CHAPTER V
A TIME-DEPENDENT COUPLED CLUSTER METHOD
STUDY OF NONADIABATIC DYNAMICS
5.1. INTRODUCTION

In the previous chapter we have studied the intra-molecular vibrational energy transfer in some model systems using **MRTDCCM formalism**. In this chapter we study the applicability of **TDCCM** to study the electronic-vibrational energy transfer in systems containing nonadiabatically coupled potential energy surfaces. The nonadiabatic dynamics on coupled electronic surfaces have attracted much interest recently. "' This is due to the fact that these nonadiabatic effects are associated with many chemically interesting phenomena such as the nonradiative decay of excited electronic states, **chemiluminescence** in atom - atom and atom - molecule inelastic collision processes etc. The nonadiabatic effects arise when the adiabatic approximation is violated.

In the adiabatic or Born-Oppenheimer approximation the nuclei are considered to be stationary when solving the electronic problem. The electronic wave functions and state energies depend parametrically on the nuclear coordinates. The dynamics of the nuclei are generated by a **matrix hamiltonian** in which the electronic state energies appear in the diagonal elements and act as the potential energy for the nuclei while the **matrix** elements of the nuclear kinetic energy operator between different electronic states provide the off diagonal couplings. It is commonly assumed that dynamics of nuclei are confined to a single electronic potential energy surface. This is the crux of the adiabatic approximation. This adiabatic approximation is valid
only when the electronic states are well separated in energy compared to the spacings associated with nuclear energy levels. When the potential energy surfaces of different electronic states are close in energy the residual coupling of the nuclear kinetic energy operator between such states becomes significant. The effects associated with this situation are called as nonadiabatic effects. It is convenient to treat the nonadiabatic effects in diabatic basis.\textsuperscript{1,22} In this basis a complete set of electronic wave functions are defined such that the nuclear kinetic energy operator is diagonal in them, however, the electronic hamiltonian is not diagonal in this basis, and thus provides both diagonal and off-diagonal coupling matrix elements to the nuclear matrix hamiltonian. In this basis the matrix hamiltonian for the nuclear motion is written as

\[ H = T_N^{1/2} + \mathcal{W}(Q), \quad (5.1.1) \]

where \( T_N^{1/2} \) is the diagonal kinetic energy operator and \( \mathcal{W}(Q) \) matrix elements are defined as

\[ W_{nm}(Q) = \int dr \phi^*_n(r,Q) H \phi_m(r,Q). \quad (5.1.2) \]

Here \( \phi_n(r,Q) \) are diabatic wave functions.

The hamiltonian \( H \) in eq.(5.1.1) is an infinite dimensional matrix operator. In most situations only a few electronic states interact strongly. Consequently only such states are included and a finite dimensional matrix operator is used to approximate \( H \). For studies of spectroscopic interest,
further approximations are made. For example expanding $W(Q)$ as a Taylor series around the ground surface equilibrium geometry and truncating after linear term in $Q$, results in the linear coupling model. In this model the terms in the Hamiltonian matrix elements are

$$H_{nn} = T_n + E_n + \sum_k k^{(n)}_k Q_k + \frac{1}{2} \sum_{RS} V_{RS} Q_R Q_S,$$

$$H_{nm} = \alpha^{(n,m)}_0 \sum_k \alpha^{(n,m)}_k Q_k,$$

Here the energies $E$ are constants and are given by $W(Q)$. $k^{(n)}_k$ are intrastate electronic-vibrational energy coupling constants and $\alpha^{(n,m)}_k$ are interstate coupling constants. In general these coupling constants are determined by ab initio methods. Generally totally symmetric normal modes give rise to nonzero intrastate coupling constants and the nontotally symmetric modes to nonzero interstate coupling constants. The totally symmetric modes modulate the energy separation between the electronic states and are termed as tuning modes and the nontotally symmetric modes are termed as coupling modes.

The use of diabatic basis is particularly advantageous when the potential energy surfaces of the concerned electronic states become degenerate in the $n$-dimensional normal coordinate space forming a conical intersection.$^1,23$ The main reason for this is the complicated behaviour of the matrix elements of nonadiabatic coupling operators in the vicinity of avoided crossings. These elements are principally singular at the
point of intersection and show rapid oscillations near it and thus are difficult to handle numerically.\textsuperscript{22,23} On the other hand the coupling matrix elements are well behaved in the diabatic basis and can often be modeled in terms of simple functions of nuclear coordinates. The linear coupling model defined above is an example of such simple parametrization and is quite successful in providing interpretation for several spectroscopic studies.

The standard theoretical method to obtain the nonadiabatic dynamics is the time-independent approach based on the Ritz-variational principle. In this method one constructs the Hamiltonian matrix in a basis formed by the product functions of electronic and vibrational states of the uncoupled system. This Hamiltonian matrix is then diagonalised to give the eigen values and eigenvectors. The required physical quantities are then determined from these. The computational requirement for the diagonalization procedure goes as $N$, where $N$ is the dimension of the Hamiltonian matrix. Moreover the number of basis functions needed to treat a coupled $d$ degree of freedom problem is proportional to $M$, where $M$ is the number of basis functions for a typical one degree of freedom problem. A more efficient procedure is to directly integrate the TDSE in the zeroth order basis without prediagonalising the Hamiltonian. Since this involves multiplication of the wave function with the Hamiltonian matrix at each step, the computational effort scale proportional to $N^2$. In addition the Hamiltonian matrix of the nonadiabatic problems are often quite sparse. Utilizing this the matrix multiplication can be reduced to $O(N)$ process. Several authors have reported such
dynamical calculations.\textsuperscript{16,7} Though these methods are dependable
the basic problem is that the size of the Hilbert space scales
exponentially as $M^d$ thus making it difficult to study systems with
more than four degrees of freedom. Alternative methods
developed for the problem are time-dependent perturbative
approach,\textsuperscript{8,9} semiclassical methods, the time-dependent self
consistent field (TDSCF) method\textsuperscript{13} and the path integral
methods\textsuperscript{18,19} etc. The time-dependent perturbation theory
separates the electronic hamiltonian into an uncoupled hamiltonian
$H$ and the perturbation $V$ and develops power series expansion for
the evolution operator in terms of the nonadiabatic coupling
constant. Coalson and Kinsey\textsuperscript{8} have applied this method to a two
state one vibrational mode model system and concluded that it
breaks down in the strong coupling limit and for the long time
dynamics.

Meyer and Miller\textsuperscript{10} have developed a classical analog for
electronic degrees of freedom. In this method one constructs the
electronic hamiltonian matrix formed by the electronic states
whose elements depend on the nuclear coordinates. The equations
for the electronic motion are obtained by solving the TDSE where
the nuclear coordinates are taken to be time-dependent and the
nuclear motion is treated classically. This method is
computationally simple to implement. Meyer\textsuperscript{10} used it to calculate
the nonradiative decay rates in $\text{C}_2\text{H}_4$ cation. Zwanziger et al.\textsuperscript{11}
performed a semiclassical quantization of classical analog model.
Application of this method to the Jahn-Teller problem in the
region of linear coupling provided results in good agreement with
exact quantum mechanical solution. Recently Stock and Miller\textsuperscript{12} developed a classical model based on the Meyer and Miller\textsuperscript{10} framework of the classical electron analog model for the determination of nonadiabatic excited state dynamics. The method is tested for the four-mode model of the $S_2$-$S_1$ intersection in pyrazine and on 3 state, 5-mode and 5-state, 16-mode models of benzene cation. This method reproduces the qualitative features of time and frequency resolved absorption spectra as in the exact quantum mechanical calculation.

The TDSCF method\textsuperscript{13} has been used by few authors to study the nonadiabatic dynamics. The computational effort in this approach scales linearly with the number of vibrational modes. As the TDSCF method does not account for the correlations between the modes it is not dependable in the long time limit and is reliable only for the short time dynamics where the correlation effects are negligible.

Another approach which is used in determining the nonadiabatic dynamics is the path-integral formulation. Coalson used the path-integral framework for spin-boson model problem and found that the spectroscopic observations can be obtained even in the strong coupling regimes using this formulation. A rigorous path-integral approach for determining the nonadiabatic dynamics of the linear coupling model was recently developed by Domcke and co workers. The time-dependent correlation functions are expressed as sums over all possible paths and for each electronic path the multi-mode vibrational propagator factorizes into a product of single-mode propagators. The summation over paths is
replaced by \textit{summation} over classes as a practical \textit{approximation}. The propagator averages are calculated by recursive \textit{scheme}. The calculations they have presented are for four-mode and twenty \textbf{four-mode} pyrazine models. In this method the numerical effort rises only moderately with the number of modes and so is useful for studying the many-mode systems.

These studies provided some qualitative aspects of the results of the nonadiabatic effects in the systems having conically intersecting potential energy surfaces. In these systems the electronic dynamics in a femtosecond time scale are driven by the velocity of the coherent motion in the tuning modes. This dependence induces a slower vibrational dephasing process which destroys the coherence of vibrational motion. When this dephasing is completed the electronic populations are trapped on the lower surface and the electronic decay becomes irreversible.

Recently Sastry et al.\textsuperscript{20} studied the dynamics of the linear coupling model using time-dependent coupled cluster method. In this study, a mixed representation was used in which all the normal modes were represented by boson ladder operators, while the electronic degree of freedom subsystem was represented in a basis set in a manner very similar to the mixed representation we used for the \textit{IVR} of system-I in Chapter IV. All states in which the vibrational mode states were \textit{v}=0 states were included in the model space. The method is quite good for short time dynamics and yields qualitatively correct spectra even when the cluster operator is restricted to have no more than one boson creation operator. At longer times however, the working equations became
stiff and can not be integrated.

Since the MRTDCCM approach in the boson operator representation is not able to provide long time dynamics, we wished to see if TDCCM in a basis set representation is able to provide a better representation. It turn out that TDCCM using stationary basis functions also suffers from the same problems that MRTDCCM approach of Sastry. However doing TDCCM in dynamical basis generated by TDSCF procedure eliminates the stiffness of the equations and we could carry out the calculation for long periods. To test the potentiality of the method we have done some model calculations. We present the working equations in sec.5.2 and the model calculations in sec.5.3. In sec.5.4 we have drawn some conclusions on the validity of the approach for the present problem.

5.2. THEORETICAL FRAMEWORK

5.2.1 Model hamiltonian

We model our systems such that only two electronic states belonging to different irreducible representations and n-vibrational modes are relevant for the dynamics. We impose following simplifications on our model. The model hamiltonian is constructed in the diabatic electronic basis. The harmonic approximation is invoked for the diabatic potential energy surfaces and the vibrational frequencies in all the unperturbed surfaces are assumed to be equal. The interstate and the intrastate coupling constants are approximated by linear terms in
the normal coordinates. After these simplifications the model
hamiltonian for the two state n-mode system can be written as

$$H = \sum |e_i\rangle (e_i + H_1) \langle e_i | + V_c \quad (5.2.1a)$$

$$H_1 = \sum_n h_{1n} = \sum_n (\omega_n (p_n^2 + q_n^2)/2 + k_{ln} q_n) \quad (5.2.1b)$$

$$V_c = |e_1\rangle \sum \langle \lambda_c q_c | e_2 \rangle + h.c., \quad (5.2.1c)$$

where \(i\) is the electronic state and \(n\) represents the vibrational
mode. Here \(p_n, q_n\) are the momentum and position operators of the
nth vibrational mode, \(\omega_n\) are the associated frequencies, \(k_{ln}\) and
\(\lambda\) are the intrastate and interstate coupling constants
respectively. The modes which contribute to \(A\) are called as
coupling modes and the modes which contribute to \(k\) are tuning
modes.

In this nonadiabatic problem the coupling mode and the
electronic degrees of freedom interact strongly so we treat them
as a single subsystem. The resulting hamiltonian for the system
can then be written as

$$H = H^{ec} + H^t, \quad (5.2.2a)$$

$$H^{ec} = \sum_i |e_i\rangle \epsilon_i \langle e_i | + |e_1\rangle \lambda_c q_c \langle e_2 |$$

$$+ \omega_c (p_c^2 + q_c^2)/2 + h.c., \quad (5.2.2b)$$
Here $H_{ec}$ is the hamiltonian corresponding to coupling mode electronic degree subsystem and $H$ is the hamiltonian for the tuning modes. We now define the basis functions required. For the tuning modes we utilize the harmonic oscillator eigenfunctions centered at the origin and their width parameters were chosen to match the frequencies of the ground surface. For the coupling mode electronic degrees subsystem the basis functions are $\{|e_i \phi^c_n; i=1,2; 0 \leq n \leq \alpha \}$. As long as the two electronic states concerned belong to two different irreducible representations, this space can be separated into different symmetry spaces. Depending on the initial conditions (i.e. the electronic surface on which the wave packet starts at $t=0$) the dynamics would be confined to one or the other subspace. Thus it is sufficient to consider any one of the two subspaces. Note that the harmonic oscillator eigenfunctions with even quantum number are always totally symmetric, while those of the odd quantum number belong to the same irreducible representation as the normal coordinate concerned. Since the coupling coordinate belongs to the direct product symmetry of the two electronic states, the two subspaces have exactly the same number of functions as the harmonic oscillator Hilbert space and thus are labeled by harmonic oscillator quantum numbers alone. The initial conditions then uniquely determine the electronic state associated with each vibrational state. We have used these subspaces in our computations. The diagrammatic notations for the hamiltonian

$$\begin{align*}
H^t &= \sum_i |e_i \rangle \langle k_{it} q_t | e_i \rangle + \sum_t \omega_t (p_t^2 + q_t^2)/2.
\end{align*}$$

(5.2.2c)
terms in this basis are presented in Fig.5.1a.

5.2.2. TDCCM ansatz:

We now turn to the parametrization of the time-dependent wave function in the TDCCM framework. The wave function $\psi$ is written as

$$\psi = U \phi_0^*.$$  \hspace{1cm} (5.2.3)

Since we are interested primarily in the spectroscopic properties of the upper surface of the two interacting electronic states, the initial state is the vibration less state of the electronic ground state transported vertically on to the upper surface. Thus we take the CCM reference wave function $\phi$ to be

$$\phi_0 = \phi^{(0)}_{ec}(r_e,q_c) \prod_t \phi^{(0)}_t(q_t).$$  \hspace{1cm} (5.2.4)

Based on the operator manifold analysis of Chapter III the operator sets for the model problem are identified. Since the model space contains zero valence particles, only $C$ and $B$ type operators sets are necessary for obtaining the dynamics in this model.

$C_0 = \{ 1 \}$

$B_0 = \{ a^+_m a^+_n a^+_i a^+_j a^+_k \ldots; i,j \in ec \text{ or } t \}.$

Here $m$ and $n$ are the basis function indices.
Fig. 5.1  (a) The diagrammatic representation of Hamiltonian terms. In the diagrams from iv to vii the top line is always ec subsystem mode and it is diagonal. (b) The diagrammatic notations for the cluster operators $S^+_1$, $S^-_2$. 
The model space evolution operator can then be written as

\[ U = U_0. \]  \hspace{1cm} (5.2.5a)

TDCCM\textsuperscript{24} posits an exponential form to the evolution operator. \( U \) can then be written as

\[ U_0 = \exp(S^0); \quad S^0 \in C_0 \cup B_0. \]  \hspace{1cm} (5.2.5b)

The cluster operator \( S^0 \) is expanded as

\[ S^0 = S^0_0 + S^0_1 + S^0_2 + \ldots \]  \hspace{1cm} (5.2.5c)

\[ S^0_0 = s^0_{0,1}, \]  \hspace{1cm} (5.2.5d)

\[ S^0_1 = \sum_{i,m} s^1_{i,m} a^+_{i,m} a^0_{0,m}, \]  \hspace{1cm} (5.2.5e)

\[ S^0_2 = \sum_{i,j,m,n} s^1_{i,j,m,n} a^+_{i,m} a^+_{j,n} a^0_{0,m} a^0_{0,n}, \]  \hspace{1cm} (5.2.5e)

where \( i,j,m,n \) are defined as earlier and the subscript 0 indicates the hole state. Some of these are depicted in the Fig.5.1b. The working equations are then derived from the equations

\[ P(U^{-1}HU - iU^{-1}\dot{U})P = 0 \]  \hspace{1cm} (5.2.6a)

for \( S^0_0 \) and

\[ Q(U^{-1}HU - iU^{-1}\dot{U})Q = 0 \]  \hspace{1cm} (5.2.6b)
for S°. Derivation of the working equations is once again carried out in the diagrammatic notation and the resulting equations for is°, iς° and iς° are presented in Fig.5.2a, Fig.5.2b and Fig.5.2c respectively. These differential equations are integrated using fourth order Runge-Kutta scheme. The equations became stiff in a very short period of time and we could not get enough information to obtain the sufficiently resolved spectra. In view of the failure of this single reference TDCCM the other alternative that strikes is the MRTDCCM formalism.

As discussed in the previous chapter the MRTDCCM\textsuperscript{25,26} generates all the higher body excitations from the multi-reference initial state. From the work of Madhavi Sastry\textsuperscript{20} on the same nonadiabatic model problem it was known that the MRTDCCM equations are more flexible than the single reference TDCCM equations but the long time dynamics (beyond 50 fs) can not be obtained even in this formalism.

In these two formalisms the dynamics are obtained by following the evolution of initial state within the TDCCM or MRTDCCM framework but using static basis functions. One problem in using the static basis functions is that the wave packet leaves the model space in exceedingly short time and the nonadiabatic coupling terms are quite large. As a consequence the intruder states with complex eigenvalues become important even in short time dynamics. This problem can be circumvented by using the dynamical basis sets in terms of which the reference state used in TDCCM has significant overlap with the exact wave function over long periods. Over the last few years several authors have
Fig. 5.2

Continued
Fig. 5.2  The diagrammatic representation of the equations for (a) $i\tilde{s}^0$, (b) $i\tilde{s}^0$ and (c) $i\tilde{s}^0$. 


discussed the advantages of these dynamical basis functions. We specifically use the basis functions generated by TDSCF approach for this system. The TDSCF calculations for this problem are already done in our group and from these calculations we knew that it performs quite well up to about 100 fs. With this background we have considered the TDSCF calculation to generate a dynamical basis to perform TDCCM calculation. In the following section we obtain the working equations in this formalism.

5.2.3. TDCCM in dynamical basis generated by TDSCF method:

We continue to consider the coupling mode and the electronic degree freedom as a single subsystem. The TDSCF function $\phi$ is written as

$$\phi^{(t)} = \prod_{t} \phi_{t}^{(t)}(q_{t})\phi_{\text{ec}}^{(t)}(r_{\text{e}}, q_{\text{c}}).$$

(5.2.7)

Here the functions $\phi_{t}$ and $\phi_{\text{ec}}$ are determined by TDSCF method. The working equations for this part are obtained by considering the trial wave function as in eq. (5.2.7) and by employing the Frenkel variational principle $\langle \delta \phi | H - i\partial/\partial t | \phi \rangle = 0$. The equations for $\phi$ and $\langle p \rangle$ are

$$i \dot{\phi}_{t} = h_{t}^{\text{SCF}} \phi_{t},$$

(5.2.8a)

$$i \dot{\phi}_{\text{ec}} = h_{\text{ec}}^{\text{SCF}} \phi_{\text{ec}},$$

(5.2.8b)

where
The initial conditions for eq.(5.2.9) are chosen such that all \( |\phi_i\rangle\) are the eigenfunctions of the decoupled oscillators at \( t=0 \). Consequently they are orthogonal at \( t=0 \) and continue to be orthogonal through out their evolution since \( h^{SCF} \) are hermitian operators.

We now invoke the TDCCM ansatz. The SCF solution for the vacuum state is taken to be the reference state for the CCM calculations. As a consequence, the operator space analysis of the previous section is valid here also. However, the single particle creation/annihilation operators are now explicitly time-dependent and obey

\[
\begin{align*}
\hat{a}_m^+ & = \hat{h}^{SCF} \hat{a}_m^+ \\
\hat{a}_m^i & = -\hat{h}^{SCF} \hat{a}_m^i
\end{align*}
\]  

(5.2.10a)

(5.2.10b)

This introduces an additional term in the working equations.
Fig. 5.3 The diagrammatic representation of the equations for (a) $i\hat{s}^0$ (b) $i\hat{s}^0$ in the DYTDCCM formalism. Note that the two body vertex is not necessarily diagonal in ec subsystem in the dynamical basis unlike in the stationary basis.
We approximate the one body cluster operator $S$ to zero because the TDSCF method effectively accounts for the one body part of the Hamiltonian. Now for the operators $S$ and $S^0$ we solve the eq. (5.2.6). The diagrammatic representation of the equations for $S^0$ and $S^0$ are presented in Fig. 5.3. We have calculated modulus of auto correlation function and the spectra of few model systems. The modulus of auto correlation function represents the probability amplitude that the system after time $t$ is still in the initial state. The spectrum is obtained by Fourier transforming the respective auto correlation functions.

The autocorrelation function is defined as

$$ C = <\phi_0|\phi(t)> = <\phi_0|\exp(S_0+S_2^0)|\phi_{\text{SCF}}>. \quad (5.2.9a) $$

In our computations we have approximated this to

$$ C \approx <\phi_0|\phi_{\text{SCF}}>|\exp(S_0^0). \quad (5.2.9b) $$

to avoid the construction of the full wave function $\exp(S)|\phi>$. The model applications and the results are presented in the next section.

5.3. MODEL APPLICATIONS AND RESULTS

Calculations were carried out on four model systems:

1. 3-mode ethylene cation,
2. $S_2$, surface of 3-mode model
pyrazine, (3) $S_2$ surface of 4-mode model pyrazine, (4) $S_z$ surface of 24-mode model pyrazine by TDCCM framework using the dynamical basis generated by TDSCF and compared with the TDSCF results. We refer our former approach as DYTDCCM from now onwards. The energies of the electronic states, the frequencies and the coupling constants of the vibrational modes we have taken from the literature and are collected in Tab. 5.1.

The parameters $k$ are the intrastate coupling constants and $\lambda$ is the interstate coupling constant and $\omega$ are the corresponding frequencies. $c$ are the energies of lower and upper electronic states.

The results of calculations on the 3-mode ethylene cation are presented in Figs. 5.4 and 5.5. In the TDSCF calculations 22 functions were used to represent the coupling mode and the tuning modes were propagated by GWP. As noted in ref. 17 the tuning modes experience harmonic potentials in the SCF approximation and so GWP is exact for these. For the coupled cluster calculations 5 of the lowest energy functions were used for each mode.

In Fig. 5.4 we have plotted the modulus of autocorrelation function (ACF) against time for the 3-mode ethylene cation calculated in the two formalisms DYTDCCM and TDSCF. For comparison the results of the exact calculations taken from ref. 2 are inserted. The initial very fast decay is reproduced by the two formalisms to a very good extent. The amplitude is very small through out its evolution which is generally associated with nonradiative decay process. [35] The ACF
by DYTDCM is generally **smaller** than by the TDSCF calculation.

Table 5.1 Parameters used in the model systems:

(All quantities are in eV.)

<table>
<thead>
<tr>
<th>el. or vib. mode</th>
<th>lower</th>
<th>upper</th>
<th>ω</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ethylene cation (ref.2)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>10.75</td>
<td>12.65</td>
<td></td>
</tr>
<tr>
<td>k₁</td>
<td>0.024</td>
<td>-0.362</td>
<td>0.360</td>
</tr>
<tr>
<td>k₂</td>
<td>-0.236</td>
<td>0.330</td>
<td>0.205</td>
</tr>
<tr>
<td>λₑ</td>
<td>0.402</td>
<td></td>
<td>0.110</td>
</tr>
<tr>
<td><strong>3-mode pyrazine (ref.5)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>3.94</td>
<td>4.84</td>
<td></td>
</tr>
<tr>
<td>k₁</td>
<td>0.037</td>
<td>-0.254</td>
<td>0.126</td>
</tr>
<tr>
<td>k₂</td>
<td>-0.105</td>
<td>0.149</td>
<td>0.074</td>
</tr>
<tr>
<td>λₑ</td>
<td>0.262</td>
<td></td>
<td>0.118</td>
</tr>
<tr>
<td><strong>4-mode pyrazine (ref.19)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>3.94</td>
<td>4.84</td>
<td></td>
</tr>
<tr>
<td>k₁</td>
<td>-0.0964</td>
<td>0.1194</td>
<td>0.0740</td>
</tr>
<tr>
<td>k₂</td>
<td>0.0470</td>
<td>0.2012</td>
<td>0.1273</td>
</tr>
<tr>
<td>k₃</td>
<td>0.1594</td>
<td>0.0484</td>
<td>0.1568</td>
</tr>
<tr>
<td>λₑ</td>
<td>0.1825</td>
<td></td>
<td>0.0936</td>
</tr>
</tbody>
</table>

continued
<table>
<thead>
<tr>
<th></th>
<th>24-mode pyrazine (19)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3.94</td>
</tr>
<tr>
<td>$c$</td>
<td></td>
</tr>
<tr>
<td>$k_1$</td>
<td>-0.0964</td>
</tr>
<tr>
<td>$k_2$</td>
<td>0.0470</td>
</tr>
<tr>
<td>$k_3$</td>
<td>0.1594</td>
</tr>
<tr>
<td>$k_4$</td>
<td>0.0069</td>
</tr>
<tr>
<td>$k_5$</td>
<td>0.0112</td>
</tr>
<tr>
<td>$k_6$</td>
<td>0.0102</td>
</tr>
<tr>
<td>$k_7$</td>
<td>0.0188</td>
</tr>
<tr>
<td>$k_8$</td>
<td>0.0261</td>
</tr>
<tr>
<td>$k_9$</td>
<td>0.0308</td>
</tr>
<tr>
<td>$k_{10}$</td>
<td>0.0210</td>
</tr>
<tr>
<td>$k_{11}$</td>
<td>0.0265</td>
</tr>
<tr>
<td>$k_{12}$</td>
<td>0.0196</td>
</tr>
<tr>
<td>$k_{13}$</td>
<td>0.0281</td>
</tr>
<tr>
<td>$k_{14}$</td>
<td>0.0284</td>
</tr>
<tr>
<td>$k_{15}$</td>
<td>0.0361</td>
</tr>
<tr>
<td>$k_{16}$</td>
<td>0.0560</td>
</tr>
<tr>
<td>$k_{17}$</td>
<td>0.0433</td>
</tr>
<tr>
<td>$k_{18}$</td>
<td>0.0625</td>
</tr>
<tr>
<td>$k_{19}$</td>
<td>0.0717</td>
</tr>
<tr>
<td>$k_{20}$</td>
<td>0.0782</td>
</tr>
<tr>
<td>$k_{21}$</td>
<td>0.0780</td>
</tr>
<tr>
<td>$k_{22}$</td>
<td>0.0269</td>
</tr>
<tr>
<td>$k_{23}$</td>
<td>0.0306</td>
</tr>
<tr>
<td>$\lambda$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.1825</td>
</tr>
</tbody>
</table>
and is closer to the exact calculation of ref.2 (insert a in the Fig.5.4).

**Fig.5.5** is the photoelectron spectrum of the ethylene cation second band. The inserts are again from ref.2. Due to the large energy gap of 1.9 eV of the two interacting states the spectral bands are well separated. The qualitative spectrum is reproduced by these two formalisms, but the gross structure of the band is missing in the two formalisms.

In Figs. 5.6 and 5.7 we present the results of the calculations carried out on 3-mode pyrazine. The basis is similar to that used for the ethylene cation. In **Fig.5.6** we have plotted the modulus of ACF verses time calculated for S state by DYTDCCM and TDSCF formalisms. The insert is from ref.36. The modulus of ACF is correctly reproduced upto 60 fs by the two formalisms. Beyond this DYTDCCM fails to gain any value and continues to be almost negligible. The underestimation of the modulus of ACF by DYTDCCM is probably due to the term we have neglected in the computation of autocorrelation function. The TDSCF also deviates from the exact calculation, for example around 100 fs the exact calculation fluctuates with the value of 0.1 but the TDSCF shows a sudden rise up to 0.3.

**Fig.5.7** is the corresponding absorption spectrum of 3-mode pyrazine upper surface. The inserts are from the calculation of Schneider et al. We can clearly see that the TDSCF spectrum is diffuse and structureless, whereas the DYTDCCM shows the humps which appear in the model exact spectrum (insert b) indicating that DYTDCCM at $S_2$ level is a better approximation.
Fig. 5.4 The modulus of ACF in 3-mode ethylene cation. Continuous line: DYTDCCM calculation. Dashed line: TDSCF calculation. The insert (a) is the exact calculation and (b) in the absence of vibronic coupling. The inserts are from ref. 2.
Fig. 5.5 The photoelectron spectrum of ethylene cation second band. The figure conventions are the same as in Fig. 5.4. The inserts are the corresponding calculations of inserts of Fig. 5.4 taken from ref. 2.
Fig. 5.6 The modulus of ACF of $S_2$ state of 3-mode pyrazine. Continuous line: DYTDCCCM calculation. Dashed line: TDSCF calculation. The insert is from ref. 36. Of the two lines of the insert continuous line: the exact calculation and the dashed line: when $\lambda = 0$. 

187
Fig. 5.7 The absorption spectrum of S state of 3-mode pyrazine. The figure conventions are the same as in Fig. 5.6. The inserts a, b, are the experimental, exact quantum mechanical calculations and c is in the absence of vibronic coupling, $\lambda=0$. The inserts are from ref. 5.
than TDSCF.

In Fig. 5.8 we plot the modulus of ACF for S state of the 4-mode pyrazine calculated by DYTDCCM and TDSCF formalisms in the same basis as above. Both DYTDCCM and the TDSCF calculations show initial very fast decay and continues to fluctuate with a variable small value throughout the evolution. Fig. 5.9 is the corresponding absorption spectrum by the two formalisms. The inserts a and b are the exact and the path integral results from ref. 19. The TDSCF spectrum is just a broad band while the DYTDCCM calculation produces the qualitative features of the spectrum correctly.

In Figs. 5.10 and 5.11 we present the results of the calculations done for 24-mode pyrazine. The SCF calculation was similar to those reported above. In the TDCCM calculation we have used a smaller basis. The first four modes were represented by 5 SCF functions each as in the previous case, and the remaining twenty modes were represented by 2 functions each. In Fig. 5.10 we plot the modulus of ACF for S state of 24-mode pyrazine by DYTDCCM and TDSCF calculations. The insert is the path integral calculations taken from ref. 19. The initial very fast decay is similar to that in the 4-mode pyrazine in both the calculations. In the long time limit the DYTDCCM result is strongly damped similar to the path-integral calculation. The TDSCF calculation does not show this strong damping. In addition, TDSCF shows strong recurrences at earlier times that are absent in the exact result. The DYTDCCM formalism corrects these anomalous recurrences. Fig. 5.11 is the corresponding absorption spectrum of
Fig. 5.8 The modulus of ACF of S state of 4-mode pyrazine. Continuous line: DYTDCM calculation. Dashed line: TDSCF calculation.
Fig. 5.9 The absorption spectrum of S state of 4-mode pyrazine. The figure conventions are the same as in Fig. 5.8. The insert a is the exact spectrum and b is the path integral calculation. These are taken from ref. 19.
Fig. 5.10 The modulus of ACF of S state of 24-mode pyrazine. Continuous line: DY TDCCM calculation. Dashed line: TDSCF calculation. The insert is path-integral calculation (ref. 19).
Fig. 5.11 The absorption spectrum of \( S_2 \) state of 24-mode pyrazine. The figure conventions are the same as in Fig. 5.10. The insert is again path-integral calculation (ref. 19).
S state of 24-mode pyrazine obtained by DYTDCCM and TDSCF formalisms. Insert a is again the path integral calculation\(^{19}\) and insert b is the spectrum calculated with \(X=0\) by path integral calculation. The DYTDCCM qualitatively reproduced the spectrum as in the path integral calculation but it differs in the sense that the sharp humps in the path integral calculation are slightly broadened in our calculations.

5.4. CONCLUSIONS

In this chapter we have studied the applicability of TDCCM approach for the description of nonadiabatic dynamics. Our goal was to see whether the TDCCM can provide a qualitatively and quantitatively correct description of the dynamics for this class of systems even with low order truncations. If it can provide such a description, what would be the best basis in which such calculations can be carried out, at what order should the cluster operator be truncated and which configurations should be included in the model space. These systems differ from the system studied in Chapter IV, in that it is known\(^{17}\) that TDSCF provides a good description for these systems unlike the IVR problem studied there, for which TDSCF gives trivial dynamics. Secondly, there are no dominating resonance sequences in these systems.

To find answers to the questions posed above, we have made two sets of calculations. Since no degeneracies exist in the system, we have assumed that a single reference state would
provide an adequate starting point. In the first approach, we carried out TDCCM calculations in a stationary basis with the initially prepared state as the reference state. The working equations in this approach became stiff very soon and could not be integrated. As noted in Chapter II the working equations became stiff when the overlap of the wave packet with the model space (the reference state in this case) approaches zero. Since the autocorrelation function is practically zero for most of the time in our calculations, this must be the reason for the stiffness of the equations. To circumvent this one must choose the model space (the reference function) such that its overlap with the exact wave packet is significant throughout the course of its time evolution. Since the TDSCF solution to this class of problems is known to have such acceptable overlap for moderately long times\textsuperscript{17}, we carried out TDCCM calculation in the dynamical basis generated by TDSCF, i.e. using the TDSCF state of the initial (t=0) state as a reference state. The resulting equations were not stiff indicating that TDSCF does indeed provide a good reference state for the TDCCM calculations.

We next turn to the approximation of the cluster operator. Due to the constraints on computational resources, we could only study one approximation $S=S_2$. The computational studies showed that this approximation considerably improved upon the TDSCF results and often is quite close to the exact result.

With these we draw the following tentative conclusions: (1) The TDSCF provides a good reference state for the dynamical calculations, (2) A single reference TDCCM at $S=S_2$ level over this
reference state is adequate to provide a good description for this class of systems. More studies are required to confirm these conclusions.
REFERENCES


22. (a) W. Lichten, Phys. Rev. 131, 229 (1963); 139, A27
(1965); 164, 131 (1967); (b) F. T. Smith, Phys. Rev. 179, 111 (1969).


