

CHEM3023: Spins, Atoms and Molecules

CHEM3006P or similar background knowledge is required for this course. This course has two parts:

Part 1: Quantum Chemistry techniques for simulations of molecular properties
(Dr Chris-Kriton Skylaris)

Part 2: Quantum theory of angular momentum (spin) and its applications to
NMR (Dr David Turner)

Textbooks for part 1:

Recommended:

- C. J. Cramer, “Essentials of Computational Chemistry: Theories and Models”, 2nd Edition, Wiley 2004

Also very useful:

- P. Atkins and R. Friedman, “Molecular Quantum Mechanics”, 4th Edition, OUP 2005
- A. Szabo and N. S. Ostlund, “Modern Quantum Chemistry”, Dover 1996

Contents of part 1 (Quantum Chemistry)

- Time-independent Schrödinger equation
- Wavefunctions and observable properties in Quantum Mechanics
- Separation of electronic from nuclear coordinates
- Approximation techniques for calculating wavefunctions: the variation principle
- First-principles computational methods for molecules. The Hartree-Fock molecular orbital method
- Setting up and running Hartree-Fock calculations, examples
- Calculations of molecular structure, spectra, electronic properties, energy levels, thermodynamic properties

Lecture 1

Introduction to molecular quantum theory

C.-K. Skylaris

Learning outcomes

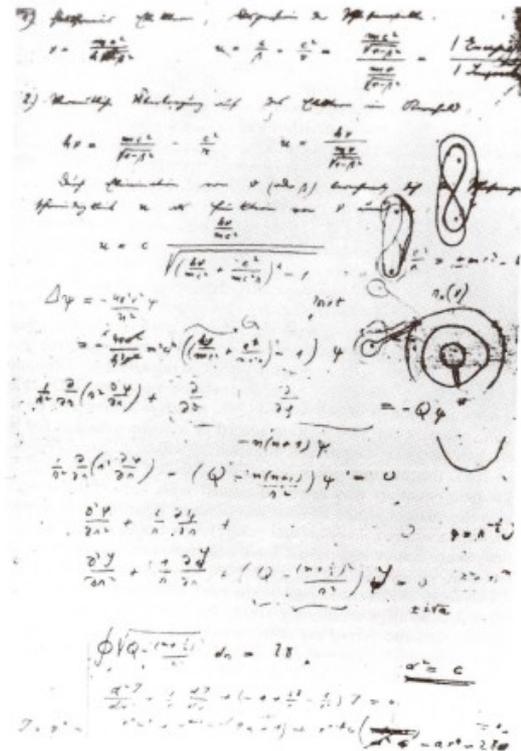
- The time-independent Schrödinger equation
- Obtaining experimentally observable properties from the wavefunction

Discovery of “modern” quantum mechanics

Work of many distinguished scientists. Discovery of Schrödinger equation was a major breakthrough. According to history, Schrödinger first wrote down his “wave equation” during a skiing Christmas holiday in 1925-26.



The Villa Hertzog, where wave mechanics was discovered during the Christmas holidays, 1925–26.



Page from Schrödinger's notebook where he first wrote his wave equation

The Schrödinger equation (time-independent version)

- Is a fundamental law of nature: It can not be proved, but we know it works. Newton's second law of motion ($\mathbf{F} = m \mathbf{a}$) is another example of a law of nature.
- Applies at the microscopic scale: electrons, atoms, molecules, etc.
- What information can it provide? Every property that can be measured experimentally.
- The solution of Schrödinger's equation yields the wavefunction. Observable properties are extracted by further processing of the wavefunction.
- Separated from classical “physics” and widely applicable, especially in chemistry and materials science.

Quantum theory of matter

Discovered (c.a. 1925). Extremely general, applies to all atomic-scale objects.



The Nobel Prize in Physics 1933

"for the discovery of new productive forms of atomic theory"



Erwin Schrödinger

🏆 1/2 of the prize

Austria

Berlin University
Berlin, Germany



Paul Adrien Maurice Dirac

🏆 1/2 of the prize

United Kingdom

University of Cambridge
Cambridge, United Kingdom

Dirac (1929): "The underlying laws necessary for the mathematical theory of ... the whole of **chemistry** are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble..."

(Computational) Quantum Chemistry

Several decades after the discovery of quantum mechanics. Further research and the availability of computers allow application of Quantum Mechanics to Chemistry

From the presentation of the Nobel prize in Chemistry 1998:

“Chemistry is not only test tubes and chemicals. In quantum chemistry, quantum mechanics is used to *compute* the properties of molecules and their interaction. This year's laureates have made it possible to use the complex equations of quantum mechanics to study molecules and chemical processes with the help of computers.”



The Nobel Prize in Chemistry 1998

"for his development of the density-functional theory"

"for his development of computational methods in quantum chemistry"

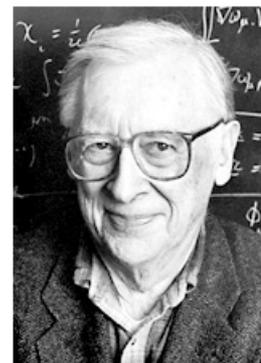


Walter Kohn

🏆 1/2 of the prize

USA

University of California
Santa Barbara, CA, USA



John A. Pople

🏆 1/2 of the prize

United Kingdom

Northwestern University
Evanston, IL, USA

The time-independent Schrödinger equation

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

Hamiltonian operator Wavefunction Energy

The diagram shows the time-independent Schrödinger equation $\hat{H}\Psi = E\Psi$. Three blue arrows point from text labels below to the corresponding terms in the equation: one from 'Hamiltonian operator' to \hat{H} , one from 'Wavefunction' to Ψ , and one from 'Energy' to E .

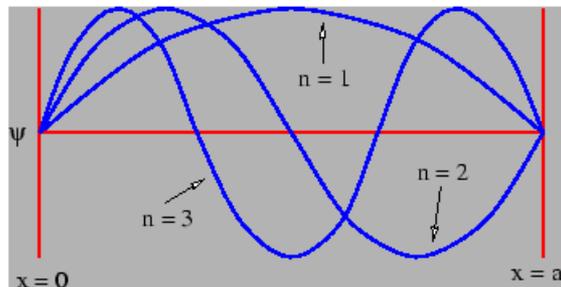
$$(\hat{T} + \hat{V})\Psi = E\Psi$$

Kinetic energy operator Potential energy operator

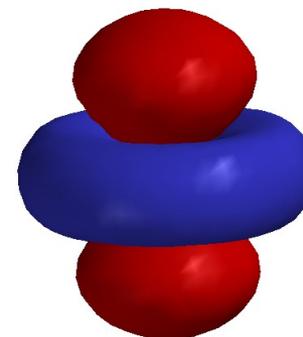
The diagram shows the expanded time-independent Schrödinger equation $(\hat{T} + \hat{V})\Psi = E\Psi$. Two blue arrows point from text labels below to the corresponding terms in the equation: one from 'Kinetic energy operator' to \hat{T} , and one from 'Potential energy operator' to \hat{V} .

Wavefunctions

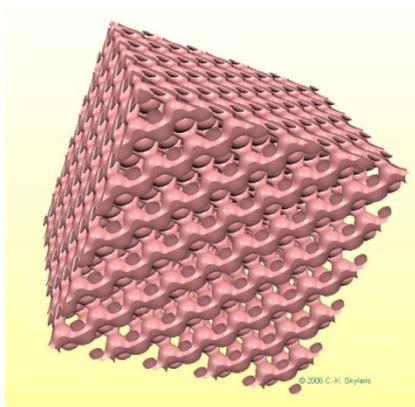
Schrödinger's equation applies to all kinds of systems (atoms, molecules, materials). Its solutions are the wavefunctions:



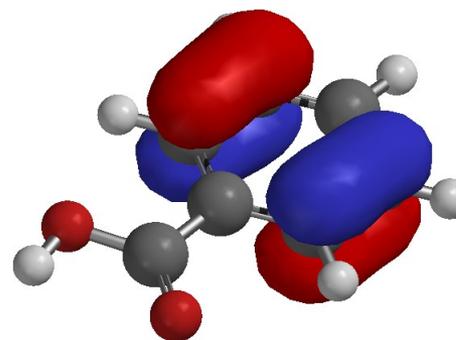
Particle in a box



Hydrogen atom



Silicon crystal



Benzoic acid

Wavefunctions

- In general, a wavefunction (often represented by the Greek letter Ψ , “psi”) is a complex function of many variables, one for each particle. For N particles it is a function of their $3N$ coordinates:

$$\Psi(x_1, y_1, z_1, x_2, y_2, z_2, \dots, x_N, y_N, z_N) = \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$$

How many variables are included in the wavefunction of

- 1) A hydrogen molecule
- 2) A benzene molecule

Acceptable wavefunctions

Whether exact or approximate, an acceptable wavefunction must obey the following properties:

- Be finite
- Be continuous
- Be single-valued
- Respect the indistinguishability of the same particles (e.g. electrons, or protons, etc)
- Its square modulus can be interpreted as a probability distribution (in other words it should be possible to normalise the wavefunction to unity – see later)

Operators

- A different way to write something that you already know
- Any change on a function can be represented by an operator
- Here are some examples of changes that can happen to a function and how these are represented by an operator “acting” on the function:

Multiplication by a number $\hat{a} f(x) = af(x)$

Differentiation $\hat{D}_y g(x, y) = \frac{\partial g(x, y)}{\partial y}$

Multiplication by a function $\hat{V}(x) f(x) = V(x)f(x)$

Operators and observable properties

- Experimental measurements of physical properties are average values
- Quantum mechanics postulates that we can calculate the result of any such measurement by “averaging” the appropriate operator and the wavefunction as follows:

$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} \Psi^*(x) \hat{x} \Psi(x) dx}{\int_{-\infty}^{\infty} \Psi^*(x) \Psi(x) dx}$$

The above example provides the expectation value (average value) of the position along the x-axis.

Complex numbers and functions

In Quantum mechanics we use the “*” superscript to denote the complex conjugate of numbers and functions. Examples:

$$2^* = 2 \qquad i^* = -i$$

$$(3 + 5i)^* = 3 - 5i$$

$$(a + ib)^* = a - ib$$

$$\Psi(x) = f(x) + ig(x) \qquad \Psi^*(x) = f(x) - ig(x)$$

The (time-independent) Schrödinger equation is an **eigenvalue equation**

$$\hat{A} f_n(x) = a_n f_n(x)$$

operator for property A eigenfunction eigenvalue

$$\hat{H} \Psi_n(x) = E_n \Psi_n(x)$$

Energy operator (Hamiltonian) wavefunction Energy eigenvalue

Quantisation: Only certain (discrete) eigenvalues are allowed by the solutions of the Schrödinger equation

Particle in a box

$$E_n = \frac{n^2 h^2}{8ml^2}$$

Harmonic oscillator

$$E_n = \left(n + \frac{1}{2}\right) h\nu$$

Hydrogen atom

$$E_n = -\frac{Z^2}{n^2} \left(\frac{e^2}{2a}\right)$$

Probability density

In principle, quantum mechanics assumes that a particle can be found anywhere in space. The probability that it will be found in the **interval between x and $x+dx$** is given by

$$P(x)dx = |\Psi(x)|^2 dx$$

Probability density

squared magnitude of wavefunction

provided that the wavefunction is normalised,

$$\int_{-\infty}^{\infty} |\Psi(x)|^2 dx = 1$$

i.e. the probability of finding the particle in all space is equal to 1

Probability density

The probability density formula contains the squared **magnitude of a complex number** which is defined as follows:

$$|z|^2 = z z^*$$

$$|a + ib|^2 = (a + ib)(a - ib) = a^2 + b^2$$

Write down the probability density for the following wavefunctions

n -th state of particle
in 1D box:

$$\Psi_n(x) = \sqrt{\frac{2}{l}} \sin\left(\frac{n\pi x}{l}\right)$$

Ground state of
hydrogen atom

$$\Psi_{100}(x, y, z) = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a}\right)^{3/2} e^{-Zr/a}$$

Summary

- Time-independent Schrödinger equation
- Wavefunctions
- Operators
- Probability density