Simulating Photodissociation of High-Dimensional Systems Using Multiconfiguration Time-Dependent Hartree Method

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Kemijski seminar 1

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Introduction

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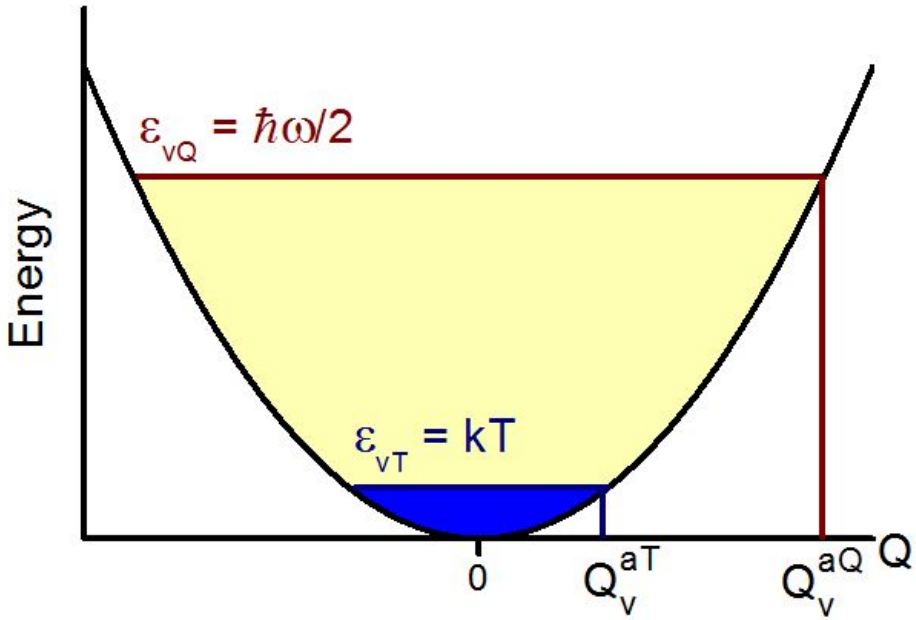

$T = 300$ K; $\omega = 1600$ cm^{-1}

Int. J. of Quantum Chemistry, **116** (2016) 762–771.

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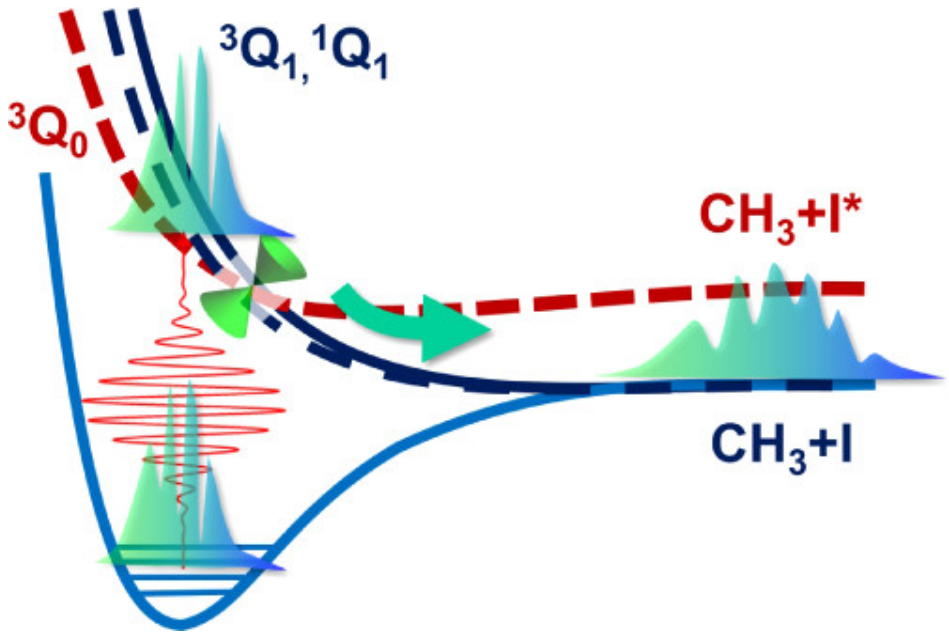
- number of Hartree products grows exponentially: 9 DOF, 32 basis functions per mode - 3.5×10^{13} Hartree products

Photodissociation



J. Chem. Theory Comput. 2025, **21**, 15, 7267–7278

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- time-dependent basis functions allow efficient truncation of the basis set

$$\Psi^{(s)}(Q_1, ..., Q_m, t) = \sum_{j_1,...,j_m} A^{(s)}_{j_1,...,j_m}(t) \prod_{\kappa=1}^{m} \phi^{(\kappa,s)}_{j_\kappa}(Q_\kappa, t)$$
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- to make the propagation uniquely defined:

$$\left\langle \phi^{(\kappa)}_j(0) \middle| \phi^{(\kappa)}_l(0) \right\rangle = \delta_{jl}$$
$$\langle \phi_j(t) | \partial_t \phi_l(t) \rangle = 0$$

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$$i\partial_t A_J^{(s)} = \sum_{s',L} \left\langle \Phi_J^{(s)} \middle| H^{(ss')} \middle| \Phi_L^{(s')} \right\rangle A_L^{(s')}$$

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$$\left\langle H^{(ss')} \right\rangle_{ab}^{(\kappa)} = \sum_{j_1} \cdots \sum_{j_{\kappa-1}} \sum_{j_{\kappa+1}} \cdots \sum_{j_m} A^{(s)*}_{j_1 \ldots j_{\kappa-1} a j_{\kappa+1} \ldots j_m} A^{(s')}_{j_1 \ldots j_{\kappa-1} b j_{\kappa+1} \ldots j_m}$$

$$\left\langle \phi_{j_1}^{(s,1)} \ldots \phi_{j_{\kappa-1}}^{(s,\kappa-1)} \phi_{j_{\kappa+1}}^{(s,\kappa+1)} \ldots \phi_{j_m}^{(s,m)} \middle| H^{(ss')} \middle| \phi_{j_1}^{(s',1)} \ldots \phi_{j_{\kappa-1}}^{(s',\kappa-1)} \phi_{j_{\kappa+1}}^{(s',\kappa+1)} \ldots \phi_{j_m}^{(s',m)} \right\rangle$$

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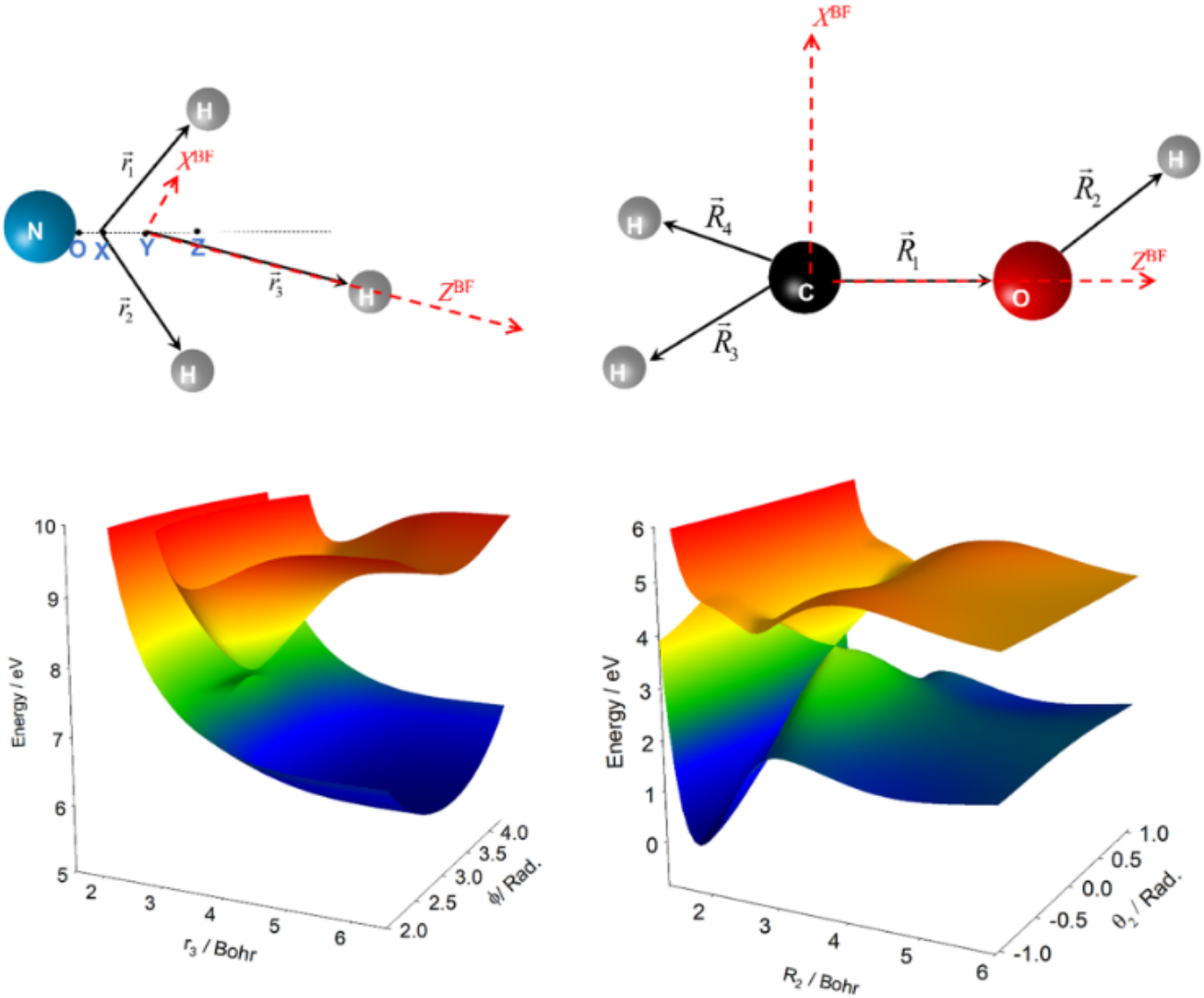
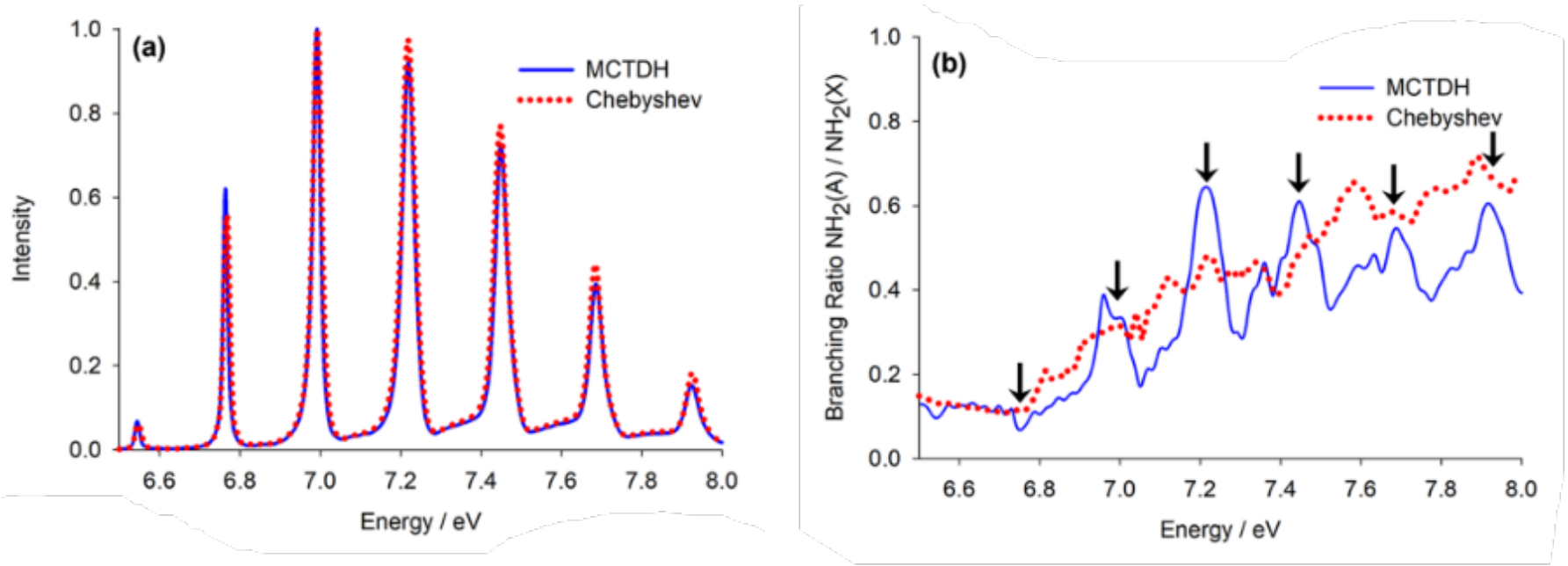
- MCCPD transforms V_{11}, V_{12} and V_{22} into a sum of products form
- Monte Carlo integrals to avoid exact numerical integration during the transformation to SOP form

Simulated Systems



source: J. Chem. Theory Comput. 2022, 18, 4627-4638

Ammonia



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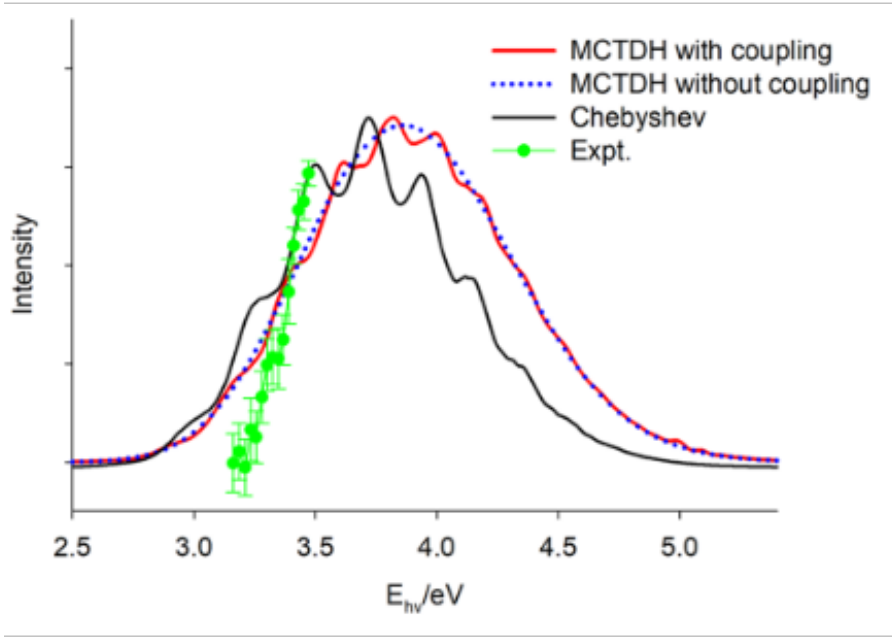
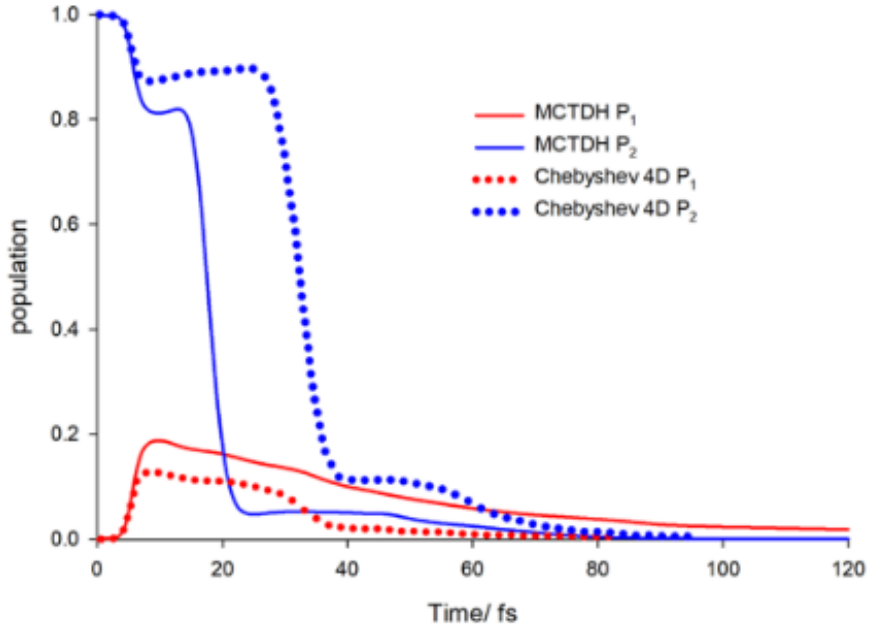
Hydroxymethyl Radical





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Conclusion

- time dependent basis functions enable quantum dynamics simulations of high dimensional systems
- long lived resonances and chaotic dynamics NH_3 remain a challenge for MCTDH
- full dimensional simulation of hydroxymethyl radical validate previous 4D model

Literature

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3. S. Han, M. Schröder, F. Gatti, H.-D. Meyer, D. Lauvergnat, D. R. Yarkony, H. Guo, *J. Chem. Theory Comput.*, **18** (2022) 4627–4638.