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A NEURAL NETWORK APPROACH TO THE STUDY OF DYNAMICS AND STRUCTURE OF MOLECULAR SYSTEMS

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ABSTRACT:

Neural networks are used to study intramolecular energy flow in molecular systems (tetratomics to macromolecules), developing new techniques for efficient analysis of data obtained from molecular-dynamics and quantum-mechanics calculations. Neural networks can map phase space points to intramolecular vibrational energies along a classical trajectory (example of complicated coordinate transformation), producing reasonably accurate values for any region of the multidimensional phase space of a tetratomic molecule. Neural network energy flow predictions are found to significantly enhance the molecular-dynamics method to longer time-scales and extensive averaging of trajectories for macromolecular systems. Pattern recognition abilities of neural networks can be used to discern phase space features. Neural networks can also expand model calculations by interpolation of costly quantum mechanical *ab initio* data, used to develop semiempirical potential energy functions.

I. INTRODUCTION

Detailed investigation of the transfer and redistribution of internal energy is fundamental to developing an understanding of the dynamics of molecular systems. In particular, the redistribution of energy within a molecule plays an essential role in its chemical reaction dynamics (Yardley, 1980; Steinfeld, 1989) A molecule that is sufficiently energized will generally undergo a physical and/or chemical change, ultimately dissociating or isomerizing to form products. The rate at which these processes occur is determined by the time scale for energy flow into the reaction coordinate of the system. Investigating the mechanisms that control internal energy redistribution is therefore an essential step in the attempt to understand and predict how various features of a chemical system control its dynamics (Uzer, 1991).

Molecular dynamics simulations provide a powerful tool for examining energy transfer processes (Sumpter and Noid, 1992). However, computational time limitations has plagued molecular dynamics studies for a number of years. While substantial improvements and simplifications can be made which allow more efficient calculations to be performed (Noid, 1990; Gray, 1994) the problem of accurate calculations on a complex potential energy surface for nanosecond times still remains. Some of the computational obstacles involved in detailed simulations of molecular energy flow include: (1) globally accurate potential energy surfaces, (2) intensive computer time required for trajectory calculations, and (3) simple means for the calculation of energy flow (from one mode to another) within a particular molecule. Fortunately, many of these shortcomings can be substantially helped by utilizing neural network techniques (Fausett, 1994).

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Local Mode Energies in a Cartesian Coordinate Reference Frame

Although the most widely spread descriptions of the vibrational motion were traditionally given in normal coordinates (Wilson, 1955) other sets of coordinates are more appropriate to describe vibrationally excited systems. In particular, local or internal coordinates (bond-angle coordinates) are useful to formulate the non-linear dynamics problem of vibrational motion, and to take account for the overtone spectra of some molecules (specially those containing XH groups).

A method for calculating local mode energies in polyatomics from Cartesian coordinates has been proposed (Getino, 1990). Basically the vibrational mode energy is calculated as the sum of the potential plus the kinetic mode energies. In general, the potential mode energy is very simple to obtain since the potential energy surface is most commonly fit to analytical functions which are quasi-separable in internal coordinates. The kinetic energy is computed in Cartesian coordinates, thus a transformation to the coordinates of the potential is necessary to obtain the kinetic mode energies. This can be achieved by using a method based on Wilson's treatment of molecular vibrations (Wilson, 1955). The kinetic mode energies can be expressed in matrix form as:

$$2T = \dot{\mathbf{r}} \mathbf{K} \dot{\mathbf{r}} \quad (1)$$

where $\dot{\mathbf{r}}$ is the vector of the time derivatives of the curvilinear coordinates (bonds, bend angles, dihedral angle, etc.), and \mathbf{K} is the kinetic energy matrix. $\dot{\mathbf{r}}$ can be calculated by transforming the Cartesian velocities, $\dot{\mathbf{x}}$:

$$\dot{\mathbf{r}} = \mathbf{B} \dot{\mathbf{x}}, \quad (2)$$

where \mathbf{B} is the transformation matrix from Cartesian to curvilinear coordinates. It can be shown that the kinetic energy matrix \mathbf{K} is the inverse of Wilson's \mathbf{G} matrix:

$$\mathbf{G} = \mathbf{B} \mathbf{M}^{-1} \mathbf{B}^T, \quad (3)$$

where \mathbf{M}^{-1} is a diagonal matrix of the reciprocal masses of the atoms and \mathbf{B}^T is the transposed \mathbf{B} matrix. Thus, one can write the kinetic energy (eq.(1)) as:

$$2T = \dot{\mathbf{r}} \mathbf{G}^{-1} \dot{\mathbf{r}} = \sum \dot{r}_i G^{-1}_{ij} \dot{r}_j . \quad (4)$$

The kinetic mode energies are approximated as the diagonal terms of the above equation:

$$T_i = (\dot{r}_i G^{-1}_{ii} \dot{r}_i) / 2 . \quad (5)$$

The analysis of mode energies can provide a means to define the pathways for energy flow that lead to chemical reaction, structural changes, and subtle or drastic transitions in the vibrational modes (quasiperiodic and chaotic motion). This type of analysis has provided the framework for much of the present understanding of energy flow in polyatomic molecules. Maybe the most useful application of the mode energy representation is to pictorially describe the energy history of the molecule, as calculated from classical trajectories. Analyzed for individual trajectories, mode energies can help elucidate the internal energy pathways and mechanisms (resonances, couplings) governing the vibrational motion and ultimately

reaction dynamics of polyatomics. When averaged over ensembles of trajectories, the mode energies show the essentials of internal energy transfer and give information on its rates.

Figure 1 illustrates an example of the first application, the pictorial representation of an individual trajectory for H_2O_2 .

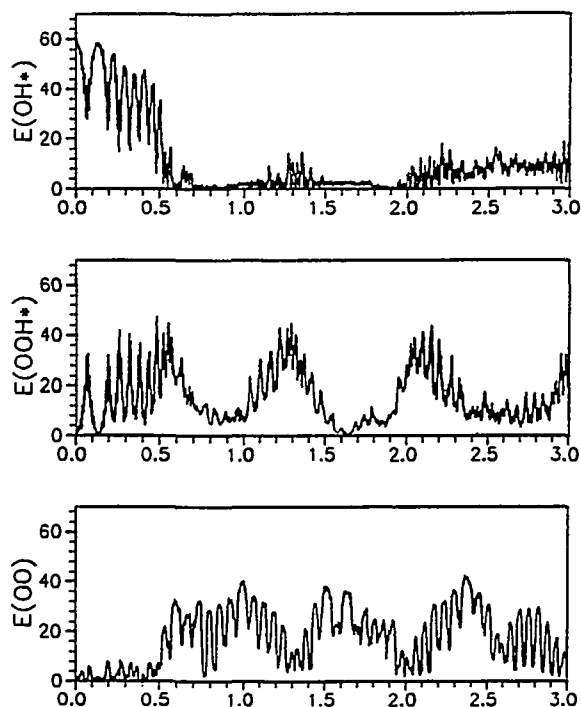


Figure 1. Local mode energy flow for H_2O_2 computed from molecular dynamics simulations.

The energy in each local mode (this molecule has six local or internal vibrations: two OH stretches, one OO stretch, two OOH bends, and a torsion) is followed as a function of time along a trajectory as a sum of potential plus kinetic mode energy as specified before. Fig. 1 shows the energy redistribution from an initially excited OH state. In this trajectory, the de-excitation of the OH overtone involves reversible energy transfer to the adjacent OOH bend for about 0.5 ps, after which some energy accumulates in the OO bond and is followed by a somewhat complicated energy flow mainly involving the OO stretch and the two OOH bends.

As it was described before, the evaluation of mode energies involves the calculation of the **B** and **G** matrices and the inversion of **G**, along the trajectory (2000 times in the 3 ps trajectory of Fig. 1). While that is more or less trivial for small molecular systems (2 - 6 atoms) it can become a problem for macromolecular systems (systems with over 1000 atoms), for which the relatively simple algebra of mode energy evaluation can greatly multiply the computer time needed for the trajectory calculation (which is naturally large since it involves the integration of over 6000 coupled equations of motion). Conceptually, the above method only involves the mathematical operations of vector transformations, summations, and products, and thus should provide a reasonable problem for the application of neural networks.

Specification of the Neural Network: Architecture and Implementation

In the present application we have trained a neural network to learn the relationship between Cartesian coordinates and momenta, and the kinetic internal mode energies of tetratomics (H_2X_2). All the information required for the algebraic transformation is provided as input data to the neural network: 12 Cartesian atom positions (x,y,z) and 12 Cartesian momenta (p_x, p_y, p_z), and the 4 atomic masses. The neural network gives the 6 kinetic internal mode energies (two XH stretches, one XX stretch, two HXX bends, and one torsion) as an output. We found that for this problem, the optimum architecture of the fully connected neural network is: 28 input nodes, two hidden layers (the first has 38 nodes and the second has 12 nodes) and an output layer of 6 nodes, giving a total of 84 nodes and 1648 connections, including bias values.

In the implementation step, the network was given a number of examples from a classical trajectory. The connection weights of the network are modified to give outputs that match the mode energies calculated algebraically, and following certain internal laws the network "learns" the relationship between input and output. In this case, that relationship it is not a simple linear dependence, but it involves (as described above): The calculation of the B , G and G^{-1} matrices, and products of those to transform linear momenta from the Cartesian into the internal curvilinear coordinate frame. Once the neural network has extracted information on how the input and output are associated, it will then be used to calculate the kinetic mode energies for other trajectories for which it was not trained. Since the calculation of mode energies is essentially a transformation, the results should be generic.

The 84 node neural network was trained using 2000 examples (phase space points and mode energies for 2000 points along the trajectory of Fig. 1 but the order of the data is randomized to eliminate any correlations) for 9400 cycles to obtain a reasonable output error. Further training did not improve the networks ability to generalize and at this point, the training was stopped and the architecture was tested to make sure that the number of nodes was adequate.

RESULTS AND DISCUSSION

The performance of the neural network to produce kinetic mode energies from Cartesian coordinates was examined for several different cases. First, to check the overall accuracy and its ability to generalize we have used single trajectories in different parts of the 24 dimensional phase space of hydrogen peroxide (H_2O_2). Cases studied include (not all the cases will be discussed):

- (a) A non-reactive trajectory (Fig. 1) that was used in training the network.
- (b) The training trajectory predicted to longer timescales ($t > 3$ ps).
- (c) A reactive trajectory ($H_2O_2 \Rightarrow 2 OH$).

The kinetic mode energies predicted by the neural network are compared to the "exact" values, algebraically calculated along the trajectory. Figure 2 shows both calculated and neural network predicted kinetic energy values in a OH local modes (the initially excited OH stretch) for the examples of case (a), the training trajectory. Energies are scaled between 0.1 and 0.9, and the trajectory data are randomized before the training step, so that the correlation between examples is lost. Thus, the abscissas axis in Fig. 2 shows the arbitrary order in which the training examples are given.

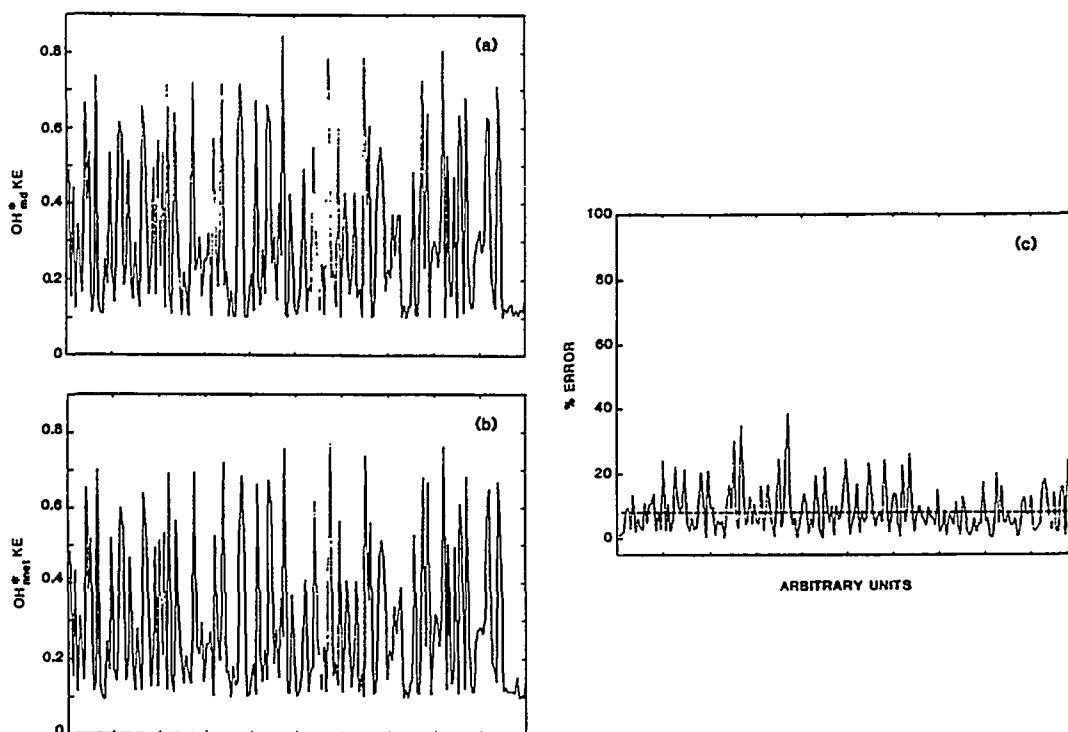


Figure 2. Local mode energy flow for H_2O_2 predicted by a trained neural network (b), computed by molecular dynamics (a), and the abs % error (c).

As can be observed in Fig. 2, the results predicted by the neural network closely resemble the kinetic mode energy calculated by algebraically transforming the molecular dynamics (MD) results. A better estimate of the accuracy of the network can be obtained from the divergence of both sets of values, calculated as the relative percent error = $\text{ABS}[(E(t)_{\text{MD}} - E(t)_{\text{NNET}})/E(t)_{\text{MD}}] * 100$, also included in Fig. 2. Although for certain points the error can be as much as almost 40%, it is also very close to zero for some other points. The dashed line shows the average value of the relative error $\langle \text{Er} \rangle$, which for each mode (all modes are not shown in Fig. 2) is: $\langle \text{Er}(\text{OH}^*) \rangle = 8.2\%$, $\langle \text{Er}(\text{OOH}^*) \rangle = 8.2\%$, $\langle \text{Er}(\text{OO}) \rangle = 2.5\%$, $\langle \text{Er}(\text{OOH}) \rangle = 5.4\%$, $\langle \text{Er}(\text{OH}) \rangle = 12.0\%$, and $\langle \text{Er}(\text{tor}) \rangle = 5.6\%$. Thus, the neural network predicted the mode energies to reasonably accurate levels. For case (b), phase space points from this trajectory at times between $t=3$ ps and $t=10$ ps (not used in the training step), the neural network was able to predict kinetic mode energies even in better agreement with the trajectory calculated values (around 5% error).

The results derived from Fig. 2 demonstrates that the neural network is able to make qualitative predictions of kinetic mode energies from Cartesian coordinates and momenta for arbitrary trajectories on a H_2O_2 potential energy surface. The predicted energies are within a reasonable range of error (1-12%), especially when taking into account that the best estimate for mode energies (the algebraic calculation) is also approximate, and that the accuracies of molecular potential energy surfaces can not be expected to be better than a few percent. For graphical purposes as depicting energy transfer pathways, these mode energies are accurate enough.

The advantage of the neural network approach to study (kinetic, potential or

total) internal mode energies is that, once the network has been properly trained, it can be used to analyze mode energies for virtually any trajectory from stored Cartesian coordinates and momenta. The training step may be tedious and time consuming, but once accomplished, the computer time for the neural network estimation of mode energies for 2000 phase space points is only a few seconds. In addition, the trained network can generalize the knowledge to other systems, as it will be discussed below. These advantages have far reaching implications and could mean substantial savings in future molecular dynamics applications.

Since the relationship between phase space points and mode energies is basically a coordinate transformation, the neural network should be able to generalize that knowledge for any given molecular system. To test the applicability of the neural network/molecular dynamics method to other molecules we have carried out kinetic mode energy calculations for a series of overtone excited tetratomic molecules: H_2X_2 , $X=C, N, O, Si, S, Se$. In a first approximation, the same potential energy surface was used, and trajectories from similar initial conditions were calculated. Since the heavy atom masses are different, vibrational frequencies and kinetic couplings of these systems are also different, thus affecting their intramolecular dynamics.

A neural network of the same architecture as described before was trained, in this case, to learn the kinetic mode energy dependence on the phase space points as a function of the atomic masses. Once the neural network has been trained to relate the mode energies to phase space points along trajectories and the atomic masses (the masses are used to distinguish between different molecular systems), it should in principle be able to make predictions for a large range of tetratomic system. Results obtained have average relative errors similar to that discussed for hydrogen peroxide. Not only for the molecules used for training, but for others of masses in between, and more interestingly, even for molecules with masses outside the training range. This suggests the ability of the neural network to generalize the results to unknown molecular systems, indicating that it should be applicable for the trained application, independently of the chemical system and without the need for any network architecture changes or further training.

Very good results have also been obtained for the study of energy flow from an overtone excited CH stretching mode in a polyethylene molecule by employing the neural network/molecular dynamics techniques (Sumpter, 1992). In this case, the inputs to the neural network were the level of the initial CH stretch excitation, temperature of the system, time and desired mode (CH-stretch for example); the output is the energy in the desired mode. Using this approach, mode energy predictions could be made at numerous times, temperatures, pressures, system sizes, and excitation levels without the need to carry out any additional molecular dynamics calculations or to perform additional training of the neural network.

SUMMARY AND CONCLUDING REMARKS

In summary, we have illustrated how a trained neural network is able to carry out qualitative mode energy calculations for a variety of molecular systems. A useful extension of this method is to use the network to give the kinetic mode energies for more complex systems such as macromolecules or proteins. Innumerable neural network applications such as this can be thought of in the dynamics study of molecular systems. For example, there is an interest in the

possibility of predicting the time dependent energy flow within a molecular system. The neural network/molecular dynamics techniques was shown to help this problem in the following way: a) The method described above could be used to analyze mode energies for a number of trajectories, which could then be processed in ensembles to give the essential energy flow components; b) Once the energy flow behavior is characterized, that information could be used to train a new neural network to "learn" the mode energies as a function of time, that is the overall dynamics of the multidimensional phase space. This information can be extracted from a reduced number of trajectory calculations, and then generalized for any given set of initial conditions, once the neural network is properly trained. For macromolecules this has proven to be extremely useful since the dimensionality of the phase space is very large and trajectory calculations are very sparse due to computer time restrictions.

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