Vibronic coupling in the Pyridine Radical Cation: Nuclear Dynamics Studied Using the Multi-configuration Time-Dependent Hartree method

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Abstract. The multi-configuration time-dependent Hartree (MCTDH) method was applied to study nuclear dynamics following transitions to a manifold of vibronically coupled ground \( ^2 \)A\(_1\) and excited \( ^2 \)A\(_2\) and \( ^2 \)B\(_1\) states of the pyridine radical cation (PRC). These states originate from ionization out of the highest occupied orbitals of pyridine, 7a\(_1\) (\( \pi \sigma \)), 1a\(_2\) (\( \pi \)), and 2b\(_1\) (\( \pi \)), respectively, and give rise to the lowest two photoelectron bands. We focus on various theoretical and computational aspects of the MCTDH method and methodology to calculate the spectrum, taking our study of the vibronically interacting \( ^2 \)A\(_1\), \( ^2 \)A\(_2\), and \( ^2 \)B\(_1\) states of PRC as an example. In particular, the choice of the single-particle functions (SPFs) and schemes to combine vibrational modes are discussed.

1. Introduction

Pyridine (Figure 1) is a fundamental heterocyclic molecule, a common fragment of many biological compounds and synthesized drugs [1–3]. Therefore, understanding the electronic structure and nuclear dynamics of pyridine in its neutral and cationic states is of current importance in modern chemistry. The electronic structure of pyridine was studied in our previous work [4,5] by means of synchrotron radiation photoelectron spectroscopy and accurate \textit{ab initio} calculations. Special emphasis was placed on the four lowest states of the pyridine radical cation (PRC), \( ^2 \)A\(_1\), \( ^2 \)A\(_2\), \( ^2 \)B\(_1\), and \( ^2 \)B\(_2\), formed upon ionization out of the 7a\(_1\) (\( \pi \sigma \)), 1a\(_2\) (\( \pi \)), 2b\(_1\) (\( \pi \)), and 5b\(_2\) (\( \pi \)) molecular orbitals, respectively. The ionization energies (ionization potentials, IPs) for these states were computed using different \textit{ab initio} methods [4]. It was shown that the very top-level electron correlation method, in particular accounting for triple excitations, such as EOM-IP-CCSDT or CC3, is required to correctly reproduce the ordering of the states and their relative energies. The IPs obtained using the EOM-IP-CCSDT and CC3 methods are found to be in very good agreement with the experimental results: 9.68 (9.66) eV, 9.84 (9.85) eV, 10.55 (10.51) eV, and 12.84 (12.45) eV, for \( ^2 \)A\(_1\), \( ^2 \)A\(_2\), \( ^2 \)B\(_1\), and \( ^2 \)B\(_2\) ionization energies, respectively, with the experimental values from Ref. [6] being given in parenthesis. The other methods, which account for electron correlation effects at lower levels, give less accurate relative energies or even predict a wrong order of the \( ^2 \)A\(_1\) and \( ^2 \)A\(_2\) states (see more details in Ref. 4).
In our recent work [5], the three lowest cationic states of pyridine, \(^1\text{A}_2\), \(^2\text{A}_2\) and \(^2\text{B}_1\), were shown to be vibronically coupled, and a three-state linear vibronic coupling (LVC) model was formulated employing the framework of model Hamiltonians. The model was parametrized based on results of our ab initio calculations for the ground state of neutral pyridine and results of the CC3 calculations for the \(^1\text{A}_2\), \(^2\text{A}_2\) and \(^2\text{B}_1\) cationic states. In the CC3 calculations, the above mentioned high-level CC3 method [7-10] in combination with the continuum orbital approach [11] was employed. Using this model, nuclear dynamics following ionization to the three cationic states under consideration were computed employing the multi-configuration time-dependent Hartree (MCTDH) method [12], with 24 vibrational modes being taken into account. In addition, the conventional time-independent approach [13] was applied, with 11 vibrational modes being taken into account. Although the time-dependent (MCTDH) approach allows for taking more vibrational modes into account, the time-independent ansatz allows for obtaining explicit solutions for vibronic levels, thus allowing to estimate the density of the vibronic levels in the spectrum. The spectra obtained using both approaches are in good qualitative agreement with the experimental high-resolution He I photoelectron spectrum of pyridine obtained by Liu et al [14], allowing for assignment of some experimental structure.

The three-state LVC model was also used to explore the potential energy surfaces (PES) of the \(^2\text{A}_1\), \(^2\text{A}_2\) and \(^2\text{B}_1\) states [5]. The PES of the \(^2\text{A}_1\) and \(^2\text{A}_2\) states were shown to intersect in the vicinity of the adiabatic minimum of the \(^2\text{A}_2\) state, while the surfaces of the \(^2\text{A}_2\) and \(^2\text{B}_1\) states intersect near the \(^2\text{B}_1\) state minimum. The PES of these three states form a whole system of low-lying conical intersections (CIs). This suggests that various fast radiationless decay processes should take place following ionization to the \(^2\text{A}_2\) and \(^2\text{B}_1\) states, eventually bringing the system to its \(^2\text{A}_1\) cationic ground state. Short lifetimes of the \(^2\text{A}_2\) and \(^2\text{B}_1\) states manifest themselves in strongly broadened spectral features, which are observed above the energy associated with the lowest CI. They are composed of very complex patterns of vibronic lines, which is characteristic of non-adiabatic nuclear dynamics (Figure 2a). The spectrum exhibits some resolved vibrational structure only in its low-energy part, below the energy of the lowest CI, where the adiabatic and Franck-Condon approximations are still valid. Since vibronic interactions affect the ground state of PRC they can be expected to have appreciable influence on physical and chemical properties of pyridine. A comprehensive review of the state-of-the-art publications on the ionization spectrum of pyridine and its vibronic structure is given in our previous work [4,5].

The MCTDH method is a powerful, universal and flexible approach for solving the time-dependent Schrödinger equation [15]. One of the important features of MCTDH is the possibility of mode combinations to set up a very compact wavefunction (wave packet), which allows for consideration of large systems with many vibrational modes (degrees of freedom). Therefore, there are numerous applications of the method [12,15-25]. There are however some subtle methodological aspects that we would like to consider here. Below we provide additional details of MCTDH computational methodology in the case of vibronic coupling modeling of the pyridine ionization spectrum.
2. Theoretical approach

Nowadays, one of the most efficient methods able to solve the time-dependent Schrödinger equation

$$\hat{H}\psi(t) = i\hbar \frac{\partial}{\partial t}\psi(t)$$

(1)

is the MCTDH method. The advantage of MCTDH over the standard numerical time propagation algorithms is due to restricted ability of the latter methods to solve relatively large problems because of the exponential increase of computational costs with the number of degrees of freedom [26].

In the MCTDH formalism, the wave function $\psi(t)$ describes the molecular dynamics of a system with $f$ degrees of freedom (DOF) using a linear combination of Hartree products of time-dependent single-particle functions (SPFs) $\phi_{i}(q_{i}, t)$:

$$\psi(q_{1}, \ldots, q_{f}, t) = \sum_{k=1}^{n} \sum_{j=1}^{n_{k}} A_{k-j} (t) \prod_{k}^{f} \phi_{i_k}(q_{i_k}, t)$$

(2)

where $q_{i}, q_{j}$ are nuclear coordinates (DOF), $A_{k-j} (t)$ denote the expansion coefficients and $n_k$ is a number of SPFs for $k$-th DOF.

SPFs are represented as a linear combination of a time-independent orthonormal primitive basis set $\chi^{\ell}_{i}(q_{i})$

$$\phi_{i}(q_{i}, t) = \sum_{k=1}^{n} a_{i}^{\ell}(t) \chi^{\ell}_{i}(q_{i})$$

(3)

These functions are optimized by the variation principle. Typically, a discrete variable representation (DVR) is used for this in wavepacket propagation calculations [27].
The MCTDH method allows to use different number of SPFs for each independent electronic state. This multistate formalism is suitable for solving the vibronic coupling problem of several states by expanding the wave function in a basis of electronic states \( \{ \alpha \} \) [15]

\[
|\psi\rangle = \sum_{\sigma} \psi_\sigma |\alpha\rangle
\]

(4)

where \( \sigma \) is a number of electronic states and each of \( \psi_\sigma \) is expanded in a basis set according to equation (2).

The main disadvantage of any standard algorithm is an exponential growth of computer resources upon increasing the number of system’s DOF. The standard methods require \( \sim N' \) bytes, where \( N \) is associated with the number of grid points. By propagating the limited set of parameters, the MCTDH reduces the memory (RAM) needed for the computation as:

\[
\sim n' + fnN \text{ bytes}
\]

(5)

The first part \( n' \) is the memory requirement for the coefficient vectors and \( fnN \) is determined by the number of SPFs.

On the other hand, one can combine physical coordinates into \( n \)-dimensional “particles” (Usually one combines up to 4 vibrational modes into one multidimensional particle).

\[
Q_i = \{ q_{i<} - q_{i>} \}
\]

(6)

The mode combination technique improves convergence and allows for considering larger systems using less computational resources, which is one of the main advantages of the MCTDH method.

According to [27, 28], the vibronic coupling model Hamiltonian reads as follows:

\[
\hat{H} = \sum_{i} \frac{\omega_i}{2} \left( -\frac{\partial^2}{\partial Q_i^2} + Q_i^2 \right) \hat{I} + W
\]

(7)

where \( Q_i \) are dimensionless normal coordinates related to normal modes \( \nu_i \) with the harmonic vibrational frequencies \( \omega_i \), and \( \hat{I} \) is a \( n \times n \) unit matrix. The Hamiltonian includes kinetic and potential energy parts and a diabatic electronic \( n \times n \) matrix \( W \) describing changes in the potential energy. The matrix elements of \( W \) are expanded in Taylor series around some configuration \( (Q_0) \) of the molecule. The matrix elements \( W_{nm} \) describe diabatic energies of the states, whereas the \( W_{nm} \) describe their coupling. In our present model used for PRC calculations, the expansion is cut after the linear terms, which leads to the LVC model. The diagonal elements of \( W_{nm} \) are written as

\[
W_{nn} = E_n + \sum_i \kappa_{i}^{(mm)} Q_i
\]

(8)

and the non-diagonal elements:

\[
W_{nm} = \sum_i \chi_{i}^{(mm)} Q_i \quad \text{for} \ n \neq m
\]

(9)

The \( E_n \) denote the vertical excitation energy of electronic states, \( \kappa_{i}^{(mm)} \) and \( \chi_{i}^{(mm)} \) are intrastate and interstate vibronic coupling constants [12].

The \( \kappa_{i}^{(mm)} \) intrastate coupling constants are defined as the gradients of the potential energy functions \( V_n \) associated with the states entering the LVC model (here the \( 1A_2, 2A_2 \) and \( 2B_1 \) states of PRC) at the expansion point \( Q_0 \), which here is the equilibrium geometry of the ground state of neutral pyridine:

\[
\kappa_{i}^{(mm)} = \left( \frac{\partial V_n}{\partial Q_i} \right)_{Q=0}
\]

(10)
The $\lambda_{ij}^{(nm)}$ interstate coupling constants describing vibronic coupling of the diabatic states are defined as follows:

$$
\lambda_{ij}^{(nm)} = \left[ \frac{1}{8} \left( V_n - V_m \right)^2 \right]^{1/2} 
$$

(11)

The parameters $\omega_i$ and $E_i$ in equation (7) are obtained from ab initio quantum chemistry calculations. For the three-state LVC model of PRC, they were calculated for the ground state of neutral pyridine using the MP2 method and cc-pVTZ basis set. The gradients in equation (10) and the quantity in equation (11) are evaluated numerically by means of finite displacements from $Q_0$ along a particular normal coordinate.

The ionization spectrum is evaluated by the Fourier transform of the autocorrelation function:

$$
\sigma(E) \sim \int \exp(iEt)g(t)c(t)dt
$$

(12)

The autocorrelation function $c(t)$ is defined as the overlap between the initial and the propagated wave function [12]. As we use multistate formalism, the autocorrelation function is calculated separately for each of an electronic state $\alpha$:

$$
c_{\alpha}(t) = \langle \psi_{\alpha}(0) | \psi_{\alpha}(t) \rangle
$$

(13)

To decrease errors due to the short time Fourier transform (as the simulation is finite), the autocorrelation function is multiplied by the window function $g(t)$:

$$
g(t) = f(t) \cos \left( \frac{\pi t}{2T} \right) \Theta \left( 1 - \frac{|t|}{T} \right)
$$

(14)

The $T$ denotes the wave packet propagation, $\Theta$ is the Heaviside function and $k = \{0,1,2\}$ (usually we use $k = 1$ as the optimal value).

To compare the calculated spectrum with the experimental one, the damping factor $f(t)$

$$
f(t) = \exp(-t/\tau)
$$

(15)

is added. This is equivalent to the convolution with the Lorentzian function, where $\tau$ is an appropriate parameter related to the spectral resolution with the full width at half maximum (FWHM) $\Gamma = 2/\tau$ [29].

3. Computational details of the MCTDH calculation for ionization spectrum

According to the discussion in the previous section, all the parameters required to set up the MCTDH calculations were obtained from accurate ab initio calculations in our previous work [5]. In particular, the ground-state geometry of neutral pyridine and the vibrational frequencies were calculated using the MP2 method in combination with the cc-pVTZ basis set by employing the Gaussian program package [30]. Using the normal vibrational modes $v_i$ and the frequencies $\omega_i$, the dimensionless normal coordinates required in equation (7) were generated. The displaced geometries $Q_i$ were obtained by applying a distortion $\Delta_j = 0.5$ (in terms of dimensionless normal coordinates) to the equilibrium ground state geometry $Q_0$ [5]. Vertical ionization energies of the optimal and displaced geometries were calculated using the above mentioned CC3 method as implemented in the CFOUR program [31]. The intra- and interstate coupling constants $\kappa_{ij}^{(nm)}$ and $\lambda_{ij}^{(nm)}$ were calculated according to equations (10) and (11).

After having set up the model Hamiltonian (7), propagations of the wave packet were performed populating a particular state, $^2A_1$, $^2A_2$ or $^2B_1$, of PRC. The wave-packet propagation calculations as well as evaluation of the autocorrelation function (13) and generation of the ionization spectrum (14)
were performed using the Heidelberg MCTDH program package [12]. For the wave-packet propagation calculations, one has to set up the number of SPFs \( q_{i}^{(k)}(q_{i},t) \), the number of grid points \( \chi_{i}^{(a)}(q_{i}) \), the mode combination (6), and the propagation time.

4. Results and discussion

One of the delicate points in setting up any MCTDH computation is the way of combining vibrational modes into 1- or n-dimensional particles [23]. In the PRC case, we considered two scenarios (schemes). The first scheme is based on combining into a particle the modes that are expected to correlate to each other. In the second schemes, we combined modes of similar vibrational frequencies (Table 1).

Table 1. Two schemes of mode combinations into particles, SPF basis for each particle and each state, vibrational frequencies of the mode and size of the primitive basis. For the clarity of the first scenario, vibrational modes are combined by (i) having the same symmetry and indicated in the first column, and (ii) by similar values of the Poisson parameter, given in the third column.

| Modes to SPFs combined | SPF basis size | Frequencies (MP2), cm\(^{-1}\) | Primitive basis size |
|-------------------------|----------------|-------------------------------|---------------------|
|                         | \( ^{2}A_{1}(\pi \sigma) \) | \( ^{2}A_{2}(\pi \pi) \) | \( ^{2}B_{1}(\pi \pi) \) |
| Scheme 1                |                |                              |                     |
| \( a_{1} \) v1          | >1             | 10                            | 8                   | 8                   | 602                      | 12                      |
| v2, v3, v5, v7          | ~0.1           | 8                             | 6                   | 6                   | 1009,1048,1242,1632      | 8,8,8,8                 |
| v4, v6, v8, v9, v10     | <0.01          | 4                             | 2                   | 2                   | 1094,1508,3200,3219,3243 | 6,6,6,6,6               |
| \( a_{2} \) v12, v13    | >1             | 8                             | 4                   | 8                   | 726,759                  | 8,8                    |
| v14, v15                | ~0.1           | 4                             | 2                   | 4                   | 953,1008                 | 6,6                    |
| \( b_{1} \) v16, v22    | ~1             | 6                             | 8                   | 8                   | 658,1622                 | 8,8                    |
| v17, v18, v19, v20, v23 | <0.1           | 2                             | 4                   | 4                   | 1079,1171,1379,1402,3199 | 6,6                    |
| \( b_{2} \) v25, v26    | >1             | 8                             | 8                   | 4                   | 382,906                  | 8,8                    |
| v27                     | ~0.1           | 4                             | 4                   | 4                   | 998                      | 6                      |
| Scheme 2                |                |                              |                     |
| v1, v25                 | 15              | 11                            | 8                   | 602,382               | 25,10                   |
| v12, v13, v16           | 8               | 8                             | 7                   | 726,759,658           | 8,8                    |
| v14, v15, v20, v27      | 11              | 9                             | 5                   | 953,1008,906,998      | 6,6,12,10               |
| v2, v3, v4, v17         | 11              | 8                             | 7                   | 1009,1048,1094,1079   | 14,14,6,6               |
| v5, v8, v9, v20         | 9               | 7                             | 7                   | 1242,1171,1379,1402   | 8,6,6,6                |
| v6, v7, v22             | 9               | 7                             | 7                   | 1508,1632,1622        | 6,6,8                  |
| v8, v9, v10, v23        | 3               | 3                             | 2                   | 3200,3219,3243,3199   | 6,6,6,6                |

In the first scheme, it is difficult to decide a priori which modes correlate (being coupled) to each other, so we combined the modes of the same symmetry and characterized by similar values of the Poisson parameter (Table 1). The Poisson parameter, which can be considered as a measure of activity of a vibrational mode is defined as follows:

\[
a_{i}^{\text{(sym)}} = \left( \frac{\chi_{i}^{(\text{sym})}}{\omega_{i}} \right)^{2}
\]  

for totally symmetric modes, and

\[
a_{i}^{\text{(asym)}} = \left( \frac{\lambda_{i}^{(\text{asym})}}{\omega_{i}} \right)^{2}
\]  

for non-totally symmetric modes.

The number of SPFs needed for MCTDH convergence depends on the combination scheme. The wavepacket propagation is considered converged if the natural weight of the last SPF remains below...
0.001 during the propagation [32]. The same holds for the primitive basis set, that is, the weight of the last primitive function should remain below 0.001. The parameters presented in Table 1 provide a sufficient convergence of the propagation in the case of both scenarios of mode combinations.

The propagation time amounted to 300fs in the case of both schemes. The CPU time of the calculations for both schemes is shown in Table 2. The second scheme is more time consuming as the larger number of SPFIs and primitive basis functions was used. The real computational time can be significantly reduced since the MCTDH program supports SMP- and MPI-parallelization.

### Table 2. The time of calculation for each electronic state per one processor (h:m)

|       | Scheme 1 | Scheme 2 |
|-------|----------|----------|
| $^2A_1 (n\sigma^{-1})$ | ~24:00   | ~24:00   |
| $^2A_2 (\pi^{-1})$     | ~25:00   | ~43:30   |
| $^2B_1 (\pi^{-1})$     | ~45:30   | ~43:20   |

The experimental photoionization spectrum of pyridine and the theoretical spectra corresponding to both scenarios of mode combinations are presented in Figure 2. Even though there is no universal algorithm for mode combinations, both spectral envelopes agree to each other and there is good qualitative agreement of theory and experiment.

For a more detailed comparison of the experimentally and theoretically obtained vibrational structure in the pyridine photoionization spectrum, the energy interval covering the low-energy shoulder of the first band is presented in Figure 3. From our point of view, both theoretical envelopes reproduce the structure of the experimental spectrum fairly well.

![Figure 3](image-url)

**Figure 3.** The low-energy shoulder of the $^2A_1 (n\sigma^{-1}) - ^2A_2 (\pi^{-1})$ band of the pyridine photoelectron spectrum: (a) the experimental spectrum [14]; (b) the theoretical spectrum computed using the MCTDH method with the mode combinations by similar frequency values; (c) theoretical spectrum computed using the MCTDH method; the modes are combined by symmetry and similar values of the Poisson parameter.
5. Conclusions
The three-state vibronic coupling problem for studying non-adiabatic nuclear dynamics in the manifold of three cationic states of pyridine and calculating the ionization spectrum has been solved using the MCTDH method. Two scenarios (schemes) of the computational settings differing in combinations of the vibrational modes have been considered. In the first scheme, the modes were combined into a “particle” based on assumption of their strong correlation to each other whereas the second scheme implies combination of the modes with similar vibrational frequencies. Both schemes produce spectral envelopes that agree fairly well with the high-resolution He I photoelectron spectrum of pyridine. The sufficient level of convergence is gained in both cases, however for the first scheme the smaller number of SPFs and primitive basis functions was required, and therefore less CPU time was needed. For larger systems the strategy for mode combinations according to scheme 1 would be preferable.

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References
[1] Bailey T D, Goe G L and Scriven E F V. 2008 Synthetic and Natural Sources of the Pyridine Ring pp 1–252
[2] Ataf Ali Altaf, Adnan Shahzad, Zarif Gul, Nasir Rasool, Amin Badshah B L 2015 A Review on the Medicinal Importance of Pyridine Derivatives J. Drug Des. Med. Chem. 1 1–11
[3] Chaubey A, Pandeya S N 2011 Pyridine: a versatile nucleuse in pharmaceutical field Asian J. Pharm. Clin. Res. 4 4
[4] Trofimov A B, Holland D M P, Powis I, Menzies R C, Potts A W, Karlsson L, Gromov E V., Badsyuk I L and Schirmer J 2017 Ionization of pyridine: Interplay of orbital relaxation and electron correlation J. Chem. Phys. 146 244307
[5] Trofimov A B, Skitnevsksaya A D, Grigoricheva E K, Gromov E V, Köppel H 2020 Vibronic coupling in the ground and excited states of the pyridine radical cation J. Chem. Phys. 153, 164307
[6] Reineck I, Maripuu R, Veenhuizen H, Karlsson L, Siegbahn K, Powar M S, Nian Zu W, Ming Rong J and Al-Shamma S H 1982 Vibrational structure in the valence electron spectra of pyridine and pyridine—d5 J. Electron Spectros. Relat. Phenomena 27 15–27
[7] Christiansen O, Koch H and Jørgensen P 1995 Response functions in the CC3 iterative triple excitation model J. Chem. Phys. 103 7429–41
[8] Koch H, Jensen H J A, Jørgensen P and Helgaker T 1990 Excitation energies from the coupled cluster singles and doubles linear response function (CCSDLR). Applications to Be, CH +, CO, and H 2 O J. Chem. Phys. 93 3345–50
[9] Koch H and Jørgensen P 1990 Coupled cluster response functions J. Chem. Phys. 93 3333–44
[10] Dalgaard E and Monkhorst H J 1983 Some aspects of the time-dependent coupled-cluster approach to dynamic response functions Phys. Rev. A 28 1217–22
[11] Stanton J F and Gauss J 1999 A simple scheme for the direct calculation of ionization potentials with coupled-cluster theory that exploits established excitation energy methods J. Chem. Phys. 111 8785–8
[12] Worth G A, Meyer H-D, Köppel H, Cederbaum L S and Burghardt I 2008 Using the MCTDH wavepacket propagation method to describe multimode non-adiabatic dynamics Int. Rev. Phys. Chem. 27 569–606
[13] Köppel H, Domcke W, Cederbaum L S 1984 Multimode molecular dynamics beyond the Born-Oppenheimer approximation Adv. Chem. Phys. 57 59–246
[14] Liu S-Y, Alnama K, Matsumoto J, Nishizawa K, Kohguchi H, Lee Y-P and Suzuki T 2011 He I Ultraviolet Photoelectron Spectroscopy of Benzene and Pyridine in Supersonic Molecular Beams Using Photoelectron Imaging J. Phys. Chem. A 115 2953–65

[15] Meyer H-D 2012 Studying molecular quantum dynamics with the multiconfiguration time-dependent Hartree method Wiley Interdiscip. Rev. Comput. Mol. Sci. 2 351–74

[16] Craig I R, Thoss M and Wang H 2011 Accurate quantum-mechanical rate constants for a linear response Azzouz-Borgis proton transfer model employing the multilayer multiconfiguration time-dependent Hartree approach J. Chem. Phys. 135 064504

[17] Neville S P and Worth G A 2014 A reinterpretation of the electronic spectrum of pyrrole: A quantum dynamics study J. Chem. Phys. 140 034317

[18] de Souza B, Farias G, Neese F and Izsák R 2019 Predicting Phosphorescence Rates of Light Organic Molecules Using Time-Dependent Density Functional Theory and the Path Integral Approach to Dynamics J. Chem. Theory Comput. 15 1896–904

[19] Neville S P, Mirmiran A, Worth G A and Schuurman M S 2019 Electron transfer in photoexcited pyrrole dimers J. Chem. Phys. 151 164304

[20] Manthe U 2017 Wavepacket dynamics and the multi-configurational time-dependent Hartree approach J. Phys. Condens. Matter 29 253001

[21] Fang J and Guo H 1994 Multiconfiguration time-dependent Hartree studies of the CH 3 I/MgO photodissociation dynamics J. Chem. Phys. 101 5831–40

[22] Viel A, Krawczyk R P, Manthe U and Domaček W 2004 Photoinduced dynamics of ethene in the N, V, and Z valence states: A six-dimensional nonadiabatic quantum dynamics investigation J. Chem. Phys. 120 11000–10

[23] Meyer H-D and Worth G A 2003 Quantum molecular dynamics: propagating wavepackets and density operators using the multiconfiguration time-dependent Hartree method Theor. Chem. Acc. 109 251–67

[24] Viel A, Eisfeld W, Neumann S, Domaček W and Manthe U 2006 Photoionization-induced dynamics of ammonia: Ab initio potential energy surfaces and time-dependent wave packet calculations for the ammonia cation J. Chem. Phys. 124 214306

[25] Teixidor M M and Huarte-Larrañaga F 2012 Methane dissociation on Ni(111): Reaction probabilities using direct and initial state selected approaches Chem. Phys. 399 264–71

[26] Gatti F, Lasorne B, Meyer H-D and Nauts A 2017 Applications of Quantum Dynamics in Chemistry vol 98 (Cham: Springer International Publishing)

[27] Domaček W, Yarkony D R and Köppel H 2004 Conical Intersections vol 15 (WORLD SCIENTIFIC)

[28] Worth G A and Cederbaum L S 2004 BEYOND BORN-OPPENHEIMER: Molecular Dynamics Through a Conical Intersection Annu. Rev. Phys. Chem. 55 127–58

[29] Raab A, Worth G A, Meyer H-D and Cederbaum L S 1999 Molecular dynamics of pyrazine after excitation to the S2 electronic state using a realistic 24-mode model Hamiltonian J. Chem. Phys. 110 936–46

[30] Frisch M J, Trucks G W, Schlegel H B, Scuseria G E, Robb M A, Cheeseman J R, Scalmani G, Barone V, Mennucci B, Petersson G A, et al 2010 Gaussian 09, Revision C.01, Gaussian, Inc., Wallingford CT

[31] CFOUR, Coupled cluster techniques for Computational Chemistry, a quantumchemical program package by Stanton J F, Gauss J, Harding M E, and Szalay P G, with contributions from Auer A A, Bartlett R J, Benedikt U, Berger C, Bernholdt D E, Bomble Y J, Cheng L, Christiansen O, Heckert M, Heun O, et al and the integral packages MOLECULE (Almlöf J and Taylor P R), PROPS (Taylor P R), ABACUS (Helgaker T, Jensen H J Aa, Jørgensen P, and Olsen J), and ECP routines by Mitin A V and van Wüllen C. For the current version, see http://www.cfour.de

[32] Meyer H, Gatti F and Worth G A 2009 Multidimensional Quantum Dynamics (Wiley)