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# Molecular Dynamics of Complex Gas-Phase Reactive Systems by Time-Dependent Groups[†]

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A novel way of assembling the total potential for performing molecular dynamical studies of complex gas-phase reactive chemical systems is introduced. The method breaks the calculation of the total potential and gradients of the potential into time-dependent groups that are governed by spatial cutoffs. These groups evolve during the course of the simulation and their number may increase or diminish as the dynamics of the system determine. In an effort to extend the simulation time of these complex reactive processes and to use high levels of theory when necessary, multiple levels of theory may be used over the groups for the calculation of both the intragroup and intergroup interactions. Representative simulations are performed to illustrate the method and a computationally facile method of obtaining the groups of a simulation are also discussed.

## I. Introduction

The development of methods for the accurate description of how a reactive chemical system changes in time is a very important field of study, but one that regrettably seems to have developed more slowly than methods for describing the stationary-state properties of chemical systems. This is unfortunate because the ability to accurately describe the time evolution of reactive chemical systems from first principles (ab initio) qualifies as a necessary step for a complete understanding of the chemical sciences. Having the ability to calculate average values of experimental observables completely on the basis of first principle molecular dynamic (MD) simulations has extremely significant possibilities. In fact, this is a necessary development for a complete understanding of chemistry—being able to follow the dynamics of reactive systems completely from first principles without having to fit parameters or functional forms to experimental data and by these simulations to obtain average values of experimental observables. When the calculation of branching ratios, internal energy-state distributions of product formation, rates of product formation, lifetimes of chemical species, etc. are based completely on first principle MD simulations, one may see the exciting potential that these first principle studies hold. The ultimate goal is for the ab initio dynamics of the system to yield the kinetics and all the details of the reaction.

There is, however, much difficulty in accomplishing this goal of MD simulations on ab initio potential energy surfaces (PESs). Two of the primary difficulties are the number of internal degrees of freedom of chemical systems ($3N - 6$, where $N$ is the number of atoms)[1] and the corresponding complexity and computational costs of obtaining accurate ab initio potential energy surface (PES) of reactive systems.[2] Due to these difficulties, the chemical systems often chosen for study by ab initio MD simulations are small, often involving 6 or fewer atoms.[3−9] A sampling of previously studied reactive systems by ab initio calculations may be found in ref 10.

The additional difficulty that the method introduced here focuses upon is that of size and complexity of the chemical system. Consider, for example, the complexity associated with gas-phase combustion processes. These gas-phase processes have very simple net reactions but often involve $\sim 10^2$ simultaneous elementary reactions and $\sim 10^3$ different chemical species in leading from reactants to products.[11−13] Certainly complexity of this magnitude adds a completely new level of difficulty when one desires to study combustion processes by ab initio MD simulations. In fact, it is only recently that effort has gone into performing MD simulations of combustion processes.[5,8,9] This effort focuses on following the dynamics of a *single* step (of the $\sim 10^2$ possible elementary steps) in isolation. Indeed, there is much room for improvement for following the dynamics of complex combustion processes. Another field in which performing MD simulations is very valuable is the chemistry of the atmosphere, where, similar to combustion processes, many simultaneous reactions occur that involve a large number of chemical species.

Part of the inherent difficulty in performing MD studies of complex combustion processes is that many of the reactive processes will involve species that require high levels of ab initio theory (with explicit methods of calculating electron correlation) to get their interactions correct (free radicals, excited electronic states, etc.), whereas some nonreactive collisional processes may involve chemical species for which much lower levels of theory may be appropriate (force fields, semiempirical, or low-level ab initio methods). Clearly, a one-size-fits-all approach to the calculation of the total potential will encounter great difficulty, falling into one of two extremes: (1) treating all the interactions with high levels of theory with explicit methods of calculating electron correlation that is sufficient to get the most demanding of interactions correct and absorb an as-yet impassable computational cost for the simplest of combustion systems or (2) treating all the interactions with a very low level of theory and very likely not capture the correct dynamics of these complex reactive systems.

To surpass this difficulty of treating the whole chemical system at too high or too low a level of theory, a combination of ab initio theory with low level force fields has been introduced and applied by others.[14−16] These QM/MM methods are extremely powerful and have been utilized in studying very important systems. A modification of these QM/MM methods

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has been introduced by combining differing levels of ab initio theory.[17−20] In fact, recently integrated QCISD(T), MP4, and MP2 methods in the IMOMO methods have proven to be very accurate when studying barrier heights and reaction energy differences of systems relevant to combustion.[21] Specific reaction parameters (SRPs) are another method that has been formulated to use multiple levels of ab initio theory.[22−27] Although these IMOMO and SRPs methods are similar to the method described in this paper, they differ in that the method of this paper is seeking to take the idea of multiple levels of theory to study the *dynamics* of chemical processes. IMOMO and SRPs have been formulated to obtain accurate calculations of stationary-state properties, such as transition states, barrier heights, and vibrational frequencies. Using multiple levels of theory in studying dynamical processes has its own unique difficulties.

Ab initio quantum chemistry has made significant contributions to the study of combustion processes by the employment of stationary-state methodologies. Kinetic mechanisms for these very complex reactions are often postulated, reduced to the smallest number of steps believed to be possible, and experimental rate coefficients are obtained by parameter estimation.[11−13,28] Sometimes, though, instead of fitting all the rate coefficients, the kinetics of some of the elementary steps of the postulated $\sim 10^2$ may be studied in isolation by cleverly devised experiments.[29−33] In the absence of experimental data, quantum chemistry is a significant help in calculating rate constants by finding and characterizing transition states of the elementary steps. Transition-state theory is then employed to obtain the rate coefficient.[13,29,34] Unfortunately, the essential veracity of the whole scheme depends on the initial postulated mechanism and ab initio methods can shed no light upon this question. Methods must be developed that can follow the dynamics of these complex reactions from reactants through to products (where the dynamics may, indeed, be spread over $\sim 10^2$ simultaneous reactions and $\sim 10^3$chemical species) by means of ab initio MD simulations. Even small progress in this area would qualify as a momentous improvement and have ubiquitous application potential.

The goal of the method developed in this manuscript is to move away from a one-size-fits-all approach to calculating the total potential energy and gradients of the potential when modeling the dynamics of gas-phase reactive systems and to move toward an approach that makes the compromise of truncating higher-order multibody terms rather than the level of theory. This approach allows the use of higher levels of ab initio theory when appropriate and lower levels of ab initio theory or force fields when appropriate. In section II discussion is given on the assembly of the total potential into these time-dependent groups over which multiple levels of theory may be employed. Discussion is also given of one of the immediate results of this formulation (discontinuity of the total potential) and illustrative simulations are given to highlight how this does not introduce problems in the simulations. This section is concluded with a discussion of the effect of van der Waals wells near where the groups change definitions. In section III the implementation of assembling the time-dependent groups in a computationally feasible way is given. In section IV the conclusions are given.

## II. Methodology

**a. Assembly of the Total Potential.** Perhaps, the greatest difficulty in performing MD simulations of complex reactive systems involves the assembly of the total potential of the system and the gradients of the total potential. This difficulty is well-known for the modeling of small systems (3−5 atoms) involving only one reactive channel; for the modeling of systems involving $\sim 10^2$ reactions and $\sim 10^3$ species the difficulty is greatly exacerbated. Again, the difficulty lies in two primary causes: the number of degrees of freedom and the computational expense associated with calculating the potential for reactive systems. An alternative approach to the assembly of the total potential involves breaking the total potential into time-dependent groups that reside inside some predetermined spatial cutoff and the group−group interactions, viz.,

$$V_{\text{total}}(t) = \sum_{i}^{N} \sum_{\alpha_i}^{N_i} V_{i\alpha_i}(t) + \frac{1}{2} \sum_{i}^{N} \sum_{j}^{N} \sum_{\alpha_i}^{N_i} \sum_{\beta_j \neq \alpha_i}^{N_j} V_{i\alpha_i j\beta_j}(t) \quad (1)$$

The total potential is assembled by calculating the total intragroup potential (the first set of sums in eq 1 over $i$ and $\alpha_i$) and the total intergroup potential (the second set of sums in eq 1 over $i$, $j$, $\alpha_i$, and $\beta_j$). The sums over $\alpha_i$ and $\beta_j$ in eq 1 are over the members of the particular groups, i.e., the total number of type $i$ groups that are throughout the whole simulation cell at the particular time of the simulation. The total number of groups, $N$, will vary during the course of the simulation as bonds are broken and formed and as chemical species evolve within the spatial cutoff of one another. Equation 1 only considers group pairwise interactions, ignoring all higher order terms and, thus, is not exact. This is deemed acceptable because the method is based on asymptotic spatial cutoffs of gas-phase systems.

To illustrate the calculation of eq 1, consider a nonreactive gas-phase chemical system (such as He) contained in a simulation cell that has been divided into all the various groups on the basis of spatial cutoffs. In other words, the inner-nucleus distance between all atoms in the simulation cell are calculated and those below a pre-defined spatial cutoff are grouped together. Those atoms outside the spatial cutoff from all other atoms are, therefore, monomers; those atoms within the spatial cutoff of one other atom form dimers, etc., until the group size is truncated. For more complex reactive systems the individual groups are defined according to the identification of the chemical species that reside inside the spatial cutoff. These groups will each be unique and may widely vary in their chemical composition. At each time step during the simulation, each of these groups may have multiple members and the members of each group will each have unique nuclear arrangements. Thus, the sum over $\alpha_i$ in this first term is a sum over the unique members of the $i$th group where $V_{i\alpha_i}$ is the intragroup interaction potential at the unique nuclear positions of this member at a particular time in the simulation. Consider a combustion reaction that, for illustrative purposes, is limited to only involving A, radical A (Ra), and $O_2$ inside a simulation cell. The total number of groups and members of the groups are formed: the A and Ra monomers (each of these monomers are isolated and the atoms lie outside the spatial cutoff from all other atoms in the simulation cell), the number of $A_2$, $O_2$, $Ra_2$, and ARa dimers (each of the atoms of these dimers are within the spatial cutoff from one another and outside the spatial cutoff of all other atoms in the simulation cell), the total number of $A_3$, $Ra_3$, $A_2Ra$, $ARa_2$, $AO_2$, and $RaO_2$ trimers, etc., until the approximation is made by truncating higher order groups. Once these groups are formed, the intragroup interactions are calculated and the level of theory employed may be adapted to whatever is appropriate for the various groups. Suppose the $A_2$, $O_2$, $AO_2$, and $A_3$ groups involve only collisional, nonreactive processes where a much lower level of theory may be employed than the remaining groups where reactive processes may take place and higher levels of theory will need to be employed. The computational cost of the intergroup calculation should be very small relative to that for the intragroup interactions. Thus, the level of theory may change with the first sum over the groups, $i$ in eq 1, but not with the sum over the members of a particular group, $\alpha_i$.

**b. Discontinuity of the Total Potential.** Breaking the total potential into time-dependent groups as given in eq 1, will yield the changing of the number of groups and the number of group members as the simulations proceed. Furthermore, as explained earlier, the interactions of the different groups may be described by varying levels of theory. The result of each of these will be discontinuities in the total potential, eq 1, as the simulation proceeds. Fortunately, for classical molecular dynamics simulations, the motion of the atoms is governed by the gradients of the potential rather than the potential itself. Because the groups are defined according to spatial cutoffs, the gradients of the potentials of the various groups will all *approach* the *same* value when the groups change identification; namely, the gradients will all approach zero. The fact that gradients approach zero at the spatial cutoff does not depend on the level of theory being employed, but, simply, that the spatial cutoffs are sufficiently large that the asymptotic region is approached regardless of the level of theory. Thus, at the spatial cutoff, the potential across the cutoff may not be continuous, but the gradients of the potential will be—provided the spatial cutoff is large enough to be near the asymptotic region. Nearness to the asymptotic region is a relative term and thus “tight” and “loose” criteria may be employed in the definition of the spatial cutoff that would reduce and increase the computational load of the simulation, respectively.

To demonstrate the principle of continuity of the gradients of eq 1 and the smooth, continuous time evolution of the atoms when the total potential undergoes significant discontinuities, a very simple grazing collision between $O_2$ and $N_2$ molecules was considered with analytic Morse potentials used to describe the O−O, N−N, and O−N interactions. This very simple test is only used to illustrate the principle of smooth and continuous forces (and the resulting smooth motion of the atoms) when the potential undergoes significant discontinuities. The point of the method is not that it will only work with, or be employed with, analytic potentials; the Morse potentials were used because they are qualitatively correct and, thus, are sufficient to *represent* what would happen when higher levels of theory are used, i.e., to illustrate the principle of the discontinuity of the potential and continuity of the kinetic energy at the spatial cutoff. Two different potential functions were used for the system: one outside the spatial cutoff where the O−N interactions are neglected and the system is two independent diatomics:

$$V_{\text{total}} = D_{N_2}[1 - \exp(-\beta_{N_2}(r_{N_2} - r_{e,N_2}))]^2 + D_{O_2}[1 - \exp(-\beta_{O_2}(r_{O_2} - r_{e,O_2}))]^2 \quad (2)$$

and one inside the spatial cutoff, where the O−N interactions are accounted for and the system is an $N_2$−$O_2$ supermolecule:

$$V_{\text{total}} = \gamma D_{N_2}[1 - \exp(-\gamma\beta_{N_2}(r_{N_2} - r_{e,N_2}))]^2 + \gamma D_{O_2}[1 - \exp(-\gamma\beta_{O_2}(r_{O_2} - r_{e,O_2}))]^2 + \sum_i [D_{NO}[1 - \exp(-\beta_{NO}(r_{NO,i} - r_{e,NO}))]^2 - D_{NO}] \quad (3)$$

The Morse potential parameters for eqs 2 and 3 are given in Table 1.[35] The $\gamma$ parameter in eq 3 was inserted to approximate the fact that when the groups switch definitions different levels of theory may be used and, thus, the intramolecular interactions of particular chemical species may not match when the groups switch. As seen in eq 3, this change in $\gamma$ affects both the well depths of the $O_2$ and $N_2$ molecules and the curvature of their interaction potentials. Shown in Figure 1 is diagram illustrating the grazing collision between $N_2$ and $O_2$ being considered as well as plots of the Morse potentials. For this $N_2$ and $O_2$ system, the spatial cutoff was defined such that if any N−O distance was below 5 bohr, then the supermolecule potential of eq 3 was used to describe the total potential and if all N−O distances were 5 bohr or above, then isolated diatomic potentials of eq 2 were used to describe the total potential. Thus, eq 1 went from being calculated as two dimers to one quadrimer at the spatial cutoff. This value of 5 bohr for the spatial cutoff was chosen to represent a rather poor choice and not quite in the asymptotic region. Thus, difficulties with the method will be more evident with this poor choice of a spatial cutoff. Furthermore, other ways exist to describe the spatial cutoff and this definition was used so that switching from inside and outside the spatial cutoff could depend on the vibrational motion of the $N_2$ and $O_2$ diatomics. This was desired to illustrate the principle that a smooth continuous simulation is still obtained even when the groups change definitions more than once during a single collision event. As illustrated in Figure 1, the $N_2$ and $O_2$ began at a large distance from one another and the total potential was given by eq 2 as two isolated diatomics. As the entities approached, an NO distance became less than the spatial cutoff and the supermolecule potential was used as given by eq 3. As the diatomics continued past one another, they, again, eventually became two isolated diatomics described by eq 2. Two separate simulations were performed: one with $\gamma = 1.0$ in the supermolecule region, as given by eq 3, and one with $\gamma = 0.8$.

**TABLE 1: Morse Potential Parameters for the Interactions of Eqs 2 and 3**

| diatoms | $D$ (eV) | $\beta$ (Å$^{-1}$) | $r_e$ (Å) |
|---|---|---|---|
| $N_2$ | 9.756 | 2.711 | 1.094 |
| $O_2$ | 5.080 | 2.689 | 1.207 |
| NO | 6.490 | 2.769 | 1.150 |

Shown in Figure 2 is the time evolution of the internuclear coordinates for the grazing collision between $O_2$ and $N_2$. The N−N, O−O, and the center of mass (COM) between the $N_2$ and $O_2$ distances are shown in Figure 2 as the black solid, blue dashed, and red dotted lines, respectively, for the was $\gamma = 1$ simulation, whereas these distances are given as the red dashed, the green solid, and black dashed−dot lines, respectively, for the $\gamma = 0.8$ simulation. For the $\gamma = 0.8$ simulation, each of the distances were increased by a fixed value of 1.0 bohr to separate the coordinates from the $\gamma = 1$ simulation. As seen in Figure 2, the two simulations are exactly the same up until $t \sim 0.125$ ps, at which time there is a change in the groups. After this time there were multiple changes in the groups; however, the coordinates for both simulations evolve in a smooth manner.

The discontinuity in the total energy for each of the grazing collisions displayed in Figure 2 is shown in Figure 3. In this figure, the difference in the total energy at every time minus the initial total energy is plotted against the time. This difference is given as the solid line for the $\gamma = 1$ simulation and as the dashed line for the $\gamma = 0.8$ simulation. From this figure it can be seen that there were six changes in the definition of the groups for both the $\gamma = 1$ and $\gamma = 0.8$ simulations: from two isolated diatomics described by eq 2 to an $N_2$−$O_2$ supermolecule described by eq 3 and back and forth for both of the simulations displayed in Figure 2. All six changes happened between times

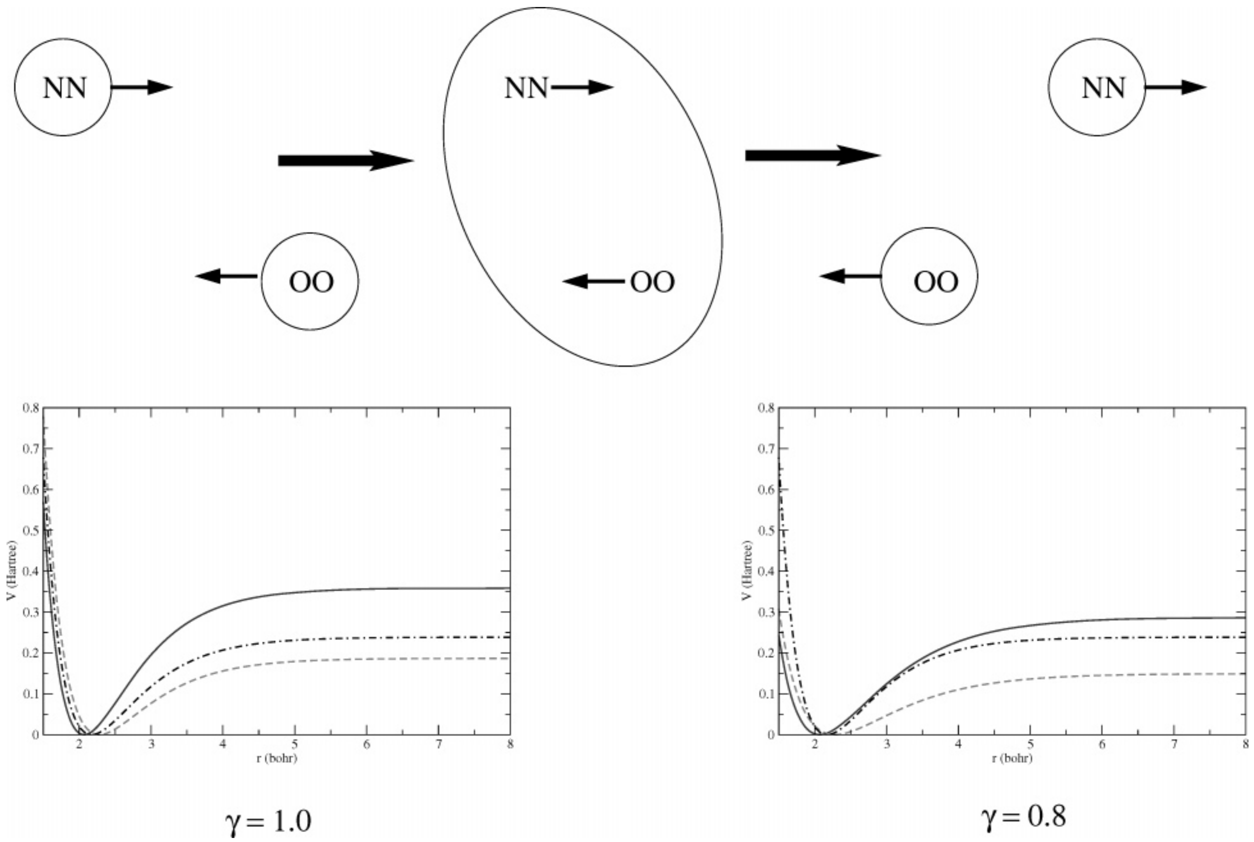

**Figure 1.** Illustration of the $N_2/O_2$ grazing collision: (left) $N_2$ (—), $O_2$ (---), and NO (—•—) Morse potentials with $\gamma = 1$, which effects only the $O_2$ and $N_2$ potentials; (right) $N_2$ (—), $O_2$ (---), and NO (—•—) Morse potentials with $\gamma = 0.8$.

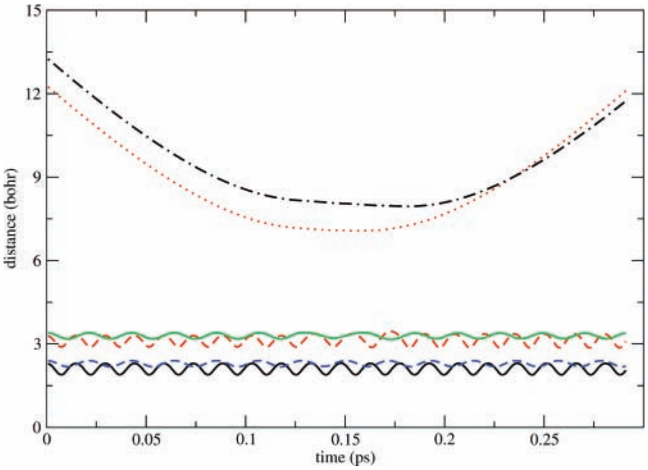

**Figure 2.** Time dependence of the $O_2$ and $N_2$ distances and the $O_2$−$N_2$ center-of-mass distances for the grazing collision in which there were six changes in the group definitions for the $\gamma = 1$ and 0.8 simulations. The N−N, O−O, and center-of-mass distances are shown as the black solid, blue dashed, and red dotted lines for the $\gamma = 1$ simulation and as the red dashed, green solid, and black dashed−dotted lines for the $\gamma = 0.8$ simulation, where these distances were increased by 1.0 bohr.

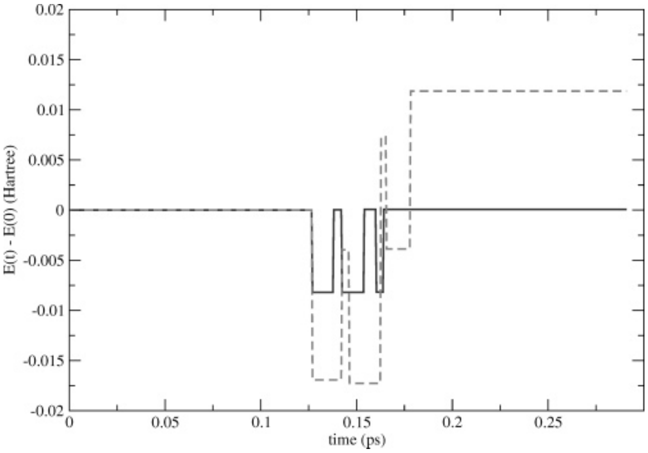

**Figure 3.** Conservation of the total energy for the grazing collision displayed in Figure 2: (—) $\gamma = 1$ simulation; (---) $\gamma = 0.8$ simulation.

0.125 and 0.180 ps when $N_2$ and $O_2$ are the closest and the changes correlate with the individual $N_2$ and $O_2$ vibrational motions. As can be seen in Figure 3, the potential changes by ∼0.008 Hartrees during this time of switching group definitions for the $\gamma = 1$ simulation, which causes the total energy to have a discontinuity of this same amount. For the $\gamma = 0.8$ simulation displayed in Figure 2, there were many more dramatic discontinuities in the total potential, up to a discontinuity of ∼0.025 Hartrees. For both simulations, the total energy only changed when the group identification changed; i.e., when the group definition remains constant, the total energy also remained constant. For the $\gamma = 1$ simulation (solid line in Figure 3), the potential changes by nearly the same amount during each change of the groups because the N−O bond lengths do not undergo drastic changes in their distances during this time window.

From Figure 2 it can also be seen that the coordinates for both simulations all evolve in time in a smooth manner even over the region where the potential is changing by as much as 0.008 and 0.025 Hartrees for the $\gamma = 1$ and 0.8 simulations, respectively. Thus, these large and repeated discontinuities in the potential do not yield the gain or loss of kinetic energy of the atoms. Further proof of this may be seen in Figure 4, where the total kinetic energy is plotted in the time window where there is a change in groups for both of the collisions displayed

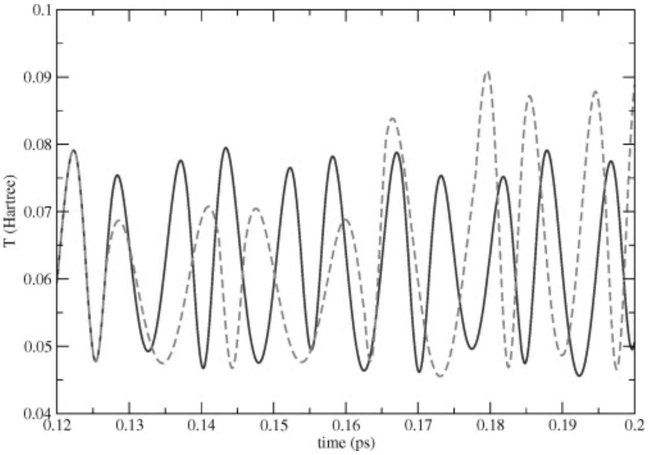

**Figure 4.** Total kinetic energy for the grazing collision displayed in Figure 2 for $\gamma = 1$ (—) and $\gamma = 0.8$ (---) during the time window where the groups change definitions.

in Figure 2. In Figure 4, the solid and the dashed lines are the total kinetic energy for the $\gamma = 1$ and $\gamma = 0.8$ simulations, respectively. As can be seen from this figure, although there are large discontinuities in the total potential, the total kinetic energy is smooth because the gradients of the potential along the coordinates defined by the spatial cutoff all approach the same value.

In summary, these two simulations simply illustrate the point of being able to define the total potential (and gradients of the potential) by time-dependent groups with levels of theory that may change at the spatial cutoff.

**c. Effect of van der Waals Wells.** The nature of the didactic Morse potentials employed in this paper ignore the possible effects of shallow van der Waals wells at the asymptote. If the chemical system had a van der Waals well and the spatial cutoff were placed in the region of the well, it could be that a lower level of theory outside the spatial cutoff would not capture the well, whereas the well was obtained with a higher level of theory inside the cutoff. The net effect could be a more significant discontinuity in the gradients than if both levels of theory captured the well or neglected the well. However, it is because of this possibility that the spatial cutoff is not a static entity but will naturally change with the chemical nature of the various groups. Thus, one could always increase the size of the cutoff so that the van der Waals well is captured with the higher level of theory. Of course this will increase the computational load of the simulation. It should also be noted that the gradients will never *exactly* match at the spatial cutoff (this was the case in both the $\gamma = 1.0$ and $\gamma = 0.8$ simulations discussed above). The gradients approach the same value at the spatial cutoff. Nevertheless, a van der Waals well will exacerbate the discontinuity of the gradients and could result in gradients at the cutoff with differing signs. However, when one examines the discontinuity in the kinetic energy that will result in a discontinuity in the gradient, it is found to go as

$$\Delta T = \frac{\Delta t^2 (\Delta \nabla E)^2}{2m} \tag{4}$$

where $\Delta t$ is the time step of the simulation and $\Delta \nabla E$ is the discontinuity in the gradient. Using a large time step of 0.25 fs and a small mass of 1.0 amu, one sees that under these difficult conditions, the discontinuity of the kinetic energy is proportional to the square of the discontinuity of the gradient divided by about 40, which greatly dampens the effect of the discontinuous gradients. Finally, given the scale of the chemical systems the methodology is designed to simulate (ab initio dynamics of $\sim 10^2$ simultaneous reactions with $\sim 10^3$ species), compromise will be necessary. Thus, the user may either decide to increase the computational cost of the simulations and move the spatial cutoff to a distance so that the van der Waals wells are captured by the higher level of theory or abide what may be a more significant gradient discontinuity at the spatial cutoff because it will likely have a small effect on the dynamics of the ensuing reactive event.

## III. Implementation

The assembly of the total potential as given in eq 1 will require the division of the chemical system into unique groups based on spatial cutoffs in a nonredundant way that is computationally efficient. The computational load for this step is overhead to the MD simulation and it is possible that the making of groups may have to be done at each time step of the simulation. Although the remaking of groups at each time step is unlikely, this step in the MD simulation must be extremely efficient. Dividing the simulation cell into subcells of much greater size than the spatial cutoff, while these subcells have linked-listed neighboring subcells, provides a computationally facile way of making the various groups and members of the groups. To form all the groups and members of the groups within the simulation cell, the subcells are looped over and for those that contain atoms within them, all the monomers, dimers, trimers, up to the truncated group size are made and the neighboring subcells are also searched to add, delete, or amend the groups of the searched subcell. After all the subcells are searched, then the total number of groups (monomers, dimers, trimers, etc.) and the members of each of these groups will have been obtained and can then be used in the calculation of the total potential from eq 1. This method of subcell division has been shown to have a computational scaling factor that is linear in the number of atoms in the simulation cell, $O(N_{\mathrm{atoms}})$.[36] The *MakeGroups* module has been written in the C programming language to perform these operations. The author may be contacted to obtain the source code.

## IV. Conclusions

In summary, a method of assembling the total potential for gas-phase reactive chemical systems in which the dynamics may be spread over many elementary steps in leading from reactants to products has been introduced. Simple tests of a grazing collision between $O_2$ and $N_2$ molecules demonstrate the principle that the total potential can be defined by groups that change definitions according to spatial cutoffs as the simulation proceeds. Although only a simple grazing collision between diatomics described by Morse potentials is illustrated here, the principle illuminated by these simple tests goes well beyond the tests and shows the direct application of the method to much more complex reactive systems where the breaking and forming of bonds will be inside the spatial cutoff and the gradient of the potential will approach the same value at the spatial cutoff just as in the examples used here. The changing of the groups at the spatial cutoff will induce discontinuities in the total potential, but the coordinates will evolve smoothly over these areas because the gradients along the coordinates between the molecular entities will approach the same value, namely zero. Because the gradients approach zero at the spatial cutoff regardless of the level of theory employed, varying levels of theory may be employed on the basis of the nature of the chemical species that define the group. The making and remaking of the groups during the course of an MD simulation is purely computational overhead. Thus, an efficient way of making groups has been given that uses link-listed subcells and only requires a maximum search of neighboring subcells to make the groups. Because the simulations will begin by performing many computationally expensive ab initio calculations over the various groups, very little simulation time will transpire for a large expense of CPU time. This difficulty is also being worked on by storing the group potential energy data to fast-access databases and combining these databases with accurate and computationally facile general methods of interpolation so that eventually the computationally expensive calculation of the ab initio intragroup interactions will yield to fast methods of interpolation. Interpolants similar to previous work[37-43] are being generalized for any dimensionality, and studies are being performed on methods of optimizing the interpolants so as to obtain general, accurate, and fast methods of PES interpolation.

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## References and Notes

(1) Schatz, G. C.; Horst, M. T.; Takayanagi, T. In *Methods for Multidimensional Dynamics Computations in Chemistry*; Thompson, D. L., Ed.; World Scientific: Singapore, 1998; p 1.

(2) Shatz, G. C. In *Reaction and Molecular Dynamics*; Lecture Notes in Chemistry, Vol. 14; Lagana, A., Riganelli, A.; Springer: Berlin, 2000; p 15.

(3) Akiya, N.; Savage, P. E. *J. Phys. Chem. A* **2000**, *104*, 4441.

(4) Skokov, S.; Wheeler, R. A. *J. Phys. Chem. A* **2000**, *104*, 6314.

(5) Moriarty, N. W.; Frenklach, M. *Proc. Combust. Inst.* **2000**, *28*, 2563.

(6) Kaledin, A. L.; Morokuma, K. *J. Chem. Phys.* **2000**, *113*, 5750.

(7) Tachikawa, H.; Igarashi, M.; Ishibashi, T. *J. Phys. Chem. A* **2002**, *106*, 10977.

(8) Scheutz, C. A.; Frenklach, M. *Proc. Combust. Inst.* **2002**, *29*, 2307.

(9) Brown, A.; McCoy, A. B.; Braams, B. J.; Jin, Z.; Bowman, J. M. *J. Chem. Phys.* **2004**, *121*, 4105.

(10) Bolton, K.; Hase, W. H.; Peslherbe, G. H. In *Methods for Multidimensional Dynamics Computations in Chemistry*; Thompson, D. L., Ed; World Scientific: Singapore, 1998; p 143.

(11) Susnow, R. G.; Dean, A. M.; Green, W. H.; Peczak, P.; Broadbelt, L. J. *J. Phys. Chem. A* **1997**, *101*, 3731.

(12) Gardiner, W. C. In *Combustion Chemistry*; Springer-Verlag: New York, 1984.

(13) Oran, E. S.; Boris, J. P. In *Numerical Approaches to Combustion Modeling*; Progress in Astronautics and Aeronautics Series, Vol. 135; American Institute of Aeronautics and Astronautics: Washington, DC, 1991.

(14) Humbel, S.; Sieber, S.; Morokuma, K. *J. Chem. Phys*. **1996**, *105*, 1959.

(15) Vreven, T.; Morokuma, K. *J. Chem. Phys*. **1999**, *111*, 8799.

(16) Kerdcharoen, T.; Morokuma, K. *J. Chem. Phys*. **2003**, *118*, 8856.

(17) Maseras, F.; Morokuma, K. *J. Comput. Chem.* **1995**, *16*, 1170.

(18) Svensson, M.; Humbel, S.; Froese, R. D. J.; Matsubara, T.; Sieber, S.; Morokuma, K. *J. Phys. Chem.* **1996**, *100*, 19357.

(19) Humbel, S.; Sieber, S.; Morokuma, K. *J. Chem. Phys*. **1996**, *105*, 1959.

(20) Svensson, M.; Humbel, S.; Morokuma, K. *J. Chem. Phys.* **1996**, *105*, 3654.

(21) Li, Q. S.; Zhao, Q.; Zhang, S. *J. Phys. Chem. A* **2004**, *108*, 6430.

(22) Gonzales-Lafont, A.; Truong, T. N.; Truhlar, D. G. *J. Phys. Chem*. **1991**, *95*, 4618.

(23) Rossi, I.; Truhlar, D. G. *Chem. Phys. Lett.* **1994**, *233*, 231.

(24) Corchado, J. C.; Espinosa-Garcia, J.; Hu, W.; Rossi, I.; Truhlar, D. G. *J. Phys. Chem*. **1995**, *99*, 687.

(25) Peslherbe, G. H.; Wang, H.; Hase, W. L. *J. Am. Chem. Soc*. **1996**, *118*, 2257.

(26) Peslherbe, G. H.; Hase, W. L. *J. Chem. Phys*. **1996**, *104*, 7882.

(27) Doubleday, C.; Bolton, K.; Peslherbe, G. H.; Hase, W. L. *J. Am. Chem. Soc*. **1996**, *118*, 9922.

(28) Matheu, D.; Dean, A. M.; Grenda, J. M.; Green, W. H. *J. Phys. Chem. A* **2003**, *107*, 8552.

(29) Stoliarov, S. I.; Knyazev, V. D.; Slagle, I. R. *J. Phys. Chem. A* **2002**, *106*, 6952.

(30) DeMore, W. B.; Bayes, K. D. *J. Phys. Chem. A* **1999**, *103*, 2649.

(31) DeMore, W. B.; Wilson, E. W. *J. Phys. Chem. A* **1999**, *103*, 573.

(32) Wilson, E. W.; Sawyer, A. A.; Sawyer, H. A. *J. Phys. Chem. A* **2001**, *105*, 1445.

(33) Wilson, E. W.; Jacoby, A. M.; Kukta, S.; Gilbert, L. E.; DeMore, W. B. *J. Phys. Chem. A* **2003**, *107*, 9357.

(34) Richter, H.; Howard, J. B. *Phys. Chem. Chem. Phys*. **2002**, *4*, 2038.

(35) Raff, L. M. In *Principles of Physical Chemistry*; Prentice Hall: Englewood Cliffs, NJ, 2001; p 857.

(36) Rapaport, D. C. In *The Art of Molecular Dynamics Simulation*, 2nd ed.; Cambridge University Press: Cambridge, U.K., 2004; p 49.

(37) Salazar, M. R.; Bell, R. L. *J. Comput. Chem*. **1998**, *19*, 1431.

(38) Salazar, M. R.; Simons, J. *J. Chem. Phys.* **1996**, *105*, 10919.

(39) Bell, R.; Simons, J. *J. Phys. Chem*. **1999**, *103*, 539.

(40) Salazar, M. R.; Simons, J. *J. Chem. Phys.* **1999**, *110*, 229.

(41) Salazar, M. R. *Chem. Phys. Lett*. **2002**, *359*, 460.

(42) Colavecchia, F. D.; Burke, J. P.; Stevens, W. J.; Salazar, M. R.; Parker, G. A.; Pack, R. T. *J. Chem. Phys*. **2003**, *118*, 5484.

(43) Salazar, M. R.; Simons, J. *J. Chem. Phys.* **2004**, *121*, 6874.