

1 Introduction

Physics is the science of the structure and properties of inanimate matter. Molecular physics is the branch of physics concerned with the examination of the structure and properties of molecules using physical methods.

Lat. *moles* = mass, *molecula* = small mass

A molecule consists of two or more atoms, held together by a chemical bond. It is the smallest unit of a (non-atomic) chemical substance.

Binding energy (96 kJ per mol \approx 1 eV per molecule):

- Chemical bonds: dissociation energy of 300 kJ mol^{-1} – 2000 kJ mol^{-1} ,
- Intermolecular interaction in liquids, molecular crystals, and molecules adsorbed at solid surfaces are in the order of magnitude of 50 kJ mol^{-1} . In gases, the interaction energy goes to zero as the pressure drops.

(Discussion of the figures given below)

The treating of problems in molecular physics is based on three pillars:

- The knowledge base of chemistry for interpreting chemical reactions, synthesis and analysis;
- The statements of quantum mechanics (quantum chemistry) for the explanation of molecular structures and properties;
- Physical measurement technology and methods.

This course is organized differently. Chapter 1 (Introduction) is followed by the chapters

2. Size, Mass and Kinetics of Molecules;
3. Molecules in Electric and Magnetic Fields;
4. Principles of Structure and Symmetry;
5. The Theory of Chemical Bonds;
6. Macromolecules;
7. Molecular Electronics;
8. Spectroscopy.

Thus, some basic theory is covered in chapters 3-5, the most important examination methods are described in chapters 2 and 8, and two examples of research areas in the field of molecular physics are treated in chapters 6 and 7. For the presentation of the most important spectroscopic methods that are integrated in this course Molecular Physics as Chapter 8 we will use some parts of another script which I use in the course "Spectroscopy for Physicists".

The course Molecular Physics put emphasis on the approaches of physicists to molecular problems. Molecular Physics is the consideration of the problems from the point of view of an experimental physicist. Other views to similar questions are chemistry, biology, material sciences and engineering including environmental engineering or environmental physics.

We could begin the history of molecular physics with Democritus [460-371 BC], who founded the atomic philosophy. This philosophy was later supported by Epicurus and Titus Carus Lucretius. Aristotle [384-322 BC] condemned it, however, and it remained unknown until the middle ages, when it was brought to light by Galileo Galilei [1564-1642]. An atomic concept of matter was supported by Robert Boyle, Isaac Newton and Christian Huygens, but opposed by Gottfried Wilhelm Leibniz. It was the basis for Daniel Bernoulli's kinetic theory of gases.



Quantitative considerations of chemical reaction led to John Dalton's law of constant and multiple proportions, which he wrote about in his book of 1808. In the same year, Louis Joseph Gay-Lussac found a relation of volumes in gas reactions which was unexplainable using Dalton's law.

A final solution was found in 1811 by the Italian physicist Avogadro [Lorenzo Romano Amedeo Carlo, Graf von Quaregna und Ceretto, 1776-1856]. His law states that the same volumes of ideal gases under the same pressure and at the same temperature have the same number of atomic groups, which he called "molecula". With that he founded an important basis for atomic and molecular physics, which needed another half century until its general acceptance.

To his honour, the number of molecules in a mole is called Avogadro's number. This number was first determined by Joseph Loschmidt in 1865 and is

$$L = N_A = 6,0221367 \times 10^{23} \text{ mol}^{-1}.$$

When Loschmidt first approximated this number, he also approximated the radius of a molecule.

It should be noted here that we use in this and other lecture scripts a comma as the decimal sign between digits in the numbers in agreement with ISO 31-0.

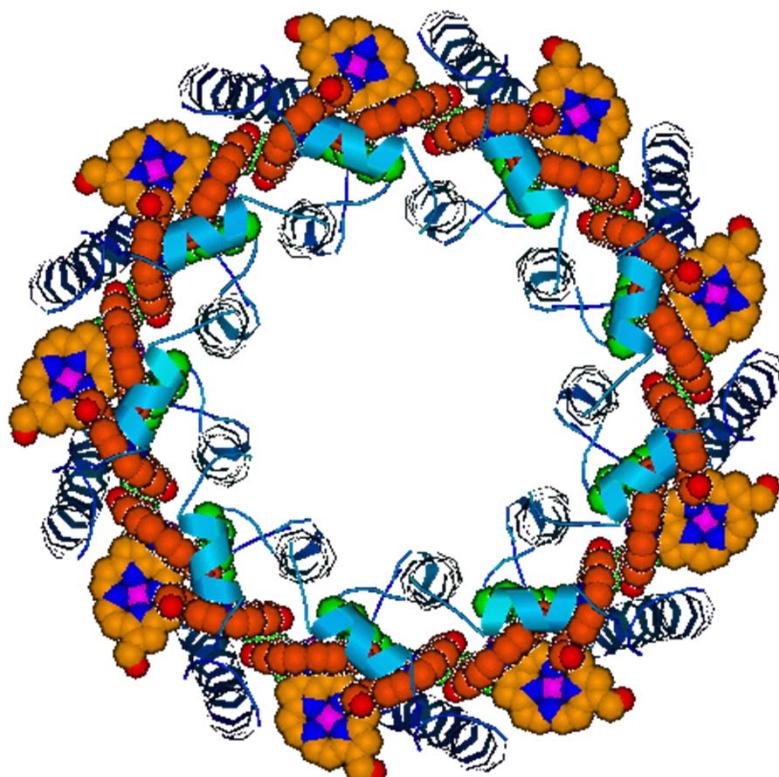
An exact understanding of chemical bonds has become possible with the advances in atomic and quantum physics. In 1915, the physicist Walter (Ludwig Julius Paschen Heinrich) Kossel developed an electrostatic model of the heteropolar chemical bond (ionic bond). He recognized the electronegativity of atoms as the source of the polarity of the bonding. The physical chemist Gilbert Newton Lewis published a paper in 1916 concerning the chemical homopolar bond caused by the creation of an electron pair. This was the fundament of the acid-base theory established in 1938/39.

Since 1927, the physicists Friedrich Hund, Walter Heinrich Heitler, and Fritz Wolfgang London laid important foundations of the quantum theory of chemical bonds, which has now become known as quantum chemistry.

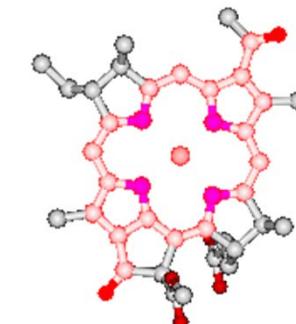
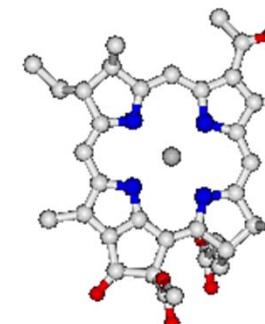
The peripheral light-harvesting complex

The light harvesting complex is a nonamer with ninefold rotational symmetry. The molecule binds 27 Bchl a and we see 9 carotenoids (rhodopin glucoside) although estimates from the native membrane of the bacteria suggest that there ought to be 18. The crystal structure has a 3-fold rotational axis intersecting the molecule - so in the crystal 1/3 of the molecule is unique: the 9-fold molecular symmetry further reduces the structure to a unit of two polypeptide chains, 1 carotenoid and 3 Bchl a molecules. There are minor departures from this (non-crystallographic) 9-fold symmetry, notably at crystal contacts, but for the vast majority of the molecule this symmetry is precise down to our current resolution of 2.0 Å.

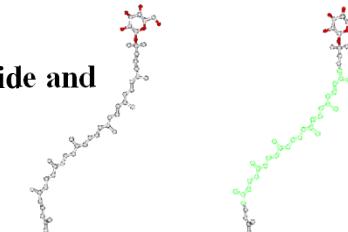
The pigments are held by the protein matrix in a systematic arrangement. At the top of the molecule is an overlapping ring of Bchl a molecules. In the diagram below these are seen edge on in orange (only the chromophore, or conjugated double bond system, is shown). At approximately the middle of the structure are 9 further Bchl a molecules. Carotenoid chromophores span the gap between the Bchl a's.



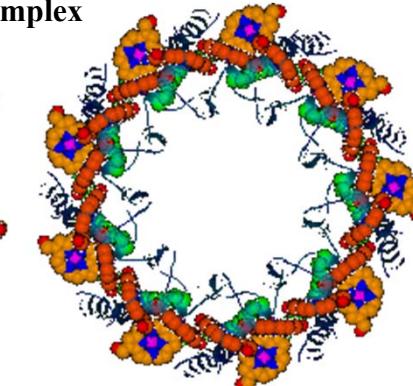
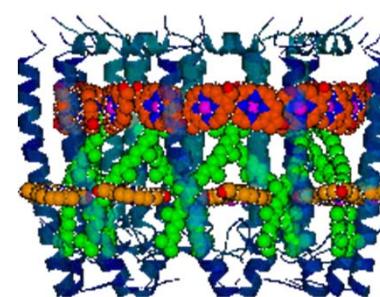
Bacteriochlorophyll a and its chromophore



Rhodopin glucoside and its chromophore

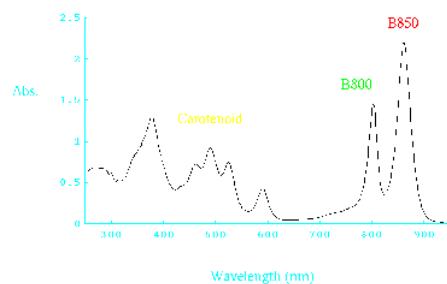


This physical arrangement of chromophores determines the gross properties of the complex



<http://www.chem.gla.ac.uk/protein/LH2/lh2struc.html>
Further information: steve@chem.gla.ac.uk

Cogdell R.J., Isaacs N.W., Freer A.A., Arrelano J., Howard T.D., Papiz M.Z., Hawthorn-thwaite-Lawless A.M. & Prince S.M. (1997) The Structure and function of the LH2 (B800-850) complex from the purple bacteria Rhodopseudomonas acidophila strain 10050. *Prog. Biophys. molec. Biol.* Vol 68 No. 1, pp 1-27.

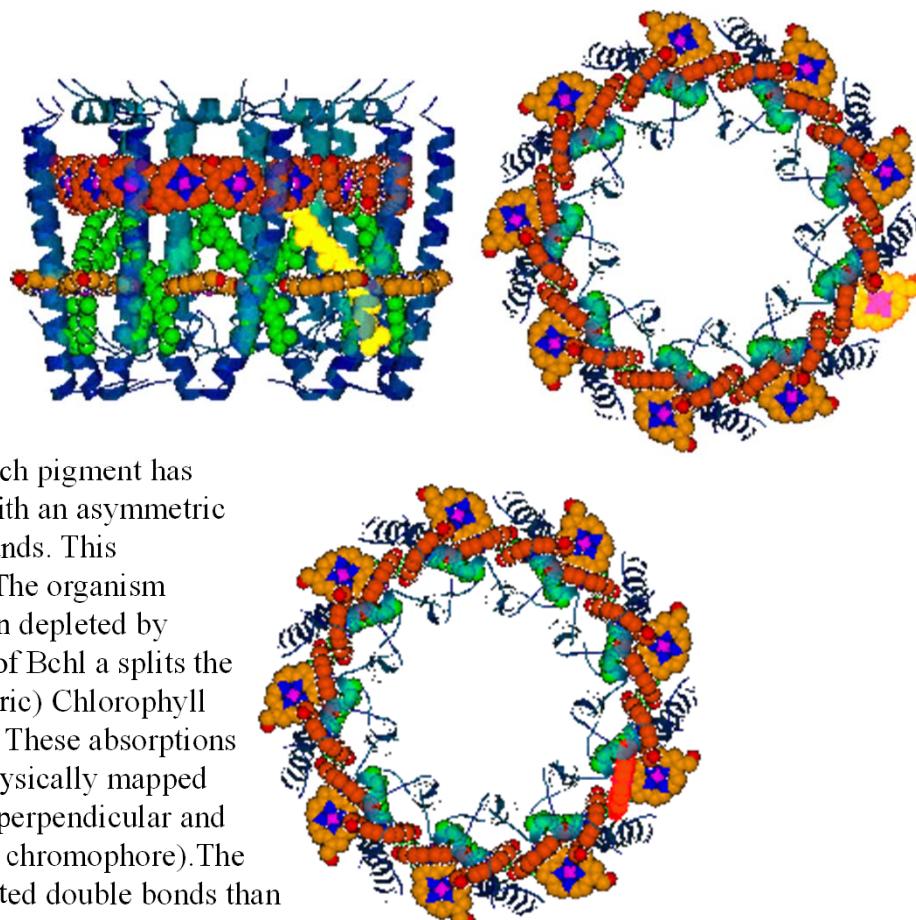


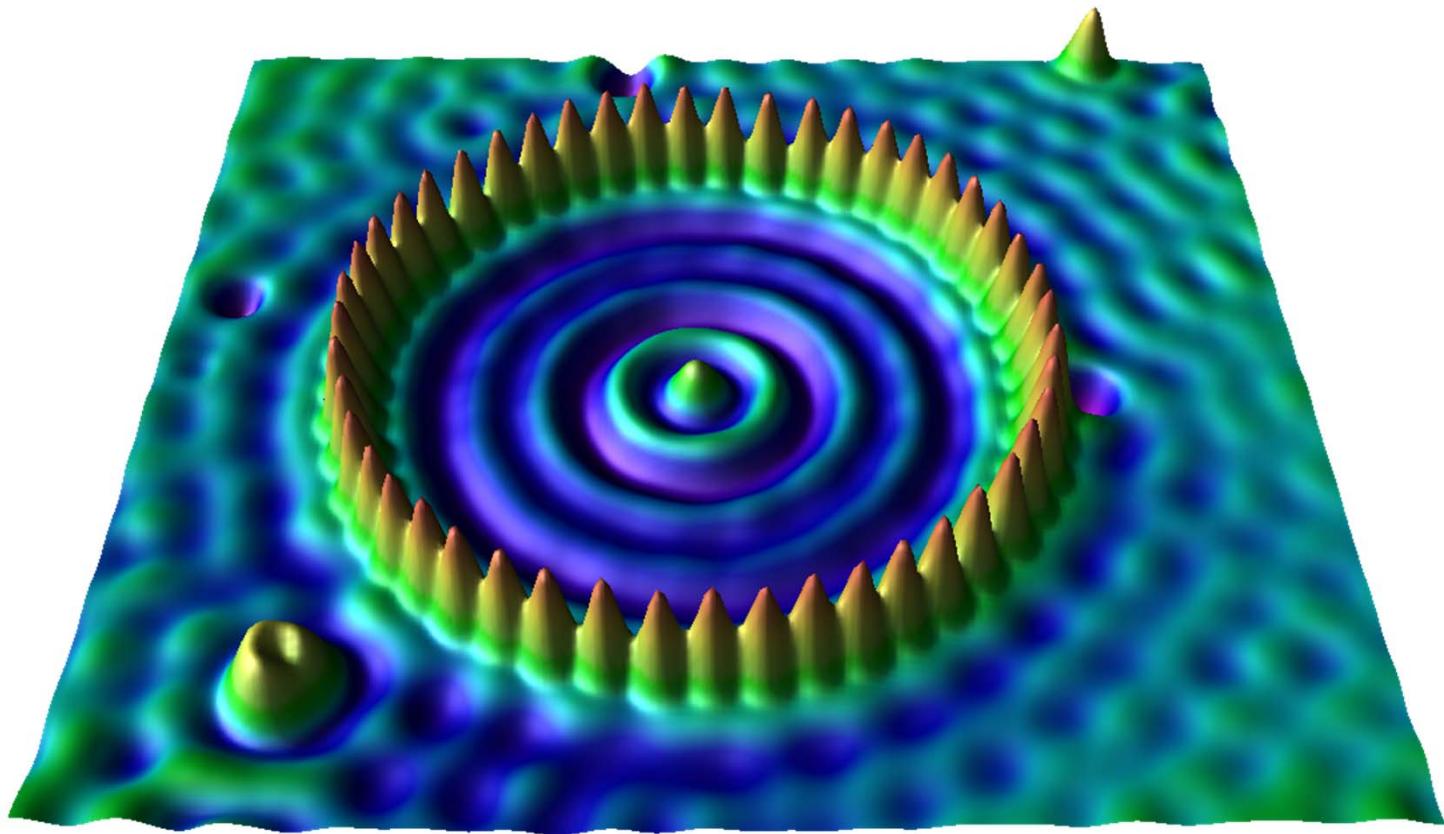
Carotenoid absorption (circa 470nm), Bchl a absorption at 800nm and Bchl a absorption at 850nm

Energy transfer in LH2

Photons may be absorbed by any of the pigments in the LH2 complex. Each pigment has characteristic resonant absorptions: Bchl a is a porphyrin like molecule with an asymmetric conjugated double bond system: this results in two resonant absorption bands. This asymmetry is the primary reason for the bacteria to choose this pigment. The organism needs to access photons from regions of the spectrum which have not been depleted by higher organisms - the asymmetry in the conjugated double bond system of Bchl a splits the resonant absorption bands of this molecule further than the (less asymmetric) Chlorophyll molecule. This allows the bacteria to find a niche in the spectrum *in vivo*. These absorptions may be mapped to transition dipoles (Q_x and Q_y) which can in turn be physically mapped onto the surface of the Bchl a molecule (the Q dipoles are approximately perpendicular and exist in the plane of the chlorin, Q_y is coincident with the long axis of the chromophore). The carotenoid molecules in purple bacteria have a greater number of conjugated double bonds than those found in higher plants. This is a consequence of having to quench a triplet energy level in Bchl a for photoprotective purposes. However a consequence of the large extent of the chromophore is again access to a less depleted portion of the spectrum. In fact purple bacteria are purple due to the absorption of their carotenoids rather than Bchl a!

Information from spectroscopy, biochemistry, and molecular biology has allowed us to assign bands in the LH2 spectrum to specific molecules in the LH2 molecule. A Q_y absorption band occurring at 800nm is due to a monomeric Bchl a pigment oriented perpendicular to the membrane normal. A Q_y absorption band occurring at 850nm may be assigned to extensively coupled Bchl a pigments with dipoles oriented parallel to the membrane normal. The Q_x dipole absorptions of all Bchl a's are at the same wavelength.

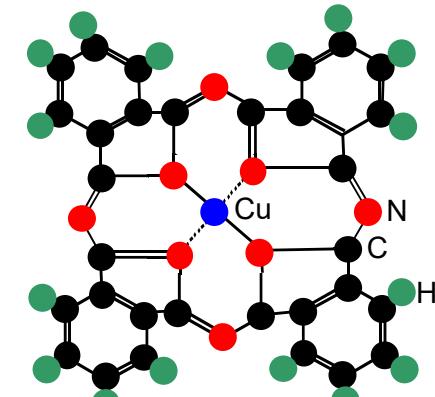
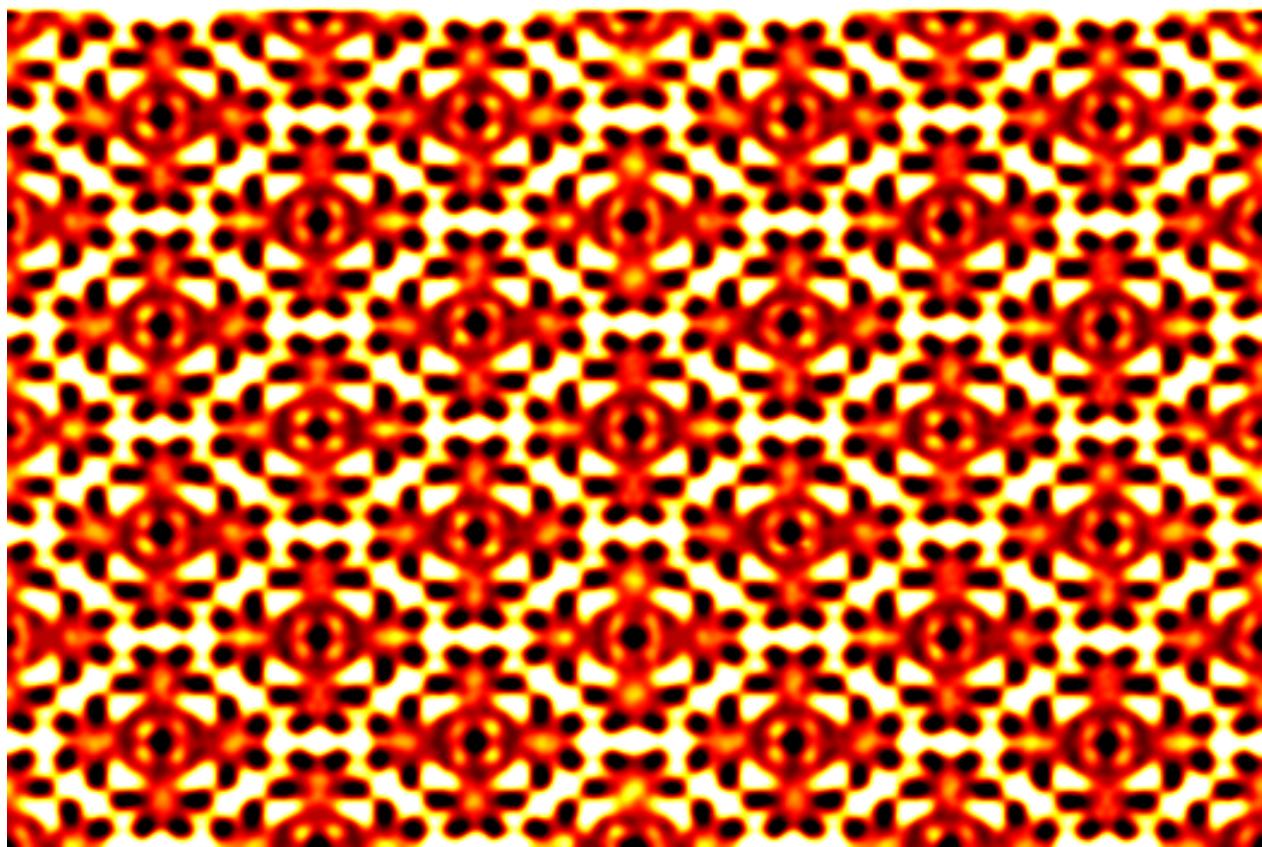




Scanning Tunneling Microscopy, IBM

Scientists discovered a new method for confining electrons to artificial structures at the nanometer lengthscale, the **Quantum Corrals**. Surface state electrons on Cu(111) were confined to closed structures (corrals) defined by barriers built from Fe adatoms. The barriers were assembled by individually positioning Fe adatoms using the tip of a low temperature scanning tunneling microscope (STM). A circular corral of radius 71.3 Angstrom was constructed in this way out of 48 Fe adatoms.

This STM image shows the direct observation of standing-wave patterns in the local density of states of the Cu(111) surface. These spatial oscillations are quantum-mechanical interference patterns caused by scattering of the two-dimensional electron gas off the Fe adatoms and point defects.



for comparison rotate around 45°

Progress of High Resolution Molecular Imaging and TEM Resolution

Using 100 kV electron microscope (JEM-100B), molecular image of chlorinated copper phthalocyanine crystal was demonstrated that molecule could be observed by many beam imaging method for the first time in the world. After that, by increasing the acceleration voltage largely the resolution was improved in photographing the same sample with 500 kV High Resolution Electron Microscope (JEM-500, HREM), which was presented at Novel symposium in 1979. The below figure was taken with new 1000 kV High Resolution Electron Spectromicroscope. The contrast inside the molecule becomes clearer, so that the benzene and the porphyrin rings appear clearer. Taken from <http://eels.kuicr.kyoto-u.ac.jp>

Literature for the course Molecular Physics

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