# Quantum Mechanics of the Diatomic Molecule (Second Edition)

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**IOP Series in Coherent Sources, Quantum Fundamentals, and Applications**

**About the Editor**

F J Duarte is a laser physicist based in Western New York, USA. His career has covered three continents while contributing within the academic, industrial, and defense sectors. Duarte is editor/author of 15 laser optics books and sole author of three books: *Tunable Laser Optics, Quantum Optics for Engineers*, and *Fundamentals of Quantum Entanglement*. Duarte has made original contributions in the fields of coherent imaging, directed energy, high-power tunable lasers, laser metrology, liquid and solid-state organic gain media, narrow-linewidth tunable laser oscillators, organic semiconductor coherent emission, *N*-slit quantum interferometry, polarization rotation, quantum entanglement, and space-to-space secure interferometric communications. He is also the author of the generalized multiple-prism grating dispersion theory and pioneered the use of Dirac's quantum notation in *N*-slit interferometry and classical optics. His contributions have found applications in numerous fields, including astronomical instrumentation, dispersive optics, femtosecond laser microscopy, geodesics, gravitational lensing, heat transfer, laser isotope separation, laser medicine, laser pulse compression, laser spectroscopy, mathematical transforms, nonlinear optics, polarization optics, and tunable diode-laser design. Duarte was elected Fellow of the Australian Institute of Physics in 1987 and Fellow of the Optical Society of America in 1993. He has received various recognitions, including the *Paul F Foreman Engineering Excellence Award* and the *David Richardson Medal* from the Optical Society.

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**Christian G Parigger**
*Former address:*
*Physics and Astronomy Department, University of Tennessee, University of Tennessee Space Institute, Center for Laser Applications, Tullahoma, TN, USA*

*Current address:*
*CGP Consulting, Manchester, TN, USA*

**James O Hornkohl**
*Hornkohl Consulting, Tullahoma, TN, USA*

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*To John, Anna, and Melissa*

*To Justin, Jason, and Jola*

# Contents

# Preface

## 0.1 First edition

The book notes from J O Hornkohl and extensive scientific discussions and research engagements in my work at the University of Tennessee Space Institute, Center for Laser Applications, motivate completion of this ebook. Communication exchanges occurred since the spring of 1987, and continued regularly until winter 2017 [1]. Over the years, several colleagues and postgraduate MSc and PhD students have contributed to applications of fundamental insights in the physics of the diatomic molecule. Thanks go to David Plemmons, Guoming Guan, Ying-Ling Chen, Wenhong Qin, Ivan Dors, Alexander Woods, David Surmick, Michael Witte, Ghaneshwar Gautam, and Christopher Helstern.

Significant emphasis has been placed on the application of the diatomic spectroscopy predictions in analysis of experimental data. For this reason, this ebook includes several chapters on applications in studies of diatomic molecules, especially important molecules such as cyanide (CN), aluminum monoxide (AlO), diatomic carbon ($C_2$), titanium monoxide (TiO), hydroxyl (OH), but also selected work on other diatomic molecules.

This text introduces insights that are essential in utilizing the inherent symmetries associated with diatomic molecules. Consequently, line positions and strengths associated with transitions from lower and upper state-manifolds are determined without invoking approximations that separate vibrations and rotations of diatomic nuclei from electron motion based on mass. The approach utilized in this work makes use of the separation of angular coordinates from electronic vibrational coordinates. Consequently, the volley of selection rules for diatomic spectroscopy is no longer required, including methodologies that rely on so-called reversed angular momentum techniques.

This work summarizes well over 30 years of quantitative analysis of temporally and spatially resolved experimental records, almost all of the experiments discussed in this ebook were conducted at the Center for Laser Applications (CLA) at the University of Tennessee Space Institute. Applications include understanding on nonequilibrium fluid and plasma physics and interpretation of stellar astrophysics spectra. In several cases of laser-induced plasma investigations, both atomic and molecular signatures or superposed spectral characteristics from molecules and atoms can be identified. Analysis of such superposition spectra requires accurate knowledge of wavelength positions and transition strengths. The revival and replacement of electrical-spark spectroscopy with laser-spark or laser-plasma spectroscopy for quantitative elemental composition analysis since the mid-1990s, viz. laser-induced breakdown spectroscopy (LIBS), extends into increased interests in molecular LIBS since (give-or-take) the mid-2000s. From an analytical and practical point of view, the requirements can be reduced to the availability of a set of diatomic line-strengths in tabular form along with programs that are designed to appropriately read the records. However, this ebook provides a reasonable account

of the quantum mechanics of the diatomic molecule, along with selected applications that were important for motivating a consistent approach and for analyzing recorded data sets from various experiments in the CLA laboratories.

The challenge of this work has been the prediction of spectra with a focus on diatomic spectroscopy. The aim of the lifetime work of Jim Hornkohl is the design of an algorithm to predict and fit computed and measured molecular spectra to provide inferences on parameters such as excitation temperature. The means to accomplish goals for various diatomic molecules are the consistent application of standard quantum theory of angular momentum. During his career, Jim engaged in efforts to overcome techniques such as Van Vleck's reversed angular momentum approach based on angular momentum commutators. The apparent difficulties included the battles with the established practice to predict and compute spectra and design programs despite the mathematical inconsistencies associated with the reversed angular momentum practice. The experimental investigations, and again the stimulating discussions, motivated refinements such as enlarging the data sets for the CN, $C_2$, or TiO diatomic molecules. In turn, the discussed applications in this book are intended to alleviate analysis of diatomic spectra composed of superpositions of a significant amount of transition lines within typical resolution for laser-plasma emission spectroscopy, to name but one example.

Christian Parigger
August 2019

## 0.2 Second edition

The second edition includes 10 additional chapters, one on the fundamentals and nine on the applications parts. Three additional appendices are included, namely: communication of NMT and BESP scripts for computation of diatomic spectra, Abel inversion scripts with one specific example, and an appendix on select recent publications that include C.G.P. as author. The additions primarily address communication of spatial profiles analyses, including Abel inversion and communication of scripts for diatomic spectroscopy and Abel inversions. However, comparisons with other existing databases clearly reveal the significance of the line strengths for the selected electronic transitions of diatomic molecules. The comparisons also include a section of $C_2$ laser-induced fluorescence. The existing databases comparisons include PGOPHER, LIFBASE, and ExoMol databases that are compared with line-strength data of diatomic molecules of interest, particularly for laser-induced plasma that is generated in gases and gas mixtures.

- New chapter 2 addresses the foundations of quantum mechanics and the mathematical implementation of specific symmetries. Application of the correspondence principle, relating classical and quantum mechanics, leads to the occurrence of the infamous sign-reversal. This chapter addresses formal treatment of symmetries in quantum mechanics. Quantum theory contra-indicates sign changes of the fundamental angular momentum algebra.

Reversed angular momentum sign changes are of a heuristic nature and are actually undesirable in the analysis of diatomic spectra.

- New chapter 15 communicates line-strength data and associated scripts for the computation and spectroscopic fitting of selected transitions of diatomic molecules. The scripts for data analysis are designed for inclusion in various software packages or program languages. Selected results demonstrate the applicability of the program for data analysis in laser-induced optical breakdown spectroscopy, primarily at the University of Tennessee Space Institute, Center for Laser Applications. Representative spectra are calculated and referenced to measured data records. Comparisons of experiment data with predictions from other tabulated diatomic molecular databases confirm the accuracy of the communicated line-strength data.
- New chapter 17 discusses cavity ring-down spectroscopy of methylidyne in a chemiluminescent plasma that is produced in a microwave cavity. Of interest are the rotational lines of selected vibrational transitions for the A–X and B–X bands. This chapter also includes recent analysis that shows excellent agreement of measured and computed data, and it communicates CH line-strength data. The CH radical is an important diatomic molecule in hydrocarbon combustion diagnosis and analysis of stellar plasma emissions, to name just two examples for analytical plasma chemistry.
- New chapter 19 discusses diatomic molecular spectroscopy of laser-induced plasma and analysis of data records, specifically signatures of cyanide (CN). Line-strength data from various databases are compared for simulation of the cyanide spectra. Of interest are recent predictions using an astrophysical database, i.e., ExoMol, a laser-induced fluorescence database, i.e., LIFBASE, and a program for simulating rotational, vibrational, and electronic spectra, i.e., PGOPHER.
- New chapter 21 presents analysis of carbon Swan bands laser-plasma emission records using line-strength data and the ExoMol database. The temperature inferences are elaborated when using nonlinear fitting with both databases. The line-strength data are also utilized for analysis of laser-induced fluorescence experiments that employ a spectral resolution of the order of 5 pm. Accurate diatomic carbon databases show many applications in laboratory diagnosis and interpretation of astrophysical plasma records.
- New chapter 23 elaborates on analysis of aluminum monoxide (AlO), laser-plasma emission records using line-strength data, and the ExoMol astrophysical database. A nonlinear fitting program computes comparisons of measured and simulated diatomic molecular spectra. This work also presents a comparison of the AlO line strength and of ExoMol data for the AlO diatomic molecule. Accurate AlO databases show a volley of applications in laboratory and astrophysical plasma diagnosis.
- New chapter 25 applies NMT and BESP scripts for the fitting of recorded experimental hydroxyl data. The fitting program also incorporates a slight, overall wavelength offset. The ExoMol and line-strength data yield close to identical temperature with a slightly different linear background.

The databases for specific hydroxyl transition yield similar predictions of the recorded laser-plasma spectra for time delays of the order of one hundred microseconds after optical breakdown initiation.

- New chapter 26 communicates measurement and analysis of diatomic molecular hydroxyl spectra after generation of laser-induced plasma, and it also shows details of the expanding plasma including associations of shadowgraphs with spectroscopy. Formation of OH is clearly discernible at time delays of several dozen microseconds after plasma initiation. Optical emissions are dispersed by a Czerny–Turner spectrometer and an intensified charge-coupled device records the data along the wavelength and slit dimensions.
- New chapter 29 combines time-resolved emission spectroscopy with Abel integral inversion techniques to obtain radial electron density values in laser-induced plasma. This chapter also includes details of the Abel transforms Hydrogen beta line profiles are recorded following optical breakdown in ultra-high-pure hydrogen gas. Asymmetric Abel inversion techniques are utilized in the analysis of collected, time-resolved data. The averaged, line-of-sight electron densities are found to be in of the order of one hundredth of an amagat for time delays close to one-half microseconds. The electron densities indicate variations across the laser-induced plasma.
- New chapter 30 elucidates the connection of measured shadowgraphs from optically induced air breakdown with emission spectroscopy in selected gas mixtures. Spectroscopic analysis explores well-above hypersonic expansion dynamics using primarily diatomic molecule cyanide and atomic hydrogen emission spectroscopy. Analysis of the air breakdown and selected gas breakdown events permits the use of Abel inversion for inference of the expanding species distribution. Typically, species are prevalent at higher density near the hypersonically expanding shock wave, measured by tracing cyanide and a specific carbon atomic line.
- New appendix J presents NMT and BESP MATLAB-scripts for computation of diatomic spectra.
- New appendix K presents Abel inversion MATLAB-scripts with one specific example.
- New appendix L summarizes select recent publications that include C.G.P. as author.

Christian Parigger
February 2024

## Reference

[1] Parigger C G and Nemes L 2017 *Int. J. Mol. Theor. Phys.* **1** 00105

# Acknowledgements

CGP and JOH appreciate the support by the Center for Laser Applications (CLA) at the University of Tennessee Space Institute during over 30 years of research engagement in spectroscopy. The research led to this book and its second edition that describe how quantum mechanics can be used to predict diatomic molecule spectra. The book and its second edition provide a comprehensive overview on diatomic molecule fundamentals and emphasize the applications of spectroscopy predictions in analysis of experimental data. Both CGP and JOH are happy to report interests and contributions by postgraduate students. Moreover, CGP is delighted about publication of the first and second editions in memoriam to JOH, a long time collaborator in analysis of laser-induced plasma spectra recorded at the CLA. Last but not least, CGP thanks researchers and colleagues at the CLA and international collaborators throughout the world for extensive discussions and motivation towards completion of both book editions.

# Author biographies

## Christian G. Parigger

Christian G. Parigger (Courtesy UTSI photo albums: L Horton.)

The research interests of Dr Christian Parigger include fundamental and applied spectroscopy, nonlinear optics, quantum optics, ultrafast phenomena, ultrasensitive diagnostics, lasers, combustion and plasma physics, optical diagnostics, biomedical applications, and, in general, atomic and molecular and optical physics. His Mag. rer. nat. degree shows work on optical bistability at the University of Innsbruck, Austria, with guidance by Dr Peter Zoller. His PhD degree studies are on the subject of polarization spectroscopy and magnetically induced switching at the University of Otago, Dunedin, New Zealand, with guidance by Drs Wes Sandle and Rob Ballagh. He also holds the Dr rer. nat. degree in Physics from the University of Innsbruck, Austria. Since 1987, his work encompasses experimental, theoretical and computational research, together with teaching, service, and outreach at the Center for Laser Applications at The University of Tennessee Space Institute, Tullahoma, Tennessee, USA.

## James O and Jeri Hornkohl

James O and Jeri Hornkohl (Courtesy UTSI photo albums: L Horton.)

The contributions of James Hornkohl, or 'Jim', encompass the spectroscopy of diatomic molecules, and the application of such spectroscopy in diagnosis of combustion, plasmas, rocket propulsion, and related problems. His support of student theses and dissertations has been especially significant, including the application of numerical methods in analysis of experiments. Moreover, his help has been greatly appreciated by his collaborators in the design of computational and experimental methods to record digital data. During the last 30 years prior to his death on February 7, 2017, Jim had been strongly engaged in the description of the very details on diatomic spectroscopy. The challenge to Jim's work has been the prediction of spectra with a focus on diatomic spectroscopy. The aim of his lifetime work was the design of an algorithm for the prediction and fitting of computed to measured molecular spectra and to provide inferences of parameters such as excitation temperature. The means to accomplish goals for various transitions of diatomic molecules are the consistent application of standard quantum theory of angular momentum.