UNIVERSITY OF
Southampton
School of Chemistry

CHEM6085

DENSITY FUNCTIONAL THEORY
for calculations on molecules and materials

Dr Chris-Kriton Skylaris

Recommended reading

On DFT theory and calculations:

- C. J. Cramer, “Essentials of Computational Chemistry: Theories and Models”, 2nd Edition, Wiley 2004.
- R. M. Martin, “Electronic Structure: Basic Theory and Practical Methods”, Cambridge University Press, 2004.

On Quantum Mechanics and Computational Chemistry:

- P. Atkins and R. Friedman, “Molecular Quantum Mechanics”, 4th Edition, OUP 2005.
- A. Szabo and N. S. Ostlund, “Modern Quantum Chemistry”, Dover 1996.
- F. Jensen, “Introduction to Computational Chemistry”, 2nd Edition, Wiley 2007.

Teaching methods

- Lectures
- Workshops
- Homework
- Questions, and end of lectures quiz

Assessment

- Christmas break assignment
- End of course exam

Programme

- Time-independent Schrödinger equation
- Wavefunctions and observable properties in Quantum Chemistry
- Electronic density (instead of the electronic wavefunction)
- Derivation of Density Functional Theory
- Kohn-Sham Density Functional Theory
- The Local Density Approximation
- More accurate approximations
- Setting up and running DFT calculations

Lecture 1

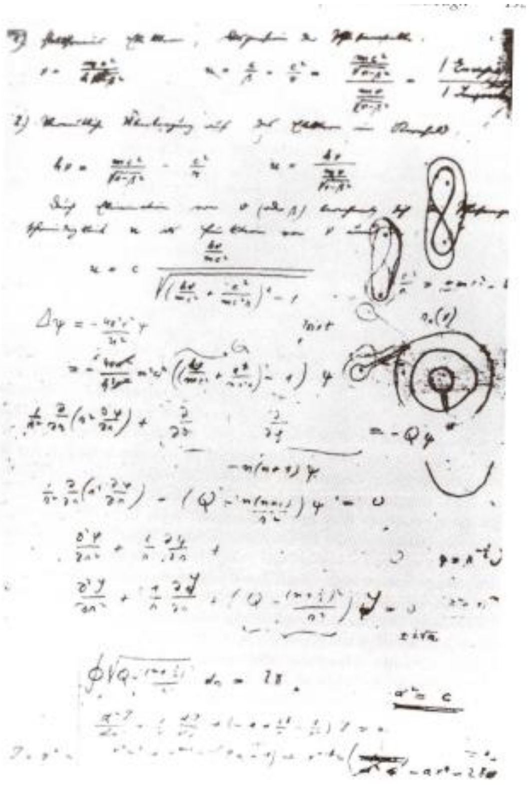
Introduction to molecular quantum theory

C.-K. Skylaris

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.

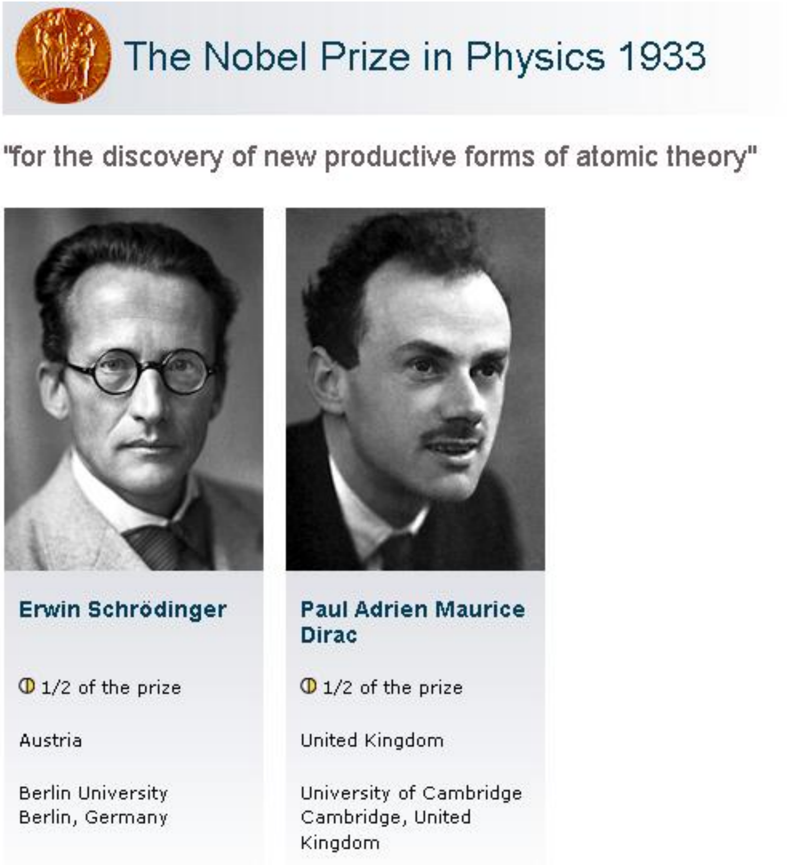
The Villa Herwig, where wave mechanics was discovered during the Christmas holidays, 1925–26.



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

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"

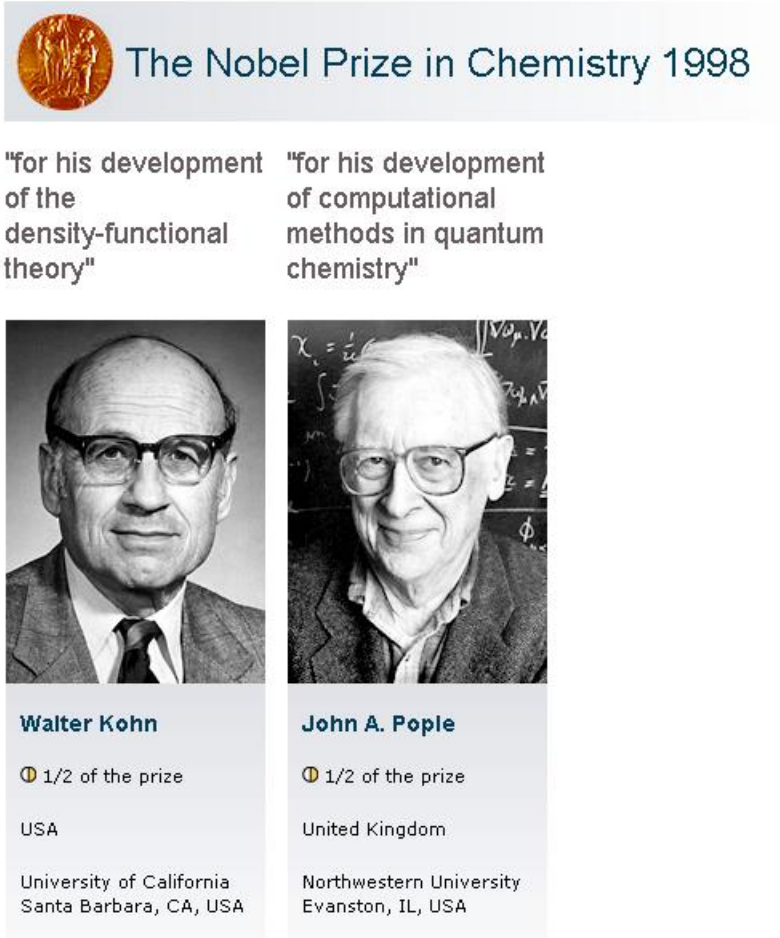
Erwin Schrödinger	**Paul Adrien Maurice Dirac**
◑ 1/2 of the prize	◑ 1/2 of the prize
Austria	United Kingdom
Berlin University Berlin, Germany	University of Cambridge Cambridge, United Kingdom

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

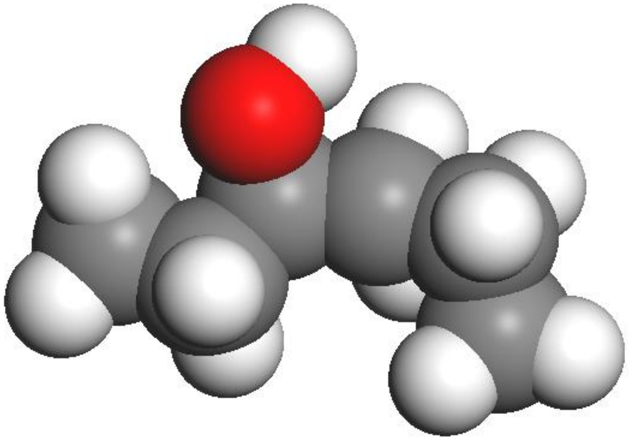
1/2 of the prize

United Kingdom

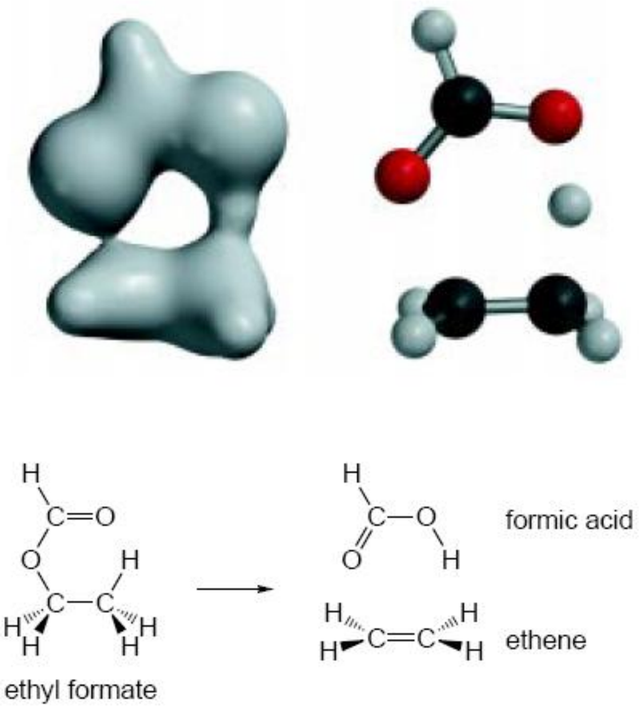
Northwestern University
Evanston, IL, USA

Relevance of DFT simulations: Molecular Interactions

Atoms in molecules

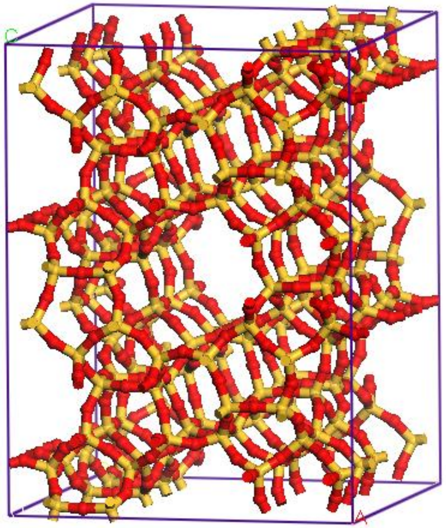


Chemical reactions

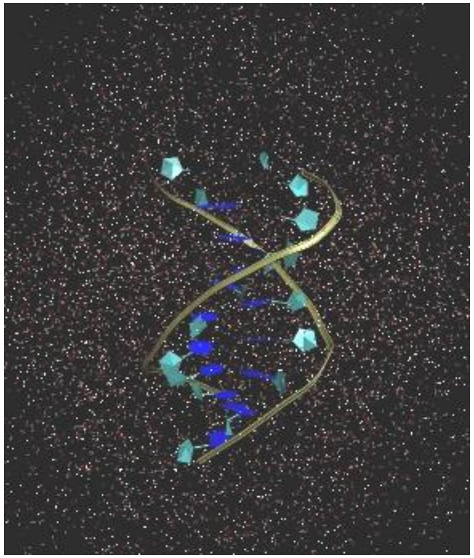


Relevance of DFT simulations: Molecular Interactions in “condensed” phases

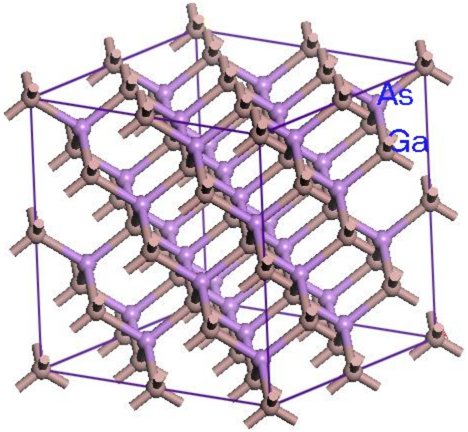
Catalysis in zeolites



DNA in water



Crystalline GaAs in semiconductors

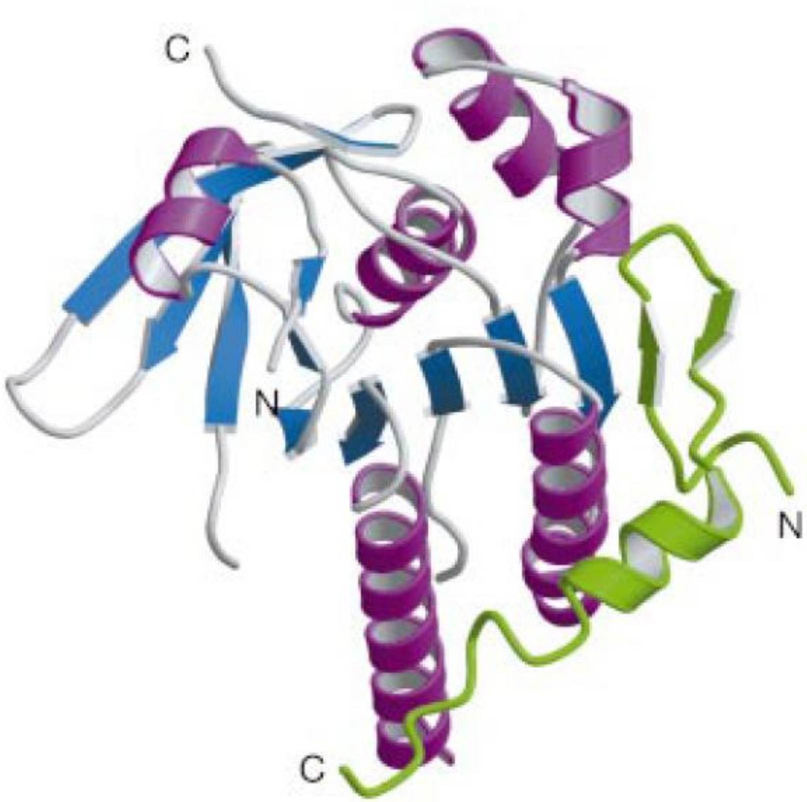


Other examples:

- Supercritical CO_2 as an easily disposable solvent for “green” chemistry
- Photo-chemistry in the atmosphere: ozone depletion, greenhouse effect

Relevance of DFT simulations: Intermolecular forces in macromolecular assemblies

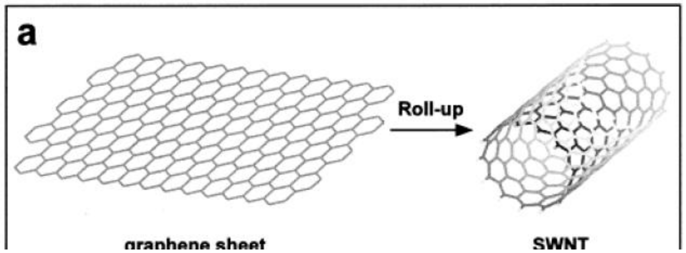
Protein-protein interface

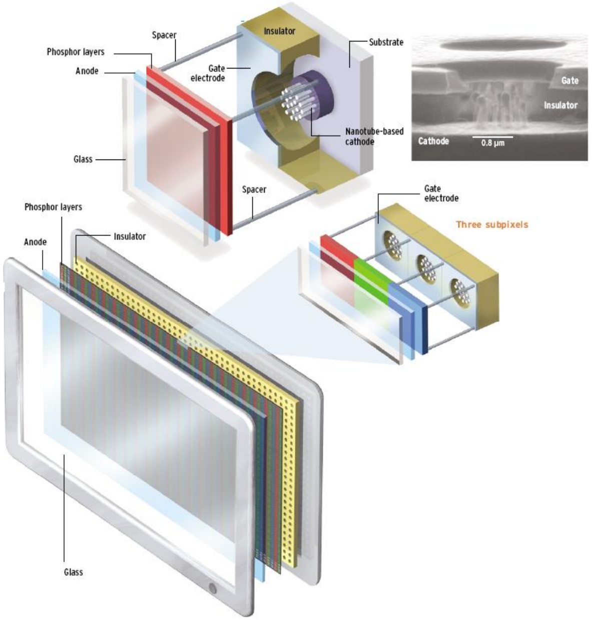


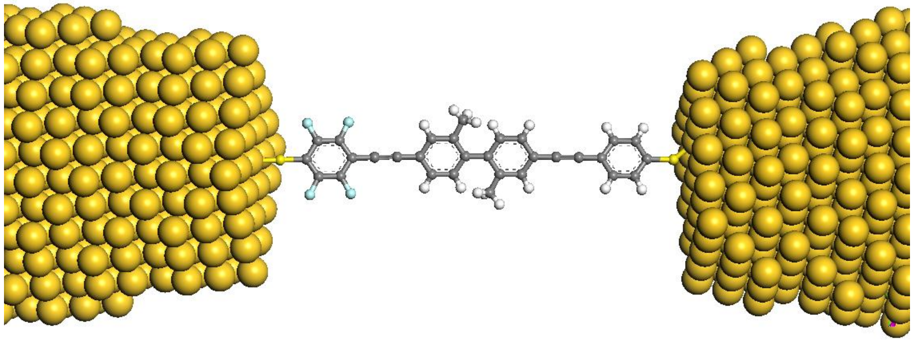
Searching for new drugs:
Protein-small molecule interactions

Relevance of DFT simulations: Nanostructures

Electronic emission from capped carbon nanotubes used for high definition screens







Molecular diode made from asymmetrically fluorinated polyene attached to gold nano-electrodes (break junction)

The wavefunction

- Quantum mechanics naturally encompasses **wave-particle duality**
- A particle such as an electron, atomic nucleus, does not travel along a definite path, but is distributed through space, like a wave
- The wave is represented by the **wavefunction**, which is a central quantity in quantum theory
- Often the wavefunction is denoted by the letter Ψ (psi)
- The wavefunction **contains** all the information that can be determined experimentally, but it is not an experimentally measurable quantity itself
- It is a very complicated function as it depends on the coordinates of every particle

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots)$$

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:

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

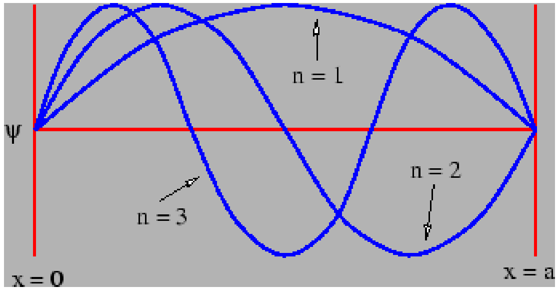
How many variables are included in the wavefunction of

1) A hydrogen molecule

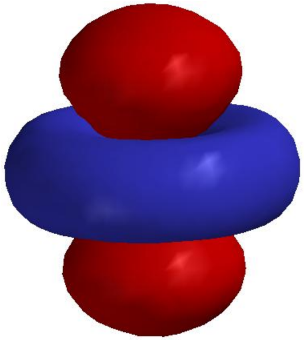
2) A benzene molecule

Wavefunctions

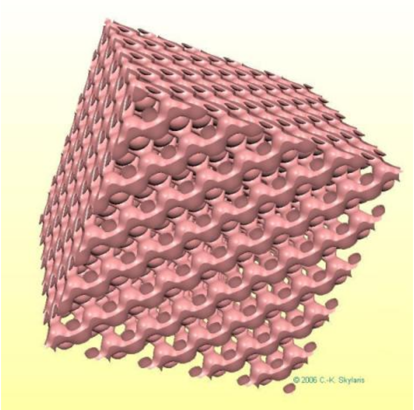
Schrödinger’s equation applies to all kinds of systems (atoms, molecules, materials). Its solutions are the wavefunctions:



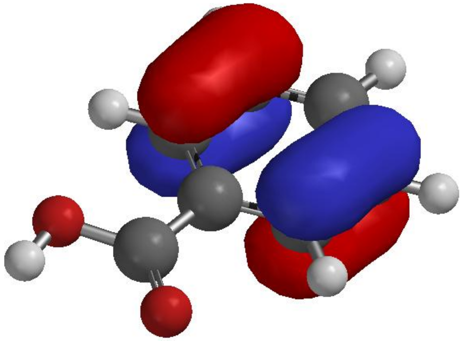
Particle in a box



Hydrogen atom



Silicon crystal



Benzoic acid

Operators in quantum theory

- 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

$$\hat{V}(x)\ f(x) = V(x)f(x)$$

The axiom: Time-dependent Schrödinger equation

$$\boxed{i\hbar\frac{\partial\Phi(\mathbf{x},t)}{\partial t} = \hat{H}\Phi(\mathbf{x},t)}$$

Hamiltonian operator

Wavefunction

$$\hat{H} = \hat{T}(\mathbf{x}) + \hat{V}(\mathbf{x},t)$$

Kinetic energy operator

Potential energy operator

What do these terms represent in molecular calculations?

When the potential energy does not change with time

$$\hat{V}(\mathbf{x},t) = \hat{V}(\mathbf{x})$$

We can try a solution which is a product of a function of position and a function of time:

$$\Phi(\mathbf{x},t) = \Psi(\mathbf{x})T(t)$$

Substitute this into the time-dependent Schrödinger equation

$$i\hbar\frac{\partial\Psi(\mathbf{x})T(t)}{\partial t} = \hat{H}\Psi(\mathbf{x})T(t)$$

$$\Psi(\mathbf{x})\ i\hbar\frac{\partial T(t)}{\partial t} = T(t)\ \hat{H}\Psi(\mathbf{x})$$

$$\boxed{i\hbar \frac{1}{T(t)} \frac{\partial T(t)}{\partial t} = \frac{\hat{H}\Psi(\mathbf{x})}{\Psi(\mathbf{x})}}$$

The lefthand side is a function of time. The righthand side is a function of position.

$$i\hbar \frac{1}{T(t)} \frac{\partial T(t)}{\partial t} = E \qquad \frac{\hat{H}\Psi(\mathbf{x})}{\Psi(\mathbf{x})} = E$$

The time-independent Schrödinger equation

$$\boxed{\hat{H}\Psi(\mathbf{x}) = E\Psi(\mathbf{x})}$$

Stationary states

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

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

Complex numbers and functions

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

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

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

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

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

Expectation values of operators

- We initially stated that any experimentally observable property can be obtained from the wavefunction
- How do we do this?
- A quantum mechanical operator is available for each experimentally observable property (e.g. Energy, position, momentum, etc)
- We obtain the property as the expectation (or "average") value of the appropriate operator

Operator for some property
(energy, position, etc)

Expectation
value of the
operator

$$\langle O \rangle = \frac{\int \psi^*(x)\,\hat{O}\,\psi(x)\,dx}{\int \psi^*(x)\,\psi(x)\,dx}$$

wavefunction

Expectation values of operators

- 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.

Homework

1) In quantum theory all operators that represent experimentally observable properties are called Hermitian operators. Look up the properties of Hermitian operators and understand how they are derived.

2) Write an expression involving the "normalisation functional" $F_{\text{Norm}}[\psi] = \int \psi^*(\mathbf{x})\psi(\mathbf{x})d\mathbf{x}$ of $\psi(\mathbf{x})$ which takes the value 0 when $\psi(\mathbf{x})$ is normalised. Can you also write an expression that takes its minimum value when $\psi(\mathbf{x})$ is normalised? Can you suggest a possible use of such expression?

3) Show that $T(t) = e^{-iEt/\hbar}$ is a solution of the equation for T(t) (slide 19).

5-minute quiz

Name :
Surname:

1) Describe under what condition the time-dependent Schrödinger equation can be reduced to the time-independent version.

2) A wavefunction $\psi(\mathbf{x})$ for which $\int \psi^*(\mathbf{x})\psi(\mathbf{x})d\mathbf{x} = 1$ is called normalised. Show how the expression for the expectation value of an operator is simplified for a normalised wavefunction.

3) How can you modify a wavefunction that is not normalised to one that is?