Dynamics of excited molecular states

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Abstract. The photo-excitation or photo-ionization of a polyatomic molecule is typically accompanied
by a strong excitation of the vibrational modes. In particular when a conical intersection of the electronic
potential energy surfaces involved lies within or close to the Frank-Condon zone, the nuclear motion
becomes very complicated, often chaotic, and the spectra become irregular and dense.

An accurate simulation of the dynamics of such excited molecules requires firstly that the multi-
dimensional and multi-state potential energy surface – or a reliable model thereof – can be determined.
Secondly, the multi-dimensional quantum dynamics have to be solved. This is a very difficult task, because
of the high dimensionality of the problem (6 to 30 degrees of freedom, say). The multi-configuration time-
dependent Hartree (MCTDH) method has proven to be very useful for the study of such problems. In
fact, an accurate treatment of the quantal dynamics of molecules like the allene cation (C$_3$H$_4$$^+$, 15D),
the butatriene cation (C$_4$H$_4$$^+$, 18D), or the pyrazine molecule (C$_4$N$_2$H$_4$, 24D) in their full dimensionality, is –
up to date – only possible with MCTDH. (The acronym nD denotes the dimensionality.)

The construction of the vibronic model Hamiltonian and the MCTDH method will be briefly discussed.
After this, the excited state dynamics of the butatriene and pyrazine molecules will be discussed.

1. Introduction
The simulation of the quantum dynamics of an (vibrationally and electronically) excited polyatomic
molecule is a difficult task because of two reasons. First, the multi-dimensional potential energy surface
(PES) has to be determined and second, the multi-dimensional quantum dynamics have to be solved.
The well known Born-Oppenheimer Approximation is usually an excellent approximation for the ground
electronic state, but for electronically excited states vibronic coupling can in general not be neglected.
Very often there are two or a few strongly coupled states and the nuclear motion evolves on these
states simultaneously. Hence a multi-dimensional multi-state PES needs to be determined. For a small
polyatomic molecule with only three atoms it is possible to determine the PES point-wise by ab initio
calculations. An analytic expression is then fitted to this set of data. In suitable cases one may do so even
for four-atomic molecules, i.e. for 6 internal degrees of freedom. But for larger molecules this approach
quickly becomes impossible. A way out is to derive a parameterized model potential and to determine
the values of the parameters (there may be hundreds of them) by comparison of the model potential with
ab initio quantum chemistry data. This approach is explained in the following section.

After the PES is determined, the multi-dimensional multi-state quantum dynamics have to be solved.
This is a difficult problem by itself, because of the large number of nuclear degrees of freedom (typically
6 to 30) which have to be accounted for. Standard quantum approaches will fail, because they require
too much computer memory, but the recently developed Multiconfiguration time-dependent Hartree
(MCTDH) method [1–4] very often is capable of treating such problems. MCTDH will be discussed
in section 3.
In section 4 we will discuss two applications, the photo-ionization spectrum of butatriene [5] and the photo-excitation spectrum of pyrazine [6, 7]. In both cases, the dynamics are strongly influenced by the presence of a conical intersection. This leads to a complicated, irregular motion, and – in particular for the pyrazine molecule – to an irregular and dense spectrum.

2. The vibronic coupling Hamiltonian

The existence of a conical intersection within or close to the Franck-Condon zone has very dramatic effects on the dynamics and hence on the spectra of polyatomic molecules. Usually the spectrum becomes very dense and only the envelope, rather than the individual line, is of interest. This allows one to concentrate on short-time dynamics. For a reliable treatment of the dynamics it is important to describe the vicinity of the Franck-Condon point accurately. However, as only short-time dynamics are required, the interaction potential away from the Franck-Condon point may be of lesser accuracy.

The adiabatic potential energy surfaces in the vicinity of a conical intersection usually exhibit a rather complicated form, i.e. they are strongly anharmonic and may show multiple minima. In contrast to the adiabatic surfaces, the diabatic ones are of simple structure. Furthermore, the diabatic coupling is well behaved, non-singular, and of potential type. All this makes the diabatic representation very attractive for numerical calculations.

We are interested in the study of absorption or ionization spectra of small polyatomic molecules. Before the absorption of a photon the molecule is assumed to be in its electronic and vibrational ground state. We use the dimensionless normal coordinates of the ground state throughout and write the ground state Hamiltonian in harmonic approximation as

\[ H_{GS} = T + \sum_{i=1}^{f} \frac{\omega_i}{2} Q_i^2 \]  

where \( f \) denotes the number of degrees of freedom and \( \omega_i \) is the \( i \)-th normal mode frequency (we use \( \hbar = 1 \)). The ground state is assumed to be well separated from all other electronic states. After excitation, however, the electronic structure is described by a set of close lying, interacting states. The vibronic Hamiltonian for this set of states reads

\[ H = T + W(Q) \]  

Assuming – for sake of simplicity – that there are only two interacting excited states of relevance and developing the diabatic potential energy matrix \( W \) in a power series around the equilibrium position of the ground state and keeping only terms up to second order, one arrives at

\[ H = T1 + \sum_{i=1}^{f} \frac{\omega_i}{2} Q_i^2 \mathbf{1} + \left( \begin{array}{cc} \varepsilon_1 & 0 \\ 0 & \varepsilon_2 \end{array} \right) \]

\[ + \sum_{i \in G_1} \left( \begin{array}{cc} \kappa_i^{(1)} & 0 \\ 0 & \kappa_i^{(2)} \end{array} \right) Q_i \]

\[ + \sum_{(i,j) \in G_2} \left( \begin{array}{cc} \gamma_{i,j}^{(1)} & 0 \\ 0 & \gamma_{i,j}^{(2)} \end{array} \right) Q_i Q_j \]
\[ + \sum_{i \in G_3} \left( \begin{array}{cc} 0 & \lambda_i \\ \lambda_i & 0 \end{array} \right) Q_i \]
\[ + \sum_{(i,j) \in G_4} \left( \begin{array}{cc} 0 & \mu_{i,j} \\ \mu_{i,j} & 0 \end{array} \right) Q_i Q_j. \] (4)

The first two terms reproduce the ground state Hamiltonian, but located on the diagonal of the electronic 2×2 matrix. The two energies \( \varepsilon_1 \) and \( \varepsilon_2 \) are the vertical excitation energies. The next four sums describe the linear and the bilinear coupling terms.

Due to symmetry considerations the sums run only over restricted sets of modes [5,8]. \( G_1 \) is the set of totally symmetric modes and \( G_3 \) is the set of asymmetric modes which provide linear coupling between the two interacting states. Similarly, \( G_2 \) and \( G_4 \) denote the sets of coordinate pairs, which provide interstate and intrastate coupling, respectively.

A high symmetry of the molecule does not only help to reduce the number of parameters, it also provides a solid basis for the vibronic coupling model Hamiltonian. When the two interacting electronic states are of different symmetry (as assumed here), the inter-state coupling must be an odd function of the coupling coordinate. Hence there cannot be a constant or quadratic term. The vibronic coupling Hamiltonian was first derived by Cederbaum et al. [9,10] and is more fully described in a review article by Köppel et al. [8].

To demonstrate that diabatic surfaces of rather simple structure may indeed produce complicated adiabatic surfaces, we show in figures 1, 2 a two-dimensional (2D) cut of the diabatic and adiabatic PES of butatriene [5].

Quantum chemistry supplies us with the adiabatic potential energy surfaces \( V_i \), and – at some higher cost – with the non-adiabatic coupling elements. Fortunately, the latter are not needed when determining the parameters of the vibronic coupling Hamiltonian, the knowledge of the adiabatic potential energy surfaces alone is sufficient. The parameters of the vibronic coupling Hamiltonian are determined by comparing the adiabatic potential energy surfaces obtained by diagonalizing the diabatic model potential with those obtained by quantum chemistry. To this end a least-squares fit is performed, i.e. the function [5]

\[
L(\kappa, \lambda, \gamma, \mu) = \\
\sum_{n=1}^{M_1} w_n^{(1)} \left[ V_1^{\text{mod}}(\varepsilon_1, \varepsilon_2, \kappa, \lambda, \gamma, \mu; Q_n) - V_1(Q_n) \right]^2 \\
+ \sum_{n=1}^{M_2} w_n^{(2)} \left[ V_2^{\text{mod}}(\varepsilon_1, \varepsilon_2, \kappa, \lambda, \gamma, \mu; Q_n) - V_2(Q_n) \right]^2. \] (5)

is minimized. Here \( \kappa, \lambda, \gamma, \mu \) stand for all the coupling constants and \( V_i^{\text{mod}} \) denote the adiabatic surfaces obtained by diagonalizing the potential part of the vibronic coupling Hamiltonian, (4).

3. Multiconfiguration time-dependent Hartree (MCTDH)

The Multiconfiguration time-dependent Hartree (MCTDH) method [1–4] is a general algorithm to solve the time-dependent Schrödinger equation. It may be understood as a time-dependent version of CASSCF, however, not for electrons but for distinguishable particles. The complete active space (CAS) of MCTDH is a direct product space of so-called single–particle functions (SPFs). The SPFs, \( \varphi(q,t) \), may be one– or multi–dimensional functions and, in the latter case, the coordinate \( q \) is a collective one, \( q = (Q_1, \ldots, Q_d) \).

As the SPFs are time–dependent, they follow the wavepacket and often a rather small number of SPFs suffices for convergence.
The ansatz for the MCTDH wavefunction reads

\[ \Psi(Q_1, \cdots, Q_f, t) = \Psi(q_1, \cdots, q_p, t) = \sum_{j_1} \sum_{j_2} \cdots \sum_{j_p} A_{j_1 \cdots j_p}(t) \prod_{\kappa=1}^p \phi_{j_\kappa}(q_\kappa, t) = \sum_j A_j \Phi_j, \]

where \( f \) denotes the number of degrees of freedom and \( p \) the number of MCTDH particles, also called combined modes. There are \( n_\kappa \) SPFs for the \( \kappa \)-th particle. The \( A_j \equiv A_{j_1 \cdots j_f} \) denote the MCTDH expansion coefficients and the configurations, or Hartree-products, \( \Phi_j \) are products of SPFs, implicitly defined by (6). The SPFs are finally represented by linear combinations of time-independent primitive basis functions.

In order to write down the equations of motion for the SPFs and coefficients in a concise way, it is necessary to introduce the single-hole functions

\[ \Psi_l^{(\kappa)} = \langle \phi_l^{(\kappa)} | \Psi \rangle. \]

Note that the coordinates of the \( \kappa \)-th particle are integrated out. The single-hole functions allow us to define mean field

\[ \langle H \rangle_j^{(\kappa)} = \langle \Psi_l^{(\kappa)} | H | \Psi_l^{(\kappa)} \rangle \]

and density matrices

\[ \rho_{jl}^{(\kappa)} = \langle \Psi_l^{(\kappa)} | \Psi_j^{(\kappa)} \rangle. \]

The mean-field matrix elements are operators on the \( \kappa \)-th particle. Finally, we define the MCTDH projector

\[ P^{(\kappa)} = \sum_{j=1}^{n_\kappa} | \phi_j^{(\kappa)} \rangle \langle \phi_j^{(\kappa)} |. \]

The MCTDH equations of motion are derived by applying the Dirac-Frenkel variational principle \[11, 12\] to the ansatz (6). After some algebra, one obtains

\[ iA_j = \sum_L \langle \Phi_j | H | \Phi_L \rangle A_L, \]
\[
\dot{\varphi}^{(k)} = \left( 1 - P^{(k)} \right) \left( \rho^{(k)} \right)^{-1} \langle H \rangle^{(k)} \varphi^{(k)},
\]
(12)

where a vector notation, \( \varphi^{(k)} = (\varphi^{(k)}_1, \cdots, \varphi^{(k)}_n)^T \), is used. Details on the derivation, as well as more general results, can be found in [2–4]. The MCTDH projector ensures that that part of the propagation of the total wavefunction, which is accomplished by the coefficients, is not re-done when propagating the SPFs. The projector also ensures that the SPFs stay orthonormal.

The MCTDH equations conserve the norm and, for time-independent Hamiltonians, the total energy. MCTDH simplifies to Time-Dependent Hartree when setting all \( n^\kappa = 1 \). Increasing the \( n^\kappa \) recovers more and more correlation, until finally, when \( n^\kappa \) equals the number of primitive functions, the standard method (i.e. propagating the wavepacket on the primitive basis) is used. It is important to note, that MCTDH uses variationally optimal SPFs, because this ensures fast convergence.

The solution of the equations of motion requires to build the mean–fields at every time–step, a fast evaluation of the mean–fields is hence essential. A fast algorithm exists, if the Hamiltonian can be written as a sum of products of mono–particle operators.

\[
H = \sum_{r=1}^s c_r \prod_{\kappa=1}^p h_r^{(\kappa)},
\]
(13)

where \( h_r^{(\kappa)} \) operates on the \( \kappa \)-th particle only and where the \( c_r \) are numbers. In this case the matrix-elements of the Hamiltonian can be expressed by a sum of products of mono–mode integrals, the evaluation of which is very fast.

\[
\langle \Phi_J | H | \Phi_L \rangle = \sum_{r=1}^s c_r \prod_{\kappa=1}^p \langle \varphi_{J_\kappa} | h_r^{(\kappa)} | \varphi_{L_\kappa} \rangle,
\]
(14)

Fortunately, the vibronic coupling Hamiltonian introduced above assumes the required product form, making this problem very suitable for MCTDH.

All quantities of interest can be generated from the knowledge of the time-evolved wavepacket. In particular, the spectrum is generated by Fourier transform of the autocorrelation function \( c(t) = \langle \Psi(0) | \Psi(t) \rangle \).

4. Applications

Several polyatomic molecules have been investigated using the vibronic coupling model Hamiltonian and the MCTDH wavepacket propagation method outlined above. In particular we note the work on pyrazine [6,7], Allene [13], butatriene [5], Benzene [14], and Furan [15]. In the following we will briefly discuss the dynamics of butatriene and pyrazine after photo-ionization and photo-excitation, respectively.

Butatriene, C_{4}H_{4}, is a planar molecule with D_{2h} symmetry. It has 18 internal degrees of freedom. A broad-band photo-absorption leads to a vertical excitation from neutral ground state to the \( X^2B^2_{2g} \) and \( A^2B^2_{2u} \) cationic states. Higher ionic states can be neglected. The two electronic states under consideration are coupled through a conical intersection. Without this coupling, the spectrum would show intensity only close to the vertical excitation energies of these states, i.e. close to 9.3 eV and 10.0 eV. There would be almost no intensity in the middle (9.5 eV – 9.8 eV) of the spectrum. The experiment and the simulation however show (cf. figure 3), that there is a considerable intensity over this region (so called mystery band). This is a clear demonstration of the importance of the vibronic coupling. Figure 4 shows, that a reduced dimensionality treatment, including only the five modes which are coupled linearly, is not sufficient. The full-dimensionality calculation reproduces the experimental spectrum considerably better.

Similar differences between the 5D and the 18D calculations are displayed by the autocorrelation functions, figures 5, 6. When the initial wavepacket is started on the (lower) \( X^2B^2_{2g} \) state, one observes
strong recurrences, indicating that the motion is still fairly regular. Starting from the (upper) $A^2B_{2u}$ generates an autocorrelation function which falls off very quickly and then shows only weak recurrences, indicating a much more irregular motion. This is because the conical intersection is easier reached by a wavepacket which starts on the upper diabatic surface.

The vibronic coupling in pyrazine is considerably stronger as compared to butatriene. Here the coupling produces an extremely dense spectrum, because none of the 24 internal modes acts as a simple spectator, they all can be excited via the vibronic coupling. Figure 7 shows the spectrum in comparison with the experimental one. The agreement is excellent. Figure 8 depicts the autocorrelation function. The rather small values of the modulus of the autocorrelation function indicates a strongly irregular motion.

The knowledge of the autocorrelation function allows to estimate the value of $1/(\Sigma p_i^2)$, where $p_i$ denotes the overlap of the $i$-th eigenstate with the initial wavepacket, i.e. $p_i$ is essentially the spectral line strength and $\Sigma p_i = 1$. Hence $1/(\Sigma p_i^2)$ may be interpreted as the number of spectral lines of
non-negligible strength. (For more information on this sum, see the appendix of [16]). We found $1/(\sum_i |p_i|^2) = 2500$, what again emphasizes the quasi-continuum character of the spectrum.

The electronic to vibrational energy conversion is very fast. Only 20 fs after excitation, most of the initial wavepacket has moved from the upper adiabatic surface to the lower one [6]. As a consequence, the radiation is quenched. The molecule strongly absorbs light of wavelengths between, say, 235 nm and 265 nm, but it does not re-emit this light. The experimentalists [17] have measured the fluorescence lifetime to be longer than 100 ps for all lines above 285 nm wavelength. Going to higher energies, however, the lifetime dramatically shortens, being 25 ps at 270 nm and not measurable at shorter wavelengths. For more information on the pyrazine molecule see [6, 7, 17–21].

All the examples discussed above belong to the category of bound state dynamics. But we want to emphasize that MCTDH has been used to treat scattering and half-scattering (e.g. photodissociation) problems as well. In fact, being a time-dependent method, MCTDH is very suitable for attacking such problems. The rather complicated scattering boundary conditions, which must be satisfied in a time-independent calculation, do not appear when propagating a wavepacket. In this respect, a recent study [22] on the dynamics of dissociative attachment of electrons to water may be of particular interest to the present audience.

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