

Multiconfiguration time-dependent Hartree (MCTDH): An efficient method for propagating wavepackets in several dimensions.

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Abstract

The multiconfiguration time-dependent Hartree (MCTDH) method [1–7] is an algorithm for propagating multi-dimensional wavepackets. This algorithm is briefly introduced and its efficiency is explained. In short, the efficiency originates from using an variationally optimized time-dependent basis set. To achieve the full efficiency, however, the Hamiltonian must be given as a sum of products of one-dimensional operators.

The efficiency of MCTDH is best demonstrated through the calculations on the absorption spectrum of pyrazine [4, 5]. There the correlated motion of all the 24 modes evolving on two coupled electronic surfaces is treated with high accuracy. To emphasize the very large gain obtained here we note that the underlying primitive basis consists of 10^{21} points, whereas there are only 3.8×10^6 configurations are needed for convergence.

Calculations on the reactive scattering process $H + D_2 \rightarrow HD + D$ [6, 7], on the other hand, demonstrate that MCTDH can be competitive even for rather small systems. The LSTH interaction potential was expanded to assume the required product form. (A special algorithm was developed to do so [8]).

MCTDH has been applied to a wide range of molecular processes, including photodissociation, surface scattering, reactive scattering and the computation of vibrational spectra. Recently MCTDH has been used to study the well known spin-boson model [9]. Here it was possible to account for 80 vibrational modes. Further information, a list of references, etc, can be found on the MCTDH home page: <http://www.pci.uni-heidelberg.de/tc/usr/mctdh/>

References

- [1] H.-D. Meyer, U. Manthe, and L. S. Cederbaum, Chem. Phys. Lett. **165**, 73 (1990).
- [2] U. Manthe, H.-D. Meyer, and L. S. Cederbaum, J. Chem. Phys. **97**, 3199 (1992).
- [3] M. H. Beck, A. Jäckle, G. A. Worth, and H.-D. Meyer, Phys. Rep. **324**, 1 (2000).
- [4] G. A. Worth, H.-D. Meyer, and L. S. Cederbaum, J. Chem. Phys. **109**, 3518 (1998).
- [5] A. Raab, G. Worth, H.-D. Meyer, and L. S. Cederbaum, J. Chem. Phys. **110**, 936 (1999).
- [6] A. Jäckle, M.-C. Heitz, and H.-D. Meyer, J. Chem. Phys. **110**, 241 (1999).
- [7] S. Sukiasyan and H.-D. Meyer, J. Phys. Chem. A **105**, 2604 (2001).
- [8] A. Jäckle and H.-D. Meyer, J. Chem. Phys. **109**, 3772 (1998).
- [9] H. Wang, J. Chem. Phys. **113**, 9948 (2000).