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量子化学

Quantum Chemistry

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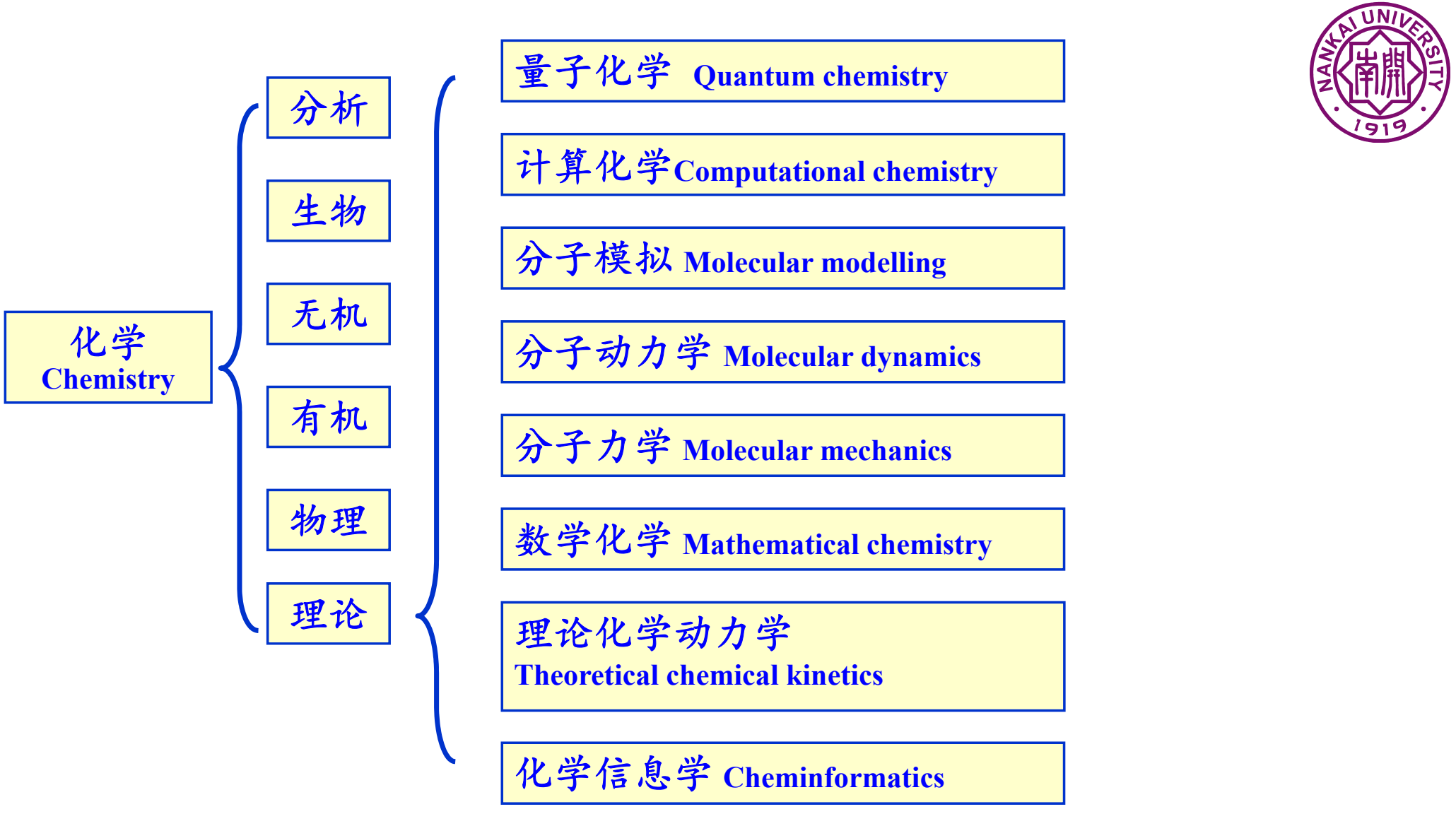

化学
Chemistry
分析
生物
无机
有机
物理
理论
量子化学 Quantum chemistry
计算化学Computational chemistry
分子模拟 Molecular modelling
分子动力学 Molecular dynamics
分子力学 Molecular mechanics
数学化学 Mathematical chemistry
理论化学动力学
Theoretical chemical kinetics
化学信息学 Cheminformatics

一、研究内容

量子化学：将量子力学原理应用于化学问题

- 方法：量子力学原理
- 内容：原子、分子和晶体的电子结构、化学键理论、分子间作用力、化学反应机理、各种光谱、波谱和电子能谱
- 应用：广泛应用于化学各个领域，成为与实验仪器一样的日常研究工具

量子化学已广泛应用于化学的各个分支

- 物理化学：计算热力学性质(结合统计力学)、解释分子光谱、确定分子的结构性质、计算化学反应过渡态、估算反应速率常数等
- 有机化学：估计分子的相对稳定性、计算反应中间物的性质、分析核磁谱等
- 分析化学：光谱的频率和强度
- 无机化学：预测解释过渡金属复合物离子的性质(配位场)
- 生物化学：生物分子的构象、了解酶与底物的作用等

二、发展历史

1. 经典物理学

十九世纪末期，经典物理学 “完美”的理论

机械运动→Newton力学

电磁现象和光→Maxwell方程

热现象→热力学和统计物理学 (Boltzmann &Gibbs)

“The more important fundamental laws and facts of physical science have all been discovered, and these are now so firmly established that the possibility of their ever being supplanted in consequence of new discoveries is exceedingly remote.... Our future discoveries must be looked for in the sixth place of decima”

Albert. A. Michelson(迈克耳逊)

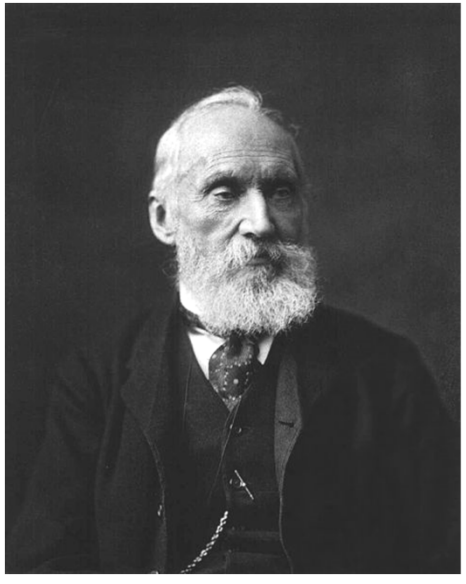
speech at the dedication of Ryerson Physics Lab, U. of Chicago 1894

Albert Michelson (1852–1931), American physicist, professor in Cleveland and Chicago, USA. He specialized in the precise measurements of the speed of light. the first American to receive a Nobel Prize in physics, 1907

There is nothing new to be discovered in physics now. All that remains is more and more precise measurement.

... The beauty and clearness of the dynamical theory, which asserts heat and light to be modes of motion, is at present obscured by two clouds.
The first came into existence with the undulatory theory of light ... it involved the question 'How could the Earth move through an elastic solid, such as essentially is the luminiferous ether?'
The second is the Maxwell-Boltzmann current doctrine regarding the partition of energy ...

- Kelvin, Lord William Thomson

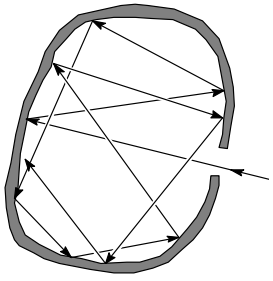


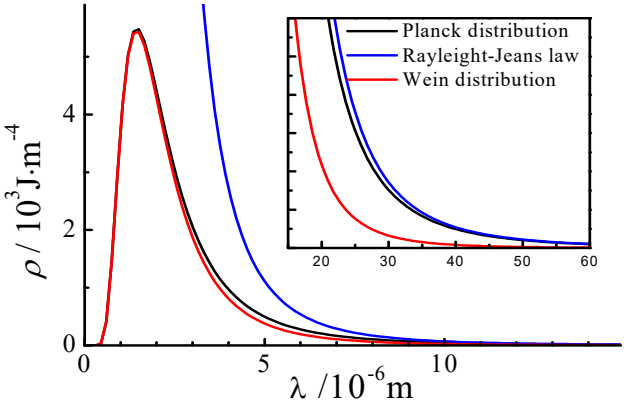
Kelvin, Lord William Thomson(1824-1907)

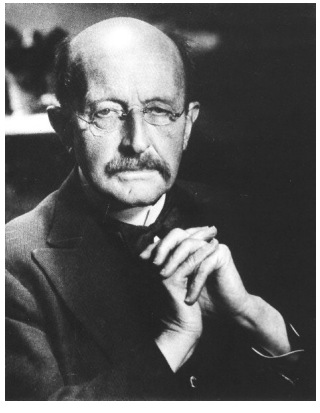
The history of quantum theory, one of most revolutionary and successful theories ever designed by man, will briefly be given below.

2. 旧量子论

1) Black body radiation 1900 – Max Planck



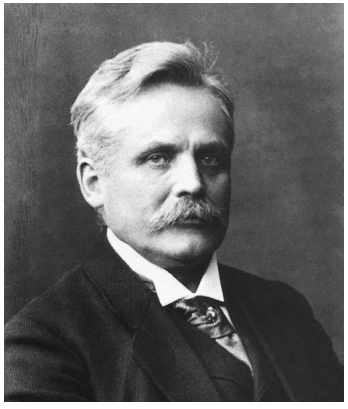




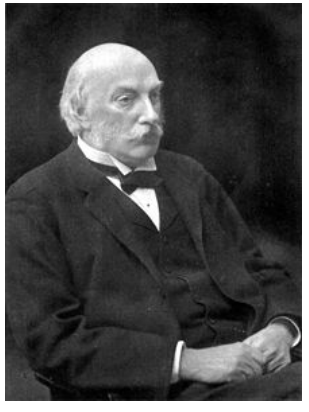
Max Karl Ernst Ludwig Planck (1858–1947), German physicist, professor at the universities in Munich, Kiel and Berlin, first director of the Institute of Theoretical Physics in Berlin. He made a major breakthrough as if in an act of scientific desperation. In 1918 Planck received the Nobel Prize "for services rendered to the advancement of Physics by his discovery of energy quanta".

1900年12月14日Planck提出能量量子化假设，成功解决了黑体辐射问题，这一天被公认为量子理论诞生日

$$h = 6.62606896\times10^{-34}\ \mathrm{J\cdot s}$$

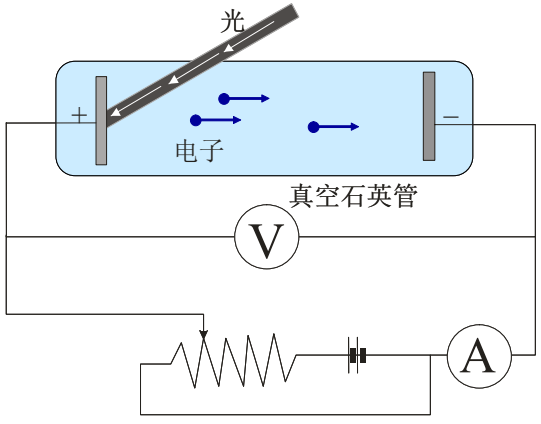


Wilhelm Wien (1864 –1928) German physicist received the 1911 Nobel Prize for his work on heat radiation.



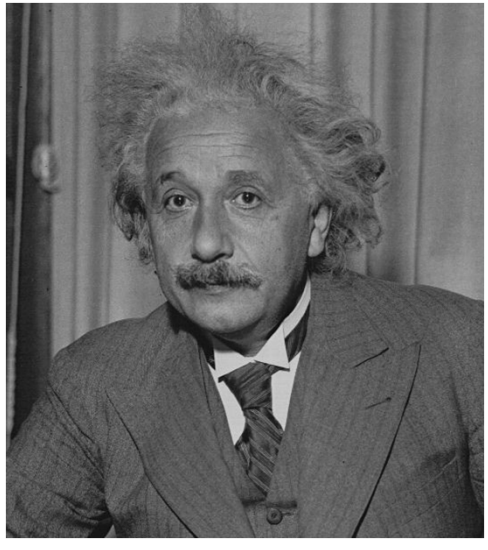
John William Strutt, Lord Rayleigh (1842–1919), British physicist, Cavendish Professor at Cambridge, received 1904 Nobel Prize "for his investigations of the densities of the most important gases and for his discovery of argon in connection with these studies".

2) Photoelectric effect 1905 – Albert Einstein

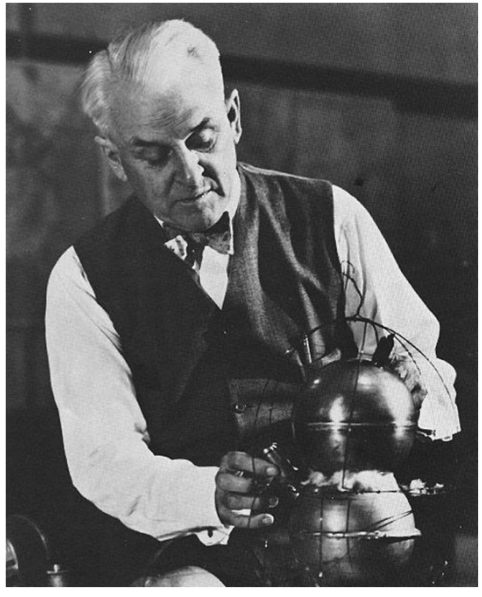


$$\varepsilon = h\nu$$

$$\frac{1}{2}mv^2 = h\nu - W_0$$



Albert Einstein (1879–1955) was a German-born theoretical physicist who developed the theory of general relativity, effecting a revolution in physics. For this achievement, Einstein is often regarded as the father of modern physics and one of the most prolific intellects in human history. He received the 1921 Nobel Prize in Physics "for his services to theoretical physics, and especially for his discovery of the law of the photoelectric effect". The latter was pivotal in establishing quantum theory within physics.



Robert A. Millikan(1868-1953) was an American experimental physicist, and Nobel laureate in physics for his measurement of the charge on the electron and for his work on the photoelectric effect

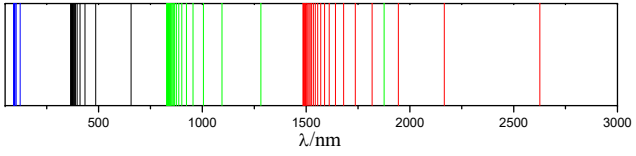
3) 1911 – Ernest Rutherford

4) The model of the hydrogen atom 1913 – Niels Bohr

5) "Old quantum theory" 1916 – Arnold Sommerfeld

$$h\nu = E'' - E'$$

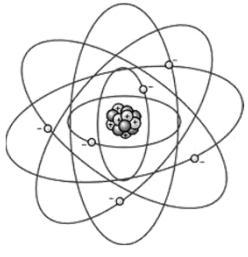
$$M = n\frac{h}{2\pi} = n\hbar$$

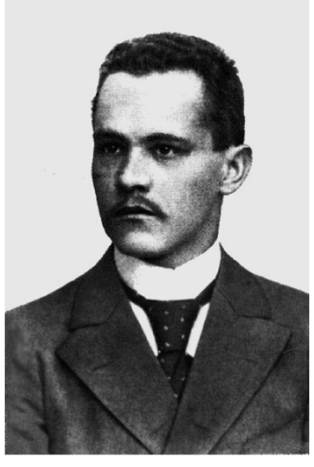


$$r = n^2 \frac{h^2 \varepsilon_0}{\pi m e^2} = n^2 a_0 \qquad \widetilde{R} = \frac{2\pi^2 m e^4}{(4\pi\varepsilon_0)^2 h^3 c} = 109737.315\ \mathrm{cm}^{-1}$$

Ernest Rutherford(1871– 1937) was a New Zealand-British chemist and physicist who became known as the father of nuclear physics. He received the 1908 Nobel Prize in Chemistry "for his investigations into the disintegration of the elements, and the chemistry of radioactive substances".

Niels Hendrik Bohr (1885–1962), Danish physicist, a professor at Copenhagen University, played a key role in the creation and interpretation of quantum mechanics. In 1922 Bohr received the Nobel Prize "for his investigation of the structure of atoms". In the same year he became the father of Aage Niels Bohr – a future winner of the Nobel Prize (1975, for studies of the structure of nuclei). Bohr has been described as one of the most influential scientists of the 20th century.

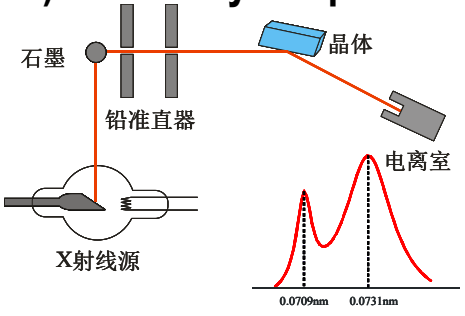




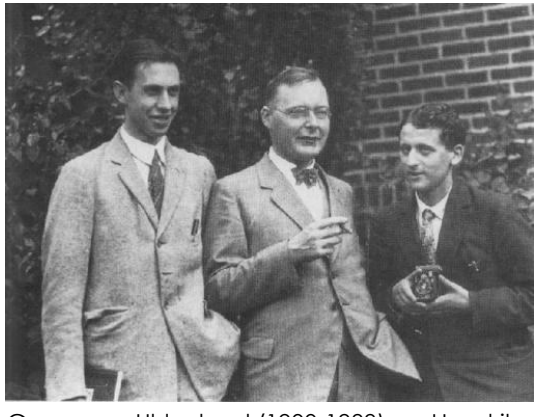
Arnold Sommerfeld (1868– 1951)
普朗克是权威，爱因斯坦是天才，索末菲是老师

3. 量子力学

1) Waves of matter 1923 – Louis de Broglie
2) Electron–photon scattering 1923 – Arthur Compton
3) Discovery of spin 1925 – George E. Uhlenbeck & Samuel A. Goudsmit



Arthur Compton (1892–1962) was an American physicist and Nobel laureate in physics for his discovery of the Compton effect.



George Uhlenbeck(1900-1988), Hendrik Kramers, and Samuel Goudsmit(1902-1978) circa 1928 in Ann Arbor

$p = h/\lambda$

Louis Victor Pierre Raymond de Broglie (1892–1987) was studying history at the Sorbonne, carefully preparing himself for a diplomatic career. His older brother Maurice, a radiographer, aroused his interest in physics. The first World War (Louis did his military service in a radio communications unit) and the study of history delayed his start in physics. He was 32 when he presented his doctoral dissertation, which embarrassed his supervisor, Paul Langevin. The thesis, on the wave nature of all particles, was so revolutionary, that only a positive opinion from Einstein, who was asked by Langevin to take a look of the dissertation, convinced the doctoral committee. Only five years later (in 1929), Louis de Broglie received the Nobel Prize "for his discovery of the wave nature of electrons".

4) Pauli Exclusion Principle 1925 – Wolfgang Pauli
5) Matrix quantum mechanics 1925 – Werner Heisenberg

Wolfgang Ernst Pauli (1900–1958) was an Austrian theoretical physicist and one of the pioneers of quantum physics. he received the 1945 Nobel Prize in Physics for his "decisive contribution through his discovery of a new law of Nature, the exclusion principle or Pauli principle," involving spin theory, underpinning the structure of matter and the whole of chemistry.

Werner Karl Heisenberg (1901–1976) was a German theoretical physicist who made foundational contributions to quantum mechanics and is best known for asserting the uncertainty principle of quantum theory. In addition, he made important contributions to nuclear physics, quantum field theory, and particle physics. Heisenberg, along with Max Born and Pascual Jordan, set forth the matrix formulation of quantum mechanics in 1925. Heisenberg was awarded the 1932 Nobel Prize in Physics for the creation of quantum mechanics, and its application especially to the discovery of the allotropic forms of hydrogen.

6) Schrödinger equation 1926 – Erwin Schrödinger
7) Statistical interpretation of wave function 1926 – Max Born

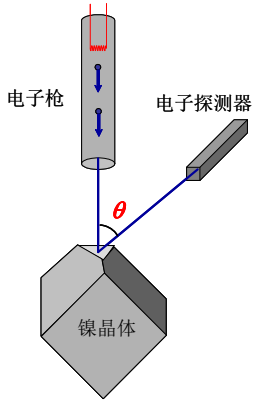
Erwin Rudolf Josef Alexander Schrödinger (1887–1961) was an Austrian born physicist and theoretical biologist who was one of the fathers of quantum mechanics, and is famed for a number of important contributions to physics, especially the Schrödinger equation, for which he received the Nobel Prize in Physics in 1933.

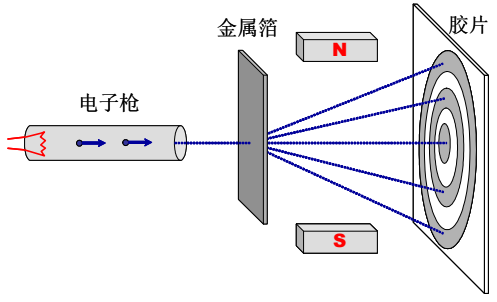
$$\hat{H}\Psi = E\Psi$$

Max Born (1882–1970) was a German-British physicist and mathematician who was instrumental in the development of quantum mechanics. He also made contributions to solid-state physics and optics and supervised the work of a number of notable physicists in the 1920s and 30s. Born won the 1954 Nobel Prize in Physics.

8) Uncertainty principle 1927 – Werner Heisenberg $\Delta x \Delta p_x \geq \frac{\hbar}{2}$

9) Electron diffraction 1927 – Clinton Davisson, Lester H. Germer, George Thomson





Clinton Joseph Davisson(1881-1958) & Lester Halbert Germer (1896-1971)

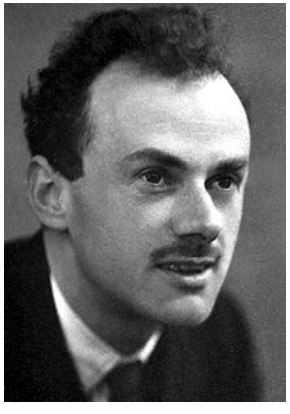
George Paget Thomson(1892-1975)

Clinton Joseph Davisson, was an American physicist. George Paget Thomson was an English physicist. They won the 1937 Nobel Prize in Physics for the discovery of the wave properties of the electron by electron diffraction.

10) Dirac equation for the electron and positron 1928 – Paul Dirac

$$i\hbar\frac{\partial}{\partial t}\psi = \left(h_D + qV\right)\psi$$

Paul Adrien Maurice Dirac (1902 – 1984) was an English theoretical physicist who made fundamental contributions to the early development of both quantum mechanics and quantum electrodynamics. Dirac shared the Nobel Prize in Physics for 1933 with Erwin Schrödinger, "for the discovery of new productive forms of atomic theory."



δ

1927年Solvay会议

I. Langmuir, M. Planck, M. Curie, H.A. Lorentz, A. Einstein, P. Langevin, C.E. Guye, C.T.R. Wilson, O.W. Richardson.
P. Debye, M. Knudsen, W.L. Bragg, H.A. Kramers, P.A.M. Dirac, A.H. Compton, L.V. de Broglie, M.Born, N. Bohr.
A. Piccard, E. Henriot, P. Ehrenfest, E. Herzen, T. De Donder, E. Schroedinger, E. Verschaffelt, W. Pauli, W. Heisenberg, R. H. Fowler, L. Brillouin.

4. 量子化学

1) The birth of Quantum chemistry 1927 –Walter Heitler, Fritz London

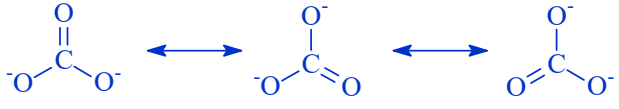
2) Heitler-London-Slater- Pauling Valence-Bond Theory

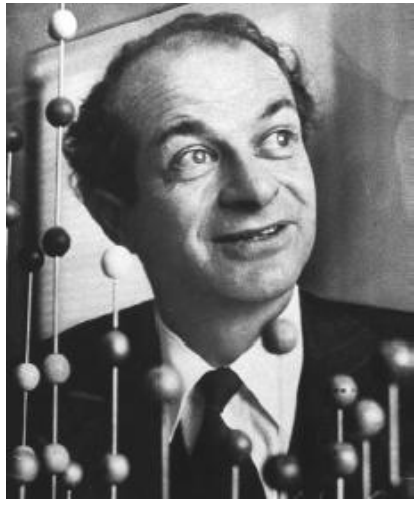
Walter Heinrich Heitler (1904–1981) was a German physicist who made contributions to quantum electrodynamics and quantum field theory. He brought chemistry under quantum mechanics through his theory of valence bonding

Fritz Wolfgang London (1900–1954) was a German theoretical physicist. His fundamental contributions to the theories of chemical bonding and of intermolecular forces.

John Clarke Slater (1900–1976) was a noted American physicist who made major contributions to the theory of the electronic structure of atoms, molecules and solids. This work is of ongoing importance in chemistry, as well as in many areas of physics.

Valence Bond Theory

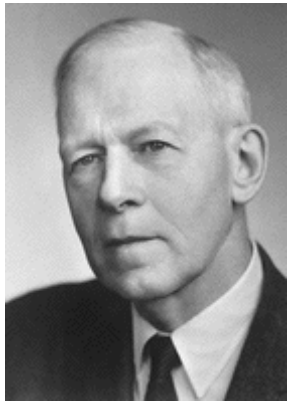




Linus Carl Pauling (1901–1994), American physicist and chemist. He received the 1954 Nobel prize: "for his research into the nature of the chemical bond and its application to the elucidation of the structure of complex substances". In 1962 he received the Nobel peace prize. His major achievements are the development of the theory of chemical bond, i.a., the VB method (also called resonance theory), and determining the structure of one of the fundamental structural elements of proteins, the a-helix.

3) Molecular Orbital Theory 1927–1931 Friedrich Hund, Robert Mulliken

Friedrich Hermann Hund (1896 -1997) was a German physicist known for his work on atoms and molecules.



Robert Sanderson Mulliken (1896 – 1986) was an American physicist and chemist, primarily responsible for the early development of molecular orbital theory. He received the Nobel Prize for chemistry in 1966.

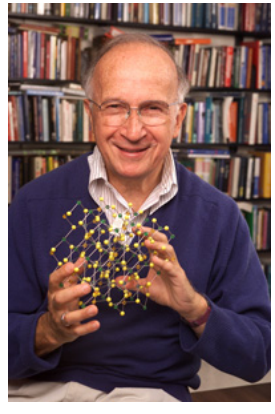
4) Frontier Molecular Orbital Theory 1952 Kenichi Fukui 福井謙一

5) Principle of the Conservation of Molecular Orbital Symmetry 1965 Woodward-Hoffmann rules

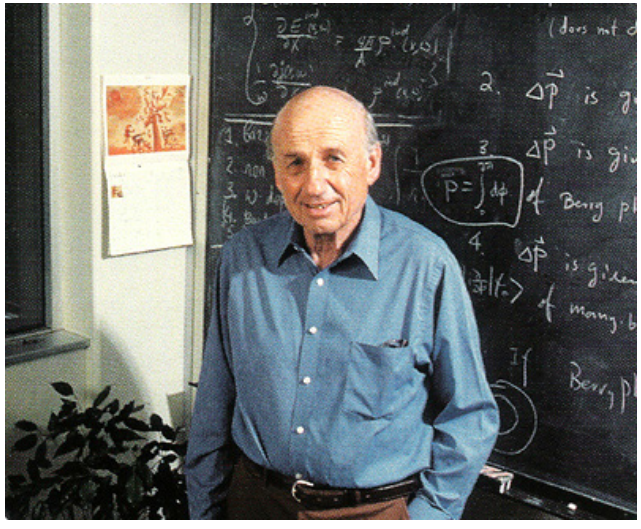
Kenichi Fukui 福井謙一 (1918–1998), Japanese chemist, One of the first scholars who stressed the importance of the IRC, and introduced what is called the frontier orbitals (mainly HOMO and LUMO), which govern practically all chemical processes. Fukui received the Nobel Prize in chemistry in 1981.

Robert Burns Woodward (1917–1979) was an American organic chemist, considered by many to be the preeminent organic chemist of the twentieth century. He was awarded the Nobel Prize in Chemistry in 1965.

Roald Hoffmann (1937-) is an American theoretical chemist who won the 1981 Nobel Prize in Chemistry.



6) Density Functional Theory 1964~1965
Walter Kohn, Pierre C. Hohenberg and 沈吕九(Lu Jeu Sham)



Walter Kohn (1923-2016), American physicist of the Austrian origin. His conviction about the primary role the electronic density plays, led him to fundamental theoretical discoveries. Kohn shared the Nobel Prize with John A. Pople in 1998, receiving it "for his development of the density functional theory".

Pierre C. Hohenberg (1934-2017) is a French-American theoretical physicist

沈吕九(Lu Jeu Sham)(1938-)

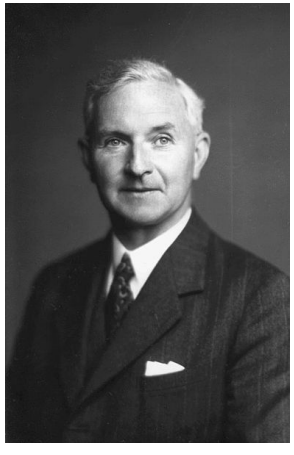
The fundamental laws necessary for the mathematical treatment of large parts of physics and the whole of chemistry are thus fully known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved -P. A. M. Dirac 1929

5. 计算量子化学

- 1928 Hartree — Self-Consistent Field method (SCF)
- 1928 J. C. Slater— Proof that the Hartree method gives the best possible variation function function
- 1929 Lennard-Jones — Linear Combination of Atomic Orbitals approximation for molecular orbitals
- 1930 Vladimir A. Fock — HF-SCF Antisymmetrized spin-orbitals

Douglas Rayner Hartree (1897–1958) was an English mathematician and physicist most famous for the development of numerical analysis and its application to the Hartree-Fock equations of atomic physics and the construction of the meccano differential analyser.

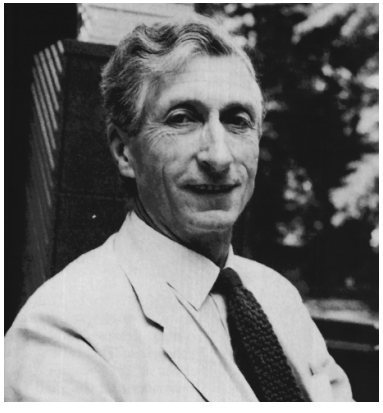
Vladimir Aleksandrovich Fock (1898 – 1974) was a Soviet physicist, who did foundational work on quantum mechanics and quantum electrodynamics.



Sir John Edward Lennard-Jones (1894–1954) was a mathematician who was a professor of theoretical physics at Bristol University, and then of theoretical science at Cambridge University. He may be regarded as the initiator of modern computational chemistry.

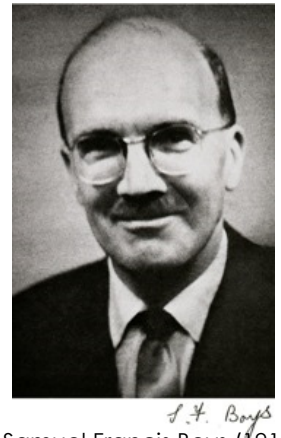
- **1930 Hückel — HMO**
- **1934 Christian Møller and Milton S. Plesset — Møller–Plesset perturbation theory (MP)**
- **1938 Coulson — The first accurate calculation of a molecular orbital wavefunction on the hydrogen molecule**
- **1950 Boys — Configuration Interaction(CI)**
- **1951 Clemens C. J. Roothaan and George G. Hall — Roothaan-Hall equations**

Erich Hückel (1896 – 1980) was a German physicist and physical chemist. He is known for two major contributions: The Debye–Hückel theory of electrolytic solutions; The Hückel method of approximate molecular orbital (MO) calculations on π electron systems.



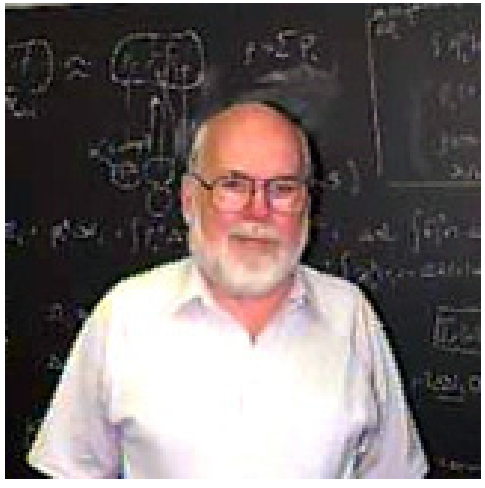
Charles Alfred Coulson (1910 – 1974) was an applied mathematician, theoretical chemist and religious author

Clemens C. J. Roothaan(1918-2019) His Important Contributions:The theory of atomic and molecular structure. Application of digital computers to scientific problems.



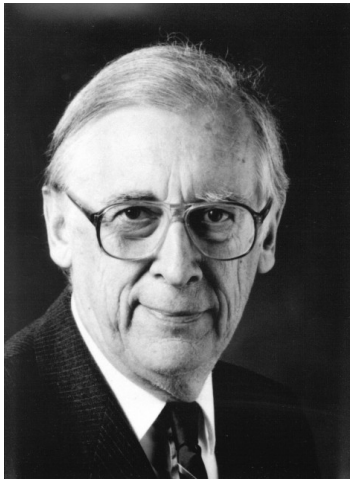
Samuel Francis Boys (1911-1972). Leader in Theoretical Chemistry, His contributions to Quantum Molecular Science are all fundamental. Gaussian functions (1950), Configuration Interaction, the counterpoise method for the basis set superposition error(BSSE)

- **1950s Rudolph Pariser, Robert Parr and John Pople — PPP Method**
- **1963 Roald Hoffmann — Extended Hückel Method(EHMO)**



Robert Ghormley Parr (1921-2017) a theoretical chemist.

Important Contributions: Ab initio methods, semiempirical methods, separability and localization, electron correlation, vibrational potential functions, internal rotation, electrostatic models, density-functional theory and methods, chemical concepts from density-functional theory, applications of information theory in quantum chemistry.



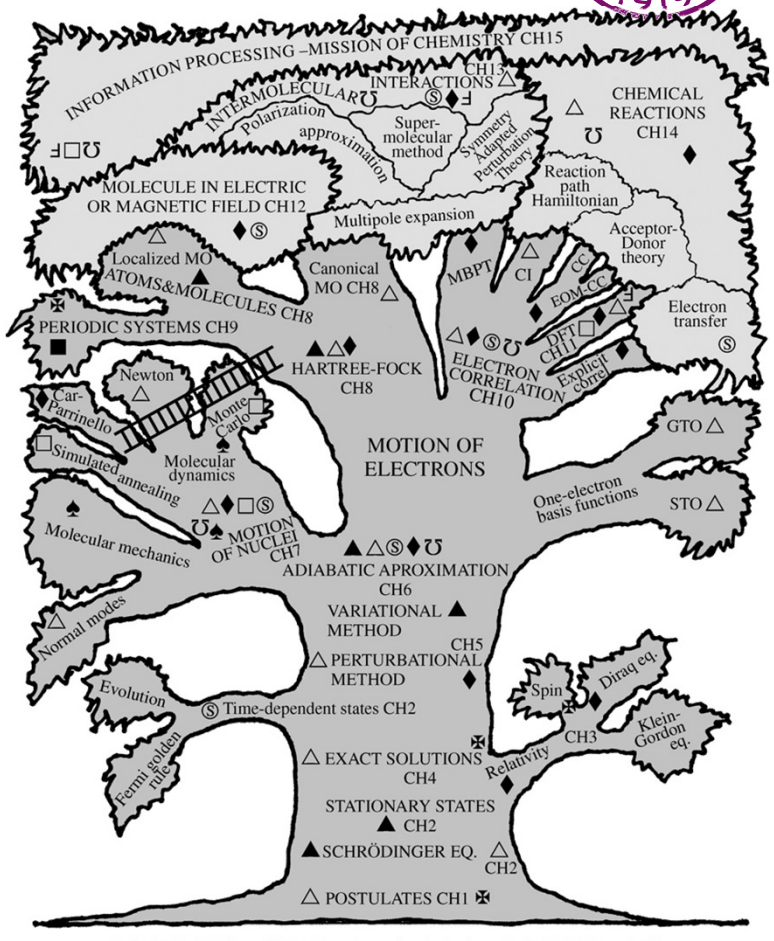
Sir John Anthony Pople, (1925 – 2004) was a Nobel-Prize(1998) winning theoretical chemist.

Important Contributions: Development of semi-empirical and ab initio molecular orbital theory

Rudolph Pariser(1923 -) a physical and polymer chemist. Pariser is best known for his work with Robert G. Parr on the method of molecular orbital computation now known as the Pariser–Parr–Pople method (PPP method). He spent most of his career as a polymer chemist working for DuPont

- **1954** Pople, Nesbet,Berthier — Unrestricted Hartree–Fock(UHF)
- **1960** Roothaan — Restricted open-shell Hartree–Fock (ROHF)
- **1965** Pople, Santry and Segal — CNDO,
- **1965** Pople, Santry and Segal — NDDO
- **1967** Pople, Beveride and Dobosh — INDO
- **1970s and 1980s** Michael Dewar — MINDO, MNDO, AM1 and PM3

Michael J. S. Dewar (1918-997) a theoretical chemist is known most famously for the development of the Semi-empirical quantum chemistry methods.



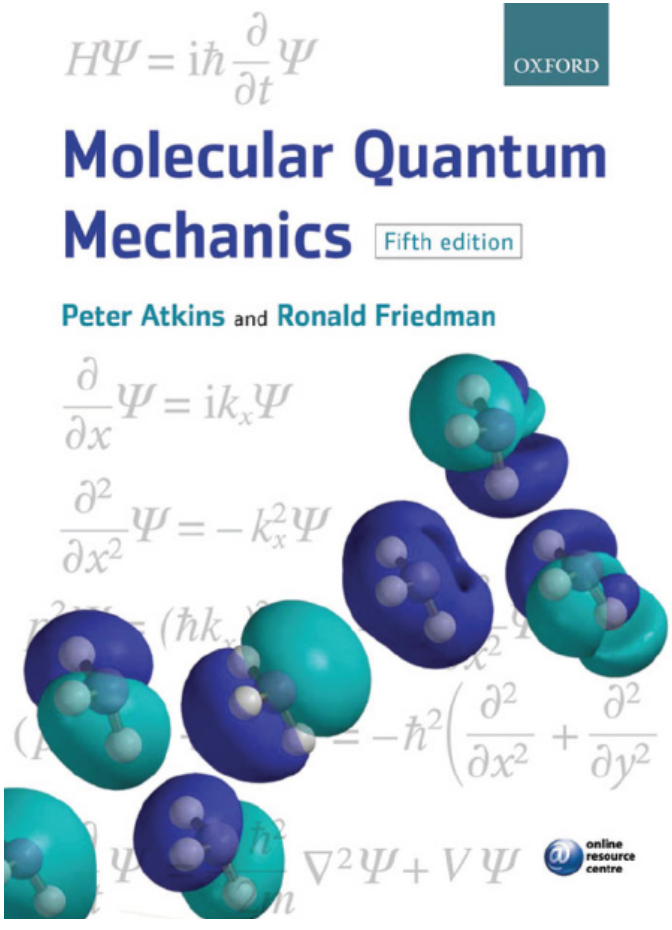
From "*Ideas of Quantum Chemistry*", Lucjan Piela, Elservier, 2007 WHERE ARE WE?

三、课程内容

- 量子力学基础
- 可精确求解的简单体系
- 角动量、自旋和原子光谱
- 近似方法
- 分子结构
- 计算化学方法

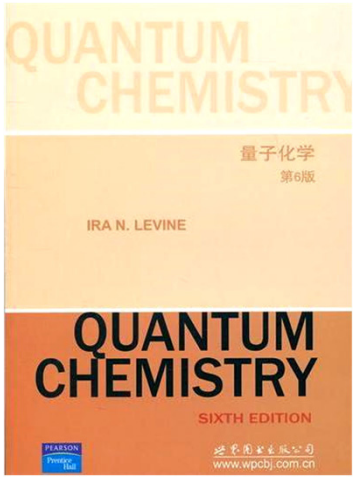
四、参考书

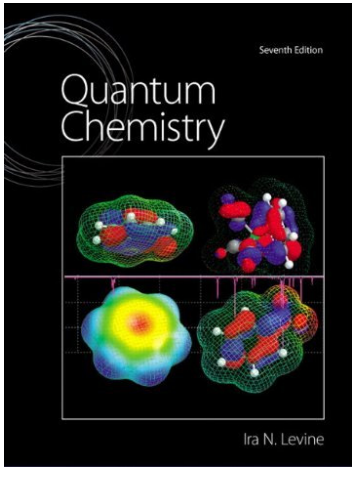
1. "*Molecular Quantum Mechanics*" 5th ed. Peter Atkins, Ronald Friedman, Oxford University Press Inc., 2011
2. "*Quantum Chemistry*" 7th ed. , Ira N. Levine, Pearson Education, Inc., 2014　6th ed. 世界图书出版公司;《量子化学》(2nd ed.)，宁世光，余敬曾，刘尚长译，人民教育出版社，1980
3. "*Quantum Chemistry*" 3th ed. John P. Lowe, Kirk A. Peterson, Elsevier Academic Press, 2006, 世界图书出版公司,2011
4. 《量子化学》(第二版)，徐光宪，黎乐民，王德民编著，科学出版社，2007(上册)，2009(中册)
5. "*Ideas of Quantum Chemistry*", Lucjan Piela, Elservier, 2007
6. 《量子化学》，艾林等著，石宝林译，科学出版社，1981
7. 《量子化学基础》，刘若庄等著，科学出版社，1983



"*Molecular Quantum Mechanics*" 5th ed. Peter Atkins, Ronald Friedman, Oxford University Press Inc., 2011

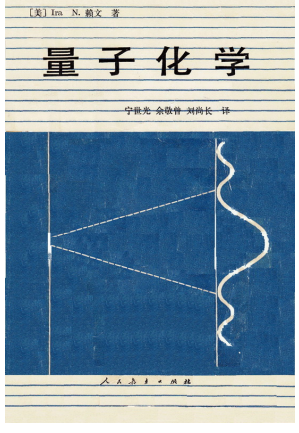
1. The foundations of quantum mechanics
2. Linear motion and the harmonic oscillator
3. Rotational motion and the hydrogen atom
4. Angular momentum
5. Group theory
6. Techniques of approximation
7. Atomic spectra and atomic structure
8. An introduction to molecular structure
9. The calculation of electronic structure
10. Molecular rotations and vibrations
11. Molecular electronic transitions
12. The electric properties of molecules
13. The magnetic properties of molecules
14. Scattering theory

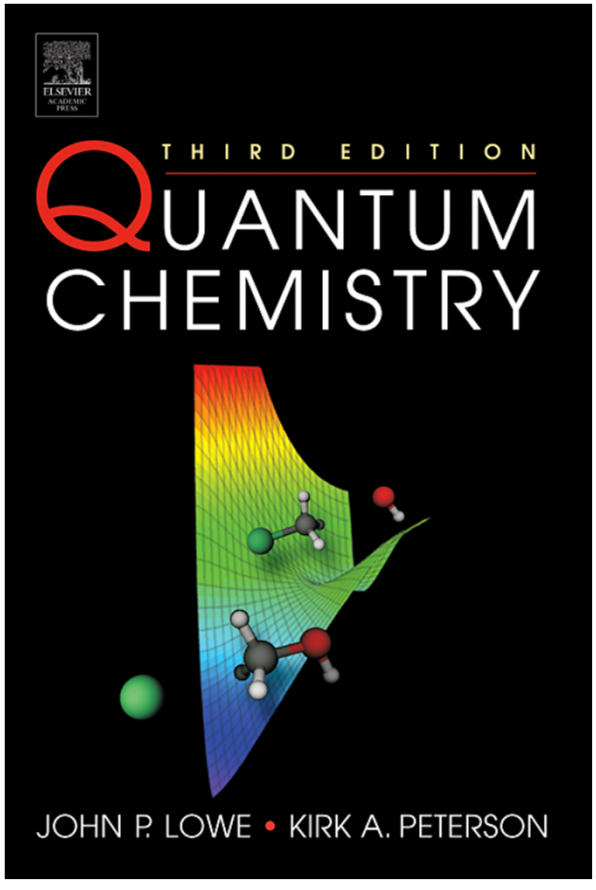




Quantum Chemistry" 7th ed. ,
Ira N. Levine, Pearson Education, Inc., 2014
《量子化学》(6th ed.) 世界图书出版公司, 2011
《量子化学》(2nd ed.)，宁世光，余敬曾，刘尚长译，人民教育出版社，1980

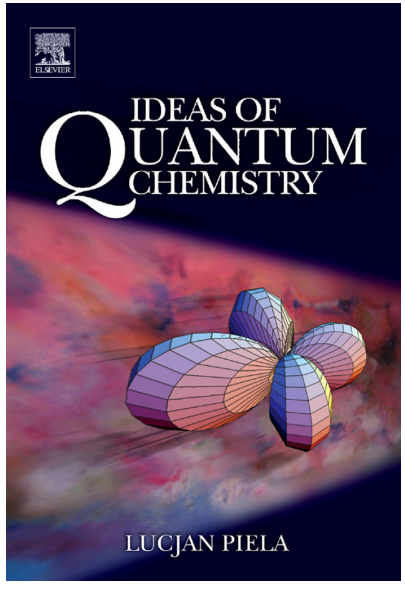
1. the schrödinger equation
2. the particle in a box
3. operators
4. the harmonic oscillator
5. angular momentum
6. the hydrogen atom
7. theorems of quantum mechanics
8. the variation method
9. perturbation theory
10. electron spin and the spin-statistics theorem
11. many-electron atoms
12. molecular symmetry
13. electronic structure of diatomic molecules
14. theorems of molecular quantum mechanics
15. molecular electronicstructure
16. electron-correlation methods
17. semiempirical and molecular-mechanics treatments of molecules
18. comparisons of methods





"*Quantum Chemistry*" 3th ed.
John P. Lowe, Kirk A. Peterson,
Elsevier Academic Press, 2006
世界图书出版公司, 2011

1. classical waves and the time-independent schrodinger wave equation
2. quantum mechanics of some simple systems
3. the one-dimensional harmonic oscillator
4. the hydrogenlike ion, angular momentum, and the rigid rotor
5. many-electron atoms
6. postulates and theorems of quantum mechanics
7. the variation method
8. the simple hückel method and applications
9. matrix formulation of the linear variation method
10. the extended hückel method
11. the scf-lcao-mo method and extensions
12. time-independent rayleigh-schrödinger perturbation theory
13. group theory
14. qualitative molecular orbital theory
15. molecular orbital theory of periodic systems



《量子化学》(第二版)，徐光宪，黎乐民，王德民编著，科学出版社，2007(上册)

第1章 量子力学基础
第2章 简单体系的精确解
第3章 氢原子和类氢离子
第4章 角动量和自旋
第5章 变分法和微扰理论
第6章 群论基础知识
第7章 群表示理论
第8章 群论在量子化学中的应用

"*Ideas of Quantum Chemistry*", Lucjan Piela, Elservier, 2007

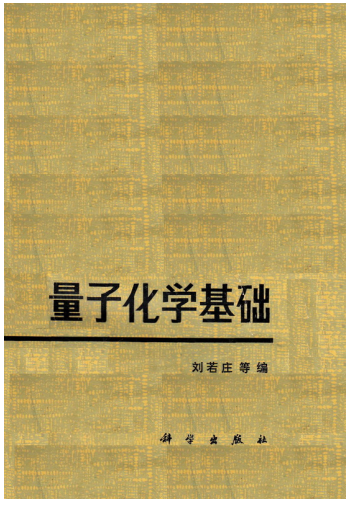
1. The Magic of QuantumMechanics
2. The Schrödinger Equation
3. Beyond the Schrödinger Equation
4. Exact Solutions –Our Beacons
5. Two Fundamental Approximate Methods
6. Separation of Electronic and Nuclear Motions
7. Motion of Nuclei
8. Electronic Motion in the MeanField:Atoms and Molecules
9. Electronic Motion in the Mean Field:Periodic Systems
10. Correlation of the Electronic Motions
11. Electronic Motion:Density Functional Theory (DFT)
12. The Molecule inan Electric or MagneticField
13. Intermolecular Interactions
14. Intermolecular Motion of Electrons and Nuclei:Chemical Reactions
15. Information Processing – the Mission of Chemistry

《量子化学》，艾林等著，石宝林译，科学出版社，1981

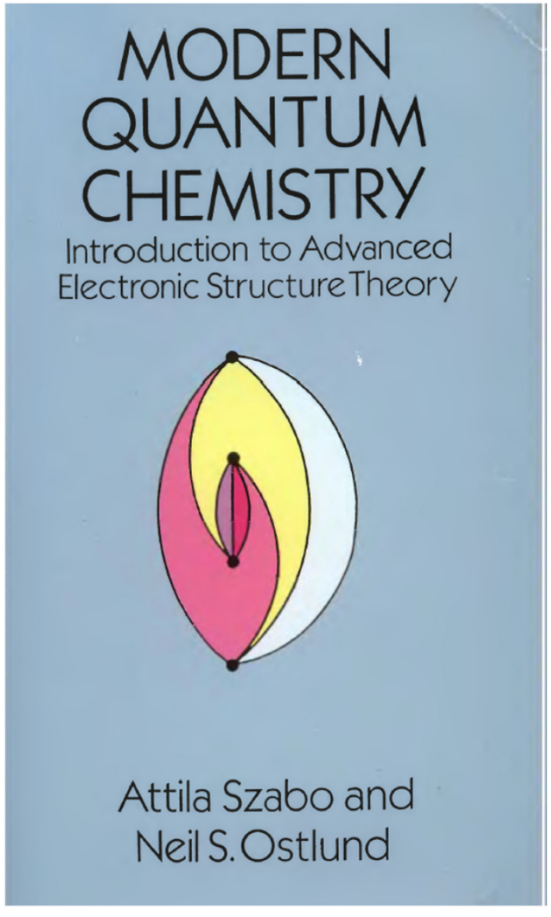
第一章 绪论:旧量子论
第二章 经典力学原理
第三章 量子力学原理
第四章 量子力学的微分方程
第五章 某些简单体系的量子力学
第六章 氢原子
第七章 近似方法
第八章 含时微扰:辐射理论
第九章 原子结构
第十章 群论
第十一章 双原子分子的电子状态
第十二章 共价键
第十三章 共振和复杂分子的结构
第十四章 分子光谱学原理
第十五章 初等量子统计力学
第十六章 反应速度的量子力学理论
第十七章 电磁现象
第十八章 特殊课题

《量子化学基础》，刘若庄等著，科学出版社，1983

第一章 量子力学基础知识
第二章 原子结构
第三章 简单分子轨道理论
第四章 共轭分子的结构与性能
第五章 分子轨道对称守恒原理
第六章 自洽场分子轨道法简介
第七章 价键法简介及其与分子轨道法对比
第八章 配位场理论



Modern Quantum Chemistry Intro to Advanced Electronic Structure Theory



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Chap 1. Mathematical Review
Chap 2. Many Electron Wave Functions and Operators
Chap 3. The Hartree-Fock Approximation
Chap 4. Configuration Interaction
Chap 5. Pair and Coupled-Pair Theories
Chap 6. Many-Body Perturbation
Chap 7. The One-Partical Many-Body Green's Function

理论化学入门

Exploring Chemistry with Electronic Structure Methods 2nd ed 基础入门

Exploring Chemistry with Electronic Structure Methods 3rd ed 计算进阶

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