CHE502 Chemical and Statistical Thermodynamics
Topic 2
The basis of Quantum Mechanics

URL: `http://theo.ism.u-bordeaux.fr/PBopp/vistec.2020.2021`

To summarize again : Purpose of these classes:

NOT to turn you into experts in computational chemistry
(especially if you are an engineer)

In chemistry in general, you should have an understanding of molecular quantities,
their orders of magnitude and which experimental findings they are related with

Demonstrate the hierarchy of theoretical and computational
methods available in chemistry (materials... , bio... , geo...)m
and their usefulness and, most importantly, limitations

Allow you to judge scientific work (publications) in this field

Give you a basis to build on if during your research work you have
to do such calculations and you must understand and evaluate them

And finally: NEVER to write in a paper (or your thesis) anything like:

"Theoretical calculations have shown ...."

You should always know which level of theory you are using,
(even if you use some expensive black box software)
and remember that there are no scientific calculations not based on some level of theory

You already learned a lot about quantum chemistry, from Aj. Montree,
in particular how to use some tools like **GaussView** and **Gaussian**
to obtain for molecules
– thermochemical data
– IR and Raman-spectra, UV-vis spectra,
– NMR shifts, ...

We will look at quantum mechanics again* from a slightly different viewpoint,
stressing more fundamental aspects, and asking ourselves (for instance):
– Under which assumptions can the code compute thermochemical data?
for isolated molecule? gas? condensed phase?
– What is an IR (or Raman) spectrum?
– What does one need to know to compute an (FT)IR spectrum of a molecule?
Will it be the same in the gas and in the liquid?
– How is the NMR shift connected with the (famous) wave function ψ?
(Equivalent question: Why does GAUSSIAN (or any other such code) sometime compute 'good' energies and 'bad' NMR shifts?)
– What do we really 'see' when we use GaussView? Are molecules just fused balls?
– ....

*"*enseigner c'est répéter" they say in French*

Quantum mechanics

You can read in any textbook about the experiments that lead scientists around 1920 to understand that some observations (experiments) could not be 'understood' by means of the physical theories known then, essentially classical (or Newton's) mechanics.

A new theory, **fully consistent with the classical theory**, which after all works very well in innumerable cases, was just needed

It had to incorporate the two following key facts

(1) Electromagnetic radiation carries energy in packages, not continuously
These packages are called **quanta**, singular **quantum**, (Max Planck 1900]

(2) Some 'particles' behave in some experiments like waves (eg. they show interferences), and some 'waves' sometimes behave like particles (eg. they scatter)

Two physicists, Erwin Schrödinger (1887-1961) and Werner Heisenberg (1901-1976) proposed two different mathematical ways to deal with these findings

In chemistry, we mostly use Schrödinger's method, even though Heisenberg's may be more general and 'elegant' (as mathematicians like to say)

It was later shown that the two methods are completely equivalent
and nobody has found another one
(except may be Paul Dirac (1802-1984) for some particular cases)

The time-independent (sufficient for us) Schrödinger Equation (S-Eq)

In principle

$$\hat{H}\ \Psi_i = E_i \cdot \Psi_i$$

with variables written out

$$\hat{H}\ \Psi_{i_1,i_2,i_3,...}(x_1, x_2, x_3, ...) = E_{i_1,i_2,i_3,...} \cdot \Psi_{i_1,i_2,i_3,...}(x_1, x_2, x_3, ...)$$

This equation can be written for any type of particles, not just electrons
(like mostly in chemistry → chemical bonding)

$\hat{H}$: the Hamilton operator, or Hamiltonian, it describes the system (n electrons, m atom, l molecule, some model system, etc.) in terms of n (or $3n$ or ... , we'll see later) variables called here x_i

$i_1 i_2 i_3$.... Quantum numbers

$\Psi_{i_1,i_2,i_3,...}(x_1, x_2, x_3, ...)$: Wavefunction, Eigenfunction, State Function (or simply state), with n (independent) variables x_j and n quantum numbers i_j

$E_{i_1,i_2,i_3,...}$: Energy Eigenvalues

The Hamiltonian $\hat{H}$ is the ONLY INPUT to the equation, it describes the system
(eg. an atom)

The S-Eq is a typical eigenvalue-eigenvector equation, you have certainly seen them in other fields and in mathematics (matrix calculations)

The distinct (counted by the quantum number(s) i) energy-eigenvalues and eigenfunctions are the output

The solutions to the equation are thus discrete (requirement 1)

The ψ_i are waves and can thus interfere (requirement 2)

It is usually very easy to write $\hat{H}$ and extremely difficult, if not impossible,
to find the many ψ_i and E_i
Actually, most of 'quantum chemistry' deals with how to find **approximate** solutions for the problem (Hamiltonian): "n electrons in the electric fields on m nuclei
(which are assumed not to move, spins are neglected and treated afterwards)"

Keyword that you may (or may not) remember: Born-Oppenheimer approximation, orbital approximation, LCAO, mean field theory, Hartree-Fock, variational principle, product wave function, Slater determinant, ...
read up if you never heard about this or cannot remember what your ajarn told you

Only very simple one-dimensional (only one variable x) Hamiltonians can be solved (ie.the E_i and ψ_i found:

For historic reasons,the quantum numbers are not called i everywhere, but v n, (later together with l m s), but it is always the same thing:
they simply number the solutions

Hamiltonian $\hat{H}$	Eigenvalues E	Eigenfunctions Ψ
particle in box	$E_n = h^2/(8mL^2) \cdot n^2, n = 1, 2, 3...$	Cosine
harmonic oscillator	$E_v = \hbar\omega(v + 1/2) \quad , v = 0, 1, 2, ..$	Hermite·Gaussian
rigid rotor	$E_l = \hbar^2/(2I)l(l + 1), l = 0, 1, 2...$	spherical harmonics (l, m)
hydrogenoid	$E_n = -\mathcal{R} \cdot 1/n^2, n = 1, 2, 3...$	*
....	......	...

We will study some of these systems qualitatively and try to gain some physical insights about:
– The energy levels
– The shapes of the wavefunctions

For a fuller treatment, in particular the manipulations of the S-Eq, check a textbook or website

First we need to look at $\hat{H}$

$\hat{H}$ is called an **operator**, it does not multiply ψ_i, it **acts on** ψ_i

'acting on' can be a simple multiplication, but also a derivative, an integral or any other mathematical operations (eg. expressed as a matrix)

Thus $\hat{H}\ \psi_i = E_i \cdot \psi_i$ means:
Find all functions $\psi_i, i = 1, 2, 3, ...$ which, when $\hat{H}$ acts on them, do not change except for the multiplication with a scalar E_i, which is to be found too

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We also need to say in which cases one must use the S-eq and in which cases one can use classical theory, ie. Newton's equation.

Louis deBroglie (1892-1987) found a simple answer:
compute the wavelength Λ (now called the deBroglie wavelength),

$$\Lambda = \frac{h}{p} \quad , \ p = m \cdot v \ \ \text{is the linear momentum}$$

and compare Λ with the 'extension' of the system
(1 or 2 Å for an atom or molecule, much less for an electron)

If $\Lambda <<$ extension the system can be described classically
If $\Lambda >>$ extension quantum mechanics must be used

Detail question: which velocity v to take? some v_{min}?, some v_{max}?, some $< v >$?
Answer. not so important, this is just an estimation
We estimate v from the average kinetic energy (or temperature, see later) and get the "de Broglie (thermal) wavelength":

$$\Lambda = \frac{h}{p} \;, \quad \text{with } p \text{ from } \;< E_{\mathrm{kin}} > \quad \Rightarrow \; \Lambda = \frac{h}{\sqrt{2\pi m k_{\mathrm{B}} T}}$$

$\Rightarrow$ the larger the mass, the higher the temperature,
the smaller Λ, and thus the more 'classical' the system

This is a general rule, we'll come back to this later

Now we (you) will look at some specific cases

→ **Study** the "one dimensional particle in the box" problem

This is a typical idealized model, it can be made to be a reasonable approximation for certain systems by using suitable masses m and length L,

see table on page 7

This is found in any textbook of physical or quantum chemistry, and on many web sites such as: `http://puccini.che.pitt.edu/~karlj/Classes/CHE2101/l10.pdf`

`Physics LibreTex 7.5: The Quantum Particle in a Box , and 100 others`

→ **Study** the "one dimensional harmonic oscillator" problem,

This is found in any textbook of physical or quantum chemistry and on many web sites GOOGLE

→ **Study** the "one electron in a radial electric field" problem,

in other words the hydrogen atom

This is found in any textbook of physical or quantum chemistry and on many web sites GOOGLE

What do these problems have in common? What is different?
Look at the table on page 7

Common features
- we can easily write the Hamiltonian $\hat{H}$
- all problems are one-dimensional (variable x or r)
  (of course an electron in the electric field of a central (fixed) proton
    is a 3-dimensional problem (variables, e.g, r, Θ, Φ)
    if the electron is in a solid, we would use the variables x, y, z (more convenient)
    it is always 3 variables, and we must select the most convenient ones for our problem
    Here we look only at the r-part)

In these simple cases, we can find (see table)
- a mathematical expression for the (countable) states (wave functions) $\psi_i(x)$ (or $\psi_i(r)$)
- a mathematical expression for the energies E_i associated with these states
- in 'real' cases (eg many particles) these quantities can only be obtained numerically

- The Hamiltonian is always $\hat{H} = \hat{T} + \hat{V}$

Differences

- The $\hat{T}$-part (kinetic energy) of the Hamiltonian
  it contains the mass(es) m of the particle(s) (electron, nucleus, atom....)
  the mathematical expression for depends only on the coordinate system (variables)
  used: x, y, z or r, Θ, Φ or ...
- The $\hat{V}$-part (potential energy) of the Hamiltonian
  This is the guts of the problem, this is where you describe your system
  What are the interactions? Coulomb? Assumed model interactions (boxes, springs ......)?

- We will later on spend a lot of time developing such $\hat{V}$s that describe some problem
  we may be interested in

(The Hamiltonian as we have studied it is also used (mutatis mutandis*)
in classical mechanics. Actually, the concept comes from there)

* Latin, GOOGLE it

more differences:

The allowed energies $E_{\mathrm{something}}$
– There is always a lowest energy, called the "ground state" energy
– This lowest energy is never $=$ zero
– Higher energies, called "excited state" energies increase in different ways:
for the 'harmonic oscillator', the spacing between two energies $\Delta E = E_{i+1} - E_i$ is constant
for the 'particle in the box', ΔE increases with increasing E
for the 'H-atom', ΔE decreases with increasing E

It is not possible to generate such a system with any other energy except one of these E_i

Wavefunction ψ

ψ is the quantity that led to most doubts about quantum mechanics
since it cannot be measured (only ψ^2 can be measured, see below)
Physical theories were not supposed to deal with things that cannot be measured

Yet this ψ, which led to the introduction of the concept of probability, has survived the test of time and proven to be very useful

We interpret ψ^2 as the probability density of finding a particle, more precisely

$$p(V) = \int_V \psi^2 \, \mathrm{d}\tau$$

where $p(V)$ is the probability (0.1 (10 %) or whatever) to find a particle
in the state ψ in some volume of space V
$\mathrm{d}\tau$ is the volume element $(\mathrm{d}x \; \mathrm{d}y \; \mathrm{d}z$ or $r^2 \mathrm{d}r \;\; \sin(\Theta)\mathrm{d}\Theta \; \mathrm{d}\Phi$ or ...)
The integral $\int_V$ is thus a multiple integral $\int \int \int$ ... over all variables of ψ

Of course, if V is the entire volume accessible to the particle $(-\infty < x < \infty$, say),
the value of the integral becomes 1, the particle is certainly inside the volume

Wavefunctions belonging to different states (eg $\psi_1, \psi_2, \psi_3,$ ...) are, and must be, different

However, in some cases, due to some symmetry in the problem, different states have the same energy. This is called **degeneracy, degenerate states**
$\psi_i \neq \psi_j$ but $E_i = E_j$

With this information in mind,
discuss the ground-state wavefunctions for the three simple cases

Also discuss their energies E_i

A little remark on energies and their units

Energy units: (see https://en.wikipedia.org/wiki/Units_of_energy)
For historic reasons, many different energy units are used in different fields
For us, it will mostly be:
erg, Joule (J), electron Volt (eV), calorie (cal) or kilocalorie (kcal)

Often, people prefer to deal with intensive rather than with extensive quantities, so the energies are divided by the quantity of matter: J/mol, kcal/mol etc

Sometimes (eg. in spectroscopy, people use (for convenience) energy-equivalent units
$\lambda \cdot \nu = c \ , \ E = h \cdot \nu \quad \rightarrow \quad E = h \cdot c/\lambda \quad \rightarrow \quad 1/\lambda = E/(h \cdot c)$
So in spectroscopy 'energies' are often given as $1/\lambda$ (cm^{-1}, ie in units of $E/(h \cdot c)$)
This is because in vibrational spectroscopies, this unit (usually called "wavenumber") gives 'nice numbers' (ie. without big positive or negative powers of 10) for the energies involved in vibrational spectroscopy

In the same way one can use the equation $E = k_\mathrm{B} T$ and report energies as
$E/k_\mathrm{B} = T$ in Kelvin

It is useful to keep in mind a few orders of magnitude:

We start from the energy of the ground state (ionization energy) of the Hydrogen atom, the famous number (which you all remember) -13.6 eV

In chemistry, this is a rather 'big' energy
(of course not in physics, think of nuclear reactions, astrophysics, galaxies, black holes .....)

Orders of magnitude (we don't care here about factors of 2 and such):

$$13.6 \text{ eV} \;\approx\; 100,000 \text{ cm}^{-1} \;\approx\; 100,000 \text{ K}$$

Chemistry 'happens' around 300 K (not at 1 K and not at 100,000 K), so our 'measure of all things' is the thermal energy at 'room temperature', 300 K

What happens, or does not happen, in chemistry, whether it is fast or slow, is often (mostly) governed by the relation between the energy involved and the energy $E = k_{\rm B}T$ with T≈300 K

An important approximation, which is frequently made
If a Hamiltonian $\hat{H}$ depending on two sets of variables (called here x and X) can be separated into two Hamiltonians $\hat{H}_1(x)$ and $\hat{H}_2(X)$:

$$\hat{H}(x, X) = \hat{H}_1(x) + \hat{H}_2(X)$$

ie into two independent problems, then one can solve the S-eqs for $\hat{H}_1(x)$ and $\hat{H}_2(X)$ independently:

$$\hat{H}_1(x)\psi_1(x) = E_1 \cdot \psi_1(x) \;\; \text{and} \;\; \hat{H}_2(X)\psi_2(X) = E_2 \cdot \psi_2(X)$$

BEWARE: here the lower indices are not quantum numbers!
(*you would know because $\hat{H}$ does not have a quantum number!*)

We then have

$$\hat{H}(x, X)\Psi = \mathbb{E} \cdot \Psi \;\; = \;\; (\hat{H}_1(x) + \hat{H}_2(X))\;(\psi_1\psi_2) \;\; = \;\; (E_1 + E_2) \cdot (\psi_1\psi_2)$$

ie the wavefunctions Ψ of $\hat{H}$ are products of ψs, and the eigenvalues (energies) are sums

This approximation is used (in a more sophisticated way because of the spin) in electronic structure calculations (may be Aj. Montree mentioned this, orbitals!).
The x could also refer to elecrons, and the X to nuclei, or ...

Corollary

'Orbitals' do not exist in reality,
they appear as mathematical objects in the
(usually quite good) approximations made to describe molecular wave functions
(or electronic densities ψ^2)