QUANTUM CHEMISTRY

量子化学
第6版

IRA N. LEVINE

QUANTUM CHEMISTRY

SIXTH EDITION

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Quantum Chemistry

Sixth Edition

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To my quantum chemistry students: Vincent Adams, Margaret Adamson, Emanuel Akinfeleye, Ricardo Alkins, Byongjae An, Salvatore Atzeni, Abe Auerbach, Andrew Auerbach, Nikolay Azar, Joseph Barbuto, David Baron, Christie Basseth, Sene Bauman, Laurance Beaton, Howard Becker, Michael Beitchman, Anna Berne, Kamal Bharucha, Susan Bienenfeld, Mark Blackman, Toby Block, Allen Bloom, Gina Bolnet, Demetrios Boyce, Diza Braksmayer, Steve Braunstein, Paul Brumer, Jean Brun, Margaret Buckley, Lynn Caporale, Richard Carter, Julianne Caton-Williams, Shih-ching Chang, Ching-hong Chen, Hongbin Chen, Huifen Chen, Kangmin Chen, Kangping Chen, Guang-Yu Cheng, Yu-Chi Cheng, El-hadi Cherchar, Jeonghwan Cho, Ting-Yi Chu, Kyu Suk Chung, Joseph Cincotta, Robert Curran, Joseph D'Amore, Ronald Davy, Jody Delsol, Aly Dominique, Xiao-Hong Dong, Barry DuRon, Azaria Eisenberg, Myron Elgart, Musa Elmagadam, Anna Eng, Stephen Engel, Quianping Fang, Nicola Farina, Larry Filler, Seymour Fishman, Donald Franceschetti, Mark Freilich, Michael Freshwater, Tobi Eisenstein Fried, Joel Friedman, Kenneth Friedman, Aryeh Frimer, Mark Froimowitz, Irina Gaberman, Paul Gallant, Hong Gan, Mark Gold, Stephen Goldman, Neil Goodman, Roy Goodman, Isaac Gorbaty, Aleksander Gorbenko, Steven Greenberg, Walter Greigg, Michael Gross, Zhijie Gu, Judy Guiseppi-Henry, Lin Guo, Hasan Hajomar, Runyu Han, Sheila Handler, Noyes Harrigan, Jun He, Warren Hirsch, Richard Hom, Kuo-zong Hong, Mohammed Hossain, Fu-juan Hsu, Bo Hu, Jong-chin Hwan, Leonard Itzkowitz, Colin John, Mark Johnson, Kirby Juengst, Abraham Karkowsky, Spiros Kassomenakis, Abdelahad Khajo, Mohammed Khan, Michael Kittay, Colette Knight, Barry Kohn, Yasemin Kopkalli, Malgorzata Kulcyk-Stanko, David Kurnit, Athanasios Ladas, Alan Lambowitz, Eirini Lampiri, Bentley Lane, Yedidyah Langsam, Noah Lansner, Surin Laosooksathit, Chi-Yin Lee, Chiu Hong Lee, Stephen Lemont, Elliot Lerner, Jiang Li, Zheng Li, Israel Liebersohn, Joel Liebman, Steven Lipp, Huiyu Liu, Letian Liu, James Liubicich, John Lobo, Rachel Loftoa, Wei Luo, Dennis Lynch, Michelle Maison, Mohammad Malik, Pietro Mangiaracina, Louis Maresca, Allen Marks, Tom McDonough, Keisha McMillan, Antonio Mennito, Leonid Metlitsky, Ira Michaels, Tziril Miller, Bin Mo, Qi Mo, Paul Mogolesko, Alim Monir, Safrudin Mustopa, Irving Nadler, Stuart Nagourney, Kwazi Ndlovu, Harold Nelson, Wen-Hui Pan, Padmanabhan Parakat, Frank Pecci, Albert Pierre-Louis, Paloma Pimenta, Eli Pines, Jerry Polesuk, Arlene Gallanter Pollin, James Pollin, Lahanda Punyasena, Cynthia Racer, Munira Rampersaud, Caleen Ramsook, Robert Richman, Richard Rigg, Bruce Rosenberg, Martin Rosenberg, Robert Rundberg, Edward Sachs, Mohamed Salem, Mahendra Sawh, David Schaeffer, Gary Schneier, Neil Schweid, Judith Rosenkranz Selwyn, Gunnar Senum, Simone Shaker, Steven Shaya, Allen Sheffron, Wu-mian Shen, Yuan Shi, Lawrence Shore, Alvin Silverstein, Barry Siskind, Jerome Solomon, De Zai Song, Henry Sperling, Joseph Springer, Charles Stimler, Helen Sussman, Sybil Tobierre, Dana McGowan Tormey, David Trauber, Choi Han Tsang, King-hung Tse, Michele Tujague, Irina Vasilkin, Natalya Voluschuk, Sammy Wainhaus, Alan Waldman, Huai Zhen Wang, Zheng Wang, Robert Washington, Janet Weaver, William Wihlborg, Peter Williamsen, Frederic Wills, Shiming Wo, Guohua Wu, Jinan Wu, Xiaowen Wu, Ming Min Xia, Wei-Guo Xia, Xiaoming Ye, Ching-Chun Yiu, Wen Young, Xue-yi Yuan, Ken Zaner, Juin-tao Zhang, Hannian Zhao, Li Li Zhou, Shan Zhou, Yun Zhou.

Preface

This book is intended for first-year graduate and advanced undergraduate courses in quantum chemistry.

The following improvements were made in the sixth edition:

- Exercises with answers were added to most of the in-chapter examples.
- The problems were revised and are now classified by section.
- Section 1.9 containing calculus formulas for review was added.
- Chapter 13 was shortened by moving three of its sections to Chapter 14.
- Chapter 15 was shortened by moving discussion of correlation methods to a new Chapter 16.
- Some of the mathematical derivations have been moved from the text to homework problems with step-by-step hints; examples are the derivations of the He $1/r_{12}$ integral (Section 9.3) and the Numerov-method formula (Section 4.4).
- References to online computer simulations of several quantum-mechanical systems were added.
- The discussion of NMR spectroscopy in Section 10.9 was expanded.
- Mention of Gaussian units was dropped.

New material in the sixth edition includes the following:

- Mayer bond orders (Section 15.6)
- The RI (density-fitting) approximation (Sections 15.16 and 16.2)
- The MP2-R12 and MP2-F12 methods (Section 16.2)
- Extrapolation to the complete-basis-set limit (Sections 15.5 and 16.3)
- The SCS-MP2 and SOS-MP2 methods (Section 16.2)
- Meta-GGA functionals (Section 16.4)
- Time-dependent DFT (Section 16.4)
- The G4 , W1, W2, W3, and W4 methods (Section 16.5)
- The PM5, PM6, RM1, PDDG/PM3, and SCC-DFTB methods (Section 17.4)

A solutions manual for the problems in the book is available.

The expanding role of quantum chemistry makes it highly desirable for students in all areas of chemistry to understand modern methods of electronic structure calculation, and this book has been written with this goal in mind.

I have tried to make explanations clear and complete, without glossing over difficult or subtle points. Derivations are given with enough detail to make them easy to follow, and I avoid resorting to the frustrating phrase "it can be shown that" wherever possible. The aim is to give students a solid understanding of the physical and mathematical aspects of quantum mechanics and molecular electronic structure. The book is

designed to be useful to students in all branches of chemistry, not just future quantum chemists. However, the presentation is such that those who do go on in quantum chemistry will have a good foundation and will not be hampered by misconceptions.

An obstacle faced by many chemistry students in learning quantum mechanics is their unfamiliarity with much of the required mathematics. In this text I have included detailed treatments of operators, differential equations, simultaneous linear equations, and other needed topics. Rather than putting all the mathematics in an introductory chapter or a series of appendices, I have integrated the mathematics with the physics and chemistry. Immediate application of the mathematics to solving a quantum-mechanical problem will make the mathematics more meaningful to students than would separate study of the mathematics. I have also kept in mind the limited physics background of many chemistry students by reviewing topics in physics.

This book has benefited from the reviews and suggestions of Leland Allen, N. Colin Baird, Steven Bernasek, James Bolton, W. David Chandler, Donald Chesnut, R. James Cross, David Farrelly, Melvyn Feinberg, Gordon A. Gallup, David Goldberg, Tracy Hamilton, John Head, Warren Hehre, Hans Jaffé, Miklos Kertesz, Neil Kestner, Harry King, Peter Kollman, Mel Levy, Errol Lewars, Joel Liebman, Frank Meeks, Robert Metzger, Pedro Muiño, William Palke, Sharon Palmer, Gary Pfeiffer, Russell Pitzer, Kenneth Sando, Harrison Shull, James J. P. Stewart, Richard Stratt, Arieh Warshel, John S. Winn, and Michael Zerner. The following people provided reviews for the sixth edition: Gary DeBoer, Douglas Doren, Daniel Gerrity, Robert Griffin, Sharon Hammes-Schiffer, James Harrison, Robert Hinde, Anna Krylov, Tien-Sung Tom Lin, Ryan McLaughlin, Charles Millner, John H. Moore, Kirk Peterson, Oleg Prezhdo, Frank Rioux, Fu-Ming Tao, Ronald Terry, Alexander Van Hook, and Peter Weber. I wish to thank these people and several anonymous reviewers.

I would appreciate receiving any suggestions that readers may have for improving the book.

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CHAPTER 1

The Schrödinger Equation

1.1 QUANTUM CHEMISTRY

In the late seventeenth century, Isaac Newton discovered **classical mechanics**, the laws of motion of macroscopic objects. In the early twentieth century, physicists found that classical mechanics does not correctly describe the behavior of very small particles such as the electrons and nuclei of atoms and molecules. The behavior of such particles is described by a set of laws called **quantum mechanics**.

Quantum chemistry applies quantum mechanics to problems in chemistry. The influence of quantum chemistry is evident in all branches of chemistry. Physical chemists use quantum mechanics to calculate (with the aid of statistical mechanics) thermodynamic properties (for example, entropy, heat capacity) of gases; to interpret molecular spectra, thereby allowing experimental determination of molecular properties (for example, molecular geometries, dipole moments, barriers to internal rotation, energy differences between conformational isomers); to calculate molecular properties theoretically; to calculate properties of transition states in chemical reactions, thereby allowing estimation of rate constants; to understand intermolecular forces; and to deal with bonding in solids.

Organic chemists use quantum mechanics to estimate the relative stabilities of molecules, to calculate properties of reaction intermediates, to investigate the mechanisms of chemical reactions, and to analyze nuclear-magnetic-resonance spectra.

Analytical chemists use spectroscopic methods extensively. The frequencies and intensities of lines in a spectrum can be properly understood and interpreted only through the use of quantum mechanics.

Inorganic chemists use ligand field theory, an approximate quantum-mechanical method, to predict and explain the properties of transition-metal complex ions.

Although the large size of biologically important molecules makes quantum-mechanical calculations on them extremely hard, biochemists are beginning to benefit from quantum-mechanical studies of conformations of biological molecules, enzyme–substrate binding, and solvation of biological molecules.

Quantum mechanics determines the properties of nanomaterials (objects with at least one dimension in the range 1 to 100 nm), and calculational methods to deal with nanomaterials are being developed (E. K. Wilson, *Chem. Eng. News,* April 28, 2003, p. 27). When one or more dimensions of a material fall below 100 nm (and especially below 20 nm), dramatic changes in the optical, electronic, chemical, and other properties from those of the bulk material can occur. A semiconductor or metal object with one dimension in the 1 to 100 nm range is called a *quantum well*; one with two dimensions in this range is a *quantum wire*; and one with all three dimensions in this range is

a *quantum dot*. The word *quantum* in these names indicates the key role played by quantum mechanics in determining the properties of such materials. Many people have speculated that nanoscience and nanotechnology will bring about the "next industrial revolution," while others have criticized this field as, so far, containing more hype than achievement.

The rapid increase in computer speed and the development of new methods (such as density functional theory—Section 16.4) of doing molecular calculations have made quantum chemistry a practical tool in all areas of chemistry. Nowadays, several companies sell quantum-chemistry software for doing molecular quantum-chemistry calculations. These programs are designed to be used by all kinds of chemists, not just quantum chemists. Because of the rapidly expanding role of quantum chemistry and related theoretical and computational methods, the American Chemical Society began publication of the new periodical the *Journal of Chemical Theory and Computation* in 2005.

"Quantum mechanics ... underlies nearly all of modern science and technology. It governs the behavior of transistors and integrated circuits ... and is ... the basis of modern chemistry and biology" (Stephen Hawking, *A Brief History of Time*, 1988, Bantam, chap. 4).

1.2 HISTORICAL BACKGROUND OF QUANTUM MECHANICS

The development of quantum mechanics began in 1900 with Planck's study of the light emitted by heated solids, so we start by discussing the nature of light.

In 1801, Thomas Young gave convincing experimental evidence for the wave nature of light by observing diffraction and interference when light went through two adjacent pinholes. (*Diffraction* is the bending of a wave around an obstacle. *Interference* is the combining of two waves of the same frequency to give a wave whose disturbance at each point in space is the algebraic or vector sum of the disturbances at that point resulting from each interfering wave. See any first-year physics text.)

In 1864, James Clerk Maxwell published four equations, known as Maxwell's equations, which unified the laws of electricity and magnetism. Maxwell's equations predicted that an accelerated electric charge would radiate energy in the form of electromagnetic waves consisting of oscillating electric and magnetic fields. The speed predicted by Maxwell's equations for these waves turned out to be the same as the experimentally measured speed of light. Maxwell concluded that light is an electromagnetic wave.

In 1888, Heinrich Hertz detected radio waves produced by accelerated electric charges in a spark, as predicted by Maxwell's equations. This convinced physicists that light is indeed an electromagnetic wave.

All electromagnetic waves travel at speed $c = 2.998 \times 10^8$ m/s in vacuum. The frequency ν and wavelength λ of an electromagnetic wave are related by

$$\boxed{\lambda \nu = c} \tag{1.1}$$

(Equations that are enclosed in a box should be memorized.) Various conventional labels are applied to electromagnetic waves depending on their frequency. In order of increasing frequency are radio waves, microwaves, infrared radiation, visible light, ultraviolet

radiation, X-rays, and gamma rays. We shall use the term **light** to denote any kind of electromagnetic radiation. Wavelengths of visible and ultraviolet radiation were formerly given in **angstroms** (Å) and are now given in **nanometers** (nm):

$$1 \text{ nm} = 10^{-9} \text{ m}, \qquad 1 \text{ Å} = 10^{-10} \text{ m} = 0.1 \text{ nm} \qquad \textbf{(1.2)}$$

In the late 1800s, physicists measured the intensity of light at various frequencies emitted by a heated blackbody at a fixed temperature. A *blackbody* is an object that absorbs all light falling on it. A good approximation to a blackbody is a cavity with a tiny hole. When physicists used statistical mechanics and the electromagnetic-wave model of light to predict the intensity-versus-frequency curve for emitted blackbody radiation, they found a result in complete disagreement with the high-frequency portion of the experimental curves.

In 1900, Max Planck developed a theory that gave excellent agreement with the observed blackbody-radiation curves. Planck assumed the radiation emitters and absorbers in the blackbody to be harmonically oscillating electric charges ("resonators") in equilibrium with electromagnetic radiation in a cavity. Planck assumed that the total energy of those resonators whose frequency is ν consisted of N indivisible "energy elements," each of magnitude $h\nu$, where N is an integer and h (**Planck's constant**) was a new constant in physics. The value $h = 6.6 \times 10^{-34}$ J·s led to curves that agreed with the experimental blackbody curves. Planck distributed these energy elements among the resonators. In effect, this restricted the energy of each resonator to be a whole-number multiple of $h\nu$ (although Planck did not explicitly say this). Thus the energy of each resonator was **quantized**, meaning that only certain discrete values were allowed for a resonator energy. Planck's work is usually considered to mark the beginning of quantum mechanics. However, historians of physics have debated whether Planck in 1900 viewed energy quantization as a description of physical reality or as merely a mathematical approximation that allowed him to obtain the correct blackbody radiation formula. [See C. A. Gearhart, *Phys. Perspect.*, **4**, 170 (2002); S. G. Brush, *Am. J. Phys.*, **70**, 119 (2002).]

The concept of energy quantization is in direct contradiction to all previous ideas of physics. According to Newtonian mechanics, the energy of a material body can vary continuously. However, only with the hypothesis of quantized energy does one obtain the correct blackbody-radiation curves.

The second application of energy quantization was to the photoelectric effect. In the *photoelectric effect,* light shining on a metal causes emission of electrons. The energy of a wave is proportional to its intensity and is not related to its frequency, so the electromagnetic-wave picture of light leads one to expect that the kinetic energy of an emitted photoelectron would increase as the light intensity increases but would not change as the light frequency changes. Instead, one observes that the kinetic energy of an emitted electron is independent of the light's intensity but increases as the light's frequency increases.

In 1905, Einstein showed that these observations could be explained by regarding light as composed of particlelike entities (called **photons**), with each photon having an energy

$$E_{\text{photon}} = h\nu \qquad \textbf{(1.3)}$$

When an electron in the metal absorbs a photon, part of the absorbed photon energy is used to overcome the forces holding the electron in the metal, and the remainder appears as kinetic energy of the electron after it has left the metal. Conservation of energy gives $h\nu = \Phi + T$, where Φ is the minimum energy needed by an electron to escape the metal (the metal's *work function*), and T is the maximum kinetic energy of an emitted electron. An increase in the light's frequency ν increases the photon energy and hence increases the kinetic energy of the emitted electron. An increase in light intensity at fixed frequency increases the rate at which photons strike the metal and hence increases the rate of emission of electrons, but does not change the kinetic energy of each emitted electron.

The photoelectric effect shows that light can exhibit particlelike behavior in addition to the wavelike behavior it shows in diffraction experiments.

In 1907, Einstein applied energy quantization to the vibrations of atoms in a solid element, assuming that each atom's vibrational energy in each direction (x, y, z) is restricted to be an integer times $h\nu_{\text{vib}}$, where the vibrational frequency ν_{vib} is characteristic of the element. Using statistical mechanics, Einstein derived an expression for the constant-volume heat capacity C_V of the solid. Einstein's equation agreed fairly well with known C_V-versus-temperature data for diamond.

Now let us consider the structure of matter.

In the late nineteenth century, investigations of electric discharge tubes and natural radioactivity showed that atoms and molecules are composed of charged particles. Electrons have a negative charge. The proton has a positive charge equal in magnitude but opposite in sign to the electron charge and is 1836 times as heavy as the electron. The third constituent of atoms, the neutron (discovered in 1932), is uncharged and slightly heavier than the proton.

Starting in 1909, Rutherford, Geiger, and Marsden repeatedly passed a beam of alpha particles through a thin metal foil and observed the deflections of the particles by allowing them to fall on a fluorescent screen. Alpha particles are positively charged helium nuclei obtained from natural radioactive decay. Most of the alpha particles passed through the foil essentially undeflected, but, surprisingly, a few underwent large deflections, some being deflected backward. To get large deflections, one needs a very close approach between the charges, so that the Coulombic repulsive force is great. If the positive charge were spread throughout the atom (as J. J. Thomson had proposed in 1904), once the high-energy alpha particle penetrated the atom, the repulsive force would fall off, becoming zero at the center of the atom, according to classical electrostatics. Hence Rutherford concluded that such large deflections could occur only if the positive charge were concentrated in a tiny, heavy nucleus.

An atom contains a tiny (10^{-13} to 10^{-12} cm radius), heavy nucleus consisting of neutrons and Z protons, where Z is the atomic number. Outside the nucleus there are Z electrons. The charged particles interact according to Coulomb's law. (The nucleons are held together in the nucleus by strong, short-range nuclear forces, which will not concern us.) The radius of an atom is about one angstrom, as shown, for example, by results from the kinetic theory of gases. Molecules have more than one nucleus.

The chemical properties of atoms and molecules are determined by their electronic structure, and so the question arises as to the nature of the motions and energies of the electrons. Since the nucleus is much more massive than the electron, we expect the motion of the nucleus to be slight compared with the electrons' motions.