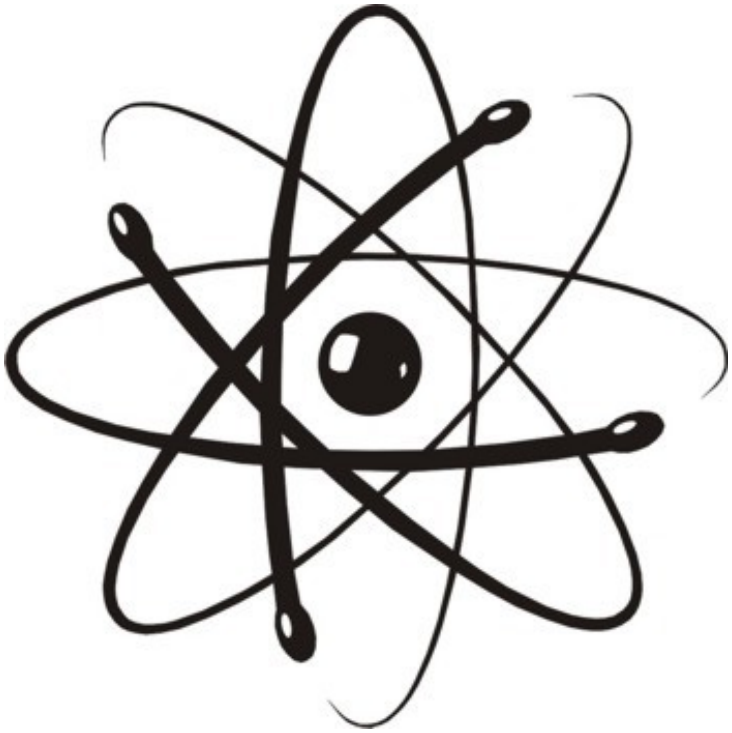
Quantum Chemistry with Applications in Spectroscopy



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Preface

This text has grown out of several years of teaching this material at several different colleges. The feedback I have received from my students has been incredibly. I have tried to choose example that seemed to work particularly well in aiding students to gain an understanding of the material while grounding complex concepts in more familiar experiences and intuitions.

In writing this text, I have tried to maintain a connection to measurable phenomena when discussing the otherwise abstract quantum mechanical models. In particular, I have attempted to follow the development of each model with specific spectroscopic examples which utilize the basic models as foundations to understand the behavior of real chemical systems. My experience is that the methodology works better than simply talking about quantum mechanics first, and then following with a discussion of spectroscopy, as though the two topics are not related.

Also toward that end, I have included a great deal of the applications of group theory into the text. While group theory is often the bailiwick of inorganic chemistry, I find that it is also very useful in the descriptions of molecular vibrations, molecular orbitals, selection rules, and other topics that are typically discussed in a course in physical chemistry.

It is my sincere hope that by feathering these two topics into the discussion of quantum chemistry that students will not simply get bogged down in the minutia of complex equations and math, but rather have the chance to see the "big picture."

The key to self-respect – a necessary component in attaining peer-respect – is to build a foundation of meaningful competence upon which one can build a solid structure of self-confidence. Quantum Chemistry, being an advanced topic, provides students with the capacity to truly stretch the boundaries of their skill-sets and extend that foundation. The hope is that this text will provide one of the supports that will help students approach this stretch and build meaningful confidence that is grounded in competence. It is meant to be part of journey, not an endpoint. The true value of an education is in how one applies it.

And, as always, I wish all students who study physical chemistry all of the best in their endeavors. May the expectation value of your experience be satisfaction!

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Physical Constants and Values

(The NIST Reference on Constants, Units, and Uncertainty, 2014)

Quantity	Symbol	Value
Speed of Light	c	299 792 458 m/s
Electron Charge	e	$1.602\ 176\ 6208(98) \times 10^{-19}$ C
Faraday Constant	F	$96\ 485.332\ 89(59)$ C mol^{-1}
Boltzmann Constant	k_B	$1.380\ 648\ 52(79) \times 10^{-23}$ J K^{-1}
Gas Law Constant	R	$8.314\ 4598(48)$ J mol^{-1} K^{-1}
Planck's Constant	h	$6.626\ 070\ 040(81) \times 10^{-34}$ J s
Avogadro's Number	N_A	$6.022\ 140\ 857(74) \times 10^{23}$ mol^{-1}
Atomic Mass Unit	amu	$1.660\ 539\ 040(20) \times 10^{-27}$ kg
Electron Mass	m_e	$9.109\ 383\ 56(11) \times 10^{-31}$ kg
Proton Mass	m_p	$1.672\ 621\ 898(21) \times 10^{-27}$ kg
Neutron Mass	m_n	$1.674\ 927\ 471(21) \times 10^{-27}$ kg
Magnetic Constant	μ_0	$12.566\ 370\ 614... \times 10^{-7}$ N A^{-2}
Electric Constant	ε_0	$8.854\ 187\ 817... \times 10^{-12}$ F m^{-1}
Rydberg Constant	R_∞	$10\ 973\ 731.568\ 508(65)$ m^{-1}

References

The NIST Reference on Constants, Units, and Uncertainty. (2014). Retrieved March 13, 2016, from CODATA Internationally recommended 2014 values of the Fundamental Physical Constants: http://physics.nist.gov/cuu/index.html

Periodic Table

(with rounded atomic masses)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
I A	II A	III B	IV B	V B	VI B	VII B	VIII B			I B	II B	III A	IV A	V A	VI A	VII A	VIII A
1 **H** 1.008																	2 **He** 4.003
3 **Li** 6.944	4 **Be** 9.012											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
11 **Na** 22.99	12 **Mg** 24.30											13 **Al** 27.00	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.06	17 **Cl** 35.45	18 **Ar** 39.95
19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.87	23 **V** 50.94	24 **Cr** 52.00	25 **Mn** 54.94	26 **Fe** 55.84	27 **Co** 58.93	28 **Ni** 58.69	29 **Cu** 63.55	30 **Zn** 65.39	31 **Ga** 69.72	32 **Ge** 72.64	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.90	36 **Kr** 83.80
37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.94	43 **Tc** (98)	44 **Ru** 101.1	45 **Rh** 102.9	46 **Pd** 106.4	47 **Ag** 107.9	48 **Cd** 112.4	49 **In** 114.8	50 **Sn** 118.7	51 **Sb** 121.8	52 **Te** 127.6	53 **I** 126.7	54 **Xe** 131.3
55 **Cs** 132.9	56 **Ba** 137.3	*	72 **Hf** 178.5	73 **Ta** 180.9	74 **W** 183.8	75 **Re** 186.2	76 **Os** 190.2	77 **Ir** 192.2	78 **Pt** 195.1	79 **Au** 197.0	80 **Hg** 200.6	81 **Tl** 204.4	82 **Pb** 207.2	83 **Bi** 209.0	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** (226)	**	104 **Rf** (261)	105 **Db** (262)	106 **Sg** (266)	107 **Bh** (264)	108 **Hs** (269)	109 **Mt** (268)	110 **Ds** (271)	111 **Rg** (272)	112 **Cn** (277)	113 **Nh** (284)	114 **Fl** (285)	115 **Mc** (288)	116 **Lv** (289)	117 **Ts** (294)	118 **Og** (294)

*Lanthanides	57 **La** 138.8	58 **Ce** 140.1	59 **Pr** 140.9	60 **Nd** 144.2	61 **Pm** (145)	62 **Sm** 150.4	63 **Eu** 152.0	64 **Gd** 157.2	65 **Tb** 158.9	66 **Dy** 162.5	67 **Ho** 164.9	68 **Er** 167.3	69 **Tm** 168.9	70 **Yb** 173.0	71 **Lu** 175.0
**Actinides	89 **Ac** (227)	90 **Th** 232.0	91 **Pa** 231.0	92 **U** 238.0	93 **Np** (237)	94 **Pu** (244)	95 **Am** (243	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (262)

Place links to chapter files here: