## Contents

*Preface*  
page xi  
1 Molecular Rydberg states  
1.1 The nature of Rydberg states  
1.2 Organization of the text  
2 The quantum defect picture  
2.1 Introduction  
2.2 Coulomb wavefunctions  
2.3 Single-channel quantization  
2.4 Coupled channels  
3 *Ab-initio* quantum defects  
3.1 Traditional quantum chemistry  
3.2 Constrained *ab-initio* wavefunctions  
3.3 The R-matrix matching procedure  
3.4 The Wigner–Eisbud R-matrix  
3.5 Variational R-matrix theory  
3.6 Rydberg–valence interactions  
3.7 The influence of positive ion dipoles  
4 Frame transformations and channel interactions  
4.1 Physical assumptions  
4.2 Rotational channel interactions  
4.3 Vibrational channel interactions  
4.4 Vibronic channel interactions  
5 Competitive fragmentation  
5.1 Perturbation model for diatomic species  
5.2 Diatomic predissociation
## Contents

5.3 Dissociative recombination and related phenomena 130  
5.4 R-matrix formulation 140  
5.5 Vibronically induced dissociative recombination of $\text{H}_3^+$ 148  

6 Photo-excitation 157  
6.1 Introduction 157  
6.2 $n$-photon discrete absorption 158  
6.3 Spherical tensor representation 163  
6.4 Spatial selectivity 167  
6.5 Resonant two-photon excitation 170  
6.6 Multiphoton band structure 171  
6.7 Angular momentum decoupling in high Rydberg states 177  
6.8 ZEKE intensities 183  

7 Photo-ionization 191  
7.1 Boundary conditions and cross-sections 192  
7.2 The photo-ionization matrix element 195  
7.3 Integrated cross-section 199  
7.4 Differential cross-section 202  
7.5 Fixed molecule angular distribution 215  
7.6 Resonant two-photon ionization 219  
7.7 Orientation and alignment 226  
7.8 Spin polarization 232  

8 Manipulating Rydberg states 239  
8.1 Rydberg wavepackets 239  
8.2 The Stark effect 255  

Appendix A MQDT normalization 273  
A.1 Open channels 273  
A.2 Closed channels 275  

Appendix B Alternative MQDT representations 278  
B.1 Standard representation 278  
B.2 Sine–cos representation 279  
B.3 Mixed representation 280  

Appendix C Rotational frame transformations 282  
C.1 Hund’s cases for diatomic molecules 282  
C.2 Parity considerations 284  
C.3 Basis functions 285  
C.4 Diatomic frame transformations 286  
C.5 Asymmetric tops 290
## Contents

<table>
<thead>
<tr>
<th>Appendix D</th>
<th>Optical transition and photo-ionization amplitudes</th>
<th>295</th>
</tr>
</thead>
<tbody>
<tr>
<td>D.1</td>
<td>Discrete absorption amplitudes</td>
<td>295</td>
</tr>
<tr>
<td>D.2</td>
<td>Photo-ionization amplitudes</td>
<td>297</td>
</tr>
<tr>
<td>D.3</td>
<td>Dipole radial matrix elements and Cooper minima</td>
<td>303</td>
</tr>
<tr>
<td>Appendix E</td>
<td>Generalized MQDT representation</td>
<td>307</td>
</tr>
<tr>
<td>Appendix F</td>
<td>Notation</td>
<td>310</td>
</tr>
<tr>
<td>F.1</td>
<td>Angular momenta</td>
<td>310</td>
</tr>
<tr>
<td>F.2</td>
<td>Reduced matrix elements</td>
<td>310</td>
</tr>
<tr>
<td>F.3</td>
<td>Other special brackets</td>
<td>312</td>
</tr>
<tr>
<td>Index</td>
<td></td>
<td>314</td>
</tr>
</tbody>
</table>