Certifying the Potential Energy Landscape

Dhagash Mehta[*]

Dept of Physics, Syracuse University, Syracuse, NY 13244, USA.

Jonathan D. Hauenstein[†]

Dept of Mathematics, North Carolina State University, Raleigh, NC 27695, USA.

David J. Wales

Dept of Chemistry, The University of Cambridge, Cambridge, CB2 1EW, UK.

It is highly desirable for numerical approximations to stationary points for a potential energy landscape to lie in the corresponding quadratic convergence basin. However, it is possible that an approximation may lie only in the linear convergence basin, or even in a chaotic region, and hence not converge to the actual stationary point when further optimization is attempted. Proving that a numerical approximation will quadratically converge to the associated stationary point is termed *certification*. Here we employ Smale's α-theory to stationary points, providing a certification that serves as a *mathematical proof* that the numerical approximation does indeed correspond to an actual stationary point, independent of the precision employed. As a practical example, employing recently developed certification algorithms, we show how the α-theory can be used to certify all the known minima and transition states of Lennard-Jones LJ_N atomic clusters for $N = 7, \ldots, 14$.

Introduction: The surface defined by a potential, $V(\mathbf{x})$, with $\mathbf{x} = (x_1, \ldots, x_n)$, is the potential energy landscape (PEL) of the corresponding physical or chemical system [1, 2]. The critical points of a PEL, defined by the solutions of the equations $\partial V(\mathbf{x})/\partial x_i = 0$ for $i = 1, \ldots, n$, provide important information about the landscape. These critical points, the stationary points (SPs) of the PEL, can be classified according to the number of negative eigenvalues of the Hessian matrix, $H_{i,j} = \partial^2 V(x)/\partial x_i \partial x_j$: the SPs with no negative eigenvalues are minima, and the SPs with exactly I negative eigenvalue are saddles of index I. SPs at which H has one or more additional zero eigenvalues to those determined by translational and rotational symmetry are called singular SPs, or non-Morse points.

Except for rare examples like the one-dimensional XY model [3] it is not usually possible to obtain the SPs analytically, and one has to rely upon computing numerical approximations. For a numerical approach, "solve" means "to compute a numerical approximation of the associated solutions." Once a numerical approximation is obtained, it is heuristically validated. Two standard approaches are to monitor iterations of Newton's method and to substitute the approximations into the equations to see if they are satisfied up to a chosen tolerance. Although such a validation usually works well in practice, it does not guarantee that the numerical approximation will indeed converge quadratically to the associated solutions using arbitrary precision. In other words, even if a numerical approximation is heuristically validated, it could correspond to a nonsolution at higher precision. Additionally, Newton iterations may have unpredictable behavior, such as attracting cycles and chaos, when applied to points that are not in a basin of attraction [4–7] of some solution.

If the given system is a set of polynomial equations, then one can use numerical polynomial homotopy continuation [8–18] to compute all the isolated solutions (see e.g. [19–21] for some related approaches). Numerical approximations of the isolated solutions are obtained and hence the aforementioned difficulties also arise.

A proper validation of a numerical approximation is termed *certification*, i.e., a verification that the given numerical approximation will converge quadratically to the nearby associated solution using arbitrary precision. Roughly speaking, quadratic convergence doubles the number of correct digits after each iteration, so that the associated solution can be approximated to a given accuracy efficiently. Starting in the 1980's, Smale and others developed a method that certifies a numerical approximation as an actual solution of the system [22]. For a given system of equations $f = 0$ and a given point x^*, one computes a number $\alpha(f, x^*)$ which, if it less than $\left(13 - 3\sqrt{17}\right)/4 \approx 0.157671$, guarantees that Newton's method starting from x^* will quadratically converge to a solution of $f = 0$. Applying this certification scheme, ensures that our numerical solutions are good enough so that more accurate approximations can be obtained easily and efficiently.

Smale's α-Theory: We summarize Smale's α-theory following Ref. [23], where we restrict ourselves to systems of equations that have the same number of equations as variables, termed square systems. We should also emphasize that Smale's α-theory is usually used to certify complex solutions for systems of polynomial equations, so we start with the key points of the theory for this case [22]. Since more can be said about real solutions, we will discuss them separately below, as well as generalizations to other types of nonlinear equations, such as the those involving exponentials and trigonometric functions.

For a system f of n multivariate polynomial equations in n variables, we denote the set of solutions of $f = 0$ as $\mathcal{V}(f) := \{\mathbf{z} \in \mathbb{C}^n | f(\mathbf{z}) = 0\}$ and the Jacobian of f at $\mathbf{x}$ as $J_f(\mathbf{x})$. Consider the Newton iteration of f starting at $\mathbf{x}$

[*]dbmehta@syr.edu
[†]hauenstein@ncsu.edu

defined by

$$N_f(\mathbf{x}) := \begin{cases} \mathbf{x} - J_f(\mathbf{x})^{-1} f(\mathbf{x}), & \text{if } J_f(\mathbf{x}) \text{ is invertible,} \\ \mathbf{x} & \text{otherwise.} \end{cases} \quad (1)$$

For $k \geq 1$, the k-th Newton iteration is simply

$$N_f^k(\mathbf{x}) := \underbrace{N_f \circ \cdots \circ N_f}_{k \text{ times}}(\mathbf{x}). \quad (2)$$

A point $\mathbf{x} \in \mathbb{C}^n$ is called an *approximate solution* of f with *associated solution* $\mathbf{z} \in \mathcal{V}(f)$ if, for each $k \geq 1$,

$$\left\| N_f^k(\mathbf{x}) - \mathbf{z} \right\| \leq \left(\frac{1}{2}\right)^{2^k - 1} \|\mathbf{x} - \mathbf{z}\|, \quad (3)$$

where $\|\cdot\|$ is the standard Euclidean norm on $\mathbb{C}^n$. In other words, $\mathbf{x}$ is an approximate solution to f if it is in the quadratic convergence basin defined by Newton's method of some solution $\mathbf{z}$. The key to Smale's α-theory, as shown in the following theorem, is a sufficient condition for proving that a given point is an approximate solution without knowledge about $\mathbf{z}$.

Theorem: If $\alpha(f, \mathbf{x}) < \left(13 - 3\sqrt{17}\right)/4$ for a square polynomial system f and point $\mathbf{x}$, then $\mathbf{x}$ is an approximate solution to f, where

$$\begin{aligned} \alpha(f, \mathbf{x}) &:= \beta(f, \mathbf{x})\gamma(f, \mathbf{x}), \\ \beta(f, \mathbf{x}) &:= \|J_f(\mathbf{x})^{-1} f(\mathbf{x})\|, \quad \text{and} \\ \gamma(f, \mathbf{x}) &:= \sup_{k \geq 2} \left\| \frac{J_f(\mathbf{x})^{-1} D^k f(\mathbf{x})}{k!} \right\|^{\frac{1}{k-1}}. \end{aligned} \quad (4)$$

In $\gamma(f, \mathbf{x})$, the term $D^k f(\mathbf{x})$ is the symmetric tensor whose components are the partial derivatives of f of order k. Additionally, for convenience, if at some $\mathbf{x} \in \mathcal{V}(f)$ where $J_f(\mathbf{x})$ is not invertible, then $\alpha(f, \mathbf{x}) := 0$, $\beta(f, \mathbf{x}) := 0$ and $\gamma(f, \mathbf{x}) := \infty$. If $\mathbf{x} \notin \mathcal{V}(f)$ such that $J_f(\mathbf{x})$ is not invertible, then $\alpha(f, \mathbf{x})$, $\beta(f, \mathbf{x})$ and $\gamma(f, \mathbf{x})$ are taken as ∞. Finally, if $\mathbf{x}$ is an approximate solution of f, then $\|\mathbf{x} - \mathbf{z}\| \leq 2\beta(f, \mathbf{x})$ where $\mathbf{z} \in \mathcal{V}(f)$ is the associated solution to $\mathbf{x}$.

We remark that since this theorem provides a sufficient condition for a point to be an approximate solution, the set of *certifiable* approximate solutions is generally much smaller than the set of approximate solutions. However, for a true approximate solution, a few Newton iterations usually generate a point that can be certified.

Given two approximate solutions $\mathbf{x}_1$ and $\mathbf{x}_2$, one often needs to verify that the corresponding associated solutions $\mathbf{z}_1$ and $\mathbf{z}_2$ are distinct. One way to show this uses the triangle inequality together with $\|\mathbf{x}_i - \mathbf{z}_i\| \leq 2\beta(f, \mathbf{x}_i)$.

Other Nonlinear Systems: The above theorem was actually proved with "polynomial" replaced by "analytic." However, we present it in this fashion since, in the polynomial case, $\gamma(f, \mathbf{x})$ is actually defined as a maximum over finitely many terms, since only finitely many partial derivatives can be nonzero. In fact, it can be bounded above based on the coefficients of f, the degree of the polynomials in f, and $J_f(\mathbf{x})$. Nonetheless, $\gamma(f, \mathbf{x})$ can also be bounded above for other nonlinear systems, in particular,

Table I. Convergence to $z = 1$ for $f(x) = x^4 - 1$ starting at $x = 1.1$.

k	1	2	3	4	5
$-\log_{10}\left(\|N_f^k(x) - z\|\right)$	1.89	3.62	7.06	13.94	27.70
$-\log_{10}\left(\|x - z\|/2^{2^k - 1}\right)$	1.30	1.90	3.11	5.52	10.33

Table II. Convergence to various roots for the 50-th Chebyshev polynomial of the first kind.

x^*	$\lim\limits_{k \to \infty} N_f^k(x^*)$
0.997	$x_2 = \cos(3\pi/100)$
0.9979	$x_3 = \cos(5\pi/100)$
0.99799	$x_5 = \cos(9\pi/100)$
0.997999	$x_6 = \cos(11\pi/100)$
0.998001	$x_6 = \cos(11\pi/100)$
0.99801	$x_9 = \cos(17\pi/100)$
0.9981	$x_1 = \cos(\pi/100)$
0.998	$x_6 = \cos(11\pi/100)$

systems of polynomial-exponential equations [24]. A system is polynomial-exponential if it is polynomial in both the variables $x_1, \ldots, x_n$ and finitely many exponentials of the form e^{ax_i} where $a \in \mathbb{C}$. Many standard functions such as $\sin(x)$, $\cos(x)$, $\sinh(x)$, and $\cosh(x)$ can be formulated as systems of polynomial-exponential functions since they are indeed polynomial functions of e^{ax} for suitable $a \in \mathbb{C}$.

Real Solutions: For a square system f such that N_f defines a real map, i.e. $N_f(\mathbf{x})$ is real whenever $\mathbf{x}$ is real, then Smale's α-theory can be extended to provide more information about real solutions [23]. For potential energy landscapes, when the potential energy function $V(\mathbf{x})$ is real for real $\mathbf{x}$, the corresponding Newton iteration is always a real map. In this case, one can determine the reality of the associated solution $\mathbf{y}$ from any approximate solution $\mathbf{x}$. If $\mathbf{x}$ is real, then $\mathbf{y}$ must also be real. However, if $\mathbf{x}$ is not real, one can show that $\mathbf{y}$ is real by showing that $\mathbf{x}$ and its real part, namely $(\mathbf{x} + \bar{\mathbf{x}})/2$ where $\bar{\mathbf{x}}$ is the conjugate of $\mathbf{x}$, have the same associated solution, namely $\mathbf{y}$. To show that $\mathbf{y}$ is not real, one simply has to verify that $\mathbf{x}$ and its conjugate $\bar{\mathbf{x}}$ have distinct associated solutions, namely $\mathbf{y}$ and $\bar{\mathbf{y}}$, since $\|\mathbf{x} - \mathbf{y}\| \leq 2\beta(f, \mathbf{x})$ via the triangle inequality.

We use a recently developed practical implementation of the α-theory, called **alphaCertified**, for certifying solutions to systems of equations [23, 24]. When using exact rational arithmetic, the implementation of α-theory in **alphaCertified** is rigorous and can be taken as a *mathematical proof of the computed results*. Hence, this approach provides an alternative to other analytic or symbolic computations. The algorithms are also implemented in arbitrary precision floating point arithmetic in **alphaCertified**, which provides certified results up to round-off errors. We also emphasise that the procedure of certifying the solutions is completely parallelizable.

An Illustrative Example: As a demonstration of computing $\alpha(f, x)$, $\beta(f, x)$, and $\gamma(f, x)$ for a single coordinate, consider the univariate polynomial $f(x) = x^4 - 1$. In this simple case, we can actually compute these quantities as a function of a variable x rather than at a specific value. We will assume $x \neq 0$ since $f'(x) = 4x^3$ is zero if and only if $x = 0$ and $f(0) \neq 0$. Clearly, $\beta(f, x) = |x - x^{-3}|/4$.

Now, in the univariate case, the term $D^k f(x)$ in $\gamma(f,x)$ is simply the k-th derivative of f at x, i.e., $f^{(k)}(x)$. Since f has degree 4, we only need to take the maximum over $k = 2, 3, 4$ to compute $\gamma(f,x)$. One can easily verify that the maximum is attained at $k = 2$ with $\gamma(f,x) = 3|x^{-1}|/2$. Thus, $\alpha(f,x) = 3|1-x^{-4}|/8$ for any $x \neq 0$. For example, $\alpha(f, 2.5) = 0.3654$ so that $x = 2.5$ cannot be certified as an approximate solution, and $x = 2.5$ is indeed outside all the quadratic convergence basins. However, since $\alpha(f, 1.1) = 0.11887$, $x = 1.1$ is certifiably an approximate solution of $f = 0$. In this case, we know that the associated solution is $z = 1$, and Table I confirms the quadratic convergence for a few iterations.

Example With Close Roots: The n-th Chebyshev polynomial of the first kind has n roots between -1 and 1. These roots, called Chebyshev nodes, are located at $x_i = \cos[(2i-1)\pi/2n]$ for $i = 1, \ldots, n$. We can use this example to demonstrate how small perturbations in a numerical approximation can change the root that Newton's method converges to. This chaotic behavior can be avoided using certification. In particular, Table II considers selected values where $f(x) = \cos(50 \cos^{-1} x)$ is the 50-th Chebyshev polynomial of the first kind.

Müller-Brown Surface: The Müller-Brown surface [25] is a well-known model landscape [26–29]. It is defined as

$$V(x,y) = \sum_{i=1}^{4} A_i \exp(a_i(x-x_i^0)^2$$
$$+ b_i(x-x_i^0)(y-y_i^0) + c_i(y-y_i^0)^2), \quad (5)$$

where

$$
\begin{aligned}
A &= (-200, -100, -170, 15), & a &= (-1, -1, -6.5, 0.7), \\
b &= (0, 0, 11, 0.6), & c &= (-10, -10, -6.5, 0.7), \\
x^0 &= (1, 0, -0.5, -1), & y^0 &= (0, 0.5, 1.5, 1).
\end{aligned}
\quad (6)
$$

Since $\nabla V = [\partial V/\partial x, \ \partial V/\partial y]$ involves polynomials as exponents, we simply add new variables to produce an equivalent polynomial-exponential form as

$$
f(x, y, z_1, \ldots, z_4, w_1, \ldots, w_4) =
\begin{bmatrix}
\sum_{i=1}^{4} A_i w_i (2a_i(x-x_i^0) + b_i(y-y_i^0)) \\
\sum_{i=1}^{4} A_i w_i (b_i(x-x_i^0) + 2c_i(y-y_i^0)) \\
a_i(x-x_i^0)^2 + b_i(x-x_i^0)(y-y_i^0) + c_i(y-y_i^0)^2 - z_i \\
\exp(z_i) - w_i, i = 1, \ldots, 4
\end{bmatrix}.
\quad (7)
$$

Given (x,y), we obtain values of z_i and w_i based on the last eight functions in f and then try to certify the result. In particular, Table III presents five numerical approximations of SPs along with an upper bound on the value of $\alpha(f, \cdot)$ and an approximation of $\beta(f, \cdot)$.

Based on the upper bounds on $\alpha(f, \cdot)$ computed by **alphaCertified**, each point is indeed an approximate solution. The bounds on the distance from each numerical approximation to the corresponding approximate solution based on $\beta(f, \cdot)$ show that they correspond to distinct SPs. Thus, we have *proved* that the five numerical approximations are indeed in the quadratic convergence basin of distinct SPs.

Table III. Five stationary points of the Müller-Brown potential and the corresponding α and β.

x	y	upper bound of $\alpha(f, \cdot)$	approximation of $\beta(f, \cdot)$
-0.5582236346	1.441725842	0.0140	$4.84 \cdot 10^{-9}$
0.6234994049	0.02803775853	0.0460	$1.94 \cdot 10^{-9}$
0.212486582	0.2929883251	0.0437	$3.05 \cdot 10^{-9}$
-0.8220015587	0.6243128028	0.0006	$6.94 \cdot 10^{-10}$
-0.050010823	0.4666941049	0.0068	$2.89 \cdot 10^{-9}$

Table IV. Summary of α, β, and γ for the known LJ_N clusters.

N	number of points	maximum upper bound of $\alpha(f_N, \cdot)$	maximum $\beta(f_N, \cdot)$	maximum upper bound of $\gamma(f_N, \cdot)$	minimum pairwise distance
7	16	$6.82 \cdot 10^{-19}$	$1.03 \cdot 10^{-28}$	$1.01 \cdot 10^{10}$	0.4354
8	50	$2.03 \cdot 10^{-19}$	$1.28 \cdot 10^{-28}$	$1.60 \cdot 10^{9}$	0.4268
9	186	$3.55 \cdot 10^{-17}$	$1.77 \cdot 10^{-27}$	$5.46 \cdot 10^{10}$	0.0559
10	699	$2.86 \cdot 10^{-14}$	$3.94 \cdot 10^{-24}$	$9.87 \cdot 10^{10}$	0.0600
11	2594	$6.40 \cdot 10^{-15}$	$2.80 \cdot 10^{-26}$	$6.04 \cdot 10^{11}$	0.0556
12	9122	$1.05 \cdot 10^{-9}$	$1.63 \cdot 10^{-21}$	$4.28 \cdot 10^{12}$	0.0093
13	30265	$2.48 \cdot 10^{-12}$	$2.84 \cdot 10^{-23}$	$2.16 \cdot 10^{13}$	0.0081
14	91415	$4.54 \cdot 10^{-8}$	$1.50 \cdot 10^{-19}$	$3.58 \cdot 10^{14}$	0.0087

Lennard-Jones Clusters: We now consider atomic clusters of N atoms bound by the Lennard-Jones potential [30], denoted LJ_N. The pairwise potential between interacting particles is defined as

$$V_N = 4\epsilon \sum_{i=1}^{N} \sum_{j=i+1}^{N} \left[\left(\frac{\sigma}{r_{i,j}}\right)^{12} - \left(\frac{\sigma}{r_{i,j}}\right)^{6} \right], \quad (8)$$

where ϵ is the pair well depth, $2^{1/6}\sigma$ is the equilibrium pair separation, and

$$r_{i,j} = \sqrt{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2}. \quad (9)$$

For convenience, we take $\epsilon = 1/4$ and $\sigma = 1$. Since V_N only depends upon the pairwise distances, the set of SPs is invariant under overall translation and rotation. Thus, we fix

$$x_1 = y_1 = z_1 = y_2 = z_2 = z_3 = 0. \quad (10)$$

Now, to construct a polynomial system equivalent to $\nabla V_N = \mathbf{0}$, we add variables $R_{i,j}$ with polynomial equations

$$R_{i,j} \left((x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2 \right) = 1. \quad (11)$$

That is, $R_{i,j} = 1/r_{i,j}^2$ so that $V_N = \sum_{i<j} \left(R_{i,j}^6 - R_{i,j}^3 \right)$. For simplicity, we define $R_{i,j} = R_{j,i}$ for $i \neq j$. Hence, for the SPs, we consider the polynomial system

$$
f_N(\mathbf{x}, \mathbf{y}, \mathbf{z}, R_{i,j}) =
\begin{bmatrix}
\sum_{j \neq i} 6R_{i,j}^4 \left(2R_{i,j}^3 - 1\right)(x_j - x_i), i = 2, \ldots, N \\
\sum_{j \neq i} 6R_{i,j}^4 \left(2R_{i,j}^3 - 1\right)(y_j - y_i), i = 3, \ldots, N \\
\sum_{j \neq i} 6R_{i,j}^4 \left(2R_{i,j}^3 - 1\right)(z_j - z_i), i = 4, \ldots, N \\
R_{i,j} \left((x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2\right) - 1, i < j
\end{bmatrix}.
\quad (12)
$$

An extensive search for minima and saddle points was carried out in [29] for this model up to $N = 13$, along with

a corresponding search for minima and saddles of index one (transition states) for $N = 14$ in [31]. All of the minima and transition states, available for download at http://doye.chem.ox.ac.uk/networks/LJn.html, were obtained using numerical methods.

To certify these solutions, we first translated and rotated each one so that condition (10) holds, and then computed $R_{i,j}$ based on (11). The downloaded points are provided to 10 decimal places, and many of them were *not* certifiable. We performed two Newton iterations using 96-bit precision to improve both the precision and accuracy so that (10) and (11) hold. Finally, using the resulting points, we employed **alphaCertified** to compute upper bounds on $\alpha(f_N, \cdot)$, which we summarize in Table IV. In particular, this table shows that, for $N = 7, \ldots, 14$, each numerical approximation of the minima and transition states does indeed correspond to a certified approximate solution. For $N = 14$, the values of $\lceil \log_{10} \gamma(f_{14}, \cdot) \rceil$ for the minima and transition states suggest that we should use numerical approaches that approximate the coordinates of each stationary point to at least 15 decimal places. Hence, certification can also provide insight into convergence conditions, which hitherto have been chosen based on physical intuition.

Since we performed two Newton iterations prior to certification, we need to perform an *a posteriori* verification that we still have distinct solutions. This was accomplished using the triangle inequality, as discussed above, with the maximum value of $\beta(f_N, \cdot)$ and the minimum pairwise distance between the x, y, z coordinates of the approximations. To summarize, Table IV *proves* that the numerically approximated SPs are indeed in the quadratic convergence basin of distinct SPs.

Conclusions: Approximate numerical solutions obtained from standard non-linear optimization methods may lie in the linear convergence basin, or even in a chaotic region, instead of the desired quadratic region of convergence. Hence, the numerical approximation may turn out to be a non-solution of the system when more Newton iterations are performed, which could fundamentally change the scientific conclusions. We have demonstrated several examples of such behaviour. To mitigate such problems, we show how Smale's α-theory can be used to certify that a numerical approximation is in the quadratic convergence region of a solution, to determine if two points correspond to distinct solutions, and to determine if the corresponding solution is real. Moreover, the procedure for certifying the solutions is completely parallelizeable. As a practical demonstration of the approach, we have refined and then certified all the known minima and transition states for the Lennard-Jones potential for up to 14 atoms. This is the first certification conducted for a set of physically relevant atomic structures that we are aware of, and it provides quantitative convergence criteria for geometry optimization. We also observe that for the stationary points of the Lennard-Jones potential, the size of the quadratic convergence basin decreases as N increases. These new insights should be applicable throughout molecular science and studies of soft and condensed matter, wherever stationary points are considered to analyze structure, dynamics and thermodynamic properties.

[1] D. J. Wales, *Energy Landscapes*, Cambridge University Press, 2004.
[2] M. Kastner, Rev. Mod. Phys. **80**, 167 (2008).
[3] D. Mehta and M. Kastner, Annals Phys. **326**, 1425 (2011).
[4] P. G. Mezey, Theo. Chim. Acta **58**, 309 (1981).
[5] P. G. Mezey, *Potential Energy Hypersurfaces*, Elsevier, Amsterdam, 1987.
[6] D. J. Wales, J. Chem. Soc. Faraday Trans. **88**, 653 (1992).
[7] D. J. Wales, J. Chem. Soc. Faraday Trans. **89**, 1305 (1993).
[8] D. Mehta, Ph.D. Thesis, The Uni. of Adelaide, Australasian Digital Theses Program (2009).
[9] D. Mehta, A. Sternbeck, L. von Smekal, and A. G. Williams, PoS **QCD-TNT09**, 025 (2009).
[10] D. Mehta, Phys.Rev. **E (R) 84**, 025702 (2011).
[11] D. Mehta, Adv.High Energy Phys. **2011**, 263937 (2011).
[12] M. Kastner and D. Mehta, Phys.Rev.Lett. **107**, 160602 (2011).
[13] M. Maniatis and D. Mehta, Eur.Phys.J.Plus **127**, 91 (2012).
[14] D. Mehta, Y.-H. He, and J. D. Hauenstein, JHEP **1207**, 018 (2012).
[15] C. Hughes, D. Mehta, and J.-I. Skullerud, (2012).
[16] D. Mehta, J. D. Hauenstein, and M. Kastner, Phys.Rev. **E85**, 061103 (2012).
[17] Y.-H. He, D. Mehta, M. Niemerg, M. Rummel, and A. Valeanu, (2013).
[18] A. J. Sommese and C. W. Wampler, *The numerical solution of systems of polynomials arising in Engineering and Science*, World Scientific Publishing Company, 2005.
[19] K. Kowalski and K. Jankowski, Phys. Rev. Lett. **81**, 1195 (1998).
[20] A. J. W. Thom and M. Head-Gordon, Phys. Rev. Lett. **101**, 193001 (2008).
[21] L. Piela, J. Kostrowicki, and H. A. Scheraga, J. Phys. Chem. **93**, 3339 (1989).
[22] L. Blum, F. Cucker, M. Shub, and S. Smale, *Complexity and real computation*, Springer-Verlag, New York, 1998, With a foreword by Richard M. Karp.
[23] J. D. Hauenstein and F. Sottile, ACM TOMS **38**, 28 (2012).
[24] J. D. Hauenstein and V. Levandovskyy, arXiv:1109.4547 (2011).
[25] K. Müller and L. Brown, Theoretica Chimica Acta **53**, 75 (1979).
[26] J.-Q. Sun and K. Ruedenberg, J. Chem. Phys. **98**, 9707 (1993).
[27] J.-Q. Sun and K. Ruedenberg, J. Chem. Phys. **100**, 1779 (1994).
[28] D. J. Wales, J. Chem. Phys. **101**, 3750 (1994).
[29] J. P. K. Doye and D. J. Wales, J. Chem. Phys. **116**, 3777 (2002).
[30] J. E. Jones and A. E. Ingham, Proc. Roy. Soc. London A **107**, 636 (1925).
[31] J. P. K. Doye and C. P. Massen, J. Chem. Phys. **122**, 084105 (2005).