step in understanding thermodynamic properties of systems as diverse as proteins, crystals or nanoscale clusters is the identification of the global minimum. Definite proof typically requires exhaustive sampling of every other minimum in configurational space, a prohibitive task given that the number of local minima on the surface grows exponentially with the number of particles in the system\textsuperscript{3,6}.

A series of approaches have been proposed to tackle this problem with various degrees of success. Most stochastic methods are variations of the Monte Carlo (MC) method with additional steps introduced to aid barrier crossing between local minima\textsuperscript{7,8,9}, although genetic-based algorithms\textsuperscript{10,11} have also been used. Deterministic approaches usually derive from global optimisation techniques\textsuperscript{12,13,14} or molecular dynamics\textsuperscript{15}. Methods that deform the potential in order to eliminate local minima include hypersurface deformation techniques\textsuperscript{16}, such as the distance scaling method\textsuperscript{17}, and the very successful MC basin-hopping method\textsuperscript{18}.

A commonality in most methods is that they require extensive sampling of the local minima of the potential energy surface itself prior to finding the global minimum. Not only is this process time consuming, sensitive to initial conditions, and susceptible to trapping due to high barriers, it crucially provides no proof that a given point on the PES is indeed the global minimum other than that it is the lowest visited to date by the algorithm. It is typically not possible to evaluate how close such a minimum would be to the correct answer to further guide the search. Furthermore, all methods rely to a greater or lesser extent on the topology of the PES being ‘well behaved’ in the sense that the global minimum is connected to other low lying local minima so that it can be reached from them.

Here we outline a different strategy that addresses the problem of locating the global minimum without sampling other minima in configurational space. As a result, it is independent of initial conditions and of any requirement that the minimum be closely related to any other. Either the exact result is found together with a proof or a lower bound is obtained. In no case is the original function deformed. A key idea is that instead of sam-
pling the underlying non-convex function, we approach it from below. A different problem is sought, whose solution coincides with the solution of the problem we are interested in. For this approach to be successful, it must be coupled both with a rigorous and systematic way to find such problems that can be easily solved, and, with a way to evaluate how close the two solutions are. An important mathematical concept that provides such a link is that many nonconvex problems turn out to be projections of higher dimensional convex problems. The great advantage of the latter is that they are efficiently solved since the local minimum is the global minimum. Furthermore, they also allow for physical insight into the system because they possess duality properties. This duality provides geometric interpretations to the original problem and allows us to monitor how close the solution of the derived problem is to the true solution we are seeking. This is coupled with a systematic way to improve on our non-exact solutions. The combination of these features makes this approach appealing because physical insight is revealed about the system while seeking the solution itself. The approach, originally developed by Parrilo for semialgebraic geometry problems in robust control, is applicable to polynomial systems and is based on obtaining a sum of squares (SOS) representation of the original function, which turns out to be convex in the coefficient space of the function, and, hence efficiently computed through semidefinite programming techniques. In Sec II we give the main concepts of the theory and its relation to physical observables and in Sec III we apply it to a series of low dimensional examples that exemplify a range of difficulties encountered in complex landscape problems and which highlight the different capabilities and versatility of this method. In Sec IV we discuss the advantages and shortcomings of the approach.

II. THEORY

A. SOS decompositions

A different approach to locating the global minimum $U^*$ of a multivariable polynomial, $U(x_i, \ldots x_n) \equiv U$ of degree $d$ is to look for the largest real number $\lambda$ such that $U - \lambda$ can be decomposed as a SOS\textsuperscript{1,2,19}, that is

$$U - \lambda = \sum_{i=1}^{r} p_i^2 \geq 0 \quad (1)$$
where \( p_i \) are polynomial functions of degree \( d/2 \) in the variables of \( U \) (Fig. 1, steps 1-3). Because being a SOS is a sufficient condition for a function to be nonnegative (although not a necessary one), it is clear that if a SOS decomposition exists, \( \lambda \) will always be a lower bound to the original function’s global minimum, \( U^* - \lambda^* \geq f^{\text{SOS}} \) where \( ^* \) denotes the optimal and \( f^{\text{SOS}} \) the SOS decomposition\(^19\). Indeed, both \( \lambda \) and \( f^{\text{SOS}} \) are guaranteed to bound the original problem from below\(^19\). The next step then becomes to obtain the SOS decomposition together with \( \lambda \) that gives the closest answer to our original problem.

A central idea is the systematic lifting of a polynomial function in its coefficient space (rather than its variables) to a SOS function. An important result from real algebraic geometry, the Positivstellensatz\(^20\), provides such a lifting.

The problem becomes tractable by additionally exploiting the theorem\(^1\) that for globally non-negative polynomial functions, there exists a positive semidefinite matrix \( Q \) such that:

\[
U(x) - \lambda = f^{\text{SOS}} = z(x)^T Q z(x), \quad \text{where } Q \succeq 0, \quad (2)
\]

so that the original problem of Eq.\(^1\) can now be formulated algebraically. \( z(x) \) is the vector of monomials of \( U \) with degree less than or equal to half the degree of \( U \) and provides a basis for the SOS function decomposition. Since the variables in \( z \) are not algebraically independent, the matrix \( Q \) is not unique and may be positive semidefinite in some representations but not in others. The problem now becomes a search for a symmetric positive definite matrix \( Q \) that satisfies the constraints imposed by Eq.\(^2\). Note that the original non-convex problem in the variables of \( U \) has been mapped to a different problem, namely obtaining the polynomial coefficients of the SOS representation, which is equivalent to obtaining the matrix elements of \( Q \). This latter problem, although in higher dimensions, is now convex and amenable to efficient solutions by SDP. Additionally, the minimisation of the potential is carried out concurrently with the search for the SOS coefficients. The theoretical elegance of this methodology coupled with efficient computational techniques, allows for SOS decompositions to be found in polynomial time (As long as either the degree of the polynomial or the number of variables are fixed) and additionally provides the proof that the result is indeed a lower bound to the global minimum. If the answer is not exact, the gap from the true solution is known.
B. SDP and Duality

SDPs\textsuperscript{21} are a class of optimisation problems over positive definite matrices solvable by polynomial time algorithms such as the very successful primal-dual interior point methods\textsuperscript{22}. Such methods compute the optimal solution as well as provide certificates (proofs) of optimality. These certificates are based upon a duality theory in which two problems are solved simultaneously. The dual problem solution provides a lower bound on the primal problem. The difference between the primal and dual solutions, referred to as the duality gap, proves whether an exact solution has been found or provides the lower bound to the solution, which is away by at most the magnitude of the duality gap.

The original polynomial minimisation can be recast as the SDP given in Eq. 4 in Fig. 1. In our case, the primal problem gives the lower bound to the global minimum as well as the SOS decomposition, while the dual provides the location of this bound in the configurational space. In the mathematical community the focus is typically on the primal, with the dual only used to provide the duality gap. However, as we show here there is relevant and interesting physics in the dual problem as well.

C. Convexity and duality

Duality appears in many places in chemical physics, albeit without this name. It is intimately connected with convexity\textsuperscript{23}. Multidimensional convex functions obey a range of useful properties, one of which is that at each point there is at least one hyperplane tangent to the graph, whose slope is the derivative of that function. In fact, this plane belongs to a family of planes that separate the entire configurational space in two parts, below and above the function. Convexity ensures that they never cross the function in more than one point. To demonstrate how duality is related to this, we restrict ourselves to a 1 dimensional parabola $f(x) = x^2$ but the argument is completely general. The separating planes now become straight lines (Fig. 1). There is a set of lines with slope $y$ which lie below the parabola as long as $yx - d \leq x^2$ where $d$ is the depth. The line will touch tangentially the parabola when $d = 1/4y^2$. Each point on the parabola can be represented as a line which touches the parabola with different slopes $y$. The envelope of these lines reproduces the parabola itself. In fact, by looking for the maximum slope $y$, we obtain simultaneously $f(x)$.
This is in fact what the Legendre transforms do in thermodynamics where for example the Gibbs and Helmholtz free energy are coupled with pressure and volume respectively. This interpretation was already recognised by Tisza. The dual emphasises the geometric interpretation of the problem, and in that sense its variables can be interpreted as generalised Lagrange multipliers. It further clarifies how we can obtain information about a function by looking outside and bounding it externally from below.

III. RESULTS

To demonstrate the SOS approach in physical applications, we apply it now to model potentials that highlight the versatility of the method in dealing with typical aspects of landscapes that make them difficult to study. Once the problem is formulated theoretically as described above, we use third party Matlab toolboxes to carry out the SOS decomposition: SOSTOOLS, a tool for producing the SOS decompositions of polynomial optimisation problems and SeDuMi or SDPT3, SDP solvers which use primal-dual interior point methods. Other minimisations for comparisons were implemented in the Matlab optimization toolbox.

A. Multi-well potential

To demonstrate the method we apply it first to a potential with many minima whose values are very close to the global minimum but are separated by high barriers (see Fig. 3). The typical ratio of barrier height/local minima energy difference is 80. In addition, the minimum closest in energy to the global minimum is furthest apart in domain space. This type of poor connectivity behaviour is not uncommon in potential energy surface problems where a number of nodes on the disconnectivity graph have energy levels that are almost identical.

The SOS approach provides the global minimum which in this case is proven to be exact from the duality gap, and, correctly identifies its location in the coordinate space (Table 1). Additionally, the SOS decomposition we obtained is a faithful representation of the original function (Fig. 3). A general feature of the SOS optimisation, once formulated theoretically, is that it is carried out once, unlike other methods which may depend on a good initial guess.
or on the location of the initial conditions, and, it provides all the information simultaneously.

We have compared to two other common minimisation approaches: the downhill simplex method\textsuperscript{29} and the BFGS quasi-newton scheme\textsuperscript{30}, which is used in the basin-hopping algorithm. Unlike SOS, both methods were applied iteratively from a grid of starting points spanning the domain space of the problem with the grid density being increased until the global minimum was obtained. In order to succeed in finding the global minimum, at least 10 separate runs from starting points on an evenly spaced grid of points spanning the domain were required. This is in fact more attempts than the number of minima in the domain. The point however remains that these algorithms have no way of establishing that the minimum that they locate is in fact the global minimum.

We note that there is nothing special about the form of the potential presented here. We have tried successfully several multiwell examples with different polynomial representations, more asymmetric wells, and, separations with identical success. Interestingly, the method can identify the global minimum even if the wells are nearly-degenerate with arbitrarily close energy. In fact, a true degeneracy is reflected in the eigenvalues of the dual solution matrix and can hence be identified and located in the dual solution matrix. This can be very useful in locating often missed degenerate minima by looking at the dual.

The formalism holds for multi-dimensional problems and so a generalisation of this problem to higher dimensions works in the same fashion. The global minimum ($U = -14.036$, location = $[-0.9798, -0.9798, -0.9798, -0.9798]$) is identified among on the order of 4100 densely spaced minima (Fig. 4) of the 4 dimensional version of the same potential. At the same time, a ten dimensional version with now disconnected minima dispersed in a higher 10 dimensional space (of the order of 59,000 minima) worked equally well (Table 1).

\textbf{B. Golf-like potential}

A different set of energy landscapes exhibit flat regions with deep and narrow wells which become especially challenging and rapidly intractable for searching algorithms. The reason is that the flat regions provide no energy differences that can guide any search. Exhaustive searching is the only option, which becomes intractable very rapidly as the domain increases. We were able to successfully locate the global minimum of a delta function embedded in a two-dimensional infinite region. Such an example is shown in Fig. 5 where the function
is almost flat everywhere except in two locations where almost identical delta function wells are present. Note that we have included the entire \( \mathbb{R}^2 \) domain. The SOS approach correctly identifies the minimum and its location (Table 1). This is also true when the higher energy well becomes wider. The power of this approach comes from the following general simultaneous reasons: (i) the solution is always approached from below so the flatness of the function does not enter (ii) the minimum is very narrow in configurational space, however, in the lifted space of the coefficients this is no longer necessarily true (iii) the set of equations linking the coefficients of the function intersect the cone of positive definite matrices. The possible solutions are now on the boundary of this space and no longer on the interior and hence easy to distinguish near degeneracies even if disconnected in configuration space.

C. Müller potential

The Müller potential\(^{31}\) is commonly used as a non-trivial test for reaction path methods due to the complexity of its minima structure that leads to a highly contorted reaction coordinate which requires a sharp change of direction at the saddle. The potential surface (Fig. 6) contains three minima, with the global minimum of \(-146.7\) at \((-0.558, 1.442)\):

\[
U(x, y) = \sum_{i=1,...,4} A_i \exp[a_i(x - x_i)^2 + b_i(x - x_i)(y - y_i) + c_i(y - y_i)^2]
\]  

(3)

where \(A = (-200, -100, -170, 15), \ a = (-1, -1, -6.5, 0.7), \ b = (0, 0, 11, 0.6), \ c = (-10, -10, -6.5, 0.7), \ x_i = (1, 0, -0.5, -1), \ y_i = (0, 0.5, 1.5, 1)\). Its domain is constrained in order to exclude areas where the function is not well behaved. The SOS approach allows for constraints, both equality and inequality, to be incorporated on an equal footing as can be seen in Eq. 3 of Fig. 1. We can take advantage of this powerful tool here by excluding parts of space that are not of interest in the formulation of the problem. The definition of this function includes an exponential so in order to apply the method here we fitted the function in a least squares sense to a polynomial of degree 16, \(U_f\), which contains 153 monomials, 67 of which are odd. (The RMS error normalised by the data range was 0.0015 over the points sampled). This leads to the minimisation of \(U_f\) subject to a series of inequality
constraints, $g_i$:

\[
\begin{align*}
\text{max: } & \lambda \\
\text{subject to: } & U_f - \sum_{i=1}^{4} s_i g_i - \lambda \geq 0 \\
& g1 : x \geq -1.5 \quad g2 : x \leq 0.7 \\
& g3 : y \geq -0.5 \quad g4 : y \leq 2.0,
\end{align*}
\]

where $s_i$ are additional SOS functions with unknown coefficients.

The SOS approach succeeded in locating the minimum which is proven to be exact by the duality gap. It is interesting to point out that the final SOS decomposition of the potential is a good representation of the original function (see Fig. [4]) which may allow for additional properties of the function to be explored in different representations. For example, we were able to correctly locate the elusive saddle through eigenvector following on the SOS function. If more faithful representations were sought, a better bound to the function can be produced by systematically augmenting the dimension of the basis (eq. 3, Fig 1) at higher computational cost.

IV. DISCUSSION

The SOS approach is a rigorous and systematic way to approaching complex problems by exploiting both their algebraic and geometric properties. We have applied it here to the identification of the global minimum of model potential energy surfaces which exemplify features that make this problem difficult in physical systems of interest such as narrow and disconnected wells embedded in flat or contorted regions. We have demonstrated the method on low dimensional problems in which it is possible to gain an understanding of how the method works and how it is different to other approaches. It is clear that no method will outperform all other methods for all problems and it may well be that heuristic approaches may outperform the more formal SOS approach on a given subset of problems. However, the appeal of the SOS approach stems from its generality due to its deep theoretical foundations and efficient computational algorithms.

Another advantage comes from the added physical insight that can be gained by formulating the problem in this way where duality holds. An immediate consequence of duality is the ability to produce a proof when the exact answer has been reached without sampling or
comparing to other minima, in contrast to almost all other methods. Secondly, the geometrical interpretation attached to the dual can lead to insight into the problem, including the identification of degeneracies and symmetries. Furthermore, there is freedom in how to pose a problem, so that constraints (equalities and inequalities) can be incorporated as variables or new variables can be introduced which can lead to efficient answers. This is particularly useful for dealing with more complex potentials that include trigonometric functions and so fitting could be avoided by introducing new variables. This may extend the applicability of the method to certain non-polynomial functions.

Unlike other methodologies that approximate the functions either by subtracting or adding extra terms, which is known to often alter the behaviour of the system especially in multidimensional problems, in this approach the original function is never deformed nor linearised. Rather, an entirely different and higher dimensional problem is sought, which is both convex solvable and whose solution in the space of the original variables coincides with that of the original question. Unlike gradient-based and Monte-Carlo methods that use the original function, this approach bounds the function externally from below. This is one of the reasons that poorly connected and/or nearly degenerate minima separated by high barriers do not pose the difficulties encountered in the usual sense.

As the complexity of problems attempted increases, it is possible that the exact solution may not be found. In many cases, a “close enough” answer may be adequate. Here, we can quantify the gap between our answer and the exact solution. If the lower bound solution is not adequately close, then further refinement can be sought by seeking a higher dimensional monomial basis or augmenting the equation of the Positivstellensatz by introducing SOS functions, which can be thought here as a generalisation of Lagrange multipliers. Accuracy can be systematically increased at the expense of more computational cost, since there is a proof of the existence of the exact answer in such liftings to higher dimensions. In that respect, this method is closer in spirit to a variational approach but one which is guaranteed to be optimal and may lead eventually, at least in principle, to the right answer of the original problem. Unlike other global approaches, the method allows for insight into the nature of the PES rather than just providing a number. For example, having an explicit SOS polynomial representation of the problem can potentially be useful for studying other properties of the system besides its global minimum.

A number of challenges remain due to the significant scaling of the number of the new
variables that occurs as a result of the lifting process which means that, for physical problems, the current limitations on size of SDPs solvable using primal-dual interior point methods need to be overcome. Excluding symmetries and symmetry operations is a promising way in that direction. This is the focus of ongoing research.

We thank Pablo Parrilo & Mauricio Barahona for helpful discussions. This work has been funded by the BBSRC, UK and the ONR, USA.
1 P. Parrilo, Ph.D. thesis, California Institute of Technology, Pasadena, CA., U.S.A. (2000).
2 P. Parrilo and B. Sturmfels, *Algorithmic and quantitative real algebraic geometry* (AMS, 2003), vol. 60, pp. 83–99.
3 R. S. Berry, Chemical Reviews 93, 2379 (1993) and references therein.
4 D. Wales and H. A. Scheraga, Science 285, 1368 (1999) and references therein.
5 L. Munro, A. Tharrington, and K. Jordan, Computer physics communications 145, 1 (2002) and references therein.
6 C. Tsai and K. Jordan, Journal of Physical Chemistry 97, 11227 (1993).
7 S. Kirkpatrick, C. Gelatt, and M. Vecchi, Science 220, 671 (1983).
8 D. D. Frantz, D. L. Freeman, and J. D. Doll, J. Chem. Phys. 93, 2769 (1990).
9 H. Grubmueller, Phys. Rev. E 52, 2893 (1995).
10 A. A. Rabow and H. A. Scheraga, Protein Science 5, 1800 (1996).
11 D. Deaven, N. Tit, J. Morris, and K. Ho, Chem. Phys. Lett. 256, 195 (1996).
12 C. Maranas and C. Floudas, Journal of Chemical Physics 97, 7667 (1992).
13 M. Damsbo, B. Kinnear, M. Hartings, P. Ruhoff, M. Jarrold, and M. Ratner, PNAS 101, 7215 (2004).
14 I. Andricioaei and J. Straub, J. Comput. Chem. 19, 1445 (1998).
15 J. Doye, D. Wales, and R. Berry, Journal of Chemical Physics 103, 4234 (1995).
16 L. Piela, J. Kostrowicki, and H. Scheraga, J. Phys. Chem. 93, 3339 (1989).
17 J. Pillardy and L. Piela, J. Phys. Chem. 99, 11805 (1995).
18 D. Wales and J. Doye, J. Phys. Chem. A 101, 5111 (1997).
19 N. Z. Shor, Cybernetics 23, 731 (1987).
20 G. Stengle, Math. Ann 207, 87 (1974).
21 L. Vandenberghe and S. Boyd, SIAM Review 38, 49 (1996).
22 Y. E. Nesterov and A. S. Nemirovsky, Ekonomika i Matem. Metody (1988).
23 G. Strang, *Introduction to Applied Mathematics* (Wellesley-Cambridge Press, 1986).
24 L. Tisza, *Generalized Thermodynamics* (MIT Press, 1966).
25 S. Prajna, A. Papachristodoulou, and P. Parrilo, *SOSTOOLS, Sum of Squares Optimization*
Toolbox for MATLAB, User’s Guide, Version 1.00, Dept. of Control and Dynamical Systems, California Institute of Technology, Pasadena, CA 91125 - USA (2002).

26 J. Sturm, Using SEDUMI 1.02, A Matlab Toolbox for Optimisation Over Symmetric Cones, Dept. of Econometrics, Tilburg University, Tilburg, The Netherlands (2001).

27 R. Tutuncu, K. Toh, and M. Todd, SDPT3 - a Matlab software package for semidefinite-quadratic-linear programming (2001).

28 O. Becker and M. Karplus, J. Chem. Phys. 106, 1495 (1997).

29 J. A. Nelder and R. Mead, Computer Journal 7, 308 (1965).

30 J. E. Dennis and R. B. Schnabel, Numerical Methods for unconstrained optimization and nonlinear equations (SIAM, 1983).

31 K. Müller, Angew. Chem. Int. Ed. Engl. 19, 1 (1980).
List of figures:

1. Convex duality in Legendre transforms.

2. Schematic flowchart of a SOS optimisation.

3. SOS optimisation on a 1D multiwell potential.

4. A 2D projection of a 4 dimensional potential of 16th degree.

5. Contour plot of a Golf-like landscape.

6. Contour plot of the original fitted Müller potential (a), and its SOS representation (b).
List of tables:

1. Summary of SOS optimisation results for the 1D, 10D multiwell, Müller and Golf-like potentials.
List of figure captions:

Fig. 1: How convexity and duality are related. A set of lines with slope $y$ lie below the parabola $f(x) = x^2$, as long as $yx - d \leq x^2$ where $d$ is the depth. The line will touch tangentially the parabola when $d = 1/4y^2$. Each point on the parabola can be represented as a line which touches the parabola with different slopes $y$. The envelope of these lines reproduces the parabola itself. In fact, by looking for the maximum slope $y$, we obtain simultaneously $f(x)$. The relationship between convexity and duality appears in many places in chemical physics. An example of such a relationship are the Legendre transforms in thermodynamics.

Fig. 2: Schematic flowchart of a SOS optimisation. The original global energy minimisation problem is reformulated in a series of steps: (1) a polynomial optimisation including any constraints is transformed to (2) a maximisation of a real number $\lambda$ which will keep the function nonnegative. A sufficient but not necessary condition for this to be true is that the function is a SOS, so the problem is rewritten as (3). The constraints can be incorporated as well and algebraic geometry guarantees the validity of this equation. The additional terms provide a series of hierarchical approximations to the true solution. (4) A function being a SOS is equivalent to finding a positive semidefinite matrix $Q$ where $z$ is a vector of monomials of $U$. Note that $Q$ relates the coefficients of $U$ and contains $\lambda$. Finding $Q$ is equivalent to the semidefinite programme given in (5), with the primal (left) and dual (right) problems. Each step is an exact reformulation of the previous apart from (3) which is guaranteed to give an optimal bound to the original problem. When expressed in the appropriate monomial basis the problem of locating the coefficients of $Q$ becomes convex and hence efficiently solvable. However, the SOS function (3) is still a non-convex function in configuration space and can be a good representation of the original function.

Fig. 3: SOS optimisation on a multiwell potential $U(\cdot)$ with 8 minima, the leftmost being the global minimum. The second minimum, farthest away in domain space, is very close in value to the global minimum. The global minimum is correctly identified. The SOS function $f^{SOS}(\cdot)$ is in excellent agreement with $U$. Here, $U = 0.01x - 128.1x^2 + 2688x^4 + (-21504x^6 + 84480x^8 - 180224x^{10} + 212992x^{12} - 131072x^{14} + 32768x^{16}$.

Fig. 4: A 2D projection of a 4 dimensional multiwell potential with 4096 minima given by:

$U(x_1, x_2, x_3, x_4) = \sum_{i=1}^{4} (a_0 + a_1 x_i + a_2 x_i^2 + a_3 x_i^4 + a_4 x_i^6 + a_5 x_i^8 + a_6 x_i^{10} + a_7 x_i^{12} + a_8 x_i^{14} + a_9 x_i^{16})$ where $a_0 = 1, a_1 = 0.5, a_2 = -130.1, a_3 = 2688, a_4 = -21504, a_5 = 84480, a_6 = -180224, a_7 = -$
212992, \( a_8 = -131072, a_9 = 32768 \). SOS optimization sucessfully identified the global minimum of \( U = -13.977 \) to within 0.026 at the point \([-0.9792, -0.9792, -0.9792, -0.9792]\).

Fig. 5: Contour plot of a Golf-like potential. \( U \) is given by
\[
\frac{1}{\pi} \left( \frac{e_1}{(x-5)^2+(y-4)^2+e_1^2} + \frac{e_2}{(x+7)^2+(y+6)^2+e_2^2} \right),
\]
\( e_1 = 0.09, e_2 = 0.1 \) defined over the entire \( \mathbb{R}^2 \) domain (left). The area close to the origin (blue circle) is reproduced at greater magnification on the right. The two minima are \( U(5, 4) = -3.5369 \) (global) and \( U(-7, 6) = -3.1832 \). In this case the SOS optimisation produces a lower bound of \( U = -3.539 \). The non-negligible duality gap (Table 1) shows that the exact answer is at most 0.0023 away. The configurational coordinates are obtained correctly to within numerical accuracy.

Fig. 6. Contour plot of the original fitted Müller potential (a), and its SOS representation (b). The global minimum was identified correctly. \( f^{SOS} \) (b) is the projection to the original domain space from the lifted space of the SOS function including the inequality constraints. Much of the original function is preserved within the first order of Eq. 3, Fig. 1.
TABLE I: Summary of SOS optimisation results for the multi-well, Müller and golf-like potentials: the cpu time in a standard PC in seconds, the lower bound value with the exact global minimum in brackets, the configurational coordinates of the minimum, the duality gap, and the final values of the primal and dual problem. The 10 dimensional multiwell example was defined as follows:

\[ U = \sum_{i=1}^{10} a_1 x_i + a_2 x_i^2 + a_3 x_i^3 + a_4 x_i^4 + a_5 x_i^5 + a_6 x_i^6 \]

where \( a_1 = 2, a_2 = 230, a_3 = -28, a_4 = -1000, a_5 = 1, a_6 = 1000 \) and the global minimum of \(-193.685 \) was located among approximately 59000 minima at (*) \((0.7369, 0.7369, 0.7369, 0.7369, 0.7369, 0.7369, 0.7369, 0.7369, 0.7369, 0.7369)\).
FIG. 1: How convexity and duality are related. A set of lines with slope $y$ lie below the parabola $f(x) = x^2$, as long as $yx - d \leq x^2$ where $d$ is the depth. The line will touch tangentially the parabola when $d = 1/4y^2$. Each point on the parabola can be represented as a line which touches the parabola with different slopes $y$. The envelope of these lines reproduces the parabola itself. In fact, by looking for the maximum slope $y$, we obtain simultaneously $f(x)$. The relationship between convexity and duality appears in many places in chemical physics. An example of such a relationship are the Legendre transforms in thermodynamics.
FIG. 2: Schematic flowchart of a SOS optimisation. The original global energy minimisation problem is reformulated in a series of steps: (1) a polynomial optimisation including any constraints is transformed to (2) a maximisation of a real number $\lambda$ which will keep the function nonnegative. A sufficient but not necessary condition for this to be true is that the function is a SOS, so the problem is rewritten as (3). The constraints can be incorporated as well and algebraic geometry guarantees the validity of this equation. The additional terms provide a series of hierarchical approximations to the true solution. (4) A function being a SOS is equivalent to finding a positive semidefinite matrix $Q$ where $z$ is a vector of monomials of $U$. Note that $Q$ relates the coefficients of $U$ and contains $\lambda$. Finding $Q$ is equivalent to the semidefinite programme given in (5), with the primal (left) and dual (right) problems. Each step is an exact reformulation of the previous apart from (3) which is guaranteed to give an optimal bound to the original problem. When expressed in the appropriate monomial basis the problem of locating the coefficients of $Q$ becomes convex and hence efficiently solvable. However, the SOS function (3) is still a non-convex function in configuration space and can be a good representation of the original function.
FIG. 3: SOS optimisation on a multiwell potential $U(-)$ with 8 minima, the leftmost being the global minimum. The second minimum, farthest away in domain space, is very close in value to the global minimum. The global minimum is correctly identified. The SOS function $f^{SOS}(\star)$ is in excellent agreement with $U$. Here, $U = 0.01x - 128.1x^2 + 2688x^4 - 21504x^6 + 84480x^8 - 180224x^{10} + 212992x^{12} - 131072x^{14} + 32768x^{16}$. 
FIG. 4: A 2D projection of a 4 dimensional multiwell potential with 4096 minima given by:

\[ U(x_1, x_2, x_3, x_4) = \sum_{i=1}^{4} a_0 + a_1 x_i + a_2 x_i^2 + a_3 x_i^4 + a_4 x_i^6 + a_5 x_i^8 + a_6 x_i^{10} + a_7 x_i^{12} + a_8 x_i^{14} + a_9 x_i^{16} \]

where \( a_0 = 1 \), \( a_1 = 0.5 \), \( a_2 = -130.1 \), \( a_3 = 2688 \), \( a_4 = -21504 \), \( a_5 = 84480 \), \( a_6 = -180224 \), \( a_7 = 212992 \), \( a_8 = -131072 \), \( a_9 = 32768 \). SOS optimization sucessfully identified the global minimum of \( U = -13.977 \) to within 0.026 at the point \([ -0.9792, -0.9792, -0.9792, -0.9792 ]\).
FIG. 5: Contour plot of a Golf-like potential. $U$ is given by

$$U = \frac{-1}{\pi} \left( \frac{e_1}{(x-5)^2+(y-4)^2+e_1^2} + \frac{e_2}{(x+7)^2+(y+6)^2+e_2^2} \right),$$

with $e_1 = 0.09, e_2 = 0.1$ defined over the entire $\mathbb{R}^2$ domain (left). The area close to the origin (blue circle) is reproduced at greater magnification on the right. The two minima are $U(5,4) = -3.5369$ (global) and $U(-7,6) = -3.1832$. In this case the SOS optimisation produces a lower bound of $U = -3.539$. The non-negligible duality gap (Table 1) shows that the exact answer is at most 0.0023 away. The configurational coordinates are obtained correctly to within numerical accuracy.
FIG. 6: Contour plot of the original fitted Müller potential (a), and its SOS representation (b). The global minimum was identified correctly. $f^{SOS}$ (b) is the projection to the original domain space from the lifted space of the SOS function including the inequality constraints. Much of the original function is preserved within the first order of Eq. 3, Fig. 1.