

Contents

1	Introduction	1
2	Classical mechanics	9
2.1	Specifying the initial parameters	9
2.2	The Monte Carlo method	10
2.3	The equations of motion	10
2.4	Initial conditions	12
2.5	The calculation of a single trajectory	13
2.6	Product analysis	14
2.7	Calculation of the reaction probability	16
2.8	Reaction cross section	16
2.9	Nonadiabatic multi-surface classical mechanics	16
3	Quantum mechanics	19
3.1	The wavepacket propagation	19
3.2	Time evolution	20
3.3	The A–BC system	21
3.3.1	Jacobi coordinates	21
3.3.2	Space-fixed and body-fixed Jacobi coordinates	22
3.4	The Hamiltonian of the 3-atomic system	23
3.4.1	The kinetic energy terms	24
3.4.2	The angular kinetic energy terms	24
3.4.3	The potential energy	25
3.5	Preparation of the initial wavepacket	25
3.6	Analysis of the propagated wavepacket	26
3.6.1	The flux analysis method	26
3.7	The cross section	27
4	H_3^+ and H_3^- PES	29
4.1	The H_3^+ potential energy surface	29
4.2	H_3^- PES	30
5	Results	37
5.1	$H^+ + H_2(v, j)$	37
5.1.1	Non-Born-Oppenheimer investigations	37
5.1.2	Reaction probabilities	37
5.1.3	The surface hopping analysis	42
5.2	$H^- + H_2(v, j)$	50
5.2.1	Quasi-classical trajectory investigations	50
5.2.2	Wave packet calculations for $H^- + H_2(v, j) \rightarrow H_2(v', j') + H^-$	58

5.3	$H^- + D_2(v, j)$	66
5.3.1	Quasi-classical trajectory calculations	66
5.3.2	Wave packet calculations for $H^- + D_2(v, j) \rightarrow HD(v', j') + D^-$	76
5.4	$D^- + H_2(v, j)$	82
5.4.1	Quasi-classical trajectory investigations	82
5.4.2	Wave packet calculations for $D^- + H_2(v, j) \rightarrow HD(v', j') + H^-$	88
5.5	$D^- + D_2(v, j)$	93
5.5.1	Quasi-classical trajectory investigations	93
5.5.2	Wave packet calculations for $D^- + D_2(v, j) \rightarrow D_2(v', j') + D^-$	99
5.6	$H^- + HD(v, j)$ and $D^- + HD(v, j)$	104
5.6.1	Reaction probabilities for the collision of D^- and H^- with $HD(v=0-1, j=0)$	104
5.6.2	Reaction cross sections for the collisions of D^- and H^- ions with $HD(v=0-1, j=0)$	107
6	Appendix	110
6.1	Associated Legendre functions	110
6.2	Legendre polynomial	110
6.3	Fortran code for calculation of turning point and vibrational period of a diatomic molecule	110