

Hiroki Nakamura
Gennady Mil'nikov

$$V = \frac{Q}{4\pi\epsilon} \sum \frac{k_n}{r^n}$$

Quantum Mechanical Tunneling in Chemical Physics

CRC Press
Taylor & Francis Group
6000 Broken Sound Parkway NW, Suite 300
Boca Raton, FL 33487-2742

© 2013 by Taylor & Francis Group, LLC
CRC Press is an imprint of Taylor & Francis Group, an Informa business

No claim to original U.S. Government works

Printed on acid-free paper
Version Date: 20121218

International Standard Book Number: 978-1-4665-0731-9 (Hardback)

This book contains information obtained from authentic and highly regarded sources. Reasonable efforts have been made to publish reliable data and information, but the author and publisher cannot assume responsibility for the validity of all materials or the consequences of their use. The authors and publishers have attempted to trace the copyright holders of all material reproduced in this publication and apologize to copyright holders if permission to publish in this form has not been obtained. If any copyright material has not been acknowledged please write and let us know so we may rectify in any future reprint.

Except as permitted under U.S. Copyright Law, no part of this book may be reprinted, reproduced, transmitted, or utilized in any form by any electronic, mechanical, or other means, now known or hereafter invented, including photocopying, microfilming, and recording, or in any information storage or retrieval system, without written permission from the publishers.

For permission to photocopy or use material electronically from this work, please access www.copyright.com (<http://www.copyright.com/>) or contact the Copyright Clearance Center, Inc. (CCC), 222 Rosewood Drive, Danvers, MA 01923, 978-750-8400. CCC is a not-for-profit organization that provides licenses and registration for a variety of users. For organizations that have been granted a photocopy license by the CCC, a separate system of payment has been arranged.

Trademark Notice: Product or corporate names may be trademarks or registered trademarks, and are used only for identification and explanation without intent to infringe.

Library of Congress Cataloging-in-Publication Data

Nakamura, Hiroki.

Quantum mechanical tunneling in chemical physics / Hiroki Nakamura, Institute of Molecular Science, National Chiao Tung University ... Taiwan, and Institute for Molecular Science, National Institutes of Natural Sciences, Okazaki, Japan, Gennady Mil'nikov, Faculty of Electrical, Electronic and Informatics Engineering, Osaka University ... Japan.

pages cm

Includes bibliographical references and index.

ISBN 978-1-4665-0731-9 (hardback)

1. Tunneling (Physics) I. Title.

QC176.8.T8N34 2013

537.6'226--dc23

2012047936

Visit the Taylor & Francis Web site at
<http://www.taylorandfrancis.com>

and the CRC Press Web site at
<http://www.crcpress.com>

Contents

Preface	ix
Chapter 1 Introduction	1
Chapter 2 One-Dimensional Theory	5
2.1 Exactly Solvable Cases	5
2.1.1 Case of Delta-Function Barrier	5
2.1.2 Case of Parabolic Potential Barrier	6
2.1.3 Case of Eckart Potential Barrier	8
2.2 WKB Approximation and Connection Formula	10
2.3 Comparison Equation Method	11
2.4 Diagrammatic Technique	13
2.5 Instanton Theory and Modified WKB Method	16
2.5.1 Instanton Theory	16
2.5.2 Modified WKB Method	24
2.6 Energy Levels in a Double Well Potential	26
2.6.1 Asymmetric Double Well Potential	26
2.6.2 Symmetric Double Well Potential	28
2.7 Decay of Metastable State	29
Chapter 3 Two-Dimensional Theory	33
3.1 WKB Theory	33
3.2 Instanton Theory	40
Chapter 4 Multidimensional Effects: Peculiar Phenomena	43
4.1 Effects of Vibrational Excitation on Tunneling Splitting	43
4.1.1 Adiabatic and Sudden Approximations	43
4.1.2 Case of Symmetric Mode Coupling Potential	44
4.1.3 Case of Antisymmetric Mode Coupling Potential	49
4.1.4 Case of Squeezed (Sqz) Double Well Potential	50
4.2 Insufficiency of Two-Dimensional Model	54
4.3 Proton Tunneling in Tropolone	54
4.3.1 Available Experimental Data	54
4.3.2 Tunneling Dynamics in the Ground \tilde{X} State	56
4.3.3 Analysis of Tunneling Dynamics of the Excited \tilde{A} State.	59
Chapter 5 Nonadiabatic Tunneling	61
5.1 Definition and Qualitative Explanation	61
5.2 One-Dimensional Theory	64
5.2.1 Case of $E \leq E_t$	67
5.2.2 Case of $E_t \leq E \leq E_b$	68
5.2.3 Case of $E_b \leq E$	68

Chapter 6	Multidimensional Theory of Tunneling Splitting	75
6.1	General Formulation	75
6.1.1	Multidimensional Extension of the Instanton Theory	75
6.1.2	WKB Approach in Cartesian Coordinates	82
6.1.3	WKB Approach in the Case of General Hamiltonian in Curved Space	85
6.2	How to Find Instanton Trajectory	89
6.3	How to Use the Theory	92
6.3.1	Evaluation of the Pre-Exponential Factor	92
6.3.2	Incorporation of High Level of <i>ab initio</i> Quantum Chemical Calculations	95
6.4	Case of Low Vibrationally Excited States	96
6.4.1	One- and Two-Dimensional Cases	96
6.4.2	Multidimensional Case in Terms of Cartesian Coordinates	99
6.4.3	Case of General Multidimensional Curved Space	103
Chapter 7	Numerical Applications to Polyatomic Molecules	109
7.1	<i>N</i> -Dimensional Separable Potential Model	109
7.2	Hydroperoxy Radical HO ₂	111
7.3	Vinyl Radical C ₂ H ₃	120
7.4	Malonaldehyde C ₃ O ₂ H ₄	128
7.5	Formic Acid Dimer (DCOOH) ₂	139
Chapter 8	Decay of Metastable States	149
8.1	General Formulation	149
8.1.1	Determination of Instanton Trajectory	149
8.1.2	Formulation in Terms of Cartesian Coordinates	151
8.1.3	General Canonically Invariant Formulation	154
8.2	Numerical Application	158
Chapter 9	Tunneling in Chemical Reactions	163
9.1	Determination of Caustics and Propagation in Tunneling Region	163
9.1.1	Caustics in Chaotic Henon-Heiles System	166
9.1.2	Caustics in Chemical Reaction Dynamics	167
9.2	Direct Evaluation of Reaction Rate Constant	174
9.2.1	Adiabatic Chemical Reaction	174
9.2.2	Nonadiabatic Chemical Reaction	178
Chapter 10	Concluding Remarks and Future Perspectives	183

Appendix A	Proofs of Equation (2.95) and Equation (2.110)	185
Appendix B	Derivation of Equation (6.80)	187
Appendix C	Herring Formula in Curved Space	189
Appendix D	Derivation of Equation (6.97)	191
Appendix E	Computer Code to Calculate Instanton Trajectory	193
Appendix F	Derivation of Some Equations in Section 6.4.2	201
Bibliography	205
Index	213