

[CH932] Quantum Chemistry

Dr. Gabriele C. Sosso

University of Warwick Department of Chemistry

Office: G Block, Office 4 E-mail: <u>G.Sosso@warwick.ac.uk</u>

Term I, 2017/2018

Why should I care?



• Spectroscopy - e.g. UV/Vis spectroscopy





Why should I care?

WARWICK THE UNIVERSITY OF WARWICK

Charge transfer in biological systems

Biological electron-transfer (ET) reactions are typically described in the framework of coherent two-state electron tunneling or multistep hopping. However, these ET reactions may involve multiple redox cofactors in van der Waals contact with each other and with vibronic broadenings on the same scale as the energy gaps among the species.

> Zhang, Y., Liu, C., Balaeff, A., Skourtis, S.S., and Beratan, D.N. (2014). Biological charge transfer via flickering resonance. PNAS 111, 10049–10054.



Figure 1. Examples of biological systems where electron transfer play a key role. (A) electron transfer initiating DNA UV-lesion repair by enzyme photolyase. (B) electron transfer triggering a cascade of charge transfer reactions in the cytochrome bc1 complex that lead to a formation of an electrostatic gradient through the plasma membrane. (C) Activation of cryptochrome protein initiated by blue light excitation of the FAD cofactor leading to a formation of a radical pair.

Sjulstok, E., Olsen, J.M.H., and Solov'yov, I.A. (2015). Quantifying electron transfer reactions in biological systems: what interactions play the major role? Scientific Reports 5, srep18446.

Why should I care?



• Computational chemistry

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

J

- Post-Hartree-Fock methods (CI, CC, MP2...)
- Density Functional Theory
- [...]

hb_1.mp4

Ļ



CH_932_outline.gif

Assessment:

Workshop (pass/fail)

Course resources

Books:

- Reading list on Moodle
- Remember: nothing is essential, everything is useful



Myself:

- Via email: <u>G.Sosso@warwick.ac.uk</u> [anytime]
- In person: G Block, Office 4. Office hours for CH932: Thursday, 2-3 PM.
 [A 24h notice via email would be highly appreciated]









Learning Objectives

By the end of this lectures you should...

- ... be familiar with the basic concepts of quantum mechanics
- ... be able to deal with a few model systems (free particle, particle in a box, hydrogen atom...)
- ... be confident about the notion of chemical bonds and intermolecular interactions

Assumptions

At this stage you should be familiar with ...

• Nothing - we shall start from scratch!

The need for quantum mechanics

- Early birds: Ludwig Boltzmann (1877) [discrete energy levels]
- Old quantum theory:
 - Max Planck (1900) [black-body radiation]
 - Albert Einstein (1905) [photoelectric effect]
 - Niels Bohr (~1910)[hydrogen line spectrum]
 - [...]
- Unified & Formalised (~1930)
 - David Hilbert
 - Paul Dirac
 - [...]

Photoelectric effect

- Energy quantisation
- Wave-particle duality

Photoelectric effect





metal



Photoelectric effect





Classical electromagnetic theory Energy transfer from the light to the electron

The more intense the light, the strongest the force applied to the electron (eventually, for a sufficiently intense light, the electron *will* leave the metal)



For each metal, there exist a characteristic cutoff frequency below which no electrons are emitted, no matter how intense the light

Photoelectric effect





Einstein interpretation

Light is *quantised* into "bundles of energy" (*particles!*) called photons, each with energy

$$E = h\nu$$

Increasing the intensity of the light increase the number of photons, but not their frequency, hence their individual energy is the same

What we need instead is photons with:

$$\nu > \frac{w_0}{h}$$

Wave-particle duality





Quantum physics

$$\lambda = \frac{h}{p}$$

de Broglie relation:

the wavelength λ of the *wave* associated with the motion of the *particle* having a momentum p

Atomic spectra



The spectra emitted by macroscopic objects upon the interaction with electromagnetic radiation are continuous



The spectra emitted by free atoms display a number of discrete wavelengths



W. Finkelnburg, Structure of Matter, Springer-Verlag, Heidelberg, 1964.)

The electronic structure of atoms is quantised

The Schrödinger equation

How do we calculate these discrete energy levels e.g. for the hydrogen atom?

The Schrödinger equation

$$\mathcal{H}|\psi(\bar{r},t)\rangle = i\hbar\frac{\partial}{\partial t}|\psi(\bar{r},t)\rangle$$
$$H\psi = E\psi$$

- Operators
- Wave function
- Time dependency

Classical mechanics:

A system (say, a free particle) is described by positions and momenta

 $\begin{array}{l} \mbox{Quantum mechanics}\\ \mbox{A system (say, a free particle) is described by its wave function } \psi \end{array}$

The wave function



All the information about the state of a quantum system are contained in the wave function ψ

It has to be:

- Continuous
- Single valued
- Finite
- Smooth
- Square integrable



• include an imaginary part

Born's interpretation of ψ

The connection between ψ and the actual behaviour of the associated system (e.g. a particle) is given by The Born Rule:

$$P(x,t) = \psi^*(\bar{r},t) \cdot \psi(\bar{r},t)$$

The probability of finding e.g. a particle at the position r(+dr) and at time t(+dt) is equal to the square of the particle's wave function at that point

- This is a probability density
- It is always real and non-negative
- It makes sense: the particle is likely to be found where/when ψ has a decent amplitude

No time dependence, one dimension (x)...



The Schrödinger equation -II

How do we calculate these discrete energy levels e.g. for the hydrogen atom?

The Schrödinger equation

$$\mathcal{H}|\psi(\bar{r},t)\rangle = i\hbar\frac{\partial}{\partial t}|\psi(\bar{r},t)\rangle$$
$$H\psi = E\psi$$

- Operators
- Wave function
- Time dependency

Operators

Objects that act on the wave function Mathematics makes it easier [matrixes and vectors]

$$\mathcal{H} \Rightarrow$$
 Hamiltonian operator
 $i\hbar \frac{\partial}{\partial t} \Rightarrow$ energy operator

- WARWICK

0

The Hamiltonian operator In analogy with classical mechanics:

$$\mathcal{H} = V + K \qquad \qquad K_{\text{one dim.}} = -\frac{\hbar^2}{2m} \cdot \frac{\partial^2}{\partial x^2}$$

The Energy operator We "get rid of this" via *separation of variables*

$$\mathcal{H}|\psi(\bar{r},t)\rangle = i\hbar\frac{\partial}{\partial t}|\psi(\bar{r},t)\rangle$$

We look for wave functions that can be written as:

$$\psi(\bar{r},t) = \psi(\bar{r}) \cdot \psi(t) \qquad \qquad \psi(t) = e^{-\frac{iEt}{\hbar}}$$

Time-independent Schrödinger equation:

$$H\psi(\bar{r}) = E\psi(\bar{r})$$

The free particle



The free particle:

- The zero potential
- Just the kinetic term
- One dimension (x)



We have to solve the Schrödinger equation:

$$H\psi(\bar{r}) = E\psi(\bar{r})$$
$$\checkmark$$
$$-\frac{\hbar^2}{2m} \cdot \frac{\partial^2 \psi(x)}{\partial x^2} = E\psi(x)$$

Remember the time dependence!

$$\psi(\bar{r},t) = \psi(\bar{r}) \cdot e^{-\frac{iEt}{\hbar}}$$

The free particle - wave function

 ψ

$$\begin{aligned} -\frac{\hbar^2}{2m} \cdot \frac{\partial^2 \psi(x)}{\partial x^2} &= E\psi(x) \\ &\frac{\partial^2 \psi(x)}{\partial x^2} &= -\frac{2mE}{\hbar^2}\psi(x) \\ \psi'' &= -k^2\psi, \text{ with } k = \frac{\sqrt{2mE}}{\hbar} \\ (x) &= \sin(kx) \text{ , or } \cos(kx) \text{ , or } e^{ikx} \end{aligned}$$

WAR

THE UNIVERSITY OF WARWICK

$$\psi(x) = \alpha \cos(kx) + \beta \sin(kx)$$

$$e^{ix} = \cos(x) + i \sin(x)$$

$$\psi(x) = e^{ikx}$$

$$\psi(x, t) = e^{ikx} \cdot e^{-\frac{iEt}{\hbar}} = e^{i \cdot (kx - \frac{Et}{\hbar})}$$

$$P(x, t) = Q^{ikx} \cdot Q^{ikx} = Q^{i} \cdot Q^{ikx}$$

The free particle - wave function

 $P(x,t) = 1 \quad \forall t$ All t $\Psi^*(x, t) \Psi(x, t)$ $\int_{-\infty}^{\infty} |\psi(x,t)^2| \, dx = 1$ 0 x $t = t_0$ x $\Psi^*(x, t) \Psi(x, t)$ Group of traveling waves... $\psi_{\text{group}}(x,t) = \sum_{i=1}^{N} A_i \cdot e^{i(k_i x - \frac{E_i t}{\hbar})}$ $t = t_0 + \Delta t$ 0 x $t = t_0 + 2\Delta t$ 0

Figure 6-2 The probability density $\Psi^*\Psi$ for a group traveling wave function of a free particle. With increasing time the group moves in the direction of increasing *x*, and also spreads.

The free particle - energy levels

There are no restrictions on the value of k...

$$E = \frac{k^2 \hbar^2}{2m} \quad \forall E \ge 0$$

- Energy levels are *not* quantised
- This is identical to the classical case



HOWIVIR

What happens if instead of V(x)=0...

The particle in the box





The box





$$V(x) = \begin{cases} 0, & \text{for } 0 \le x \le L \\ \infty, & \text{for } x < 0 \text{ or } x > L \end{cases}$$

Not so boring!





Particle in a box ~ conjugated systems



WAR THE UNIVERSI

- Conjugated system (22 conjugated C-C bonds)
- The (22) conjugated electrons are delocalised across the whole chain
- They are (more or less) free to move across the chain
- They (roughly) feel the same potential at each point



Lauric Acid

- Saturated bonds
- Localised states electrons are mostly bound
- Functional (polar!) group unbalance the potential across the chain

Particle in a box - the wave function



The wave function has to be continuous everywhere

$$\psi(x=0) = \psi(x=L) = 0$$

(1.)
$$\psi(x=0) = \alpha \cos(0) + \beta \sin(0) = 0 \Rightarrow \alpha = 0$$

(2.)
$$\psi(x = L) = \alpha \cos(kL) + \beta \sin(kL) = 0 \implies \beta \sin(kL) = 0$$

 $\implies kL = n\pi , 1, 2... \implies k = \frac{n\pi}{L} , 1, 2...$

Particle in a box - the wave function



The wave function has to be continuous everywhere

$$\psi(x) = \alpha \cos(kx) + \beta \sin(kx)$$

(1.)
$$\alpha = 0$$
 and $k = \frac{n\pi}{L}$, 1, 2... (2.)

Particle in a Box Wave Function

$$\psi_n(x) = \beta \sin\left(\frac{n\pi}{L}x\right)$$

Particle in a box - the wave function

 $\psi_n(x)$ has n-1 nodes (points other than x=0 and x=L for which $\psi_n(x)=0$)

WA



Particle in a box - probability density

Where is the particle? Probability density $\psi_n^*(x) \cdot \psi_n(x) = |\psi_n(x)|^2$ WAR

THE UNIVERSITY OF WARWIG

For (infinitely) large values of $n\,$ the particle can be found anywhere in the box with the same probability



Correspondence principle

For (infinitely) large values of n the particle can be found anywhere in the box with the same probability Probability density $V = \psi_n^*(x) \cdot \psi_n(x) = |\psi_n(x)|^2$ $V(x) = \infty$ $V(x) = \infty$ $V(x) = \infty$ x = 0x = L

Correspondence Principle In the limit of large quantum numbers, we recover classical mechanics

Particle in a box - energy levels

$$k = \frac{\sqrt{2mE}}{\hbar} \text{ and } k = \frac{n\pi}{L}$$
$$\clubsuit$$
$$E_n = \frac{\hbar^2 n^2 \pi^2}{2mL^2}, \text{ with } n = 1, 2, .$$



- Energy levels are quantised
- There exist a zero point energy
- 2D box introduces *degeneracy*

$$E_{n_x,n_y} = \frac{\hbar^2 \pi^2}{2mL^2} \cdot (n_x^2 + n_y^2),$$

with $n_x = 1, 2, ...$ and $n_y = 1, 2, ...$



Particle in a box - degenerate states

If
$$A[n_x = 1, n_y = 2]$$
 and $B[n_x = 2, n_y = 1]$
 $E(A) = \frac{\hbar^2 \pi^2}{2mL^2} \cdot 5 = E(B)$
 $\psi(A) = \sqrt{\frac{2}{L}} \cdot \sin\left(\frac{\pi x}{L}\right) \cdot \sqrt{\frac{2}{L}} \cdot \sin\left(\frac{2\pi y}{L}\right) \neq \sqrt{\frac{2}{L}} \cdot \sin\left(\frac{2\pi x}{L}\right) \cdot \sqrt{\frac{2}{L}} \cdot \sin\left(\frac{\pi y}{L}\right)$

THE UNIT



Coffee!





This is one of the *very* few cases where we can solve Schrödinger equation analytically As in the case of e.g. the free particle and the particle in the box

HOWIVIR

Even just for the helium atom, no closed-form solution can be found

The Schrödinger equation for the hydrogen atom

1. Reduced mass μ



The hydrogen atom

So that we have an electron with reduced mass μ interacting with the nucleus via the Coulomb potential

 $V = \frac{q_{\text{nucleus}} \cdot q_{\text{electron}}}{4\pi\epsilon_0 \bar{r}_{\text{nucleus-electron}}} = \frac{Ze \cdot -e}{4\pi\epsilon_0 \cdot \bar{r}} = -\frac{e^2}{4\pi\epsilon_0 \cdot \bar{r}}$

The Hamiltonian of the system is thus:

$$\mathcal{H} = -\frac{\hbar^2}{2\mu} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 \cdot \bar{r}}$$

(Spherical) polar coordinates & separation of variables (radial and angular [polar + azimuth] parts)...

Energy levels

$$E_n = -\frac{\mu Z^2 e^4}{(4\pi\epsilon_0)^2 2\hbar^2 n^2}$$
The hydrogen atom - energy levels

$$E_n = -\frac{\mu Z^2 e^4}{(4\pi\epsilon_0)^2 2\hbar^2 n^2}$$

 $n = 1, 2, ..., \infty$ Principal quantum number THE UNIVERSI



Quantitative agreement with the experimental spectrum

The hydrogen atom - zero point energy

$$E_n = -\frac{\mu Z^2 e^4}{(4\pi\epsilon_0)^2 2\hbar^2 n^2}$$

 $n = 1, 2, ..., \infty$ Principal quantum number


The hydrogen atom - wave functions

$$\psi_{n,l,m_l}(r,\theta,\phi) = R_{n,l}(r) \cdot Y_{l,m_l}(\theta,\phi)$$

 $R_{n,l}(r) = e^{-\frac{\text{constant} \cdot r}{n}} \cdot r^l \Rightarrow \text{ polynomial in } r \text{ [Radial part]}$

 $Y_{l,m_l}(\theta,\phi) = e^{im_l\phi} \cdot \sin^{|m_l|}\theta \Rightarrow \text{ spherical harmonics [Angular part]}$

Quan	tum N	lumbers	
n	l	m_l	Eigenfunctions
1	0	0	$\psi_{100} = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$
2	0	0	$\psi_{200} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(2 - \frac{Zr}{a_0}\right) e^{-Zr/2a_0}$
2	1	0	$\psi_{210} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \cos\theta$
2	1	<u>+</u> 1	$\psi_{21\pm 1} = \frac{1}{8\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \sin \theta e^{\pm i\varphi}$

- The principal quantum number n is related to energy [n > 0]
- The orbital quantum number *l* is related to angular momentum [0 < l < n-1]
- The magnetic quantum number m_l is related to direction of the angular momentum of the electron $[-l < m_l < +l]$

The hydrogen atom - probability densities



Radial probability density

$$P_{n,l}(r)dr = R_{n,l}^*(r) \cdot R_{n,l}(r) 4\pi r^2 dr$$

- *n* determines:
 - the *extent* (r) of the probability
 - the number of nodes N_N in ψ (and thus P(r) as well) $[N_N=n-1]$

• I determines the *shape* of the probability

- *P*(*r*) decays quite rapidly
- *P*(*r*) is *not* homogeneous



The hydrogen atom - probability densities

Angular probability density

$$P_{l,m_l}(\theta) = Y_{l,m_l}^*(\theta,\phi) \cdot Y_{l,m_l}(\theta,\phi)$$



The hydrogen atom - atomic orbitals



Radial and angular results together...

Atomic (hydrogen-like) orbitals





Each atomic orbital can host up to two electrons Spin quantum number *m*_s from Dirac equation

Orbital angular momentum (L)

The quantum number I is related to the orbital angular momentum L of the electron

The two quantities are related by the following equation:

$$\mathcal{L}^2|\psi\rangle = \hbar^2 l(l+1)|\psi\rangle$$

L describes the "orbital" motion of the electron about the center of the atom



This motion can be described in terms of spherical harmonics



Spin (S)



Electrons (well, in fact *any* elementary particle!) have an *intrinsic angular momentum* as well, *S*

Exactly as in the case of L...

$$\mathcal{S}^2|\psi\rangle = \hbar^2 s(s+1)|\psi\rangle$$

S describes the "intrinsic" motion of the electron about its center of mass...



- There is *no* direct analogy with classical mechanics
- *s* is *not* related to positions and/or angles
- It is something so fundamental that every particle has its own spin its own value os s

Spin - electrons



Gasser, U., et al. (2001). Real-Space Imaging of Nucleation and Growth in Colloidal Crystallization. Science 292, 258–262.

Spin - electrons

In quantum mechanics, usually we cannot: particles are *indistinguishable*

Suppose we have two particles (say, two electrons), 1 and 2 and two states, A and B (four quantum number included in one letter!)

The combined wave functions of the system are:

$$\psi_{\text{Combined}} = \psi_A(1)\psi_B(2) \text{ or } \psi_B(1)\psi_A(2)$$

This does not work, though! The probability density is not the same if I swap 1 with 2!

 $\psi_A^*(1)\psi_B^*(2)\cdot\psi_A(1)\psi_B(2)\neq\psi_A^*(2)\psi_B^*(1)\cdot\psi_A(2)\psi_B(1)$

However, we can construct linear combinations in order to make things right:

$$\psi_{\text{Combined}}^{\text{Symmetric}} = \frac{1}{2} [\psi_A(1)\psi_B(2) + \psi_B(1)\psi_A(2)] \quad \text{Integral or zero spin: bosons}$$

$$\psi_{\text{Combined}}^{\text{Antisymmetric}} = \frac{1}{2} [\psi_A(1)\psi_B(2) - \psi_B(1)\psi_A(2)] \quad \text{Half-integral spin: fermions}$$

The exclusion principle



Consider two electrons in *exactly* the same state A:

$$\psi_{\text{Combined}}^{\text{Antisymmetric}} = \frac{1}{2} [\psi_A(1)\psi_A(2) - \psi_A(1)\psi_A(2)]$$

Pauli expulsion principle: Two electrons *cannot* occupy *exactly* the same state

Singlet and Triplet states

Note that for fermions/bosons the *total* wave function has to be antisymmetric/symmetric

$$\psi = \psi_{\rm Spatial} \cdot \psi_{\rm Spin}$$

For fermions (e.g. electrons):

 $\psi = \psi_{\text{Spatial}}^{\text{Antisymmetric}} \cdot \psi_{\text{Spin}}^{\text{Symmetric}} \text{ or } \psi_{\text{Spatial}}^{\text{Symmetric}} \cdot \psi_{\text{Spin}}^{\text{Antisymmetric}}$

antisymmetric spin eigenfunction: $\frac{1}{\sqrt{2}} \left[(+1/2, -1/2) - (-1/2, +1/2) \right] \text{ (singlet)}$

symmetric spin
eigenfunctions:
$$\frac{1}{\sqrt{2}} [(+1/2, -1/2) + (-1/2, +1/2) \text{ (triplet)} \\ (-1/2, -1/2)$$

Singlet and Triplet states

Singlet and triplet states have different energies!

e.g. energy levels of the helium atom





8

Wait, no triplet state?

H₂+ and the Born-Oppenheimer approx.

Even in the case of the H₂+ molecule (2 protons, 1 electron), it is impossible to solve the Schrödinger equation analytically



The Born-Oppenheimer approximation:

$$\psi(z, Z_1, Z_2) = \psi(z, \{Z_1, Z_2\}) \cdot \psi(Z_1, Z_2)$$

$$\psi(\bar{r}_e, \bar{R}_N) = \psi(\bar{r}_e, \{\bar{R}_N\}) \cdot \psi(\bar{R}_N)$$

The Born-Oppenheimer approximation

$$\psi(\bar{r}_e, \bar{R}_N) = \psi(\bar{r}_e, \{\bar{R}_N\}) \cdot \psi(\bar{R}_N)$$

The wave function for the electrons depend on the position of the electrons and, *parametrically*, on the position of the nuclei

For each nuclear configuration $\{\mathbf{R}_N\}$, we have a different electronic wave function



The Born-Oppenheimer approximation



Electrons are *much* ($\sim 10^{3-4}$) lighter than the nuclei, so for each movement of the nuclei, the electrons follows *immediately*

Electrons are immobile on the timescale of nuclear motion

The electron-nuclei interaction is still there

HOWIVIR

We discard the kinetic terms for the nuclei (and the mixed electron-nuclei terms) in the Hamiltonian

$$\mathcal{H} = -\frac{\hbar^2}{2m_e} \frac{\partial^2}{\partial z^2} - \frac{\hbar^2}{2M_1} \frac{\partial^2}{\partial Z_1^2} - \frac{\hbar^2}{2M_2} \frac{\partial^2}{\partial Z_2^2} + V(z, Z_1, Z_2)$$
$$\mathcal{H} = -\frac{\hbar^2}{2m_e} \frac{\partial^2}{\partial z^2} + V(z, \{Z_1, Z_2\})$$
$$\mathcal{H} = -\frac{\hbar^2}{2m_e} \frac{\partial^2}{\partial z^2} - \frac{e^2}{4\pi\epsilon_0 z_{e-1}} - \frac{e^2}{4\pi\epsilon_0 z_{e-2}} + \frac{e^2}{4\pi\epsilon_0 Z_{1-2}}$$

The Born-Oppenheimer approximation



Comparison with the Hamiltonian for the hydrogen atom:

$$\mathcal{H} = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{4\pi\epsilon_0\cdot\bar{r}}$$

We can do this - analytically! (*ellipsoidal instead of spherical polar coordinates*)

H₂+ - molecular orbitals

Solving the Schrödinger equation for H₂+ in the Born-Oppenheimer approximation leads to...





WARM

THE UNIVERSITY OF WARWIG







H₂+ - molecular orbitals

Solving the Schrödinger equation for H₂+ in the Born-Oppenheimer approximation leads to...





WAR



Molecular Orbitals (MO) Look at the probability density!

- $1\sigma \implies$ Bonding orbital
- $2\sigma \implies$ Antibonding orbital

LCAO

Actually, we cannot solve the Schrödinger equation for anything more complicated than H₂+ - even when using the Born-Oppenheimer approximation





WAR Linear Combination of Atomic Orbitals LCAO $c_i\psi_{
m Atomic}$ Orbital $\psi_{
m Molecular}$ Orbital iThe case of H_{2}^{+} again: ψ₂ ► z ψ_1 е $\psi_{\mathrm{H}_2^+}^{1\sigma} \approx \psi_1 + \psi_2$ Symmetry Are the MO invariant upon inversion of electronic coordinates? • 1σ is! g (gerade) $\psi_{\rm H_2^+}^{2\sigma} \approx \psi_1 - \psi_2$ • 2σ is not! u (*ungerade*)

LCAO diagrams

WARWICK

The hydrogen molecule



Bond order



THE UNIVERSITY OF WARWICH

LCAO diagrams



LCAO how to:

- 1. Find the valence electrons for each atom in the molecule
- 2. Homo- vs hetero- nuclear molecule (the more electronegative atom will be placed lower on the diagram)
- 3. Build the MOs, keeping in mind that:
 - More nodes = higher MOs
 - Sigma orbitals are stronger than pi bonds
 - Antibonding MOs are higher in energy than bonding MOs
 - Constructive overlap = fewer nodes = more stable (less energetic)
 - Destructive overlap = more nodes = less stable (more energetic)
- 4. Double check: the number of individual atomic orbitals should equal the number of MOs

LCAO diagrams

WARVICK

The *nitrogen* molecule

Electronic configuration of the nitrogen atom:

[He] 2s²2p³



Bond order?

Molecular orbitals



The *HF* molecule

Electronic configuration of the fluorine atom: [He] $2s^22p^5$

The σ atomic orbital of F cannot interact with the σ atomic orbital of H



Molecular orbitals



The *HF* molecule

Electronic configuration of the fluorine atom: [He] 2s²2p⁵

The σ atomic orbital of F cannot interact with the σ atomic orbital of H



Coffee!





Intra- & Inter- molecular interactions



Typically much weaker No need to do chemistry, electrostatic is usually enough...

Covalent bond

Covalent bonds are the realm of LCAO

THE UN

Non polar





on the electronegativity scale)

lonic bond

Na donates electron CI accepts electron CI accepts electron

WAR

THE UNIVERSITY OF WARWICK

Chemistry in solution

nacl_2.mp4







Intramolecular force	Basis of formation	Relative strength
Metallic bond	Metal cations to delocalized electrons	1, strongest
lonic bond	Cations to anions	2
Polar covalent bond	Partially charged cation to partially charged anion	3
Nonpolar covalent bond	Nuclei to shared electrons	4, weakest

Intermolecular forces



Intermolecular forces according to Jacob Israelachvili, commenting upon a corollary of the Hellmann-Feynman theorem...



"[...] all intermolecular forces are essentially electrostatic in origin [...] once the spatial distribution of the electron clouds has been determined by solving the Schrödinger equation, the intermolecular forces may be calculated on the basis of straightforward classical electrostatic"



- Van der Waals forces:
 - Keesom forces (permanent dipole-permanent dipole)
 - Debye forces (permanent dipole-induced dipole)
 - London dispersion forces (fluctuating dipole-induced dipole)
- Ion-(induced or permanent...) dipole
- Hydrogen bonding
- Halogen bonding [...]

Molecular dipoles

- WARWICK



 $\bar{\mu} = q \cdot \bar{d}$



Beware the sign!

- Chemists: from + to -
- Physicists: from to +




Molecular dipoles



Molecular dipoles

- Permanent dipoles
- Induced dipoles
- Fluctuating dipoles

Permanent dipole



Keesom forces





Molecular dipoles



Molecular dipoles

- Permanent dipoles
- Induced dipoles
- Fluctuating dipoles

Induced dipole



Molecular dipoles

WARVICK THE UNIVERSITY OF WARWICK

Molecular dipoles

- Permanent dipoles
- Induced dipoles
- Fluctuating dipoles

Fluctuating dipole



The strength of these dipoles depends upon the *polarizability* of the electrons involved i.e. how electrons respond to an electric field

How many electrons? How tightly are they bound to the nuclei?

The case of methanol











Electrostatic interactions

THE U

The electrostatic potential energy between two charges q_1 and q_2 is:

1

3

distance (r, or d) [Å]

4

Intra- & Inter- molecular forces

A long-standing challenge for molecular simulations

The energy (and thus the forces) of the system depends on both intra- and inter- molecular interactions

ab initio vs classical methods

How do we represent intra- and inter- molecular interactions?



The case of water...

0. Keep it simple:



The case of water





1. Molecules cannot overlap

Hard spheres [colloidal particles]



The case of water

2. Repulsive and attractive terms

Lennard-Jones potential [e.g. metallic liquids]

$$V_{LJ}(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right]$$





THE U

The case of water

- 3. Back to the water molecule Bond and angles
- 4. What about the dipole moment? Point charges
- 5. Liquid water LJ + point charges
- 6. Polarisable liquid water LJ + point charges that can vary in time
- 7. Proton transfer in water DFT (or machine-learning based potentials)
- 8. Nuclear quantum effects in water Path Integral simulations
- 9. Heterogeneous ice nucleation Different interactions for different components...





Learning Objectives

By the end of this lectures you should...

- ... be familiar with the basic concepts of quantum mechanics
- ... be able to deal with a few model systems (free particle, particle in a box, hydrogen atom...)
- ... be confident about the notion of chemical bonds and intermolecular interactions



CH932: Quantum Chemistry (2017/18)

Additional reading with respect to the Quantum Chemistry part of the CH932 module [Introduction to Chemistry and Biochemistry]

View Online

2 items

Quantum physics of atoms, molecules, solids, nuclei, and particles - Robert M. Eisberg, Robert Resnick, c1985

Book | recommended | This is a classic textbook, encompassing most of the basic concepts of quantum mechanics. It is amazingly clear, and avoids as much mathematics as possible in illustrating concepts and examples. It also contains a number of problems for which solutions are available (separate book). It can very well level the playfield when dealing with interdisciplinary content/research anytime quantum chemistry is involved.

Molecular Quantum Mechanics - Peter W. Atkins, Ronald S. Friedman, 2010 Book | recommended | This book cover an incredible collection of topics. While never entering into the very details, it offer a fairly rigorous treatment of many aspect of quantum chemistry. It also included several excellent examples plus a diverse array of problems - solutions to which can be easily found.



The workshop





Pen, paper & calculator 14:00, MOAC seminar room



