# [CH932] <br> Quantum Chemistry 

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## Why should I care?

- Spectroscopy - e.g. UV/Vis spectroscopy



$$
E=h \nu=\frac{h c}{\nu}
$$

$\lambda_{\mathrm{HOMO} \text {-LUMO }}=\frac{h c}{\Delta E_{\text {HOMO-LUMO }}}$

## Why should I care?

## - 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 bcl 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.

## Why should I care?

- Computational chemistry

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

$\downarrow$

- Post-Hartree-Fock methods (CI, CC, MP2...)
- Density Functional Theory
- [...]
$\downarrow$
hb_1.mp4

CH_932_outline.gif

## Assessment:

Workshop (pass/fail)

## Course resources

## Books:

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


## Moodle:

- Lecture notes [plus Lecture Capture]



## Myself:

- Via email: G.Sosso@warwick.ac.uk [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
Free electron model
metal ion in fixed position
delocalised electrons


## 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,

## 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 $\lambda$ 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


## HOWEVER

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


Figure 4-10 A photograph of the visible part of the hydrogen spectrum. (Spectrum from 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

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

- Operators
- Wave function
- Time dependency

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

Quantum mechanics
A system (say, a free particle) is described by its wave function $\psi$

## The wave function

All the information about the state of a quantum system are contained in the wave function $\psi$

It has to be:

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


It can:

- be time dependent
- include an imaginary part


## Born's interpretation of $\psi$

The connection between $\psi$ 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 $r(+d r)$ and at time $t(+d t)$ 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 $\psi$ has a decent amplitude

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


$$
P(a<x<b)=\int_{a}^{b}|\psi(x)|^{2} d x
$$

## The Schrödinger equation -II

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

The Schrödinger equation

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

- Operators
- Wave function
- Time dependency


## Operators

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

$$
\begin{aligned}
\mathcal{H} & \Rightarrow \text { Hamiltonian operator } \\
i \hbar \frac{\partial}{\partial t} & \Rightarrow \text { energy operator }
\end{aligned}
$$

## Operators

The Hamiltonian operator
In analogy with classical mechanics:

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

## 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:

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

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:

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

Remember the time dependence!

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

## The free particle - wave function

$$
\begin{gathered}
-\frac{\hbar^{2}}{2 m} \cdot \frac{\partial^{2} \psi(x)}{\partial x^{2}}=E \psi(x) \\
\frac{\partial^{2} \psi(x)}{\partial x^{2}}=-\frac{2 m E}{\hbar^{2}} \psi(x) \\
\psi^{\prime \prime}=-k^{2} \psi, \text { with } k=\frac{\sqrt{2 m E}}{\hbar} \\
\psi(x)=\sin (k x), \text { or } \cos (k x), \text { or } e^{i k x} \\
\psi(x)=\alpha \cos (k x)+\beta \sin (k x) \\
e^{i x}=\cos (x)+i \sin (x) \\
\psi(x)=e^{i k x} \\
\psi(x, t)=e^{i k x} \cdot e^{-\frac{i E t}{\hbar}}=e^{i \cdot\left(k x-\frac{E t}{\hbar}\right)} \\
P(x, t)
\end{gathered}
$$

## The free particle - wave function

$$
P(x, t)=1 \quad \forall t
$$



Group of traveling waves...

$$
\psi_{\text {group }}(x, t)=\sum_{i=1}^{N} A_{i} \cdot e^{i\left(k_{i} x-\frac{E_{i} t}{\hbar}\right)}
$$



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 $k \ldots$

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

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


HOWジきス

What happens if instead of $V(x)=0 \ldots$

The particle in the box


The box


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

## Not so boring!



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



2

##  <br> 3

## Particle in a box ~ conjugated systems

## Beta-Carotene



- 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



Within the box $\Rightarrow V(x)=0$
The wave function if that of the free particle in one dimension!

$$
\psi(x)=\alpha \cos (k x)+\beta \sin (k x), k=\frac{\sqrt{2 m E}}{\hbar}
$$

Particle in a Box:
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.) $\psi(x=L)=\alpha \cos (k L)+\beta \sin (k L)=0 \Rightarrow \beta \sin (k L)=0$

$$
\Rightarrow k L=n \pi, 1,2 \ldots \Rightarrow k=\frac{n \pi}{L}, 1,2 \ldots
$$

## Particle in a box - the wave function



Within the box $\Rightarrow V(x)=0$
The wave function if that of the free particle in one dimension!

$$
\psi(x)=\alpha \cos (k x)+\beta \sin (k x), k=\frac{\sqrt{2 m E}}{\hbar}
$$

Particle in a Box:
The wave function has to be continuous everywhere


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



## Particle in a box - probability density

$$
\begin{gathered}
\text { Where is the particle? } \\
\text { Probability density } \\
\psi_{n}^{*}(x) \cdot \psi_{n}(x)=\left|\psi_{n}(x)\right|^{2}
\end{gathered}
$$

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


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

## Particle in a box - energy levels

$$
\begin{gathered}
k=\frac{\sqrt{2 m E}}{\hbar} \text { and } k=\frac{n \pi}{L} \\
E_{n}=\frac{\hbar^{2} n^{2} \pi^{2}}{2 m L^{2}}, \text { with } n=1,2, \ldots
\end{gathered}
$$



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

$$
\begin{aligned}
E_{n_{x}, n_{y}} & =\frac{\hbar^{2} \pi^{2}}{2 m L^{2}} \cdot\left(n_{x}^{2}+n_{y}^{2}\right), \\
\text { with } n_{x} & =1,2, \ldots \text { and } n_{y}=1,2, \ldots
\end{aligned}
$$



## Particle in a box - degenerate states

$$
\begin{gathered}
\text { If } A\left[n_{x}=1, n_{y}=2\right] \text { and } B\left[n_{x}=2, n_{y}=1\right] \\
E(A)=\frac{\hbar^{2} \pi^{2}}{2 m L^{2}} \cdot 5=E(B) \\
\psi(A)=\sqrt{\frac{2}{L}} \cdot \sin \left(\frac{\pi x}{L}\right) \cdot \sqrt{\frac{2}{L}} \cdot \sin \left(\frac{2 \pi y}{L}\right) \neq \sqrt{\frac{2}{L}} \cdot \sin \left(\frac{2 \pi x}{L}\right) \cdot \sqrt{\frac{2}{L}} \cdot \sin \left(\frac{\pi y}{L}\right)
\end{gathered}
$$

## Coffee!

## The hydrogen atom

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

## HOWEVER

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

## The Schrödinger equation for the hydrogen atom

1. Reduced mass $\mu$


Actual system


Model system

$$
\mu=\left(\frac{M_{\text {nucleus }}}{m_{\text {electron }}+M_{\text {nucleus }}}\right) \cdot m_{\text {electron }}=0.995 m_{\text {electron }}
$$

## The hydrogen atom

So that we have an electron with reduced mass $\mu$ interacting with the nucleus via the Coulomb potential

$$
V=\frac{q_{\text {nucleus }} \cdot q_{\text {electron }}}{4 \pi \epsilon_{0} \bar{r}_{\text {nucleus-electron }}}=\frac{Z e \cdot-e}{4 \pi \epsilon_{0} \cdot \bar{r}}=-\frac{e^{2}}{4 \pi \epsilon_{0} \cdot \bar{r}}
$$

The Hamiltonian of the system is thus:

$$
\begin{gathered}
\mathcal{H}=-\frac{\hbar^{2}}{2 \mu} \nabla^{2}-\frac{e^{2}}{4 \pi \epsilon_{0} \cdot \bar{r}} \\
\downarrow
\end{gathered}
$$

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

$$
\begin{gathered}
\stackrel{\downarrow}{\text { Energy levels }} \\
E_{n}=-\frac{\mu Z^{2} e^{4}}{\left(4 \pi \epsilon_{0}\right)^{2} 2 \hbar^{2} n^{2}}
\end{gathered}
$$

## The hydrogen atom - energy levels

$$
E_{n}=-\frac{\mu Z^{2} e^{4}}{\left(4 \pi \epsilon_{0}\right)^{2} 2 \hbar^{2} n^{2}} \quad \begin{gathered}
n=1,2, \ldots, \infty \\
\text { Principal quantum number }
\end{gathered}
$$



Quantitative agreement with the experimental spectrum

## The hydrogen atom - zero point energy

$$
E_{n}=-\frac{\mu Z^{2} e^{4}}{\left(4 \pi \epsilon_{0}\right)^{2} 2 \hbar^{2} n^{2}}
$$

$$
n=1,2, \ldots, \infty
$$

Principal quantum number


## The hydrogen atom - wave functions

$$
\begin{aligned}
\psi_{n, l, m_{l}}(r, \theta, \phi) & =R_{n, l}(r) \cdot Y_{l, m_{l}}(\theta, \phi) \\
R_{n, l}(r)=e^{-\frac{\text { constant.r }}{n}} \cdot r^{l} & \Rightarrow \text { polynomial in } r \text { [Radial part] } \\
Y_{l, m_{l}}(\theta, \phi)=e^{i m_{l} \phi} \cdot \sin ^{\left|m_{l}\right|} \theta & \Rightarrow \text { spherical harmonics [Angular part] }
\end{aligned}
$$

Quantum Numbers.

| $n$ | $l$ | $m_{l}$ | Eigenfunctions |
| :---: | :---: | :---: | :---: |
| 1 | 0 | 0 | $\psi_{100}=\frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_{0}}\right)^{3 / 2} e^{-Z r / a_{0}}$ |
| 2 | 0 | 0 | $\psi_{200}=\frac{1}{4 \sqrt{2 \pi}}\left(\frac{Z}{a_{0}}\right)^{3 / 2}\left(2-\frac{Z r}{a_{0}}\right) e^{-Z r / 2 a_{0}}$ |
| 2 | 1 | 0 | $\psi_{210}=\frac{1}{4 \sqrt{2 \pi}}\left(\frac{Z}{a_{0}}\right)^{3 / 2} \frac{Z r}{a_{0}} e^{-Z r / 2 a_{0}} \cos \theta$ |
| 2 | 1 | $\pm 1$ | $\psi_{21 \pm 1}=\frac{1}{8 \sqrt{\pi}}\left(\frac{Z}{a_{0}}\right)^{3 / 2} \frac{Z r}{a_{0}} e^{-Z r / 2 a_{0}} \sin \theta e^{ \pm i \varphi}$ |

- The principal quantum number $n$ is related to energy [ $n>0$ ]
- The orbital quantum number / is related to angular momentum $[0<1<n-1]$
- The magnetic quantum number $m_{l}$ is related to direction of the angular momentum of the electron $\left[-1<m_{l}<+l\right]$


## The hydrogen atom - probability densities







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



## The hydrogen atom - probability densities

## Angular probability density

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


$l=3, m_{l}= \pm 3$

$\mathrm{m} /$ determines the orientational dependence of the probability
$\Rightarrow \quad$ I determines


## The hydrogen atom - atomic orbitals

Radial and angular results together..

Atomic (hydrogen-like) orbitals


- $n$ " m size
- / $" \rightarrow$ shape
- $m_{l}$ " $\rightarrow$ orientation

Labelling:
$n l(s, p, d \ldots)^{\text {n. electrons }}$ e.g. $3 d^{2}$

Each atomic orbital can host up to two electrons
Spin quantum number $m_{S}$ from Dirac equation

## Orbital angular momentum (L)

The quantum number / 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

Electrons (well, in fact any elementary particle!) have an
intrinsic angular momentum as well, $S$
Exactly as in the case of $L \ldots$

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

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 $s$
"Ordinary" matter has $s=1 / 2$
The Higgs boson has $s=0$


Integral or zero spin: bosons
$\downarrow$
The wave function is
symmetric
under particle interchange

Half-integral spin: fermions $\downarrow$

The wave function is
antisymmetric under particle interchange


In classical mechanics we can label particles:


Gasser, U., et al. (2001).

## 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:
$\psi_{\text {Combined }}^{\text {Symmetric }}=\frac{1}{2}\left[\psi_{A}(1) \psi_{B}(2)+\psi_{B}(1) \psi_{A}(2)\right] \quad$ integral or zero spin: bosons
$\psi_{\text {Combined }}^{\text {Antisymetric }}=\frac{1}{2}\left[\psi_{A}(1) \psi_{B}(2)-\psi_{B}(1) \psi_{A}(2)\right] \quad$ Halt-integral spin: fermions

## The exclusion principle

$$
\psi_{\text {Combined }}^{\text {Antisymmetric }}=\frac{1}{2}\left[\psi_{A}(1) \psi_{B}(2)-\psi_{B}(1) \psi_{A}(2)\right]
$$

Consider two electrons in exactly the same state A:

$\psi_{\text {Combined }}^{\text {Antisymetric }}=\frac{1}{2}\left[\psi_{A}(1) \psi_{A}(2)-\psi_{A}(1) \psi_{A}(2)\right]$


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

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

For fermions (e.g. electrons):
$\psi=\psi_{\text {Spatial }}^{\text {Antisymmetric }} \cdot \psi_{\text {Spin }}^{\text {Symmetric }}$ or $\psi_{\text {Spatial }}^{\text {Symmetric }} \cdot \psi_{\text {Spin }}^{\text {Antisymmetric }}$
$\underset{\text { eigenfunction: }}{\operatorname{antisymmetric~spin}} \quad \frac{1}{\sqrt{2}}[(+1 / 2,-1 / 2)-(-1 / 2,+1 / 2)] \quad$ (singlet)

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

## Singlet and Triplet states

Singlet and triplet states have different energies!
e.g. energy levels of the helium atom


## $\mathrm{H}_{2}{ }^{+}$and the Born-Oppenheimer approx.

Even in the case of the $\mathrm{H}_{2}{ }^{+}$molecule ( 2 protons, 1 electron), it is impossible to solve the Schrödinger equation analytically

$$
\begin{gathered}
\mathcal{H}=-\frac{\hbar^{2}}{2 m_{e}} \frac{\partial^{2}}{\partial z^{2}}-\frac{\hbar^{2}}{2 M_{1}} \frac{\partial^{2}}{\partial Z_{1}^{2}}-\frac{\hbar^{2}}{2 M_{2}} \frac{\partial^{2}}{\partial Z_{2}^{2}}+V\left(z, Z_{1}, Z_{2}\right) \\
\mathcal{H} \psi\left(z, Z_{1}, Z_{2}\right)=E \psi\left(z, Z_{1}, Z_{2}\right) \\
\downarrow
\end{gathered}
$$

The Born-Oppenheimer approximation:

$$
\begin{aligned}
\psi\left(z, Z_{1}, Z_{2}\right) & =\psi\left(z,\left\{Z_{1}, Z_{2}\right\}\right) \cdot \psi\left(Z_{1}, Z_{2}\right) \\
\psi\left(\bar{r}_{e}, \bar{R}_{N}\right) & =\psi\left(\bar{r}_{e},\left\{\bar{R}_{N}\right\}\right) \cdot \psi\left(\bar{R}_{N}\right)
\end{aligned}
$$

## The Born-Oppenheimer approximation

$$
\psi\left(\bar{r}_{e}, \bar{R}_{N}\right)=\psi\left(\bar{r}_{e},\left\{\bar{R}_{N}\right\}\right) \cdot \psi\left(\bar{R}_{N}\right)
$$

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 $\left\{\mathbf{R}_{N}\right\}$, 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

## HOWEV淂

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

$$
\begin{gathered}
\mathcal{H}=-\frac{\hbar^{2}}{2 m_{e}} \frac{\partial^{2}}{\partial z^{2}}-\frac{\hbar^{2}}{2 M_{1}} \frac{\partial^{2}}{\partial Z_{1}^{2}}-\frac{\hbar^{2}}{2 M_{2}} \frac{\partial^{2}}{\partial Z_{2}^{2}}+V\left(z, Z_{1}, Z_{2}\right) \\
\mathcal{H}=-\frac{\hbar^{2}}{2 m_{e}} \frac{\partial^{2}}{\partial z^{2}}+V\left(z,\left\{Z_{1}, Z_{2}\right\}\right) \\
\mathcal{H}=-\frac{\hbar^{2}}{2 m_{e}} \frac{\partial^{2}}{\partial z^{2}}-\frac{e^{2}}{4 \pi \epsilon_{0} z_{e-1}}-\frac{e^{2}}{4 \pi \epsilon_{0} z_{e-2}}+\frac{e^{2}}{4 \pi \epsilon_{0} Z_{1-2}}
\end{gathered}
$$

## The Born-Oppenheimer approximation

$$
\mathcal{H}=-\frac{\hbar^{2}}{2 m_{e}} \frac{\partial^{2}}{\partial z^{2}}-\frac{e^{2}}{4 \pi \epsilon_{0} z_{e-1}}-\frac{e^{2}}{4 \pi \epsilon_{0} z_{e-2}}+\frac{e^{2}}{4 \pi \epsilon_{0} Z_{1-2}}
$$



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)

## $\mathrm{H}_{2}{ }^{+}$- molecular orbitals

Solving the Schrödinger equation for $\mathrm{H}_{2}{ }^{+}$
in the Born-Oppenheimer approximation leads to...



## $\mathrm{H}_{2}{ }^{+}$- molecular orbitals

Solving the Schrödinger equation for $\mathrm{H}_{2}{ }^{+}$ in the Born-Oppenheimer approximation leads to...



Actually, we cannot solve the Schrödinger equation for anything more complicated than $\mathrm{H}_{2}{ }^{+}$

- even when using the Born-Oppenheimer approximation


## HOWシV浮

Inspired by the $\mathrm{H}_{2}+\mathrm{MO}$, we can think that building MO is a matter of constructive/destructive interference

In the case of $\mathrm{H}_{2}{ }^{+}$constructive/destructive interference between the two atomic $(\sigma)$ orbitals of the hydrogen atom


## CAO

## Linear Combination of Atomic Orbitals

LCAO

$$
\psi_{\text {Molecular Orbital }}=\sum_{i} c_{i} \psi_{\text {Atomic Orbital }}
$$

The case of $\mathrm{H}_{2}+$ again:

$\psi_{\mathrm{H}_{2}^{+}}^{1 \sigma} \approx \psi_{1}+\psi_{2}$


$$
\psi_{\mathrm{H}_{2}^{+}}^{2 \sigma} \approx \psi_{1}-\psi_{2}
$$



Symmetry
Are the MO invariant upon inversion of electronic coordinates?

- $1 \sigma$ is! g (gerade)
- $2 \sigma$ is not! u (ungerade)


## LCAO diagrams

The hydrogen molecule


The helium molecule


## Bond order

$$
\text { Bond order: } \frac{\text { N. of bonding } e-\mathrm{N} \text {. of antibonding } e}{2}
$$

The higher the bond order (BO), the stronger the bond [length, enthalpy]

- Hydrogen molecule: $\mathrm{BO}=1$
- Helium molecule: $\mathrm{BO}=0$



## 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

The nitrogen molecule
Electronic configuration of the nitrogen atom:
[He] 2s²2p3


Bond order?

Electronic configuration of the fluorine atom:
[He] 2s²2p5
The $\sigma$ atomic orbital of $F$ cannot interact with the $\sigma$ atomic orbital of $H$


The HF molecule
Electronic configuration of the fluorine atom:
[He] 2s²2p5
The $\sigma$ atomic orbital of $F$ cannot interact with the $\sigma$ atomic orbital of $H$


The $2 \sigma$ orbital is non-bonding because the $\mathrm{H} 1 s$ and $\mathrm{F} 2 s$ orbitals are too far apart in energy to interact


H
HF
F
(1s ${ }^{1}$ )
$\left(2 s^{2} 2 p^{5}\right)$
Bond order = 1

## Coffee!

## Intra- \& Inter- molecular interactions



You have to do chemistry to break/form them
Typically much weaker
No need to do chemistry, electrostatic is usually enough...

## Covalent bond

## Covalent bonds are the realm of LCAO

Non polar



## Ionic bond



Chemistry in solution
nacl_2.mp4

## Metallic bond



## Ranking [?]



## 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"

## Intermolecular forces

## A rather subjective list:

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


## Molecular dipoles

$$
\begin{aligned}
& \text { (electric) Dipole moment } \\
& \qquad \bar{\mu}=q \cdot \bar{d}
\end{aligned}
$$



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

Molecular dipoles

- Permanent dipoles
- Induced dipoles
- Fluctuating dipoles

Fluctuating dipole


Spherical atom, or molecule with no net dipole moment


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

The case of methanol


H
$\mathrm{H}_{\mathrm{H}} \mathrm{C}-\mathrm{O}-\mathrm{H}$
$\mathrm{H}^{\prime}$

12


## Electrostatic interactions

The electrostatic potential energy between two charges $q_{1}$ and $q_{2}$ is:

$$
E_{\text {Electrostatic }}(\bar{d})= \pm \frac{q_{1} \cdot q_{2}}{4 \pi \epsilon_{0} \bar{d}}
$$


$F_{\text {Electrostatic }}(\bar{d})=-\nabla E_{\text {Electrostatic }}(\bar{d})= \pm \frac{q_{1} \cdot q_{2}}{4 \pi \epsilon_{0} \bar{d}^{2}}$


## 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]


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

## The case of water

2. Repulsive and attractive terms

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

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




## The case of water

3. Back to the water molecule - Bond and angles
4. What about the dipole moment? - Point charges
5. Liquid water $-L J+$ point charges
6. Polarisable liquid water $-L J+$ 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



## Additional reading

## 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


