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A Self-Starting Method for Obtaining Analytic Potential-Energy Surfaces from ab Initio Electronic Structure Calculations

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Previous methods proposed for obtaining analytic potential-energy surfaces (PES) from ab initio electronic structure calculations are not self-starting. They generally require that the sampling of configuration space important in the reaction dynamics of the process being investigated be initiated by using chemical intuition or a previously developed semiempirical potential-energy surface. When the system under investigation contains four or more atoms undergoing three- and four-center reactions in addition to bond scission processes, obtaining a sufficiently converged initial sampling can be very difficult due to the extremely large volume of configuration space that is important in the reaction dynamics. It is shown that by combining direct dynamics (DD) with previously reported molecular dynamics (MD), novelty sampling (NS), and neural network (NN) methods, an analytical surface suitable for MD computations for large systems may be obtained. Application of the method to the investigation of N−O bond scission and cis−trans isomerization reactions of HONO followed by comparison of the resulting neural network potential-energy surface to one obtained by using a semiempirical potential to initiate the sampling shows that the two potential surfaces are the same within the fitting accuracy of the surfaces. It is concluded that the combination of direct dynamics, molecular dynamics, novelty sampling, and neural network fitting provides a self-starting, robust, and accurate DD/MD/NS/NN method for the execution of first-principles, ab initio, molecular dynamics studies in systems containing four or more atoms which are undergoing simultaneous two-, three-, and four-center reactions.

I. Introduction

Molecular dynamics (MD) and Monte Carlo (MC) simulations are the most powerful and robust existing methods for the investigation of the dynamical behavior of atomic and molecular motions of complex systems. With the advent of relatively inexpensive, powerful workstations, molecular dynamics simulations have become routine. Once the potential-energy surface (PES) for the system has been obtained, the MD or MC computations are straightforward. In the majority of cases, the computational time required is on the order of hours to a few days. However, the accuracy of these simulations depends critically on the accuracy of the potential hypersurface used.

In many investigations, an empirical or semiempirical PES is employed to represent the force field of the system under investigation. Such potentials generally yield only qualitative or semiquantitative descriptions of the system dynamics. Empirical potential surfaces can be significantly improved by fitting the chosen functional form for the potential to the force fields obtained from trajectories by using ab initio Car−Parrinello[1] molecular dynamics simulations. This method has been employed by several research groups.[2−5]

If the system under investigation is not too large and complex, ab initio electronic structure calculations offer a route to obtaining extremely large databases, which can be employed to obtain the PES for the system. Malshe et al.[6] have recently developed a method that reduces or eliminates many of the problems associated with fitting empirical potentials particularly when some of the parameters are made functions of the system configuration. The method completely obviates the problem of selecting the form of the functional dependence of the parameters upon the system's coordinates. This form is, in effect, determined automatically by a neural network (NN).

Several research groups have employed methods that obviate the need to select arbitrary functional forms for the potential surface. These methods attempt to accurately sample the configuration space of the system and then fit the resulting database of ab initio energies and perhaps experimental data by using some generalized numerical procedure. To date, four such methods have been used in a variety of systems. They are (i) moving interpolation techniques,[7−9] (ii) reproducing kernel Hilbert space (RKHS),[10,11] (iii) interpolating moving least-squares (IMLS),[12,13,15−18] and (iv) neural network methods.[19−28] The following discussion briefly describes these methods.

Ischtwan and Collins[7] have developed a moving interpolation technique in which the potential energy in the neighborhood of any point is approximated by a Taylor series, using inverse bond length coordinates as the expansion variables. Initially, a set of system configurations along the reaction path is selected by using chemical intuition. Ab initio electronic structure calculations of the system energy and gradients in these configurations are then executed. The data thus produced are employed to obtain the set of Taylor series expansions. A Shepard method[8] is used to effect the required interpolations. This procedure expresses

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the potential at any configuration as a weighted average of the Taylor series about all N points in the data set, or alternatively, those points within a specified cutoff radius. Subsequently, the results are iteratively improved by computing trajectories on the Taylor series fitted surface and recording the internal coordinates at a series of successive configurations encountered in the trajectories. In part, these new points are added to the data set according to a weight factor that is determined by the relative density of points in the data set in the region of the new points. For systems which are undergoing two-center, bond dissociation or formation reactions, the fitting error with a test set of ab initio energies is usually found to be in the range of from 0.0010 to 0.031 eV depending upon the complexity of the system. For a review of this method and results, the review by Collins may be consulted.[9]

The second method for obtaining ab initio potential surfaces for three- and four-body systems employs the criterion of reproducing kernel Hilbert space (RKHS) as the means to effect the required fitting of the ab initio energies. Ho et al.[10] have employed this procedure to investigate the $O(^1D) + H_2 \rightarrow OH + H$ reaction. When 1280 ab initio data points were employed to define the surface, the fitting yielded a surface whose absolute root-mean-square error compared to ab initio energies was 0.0131 eV. Pederson et al.[11] have used the same method to study the dynamics of the $N(^2D) + H_2$ reaction.

Maisuradze et al.[12] have introduced the third method, namely, an interpolating moving least-squares (IMLS) method, to effect the fitting between the computed ab initio points. When the method is unrestricted, the least-squares coefficients are obtained from the solution of a large matrix equation that must be solved repeatedly during a trajectory study. In this form, the required computational time increases with NM^2, where N is the number of data points to be fitted and M is the number of basis functions used in the linear combination that provides the fit. Guo et al.[13] have evaluated the IMLS method using the analytic surface of Kuhn et al.[14] for simple O−O bond rupture of HOOH. With $N = 300$, the results showed the statistical fitting errors to lie in the range of 0.085 to 0.171 eV. Kawano et al.[15] have compared the accuracy of the IMLS method with that of the modified Shepard procedure for the HOOH bond scission reaction. With $N = 6489$, the root-mean-square errors for IMLS and modified Shepard were 0.0468 and 0.0202 eV, respectively. Guo et al.[16] have recently reported IMLS results for the unimolecular dissociation reaction of $H_2CN \rightarrow H + HCN$. Their results show root-mean-square fitting errors that vary between 0.0055 and 0.0290 eV.

The major problem with the IMLS method is the extremely large computational time required for its execution. When more than four atoms are involved, the computation time increases rapidly due to the M^2 factor. The time also increases linearly with the number of ab initio data points employed. Guo et al. have reported a computational time of about 100 min for one H_2CN dissociation trajectory lasting 2.5 ps when 830 data points are employed.[16]

The computational difficulties associated with IMLS methods have recently been addressed by Dawes et al.[17a] and by Guo et al.[17b] By converting the IMLS method to what is essentially a modified Shepard method,[8] the large computational bottleneck present in IMLS calculations is avoided. The authors[17] term this hybrid method a “local IMLS” or L-IMLS method. To date, this hybrid procedure has been applied only to molecules containing four or less atoms undergoing a single, two-center, bond-dissociation reaction. Ishida and Schatz have also proposed a procedure that combines the IMLS and Shepard methods.[18a] This combined method has been applied to the investigation of the three-body reaction dynamics of the $O(^1D) + H_2$ reaction.[18b]

The fourth method involves the use of neural networks (NN). Neural networks provide a powerful method to effect the fitting of an ensemble of potential energy points in a database. Blank et al.[19,20] have employed a NN to fit data derived from an empirical potential model for CO chemisorbed on a Ni(111) surface. These same investigators also examined the interaction potential of H_2 on a Si(100)−2×1 surface using a data set comprised of 750 energies computed from local density functional theory. Hobday et al.[21] have used similar methods to investigate the energies of C−H systems with a NN comprised of five input nodes, one hidden layer with six nodes and an output layer. Tafeit et al.[22] and Gassner et al.[23] have successfully employed NN methods to fit the torsional energies in large biological systems and for the $H_2O-Al^{3+}-H_2O$ system, respectively. Brown et al.[24] have employed a two-layer NN with 32 neurons in the hidden layer to obtain a fit to the PES for the van der Waals systems HF−HF and HF−HCl. More recently, Lorenz et al.[25] have used a NN to represent the PES for H_2 dissociative adsorption on the (2×2) potassium-covered, Pd(100) surface. The authors conclude that NNs provide an efficient tool to study reaction processes where extensive statistics are required.

Manzhos et al.[26] have employed a nested NN approach to obtain extremely accurate fits to the PES for systems in the neighborhood of their equilibrium configurations. In this approach, one NN is employed to obtain a PES that is reasonably close to the points in the database. A second NN is then developed that fits the difference between predictions of the first NN and the points in the database. Using this approach, the authors report fitting errors on the order of 1 cm^{-1} for H_2O and 2 cm^{-1} for HOOH and H_2CO.

In most applications of two-layer NNs, the transfer functions used between the hidden layer and the output layer are sigmoid functions. Manzhos and Carrington[27] have recently reported an investigation of the use of exponential transfer functions. The potential advantage of such transfer functions lies in the fact that the exponential of a sum is the product of the individual exponentials. This property permits the resulting PES to be written in a sum of products form, which is desirable from the point of view of executing quantum dynamics calculations. Their investigations[27] show that the fitting accuracy of exponential transfer functions is only slightly less than that of sigmoid functions for NNs containing an equal number of neurons. Consequently, this finding may lead to more efficient NN representations of potential surfaces for quantum dynamics.

In more recent work, Manzhos and Carrington[28] have combined the high dimensional model representation (HDMR) suggested by Rabitz and co-workers[29] with NNs that employ exponential transfer functions to obtain a practical method for building multidimensional potentials. Using this method, it is possible to accurately represent the PES for an N-atom system using terms that contain only M-body and lower terms where $M < N$.

Raff et al.[30] have developed a novelty sampling-neural network method for sampling multidimensional configuration space and then obtaining an accurate fit to the ab initio database using neural networks. The novelty sampling provides the means by which to both ensure adequate sampling of the multidimensional configuration hyperspace and to test for convergence of the resulting NN potential surface. NN fitting permits either the potential, the surface gradients, or both to be fitted.[31,32] To date, the method has been used to investigate the nonadiabatic unimolecular dissociation of SiO_2,[33] four-center, cis−trans isomerization and two-center, N−O bond dissociation in HONO,[34] the simultaneous dissociation reactions of the six-atom vinyl bromide system that include four, two-center, bond dissociation processes and two, three-center dissociation reactions,[35] and the exchange and abstraction reactions of HBr reacting with H′ atoms to form H′Br or H_2, respectively.[36] The H + HBr investigation is an application of NNs being used to simultaneously fit both the potential surface and its gradients.[31,32] The fitting accuracy thereby achieved is extremely high with a median rms fitting error of 0.00015 eV, which is sufficiently small to produce point-by-point agreement between trajectories integrated on the NN and analytic surfaces.

While the above numerical procedures provide powerful and robust methods for obtaining fits to ab initio or other databases once those databases have been obtained, none of the presently available methods provide an efficient, robust, self-starting procedure for sampling the configuration space of the system to obtain that database when the volume of configuration space that must be sampled is extremely large, as will be the case when the system is at high energy and is undergoing several simultaneous two-, three-, and four-center reactions.

Ludwig and Vlachos[37] have recently reported an investigation of the molecular dynamics of H_2 dissociation on Pt(111) and Cu(111) surfaces using neural networks and novelty sampling methods. In their investigation, the database for the NN fitting was obtained by using novelty sampling methods to examine the configuration points resulting from running direct dynamics (DD) trajectories in which density functional theory (DFT) was employed at each integration point to obtain the force field required for the solution of the Hamiltonian equations of motion for the system. In this paper, we show how this method may be extended to complex systems undergoing multiple two-, three-, and four-center reactions. By suitable modification of the manner in which the DD trajectories are employed and using our previously described novelty sampling (NS) precedures[30,35] that simultaneously provide a method to guide the selection of configuration points to be included in the database and test for convergence of the PES, we obtain a robust, self-starting method for efficient sampling of the dynamically important regions of configuration space in systems where the volume of configuration space that must be sampled is extremely large.

Section II of the paper describes the details of this DD/MD/NS/NN method. In Section III, the procedure is employed to obtain a PES for the HONO system that is undergoing four-center cis−trans isomerization and simultaneous N−O bond dissociation. This PES is compared to one previously reported by Le and Raff.[34] The comparison shows the two surfaces to be nearly identical. The conclusions are given in Section IV.

II. The DD/MD/NS/NN Method: Self-Starting with Direct Dynamics

A crucial element in any general ab initio dynamics method is the development of an importance sampling procedure that adequately samples the subset of configuration space that is important in the dynamics being investigated rather than the entire configuration space. If this is not done, the electronic structure calculations will immediately overwhelm our computational resources for any complex system with four or more atoms.

The methods to initiate the importance sampling are (a) chemical intuition[7] and (b) sampling by using MD calculations on semiempirical potential surfaces.[9,30,34,35] When chemical intuition is employed, the investigator attempts to deduce the motions the system will undergo as it moves along the reaction coordinates for each open channel. An ensemble of configurations is then developed that represents these motions and electronic structure calculations of the potential and force fields for these configurations are performed. It is assumed that the configurations so investigated are among the more influential ones in controlling the reaction dynamics. When the reaction under consideration is relatively simple, sampling based on chemical intuition is more likely to succeed than is the case for complex reactions involving multiple channels and high energy.[34,28] Ischtwan and Collins[7] used this method effectively in their study of the NH + H_2 → NH_2 + H reaction.

The most efficient procedure to obtain the configurations of importance in the dynamics is MD calculations. The nuclear configurations that are generated in an ensemble of trajectories comprise the subset of configuration space that we wish to sample. Such methods were first introduced by Collins and co-workers.[9] There is, however, one significant problem associated with the implementation of such a procedure. The computation of trajectories requires that we already have the PES that we are seeking to develop. Basically, we must have a means to initiate the procedure. This is the self-starting problem to which we have referred.

To date, two methods have been employed to obtain an initial potential surface that permits trajectories to be computed and the configurations generated sampled. Collins and co-workers[9] have generated an initial database using chemical intuition, as previously described. Interpolation between these points is achieved by using a moving Shepard interpolation procedure.[8,9] Once this initial PES is obtained, classical trajectories are initiated by using efficient microcanonical sampling[38,39] to select the initial conditions and additional configuration points are added to the database by using some appropriate selection method. At this point, a new PES is generated by using the same method. Additional trajectories are computed on this new PES, and the database is again improved iteratively until convergence is attained by using some appropriate criterion.

The MD/NS/NN method employs a semiempirical PES to initiate the trajectory sampling procedure.[30] Our recent studies of the HONO[34] and vinyl bromide[35] systems show that this procedure yields excellent results, but it is not self-starting in that a reasonably accurate, semiempirical, analytic surface must be available to initiate the sampling. This places a severe restriction on the method.

When a semiempirical PES is available, we simply compute an ensemble of trajectories under conditions identical with those for which we wish to investigate the reaction dynamics. A subset of these trajectories is selected that exhibit reactions into all open channels. As these trajectories proceed, we store the nuclear configurations at equally spaced time intervals. This is continued until we have several thousand such configurations. The energies and forces present in these configurations are then computed by using the desired level of ab initio theory and basis set. These results comprise the first approximation to the database describing the potential and force field for the system.

In the second step of the MD/NS/NN method, we fit a feedforward NN to the ab initio database for the energies obtained by using the empirical PES. A second set of MD trajectories is now computed by using the NN force field rather than the original semiempirical potential. During these calculations, additional nuclear configurations are stored and their energies and forces subsequently computed. Modified novelty sampling algorithms[30,35] based on the current density of configuration points in the database guide our selection of new configurations. Regions with a low density are preferentially included in our sample. The energies and forces obtained for the newly selected configurations are added to the overall database characterizing the PES and force field. New neural networks are trained to fit to this expanded database and the entire procedure repeated until convergence is achieved. An additional advantage of the modified novelty sampling methods being employed is that they provide convergence criteria without requiring a molecular dynamics investigation of the reactions of interest.

In its present form, the MD/NS/NN method is essentially restricted to those systems for which a reasonable empirical or semiempirical PES exists. To conduct ab initio dynamics studies in a new complex system, the investigators must first develop an analytic semiempirical potential that describes all open reaction channels for the system. If the system involves only a two-center bond dissociation reaction, this is not a difficult problem. However, for a complex system undergoing several two-center bond dissociations as well as three- and four-center reactions, this is a formidable task that can require many months of intensive human effort.[40]

A sense of the magnitude of the sampling difficulty can be obtained by comparing the size of the databases required to obtain a converged PES for systems involving only a single, two-center bond dissociation reaction with the size required when multiple two-, three-, and four-center reactions are involved. When the reaction of interest is a single, two-center bond dissociation gas-phase reaction in a three- or four-atom system, the database required for obtaining a reasonably accurate PES usually contains between 300 to 6500 points. For a representative sampling of 23 such systems, the reader may consult Table 2 of ref 6. For single, two-center bond dissociation reactions on surfaces, the situation is the same. In their investigation of H_2 dissociation on Pt(111) and Cu(111) surfaces, Ludwig and Vlachos[37] employed databases containing between 1000 and 4000 configurations. Lorenz et al.[25] used a database comprised of 659 configurations to investigate the dissociative adsorption probabilities of H_2 on a (2×2) potassium-covered Pd(100) surface.

In contrast, the study of the simultaneous four-center, cis−trans isomerization and two-center N−O bond dissociation reactions of HONO required a database of 21 584 configurations.[34] To study vibrational energies of the five-atom $H_3O_2^-$ system, Huang et al.[41] had to employ a database of 66 965 ab initio electronic energies. This large database was necessitated because of the high dimensionality of the five-atom system and also because of the "floppy" nature of the vibrational motions. To investigate the four distinct, two-center bond dissociations and two, three-center dissociation processes occurring simultaneously in the six-atom vinyl bromide system, the converged database had to contain almost 72 000 points.[35]

One of the objectives of the present research is to enhance the power of methods whose purpose is to fit databases obtained from ab initio electronic structure calculations by developing a self-starting procedure that will handle complex systems involving multiple two-, three-, and four-center reactions in which the volume of the configuration space important in the reaction dynamics is very large.

To achieve this objective, we extend the direct dynamics (DD) method employed by Ludwig and Vlachos[37] to investigate H_2 dissociation of Pt(111) and Cu(111) surfaces. In DD, trajectories are computed by calculation of the force field at each integration point by using some ab initio quantum mechanical method. Because of the huge number of computations required for each trajectory, the ab initio method chosen must usually be some form of DFT. As a result, only a very limited number of trajectories can be obtained. As the system under investigation increases in size, the computational requirements will quickly overwhelm the available computational resources. The basic problem is that all the information obtained about the potential-energy surface and the corresponding force field during the integration of the trajectory is discarded after the completion of the calculation. Therefore, each subsequent trajectory fails to profit from all the computational effort expended in obtaining the previous trajectories. As a result, DD has seen only limited usage.

By combining DD with the MD/NS/NN method, we can make both procedures far more powerful. Instead of employing an empirical PES, we initiate the sampling using trajectories computed by DD methods. Such a procedure obviates the need to develop an empirical PES prior to conducting ab initio investigations of the dynamics. This DD/MD/NS/NN method, therefore, becomes self-starting as well as efficient due to the fact that the advantages of MD/NS/NN also become available.

We have previously shown[30] that the final, converged potential surface is not sensitive to the choice of the particular empirical PES employed in the initial step provided it is reasonably accurate for all reaction channels occurring in the process. The evidence for this is contained in Figures 2 and 3 of ref 30 along with the associated discussion. Therefore, we expect that the ensemble of configurations generated by the DD trajectories in the initial step will be sufficiently representative of the configuration space important in the dynamics that our NS procedures will lead to convergence of the final database to the desired NN potential surface. Moreover, although the DD trajectories are executed by using DFT methods with perhaps a smaller basis set, the electronic structure calculations on the stored configurations obtained in these trajectories can be carried out at any desired level of theory with a substantially larger basis set. In the present studies, we adopt this strategy by running the DD trajectories at the DFT level and carrying out the final calculations at the MP4(SDQ)/6-311G(d) level.

Proper sampling of configurations associated with reaction channels of minor importance can present difficulties when the DD/MD/NS/NN method is used. When an empirical potential surface is employed to initiate the sampling, thousands of trajectories can be computed in acceptable computational times. Those trajectories reacting in minor reaction channels can then be selected for sampling to ensure that all the important regions of configuration space are included in the database. When DD is used, we do not have the luxury of computing thousands of trajectories. Therefore, a different approach is required.

The problem can be addressed in many ways. First, one can employ a nonstatistical selection of initial conditions for the DD trajectories. For example, one can employ projection methods to partition the initial excitation energy among the various vibrational and rotational degrees of the system under study.[42] This method permits the initial energy to be preferentially inserted into those modes that chemical intuition suggests will enhance the probability of reaction into selected channels. By combining this procedure with enhanced excitation energy, the DD trajectories can often be forced to sample the important regions of configuration space for minor reaction channels.

Second, if necessary, the DD trajectories for the reverse reaction can be computed. That is, the DD calculations are initiated by starting in the product channel for the minor reactions of interest. These trajectories are followed until the system reaches the reactant configuration for the process of interest. Since microscopic reversibility ensures that the reaction pathways for both forward and reverse processes will be identical, a proper sampling of the reverse trajectory will provide the configurations required to make the MD/NS/NN method self-starting. It is reasonable to anticipate that this reverse method will be effective since processes that are severely constrained in one direction are often facile in the opposite direction. Finally, one can initiate the DD trajectories starting at the saddle point on the PES. By proper selection of the initial momenta, the DD trajectory can be forced to proceed either toward the product or the reactant configuration space. Making both selections in turn permits the entire configuration space for the process to be sampled. In the present studies of HONO, we achieved this goal by running a few DD trajectories with the initial conditions corresponding to high values of the bond length which is expected to be broken.

It may be noted that the DD procedure will not only produce a new DD/MD/NS/NN method that is self-starting, it will also serve to greatly enhance the efficiency of DD calculations if one is interested in the ab initio surface at the level at which the DD trajectories have been run. No longer will DD suffer from the fact that all the information obtained about the PES and the corresponding force field during the integration of a trajectory is discarded after the completion of the calculation. This information can be retained in a database. A NN is then fitted to this database. After this, the investigation can proceed on the NN surface without the need for further DFT calculations.

III. Application to N−O Bond Dissociation in HONO: Results and Discussion

As an illustrative example of the operation of the DD/MD/NS/NN method, we have applied it to the investigation of the N−O bond dissociation reaction of HONO. With four atoms and both the four-center, cis−trans isomerization and two-center, N−O dissociation reaction channels open, this system is sufficiently complex to be a good test of the method.

In this investigation, we focus our attention on the question of whether the final results given by the neural networks obtained by employing (1) direct dynamics and (2) an empirical potential to effect the initial sampling are in agreement. Since we generally initially sample only a few thousand points in the very large configuration space important in complex reactions, it is possible that the two methods will lead to final NN networks that predict very different dynamics. On the other hand, if the two methods lead to very similar NNs that predict similar dynamics, this would suggest that the two initial sampling methods are essentially equivalent. Since an ab initio investigation of the HONO reaction dynamics has recently been reported by Le and Raff[34] using MD/NS/NN methods, there exists a good benchmark against which the DD/MD/NS/NN results can be compared.

Le and Raff[34] investigated the isomerization and dissociation dynamics of HONO on an ab initio potential surface obtained by fitting the results of electronic structure calculations at 21 584 configurations using previously described MD/NS/NN methods and a semiempirical PES developed by Guan and Thompson.[43] The electronic structure calculations were executed by using GAUSSIAN 98 with a 6-311G(d) basis set at the MP4(SDQ) level of accuracy. The average absolute fitting error of the NN was found to be 0.017 eV. The reader is referred to ref 34 for the details of these calculations. For brevity, we shall only discuss the portions of the DD/MD/NS/NN calculations that differ from those reported in that reference.

In this investigation, we initiate the sampling of the HONO configuration space by using DD with the "ADMP" command of Gaussian-03[44] at the B3LYP/6-31G(d) level with a time step of 0.10 fs. To ensure that some trajectories reach the phase space corresponding to the product space (NO + OH), the initial configuration corresponding to bond length r(N−O) for the N−O bond has been taken as ∼2.5 Å while keeping other internal coordinates r(N=O), r(O−H), ∠ONO, ∠ONH, and torsion angle nearly equal to those of the cis or trans ground state. The DD trajectories have been run for 4000 time steps with the initial nuclear kinetic energy equal to ∼2.7 eV. One trajectory starting from the cis equilibrium as well as one trajectory starting from the trans equilibrium state with nuclear kinetic energy equal to 0.14 eV has been run for 500 time steps to sample the configurations near the equilibrium states of the system.

Configuration points are selected for inclusion in the database on the basis of distance criteria. A point i occurring during the sampling trajectories is accepted if its distance d_{ij} from each of the previously accepted n points is greater than d_{lim}. Here, d_{ij} is the distance between the points in the six-dimensional hyperspace spanned by the six internuclear distances, (r_1, r_2,..., r_6). It is defined by

$$d_{ij} = [\sum (r_k^{(i)} - r_k^{(j)})^2]^{1/2}$$

where the summation runs over all six internuclear distances. The value of d_{lim} is chosen to be 0.1 Å except for the trajectories run near cis and trans ground states for which d_{lim} is chosen to be 0.01 Å. The initial sampling comprises 6085 configurations selected from 25 DD trajectories. MP4(SDQ)/6-311G(d) calculations have been performed to obtain the potential energy for each of these configurations.

A two-layer (6−40−1) neural network (NN)[45] is employed to fit the ab initio database generated from the results of the DD trajectories. The data to be interpolated have been divided randomly into three parts: training set (∼80%), validation set (∼10%), and testing set (10%). The fitting to the database is accomplished iteratively by using 3000 cycles with the Levenberg−Marquardt algorithm.[46] Overfitting[47] has been avoided by monitoring the error associated with the validation set. The input variables to the NN comprise the six atomic distances r_1, r_2, r_3, r_4, r_5, and r_6. The corresponding ab initio energy value relative to that in the cis equilibrium state is used as the output variable for the NN. The Matlab Neural Network software[45] has been used to determine $\mathbf{W}_1$, $\mathbf{b}_1$, $\mathbf{W}_2$, and $\mathbf{b}_2$ matrices of dimensions (40×6), (40×1), (1×40), and (1×1), respectively. Using these matrices, the output potential V for an input vector

$$\mathbf{p} = [r_1,r_2,r_3,r_4,r_5,r_6]^{\dagger} \tag{1}$$

can be computed as follows:

$$V = \mathbf{W}_2\, \mathrm{f}(n) + \mathbf{b}_2 \tag{2}$$

Here, the transfer function f($\mathbf{n}$) is the hyperbolic tangent function of $\mathbf{n}$, and

$$\mathbf{n} = \mathbf{W}_1\mathbf{p} + \mathbf{b}_1 \tag{3}$$

In these equations, r_1, r_2, r_3, r_4, r_5, r_6, and V are normalized input and output variables in the range −1 to +1. The normalized or scaled value of a variable $A_{i,\mathrm{norm}}$ is related to the unnormalized or unscaled value A_i as follows:

$$A_{i,\mathrm{norm}} = 2(A_i - A_{\mathrm{min}})/(A_{\mathrm{max}} - A_{\mathrm{min}}) - 1 \tag{4}$$

Here, A_{max} and A_{min} refer to the maximum and minimum value of the variable A used in fitting the neural network.

Using the 6 085 configurations from the DD trajectories as the database, an initial NN is fitted. This NN-fitted potential-energy surface is employed to compute 10 000 trajectories, each with an energy in the range 3.1−3.3 eV. These trajectories are integrated for 5 ps or until N−O bond scission occurs. From these trajectories, 3 827 new configurations have been obtained by using novelty sampling procedures[30,34,35] to guide the selection of new configurations. These new configurations are then added to the already existing 6085 configurations and a new NN is fitted to this database. This iterative procedure is repeated five times to obtain a database comprising 20 192 configurations. Convergence of the final NN PES is determined by using NS criteria.[30,35] The NN fit to this database is taken as our final HONO potential surface. The salient features of this NN are as follows.

Figure 1 shows the variation of the potential energy V given by eq 2 with the ab initio energy values for all configurations. The difference of V and the ab initio value of energy is the fitting error. The value of the absolute error averaged over all configurations is found to be 0.022 eV. As expected,[34,35] the error tends to increase as the energy increases. This result is a consequence of the increased size of the configuration space energetically available to the HONO system at higher energies. As the size of the configuration space increases, the sampling becomes more sparse, and the fitting error increases. Figure 2 gives the error distribution curve. We note that more than 67% of the configurations have an absolute error less than 0.03 eV.

One of the objectives of the present investigation is to compare the NN fitting results generated by the fitting of data starting from the configurations obtained by (1) the use of DD and (2) the use of a semiempirical analytical potential.[43] For this purpose, we shall compare the present NN for the HONO system with the one obtained by Le and Raff[34] that is denoted as Surface 1. For reference purposes, we shall denote the NN obtained using DD as method A and the resulting potential as V_A. The NN obtained by Le and Raff[34] will be denoted as method B and V_B, respectively.

As a first test of the interpolated potential, we have computed the normal-mode frequencies of cis and trans HONO. These are listed in Table 1 along with those determined in ref 34 and those given by Gaussian MP4(SDQ)/6-311G(d) calculations as well as by experiment.[48] We note that the average absolute deviation between the computed frequencies obtained in the present work and those reported by Le and Raff[34] is 4%.

To obtain the barrier height for the dissociation channel, we have computed the minimum value of the potential as a function of the N−O bond length. The minimum potential energy at each value of r(N−O) has been determined by freezing two atoms, N and O associated with the bond, and allowing the other two atoms to move. We computed this energy by two methods: (1) by directly using the "opt=ModRedundant" feature of Gaussian-03 at the level MP4(SDQ)/6-311G(d)[44] and (2) by using the present NN that yields the potential V_A. The results obtained by both methods are shown in Figure 3. We note that the results given by the two methods agree to within 0.02 eV. A similar computation using the NN obtained in ref 34 also leads to the same level of agreement. This agreement suggests that sampling initiated by using DD methods leads to a final NN very similar to the one obtained when the sampling is initiated by using a semiempirical PES. The barrier height E_o for N−O dissociation is found to be 2.58 eV.[49]

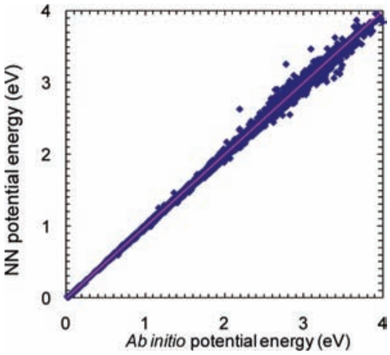

Figure 1. Comparison of the potential (in eV) predicted by the feedforward (6-40-1) NN obtained with novelty sampling of configuration space initiated by using DD trajectories with the computed ab initio MP4(SDQ)/6-311G(d) energies the final database comprising 20 192 HONO configurations.

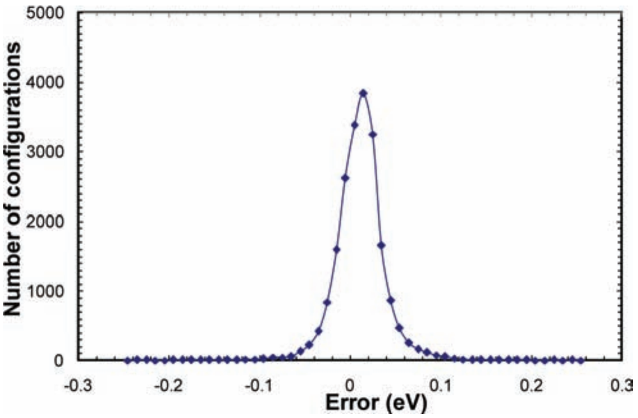

Figure 2. Distribution of differences between (6-40-1) NN obtained in this work and the computed ab initio MP4(SDQ)/6-311G(d) energies for the final database comprising 20 192 HONO configurations. The average absolute difference is 0.022 eV.

The dissociation rate for N−O bond scission has been studied at five values of the vibrational energy ranging from 2.8 to 3.3 eV. N_o = 1000 trajectories on the NN PES have been computed at each energy to obtain the dissociation rate given by

$$N = N_o \exp(-kt) \tag{5}$$

A typical decay curve is shown in Figure 4. This curve corresponds to a total vibrational energy E = 3.1 eV initially partitioned equally among all normal modes after inserting the zero-point energy in each mode. The computed rate coefficients,

TABLE 1: Experimental and Computed Wave Numbers (cm^{-1}) for Cis and Trans HONO[a]

vibrational modes	OH	N=O	HON	O−N	ONO	torsion
cis HONO						
exptl[b]	3426	1641	1302	852	609	640
Gaussian MP4(SDQ)	3647	1720	1416	964	683	724
present work	3646	1726	1434	939	693	748
ref 34	3597	1639	1370	968	671	710
trans HONO						
exptl[b]	3591	1700	1263	790	596	544
Gaussian MP4(SDQ)	3813	1778	1375	894	669	594
calcd: NN surface						
present work	3820	1751	1359	877	678	626
ref 34	3799	1738	1348	967	708	549

[a] The Gaussian calculations were done at MP4(SDQ) level, using the same basis set described in the text. [b] Reference 48.

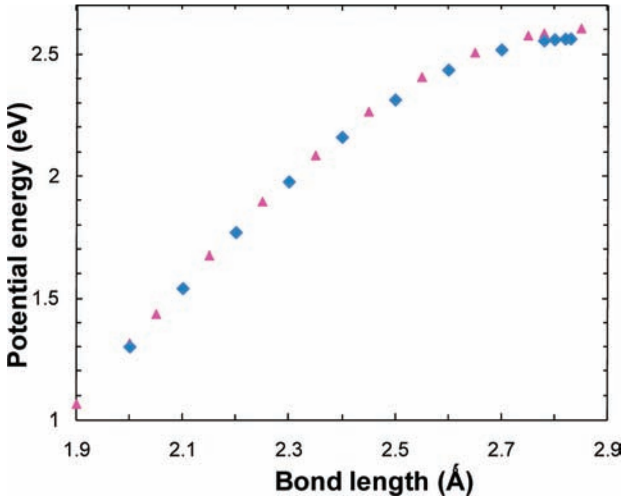

Figure 3. Comparison of the N−O bond dissociation reaction profiles as a function of N−O bond length (in Å) for the present (6-40-1) NN and the results of ab initio MP4(SDQ)/6-311G(d) calculations: (▲) present NN results and (◆) MP4(SDQ)/6-311G(d) calculations.

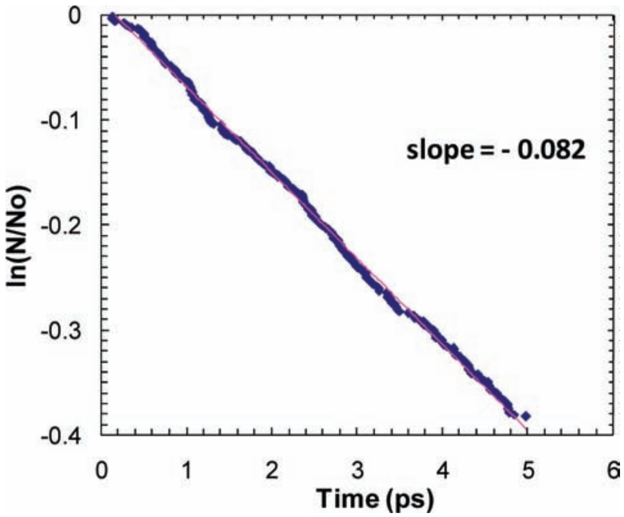

Figure 4. Decay curve for N−O bond dissociation. This curve corresponds to a total vibrational energy $E = 3.1$ eV initially partitioned equally among all normal modes after inserting the zero-point energy in each mode. The slope of the best least-squares line to the data gives a dissociation rate coefficient of 0.082 ps^{-1}.

k, at these values of energies are found to satisfy the RRK equation:

$$k = f(1 - E_o/E)^{s-1} \quad (6)$$

The variation of ln(k) with ln($1 - E_o/E$) is shown in Figure 5. From the slope and intercept of the least-squares fit, we obtain $f = 2.77 \times 10^{13}$ s^{-1} and $s = 4.3$. This frequency factor corresponds to a vibrational wavenumber of 924 cm^{-1}, which is in very good agreement with the computed frequency of the related mode of vibration, i.e., the N−O stretching mode whose fundamental frequency is 939 cm^{-1}.

In RRK theory, the value of s signifies the effective number of vibrational modes participating in the dissociation process. It may be noted that for large molecules, the value of s is usually found[50] to be approximately half the total number of vibrational modes. For small systems or in systems where the energy transfer among all vibrational modes is very rapid, the value of s approaches the total number of vibrational modes.[33]

Using a NN in which the configuration space sampling was initiated by using a semiempirical potential, Le and Raff[34] have reported values of the N−O dissociation rate coefficient of 0.092 and 0.157 ps^{-1} at 3.1 and 3.3 eV, respectively, with zero-point energy in each mode and the remainder distributed equally among all modes. The present results obtained by using a NN generated by initiating the sampling with DD are 0.082 and 0.186 ps^{-1} (see Table 2) at the same energies and equivalent energy partitioning. The 15% difference in the results may be attributed to the error associated with the inaccuracy in the potential (~0.02 eV) and the Monte Carlo error associated with the finite number of trajectories run in both the studies. It may be noted that k is very sensitive to the energy. By comparing the values of k at 3.1 and 3.3 eV, we find that a difference in internal vibrational energy of 0.01 eV leads to a ~5% difference in the value of k.

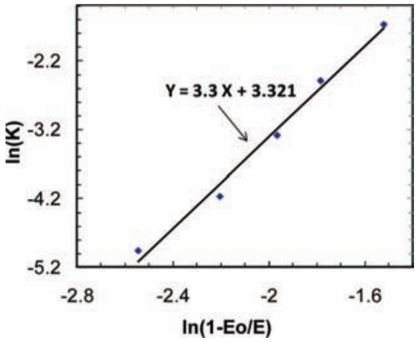

Figure 5. RRK plot for N−O bond dissociation. Each rate coefficent is obtained by partitioning the energy in excess of zero-point energy equally among all vibrational modes. The best least-squares line gives an RRK frequency factor of 2.77 × 10^{13} s^{-1} and $s = 4.3$.

To obtain a direct comparison of potentials V_A and V_B, we consider the configuration space covered by 1 000 trajectories run at an internal energy of 3.1 eV. By recording the configurations at periodic intervals, 75 388 configurations have been recorded. At each of these configurations, the difference in the potentials V_A and V_B has been computed. The average of the absolute value of this difference is found to be 0.029 eV. The distribution curve, i.e, the number of configurations as a function of the difference ($V_B - V_A$), is shown in Figure 6. A comparison of Figures 2 and 6 shows that the difference of the potential given by the present network and the actual ab initio potential (Figure 2) is comparable to the difference in the potential between the two neural networks obtained by methods A and B.

The results shown in Figure 6 allow us to infer that the configuration space covered by both networks A and B is appropriate for the purpose of computation of the chemical properties in the range of energy considered. Had there been a significant number of "holes" in the configuration space obtained by either method A or method B, it would have been reflected in the computed dissociation rates and in the magnitude of $V_A - V_B$. This agreement between A and B is neither surprising nor a matter of chance as more than a billion configurations have been scanned in the process of novelty sampling in five iterations.

IV. Summary and Conclusions

We have introduced a DD/MD/NS/NN method that combines direct dynamics (DD) with NNs and modified novelty sampling (NS) procedures[30,35] for the execution of first-principles, ab initio, molecular dynamics studies. This combination makes both DD and MD/NS/NN methods far more powerful and produces a self-starting, robust, and accurate method for efficient sampling

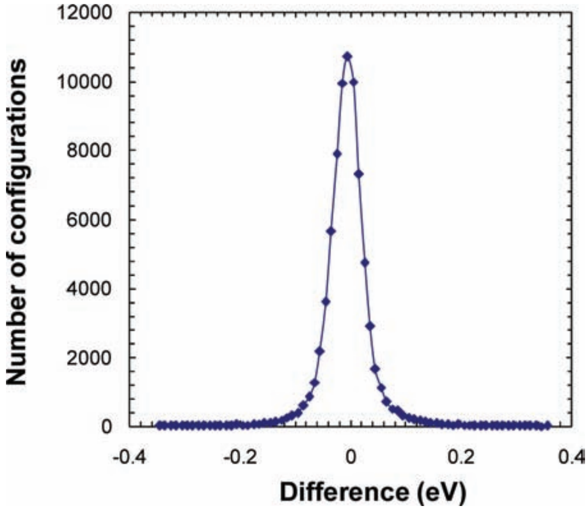

Figure 6. Distribution of the differences in energies (in eV) predicted by the present NN obtained by using DD to initiate the sampling of configuration space and that reported in ref 34,where a semiempirical PES was employed for 75 388 HONO configurations obtained in 1 000 trajectories at an internal energy of 3.1 eV. The average absolute difference is 0.029 eV.

TABLE 2: N−O Bond Dissociation Computed Rate Coefficients

	rate coefficient (ps^{-1})	
total energy (eV)	present results	ref 34
3.1	0.082	0.092
3.3	0.186	0.157

of the dynamically important regions of configuration space for complex reactions involving simultaneous two- and four-center reactions to produce an ab initio database to which NNs can be fitted and MD calculations carried out. Also, the configurations and associated energies obtained during the DD calculations can be stored and then fitted by using NN methods to provide a PES on which further trajectories can be computed without the need for further DFT calculations.

To validate the DD/MD/NS/NN method, we have investigated the N−O bond dissociation dynamics of HONO on an ab initio PES obtained using DD with the B3LYP/6-31G(d) procedure of Gaussian-03[44] to initiate the sampling of the HONO configuration space. The energies of the configurations obtained in the DD sampling are computed at the MP4(SDQ)/6-311G(d) level of accuracy to obtain the initial database to which we fit a feedforward (6-40-1) NN. Additional trajectories are computed on this NN and the resulting configurations are either accepted or rejected by using previously formulated novelty sampling methods.[30,35] The MP4(SDQ)/6-311G(d) energies of the accepted configurations are added to the database and a new (6-40-1) NN is fitted to the results. This procedure is repeated iteratively until convergence of the database is obtained by using novelty sampling criteria. Convergence is obtained after five iterations during which approximately 50 000 trajectories were computed by using the intermediate NN-fitted potential-energy surfaces and more than a billion HONO configurations examined. This is the same number of iterations that were required when a semiempirical PES[43] was employed to initiate the sampling.[34]

The final database comprises 20 192 HONO configurations and their associated MP4(SDQ)/6-311G(d) energies. The mean absolute fitting error of the NN to this database is 0.022 eV. The number of configurations required to achieve convergence under NS criteria is very close to that required (21 584) when the sampling was initiated by using a semiempirical PES.[34]

To determine if the NN obtained using DD to initiate configuration space sampling is in accord with a NN obtained using a previously reported semiempirical potential surface,[34] we have compared the energies predicted by the two NNs for 75 388 HONO configurations obtained in 1 000 trajectories at an internal energy of 3.1 eV. The average absolute value of the difference of the energies predicted by the two NNs is 0.029 eV, which is close to the agreement of the NNs with the computed MP4(SDQ)/6-311G(d) energies.

The minimum energy path and the barrier height given by the interpolated surface are found to be in excellent agreement with those given directly by the Gaussian [MP4(SDQ)/6-311G(d)] calculations. The calculated fundamental HONO vibrational frequencies predicted by the two NNs show an average difference of about 4%. The trajectory-computed N−O dissociation rates at 3.1 and 3.3 eV internal energy with the energy in excess of zero-point energy equally distributed across all vibrational modes differ by about 15%. The rate coefficient deviation expected because of the 0.029 eV average difference in energy between the two NNs is sufficient to account for this 15% variation. Further, the dissociation rates are found to satisfy the RRK equation leading to a frequency factor in agreement with the fundamental frequency of vibration corresponding to the N−O stretching mode.

We conclude that DD dynamics trajectories executed at the density functional level of theory with the B3LYP/6-31G(d) procedure for incorporation of the correlation energy provide a robust and powerful self-starting method for initiation of configuration space sampling that obviates the need for a semiempirical PES.

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