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The Construction of Semi-diabatic Potential Energy Surfaces of Excited States for Use in Excited State AIMD Studies by the Equation-of-Motion Coupled-Cluster Method

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The semi-diabatic potential energy surfaces (PESs) of the excited states of polyatomic molecules can be constructed for use in *ab initio* molecular dynamics (AIMD) studies by relying on the continuity of the electronic energy, oscillator strength, and spherical extent of an excited state along with first derivatives of these quantities as computed by using the equation-of-motion coupled-cluster (EOM-CC) method. The semi-diabatic PESs of both the $\pi \to \pi^*$ valence excited state and the 3s-type Rydberg state of ethylene are presented and discussed in this paper, in conjunction with some of the AIMD results we obtained for these states.

Key Words : Semi-diabatic PES, AIMD, Equation-of-motion coupled-culster, Excited state

Introduction

The development of an *ab initio* molecular dynamics (AIMD) method for the study of dynamical phenomena involving excited electronic states of polyatomic molecules is one of the most important recent advances in theoretical and computational chemistry research. When excited electronic states are involved, avoided and true crossings of electronic states are usually encountered. This means that in principle it is necessary to also confront the multi-electronic state problem, that is to say the breakdown of the Born-Oppenheimer approximation. In this case, one can choose to define the electronic states in either adiabatic or diabatic representations. Since the potential energy curves are often smoother in the diabatic representation, diabatic PESs can make the study of multi-electronic state molecular dynamics considerably simpler than is the case for the adiabatic representation. However, there is no unique method of diabatization of the PESs of polyatomic molecules,[1] and diabatization schemes usually require global information about the PESs. This makes the adiabatic representation indispensable for practical AIMD studies, where only local information about the PESs is available at any given point in time. Solution of the dynamical problem including all of the coupled electronic states in the adiabatic representation also requires the computation of the nonadiabatic coupling matrix elements (NACME).[2] These are not always available, in which case one would still like to be able to follow the dynamics. An approximate way to accomplish this is by following an individual adiabatic excited state surface. This becomes ambiguous when the energy gap between states vanishes, but a useful first approximation in these cases is to follow an adiabatic state according to auxiliary conditions which lead to diabatic propagation. In this paper, we call the resulting PESs semi-diabatic. Strictly speaking, these are adiabats because they diagonalize the electronic Hamiltonian.

However, we will choose the adiabat which is being followed according to continuity criteria applied to both the energy and properties computed from the electronic wavefunction.

The reliability of an AIMD study depends on the accuracy of the PES it uses. Among the several *ab initio* methods available for the calculation of electronic structure, the use of the coupled-cluster and the equation-of-motion coupled-cluster (CC/EOM-CC) theories for the ground and excited electronic states respectively is now established as one of the best single-reference theories.[3,4] The analytic method of evaluating the energy gradient of the ground and excited electronic states by the CC/EOM-CC theory has been implemented[5] in computer programs like Aces-2.[6] The availability of analytic energy gradient is crucial to the efficient AIMD study of polyatomic molecules.

Several kinds of semi-diabatic PESs have been suggested and used in molecular dynamics studies. These PESs were constructed based on the continuity of some of the properties of electronic states, such as the dipole moment and polarizability.[7] Another way of constructing a semi-diabatic PES, based on the continuity of the oscillator strength and of the spherical extent ($<r^2>$) of an excited state, is suggested in this work. This approach is applied here to the AIMD simulation of the nuclear motions of ethylene in an excited state reached by photoabsorption.

Methods

The initial values of the positions and momenta of all the atoms of ethylene were sampled from a Wigner distribution,[8] corresponding to the ground state vibrational wavefunction in the harmonic approximation. The dynamic changes in the positions and momenta of the atoms of ethylene, referred to here as a trajectory, were then computed by solving the classical equations of motion with the velocity Verlet method.[9] The time step of the classical molecular dynamics

(MD) calculation was set at 10 atomic time units, about 0.242 fs. At each time step of the classical MD calculation, the ground and excited electronic states were computed on the fly by using the coupled-cluster singles and doubles (CCSD) and the equation-of-motion coupled-cluster singles and doubles (EOM-CCSD) methods.[3,4] The roots of the similarity transformed Hamiltonian matrix correspond to the excitation energies of the excited states.[4] The Davidson procedure[10] for finding the roots was slightly modified in our approach by the use of the eigenvector of the specific state from the previous MD step as the initial guess for the current MD step, and by the search for at least four additional nearest roots. The oscillator strength and the spherical extent ($<r^2>$) of the electronic wavefunction were calculated by using the L- and the R-vector of the similarity transformed Hamiltonian matrix, as described elsewhere.[4] Because the PES is not predefined in AIMD methods, we have to select an electronic state at each MD step and then extend the PES on the fly by using the *ab initio* results of the current MD step. The correct state is selected by comparing not only the electronic energy (i.e. the continuity of the PES, which is the basic requirement) but also the oscillator strength and the spherical extent at the current MD step with those of the previous MD step. We also insisted on the continuity of the first derivatives of these properties. Although the excited state obtained by using the eigenvector of the state from the previous MD step as the initial guess of the Davidson procedure usually corresponds to the same state, this is not always guaranteed. The roots of the excited states are also not always found in the correct order, especially when a two-electron excited state appears nearby. To make sure we found the correct state in the correct order in the examination of the possible nearby states, we insisted on finding four additional states, which meant that we examined a total of five excited states in the construction of a semi-diabatic PES of a particular excited state.

Results and Discussion

The semi-diabatic PESs of the $\pi \rightarrow \pi^*$ valence excited state (V-state) and the 3s-type Rydberg state (R_{3s}-state) of ethylene[11] were constructed and examined along about thirty classical trajectories for the initial 50 fs after photoabsorption. When a classical trajectory proceeds far from any intersection involving the target electronic state, no special attention is required and the construction of a PES is so simple it need not be discussed further here. When a classical trajectory crosses or approaches a conical intersection involving the target electronic state, the semi-diabatic PES was constructed as described above. Only some of the potential energy curves we obtained in our thirty AIMD cases are presented and discussed below. The PES of the ground state is not shown in the following figures because it is typically located about 0.25 Hartrees (a.u.) below the energies shown in the figures. When the 6-31G electronic basis set was used for the PESs as in Figures 1-3, the difference between the spherical extents of the two states
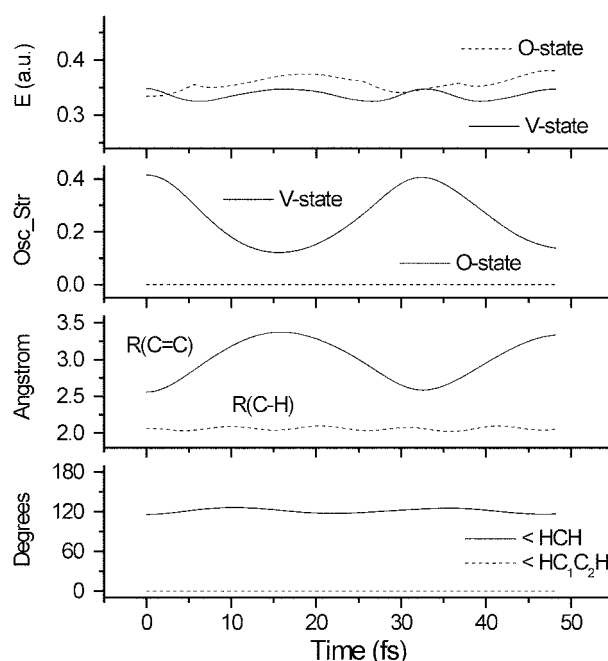
Figure 1. The changes in potential energy, oscillator strength, bond lengths, and angles of ethylene obtained by a single-trajectory AIMD simulation on the PES of the V-state along the centroid trajectory. The V-state and the O-state represent the valence $\pi \rightarrow \pi^*$ excited state and the nearest other state respectively, as computed by the EOM-CCSD/6-31G method.

was found to be too small to be useful in the construction of the semi-diabatic PES, and so the changes in spherical extent are not included in Figures 1-3.

Figure 1 shows the AIMD results for the centroid trajectory, which starts from the geometry of the equilibrium molecular structure of the ground state with no initial velocity. The x-axis represents the elapsed time (in fs) after the start of the AIMD simulation. In this trajectory the molecular structure retains a planar geometry, and the dihedral angle $\angle HC_1C_2H$ does not deviate from zero, as shown in the fourth panel. The solid line in the first panel is the PES of the V-state, while the dotted line represents that of the nearest electronic state, which we will call the O-state. The O-state may have different character at different points in the trajectory, as discussed at various points later in the text. The potential energy E (in a.u.) in the first panel is defined with respect to the energy of the ground state at its equilibrium geometry. The discontinuities of the first derivative of the O-state energy at 6 and 37 fs stem from the fact that it changes electronic character at these points, i.e. it is involved in a true or avoided crossing with another electronic state. The solid and dotted lines in the second panel represent the changes in the oscillator strengths of the V-state and the O-state respectively. The changes in bond lengths and angles are shown in the third and fourth panels respectively. The electronic energies of the V-state and the O-state become equal at around 31-34 fs, which implies that the trajectory crosses a conical intersection involving these states. Though for such a crossing the continuity of the PES or of the first
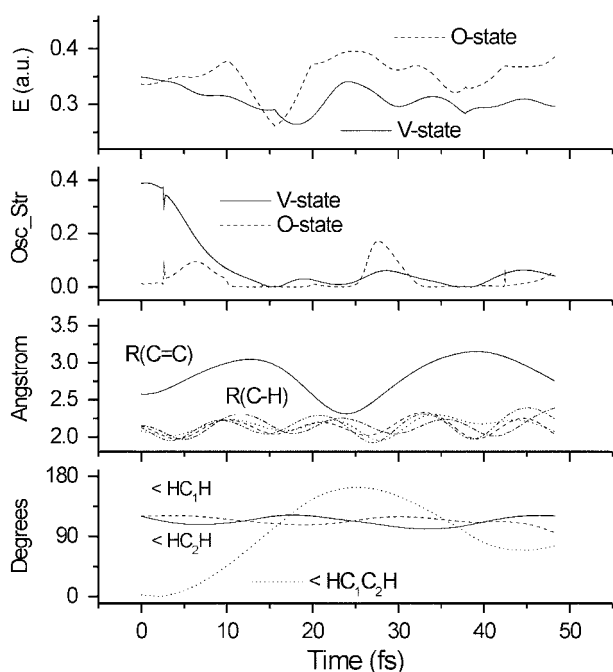
Figure 2. AIMD results with the EOM-CCSD/6-31G basis for a trajectory showing a large torsional motion.

Figure 3. AIMD results with the EOM-CCSD/6-31G basis for a trajectory with several encounters between two states.

derivative of PES are not sufficient conditions for the unambiguous construction of the PES, semi-diabatic PESs of the two states are easily constructed because of the clearly distinguishable oscillator strengths of the two states, as shown in the second panel.

When the initial geometry of a classical trajectory is one that is slightly distorted from the equilibrium structure of the ground state, as shown in the third and fourth panels of Fig. 2, the two states approach each other at 14 fs, earlier than in the case of the centroid trajectory shown in Figure 1. The oscillator strengths are very similar, and are of little help in the construction of the PESs. However, the continuity of the first derivative of the electronic energy is sufficient for the construction of the PES in this case. In this instance, the shape of the PES of the O-state resembles that of the two-electron excited state, the Z-state, as has been described in several earlier works.[12] The dihedral angle $\angle HC_1C_2H$ shown in the fourth panel indicates that the ethylene molecule is twisted about the C=C double bond. The detailed analysis of the structure also reveals that half of the ethylene moiety, the -CH_2 unit, has a pyramidal shape at this point. All these aspects are in accordance with the Z-state described previously. It has to be mentioned here that not only the PESs of both the V-state and the O-state but also the PES of the ground state (not shown here) have small cusp shapes at 16 and 38 fs. These are artifacts due to the limitations of the single reference CCSD method, which have been discussed elsewhere.[13] These cusps indicate the divergence of the first derivatives of the PESs. Because we use fixed time steps, we effectively average over these discontinuities which could nevertheless cause difficulties even when using analytic gradients if the trajectory came sufficiently close to the
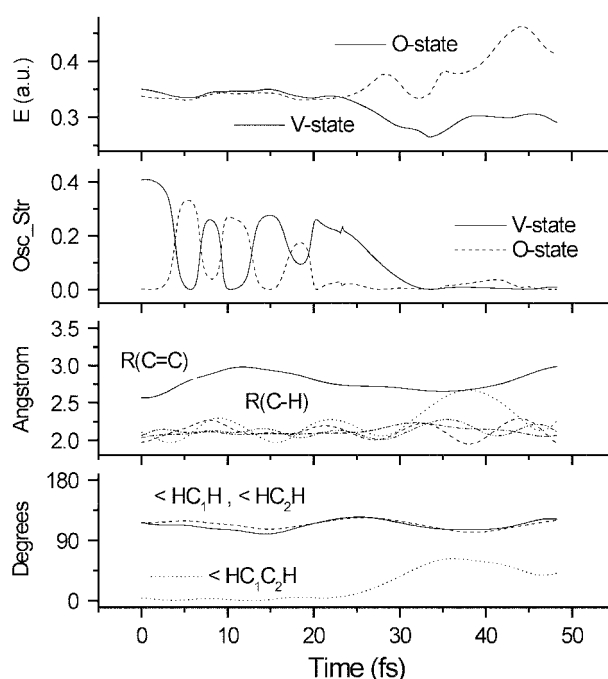
problematic region. Though these artificial cusps can be removed by some arbitrary adjustments, we did not make any such adjustment here because the additional potential energies produced by the artificial cusps are two orders of magnitude smaller than the kinetic energies of the atoms at these points. In spite of the appearance of these artificial cusps, the present results show that the single reference EOM-CCSD method used in this work is able to describe such demanding situations successfully.

The most difficult situation for constructing the semi-diabatic PES that we observed in our test work is shown in Figure 3. The two PESs in the first panel show that there are about four possible points at which the nonadiabatic coupling vector is very large. In this case, insisting on the continuity of the first derivative of the oscillator strength was necessary for the construction of the PESs. Though the situation here looks quite troublesome, the probability of this trajectory as computed by the Wigner method[8] is two orders of magnitude smaller than those of other trajectories such as those in Figures 1 and 2. Most of the other thirty trajectories are more similar to those presented in Figures 1 and 2. As a result, the contribution of the trajectory shown in Figure 3 to the overall AIMD results is expected to be marginal. It is interesting to note that one of the C-H bonds is significantly extended at 37 fs. The dihedral angle $\angle H-C_1-C_2-H$ is about 75 degrees. This could be a movement toward H-atom migration[14] from one C-atom to another C-atom on the excited PES, but the consequences of this trajectory for the overall dynamics of ethylene are not explored here.

Although the results presented here using the 6-31G electronic basis set demonstrate our procedure for constructing semi-diabatic PESs, this basis is too small to properly
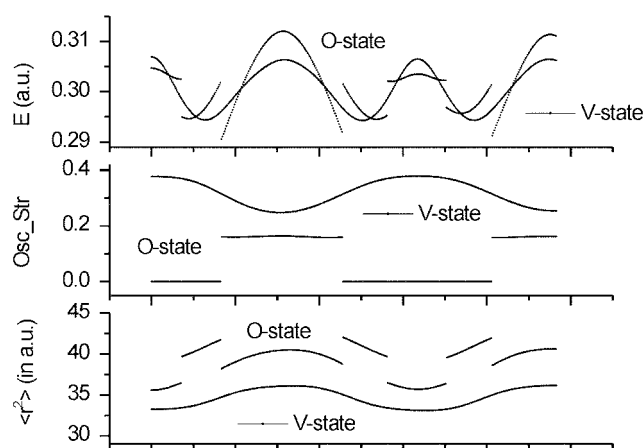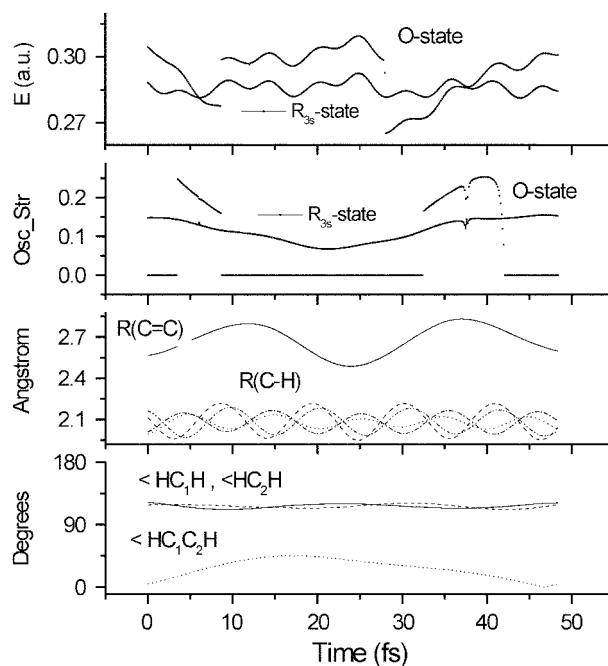
Figure 4. AIMD results with the EOM-CCSD/6-31+G basis for the centroid trajectory. The third panel shows the changes in the spherical extents ($<r^2>$) of the excited states. The changes in bond lengths and angles are not shown here because the molecule remains in a planar structure, as shown in the fourth panel of Fig. 1.

Figure 5. AIMD results with the EOM-CCSD/6-31+G basis for a trajectory on the PES of the 3s type Rydberg state, R_{3s}-state. The nearest state, the O-state, is either the $\pi \rightarrow \pi^*$ excited V-state or the $3p_z/3p_y$ Rydberg state.

balance the effects of dynamic correlation and Rydberg character in the electronic wavefunctions. The excitation energy of the V-state was calculated to be about 1.5 eV larger than its experimental value.[11] Further, the ordering of the four lowest excited states is not correctly described by calculations using the 6-31G basis. According to our study with several different basis-set sizes, the 6-31+G basis turns out to be the smallest electronic basis set that can describe the V-state and the other three nearby Rydberg states quantitatively and qualitatively.[15] The semi-diabatic PESs of the $\pi \rightarrow \pi^*$ excited state (V-state) and the 3s type Rydberg state (R_{3s}-state) were constructed with the 6-31+G basis, as shown in Figures 4 and 5.

The PES of the V-state was calculated by the EOM-CCSD/6-31+G method along the centroid trajectory and is shown in the first panel of Figure 4. It shows that the V-state crosses the 3pz-, 3py-, and 3s-type Rydberg states at 3, 5, and 12 fs respectively, and crosses those states again in reverse order at 21, 27, and 29 fs. All these Rydberg states are designated by the O-state here. The semi-diabatic PES of the V-state was easily constructed by using the changes in the oscillator strength and the spherical extent shown in the second and third panels respectively. Due to the diffuse s- and p-type basis functions included in the 6-31+G basis set, the spherical extents of the Rydberg states are distinctly larger than that of the V-state, and this difference can be an additional help in the construction of the semi-diabatic PES of a state. The semi-diabatic PES of the V-state was calculated with the EOM-CCSD/6-31+G method along a trajectory starting from a slightly distorted structure as in the cases of Figures 2 and 3, and is virtually identical to that calculated with the EOM-CCSD/6-31+G method shown in Figures 2 and 3. The use of diffuse functions in the 6-31+G basis set means that spherical extent may also be an additional property that is useful in the construction of semi-diabatic PESs.

When the electronic states of ethylene are calculated by

the EOM-CCSD/6-31+G method, the 3s-type Rydberg state (R_{3s}-state) is found to be the lowest singlet excited state. Other singlet excited states are located about 0.5 eV above the R_{3s}-state for most domains of the trajectories, so the construction of its PES is a simple matter. However, the PES in Figure 5 has an interesting feature: the PES of the R_{3s}-state crosses the PES of another state at 6 and 37 fs. These crossings imply the existence of a conical intersection responsible for radiationless quenching to the ground state. Though the conical intersection between the V-state and the ground state is well known,[14] the conical intersection shown in Figure 5 has not previously been studied. The changes in the C-H bond lengths in the third panel suggest that the main characteristics of this trajectory correspond to an asymmetric stretch mode, *i.e.* the v_8 or the v_{10} mode.[11] Further exploration of this new conical intersection is not carried out here.

Conclusions

A method for constructing the semi-diabatic PES of a specific excited electronic state, based on the continuity of the electronic energy, the oscillator strength, and the spherical extent of the state, as well as the first derivatives of these quantities, was suggested and tested by conducting actual AIMD studies. It was shown that insisting on the continuity of the first derivatives of the electronic energy and of the oscillator strength is sufficient for the construction of the semi-diabatic PES. When Rydberg states are involved and the electronic basis set includes the diffuse basis functions necessary for the description of Rydberg states, spherical extent of the electronic wavefunction can offer an

additional guide to the construction of the PES.

Our results demonstrate the potential of the use of the equation-of-motion coupled-cluster singles and doubles (EOM-CCSD) method for the handling of excited states in the AIMD study of phenomena involving excited electronic states. The PESs discussed in this work also reveal several interesting features of the overall PES for the photo-absorption dynamics of ethylene. A new AIMD method is under development that combines the EOM-CCSD method for calculating electronic structure with the full-multiple-spawning (FMS) method[16] for calculating the nuclear wavefunction. Results of AIMD (EOM-CCSD/FMS) studies that use semi-diabatic PESs as constructed in this work will be presented elsewhere.[15]

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