Using Hessian update formulae to construct modified Shepard interpolated potential energy surfaces: Application to vibrating surface atoms

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Using Hessian update formulae to construct modified Shepard interpolated potential energy surfaces: Application to vibrating surface atoms

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Modified Shepard interpolation based on second order Taylor series expansions has proven to be a flexible tool for constructing potential energy surfaces in a range of situations. Extending this to gas–surface dynamics where surface atoms are allowed to move represents a substantial increase in the dimensionality of the problem, reflected in a dramatic increase in the computational cost of the required Hessian (matrix of second derivatives) evaluations. This work demonstrates that using approximate Hessians derived from well known Hessian update formulae and a single accurate Hessian can provide an effective way to avoid this expensive accurate Hessian determination. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4868637]

I. INTRODUCTION

There has been sustained development in the application of electronic structure theory to calculating the energies of molecular and condensed phase systems over the past 50 years. Nonetheless, an enduring problem is how to use the results of such calculations in realistic atomistic simulations of the dynamics of the system. Even within the simplest Born-Oppenheimer approximation, a continuous representation of the potential energy surface (PES) as a function of atomic coordinates is usually required. Electronic structure theory calculations almost universally provide PES information only at a single point.

Many methods have been developed to construct continuous PESs from discrete calculated PES data. A suitable continuous functional form can be fit to the sampled data.[1–3] A neural network representation is a special case of this approach.[4–6] Cluster, "*n*-mode" or reproducing kernel Hilbert space expansions[7–9] can be used, or the potential energy data can be interpolated with multidimensional splines or other styles of interpolation.[10–13] A method of the latter type that has been used in a range of scenarios is a modified Shepard interpolation, in which the "global" representation of the PES is an interpolating weighted sum of (usually) second order Taylor series expansions around scattered geometries.

A modified Shepard interpolation of PES data was used in the pioneering work of Ischtwan and Collins[14] to develop an automated procedure to build PESs for bi-molecular reactions using classical dynamics. Termed *Grow*, the procedure has proven reliable and flexible.[15] The PESs are constructed specifically for classical molecular dynamics, but quantum calculations can equally be performed on these PESs.[16,17] Methods are also being developed for sampling based on quantum dynamics.[18,19]

Modified Shepard interpolation and the *Grow* procedure have been generalised to describe gas–surface reactions in at least three formalisms. In one implementation, the solid surface atoms were treated as an extension of the gas phase description.[20] More recent work uses systematic molecular fragmentation to express the gas–surface PES as a sum of fragment PESs,[21] or constructs a custom set of coordinates to take more explicit account of the symmetry present in gas–surface interactions.[22]

A desirable extension of the work on interpolating gas–surface PESs would be to incorporate the effect of motion of the surface atoms explicitly. In principle, one could incorporate coordinates describing surface atom motion with appropriate consideration of the symmetry of the system. There are a number of ways in which this could be done, such as using coordinates to describe specific phonons or by allowing certain atoms to move independently with Cartesian coordinates for each.

Allowing a useful range of solid surface vibrational modes would require explicit consideration of a supercell of the surface lattice. However, this presents a practical difficulty. Electronic structure theory calculations describing gas–surface interactions, particularly with metal surfaces, are currently performed almost exclusively using periodic density functional theory (DFT). Available codes for performing periodic DFT calculations do not allow the calculation of second derivatives of the energy analytically. Thus, the second derivative matrix (known as the Hessian) that is required to construct a second order Taylor series expansion around a geometry must be calculated by a finite difference of the first derivatives or energies, performing a series of DFT calculations with each coordinate stepped up and down. For example, accurately calculating the required Hessian for a diatomic interacting with a static surface from forces requires 12 additional DFT calculations to be performed, two for each degree of freedom. For a diatomic interacting with a metal surface in which one surface atom is allowed to move in each surface unit cell, calculating the full Hessian for a 3×3 supercell by differencing requires 66 additional DFT calculations. When combined with the likelihood that the higher dimensional domain of the PES would require an increase in the number of points required to converge the interpolated PES, and the fact

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that often more than one surface atom per unit cell should be allowed to move,[23] the additional computational time required to calculate the Hessian by finite difference becomes problematic. The general unavailability of analytic second derivatives in periodic DFT programs will continue for the foreseeable future.

Experience in interpolating molecular PESs suggests that neglecting the second order term of the Taylor series does not offer a solution.[24] However, interpolating between second order Taylor series expansions using imprecise Hessians has been successful in particular contexts.[25,26] This suggests the question to be addressed in this work: Can we construct a useful modified Shepard interpolation for PESs using a computationally convenient approximation for the Hessian of surface atom degrees of freedom?

The field of nonlinear optimisation provides a rich set of methods for estimating Hessian information without explicitly evaluating second derivatives. The quasi-Newton or variable metric methods, in particular, define useful means of accumulating Hessian information from the gradients of a function calculated at a number of different points in a high dimensional domain. Developed from the 1950s,[27] these methods start from an estimate of the Hessian at a starting point (which does not need to be accurate) and update the Hessian as the optimisation algorithm proceeds toward the desired minimum of the target function. Often, the Hessian approximation converges to the true Hessian at the function minimum.

In this work, we turn that process around. Starting from a known minimum of a potential function and the Hessian at that point, can we use Hessian update formulae to construct approximations to the Hessian at points displaced from the minimum that are useful in constructing modified Shepard interpolations?

II. FORMALISM

Loosely, the modified Shepard interpolation of a potential function as a function of atomic coordinates $\mathbf{x}$, including symmetry, is given by[14,15,22,28]

$$V_{\text{interp}}(\mathbf{x}) = \sum_i \sum_{g\in G} w_{(g\circ i)}(\mathbf{x})\, T_{(g\circ i)}(\mathbf{x}), \tag{1}$$

where the sum over i sums over all known *data points* where the potential energy and its derivatives have been calculated, $\{\mathbf{x}_{(i)}\}$. G represents the set of symmetry operations to be applied under which the potential is invariant, with $g\circ i$ indicating that the quantity for data point i is to be transformed according to the symmetry element g. T are the Taylor series expansions

$$T_{(i)}(\mathbf{x}) = E_{(i)} + \Delta\mathbf{E}^T_{(i)}(\mathbf{x}-\mathbf{x}_{(i)}) + \frac{1}{2}(\mathbf{x}-\mathbf{x}_{(i)})^T B_{(i)}(\mathbf{x}-\mathbf{x}_{(i)}) \tag{2}$$

in which $E_{(i)}$, $\Delta\mathbf{E}_{(i)}$, and $B_{(i)}$ are the potential energy, its gradient and Hessian, respectively, evaluated at $\mathbf{x}_{(i)}$. Finally, the w in Eq. (1) are the interpolating weight functions. In this work, we use the simple weight functions

$$w_{(g\circ i)}(\mathbf{x}) = \frac{\nu_{(g\circ i)}(\mathbf{x})}{\sum_j \sum_{h\in G} \nu_{(h\circ j)}(\mathbf{x})} \tag{3}$$

with

$$\nu_{(i)}(\mathbf{x}) = \|\mathbf{x}-\mathbf{x}_{(i)}\|^{-2p} \tag{4}$$

and $p > 0$. In *Grow* parlance, this is a "1-part" weight function.[29]

Three Hessian update formulae commonly used in quasi-Newton optimisation algorithms[30] are used in this work. Given a gradient $\mathbf{g}$ and Hessian matrix B at a point $\mathbf{x}$ and a gradient $\mathbf{g}'$ at a point $\mathbf{x}'$, for convenience we define

$$\boldsymbol{\delta} = \mathbf{x}' - \mathbf{x}, \tag{5}$$

$$\boldsymbol{\gamma} = \mathbf{g}' - \mathbf{g}, \tag{6}$$

and

$$\boldsymbol{\epsilon} = \boldsymbol{\gamma} - B\boldsymbol{\delta}. \tag{7}$$

We can then approximate the Hessian at point $\mathbf{x}'$ using the symmetric rank one update given by

$$B'_{\text{SR1}} = B + \frac{1}{\boldsymbol{\epsilon}^T\boldsymbol{\delta}}\boldsymbol{\epsilon}\boldsymbol{\epsilon}^T, \tag{8}$$

the Powell update given by

$$B'_{\text{Powell}} = B + \frac{1}{\boldsymbol{\delta}^T\boldsymbol{\delta}}(\boldsymbol{\epsilon}\boldsymbol{\delta}^T + \boldsymbol{\delta}\boldsymbol{\epsilon}^T) - \frac{\boldsymbol{\epsilon}^T\boldsymbol{\delta}}{(\boldsymbol{\delta}^T\boldsymbol{\delta})^2}\boldsymbol{\delta}\boldsymbol{\delta}^T \tag{9}$$

or the Broyden-Fletcher-Goldfarb-Shanno (BFGS) update given by

$$B'_{\text{BFGS}} = B + \frac{1}{\boldsymbol{\delta}^T\boldsymbol{\gamma}}\boldsymbol{\gamma}\boldsymbol{\gamma}^T - \frac{1}{\boldsymbol{\delta}^T B\boldsymbol{\delta}} B\boldsymbol{\delta}\boldsymbol{\delta}^T B. \tag{10}$$

In the context of a central point where the Hessian is known and a cluster of points around this central point where the Hessian is to be estimated, these update formulae can be applied in a number of ways. Three methods are applied in this work: the "from centre" scheme where the update formulae are applied to infer the Hessian at each point directly from the central point, the "from nearest" scheme in which the Hessians are propagated outward from the central point, using the update formulae only between points where the Hessian is known or has already been approximated and the nearest points, and the "weighted" scheme where Hessians are propagated outward using update formulae for all known or already approximated Hessians in a weighted sum with distance-based weight functions similar to those of Eqs. (3) and (4). If data points are added sequentially (as would be the case in the *Grow* procedure), the second and third of these schemes would require reassessment of the Hessians for all previous points when data points are added, as new points will often be closer to the central point (where the Hessian is known precisely) than previous points.

Two test potentials have been used to test the utility of these updates for modified Shepard interpolation. The first

was a simple two-dimensional function composed of coupled quartic and Morse potential terms,

$$V_2 = 0.7(1.9x^2 + 1.65x^4) + [1.17 - 0.7(1.9x^2 + 1.65x^4)](1 - e^{1.03(z+1.5z^2)}). \quad (11)$$

The second was designed to represent a lattice of surface atoms. A 3 × 3 grid of atoms arranged in a two-dimensional hexagonal lattice with a lattice parameter of 6 was considered explicitly, with each atom allowed to move in three dimensions. Thus, the potential energy was a function of 27 degrees of freedom. The potential was comprised of a sum of anharmonic vibrational terms centred on the equilibrium position of each of the nine atoms and Lennard-Jones potentials between each atom and its six nearest neighbours in the lattice, treated periodically in x and y

$$V_{27} = \sum_{i=1}^{9} \left\{ 0.015\left|x_i^2+y_i^2\right| + 0.05\left(x_i^2+y_i^2\right)^2 + \frac{1}{3}(1-e^{-z/3})^2 + 0.05 \sum_{j\in\mathcal{N}_i} \left[\left(\frac{6}{r_{ij}}\right)^{12} - 2\left(\frac{6}{r_{ij}}\right)^{6} \right] \right\}, \quad (12)$$

where x_i, y_i, and z_i are the displacements of the ith atom from its equilibrium lattice position, the sets $\mathcal{N}_i$ contain the identities of the six nearest neighbours to atom i, and r_{ij} is the distance from atom i to atom j under the minimum image convention.

III. RESULTS

In this work, the utility of the modified Shepard interpolation using Hessian update formulae was tested in three ways.

A. Optimal interpolation of V_2

The first test was for an interpolation of V_2. An energy parameter Λ defines a domain $\mathcal{D}_\Lambda$ in which $V_2 \leq \Lambda$. With a fixed number of data points n defining the interpolated potential V_{interp}, the function

$$f_\Lambda = \max_{(x,z)\in\mathcal{D}_\Lambda} (|V_{\text{interp}} - V_2|) \quad (13)$$

was minimised with respect to the coordinates of the n data points $(x_i, z_i) \in \mathcal{D}_\Lambda$. The simulated annealing implementation of Goffe *et al.*[31] was used to perform the minimisation. Minimisations were carried out for a range of values of Λ and n.

Tests were conducted for the interpolated potential V_{interp} being constructed with different approaches based on Eqs. (1)–(4), with $p = 4$. In all cases, one data point was located at the potential minimum position at the origin, whose second order Taylor series expansion was constructed using the correct, analytic Hessian evaluated at that point. The remaining $n - 1$ data points were treated with six different approaches, namely:

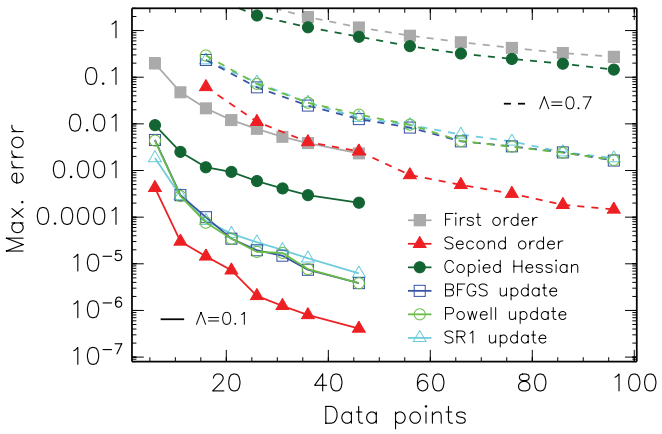

FIG. 1. Optimum values of f_Λ [Eq. (13)] as a function of the number of data points for $\Lambda = 0.1$ and $\Lambda = 0.7$ using six different interpolation schemes (see text). Symbols representing calculations are connected by straight lines.

1. second order Taylor series expansions using analytic Hessians;
2. first order Taylor series expansions, neglecting the second order term of Eq. (2);
3. second order Taylor series expansions using Hessians approximated from that at the origin by the rank one formula, Eq. (8);
4. second order Taylor series expansions using Hessians approximated from that at the origin by the Powell formula, Eq. (9);
5. second order Taylor series expansions using Hessians approximated from that at the origin by the BFGS formula, Eq. (10);
6. second order Taylor series expansions using the Hessian evaluated at the origin as the Hessian everywhere.

The $n - 1$ data points were replicated according to the $V_2(x, z) = V_2(-x, z)$ symmetry of V_2.

The optimum values of f_Λ (the maximum absolute interpolation error) are shown in Figure 1 for $\Lambda = 0.1$ and $\Lambda = 0.7$. Consistent with previous work,[24] using mostly first order Taylor series expansions for the modified Shepard interpolation gave a maximum interpolation error several orders of magnitude larger than using second order Taylor series expansions. Using the Hessian from the potential minimum everywhere did improve the interpolation error (at no significant computational cost), but still fell several orders of magnitude short of the performance of the second order expansions.

Using one of the three Hessian update formulae reduced the interpolation error substantially, generally to within an order of magnitude of the full second order expansion result. The three Hessian update formulae performed approximately equivalently.

B. 3 × 3 lattice: Defined path

The second test was for an interpolation of the two-dimensional periodic lattice potential V_{27}. A continuous predefined path was devised starting and finishing at the origin, passing through a number of random points and high symmetry points in the 27-dimensional space describing the

locations of the lattice atoms. Along this path V_{27} varied from its minimum at −2.7 up to a maximum of −1.74. The energies along this path were calculated for a modified Shepard interpolation, initially using only a data point with an accurate Hessian at the origin. Subsequently, the point of maximum deviation between V_{interp} and V_{27} along this path was determined, and a data point added at that location. This can be considered to be an idealised simulation of the *Grow* procedure, as the point of maximum error would be an attractive geometry to add in *Grow* were it to be identifiable. Points were added until the maximum deviation between V_{interp} and V_{27} was smaller than 0.005 (0.5% of the energy range along the path).

The six interpolation schemes described in Sec. III A were used in this test. The update formulae were used in the three different modes described in Sec. II, being directly from the central potential minimum data point, propagated from the nearest already known Hessian, or propagated in a weighted average update from all nearby known Hessians.

For simplicity in this proof of principle work only a subset of the symmetries present in V_{27} were implemented for the g sum of Eq. (1), being the translational symmetry of the underlying lattice. Thus, a displacement of one of the nine atoms in the lattice is exactly equivalent in the interpolated PES to a similar displacement (in the same direction) of any of the other atoms. Other symmetries of the appropriate hexagonal plane group (accounting for equivalent displacements in different directions) were not implemented.

General features of the energetics and interpolations along this predefined path are shown in Figure 2. As V_{27} is a concave function in the region being examined, errors in the interpolation using first order Taylor series expansions always underestimated the value of the function. On the scale of the plot in Figure 2 an interpolation based on 12 data points and second order Taylor series expansions reproduced the potential profile well, whether the Hessian was evaluated analytically or by using an update formula from the potential minimum.

Figure 3 examines the performance of the modified Shepard interpolation schemes in more detail. Plotted is the mean absolute interpolation error along the predefined path as a function of the number of data points, for the various interpolation schemes tested. Data points were added until the maximum absolute interpolation error dropped below 0.005.

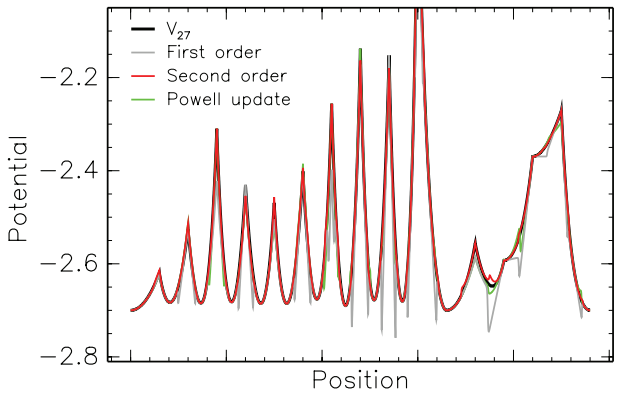

FIG. 2. V_{27} along the predefined test path as well as the 12 data point interpolations using first order, correct second order, and Powell-updated Taylor series expansions.

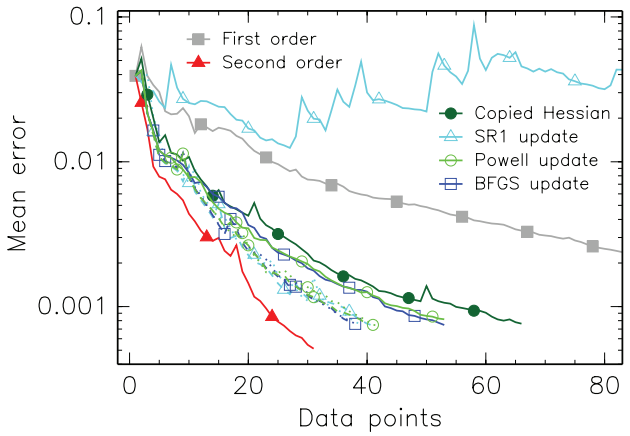

FIG. 3. The average error along the predefined path under a range of interpolation schemes for V_{27}. Hessian update formulae applied from the central point (solid lines), from the nearest available Hessian (dashed lines) and as a weighted sum of available Hessians (dotted lines).

Extending beyond the range shown in Figure 3, an interpolation based on first order Taylor series expansions required 140 points to achieve the 0.005 maximum error criterion. Approximating Hessians with the symmetric rank one formula from the central point was not continued beyond 100 data points due its apparent instability.

Like in the previous example, using first order Taylor series expansions exhibited the worst convergence and the standard second order interpolation the best, with using the Hessian from the potential minimum copied for all data points providing intermediate performance. Estimating Hessians with the BFGS or Powell formulae determining the unknown Hessians from the central potential minimum point directly ("From centre") gave somewhat smaller interpolation errors than simply copying the potential minimum Hessian. Using the update formulae to estimate Hessians sequentially, either propagating outward from centre to the nearest point ("From nearest") or using a number of estimates in a distance weighted scheme ("Weighted") gave errors that were substantially smaller still. Little difference was observed in the performance of the sequential update schemes. Notably, this included the symmetric rank one formula, despite the non-convergence of applying this update from the central point.

C. 3 × 3 lattice: Classical trajectory

The *Grow* procedure is usually applied by monitoring dynamical results as data points are added to the interpolation of the potential function.[15] Thus, it is desirable to test the utility of the Hessian update formulae in a similar manner. In the context of vibrational motion of surface atoms, there is not a single dynamical quantity that is easily monitored in the same way as, for example, the reaction probability in a reactive system. Instead, a classical trajectory was calculated for a short time on the interpolated PES, using the error in the interpolated PES along the trajectory to select points akin to the dynamics-guided sampling used for *Grow*.

Being subject to classical mechanics, changes to the PES caused by adding data points to the modified Shepard interpolation could lead to the trajectory exploring completely different regions of configuration space than under the PES from the interpolation without those data points. To allow convergence in an easily manageable number of data points, for this proof of principle calculation the length of the trajectory was progressively extended, adding data points until the maximum error was small between extensions. Note that the maximum interpolation error increased dramatically when the trajectory was extended to longer time, as the trajectory explored new regions far from the existing data points.

For the dynamics, the value of the potential function V_{27} was interpreted as electron volts and the atoms were taken to have a mass of 60 u, approximately the mass of nickel. The resulting dynamics explored the PES over a range of a little over 0.4 eV, or around 5000 K.

Using second order Taylor series expansion in the modified Shepard interpolation of V_{27} achieved the desired accuracy along the entire trajectory with 80 data points, as shown in the upper panel of Figure 4. Using a first order Taylor series expansion everywhere except the potential minimum did not yield satisfactory results, with errors around 0.002 from a 700 point interpolation along only three quarters of the desired trajectory length. Copying the potential minimum Hessian to all points performed remarkably well, giving the desired accuracy with around 200 data points (second panel, Figure 4).

The Powell and BFGS update formulae, applied either from the nearest assigned data point or through weighted updates, also performed well. The lower panels of Figure 4 show the best (BFGS from nearest points) and worst (weighted Powell update) combinations. Using the BFGS update converged substantially faster than the Powell update. Nonetheless, even the worst case achieved the desired accuracy with about three times the number of data points as the second order case using accurate Hessians.

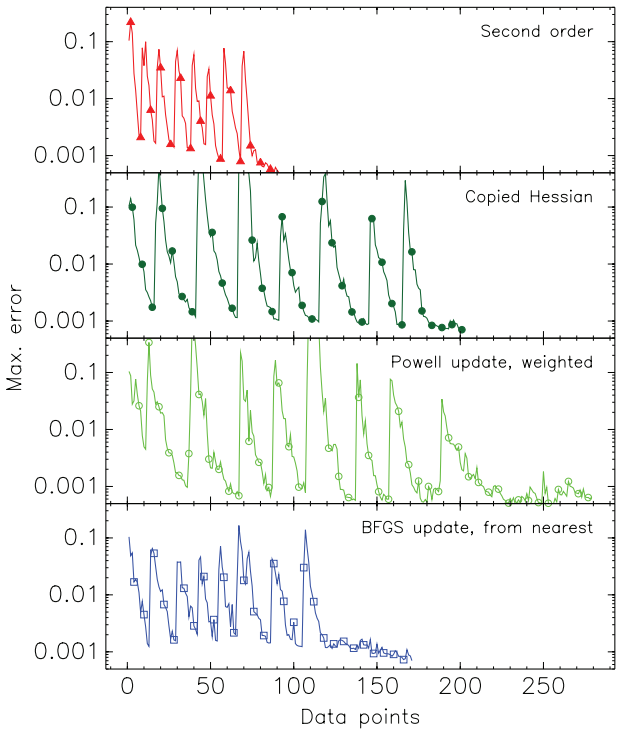

FIG. 4. The maximum error along a trajectory under a range of interpolation schemes for V_{27}. Spikes in the interpolation error generally coincide with extending the trajectory to longer times.

The symmetric rank one update performed poorly in this test. Although the errors along the early parts of the trajectory could be made small, longer trajectories proved very unstable on adding data points. Overall, the symmetric rank one update was even less effective in this context than using only first order expansions, irrespective of which Hessian propagation scheme was used.

IV. DISCUSSION

An important aspect of this work is that the Hessian update formulae can be applied at negligible computational cost, when compared to accurately calculating Hessians using periodic DFT electronic structure calculations. Thus, constructing an interpolation based on first order Taylor series expansions, copying a known Hessian to approximate a nearby point or using a Hessian update formula to approximate a nearby point all cost essentially the same computational time per data point. Any of these approaches are significantly cheaper than evaluating Hessians accurately for interpolating accurate second order Taylor series expansions. Even seemingly more complicated schemes requiring reassignment of Hessians over all data points with repeated nearest neighbour searches when a data point is added to the interpolation set (such as the weighted scheme used here) pale into insignificance when compared with the cost of calculating a Hessian accurately. While the straight-forward use of the potential minimum Hessian copied everywhere gives a decent interpolation for the vibrational scenarios studied here, any increase in accuracy by using a Hessian update formula is an improvement from the point of view of computational efficiency.

The Powell and BFGS updates are both rank two update formulae. Both of these updates were effective in this work. The symmetry rank one update of Eq. (8) was effective for the interpolation of the two-dimensional function V_2, but not for the higher dimensional case of V_{27}. Examining the interpolated PES along the predefined path of Sec. III B as data points were added under the rank one update suggests that using Eq. (8) to update a Hessian over a longer distance resulted in a data point with excessively high positive curvature. Such data points introduce large errors into the interpolated PES. Adding data points to correct these errors induced further high curvature points, as new data points are added even further from the central potential minimum. For the predefined path, using previously approximated Hessians involved major contributions from closer points only, avoiding the long-distance updates that apparently cause problems for the rank one update. This did not work for the classical trajectory of Sec. III C. The rank one formula's success for interpolating V_2 may be due to smaller average distances in the substantially lower dimensional space, or it may have been due to the optimal placement of all data points simultaneously through the simulated annealing procedure used.

In this work, Hessian update formulae have been used to propagate Hessians everywhere from a Hessian determined accurately at a single geometry. An obvious extension would be to accurately determine the Hessian at a number of judiciously chosen geometries. Such an approach has not been explored in this work.

In the context of nonlinear optimisation, another very effective method that incorporates updates to approximations to the Hessian of a system based on incomplete information is that derived from the work of Schlegel.[32] This method is known to many in the computational chemistry community as the Berny algorithm. The Berny Hessian update is effectively a prediction–correction method which includes historical information. It cannot be easily expressed in the "from this Hessian and these gradients give that Hessian" form of Eqs. (8)–(10), which is why it has not been used in this work.

V. CONCLUSION

The results given above confirm the conclusion of Ref. 24 that modified Shepard interpolation based on first order Taylor series expansions performs extremely poorly compared to the second order version. This work shows that this holds even in vibrational scenarios with a second order term included at the potential minimum, which might be expected to be substantially beneficial.

Using approximate Hessians in the Taylor series expansions, on the other hand, has proven to be useful. Approximating the Hessian at data points using well-known updates (such as the BFGS update) generally allowed convergence of the interpolated PES with around twice the number of data points as required when using accurate Hessians. When the Hessian is expensive to calculate (such as when the energies come from electronic structure theory calculations) this represents a significant saving of computational effort.

For the test problems considered in this work, approximating the Hessian everywhere to be that calculated at the potential minimum in a second order modified Shepard interpolation gave a significant improvement over the first order case. At times this approach was competitive with using the BFGS or Powell updates. In other cases, copying the potential minimum Hessian gave significantly worse performance than using update formulae. Copying the Hessian represents no significant computational saving over the update formulae so is not recommended in general.

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