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Accuracy of Low-level Surface in Hierarchical Construction of Potential Energy Surface

Chun-rui Wang, Dong H. Zhang*

State Key Laboratory of Molecular Reaction Dynamics & Center for Theoretical and Computational Chemistry, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

The effects of low-level PES on the overall accuracy of the final surface constructed by using hierarchical construction were investigated with the constructions of a number of global surfaces for the H3 system at UHF (UMP2, DFT-B3LYP, UCCSD(T))/vtz, and UCCSD(T)/avqz levels of theory. The total reaction probabilities for the $H+H_2$ reaction calculated on these surfaces revealed that the accuracy of UCCSD(T)/avqz surface is very close to the well-known BKMP2 surface, while the UCCSD(T)/vtz PES has a slightly higher barrier. In contrast, the low-level theories (UHF, UMP2, DFT-B3LYP) with vtz basis set can only provide a qualitative description of this simplest reaction despite the fact that they are widely used to study reactions in complex systems. On the other hand, although these theories are not accurate on describing the reaction, they can be used to provide the low-level PESs for hierarchical construction of the UCCSD(T)/avqz PES with the number of UCCSD(T)/avqz energies substantially reduced.

Key words: Hierarchical construction scheme, Accuracy of potential energy surface, Three-dimensional cubic spline

I. INTRODUCTION

Accurate potential energy surfaces (PES) are a prerequisite for many types of chemical calculations, ranging from spectroscopy to reaction dynamics. The construction of PES starts from electronic structures calculations by either *ab initio* methods or density functional theory (DFT) on a large number of molecular configurations, followed by PES generation by using various PES generation methods, such as functional fitting [1, 2], spline [3, 4], reproducing kernel Hilbert space (RKHS) [5], modified Shepard interpolation [6], interpolating moving least-squares [7], and neural networks [8]. The accuracy of a constructed PES, which is crucial to the final output, depends on the *ab initio* level used for electronic structure calculations, the number of *ab initio* data points calculated to sample the molecular configuration, as well as the generation method used to construct the PES. One main difficulty for PES generation comes from the fact that the overall magnitude of potential energy variation for a molecular system is much larger than the required accuracy in important energy region. For example, for a reaction system the potential energy may vary a few tenths of eV along the reaction path, and a few percents of eV in error may deteriorate the accuracy of a PES considerably. While on

the coordinates perpendicular to the reaction path, the variation of the potential energy typically is a few eV. It is certainly not a trivial task to construct a global PES spanning such a large energy scale accurately. On the other hand, because the computational cost increases fast with the level of the electronic structure calculations, it is very expensive to sample the many molecular configurations using high level data points. Therefore, it is of great importance to develop practical generation methods to construct accurate PES at minimum computational cost for energy calculations.

Some time ago, Fu *et al.* proposed a hierarchical construction scheme for accurate *ab initio* PES generation [9]. The scheme is based on a simple observation that when molecular configuration changes, the variation in the potential energy difference between different *ab initio* methods is significantly smaller than the variation for potential energy itself. This means it is much easier to numerically represent energy difference instead of energy itself. Because the computational cost for *ab initio* calculations increases very rapidly with accuracy, one can gain substantial saving on computational cost by constructing a high accurate potential energy surface as a sum of a low accurate surface based on extensive low-level *ab initio* data points and an energy difference surface for low and high accuracy *ab initio* methods based on much fewer data points.

The new scheme was applied to construct an accurate ground potential energy surface, known as FXZ PES, for the FH_2 system by three-dimensional spline method

*Author to whom correspondence should be addressed. E-mail: zhangdh@dicp.ac.cn, FAX: +86-411-84675584

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with 15×10^3 UCCSD(T)/avqz energies for the low-level PES, and 1.4×10^3 UCCSD(T)/av5z energies for the energy difference PES. In another word, they used 15×10^3 points of UCCSD(T)/avqz energies and 1.4×10^3 points of UCCSD(T)/av5z energies to yield a smooth UCCSD(T)/av5z PES, reducing the total computational time by about a factor of 4.5 if one simply calculated 15×10^3 points of UCCSD(T)/av5z energies. The PES has been widely used to study dynamical resonances in the $F+H_2/HD$ reactions [10, 11] as well as many other properties in the reaction system [12, 13]. The overall accuracy has been found to be remarkable.

The rationale to choose the UCCSD(T)/avqz PES as the low-level PES for the FH_2 system is to reduce the fitting error to the maximum degree in order to predict the resonances in the $F+H_2/HD$ reactions at spectroscopic accuracy. However, for theoretical studies of most chemical reactions, this level of accuracy is not achievable or desired. As a result, one may consider to use a lower accuracy PES, which can be constructed very easily, as the low-level surface to cut the overall computational cost further.

In this work, we use the H3 system as the model to investigate the effects of the accuracy of the low-level PES on the overall accuracy of the final PES. The $H+H_2$ system is the simplest gas-phase reaction, which has played an extremely important role in chemical reaction dynamics studies. Many global analytic potential energy surfaces for the $H+H_2$ system, such as LSTH [14−18], BKMP [19], and BKMP2 [20] PESs, have been extensively used in the quantum reaction dynamics calculations. Excellent agreements with the experiments have been achieved on the BKMP2 PES, which was fitted to 8701 *ab initio* energies.

II. THEORY

A. Hierarchical construction scheme for accurate PES generation

The basic idea of hierarchical construction (HC) scheme can be explained as follows:

$$\mathbf{V}_{\text{high}}(\mathbf{R}) = \mathbf{V}_{\text{low}}(\mathbf{R}) + \Delta\mathbf{V}_{\text{high-low}}(\mathbf{R}) \tag{1}$$

$$\mathbf{V}_{\text{low}}(\mathbf{R}) \leftarrow V_{\text{low}}, \quad \text{dense points} \tag{2}$$

$$\Delta\mathbf{V}_{\text{high-low}}(\mathbf{R}) \leftarrow V_{\text{high}} - V_{\text{low}}, \quad \text{sparse points} \tag{3}$$

where $\mathbf{V}_{\text{high}}$ is a high accuracy PES, $\mathbf{V}_{\text{low}}$ is a low accuracy PES, $\Delta\mathbf{V}_{\text{high-low}}$ is the energy difference PES between high and low accuracy methods, $\mathbf{R}$ represents the nuclear coordinates, and V represents quantum chemistry calculation data points. Eqs. (1)−(3) mean that a high accuracy PES can be constructed by a sum of a low accuracy PES based on extensive data points and an energy difference surface based on much fewer data points. Because the dense data points for low accuracy PES can be calculated by simple quantum chem-
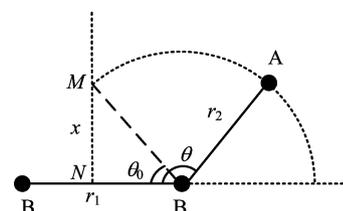

FIG. 1 The internal coordinates used for three-dimensional spline for a triatomic AB2 system, where $\theta_0 = a\cos(r_1/(2r_2))$.

istry methods, the computational cost can be greatly reduced.

In Fu's work [9], they have chosen UCCSD(T)/avqz as the low accuracy method and UCCSD(T)/av5z as the high accuracy method, which reduced the total computational time by a factor of about 4.5. In this work, we will investigate the effects of low-level PES on the final accuracy of the PES, to further reduce the computational cost.

B. Spline scheme for AB2 and B3 system

For a triatomic system, the internal coordinates shown in Fig.1 are the most commonly used coordinate system for spline. For an AB2 system, because the potential is symmetric with respect to the perpendicular line equally bisecting the B2 bond as shown in Fig.1, one can utilize the symmetry to reduce the number of energy points required for spline.

Suppose we perform spline on θ first for fixed r_1 and r_2, we can utilize the symmetry to limit the range of θ as following: when $r_2 \le r_1/2$, $0° \le \theta \le 180°$; otherwise, $\theta_0 \le \theta \le 180°$, where $\theta_0 = a\cos(r_1/(2r_2))$. As we know, for the first case ($r_2 \le r_1/2$) the first order derivates of the potential with respect to θ, $dV/d\theta$, are zero at both end. For the second case, $dV/d\theta(\theta=\theta_0)=dV/dxr_2\cos(\theta_0)$. To perform spline for r_2, one can also use $dV/dr_2 = dV/dx\sin\theta_0$ on the dividing line. And dV/dx can be obtained from the spline straightforwardly by calculating sufficient energy points on the dividing line. In this way, we can carry out the three-dimensional spline without any energy points on the other side of the dividing line.

For a B3 system, in addition to the symmetry of an AB2 system we can use $r_1 \ge r_2$, or $\theta \ge 60°$, to reduce the number of energy points further.

III. RESULTS

We use the spline scheme for B3 system to construct the potentials using HC method. For the set of dense points, the grid is specified as follows: r_1 and r_2 are chosen from 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 2.0, 2.2, 2.4, 2.6, 2.8, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0,
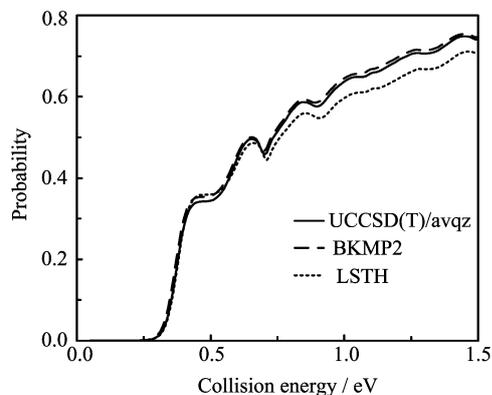
FIG. 2 Total reaction probabilities for the H+H$_2$ reaction as a function of collision energy calculated on the UCCSD(T)/avqz PES, in comparison with those from the BKMP2 and LSTH PES.

FIG. 3 Total reaction probabilities for the H+H$_2$ reaction as a function of collision energy calculated on the UHF(UMP2, B3LYP, UCCSD(T))/vtz PES, in comparison with those from UCCSD(T)/avqz PES.

7.0, 8.0, 9.0, 10.0, 11.0, 12.0, and 13.0 a_0 with the restriction of $r_1 \geq r_2$, and the angle θ runs from θ_0 to 180° in increments of 10°. This grid contains 5888 conformations. In addition, 496 points on the perpendicular bisector lines are added to calculate energies and first order derivatives at the endpoints on the dividing lines. For the set of sparse points, the grid dense is reduced as follows: r_1 and r_2 are chosen from 0.7, 0.9, 1.2, 1.5, 1.8, 2.2, 2.8, 3.5, 5.0, 7.0, 10.0, and 13.0 a_0, and the increments of θ are 20°. Similarly 96 points on the dividing line are prepared to calculate the first order derivatives. It yields a total number of 767 configurations, which is much smaller than that for the dense grid.

In order to provide a standard PES to examine the accuracy of the HC PESs, we calculated UCCSD(T)/avqz (spin unrestricted coupled cluster method with all single and double excitations and perturbative accounts of triple excitations, using an augmented correlation consistent polarized valence quadruple zeta quality basis set) energies on the set of dense points to construct a high accuracy PES (denoted as UCCSD(T)/avqz PES). Figure 2 shows the total reaction probabilities for the H+H$_2$ reaction with the total angular momentum $J=0$ obtained on the UCCSD(T)/avqz, BKMP2, and LSTH PESs using the time-dependent wave packet method. The reaction probabilities obtained from the UCCSD(T)/avqz PES agree well with those from BKMP2 which has been proved to be very accurate for the H3 system, and are much better than those from LSTH. The fact that one can obtain a smooth PES for the H3 system by using about 6×10^3 energy points clearly shows that three-dimensional spline is indeed a good choice for PES construction for triatomic systems, in particular for those involving identical atoms.

Figure 3 shows the total reaction probabilities for the H+H$_2$ reaction with $J=0$ obtained on the PESs calculated by the UHF, UMP2, DFT with B3LYP functional, and UCCSD(T) methods, all with basis set of vtz, in comparison with that from the UCCSD(T)/avqz PES.
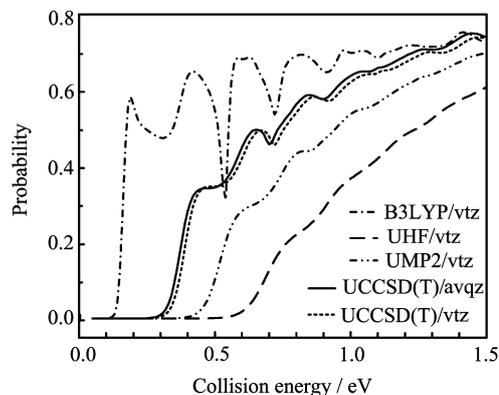
Here all the potentials are constructed based on the set of dense points. First of all, one can see the reaction probabilities on the UCCSD(T)/vtz PES agree rather well with that on the UCCSD(T)/avqz PES, except an energy shift of 15 meV. This energy shift is rather small, but it still shows that vtz basis set is not sufficient even for such a simple reaction to achieve the level of accuracy commonly pursued nowadays for triatomic systems.

In strong contrast, the reaction probabilities obtained on the UHF, UMP2, and B3LYP PESs differ substantially from those on both UCCSD(T)/avqz and UCCSD(T)/vtz PESs. Because the UHF, UMP2, and B3LYP PESs were constructed with the same basis set as the UCCSD(T)/vtz PES, the substantial differences clearly reveal that UHF, UMP2, and DFT with B3LYP functional are very poor on describing the reaction. It can be seen that the reaction probabilities on the UHF PES are substantially smaller than on the UCCSD(T)/vtz PES, with a threshold energy of 0.52 eV which is higher than those on the UCCSD(T)/vtz PES by 0.24 eV. The reaction probabilities on the UMP2 PES are also considerably smaller than those on the UCCSD(T)/vtz PES, with a threshold energy of 0.40 eV which is higher than that on the UCCSD(T)/vtz PES by 0.12 eV. On the other hand, the threshold for the B3LYP PES is only 0.1 eV, lower than that of UCCSD(T)/vtz PES by about 0.18 eV. And the reaction probabilities on the B3LYP PES are larger than those of UCCSD(T)/vtz PES, in particular in low collision energy region. Furthermore, the reaction probability curve is substantially more oscillatory than that of UCCSD(T)/vtz. Therefore, UMP2 and DFT with B3LYP functional can only provide a qualitative description of this simplest reaction despite the fact they have been used widely to study complex reactions.

From Fig.3, one can see that the UHF, UMP2, and B3LYP PESs differ substantially from the
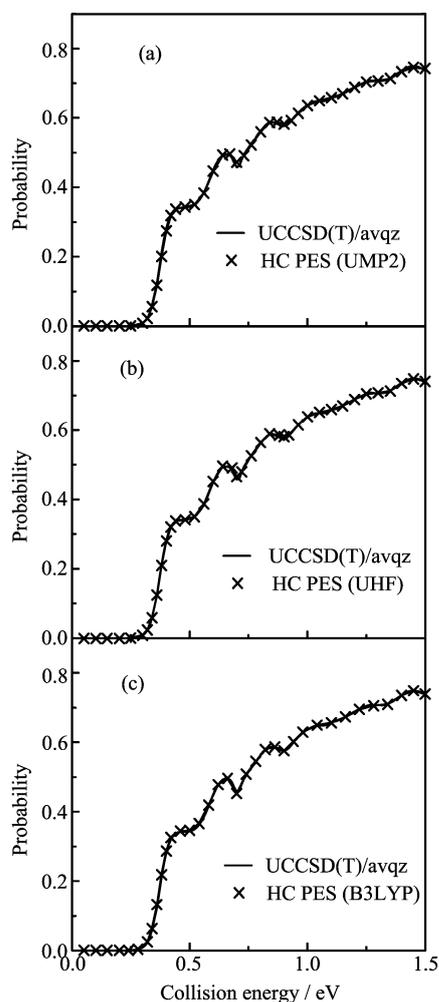
FIG. 4 Comparison of the total reaction probabilities for the H+H$_2$ reaction from the UCCSD(T)/avqz PES with the HC PES using (a) UHF/vtz, (b) UMP2/vtz, and (c) B3LYP/vtz PES, as low-level surfaces.
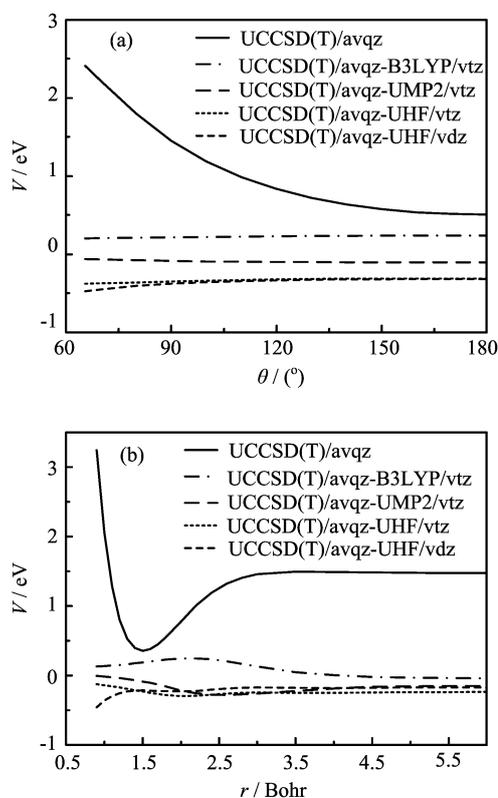

FIG. 5 Representative potential curves for UCCSD(T)/avqz PES, in comparison with energy differences as a function of (a) θ with $r_1=1.5a_0$ and $r_2=1.8a_0$ and (b) r_1 with $r_2=2.2a_0$ and $\theta=180°$.

UCCSD(T)/vtz and UCCSD(T)/avqz PESs. Can they be used as low-level PESs for hierarchical construction of accurate PES for the system to reduce the number of high level *ab initio* energy points? We used them as the low-level PESs for hierarchical construction of the UCCSD(T)/avqz PES by only calculating UCCSD(T)/avqz energy points on the sparse grid points.

Figure 4 shows the total reaction probabilities for the H+H$_2$ reaction with the total angular momentum $J=0$ obtained on HC PESs. As can be seen, no matter with the UHF, UMP2, or B3LYP PES as the low-level PES, the HC PES is able to produce the total reaction probabilities for the reaction in perfect agreement with that from the UCCSD(T)/avqz PES. Because the number of energy points for the sparse grid is only about 800, in comparison with that of 6×10^3 points for the dense grid, it is clear that the UHF, UMP2, and B3LYP PESs can be used as the low-level PES for hierarchical con-

struction of accurate PES to substantially reduce computational costs for *ab initio* calculations.

To help understand why the UHF, UMP2, and B3LYP PESs can be used as low-level PES despite the fact they are very poor on describing the reaction, we plot in Fig.5 two UCCSD(T)/avqz potential curves, for which one needs to do spline accurately in order to obtain an accurate UCCSD(T)/avqz PES. As can be seen, the potential values change substantially no matter with r or with θ. Consequently one has to use a set of dense grids to achieve an accurate spline PES. In contrast, the energy differences between the UCCSD(T)/avqz and UHF(UMP2, B3LYP)/vtz are considerably smaller in magnitude, as a result one can use a set of sparse grids to reduce substantial computational cost. Furthermore, even if we use the UHF/vdz level of *ab initio* method for the low-level PES, we are still able to obtain a HC PES with the same level of accuracy as the standard UCCSD(T)/avqz PES, simply because the energy differences between UCCSD(T)/avqz and UHF/vdz energies are quite close to those between UCCSD(T)/avqz and UHF/vtz energies as shown in Fig.5. UHF/vdz is essentially the simplest *ab initio* method with a very small basis set, in which the computational time can be negligible compared with UCCSD(T)/avqz, yet it still can be used as the low-level *ab initio* method to

substantially reduce the number of high-level *ab initio* energy points for accurate PES construction.

IV. CONCLUSION

On the H3 system, we investigated the effects of low-level PES on the overall accuracy of the final PES constructed by HC scheme. We constructed a number of global PESs for the H3 system at UHF(UMP2, DFT-B3LYP, UCCSD(T))/vtz, and UCCSD(T)/avqz levels of theory, utilizing three-dimensional spline by taking full advantage of exchange symmetry of the system. The total reaction probabilities for the H+H$_2$ reaction calculated on these PESs using the time-dependent wave packet method revealed that the accuracy of UCCSD(T)/avqz PES is very close to the well-known BKMP2 PES, while the UCCSD(T)/vtz PES has a slightly higher barrier. In contrast, the low-level theories (UHF, UMP2, DFT-B3LYP) with vtz basis set can only provide a qualitative description of this simplest reaction despite the fact that they are widely used to study reactions in complex systems. On the other hand, although these theories are not accurate on describing the reaction, they can be used to provide the low-level PESs for hierarchical construction of the UCCSD(T)/avqz PES with the number of UCCSD(T)/avqz energies substantially reduced. Because the computational cost for these low-level theories with a small basis set is essentially negligible compared to UCCSD(T) with a large basis set, one should use HC method to construct accurate PES to substantially reduce the overall computational cost for *ab initio* calculations.

V. ACKNOWLEDGMENTS

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