

FEEG6016

Simulation and modelling: Quantum Chemistry

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FEEG6016: Quantum Chemistry

Textbooks:

Recommended:

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

Also very useful:

- F. Jensen. “Introduction to Computational Chemistry”, 2nd Edition, Wiley 2006
- P. Atkins and R. Friedman, “Molecular Quantum Mechanics”, 5th Edition, OUP 2011
- A. Szabo and N. S. Ostlund, “Modern Quantum Chemistry”, Dover 1996

Lecture summary: basics of quantum chemistry

- Schrödinger equation
- Observable properties in quantum mechanics
- Hamiltonian operators for molecules
- Molecular orbitals and many-electron wavefunctions
- Energy of the many-electron wavefunction
- Molecular integrals (core Hamiltonian, Coulomb, Exchange)
- The Hartree-Fock method for calculating the energy of a many-electron wavefunction

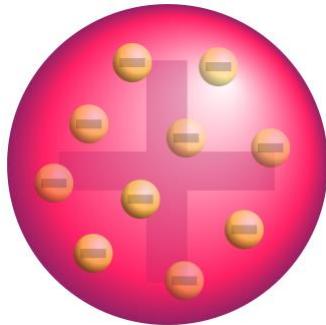
Part 1

Schrödinger's equation and Dirac's bra-ket notation

Atomic models

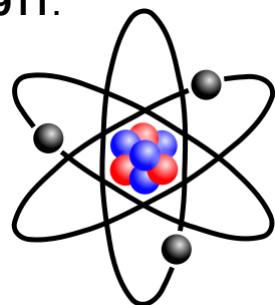
J. J. Thomson's "plum pudding model"

After the discovery of the electron in 1897, J. J. Thompson proposed his model in **1904**, before the discovery of the atomic nucleus



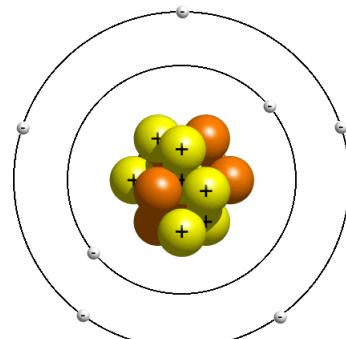
E. Rutherford's "planetary model"

The discovery of atomic nuclei suggested that J. J. Thomson's "plum pudding model" was incorrect. Rutherford proposed the planetary model in **1911**.



The Bohr model

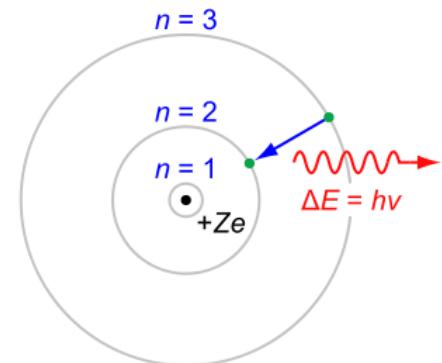
The first "quantum" theory (**1913**). Explains atomic spectra of hydrogen and its stability. But only works for one-electron atoms and the "quantisation" is imposed artificially



The breakthrough: Schrödinger's equation (1925)

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

Naturally includes **wave-particle duality and energy quantisation**. Applies to **any microscopic system**.



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.

Handwritten notes from Schrödinger's notebook, likely the original derivation of the Schrödinger equation. The notes include:

$$\begin{aligned} \text{1) } & \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} = \frac{1}{m^2} \frac{\partial^2 \psi}{\partial t^2} \\ \text{2) } & \text{Kinetic Energy } T = \frac{1}{2m} (\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2}) \\ & \text{Schrödinger's wave equation: } \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} = -\frac{2m}{\hbar^2} E \psi \\ & \frac{\partial^2 \psi}{\partial x^2} = -\frac{2m}{\hbar^2} E \psi \\ & \frac{\partial^2 \psi}{\partial y^2} = -\frac{2m}{\hbar^2} E \psi \\ & \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} = -\frac{2m}{\hbar^2} E \psi \\ & \frac{\partial^2 \psi}{\partial x^2} = -\frac{2m}{\hbar^2} E \psi \\ & \frac{\partial^2 \psi}{\partial y^2} = -\frac{2m}{\hbar^2} E \psi \\ & \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} = -\frac{2m}{\hbar^2} E \psi \\ & \frac{\partial^2 \psi}{\partial x^2} = -\frac{2m}{\hbar^2} E \psi \\ & \frac{\partial^2 \psi}{\partial y^2} = -\frac{2m}{\hbar^2} E \psi \\ & \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} = -\frac{2m}{\hbar^2} E \psi \end{aligned}$$

Page from Schrödinger's notebook, with his wave equation

Quantisation: Only certain (discrete) energy levels eigenvalues are produced by 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

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

Quantum theory of matter



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

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"

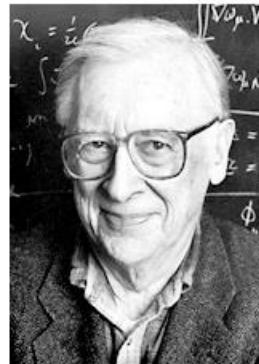


Walter Kohn

1/2 of the prize

USA

University of California
Santa Barbara, CA, USA



John A. Pople

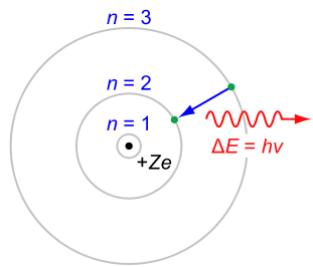
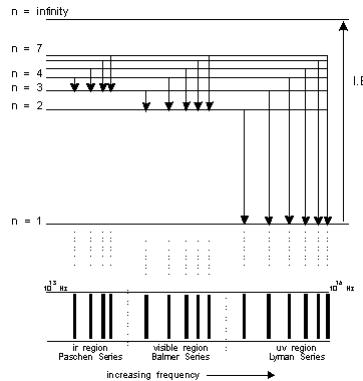
1/2 of the prize

United Kingdom

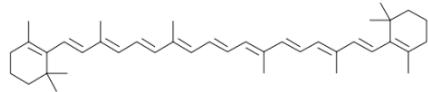
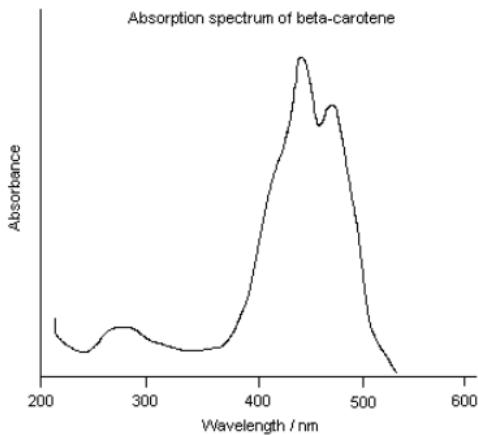
Northwestern University
Evanston, IL, USA

Quantum theory

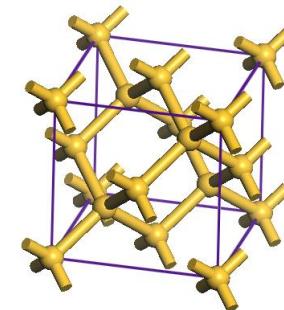
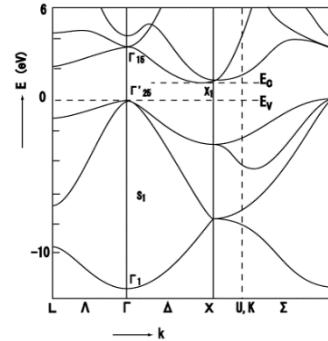
General and transferable: applies to all materials and their properties



atoms



molecules



materials

The (time-independent) Schrödinger equation

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

Hamiltonian operator Wavefunction Energy

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

Kinetic energy operator Potential energy operator

Operators

- A different way to write something that you already know
- Any change on a function can be represented by an operator
- 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

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

Wavefunctions

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

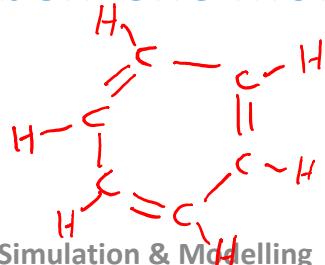
$$\Psi(x_1, y_1, z_1, x_2, y_2, z_2, \dots, x_N, y_N, z_N) = \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$$

How many variables are contained in the wavefunction of



1) A hydrogen molecule $H_{\text{nucleus}} \times 2 + e^- \times 2 = 4 \times 3 = 12$

2) A benzene molecule $C_{\text{nucleus}} \times 6 + H_{\text{nucleus}} \times 6 + e^- \times 6 \times 6 + e^- \times 6 = 54 \times 3 = 162$



Using operators to compute observables

- “Observables” or “expectation values”: Experimental measurements (e.g. energy, position of electron, etc)
- According to Quantum theory we can compute the outcome of any such measurement by **“averaging” the appropriate operator and the wavefunction** as follows:

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

*operator for position
X*

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

Dirac's “bra-ket” shorthand notation

- Paul Dirac introduced a shorthand notation for quantum chemical integrals that greatly simplifies written expressions without any loss of information
- This notation has become the standard in quantum theory and we will use it throughout this course

$$\int \Psi^*(\mathbf{x}) \hat{C} \Phi(\mathbf{x}) d\mathbf{x} \quad \text{becomes} \quad \langle \Psi | \hat{C} | \Phi \rangle$$

A “bra” *bra* \hat{C} *ket* A “ket”

$$\langle \Psi | \equiv \int d\mathbf{x} \Psi^*(\mathbf{x}) \quad | \Phi \rangle \equiv \Phi(\mathbf{x})$$

Example: Write the Schrödinger equation in bra-ket notation

$$\hat{H} \psi(x) = E \psi(x) \quad \text{becomes} \quad \hat{H} |\psi\rangle = E |\psi\rangle$$

Bra-ket notation practice

Example: Write the following expressions in bra-ket notation

$$\int f(\mathbf{x}) g^*(\mathbf{x}) d\mathbf{x} \quad \int f(\mathbf{x}) g(\mathbf{x}) d\mathbf{x} \quad \int f^*(\mathbf{x}) g(\mathbf{x}) d\mathbf{x} \quad \int f^*(\mathbf{x}) g^*(\mathbf{x}) d\mathbf{x}$$

$\langle f^* | g^* \rangle$ $\langle f^* | g \rangle$ $\langle f | g \rangle$ $\langle f | g^* \rangle$

$$\psi(\mathbf{x}) \int \psi^*(\mathbf{x}') f(\mathbf{x}') d\mathbf{x}' \quad \int f^*(\mathbf{x}) [a g(\mathbf{x}) + b h(\mathbf{x})] d\mathbf{x}$$

$\langle \psi | \psi | f \rangle$ $\langle f | a g(x) + b h(x) \rangle =$
 $= a \langle f | g \rangle + b \langle f | h \rangle$

Bra-ket notation practice

Homework: write these expressions in bra-ket notation

$$\int f^*(\mathbf{x}) \hat{H} \hat{H} g(\mathbf{x}) d\mathbf{x}$$

$$\int f^*(\mathbf{x}) (\hat{H}_1 + \hat{H}_2) g(\mathbf{x}) d\mathbf{x}$$

$$\int \psi^*(x) \frac{d}{dx} \phi(x) dx$$

$$\int \psi_i^*(x_1) \psi_i(x_1) dx_1 \int \psi_j^*(x_2) \psi_j(x_2) dx_2$$

Bra-ket notation practice

Starting from the Schrödinger equation, write down an expression for the energy

Integral form

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

$$\psi^*(\mathbf{x})\hat{H}\psi(\mathbf{x}) = \psi^*(\mathbf{x})E\psi(\mathbf{x})$$

$$\int \psi^*(\mathbf{x})\hat{H}\psi(\mathbf{x})d\mathbf{x} = \int \psi^*(\mathbf{x})E\psi(\mathbf{x})d\mathbf{x}$$

$$\int \psi^*(\mathbf{x})\hat{H}\psi(\mathbf{x})d\mathbf{x} = E \int \psi^*(\mathbf{x})\psi(\mathbf{x})d\mathbf{x}$$

$$E = \frac{\int \psi^*(\mathbf{x})\hat{H}\psi(\mathbf{x})d\mathbf{x}}{\int \psi^*(\mathbf{x})\psi(\mathbf{x})d\mathbf{x}}$$

Bra-ket form

$$\hat{H}|\psi\rangle = E|\psi\rangle$$

$$\psi^*(\mathbf{x})\hat{H}|\psi\rangle = \psi^*(\mathbf{x})E|\psi\rangle$$

$$\langle\psi|\hat{H}|\psi\rangle = \langle\psi|E|\psi\rangle$$

$$\langle\psi|\hat{H}|\psi\rangle = E\langle\psi|\psi\rangle$$

$$E = \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle}$$

Part 2

Hamiltonian operators for molecules

Constructing operators in Quantum Mechanics

Quantum operators **have the same expressions** as classical quantities

Classical quantity	Quantum operator
position	$x \longrightarrow x$

Potential (e.g.
energy of attraction
of an electron by an
atomic nucleus)

$$V(x) \longrightarrow V(x)$$

With one exception!

**The momentum operator
is completely different:**

$$mv_x \longrightarrow -i\hbar \frac{d}{dx}$$

Constructing Hamiltonian operators

The Hamiltonian operator is the total energy operator and is a sum of

$$\hat{H} = \hat{T} + \hat{V}$$

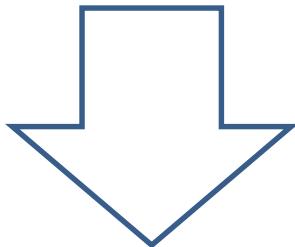
- (1) the kinetic energy operator
- (2) the potential energy operator

Constructing Hamiltonian operators

(1) the kinetic energy operator

Classical theory: kinetic energy

$$T = \frac{1}{2}mv_x^2 = \frac{(mv_x)^2}{2m} = \frac{1}{2m} p_x^2$$



Quantum theory: kinetic energy **operator**

$$\hat{T} = \frac{1}{2m} \hat{p}_x^2 = \frac{1}{2m} \hat{p}_x \hat{p}_x$$

therefore

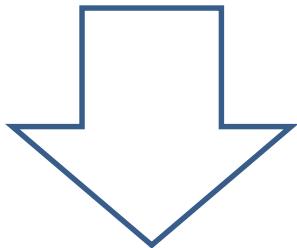
$$\hbar = \frac{\hbar}{2n}$$

$$\begin{aligned} \hat{T} &= \frac{1}{2m} \left[-i\hbar \frac{d}{dx} \right] \left[-i\hbar \frac{d}{dx} \right] \\ &= -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \end{aligned}$$

Constructing Hamiltonian operators

(2) the potential energy operator

Classical theory: potential energy $V = V(x)$



Quantum theory: potential energy **operator** $\hat{V} = V(x)$

That's all!

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

Constructing Hamiltonian operators

The Hamiltonian operator

$$\hat{H} = \hat{T} + \hat{V}$$

is a sum of

(1) the kinetic energy operator

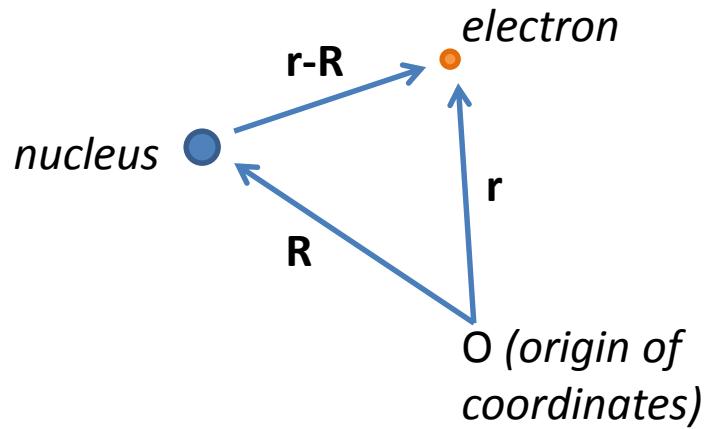
$$\hat{T} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$$

(2) the potential energy operator

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

So the Hamiltonian operator is: $\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)$

Hamiltonian operator for Hydrogen atom



$$\hat{H} = \hat{T} + \hat{V}$$

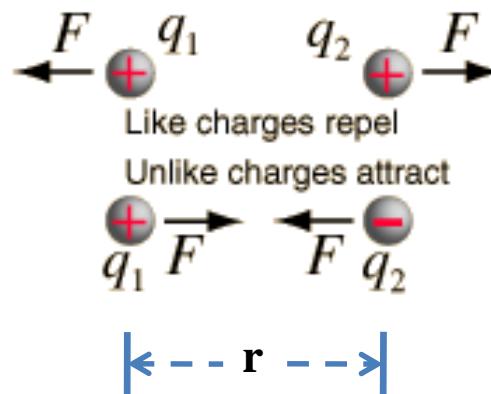
electronic
kinetic energy

electron-nucleus
attraction energy

nuclear kinetic
energy

Background: Force between two charges: Coulomb's Law

Electrons and nuclei are charged particles


$$F = \frac{kq_1q_2}{r^2} = \frac{q_1q_2}{4\pi\epsilon_0 r^2} \quad \text{Coulomb's Law}$$

Distance between charge q_1 at point \mathbf{r}_1 and charge q_2 at point \mathbf{r}_2

$$|\mathbf{r}| = \sqrt{(x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2} = |\mathbf{r}_2 - \mathbf{r}_1|$$

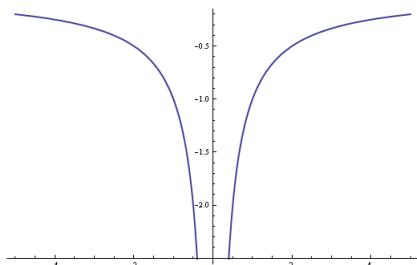
Coulomb potential energy

$$V_{q_1, q_2}(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{|\mathbf{r}|}$$

Examples:

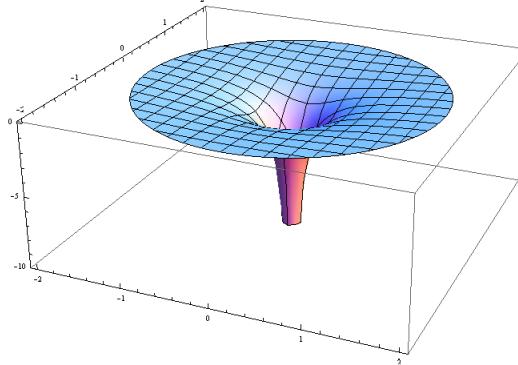
In one dimension

$$-\frac{1}{|\mathbf{r}|} = -\frac{1}{|x|}$$



In 2 dimensions

$$-\frac{1}{|\mathbf{r}|} = -\frac{1}{\sqrt{x^2 + y^2}}$$

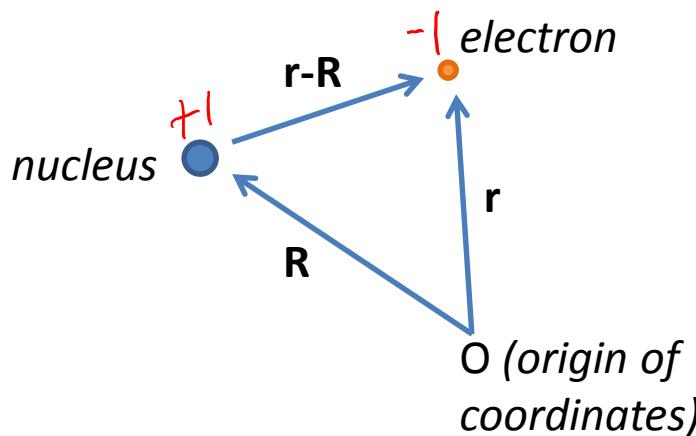


In 3 dimensions

$$-\frac{1}{|\mathbf{r}|} = -\frac{1}{\sqrt{x^2 + y^2 + z^2}}$$

- Difficult to visualise (would require a 4-dimensional plot!)
- We live in a 3-dimensional world so this is the potential we use

Hamiltonian operator for Hydrogen atom



nuclear kinetic energy

$$\hat{H} = -\frac{\hbar^2}{2M} \left(\frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2} \right) - \frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) - \frac{1}{4\pi\varepsilon_0} \frac{e^2}{|\mathbf{r} - \mathbf{R}|}$$

electronic kinetic energy

$$\hat{H} = -\frac{\hbar^2}{2M}\nabla_{\mathbf{R}}^2 - \frac{\hbar^2}{2m}\nabla_{\mathbf{r}}^2 - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{|\mathbf{r} - \mathbf{R}|}$$

electron-nucleus attraction

Atomic units

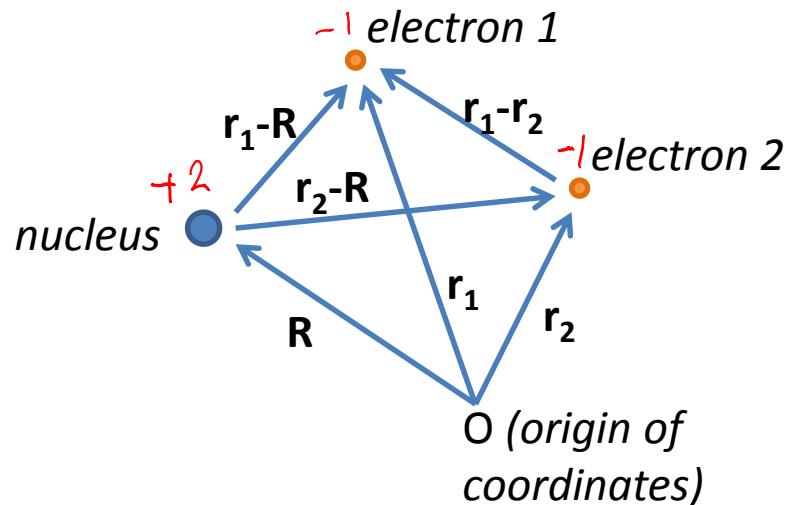
Simplify quantum chemistry expressions

In SI units: $\hat{H} = -\frac{\hbar^2}{2M}\nabla_{\mathbf{R}}^2 - \frac{\hbar^2}{2m}\nabla_{\mathbf{r}}^2 - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{|\mathbf{r} - \mathbf{R}|}$

In atomic units: $\hat{H} = -\frac{1}{2M}\nabla_{\mathbf{R}}^2 - \frac{1}{2}\nabla_{\mathbf{r}}^2 - \frac{1}{|\mathbf{r} - \mathbf{R}|}$

Quantity	Atomic Unit	Value in SI
Energy	$e^2/4\pi\varepsilon_0a_0$ (Hartree, E_h)	4.36×10^{-18} J
Charge	e	1.60×10^{-19} C
Length	a_0	5.29×10^{-11} m
Mass	m_e	9.11×10^{-31} kg

Hamiltonian for the Helium atom



$$\hat{H} = -\frac{1}{2M}\nabla_{\mathbf{R}}^2 - \frac{1}{2}\nabla_{\mathbf{r}_1}^2 - \frac{1}{2}\nabla_{\mathbf{r}_2}^2 - \frac{2}{|\mathbf{r}_1 - \mathbf{R}|} - \frac{2}{|\mathbf{r}_2 - \mathbf{R}|} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

kinetic
energy of
nucleus

kinetic
energy of
electron 1

kinetic
energy of
electron 2

attraction of
electron 1 by
nucleus

attraction of
electron 2 by
nucleus

repulsion
between
electrons 1
and 2

Hamiltonian operator for a water molecule

Water contains 10 electrons and 3 nuclei. We will use the symbols “O” for the oxygen (atomic number $Z_O=8$) nucleus, “H1” and “H2” (atomic numbers $Z_{H1}=1$ and $Z_{H2}=1$) for the hydrogen nuclei.

$$\hat{H}_{H_2O} = -\frac{1}{2M_O}\nabla_{\mathbf{R}_O}^2 - \frac{1}{2M_{H1}}\nabla_{\mathbf{R}_{H1}}^2 - \frac{1}{2M_{H2}}\nabla_{\mathbf{R}_{H2}}^2 - \sum_{i=1}^{10} \frac{1}{2}\nabla_{\mathbf{r}_i}^2$$

Kinetic energy of O Kinetic energy of H1 Kinetic energy of H2 Kinetic energy of electron i

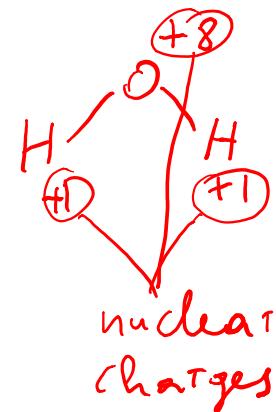
$$-\sum_{i=1}^{10} \frac{8}{|\mathbf{r}_i - \mathbf{R}_O|} - \sum_{i=1}^{10} \frac{1}{|\mathbf{r}_i - \mathbf{R}_{H1}|} - \sum_{i=1}^{10} \frac{1}{|\mathbf{r}_i - \mathbf{R}_{H2}|}$$

Electron attraction to O Electron attraction to H1 Electron attraction to H2

$$+\sum_{i=1}^{10} \sum_{j=i+1}^{10} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{I=1}^3 \sum_{J=I+1}^3 \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}$$

Electron-electron repulsion nucleus-nucleus repulsion

E.g. Assume
 $Z_1 = Z_O$
 $Z_2 = Z_{H1}$
 $Z_3 = Z_{H2}$



- Quite a complicated expression! Hamiltonians for molecules become intractable
- Fortunately, we do not need to write all this for every molecule we study. We can develop expressions that are much more compact and apply to any molecule, irrespective of size

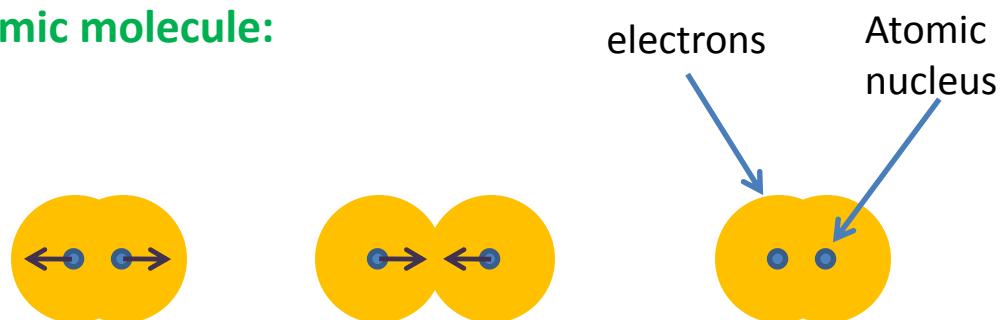
Separating electronic from nuclear coordinates

Nuclei are much heavier than electrons (e.g. Proton mass \approx 1800 times the mass of an electron => compare kinetic energy operators of proton and electron).

As a result nuclei move much slower than electrons. To a very good approximation, we can assume that the electronic motions are instantaneously “equilibrated” at each nuclear position.

Example: Vibration of diatomic molecule:

“electron cloud”
instantaneously re-adjusts
its shape to follow moving
nuclei



Born-Oppenheimer approximation

Solve Schrödinger's equation **only in the electronic coordinates** for fixed nuclear coordinates.

$$\hat{H} = - \sum_I \frac{1}{2M_I} \nabla_I^2 + \sum_I \sum_{J>I} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} - \sum_i \frac{1}{2} \nabla_i^2 + \sum_i \sum_{j>i} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_i \sum_I - \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|}$$

$\hat{H}_{elec} \Phi_{elec} = E_{elec} \Phi_{elec}$

$$\Phi_{elec} = \Phi_{elec}(\{\mathbf{r}_i\}; \{\mathbf{R}_I\})$$

variables 1 parameter

$$E_{elec} = E_{elec}(\{\mathbf{R}_I\})$$

The resulting wavefunctions and energies have a **parametric dependence** in the coordinates of the nuclei

- Important for Chemistry: used to determine structures of reactants, products, transition states, reaction paths
- We will always assume the Born-Oppenheimer approximation

Electronic Hamiltonian operator for water molecule

Water contains 10 electrons and 3 nuclei. We will use the symbols “O” for the oxygen (atomic number $Z_O=8$) nucleus, “H1” and “H2” (atomic numbers $Z_{H1}=1$ and $Z_{H2}=1$) for the hydrogen nuclei.

Apply the B.O. approximation to obtain the electronic Hamiltonian:

$$\hat{H}_{H_2O} = -\frac{1}{2M_O}\nabla_{\mathbf{R}_O}^2 - \frac{1}{2M_{H1}}\nabla_{\mathbf{R}_{H1}}^2 - \frac{1}{2M_{H2}}\nabla_{\mathbf{R}_{H2}}^2 - \sum_{i=1}^{10} \frac{1}{2}\nabla_{\mathbf{r}_i}^2$$

~~Kinetic energy of O~~ ~~Kinetic energy of H1~~ ~~Kinetic energy of H2~~ Kinetic energy of electron i

$$- \sum_{i=1}^{10} \frac{8}{|\mathbf{r}_i - \mathbf{R}_O|} - \sum_{i=1}^{10} \frac{1}{|\mathbf{r}_i - \mathbf{R}_{H1}|} - \sum_{i=1}^{10} \frac{1}{|\mathbf{r}_i - \mathbf{R}_{H2}|}$$

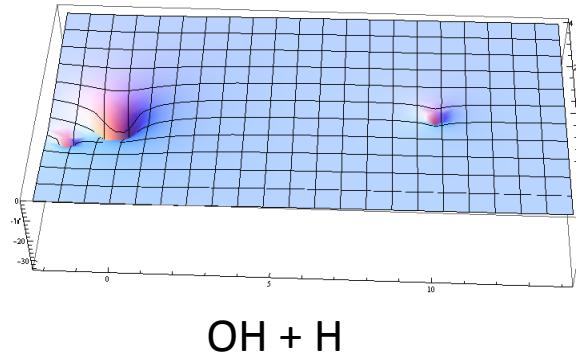
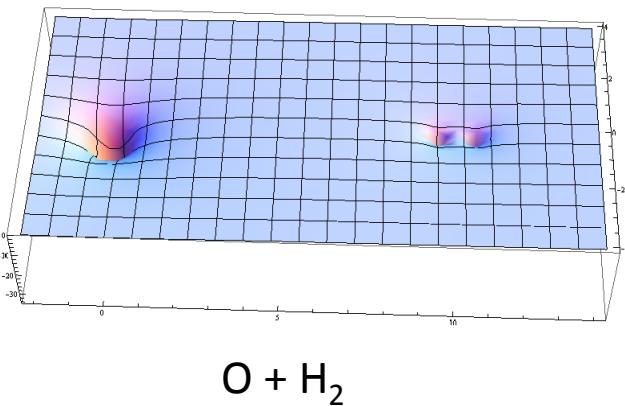
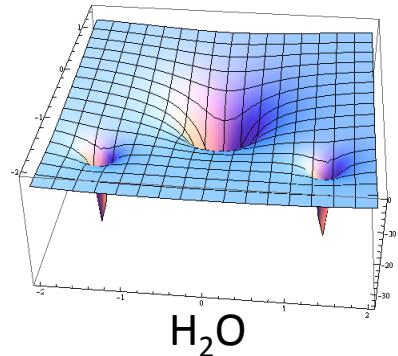
Electron attraction to O Electron attraction to H1 Electron attraction to H2

$$+ \sum_{i=1}^{10} \sum_{j=i+1}^{10} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{I=1}^3 \sum_{J=I+1}^3 \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}$$

Electron-electron repulsion nucleus-nucleus repulsion

E.g. Assume
 $Z_1 = Z_O$
 $Z_2 = Z_{H1}$
 $Z_3 = Z_{H2}$

Example: Nuclear attraction potential for one O and two H



Homework

- Write the electronic Hamiltonian operator for these 3 cases
- What is different between these 3 operators?
- Can you suggest how you may model the reaction $\text{OH}+\text{H} \rightarrow \text{H}_2\text{O}$?

Part 3

Slater determinant wavefunctions

Molecular orbitals

- A wavefunction for a single electron is called a molecular orbital (MO)
- MOs with spatial and spin coordinates are called **spin orbitals** and are products of a spatial orbital and a spin function
- There is an infinite number of possible spatial orbitals but only two kinds of spin function: the “up spin” $\alpha(\omega)$ and the “down spin” $\beta(\omega)$

$$\begin{array}{c} \chi^{\uparrow}(\mathbf{x}) = \psi(\mathbf{r})\alpha(\omega) \\ \text{Spin orbital} \quad \text{Spatial orbital} \quad \text{Spin function} \\ \downarrow \qquad \qquad \qquad \downarrow \\ \chi^{\downarrow}(\mathbf{x}) = \psi(\mathbf{r})\beta(\omega) \end{array}$$

- Molecules contain many electrons. Can we use MOs to build simple many-electron wavefunctions?

Slater determinant wavefunction

For two electrons, a suitable many-electron wavefunction from spin orbitals is

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) \end{vmatrix}$$

Electron labels

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) - \chi_2(\mathbf{x}_1)\chi_1(\mathbf{x}_2)$$

Orbital labels

- A wavefunction of this form is called a **Slater determinant**
- It obeys the antisymmetry principle $\Psi(\mathbf{x}_2, \mathbf{x}_1) = -\Psi(\mathbf{x}_1, \mathbf{x}_2)$

$$\begin{aligned}\Psi(\vec{\mathbf{x}}_2, \vec{\mathbf{x}}_1) &= \chi_1(\vec{\mathbf{x}}_2)\chi_2(\vec{\mathbf{x}}_1) - \chi_2(\vec{\mathbf{x}}_2)\chi_1(\vec{\mathbf{x}}_1) = \\ &= -[\chi_1(\vec{\mathbf{x}}_1)\chi_2(\vec{\mathbf{x}}_2) - \chi_2(\vec{\mathbf{x}}_1)\chi_1(\vec{\mathbf{x}}_2)] = \\ &= -\Psi(\vec{\mathbf{x}}_1, \vec{\mathbf{x}}_2)\end{aligned}$$

Hartree product
 $\Psi(\vec{\mathbf{x}}_1, \vec{\mathbf{x}}_2) = \chi_1(\vec{\mathbf{x}}_1)\chi_2(\vec{\mathbf{x}}_2)$

Slater determinants

Slater determinant for N electrons:

$$\Psi_{SD}(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \dots & \chi_N(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \dots & \chi_N(\mathbf{x}_2) \\ \vdots & \vdots & & \vdots \\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \dots & \chi_N(\mathbf{x}_N) \end{vmatrix}$$

Normalisation constant

$\langle \Psi_{SD} | \Psi_{SD} \rangle = 1$ — Normalisation condition

Shorthand representation, as a ket:

$$\Psi_{SD}(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = |\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2)\dots\chi_N(\mathbf{x}_N)\rangle$$

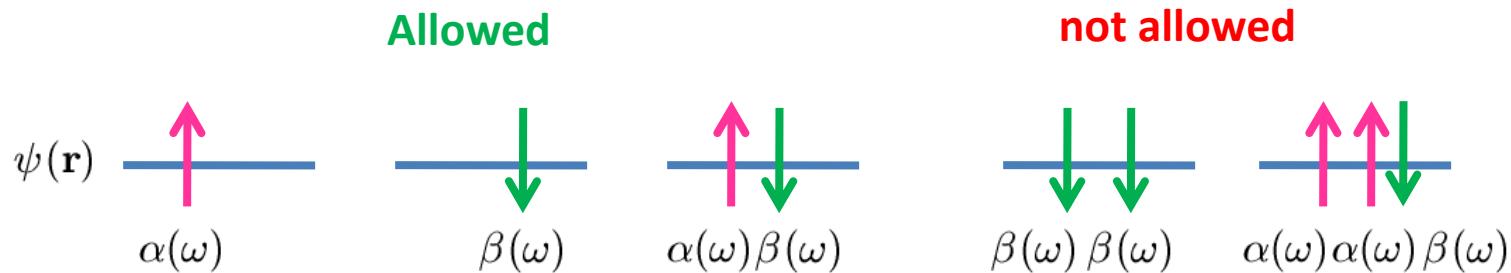
- Spin orbitals in Slater determinants are always orthonormal, i.e.

$$\langle \chi_i | \chi_j \rangle = 0 \text{ if } i \neq j$$

$$\langle \chi_i | \chi_j \rangle = 1 \text{ if } i = j$$

The Pauli principle

- A determinant is zero if two or more of its rows or columns are identical
- A wavefunction which is zero everywhere in space is not physically acceptable
- Therefore a spin orbital can be included **only once** in a Slater determinant



- The Pauli principle follows naturally as a spatial orbital can result in at most two spin orbitals (one with up and one with down spin function)
- In other words, a spatial orbital can be occupied by no more than two electrons of opposite spins

Electronic energy of a Slater determinant

- We need to derive an expression for the electronic energy of a SD

$$E_{SD} = \frac{\langle \Psi_{SD} | \hat{H}_{elec} | \Psi_{SD} \rangle}{\langle \Psi_{SD} | \Psi_{SD} \rangle}$$

=] as Slater determinants
are always normalised

$$\hat{H}_{elec} = - \sum_{i=1}^{N_{elec}} \frac{1}{2} \nabla_i^2 - \sum_{I=1}^{N_{nuc}} \sum_{i=1}^{N_{elec}} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \sum_{i=1}^{N_{elec}} \sum_{j=i+1}^{N_{elec}} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

Kinetic Nuclear attraction Electron-electron repulsion

1) Kinetic energy

- The expectation value of the kinetic energy is

$$E_{kin} = \int \dots \int \Psi_{SD}^*(\mathbf{x}_1, \dots, \mathbf{x}_{N_{elec}}) \left(\sum_{i=1}^{N_{elec}} -\frac{1}{2} \nabla_i^2 \right) \Psi_{SD}(\mathbf{x}_1, \dots, \mathbf{x}_{N_{elec}}) d\mathbf{x}_1 \dots d\mathbf{x}_{N_{elec}}$$

In bra-ket notation:

$$E_{kin} = \langle \Psi_{SD} | \hat{T}_{elec} | \Psi_{SD} \rangle = \langle \Psi_{SD} | \left(\sum_{i=1}^{N_{elec}} -\frac{1}{2} \nabla_i^2 \right) | \Psi_{SD} \rangle$$

It can be shown (using the properties of determinants) that this is equal to:

$$= \sum_{i=1}^{N_{elec}} \int \chi_i^*(\mathbf{x}) \left(-\frac{1}{2} \nabla^2 \right) \chi_i(\mathbf{x}) d\mathbf{x} = \sum_{i=1}^{N_{elec}} \langle \chi_i | -\frac{1}{2} \nabla^2 | \chi_i \rangle$$

- a sum of the kinetic energies of the N_{elec} spin orbitals (i.e. a sum of N_{elec} integrals, each of which involves the coordinates of one electron).

2) Nuclear attraction energy

- Leads to an expression similar to the kinetic energy:

$$E_{e-n} = \langle \Psi_{SD} | \hat{V}_{e-n} | \Psi_{SD} \rangle = \langle \Psi_{SD} | \sum_{i=1}^{N_{elec}} \left(\sum_{I=1}^{N_{nuc}} \frac{-Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} \right) | \Psi_{SD} \rangle$$

$\underbrace{\quad\quad\quad}_{\hat{v}_{ext}(\vec{r})}$

$$= \sum_{i=1}^{N_{elec}} \int \chi_i^*(\mathbf{x}) \left(\sum_{I=1}^{N_{nuc}} \frac{-Z_I}{|\mathbf{r} - \mathbf{R}_I|} \right) \chi_i(\mathbf{x}) d\mathbf{x} = \sum_{i=1}^{N_{elec}} \langle \chi_i | \sum_{I=1}^{N_{nuc}} \frac{-Z_I}{|\mathbf{r} - \mathbf{R}_I|} | \chi_i \rangle$$

- which is equal to the sum of the nuclear attraction energies of N_{elec} spin orbitals (**again, a sum of N_{elec} integrals, each of which involves the coordinates of one electron**).
- The nuclear attraction potential for each electron (also called “the external potential”) is :

$$\hat{v}_{ext}(\mathbf{r}) = \sum_{I=1}^{N_{nuc}} \frac{-Z_I}{|\mathbf{r} - \mathbf{R}_I|}$$

3) Electron-electron repulsion energy

$$E_{e-e} = \langle \Psi_{SD} | \hat{V}_{e-e} | \Psi_{SD} \rangle = \langle \Psi_{SD} | \left(\sum_{i=1}^{N_{elec}} \sum_{j=i+1}^{N_{elec}} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right) | \Psi_{SD} \rangle$$

is written as a double sum of “two-electron integrals”:

$$= \frac{1}{2} \sum_{i=1}^{N_{elec}} \sum_{j=1}^{N_{elec}} \left[\int \int \chi_i^*(\mathbf{x}_1) \chi_j^*(\mathbf{x}_2) \frac{1}{r_{12}} \chi_i(\mathbf{x}_1) \chi_j(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 - \int \int \chi_i^*(\mathbf{x}_1) \chi_j^*(\mathbf{x}_2) \frac{1}{r_{12}} \chi_j(\mathbf{x}_1) \chi_i(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \right]$$
$$\frac{1}{|\vec{r}_1 - \vec{r}_2|}$$

- In total, this is a sum of $N_{elec}(N_{elec}-1)/2$ integrals, **each of which involves the coordinates of two electrons**

Electronic energy of Slater determinant

- By summing the expressions for kinetic, nuclear attraction and electron-electron energies we obtain the total electronic energy of a Slater determinant

$$E_{SD} = \sum_{i=1}^{N_{elec}} \int \chi_i^*(\mathbf{x}) \hat{h} \chi_i(\mathbf{x}) d\mathbf{x}$$
$$+ \frac{1}{2} \sum_{i=1}^{N_{elec}} \sum_{j=1}^{N_{elec}} \left[\int \int \chi_i^*(\mathbf{x}_1) \chi_j^*(\mathbf{x}_2) \frac{1}{r_{12}} \chi_i(\mathbf{x}_1) \chi_j(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 - \int \int \chi_i^*(\mathbf{x}_1) \chi_j^*(\mathbf{x}_2) \frac{1}{r_{12}} \chi_j(\mathbf{x}_1) \chi_i(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \right]$$

where $\hat{h} = -\frac{1}{2}\nabla^2 + \sum_{I=1}^{N_{nuc}} \frac{-Z_I}{|\mathbf{r} - \mathbf{R}_I|}$ This is the “core Hamiltonian” operator


 N_{ext+}

- To understand the meaning of the terms in the above energy expression, we need to re-write it in terms of spatial orbitals 
- Lets first look at the case of an even number of electrons and each spatial orbital being doubly occupied: 




$$|\Psi_{SD}\rangle = |\psi_1(\mathbf{r}_1)\alpha(\omega_1) \psi_1(\mathbf{r}_2)\beta(\omega_2) \psi_2(\mathbf{r}_3)\alpha(\omega_3) \dots \psi_{N_{elec}/2}(\mathbf{r}_{N_{elec}-1})\alpha(\omega_{N_{elec}-1}) \psi_{N_{elec}/2}(\mathbf{r}_{N_{elec}})\beta(\omega_{N_{elec}})\rangle$$

Electronic energy in terms of the spatial orbitals

- After we integrate out the spin variable, it can be shown that the energy of a Slater determinant in terms of spatial orbitals is:

$$E_{SD} = 2 \sum_{i=1}^{N_{elec}/2} \int \psi_i^*(\mathbf{r}) \hat{h} \psi_i(\mathbf{r}) d\mathbf{r} + \sum_{i=1}^{N_{elec}/2} \sum_{j=1}^{N_{elec}/2} \left[2 \int \int \psi_i^*(\mathbf{r}_1) \psi_j^*(\mathbf{r}_2) \frac{1}{r_{12}} \psi_i(\mathbf{r}_1) \psi_j(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 - \int \int \psi_i^*(\mathbf{r}_1) \psi_j^*(\mathbf{r}_2) \frac{1}{r_{12}} \psi_j(\mathbf{r}_1) \psi_i(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \right]$$

Core hamiltonian integral, h_i

- There are two kinds of electron-electron integrals above :

$$\int \int \frac{|\psi_i(\mathbf{r}_1)|^2 |\psi_j(\mathbf{r}_2)|^2}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 = J_{ij} > 0$$

Coulomb integral

$$\int \int \frac{[\psi_i^*(\mathbf{r}_1) \psi_j(\mathbf{r}_1)][\psi_i^*(\mathbf{r}_2) \psi_j(\mathbf{r}_2)]^*}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 = K_{ij} > 0$$

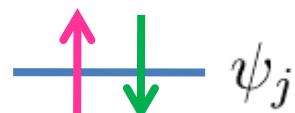
Exchange integral

You need to know these formulas!

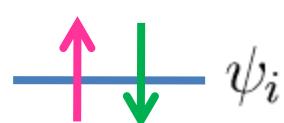
Electronic energy of a Slater determinant: physical interpretation



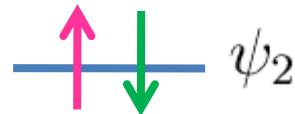
$$E_{SD} = 2 \sum_{i=1}^{N_{elec}/2} h_i + \sum_{i=1}^{N_{elec}/2} \sum_{j=1}^{N_{elec}/2} (2J_{ij} - K_{ij})$$



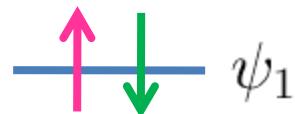
- An electron in orbital ψ_i has kinetic and nuclear attraction energy h_i



- It has a Coulomb (electrostatic) interaction energy J_{ij} with each of the other electrons, in orbitals ψ_j

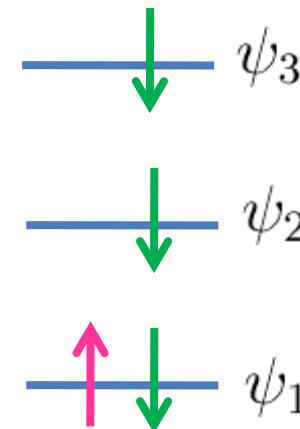
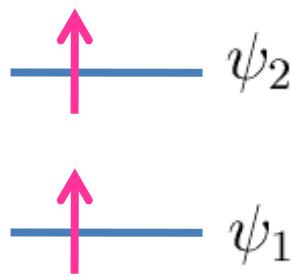


- It also has an exchange interaction energy K_{ij} **only with electrons of the same spin** in orbitals ψ_j . This is a purely quantum effect and is a consequence of the antisymmetry we have introduced in our wavefunctions



Electronic configurations

- Now that we know what interactions make up the energy of a Slater determinant wavefunction we can write down the energy of any electronic configuration
- Let's try the following examples:

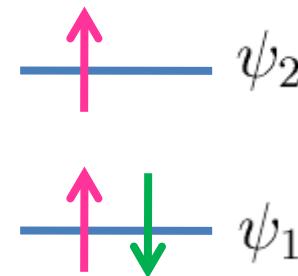
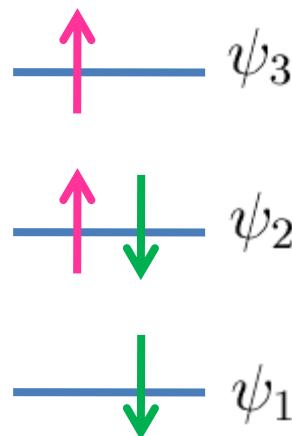


$$E = h_1 + h_2 + J_{12} - k_{12}$$

$$\begin{aligned} E = & 2h_1 + h_2 + h_3 + J_{11} + 2J_{12} + 2J_{13} \\ & + J_{23} - k_{12} - k_{13} - k_{23} \end{aligned}$$

Electronic configurations

Homework: write down the energy of the following electronic configurations in terms of core Hamiltonian, Coulomb and exchange integrals



Part 4

Hartree-Fock calculations

So far:

- A spin orbital is a one-electron wavefunction
- The simplest possible many-electron wavefunction which is antisymmetric is a Slater determinant of spin orbitals

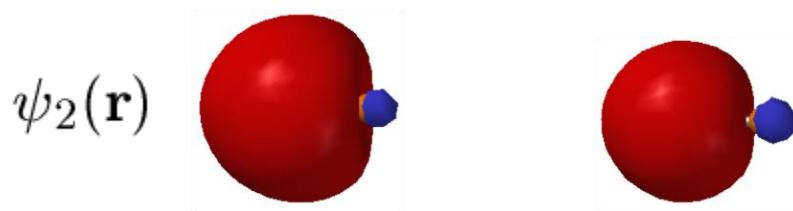
$$\Psi_{SD}(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \dots & \chi_N(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \dots & \chi_N(\mathbf{x}_2) \\ \vdots & \vdots & & \vdots \\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \dots & \chi_N(\mathbf{x}_N) \end{vmatrix}$$

- Spin orbitals have a spatial part and a spin part (either “up” or “down”)

$$\begin{aligned}\chi^\uparrow(\mathbf{x}) &= \psi(\mathbf{r})\alpha(\omega) \\ \text{Spin} &\quad \text{Spatial} \quad \text{Spin} \\ \text{orbital} &\quad \text{orbital} \quad \text{function} \\ \chi^\downarrow(\mathbf{x}) &= \psi(\mathbf{r})\beta(\omega)\end{aligned}$$

Selecting the spatial orbitals

- There are infinite choices possible for the spatial molecular orbitals in a Slater determinant. Which one is “best” ?
- Example: Two (out of infinite) sets of spatial orbitals for the 4 electrons of the LiH molecule:



Finding the optimum spatial molecular orbitals

- How do we decide what are the “best” spatial orbitals for a molecule?
- We need a guiding principle
- This is the variation principle: It can be applied to any approximate wavefunction.
- It forms the basis of many quantum chemistry computational techniques

Variation principle

- The **Variation principle** states that if the energy E is calculated from an approximate wavefunction Ψ_{ap} ,

$$E_{\text{ap}} = \frac{\int \Psi_{\text{ap}}^*(x) \hat{H} \Psi_{\text{ap}}(x) dx}{\int \Psi_{\text{ap}}^*(x) \Psi_{\text{ap}}(x) dx} \geq E_{\text{exact}}$$

then this energy is always greater than or equal to the true (exact) energy of the system

- The variation principle can be used to develop schemes for computing the spatial MOs: we search for the spatial MOs that produce the lowest (total) electronic energy

E₉: Assume we have two Slater determinants for a molecule, Ψ_{SD}^A and Ψ_{SD}^B , with energies

$$E_{SD}^A = \langle \Psi_{SD}^A | \hat{H} | \Psi_{SD}^A \rangle \quad E_{SD}^B = \langle \Psi_{SD}^B | \hat{H} | \Psi_{SD}^B \rangle$$

If $E_{SD}^A > E_{SD}^B$ then (according to variation principle) Ψ_{SD}^B is a better approximation to the exact wave function.

The Hartree-Fock equations

Starting from the energy of a Slater determinant wavefunction:

$$E_{SD} = 2 \sum_{i=1}^{N_{elec}/2} h_i + \sum_{i=1}^{N_{elec}/2} \sum_{j=1}^{N_{elec}/2} (2J_{ij} - K_{ij})$$

It can be shown (this is optional - see e.g. Szabo & Ostlund – or ask me outside the lectures) that the energy of the Slater determinant is minimised when the molecular orbitals are solutions of the following eigenvalue equation (known as the Hartree-Fock equation):

$$\hat{f}\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$

This is the **Fock** operator

The Fock operator

Is built from three operators:

- Core Hamiltonian
- Coulomb
- Exchange

$$\hat{f} = \hat{h} + \sum_{i=1}^{N_{elec}/2} (2\hat{J}_i - \hat{K}_i)$$

$$\hat{h} = -\frac{1}{2}\nabla^2 + \sum_{I=1}^{N_{nuc}} \frac{-Z_I}{|\mathbf{r} - \mathbf{R}_I|}$$

Core Hamiltonian operator

$$\hat{J}_i(\vec{r}_1) = \int \frac{|\psi_i(\vec{r}_2)|^2}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_2$$

$$\hat{J}_i(\mathbf{r}_1)\psi_k(\mathbf{r}_1) = \left[\int \psi_i^*(\mathbf{r}_2) \frac{1}{r_{12}} \psi_i(\mathbf{r}_2) d\mathbf{r}_2 \right] \psi_k(\mathbf{r}_1)$$

Coulomb operator

$$\hat{K}_i(\mathbf{r}_1)\psi_k(\mathbf{r}_1) = \left[\int \psi_i^*(\mathbf{r}_2) \frac{1}{r_{12}} \psi_k(\mathbf{r}_2) d\mathbf{r}_2 \right] \psi_i(\mathbf{r}_1)$$

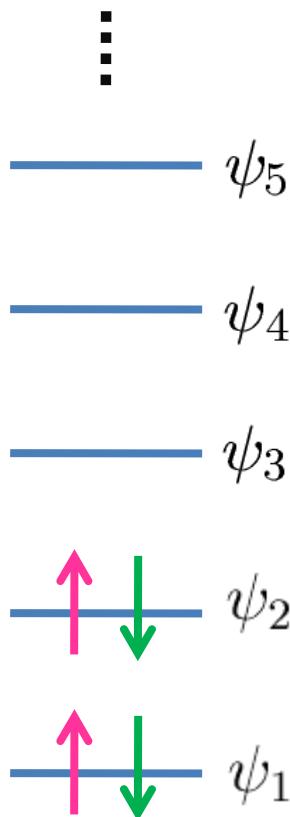
Exchange operator

this is not a typo!

The Fock operator (continued)

- Its **eigenfunctions** are the optimal spatial **molecular orbitals**
- Its **eigenvalues** are the molecular orbital energies
- It consists of three parts:
 - Core Hamiltonian operator: kinetic energy of an electron and its electrostatic attraction to all the nuclei
 - Coulomb operator: Electrostatic repulsion of an electron from all other electrons
 - Exchange operator: A purely quantum effect (no classical analogue), consequence of the antisymmetry of the electronic wavefunction

Fock operator example with 4 electrons



Fock operator

$$\hat{f} = \hat{h} + 2\hat{J}_1 - \hat{K}_1 + 2\hat{J}_2 - \hat{K}_2$$

Acting on occupied orbital ψ_1

$$\begin{aligned}\hat{f}\psi_1(\mathbf{r}) &= \hat{h}\psi_1(\mathbf{r}) + 2\hat{J}_1\psi_1(\mathbf{r}) - \hat{K}_1\cancel{\psi_1}(\mathbf{r}) + 2\hat{J}_2\psi_1(\mathbf{r}) - \hat{K}_2\psi_1(\mathbf{r}) \\ &= \hat{h}\psi_1(\mathbf{r}) + \hat{J}_1\psi_1(\mathbf{r}) + 2\hat{J}_2\psi_1(\mathbf{r}) - \hat{K}_2\psi_1(\mathbf{r})\end{aligned}$$

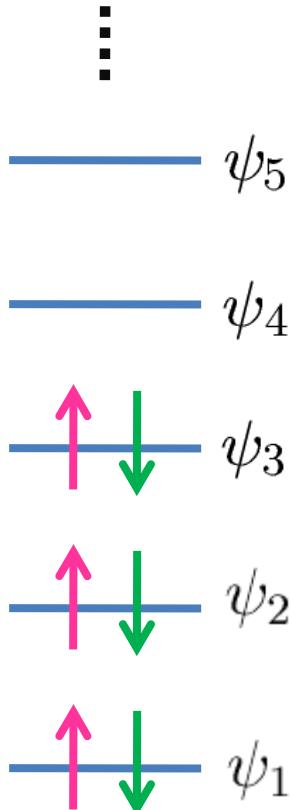
Cancellation of self-interaction for electron 1

because $\hat{J}_1\psi_1(\mathbf{r}) = \hat{K}_1\psi_1(\mathbf{r})$ (prove this)

Acting on unoccupied (virtual) orbital ψ_3

$$\hat{f}\psi_3(\mathbf{r}) = \hat{h}\psi_3(\mathbf{r}) + 2\hat{J}_1\psi_3(\mathbf{r}) - \hat{K}_1\psi_3(\mathbf{r}) + 2\hat{J}_2\psi_3(\mathbf{r}) - \hat{K}_2\psi_3(\mathbf{r})$$

Example of the Hartree-Fock equations



- Let's write down the Hartree-Fock eigenvalue equation for a molecule with 6 electrons, e.g. BeH₂, using the form of the Fock operator from slide 56

$$\left[\hat{h} + \sum_{i=1}^3 (2\hat{j}_i - \hat{k}_i) \right] \psi_j(\vec{r}) = \varepsilon_j \psi_j(\vec{r})$$

\hat{f} , the Fock operator
which is made of Ψ_1, Ψ_2, Ψ_3

$j=1, 2, 3, 4\dots$

- Observe the structure of this equation. Can you suggest a way of solving it?

The Self-Consistent Field (SCF) procedure

- The Fock operator depends on the molecular orbitals
- Thus, an iterative procedure is used to find these orbitals
- It is called the **Self-Consistent Field (SCF)** procedure

