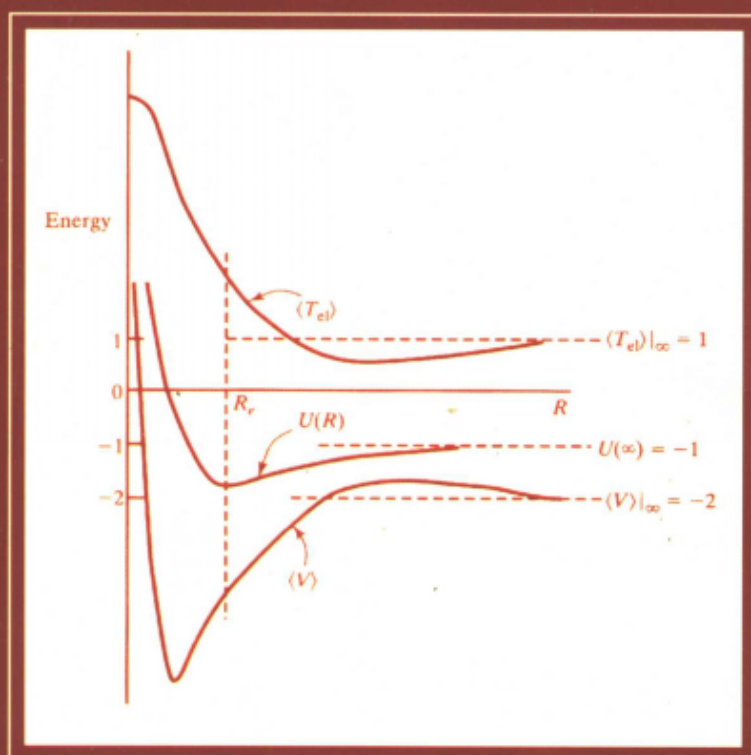


FIFTH EDITION

Quantum Chemistry

量子化学 第5版



IRA N. LEVINE

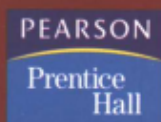
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Fifth Edition

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To my quantum chemistry students: Vincent Adams, Ricardo Alkins, Byongjae An, Salvatore Atzeni, Abe Auerbach, Andrew Auerbach, Joseph Barbuto, David Baron, Christie Basseth, Sene Bauman, Howard Becker, Michael Beitchman, Anna Berne, Kamal Bharucha, Susan Bienenfeld, Mark Blackman, Toby Block, Allen Bloom, Demetrios Boyce, Diza Braksmayer, Steve Braunstein, Paul Brumer, Jean Brun, Lynn Caporale, Richard Carter, 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, Aly Dominique, Xiao-Hong Dong, Barry DuRon, Azaria Eisenberg, Myron Elgart, Musa Elmagadam, Anna Eng, Stephen Engel, Quianping Fang, Larry Filler, Seymour Fishman, Donald Franceschetti, Mark Freilich, Michael Freshwater, Tobi Eisenstein Fried, Joel Friedman, Kenneth Friedman, Aryeh Frimer, Mark Froimowitz, Paul Gallant, Hong Gan, Mark Gold, Stephen Goldman, Neil Goodman, Roy Goodman, Isaac Gorbaty, Steven Greenberg, Michael Gross, Zhijie Gu, Judy Guiseppi-Henry, Lin Guo, Runyu Han, Sheila Handler, Warren Hirsch, Richard Hom, Kuo-zong Hong, Mohammed Hossain, Fu-juan Hsu, Bo Hu, Jong-chin Hwan, Leonard Itzkowitz, Mark Johnson, Kirby Juengst, Abraham Karkowsky, Spiros Kassomenakis, Michael Kittay, Colette Knight, Barry Kohn, Yasemin Kopkalli, David Kurnit, Athanasios Ladas, Alan Lambowitz, Bentley Lane, Yedidyah Langsam, Surin Laosooksathit, Chi-Yin Lee, Stephen Lemont, Elliot Lerner, Jiang Li, Zheng Li, Israel Liebersohn, Joel Liebman, Steven Lipp, Letian Liu, James Liubicich, John Lobo, Rachel Loftoa, Wei Luo, Dennis Lynch, Mohammad Malik, Pietro Mangiaracina, Louis Maresca, Allen Marks, Tom McDonough, Antonio Mennito, Ira Michaels, Bin Mo, Paul Mogolesko, 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, Cateen Ramsook, Robert Richman, Richard Rigg, Bruce Rosenberg, Martin Rosenberg, Robert Rundberg, Edward Sachs, Mahendra Sawh, David Schaeffer, Gary Schneier, Neil Schweid, Judith Rosenkranz Selwyn, Gunnar Senum, 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, 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, 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.

New material in the fifth edition includes:

- The Numerov method for numerical solution of the one-dimensional Schrödinger equation (Sections 4.4, 6.9, and 13.2)
- Linear-scaling methods (Section 15.5)
- Molecular electrostatic potentials (Section 15.8)
- Conformational searching (Section 15.12)
- Vibrational frequencies (Section 15.13)
- Thermodynamic properties (Section 15.14)
- Ab initio quantum chemistry programs (Sections 15.15 and 15.16)
- Composite methods (Section 15.21)
- Solvent effects (Sections 15.22 and 16.7)
- The ONIOM, IMOMO, and IMOMM methods (Section 15.26)

The following topics have been substantially expanded:

- Density-functional theory (Section 15.20)
- The molecular-mechanics method (Section 16.6)
- Semiempirical methods (Section 16.5)
- Geometry optimization (Section 15.11)
- Comparison of methods (Chapter 17)

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, James Bolton, Donald Chesnut, Melvyn Feinberg, Gordon A. Gallup, David Goldberg, Warren Hehre, Hans Jaffé, Neil Kestner, Harry King, Peter Kollman, Errol Lewars, Joel Liebman, Frank Meeks, Robert Metzger, William Palke, Gary Pfeiffer, Russell Pitzer, Kenneth Sando, Harrison Shull, James J. P. Stewart, Richard Stratt, Arie Warshel, and Michael Zerner. Portions of the fifth edition were reviewed by Steven Bernasek, W. David Chandler, R. James Cross, David Farrelly, Tracy Hamilton, John Head, Miklos Kertesz, Mel Levy, Pedro Muñio, Sharon Palmer, and John S. Winn. Robert Gotwals' online computational chemistry course at the North Carolina Supercomputing Center allowed me to get experience using a supercomputer. 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, bond lengths and bond angles, 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 NMR 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.

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.

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.)

About 1860, James Clerk Maxwell developed 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

$$\lambda\nu = c \quad (1.1)^*$$

(An equation with an asterisk after its number 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* (\AA) and are now given in *nanometers* (nm):

$$1 \text{ nm} = 10^{-9} \text{ m}, \quad 1 \text{ \AA} = 10^{-10} \text{ m} = 0.1 \text{ nm} \quad (1.2)^*$$

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 that the atoms of the blackbody could emit light energy only in amounts given by $h\nu$, where ν is the radiation's frequency and h is a proportionality constant, called *Planck's constant*. The value $h = 6.6 \times 10^{-34}$ J · s gave curves that agreed with the experimental blackbody curves. Planck's work marks the beginning of quantum mechanics.

Planck's hypothesis that only certain quantities of light energy can be emitted

(that the emission is *quantized*) was in direct contradiction to all previous ideas of physics. The energy of a wave is related to its amplitude, and the amplitude varies continuously from zero on up. Moreover, according to Newtonian mechanics, the energy of a material body can vary continuously. Hence physicists expected the energy of an atom to vary continuously. If one expects the energies of atoms and of electromagnetic waves to vary continuously, one also expects the electromagnetic-radiation energy emitted by atoms to vary continuously. However, only with the hypothesis of quantized energy emission 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

$$E_{\text{photon}} = h\nu \quad (1.3)*$$

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.

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.

In 1911, Rutherford proposed his planetary model of the atom in which the electrons revolved about the nucleus in various orbits, just as the planets revolve about the sun. However, there is a fundamental difficulty with this model. According to classical electromagnetic theory, an accelerated charged particle radiates energy in the form of electromagnetic (light) waves. An electron circling the nucleus at constant speed is being accelerated, since the direction of its velocity vector is continually changing. Hence the electrons in the Rutherford model should continually lose energy by radiation and therefore would spiral toward the nucleus. Thus, according to classical (nineteenth-century) physics, the Rutherford atom is unstable and would collapse.

A possible way out of this difficulty was proposed by Niels Bohr in 1913, when he applied the concept of quantization of energy to the hydrogen atom. Bohr assumed that the energy of the electron in a hydrogen atom was quantized, with the electron constrained to move only on one of a number of allowed circles. When an electron makes a transition from one Bohr orbit to another, a photon of light whose frequency ν satisfies

$$E_{\text{upper}} - E_{\text{lower}} = h\nu \quad (1.4)^*$$

is absorbed or emitted, where E_{upper} and E_{lower} are the energies of the upper and lower states (conservation of energy). With the assumption that an electron making a transition from a free (ionized) state to one of the bound orbits emits a photon whose frequency is an integral multiple of one-half the classical frequency of revolution of the electron in the bound orbit, Bohr used classical mechanics to derive a formula for the hydrogen-atom energy levels. Using (1.4), he obtained agreement with the observed hydrogen spectrum. However, attempts to fit the helium spectrum using the Bohr theory failed. Moreover, the theory could not account for chemical bonds in molecules.

The basic difficulty in the Bohr model arises from the use of classical mechanics to describe the electronic motions in atoms. The evidence of atomic spectra, which show discrete frequencies, indicates that only certain energies of motion are allowed; the electronic energy is quantized. However, classical mechanics allows a continuous range of energies. Quantization does occur in wave motion; for example, the fundamental and overtone frequencies of a violin string. Hence Louis de Broglie suggested

in 1923 that the motion of electrons might have a wave aspect; that an electron of mass m and speed v would have a wavelength

$$\lambda = \frac{h}{mv} = \frac{h}{p} \quad (1.5)$$

associated with it, where p is the linear momentum. De Broglie arrived at Eq. (1.5) by reasoning in analogy with photons. The energy of any particle (including a photon) can be expressed, according to Einstein's special theory of relativity, as $E = mc^2$, where c is the speed of light and m is the particle's relativistic mass (not its rest mass). Using $E_{\text{photon}} = h\nu$, we get $mc^2 = h\nu = hc/\lambda$ and $\lambda = h/mc = h/p$ for a photon traveling at speed c . Equation (1.5) is the corresponding equation for an electron.

In 1927, Davisson and Germer experimentally confirmed de Broglie's hypothesis by reflecting electrons from metals and observing diffraction effects. In 1932, Stern observed the same effects with helium atoms and hydrogen molecules, thus verifying that the wave effects are not peculiar to electrons, but result from some general law of motion for microscopic particles.

Thus electrons behave in some respects like particles and in other respects like waves. We are faced with the apparently contradictory "wave-particle duality" of matter (and of light). How can an electron be both a particle, which is a localized entity, and a wave, which is nonlocalized? The answer is that an electron is neither a wave nor a particle, but something else. An accurate pictorial description of an electron's behavior is impossible using the wave or particle concept of classical physics. The concepts of classical physics have been developed from experience in the macroscopic world and do not properly describe the microscopic world. Evolution has shaped the human brain to allow it to understand and deal effectively with macroscopic phenomena. The human nervous system was not developed to deal with phenomena at the atomic and molecular level, so it is not surprising if we cannot fully understand such phenomena.

Although both photons and electrons show an apparent duality, they are not the same kinds of entities. Photons always travel at speed c and have zero rest mass; electrons always have $v < c$ and a nonzero rest mass. Photons must always be treated relativistically, but electrons whose speed is much less than c can be treated nonrelativistically.

1.3 THE UNCERTAINTY PRINCIPLE

Let us consider what effect the wave-particle duality has on attempts to measure simultaneously the x coordinate and the x component of linear momentum of a microscopic particle. We start with a beam of particles with momentum p , traveling in the y direction, and we let the beam fall on a narrow slit. Behind this slit is a photographic plate. See Fig. 1.1.

Particles that pass through the slit of width w have an uncertainty w in their x coordinate at the time of going through the slit. Calling this spread in x values Δx , we have $\Delta x = w$.

Since microscopic particles have wave properties, they are diffracted by the slit producing (as would a light beam) a diffraction pattern on the plate. The height of the graph in Fig. 1.1 is a measure of the number of particles reaching a given point. The dif-