Growing multiconfigurational potential energy surfaces with applications to $X+H_2$ ($X=C, N, O$) reactions

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A previously developed method, based on a Shepard interpolation procedure to automatically construct a quantum mechanical potential energy surface (PES), is extended to the construction of multiple potential energy surfaces using multiconfigurational wave functions. These calculations are accomplished with the interface of the PES-building program, GROW, and the GAMESS suite of electronic structure programs. The efficient computation of multiconfigurational self-consistent field surfaces is illustrated with the $C+H_2$, $N+H_2$, and $O+H_2$ reactions. © 2006 American Institute of Physics. [DOI: 10.1063/1.2185641]

I. INTRODUCTION

The investigation of the chemical dynamics of a molecular system allows both time-independent and time-dependent phenomena to be calculated. This facilitates both comparisons with experimental data and the prediction and interpretation of details not easily obtainable from experiments. In order to perform dynamics calculations over a large range of configurations, knowledge of the corresponding molecular potential energy surface (PES) must cover a broad range of coordinate space. The least biased and most accurate method to obtain data about the surface is through first principles or quantum mechanics (QM) electronic structure calculations. With the advancement of high performance computing and scalable codes, QM methods can provide very accurate calculations of small molecules and molecular systems. But, in most cases, QM calculations can only provide an incomplete picture of the PES due to the large computational cost of such methods. The calculation of QM energies and first and second derivatives (gradients and Hessians) at selected discrete points only gives the overall *shape* of the PES. The difficulty arises in that a finite number of unrelated energy and derivative values *alone* do not constitute a molecular PES. The PES may be more formally defined as a function or algorithm that is capable of accurately describing the molecular energy while some interatomic distances change by several angstroms and others by no more than 0.1 Å.

Many methods have been used to obtain a PES: fitting an assumed global functional form to the available QM data,^{1,2} using some expansion of the potential about a reaction path,³ or interpolating in some way between known data points.^{4,5} Direct dynamics can also be carried out “on the fly,” with *ab initio* or semiempirical calculations at every molecular con-

figuration generated by the dynamics calculation.^{6,7} The bottleneck in using electronic structure theory to build a PES and, therefore, the study of reaction dynamics, is the dimensionality of the system and the number of points needed in each dimension to accurately describe the PES. For a diatomic molecule, the PES is just a one-dimensional curve. For a triatomic system, a global, three-dimensional surface must be constructed. Four atoms require the determination of a six-dimensional surface. Beyond four atoms, the determination of a global PES in this manner is almost impossible. Of course, most interesting chemical systems contain more than four atoms. The number of points needed in each dimension depends on the molecular system and the desired properties. It is therefore desirable to design a method for constructing a global PES that is accurate, computationally cost-effective, and generic.

Collins and co-workers^{4,8–13} have derived and developed a method based on a modified Shepard interpolation procedure to construct a molecular PES. The goal is to produce an accurate PES with the smallest number of QM calculations by carefully selecting the location of data points. The interpolation method used to construct the PES is combined with classical trajectory simulations to provide an iterative scheme for successively improving and updating the PES. The simulations allow the configuration space to be broadly sampled. This methodology, implemented in the program GROW, has been developed to minimize the interpolation error for a given number of data points, thereby ensuring that the PES can be reliably constructed for a small set of data points without the need to fit to a functional form. Thus, reliance on chemical intuition and the inadvertent introduction of unphysical features can be avoided. Each iteration automatically places new data points only in dynamically important parts of the configuration space; QM calculations are then performed at those points. For example, the OH

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$+H_2 \rightarrow H_2O + H$ reaction only required ~ 200 data points to accurately describe the PES;^{8,11,12} ~ 1500 data points were needed for a reasonably accurate interpolation of the $H + CH_4 \rightarrow H_2 + CH_3$ reaction.¹³

The original implementation of GROW was confined to the construction of potential energy surfaces for ground electronic states. This paper describes the extension of GROW to enable the study of reactions on multiple surfaces and problems that require a multireference description. Since GROW requires QM energies and derivatives at a selected number of data points in order to “grow” the PES, the interface of GROW and the quantum chemistry program GAMESS (Ref. 14) is implemented. The paper begins with a brief introduction to the essential features of GROW, followed by a description of the ability to generate multiple multiconfiguration self-consistent field (MCSCF) surfaces with the GROW-GAMESS interface. Finally, applications to $X + H_2$ reactions ($X = C, N, O$) will be discussed.

II. METHOD DESCRIPTION AND DEVELOPMENT

A. GROW

The features of GROW have been described elsewhere^{4,8–13} so only a brief description is given here. GROW constructs a PES as an interpolation of Taylor expansions centered at data points scattered throughout the configuration space of the system.⁴ In general, a surface is constructed by expanding the surface in the vicinity of a “data point” as a Taylor series in the inverse distances, $\mathbf{Z}$, where $Z_k = 1/R_k$ and $\mathbf{R}$ is the set of interatomic distances. More physically reasonable behavior is obtained when the Taylor expansion is written in terms of inverse distances $\mathbf{Z}$ rather than interatomic distances,⁴

$$T_i(\mathbf{Z}) = V[\mathbf{Z}(i)] + \sum_{k=1}^{3N-6} [Z_k - Z_k(i)] \left. \frac{\partial V}{\partial Z_k} \right|_{\mathbf{Z}=\mathbf{Z}(i)} + \frac{1}{2!} \sum_{k=1}^{3N-6} \sum_{j=1}^{3N-6} [Z_k - Z_k(i)][Z_j - Z_j(i)] \times \left. \frac{\partial^2 V}{\partial Z_k \partial Z_j} \right|_{\mathbf{Z}=\mathbf{Z}(i)} + \dots, \quad (1)$$

where $V[\mathbf{Z}(i)]$ is the potential energy at $\mathbf{Z}(i)$ and derivatives are taken with respect to inverse distances at the i th data point $\mathbf{Z}(i)$. The expansion is truncated to second order.

For a system with more than four atoms, redundant internal coordinates can occur since the number of internuclear distances is greater than the number of independent internal coordinates, $3N-6$. In this case, a set of $3N-6$ local internal coordinates ζ are constructed as linear combinations of the $N(N-1)/2$ reciprocal distances for each $\mathbf{Z}(i)$,¹³

$$\zeta^{(X_0)}(X) = \tilde{U}^T \mathbf{Z} \quad \text{for } \mathbf{Z} \text{ close to } \mathbf{Z}_0 = \mathbf{Z}(X_0),$$

where X_0 refers to the initial set of Cartesian coordinates.

The matrix $\mathbf{U}$ is defined in terms of molecular fragments, using both intra- and intermolecular distances. The QM Cartesian derivatives of the PES at $\mathbf{X}(i)$ must then be trans-

formed into these internal coordinates. The Taylor series in Eq. (1) is then evaluated using these internal coordinates in place of the reciprocal distances.

Once the required QM energy and derivatives have been evaluated at some number (N_d) of molecular configurations, a modified Shepard interpolation^{15,16} defines the total potential energy (PE) $V(\mathbf{Z})$ at any configuration $\mathbf{Z}$ as a weighted average of Taylor series about all N_d initial data points and their symmetry-determined equivalents,⁸

$$V(\mathbf{Z}) = \sum_{g \in G} \sum_{i=1}^{N_d} w_{g \circ i}(\mathbf{Z}) T_{g \circ i}(\mathbf{Z}), \quad (2)$$

where G indicates the molecular symmetry group [usually the complete nuclear permutation (CNP) group] and $g \circ i$ indicates that the i th data point $\mathbf{Z}(i)$ is replaced by a data point transformed by group element g . The sum over the set of symmetry elements g means that all permutationally equivalent data points are included in the energy expression; no new QM calculations need to be performed for these symmetrically equivalent points. This procedure results in a symmetrized data set, and a PES that exhibits the full molecular symmetry.¹⁷

The normalized weight function w_i weights the contribution of a Taylor expansion at $\mathbf{Z}(i)$ to the total PE at configuration $\mathbf{Z}$,

$$w_i(\mathbf{Z}) = \frac{\nu_i(\mathbf{Z})}{\sum_{g \in G} \sum_{k=1}^{N_d} \nu_{g \circ k}(\mathbf{Z})}. \quad (3)$$

Data points that are spatially close to $\mathbf{Z}$ will have a larger weight. The biasing of data is achieved using the unnormalized weight function $\nu_i(\mathbf{Z})$,

$$\nu_i(\mathbf{Z}) = \left(\left[\sum_{l=1}^{N(N-1)/2} \left(\frac{Z_l - Z_l(i)}{d_l(i)} \right)^2 \right]^q + \left[\sum_{l=1}^{N(N-1)/2} \left(\frac{Z_l - Z_l(i)}{d_l(i)} \right)^2 \right]^p \right)^{-1} \quad \text{for } q \ll p. \quad (4)$$

Here $q=2$ and $2p \gg 3N-3$,¹⁴ and the $\{d_l(i)\}$ effectively define a type of confidence volume about $\mathbf{Z}(i)$. If the components of $\mathbf{Z}$ fall within the “confidence lengths” of $\mathbf{Z}(i)$, the weight assigned to $\mathbf{Z}(i)$ will fall slowly as the effective distance, $\|\mathbf{Z} - \mathbf{Z}(i)\|$, increases. If $\mathbf{Z}$ falls outside the confidence length, the weight assigned to $\mathbf{Z}(i)$ falls quickly with an increase in distance. As described elsewhere, the confidence lengths are determined through a Bayesian analysis.⁹ This two-part weight function allows the relative weights of two or more data points near $\mathbf{Z}$ to vary only slowly with varying $\mathbf{Z}$; this reduces the error in the PES gradient and is especially important for larger systems.¹³

The basic iterative procedure is as follows (see Fig. 1).^{4,8,11} After a small initial data set is constructed, usually on a relevant reaction path (the Shepard interpolation is thus well defined on this reaction path), GROW runs a small number of trajectories with initial conditions appropriate to the reaction under study. Molecular configurations are periodically recorded to obtain a set of several thousands of geometries. One or more of these geometries is chosen to be added

FIG. 1. Schematic for the iterative procedure in GROW.

to the data set, and the required QM energies and derivatives are calculated for these points. Finally, the new data points are incorporated into the data set to form an updated PES. This process continues with the calculation of more trajectories. As the data set grows, the interpolated PES becomes more accurate. The PES is considered to be converged to chemical accuracy when the average values of observables of interest (obtained from large sets of classical trajectories) are unchanged by further iterations and increase in the size of the data set.

The methods for choosing a new data point have been described in detail elsewhere.⁸ The variance sampling method attempts to place data points at configurations where the uncertainty in the interpolated PE is the highest. The “*h*-weight” method^{4,11} attempts to place data in regions that the trajectories often visit, but where few data points are already present. Both methods are used alternately to give a more “well-rounded” description of the PES.

B. MCSCF surfaces

The initial implementation of the interpolation procedure for growing potential energy surfaces was limited to ground state surfaces and single configuration wave functions. For problems that involve significant diradical character (frequently bond-breaking processes) or multiple electronic states, multideterminant methods must be employed. The introduction of MCSCF wave functions requires the addition of new features to facilitate efficient construction of potential energy surfaces. For example, physically meaningful starting orbitals are especially important when performing MCSCF calculations. Also, when computing surfaces with multireference wave functions, it is critical to regularly update the orbitals. In a chemical reaction, bonds are breaking and forming, and orbital occupation numbers can change rapidly. The energies and occupation numbers of the orbitals must therefore be monitored, as well as the active space of the MCSCF calculation.

The interpolation procedure in GROW is initiated using data points from a reaction path calculation with GAMESS [usually an intrinsic reaction coordinate¹⁸ (IRC) calculation].

These geometries are used to generate an initial data file for the interpolated PES. The energy, gradient, and/or Hessian are calculated at each of these initial points and saved in the PES data file. The MCSCF interface also saves each geometry and wave function in libraries to be used while growing the PES. The iterative growing procedure eventually chooses a new point to add to the data set. The geometry library is searched to find the closest possible matching geometry to this new point. The corresponding wave function is then used as the initial wave function for the MCSCF calculation on the new data point. A better guess for the initial wave function allows for a much more efficient calculation.

III. APPLICATION TO X+H₂

The X+H₂ system on the ground state PES of the separated reactants is chosen to illustrate the new MCSCF potential energy surface growing process. There are three basic reactions to consider,

Following a brief discussion of the X+H₂ reactions (X = C, N, O), the specific potential energy surfaces will be discussed.

A. Background of N, C, and O reactions

The N+H₂ reaction network has been the subject of several previous experimental and theoretical studies.^{19–21} The forward abstraction reaction [Eq. (6)] is of interest in the study of rocket fuel propellants,²² and the reverse abstraction reaction is relevant to the pyrolysis of ammonia.²³ Most experimental studies of the forward and reverse abstraction reactions have been focused on reaction rate constants.^{19,23} Electronic structure calculations have also been done to predict and confirm stationary point properties and rate constants for these reactions.^{20,21} Xu *et al.*²⁰ found that the energy of reaction strongly depends on electron correlation and basis set size. For example, energies calculated at the unrestricted Hartree-Fock (UHF) level were overestimated in comparison with experimental values; the addition of polarization functions reduced the theoretical-experimental difference by ~10 kcal/mol. After the addition of electron correlation to UHF/6-311G(*d,p*) energies, barrier heights also dropped at the second order (UMP2) and fourth order (UMP4) of spin-unrestricted Møller-Plesset perturbation theory.

No experimental studies of the ground state N(⁴S) abstraction reaction have been done to determine differential cross sections and characterize rovibrational and angular distributions of the products, due to the difficulty in preparation of N atoms and NH radicals. Since ground state N(⁴S) is also not very reactive, most theoretical (and experimental) dynamics studies²¹ focused on the dynamics of the more reactive lowest excited state N(²D), as it is more reactive. Recently, Pascual *et al.*²⁴ used quasiclassical trajectory (QCT)

and variational transition state theory to study the dynamics of the forward and reverse abstraction and exchange reactions for ground state $N(^4S)$ using an accurate PES derived from high level electronic structure calculations. Their motivation was to determine rate constants, as well as to provide information about reaction cross sections and product state distributions that would be useful to experimentalists. Since the level of theory and computation time must be balanced in a dynamics study, Pascual *et al.*, after assessing several alternative levels of theory and basis set sizes, settled on multiconfigurational, quasidegenerate second order perturbation theory (MCQDPT2) calculations with fully optimized reaction space (FORS) MCSCF [FORS-MCSCF(7,6)/6-311++G(*d,p*)] molecular orbitals. GAMESS was used for the electronic structure calculations and GROW was used to generate the PES for the QCT studies. The two transition states and the PES were accurately described based on 156 points, and the predicted rate constants are in reasonable agreement with available experimental and theoretical results.

C and O are adjacent to N, each with a 3P ground state. Thus, both $C+H_2$ and $O+H_2$ are reported here for the triplet surfaces. Several theoretical dynamics studies of the CH_2 reaction on the triplet surface have been performed.^{25,26} The study done by Harding *et al.*²⁶ fits multireference configuration interaction calculations to a functional form to characterize the PES. They found no barrier for the $CH+H$ addition reaction or $C+H_2$ insertion reaction (both giving CH_2), and determined that reaction kinetics are dominated by activationless processes versus, for example, the abstraction reaction. The triplet $O+H_2$ surface has also been studied in detail.²⁷⁻²⁹ A late barrier in the abstraction reaction [Eq. (6)], ranging from 35.2 to 11.8 kcal/mol (depending on the calculation method and PES), exists for collinear reactant geometries. The saddle point features of the PES depend very strongly on the H–H–O angle, with the barrier to products increasing as this angle increases.²⁷ It has also been reported²⁸ that collinear reactant geometries in the abstraction reaction produce $^3\Pi$ and $^3\Sigma^-$ states with the $^3\Pi$ state correlating to the products. In noncollinear geometries, the doubly degenerate $^3\Pi$ state splits into the $^3A'$ and $^3A''$ electronic states. The rates of reaction for these two surfaces are very different at different temperatures as there is a more constricted bending potential for the $^3A'$ surface.²⁸

In order to demonstrate the extension of GROW to multiple PESs, results are also presented for the HCH exchange in the two lowest singlet states of the $HC+H$ exchange reaction [Eq. (7)]. Note that the first singlet state of CH_2 is only slightly higher in energy (9.025 kcal/mol) than the triplet ground state; the second singlet state is 24.2 kcal/mol above the lowest singlet state.³⁰ Past studies³¹ of the singlet surface have shown that there is no barrier for the C_{2v} perpendicular insertion [Eq. (5)] of $C(^1D)$ into H_2 , but a very high barrier (12.35 kcal/mol) for $C_{\infty v}$ collinear abstraction [Eq. (6)]. The perpendicular approach is, in fact, the minimum energy path to reach the first singlet state of CH_2 . For a fixed HCH angle (102.5°), there is no potential energy barrier to dissociation of CH_2 into $CH+H$.

B. General methods

1. Electronic structure methods

The first step in growing a global PES is to choose an appropriate level of theory and basis set. Since a PES constructed using the procedure outlined above is an accurate interpolation of the exact PES *for the level of theory employed*, an inadequate level of theory can result in a PES that does not reflect experimental observables. MCSCF calculations can provide qualitatively correct chemical insights, but dynamic correlation needs to be added to obtain quantitatively correct energies. The PESs reported here will be used to illustrate the ability to build MCSCF global surfaces and provide fundamental insights about the chemical processes of interest here, not to provide quantitative rate constants.

For $N+H_2$, the Pascual-Schatz²⁴ basic method is a FORS-MCSCF wave function with a full valence active space of seven active electrons in six active orbitals [FORS-MCSCF(7,6)/6-311++G(*d,p*)]. The active orbitals are the H–H sigma bonding and antibonding molecular orbitals (MO) and the $2s$ and $2p$ atomic orbitals on N. The N $1s$ orbital is kept doubly occupied. Once this FORS-MCSCF PES was generated, single point MCQDPT energies were obtained at selected geometries for improved relative energies. Following the lead of Pascual *et al.*, the PES developed in this work, for $X=C$, N, and O, was generated with FORS-MCSCF wave functions: FORS-MCSCF(6,6), FORS-MCSCF(7,6), and FORS-MCSCF(8,6) with the 6-311++G(*d,p*) basis set for C, N, and O, respectively. Since both C and O are ground state triplets, for consistency with the ground state $N(^4S)$ analog, both $C+H_2$ and $O+H_2$ PES generation and classical trajectory studies were done on the triplet surface. Of course, for C, the triplet and singlet surfaces are very close in energy and both are chemically interesting. Since a major motivation of this study is the new ability to build multiple potential energy surfaces, the two lowest CH_2 singlet surfaces will also be presented.

As with the Pascual-Schatz calculations, the abstraction and exchange reactions were considered for the triplet $C+H_2$ and $N+H_2$ systems. Only the abstraction transition state (TS) was pursued for the $O+H_2$ system in order to test the sampling ability of GROW. The ground state singlet was also considered for the $HC+H$ exchange surface. Transition states were located, and Hessians were calculated for the structures (reactants, products, and TSs) to determine if they are minima (positive definite Hessian) or transition states (one negative eigenvalue). IRC pathways¹⁸ were employed in order to connect reactants, transition states, and products.

Since many low-lying surfaces are very close together in the $C+H_2$ system (as mentioned above), many convergence problems were encountered with the $C+H_2$ MCSCF calculations on the triplet surface. Restricted open-shell Hartree-Fock [ROHF/6-311++G(*d,p*)] theory was thus employed to define the reactants and products, locate the TSs, and calculate IRC pathways since GROW only requires a rough estimate of a reaction path for the initial data set. No TS was found for the collinear triplet $C+H_2$ exchange reaction, as the system falls into the deep CH_2 well (see below).

Only selected points from the IRC pathways (approx-

mately every third IRC point) are used to define an initial surface for the Shepard interpolation procedure. These points were used to provide an energy profile for each IRC pathway (energy profiles will be given in the following sections). For $N+H_2$, this set of initial data consisted of 30 points from the abstraction IRC and 30 points from the exchange IRC. The triplet $C+H_2$ and $O+H_2$ systems consisted of 50 and 80 points, respectively, from the abstraction IRC. The first and second singlet states of the $HC+H$ exchange surface contained 42 IRC points. Finally, all electronic structure calculations were performed using the GAMESS suite of programs.^{14,32}

2. Classical trajectory methods

There are several controls for the classical simulation portion of the PES growth process; explicit details about these controls have been described elsewhere.^{4,13} Initial reference geometries for the classical trajectories are required, but different parts of a PES can be grown from different reference conditions and may give a more well-rounded characterization of the final surface. The PESs in this study were constructed starting from the forward and reverse IRCs; reference geometries were reactants and products, respectively. Trajectories for building a PES were also initiated at each abstraction TS.

The initial internal energies of the reference fragments and the relative translational energy of the system must also be supplied in the growth process. These values will be presented for each reaction in the descriptions given below. The tables should be interpreted to mean that if the reactants are used as the reference, the values for the energy of H_2 will be supplied to GROW (since the atom X has no vibrational energy). If products are used as the reference, the energy of XH will be supplied, and if the TS is used as the reference geometry, the energy of the abstraction TS, $H-H-X$ (all atoms in one fragment), will be used. The initial fragment separation was set at 5.0 Å for all studies unless there is only one fragment (e.g., starting from a TS). All trajectories start with the fragments separated by this distance, and any trajectory is discontinued if fragments move out of this range. The interpolation scheme employed $q=2$ and $p=6$ (for $N+H_2$) or $p=9$ (for triplet $C+H_2$, singlet $HC+H$, and $O+H_2$) [see Eq. (4)]; these values have been tested and used for other small systems.^{3,11} All permutations of the molecular systems were allowed so that the molecular and PES symmetry group is the CNP group.

A velocity Verlet integrator was used to calculate classical trajectories with a time step of 0.01 fs. A Markov walk was used to generate a microcanonical distribution of initial atomic positions and velocities for the classical trajectories.³³ The number of Markov chain steps per trajectory and Markov step length were set at 500 and 0.15 Å, respectively, for all fragments. If a saddle point is used as the initial reference geometry, the Markov walk will wander downhill to products or reactants unless constrained to remain in the saddle point vicinity. The $X-H$ bond is held fixed during the PES construction to avoid this scenario.

In order to decrease the number of time-consuming calculations, a neighbor list scheme is employed. Inner and

FIG. 2. Reaction cross sections for $H_2(^1\Sigma_g^+) + C(^3P) \rightarrow HC(^2\Pi) + H(^2S)$ are shown as a function of the number of data points defining the PES, for four values of the relative translational energy. The error bars indicate two standard deviations resulting from the finite number of trajectories.

outer neighbor lists are defined with weight cutoffs, as well as the number of time steps between which both lists must be updated.⁴ The calculations described below set the outer neighbor list to be evaluated every 10 time steps and used a distance-dependent weight cutoff of 10^{-10} . The inner neighbor list was evaluated every 5 time steps with a cutoff of 10^{-4} . These values are appropriate for the time step of 0.01 fs. The growth cycles were discontinued when the PES data file contained approximately 300–500 points in accord with the number of points needed to describe the PES with this process in many previous studies of small systems.^{3,11,13}

Figure 2 shows the cross section for the $C+H_2 \rightarrow CH+H$ reaction on the triplet surface, as a function of the number of data points defining the PES, for four values of the relative translational energy. The cross sections were calculated using a maximum impact parameter of 2.0 Å, and the error bars indicate the statistical uncertainty arising from the finite trajectory samples. The figure indicates that the cross sections are reasonably converged in this energy range. Similar convergence results were found for the $N+H_2$, $O+H_2$, and singlet $HC+H$ PESs. Note that the lowest translational energy used in Fig. 2 is below the barrier energy for this

TABLE I. Optimized bond distances [FORS-MCSCF(x,y)/6-311++G(d,p)]. Values in parentheses indicate the number of active electrons and orbitals in the MCSCF calculation.

Diatom	MCSCF active space (electrons/orbitals)	R (Å)
H_2 singlet	(2,2)	0.757
CH quartet	(5,5)	1.094
NH triplet	(6,5)	1.050
OH doublet	(7,5)	0.975

TABLE II. Geometric parameters of transition state structures (all structures are colinear).

Transition state ^a	$R_{12}(\text{\AA})$	$R_{23}(\text{\AA})$
Abs. C (triplet): H1–H2–C3	1.033	1.265
Abs. N (quartet): H1–H2–N3	1.164	1.157
Ex. N (quartet): H1–N2–H3	1.292	1.292
Abs. O (triplet): H1–H2–O3	0.969	1.183

^aAbs. and ex. indicate abstraction and exchange reactions.

reaction. This indicates that the classical dynamics produces a cross section of about $1 \text{ \AA}^2$ as an “unphysical” consequence of the classical vibrational motion at zero point vibrational energy. This should be taken into account when considering the physical relevance of the classical cross sections.

C. C+H₂

Reactant, product, and transition state bond lengths for the triplet surface are given in Tables I and II; PE energy barriers are given in Table III. The initial data supplied to the PES growing process were calculated at the ROHF level of theory (as mentioned above), but, in order to test the MCSCF PES growing procedure, all new PES data points, as well as the recalculation of the energies of the initial data set geometries were calculated at the MCSCF level of theory only. The approach of using initial ROHF stationary point calculations and MCSCF growth/dynamics is sensible as the interpolation process has the ability to sample configuration space and only requires a rough estimate of reaction path data. Table II shows that the abstraction TS has considerable CH (product) character since the C–H bond is nearly formed. This is reinforced by the data presented in Table III, in that the forward barrier to reach the abstraction saddle point is much larger than the reverse barrier. The energy profile in the vicinity of the abstraction IRC pathway (Fig. 3) also illustrates this feature.

The initial internal energies of the reference fragments and the relative translational energy of the system for the classical trajectories are shown in Table IV. Initial internal energies were chosen based on the zero point energy of each fragment; low translational energies were supplied to the system. If the abstraction saddle point was used as the reference geometry, the C–H bond was held fixed at $1.3 \text{ \AA}$ during the generation of initial atomic positions and momenta.

Energy and atom distance distributions (Fig. 4) are reported for a data set that contains 349 points. This data set defines the PES for this reaction. In order to get the energy

FIG. 3. Energy profile in the abstraction IRC region for $\text{H}_2(^1\Sigma_g^+) + \text{C}(^3P)$. (The IRC pathway was calculated at the ROHF level, but MCSCF single point energy calculations were done at the initial points for the PES growing process; the MCSCF energies are shown here.)

distribution of data points, all energies were collected and “binned” in intervals of 0.01 a.u. These values were then plotted in histogram form; thus, the histogram with energy between -38.87 and -38.86 a.u. shows the frequency of data points with energies that fall in this range. The energy values of the reactants, products, and TSs are indicated on the graph for reference. The energy distribution of the PES data points [Fig. 4(a)] is concentrated around the abstraction reaction, but, in sampling other parts of space, GROW has found the CH_2 well (indicated by points with much lower energies). The atom distance distribution plot is shown in Fig. 4(b). The H1–H2 and H1–C3 distances are calculated for each data point; data point geometries are then plotted as a function of the H1–H2 vs H1–C3 distance (the system is defined as H1–H2–C3); the initial IRC data points are indicated on the plot. The shift of most data points away from the IRC is indicative of the fact that the molecule is not constrained by the dynamics to be close to the linear HHC configuration of the IRC. The energy contour plot is shown in Fig. 5. Energy has been plotted as a function of the two CH bond lengths, finding the minimum in the HH bond length for each CH, CH pair. Zero is defined as the lowest energy in the PES data file, in this case, equilibrium CH_2 . The deep CH_2 well is readily apparent in the lower left-hand corner of the plot. As indicated in

TABLE III. FORS-MCSCF potential energy barriers and energies of reaction (kcal/mol); zero point energy corrections are included. ROHF energies are provided for the $\text{C}(^3P) + \text{H}_2(^1\Sigma_g^+)$ system.

Reaction	Forward barrier	Reverse barrier	Reaction energy
$\text{H}_2(^1\Sigma_g^+) + \text{C}(^3P) \rightleftharpoons \text{HC}(^2\Pi) + \text{H}(^2S)$	41.9	23.6	18.3
$\text{H}_2(^1\Sigma_g^+) + \text{N}(^4S) \rightleftharpoons \text{HN}(^3\Sigma^-) + \text{H}(^2S)$	36.4	7.4	29.0
$\text{H}(^2S) + \text{NH}(^3\Sigma^-) \rightleftharpoons \text{HN}(^3\Sigma^-) + \text{H}(^2S)$	32.6	32.6	0.0
$\text{H}_2(^1\Sigma_g^+) + \text{O}(^3P) \rightleftharpoons \text{HO}(^2\Pi) + \text{H}(^2S)$	25.4	15.5	9.9
$\text{HC}(^2\Pi) + \text{H}(^2S) \rightleftharpoons \text{CH}_2(^1A_1)$	8.1	83.3	91.4

TABLE IV. Reaction conditions for C+H₂ system (triplet and singlet states).

Initial energy of H ₂	5.7 kcal/mol
Initial energy of CH	5.7 kcal/mol
Initial energy of TS (H-H-C or H-C-H)	6.2 kcal/mol
Relative translational energy (H ₂ +C or H+CH)	6.2 kcal/mol

the initial QM calculations, no TS is found in the exchange reaction; reactions directly go downhill to CH₂. The abstraction saddle point, indicated by an X, is shown in the “ridge” of higher energy separating C+H₂ and H+CH (or HC+H).

FIG. 4. H₂(¹Σ_g⁺)+C(³P). (a) Energy distribution (dots represent energies of reactants, products, and TS; this shows where these energies would be placed in the histogram). (b) Atom distance distribution (bold dots indicate initial IRC data).

FIG. 5. Energy (kJ/mol) contour for the H₂(¹Σ_g⁺)+C(³P) PES [zero is defined as the lowest energy in the PES data file, equilibrium CH₂(³B₁)]. The abstraction TS is indicated with an X.

As previously mentioned, the HC+H exchange reaction was considered for the ground state singlet surface. It was discovered that the atoms must be noncollinear in order to find a MCSCF TS for the reaction. The same type of wave function and basis set were used for the singlet as for the triplet (see Sec. III B). A TS with a very small barrier leading to CH₂ was detected; a Hessian was calculated to assure that this was a saddle point (one imaginary frequency), and IRC pathways were employed to connect the TS with reactants (HC+H) and products (CH₂). The TS geometry is shown in Fig. 6. Energies of the reactants and TS are given in Table V, as well as those of the first three states of CH₂ (³B₁, ¹A₁, and ¹B₁). The barrier heights and net reaction energies are given in Table III. The energy profile along the HC+H→CH₂ IRC for the first singlet state is shown in Fig. 7. Note that the TS structure is very much like that of the reactants (HC+H) as reflected by the TS geometry (Fig. 6) and the fact that the barrier is very small (Fig. 7 and Table III).

In order to study the second singlet state, the initial geometries from the first singlet state IRC were recalculated to give second singlet state energies and wave functions (GAMESS) and numerical gradients and Hessians (GROW). State averaged (SA) MCSCF calculations with weights of 0.5 on both singlet states were employed to form the two-particle density matrix. It is recommended that this approach

FIG. 6. MCSCF TS for the ground state singlet reaction, HC(²II)+H(²S)→CH₂(¹A₁).

TABLE V. Relative energies (kcal/mol) of reactants, products, and transition states (FORS-MCSCF) for the singlet $\text{HC}+\text{H}\rightarrow\text{CH}_2$ surface. Zero energy is taken at the ground state of $\text{CH}_2(^3B_1)$.

Species	Energy
$\text{HC}(X^2\Pi)+\text{H}(^2S)$	103.5
$\text{CH}_2(^3B_1)$	0.0
$\text{CH}_2(^1A_1)$	12.1
$\text{CH}_2(^1B_1)$	71.6
First singlet state TS	95.4
Pure second singlet TS ^a	173.5
50/50 second singlet TS ^b	137.5

^aPure second singlet TS denotes the energy of the second singlet state (weights of 0.0 and 1.0 for the first two singlet states) at the ground state singlet TS geometry.

^b50/50 second singlet TS denotes the energy of the second singlet state (weights of 0.5 and 0.5 for the first two singlet states) at the ground state singlet TS geometry.

be considered when studying multiple MCSCF excited states. The energies of the pure (weights=0.0,1.0) second singlet state and 50/50 (weights=0.5,0.5) second singlet state at the geometry of the first singlet state TS are given in Table V for reference.

The initial internal energies of the reference fragments and the relative translational energy of the system for the classical trajectories are shown in Table IV (the same as for the triplet surface). Initial internal energies were chosen based on the zero point energy of each fragment; low translational energies were supplied to the system.

The energy contour plots for both the first and second singlet states are shown in Figs. 8 and 9, respectively. The lowest (second) singlet state surface is reported for a data set containing 342 (500) points. Energy is plotted as a function of the two CH bond lengths, with the zero of energy taken to be the lowest energy in the PES data file: either equilibrium $\text{CH}_2(^1A_1)$ or $\text{CH}_2(^1B_1)$. As for the triplet, the deep CH_2 well is readily apparent. Reactants quickly go downhill to CH_2 ,

FIG. 7. Energy profile in the exchange IRC region for $\text{HC}(^2\Pi)+\text{H}(^2S)\rightarrow\text{CH}_2(^1A_1)$.

FIG. 8. Energy (kJ/mol) contour for the ground state singlet reaction, $\text{HC}(^2\Pi)+\text{H}(^2S)\rightarrow\text{CH}_2(^1A_1)$ PES [zero is defined as the lowest energy in the PES data file, equilibrium $\text{CH}_2(^1A_1)$].

therefore $\text{C}+\text{H}_2$ is not visible. As expected, the second singlet state is very much like the lowest singlet state but higher in energy.

D. $\text{N}+\text{H}_2$

Reactant, product, and transition state bond lengths for both abstraction and exchange reactions are given in Tables I and II; PE energy barriers are given in Table III. Again, Table II shows that the N-H bond is almost formed by the time that the abstraction TS is reached. The barrier to go from N

FIG. 9. Energy (kJ/mol) contour for the second singlet state reaction, $\text{HC}(^2\Pi)+\text{H}(^2S)\rightarrow\text{CH}_2(^1B_1)$ PES [zero is defined as the lowest energy in the PES data file, equilibrium $\text{CH}_2(^1B_1)$].

FIG. 10. Energy profile in the (a) exchange and (b) abstraction IRC regions for the $\text{N}+\text{H}_2$ system.

$+\text{H}_2$ to this abstraction TS is even larger than that for $\text{C}+\text{H}_2$ (see Table III). Energy profiles in the vicinity of both IRC pathways are shown in Fig. 10.

The initial internal energies of the reference fragments and the relative translational energy of the system for the classical trajectories are shown in Table VI. Larger translational energies were supplied to this system, as compared

TABLE VI. Reaction conditions for $\text{N}+\text{H}_2$ system.

Initial energy of H_2	5.7 kcal/mol
Initial energy of NH	12.7 kcal/mol
Initial energy of abstraction TS ($\text{H}-\text{H}-\text{N}$)	6.2 kcal/mol
Relative translational energy (H_2+N or $\text{H}+\text{NH}$)	37.8 kcal/mol

FIG. 11. $\text{N}+\text{H}_2$ (a) Energy distribution (dots represent energies of reactants, products, and TSs; this shows where these energies would be placed in the histogram). (b) Atom distance distribution (bold outline of dots, lower left-hand corner, indicate initial IRC data).

with $\text{C}+\text{H}_2$. When the abstraction saddle point was used as the reference geometry, the $\text{N}-\text{H}$ bond was held fixed at 1.2 Å during the generation of the initial atomic positions and momenta.

Energy and atom distance distributions and a PES contour are reported for a data set that contains 585 points in Fig. 11. The energy distribution of the PES data points [Fig. 11(a)] is mainly concentrated around the abstraction reaction TS and product, $\text{H}+\text{NH}$, but other areas are also sampled. The atom distance distribution plot [Fig. 11(b)] gives another view of the sampling of data points. Data point geometries are plotted as a function of the $\text{H1}-\text{H2}$ distance versus the $\text{H1}-\text{N3}$ distance (the system is defined as $\text{H1}-\text{H2}-\text{N3}$); the initial IRC data points are indicated on the plot. While GROW mainly generates points around the IRC data (the Shepard

FIG. 12. Energy (kJ/mol) contour for the $N+H_2$ PES (zero is defined as the lowest energy in the PES data file). The abstraction and exchange TSs are indicated with an X and bold dot, respectively.

interpolation is well defined in this area), it also samples configurations in other regions of space as seen by the “tails” extending in both directions from the initial IRC data. The energy contour plot is shown in Fig. 12. Energy has been plotted as a function of the two NH bond lengths, finding the minimum in the HH bond length for each NH, NH pair. Zero is defined as the lowest energy in the PES data file. The abstraction saddle point is located on the “curve” between the $N+H_2$ and $NH+H$ and is indicated on the plot. There is no deep well with the $N+H_2$ reaction, as there was for $C+H_2$. The exchange saddle point is located in the horseshoe-shaped region in the lower left-hand corner. This also agrees with the equal N–H distances in the geometry of the exchange saddle point.

E. $O+H_2$

Reactant, product, and transition state bond lengths are given in Tables I and II; PE energy barriers are given in Table III. The abstraction reaction TS shows O–H bond character (Table II), and the forward barrier to the abstraction reaction is again larger than the reverse. The energy profile along the abstraction IRC is shown in Fig. 13.

The initial internal energies of the reference fragments and the relative translational energy of the system for the classical trajectories are shown in Table VII. Large translational energies were supplied to the system since smaller energies gave no reaction and added no new points to the surface. When the abstraction saddle point was used as the reference geometry, the O–H bond was held fixed at 1.2 Å during the generation of the initial atomic positions and momenta.

Energy and atom distance distributions and a PES contour are reported in Fig. 14 for a data set that contains 430 points. The energy distribution of the PES data points [Fig.

FIG. 13. Energy profile in the abstraction IRC region for $O+H_2$.

14(a)] shows that configuration space around the abstraction reaction has been sampled the most but that the other areas have also been explored and that sampling was not exclusive to the reaction path. The atom distance distribution plot is shown in Fig. 14(b). Data point geometries are plotted as a function of the H1–H2 distance versus the H1–O3 distance (the system is defined as H1–H2–O3), and the initial IRC data points are indicated on the plot. Again, sampling was focused around the reaction path, but other configurations are also included in the PES. For example, the “tail” on the right side of the graph places data points in regions not accounted for in the static IRC pathway.

The contour energy plot is shown in Fig. 15. Energy has been plotted as a function of the two OH bond lengths, finding the minimum in the HH bond length for each OH, OH pair. Zero is defined as the lowest energy in the PES data file. This plot is very similar to the NH_2 plot in that the abstraction saddle point is located on the curve between $O+H_2$ and $OH+H$. Even though no exchange reaction information was supplied to the MCSCF PES growing process, there appears to be an exchange saddle point in the horseshoe-shaped region in the lower left-hand corner.

IV. CONCLUSIONS

The new MCSCF PES growing process samples the appropriate configuration space to describe the $X+H_2$ reactions. Even though C, N, and O are neighbors on the Periodic Table, the PES studies show that they have very different

TABLE VII. Reaction conditions for the $O+H_2$ system.

Initial energy of H_2	5.7 kcal/mol
Initial energy of OH	12.7 kcal/mol
Initial energy of abstraction TS (H–H–O)	6.2 kcal/mol
Relative translational energy (H_2+O or $H+OH$)	50.2 kcal/mol

FIG. 14. $O+H_2$. (a) Energy distribution (dots represent energies of reactants, products, and TS; this shows where these energies would be placed in the histogram). (b) Atom distance distribution (bold outline of dots, lower left-hand corner, indicate initial IRC data).

behaviors in terms of a global, ground state PES for these reactions. The triplet $C+H_2$ surface exhibits the deep CH_2 well, while both $N+H_2$ (quartet) and $O+H_2$ (triplet) surfaces indicate that a barrier exists in the exchange reaction. There is also a large contrast between the singlet and triplet $C+H_2$ ($HC+H$) surfaces with the singlet showing no explicit way to get to the abstraction or insertion reactants. The first and second singlet surfaces for the $HC+H$ exchange reaction are very similar, as expected. All surfaces were characterized with very few data points and QM calculations, making the process very efficient. The new MCSCF process also makes it possible to build potential energy surfaces using multiconfigurational wave functions. This opens up a wide range of new, important applications that cannot be studied with

FIG. 15. Energy (kJ/mol) contour for the $O+H_2$ PES (zero is defined as the lowest energy in the PES data file). The abstraction TS is indicated with an X.

single determinant methods. However, many reactions do not take place on a single adiabatic surface when multiple surfaces are in close proximity. The dynamics of reactions that take place on multiple electronic states are governed by multiple PESs. These descriptions are very important in regions of surface crossings and conical intersections, as well as in chemical reactions that take place in excited electronic states and proceed via multiple electronic states. The extension to treating multisurface problems is an important tool for a vast number of scientific problems, ranging from atmospheric chemistry to photochemical reaction mechanisms in organic and inorganic chemistry to fundamental biological phenomena such as photosynthesis. The calculation of an accurate PES to be used for dynamic simulations is very important to our understanding of the chemical world at a molecular level. A central aspect of chemistry is unraveling complex chemical mechanisms, including multiple surfaces and competition among the many competing reactions. Accurately representing the PES with a small amount of data, based on accurate, high level *ab initio* quantum chemistry, allows an efficient and effective approach to understanding these reactions and processes.

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