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Modified Shepard interpolation of gas-surface potential energy surfaces with strict plane group symmetry and translational periodicity

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A new formulation of modified Shepard interpolation of potential energy surface data for gas-surface reactions has been developed. The approach has been formulated for monoatomic or polyatomic adsorbates interacting with crystalline solid surfaces of any plane group symmetry. The interpolation obeys the two dimensional translational periodicity and plane group symmetry of the solid surface by construction. The interpolation remains continuous and smooth everywhere. The interpolation developed here is suitable for constructing potential energy surfaces by sampling classical trajectories using the *Grow* procedure. A model function has been used to demonstrate the method, showing the convergence of the classical gas-surface reaction probability. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4757149>]

I. INTRODUCTION

Gas-surface interactions and gas-surface chemistry are vitally important to a wide range of scientific, technological, and industrial applications.^{1–16} This importance has given rise to a long history of modelling and calculating gas-surface interaction energies, and developing compact representations of these energies.^{15–27}

In the Born-Oppenheimer approximation, the energy of a gas phase molecule or adsorbate interacting with a solid surface is dependent only on the positions of the atoms and forms a single valued potential energy surface (PES). Electronic structure theory methods such as periodic density functional theory (DFT) can be used to calculate the value of the PES at any particular gas-surface geometry. For interactions with metal surfaces, the DFT approach has been quite successful.^{14–19,28} Interactions with non-metallic crystal surfaces are harder to describe with DFT, though recent developments with molecular fragmentation descriptions of adsorbates interacting with wide band gap materials show promise.^{29,30}

Even when one has an electronic structure theory method that can calculate gas-surface interaction energies suitably accurately at discrete points, for dynamics calculations, a continuous representation of the PES is usually required. As is the case for molecular PESs, there are a number of viable approaches. For example, the energies calculated at particular geometries can be fit to an analytic functional form.^{28,31–37} The PES can be expressed in a neural network^{38,39} or cluster-type^{40–42} representation. Alternatively, there are several approaches based on local expansions around geometries where the energy and other properties have been calculated explicitly.^{42–44}

A method that falls into the last category above is modified Shepard interpolation. Building on the success of modified Shepard interpolation for building the PESs for gas phase reactions in an algorithm often called *Grow*,^{45–51} modified Shepard interpolation has been used to represent the PES in gas-surface reactions.^{44,52–55} This approach has several advantages, including being able to treat polyatomic adsorbates, simple and seamless treatment of reactive or non-reactive collisions, physisorption, chemisorption and surface catalysed reactions, and strict interpolation of known energies. While the formalism that has been used to date has been successful,^{16,44,52–57} it has a number of weaknesses. The most significant of these is difficulty in ensuring that the PES maintains the correct behaviour as the adsorbate crosses the edges of the periodic surface unit cell. In the current work, we develop a new approach to modified Shepard interpolation of PESs for gas-surface interactions. The new formalism retains the advantages of the previous approach, while rigorously maintaining the symmetry implied by the structure of the solid surface.

Most investigations of gas-surface interactions assume the solid surface to be crystalline, meaning that the interaction exhibits translational periodicity. Strict 2D periodicity idealises the interaction to be between a molecule and an infinite extent 2D surface. This is the case we deal with in the current work. The assumption of periodicity does not imply that the surface has to be static. Phonon motion is allowed in a general 2D periodic treatment, provided that the relevant phonons are commensurate with the 2D periodic lattice. Both single surface oscillator models⁵⁸ and the population of multiple phonon modes are compatible with a 2D periodic description. However, in this work we assume a static solid surface, conforming to what has been termed the BOSS approximation (for Born-Oppenheimer static surface⁵⁹). Explicitly incorporating the effect of surface motion commensurate with

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the 2D periodicity in the interpolated PES may be possible in the future, by including appropriate additional coordinates to describe the surface motion.

Note that throughout the following, we talk of *the adsorbate* interacting with the solid surface. This should not be interpreted as suggesting that only a single species can interact with the solid surface in this formalism. The term “adsorbate” is here being used to refer to the non-crystalline part of the modelled system. The approach being described can equally interpolate PESs for multiple atomic or molecular fragments interacting with the solid surface, allowing the investigation of reactions that occur through, for example, Langmuir-Hinshelwood or Eley-Rideal mechanisms.

II. THEORY

A. Modified Shepard interpolation

The representation of the gas-surface PES is similar in both spirit and implementation to the modified Shepard interpolation that has been used for some time for representing molecular^{45–50} and gas-surface^{16,44,52–57} PESs. The PES is determined by the energies and the first and second order derivatives of the energy at a set of “data point” geometries. The resulting continuous PES interpolates the energies and first and second order derivatives of the underlying energy landscape, which must be calculated at the data points by, for example, some electronic structure theory such as DFT. (In this work, we are not concerned with how one *calculates* the potential energies at the data points, but how these discrete calculations are *interpolated* into a complete PES that obeys 2D periodic and plane group symmetries.)

For a static surface, the PES is a function of the positions of the adsorbate atoms relative to the solid surface. For N adsorbate atoms, the PES is $3N$ dimensional. There are many possible coordinate sets that can be used to describe the positions of N adsorbate atoms relative to each other and to the solid surface. The $3N$ Cartesian coordinates of the atoms (with the Cartesian axes fixed with respect to the solid surface) are one possible set, and in this work, we assume that the first and second derivatives of the energy with respect to the $3N$ Cartesian coordinates can be calculated at data point geometries by, for example, the underlying DFT method. In general, the number of coordinates contained in any set that can describe the positions of all the adsorbate atoms exceeds $3N$. For example, one could use the $N(N-1)/2$ distances between the N adsorbate atoms and the distances from each adsorbate atom to a series of fixed points on the solid surface (e.g., surface atoms). Thus, the basic coordinates are here described as a *redundant* set of internal coordinates. In Sec. II B, we describe the particular choice of coordinates we use in this work, that are consistent with the symmetry of crystalline surfaces. There are N_{red} redundant internal coordinates, $N_{\text{red}} \geq 3N$.

Cartesian coordinates are not optimal for accurate interpolation⁴⁷ and are not convenient for implementing the required symmetry of the PES. Redundant coordinates, while being convenient for implementing the symmetry of the PES if carefully chosen, are also not optimal for accurate interpolation. Therefore, we define a set of $3N$ *local* internal coor-

dinates associated with each data point where the energy and derivatives are known, which are optimised to describe motion in the vicinity of the data point geometry. These $3N$ local internal coordinates are linear combinations of the redundant internal coordinates.

We denote the redundant internal coordinates by the vector $\mathbf{Z}$ and the full set of Cartesian coordinates for all N atoms by the vector $\mathbf{X}$. The $3N$ local internal coordinates are defined from the relation between the redundant internal coordinates and the Cartesian coordinates of the N adsorbate atoms embodied in the Wilson B matrix. Noting that we use the notation (i) to indicate a quantity associated with the i th data point, the α, β element of the variant of the Wilson matrix used here is given by

$$B_{\alpha\beta}(i) = \frac{\partial Z_{\alpha}}{\partial X_{\beta}}, \quad (1)$$

for $1 \leq \alpha \leq N_{\text{red}}$ and $1 \leq \beta \leq 3N$, and where the derivative is evaluated at the $\mathbf{X}$ and $\mathbf{Z}$ coordinates of the i th data point geometry. The local internal coordinates are formed from the singular value decomposition (SVD) of this matrix

$$B(i) = U(i)\Lambda(i)V(i)^T, \quad (2)$$

where U is an $N_{\text{red}} \times N_{\text{red}}$ matrix, Λ is an $N_{\text{red}} \times 3N$ matrix, and V is a $3N \times 3N$ matrix. U and V are unitary matrices containing the left and right singular vectors as columns, while Λ is a diagonal matrix with the $3N$ singular values of B on the diagonal. $3N$ local internal coordinates are defined in the vicinity of the geometry of data point i as

$$\boldsymbol{\zeta}(i) = \Lambda(i)^{-1}U(i)^T\mathbf{Z}. \quad (3)$$

Formally, the $\Lambda(i)^{-1}$ appearing in Eq. (3) is the inverse of the $3N \times 3N$ diagonal matrix obtained by dropping the last $N_{\text{red}} - 3N$ rows of $\Lambda(i)$ that contain only zeros.

Whereas the general gas phase case requires $3N - 6$ local internal coordinates,⁴⁷ in this work, we require exactly $3N$. Hence, the SVD in Eq. (2) can explicitly be the convenient “thin” SVD, in which exactly $3N$ non-zero singular values and their corresponding singular vectors are calculated, rather than the full $N_{\text{red}} \times N_{\text{red}}$ U matrix.

The result of Eqs. (1)–(3) is to produce a set of $3N$ independent internal coordinates, which describe changes in geometry in the vicinity of the data point i . The Jacobean matrix of the transformation from Cartesian coordinates to the internal $\boldsymbol{\zeta}$ coordinates is given by the matrix of right singular vectors $V(i)$, and is thus unitary. This matrix can then be used to reliably transform Cartesian derivatives into derivatives with respect to the internal coordinates.^{46,47}

In the vicinity of the geometry of data point i , the Taylor series expansion of the PES is expressed as

$$T_{(i)}(\mathbf{Z}) = E(i) + \Delta\mathbf{E}(i)^T\Delta\boldsymbol{\zeta}(i) + \frac{1}{2}\Delta\boldsymbol{\zeta}(i)^TF(i)\Delta\boldsymbol{\zeta}(i) + \text{higher order terms}, \quad (4)$$

where $E(i)$ is the energy at the data point geometry [equivalently expressed as $\mathbf{X}(i)$, $\mathbf{Z}(i)$ or $\boldsymbol{\zeta}(i)$], $\Delta\mathbf{E}(i)$ is the vector of first derivatives at data point i with respect to elements of $\boldsymbol{\zeta}(i)$, $F(i)$ is the matrix of second derivatives at data point i with respect to elements of $\boldsymbol{\zeta}(i)$, and $\Delta\boldsymbol{\zeta}_i$ is the displacement of the

point $\mathbf{Z}$ from the data point geometry $\mathbf{Z}(i)$ in $\xi(i)$ coordinates,

$$\Delta\xi(i) = \Lambda(i)^{-1}U(i)^T [\mathbf{Z} - \mathbf{Z}(i)]. \quad (5)$$

In this work, as in similar gas phase calculations, the Taylor series expansions are truncated at second order.^{60,61} It is straightforward to calculate the local coordinate derivatives and force constants $\Delta\mathbf{E}(i)$ and $F(i)$ from the Cartesian first and second derivatives at the data point geometry.⁴⁷

The global approximation to the PES is defined by a modified Shepard interpolation of the second order Taylor series expansions centred on the set of N_{data} data point geometries and all symmetry-equivalent copies of these data point geometries

$$V(\mathbf{Z}) = \sum_{i=1}^{N_{\text{data}}} \sum_{g \in G_{\text{CNP}} \times G_{\text{PG}}} w_{(g \circ i)}(\mathbf{Z}) T_{(g \circ i)}(\mathbf{Z}). \quad (6)$$

In this equation, the w are weight functions, and G_{CNP} and G_{PG} are the molecular permutation and plane group⁶² symmetry groups, respectively, describing the symmetry of the gas-surface interaction. Generally, G_{CNP} is the complete nuclear permutation group for the atoms of the adsorbate, while G_{PG} describes the symmetry of the solid surface the adsorbate is interacting with. The subscript $(g \circ i)$ denotes that the quantity for data point i has been transformed according to the symmetry operation $g \in G_{\text{CNP}} \times G_{\text{PG}}$. By adding a term for each data point transformed according to the elements of $G_{\text{CNP}} \times G_{\text{PG}}$, the interpolated PES exhibits the symmetry embodied in $G_{\text{CNP}} \times G_{\text{PG}}$ globally.

The PES defined by Eq. (6) is constrained to being an interpolation of the energies at the data points by requiring that

$$w_{(g \circ i)}(\mathbf{Z}(g \circ i)) = 1, \quad (7)$$

at the data points and

$$\sum_{i=1}^{N_{\text{data}}} \sum_{g \in G_{\text{CNP}} \times G_{\text{PG}}} w_{(g \circ i)}(\mathbf{Z}) = 1, \quad (8)$$

for all valid $\mathbf{Z}$. Here, we follow the approach that has been developed for the *Grow* procedure for gas phase reactions. We ensure Eqs. (7) and (8) are satisfied by defining the weight functions in terms of primitive weights v according to

$$w_{(i)}(\mathbf{Z}) = \frac{v_{(i)}(\mathbf{Z})}{\sum_j \sum_{g \in G_{\text{CNP}} \times G_{\text{PG}}} v_{(g \circ j)}(\mathbf{Z})}. \quad (9)$$

The primitive weights are required to obey $\lim_{\mathbf{Z} \rightarrow \mathbf{Z}(i)} v_i(\mathbf{Z}) \rightarrow \infty$, and $v_{(i)}(\mathbf{Z})$ must decay sufficiently quickly as $\|\mathbf{Z} - \mathbf{Z}(i)\|$ grows.

When N_{data} is small, we use the “one part” weights

$$v_{(i)}(\mathbf{Z}) = \|\mathbf{Z} - \mathbf{Z}(i)\|^{-2p}. \quad (10)$$

The decay rate of this weight function depends on the value of p . For redundant coordinates $\mathbf{Z}$ comprised solely of inverse distances and a “uniform” distribution of data points, one can show that the PES converges with increasing N_{data} as long as p is larger than the number of degrees of freedom in the system ($3N - 6$ for gas phase PESs).⁴⁵ Similar bounds have not

been proven for the redundant coordinates used in this work, but we expect $p > 3N$ would be a minimum requirement for convergence.

The larger density of data points arising from larger N_{data} allows the definition of an elliptical confidence volume for the truncated Taylor series expansion around $\mathbf{Z}(i)$.⁴⁸ Thus, for larger numbers of data points, we use the “two part” weight function

$$v_{(i)}(\mathbf{Z}) = [\varepsilon_{(i)}(\mathbf{Z})^{2p} + \varepsilon_{(i)}(\mathbf{Z})^{2q}]^{-1}, \quad (11)$$

where q is a small integer (here, $q = 2$) and $\varepsilon_{(i)}(\mathbf{Z})$ is a local weighted distance in the redundant internal coordinate space,

$$\varepsilon_{(i)}(\mathbf{Z})^2 = \sum_{j=1}^{N_{\text{red}}} \left(\frac{Z_j - Z_j(i)}{d_j(i)} \right)^2, \quad (12)$$

in which Z_j , $Z_j(i)$, and $d_j(i)$ are the j th elements of $\mathbf{Z}$, $\mathbf{Z}(i)$, and $\mathbf{d}(i)$, respectively, where the vector $\mathbf{d}(i)$ contains the lengths defining the confidence volume for data point i . The expressions for the elements of $\mathbf{d}(i)$ are derived using Bayesian arguments.⁴⁸ The effect of this approach is that inside the confidence volume, the slower decay of the q term dominates, while outside the confidence region, the decay of weights returns to decaying faster according to the magnitude of p .

With the exception of defining the redundant internal coordinates $\mathbf{Z}$ appropriate for describing periodic gas-surface reactions, this defines the interpolated PES based on sampling some underlying force field at N_{data} discrete geometries. In terms of building a PES for a gas-surface reaction, little is different to the gas phase case, where the *Grow* procedure is well established.^{45–50} Starting from an initial small set of data points (for example, a sampling of geometries along a minimum energy path), classical trajectories can be integrated on the PES. Geometries are then selected from the set of geometries visited by the classical trajectories using measures that probe the accuracy of the interpolated PES, and the importance of various geometrical regions to the classical dynamics. The energy and derivatives of the selected geometries are evaluated according to the underlying force field and the selected geometries are added to the set of data points, nominally improving the interpolated PES. The cycle is repeated until the dynamical quantities of interest converge to a suitable level with respect to the number of data points.

A similar procedure has recently been demonstrated for building gas-surface PESs based on systematic molecular fragmentation of non-metallic crystals.³⁰ Note that the sampling procedure used in the current work for selecting new data points is essentially the same as that for the gas phase case. This is different to the procedure used in the fragmented gas-surface PES case, where modifications were required to handle each gas-surface PES evaluation relying on hundreds of fragment geometries.

B. Redundant coordinates for gas-surface interpolation

Different sets of redundant internal coordinates, $\mathbf{Z}$, have been used previously to build PESs for different situations. The inverses of the full set of $N(N - 1)/2$ internuclear

distances are used for adiabatic PESs of gas phase molecules and molecular fragments. The interpolation of diabatic potential matrices, which are not invariant under inversion, uses scalar triple product combinations of internuclear vectors in addition to the internuclear distances.^{49,63}

Previous work on interpolating gas-surface PESs used inverse internuclear distances within the adsorbate, along with additional inverse distances to surface atoms (lattice sites).^{44,52–55} As was noted in the Introduction, these inverse internuclear and lattice site distance coordinates for gas-surface interpolation have proven to be problematic in terms of correct behaviour with respect to translation of the adsorbate in the plane of the solid surface, particularly when the adsorbate moves across the boundary of the periodic surface unit cell. To circumvent these problems, we have identified a number of general desirable properties for the redundant gas-surface coordinate system. The coordinates should

1. be complete with respect to the $3N$ degrees of freedom of the system, being the adsorbate orientation and position relative to the surface lattice in addition to the molecular shape space of the adsorbate (that is, the redundant coordinates must span the $3N$ Cartesian space);
2. be a faithful representation of the nuclear permutation group of the adsorbate;
3. be a faithful representation of the plane group of the periodic surface;
4. be invariant to lattice translation;
5. reduce to coordinates appropriate for the isolated gas phase species (independent of rotation and translation) when the adsorbate is far from the solid surface.

The inverse internuclear and lattice site distance coordinates used previously^{44,52} rigorously obey properties 1, 2, and 5 on this list. Property 3 is only partially obeyed, with reflections, etc., across the edges of the periodic surface unit cell being problematic. This is closely related to the fact that the coordinates were never intended to have property 4 globally, relying on external translation to a particular origin.

In this work, we use a set of coordinates specifically designed to possess these beneficial properties. These coordinates are comprised of

- the full set of $N(N - 1)/2$ inverse nuclear distances between adsorbate atoms,
- the inverse of the height of each adsorbate above a plane parallel to the solid surface, and
- a modified redundant set of sines and cosines of the projection of each atom on the reciprocal lattice of the surface lattice.

The first of these are the same as used in the gas phase case

$$\chi_{ij} = \|\mathbf{x}_i - \mathbf{x}_j\|^{-1}, \quad (13)$$

for all $1 \leq i < j \leq N$, where $\mathbf{x}_i = (x_i, y_i, z_i)^T$ is the vector of the Cartesian coordinates of the i th adsorbate atom.

The inverse height coordinates are measured relative to some origin located a distance Δ below the nominal surface plane. In the following, we take the z Cartesian axis to be normal to the plane of the solid surface, which is located at $z = 0$, with positive z values in the vacuum. Therefore, the

inverse height coordinates are

$$h_i = (z_i + \Delta)^{-1}, \quad (14)$$

for the i th atom. The inverse of the height above the solid surface has been used to reflect that the potential energy is expected to vary with height above the solid surface most strongly near the surface. Far from the solid surface, the potential barely changes with respect to translation normal to the solid surface, so the corresponding coordinates should barely change. The offset of the origin to below the nominal surface plane (e.g., the plane of the uppermost surface atoms) is to allow adsorbate atoms to penetrate below the uppermost plane of surface atoms (important for deeply corrugated solid surfaces), and to prevent the coordinates from changing too rapidly very close to the solid surface.

From the surface lattice vectors $\mathbf{a} = (a_1, a_2, 0)^T$ and $\mathbf{b} = (b_1, b_2, 0)^T$, we define the reciprocal lattice vectors

$$\hat{\mathbf{a}} = \frac{1}{a_1 b_2 - a_2 b_1} \begin{pmatrix} b_2 \\ -b_1 \\ 0 \end{pmatrix} \quad (15)$$

and

$$\hat{\mathbf{b}} = \frac{1}{a_1 b_2 - a_2 b_1} \begin{pmatrix} -a_2 \\ a_1 \\ 0 \end{pmatrix}. \quad (16)$$

In order to satisfy property 3 above for hexagonal lattices, we also define a third vector

$$\hat{\mathbf{c}} = \frac{1}{a_1 b_2 - a_2 b_1} \begin{pmatrix} a_2 - b_2 \\ b_1 - a_1 \\ 0 \end{pmatrix}. \quad (17)$$

The vectors $\hat{\mathbf{a}}$ and $\hat{\mathbf{b}}$ lie in the plane of the solid surface perpendicular to the lattice vectors $\mathbf{b}$ and $\mathbf{a}$, respectively. The vector $\hat{\mathbf{c}}$ is similarly perpendicular to the $\mathbf{a} - \mathbf{b}$ direction, which is the third direction equivalent to $\mathbf{a}$ and $\mathbf{b}$ in hexagonal symmetry. The $\hat{\mathbf{a}}$, $\hat{\mathbf{b}}$, and $\hat{\mathbf{c}}$ vectors are illustrated in Figure 1. Then defining

$$\begin{aligned} \alpha_i &= \mathbf{x}_i^T \hat{\mathbf{a}}, \\ \beta_i &= \mathbf{x}_i^T \hat{\mathbf{b}}, \\ \gamma_i &= \mathbf{x}_i^T \hat{\mathbf{c}}, \end{aligned} \quad (18)$$

for each adsorbate atom i yields a set of coordinates whose values change by whole integers for lattice translations of the adsorbate. Further, we define

$$\begin{aligned} s_{1i} &= \sin 2\pi \alpha_i, \\ s_{2i} &= \cos 2\pi \alpha_i, \\ s_{3i} &= \sin 2\pi \beta_i, \\ s_{4i} &= \cos 2\pi \beta_i, \\ s_{5i} &= \sin 2\pi \gamma_i, \\ s_{6i} &= \cos 2\pi \gamma_i, \end{aligned} \quad (19)$$

FIG. 1. Illustration of the reciprocal lattice vectors underlying the definition of the in-plane coordinates η_{ki} (Eqs. (15)–(20)). The circles represent 2D periodic images of a surface atom located at the origin of the surface unit cell, with the surface unit cell shaded. The blue arrows represent the surface unit cell lattice vectors $\mathbf{a}$ and $\mathbf{b}$, while the green arrows represent $\hat{\mathbf{a}}$, $\hat{\mathbf{b}}$, and $\hat{\mathbf{c}}$. The $\hat{\mathbf{c}}$ vector is not considered for non-hexagonal plane groups (crystalline surfaces without three-fold rotation symmetry elements).

for each adsorbate atom i . These coordinates are invariant under lattice translation. Both sine and cosine terms are included as redundant coordinates as either function alone takes the same value in two locations within each periodic surface unit cell, whereas the pair uniquely determines positions within a cell. The final “in-plane” coordinates to be added to the set of redundant internal coordinates $\mathbf{Z}$ are then taken to be

$$\eta_{ki} = h_i^2 s_{ki}, \quad (20)$$

with the dependence on the inverse height introduced in order to satisfy property 5 above. The power 2 that appears in (20) for the inverse height dependence is not required from theoretical considerations, but has been selected for convenience. Numerical experiments show that this power works well.

For non-hexagonal periodic surfaces (exhibiting symmetry of plane groups⁶² #1–#12), only four of these coordinates are required for each atom, η_{1i} to η_{4i} . For hexagonal symmetry solid surfaces (plane groups #13–#17), the coordinates η_{5i} and η_{6i} are added to allow plane group symmetry operations to be applied as a linear transformation among the η_{ki} . This ensures that the η_{ki} coordinates form a faithful representation of the plane group symmetry of the solid surface. Extending the coordinates to a third in-plane direction for hexagonal plane groups (adding coordinates in the direction of $\hat{\mathbf{c}}$) is analogous to the use of a redundant set of four Miller indices to specify planes and directions in hexagonal crystals, where certain symmetries are not obvious with the standard set of three Miller indices. The transformation of these coordinates under plane group symmetry operations is described in Appendix A.

Clearly, when the adsorbate is monoatomic, there are no inverse internuclear distances. In this case, the redundant coordinates are four or six in plane coordinates η_{ki} (depending on the symmetry of the solid surface) and a single inverse height.

When using the two part weight function of Eq. (11), confidence lengths must be defined for each of the redundant internal coordinates. For the inverse adsorbate bond length coordinates, χ_{ij} , and the inverse height coordinates, h_i , these are calculated according to the original formulae of Ref. 48. However, the η_{ki} coordinates are sinusoidal, meaning that they are

multivalued. This means that the analysis of Ref. 48 does not give an accurate reflection of the accuracy of the Taylor series expansions in η_{ki} directions around data points for which the s_{ki} values are near ± 1 (i.e., atoms above the edges of the surface unit cell, etc.) To combat this, in this work we consider sine and cosine pairs together when determining confidence intervals. At each data point, for each atom i , η_{1i} and η_{2i} are assigned the same confidence interval, and similarly for the pair η_{3i} and η_{4i} , and the pair η_{5i} and η_{6i} . For each pair of coordinates, contributions from the differences in predicted and observed gradients in both coordinates are added together to determine the combined confidence interval. As the sine coordinate is well behaved where the cosine coordinate is problematic, and also the converse, this approach yields reasonable confidence lengths for both redundant coordinates in the pair.

It is worth noting that both the position and orientation of adsorbate species relative to the surface lattice is well described by the set of h_i and η_{ki} coordinates. As a consequence, there is no compelling need to “buckle” data point geometries away from difficult to describe configurations, as is necessary in the gas phase case.⁴⁷ However, when the adsorbate is far from the solid surface, these coordinates tend to zero. Distortion away from planar geometries may be required if data points with the adsorbate very far from the solid surface are included.

III. DEMONSTRATION OF THE METHOD

A. Model gas-surface force field

A model PES for an H_2 -like diatomic interacting with a hexagonal periodic surface has been used as a test case in this work. The model PES is described in Appendix B. The solid surface was taken to be hexagonal with lattice constant $6 a_0$. The model PES was designed with full $p6mm$ plane group symmetry (#17). This is the symmetry often imposed on PESs for adsorbates interacting with fcc(111) and hcp(0001) metal surfaces (although strictly these surfaces are of lower $p3m1$ symmetry, with inequivalent hollow sites).

There are no surface atoms in the model PES, and it is not supposed to represent any particular system. Nonetheless, because of the obvious analogy with the important case of hexagonal surfaces of close packed metals, we use somewhat analogous terminology. Thus, the hexagonal lattice of points that are equivalent by symmetry to the lattice origin are termed “top sites” when referred to in opposition to other sites, or as lattice points or the lattice origin when convenient.

As a benchmark, 5000 classical trajectories were run for gas-surface collisions using the model PES, with atom masses taken to be that of hydrogen. The diatomic started $15 a_0$ ($7.94 \text{ \AA}$) from the solid surface, with the position of the centre of mass in the plane parallel to the solid surface being selected from a uniform random distribution. The initial orientation and vibrational phase of the diatomic was random, with the internal vibrational energy set at $20 mE_h$ (52.5 kJ/mol). The initial velocity for the diatomic was at normal incidence to the solid surface, with $30 mE_h$ (78.8 kJ/mol) of translational energy. The total initial energy ($50 mE_h$) is indicated in the

plots of the potential in Appendix B. This energy is insufficient to react at the “top sites,” but the translational energy alone is sufficient to cross the dissociative adsorption barrier elsewhere on the solid surface.

The most common outcome of the trajectories was dissociative adsorption of the diatomic yielding two independent adsorbed atoms, which was the behaviour in 75% of the gas-surface collisions. In a small proportion of collisions ($<1\%$), the adsorbed atoms were close together at the end of the trajectory; these have been categorised separately as an adsorbed diatomic. Non-reactive scattering of the diatomic occurred with a probability of 17%. The total initial energy of 50 mE_h was sufficient to allow the diatomic to dissociate, but for one atom to escape to the gas phase with the other remaining adsorbed to the solid surface. This could occur either at the point of adsorption and dissociation, or later after the atoms had migrated away from one another. “Atom release,” as we denote this surface catalysis process, accounted for the remaining trajectories, at a probability around 8%.

B. The interpolated PES

The interpolated PES for the gas-surface reaction was constructed using the *Grow* procedure. The initial PES was defined by data points at a set of 31 geometries approximating a constrained minimum energy pathway for a dissociative adsorption. Along this constrained path, the diatomic remained parallel to the solid surface, directly above the lattice origin (“top site”) with the centre of the diatomic aligned with the lattice point, and with the diatomic axis parallel with a lattice vector. It is notable that the barrier along this constrained path is higher than the total initial energy for the trajectories.

From each small batch of trajectories, new geometries were selected for adding as data points by alternating between the “variance” and “*h*-weight” criteria regularly used in constructing gas phase potentials with the *Grow* procedure.⁴⁶ Geometries for which the interpolated PES gave an energy significantly below the energy of the lowest energy data point known were also selected as new data points.

Periodically, larger batches of trajectories were run to monitor the reaction probabilities on the interpolated PES. Using the one part weight function with $p = 8$, the resulting probabilities are shown in Figure 2. After adding several hundred data points, the calculated reaction probabilities were of the correct magnitude. However, the probabilities were clearly not converged to the values obtained for the underlying analytic PES as the number of data points approached 900.

Using the two part weight function of Eq. (11) has proven to be superior in the gas phase case. The two part weight function was also used in this work, with $p = 8$ and $q = 2$. The two part weight function with Bayesian confidence volumes can only be used if a sufficient number of well-distributed data points are known to reasonably assign confidence lengths. Thus, for the two part weight function, the *Grow* PES construction procedure was restarted from the first 150 data points selected with the one part weight function. The two part weight function was used exclusively from that

FIG. 2. Reaction probabilities calculated for the interpolated gas-surface PES as a function of the number of data points. The PES was interpolated using the one part weight function. Error bars indicate 95% score confidence intervals due to statistical sampling. Horizontal dashed lines indicate the probabilities from the model potential (see Sec. III A), with the associated confidence intervals shaded.

point. The resulting reaction probabilities as the number of data points increased are shown in Figure 3.

Figure 3 shows that the reaction probabilities calculated from the interpolated PES converged to the probabilities calculated for the underlying analytic PES as the number of data points increased beyond 800. With only a few exceptions, from this point onwards, the confidence intervals of the probabilities calculated with the interpolated PES contained the probabilities calculated directly from the analytic PES. This applied to all four of the monitored probabilities. For lower numbers of data points (400–800), the calculated probabilities were generally more consistent with the probabilities from the analytic PES than those produced using the one part weight function (cf. Fig. 2).

The data point selection procedure that has been used in this work placed most of the data points near to the solid surface. This is examined in Figure 4, which shows the distribution of the z coordinate of the centre of mass of the adsorbate for all the data points defining the final PES. Almost 60% of the data points have the adsorbate centre of mass closer to the solid surface than $z = 3 a_0$. Figure 4 also shows the distribution of the z coordinates of the centre of mass considering only data points for which the adsorbate atoms were closer than $2 a_0$ to one another. The partitioning of data points into

FIG. 3. Reaction probabilities as in Fig. 2, but using the two part weight function.

FIG. 4. Histogram of z values for the centre of mass of the diatomic at the data point geometries. Separate histograms are shown for all data points and those in which the adsorbate atoms are closer than $2 a_0$ to each other in an intact diatomic ("Bond length $< 2 a_0$ "). Also shown is the distribution of diatomic centres of mass from the one part weight function case.

those with adsorbate atom distances less than and greater than $2 a_0$ allows the comparison of the distribution of data point geometries contributing to the PES for the system in the molecular state and in the dissociation barrier regions (which can be expected to strongly influence the reaction probabilities) with those in which the diatomic has clearly passed over the dissociation barrier (which may be more relevant for properties such as product state distributions). Almost all of the data points with the adsorbate diatomic dissociated into atoms lie close to the solid surface, as represented by the difference in these two distributions in the $0.5 a_0 \leq z \leq 2 a_0$ region in Fig. 4.

The distribution of the adsorbate centres of mass in the data point geometries with intact diatomics (bond lengths less than $2 a_0$) when using the one part weight function is shown in Fig. 4 as connected points. This distribution extends to lower z values than in the two part weight function case. Using the two part weight function resulted in a substantial increase in intact diatomic data points in the $1.5 a_0 \leq z \leq 3.2 a_0$ region compared to the one part weight function. As indicated in Appendix B, the saddle points along the minimum energy paths for dissociative adsorption lie in this region. It is reasonable to assume that the dissociative adsorption probability is sensitive to the PES in this region, suggesting that the success of the two part weight function in giving probabilities converging to the expected values can be attributed in part to this higher density of points in the critical barrier region.

Figure 5 shows the distribution across the periodic surface unit cell of data point geometries in which the diatomic bond length was less than $2 a_0$. Again, this criterion is used to focus on geometrical regions that are expected to be critical for the observed reaction rates. At the energies used in this work, collision at the "top site," directly above the lattice origin, does not lead to reaction. As might be expected, this is reflected in the distribution of data point geometries, which favour reactive sites away from the lattice points. What may be less expected is the degree to which the initial 31 data points located above the lattice origin allows the data point selection procedure to not need to add any more data points in the vicinity of the lattice points. When the adsorbate diatomic remained intact with a separation of less than $2 a_0$, only a single data point geometry was selected within a cylinder of radius $0.7 a_0$ centred on the lattice origin; that single point was far from the solid surface, with the diatomic centre of mass located at $z = 14.9 a_0$. This was despite the fact that the trajectory simulations for sampling were run at energies where the model PES would allow the adsorbate to approach to within $3 a_0$ of the solid surface above the lattice points. Away from the lattice points, the classical turning point lies even closer to the solid surface.

A more detailed examination of the diatomic centre of mass distribution for data point geometries with intact diatomics reveals that, with the two part weight function, the PES away from the solid surface is well described by a small number of data points. After switching to the two part weight function, only 7 of 459 intact diatomic data points were added with the diatomic centre of mass further than $6 a_0$ from the solid surface. All seven of these points were located near the $15 a_0$ starting separation. On the other hand, sampling based on the one part weight function continued to add data points far from the solid surface.

IV. CONCLUSION

The modified Shepard interpolation scheme described in this work provides an interpolation of potential energies for gas-surface interactions. The two-dimensional periodicity and plane group symmetry of the interactions with crystalline surfaces is rigorously reproduced. The symmetry implied by any of the 17 plane groups can be readily implemented through simple transformations of the coordinates described in

FIG. 5. The x, y projection of the diatomic centre of mass of the data point geometries. Only data points in which the diatomic atoms are closer together than $2 a_0$ are shown. The x, y coordinates have been folded into the asymmetric unit of the $p6mm$ surface unit cell, then reflected across the centre line for clarity. The dark lines connect lattice points ("top sites"), whereas the dashed lines represent the reflections present in the $p6mm$ plane group.

Sec. II B, which is used to give the required symmetry in the interpolated PES.

Furthermore, in this work, we have demonstrated that the classical dynamics sampling method known as *Grow* is effective for constructing interpolations using the coordinates developed here. A model gas-surface reaction with a diatomic adsorbate has been used as a test case. Reaction rates from classical trajectories run on the interpolated PES converged to the same values as those for the model PES (to within statistical uncertainty). There were no significant problems with energy conservation during trajectories, as the interpolated PES constructed here has been designed to ensure continuity and smoothness at the boundaries of the periodic surface unit cell.

This work makes no assumptions about the source of the energies being interpolated, other than that they can be evaluated at arbitrary geometries and form a smooth BOSS potential surface. Analytic first and second derivatives of the energy with respect to the positions of the adsorbate atoms are desirable (as they are generally faster than finite difference calculations), but not essential. The current state of computational surface science suggests that the most likely source of these energies are from periodic DFT calculations on slabs representing the crystalline surface. There are no differences in interpolating PESs for interactions with the surface of metallic, semiconducting, or insulating materials. The current interpolation scheme could equally be used to interpolate energies derived from systematic molecular fragmentation of crystal surfaces.

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APPENDIX A: PLANE GROUP SYMMETRY AND COORDINATE TRANSFORMATIONS

A plane group is described by a set of symmetry elements, being rotations, reflections, and glides. The presence of a set of these elements can imply the presence of others, to make the full plane group. Thus, the symmetry of the 17 plane groups can be fully specified in terms of any one of several different subsets of symmetry elements. Therefore, only a limited number of elements need be implemented explicitly, with the remaining symmetry being applied by successive application of different implemented elements. Table I lists one such set of symmetry operations. Using these symmetry operations, the symmetry present in each plane group is listed in Table II. This is the decomposition used in the implementation developed in the current work. Note that for hexagonal plane groups we take **a** and **b** to form an angle of 60°.

To transform the in-plane coordinates η_{ki} according to some plane group symmetry element g to form the transformed geometry, we sequentially apply the relevant combination of operations from Table I. Each operation transforms η_{ki} to the transformed $g \circ \eta_{ki}$ according to Table III.

TABLE I. The particular symmetry operations used to decompose the plane groups in this work, and the shorthand notation used in Tables II and III.

Element	Notation
Twofold rotation around the origin	2
Reflection across the y axis	mx
Reflection across $x = a/2$ axis	mx/2
Glide along the y axis	gx
Glide along $x = a/2$	gx/2
90° rotation around the origin	4/2
Threefold rotation around the origin ^a	3 [±]
Reflection across a + b (long diagonal)	mld
Reflection across b − a (short diagonal)	msd

^aThe presence of 3⁺ implies 3[−], and the converse.

TABLE II. The decomposition of each plane group into the elements listed in Table I.

Group	#	2	mx	mx/2	gx	gx/2	4/2	3 [±]	mld	msd
<i>p1</i>	1									
<i>p2</i>	2	✓								
<i>pm</i>	3		✓							
<i>pg</i>	4				✓					
<i>cm</i>	5		✓			✓				
<i>p2mm</i>	6	✓	✓							
<i>p2mg</i>	7	✓		✓						
<i>p2gg</i>	8	✓				✓				
<i>c2mm</i>	9	✓	✓			✓				
<i>p4</i>	10	✓					✓			
<i>p4mm</i>	11	✓	✓				✓			
<i>p4gm</i>	12	✓				✓	✓			
<i>p3</i>	13							✓		
<i>p3m1</i>	14							✓	✓	
<i>p31m</i>	15							✓		✓
<i>p6</i>	16	✓						✓		
<i>p6mm</i>	17							✓	✓	✓

TABLE III. How the η_{ki} coordinates transform under each symmetry operation from Table I.

Element	$g \circ \eta_{1i}$	$g \circ \eta_{2i}$	$g \circ \eta_{3i}$	$g \circ \eta_{4i}$	$g \circ \eta_{5i}$	$g \circ \eta_{6i}$
2	$-\eta_{1i}$	η_{2i}	$-\eta_{3i}$	η_{4i}	$-\eta_{5i}$	η_{6i}
mx	η_{1i}	η_{2i}	$-\eta_{3i}$	η_{4i}		
mx/2	η_{1i}	η_{2i}	η_{3i}	$-\eta_{4i}$		
gx	$-\eta_{1i}$	$-\eta_{2i}$	$-\eta_{3i}$	η_{4i}		
gx/2	$-\eta_{1i}$	$-\eta_{2i}$	η_{3i}	$-\eta_{4i}$		
4/2	η_{3i}	η_{4i}	$-\eta_{1i}$	η_{2i}		
3 ⁺	η_{3i}	η_{4i}	η_{5i}	η_{6i}	η_{1i}	η_{2i}
3 [−]	η_{5i}	η_{6i}	η_{1i}	η_{2i}	η_{3i}	η_{4i}
mld	η_{3i}	η_{4i}	η_{1i}	η_{2i}	η_{5i}	η_{6i}
msd	$-\eta_{3i}$	η_{4i}	$-\eta_{1i}$	η_{2i}	$-\eta_{5i}$	η_{6i}

APPENDIX B: THE MODEL GAS-SURFACE POTENTIAL ENERGY FUNCTION

The model gas-surface potential energy surface is given by

$$V = D_1[R^{-12} - 2(r_0 + \tilde{z}^{-3})^{-6}R^{-6}] + D_2 \sum_{i=1,2} [(1 - e^{-\alpha_s(z_i - z_s)})^2 - 1] + \frac{D_3}{2} \sum_{i=1,2} (1 + \cos 2\pi\rho_i), \quad (\text{B1})$$

where $R = \|\mathbf{x}_1 - \mathbf{x}_2\|$ is the diatomic bond length and $\tilde{z} = (z_1 + z_2)/2$ is the z coordinate of the centre of the diatomic, with z_i the z coordinate of atom i . The first term on the right of Eq. (B1) is a Lennard-Jones-like function in which the potential minimum increases as the diatomic centre approaches the solid surface. The second term binds dissociated atoms to the solid surface. In the third term

$$\rho_i = \min(d_i/a, 1/2), \quad (\text{B2})$$

FIG. 6. Contour plots of the model potential. The diatomic is centred on the “top site” directly above a lattice point (a) and on the “3-fold site” equidistant from three lattice points (b). The diatomic is aligned in the plane of the solid surface and parallel to a lattice vector, with the potential plotted as a function of the diatomic bond length R and the height above the solid surface z . Solid contours are spaced 20 mE_h apart, with the contours below, above, and at the gas phase diatomic minimum separation energy in blue, red, and black, respectively. The dashed contour in the entrance valley lies at 50 mE_h , the initial kinetic energy used in the classical trajectories. The location of the initial data points are indicated with dots in (a).

where a is the lattice constant of the hexagonal lattice (so that the surface lattice vectors are, for example, $\mathbf{a} \equiv (a_1, a_2, 0)^T = (a, 0, 0)^T$ and $\mathbf{b} \equiv (b_1, b_2, 0)^T = (a/2, \sqrt{3}a/2, 0)^T$) and d_i is the distance from atom i to the nearest lattice point with the z component scaled by a factor α ,

$$d_i = \min_{h,k \in \mathbb{Z}} [(x_i - ha_1 - kb_1)^2 + (y_i - ha_2 - kb_2)^2 + (\alpha z_i)^2]^{1/2}. \quad (\text{B3})$$

Thus, the interaction with the solid surface is corrugated in accord with the $p6mm$ plane group symmetry of a hexagonal lattice.

In this work, the potential is defined by the constants $D_1 = 9 E_h$, $D_2 = 1/7 E_h$, $D_3 = 1/10 E_h$, $r_0 = 1.4 a_0$, $\alpha_s = 1.5 a_0^{-1}$, $z_s = 0.9 a_0$, $\alpha = 1/\sqrt{2}$, and $a = 6 a_0$. This yields a PES with a barrier to dissociative adsorption directly above the lattice points (the “top site”) that is 75 mE_h above the asymptotic energy. Away from the top sites in “bridge” and “3-fold” regions, the potential is more reactive, with the corresponding barrier height being less than 11 mE_h . Some illustrative slices through the PES are shown in Figure 6. Appropriate scans of the PES parallel to the solid surface show the hexagonal symmetry built into the PES, as do the dissociation barrier energy and location.

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