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Gradient-based multiconfiguration Shepard interpolation for generating potential energy surfaces for polyatomic reactions

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This paper describes and illustrates a way to construct multidimensional representations of reactive potential energy surfaces (PESs) by a multiconfiguration Shepard interpolation (MCSI) method based only on gradient information, that is, without using any Hessian information from electronic structure calculations. MCSI, which is called multiconfiguration molecular mechanics (MCMM) in previous articles, is a semiautomated method designed for constructing full-dimensional PESs for subsequent dynamics calculations (classical trajectories, full quantum dynamics, or variational transition state theory with multidimensional tunneling). The MCSI method is based on Shepard interpolation of Taylor series expansions of the coupling term of a 2×2 electronically diabatic Hamiltonian matrix with the diagonal elements representing nonreactive analytical PESs for reactants and products. In contrast to the previously developed method, these expansions are truncated in the present version at the first order, and, therefore, no input of electronic structure Hessians is required. The accuracy of the interpolated energies is evaluated for two test reactions, namely, the reaction $OH + H_2 \rightarrow H_2O + H$ and the hydrogen atom abstraction from a model of α-tocopherol by methyl radical. The latter reaction involves 38 atoms and a 108-dimensional PES. The mean unsigned errors averaged over a wide range of representative nuclear configurations (corresponding to an energy range of 19.5 kcal/mol in the former case and 32 kcal/mol in the latter) are found to be within 1 kcal/mol for both reactions, based on 13 gradients in one case and 11 in the other. The gradient-based MCMM method can be applied for efficient representations of multidimensional PESs in cases where analytical electronic structure Hessians are too expensive or unavailable, and it provides new opportunities to employ high-level electronic structure calculations for dynamics at an affordable cost. © *2010 American Institute of Physics*. [doi:10.1063/1.3310296]

I. INTRODUCTION

The analytical representation of potential energy surfaces for reactive systems is a problem that has challenged quantum chemistry since its early days,[1,2] and several reviews and book chapters discussing the subject are available.[1–14] Some particular promising recent methods for fitting reactive potential energy surfaces are Shepard interpolation,[13,15] spine interpolation,[12] interpolating moving-least-squares,[16–18] and least-squares fitting of permutationally symmetrized multinomials of bond-order-like functions of internuclear distances.[19,20] In addition, our group has developed a method based on Shepard interpolation of the off-diagonal elements of a configuration interaction matrix.[21–25] We will call this method multiconfiguration Shepard interpolation (MCSI). Another name for it, which we and others have used in the past, is multiconfiguration molecular mechanics (MCMM),[21–33] and the extension to combined quantum mechanics and molecular mechanics has been called electrostatically embedded MCMM (EE-MCMM).[24,34,35] The MCMM name emphasizes that the speed of evaluating the potential during dynamics computations is comparable to that for molecular mechanics. The

MCSI name emphasizes that the method is not a semiempirical model for predicting potential energy surfaces but rather a method for interpolating electronic structure data. Both names emphasize that the method is based on two or more configurations—usually two, with one corresponding to reactants and one corresponding to products.

All fitting methods have advantages and disadvantages. The tradeoff between Shepard interpolation and interpolated moving least squares is often seen as follows: Shepard interpolation requires input Hessians to carry out the fit, but the resulting fit is inexpensive to evaluate during dynamics calculations, whereas interpolating moving least-squares has more flexibility in the input data but requires an expensive solution of a weighted least-squares problem at every dynamics step, storage of fitting parameters at geometries spanning the coordinate space, or both. The MCSI method has been shown to ameliorate the cost of Hessians by greatly cutting back on the number needed, for example, from hundreds or a thousand in straight Shepard interpolation of the potential energy surface itself to a few[31] or at most a few dozen[23] in MCSI; furthermore, one can substitute partial Hessians for many of the Hessians.[28] In the present article we cut the cost even more by showing that we can eliminate the need for Hessians altogether.

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II. KEY ELEMENTS OF THE METHOD

In non-Hermitian MCSI,[25] the interpolated potential energy V at a molecular geometry $\mathbf{x}$ is given by the lowest eigenvalue of a valence bond configuration interaction Hamiltonian matrix $\mathbf{H}$, defined by

$$\mathbf{H} = \begin{pmatrix} H_{11}(\mathbf{x}) & \beta(\mathbf{x}) \\ \beta(\mathbf{x}) & H_{22}(\mathbf{x}) \end{pmatrix}, \tag{1}$$

where H_{11} and H_{22} are analytical representations of valence bond configurations of the reactant and the product (ordinarily, molecular mechanics potentials), and β is an approximation to the off-diagonal matrix element, H_{12}. $H_{11}(\mathbf{x})$ and $H_{22}(\mathbf{x})$ and their derivatives are calculated at every geometry $\mathbf{x}$ wherever the dynamics code needs potential energy and its gradient, whereas β at $\mathbf{x}$ is obtained via Shepard interpolation from data at a set of geometries called Shepard points. If the invariance of the potential energy surface with respect to the exchange of identical nuclei (nuclear permutation symmetry) is required, the matrix elements are symmetrized as described previously.[22]

The quantity β is the key variable of the MCSI method. We obtain β as follows. First, we obtain β_o^2 via a Shepard interpolation step

$$\beta_o^2 = \sum_{k=1}^{N} \sum_{i=1}^{m!} w_{ki}(\mathbf{r}) T_{12}^2(\mathbf{r}, k, i), \tag{2}$$

where w_{ki} is a Shepard-interpolation weight function, each quantity $T_{12}^2(\mathbf{r}, k, i)$ is a Taylor series expansion of $H_{12}^{2(k,i)}$ at a geometry $\mathbf{r}(\mathbf{x})$, and m is the number of identical nuclei to be treated as permutationally equivalent. At this step, the nuclear permutation symmetry is imposed as in the method proposed by Collins,[13] with the exception that the interpolated quantity is the coupling term β rather than the potential energy itself. To maintain orientational invariance, Shepard interpolation given by Eq. (2) is performed in internal (denoted $\mathbf{r}$) rather than in Cartesian coordinates (denoted $\mathbf{x}$) in the same way as described in Ref. 21. The coupling element β is then given by

$$\beta = \begin{cases} |\beta_o(\mathbf{x})|; & \beta_o^2(\mathbf{x}) \geq 0 \\ iu|\beta_o(\mathbf{x})|; & \beta_o^2(\mathbf{x}) < 0, \end{cases} \tag{3}$$

where

$$u = \begin{cases} 1; & \beta_o^2(\mathbf{x}) \geq -\Delta^2/4 \\ \Delta/(2|\beta_o|); & \beta_o^2(\mathbf{x}) < -\Delta^2/4, \end{cases} \tag{4}$$

and

$$\Delta = H_{11}(\mathbf{x}) - H_{22}(\mathbf{x}). \tag{5}$$

In Eq. (3), the condition $\beta_o^2 > 0$ corresponds to a case in which the target potential energy surface is lower than both diagonal elements; in this situation, one can always improve the MCSI fit by choosing an appropriate real β, i.e., by placing a Shepard point in the vicinity of a given geometry. By allowing β_o^2 to be negative, one extends the range of molecular geometries at which one can obtain an accurate fit, i.e., where one can make the fit agree exactly with the target data, as explained in Ref. 25. In Eq. (4), the condition $\beta = \Delta^2/4$

corresponds to the limit of where one can make the fit agree exactly with the target data with imaginary β. This is also discussed in Ref. 25.

The Taylor series expansions T_{12}^2 around each Shepard point (k, i) used in Shepard interpolation are obtained as follows. First, we define a matrix $\mathbf{H}^{(k,i)}$ at each geometry (k, i) by

$$\mathbf{H}^{(k,i)} = \begin{pmatrix} H_{11}^{(k,i)}(\mathbf{r}) & H_{12}(\mathbf{r}, k, i) \\ H_{12}(\mathbf{r}, k, i) & H_{22}^{(k,i)}(\mathbf{r}) \end{pmatrix}. \tag{6}$$

Using Taylor series reversion for H_{12}, one obtains

$$\begin{aligned} H_{12}(\mathbf{r}, k, i)^2 \approx & (H_{11}^{(k,i)} - H^{(k,i)})(H_{22}^{(k,i)} - H^{(k,i)}) \\ & + (H_{22}^{(k,i)} - H^{(k,i)})(\mathbf{g}_{11}^{(k,i)} - \mathbf{g}^{(k,i)})^{\mathsf{T}} \Delta\mathbf{r}^{(k,i)} \\ & + (H_{11}^{(k,i)} - H^{(k,i)})(\mathbf{g}_{22}^{(k,i)} - \mathbf{g}^{(k,i)})^{\mathsf{T}} \Delta\mathbf{r}^{(k,i)}, \end{aligned} \tag{7}$$

where H_{nn} and $\mathbf{g}_{nn}(n=1,2)$ are molecular mechanics energies and gradients of configurations 1 and 2 at a Shepard point (k, i), and H and $\mathbf{g}$ are the energy and the gradient obtained from the electronic structure calculations at the same geometry, T denotes a transpose, and

$$\Delta\mathbf{r}^{(k,i)} = \mathbf{r}(\mathbf{x}) - \mathbf{r}(\mathbf{x}^{(k,i)}). \tag{8}$$

Note that there are two ways to eliminate the use of Hessians in the present context. One way is to truncate the Taylor series expansion at the first order as in Eq. (7). The other way is to truncate at the second order, but set all Hessian matrix elements to zero, in which case, the results will be different from the former case due to the contribution of the gradient times gradient term in the second derivatives of H_{12}. The present paper only considers truncation at the first order. Yet another way to reduce the number of the input electronic structure Hessians is by using a combination of the first- and second-order Taylor series expansions in Eq. (2). For example, one may want to use the second-order expansion at the reaction saddle point and one of the gradient-only approaches mentioned above at the other Shepard points. This may be useful, for instance, in quasiclassical trajectory calculations if one wants to start a trajectory from the reaction saddle point. The goal of the present article, though, is to show that we can obtain good results with only gradient data.

The normalized weight function used in Eq. (2) is

$$w_{ki} = \frac{\dfrac{Y_{ki}(\mathbf{r})}{d_{ki}(\mathbf{s})^4}}{\displaystyle\sum_{k=1}^{(N+2)} \sum_{i=1}^{m!} \dfrac{Y_{ki}(\mathbf{r})}{d_{ki}(\mathbf{s})^4}}, \tag{9}$$

where d_{ki} is the generalized distance between $\mathbf{s}$ and $\mathbf{s}^{(k,i)}$ defined as

$$d_{ki}(\mathbf{s}) = \sqrt{\sum_{\gamma=1}^{\Gamma m!} (s_\gamma - s_\gamma^{(k,i)})^2}, \tag{10}$$

where $\mathbf{s} \equiv \{s_1, s_2, \ldots s_\gamma, \ldots s_\Gamma\}$ is a set of internal coordinates, generally different form $\mathbf{r}$.

The scaling coefficients $Y_{ki}(\mathbf{r})$ are chosen either as unity or as a function that ensures that the reactive system is de-

scribed by pure molecular mechanics in the asymptotic regions. To ensure that, we define Y_{ki} at a geometry $\mathbf{r}$ as

$$Y_{ki}(\mathbf{r}) = \frac{1}{1 + \left(\dfrac{V'_{12}(\mathbf{r},k,i)^2 - D^{(k)}}{A^2} \right)^{\mu}}, \quad (11)$$

where A and m are parameters. In the work presented below, we used Eq. (11) with $A = 0.002 \; E_h$ and $\mu = 4$ in Sec. III.A and $Y = 1$ in Sec. III.B.

III. INTERPOLATED SURFACES FOR MODEL SYSTEMS

In the present work, we assess the accuracy of the interpolated potential energy surfaces by comparing interpolated energies to the "accurate" energies obtained directly by the electronic structure calculations for a representative set of dynamically important nuclear configurations.

III.A. OH + H₂ → H₂O + H

The first system is OH_3 as in the reaction

$$OH + H_2 \rightarrow H_2O + H \quad (R1).$$

For this system, we constructed potential energy surfaces that are invariant under the complete nuclear permutation (CNP) group, that is, which are invariant under the exchange of all indistinguishable nuclei. Since there are three identical nuclei, there are $N \cdot 3!$ terms in the Shepard interpolation of Eq. (2), where N is the number of unique Shepard points. The electronic structure level for the target potential energy surface and molecular mechanics force field are the same as in the previous work.[23] In particular, the target results for the present study are obtained using the MPWB1K (Ref. 36) density functional with the 6-31+G(d,p) basis set.[37] Locations of the Shepard points are the same as in the previous work;[23] the three potential energy surfaces considered in this paper have been constructed using subsets of the 37 Shepard points used in Ref. 23. We used 13, 27, and 35 gradients in the three examples, so these surfaces are labeled MCSI(13g), MCSI(27g), and MCSI(35g), respectively. In keeping with the previous work,[23,25,31] the number N in parentheses indicates the number of unique electronic structure Shepard points in Shepard interpolation of H_{12}^2 given by Eq. (2). The difference of this work from previous work is that at each Shepard point, only the gradients (but no Hessian) have been used, which is indicated by "g" following the number of Shepard points. Two additional Shepard points representing reactant and product configurations (see, e.g., Ref. 21) have also been included in Shepard interpolation. At both of these points H_{12} and its gradients are assumed to be zero; therefore, these points do not occur in Eq. (2), but they do occur in Eq. (9). Thus, Eq. (2) actually corresponds to an ($N + 2$)·3!-point interpolation with $N \cdot 3!$ nonzero terms. The choice of the force field is the same as in the previous paper,[23] in particular we used a modified MM3 (Ref. 38) force field with the parameters (set p2) given in Ref. 23.

The sets of internal coordinates $\mathbf{r}$ and $\mathbf{s}$ used in Eqs. (2) and (9) involved all six internuclear distances ($\mathbf{s} \equiv \mathbf{r}$ in the present case) due to the requirement of the invariance of the

TABLE I. MUE for MCSI(13g), MCSI(25g), and MCSI(35g) for different ranges of potential energy (the zero of potential energy corresponds to the product asymptote; the reaction saddle point is 18.6 kcal/mol higher than the product asymptote) for the reaction OH+H₂, averaged over a number of dynamically important molecular geometries visited by quasiclassical trajectories.

Energy range	MCSI(13g)	MCSI(27g)	MCSI(35g)	N_{geom} [a]
<7.6	0.44	0.40	0.39	133
<10.6	0.55	0.50	0.48	183
<19.6	0.93	0.80	0.80	468
<25.6	1.31	0.98	0.98	623
<33.6	1.78	1.18	1.14	722

[a]Number of geometries in the energy range indicated in the first column. The number of geometries varies from 133 to 722, depending on the upper limit of the energy range considered.

surface under the operations of the CNP group. The set of geometries used to evaluate the accuracy of the interpolated energies was generated by "saving" a molecular geometry every 10 fs during quasiclassical trajectory simulations on interpolated potential energy surfaces and comparing the energy at this geometry to the potential energy obtained by the electronic structure calculations at the target level. In this way, one identifies the dynamically important regions of the potential energy surface most "visited" by quasiclassical trajectories. Initial conditions for trajectories are the same as in the previous work.[23]

Table I summarizes mean unsigned errors (MUEs) for MCSI(13g), MCSI(27g), and MCSI(35g) averaged over the wide range of dynamically relevant geometries, obtained by sampling trajectories as explained in the previous paragraph. The MUEs in this table are given for the energy range from zero to ~34 kcal/mol, with the zero of energy at the reaction product, i.e., at the H₂O+H asymptote. The reaction energy and the forward and reverse barrier heights on each interpolated surface are −13.6, 4.9, and 18.6 kcal/mol, respectively, for both the target electronic structure level and the interpolation; the interpolation reproduces these values precisely because one of the Shepard points is at the reaction saddle point and because the method involves adjusting the relative energies of the reactant and of the product asymptotes that are described by pure molecular mechanics,[38,39] as described elsewhere.[21,40] The energy range covered in Table I thus goes from zero (actually, the lowest energy point in the data set is ~0.1 kcal/mol) up to 33.6 kcal/mol, that is, up to 15 kcal/mol above the reaction saddle point, which is higher than needed for studying collisions under thermal conditions, even at combustion temperatures.

The results in Table I indicate that the MUEs for the MCSI(27g) and MCSI(35g) surfaces are, on the average, within chemical accuracy (defined here as 1 kcal/mol) up to 25.6 kcal/mol; the MCSI(13g) surface is equally accurate up to 19.6 kcal/mol, which corresponds to a range of 19.5 kcal/mol. Note that no Shepard points have been placed above the reaction saddle point in the latter case, therefore, the MCSI(13g) surface is less accurate in the higher-energy range. Table I also shows that the source of the error for MCSI(27g) and MCSI(35g) is primarily due to the molecular mechanics force field because there is no significant im-
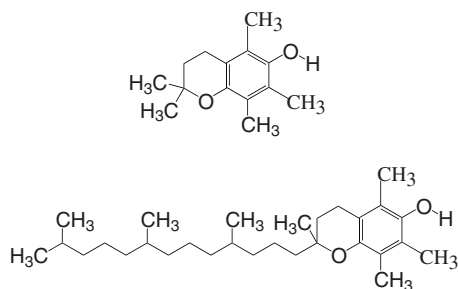
FIG. 1. Structure of the reactant in reaction R2 (top). Structure of α-tocopherol (bottom).

provement in going from 27 Shepard points to 35 Shepard points. The inclusion of Hessians, or, equivalently, the inclusion of a second derivative term into Eq. (7) does not change this situation. This, again, indicates that the error is dominated by the molecular mechanics. In fact, although we do not present the details of a fit including Hessians in this paper, we did carry out such a fit, and we found that at most points there is a little change in accuracy, in either direction, but at a few points in a higher energy region the results actually become worse than for the surface obtained without using the Hessians. This is not necessarily surprising because in any computational method that involves several sources of error, reducing a particular error which is not the dominant error does not necessarily improve the final result; the overall error might get better or it might get worse. One therefore can conclude that if one desires to get a more accurate global representation of a potential energy surface with an error of a few tenths of kcal/mol, one has to adopt a better molecular mechanics force field, which appears to be the dominant source of error. The latter task involves adjusting the functional forms and/or parameters for one-dimensional functions to describe individual bond stretches, valence angles, and torsions and for the van der Waals interactions, and as such, is significantly less involved than conventional fitting of a full-dimensional potential for a reactive system.

III.B. Hydrogen atom abstraction from 5,7,8-trimethyl-croman-6-ol (a model of α-tocopherol) by methyl radical

The second reaction studied in the present article is a hydrogen transfer from a model compound representing a phenolic antioxidant related to vitamin E. In particular we consider

$$CH_3^\bullet + ROH \rightarrow CH_4 + RO^\bullet \quad (R2),$$

where R is illustrated in Fig. 1 both for the α-tocopherol molecule and its model used in the present paper. The R group studied here has 32 atoms so the whole system has $N=38$ atoms, and the dimensionality of the potential energy surface is $3N-6=108$. Hydrogen atom abstraction from phenolic antioxidants related to vitamin E has been extensively studied in the past.[41–45] With few exceptions,[45] theoretical studies have primarily been focused on calculations of reaction barrier heights[42] or reaction energies.[44] In the present work, we applied the MCMM method to generate the full-dimensional lowest adiabatic potential energy surface for hy-

drogen atom abstraction from 5,7,8-trimethyl-croman-6-ol by methyl radical, and we have assessed the accuracy of the interpolated surface.

Potential energies and gradients at Shepard points have been obtained using the MPWB1K density functional[36] with the 6-31G(d,p) basis set.[37] Since our goal here is to test the ability of the MCSI method to interpolate potential energy surfaces rather than to get quantitative results for a particular reaction, this choice of the electronic structure method is adequate. Nuclear permutation symmetry has not been imposed for reaction R2. We used the MM3 (Ref. 38) molecular mechanics force field as a starting point for this reaction. The missing parameters have been roughly optimized to make the contour plots of the interpolated surface qualitatively agree with the contour plots of the target (uninterpolated) surface. Furthermore, a few molecular mechanics parameters that already exist in MM3 have been roughly readjusted in a similar way. The new molecular mechanics atom types and new molecular mechanics parameters, i.e., those which are not present in the original MM3 (Ref. 38) force field, along with the modified parameters, are given in the supporting information.[46]

Shepard interpolation [Eq. (2)] has been performed in nonredundant internal coordinates; the total number of coordinates is 108. The set of coordinates **s** used in calculation of the weight function of Eq. (9) involved the three internuclear distances of the three atoms involved in the hydrogen transfer, namely, the $O-H_t$, $C-H_t$, and $C-O$ distances (where the subscript t denotes the transferring hydrogen atom).

The electronic-structure Shepard points have been placed as follows. The first six points have been placed along the minimum energy path for the reaction calculated in mass-scaled Cartesian coordinates. When starting from the reaction saddle point and going down toward both the reactants and the products, the reaction coordinate initially corresponds largely to the motion of the hydrogen atom while the positions of the rest of the atoms remain nearly unchanged; and the first six Shepard points correspond to geometries with varying $O-H_t$ distance with the rest of the internal coordinates being approximately fixed at their values at the reaction saddle point. In particular, the O–H distance at these Shepard points changes from 1.02 to 1.45 Å, whereas the O–C distance is about 2.5 Å at each of these geometries. The other four Shepard points have been placed at (1.68; 2.70), (0.96; 2.70), (1.11; 2.66), and (0.97; 2.77), where the numbers in parentheses indicate the $O-H_t$ and $C-O$ distances (in angstroms), respectively, with the remaining internal coordinates fixed at their values at the reaction saddle point. Finally, one Shepard point has been placed in the energy well of the hydrogen-bonded complex of the products, at a geometry where the gradient calculated at the target level is relatively small; in particular, where the magnitude of the largest Cartesian component of the gradient is 5.0×10^{-5} hartree/bohr. At this geometry, the $O-H_t$ and C–O distances are 2.58 and 3.67 Å, respectively. Figures 2 and 3 show contour plots of the interpolated and accurate potential energy surfaces for this system as functions of the $O-H_t$ and C–O internal coordinates. The molecular geometries used to generate these contour plots have also been
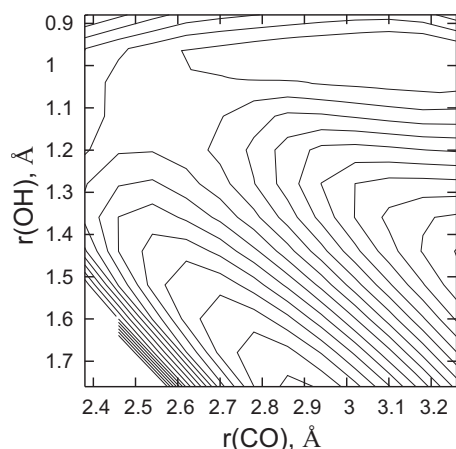
FIG. 2. Equipotential contour plot of the interpolated MCSI(11g) potential energy surface as a function of the OC and OH distances. The remaining internal coordinates (bond distances, bond angles, and torsions) are fixed at their values at the reaction saddle point. Contours start at 14.3 kcal/mol and are equally spaced by 3 kcal/mol with the zero of energy at the product asymptote. Bond distances are in angstroms.

used to generate statistics on the accuracy of the interpolated surface. In this 12×12 grid of geometries, the O–H$_t$ distance changes from 0.88 to 1.76 Å, and C–O changes from 2.38 to 3.22 Å.

The MUEs for the interpolated surface using input of only energies and gradients at the 11 Shepard points are given in Table II. For this system, we only considered the surface up to ~9 kcal/mol above the reaction saddle points due to the possibility of a low-energy conical intersection in a reaction of this kind.[45] For this reason, the higher-energy nuclear configurations have not been included in the statistics. As one can see from Table I, the MUEs are within the chemical accuracy over an energy range of 32 kcal/mol, from 14.3 to 46.3 kcal/mol. These are very encouraging results considering that the molecular mechanics force field has not been optimized for this reaction and only very rough optimization was performed for the new parameters. One could reduce the MUEs further by optimizing reaction-specific molecular force field.
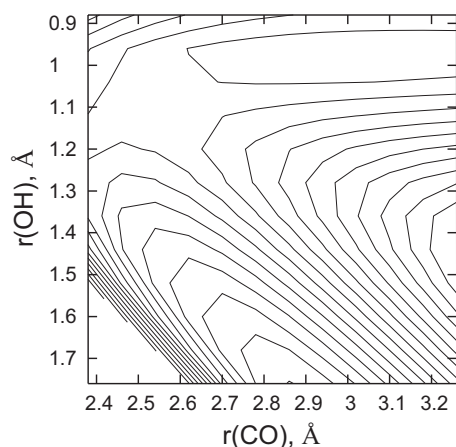

FIG. 3. Same as Fig. 2 except for the accurate (uninterpolated) potential energy surface.

TABLE II. MUE for MCSI(11g) for different ranges of potential energy (the zero of potential energy corresponds to the product asymptote; the reaction saddle point is 36.85 kcal/mol higher than the product asymptote, and the reactant potential energy is 31.33 kcal/mol higher than the product) for reaction of hydrogen atom abstraction from 5,7,8-trimethyl-croman-6-ol (a model of α-tocopherol) by methyl radical, averaged over a number of molecular geometries.

Energy range	MCSI(11g)	N_{geom} [a]
14.3–37.3	0.67	65
14.3–40.3	0.87	88
14.3–42.3	0.88	94
14.3–46.3	0.98	108

[a]Number of geometries in the energy range; this is a subset of the 144 geometries on the grid used for Figs. 2 and 3.

IV. CONCLUDING REMARKS

In this paper, we have tested an MCSI interpolation scheme which only uses gradient information (and no Hessians) from electronic structure calculations. The quality of the interpolated surfaces is assessed by comparing the interpolated potential energies to the potential energies obtained directly from electronic structure calculations for representative sets of molecular geometries. The assessment is performed for small and medium-sized reactive systems, with respectively four and 38 atoms, for which the interpolated potential energy surfaces have been generated from a small number of Shepard points. In each case the surfaces are found to be chemically accurate (to within 1 kcal/mol) in the range of potential energy up to a few kcal/mol above the reaction saddle point. The accuracy of the surfaces in higher energy ranges could be improved by placing Shepard points in these energy ranges, and the overall MUEs of the surfaces could be reduced by adopting reaction-specific molecular mechanics force fields. We have also found that the inclusion of the Hessians does not necessarily improve the surface in all energy ranges considered. The inclusion of Hessians is recommended in cases when one is interested in accurate second derivatives of a potential energy surface at or close to stationary points (such as, e.g., in the use of the interpolated surface for variational transition theory calculations) but we can now conclude that Hessians are not required if the goal is to obtain reasonable global representations of potential energy surfaces without necessarily having precisely fitted vibrational force constants.

The method presented in this article has significant advantages for fitting reactive potential energy surfaces for systems with many degrees of freedom. It requires only a small number of gradients and no Hessians, the potential can be evaluated during dynamics calculations without solving linear equations, and the method is applicable to potential energy surfaces with many degrees of freedom, such as the 108-degree-of-freedom system considered here. Additional improvements are still possible. For example, we showed previously in the Hessian-based version of MCSI that it is not necessary to use full Hessians,[28] and a similar partial-gradient scheme might be useful. Similarly we showed how the Hessian-based scheme could efficiently be applied in the context of electronically embedded combined quantum me-

chanical and molecular mechanical methods,[24,34,35] and this could also be applied to the present gradient-only version.

ACKNOWLEDGMENTS

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