

**Appendices to the**  
**"Revised guide of the *van Quantum tot Molecuul* course"**

**Juan Rojo**

**Appendix 1)** Original course guide

**Appendix 2)** Handout for one of my lessons in the course

**Appendix 3)** Slides of the introductory lesson of the course

**Appendix 4)** Slides of the presentation "*Assessing, Testing, and Evaluating*" given on the 5th of October 2017

**Appendix 5)** Handout for the presentation "*Assessing, Testing, and Evaluating*" given on the 5th of October 2017, which complement the slides of Appendix 4.



**Appendices to the**  
**"Revised guide of the *van Quantum tot Molecuul* course"**

**Juan Rojo**

**Appendix 1) Original course guide**

**studiehandleiding**  
***van Quantum tot Molecuul***  
**6 EC**  
**2015 - 2016**

***Vrije Universiteit***  
**Faculteit Exacte Wetenschappen**  
**BSc Programma**  
**Medische Natuurwetenschappen**

## **Van Quantum tot Molecuul**

**code**

X\_420545

**Credits**

6 EC

**Niveau**

200

**Doelgroep**

2MNW

**Docenten**

Prof. Dr. John Kennis en Prof. Dr. Ir. Erwin Peterman

**Periode**

3 - 4

**Leerdoel**

Doel van het college is de introductie van de basis-concepten voor het beschrijven van atomen, elektronische orbitals en moleculen m.b.v. quantummechanische principes. Beoogd wordt enerzijds een beter inzicht te verkrijgen in de fysische achtergronden van chemische eigenschappen en anderzijds te zien hoe quantummechanische concepten zich vertalen in meetbare grootheden. Specifieke leerdoelen per hoor/werkcollege staan vermeld op p. 7.

**Inhoud**

De cursus is opgebouwd uit de volgende onderwerpen

- Introductie in de quantum wereld, golf-deeltje dualisme, de Broglie relatie, Heisenberg onzekerheidsprincipe, Schrödinger vergelijking, deeltje in een doosje, tunnelling, harmonische oscillator, waterstofatoom, electronspin, de opbouw van het periodiek systeem
- Binding tussen atomen en opbouw van moleculen; valence bond theorie, molecular orbital theorie, variatieprincipe, hybridisatie, moleculaire interacties, waterstofbruggen, Hückel theorie
- Moleculaire spectroscopie: vibratoire en elektronische spectroscopie
- magnetische resonantie

**onderwijsvorm**

- Hoorcollege
- werkcollege

**Literatuur**

'Physical Chemistry' van Atkins en De Paula, 10e editie, Oxford University Press.

**Tentaminering en becijfering**

Schriftelijk deeltentamen

Schriftelijk tentamen

**voorkennis**

Calculus, Mathematische Methoden, Thermodynamica, FMF1, FMF2

**Doelgroep**

2MNW, geïnteresseerde 2SBI of 3SBI studenten.

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## Werkcolleges

### Werkcollege assistenten

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Er worden in totaal 9 werkcolleges gegeven. Voor de werkcolleges worden jullie geacht je in groepjes van 3-4 te organiseren. Voorafgaand aan elk werkcollege dien je een aantal eenvoudige opgaven gemaakt te hebben die kort besproken worden in het werkcollege. Tijdens het werkcollege maak je groepsgewijs ter plekke een aantal meer complexe opgaven. De assistenten lopen rond en helpen jullie hiermee. In principe worden de opgaven niet op het bord gemaakt, echter in het geval dat een groot aantal mensen met hetzelfde probleem zit kan er ad hoc besloten worden om iets centraal uit te leggen. Alle thuis- en werkcollegeopgaven worden vooraf aangekondigd op blackboard.

### Deelname aan het werkcollege is verplicht.

-deelname aan het werkcollege is verplicht om aan het tentamen te mogen deelnemen. Deze regel geldt niet als je in voorgaande jaren het vak (en de werkcolleges) gevolgd hebt.

-zet je handtekening op presentielijst bij begin en eind werkcollege

-Als je echt verhinderd bent, bijv. i.v.m. ziekte of familieomstandigheden, laat het weten, via email, aan docenten en assistenten!

## Tentamenstof

Uit Atkins en De Paula, 10<sup>th</sup> edition:

Hoofdstuk 7 geheel, behalve 7A1b

Hoofdstuk 8 geheel

Hoofdstuk 9 9A, 9B, 9C1, 9C2a

Hoofdstuk 10 10A, 10B, 10C1, 10D, 10E1, 10E2

Hoofdstuk 11 NIET

Hoofdstuk 12 12A1, 12D1-3, 12E1-3, behalve 3(a), 3(c)

Hoofdstuk 13 13A1(c), 13A2a-b, 13B1, 13C

Hoofdstuk 14 14A1, 14A2, 14B1, 14C1-2

Hoofdstuk 16 16B3

### **Vragenuur**

Voorafgaand aan het tentamen zijn de docenten beschikbaar voor vragen over de stof, in hun kantoor T130 (JK) en T054A (EP). Exacte tijd wordt aangekondigd op blackboard.

### **Tentamen**

Er worden een tussententamen en een volledig eindtentamen afgenomen. Het tussententamen betreft de stof behandeld in HC1 t/m HC6 (hoofdstukken 7 – 9) en vindt plaats op donderdag 4 februari.

Aan het eind van de cursus wordt een eindtentamen afgenomen over de volledige stof, op 22 maart. Dit tentamen bestaat uit Deel I (stof HC 1 – HC 6) en Deel II (stof HC7 – HC12).

De regels voor becijfering:

1. indien je een onvoldoende haalt voor het tussententamen dien je het volledige eindtentamen te maken.
2. indien je een voldoende haalt voor het tussententamen heb jij de keuze om Deel I van het eindtentamen wel of niet te maken. Als je het wel maakt dan telt het hoogste cijfer (van het tussententamen of Deel I van het eindtentamen).
3. Voor het eindcijfer worden de cijfers van Deel I van het eindtentamen (of het tussententamen) en Deel II van het eindtentamen gemiddeld.
4. Het hertentamen moet altijd helemaal gemaakt worden, het cijfer van het tussententamen telt niet mee. Het tussententamen kan ook niet meegenomen worden naar volgend jaar.

Tijdens het tentamen mag geen gebruik gemaakt worden van cursusmateriaal. Ook programmeerbare rekenmachines zijn verboden. Een lijst van uit het hoofd te kennen formules wordt op blackboard gezet.

### **Oefententamen**

Een tentamen van voorgaande jaren wordt op blackboard gezet.

### **Leerdoelen per hoorcollege**

#### HC1

- begrijpen hoe experimentele resultaten ertoe geleid hebben dat Quantumtheorie ontwikkeld werd
- begrijpen dat quantumtheorie nodig is om de structuur en eigenschappen van kleine deeltjes zoals electronen, atomen en moleculen te beschrijven
- begrijpen dat zowel materie als licht een deeltjeskarakter en een golfkarakter hebben.

#### HC2

- begrijpen dat de toestand van een quantumstelsel beschreven wordt met een golf functie, die een oplossing is van de Schrodinger vergelijking.
- begrijpen en toepassen van de wiskundige beschrijving van de quantumfysica, waaronder hermitische operatoren, eigenwaarden vergelijkingen en orthogonaliteit.
- begrijpen hoe experimentele observabelen kunnen worden berekend uit de golf functie, en deze berekening uitvoeren.
- De Born interpretatie aangaande de fysische betekenis van de golf functie begrijpen en toepassen.
- het onzekerheidsprincipe van Heisenberg begrijpen en toepassen

#### HC3

- het kunnen oplossen van de Schrodinger vergelijking voor eenvoudige systemen: vrij deeltje in 1 dimensie, deeltje in een doosje in 1 en 3 dimensies, de harmonische oscillator.
- begrijpen waardoor opsluiting van een deeltje in een beperkte ruimte leidt tot kwantisatie van toegestane energieniveaus, en dat de nulpuntsenergie niet gelijk is aan 0.

- het fysisch kunnen interpreteren van golffuncties die een oplossing zijn van de Schrödinger vergelijking
- het begrijpen en toepassen van de scheiding-van-variabelen wiskundige techniek.
- het begrijpen en toepassen van het tunneling fenomeen.

#### HC 4

- het kunnen oplossen van de Schrödinger vergelijking voor rotationele beweging: deeltje op een ring, deeltje op een bol.
- begrijpen hoe cirkel- of bolsymmetrie in rotationele beweging leidt tot kwantisatie van toegestane energieniveaus.
- het fysisch kunnen interpreteren van golffuncties die een oplossing zijn van de Schrödinger vergelijking
- het begrip spin begrijpen.

#### HC5

- de fysische basis kunnen begrijpen van de Schrödinger vergelijking van het waterstofatoom.
- het kunnen oplossen van de Schrödinger vergelijking voor het waterstofatoom met scheiding van variabelen.
- het kunnen interpreteren van de radiale en angulaire golffuncties.
- het begrijpen van, kunnen rekenen met, een beeld vormen van de atomaire orbitalen en de bijbehorende kwantumgetallen, schillen en subschillen.

#### HC6

- het kunnen oplossen van de Schrödinger vergelijking voor multi-electron atomen met de orbitaalbenadering.
- het begrijpen van en kunnen werken met 'shielding', het Pauli- en het 'Aufbau'principe.
- het begrijpen van singlet- en triplet spintoestanden

#### HC7

- het begrijpen en kunnen toepassen van 'valence-bond' theorie op homonucleaire diatomaire moleculen en multiatomaire molecule
- het kunnen visualiseren van moleculaire orbitalen
- het begrijpen van en kunnen werken met de Born-Oppenheimer benadering
- het begrijpen van het begrip hybride orbitalen; hybride orbitalen kunnen visualiseren.

#### HC8

- het begrijpen en kunnen toepassen van moleculaire orbital theorie (lineaire combinaties van atomaire orbitalen) op  $H_2^+$ .
- het kunnen voorspellen of een orbitaal bonding of antibonding is.
- het kunnen opstellen van een moleculaire orbitaal energie diagram voor homonucleaire diatomaire moleculen.
- het kunnen visualiseren en het begrijpen van de symmetrie eigenschappen van moleculaire orbitalen

#### HC9

- het begrijpen en kunnen toepassen van het variatieprincipe op heteronucleaire diatomaire molecule.
- het begrijpen van de wiskunde en natuurkunde achter de Hückelbenadering.
- het kunnen opstellen van de Hückel matrix voor een willekeurig, niet al te groot, molecuul.

#### HC10

- begrijpen en toepassen van de basiskenmerken van absorptie en emissie in termen van macroscopische grootheden.
- begrijpen van elementaire experimentele technieken in de spectroscopie
- begrijpen van vibrationele toestanden en overgangen in twee-atomige en poly-atomige moleculen, begrijpen dat vibrationele overgangen interactie hebben met infrarood licht en Ramanverstrooiing kunnen veroorzaken, en het toepassen van deze kennis.

#### HC11

- begrijpen dat elektronische overgangen onder absorptie of emissie van een foton plaatsvinden terwijl de kernen stationair zijn (Franck-Condon principe), inclusief de wiskundige beschrijving en de gevolgen daarvan voor absorptie- en emissiespectra
- begrijpen van het overgangsdipoolmoment en toepassing op d-metal complexen,  $\pi$ - $\pi^*$  en  $n$ - $p^*$  overgangen.
- begrijpen en toepassen van de principes van fluorescentie en fosforescentie, inclusief de spiegelsymmetrie zoals die geobserveerd wordt in absorptie en emissie spectra.

#### HC12

## Programma vQtM 2015-2016

Week	Dag	Datum	Tijd	HC/WC	Docent	Topic
1	Ma	4-1	13:30	HC1	JK	Overzicht cursus, introductie quantum, Ch 7
1	Di	5-1	13:30	HC2	JK	Ch 7: Schrodinger vergelijking, interpretatie vd golffunctie, wiskundig gereedschap
1	Vr	8-1	11:00	WC1		
2	Ma	11-1	13:30	HC3	JK	Ch7: Heisenberg onzekerheidsrelaties Ch 8: vrije deeltje, deeltje in 'n doosje, tunneling, harmonische oscillator
2	Di	12-1	13:30	HC4	EP	Ch 8: Deeltje op 'n ring, deeltje op 'n bol
2	Vr	15-1	11:00	WC2		
3	Ma	18-1	13:30	HC5	EP	Ch 9: waterstofatoom
3	Di	19-1				GEEN COLLEGE
3	Vr	22-1	11:00	WC3		
4	Ma	25-1	13:30	HC6	EP	Ch 9: electronspin, meer-electron atomen
4	Di	26-1				GEEN COLLEGE
4	Vr	29-1	11:00	WC4		
5	Ma	1-2	13:30	HC7	EP	Ch 10: moleculaire structuur, valence bond theorie, MO theorie,
5	Do	4-2	13:30			TUSSENTENTAMEN
6	Ma	8-2	13:30	HC8	EP	Ch 10: MO theorie hybridisatie, variatieprincipe
6	Do	11-2	13:30	WC5		
7	Ma	15-2	13:30	HC9	EP	Ch10: Hueckel theorie

7	Do	18-2	13:30	WC6		
8	Ma	22-2	13:30	HC10	JK	Ch 12: moleculaire spectroscopie, vibratoire spectroscopie
8	Do	25-2	13:30	WC7		
9	Ma	29-2	13:30	HC11	JK	Ch 13: moleculaire spectroscopie, elektronische overgangen
9	Do	3-3	13:30	WC8		
10	Ma	7-3	13:30	HC12	JK	Ch 14: NMR
10	Do	10-3	13:30	WC9		
11	Do	17-3	13:30			VRAGENUUR
12	Di	22-3	15:15-18:00			TENTAMEN

12 HC hoorcollege

9 WC werkcollege



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**Appendix 2)** Handout for one of my lessons in the course



## van Quantum tot Molecuul

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Lecture notes, current version: February 13, 2017

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# 1 HC1: Introduction to Quantum Theory

General introduction to Quantum Theory

Based on Atkins and de Paula, *Physical Chemistry* 10th edition, Chapter 7

Learning goals of the lecture:

- (a) Understand the experimental results that led to the development of Quantum Theory.
- (b) Understand that quantum theory is necessary to describe the structure and properties of electrons, atoms and molecules.
- (c) Understand that both matter particles and light have a dual wave/particle character.

The small  $\lambda$  limit of Planck's distribution

$$\rho = \frac{8\pi hc}{\lambda^5 (e^{hc/\lambda kT} - 1)} \simeq \frac{8\pi hc}{\lambda^5} e^{-hc/\lambda kT} \rightarrow 0 \quad (1.1)$$

The De Broglie relation for matter particles

$$\lambda(p) = \frac{h}{p} \quad (1.2)$$

Photoelectric effect

$$E(\nu) = h\nu \quad (1.3)$$

Condition on the incident radiation

$$E(\nu) \geq \Phi \rightarrow \nu_{\min} = \Phi/h \quad (1.4)$$

$$E_{\text{kin}} = \frac{1}{2} m_e v_e^2 = E(\nu) - \Phi \rightarrow v_e = \sqrt{\frac{2(h\nu - \Phi)}{m_e}} \quad (1.5)$$

Planck's hypothesis

$$E = nh\nu = nh \frac{c}{\lambda} \quad (1.6)$$

Planck's constant

$$h = 6.6 \cdot 10^{-34} \text{ J} \cdot \text{s} \quad (1.7)$$

Electromagnetic wave

$$E = A \cos(\omega t - kx), \omega = 2\pi\nu, k = \frac{2\pi}{\lambda} \quad (1.8)$$

De Broglie example

$$p = mv = 2.8 \cdot 10^4 \text{ kg m/s}, \lambda = \frac{h}{p} = 2 \cdot 10^{-38} \text{ m} \quad (1.9)$$



## van Quantum tot Molecuul

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## 2 HC2: The quantum wave-function and Schroedinger equation

The Schroedinger equation, the quantum wave-function, the Born interpretation, mathematical tools of quantum mechanics, the free particle, Heisenberg's uncertainty principle.  
Based on Atkins and de Paula, *Physical Chemistry*, 10th edition, Chapter 7.

In this lecture we present the mathematical framework of quantum theory, where the main entity is the *quantum wave-function*, and the dynamical equation that this wave-function must obey, the Schroedinger equation. We also introduce a number of mathematical tools which are required in the quantum formalism. We discuss Heisenberg's uncertainty principle, and show that it entails a fundamental limitation about the physical knowledge that we can have about quantum systems.

Learning goals of the lecture:

- (a) Understand that the state of a quantum system is described by the quantum wave-function, which is a solution of the Schroedinger equation.
- (b) Understand and apply the mathematical description of quantum physics, including hermitian operators, eigenvalue equations and orthogonality.
- (c) Understand how experimental observables can be calculated from the wave-function, and perform these calculations in simple systems.
- (d) Understand the Copenhagen interpretation of the physical meaning of the wave-function.
- (e) Understand and apply Heisenberg's uncertainty principle.

## 2.1 The quantum wave-function and Schroedinger's equation

The double slit experiment that we discussed in HC1 demonstrated the wave-like character of particles such as electrons. In quantum theory, the mathematical entity which is used to describe this and related phenomena is known as the *quantum wave-function*  $\Psi$ . More in general, the *complete physical properties of any quantum system* are uniquely determined once its wave-function  $\Psi$  is specified. The wave-function depends on the spatial and time coordinates of the  $N$  particles that constitute the quantum system,

$$\Psi = \Psi(x_1, y_1, z_1, t_1, \dots, x_N, y_N, z_N, t_N), \quad (2.1)$$

though in this course we will restrict ourselves to time-independent wave-functions.

The wave-function  $\Psi$  for a quantum system composed by a single particle satisfies the *Schroedinger equation*, which in one dimension  $x$  reads

$$-\frac{\hbar^2}{2m} \frac{d^2\Psi(x)}{dx^2} + V(x)\Psi(x) = E\Psi(x) \quad (2.2)$$

where the various components of this equation are:

- $m$ , the particle's mass.
- $V(x)$ , the potential energy as a function of the position,
- $E$ , the total energy of the system (which is a conserved quantity), and
- $\hbar \equiv h/2\pi$  is the *reduced Planck's constant*.

The Schroedinger equation is an *equation of motion* for quantum particles, playing a similar role that Newton's equation  $F = ma$  has in classical mechanics.

The physical meaning of the wave-function can be interpreted as follows: if the wave-function of a particle takes the value  $\Psi(x)$  for some point  $x$ , then  $|\Psi(x)|^2 dx$  represents the *probability* that, upon performing a *measurement*, one will detect this particle in the region  $[x, x + dx]$ . In other words,  $|\Psi(x)|^2$  represents the *probability density* in the coordinate  $x$  for this particle. Regions in  $x$  where  $|\Psi(x)|^2$  is higher correspond to those regions where the particle has a higher likelihood to be found when a measurement is performed. This interpretation is known as the *Born interpretation of the wave-function*, and is illustrated in Fig. 2.1. Note that since in general the wave-function is a *complex function*, what is meant by “the square of the wave-function” has to be understood as

$$|\Psi|^2 = \Psi^*\Psi = [\text{Re}(\Psi) - i\text{Im}(\Psi)] [\text{Re}(\Psi) + i\text{Im}(\Psi)], \quad (2.3)$$

and where the symbol  $*$  stands for the complex conjugate operation.

Given that  $|\Psi|^2$  is a probability density, it needs to be normalized appropriately. Since the probability of finding the particle *anywhere in space* must be unity, the wave-function must be normalized to ensure that

$$\int_{-\infty}^{\infty} dx |\Psi|^2(x) = 1. \quad (2.4)$$

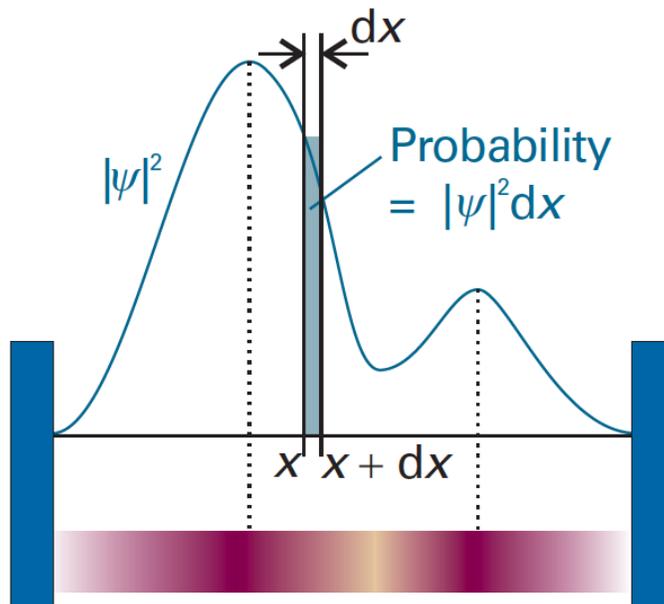


Figure 2.1: The physical interpretation of the quantum wave-function  $\Psi(x)$  is that its square  $|\Psi(x)|^2$  is the *probability density* associated to measuring the particle in a position  $x$  in space. Therefore, the *probability* to find the particle at position  $x$  in the range  $dx$  will be given by  $|\Psi(x)|^2 dx$ .

A wave-function  $\tilde{\Psi}$  that does not satisfy this normalization condition can be rescaled by a constant factor  $\Psi(x) = N \tilde{\Psi}$  given by

$$N = \left( \int_{-\infty}^{\infty} dx |\tilde{\Psi}^2(x) \right)^{-1/2}, \quad (2.5)$$

so that the rescaled wave function  $\Psi$  satisfies the correct normalization requirement of Eq. (2.4).

The quantum wave-function  $\Psi$  needs to satisfy a number of important conditions everywhere in space:

- (a) it must be continuous,
- (b) its slope (first derivative) needs to be continuous as well,
- (c) it must be single-valued, and
- (d) it must be squared-integrable, Eq. (2.4), else the Born interpretation would lead to infinite (unphysical) probabilities.

As we will show now, for most physical systems these requirements imply that the energies that arise in the solution of the Schroedinger equation Eq. (2.2) can take only a finite set of values, that is, they lead to the *quantization of the energy*, which is one of the basic tenets of quantum theory.

## 2.2 The Schroedinger equation for a free particle

The simplest case that we can study with the Schroedinger equation is that of the motion of a *free particle*, that is, a particle which is not subjected to any form of potential, and thus has  $V(x) = 0$ . In this case the

Schroedinger equation Eq. (2.2) takes the following particular simple form:

$$-\frac{\hbar^2}{2m} \frac{d^2\Psi(x)}{dx^2} = E\Psi(x) \quad (2.6)$$

which is a second-order ordinary differential equation (ODE) that admits a solution in terms of a sum of exponentials (also known as *plane-wave* solutions):

$$\Psi(x) = Ae^{ikx} + Be^{-ikx}, \quad (2.7)$$

where  $A$  and  $B$  are the *integration constants*, to be fixed by the initial conditions of the system, and the energy  $E$  and the *wave number*  $k$  are related by

$$E = \frac{\hbar^2 k^2}{2m}. \quad (2.8)$$

It is easy to show that  $\Psi = Ae^{\pm ikx}$  is a solution of Eq. (2.6), since

$$-\frac{\hbar^2}{2m} \frac{d^2 Ae^{\pm ikx}}{dx^2} = -\frac{\hbar^2}{2m} (\pm ik)^2 Ae^{\pm ikx} = \frac{\hbar^2 k^2}{2m} Ae^{\pm ikx} = EAe^{\pm ikx}. \quad (2.9)$$

In general, rather than solving a Schroedinger equation from first principles, is also possible to assume a given solution and verify then if it is indeed a solution to this equation. Note that this system,  $E$ , the particle's kinetic energy, is *not quantized* and can take any value.

The solution of the free-particle Schroedinger's equation, Eq. (2.7), has the physical interpretation of the *superposition of two waves*, one moving in the positive and the other in the negative  $x$  direction - we will motivate more this interpretation below. For simplicity, let us set  $B = 0$ , and keep only the solution corresponding to a wave propagating in the positive  $x$  direction,

$$\Psi(x) = Ae^{ikx}. \quad (2.10)$$

At this point we can ask ourselves what is the *probability of finding the particle at a given point  $x$  in space*. Following Born's interpretation, the probability density for the position  $x$  of the particle will be given by the square of its wave-function,

$$|\Psi|^2 = (A^* e^{-ikx}) \cdot (A e^{ikx}) = |A|^2, \quad (2.11)$$

so we find the remarkable result that the particle has *exactly the same probability* of being found *anywhere in space*. In other words, its position is maximally undetermined. As we will show below, this indetermination is a direct consequence that we are assuming (unphysically) that the momentum  $p = \sqrt{2mE} = \hbar k$  of the particle is known with infinite precision.

### 2.3 Eigenvalue equations in quantum theory

As we have mentioned above, the wave-function  $\Psi$  of a quantum system contains the complete physical information on a quantum system. In particular, the various properties of the system should be calculable from the knowledge of the wave-function. In quantum theory, we denote as an *observable* a given property of a quantum system (energy, momentum, angular momentum, electric charge, ...) that can be extracted

from a *measurement* of this system.

Mathematically, the tools that we will use to compute the expected outcome of a measurement of a quantum system are known as *operators*, which can be expressed in the language of *eigenfunctions* and *eigenvectors*. Formally, an *operator* is a way to represent the action of a specific mathematical function onto the wave-function  $\Psi$ . For instance, Schroedinger's equation Eq. (2.2) can be expressed in operator form as follows

$$\hat{H}\Psi(x) = E\Psi(x), \quad (2.12)$$

where the  $\hat{\phantom{H}}$  symbol indicates an operator, in this case the *Hamiltonian operator*, defined as

$$\hat{H} \equiv -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x). \quad (2.13)$$

An equation of the form of Eq. (2.12) is known as an *eigenvalue equation*. In this case the application of the Hamiltonian operator to the wave-function returns the total energy  $E$ , since  $\hat{H}$  is the operator that represents the total energy of the quantum system.

In general, an eigenvalue equation will take the general form

$$\hat{\Omega} \Psi = \omega \Psi, \quad (2.14)$$

where:

- $\hat{\Omega}$  represents a generic operator associated to the observable property  $\Omega$ ,
- $\Psi$  is the *eigenfunction* this operator is acting upon, and
- $\omega$  is the eigenvalue of the operator  $\hat{\Omega}$  associated with the eigenfunction  $\Psi$ .

Note that the eigenvalues  $\omega$  are *constant numbers*, and cannot be functions of other variables. In general, eigenvalues will be complex numbers.

Let us try to become familiar with the concept of *eigenvalue equation* with a couple of examples:

- (a) Is  $\Psi(x) = e^{\alpha x}$  an eigenfunction of the operator  $\hat{\Omega} \equiv d/dx$ ? To verify if this is the case, we apply the operator to the wave-function to find

$$\hat{\Omega}\Psi = \frac{d}{dx}e^{\alpha x} = \alpha e^{\alpha x} = \alpha\Psi, \quad (2.15)$$

so indeed in this case  $\Psi(x)$  is an eigenfunction, with  $\alpha$  being the associated eigenvalue.

- (b) Is  $\Psi(x) = e^{\alpha x^2}$  an eigenfunction of the same operator? Let us check it in the same way as before:

$$\hat{\Omega}\Psi = \frac{d}{dx}e^{\alpha x^2} = (2\alpha x)e^{\alpha x^2} = 2\alpha x\Psi \neq \omega\Psi, \quad (2.16)$$

thus now  $\Psi$  is *not* an eigenfunction, since it would have a non-constant eigenvalue, and this is not allowed.

As mentioned above, the Schroedinger equation itself is an eigenvalue equation, Eq. (2.12). For each state with a definite energy (eigenvalue)  $E$ , there corresponds a unique wave-function  $\Psi$  (the eigenfunction).

Note that in general the Schroedinger equation Eq. (2.12) will admit different solutions for the wave-function  $\Psi_n$ , each with their associated energy  $E_n$ , where by  $n$  we indicate a general quantum number which is used to label the solutions of the eigensystem.

## 2.4 Operators and physical observables

In quantum theory, the eigenvalues of specific operators such as the Hamiltonian  $\hat{H}$  correspond to *observables* of the system, in this case the total energy. Indeed, *each observable* of a quantum system, such as position, momentum, or angular momentum of the constituent particles, will have *associated an operator* that, when acting on the wave-function, will return the corresponding physical property as the eigenvalue. We now discuss this property in more detail.

In quantum mechanics, any *observable property*  $\Omega$  of the quantum system will be represented by an operator  $\hat{\Omega}$  built up from the *position* and *momentum* operators, defined respectively as

$$\hat{x} \equiv x, \quad (2.17)$$

$$\hat{p}_x \equiv \frac{\hbar}{i} \frac{d}{dx}. \quad (2.18)$$

For example, let us consider the free-particle solution of Schroedinger's equation, Eq. (2.7), and compute what happens if we apply to it the momentum operator  $\hat{p}$ . Setting  $B = 0$  first, we get that

$$\hat{p}\Psi(x) = \left(\frac{\hbar}{i} \frac{d}{dx}\right) A e^{ikx} = \hbar k A e^{ikx} = \hbar k \Psi(x), \quad (2.19)$$

so the momentum along the  $x$  direction  $p_x$  that can be associated to the free particle is  $p_x = +\hbar k$ . This is consistent with the fact that for a given value of  $k$ , the kinetic energy is  $E = \hbar^2 k^2 / 2m$  and thus  $p = \sqrt{2mE} = \hbar k$ . It can similarly be shown that the  $A = 0$  solution has associated momentum  $p_x = -\hbar k$ . Therefore, the case  $B = 0$  corresponds to a particle moving in the positive  $x$  direction with momentum  $p_x = +\hbar k$ . This calculation indicates that the free-particle solutions of Schroedinger's equation are *eigenfunctions of the momentum operator* in addition to of the Hamiltonian, that is, they represent solutions with well-defined momentum.

Similar considerations apply to other examples. First, the potential energy operator in the case of an harmonic-like potential (such as that for an harmonic oscillator) will be represented by the operator

$$\hat{V} = V(x) = \frac{1}{2} k x^2, \quad (2.20)$$

which is representative of the simplest type of operators, those whose effect correspond to multiply  $\Psi$  by a function (as compared to more complex manipulations like taking derivatives). For the kinetic energy,  $E_k = mv^2/2 = p^2/2m$ , the corresponding operator can be constructed from the momentum operator

$$\hat{E}_k = \frac{1}{2m} (\hat{p})^2 = \frac{1}{2m} \left(\frac{\hbar}{i} \frac{d}{dx}\right) \left(\frac{\hbar}{i} \frac{d}{dx}\right) = -\frac{\hbar}{2m} \frac{d^2}{dx^2}. \quad (2.21)$$

Of course, the combination of the kinetic energy and the potential energy operators corresponds to the

Hamiltonian operator, whose eigenvalue is the total energy of the system

$$\hat{H} = \hat{E}_k + \hat{V} = -\frac{\hbar}{2m} \frac{d^2}{dx^2} + \hat{V}. \quad (2.22)$$

Before continuing, it is important to consider the mathematical properties that operators must satisfy in order to represent observables of a quantum system.

## 2.5 Hermitian operators and orthogonality

We have just mentioned that, in quantum mechanics, observable properties of a system have associated operators, whose eigenvalues correspond to the values than these observables can take when the measurement is performed. However, not all operators will lead to physically sensible observables. In particular, only operators which are *Hermitian* are physically allowed. Hermitian operators have important properties, such as they always lead to real (as opposed to complex) eigenvalues, and that the eigenfunctions of Hermitian operators are *orthogonal* among them.

An Hermitian operator  $\hat{\Omega}$  is such that, given two arbitrary wave-functions  $\Psi_i$  and  $\Psi_j$ , it satisfies the following property:

$$\int dx \Psi_i^* \hat{\Omega} \Psi_j = \left( \int dx \Psi_i^* \hat{\Omega} \Psi_j \right)^\dagger. \quad (2.23)$$

It is easy to check that both the momentum and position operators  $\hat{x}$  and  $\hat{p}$  are Hermitian. For instance, in the case of  $\hat{p}$  we have

$$\int dx \Psi_i^* \hat{p} \Psi_j = \int dx \Psi_i^* \frac{\hbar}{i} \frac{d}{dx} \Psi_j = \frac{\hbar}{i} \left( \Psi_i^* \Psi_j \Big|_{-\infty}^{+\infty} - \int dx \Psi_j \frac{d}{dx} \Psi_i^* \right) = - \int dx \Psi_j \frac{\hbar}{i} \frac{d}{dx} \Psi_i^* \quad (2.24)$$

where we have used integration by parts, and exploited the facts that wave-functions must vanish at infinity. Noting that the  $\dagger$  in Eq. (2.23) indicates that the operator now acts to its left, then we have demonstrated that  $\hat{p}$  is Hermitian. In quantum theory, all observables are indeed represented by Hermitian operators, ensuring that the expectation values of these observables in physical systems are real (a system cannot have *i.e.* complex energy).

This key property that the eigenvalues of an Hermitian operator  $\hat{\Omega}$  are real can be demonstrated from its definition Eq. (2.23) as follows. Let us assume that  $\Psi_i = \Psi_j = \psi$  is an eigenfunction of this operator with eigenvalue  $\omega$ , that is  $\hat{\Omega}\psi = \omega\psi$ . Then we have that

$$\int dx \psi^* \hat{\Omega} \psi = \int dx \psi^* \omega \psi = \omega \int dx \psi^* \psi = \omega, \quad (2.25)$$

since the wave-function is normalized to one, and that also we have that the conjugate of the above expression gives

$$\left( \int dx \psi^* \hat{\Omega} \psi \right)^\dagger = \left( \omega \int dx \psi^\dagger \psi \right)^* = \omega^* \quad (2.26)$$

and since  $\hat{\Omega}$  is hermitian, then  $\omega^* = \omega$ , that is,  $\omega$  is a real number.

It is also possible to show that, for an hermitian operator, its eigenfunctions are *orthogonal* among them. In other words, they constitute a *set of linearly independent basis functions*. Mathematically, the

orthogonality property implies that

$$\int dx \Psi_i^*(x) \Psi_j(x) = \delta_{ij}, \quad (2.27)$$

that is, the integral vanishes unless the eigenfunctions are the same,  $i = j$ , in which case the integral equals one because of the normalization condition. This important property allows to express a general quantum state as a *linear superposition* of eigenfunctions of an Hermitian operator.

## 2.6 Quantum superposition and expectation values

The wave-function  $\Psi$  can be used to determine the *expectation value* of physical observables of a quantum system. In general, there will be multiple solutions  $\Psi_n$  of the Schroedinger equation, each of them being a specific eigenfunction of the Hamiltonian and thus characterized by well-defined energies  $E_n$ . Since Schroedinger's equation is a *linear* differential equation, it exhibits the property that the *superposition* of  $N$  independent solutions,

$$\tilde{\Psi} \equiv \sum_{n=1}^N \Psi_n \quad (2.28)$$

is itself *also be a solution* of the same equation. On the other hand, the new solution Eq. (2.28) will in general *not be an eigenfunction* of the Hamiltonian operator  $\hat{H}$ , and thus will not have associated a well-defined energy  $E$ . Indeed, if we apply the Hamiltonian operator to Eq. (2.28) we find that

$$\hat{H}\tilde{\Psi} = \sum_{n=1}^N \hat{H}\Psi_n = \sum_{n=1}^N E_n \Psi_n \neq E\tilde{\Psi}. \quad (2.29)$$

Therefore, while a superposition of eigenfunctions constitutes a valid solution of the original Schroedinger equation, it is not an eigenfunction itself. Crucially, in the limit  $N \rightarrow \infty$  the basis provided by the  $\{\Psi_n\}$  eigenfunctions of an Hermitian operator is *complete*, that is, any arbitrary function can be expressed as a linear combination of the elements of the  $\{\Psi_n\}$  basis.

An explicit example of the fact that a superposition of eigenfunctions of a given Hermitian operator is not necessarily an eigenfunction itself is provided by the free particle solution, Eq. (2.7) in the case that we set  $B = A$ . In this case, the wave-function can be written as

$$\Psi = A(e^{ikx} + e^{-ikx}) = 2A \cos(kx), \quad (2.30)$$

which as shown above corresponds to the superposition of one plane wave moving to the right with momentum  $p_x = +\hbar k$  and another one moving to the left with  $p_x = -\hbar k$ . If now we apply the momentum operator to this wave-function, we find

$$\hat{p}_x \Psi = \frac{\hbar}{i} \frac{d\Psi}{dx} = -\frac{2k\hbar}{i} A \sin(kx) \neq p_x \Psi, \quad (2.31)$$

therefore showing that the superposition of two wave-functions with well-defined momentum  $p_x$  is not itself an eigenfunction of this same operator, and therefore does not have a well-defined momentum. Note that, on the other hand, the solution Eq. (2.30) *is* of course an eigenvalue of the Hamiltonian operator, since

$$\hat{H}\Psi = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} 2A \cos(kx) = \frac{\hbar^2}{2m} 2Ak^2 \cos(kx) = \frac{\hbar^2 k^2}{2m} \Psi = E\Psi, \quad (2.32)$$

with the eigenvalue being the total energy of the system, as expected from the linear property of  $\hat{H}$ .

The example above demonstrate that eigenfunctions of the Hamiltonian operator, that is, the solutions of the Schroedinger equation, are not necessarily eigenfunctions of other Hermitian operators. Therefore, how it is possible to determine the expectation values for generic observables of quantum states?

To answer this question, let us start by assuming that we have a quantum state such as Eq. (2.30). In this system, each measurement of the momentum of the particle will return either  $+k\hbar$  or  $-k\hbar$  with equal probability. Therefore the *expectation value* for the operator  $\hat{p}_x$  for the quantum state Eq. (2.30) will be given by

$$\langle p_x \rangle = \frac{1}{2} \cdot (+k\hbar) + \frac{1}{2} \cdot (-k\hbar) = 0, \quad (2.33)$$

where we have weighted each eigenvalue by its probability. Therefore, while individual measurements will always return one of the two possible values of the momentum, either  $+k\hbar$  or  $-k\hbar$ , the average value over many measurements will vanish.

More in general, if we express a given wave-function as a linear superposition of eigenfunctions of an Hermitian operator  $\hat{\Omega}$ , which we can always do since these eigenfunctions form a complete basis, we have

$$\Psi = \sum_k c_k \Psi_k, \quad \hat{\Omega} \Psi_k = \omega_k \Psi_k, \quad (2.34)$$

and then the probability that a given measurement of the physical observable  $\Omega$  will yield  $\omega_k$  will be

$$P(\omega_k) = \frac{c_k^2}{\sum_j c_j^2}. \quad (2.35)$$

Therefore, the expectation value of the observable  $\Omega$  (that is, the average over a large number of measurements) will then be given by

$$\langle \Omega \rangle = \sum_k \left( \frac{c_k^2}{\sum_j c_j^2} \right) \omega_k, \quad (2.36)$$

where each possible value of that the observable  $\Omega$  can take in this quantum system (*i. e.* each possible eigenvalue) is weighted by its associated probability.

An equivalent way of computing the expectation value of the observable  $\Omega$  in terms of the wave-function is given by the following expression:

$$\langle \Omega \rangle = \int dx \Psi^* \hat{\Omega} \Psi, \quad (2.37)$$

which can be shown to be equivalent to above. Moreover, it is also easy to show that, using the definition Eq. (2.37) the expectation value of an Hermitian operator  $\hat{\Omega}$  for a quantum state where the wave function is an eigenfunction  $\Psi$  of this operator is nothing but the eigenvalue  $\omega$ . Indeed one has

$$\langle \Omega \rangle = \int dx \Psi^* \hat{\Omega} \Psi = \int dx \Psi^* \omega \Psi = \omega \int dx \Psi^* \Psi = \omega, \quad (2.38)$$

due to the normalization of the wave-function.

Thus if a quantum state  $\Psi$  is not an eigenfunction of  $\hat{\Omega}$ , but rather a linear combination of its eigenfunctions  $\Psi_k$  each with eigenvalue  $\omega_k$ ,

$$\Psi = \sum_k c_k \Psi_k, \quad (2.39)$$

then the expectation value will be given by the weighted sum of eigenvalues, with weight  $|c_k|^2$ :

$$\langle \Omega \rangle = \int dx \left( \sum_k c_k \Psi_k \right)^* \hat{\Omega} \left( \sum_j c_j \Psi_j \right) = \sum_{k,j} c_k^* c_j \omega_j \int dx \Psi_k^* \Psi_j = \sum_{k,j} c_k^* c_j \omega_j \delta_{ij} = \sum_k |c_k|^2 \omega_k, \quad (2.40)$$

where we have used the orthogonality property of the eigenfunctions of an Hermitian operator, namely Eq. (2.27). Note that in this derivation we assume that the coefficients of the linear superposition Eq. (2.39) are canonically normalized, that is, they satisfy

$$\sum_k |c_k|^2 = 1, \quad (2.41)$$

which physically means that the probability of finding the quantum state  $\Psi$  in any of the eigenfunction  $\Phi_k$  is simply unity (conservation of probability).

## 2.7 Heisenberg's uncertainty principle

Let us now go back to the free-particle solution of Schroedinger's equation for a plane wave propagating in the positive  $x$  direction,

$$\Psi = A e^{ikx}, \quad (2.42)$$

where we found that the probability distribution for the position of the particle was  $|\Psi|^2 = A^2$ , namely flat: the position of a free particle is maximally undetermined. We also found that, on the other hand, the momentum of this free particle  $\hat{p}_x \Psi = (\hbar/i)(d/dx)\Psi = p_x \Psi$  was  $+k\hbar$ , a well defined value. So why for a free particle we have *maximum uncertainty concerning its position* but instead *perfect information concerning its momentum*?

The reason for this is another of the central principles of quantum mechanics, *Heisenberg's uncertainty principle*. This principle states that *it is impossible to specify simultaneously, with arbitrary precision, both the momentum and the position of a particle*. Note that this is not a mere practical limitation due to for example the finite resolution of our measurement apparatus, but a *fundamental limitation* of the theory that holds true even in the case of ideal measurements. Mathematically, Heisenberg's uncertainty principle takes the following form:

$$\Delta x \Delta p_x \geq \frac{\hbar}{2}, \quad (2.43)$$

or in other words, the better the position of a particle is known, the greater the uncertainty concerning its momentum will be. This explains the expectation values of  $\hat{x}$  and  $\hat{p}$  in the case of a free particle: since the uncertainty on its momentum is zero ( $p = \hbar k$ ) then the uncertainty on its position, due to Eq. (2.43), must be *infinite*, and indeed the probability distribution for the position of the free particle is the same everywhere in space.

Mathematically, the uncertainty in the two observables,  $x$  and  $p$ , is computed from the square root of the *variance*, known as the *standard deviation*, of the distribution of values that these two operators can take, that is

$$\Delta x \equiv \left( \langle x^2 \rangle - \langle x \rangle^2 \right)^{1/2}, \quad (2.44)$$

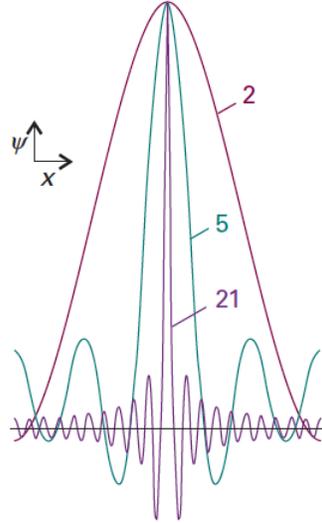


Figure 2.2: The wave function Eq. (2.47) corresponding to the superposition of  $N$  plane-wave free particle solutions, each with a different value of  $k = n\pi$ . We show the results from the addition of  $N = 2, 5, 21$  terms in Eq. (2.47), showing that the more terms we include, the better the localization of the free particle (since the higher is the indetermination of its momentum  $p_x$ ).

$$\Delta p \equiv \left( \langle p^2 \rangle - \langle p \rangle^2 \right)^{1/2}, \quad (2.45)$$

where  $\langle x^2 \rangle$  stands for the expectation value of the  $\hat{x}^2$  operator and so on.

Does this imply that the position of a free particle is always maximally uncertainty? No, if we take into account that physically, from Eq. (2.43), there should be an uncertainty associated also to the expectation value of  $\hat{p}$ , the momentum of the quantum state. A wave function for a free particle with a *finite momentum resolution* can be achieved by constructing a *superposition* of free-particle solutions, each with *different wave numbers*  $k$ , namely

$$\Psi(x) = \sum_k^N c_k e^{ikx}. \quad (2.46)$$

The more the number of contributions  $N$  to the above sum, the higher the uncertainty on the momentum of the particle, and thus we obtain an increased localization of the particle in  $x$ . This can be seen by plotting the free-particle wave-function superposition:

$$\Psi(x) = \sum_{n=1}^N \cos(n\pi x), \quad (2.47)$$

which is shown in Fig. 2.2: the more terms we add in the sum, the more values the momentum  $\hbar k$  of the particle can take, hence  $\Delta p$  is higher (more uncertain) and  $\Delta x$  smaller (increased localization in space).

To be more precise about Eq. (2.43), there are two important remarks to be done. First of all, Heisenberg's uncertainty principle applies only to position and momentum *along the same spatial direction*. So actually we have

$$\Delta x \Delta p_x \geq \frac{\hbar}{2}, \quad \Delta y \Delta p_y \geq \frac{\hbar}{2}, \quad \Delta z \Delta p_z \geq \frac{\hbar}{2}, \quad (2.48)$$

but on the other hand we can also have for instance  $\Delta x \Delta p_y = 0$ , that is, it is possible to *simultaneously*

measure  $x$  and  $p_x$  with arbitrary precision.

The second important implication of Heisenberg's uncertainty principle is that it illustrates a more general concept of quantum theory known as *complementary observables*. We define two observables  $\Omega_1$  and  $\Omega_2$  to be *complementary* if the sequential application of the corresponding operators  $\hat{\Omega}_1$  and  $\hat{\Omega}_2$  does not *commute*, that is,

$$\hat{\Omega}_1 (\hat{\Omega}_2 \Psi) \neq \hat{\Omega}_2 (\hat{\Omega}_1 \Psi), \quad (2.49)$$

or in other words, the results of applying the two operators  $\hat{\Omega}_1$  and  $\hat{\Omega}_2$  to a generic wave-function depends on the *order in which they have been applied*. It can be demonstrated that for each pair of complementary observables there will be a relation of the form of Eq. (2.43), implying that a simultaneous measurement of  $\Omega_1$  and  $\Omega_2$  with arbitrary precision is not possible.

The result that in quantum theory the subsequent application of Hermitian operators to a quantum system does not necessarily commute can be represented introducing another useful mathematical concept, the *commutator* between two operators, defined as

$$[\hat{\Omega}_1, \hat{\Omega}_2] \equiv \hat{\Omega}_1 \hat{\Omega}_2 - \hat{\Omega}_2 \hat{\Omega}_1, \quad (2.50)$$

where note that the commutator of two operators *is another operator*, that is, it should be understood as being applied to a wave-function. With this definition, for the position and momentum operators we find

$$[\hat{x}, \hat{p}_x] = i\hbar, \quad (2.51)$$

as is easy to verify explicitly. Indeed, since

$$\hat{x} \hat{p}_x \Psi = x \left( \frac{\hbar}{i} \frac{d}{dx} \right) \Psi = \frac{\hbar}{i} x \frac{d\Psi}{dx}, \quad (2.52)$$

$$\hat{p}_x \hat{x} \Psi = \left( \frac{\hbar}{i} \frac{d}{dx} \right) (x\Psi) = \frac{\hbar}{i} \Psi + \frac{\hbar}{i} x \frac{d\Psi}{dx}, \quad (2.53)$$

then their commutator gives

$$[\hat{x}, \hat{p}_x] \Psi = -\frac{\hbar}{i} \Psi = i\hbar \Psi, \quad (2.54)$$

which is the sought-for result Eq. (2.51). Therefore,  $x$  and  $p$  are *complementary observables* (their operators do not commute) and thus they cannot be measured simultaneously with arbitrary precision. This is another way of representing Heisenberg's uncertainty principle.

## 2.8 Overview of the postulates of quantum theory

We can now recapitulate what we have learned in this lecture about the *basic postulates of quantum mechanics*. These are fundamental assumptions, not derived from any other theory (at least so far), and play a similar role as the axioms of a mathematical system. These postulates are:

- (a) All the physical information about a quantum system is contained in its *wave-function*  $\Psi$ .
- (b) This wave-function satisfies a specific equation of motion, known as the *Schroedinger equation*.

- (c) The square of the wave-function  $|\Psi(\{\Omega_k\})|^2$  represents the *probability density* associated to a measurement of the  $\{\Omega_k\}$  set of physical observables.
- (d) The wave-function  $\Psi$  must be continuous, have a continuous first derivative, be single valued and be squared-integrable.
- (e) Observables  $\Omega$  are represented by *Hermitian operators*  $\hat{\Omega}$  built upon the position  $\hat{x}$  and momentum  $\hat{p}$  operators.
- (f) Some observables are *complementary*, that is, they can not be measured simultaneously with arbitrary precision. Mathematically, their associated observables *do not commute*. Complementary observables obey then relations of the form of *Heisenberg's uncertainty principle*.



## van Quantum tot Molecuul

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### 3 HC3: Quantum mechanics of simple systems

Quantum mechanics of simple systems: the particle in a box, quantum tunneling, the quantum harmonic oscillator, particle in a box with finite potential barriers.

Based on Atkins and de Paula, *Physical Chemistry*, 10th edition, Chapter 8.

In this lecture we discuss quantum mechanics applied to relatively simple systems such as the particle in a confining box and the quantum harmonic oscillator. We will study some remarkable phenomena that appear in these systems that do not have an analog in classical mechanics, such as that the *quantization of energies* and the *quantum tunneling*.

The *learning goals* of this lecture are:

- (a) Solving the Schrodinger equation for simple quantum systems.
- (b) Understanding that confinement of a quantum particle in space leads to the quantization of its energy levels, with a non-vanishing energy for the ground state.
- (c) Interpret the physical content of the wave-functions from the solutions of the Schrodinger equation.
- (d) Understanding and applying the mathematical technique of separation of variables.
- (e) Understanding and applying the phenomenon of quantum tunneling.

#### 3.1 Particle in a box and energy quantization

In HC2, when we solved the Schrodinger equation for a free particle, we found that its energy was given by  $E_k = k^2\hbar^2/2m$ , where  $k$  was a real parameter that could take any value. Therefore, for a free particle, energy

levels *are not quantized*. We now will see how once the particle is confined into a limited region of space, energy levels become automatically quantized. One of the simplest system in which energy quantization arises is for the so-called *particle in a box* system.

This system is defined by a single particle moving under the effects of a potential of the form

$$\begin{aligned} V(x) &= 0 \quad \text{for } 0 \leq x \leq L \\ V(x) &= +\infty \quad \text{for } x < 0 \quad \text{and } x > L \end{aligned} \quad (3.1)$$

In other words, the particle undergoes free motion for  $0 \leq x \leq L$ , but cannot move outside this range because it is *confined* by the potential Eq. (3.1) (since the particle would need an infinite energy to overcome that potential barrier).

Inside the region limited by the confining potential,  $0 \leq x \leq L$ , the solution of Schroedinger's equation will be the same as for a free particle (since the potential vanishes there) and thus we have

$$\Psi_k = Ae^{ikx} + B^{-ikx} = (A + B) \cos(kx) + (A - B)i \sin(kx) \equiv D \cos(kx) + C \sin(kx), \quad (3.2)$$

where we have expanded the exponentials using  $e^{ix} = \cos(x) + i \sin(x)$  and then redefined the (arbitrary) integration coefficients for reason that will become apparent below.

Since for  $x > L$  and  $x < 0$  we have that  $V(x) = \infty$ , the particle cannot travel to this region (since it would require infinite energy) and thus the wave-function will be zero there. In particular this means that

$$\Psi_k(x = 0) = 0, \quad \Psi_k(x = L) = 0. \quad (3.3)$$

Now, since as discussed in HC2, the wave-function must be *continuous*, we can use the *boundary conditions* Eq. (3.3) to fix the coefficients in Eq. (3.2):

$$\Psi_k(x = 0) = D \rightarrow D = 0, \quad (3.4)$$

$$\Psi_k(x = L) = C \sin(kL) = 0 \rightarrow k = \frac{n\pi}{L}, \quad (3.5)$$

where  $n$  is an arbitrary *integer number*. Therefore we find that for a particle in a box the quantum wave-functions and energies are given by

$$\Psi_n(x) = C \sin\left(\frac{n\pi x}{L}\right), \quad E_n = \frac{\hbar^2 \pi^2 n^2}{2mL^2}. \quad (3.6)$$

Therefore, we now find that the *energies of the particle are quantized*, and labeled by an integer number  $n$  rather than by a real number  $k$  as was the case for a free particle. Finally, the coefficient  $C = (2/L)^{1/2}$  can be determined from requiring the normalization of the wave-function.

Remarkably, we note that the lowest energy that a particle can have in this system is not zero, but rather  $E_1 = \hbar^2 \pi^2 / 2mL^2 \neq 0$ . This is known as the *zero-point energy*, and is a consequence of the fact that a quantum particle in a confining potential cannot be at rest (because else we would know its momentum with arbitrary precision, contradicting Heisenberg's uncertainty principle). Note also that the solution  $n = 0$  corresponds to  $\Psi_0 = 0$ , that is, the absence of any particle in the system, so it cannot really be associated

with the group state (which is instead the  $n = 1$  state).

The conclusions that we can extract from the particle in a box system are fully general and apply to other systems: in quantum mechanics, *energy quantization* arises from the wave nature of the wave-function in the presence of boundary conditions.

Let us now compute the expectation value of the momentum  $p_x$  for this system. As we have shown, the wave-function that solves the Schroedinger equation accounting for the boundary conditions of the system is given by

$$\Psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi n x}{L}\right), \quad (3.7)$$

and if we compute the expectation value of  $p_x$ , using the definition of Eq. (2.37), we find that

$$\langle p_x \rangle = \frac{2}{L} \int_0^L dx \sin\left(\frac{\pi n x}{L}\right) \left(\frac{\hbar}{i} \frac{d}{dx}\right) \sin\left(\frac{\pi n x}{L}\right) = \frac{2\hbar n \pi}{i L^2} \int_0^L \sin\left(\frac{\pi n x}{L}\right) \cos\left(\frac{\pi n x}{L}\right) dx = 0, \quad (3.8)$$

since the integral vanishes for any value of  $n$ , as can be checked using trigonometric identities. So therefore we find that the expectation value of the momentum for the particle in a box is  $\langle p_x \rangle = 0$ . This can be understood if we expand the solution Eq. (3.7) as follows

$$\Psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi n x}{L}\right) = \sqrt{\frac{1}{2L}} \frac{1}{i} \left( e^{i\pi n x/L} - e^{-i\pi n x/L} \right), \quad (3.9)$$

which correspond to the superposition (with equal amplitude) of a plane wave moving in the positive direction with momentum  $p_x = \hbar \pi n/L$  and another moving in the opposite direction with  $p_x = -\hbar \pi n/L$ , hence when averaging the two components of the wave-function cancel to each other leading to  $\langle p_x \rangle = 0$ .

Note also that in the limit where  $n \rightarrow \infty$  the energies of the particle become *effectively continuous*, as expected in classical physics. This is the realization of the so-called *correspondence principle* of quantum theory: for large values of the quantum numbers, the behaviour of the quantum theory becomes effectively classical.

### 3.2 Particle in a two-dimensional box

The next system that we will consider is similar than the previous one, but now the box has *two dimensions* in space, which we will denote by  $x$  and  $y$ . Therefore, the confining 2D potential of this system will take the following form:

$$\begin{aligned} V(x, y) &= 0 \quad \text{for } 0 \leq x \leq L_x \quad \text{and} \quad 0 \leq y \leq L_y \\ V(x, y) &= +\infty \quad \text{for } y < 0, \quad y > L_y, \quad x < 0, \quad x > L_x \end{aligned} \quad (3.10)$$

Inside the box, the Schroedinger equation is the same as that of the free particle but now in two dimensions, namely

$$-\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) \Psi(x, y) = E \Psi(x, y), \quad (3.11)$$

where note that now the wave-function depends on two variables,  $x$  and  $y$ , and thus the derivatives that appear are *partial derivatives* rather than total derivatives.

To solve this differential equation, we need to adopt the method of *separation of variables*, namely

assuming that the full wave-function  $\Psi(x, y)$  can be expressed as a product of two functions, each depending separately on  $x$  and  $y$  only, that is,

$$\Psi(x, y) = \Psi_X(x)\Psi_Y(y). \quad (3.12)$$

If we plug this *ansatz* on the two-dimensional Schroedinger equation Eq. (3.11), we find that

$$-\frac{\hbar^2}{2m}\Psi_Y(y)\left(\frac{\partial^2}{\partial x^2}\right)\Psi_X(x) - \frac{\hbar^2}{2m}\Psi_X(x)\left(\frac{\partial^2}{\partial y^2}\right)\Psi_Y(y) = E\Psi_X(x)\Psi_Y(y), \quad (3.13)$$

and now, if we divide each side of the equation by  $\Psi(x, y)$ , we find that

$$-\frac{\hbar^2}{2m}\frac{1}{\Psi_X(x)}\left(\frac{\partial^2}{\partial x^2}\right)\Psi_X(x) - \frac{\hbar^2}{2m}\frac{1}{\Psi_Y(y)}\left(\frac{\partial^2}{\partial y^2}\right)\Psi_Y(y) = E. \quad (3.14)$$

In Eq. (3.14), the RHS is independent of both  $x$  and  $y$ , and in the LHS we have the sum of two pieces, the first one depending *only on*  $x$  and the second one depending *only on*  $y$ . Therefore, the only way the equation can be true is if each piece is separately equal to a *constant*. If these two constants are denoted respectively by  $E_X$  and  $E_Y$  respectively, we find

$$-\frac{\hbar^2}{2m}\frac{1}{\Psi_X(x)}\left(\frac{\partial^2}{\partial x^2}\right)\Psi_X(x) = E_X, \quad (3.15)$$

$$-\frac{\hbar^2}{2m}\frac{1}{\Psi_Y(y)}\left(\frac{\partial^2}{\partial y^2}\right)\Psi_Y(y) = E_Y, \quad (3.16)$$

which are of course nothing but *two separate Schroedinger equations*, one for the  $x$  component of the wave function,  $\Psi_X(x)$ , and another for the  $y$  component of the wave function,  $\Psi_Y(y)$ . The total energy of the system is then  $E = E_X + E_Y$ , which justifies our choice of notation for the integration constants.

From the discussion above, we see that the solution of the Schroedinger equation for a particle in a 2D box will be given by the product of solutions to the same equation in a 1D box. That is, we will have that the  $x$ - and  $y$ -components of the wave functions are

$$\Psi_x(x) = \sqrt{\frac{2}{L_x}} \sin\left(\frac{n_x\pi x}{L_x}\right), \quad (3.17)$$

$$\Psi_y(y) = \sqrt{\frac{2}{L_y}} \sin\left(\frac{n_y\pi y}{L_y}\right), \quad (3.18)$$

and thus the *quantum state of the system* is now being defined by *two independent integer numbers* ( $n_x, n_y$ ) (the two quantum numbers of the system), and therefore the total wave-function is

$$\Psi(x, y) = \Psi_x(x)\Psi_y(y) = \sqrt{\frac{4}{L_x L_y}} \sin\left(\frac{n_x\pi x}{L_x}\right) \sin\left(\frac{n_y\pi y}{L_y}\right). \quad (3.19)$$

The total energy of a given quantum state of the system will be specified by the quantum numbers of this state,  $n_x$  and  $n_y$ , and thus reads

$$E_{n_x, n_y} = \frac{\hbar^2}{8m} \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right). \quad (3.20)$$

Note that in the limit in which  $L_x = L_y = L$  there will be a *degeneracy* of quantum states, meaning that different quantum states, defined by different pairs of quantum numbers  $(n_x, n_y)$  will have associated the *same total energy*. In this limit indeed the total energy becomes

$$E_{n_x, n_y} = \frac{\hbar^2}{8m} \left( \frac{n_x^2 + n_y^2}{L^2} \right), \quad (3.21)$$

so for example the quantum state  $(n_x = 1, n_y = 2)$  will correspond to a state with the same energy as that with  $(n_x = 2, n_y = 1)$ . Degeneracy is a generic property of quantum states: in general, many different states can have associated the same total energy.

### 3.3 Quantum tunneling

In classical physics, when we have a particle with total energy  $E$  moving inside a conservative potential  $V(x)$ , the particle will *confined* to the region defined by  $E \geq V(x)$ . Indeed, from energy conservation we have that the sum

$$E = E_k + V(x) = \frac{1}{2}mv^2 + V(x), \quad (3.22)$$

where  $E_k$  is the particle's kinetic energy, is a constant of motion and must hold for all values of  $x$ . Therefore, we have that

$$v^2 = \frac{2}{m} (E - V(x)) \quad (3.23)$$

can only be satisfied if  $E \geq V(x)$ , else the velocity would be an unphysical complex number. Therefore, the particle cannot move in the region of  $x$  for which  $V(x) > E$ : we know that this region is *classically forbidden*.

However, in quantum physics this is *not* necessarily the case: a particle can cross a potential barrier even when its kinetic energy is smaller than the potential energy of the barrier. This remarkable phenomenon is known as the *quantum tunneling* effect, and is schematically represented in Fig. 3.1, where we show how the wave function of a particle is non-zero even in the classically forbidden region with  $V > E_k$ , and thus leads to a finite probability of finding the particle at the right of the potential barrier.

The quantum tunneling effect is a direct consequence of the wave-like nature of the wave function. We can now quantify and compute explicitly the value of the wave-function inside and on the other side of the potential barrier. As indicated in Fig. 3.1, at the left of the barrier we have  $V = 0$ , and thus the solution of the Schroedinger equation there is the usual free-particle solution, namely

$$\Phi_k(x) = Ae^{ikx} + Be^{-ikx}, \quad (3.24)$$

where the kinetic energy is  $E_k = \hbar^2 k^2 / 2m$  and thus the linear momentum is  $p_x = \hbar k = \sqrt{2mE_k}$ .

Now, in the region *inside the barrier* the Schroedinger equation looks like

$$-\frac{\hbar^2}{2m} \frac{d^2 \Psi}{dx^2} + V\Psi = E_k \Psi, \quad \text{with } V \geq E_k. \quad (3.25)$$

Note that here I have identified the total energy  $E$  with the kinetic energy at the left side of the barrier,  $E = E_k$ , in order to *energy conservation* to be satisfied. Moreover, since the potential  $V$  is constant, this

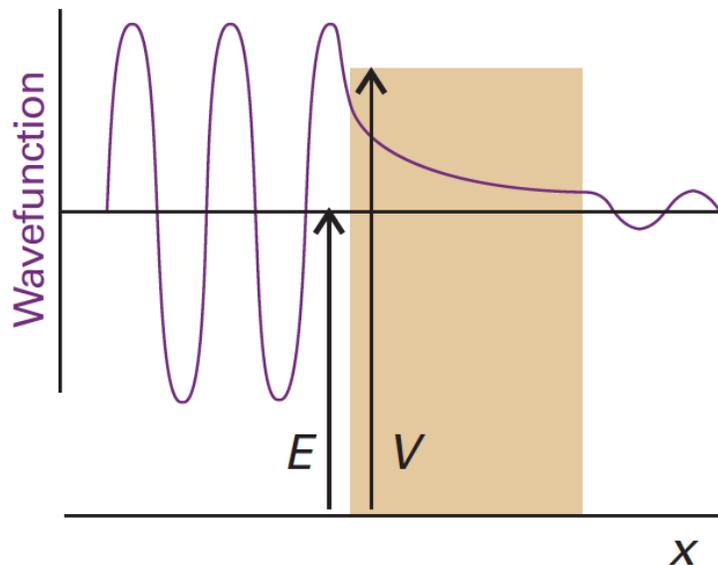


Figure 3.1: Schematic representation of the *quantum tunneling effect*: the wave-function of a particle with kinetic energy  $E_k$  is non-zero inside a barrier with potential energy  $V > E_k$ , and therefore has a finite probability (non-zero wave-function) to be found at the other side of the barrier.

equation can be rewritten as

$$-\frac{\hbar^2}{2m} \frac{d^2\Psi}{dx^2} = -(V - E_k)\Psi, \quad (3.26)$$

which has the form of a free-particle equation, but this time with a *negative energy*,  $E = -(V - E_k)$ . Using the same method as solution as for a free particle, we get that the wave-function inside the barrier is now

$$\Psi = C e^{\kappa x} + D e^{-\kappa x}, \quad \kappa \hbar = \sqrt{2m(V - E_k)} \geq 0, \quad (3.27)$$

which as an *exponential solution*, rather than the oscillatory solution of the free particle equation. Therefore, the wave-function is non-zero inside the barrier, despite  $V > E_k$  and thus of being forbidden in classical physics.

Finally, in the region right to the barrier, we have again a free-particle solution for a particle moving in the positive  $x$  direction, that is

$$\Psi = A' e^{ikx}, \quad k \hbar = \sqrt{2mE_k}, \quad (3.28)$$

with equal momentum and energy as in the left side of the barrier. In order to determine the values of the five integration constants introduced above,  $A, B, C, D, A'$ , we need exploit two properties of the wave-function: it is *continuous everywhere*, and its *derivative is also continuous* for any value of  $x$ . If we label as  $x = 0$  and  $x = L$  the start and end points of the potential barrier, continuity of the wave-function there implies that

$$\begin{aligned} A + B &= C + D, \\ C e^{\kappa L} + D e^{-\kappa L} &= A' e^{ikL}, \end{aligned} \quad (3.29)$$

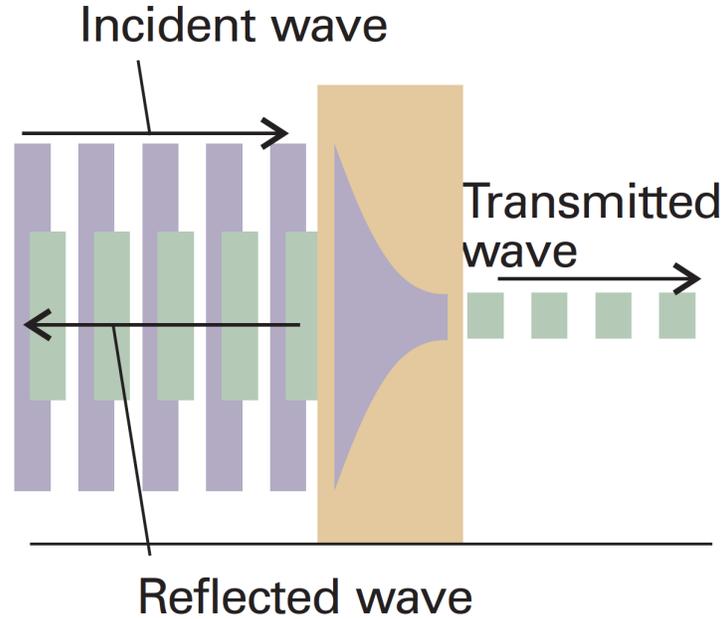


Figure 3.2: The physical interpretation of the quantum tunneling effect: an incident wave  $Ae^{ikx}$  left to the barrier is partially transmitted to the other side of the barrier with wave function  $A' = e^{ikx}$  and partially reflected, with momentum in the opposite direction as compared to the incident wave,  $Be^{-ikx}$ . The ratio  $T = A'/A$  of the transmitted over the incident amplitude is known as the *transmission coefficient*.

while the continuity of the first derivative of the wave-function at the same endpoints implies that

$$\begin{aligned} ikA - ikB &= \kappa C - \kappa D, \\ \kappa C e^{\kappa L} - \kappa D e^{-\kappa L} &= ikA' e^{ikL}. \end{aligned} \quad (3.30)$$

Note that we have five unknowns and four equations, and therefore we can express four of these unknowns in terms of a single one, say  $A$ .

As we saw in the free-particle case, for the solution in the left side of the barrier, Eq. (3.24) we could make the interpretation that the  $Ae^{ikx}$  component of the wave function can be associated with the *incident wave* (since its momentum was  $p_x = +\hbar k$ ), while the  $Be^{-ikx}$  instead would be the *reflected wave* (with momentum  $p_x = -\hbar k$  pointing in the negative  $x$  direction). Therefore, we can define a ratio  $T = A'/A$  which physically can be interpreted as the ratio of the amplitude of the *transmitted* wave over the *incident* wave, see Fig. 3.2. This *transmission coefficient*  $T$  can be computed using the values of the integration coefficients  $B, C, D, A'$  obtained as explained above, resulting in the following expression:

$$T(\kappa L, \epsilon) = \left( 1 + \frac{(e^{\kappa L} - e^{-\kappa L})^2}{16\epsilon(1 - \epsilon)} \right)^{-1}, \quad \epsilon \equiv E/V, \quad (3.31)$$

and where  $\kappa$  has been defined in Eq. (3.27). The transmission amplitude  $T$  has a number of important limiting cases. When taking the various limits, note that  $\kappa$  depends implicitly on  $\epsilon$  as well, since

$$\kappa \hbar = \sqrt{2m(V - E_k)} = \sqrt{2mV} \sqrt{1 - \epsilon}. \quad (3.32)$$

With this caveat, it is possible to derive the following important properties of the transmission amplitude  $T$ :

- In the limit  $L \rightarrow 0$  for fixed  $\kappa$ , then the transmission coefficient  $T \rightarrow 1$ .

This limit corresponds either to *very short barriers*  $L$ . In this two cases, it makes sense physically that the probability of tunneling becomes very high (and the amplitude of the *reflected way* conversely very small).

- In the limit  $\kappa \rightarrow 0$  ( $\epsilon \rightarrow 1$ ) for fixed  $L$ , then the transmission coefficient goes to

$$T \rightarrow \left(1 + \frac{mVL^2}{\hbar}\right)^{-1}, \quad (3.33)$$

so it does *not* tend to one even if  $E_k \lesssim V$  (only in the case of very short barriers  $L \rightarrow 0$  then  $T \rightarrow 1$ ).

- For  $E_k \ll V$ , or what is the same  $\epsilon \rightarrow 0$ , we find that  $T \rightarrow 0$ .

This can be physically understood from the fact that for a steep enough barrier, eventually the probability of transmission will become vanishingly small, in agreement with the *classical expectation*.

- As  $E_k \rightarrow V$  ( $\epsilon \rightarrow 1$ ), the value of the transmission amplitude increases monotonically, until the limiting value Eq. (3.33) is achieved.
- in the limit  $\kappa L \gg 1$  the transmission amplitude Eq. (3.31) becomes

$$T \simeq 16\epsilon(1 - \epsilon)e^{-2\kappa L}. \quad (3.34)$$

This limit corresponds to either very steep ( $\kappa \rightarrow \infty$ ) or very long ( $L \rightarrow \infty$ ) barriers, or the two at the same time. In this case we intuitively expect that the transmission probability will be small, and what Eq. (3.34) indeed shows is that  $T$  is *exponentially small* in this limit. We also note that  $T \sim e^{-2L\sqrt{2mV}/\hbar}$ , and thus that *lighter particles* will have a higher probability of tunneling than heavier particles.

The fact that the transmission coefficient Eq. (3.31) is different from zero is a striking deviation of quantum theory with respect to classical physics. The quantum tunneling effect indicates that for instance a naive particle picture of electrons or other quantum particles is far from adequate to describe the phenomena of the microcosm.

To conclude this discussion of the tunneling effect, recall that in HC2 we mentioned the *correspondence principle* of quantum theory, namely that in the appropriate limits the quantum behaviour should become effectively classical. In the case of the quantum tunneling effect, since we have that

$$\kappa = \frac{1}{\hbar} \sqrt{2m(V - E_k)}, \quad (3.35)$$

we find that, for fixed values of  $V$  and  $E_k$ , if  $\kappa \rightarrow \infty$  then from Eq. (3.31) we see that  $T \rightarrow 0$ . This limit can be realized if

$$\hbar \ll \sqrt{2m(V - E_k)}. \quad (3.36)$$

Therefore, in this limit (where Planck's constant can be set to zero) we find that the tunneling probability goes to zero and this recover the classically expected behaviour.

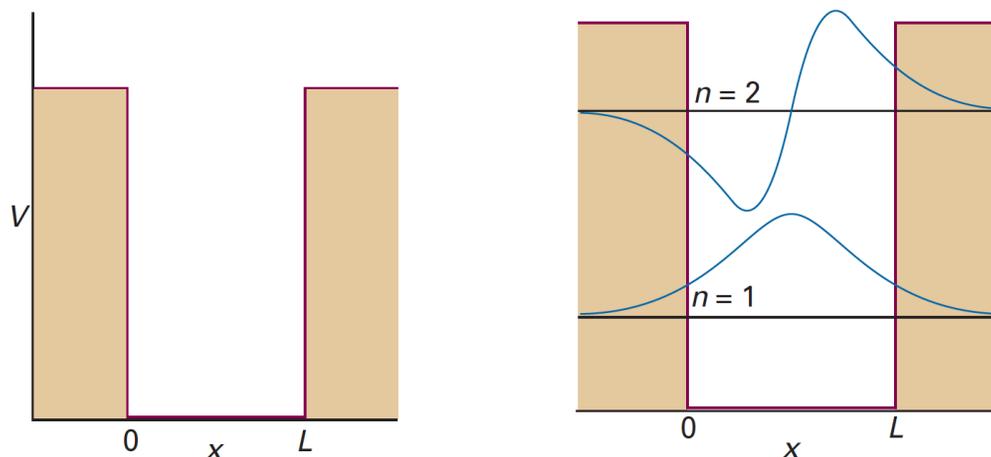


Figure 3.3: Schematic representation of the particle-in-a-box quantum system, characterized by finite potential barriers  $V$  at the two sides of the box (left plot). In the right plot we show the wave function for the first two quantum states of the system,  $n = 1$  and  $n = 2$ , which exhibit oscillatory behaviour inside the box but decay exponentially fast in the classically forbidden region with  $E < V$ .

### 3.4 Particle in a box with finite potential walls

The next quantum system that one could study is a modification of the particle-in-a-box system discussed above, with the difference that the potential barriers  $V$  at the two sides of the box now are *finite* (as opposed to infinite as before). In other words, the potential function in this system now reads

$$\begin{aligned} V(x) &= 0 \quad \text{for } 0 \leq x \leq L, \\ V(x) &= +|V| \quad \text{for } x < 0 \quad \text{and} \quad x > L. \end{aligned} \tag{3.37}$$

Although we will not work out this case explicitly in the lectures, the solution to the Schroedinger equation here follows quite directly the tunneling derivation that was presented above. Indeed, one has to solve the Schroedinger equation both inside the potential well (where we have the free-particle, oscillatory, solution) and in the classically forbidden regime *inside* the left and the right barriers, where we find a exponentially decaying solution. The integration constants of this problem can be uniquely determine by the conditions condition that the wave-function and its derivate should be continuous at both sides of the potential barrier,  $x = 0$  and  $x = L$ , as well as by the overall normalization of the wave function.

In Fig. 3.3 we show in the left plot the schematic representation of the particle-in-a-box quantum system, characterized by finite potential barriers  $V$  at the two sides of the box. In the right plot, we show the wave function for the first two quantum states of the system,  $n = 1$  and  $n = 2$ , which exhibit oscillatory behaviour inside the box but *decay exponentially fast* in the classically forbidden region with  $E < V$ . Note that, as in the quantum tunneling case discussed above, the wave-function is non-zero even inside the potential barrier, where  $V > E_k$  with  $E_k$  being the kinetic energy of the particle inside the box, but quickly becomes very small if  $V \gg E_k$ .

### 3.5 The harmonic oscillator in quantum mechanics

In classical mechanics, an *harmonic oscillator* is defined in general as particle moving under the effects of a *quadratic potential*, that is

$$V(x) = \frac{1}{2}k_f x^2, \quad (3.38)$$

where  $k_f$  is known as the *spring constant* or *Hooke's constant*. Though physically this potential is usually associated to a system based on a frictionless body attached to a flexible spring, the form Eq. (3.38) is fully general and applies to many other potentials. In particular, any potential can be approximated by Eq. (3.38) in the region near local minima (as can be seen by doing a Taylor expansion).

The harmonic potential Eq. (3.38) vanishes at  $x = 0$ , the *equilibrium* position of the particle. Note that this potential is *confining*, since it increases quadratically as  $|x|$  increases, and thus a particle in this potential would never be able to completely escape from it, no matter how large its energy is. From this potential, we can compute the force that the particle will experience, namely

$$F = -\frac{dV(x)}{dx} = -k_f x, \quad (3.39)$$

which is known as *Hooke's law*: in an harmonic oscillator (or in general, for a quadratic potential) the force is attractive and proportional to the deviation with respect to the equilibrium position.

Let us now study the behaviour of a quantum particle under the effects of the potential Eq. (3.38), that is, a *quantum harmonic oscillator*. The Schroedinger equation associated to this system will now be:

$$-\frac{\hbar^2}{2m} \frac{d^2\Psi}{dx^2} + \frac{1}{2}k_f x^2 \Psi = E\Psi. \quad (3.40)$$

Solving this equation is beyond the scope of this course, though for completeness let me show here the explicit form of the solutions for the wave function:

$$\Psi_n(x) = \frac{1}{\sqrt{2^n n!}} \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-m\omega x^2/2\hbar} H_n\left(\sqrt{\frac{m\omega}{\hbar}}x\right), \quad (3.41)$$

where  $H_n(x)$  are as special family of orthogonal polynomials known as *Hermite* polynomials, and we have defined the *frequency* of the oscillator as  $\omega \equiv \sqrt{k/m}$ , in analogy with the classical treatment. The solutions of Eq. (3.40) are labeled by the quantum number  $n$ , which takes only integer values  $n = 0, 1, 2, 3, \dots$

As a consequence of the potential barrier that confines the particle, the energies of the quantum harmonic oscillator are *quantized*, and it is possible to show that they are given by

$$E_n = \hbar\omega \left(n + \frac{1}{2}\right). \quad (3.42)$$

There are two important consequences of this result. First of all, we note that the difference in energy between two adjacent quantum levels  $n$  and  $n + 1$  is constant, that is

$$E_{n+1} - E_n = \hbar\omega, \quad (3.43)$$

independently of the value of  $n$ . Second, and more strikingly, we find that the energy of the *ground state*

(that is, the *vacuum*) of the system, the eigenfunction with the smallest associated energy, is *different from zero*. Indeed we find that for  $n = 0$  we get

$$E_0 = \frac{1}{2}\hbar\omega, \quad (3.44)$$

which is known as the *zero-point energy* of a quantum harmonic oscillator. This is a direct consequence of Heisenberg's uncertainty principle: if the energy and momentum were zero, the particle would be at rest, and we would know  $p$  with arbitrary precision. But then the indetermination on its position  $x$  would be maximal, as in the free particle case, and this is not possible due to the confining harmonic potential.

For small values of  $n$ , the Hermite polynomials that appear in the quantum wave-function Eq. (3.41) take relatively simple forms,

$$\begin{aligned} H_0(x) &= 1, \\ H_1(x) &= 2y, \\ H_2(x) &= 4y^2 - 2, \\ H_3(x) &= 8y^3 - 12y, \end{aligned} \quad (3.45)$$

and so on. Therefore, for the ground state of the system,  $n = 0$ , the wave-functions takes the particularly simple form

$$\Psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-m\omega x^2/2\hbar}, \quad (3.46)$$

which is known as a *Gaussian function*. It is easy to check explicitly that these wave-function is correctly normalized (as is the case for other values of  $n$ ), by verifying that

$$\int_{-\infty}^{\infty} dx |\Psi_0(x)|^2 = 1. \quad (3.47)$$

To show this, first one should make the change of variable  $y \equiv \sqrt{m\omega/\hbar}x$  and then use the result for the Gaussian integral that

$$\int_{-\infty}^{\infty} dx e^{-x^2} = \sqrt{\pi}. \quad (3.48)$$

It is interesting to compare the probability densities for the position  $x$  for the first two energy levels, namely  $|\Psi_0(x)|^2$  with  $|\Psi_1(x)|^2$ , where

$$\Psi_1(x) = \sqrt{2} \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \sqrt{\frac{m\omega}{\hbar}} x e^{-m\omega x^2/2\hbar}, \quad (3.49)$$

This comparison is shown in Fig. 3.4, where we show the wave-function  $\Psi_n(x)$  and its square  $|\Psi_n(x)|^2$  (which remember represents the probability density for the position  $x$ ) in the quantum harmonic oscillator for the first two eigenstates,  $n = 0$  (left plot) and  $n = 1$  (right plot). We observe that while for  $n = 0$  (the ground state) the maximum probability  $|\Psi|^2$  is found for  $x = 0$  (the classical equilibrium position), for the excited state  $n = 1$  it is rather more likely to find the particle far from the equilibrium position. This property holds for other excited states: the higher the value of  $n$ , the more likely is to find the particle far from  $x = 0$ . This behaviour is consistent with the classical theory, where the harmonic oscillator spends more time in the turning points than in the equilibrium point because its velocity is the smallest in the former positions.

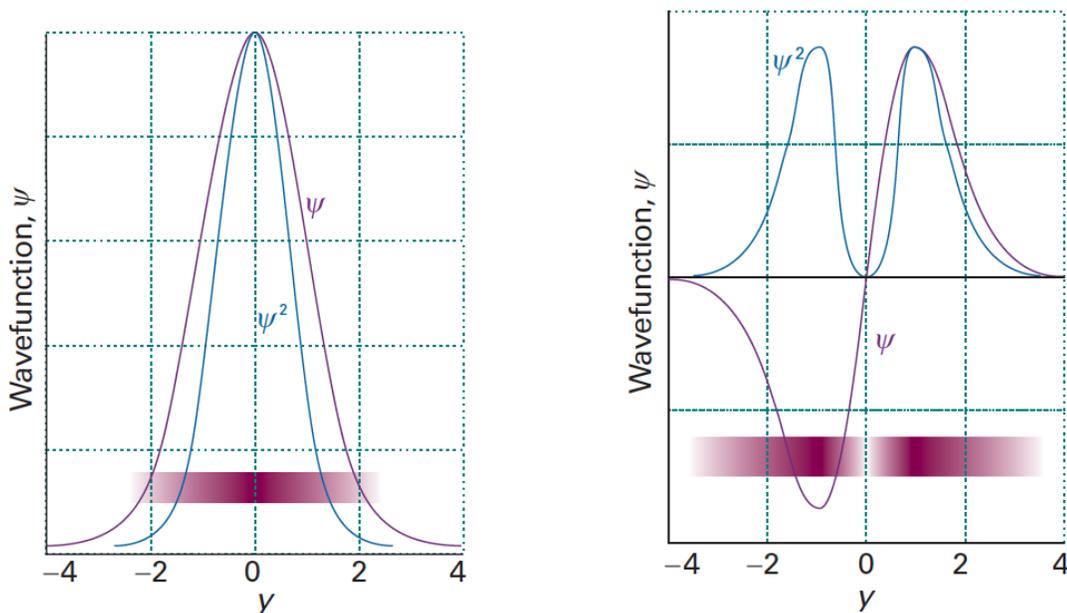


Figure 3.4: The wave-function  $\Psi_n(x)$  and its square  $|\Psi_n(x)|^2$  (which represents the probability density for the position  $x$ ) in the quantum harmonic oscillator for the first two eigenstates,  $n = 0$  (left plot) and  $n = 1$  (right plot). We observe that while for  $n = 0$  (the ground state) the maximum probability  $|\Psi|^2$  is found for  $x = 0$ , for the excited state  $n = 1$  it is rather more likely to find the particle far from the equilibrium position.

The exponential suppression in the wave function of the quantum harmonic oscillator, Eq. (3.41) implies that it goes to zero for  $x \rightarrow \pm\infty$ , no matter the value of  $n$  (that is, of how energetic is the particle). This is because the particle has a oscillatory behaviour in the region  $E > V(x)$ , but then decays exponentially in the classically forbidden region  $E < V(x)$ , which is eventually reached no matter how large is  $E$  (because of the form of the potential).

Since we have the wave-functions for all values of  $n$ , Eq. (3.41), we know that we have a complete knowledge of this quantum system, and thus we can compute the *expectation values* of arbitrary physical observables. First of all, we can show that the expectation value of the position  $x$  of the harmonic oscillator is, for any value of the quantum number  $n$ ,

$$\langle x \rangle = 0, \quad (3.50)$$

in other words, the particle has a symmetric distribution of positions around the classical equilibrium position  $x = 0$ . This can be easily shown by noting that

$$\langle x \rangle = \int_{-\infty}^{\infty} dx x |\Psi(x)|^2 \sim \int_{-\infty}^{\infty} dx x e^{-m\omega x^2/\hbar} \left[ H_n \left( \sqrt{\frac{m\omega}{\hbar}} x \right) \right]^2 = 0, \quad (3.51)$$

since the *integrand is an odd function*,  $f(x) = f(-x)$ , and the integration range is symmetrical. To see this, note that  $H_n(-x) = \pm H_n(x)$  for any values of  $n$ .

Having established that in the quantum harmonic oscillator the particle can be found with equal probability at the right and at the left of the equilibrium position, it is perhaps more interesting to now compute

its *mean square displacement*, given by

$$\langle x^2 \rangle = \left( n + \frac{1}{2} \right) \frac{\hbar}{\sqrt{mk_f}}. \quad (3.52)$$

Therefore, the *standard deviation* of the position  $x$  is

$$\Delta x \equiv \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = \sqrt{\left( n + \frac{1}{2} \right) \frac{\hbar}{(mk_f)^{1/2}}} \quad (3.53)$$

which for large values of  $n$  grows like  $\Delta x \sim \sqrt{n}$ : the likelihood of finding the particle at a greater distance from  $x = 0$  increases as the square root of the quantum number  $n$ , despite the fact that on average the expectation value will still be  $\langle x \rangle = 0$ . These results are consistent with the previous discussion above, based on the behaviour of the wave functions  $\Psi_n$ . From Heisenberg's uncertainty principle, Eq. (2.43) we can determine the standard deviation associated to measurements of the linear momentum of the quantum harmonic oscillator in this limit,

$$\Delta p_x \sim \frac{\hbar}{\Delta x} \sim \frac{\hbar}{n^{1/2}}, \quad (3.54)$$

so the higher the value of  $n$ , the better the momentum of the harmonic oscillator can be predicted (in the *correspondence limit*, we recover the classical expectation that  $p_x$  can be determined with vanishingly small uncertainty.)

There are other properties of this quantum system that are useful to compute. The expectation value of the potential energy is given by

$$\langle V \rangle = \frac{1}{2} k_f \langle x^2 \rangle = \frac{1}{2} \left( n + \frac{1}{2} \right) \hbar \left( \frac{k_f}{m} \right)^{1/2} = \frac{1}{2} \left( n + \frac{1}{2} \right) \hbar \omega, \quad (3.55)$$

where we have used the fact that the expectation value of an operator is *linear*, and the result for  $\langle x^2 \rangle$  just computed above. Therefore, given that the complete energy of the quantum harmonic oscillator was Eq. (3.42), we find that  $\langle V \rangle = E_n/2$ , and thus for the kinetic energy  $\langle E_k \rangle = E_n/2$ . So in the quantum harmonic oscillator, the energy is *equally shared* between kinetic and potential, for any value of  $n$ . This is actually a consequence of a deep principle called the *equipartition theorem*. In other words, we have that for this quantum system

$$\langle E \rangle = \langle E_k \rangle + \langle V \rangle = \frac{1}{2} \langle E \rangle + \frac{1}{2} \langle E \rangle. \quad (3.56)$$

### 3.6 Summary

To summarize, some important concepts that we have learned in this lecture are:

- The boundary conditions on the wave-function induced by a confining potential lead to the *quantization of the allowed energy levels*. This is a generic property of quantum systems, as we have seen in various examples such as the particle in a box with finite barriers and the quantum harmonic oscillator.
- In many quantum systems, the energy of the ground state is different to zero, unlike classical physics. We denote this effect as the *zero-point energy*.

- Quantum particles have a non-zero probability of being measured *within classically forbidden regions*, and to tunnel potential barriers even when their kinetic energy is smaller than the energy of the barrier.
- In some circumstances, quantum states can be *degenerate*, meaning that different states, characterized by different quantum numbers, can have associated the *same total energy*.
- In the *correspondence limit*, usually associated to high values of the quantum numbers of the system, quantum theory predictions should *reproduce their classical counterparts*.

4 HC4

5 HC5

6 HC6

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8 HC8

9 HC9

## 10 HC10: Molecular and vibrational spectroscopy



### van Quantum tot Molecuul

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Molecular and Vibrational Spectroscopy

Based on Atkins and de Paula, *Physical Chemistry* 10th edition, Chapter 12

HC10 is the first of the last three lectures of the course. In this final part, we will discuss the *interaction of molecules and nuclei with different types of electromagnetic radiation*. First of all, in HC10 we will discuss the general properties of *molecular spectroscopy and vibrational spectra*, where by *spectroscopy* we understand the study of the interaction between electromagnetic radiation and matter using different experimental techniques. Then in HC11 we will study electronic transitions in molecules. Finally, in HC12 we will illustrate the underpinnings of Nuclear Magnetic Resonance (MNR), highlighting how quantum physics is central to one of the most widely used methods of medical imaging.

The *learning goals* of this lecture are:

- Understanding and applying the basic properties of absorption and emission of electromagnetic radiation in molecules.
- Become familiar with the vibrational states and the corresponding transitions among them for di- and poly-atomic molecules.
- Understand that vibrational transitions lead the interactions with infrared light via Raman scattering, and learn how to exploit this knowledge for practical applications.

### 10.1 Basics of molecular spectroscopy

We start this lecture by presenting the basic aspects of the interactions between light and molecules. As mentioned above, the term *spectroscopy* stands for the study of the interactions between electromagnetic radiation and matter. This interaction can take place in two ways:

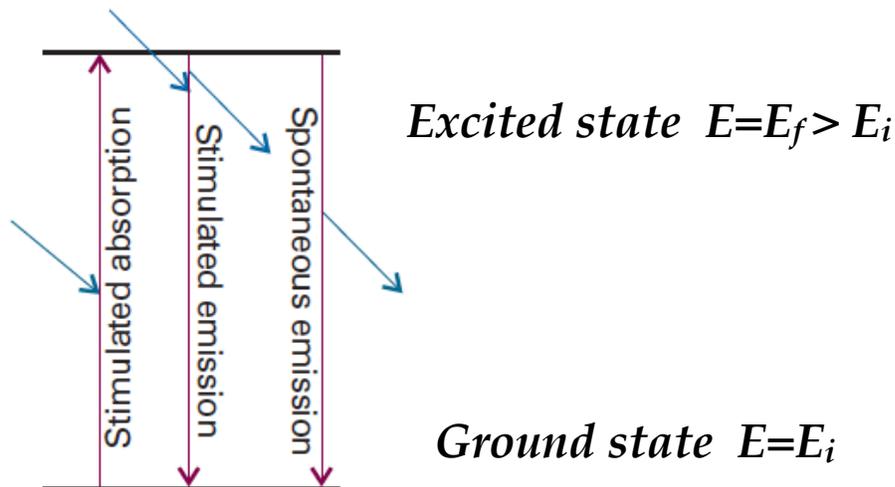


Figure 10.1: Schematic representation of the possible interactions between light and matter for a two-level quantum system, defined by a ground state with energy  $E_i$  and an excited state with energy  $E_f > E_i$ .

- by *absorption* of electromagnetic radiation by matter,
- or by the complementary process, the *emission* of electromagnetic radiation. This emission can be either *spontaneous* or *stimulated*, as we explain below.

Let us start by considering a *two-level system*, represented in Fig. 10.1. This is a quantum system in which a given particle, say an electron in a molecular orbital, can only occupy *two quantum states*, one with energy  $E_i$ , called the *ground state*, and the other with energy  $E_f$  with  $E_f > E_i$ , called the *excited state*. In this system, *spontaneous emission* of electromagnetic radiation (in the absence of external radiation) will take place via the transition  $E_f \rightarrow E_i$ , that is, where the system moves from the excited state to the ground state. By energy conservation, the energy of the emitted photon will be

$$E_\gamma = h\nu = E_f - E_i, \quad \text{and thus} \quad \nu = (E_f - E_i) / h \quad (10.1)$$

will be the frequency of the emitted radiation by this system.

The complementary process to spontaneous emission is that of the *stimulated absorption* of a photon with energy  $E_\gamma = (E_f - E_i)$ , which excites the system from the ground state  $E_i$  to the excited state  $E_f$ . This process has an associated *transition rate* given by

$$w_{f \leftarrow i} = B_{fi} \rho(\nu), \quad (10.2)$$

where  $w_{f \leftarrow i}$  stands for the number of transitions  $i \rightarrow f$  which take place per unit time and per molecule in the system,  $B_{fi}$  is known as the *Einstein coefficient* for stimulated absorption, and  $\rho(\nu)$  is the *spectral energy density* of the isotropic radiation field at the frequency  $\nu$  of the transition, in other words, the density of states available for a photon of frequency  $\nu$ . From Eq. (10.2), we can derive that the *total number of*

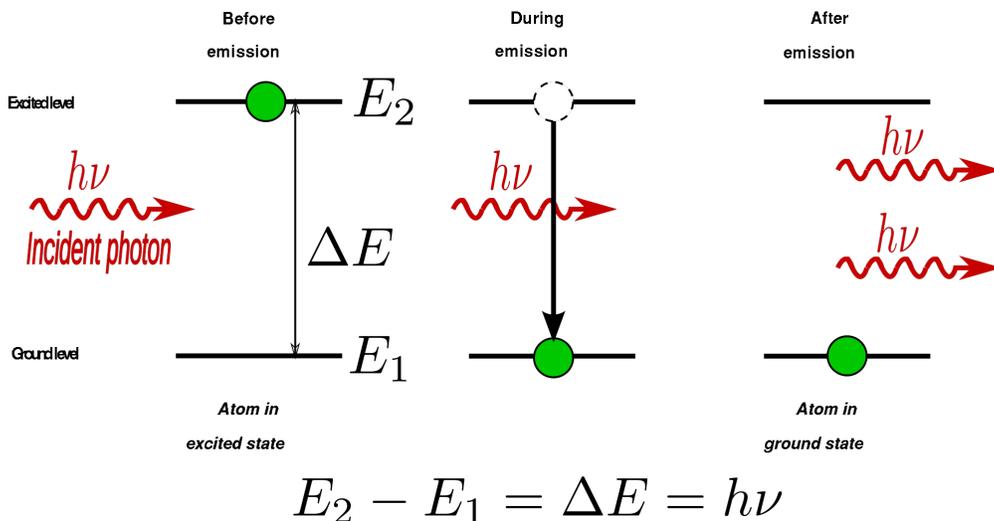


Figure 10.2: Stimulated emission of electromagnetic radiation in a two-level quantum system. The system is found in the excited state  $E_2$ , and as result of the interaction with an incident photon with energy  $E_\gamma = h\nu = E_2 - E_1$ , the system ends up in the ground state and *two photons* with energy  $E_\gamma$  are emitted from the system.

*stimulated absorptions*  $W_{f \leftarrow i}$  that take place in our system is

$$W_{f \leftarrow i} = N_i w_{f \leftarrow i} = N_i B_{fi} \rho(\nu), \quad (10.3)$$

where  $N_i$  is the number (or its density) of molecules in the system in the ground state.

The spontaneous emission of photons is not the only possible way to induce a  $f \rightarrow i$  transition in our system. In the presence of external electromagnetic radiation (incoming photons) in our two-level system, as illustrated in Fig. 10.2, an *stimulated emission* of a photon will also take place, and the associated transition rate is

$$w_{f \rightarrow i} = B_{if} \rho(\nu), \quad (10.4)$$

where  $B_{if}$  is the *Einstein coefficient for stimulated emission*. Note that the difference between spontaneous and stimulated emission is that in the latter case the system of molecules is already in the presence of electromagnetic radiation with frequency Eq. (10.1). In contrast, *spontaneous emission* of a photon corresponds to the case where no external electromagnetic radiation is incident in our system.

Now, we will show below that  $B_{fi} = B_{if}$ . Therefore we find that in *thermal equilibrium*, where the transition rate  $i \rightarrow j$  must be the same as that of  $j \rightarrow i$  (else the system would not be in equilibrium), and ignoring the effects of spontaneous emission, one has that

$$W_{f \leftarrow i} = W_{i \leftarrow j} \quad \rightarrow \quad N_i = N_j, \quad (10.5)$$

that is, the population of the ground and the excited state is the same. This is in contradiction with thermodynamics, since according to the Boltzmann distribution the occupation number of a state with

energy  $E$  at temperature  $T$  should be

$$N(E) \sim \exp\left(-\frac{E}{k_B T}\right), \quad (10.6)$$

with  $k_B$  being Boltzmann constant, and then the ratio between the population of a state with energy  $E_f$  and another one with density  $E_i$  should be classically be given by

$$\frac{N_f}{N_i} = \exp\left(-\frac{(E_f - E_i)}{k_B T}\right), \quad (10.7)$$

which is inconsistent with Eq. (10.5).

As the reader might have imagined, the incorrect assumption in the derivation above has been neglecting the effects of spontaneous emission. The rate of this process is given by  $A$ , the *Einstein coefficient for spontaneous emission*, which is independent of  $\rho$ . Therefore, the total rate for electromagnetic emission in our system per molecule will be given by the sum of the rates for spontaneous and stimulated emission,

$$w_{f \rightarrow i} = A + B_{if}\rho. \quad (10.8)$$

Therefore, in thermal equilibrium, where populations of the two levels,  $N_i$  and  $N_f$ , do not vary with time, we find that

$$N_i B_{fi} \rho(\nu) = N_f (A + B_{if} \rho)(\nu), \quad (10.9)$$

and therefore we obtain the following condition on the density of states for photons of frequency  $\nu$ ,

$$\rho(\nu) = \frac{N_f A}{N_i B_{fi} - N_f B_{if}} = \frac{A/B_{fi}}{N_i/N_f - B_{if}/B_{fi}} = \frac{A/B_{fi}}{e^{h\nu/k_B T} - B_{if}/B_{fi}}, \quad (10.10)$$

where in the last step we have used the condition that  $N_f/N_i$  should be determined by the Boltzmann distribution Eq. (10.7).

For electromagnetic radiation off a black body, or in other words, for electromagnetic radiation in thermal equilibrium at temperature  $T$ , we know that the density of states for photons of energy  $\nu$  is given by *Planck's distribution*,

$$\rho(\nu) = \frac{8\pi h\nu^3/c^3}{e^{h\nu/k_B T} - 1}, \quad (10.11)$$

and then the comparison with Eq. (10.10) allows us to identify  $B_{fi} = B_{if} \equiv B$  as well as to determine the Einstein coefficient for spontaneous emission, which is given by

$$A = \left(\frac{8\pi h\nu^3}{c^3}\right) B. \quad (10.12)$$

There are a number of important implications of this derivation:

- The Einstein coefficients for stimulated absorption and emission are *identical*.
- The Einstein coefficient  $A$  for spontaneous emission is proportional to  $B$ , that of spontaneous emission.
- Since  $A \sim \nu^3$ , we find that *spontaneous emission becomes important for high frequencies, i.e.* is important for light emission but much less for radio emission.

**Selection rules** In general, not all transitions that are consistent with energy conservation will be allowed in a given quantum system. There are two main conditions for emission and absorption to take place for a specific quantum system, and these are:

- (a) *Resonance*: the energy of the photon must be the same as the difference in energy between ground level and the excited state,  $h\nu = E_f - E_i$ .
- (b) *Selection rules*: conditions on the quantum numbers of the states  $f$  and  $i$  which restrict the allowed transitions, arising for instance from the conservation of angular momentum (since the photon is a spin-1 particle).

Let us briefly recall the origin of these selection rules. The interactions between matter and electromagnetic radiation can be described in quantum mechanics using the *time independent perturbation theory*, since the EM field oscillates in time. Classically, for a molecule to interact with an electromagnetic field and emit or absorb a photon with frequency  $\nu$ , it must possess, even if for a short amount of time, a *dipole* oscillating at that frequency. In quantum theory, the corresponding Hamiltonian for this interaction is

$$\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)}(t) \quad \hat{H}^{(1)}(t) = -\mu_z \mathcal{E} \cos(\omega t), \quad (10.13)$$

where  $\hat{H}^{(1)}(t)$  is the interaction term between the oscillating electric field of frequency  $\omega$  and amplitude  $\mathcal{E}$  and the molecular dipole moment  $\mu_z$ . Assuming that the perturbation is switched on at  $t = 0$ , it is possible to show that the rate of change of the population of the quantum state  $\Psi_f$  due to transitions from  $\Psi_i$  induced by  $\hat{H}^{(1)}(t)$  (where  $\Psi_f$  and  $\Psi_i$  are eigenstates of the time-independent Hamiltonian  $\hat{H}^{(0)}$ ) is given by

$$w_{f \leftarrow i} \propto |H_{fi}^{(1)}|^2 \quad H_{fi} = \int \Psi_f^* \hat{H}^{(1)}(t) \Psi_i d\tau, \quad (10.14)$$

which in the case of electromagnetic radiation corresponds to

$$w_{f \leftarrow i} \propto |\mu_{fi}|^2 \mathcal{E}^2 \quad \mu_{fi} = \int \Psi_f^* \hat{\mu}_z \Psi_i d\tau, \quad (10.15)$$

and therefore the rate of this transition is proportional to the square of the *transition dipole moment*  $\mu_{fi}$ . For  $\mu_{fi} = 0$ , the rate vanishes and thus such specific transition is not allowed. This is the main condition that underlies the selection rules for electronic transitions in a molecule. Recall that for atoms we have that

$$\hat{\mu} = -e\vec{r}, \quad (10.16)$$

so that its components are  $\mu_x = -ex$  and so on, and a similar expression holds for molecules but summing over all its individual components.

As we have mentioned, electronic transition can only take place if the dipole matrix element is different from zero,  $\mu_{fi} \neq 0$ . Qualitatively,  $\mu_{fi} \neq 0$  corresponds of a modification in the *geometric distribution of the electric charge* within a given atomic state. For example, the transition  $1s \rightarrow 2s$  does not have associated charge shape redistribution, so  $\mu_{fi} = 0$  and this transition is not allowed. On the other hand, for the transition  $1s \rightarrow 2p$  there is a charge redistribution, so  $\mu_{fi} \neq 0$  and this this transition is allowed. This is illustrated in Fig. 10.3, which represents the changes in the electric charge distribution in the  $1s \rightarrow 2s$  transition (forbidden) and in the  $1s \rightarrow 2p$  transition (allowed).

### Selection rules for electronic transitions

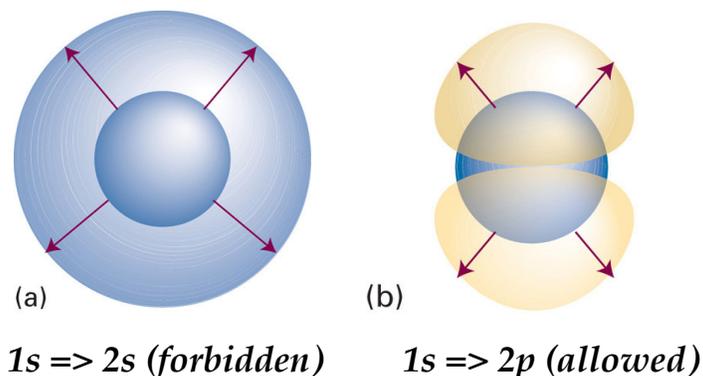


Figure 10.3: In electronic transitions, only those transitions which involve a charge redistribution, and thus a non-zero value of the electric dipole moment matrix element  $\mu_{fi}$ , are allowed by the selection sum rules. For instance, the  $1s \rightarrow 2s$  transition (left plot) does not involve a change of shape of the charge distribution, and thus is forbidden, unlike the  $1s \rightarrow 2p$  transition which is instead allowed.

**The Beer-Lambert law** From the *macroscopic point of view*, absorption of electromagnetic radiation can be described by the so-called *Beer-Lambert law*, which states that

$$I = I_0 10^{-\epsilon[J]L}, \quad (10.17)$$

where  $I_0$  and  $I$  are the intensities of the electromagnetic radiation beam before and after crossing a material,  $[J]$  is the concentration of absorbing molecules,  $\epsilon$  is the *molar absorption coefficient*, also now as *extinction coefficient*, and  $L$  is the *optical path length* (which differs from the geometrical path length in mediums other than vacuum). In other words, the Beer-Lambert law states that absorption increases exponentially with the optical path length  $L$ , the molar absorption coefficient  $\epsilon$  (which is specific of the material) and the concentration of absorbing molecules. It then follows that the *absorbance* of the sample is given by

$$A \equiv \log \frac{I_0}{I} = \epsilon[J]L. \quad (10.18)$$

Similarly, a transmission coefficient  $T = I/I_0$  can be defined, which related to the absorbance as  $A = -\log T$ .

This law can be derived as follows: consider the change of intensity of the incident electromagnetic radiation over an infinitesimal length,

$$dI = -\kappa[J]I dx, \quad (10.19)$$

where  $\kappa$  is an undetermined proportionality constant. Integrating over the total length  $L$ , and redefining  $\epsilon = \kappa/10$ , the sought-for result Eq. (10.17) is recovered. The molar absorption coefficient  $\epsilon$  depends on the wavelength of the incident light. Thus for some applications it is advantageous to define an *integrated absorption coefficient*  $\mathcal{A}$  as follows

$$\mathcal{A} = \int \epsilon(\nu) d\nu, \quad (10.20)$$

which takes into account the contribution to the total absorption from all relevant frequencies.

**Summary of this section** In this part of the lecture we have seen that:

- The Einstein coefficients  $A$ ,  $B_{fi}$  and  $B_{if}$  describe the (spontaneous and stimulated) absorption and emission of electromagnetic radiation (photons) in a two-level quantum system.
- The Einstein coefficients for stimulated absorption and emission are equal  $B_{fi} = B_{if} = B$ .
- The Einstein coefficient for spontaneous emission  $A$  is proportional to both  $B$  and to  $\nu^3$ , and thus spontaneous emission can be neglected for long wavelengths.
- The selection rules determine which transitions between atomic levels are allowed. Only those transitions for which the dipole matrix element  $\mu_{fi} \neq 0$  are possible. The condition  $\mu_{fi} \neq 0$  can be understood as a redistribution of the geometrical charge configuration.
- The Beer-Lambert law can be used to describe macroscopically the phenomenon of the absorption of electromagnetic radiation

## 10.2 Vibrational modes and light interaction in diatomic molecules

We now discuss the important topic of *vibrational modes* and their interaction with electromagnetic radiation in molecules, a topic known as *vibrational spectroscopy*. To begin with, we will restrict ourselves to *diatomic molecules*, and then move to more complex poly-atomic molecules.

As a representative diatomic molecule, we can consider ionized deuterium,  $H_2^+$ . The potential energy of the ionized deuterium molecule can be represented by a potential  $V(r)$  of the form of Fig. 10.4, where  $r$  is the distance between the atoms that constitute the molecule, the proton and the neutron. This potential is characterized by an equilibrium distance  $r_e$  where it has an absolute minimum (thus  $V'(r = r_e) = 0$ ), so that for smaller or larger values of the inter-atomic separation  $r$  the potential energy increases. This potential is known as the *Morse potential*, and can be described by the equation

$$V(r) = D_e \left(1 - e^{-a(r-r_e)}\right)^2, \quad (10.21)$$

where  $r$  is the inter-atomic distance,  $r_e$  the equilibrium distance,  $a$  is a parameter that determines the width of the potential well, and  $D_e$  is the *dissociation energy*, the energy above which the molecule separates into its two constituents atoms separately (in other words,  $r \rightarrow \infty$ ). When  $r \rightarrow 0$  the potential becomes highly repulsive, in this case due to nuclear effects that present the neutron and the proton to be too close to each other.

For small deviations of  $r$  with respect the equilibrium position, the Morse potential reduces to the *harmonic oscillator potential*. Indeed, starting from Eq. (10.21) we find that that

$$V(r = r_e) = 0 \quad (10.22)$$

$$\frac{dV(r)}{dr} = 2D_e \left(1 - e^{-a(r-r_e)}\right) \left(-ae^{-a(r-r_e)}\right) = 0 \rightarrow r = r_e \quad (10.23)$$

$$\frac{d^2V(r)}{dr^2}(r = r_e) = 2a^2D_e, \quad (10.24)$$

and therefore the Taylor expansion of the Morse potential up to second order reads

$$V(r) \simeq a^2D_e (r - r_e)^2 + \mathcal{O}\left((r - r_e)^3\right), \quad (10.25)$$

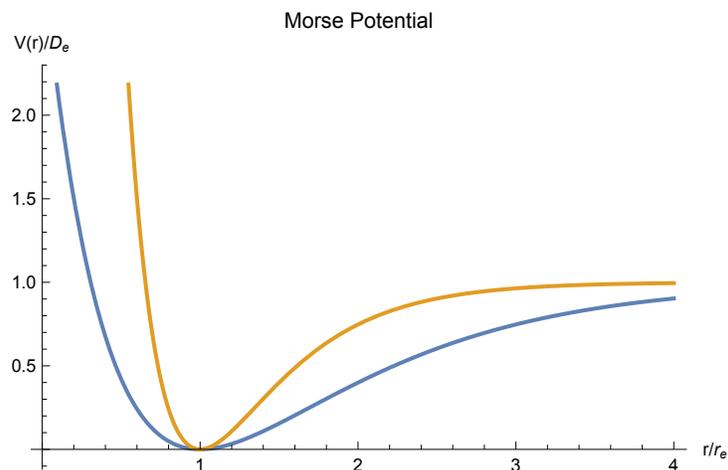


Figure 10.4: The Morse potential  $V(r)/D_e$  Eq. (10.21) as a function of  $r/r_e$ , for two values of the parameter  $a$ . We note that when the separation is large,  $r \gg r_e$ , the Morse potential  $V(r)$  tends to the dissociation energy  $D_e$ : even small energy fluctuations can break the molecule in this limit. For small values of  $r$  the Morse potential becomes highly repulsive because of strong nuclear force effects.

which can be identified with an harmonic oscillator potential, such as the one we studied in some detail in HC3, with spring constant now set to  $k_f = 2a^2 D_e$ . In other words, the larger the value of  $a$ , the *stiffer* the potential between the two atoms that form the diatomic molecule. Therefore, the vibrational modes of a diatomic molecule can be described to good approximation by the quantum states of a quantum harmonic oscillator of spring constant  $k_f = 2a^2 D_e$ .

In HC3, we showed that the Schrodinger equation for a quantum harmonic oscillator was

$$-\frac{\hbar^2}{2m_{\text{eff}}} \frac{d^2\Psi}{dx^2} + \frac{1}{2}k_f x^2 \Psi = E\Psi, \quad (10.26)$$

where since vibrations are with respect the center of mass of the diatomic system, the effective mass is given by the reduced mass  $m_{\text{eff}} = m_1 m_2 / (m_1 + m_2)$ . The energies of the quantum harmonic oscillator are quantized and given by

$$E_n = \left(n + \frac{1}{2}\right) \hbar\omega, \quad \omega = \sqrt{\frac{k_f}{m_{\text{eff}}}}, \quad (10.27)$$

and thus the quantum states are equally spaced in energy among them. Eq. (10.27) can be rewritten as

$$E_n = hc\tilde{G}_n, \quad \tilde{G}_n \equiv \left(n + \frac{1}{2}\right) \tilde{\nu}, \quad \tilde{\nu} = \frac{1}{2\pi c} \left(\frac{k_f}{m_{\text{eff}}}\right)^{1/2}, \quad (10.28)$$

which is sometimes useful since now  $G_n$  has units of *wave numbers*, that is, units of inverse length. The angular frequency of the oscillations is given by  $\omega$ . What is the order of magnitude for frequencies associated to these transitions between different vibrational states in a diatomic molecule? In the case of the HCl molecule for instance, we have that the effective spring constant is found to be  $k_f = 520 \text{ N/m}$ , and then it is possible to show that  $\lambda \simeq 3.4 \mu\text{m}$ , which corresponds to the *infrared region* of the electromagnetic spectrum. Therefore, molecular vibrational modes can be explored by means of *infrared (IR) spectroscopy*.

As in the case of transitions between electronic states, also for the transitions between vibrational states that involve the emission or absorption of a photon there exist a number of *selection rules* that restrict the

allowed transitions. As in the case of individual atoms, the allowed transitions will be determined by the dipole moment matrix element

$$\vec{\mu}_{fi} = \int \Psi_i^* \hat{\vec{\mu}} \Psi_i d\tau \quad (10.29)$$

where in the case of molecules the dipole moment operator reads

$$\hat{\vec{\mu}} = \sum_{i=1}^N q_i \vec{r}_i, \quad (10.30)$$

and the sum runs over the components of the system. In atoms, only transitions for which  $\vec{\mu}_{fi} \neq 0$ , and thus involving a charge redistribution, were allowed. For infrared transitions between vibrational states of a molecule, the condition for allowed transitions is that the electric dipole moment of the molecule changes when the atoms are displaced relative to each other. From the harmonic oscillator, we know that the selection rules tells us that  $\Delta n = \pm 1$ , with  $n$  the principal quantum number, which involve a change in wave number of

$$\Delta \tilde{G}_n = \tilde{G}_{n+1} - \tilde{G}_n = \tilde{\nu}, \quad (10.31)$$

which is of course independent of  $n$ . At room temperatures we have that  $KT/hc \simeq 200 \text{ cm}^{-1}$ , so this will be the typical wave number of infrared absorptions by vibrational modes. Since from thermodynamics we know that the ground state  $n = 0$  will be the one with higher occupation, this implies that infrared absorption by molecules will be dominated by the fundamental transition  $1 \leftarrow 0$ .

**Anharmonicity** While for small values of  $n$  the harmonic approximation Eq. (10.25) to the Morse potential Eq. (10.21) is reasonable, for excited states with high values of the quantum number  $n$  eventually the quadratic approximation will break down. To see this, let us first of all rewrite the Morse potential as

$$V(r) = hc\tilde{D}_e \left(1 - e^{-a(r-r_e)}\right)^2, \quad a = \left(\frac{m_{\text{eff}}\omega^2}{2hc\tilde{D}_e}\right)^2. \quad (10.32)$$

Then, as  $n$  is increased, the energy levels become more densely packed, as opposed to the result with the quadratic potential where  $\Delta E_n = E_{n+1} - E_n = \hbar\omega$  was constant and independent of  $n$ . It can be shown that the energy of the harmonic oscillator for larger values of  $n$  is better approximated by

$$G_n = \left(n + \frac{1}{2}\right)\tilde{\nu} - \left(n + \frac{1}{2}\right)^2 x_e \tilde{\nu}, \quad x_e \equiv \frac{a^2 \hbar}{2m_{\text{eff}}\omega} = \frac{\tilde{\nu}}{4\tilde{D}_e}, \quad (10.33)$$

and  $x_e$  is defined as the *anharmonicity constant*, which quantifies the deviations of the energy of the vibrational modes of a diatomic molecule with respect to the quadratic approximation. What this means is that now the differences in *wavenumber* between two adjacent quantum states will be given by

$$\Delta \tilde{G}_n \equiv \tilde{G}_{n+1} - \tilde{G}_n = \tilde{\nu} - 2(n+1)x_e \tilde{\nu} + \mathcal{O}(n^2), \quad (10.34)$$

so we see that for high values of  $n$  the separation between adjacent energy levels will be reduced due to these anharmonicity effects. We also note that anharmonicity also leads to the *partial lifting of the  $\Delta n = \pm 1$  selection rule* for vibrational modes, since that rule was derived assuming an harmonic potential.

## Normal vibration modes

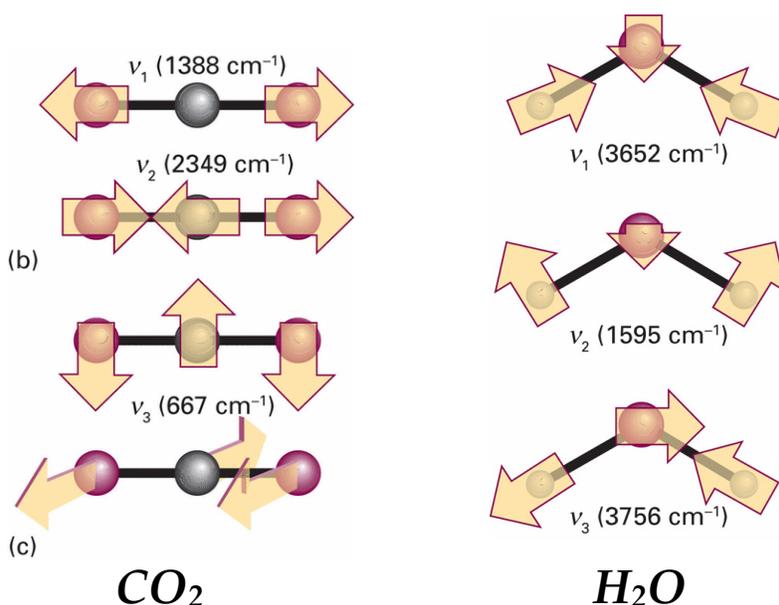


Figure 10.5: Some of the normal vibration modes that appear in  $CO_2$  (left plot) and in  $H_2O$  (right plot) molecules, where we also indicate the associated value of the wave number associated to each mode. In the case of  $CO_2$ , the first two modes are known as *symmetric stretch* and *antisymmetric stretch* respectively, while the two bottom ones are the *bending modes*.

### 10.3 Vibration modes and light interaction in poly-atomic molecules

Up to here the discussions concerning the vibration modes in the simplest possible molecules, the diatomic molecules. Next we turn to discuss the effects of vibrational models in more complex molecules composed by more than two atoms. In molecules composed by two atoms, there can only be *one possible vibration mode*, corresponding to vibrations with respect to the equilibrium position of the inter-atomic potential. On the other hand, for a molecule composed by  $N$  atoms, in general we can have up to  $3N - 5$  *vibrational modes*. Of particular interest are the so called *normal modes* of vibration, which is another name of the *independent vibration modes*. In other words, the excitation of a normal vibration mode, which affects the motion of a number of atoms, does not lead to the excitation of any other normal mode or group of atomic motions.

An suitable example of a poly-atomic molecule is carbon dioxide,  $CO_2$ . Since this molecule has three atoms,  $N = 3$ , it will be characterized by  $3N - 5 = 4$  normal modes. An interesting question here is: can the first and the third atom in the molecule vibrate in a fully independent way? As illustrated in Fig. 10.5, there are various possible vibration models of the  $CO_2$  molecule. The first two modes are known as *symmetric stretch* and *antisymmetric stretch* respectively, while the two bottom ones are the *bending modes*. We also indicate the associated value of the wave number associated to each mode. Every normal mode behaves as a *fully independent harmonic oscillator*, characterized by their own set of vibrational energy levels,

$$\tilde{G}_q(n) = \left(n + \frac{1}{2}\right) \tilde{\nu}_q \quad \tilde{\nu}_q = \frac{1}{2\pi c} \left(\frac{k_q}{m_q}\right)^{1/2}. \quad (10.35)$$

Given that the selection rules require a *change in the electric dipole moment* to activate a given vibration

mode, we see that the *symmetric stretch* mode is infrared active (since the electric dipole moment is unchanged) but that on the other hand the other three normal modes of the CO<sub>2</sub> molecule are IR active. So therefore not all possible vibrational modes of a molecule can be probed with infrared spectroscopy.

## 10.4 Raman spectroscopy

Raman spectroscopy is based on the scattering via molecules of incident monochromatic light. With this technique the vibrational and rotational modes of a molecule can be observed. The inelastic scattering of the incoming Raman photons with these vibrational states changes the energy of the scattered photon, which then can be detected providing information on the vibrational spectrum of the molecule (for example allowing to identify which kind of molecules we have in our system). The vibrational transitions underlying Raman scattering are represented in Fig. 10.6. If the outgoing photon has a higher energy than the incoming radiation, the associated transition is called a *anti-Stokes* transition, and in the opposite case they have a Stokes transition.

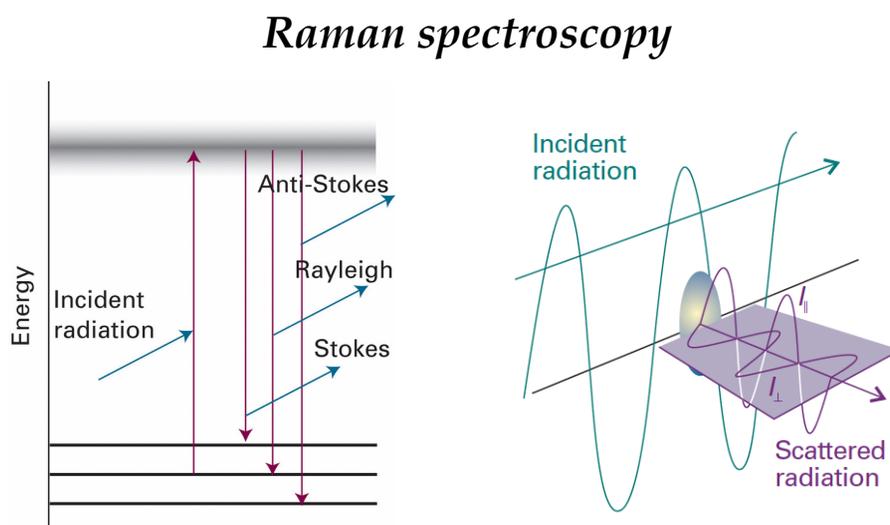


Figure 10.6: Schematic representation of Raman spectroscopy: incident monochromatic radiation undergoes inelastic scattering with the vibrational energy levels of a molecule, and thus in general the outgoing photon will have both different energy and polarization as the incoming photon (as shown in the right plot).

Also in Raman scattering only transitions that comply with a set of *selection rules* will be physically allowed. For instance, in general if the molecular vibrational state changes due to the Raman scattering the polarizability of the molecule will be also modified. As a rule of thumb, weak infrared transitions will lead to strong Raman transitions, and conversely. We know that in the quantum harmonic oscillator the selection rule  $\Delta n = \pm 1$  should hold. Transitions with  $\Delta n = +1$  are the Stokes transitions and those with  $\Delta n = -1$  are the anti-Stokes one, that in general will have associated low intensities since higher vibrational states are scarcely populated at room temperatures.

What is the main difference then between Raman spectroscopy and IR spectroscopy? That in the latter case the motion corresponding to a normal mode should be accompanied by a change of the electric dipole moment, while in the former case we require instead a change in the molecule's *polarizability* as it changes its vibrational state. Therefore we can probe complementary vibration modes in Raman as compared to

IR spectroscopy. And here a useful *exclusion rule* follows: if a molecule has a centre of symmetry, then no normal modes can be at the same time infrared and Raman active.

A specific example of Raman spectroscopy is known as *resonant Raman spectroscopy*, where the incident radiation has a frequency corresponding to almost the actual electronic excitation of the molecule. In these conditions, a photon is emitted when the excited state returns to a state close to the ground state.

**Vibrational spectroscopy of molecules** To summarize, some of the important concepts that we have learned in the second part of this lecture, about vibrational modes in diatomic and poly-atomic molecules, are the following:

- The quantum vibrational states of molecules can be modeled using the harmonic oscillator with a given effective mass and effective spring constant  $k_f$  upon approximating the inter-atomic potential by a quadratic expansion.
- There are *selection rules* which restrict the vibrational transitions, and only those that change the electric dipole moment of the molecule are allowed.
- For excited vibrational states, deviations of the quadratic potential become important, and are quantified by  $x_e$ , the anharmonicity constant.
- In a poly-atomic molecule, the normal modes represent the independent motion of groups of atoms, and each normal mode can be treated as fully independent harmonic oscillator.
- Raman spectroscopy can be used to probe some of the infrared transitions between vibrational modes of a molecule that cannot be accessed by IR spectroscopy.

## 11 HC11: Molecular spectroscopy and electronic transitions



### van Quantum tot Molecuul

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Molecular Spectroscopy and Electronic Transitions

Based on Atkins and de Paula, *Physical Chemistry* 10th edition, Chapter 13

In this lecture, we will study electronic transitions in *p-electron conjugate systems*, the Franck-Condon principle, the physics underlying the phenomena of *fluorescence* and *phosphorescence*, as well as the basic principles of operation of a *laser*. We will also present an application of these ideas in the medical context, namely the *photo-dynamic therapy* (PDT).

The *learning goals* of this lecture are:

- (a) Understanding and applying  $\pi$ - $\pi^*$  electronic transitions in molecules.
- (b) Understanding which electronic transitions can take place for either absorption or emission of a photon while the atomic nuclei are at rest (the Franck-Condon principle), including the mathematical description and implications of absorption and emission spectra.
- (c) Understanding and applying the principles of fluorescence and phosphorescence.
- (d) Understanding the basic principles that underlie the operation of a laser, such as the concept of population inversion.

### 11.1 Electronic transitions in molecules

In HC10 we studied the transitions between different vibrational states of a molecule. We now consider instead the *electronic transitions* that take place between different electronic states of a molecule. As opposed to vibrational transitions, which were associated to *infrared frequencies*, electronic molecular transitions take place mainly in the *visible and ultraviolet* regions of the electromagnetic spectrum, and therefore, among

## Molecular Orbitals

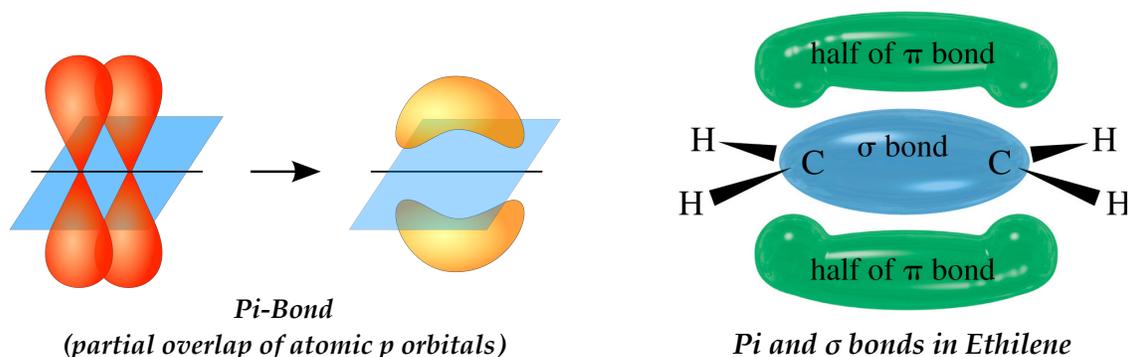


Figure 11.1: Left plot: a  $\pi$ -bond in a molecule is formed by the partial overlap between atomic  $p$ -type orbitals. Right plot: the bonding structure of ethylene,  $C_2H_4$ , showing a  $\sigma$  bond between the two  $C$  atoms (rotationally symmetric with respect to the bond axis) and the two halves of the  $\pi$  bond arising from the  $p$  atomic orbitals.

the many important properties of these transitions, they are also responsible of the *color* of materials and substances.

**Molecular orbitals** It is useful at this point to recall some important properties of *molecular orbitals*. We know that that electronic orbitals in atoms can have different principal quantum numbers:  $s$ ,  $p$ ,  $d$  and so on. In molecules, under the right circumstances, the electrons might become *de-localized* by means of the overlap between individual atomic orbitals, that is, they cannot be assigned to any of the specific components of the molecule.

The strongest type of *chemical covalent bonds* in molecules are known as  $\sigma$ -bonds, formed by a head-on overlapping between atomic orbitals leading to a molecular orbital. The key property of this bond is that the resulting orbitals are *rotationally symmetric with respect to the bond axis*. Another important type of molecular bonds are the so-called  $\pi$ -bonds, covalent chemical bonds where two lobes of one atomic orbital overlap with the two lobes of another atomic orbital, resulting in the bonding between the two atoms. In Fig. 11.1 we show how a  $\pi$ -bond in a di-atomic molecule is formed by the partial overlap between atomic  $p$ -type orbitals. In the same figure we also show the bonding structure of the ethylene molecule,  $C_2H_4$ , showing a  $\sigma$  bond between the two  $C$  atoms (rotationally symmetric with respect to the bond axis) and the two halves of the  $\pi$  bond arising from the  $p$  atomic orbitals.

In this lecture we will focus on *conjugate p-electron systems*, which denote molecules where atomic  $p$ -type orbitals are connected by means of de-localized electrons, thus giving place to  $\pi$ -type covalent bonds. These molecules are very important in organic chemistry and biology, and the wide majority of light-absorbing molecules, known as *chromophores*, that appear biology are indeed  $p$ -electron conjugate systems.

The electronic transitions within a conjugate  $p$ -electron molecular system are known as the  $\pi \rightarrow \pi^*$  transitions. This is a specific type of molecular electronic transitions, others include the  $\sigma \rightarrow \sigma^*$  and the  $n \rightarrow \sigma^*$  transitions. Here by  $\pi^*$  we indicate an *anti-bonding molecular orbital* of the  $\pi$ -type, that is, a molecular orbital that when occupied by electrons *weakens* the bond between the constituents atoms of the molecule and thus increases (rather than decreases) the energy of the molecule relative to the separated individual atoms. These  $\pi \rightarrow \pi^*$  transitions, involving de-localized  $p$ -orbitals, can be described by *Huckel theory* and are characterized by *strong light absorption*. Recall that *Huckel theory* can be used to construct

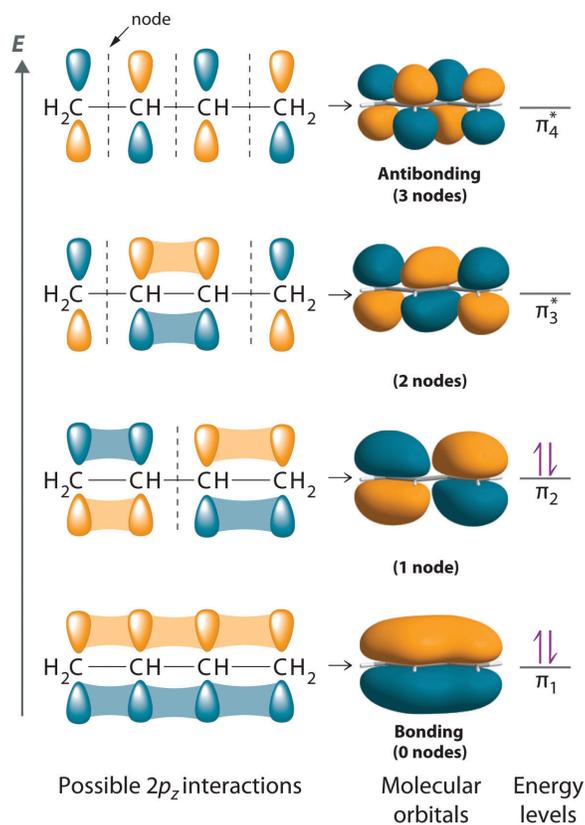


Figure 11.2: Schematic representation of the molecular orbitals of the butadiene molecule,  $C_4H_8$ . The two bottom orbitals are *bonding*  $\pi$  molecular orbitals, while the top two ones are instead *anti-bonding*  $\pi^*$  molecular orbitals. The highest occupied molecular orbital (HOMO) is here  $\pi_2$ , while the lowest unoccupied molecular orbital (LUMO) is instead  $\pi_3^*$ . Note that in the HOMO the two electrons are paired (opposite spins).

linear combinations of atomic orbitals (LCAO) into molecular orbitals to determine the energies of  $\pi$  electrons in general conjugated molecules.

For molecular orbitals, we often make the distinction between *HOMO*, the *highest occupied molecular orbital* and *LUMO*, the *lowest unoccupied molecular orbital*. Let us consider the representative case of the butadiene molecule  $C_4H_6$ . In Fig. 11.2 we show a schematic representation of the molecular orbitals of butadiene. The two bottom orbitals are *bonding*  $\pi$  molecular orbitals, while the top two are instead *anti-bonding*  $\pi^*$  molecular orbitals. The highest occupied molecular orbital (HOMO) is here  $\pi_2$ , while the lowest unoccupied molecular orbital (LUMO) is instead  $\pi_3^*$ . Note that in the HOMO the two electrons are paired, that is, they have opposite spins.

**Allowed molecular transitions** In order to determine which electronic molecular transitions are possible, we need to take into account the corresponding *selection rules*. In the case of individual atoms and of vibrational transitions in molecules, these selection rules have been reviewed in HC10. Similarly as in the case of the selection rules for electronic transitions in individual atoms, also for electronic transitions in molecules, only if the dipole moment matrix element satisfies  $\mu_{fi} \neq 0$  a given transition will be allowed.

Therefore, in the case of electronic transitions between the molecular orbitals of butadiene represented in Fig. 11.2, only those that are characterized by a non-zero electric dipole matrix element,  $\mu_{fi} \neq 0$ , will be

physically allowed. Using the wave function for the molecular orbitals of butadiene, it can be shown that

$$\int \Psi_{\pi_3^*}^* \hat{\mu} \Psi_{\pi_2} d\tau \neq 0, \quad (11.1)$$

and therefore a transition between the HOMO and LUMO levels, that is, a  $\pi \rightarrow \pi^*$  transition, is allowed. This transition will have associated the absorption of visible light by the butadiene molecule. It can also be shown that if  $x$  is the molecular bonding axis, only  $\mu_{x,fi} \neq 0$ , while instead  $\mu_{y,fi} = \mu_{z,fi} = 0$ . This has the consequence that the optical transition  $\pi_2 \rightarrow \pi_3^*$  will only be possible for *light polarized along the  $x$  axis*. On the other hand, the absorption of a photon by the HOMO-1 level, that is, the electronic state immediately below HOMO, labeled  $\pi_1$  in Fig. 11.2, resulting into a transition to the LUMO level  $\pi_3^*$  turns out not to be allowed by the selection rules, since all the possible dipole moment matrix elements vanish,

$$\int \Psi_{\pi_3^*}^* \hat{\mu} \Psi_{\pi_1} d\tau = 0. \quad (11.2)$$

By computing the energy of allowed electronic molecular transitions, it can be shown that often organic molecules actually absorb light in the *ultraviolet range*, for instance ethylene absorbs at  $\lambda = 163$  nm while butadiene at  $\lambda = 220$  nm.

**More about electronic molecular transitions** We can now present some additional facts that are important for the understanding of the physics underlying electronic transitions between molecular orbitals:

- In molecular orbitals, the *conjugation length* is defined as the length of the orbital resulting from the partial overlap of atomic  $p$ -orbitals. The more  $p$ -orbitals that contribute to a molecular orbital, the larger its conjugation length will be. This means that an electron that belongs to this orbital will be *more de-localized* the larger the conjugating length of that orbital, since it will be able to *hop* between more atoms that compose the molecule. As a general rule, the greater the conjugation length of a molecular orbital, and thus the greater the amount of de-localization of the electrons that belong to this orbital, the smaller its energy, or in other words, the *stronger its contribution to the molecular bonding*.

Recall that a similar behaviour was observed when studying the particle in a box system using the Schrodinger equation in HC3. There we saw that the energy of the allowed quantum states of the particle scaled with the length of the box  $L$  as  $E \sim L^{-2}$ , in other words, the greater the box (and thus the de-localization) the smaller the energy of the particle, qualitatively the same behaviour as for molecular orbitals.

- Another important type of electronic molecular transitions are the  $n \rightarrow \pi^*$  optical transitions. Recall that by  $n$  we denote the molecular orbital of an *auxochrome*, a functional group of atoms with free (unbounded) electron pairs that when attached to a *chromophore* (that is, a light-absorbing molecule) modifies both the wavelength and intensity of absorption. In some circumstances, an electron might transition between a  $n$  orbital of an *auxochrome* to the  $\pi^*$  orbital of a *chromophore*. In these transitions, the larger the conjugation length, the larger the *extinction coefficient* that determines how strongly this specific molecule will absorb light of a given wavelength.
- It can be shown that there is a direct connection between the value of the dipole moment transition

matrix element  $\mu_{fi}$  and the extinction coefficient  $\epsilon(\nu)$  for light of a given frequency, that determines how strongly this molecule does absorb light of this specific frequency. Intuitively, one could expect that the greater the value of the electric dipole moment transition matrix element  $\mu_{fi}$ , the stronger the absorption of light with wavelengths corresponding to this specific electronic transition. And indeed, the integral over all frequencies of  $\epsilon(\nu)$  is proportional to the square of  $\mu_{fi}$ , in other words

$$\int \epsilon(\nu) d\nu \propto |\mu_{fi}|^2. \quad (11.3)$$

Therefore, for very *narrow* transitions, the extinction coefficient  $\epsilon$  is simply proportional to  $|\mu_{fi}|^2$ .

## 11.2 The Franck-Condon principle

We now turn to discuss the *Franck-Condon principle*, which describes the transitions in which a *simultaneous* change in the vibrational and electronic states of a molecule takes place, due to the emission or absorption of a photon of the appropriate energy. This principle is important to explain the *vibrational fine structure* in the optical absorption spectrum. Recall that vibrational transitions (in the *infrared* range of the EM spectrum) have associated much smaller energies than optical transitions (in the *visible* range), and thus appear in the optical absorption spectrum as small splittings of the main absorption lines. In general, we denote as a *vibronic transition* a transition that involves simultaneous modifications in the vibrational and electronic energy states of a given molecule.

The Franck-Condon (FC) principle states that since nuclei are so much more massive than electrons,  $m_e \ll m_N$ , *electronic transitions* between different quantum states take place at much shorter time-scales than those for which the nuclei can respond, therefore the *vibrational transitions* take place at slower rates. In other words, the probability of an *electronic molecular transition* is the highest where the *relative separation between two atomic nuclei* is unchanged. This phenomenon is thus also known as a *vertical transition*, since in a  $(r, E)$  plane the transition takes place vertically along the  $y$  axis, as shown in Fig. 11.3. As in general in quantum mechanics, the transition probability will be proportional to the overlap between vibrational wave functions in the ground electronic and in an excited electronic states, and it can be shown that this overlap is maximal when the relative separation between nuclei  $r$  is unchanged.

The physical interpretation of the Franck-Condon principle is summarized in Fig. 11.3, where we show a schematic representation of the molecular potential energies for the ground and the excited electronic states in a molecule. This molecular potential energy is nothing by the Morse potential that we discussed in HC10, Eq. (10.21). According to the Franck-Condon principle, the most intense vibronic transitions take place between the ground vibrational state in the electronic ground state to to the vibrational state *lying immediately above it* in the electronic excited state. Transitions to other vibrational states also occur, but with lower intensities.

In the quantum mechanical description of the FC principle, the molecule undergoes a transition to the upper vibrational state that most closely resembles the vibrational wave-function of the vibrational ground state of the lower electronic state. The two wave functions shown here exhibit the greatest overlap and hence the matrix element for the transition probability among them is the highest.

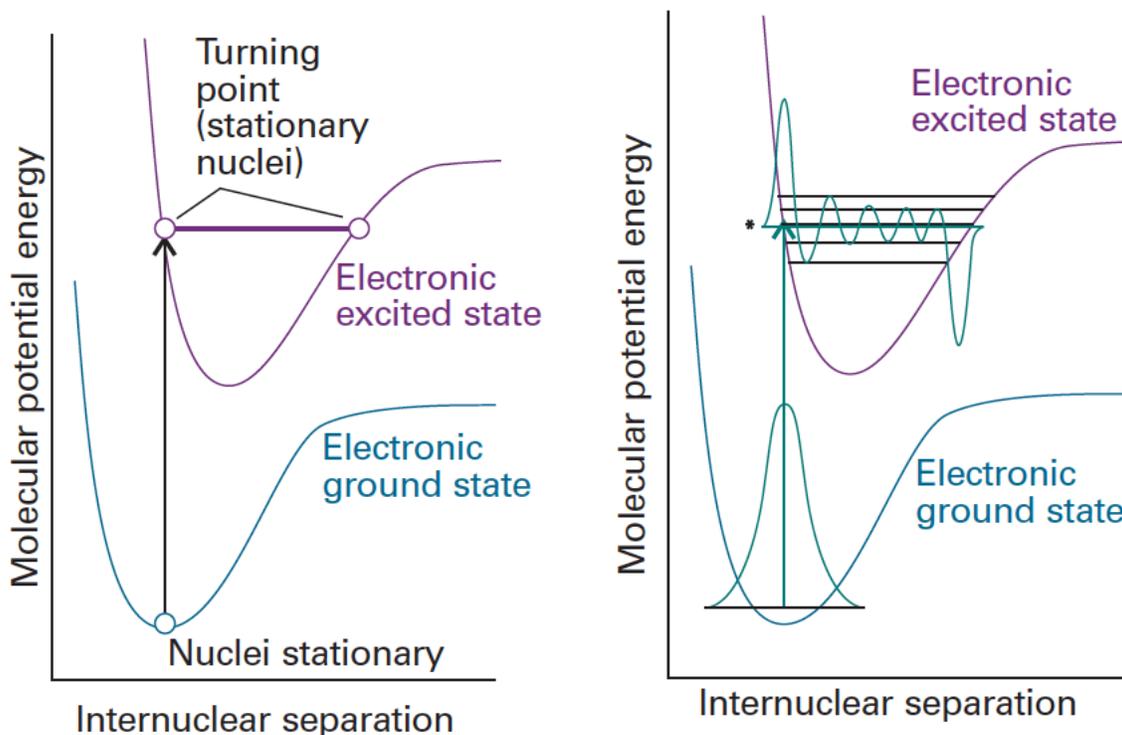


Figure 11.3: Schematic representation of the molecular potential energy (Morse potential Eq. (10.21)) for the ground and the excited electronic states in a molecule. Left plot: according to the Franck-Condon principle, the most intense vibronic transitions takes place between the ground vibrational state in the electronic ground state to the vibrational state lying immediately above it in the electronic excited state, in a way that the *inter-nuclei separation* is kept constant. Transitions to other vibrational states also occur, but this lower intensities. Right plot: in the quantum mechanical description of the FC principle, the molecule undergoes a transition to the upper vibrational state that most closely resembles the vibrational wave-function of the vibrational ground state of the lower electronic state. The two wave functions shown here exhibit the greatest overlap, and hence the matrix element for the transition probability among them is the highest, corresponding to a transition with fixed inter-nuclear separation.

**Dipole matrix element for vibronic transitions** In order to compute the matrix element for the electric dipole moment of such a vibronic transition, we need to take into account the sum of electronic and of nuclear contributions to the total molecular dipole moment operator, that is

$$\hat{\vec{\mu}} = -e \sum_j \vec{r}_j + e \sum_I Z_I \vec{R}_I, \quad (11.4)$$

where  $j$  runs over the electrons and  $I$  over the nuclei in our molecule, and  $Z_I$  is the total positive charge of the nucleus  $I$ . In order to compute the dipole transition matrix element, for both the initial and final states we separate the wave function into its electronic  $\Psi_\epsilon$  and vibrational  $\Psi_\nu$  components. This way the dipole matrix element for a given vibronic transition between an initial  $\Psi_i = \Psi_{\epsilon_i} \Psi_{\nu_i}$  and final  $\Psi_f = \Psi_{\epsilon_f} \Psi_{\nu_f}$  final state, will be given by

$$\vec{\mu}_{fi} = \int \Psi_{\epsilon_f}^* \Psi_{\nu_f}^* \left[ -e \sum_j \vec{r}_j + e \sum_I Z_I \vec{R}_I \right] \Psi_{\epsilon_i} \Psi_{\nu_i} d\tau, \quad (11.5)$$

which can be rearranged as follows:

$$\vec{\mu}_{fi} = -e \sum_j \int \Psi_{\epsilon_f}^* \vec{r}_j \Psi_{\epsilon_i} d\tau_\epsilon \int \Psi_{\nu_f}^* \Psi_{\nu_i} d\tau_\nu + e \sum_I Z_I \int \Psi_{\epsilon_f}^* \Psi_{\epsilon_i} d\tau_\epsilon \int \Psi_{\nu_f}^* \vec{R}_I \Psi_{\nu_i} d\tau_\nu, \quad (11.6)$$

where we have used that the vibrational wave functions  $\Psi_\nu$  depend only on the inter-nuclei separation  $\vec{R}_I$  while the electronic wave functions  $\Psi_{\epsilon_i}$  depend only on the position of the electrons  $\vec{r}_i$ .

The second term in Eq. (11.6) vanishes since the electronic wave functions are *orthogonal among them*,

$$\int \Psi_{\epsilon_f}^* \Psi_{\epsilon_i} d\tau_\epsilon = 0 \quad \text{for } i \neq f, \quad (11.7)$$

but note that this does not apply to the *vibrational wave functions* necessarily, they correspond to different electronic states so they do not need to be orthogonal among them. Taking this property into account, we find that the dipole matrix element can be written as

$$\vec{\mu}_{fi} = -e \sum_j \int \Psi_{\epsilon_f}^* \vec{r}_j \Psi_{\epsilon_i} d\tau_\epsilon \int \Psi_{\nu_f}^* \Psi_{\nu_i} d\tau_\nu \equiv \mu_{\epsilon_f \epsilon_i} S(\nu_f, \nu_i), \quad (11.8)$$

where we have introduced the following definitions:

$$\mu_{\epsilon_f \epsilon_i} \equiv -e \sum_j \int \Psi_{\epsilon_f}^* \vec{r}_j \Psi_{\epsilon_i} d\tau_\epsilon. \quad (11.9)$$

$$S(\nu_f, \nu_i) \equiv \int \Psi_{\nu_f}^* \Psi_{\nu_i} d\tau_\nu. \quad (11.10)$$

The first of these expressions,  $\mu_{\epsilon_f \epsilon_i}$ , corresponds to the *electronic dipole transition matrix element* between two molecular electronic states. The second of these expressions,  $S(\nu_f, \nu_i)$ , corresponds instead to the *overlap between the vibrational wave functions in the ground and in the excited states*. Therefore, the rate for a vibronic transition that involves simultaneously the change in the electronic and vibrational states of a molecule will be proportional to the *Franck-Condon factor*,

$$|S(\nu_f, \nu_i)|^2, \quad (11.11)$$

which states quantitatively what was qualitatively illustrated in Fig. 11.3, namely that the rate for vibronic transitions is maximal when the vibrational wave functions in the ground and excited electronic states resemble the most.

### 11.3 Fluorescence and phosphorescence

We now describe to important phenomena related to light emission by molecules:

- *Phosphorescence* is the *slow emission of light* in molecules, taking place in an interval of *microseconds or more*.
- *Fluorescence* is the *fast emission of light* in molecules, taking place within a time interval of *nanoseconds or less*.

Therefore, these two phenomena related to light emission in molecules have time scales that differ by several orders of magnitude, and now we explain the reason for this behaviour.

**Fluorescence** Let us start by discussing the phenomenon of *fluorescence*. From our discussion of HC10, we can recall a number of important properties of the electronic transitions within the two-level system, represented in Figs. 10.1 and 10.2, in particular we found that:

- The Einstein coefficient for stimulated absorption  $B_{fi}$  was proportional to the integral of the extinction coefficient over the relevant absorption band. It is therefore an intrinsic property of a given molecule.
- The Einstein coefficients for stimulated absorption and emission are identical,  $B_{fi} = B_{if} \equiv B$ .
- The Einstein coefficient for spontaneous emission  $A$  was proportional to both  $B$  and  $\nu^3$ , with  $\nu$  being the frequency of the emitted light:

$$A = \left( \frac{8\pi h\nu^3}{c^3} \right) B, \quad (11.12)$$

implying that spontaneous emission become relevant only at relatively high frequencies.

With these properties, we can compute rate of variation in time of the population of molecules in the excited electronic state  $f$  due to emission and absorption as follows

$$\frac{dN_f}{dt} = -N_f A - N_f B_{if} \rho(\nu) + N_i B_{fi} \rho(\nu). \quad (11.13)$$

In normal circumstances  $\rho(\nu)$ , the density of states of the EM field is small (unless a very powerful illumination is used) and can be neglected. This leaves a simple differential equation which depends only on the probability of spontaneous emission  $A$ ,

$$\frac{dN_f}{dt} = -N_f A \quad \rightarrow \quad N_f(t) = N_0 e^{-At} = N_0 e^{-t/\tau_R}, \quad (11.14)$$

where  $\tau_R = 1/A$  is the *radiative lifetime* of this specific electronic state of the molecule. The higher the rate for spontaneous emission, the smaller the radiative lifetime of the molecule will be. In the absence of other processes that decrease the population of the state  $f$ , the radiative lifetime  $\tau_R$  is equal to the total lifetime of the excited state.

In general however there are other contributions to this process that need to be taken into account. Indeed, the total life time of an excited state  $f$  will receive contributions from various mechanisms, in addition to spontaneous emission. The most important ones are:

- The internal conversion (IC) from an excited vibrational state to the vibrational ground state of a given electronic level, with constant rate  $k_{IC}$ .
- An inter-system crossing (ISC) from a singlet to a triplet state, with constant rate  $k_{ISC}$
- Other processes such as *electron transfer*, with constant rate  $k_Q$ .

To study these electronic transitions within molecules, in general it is useful to use a special type of diagrams known as *Jablonski diagram*, which schematically indicates the transitions that can take place starting from an excited state. In Fig. 11.4 we show the schematic representation of the fluorescence and

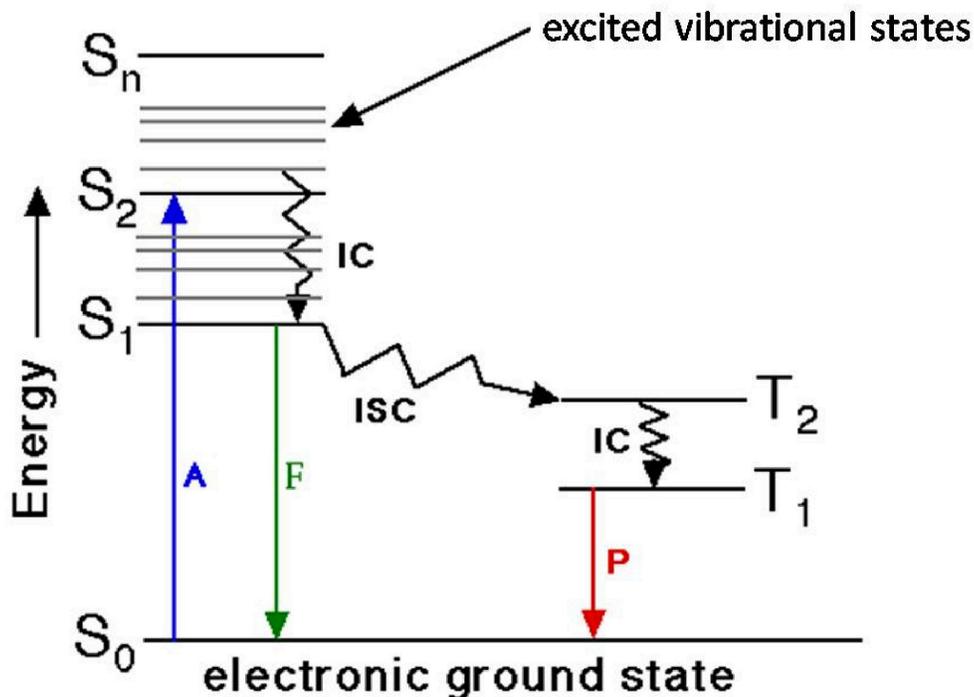


Figure 11.4: Schematic representation of the fluorescence and phosphorescence phenomena by means of the *Jablonski diagram*. In this diagram, *A* indicates the absorption of a photon, *F* and *P* represent the fluorescence and phosphorescence transitions respectively, *S* and *T* denote singlet and triplet states, and finally *IC* and *ISC* label the internal conversion and the inter-system crossing respectively.

phosphorescence phenomena by means of a Jablonski diagram. In this diagram, *A* indicates the absorption of a photon, *F* and *P* represent the fluorescence and phosphorescence transitions respectively, *S* and *T* denote singlet and triplet states, and finally *IC* and *ISC* label the internal conversion and the inter-system crossing respectively.

Let us discuss the Jablonski diagram of Fig. 11.4. First of all, an electron in the electronic ground state absorbs an incoming photon and is promoted to an excited electronic state, as well as to an excited vibrational state. From the internal conversion (*IC*) process, this electron loses energy via non-radiative (vibrational) transitions until it is found in the ground vibrational state of the first excited electronic state  $S_1$ . From there on, two things can happen: either decay to the electronic ground state (*fluorescence*) or a inter-system crossing (*ISC*) to a triplet state, which eventually gives rise to a much slower light emission (*phosphoresce*) since the triplet to singlet transition is suppressed. We therefore see that an important component of the fluorescence process involves the molecule relaxing from an excited vibrational state to the lowest vibrational state via non-radiative transitions.

As a result of the competition between the various processes that de-populate the excited state  $f$ , its total lifetime  $\tau$  will be in general shorter than the radiation lifetime  $\tau_R$ . The *total lifetime of the excited state* is called the *fluorescence lifetime*  $\tau_F$ . Therefore, in general the radiative lifetime will be different (larger) from the fluorescence lifetime. Let us make this statement more quantitative. In the presence of these additional

processes, the *occupancy number* of the electronic state  $f$ ,  $N_f$ , will vary with time as follows:

$$\frac{dN_f}{dt} = -N_f (A + k_{IC} + k_{ISC} + k_Q) \quad \rightarrow \quad N_f(t) = N_0 e^{-(A+k_{IC}+k_{ISC}+k_Q)t}, \quad (11.15)$$

from where we readily see that the fluorescence lifetime  $\tau_F$  will be determined by the sum of the rates of all processes that de-populate  $f$ , namely,

$$1/\tau_F = A + k_{IC} + k_{ISC} + k_Q, \quad (11.16)$$

In the fluorescence process, one usually introduces the *quantum yield*  $\Phi_F$  defined as the number of emitted photons divided by the number of absorbed photons

$$\Phi_F \equiv \frac{\# \text{ Emitted Photons}}{\# \text{ Absorbed Photons}} = \frac{A}{A + k_{IC} + k_{ISC} + k_Q}, \quad (11.17)$$

Let us now take a look at the rates for these various processes in a representative molecule, in this case *chlorophyll*. In this molecule, the rates for the various processes that de-populate the quantum state  $f$  are

$$\begin{aligned} k_R = A &= 0.5 \times 10^8 \text{ s}^{-1} &\rightarrow &\tau_R = 20 \text{ ns} \\ k_{ISC} &= 1.0 \times 10^8 \text{ s}^{-1} &\rightarrow &\tau_{ISC} = 10 \text{ ns} \\ k_{IC} &= 1.5 \times 10^8 \text{ s}^{-1} &\rightarrow &\tau_{IC} = 16.6 \text{ ns} \end{aligned} \quad (11.18)$$

from where the fluorescence lifetime is  $\tau_F = 3.3$  ns, and the fluorescence quantum yield  $\Phi_F = 0.166$ , meaning that for each 100 absorbed photons by the molecule, there will be 16 emitted photons.

As can be seen from the Jablonski diagram in Fig. 11.4, in general fluorescence radiation will correspond to longer wavelengths (that is, smaller energies) than the absorbed light, since the electrons undergo internal transitions losing energy before a photon is radiated. This difference is as known as the *Stokes shift*: the difference, either in wavelength or in wave number, between the absorption and fluorescence emission maxima.

**Phosphorescence** In the *phosphorescence* radiation phenomenon, the molecule goes from a *singlet* excited state to a *triplet* excited state, via the so-called inter-system crossing. as illustrated in Fig. 11.4 (see also the left plot of Fig. 11.7). The resulting triplet states are long-lived, with lifetimes that can range from microseconds to seconds, since a transition to the ground state is forbidden by the selection rules (Pauli exclusion principle). Recall that a *singlet to triplet conversion* is a transition from paired spin to unpaired spin in a given molecular electronic state.

Therefore, as shown in Fig. 11.5, the origin of a *phosphorescence* transition is a transition from a ground singlet state (with paired spins) to the excited LUMO state where the electron spin remains the same. From there, a transition from the excited singlet state to the excluded triplet state via inter-system crossing will take place, since the latter has lower energy due to Hund's rule. This inter-system crossing is enhanced by the spin-orbit coupling, and thus mostly occurs when heavy nuclei are nearby, such as S, Fe or Mg. The longevity of the *phosphorescence* radiation is then explained since the relaxation of a triplet to a singlet ground state is spin-forbidden.

The key property of phosphorescence is that, following light absorption, the subsequent re-emission takes

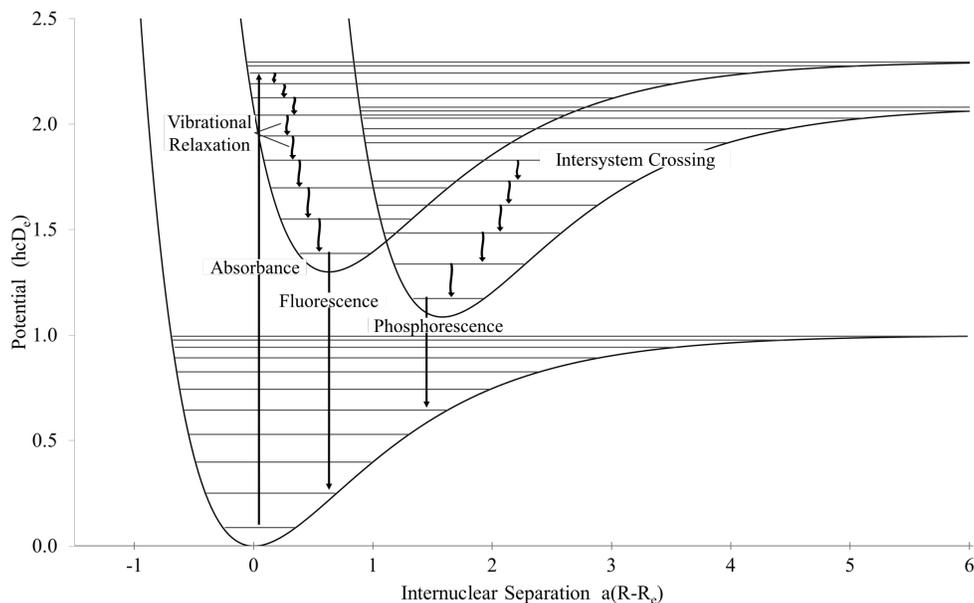


Figure 11.5: In *phosphorescence transitions*, the molecule undergoes an inter-system crossing from a singlet to a triplet state, and the resulting state has a very long lifetime since the relaxation from the excited triplet to the singlet ground state is not allowed by Pauli's exclusion principle.

place at a lower intensity for up to several hours after the original excitation. It is thus a very slow transition.

## 11.4 Lasers

The use of lasers is ubiquitous in spectroscopy, as well as in many forms of microscopy and in a wealth of medical applications. Therefore, it is important to understand how a laser works. The name *laser* was originally an acronym of *Light Amplification by Stimulated Emission of Radiation*, since it is a device that *amplifies the intensity* of the incident electromagnetic radiation. Let us now show how this is possible.

To illustrate how a laser works, we consider first of all the usual two-level system, such as the one depicted in Fig. 10.1. Since the Einstein coefficient for stimulated emission is  $B_{if}$ , the rate of  $f \rightarrow i$  transitions leading to light *stimulated emission* will be given by  $N_f B_{if} \rho(\nu)$ , as we have demonstrated in HC10. Now, a necessary condition for *lasing* is achieving *population inversion* in the system, that is, a situation such that in thermal equilibrium the population of excited states is higher than the population of lower energy states. Only under this condition it will be possible to achieve more stimulated emission than stimulated absorption, and this achieve amplification of the incident radiation intensity. Otherwise, given that the Einstein coefficients for stimulated absorption and emission are the same,  $B_{fi} = B_{if}$ , and that in thermal equilibrium the ratio of populations of the ground state and the excited state are given by the Boltzmann distribution

$$\frac{N_f}{N_i} = \exp\left(-\frac{E_f - E_i}{k_B T}\right), \quad (11.19)$$

it would be impossible to achieve more emission than absorption.

The concept of population inversion in the simple case of a two-level system is illustrated in Fig. 11.6: starting from a system in thermal equilibrium, obeying Boltzmann statistics and thus where the population

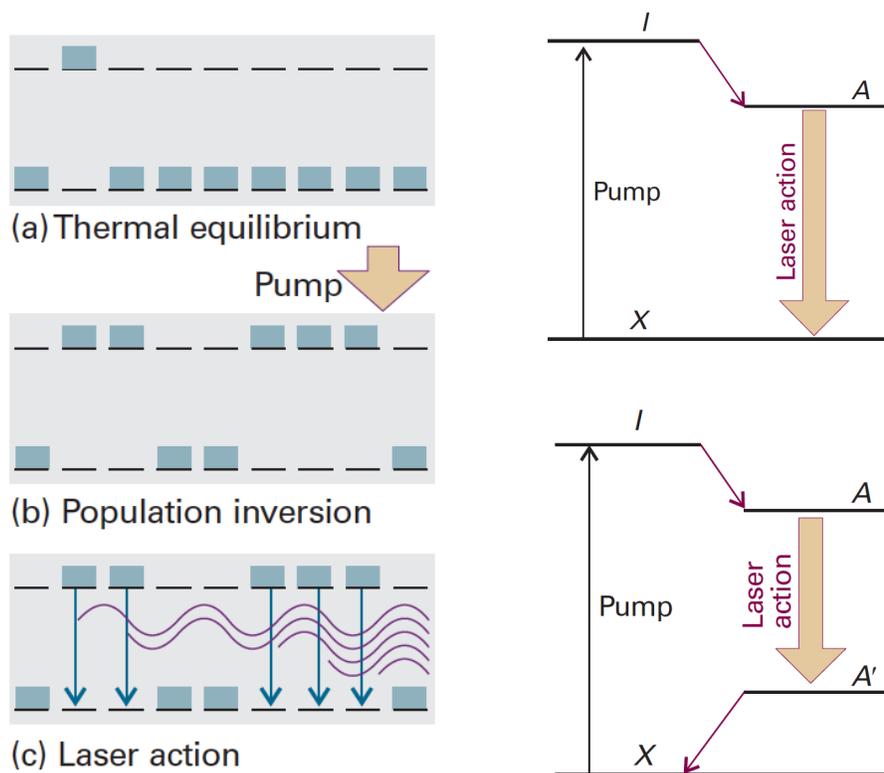


Figure 11.6: Left plot: the operation of a laser is based on the principle of *population inversion*: starting from a system in thermal equilibrium, obeying Boltzmann statistics and thus where the population of the excited state is smaller than that of the ground state, a *pumping system* increases the population of the excited state until it becomes larger than that of the ground state. In these conditions, stimulated emission will dominate over absorption and this the laser will indeed enhance light intensity. Right plot: The schematic operation of a three-level (upper diagram) and four-level (lower diagram) laser, where we indicate the specific transition that is responsible for the lasing.

of the excited state is smaller than that of the ground state,  $N_f < N_i$ , a *pumping system* increases the population of the excited state until it becomes larger than that of the ground state. Under these conditions, the overall rates for stimulated emission will be higher than those of the stimulated absorption, and lasing (light amplification) will take place. The crucial point for the laser operation is therefore how to best implement this pumping to achieve population inversion.

It is easy to realize is that actually *lasing is impossible in a two level system*. To see this, note that due to the equality of the Einstein coefficients,  $B_{if} = B_{fi}$ , the population of  $N_f$  can only be as large as 50% of the total population of the system,  $N_T = N_i + N_f$ , no matter how hard we pump. To implement the lasing concept one needs at least a system with three quantum states or even four. In Fig. 11.6 we show the schematic operation of a three-level and four-level laser, where we indicate the specific transition that is responsible for the lasing. Of all the possible transitions in the system, the one that is responsible for the lasing effect (and that requires population inversion) is  $A \rightarrow X$  for the three-level laser and  $A \rightarrow A'$  for the four-level laser, and therefore the pumping should be such that in equilibrium  $N_A \geq N_X$  ( $N_A \geq N_{A'}$ ) for the three (four) level laser. The best molecules to be used for lasing are thus for which the rates of inter-system transitions are those that facilitate the most achieving population inversion.

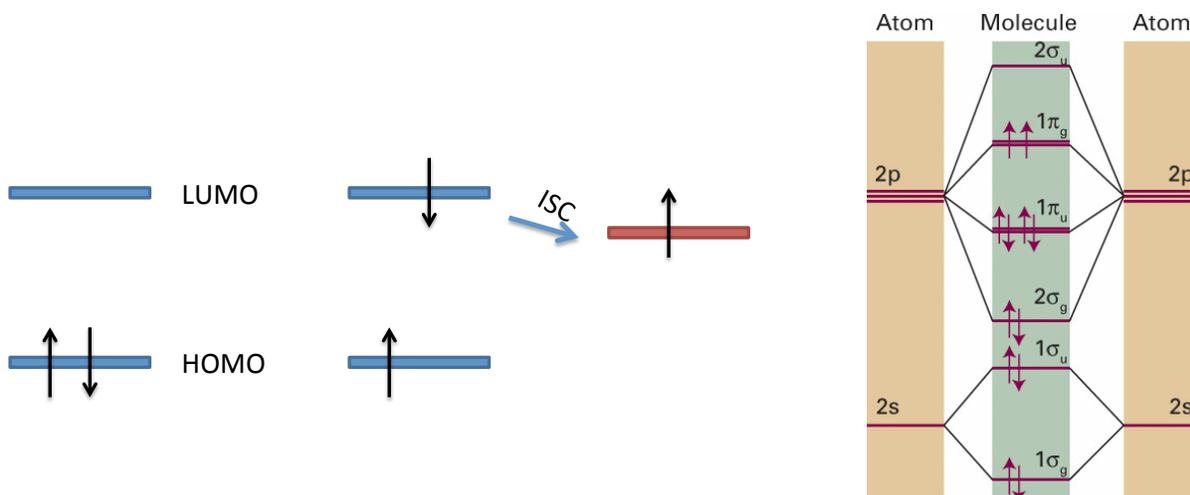


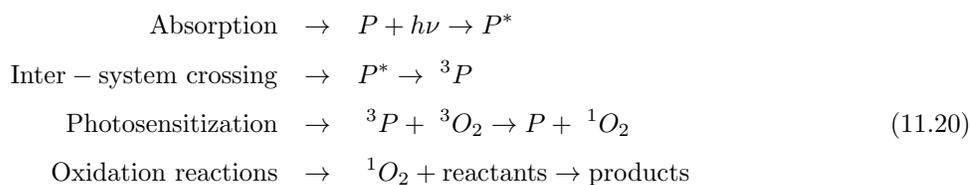
Figure 11.7: Left plot: the basic molecular electronic transition in *Photodynamic Therapy* is the one from a singlet state with paired electrons to a triplet state where the two electrons have unpaired spin via an inter-system crossing. Right plot: schematic representation of the molecular orbitals in the  $O_2$  molecule, where the  $2s$  orbitals form two  $\sigma$ -bonds and the  $2p$  orbitals form two  $\sigma$  and two  $\pi$  bonds.

The basic mechanism of light amplification in a laser arises from the *snowball effect* applied to stimulated emission: each time that a stimulated emission takes place, additional photons with the correct energy are produced, inducing yet further additional simulated emissions, with an exponential grow of the intensity of the incident electromagnetic radiation.

## 11.5 Photodynamic Therapy (PDT)

*Photodynamic therapy*, or PDT for short, is a representative example of a medical application which is based on the optical transitions between different molecular electronic states. PDT, also known as *photo-chemotherapy*, is a form of photo-therapy involving light and a photosensitizing chemical substance, which in conjunction with molecular oxygen can eliminate cancerous tissue.

PDT works as follows. We start from a molecular singlet state, with two paired electrons (opposite spin) in the same electronic quantum level. This level will be the HOMO, the Higher Occupied Molecular Orbital, as illustrated in Fig. 11.7. Using laser radiation, an electron is excited to first the LUMO orbital and then via an inter-system crossing it ends up in its first excited triplet state  $^3P$ . The resulting state photosensitizes the formation of an excited singlet state of  $O_2$ ,  $^1O_2$ , which are extremely reactive and destroy cellular components. Therefore, the photochemical cycle that leads to the shrinkage of diseased tissue is the following:



Note that the energy in the triplet state is lower than that of the singlet state due to Hund's rule, as

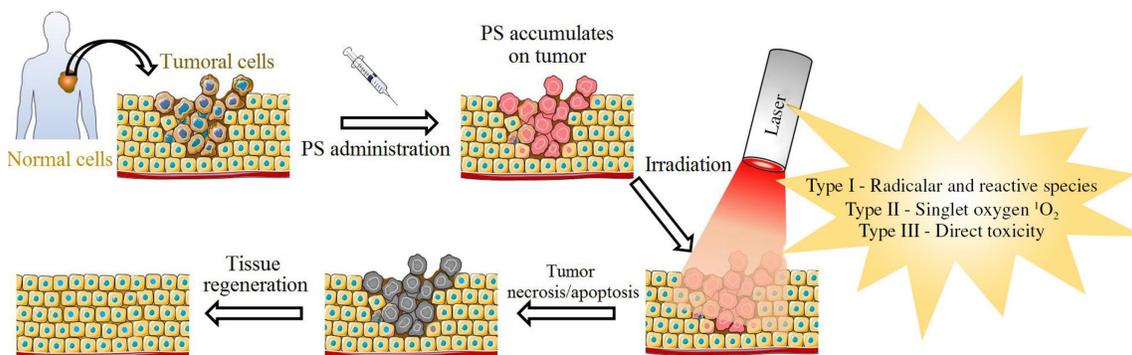


Figure 11.8: In photo-dynamic therapy, a photo-sensitive (PS) molecule is injected on the patient and accumulates on tumor. The subsequent irradiation activates a chemical reaction which creates reactive oxygen molecules  $^1O_2$  which destroy the cancerous tissue.

illustrated in Fig. 11.7. In the right plot of Fig. 11.7 we show a schematic representation of the molecular orbitals in the  $O_2$  molecule, where the  $2s$  orbitals form two  $\sigma$ -bonds and the  $2p$  orbitals form two  $\sigma$  and two  $\pi$  bonds. As we mentioned above, an inter-system crossing transition is enhanced by large spin-orbit couplings, and therefore occurs mostly where heavy nuclei such as S, Fe and Mg are nearby. Since the relaxation from the triplet state to the singlet ground state is forbidden by Pauli exclusion system (which forbids two electrons with the same spin in the same quantum state), the electronic configuration displayed in Fig. 11.7 has a remarkable longevity, which facilitates the photosensitization of a large number oxygen molecules. This is the same mechanism that explained the very long lifetime of phosphorescence.

Therefore, PDT is based on the photosensitization of  $O_2$  molecules to turn them into extremely reactive and destroy cancerous tissue. In this technique, first of all the patient is injected with a photosensitive molecule, and one waits until this substance accumulates in the tumor. Then the tumor is illuminated with laser light, induces the singlet to triplet transition in the molecule and which leads to the selective formation of reactive  $^1O_2$  and the restriction of cancerous tissue. This technique is mostly used for cancer present in body cavities such as mouth, throat or bladder. A summary of the PDT mechanism is shown in Fig. 11.5.

## 11.6 Summary and outlook

Some of the important lessons that we have learned in this lecture are the following:

- The absorption of light (visible and UV) in biological molecules takes place predominantly by means of  $\pi \rightarrow \pi^*$  transitions in  $p$ -conjugated electron systems.
- A larger  $p$ -electron conjugation length leads to absorption at longer wavelengths, that is, at smaller photon energies. This is explained by the reduced electron confinement for large conjugation lengths.
- Symmetry considerations are important when determining whether or not an given optical transition is possible within a specific molecule.
- The Franck-Condon principle explains the transitions in which a *simultaneous* change in the vibrational and electronic states of a molecule takes place, the so-called *vibronic transitions*.

- The Einstein coefficient for spontaneous emission determines the radiation lifetime of a molecule  $\tau_R$ , which in general is different (larger) than its total lifetime.
- The fluorescence lifetime  $\tau_F$  is usually shorter than the radiative lifetime  $\tau_R$  due to competing processes that de-populate the excited states.
- The phosphorescence phenomenon is explained by the long-lived emissions from a triplet excited state to a singlet ground state.
- The light amplification achieved in a laser is based on the concept of *population inversion*.
- The Photodynamic Therapy is an representative example of a medical application based on optical transitions in biomolecules.

## 12 HC12: Magnetic Nuclear Resonance



### van Quantum tot Molecuul

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Magnetic Nuclear Resonance

Based on Atkins and de Paula, *Physical Chemistry* 10th edition, Chapter 14

In this final lecture of the course, we will explore the important topic of Magnetic Nuclear Resonance and show it is the basis for one of the most important applications of quantum theory in medical therapy, namely *Magnetic Resonance Imaging*.

The *learning goals* of this lecture are:

- (a) Understand that the atomic nucleus has a magnetic moment, and that upon interaction with a magnetic field its energy levels split for different values of  $z$  component of the nuclear spin.
- (b) Understand and be able to interpret Nuclear Magnetic Resonance (NMR) spectra.
- (c) Understand how pulse techniques can be employed in order to measure NMR spectra.
- (d) Become familiar with the basic principles of Magnetic Resonance Imaging (MRI).

### 12.1 Nuclear spin

Classically in the presence of an external magnetic field  $\vec{B}$  a particle with a magnetic moment  $\vec{\mu}$  has associated an energy  $E = -\vec{\mu} \cdot \vec{B}$ . In quantum theory, promoting observables to operators, we find that the Hamiltonian that describes this interaction is

$$\hat{H} = -\hat{\vec{\mu}} \cdot \vec{B}. \quad (12.1)$$

An electron moving around an atomic nucleus has associated an associated *angular momentum*  $\vec{l}$  and thus a magnetic moment, so in this case the Hamiltonian operator reads

$$\hat{H} = -\gamma_e \hat{\vec{l}} \cdot \vec{B}, \quad \gamma_e \equiv -\frac{e}{2m_e}, \quad (12.2)$$

where  $\gamma_e$  is the *magnetogyric ratio of the electron*, also known as gyro-magnetic ratio.

Considering without loss of generality a magnetic field with magnitude  $B_0$  pointing in the  $z$  direction, the Hamiltonian will be  $\hat{H} = -\gamma_e B_0 \hat{l}_z$ . From our previous discussion of angular momentum in quantum mechanics, we know that this Hamiltonian will have as eigenvalues:

$$E_{m_l} = -\gamma_e m_l \hbar B_0 \equiv \mu_B m_l B_0, \quad \mu_B \equiv \frac{e\hbar}{2m_e} = 9.27 \times 10^{-24} \text{ J T}^{-1}, \quad (12.3)$$

where the constant  $\mu_B$  is known as *Bohr's magneton*, and  $m_l$  is the quantum number of angular momentum in the  $z$  direction.

The result above is the contribution from the electron energy from the interaction of its *orbital angular momentum* with an external magnetic field. However, an electron also has an *intrinsic angular momentum*, its spin, which will also need to be accounted for. In this case the corresponding Hamiltonian will be

$$\hat{H} = -g_e \gamma_e \vec{B} \cdot \hat{\vec{s}}, \quad (12.4)$$

with  $g_e \simeq 2.002319$  is known as the *electron's g-factor*, which deviates from 2 due to relativistic quantum effects, and  $\hat{\vec{s}}$  is the spin operator. As in the case of the angular momentum, for a magnetic field in the  $z$  direction, the contribution to the total electron energy of the interaction between the electron spin and the magnetic field will be:

$$E_{m_s} = g_e \mu_B m_s B_0, \quad (12.5)$$

where of course now  $m_s = \pm 1/2$ . Therefore, for  $B_0 \neq 0$  a given energy level will split due to this effect by an amount  $\Delta E = g_e \mu_B B_0$ , as shown in Fig. 12.1.

The interaction between a magnetic moment and an external field can also be represented within the *vector model of the spin*, illustrated in Fig. 12.2. In this picture, the external magnetic field induces a *precession* of the electron spin, defined in general as the change in the orientation of the rotational axis of a rotating body. The magnetic moment of the electron will experience a torque  $\vec{\Gamma} = \vec{\mu} \otimes \vec{B}$ , and thus the magnetic moment will rotate around the axis defined by the magnetic field with frequency

$$\nu_L = \frac{|\gamma_e B_0|}{2\pi}, \quad (12.6)$$

which is known as the *Larmor frequency*, and play an important role in the following discussion.

The splitting of energy levels due to the interaction between a magnetic field and an angular momentum can be used for the so-called *magnetic resonance*. Let us first discuss we case of electrons, and then we will turn to nuclei. Since the magnetic field induces an energy splitting of  $\Delta E = g_e \mu_B B_0$ , a transition between these two energy levels will have associated a frequency

$$\nu = \frac{g_e \mu_B B_0}{h} = \frac{g_e e B_0}{4\pi m_e}, \quad (12.7)$$

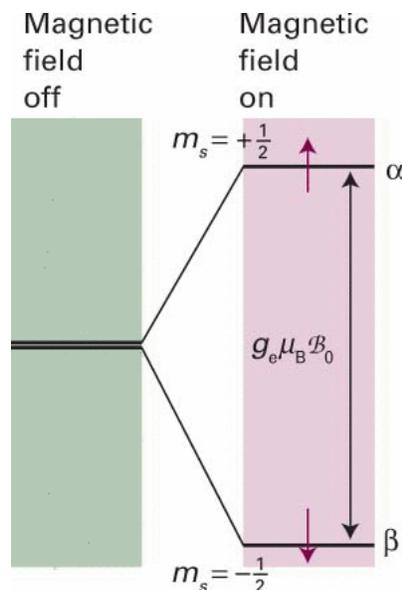


Figure 12.1: In the presence of an external magnetic field  $B_0$ , a given electronic energy state splits into two different states due to the different contribution to the  $\vec{s} \cdot \vec{B}$  coupling to the total energy. These two states are separated by an energy shift of  $\Delta E = g_e \mu_B B_0$ .

where we have use the definition of Bohr's magneton. Eq. (12.7) is known as the *resonance frequency* for electrons: absorption of electromagnetic radiation for this value of  $\nu$  will thus be favored. For a reasonably strong magnetic field of  $B = 0.3$  T, we find that this frequency is  $\nu \simeq 10$  GHz, in the domain of *microwave radiation*. Note that the Boltzmann distribution predicts that the state with lower energy will have higher population, and this the absorption of EM radiation at these frequencies will be facilitated. Note also that this transition can take place only with the condition of paired electrons between the initial and final levels.

Now, *any* particle that has associated an angular momentum will exhibit similar interactions with an external electric field. What about the *atomic nucleus* then? Atomic nuclei are composed by protons and neutrons, each of which are fermions, that is, *spin 1/2* particles. Their angular momenta will add up and in general the nuclear spin  $I$  will be different from zero. And from there on the usual properties of angular momentum follow, for instance, a nucleus with spin  $I$  will have associated an intrinsic angular momentum of  $\sqrt{I(I+1)}\hbar$ , and its components  $m_I\hbar$  along a given axis will take the values  $m_I = I, I-1, \dots, -I+1, -I$ .

The resulting splitting of the energy levels will be similar to the electron case, with the only difference that now the atomic nucleus has a different magnetic moment. Therefore, we will have that the energies associated to the nuclear spin in a external magnetic field are given by

$$E_{m_I} = -\gamma\hbar B_0 m_I, \quad \gamma\hbar \equiv g_I \mu_N \quad \mu_N = \frac{e\hbar}{2m_p} = 5.051 \times 10^{-27} \text{ J T}^{-1}, \quad (12.8)$$

where we have introduced the *nuclear magneton*  $\mu_N$  and the nuclear  $g$ -factor  $g_I$ . In the specific case of a  $I = 1/2$  nucleus, the energy levels will split into two with a energy difference  $\gamma\hbar B_0$ , and now the resonance frequency Eq. (12.7) for  $B = 12$  T will be  $\nu \simeq 500$  MHz, in the regime of *radio-waves*. This very significant change in the resonant frequency of nuclei as compared to electrons is explained from the fact that  $\mu_N \ll \mu_e$  because of the much larger nucleon mass  $m_N \gg m_e$ . Therefore, nuclear magnetic resonance can be achieved for radiation *much smaller energies* (longer wavelengths) than those of the electron case.

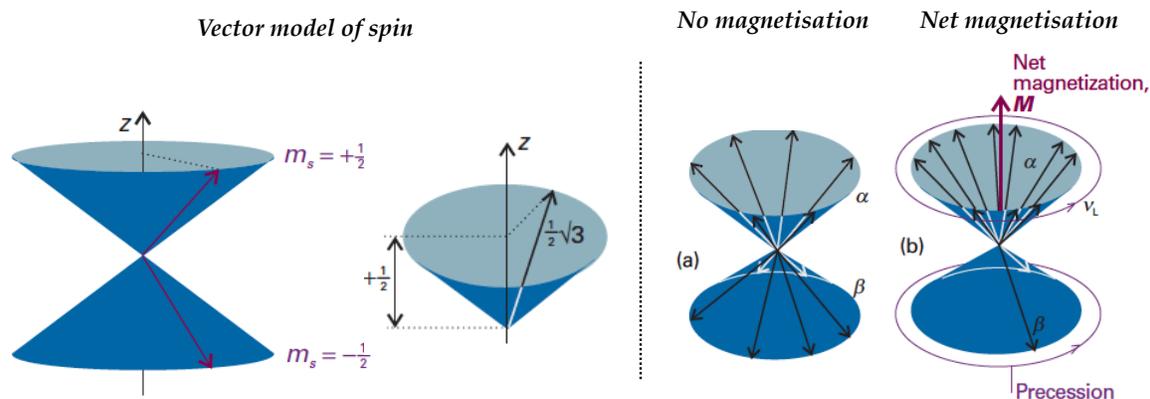


Figure 12.2: Left plot: in the vector model of electron spin, spin can be represented by a vector of length  $\sqrt{3}/2$  whose component in the  $z$  direction is  $\pm 1/2$ . Right plot: in the absence of an external field, there is no net magnetization of the electron spin. For an external magnetic field, the electron spin develops a net magnetization, represented as a precession around the  $z$  axis.

## 12.2 The chemical shift

In practice, the interaction between atomic nuclei and external magnetic fields will be partially shielded due to the surrounding electrons (atomic and/or molecular), and therefore nuclei experience a smaller magnetic field,

$$\tilde{B}_0 = B_0 - \delta B \equiv B_0(1 - \sigma), \quad (12.9)$$

where  $\sigma$  is the so-called *shielding constant*, and its value depends very sensitively on the specific chemical structure surrounding the nucleus. As a consequence of this shielding, for a fixed value of the external magnetic field  $B_0$ , nuclei of different chemical identify will have associated *different resonant frequencies*. We call this *chemical shift* the measure of the differences in the resonance frequency due to the shielding effects of the electrons, which allows to discriminate not only between different chemical elements but also between the same element in different locations within a molecule.

Given that the local magnetic field experienced by the nucleus is  $B_0(1 - \sigma)$ , the associated Larmor frequency will also be reduced, and will be given by

$$\nu_L = (1 - \sigma) \frac{\gamma B_0}{2\pi}. \quad (12.10)$$

Then we can define the *chemical shift*  $\delta$  as the shift of the Larmor frequency relative to a reference value  $\nu_0$ , that is

$$\delta \equiv \frac{\nu_L - \nu_{L,0}}{\nu_{L,0}} \times 10^6, \quad (12.11)$$

which is roughly independent of the specific value of  $B_0$ , which cancels partially in the ratio. Therefore, if for example we have a reference Larmor frequency of 500 MHz for a given field  $B_0$ , then a chemical shift of  $\delta = 1$  ppm (parts per million) corresponds to a shift in the Larmor frequency  $\nu_L$  as compared to the reference value of 500 Hz.

To illustrate the concept of chemical shift, in Fig. 12.3 we show a schematic representation of the ethanol molecule,  $\text{CH}_3\text{CH}_2\text{OH}$ . In the same figure we also show chemical shift  $\delta$  associated to different hydrogen nucleus in the ethanol molecule. We observe that the closer to the oxygen nucleus, the larger the chemical

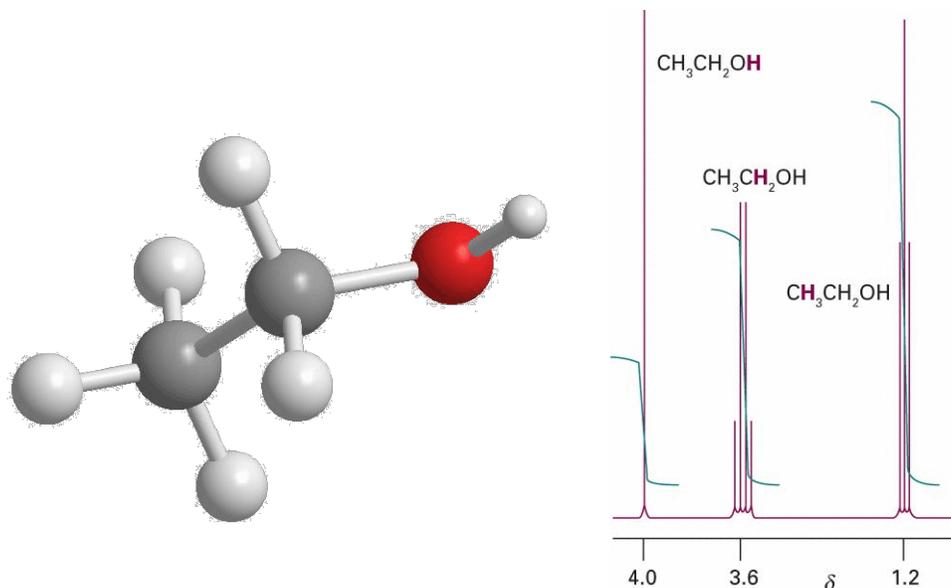


Figure 12.3: Right plot: schematic representation of the ethanol molecule,  $\text{CH}_3\text{CH}_2\text{OH}$ . Left plot: the chemical shift  $\delta$  associated to different hydrogen nucleus in the ethanol molecule. We observe that the closer to the O nucleus, the larger the chemical shift.

shift. This can be explained since oxygen is the most electro-negative element of the molecule and thus attracts the most the molecular electron density, leading to an enhanced chemical shift of the neighboring hydrogen nucleus. From Fig. 12.3 we also see that there is a *fine structure* for the each nucleus in the ethanol molecule. This fine structure arises from the *spin-spin coupling*, where the spin from one nucleus contributes to the local magnetic field of a neighboring nucleus.

### 12.3 NMR spectroscopy

We now want to illustrate how we can measure NMR spectra and chemical shifts, as required for medical applications. This can be achieved by means of the *NMR spectrometer*, and requires introducing the concept of the *pulsed technique*.

The basic ingredient of NMR is the measurement of the *chemical shifts* for each atom in a molecule of the analysed sample, which then allows its identification by comparing with the reference spectra. One possibility would be to measure the *rate of absorption of radio waves* as a function of their frequency  $\nu$ , which should be dominated by the Larmor frequencies of the nuclei in the sample. As illustrated by Fig. 12.1 (applied to the magnetic moment of nuclei), the value of the photon energy that induces the resonant transition  $\beta \rightarrow \alpha$ ,  $E_\gamma = \gamma B_0 / 2\pi$ , lies in the radio part of the EM spectrum. This approach is however challenging, since first of all the population difference between  $\alpha$  and  $\beta$ , the nuclear atomic states with different spin, is small, and second because such a frequency scan is a rather slow process. Indeed, the difference in population between  $\alpha$  and  $\beta$  can be as small as  $\mathcal{O}(10^{-5})$ .

The alternative is to use *pulse techniques*, which are much more efficient. To understand the pulse method works, we consider a vector model for the nuclear spin, such as that shown in Fig. 12.2 for the electron. Let us assume that the nuclear spin is  $I = 1/2$  for simplicity. The length of this vector is  $\sqrt{I(I+1)} = \sqrt{3}/2$  (in units of  $\hbar$ ), and the projection in the  $z$  direction is fixed to be  $I_z = \pm 1/2$ . Recall that the operators  $\hat{I}_x$ ,  $\hat{I}_y$

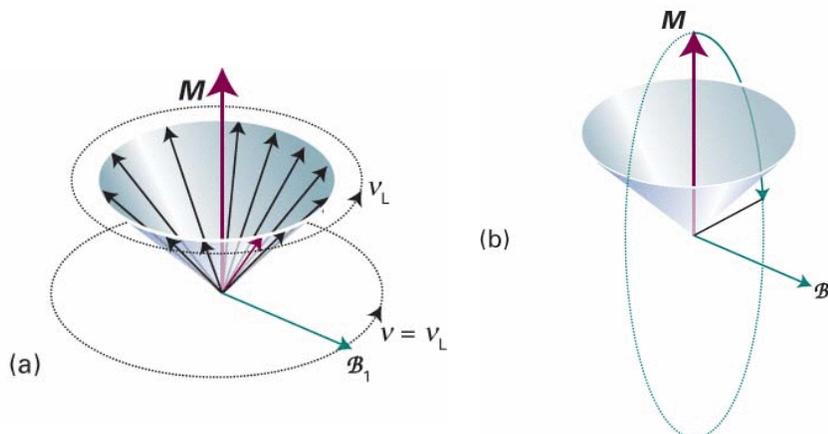


Figure 12.4: In the pulse method, a magnetic field polarized in the  $(x, y)$  plane oscillates with frequency  $\nu_L$  (left plot), perpendicular to the nuclear spin. In the rotating reference frame, the nuclear spin experiences a constant magnetic field  $B_1$  (right plot).

and  $\hat{I}_z$  do not commute among them.

For a vanishing external magnetic field,  $B_0 = 0$ , the energy of the two states  $\alpha$  and  $\beta$  are the same, and so they have the same average population. Once we switch on the external magnetic field,  $B_0 \neq 0$ , the energy of the two levels splits, with  $E_\beta < E_\alpha$  (see Fig. 12.1). Due to Boltzmann statistics, we know that the population of the lower energy state  $\alpha$  will be larger than that of the higher energy one  $\beta$ ,  $N_\alpha < N_\beta$ . This implies that a *net magnetization* is created in the analyzed material, proportional to  $N_\beta - N_\alpha$ .

The next step in the pulse method is that, in addition to the static magnetic field  $B_0$ , we also add an *oscillatory magnetic field* in the  $(x, y)$  plane, with Larmor frequency  $\nu_L$  and circular polarization so that  $B_1$  rotates in the  $(x, y)$  plane with frequency  $\nu_L$ . Recall that the static magnetic field  $B_0$  is applied along the  $z$  direction, and is thus perpendicular to the new oscillatory magnetic field. This additional field will induce the transition  $\alpha \leftarrow \beta$ , that is, from the lower to the higher energy nuclear magnetic states. If we now transform to the *rotating frame* with Larmor frequency  $\nu_L$ , the nuclear spins will experience a *constant magnetic field*  $B_1$ . Therefore, in this frame, the nuclear spins will exhibit a precession with a different value of  $\nu_L$ , as illustrated in Fig. 12.4. This new Larmor frequency will be

$$\tilde{\nu}_L = \frac{\gamma B_1}{2\pi}, \quad (12.12)$$

and thus the period of the new Larmor precession will be

$$T = \frac{2\pi}{\gamma B_1}. \quad (12.13)$$

In the pulse method, rather than having the oscillatory field  $B_1$  activated the whole time, we have it on only for a small amount of time, the *pulses*. In particular the duration of this pulses should be one quarter of the total precession period,  $(1/4) \cdot (2\pi)/\gamma B_1$ , corresponding to an angular rotation of  $\pi/2$ , which typically corresponds to a duration of microseconds. Now, while in the rotating frame the magnetization  $M$  is constant in the  $(x, y)$  plane, in the *laboratory frame* it will rotate with Larmor frequency  $\nu_L$ . This oscillatory magnetization can be detected in the *coil* of an *NMR spectrometer*, where it can be transformed

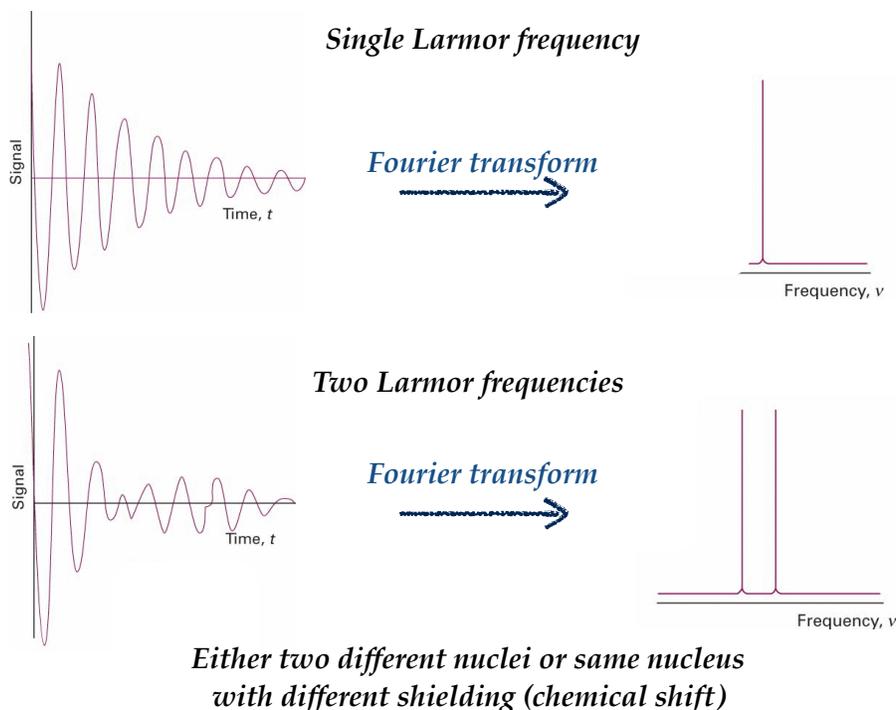


Figure 12.5: The oscillating signal measured in the MNR spectrometer can be Fourier transformed to determine the values of the Larmor frequencies present for the studied sample. In a sample with different nuclei and/or nuclei with different chemical shifts, the Fourier transform will exhibit multiple peaks corresponding to each of the relevant Larmor frequencies.

into output electromagnetic radiation in the radio spectrum.

A characteristic signal of the measured MNR signal is that it will appear as a Free Induction Decay (FID), which oscillates with Larmor frequency  $\nu_L$  but whose amplitude decays exponentially due to the finite duration of the length of the pulse. The oscillating signal detected in the MNR spectrometer can then be Fourier-transformed to determine the values of the Larmor frequencies for each of the nuclei in the studied sample, as shown in Fig. 12.5. This way, in a sample with different nuclei and/or nuclei with different chemical shifts, the Fourier transform will exhibit multiple peaks corresponding to each of the relevant Larmor frequencies.

The reason why the MNR signal in Fig. 12.5 decays exponentially with time can be understood as follows. After a  $\pi/4$  pulse, the magnetization of the atomic nuclei is not in thermal equilibrium with its surroundings. In particular, since  $\beta$  has a higher population than  $\alpha$ , the pulse will affect more the former level and thus contradict the expected Boltzmann populations. Indeed, after the  $\pi/4$  pulse the population of spins in the two levels is similar. After a some time, following the pulse, the system will be back to thermal equilibrium where

$$\frac{N_\alpha}{N_\beta} = e^{-h\nu_L/k_B T}. \quad (12.14)$$

This *longitudinal relaxation time*  $T_1$  will be given by the time it takes for the system to recover its original magnetization  $M_0$  along the  $z$  direction, namely

$$(M_z(t) - M_0) \propto e^{-t/T_1}, \quad (12.15)$$

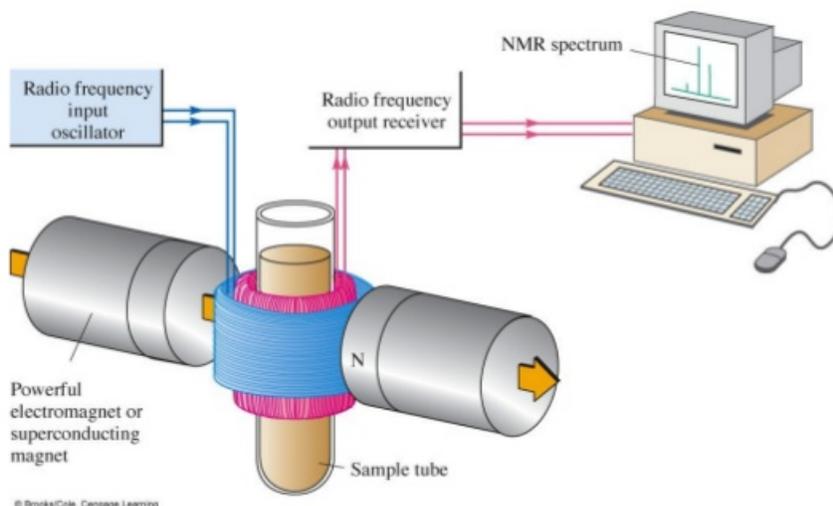


Figure 12.6: In an NMR spectrometer, a powerful magnet is used to apply a strong magnetic field to the studied sample. Then, the sample is irradiated with pulsed electromagnetic radio waves and the response of the system under this radiation (which frequencies are absorbed) is monitored to determine the resultant NMR spectra.

where we see that for  $t \gg T_1$  the magnetization will be  $M_z(t) = M_0$ , as was the case before the pulse.

Moreover, after the  $\pi/4$  pulse there will also be a new magnetization  $M_y$  along a given direction in the  $(x, y)$  plane, that is, the phase of individual nuclear spins along this plane (in the vector model of the atomic spin) will be common. Some time after the pulse, this common phase will be lost and the associated macroscopic magnetization in the transverse direction  $M_y$  will disappear. We can then define the *transverse relaxation time*  $T_2$  as

$$M_y(t) \propto e^{-t/T_2}, \quad (12.16)$$

so that for  $t \gg T_2$  we have that  $M_y \rightarrow 0$ , as was the case before the pulse. The longitudinal relaxation mechanism also affects the transversal one, so typically  $T_1 \geq T_2$ , of the order of a few seconds. The main impact of the  $T_2$  relaxation is the *broadening of spectral lines*. Indeed, it can be shown that the *width at half-maximum* of a MNR line is given by

$$\nu_{1/2} = \frac{1}{\pi T_2}. \quad (12.17)$$

The experimental apparatus for the measurement of NMR spectra is illustrated in Fig. 12.6. First of all, in an NMR spectrometer, a powerful magnet is used to apply a strong magnetic field  $B_1$  to the studied sample. Then, *pulsed electromagnetic radio waves* and the response of the system under this radiation (which frequencies are absorbed) is monitored to determine the resultant NMR spectra. The frequency of the pulsed radio waves is tuned to reproduce the Larmor frequencies of specific magnetic nuclear resonances, as explained above. The Fourier transform of the output radio frequency, as indicated in Fig. 12.5, indicates the Larmor frequencies of the various atomic components of the sample.

## 12.4 Magnetic resonance imaging (MRI)

Magnetic Nuclear Resonance is the key principle underlying *Magnetic Resonance Imaging*. This imaging method is based on the deliberate application of an *inhomogeneous magnetic field*, in other words, a *magnetic*

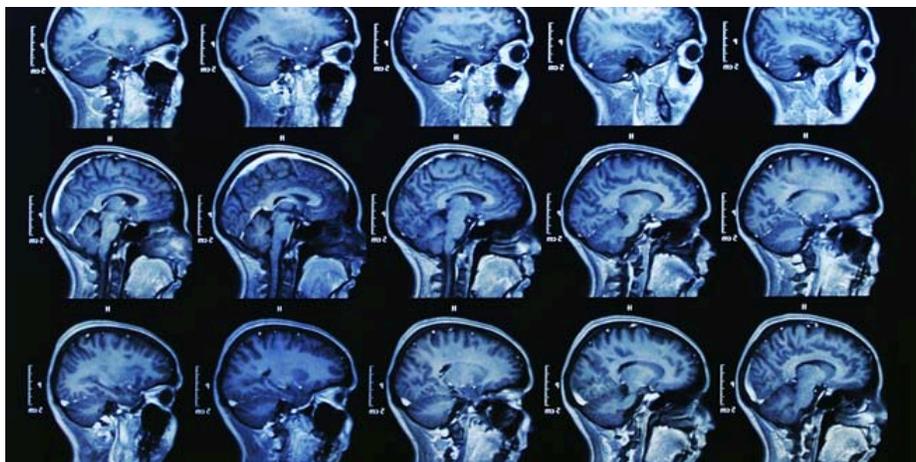


Figure 12.7: By means of Molecular Resonance Imaging, it is possible to obtain three-dimensional images of soft tissue, in this case white and grey matter inside the skull.

*field gradient.* As we have discussed, each molecule of the imaged sample, in the presence of a external magnetic field, will have associated a Larmor frequency of

$$\nu_L(\vec{r}) = (1 - \sigma) \frac{\gamma B_0(\vec{r})}{2\pi}, \quad (12.18)$$

which now will be different for each position  $\vec{r}$  of the sample, due to the inhomogeneity of the magnetic field. By comparing the observed Larmor frequencies with the expected values for some molecules and taking into account the magnetic field gradient applied to the sample, we can reconstruct a *three-dimensional* image of the chemical components of the sample.

The typical MRI application is based on the proton resonance, therefore the largest signal will come from those body parts with the highest concentration of water. To enhanced the contract, it is possible to use that the longitudinal and transverse relaxation times  $T_1$  and  $T_2$  depend on the time of local environment, for example they are different in membranes than in bulk water. This way, it is possible to image separately using MRI different types of soft tissue such as gray matter, white matter or spinal fluid. In Fig. 12.7 we illustrate how by means of Molecular Resonance Imaging it is possible to obtain three-dimensional images of soft tissue, in this case white and grey matter inside the skull.

## 12.5 Summary

Let us summarize some of the important topics that have been covered in this lecture:

- A moving electric charge has an associated *angular momentum*  $\vec{l}$ , which can then interact with a external magnetic field  $\vec{B}$ .
- The interaction of the electron spin with an external magnetic field induces an energy splitting that can be proved by resonant absorption at microwave frequencies.
- Atomic nucleus also have an intrinsic angular momentum, spin, built upon the spin of its components, protons and neutrinos. Depending on the specific nucleus, this spin can be zero, half-integer or integer.

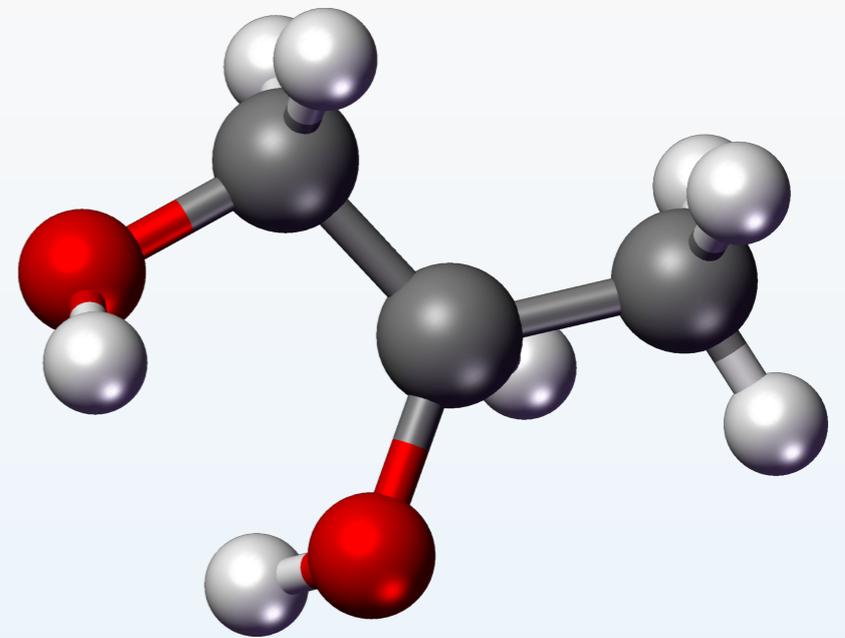
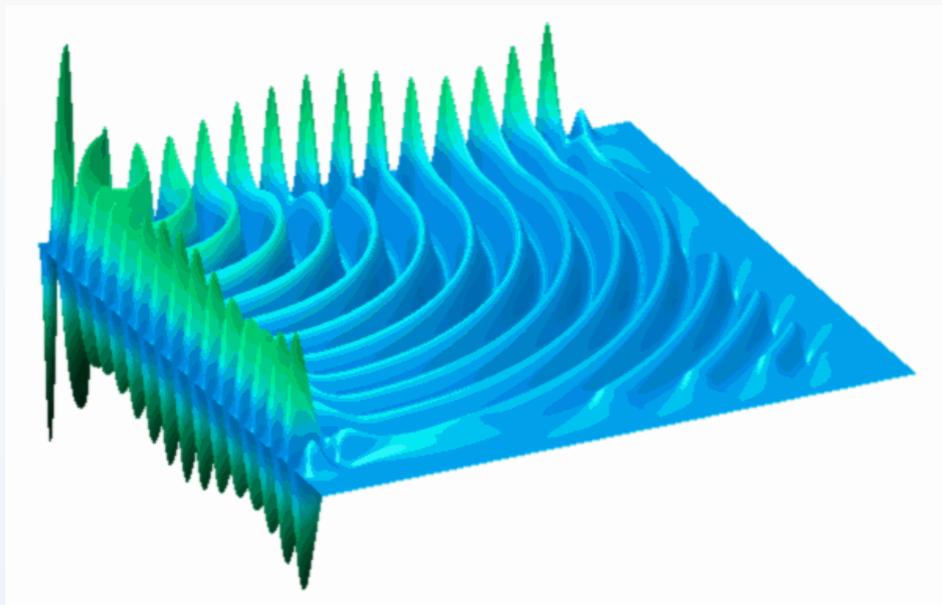
- The nuclear magneton  $\mu_N$  is much smaller than the electron magneton  $\mu_B$  due to the mass suppression of the atomic nuclei as compared to the electron mass.
- Magnetic resonance absorption in nuclei takes place at radio frequencies.
- The chemical shift quantifies the degree of shielding of nucleus by core electrons in the presence of external magnetic field.
- Magnetic nuclear resonances can be efficiently probed using the *pulse method*, where short pulses of  $\pi/4$  angle are used to excite the magnetic resonances.
- The MNR signal decays exponentially due to the longitudinal and transverse mechanism of spin relaxation.
- Magnetic nuclear resonance is the key for Magnetic Resonance Imaging, where a magnetic field gradient can be used to obtain a three-dimensional image of soft tissues.



**Appendices to the**  
**"Revised guide of the *van Quantum tot Molecuul* course"**

**Juan Rojo**

**Appendix 3)** Slides of the introductory lesson of the course



*Van Quantum tot Molecuul (X\_420545)*  
*academic year 2016-2017*

Vrije Universiteit Amsterdam  
Faculteit Exacte Wetenschappen  
BSc Programma Medische Natuurwetenschappen

## Course overview

# Basic Information

## Course Lecturers (*docenten*)

**Dr. Juan Rojo** (HC1-3 and HC10-12)  
Kamer T230 Wis- en Natuurkundegebouw  
Tel. 020-5987212  
email [j.rojo@vu.nl](mailto:j.rojo@vu.nl)



**Prof. Dr. Ir. Erwin Peterman** (HC4-10)  
Kamer U022, Wis- en Natuurkundegebouw  
Tel. 020-59 87576  
email [e.j.g.peterman@vu.nl](mailto:e.j.g.peterman@vu.nl)

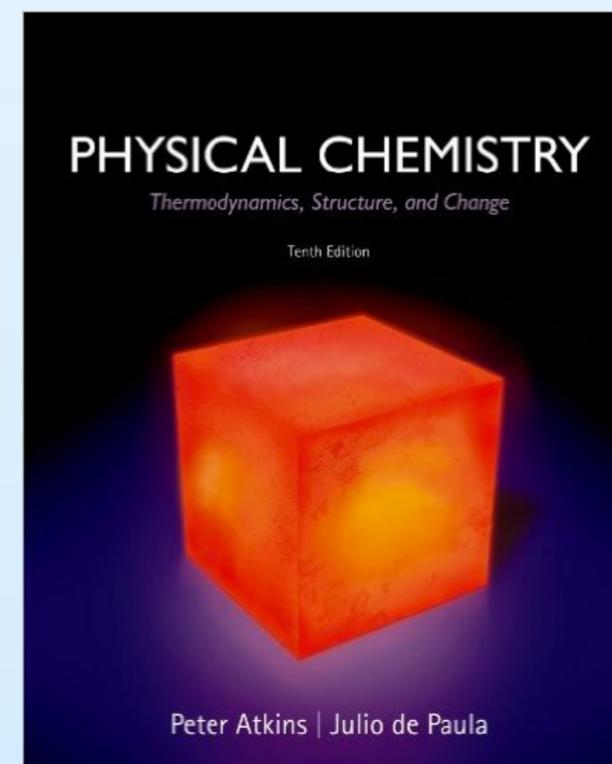


## Werkcollege assistenten

Margherita Marchetti ([m.marchetti@vu.nl](mailto:m.marchetti@vu.nl))  
Luuk Geelen ([l.h.c.geelen@student.vu.nl](mailto:l.h.c.geelen@student.vu.nl))  
Veerle Brans ([v.a.brans@student.vu.nl](mailto:v.a.brans@student.vu.nl))

## Tekstboek

**Physical Chemistry, Atkins & De Paula,**  
**10<sup>th</sup> edition, Oxford University Press**



# Course Schedule

<i>Week</i>	<i>Dag</i>	<i>Datum</i>	<i>Tijd</i>	<i>HC/WC</i>	<i>Docent</i>	<i>Topic</i>
2	Ma	9-1	13:30	-	JR	GEEN COLLEGE
2	Di	10-1	13:30	HC1	JR	Overzicht cursus, introductie quantum, Ch 7
2	Vr	13-1	11:00	WC1		WC1
3	Ma	16-1	13:30	HC2	JR	Ch 7: Schrodinger vergelijking, interpretatie vd golffunctie, wiskundig gereedschap
3	Di	17-1	13:30	HC3	JR	Ch7: Heisenberg onzekerheidsrelaties Ch 8: vrije deeltje, deeltje in 'n doosje, tunneling, harmonische oscillator
3	Vr	20-1	11:00	WC2		WC2
4	Ma	23-1	13:30	HC4	EP	Ch 8: Deeltje op 'n ring, deeltje op 'n bol
4	Di	24-1		HC5		Ch 9: waterstofatoom
4	Vr	27-1	11:00	WC3		WC3
5	Ma	30-1	13:30	HC6	EP	Ch 9: electronspin, meer-electron atomen
5	Di	31-1		HC7	EP	Ch 10: moleculaire structuur, valence bond theorie, MO theorie,
5	Vr	3-2	11:00	WC4	TAs	WC4
6	Di	7-2	13:30	WC5	TAs	WC5
6	Vr	10-2	11:00			GEEN COLLEGE
7	Di	14-2	13:30			GEEN COLLEGE

# Course Schedule

Week	Dag	Datum	Tijd	HC/WC	Docent	Topic
2	Ma	9-1	13:30	-	JR	GEEN COLLEGE
2	Di	10-1	13:30	HC1	JR	Overzicht cursus, introductie quantum, Ch 7
2	Vr	13-1	11:00	WC1		WC1
3	Ma	16-1	13:30	HC2	JR	Ch 7: Schrodinger vergelijking, interpretatie vd golffunctie, wiskundig gereedschap
3	Di	17-1	13:30	HC3	JR	Ch7: Heisenberg onzekerheidsrelaties Ch 8: vrije deeltje, deeltje in 'n doosje, tunneling, harmonische oscillator
3	Vr	20-1	11:00	WC2		WC2
4	Ma	23-1	13:30	HC4	EP	Ch 8: Deeltje op 'n ring, deeltje op 'n bol
4	Di	24-1		HC5		Ch 9: waterstofatoom
4	Vr	27-1	11:00	WC3		WC3
5	Ma	30-1	13:30	HC6	EP	Ch 9: electronspin, meer-electron atomen
5	Di	31-1		HC7	EP	Ch 10: moleculaire structuur, valence bond theorie, MO theorie,
5	Vr	3-2	11:00	WC4	TAs	WC4
6	Di	7-2	13:30	WC5	TAs	WC5
6	Vr	10-2	11:00			GEEN COLLEGE
7	Di	14-2	13:30			GEEN COLLEGE



Course Overview +  
Introduction to Quantum Physics

# Course Schedule

Week	Dag	Datum	Tijd	HC/WC	Docent	Topic
2	Ma	9-1	13:30	-	JR	GEEN COLLEGE
2	Di	10-1	13:30	HC1	JR	Overzicht cursus, introductie quantum, Ch 7
2	Vr	13-1	11:00	WC1		WC1
3	Ma	16-1	13:30	HC2	JR	Ch 7: Schrodinger vergelijking, interpretatie vd golffunctie, wiskundig gereedschap
3	Di	17-1	13:30	HC3	JR	Ch7: Heisenberg onzekerheidsrelaties Ch 8: vrije deeltje, deeltje in 'n doosje, tunneling, harmonische oscillator
3	Vr	20-1	11:00	WC2		WC2
4	Ma	23-1	13:30	HC4	EP	Ch 8: Deeltje op 'n ring, deeltje op 'n bol
4	Di	24-1		HC5		Ch 9: waterstofatoom
4	Vr	27-1	11:00	WC3		WC3
5	Ma	30-1	13:30	HC6	EP	Ch 9: electronspin, meer-electron atomen
5	Di	31-1		HC7	EP	Ch 10: moleculaire structuur, valence bond theorie, MO theorie,
5	Vr	3-2	11:00	WC4	TAs	WC4
6	Di	7-2	13:30	WC5	TAs	WC5
6	Vr	10-2	11:00			GEEN COLLEGE
7	Di	14-2	13:30			GEEN COLLEGE



Course Overview +  
Introduction to Quantum Physics



Schrodinger equation and the  
quantum wave function

# Course Schedule

Week	Dag	Datum	Tijd	HC/WC	Docent	Topic
2	Ma	9-1	13:30	-	JR	GEEN COLLEGE
2	Di	10-1	13:30	HC1	JR	Overzicht cursus, introductie quantum, Ch 7
2	Vr	13-1	11:00	WC1		WC1
3	Ma	16-1	13:30	HC2	JR	Ch 7: Schrodinger vergelijking, interpretatie vd golffunctie, wiskundig gereedschap
3	Di	17-1	13:30	HC3	JR	Ch7: Heisenberg onzekerheidsrelaties Ch 8: vrije deeltje, deeltje in 'n doosje, tunneling, harmonische oscillator
3	Vr	20-1	11:00	WC2		WC2
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4	Di	24-1		HC5		Ch 9: waterstofatoom
4	Vr	27-1	11:00	WC3		WC3
5	Ma	30-1	13:30	HC6	EP	Ch 9: electronspin, meer-electron atomen
5	Di	31-1		HC7	EP	Ch 10: moleculaire structuur, valence bond theorie, MO theorie,
5	Vr	3-2	11:00	WC4	TAs	WC4
6	Di	7-2	13:30	WC5	TAs	WC5
6	Vr	10-2	11:00			GEEN COLLEGE
7	Di	14-2	13:30			GEEN COLLEGE

→ **Course Overview + Introduction to Quantum Physics**

→ **Schrodinger equation and the quantum wave function**

→ **Heisenberg uncertainty principle quantum mechanics of simple systems (particle in box, oscillator)**

*NB the chapter numbers correspond to the 10th edition of Atkins & De Paula*

# Course Schedule

7	Vr	17-2	11:00			TUSSENTOETS
8	Di	21-2	13:30	HC8	EP	Ch 10: MO theorie hybridisatie, variatieprincipe
8	Vr	24-2	11:00	HC9	EP	Ch10: Hückel theorie
9	Di	28-2	13:30	WC6	TAs	WC6
9	Vr	3-3	11:00	HC10	JR	Ch 12: moleculaire spectroscopie, vibrationele spectroscopie
10	Di	7-3	13:30	WC7	TAs	WC8
10	Vr	10-3	11:00	HC11	JR	Ch 13: moleculaire spectroscopie, electronische overgangen
11	Di	14-3	13:30	WC8	TAs	WC9
11	Vr	17-3	11:00	HC12	JR	Ch 14: NMR
12	Di	21-3	13:30	WC9	TAs	WC9
12	Vr	24-3	11:00	VRAGEN	JR/EP	VRAGENUUR
13	Di	28-3	15:15- 18:00			TENTAMEN

# Werkcollegen

- 📍 In total there will be **9 tutorial sessions** (*werkcolleges*)
- 📍 **Attendance to the tutorials is compulsory** (else examination will not be allowed)
- 📍 Write your name in the attendance list at the start and end of the *werkcollege*
- 📍 If unable to attend due to illness or other circumstances, **inform the TAs** (*assistenten*) by email **before the session** that you will miss

It is crucial that you **prepare in advance the tutorial work:**

- 📍 Read the corresponding chapters in the **textbook and the lecture notes** in advance
- 📍 The exercises corresponding to each tutorial session will be **announced in advance**
- 📍 Self-organise yourselves in groups of 3/4 students to prepare beforehand the tutorial work for each session
- 📍 It is possible to submit specific questions by email about the exercises to the TAs before each session

# Communications

- Relevant **information** about the course, tutorial sessions, and evaluations and exams will take place through your **VU student email**
- **Check regularly your VU email**, at least once per day during term
- It might be in your interest to **configure a forward** to the email account you check more frequently

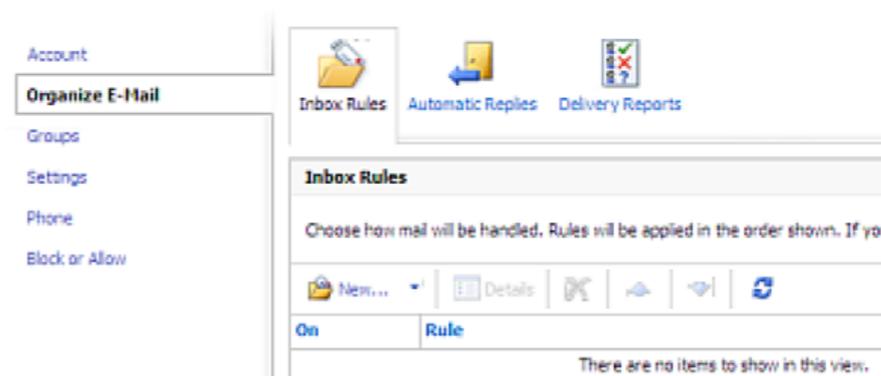
## 7. Configure a forward

When activating a forward a copy of all e-mails will be sent to the e-mail address you specify. This will only be done as long as the specified e-mail address is active. Make sure you still login to your VU-Mail regularly as to delete e-mail from the server to prevent you from running into the quota limit.

- Go to *options* in the top right corner.



- In the left column select *Organize E-Mail*.
- Select **Inbox Rules**
- Click **New...**



# Evaluation

- There will be first an **intermediate examination** (*tussentoets*) followed by a **final examination** (*volledig eindtentamen*)
- **Tussentoets:** Friday 17th February 2017, 11am, covering HC1 to HC6
- **Tentamen:** Tuesday 28th March 2017, 3.15pm, covering HC1 to HC6 (Part I) and HC7 to HC12 (Part II)
- If the mark obtained in the intermediate exam is *insufficient*, the complete final exam needs to be performed (**Parts I+II**)
- If the mark obtained in this exam is a *pass*, there is the option to **either skipping or attempting Part I in the final exam**. In the latter case, the **best of the two marks** will be the one that counts for the course evaluation
- The final exam mark will be **the sum of Part I** (or of the intermediate exam, if higher) and **Part II**
- During the exams, the **use of any material from the course is forbidden**. Scientific (programmable) calculators are likewise not allowed
- Those students repeating the course need to perform the **complete final exam** (Part I + Part II). Marks from intermediate examinations cannot be carried forward from previous years

# Office hours

- 📌 Lecturers will be **available for up to 30 minutes after the lecture** to address questions related to the content covered in each lecture
- 📌 In addition, it is possible to schedule further discussion time via email
- 📌 Questions about **tutorial exercises/sessions** should be addressed to the **course TAs**
- 📌 Do not wait to the last minute to ask questions or to discuss the course material!



# Course overview

- Basic principles of **quantum mechanics**
- The **Schrodinger equation** and the quantum wave function
- Application to **simple systems**: free particle, particle in a box, harmonic oscillator
- The **electronic structure of atoms**
- **Molecular structure and chemical bonding** from quantum mechanics
- **Quantitative description of molecules**: vibration, rotation, optical transitions, spectroscopy
- **Magnetic resonance spectroscopy** and Magnetic Resonance Imaging (MRI)

*The detailed list of topics for each lecture (and where they are covered in Atkins & De Paula) can be found in the course Study Guide in BlackBoard*



**Appendices to the**  
**"Revised guide of the *van Quantum tot Molecuul* course"**

**Juan Rojo**

**Appendix 4)** Slides of the presentation "*Assessing, Testing, and Evaluating*" given on the 5th of October 2017



# Assessing, Testing, and Evaluating

**Valerie Duplat**  
VU Amsterdam

**Elisa Giovannetti**  
VU University Medical Center, Lab Medical Oncology

**Juan Rojo**  
VU Amsterdam & Theory group, Nikhef

**University Teaching Qualification (fast track) Course**  
**VU Amsterdam, 04/10/2017**

# Outline

- ☑ **General context of assessment activities**
- ☑ **Planning methods of assessment**
- ☑ **Methods of assessing learning**
- ☑ **Summary and discussion**

The following material is based on Chapter 7 of *McKeachie's Teaching Tips: Strategies, Research, and Theory for College and University Teachers*, 14th Edition.

# General context - 1

Every course must have some specific **methods of assessment**, aiming to evaluate if students have satisfactorily achieved **their learning goals**

Some learning goals are not measurable by conventional tests

Look for other evidence

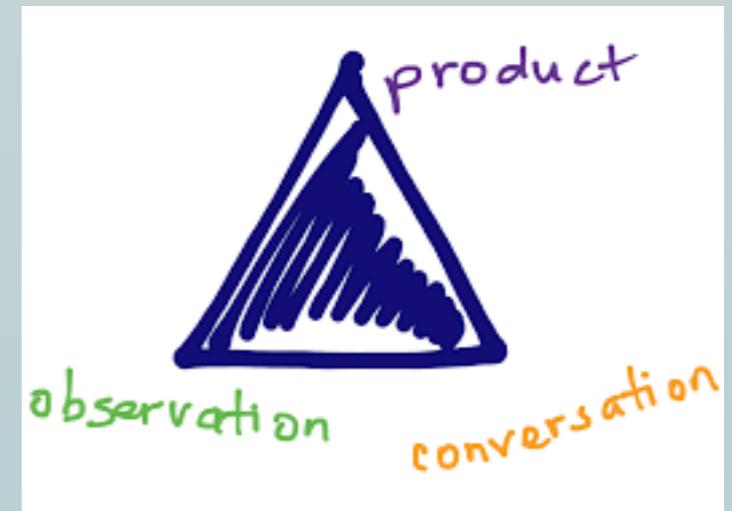


**Assessing should not be limited to testing:** classroom, lab, and out-of-class activities should play an important role (*“embedded assessment”*)

# General context - 2

Crucial to avoid using exclusively a **single assessment method** for all cases

- ☑ Some students perform badly in written tests, while they perform better with assignments or small projects that they can work on their own
- ☑ Better use variety of complementary assessment methods: *“triangulation of data”*



The specific assessment method adopted influences **what the students learn**

Assessment should not be limited to a method to grade students: it can and should be also a learning opportunity for the students (and their teachers).

# Triangulation of Data

## Observations

- Assessment checklists
- Anecdotal notes

Generate-Get-Connect-Elaborate Assessment Tracking Form						Teacher:	
<input checked="" type="checkbox"/> Constantly						<input type="checkbox"/> Sometimes	<input type="checkbox"/> Rarely
Generate-Get-Connect-Elaborate							
students can:							
Students	Generate an original idea	Get feedback from peers and teacher	Connect to other ideas and learning	Elaborate on ideas and learning	Assess the quality of learning	Notes	



Making  
Student  
Thinking  
Visible

## Conversations:

- Between peers
- With the teacher

## Products

- Students work
- Student thinking recorded
- Variety of thinking routines explored



# General context - 2

Let's make a "test"!

How would you evaluate those learning goals?

- Our students are aware/sensitive to a disrupted world
- Our students master business basics and are able to anticipate business transformation
- Students develop a creative mindset and are able to make ideas happen
- Students reflect on themselves and project themselves in the future
- Students are able to identify issues in their own area of expertise

# Planning methods of assessment

Firstly list the main **learning goals and objectives** for the course

Determine **which kind of assessment is most suitable** for each objective

Use assessment material with **greater relevance to the course contents** and assessment to increase the motivation of the students

<b>Learning Outcomes</b>	<b>Understanding of theory basics</b>	<b>Recognize examples of theories in real life</b>	<b>Use theories in designing instruction</b>	<b>Choose instructional design appropriate for situation</b>
<b>Knowledge</b>	X (exams)			
<b>Comprehension</b>	X (exams and in-class activities)	X (exams and in-class activities)		
<b>Application</b>			X (in-class design activities)	
<b>Analysis</b>				X (case analysis)
<b>Synthesis</b>			X (design project)	
<b>Evaluation</b>				X (case critique)

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FIGURE 2.2 A Planning Chart for Use in Setting Up a Course

... and an assessment

# Institutional purposes for course assessment

- Many institutions monitor **learning outcomes of their programs**
  - ☑ More **challenging task** than monitoring at the level of individual courses.
- **Involvement of faculty** is critical here, but requires appropriate guidance from university management
- Faculty members can provide valuable data by incorporating **the assessment information from their courses into the overall process**
- Designing **assessment methods for the course that provide information useful for the improvement of a whole degree or the university** leads to a double benefit

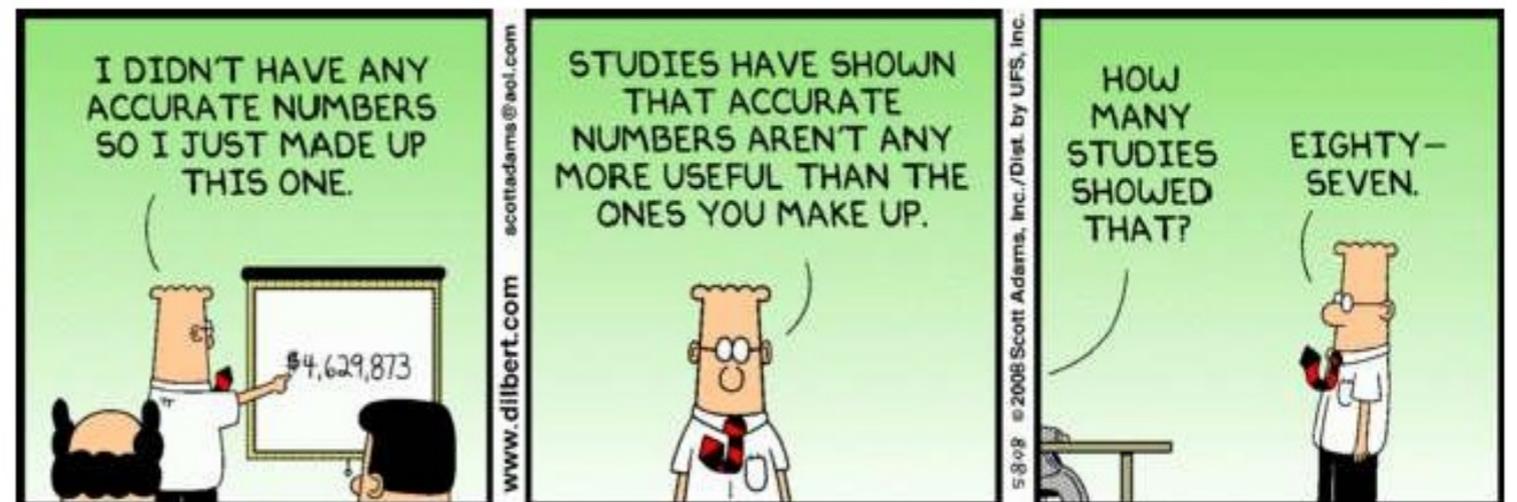
# Methods of assessing learning - 1

Consider a **variety of assessment methods**:

- ☑ some students do well in **high-stakes tests** (like in the end-of-year exam)
- ☑ others do better in **out-of-class assignments** or **short projects**

Possible pitfall of more innovative assessment methods: how to ensure the **same level of objectivity** as in a traditional test?

“Not everything that can be counted counts, and not everything that counts can be counted”



# Methods of assessing learning - 2

There exist different methods that can be used to assess learning, in other words, to evaluate if the original learning goals of the course have been fulfilled by the students.

- ❖ **Tests: in- and out-of-class**
- ❖ **Performance assessment**
- ❖ **Journals and research papers**
- ❖ **Portfolios**
- ❖ **Peer assessment**
- ❖ **Assessing group work**
- ❖ **Embedded assessment**

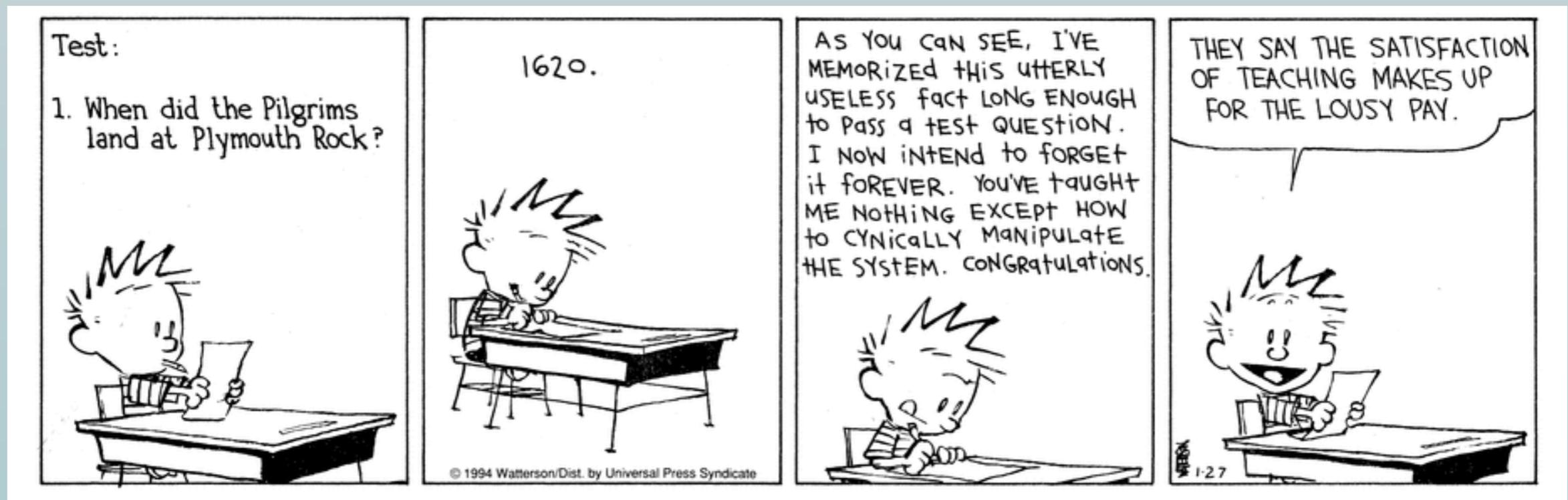
... many others!

# ❖ Tests: in- and out-of-class

Tests represent an **unavoidable part of the assessment**, but often lead to frustration / underperformance in students

Tests should focus on assessing **how students deal with the information that they have at their disposal**, not with the sheer fact of memorising a given chunk of information.

- ☑ Tests which are based on **simple fact recalling** are not appropriate anymore

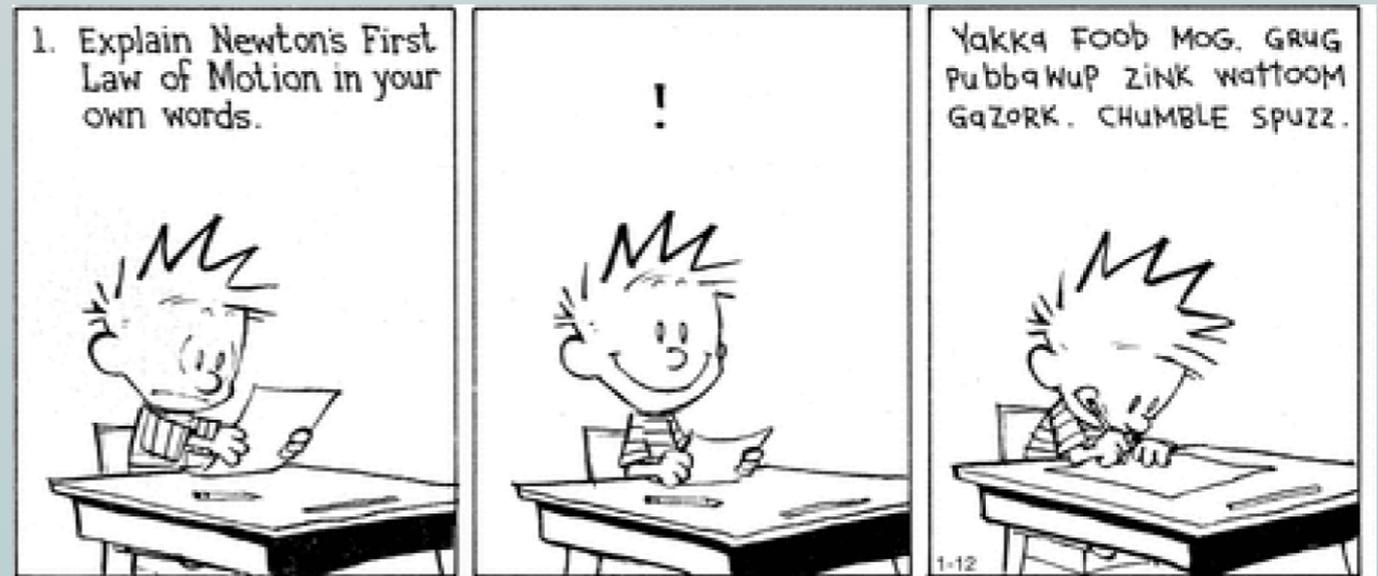


# ❖ Tests: in- and out-of-class

Tests should emphasise **the student's abilities to use the acquired knowledge**

But some students are more flexible than others at addressing novel situations, so one should:

- 1) avoid the **“happy idea” tests** which require a lot of intuition to tackle
- 2) use **higher frequency of tests/quizzes** (>2/term leads to improved performance)



It has been demonstrated that tests requiring inferences enhance learning more than those requiring memorized knowledge, and therefore should be used more often.

# ❖ Performance assessment

*Authentic assessment* favors problems that can be admit different alternative solutions, rather than those that can be solved in a fully algorithmic way.

• Focuses on assessing the degree with which students have grasped the learning objectives

✓ proposing assignments that can be **addressed from different points of view**

• Exploit assessment methods **closely related to later use of learning**

✓ simulations (computer and role-play), hands-on field or laboratory exercises, research project, juried presentations

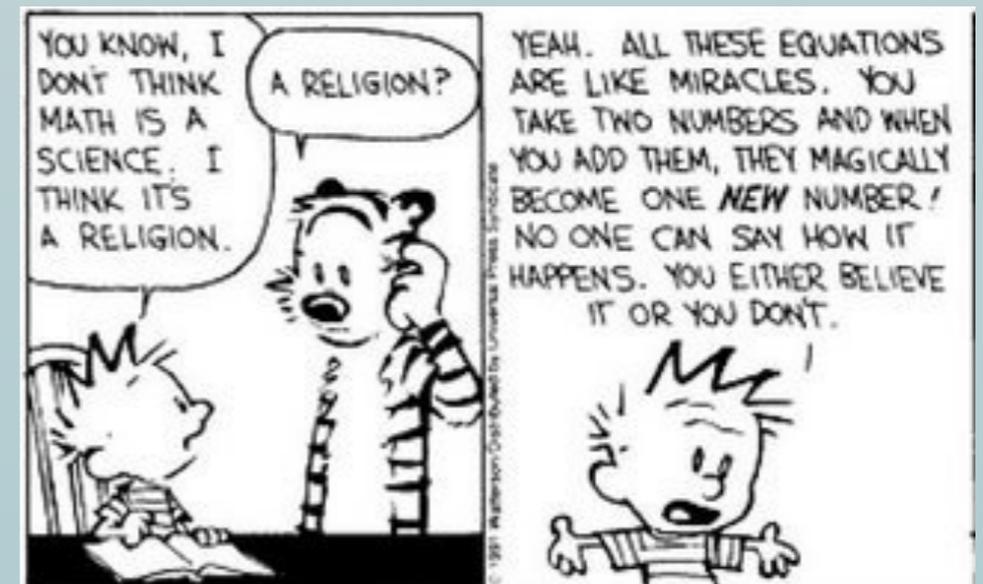
But:

1) It depends on the subject

2) They require **additional time**

✓ Both from the point of view of **preparing** the assessment methods

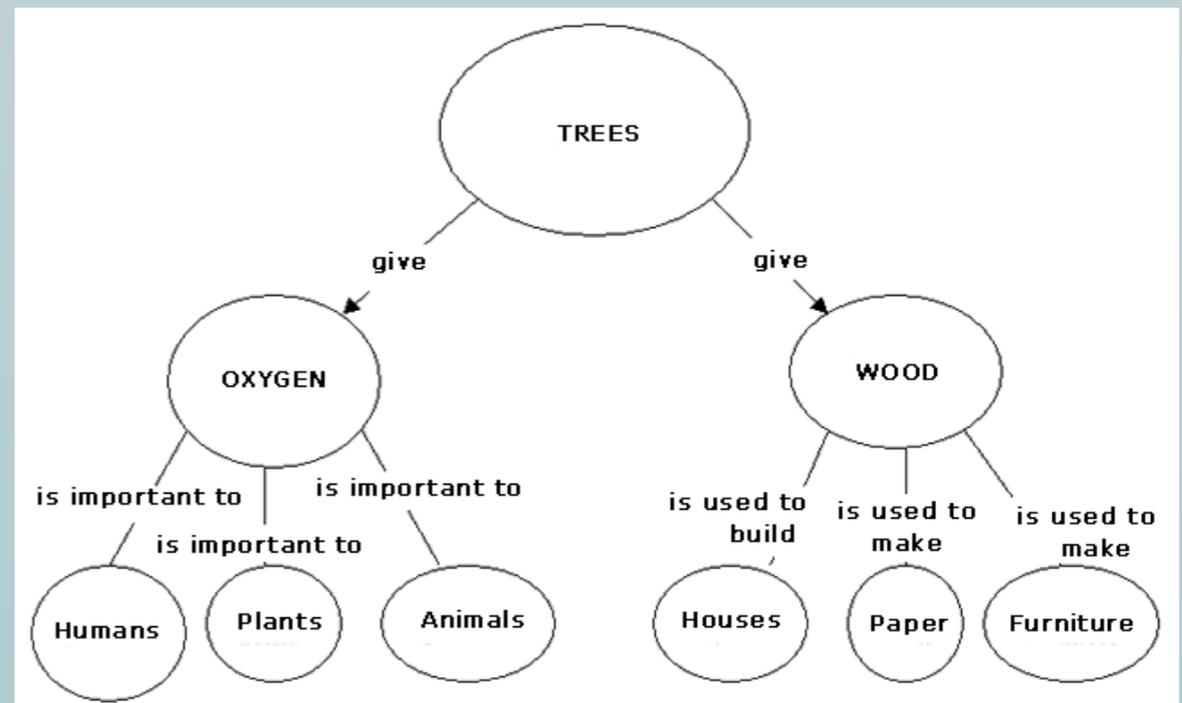
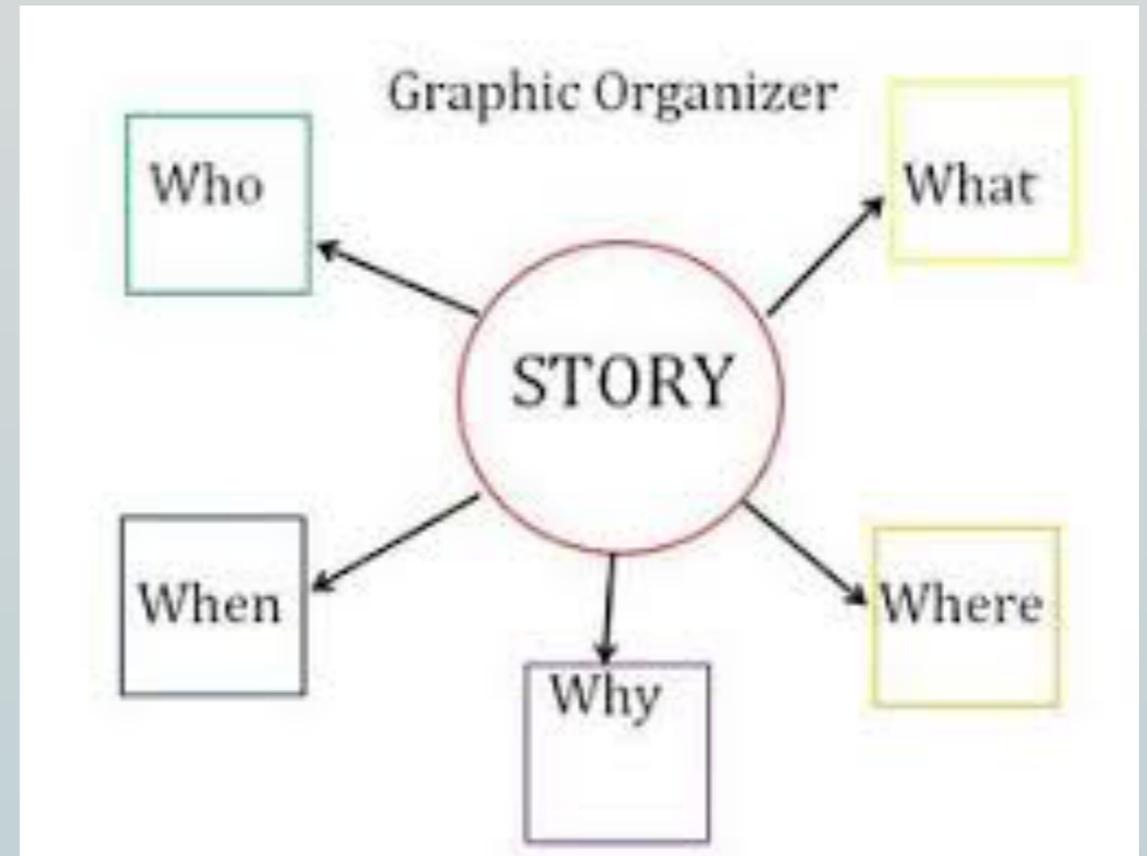
✓ and for **evaluating and marking** them in an objective and fair way



# ❖ Graphic representations

• An organized framework of (graphic organizer or concept map) is important for both thinking and learning

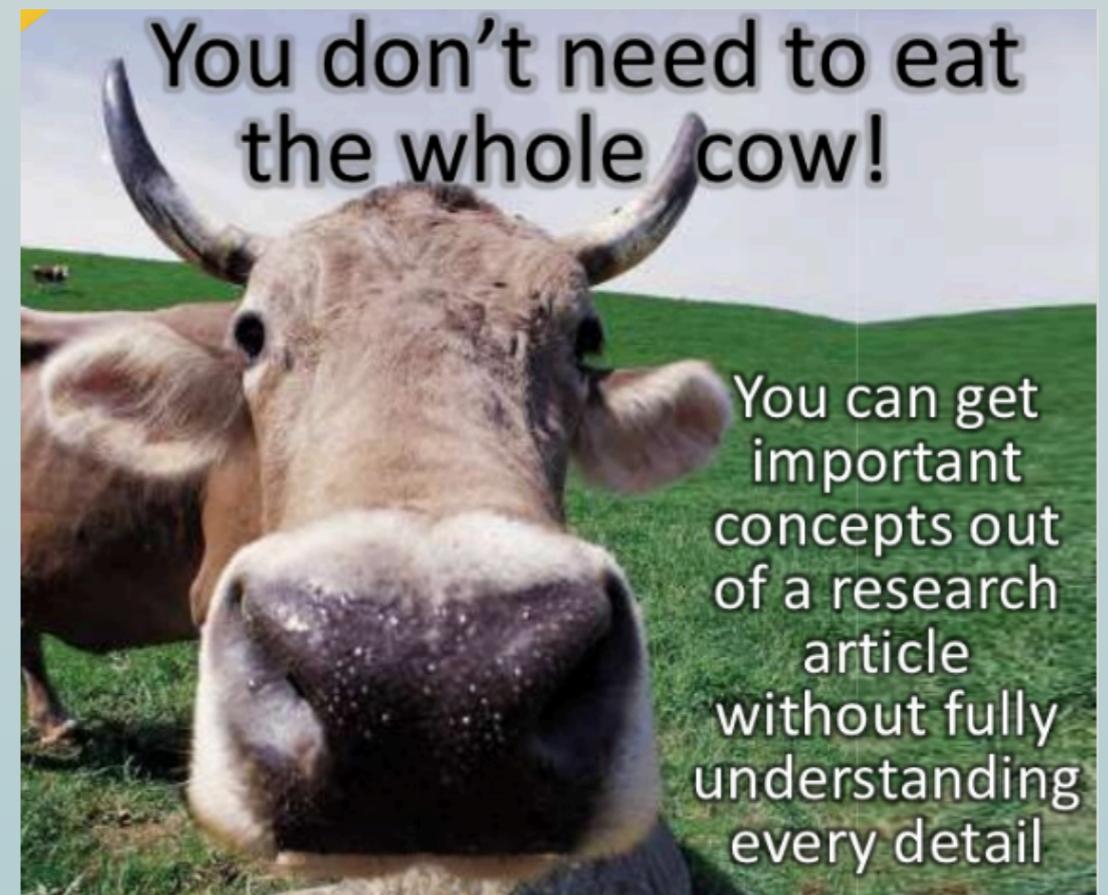
- ✓ proposing assignments with a copy of a basic structure with concepts missing, that should be filled by the students



# Journals and research papers

- Demonstrate that students can **read, understand, and explain a real research paper**
- Powerful method to gauge if the students have properly grasped the learning objectives
- Improves **critical reflection** and **self-awareness**
- Constitutes a direct motivation showing the **usefulness of the contents learned during the course**
- Valuable training preparation for **oral and presentation skills**

**Abstract:** Do I care?  
**Tables:** What did they really find?  
**Methods:** Do I believe the table?  
**Discussion:** So what?  
**Lit. Review:** What did we already know?



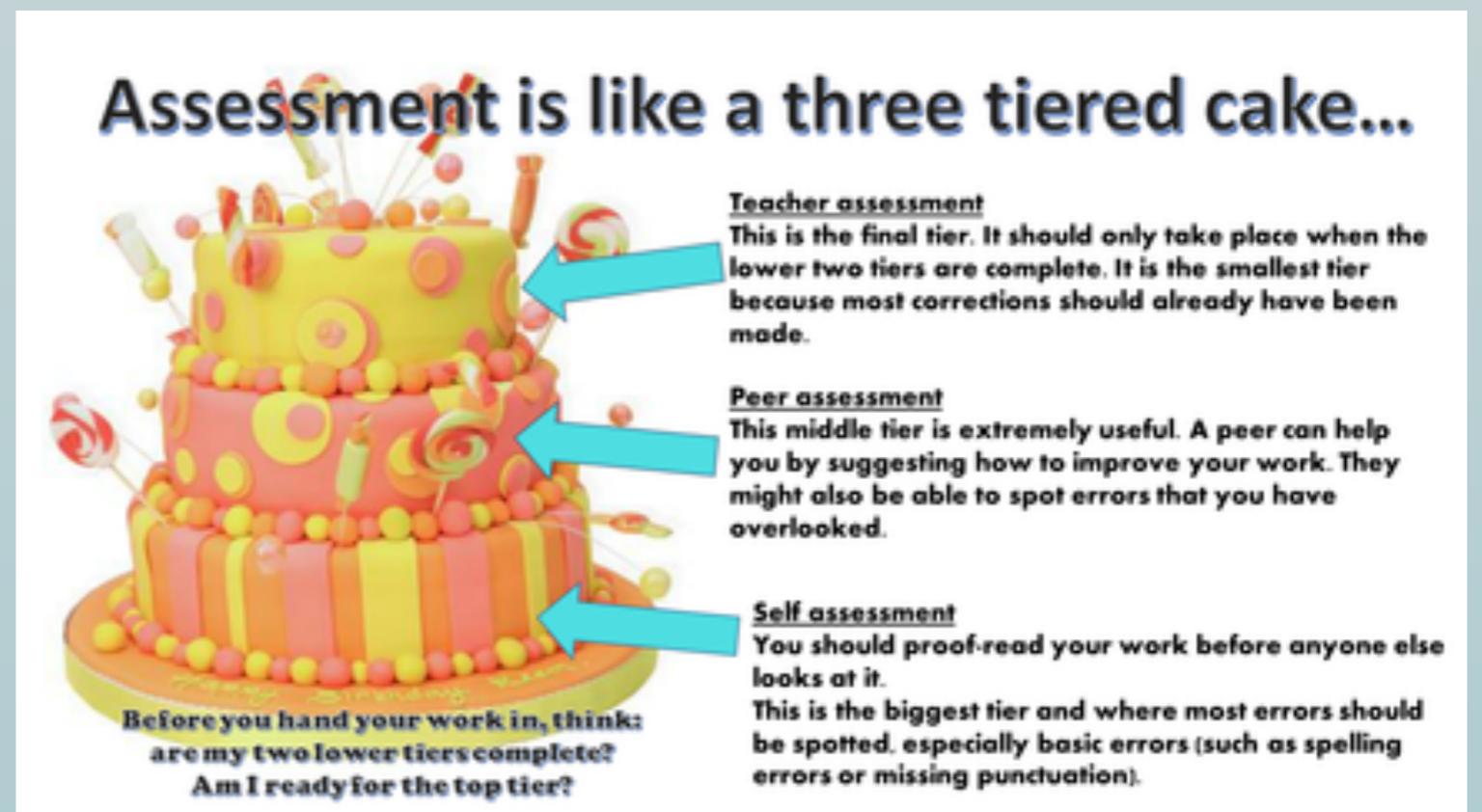
# Portfolios

- **Portfolios** not restricted to arts and architecture, they also make sense in **scientific subjects**
- They might include only student's **best work** or its **development**
- Some courses involve creating a portfolio of **computer programs** as part of its assessment (Skills in computer programming are a **highly valued asset both in academia and in private sector companies**)



# Peer Assessment

- Fellow students **help each other** to provide feedback about some of the assessment tasks
- Difficult to implement unless for **relatively small groups**, and where moreover only when **their level and background** is rather similar
- Delicate issues like **plagiarism**, or **harassing**, when the topics of the assignment are sensitive. Should be limited to situations where it can really help to attain the LOs



# Assessing group work

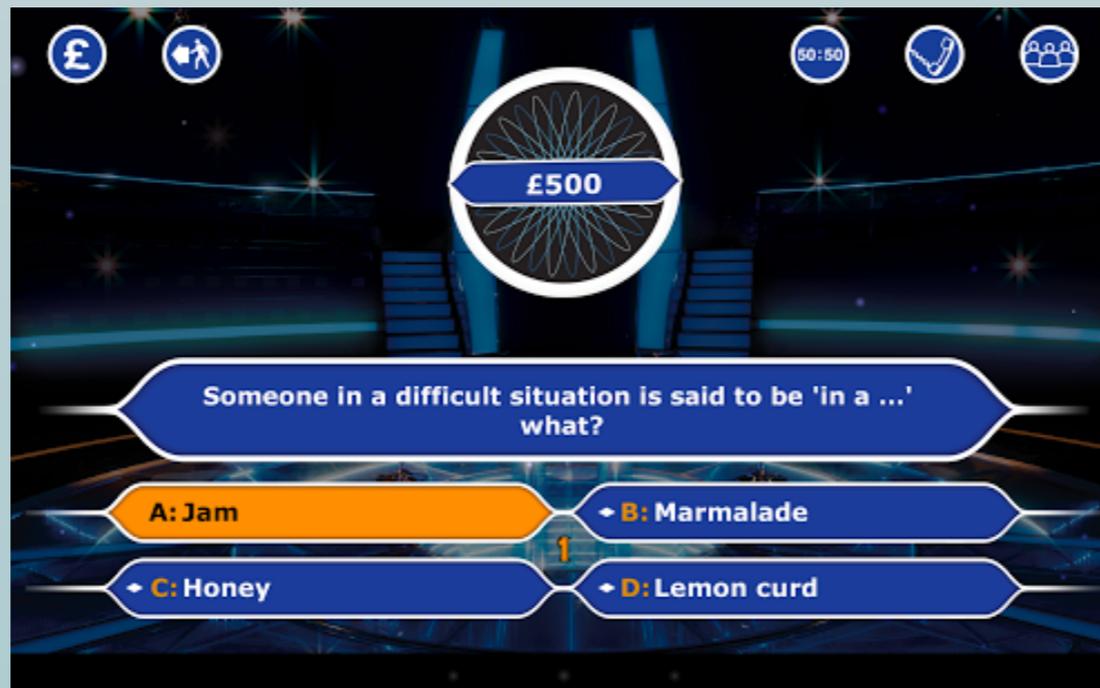
- Assessing team work individually is a **notoriously difficult task**
- Perhaps only meaningful method is a **common mark to the whole group**, but ensure that beforehand the group is well balanced (in terms of preparation, skills, and commitment)
- One suggestion has been to write individual reports, but this increases the workload while **reducing the overall quality of the final joint report**
- **Assessing each other's performance within a group** is highly delicate and difficult to be really objective

# Example of a grid for assessing group work

	Very Good	Good	Developing
<b>Research and collecting information</b> 6	I collected <i>lots of</i> information from various places, such as books, the internet etc. 6 - 5	I collected <i>some</i> information from a few places. 4 - 3	I only collected <i>a little</i> information from few places. 2 - 1
<b>Sharing</b> 8	I <i>always</i> shared my information or ideas with <i>all</i> my team members. 8 - 7	I <i>sometimes</i> shared information or ideas with my team members. 6 - 5 - 4	I shared <i>little</i> information or ideas with my team members. 3 - 2 - 1
<b>Completing tasks</b> 8	I met <i>all</i> deadlines and I was not late for meetings or to complete work. 8 - 7	I met <i>most</i> deadlines and was only late for <i>some</i> meetings and to complete work. 6 - 5 - 4	I missed <i>many</i> deadlines and was <i>often</i> late for meetings or to complete work. 3 - 2 - 1
<b>Contribution</b> 8	I <i>always</i> helped <i>every</i> team member with all tasks, such as gathering information, editing work. 8 - 7	I helped <i>some</i> of my team members, but not all to gather information and edit work. 6 - 5 - 4	I <i>didn't</i> help my team mates to gather information, edit work etc. 3 - 2 - 1
<b>Listening to other group members</b> 5	I <i>always</i> listened to the ideas and suggestions from my team. 5 - 4	I <i>sometimes</i> listened to ideas and suggestions from my team. 3 - 2	I <i>didn't</i> listen to my other team members. I often did it my own way. 1
<b>Co-operating with my team</b> 5	I <i>never</i> argued with my team members. I <i>always</i> talked about ideas and got everyone's opinion. 5 - 4	I <i>sometimes</i> argued with my team. I <i>sometimes</i> talked about ideas and thought about some opinions. 3 - 2	I <i>often</i> argued with my team mates. I <i>never</i> listened to their ideas and didn't think about their opinions. 1

# Embedded assessment

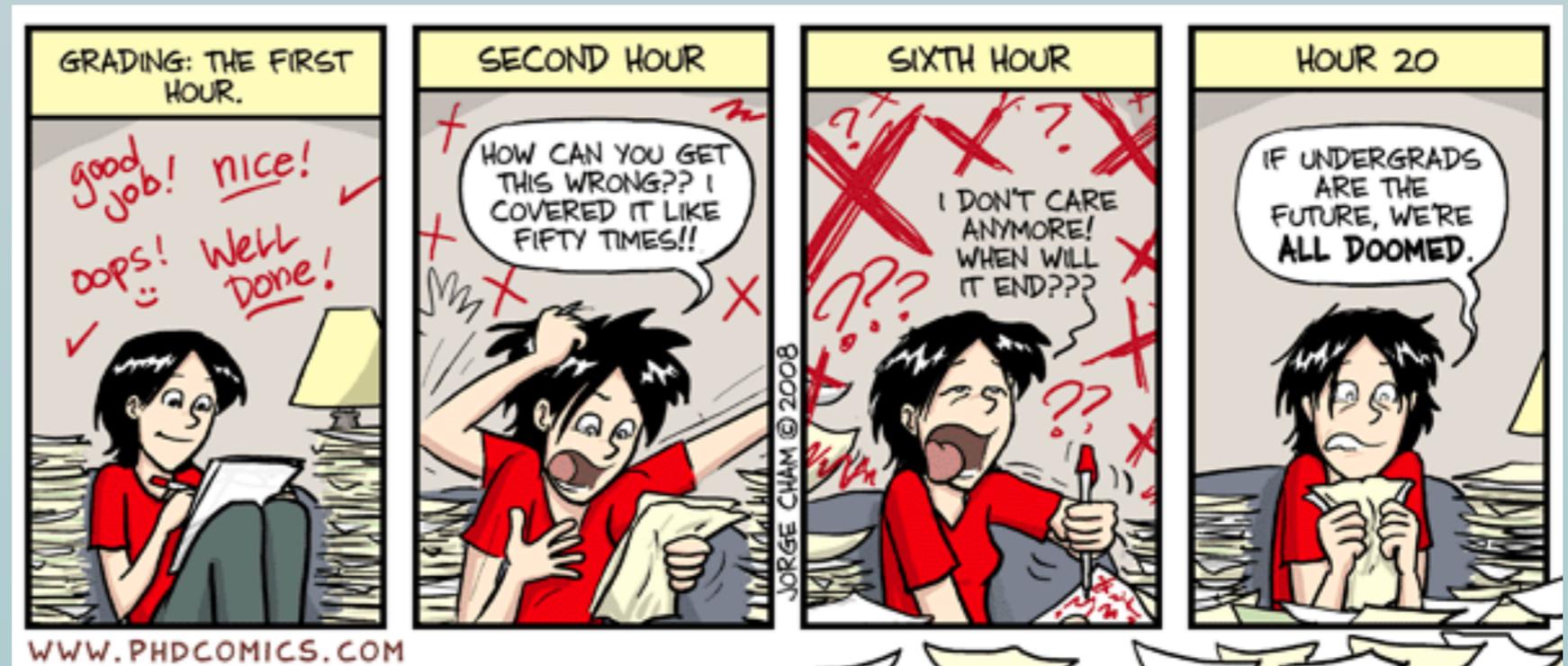
- Design assessment methods that are integral part of the **standard classroom activities**
- One popular example: **personal response systems within the lecture**
  - ✓ but biased towards easy questions that can be quickly answered
  - ✓ does not allow detailed and nuanced answers to difficult questions.
- Information collected during course activities can also be used for assessment, such as laboratory notes or field trip reports



# Assessing: some food for thought - 1

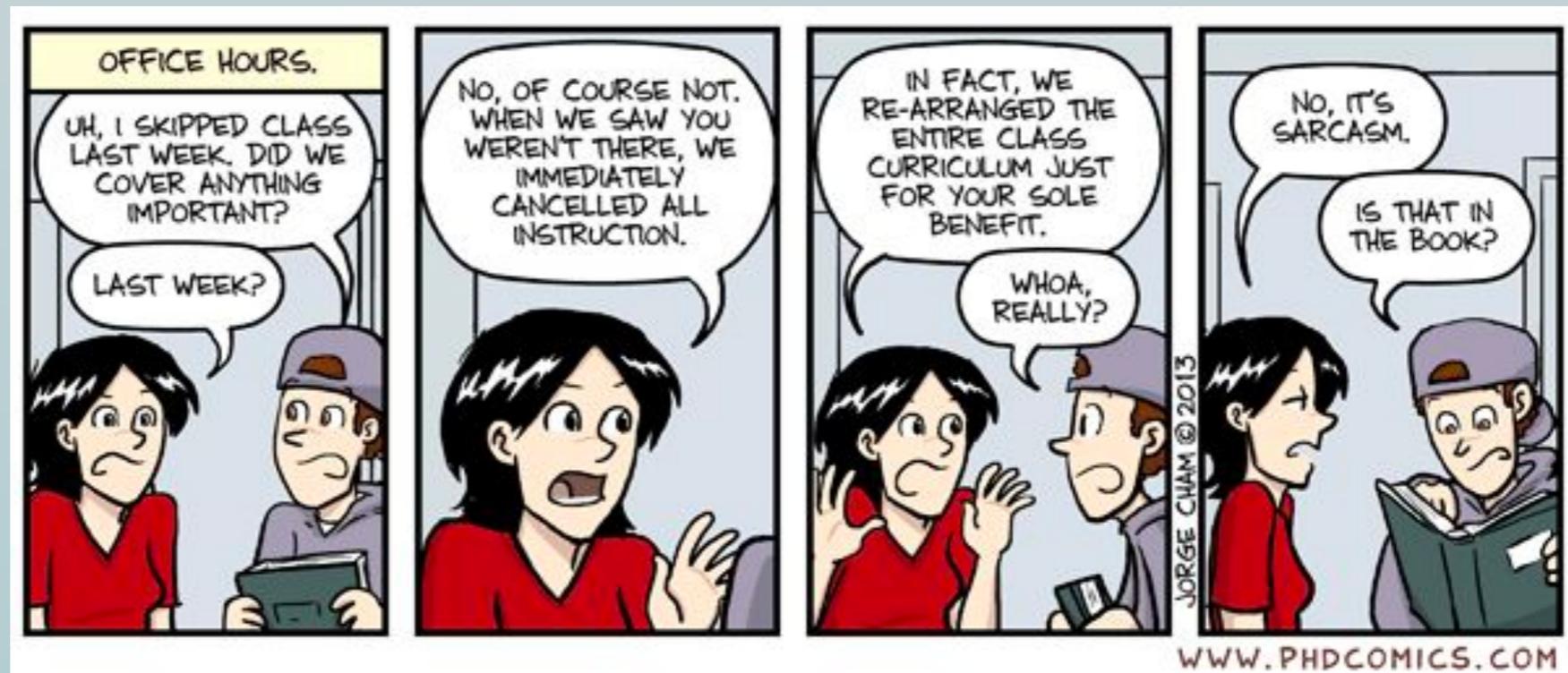
All the principles stated above sound great in theory, but can then be realistically carried out?  
What are the main concerns of experienced lecturers in this respect?

- The **many assessment methods** are all potentially useful both for the students and the instructors, but are they realistic?
- How can **overworked lecturers** with several deadlines looming provide continuous, individual feedback and partial assessment to large groups of students?
  - ✓ the contribution from **teaching and laboratory assistants** is really instrumental



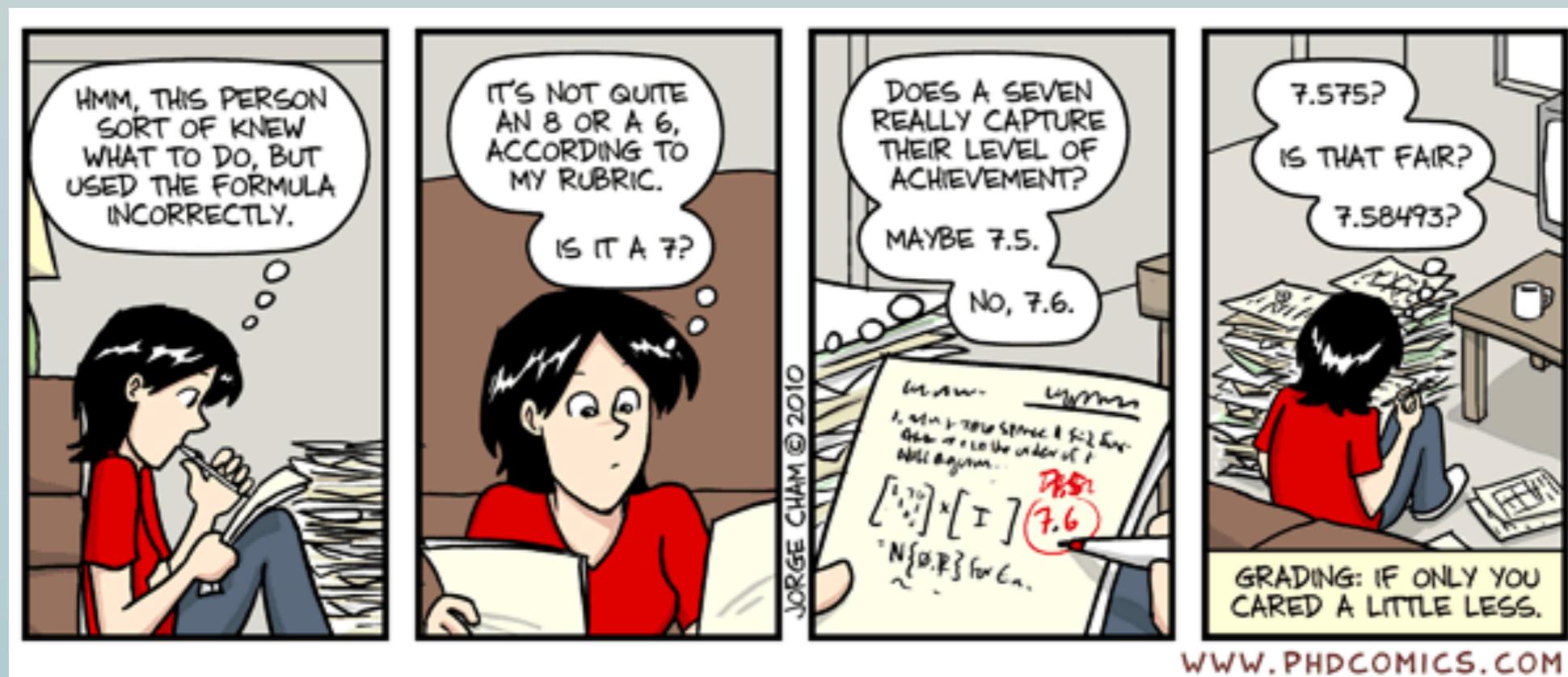
# Assessing: some food for thought - 2

- Some **competition and tension** in the assessment process can be beneficial:
  - else, how can we claim that the students are prepared for the **real world**?



# Assessing: some food for thought - 3

- A combination of assessment methods, traditional tests together with small projects and assignments to be carried out outside the classroom, is probably **best combination**
- Avoid grading the whole course based on a **single very final test!**



# Assessing the assessors (?)

- The **subjective student satisfaction** might not reflect objectively if the course has been useful for them
  - ☑ A light course with an easy exam might lead to a higher degree of satisfaction, but unlikely to lead to higher chance of employability



- Student evaluations have been shown to be **disproportionately biased against women and racial minorities**
- Crucial to devise **objective measurements of student satisfaction**, perhaps related to how well do they perform in follow-up courses and on their employability

# The art of assessing: take home messages

- **Learning is more important than grading**
- The value of a **learning experience** cannot be reduced to a **single mark** at the end of course test.
- The **assessment process itself** should also be a learning experience
- A combination of **more traditional and more innovative assessment methods** is possibly the optimal combination
- Providing **continuous feedback to the student's learning process** is very important, and cannot be restricted to the final grade

The primary goal of assessment is to provide feedback to both students and the instructors so that learning can be facilitated



**Appendices to the**  
**"Revised guide of the *van Quantum tot Molecuul* course"**

**Juan Rojo**

**Appendix 5)** Handout for the presentation "*Assessing, Testing, and Evaluating*" given on the 5th of October 2017, which complement the slides of Appendix 4.



## Assessing, Testing, and Evaluating

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Presentation Handout, current version: October 2, 2017

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The following material is based on Chapter 7 of “*McKeachie’s Teaching Tips: Strategies, Research, and Theory for College and University Teachers*”, 14th Edition.

## 1 General context

- Every course must come with some method of assessment, aiming to evaluate if the students have satisfactorily achieved its original learning goals.
- There exist different methods to carry out this assessment, some of them more conventional, others more innovative.
- It is important to avoid using exclusively a single assessment method for all cases. Some students, for instance, perform very badly in written tests, while they perform much better in case of assignments or small projects that they can work on their own.
- To some extent, the specific assessment method adopted influence what the students learn. For instance, if the exam only contains numerical problem-solving, the students will focus less on the more conceptual issues of the course.
- Some goals (such as motivation and attitudes) are not measurable by conventional tests, and need other ways to gauge their development in the students.
- Assessing is not limited to testing: classroom, laboratory, and out-of-class activities should play an important role as well in the process. This concept is know as *embedded assessment*.
- Relying on one or two tests only to determine the grades can be dangerous. Use better a variety of complementary assessment methods, what the students call *triangulation of data*. Avoid situations like the UK system, where until recently (for example in Oxford) a whole three-year course was assessed based on a single test.

Assessment should not be limited to a method to grade students: it can and should be also a learning opportunity for the students (and their teachers).

## 2 Planning methods of assessment

- Prerequisite: list the goals and objectives for the course.
- Then determine which kind of assessment is most suitable for each specific objective.
- Consider an appropriate variety of assessment methods: some students do well in high-stakes tests (like in the end of year exam) while others do better in out-of-class assignments or short projects.
- The reflection upon the interplay between goals and objectives to be achieved and the corresponding assessment methods often leads to exploring innovative forms of testing.
- Using assessment material with greater relevance to the course contents motivates better the students taking them.
- One possible pitfall of more innovative assessment methods is that it becomes more difficult to ensure objectivity. In a traditional test it is much easier to be objective in the grading, at least within scientific subjects.

### Institutional purposes for your course assessments

- Many institutions are monitoring learning outcomes of their programs, although of course this monitoring is rather more challenging at the level of individual courses.
- Involvement of faculty is critical here, but requires appropriate guidance from the university management as well as the possibility of devoting an appropriate amount of time. In this respect, the faculty members can provide very valuable data by incorporating the assessment information from their courses into the overall process.
- Designing assessment methods for the course that moreover provide information that can be used for the improvement of a whole degree or the university in general leads to a double benefit, but specific preparation is required in order to prepare such tailored assessment methods.

## 3 Methods of assessing learning

There exist different methods that can be used to assess learning, in other words, to evaluate if the original learning goals of the course have been fulfilled by the students.

### Tests: in- and out-of-class

- Tests are an unavoidable part of the assessment of many courses, but often lead to frustration in students.
- It is very well known that perfectly able students underperform in tests, even if they have appropriately achieved the learning goals of the course.

- In the information age, tests which are based on simple fact recalling are not appropriate anymore. Tests should focus on assess how students deal with the information that they have at their disposal, not with the sheer fact of whether or not students are able to memorize a given chunk of information.
- The specific ways to assess a course affect how students study for these course.
- While it is preferable to devise tests that emphasize their abilities to use the acquired knowledge, as opposed to just dump memorized information, it is also important to realize that some students are not flexible than others at addressing novel situations, so one should avoid the “*happy idea*” tests which require a lot of intuition to tackle for instance a specific problem that the students have never encountered beforehand.
- A higher frequency of tests/quizzes (meaning more than 2 per term) has been demonstrated to lead to an improved student performance.

It has been demonstrated that tests requiring inferences enhance learning more than those requiring memorized knowledge, and therefore should be used more often.

### Performance assessment (authentic assessment)

*Authentic assessment* favors problems that can be admit different alternative solutions, rather than those that can be solved in a fully algorithmic way.

- Other assessment methods more closely related to later use of learning are simulations (computers, role play) hands-on field or laboratory exercises, research project and juried presentations.
- The downside of these methods, as opposed to a traditional tests, is that they require to devote a significant amount of additional time, both from the point of view of preparing the assessment methods, and then for evaluating and marking them in an objective and fair way.

### Graphic representation of concepts

- Specially in scientific subjects, graphical representation of concepts is a rather standard assessment technique.

### Journals and research papers

- Demonstrate that one can read, understand, and explain a real research paper is a powerful assessment method to gauge if the students have properly grasped the learning objectives of the course.
- This method specifically improves critical reflection and self-awareness, as well as direct motivation when demonstrating the usefulness of the contents that have been learned during the course.
- Moreover, this provides valuable training preparation for instance for oral and presentation skills, which are then very valuable in many different contexts.

## Portfolios

- Portfolios are not restricted to artistic subjects and architecture: they also make a lot of sense in scientific subjects.
- For instance, many courses include the creating of a portfolio of computer programs to be part of the course assessment. Such virtual portfolio could be based on commercial packages such as **Mathematica** or **Matlab**, or in more general-use computer languages such as **Python**.
- Skills in computer programming are a very valued asset both in academia and in private sector companies, so we should encourage them as much as possible as part of the evaluation of scientific subjects.

## Peer assessment

- This concept means that fellow students help each other to provide feedback about some of the assessment tasks.
- A major limitation of this method is that it requires a relatively small group, and where moreover their level and background should all be rather similar, else it is difficult to meaningfully assess the progress of your fellow students.
- Here there are also delicate issues like plagiarism, or harassing when the topics of the assignment are rather sensitive. So this method of assessment should be limited to situations where it can really help.

## Assessing group work

- Assessing team work individually is a notoriously difficult task
- Here perhaps the only meaningful assessment method is to give a common mark to the whole group, but ensure that beforehand the group is well balanced among its members (both in terms of preparation, skills, and commitment to the specific project).
- One suggestion is to write individual reports, but this increases the workload while reducing the overall quality if the final joint report due to the limited time that can be devoted to its writing.
- Assessing each other's performance within a group is highly delicate and difficult to be objective.
- Overall, aiming for balanced groups and ensure that there is good communication between them is the most important ingredient for the success of group work.

## Embedded assessment

Embedded assessment means that opportunities to assess student progress and performance are integrated into the instructional materials and are indistinguishable from everyday classroom activities.

- One example is the use of personal response systems within the lecture, but of course this is biased towards easy questions that can be answered more or less intuitively, and does not allow detailed reasoned answers to difficult questions.
- Information collected during course activities can also be used for assessment, such as laboratory notes or field trip reports. Though again this represents a significant burden for assessors.

## 4 Summary

The primary goal of assessment is to provide feedback to both students and the instructors so that learning can be facilitated

The most important points of the above discussion can be summarized as follows:

- Learning is more important than grading. The value of a learning experience cannot be reduced to a single mark in the end of course test.
- The assessment process itself should also be a learning experience.
- Providing continuous feedback to the student's learning process is very important, and cannot be limited to the final grade.
- A combination of more traditional and more innovative assessment methods is possibly the optimal combination.

All the principles stated above sound great in theory, but can then be realistically carried out?  
What are the main concerns of experienced lecturers in this respect?

- The detailed assessment methods discussed in this presentation are all potentially useful both for the students and the instructors to enhance learning output, but how can overworked lecturers with several deadlines looming provide continuous, individual feedback to large groups of students? Here the contribution from teaching and laboratory assistants is really instrumental, specially in the marking and evaluation of the different assessment methods.
- Some competition and anxiety in the assessment process is essential: else, how can we claim that the students are prepared for the real world? They need to learn how to function properly under pressure, which does not mean that their value is only limited to that of their marks. A combination of assessment methods (say traditional tests together with small projects and assignments to be carried out outside the classroom) are probably the best combination. And avoid grading the whole course on a single very final test!
- Should we care about student evaluations at all? The subjective student satisfaction might very well not reflect objectively if the course has been useful for them. A light course with a very easy exam might lead to a higher degree of satisfaction, but it is unlikely to lead say to a higher chance of student

employability. In this respect, the very same questions that are asked to the students when they evaluate their courses can have a dramatic effect in the actual outcome. This reasoning also includes the student evaluation of the various assessment methods used during the course.

- Another important fact that should make us very way of student evaluations is that they have been shown to be disproportionately biased against women and racial minorities (as quantified by several studies). So it is important to devise objective measurements of student satisfaction (perhaps related as how well do they perform in follow-up courses and their employability), while the subjective satisfaction is much more difficult to extract sense from it.