

Contents

<i>Preface</i>	<i>page</i> xv
<i>Summary of notation</i>	xix
<i>Figure acknowledgements</i>	xxiii
1 General introduction	1
1.1 Electromagnetic spectrum	1
1.2 Electromagnetic radiation	3
1.3 Intramolecular nuclear and electronic dynamics	5
1.4 Rotational levels	9
1.5 Historical perspectives	12
1.6 Fine structure and hyperfine structure of rotational levels	14
1.6.1 Introduction	14
1.6.2 $^1\Sigma^+$ states	15
1.6.3 Open shell Σ states	21
1.6.4 Open shell states with both spin and orbital angular momentum	26
1.7 The effective Hamiltonian	29
1.8 Bibliography	32
Appendix 1.1 Maxwell's equations	33
Appendix 1.2 Electromagnetic radiation	35
References	36
2 The separation of nuclear and electronic motion	38
2.1 Introduction	38
2.2 Electronic and nuclear kinetic energy	40
2.2.1 Introduction	40
2.2.2 Origin at centre of mass of molecule	41
2.2.3 Origin at centre of mass of nuclei	43
2.2.4 Origin at geometrical centre of the nuclei	44
2.3 The total Hamiltonian in field-free space	44
2.4 The nuclear kinetic energy operator	45
2.5 Transformation of the electronic coordinates to molecule-fixed axes	51
2.5.1 Introduction	51
2.5.2 Space transformations	52
2.5.3 Spin transformations	54
2.6 Schrödinger equation for the total wave function	59
2.7 The Born–Oppenheimer and Born adiabatic approximations	60

2.8 Separation of the vibrational and rotational wave equations	61
2.9 The vibrational wave equation	63
2.10 Rotational Hamiltonian for space-quantised electron spin	67
2.11 Non-adiabatic terms	67
2.12 Effects of external electric and magnetic fields	68
Appendix 2.1 Derivation of the momentum operator	71
References	72
3 The electronic Hamiltonian	73
3.1 The Dirac equation	73
3.2 Solutions of the Dirac equation in field-free space	76
3.3 Electron spin magnetic moment and angular momentum	77
3.4 The Foldy–Wouthuysen transformation	80
3.5 The Foldy–Wouthuysen and Dirac representations for a free particle	85
3.6 Derivation of the many-electron Hamiltonian	89
3.7 Effects of applied static magnetic and electric fields	94
3.8 Retarded electromagnetic interaction between electrons	97
3.8.1 Introduction	97
3.8.2 Lorentz transformation	98
3.8.3 Electromagnetic potentials due to a moving electron	99
3.8.4 Gauge invariance	101
3.8.5 Classical Lagrangian and Hamiltonian	103
3.9 The Breit Hamiltonian	104
3.9.1 Introduction	104
3.9.2 Reduction of the Breit Hamiltonian to non-relativistic form	105
3.10 Electronic interactions in the nuclear Hamiltonian	109
3.11 Transformation of coordinates in the field-free total Hamiltonian	110
3.12 Transformation of coordinates for the Zeeman and Stark terms in the total Hamiltonian	114
3.13 Conclusions	118
Appendix 3.1 Power series expansion of the transformed Hamiltonian	121
References	122
4 Interactions arising from nuclear magnetic and electric moments	123
4.1 Nuclear spins and magnetic moments	123
4.2 Derivation of nuclear spin magnetic interactions through the magnetic vector potential	125
4.3 Derivation of nuclear spin interactions from the Breit equation	130
4.4 Nuclear electric quadrupole interactions	131
4.4.1 Spherical tensor form of the Hamiltonian operator	131
4.4.2 Cartesian form of the Hamiltonian operator	133
4.4.3 Matrix elements of the quadrupole Hamiltonian	134
4.5 Transformation of coordinates for the nuclear magnetic dipole and electric quadrupole terms	136
References	138

5 Angular momentum theory and spherical tensor algebra	139
5.1 Introduction	139
5.2 Rotation operators	140
5.2.1 Introduction	140
5.2.2 Decomposition of rotational operators	142
5.2.3 Commutation relations	142
5.2.4 Representations of the rotation group	143
5.2.5 Orbital angular momentum and spherical harmonics	144
5.3 Rotations of a rigid body	146
5.3.1 Introduction	146
5.3.2 Rotation matrices	148
5.3.3 Spin 1/2 systems	150
5.3.4 Symmetric top wave functions	150
5.4 Addition of angular momenta	152
5.4.1 Introduction	152
5.4.2 Wigner 3- j symbols	154
5.4.3 Coupling of three or more angular momenta: Racah algebra, Wigner 6- j and 9- j symbols	155
5.4.4 Clebsch–Gordan series	157
5.4.5 Integrals over products of rotation matrices	158
5.5 Irreducible spherical tensor operators	159
5.5.1 Introduction	159
5.5.2 Examples of spherical tensor operators	160
5.5.3 Matrix elements of spherical tensor operators: the Wigner–Eckart theorem	163
5.5.4 Matrix elements for composite systems	165
5.5.5 Relationship between operators in space-fixed and molecule-fixed coordinate systems	167
5.5.6 Treatment of the anomalous commutation relationships of rota- tional angular momenta by spherical tensor methods	168
Appendix 5.1 Summary of standard results from spherical tensor algebra	171
References	175
6 Electronic and vibrational states	177
6.1 Introduction	177
6.2 Atomic structure and atomic orbitals	178
6.2.1 The hydrogen atom	178
6.2.2 Many-electron atoms	181
6.2.3 Russell–Saunders coupling	184
6.2.4 Wave functions for the helium atom	187
6.2.5 Many-electron wave functions: the Hartree–Fock equation	190
6.2.6 Atomic orbital basis set	194
6.2.7 Configuration interaction	196
6.3 Molecular orbital theory	197

6.4	Correlation of molecular and atomic electronic states	203
6.5	Calculation of molecular electronic wave functions and energies	206
6.5.1	Introduction	206
6.5.2	Electronic wave function for the H_2^+ molecular ion	207
6.5.3	Electronic wave function for the H_2 molecule	208
6.5.4	Many-electron molecular wave functions	212
6.6	Corrections to Born–Oppenheimer calculations for H_2^+ and H_2	219
6.7	Coupling of electronic and rotational motion: Hund’s coupling cases	224
6.7.1	Introduction	224
6.7.2	Hund’s coupling case (a)	225
6.7.3	Hund’s coupling case (b)	226
6.7.4	Hund’s coupling case (c)	228
6.7.5	Hund’s coupling case (d)	228
6.7.6	Hund’s coupling case (e)	229
6.7.7	Intermediate coupling	230
6.7.8	Nuclear spin coupling cases	232
6.8	Rotations and vibrations of the diatomic molecule	233
6.8.1	The rigid rotor	233
6.8.2	The harmonic oscillator	235
6.8.3	The anharmonic oscillator	238
6.8.4	The non-rigid rotor	242
6.8.5	The vibrating rotor	243
6.9	Inversion symmetry of rotational levels	244
6.9.1	The space-fixed inversion operator	244
6.9.2	The effect of space-fixed inversion on the Euler angles and on molecule-fixed coordinates	245
6.9.3	The transformation of general Hund’s case (a) and case (b) functions under space-fixed inversion	246
6.9.4	Parity combinations of basis functions	251
6.10	Permutation symmetry of rotational levels	251
6.10.1	The nuclear permutation operator for a homonuclear diatomic molecule	251
6.10.2	The transformation of general Hund’s case (a) and case (b) functions under nuclear permutation P_{12}	252
6.10.3	Nuclear statistical weights	254
6.11	Theory of transition probabilities	256
6.11.1	Time-dependent perturbation theory	256
6.11.2	The Einstein transition probabilities	258
6.11.3	Einstein transition probabilities for electric dipole transitions	261
6.11.4	Rotational transition probabilities	263
6.11.5	Vibrational transition probabilities	266
6.11.6	Electronic transition probabilities	267
6.11.7	Magnetic dipole transition probabilities	269

6.12 Line widths and spectroscopic resolution	273
6.12.1 Natural line width	273
6.12.2 Transit time broadening	273
6.12.3 Doppler broadening	274
6.12.4 Collision broadening	275
6.13 Relationships between potential functions and the vibration–rotation levels	276
6.13.1 Introduction	276
6.13.2 The JWKB semiclassical method	277
6.13.3 Inversion of experimental data to calculate the potential function (RKR)	280
6.14 Long-range near-dissociation interactions	282
6.15 Predissociation	286
Appendix 6.1 Calculation of the Born–Oppenheimer potential for the H_2^+ ion	289
References	298
7 Derivation of the effective Hamiltonian	302
7.1 Introduction	302
7.2 Derivation of the effective Hamiltonian by degenerate perturbation theory: general principles	303
7.3 The Van Vleck and contact transformations	312
7.4 Effective Hamiltonian for a diatomic molecule in a given electronic state	316
7.4.1 Introduction	316
7.4.2 The rotational Hamiltonian	319
7.4.3 Hougen’s isomorphic Hamiltonian	320
7.4.4 Fine structure terms: spin–orbit, spin–spin and spin–rotation operators	323
7.4.5 Λ -doubling terms for a Π electronic state	328
7.4.6 Nuclear hyperfine terms	331
7.4.7 Higher-order fine structure terms	335
7.5 Effective Hamiltonian for a single vibrational level	338
7.5.1 Vibrational averaging and centrifugal distortion corrections	338
7.5.2 The form of the effective Hamiltonian	341
7.5.3 The N^2 formulation of the effective Hamiltonian	343
7.5.4 The isotopic dependence of parameters in the effective Hamiltonian	344
7.6 Effective Zeeman Hamiltonian	347
7.7 Indeterminacies: rotational contact transformations	352
7.8 Estimates and interpretation of parameters in the effective Hamiltonian	356
7.8.1 Introduction	356
7.8.2 Rotational constant	356
7.8.3 Spin–orbit coupling constant, A	357
7.8.4 Spin–spin and spin–rotation parameters, λ and γ	360

7.8.5 A -doubling parameters	362
7.8.6 Magnetic hyperfine interactions	363
7.8.7 Electric quadrupole hyperfine interaction	365
Appendix 7.1 Molecular parameters or constants	368
References	369
8 Molecular beam magnetic and electric resonance	371
8.1 Introduction	371
8.2 Molecular beam magnetic resonance of closed shell molecules	372
8.2.1 H_2 , D_2 and HD in their $X^1\Sigma^+$ ground states	372
8.2.2 Theory of Zeeman interactions in $^1\Sigma^+$ states	390
8.2.3 Na_2 in the $X^1\Sigma_g^+$ ground state: optical state selection and detection	416
8.2.4 Other $^1\Sigma^+$ molecules	421
8.3 Molecular beam magnetic resonance of electronically excited molecules	422
8.3.1 H_2 in the $c^3\Pi_u$ state	422
8.3.2 N_2 in the $A^3\Sigma_u^+$ state	446
8.4 Molecular beam electric resonance of closed shell molecules	463
8.4.1 Principles of electric resonance methods	463
8.4.2 CsF in the $X^1\Sigma^+$ ground state	465
8.4.3 LiBr in the $X^1\Sigma^+$ ground state	483
8.4.4 Alkaline earth and group IV oxides	487
8.4.5 HF in the $X^1\Sigma^+$ ground state	489
8.4.6 HCl in the $X^1\Sigma^+$ ground state	500
8.5 Molecular beam electric resonance of open shell molecules	508
8.5.1 Introduction	508
8.5.2 LiO in the $X^2\Pi$ ground state	509
8.5.3 NO in the $X^2\Pi$ ground state	526
8.5.4 OH in the $X^2\Pi$ ground state	538
8.5.5 CO in the $a^3\Pi$ state	552
Appendix 8.1 Nuclear spin dipolar interaction	558
Appendix 8.2 Relationship between the cartesian and spherical tensor forms of the electron spin–nuclear spin dipolar interaction	561
Appendix 8.3 Electron spin–electron spin dipolar interaction	563
Appendix 8.4 Matrix elements of the quadrupole Hamiltonian	568
Appendix 8.5 Magnetic hyperfine Hamiltonian and hyperfine constants	573
References	574
9 Microwave and far-infrared magnetic resonance	579
9.1 Introduction	579
9.2 Experimental methods	579
9.2.1 Microwave magnetic resonance	579
9.2.2 Far-infrared laser magnetic resonance	584
9.3 $^1\Delta$ states	587
9.3.1 SO in the $a^1\Delta$ state	587
9.3.2 NF in the $a^1\Delta$ state	591

9.4 $^2\Pi$ states	596
9.4.1 Introduction	596
9.4.2 ClO in the $X^2\Pi$ ground state	597
9.4.3 OH in the $X^2\Pi$ ground state	613
9.4.4 Far-infrared laser magnetic resonance of CH in the $X^2\Pi$ ground state	624
9.5 $^2\Sigma$ states	633
9.5.1 Introduction	633
9.5.2 CN in the $X^2\Sigma^+$ ground state	633
9.6 $^3\Sigma$ states	641
9.6.1 SO in the $X^3\Sigma^-$ ground state	641
9.6.2 SeO in the $X^3\Sigma^-$ ground state	649
9.6.3 NH in the $X^3\Sigma^-$ ground state	652
9.7 $^3\Pi$ states	655
9.7.1 CO in the $a^3\Pi$ state	655
9.8 $^4\Sigma$ states	661
9.8.1 CH in the $a^4\Sigma^-$ state	661
9.9 $^4\Delta$, $^3\Phi$, $^2\Delta$ and $^6\Sigma^+$ states	665
9.9.1 Introduction	665
9.9.2 CrH in the $X^6\Sigma^+$ ground state	666
9.9.3 FeH in the $X^4\Delta$ ground state	669
9.9.4 CoH in the $X^3\Phi$ ground state	669
9.9.5 NiH in the $X^2\Delta$ ground state	674
Appendix 9.1 Evaluation of the reduced matrix element of $T^3(S, S, S)$	678
References	680
10 Pure rotational spectroscopy	683
10.1 Introduction and experimental methods	683
10.1.1 Simple absorption spectrograph	683
10.1.2 Microwave radiation sources	685
10.1.3 Modulation spectrometers	688
10.1.4 Superheterodyne detection	701
10.1.5 Fourier transform spectrometer	703
10.1.6 Radio telescopes and radio astronomy	713
10.1.7 Terahertz (far-infrared) spectrometers	723
10.1.8 Ion beam techniques	728
10.2 $^1\Sigma^+$ states	732
10.2.1 CO in the $X^1\Sigma^+$ ground state	732
10.2.2 HeH ⁺ in the $X^1\Sigma^+$ ground state	736
10.2.3 CuCl and CuBr in their $X^1\Sigma^+$ ground states	738
10.2.4 SO, NF and NCl in their $b^1\Sigma^+$ states	741
10.2.5 Hydrides (LiH, NaH, KH, CuH, AlH, AgH) in their $X^1\Sigma^+$ ground states	743

10.3 $^2\Sigma$ states	745
10.3.1 CO^+ in the $X^2\Sigma^+$ ground state	745
10.3.2 CN in the $X^2\Sigma^+$ ground state	749
10.4 $^3\Sigma$ states	752
10.4.1 Introduction	752
10.4.2 O_2 in its $X^3\Sigma_g^-$ ground state	754
10.4.3 SO , S_2 and NiO in their $X^3\Sigma^-$ ground states	759
10.4.4 PF , NCl , NBr and NI in their $X^3\Sigma^-$ ground states	763
10.5 $^1\Delta$ states	776
10.5.1 O_2 in its $a^1\Delta_g$ state	776
10.5.2 SO and NCl in their $a^1\Delta$ states	779
10.6 $^2\Pi$ states	782
10.6.1 NO in the $X^2\Pi$ ground state	782
10.6.2 OH in the $X^2\Pi$ ground state	788
10.6.3 CH in the $X^2\Pi$ ground state	794
10.6.4 CF , SiF , GeF in their $X^2\Pi$ ground states	810
10.6.5 Other free radicals with $^2\Pi$ ground states	811
10.7 Case (c) doublet state molecules	813
10.7.1 Studies of the HeAr^+ ion	813
10.7.2 Studies of the HeKr^+ ion	832
10.8 Higher spin/orbital states	834
10.8.1 CO in the $a^3\Pi$ state	834
10.8.2 SiC in the $X^3\Pi$ ground state	836
10.8.3 FeC in the $X^3\Delta$ ground state	841
10.8.4 VO and NbO in their $X^4\Sigma^-$ ground states	841
10.8.5 FeF and FeCl in their $X^6\Delta$ ground states	845
10.8.6 CrF , CrCl and MnO in their $X^6\Sigma^+$ ground states	850
10.8.7 FeO in the $X^5\Delta$ ground state	853
10.8.8 TiCl in the $X^4\Phi$ ground state	854
10.9 Observation of a pure rotational transition in the H_2^+ molecular ion	856
References	862
11 Double resonance spectroscopy	870
11.1 Introduction	870
11.2 Radiofrequency and microwave studies of CN in its excited electronic states	871
11.3 Early radiofrequency or microwave/optical double resonance studies	876
11.3.1 Radiofrequency/optical double resonance of CS in its excited $A^1\Pi$ state	876
11.3.2 Radiofrequency/optical double resonance of OH in its excited $A^2\Sigma^+$ state	880
11.3.3 Microwave/optical double resonance of BaO in its ground $X^1\Sigma^+$ and excited $A^1\Sigma^+$ states	883

11.4 Microwave/optical magnetic resonance studies of electronically excited H ₂	885
11.4.1 Introduction	885
11.4.2 H ₂ in the $G^1\Sigma_g^+$ state	885
11.4.3 H ₂ in the $d^3\Pi_u$ state	892
11.4.4 H ₂ in the $k^3\Pi_u$ state	900
11.5 Radiofrequency or microwave/optical double resonance of alkaline earth molecules	902
11.5.1 Introduction	902
11.5.2 SrF, CaF and CaCl in their $X^2\Sigma^+$ ground states	902
11.6 Radiofrequency or microwave/optical double resonance of transition metal molecules	906
11.6.1 Introduction	906
11.6.2 FeO in the $X^5\Delta$ ground state	909
11.6.3 CuF in the $b^3\Pi$ excited state	913
11.6.4 CuO in the $X^2\Pi$ ground state	917
11.6.5 ScO in the $X^2\Sigma^+$ ground state	919
11.6.6 TiO in the $X^3\Delta$ ground state and TiN in the $X^2\Sigma^+$ ground state	922
11.6.7 CrN and MoN in their $X^4\Sigma^-$ ground states	924
11.6.8 NiH in the $X^2\Delta$ ground state	927
11.6.9 $4d$ transition metal molecules: YF in the $X^1\Sigma^+$ ground state, YO and YS in their $X^2\Sigma^+$ ground states	930
11.7 Microwave/optical double resonance of rare earth molecules	936
11.7.1 Radiofrequency/optical double resonance of YbF in its $X^2\Sigma^+$ ground state	936
11.7.2 Radiofrequency/optical double resonance of LaO in its $X^2\Sigma^+$ and $B^2\Sigma^+$ states	938
11.8 Double resonance spectroscopy of molecular ion beams	942
11.8.1 Radiofrequency and microwave/infrared double resonance of HD ⁺ in the $X^2\Sigma^+$ ground state	942
11.8.2 Radiofrequency/optical double resonance of N ₂ ⁺ in the $X^2\Sigma_g^+$ ground state	953
11.8.3 Microwave/optical double resonance of CO ⁺ in the $X^2\Sigma^+$ ground state	958
11.9 Quadrupole trap radiofrequency spectroscopy of the H ₂ ⁺ ion	960
11.9.1 Introduction	960
11.9.2 Principles of photo-alignment	960
11.9.3 Experimental methods and results	962
11.9.4 Analysis of the spectra	964
11.9.5 Quantitative interpretation of the molecular parameters	972
References	974
General appendices	978
Appendix A Values of the fundamental constants	978

Appendix B Selected set of nuclear properties for naturally occurring isotopes	979
Appendix C Compilation of Wigner 3- j symbols	987
Appendix D Compilation of Wigner 6- j symbols	991
Appendix E Relationships between cgs and SI units	993
<i>Author index</i>	994
<i>Subject index</i>	1004