

Contents

Acknowledgements	i
Abstract	iii
Résumé	v
List of Figures	ix
List of Tables	xiii
List of Acronyms	xv
Chapter 1 Introduction	1
1.1 Overview	1
1.2 Time-dependent picture of linear spectroscopy	3
1.3 Multi-trajectory semiclassical methods	7
1.3.1 Dephasing representation of quantum fidelity	8
1.4 Thawed Gaussian approximation	10
1.5 On-the-fly scheme	13
1.5.1 On-the-fly <i>ab initio</i> thawed Gaussian wave packet dynamics	14
Chapter 2 Accelerating calculations of ultrafast time-resolved electronic spectra with efficient quantum dynamics methods	19
2.1 Abstract	19
2.2 Introduction	20
2.3 Finding a minimum set of sufficiently accurate electronic surfaces	21
2.4 Accelerating quantum dynamics with high order split operator methods	22
2.5 Semiclassical dynamics for time-resolved spectroscopy	24
2.6 Results and discussion	26
2.6.1 The system	26
2.6.2 Efficiency of various split-operator methods	27
2.6.3 Time-resolved spectra and correlation functions	29
2.7 Conclusion	31
Chapter 3 On-the-fly <i>ab initio</i> semiclassical dynamics: Identifying degrees of freedom essential for emission spectra of oligothiophenes	33
3.1 Abstract	33
3.2 Introduction	34
3.3 Theory	36
3.3.1 Emission spectrum calculation	36

...

3.3.2	Stability matrix propagation: Symplecticity and effect of Hessian interpolation	36
3.3.3	Identification of the essential DOFs	39
3.3.4	TGA in subspaces of reduced dimensionality	42
3.4	Computational details	44
3.5	Results and discussion	45
3.5.1	Comparison with experimental spectra	45
3.5.2	Vibrational analysis	49
3.5.3	Quinoid structure of S1	53
3.5.4	Analysis of the effective conjugation coordinate	54
3.5.5	Time dependence of the width matrix of the OTF-AI-TGA GWP	57
3.5.6	Comparison of the OTF-AI-TGA approach to the global harmonic approximation	57
3.6	Conclusion	59
Chapter 4 On-the-fly ab initio semiclassical dynamics of floppy molecules: Absorption and photoelectron spectra of ammonia		61
4.1	Abstract	61
4.2	Introduction	62
4.3	Theory	64
4.3.1	Absorption and photoelectron spectra calculations	64
4.3.2	Global harmonic potential construction	64
4.3.3	Derivation of the TGA Gaussian wave packet energy	65
4.4	Computational Methods	67
4.5	Results and discussion	68
4.5.1	Absorption spectrum	68
4.5.2	Photoelectron spectrum	69
4.6	Conclusion	71
Chapter 5 Influence of decoupling a thawed Gaussian wave packet dynamics on spectrum calculations		73
5.1	Abstract	73
5.2	Introduction	74
5.3	Theory	75
5.3.1	Spectrum calculation	75
5.3.2	Harmonic model	76
5.3.3	Construction of the information flow matrix B	78
5.4	Computational details	79
5.5	Results and discussion	80
5.5.1	Effect of fully decoupled harmonic models on the spectrum	80
5.5.2	Effect of consecutive decoupling on the spectrum	81
5.6	Conclusions	88
Chapter 6 Conclusion and outlook		91
Chapter 7 Bibliography		95