Introduction to quantum mechanics for chemistry

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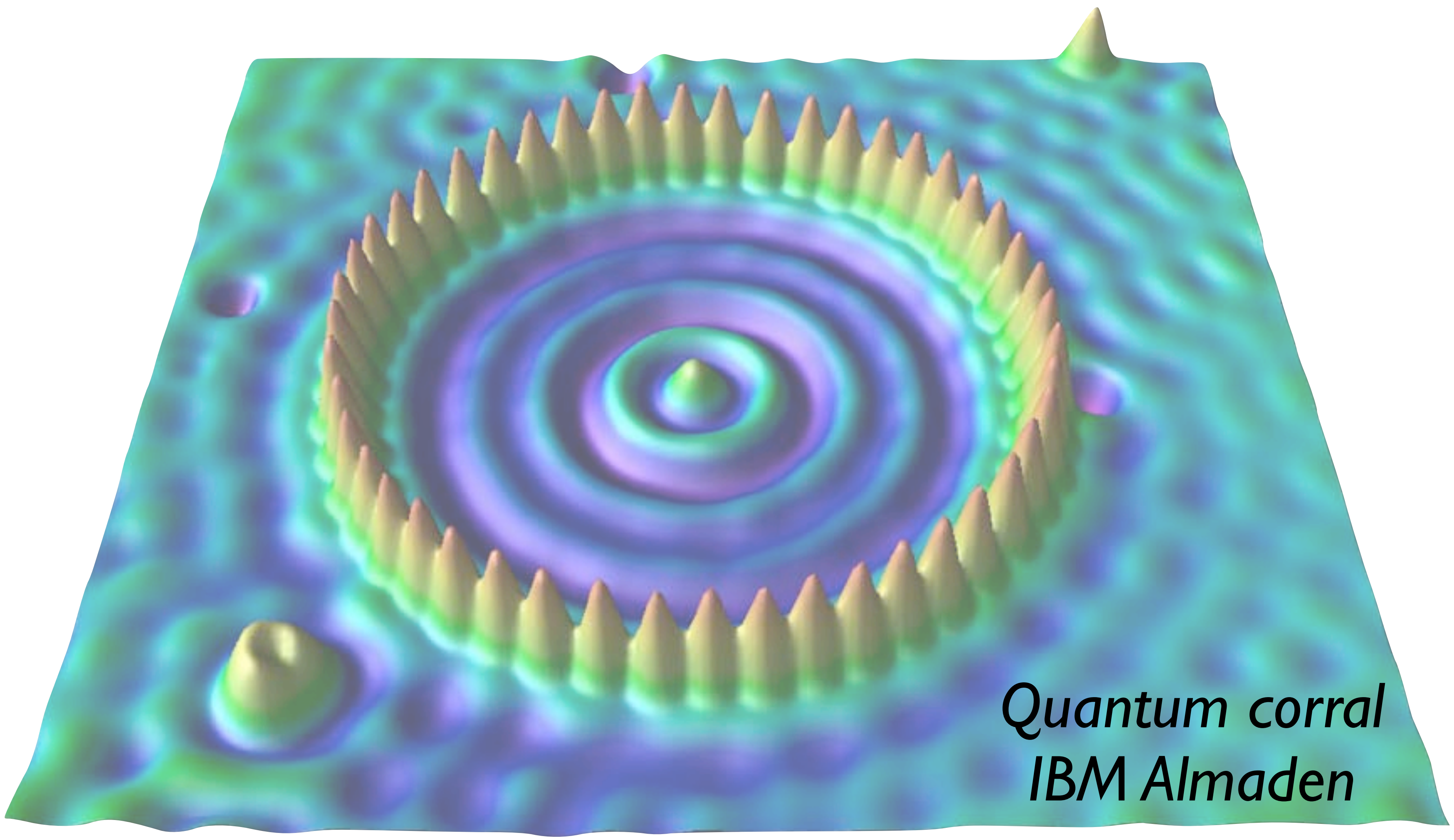
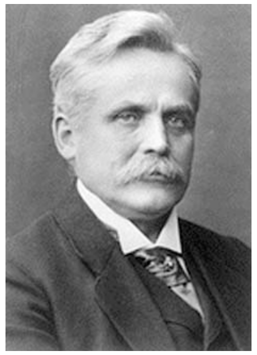
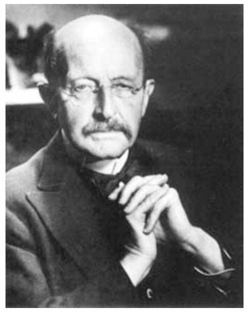
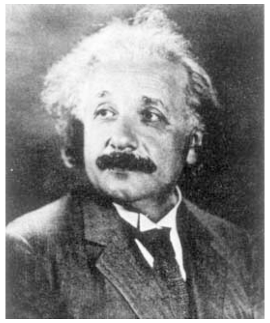





Unusual experiments

- At the turn of the 20th century some physical observations remained unexplained by "classical" theories
- **Black body radiation:** Kirchhoff (1859) Explained by Stefan, Boltzmann, Wien & Planck (1879 – 1900)
- **Photoelectric effect:** Hertz (1887) Explained by Einstein (1905)
- **Hydrogen spectrum:** Kirchhoff & Bunsen (1860); Balmer (1885), Rydberg (1888), Lymann (1906). Explained by Bohr (1913)

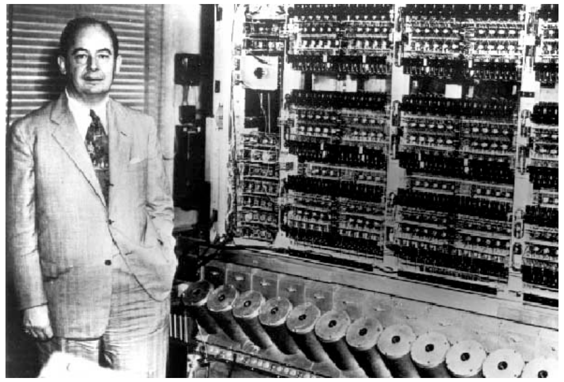





Birth of quantum theory

- De Broglie in 1924 introduces wave–particle duality
- In1926, Schrödinger and Heisenberg formulate independently a general quantum theory
- Schrödinger’s approach uses differential equations but Heisenberg’s formulation uses matrices

- 1932: Von Neumann “*Mathematical Foundations of Quantum Mechanics*”

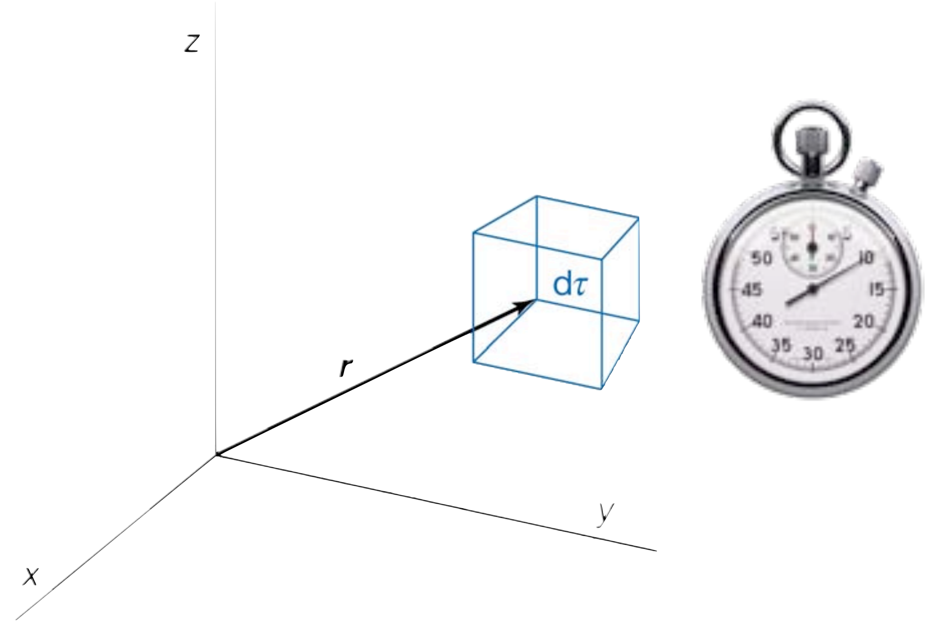


Postulates of quantum mechanics

- Quantum mechanics has a number of postulates (*Axiom*) that define the theory
- A postulate is a statement of assumption NOT necessarily a statement of fact
- Two main concepts:
  - State of a system
  - Physical observables (measurable quantities: position, momentum, energy, ...)

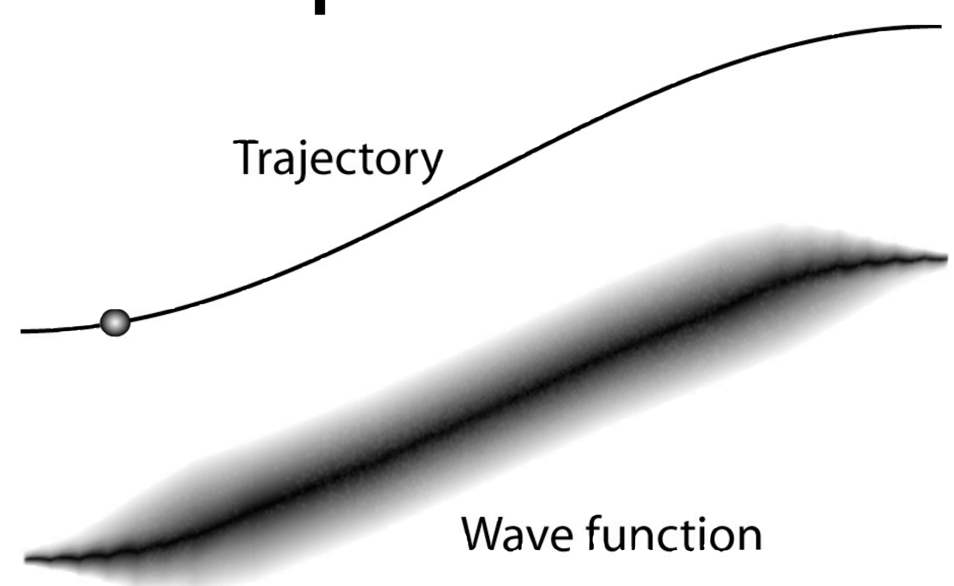
Postulate 1

- *"The state of a system is completely determined by a function that depends on the coordinates of the particle and the time"*
- *"This function,* $\Psi(\mathbf{r}, t)$*, is called the wave function (or state function) and its square modulus represents the probability of finding that particle in a volume element* $d\tau$*, at* $\mathbf{r}$ *and at time* t *"*



What does this mean?

- Postulate 1 implies that a wave function exists for any given system and can be determined
- If the wave function is known, we can predict the evolution of the state of the system with time
- Note: there are no mention of exact position or momentum, just a *probability*

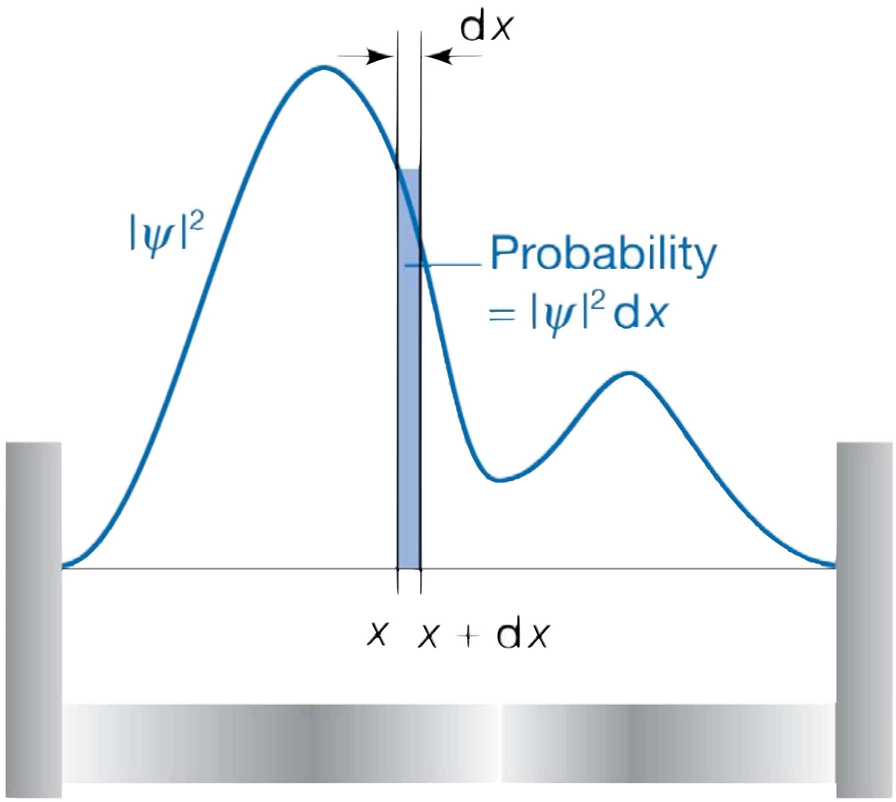


Square modulus as probability density

- If the square modulus of the wave function is a probability density, we must have:

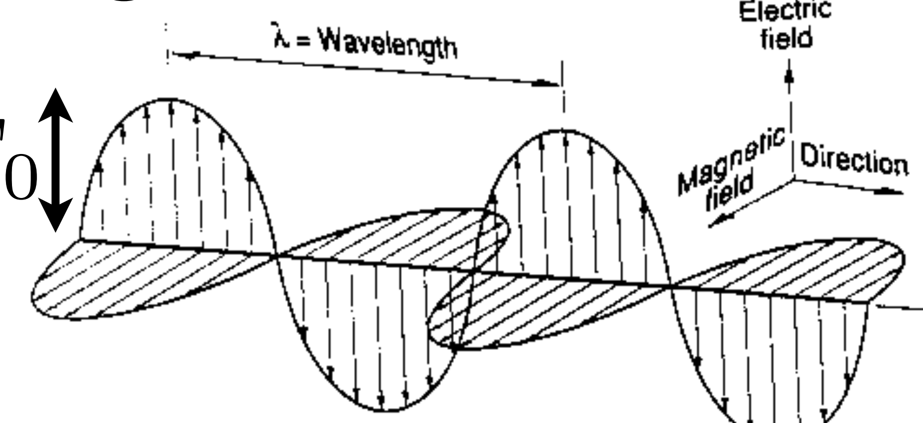
$$\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} |\Psi(\mathbf{r},t)|^2 \underbrace{dxdydz}_{d\tau} = 1$$

- So that there is a certainty to find the particle if we look far enough!
- The wave function must also:
  - be finite over coordinate range
  - be single valued and continuous



Max Born's interpretation

- Light is an electro-magnetic wave



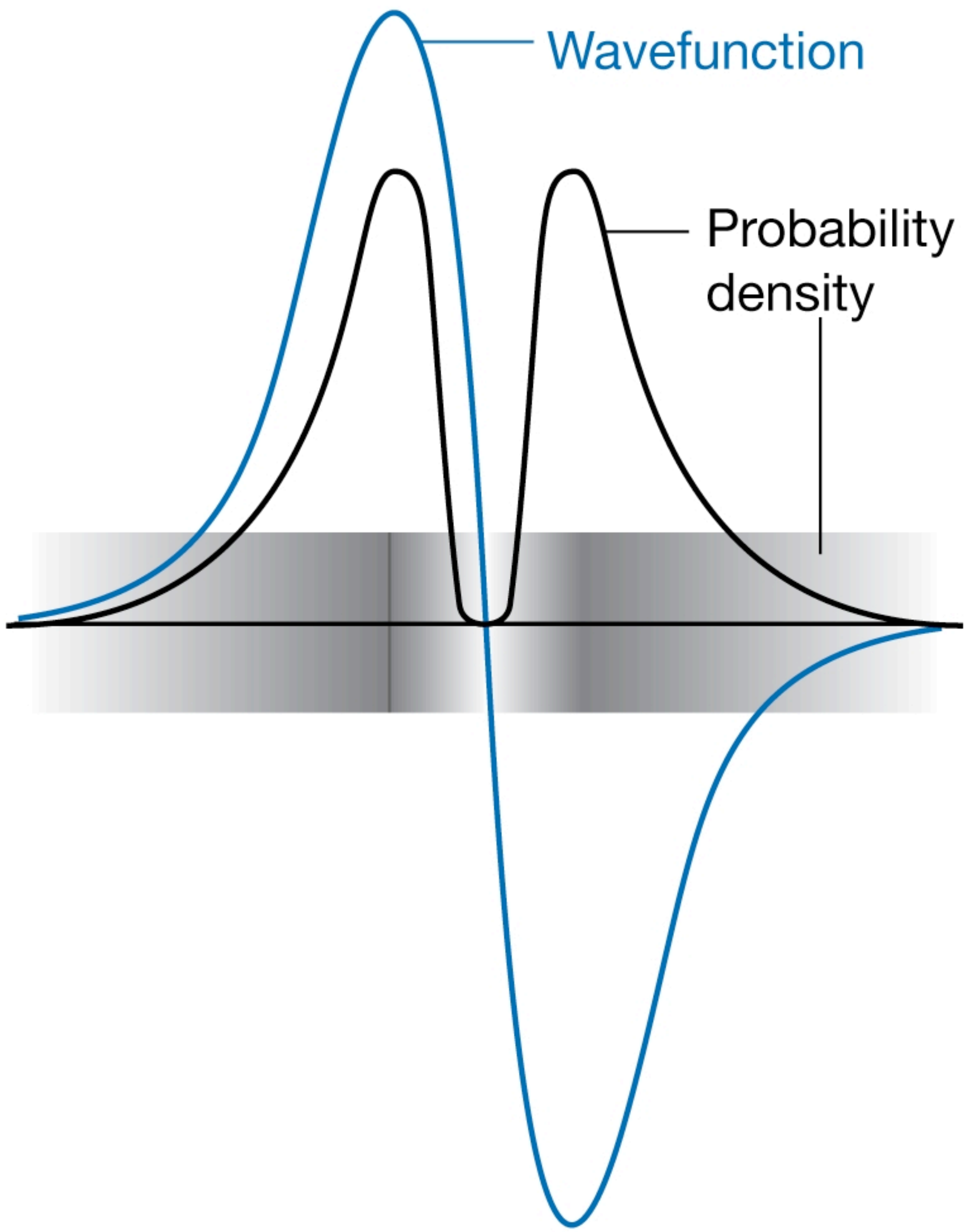
$$E = E_0 \cos\left[2\pi\left(\frac{x}{\lambda} - \nu t\right)\right]$$

- Einstein (1905): light is made of photons with energy $E = h\nu$

- Wave–particle duality suggests both descriptions are correct, depending on the type of observation

Probability density

- If $|\Psi(\mathbf{r},t)|^2$ is large, there is a high probability of finding the particle
- If $|\Psi(\mathbf{r},t)|^2$ is small there is only a small chance of finding the particle
- Note that wave function itself has no physical interpretation. Only its square modulus does!



Postulate 2

- *"To each physical observable in classical mechanics, there correspond a linear Hermitian operator in quantum mechanics"*
- What is a linear Hermitian operator?
- How do we define these operators for our purpose?

Operators

- Definition: mathematical construct that transforms a function into another function
- Examples: $\frac{d}{dx}$; x^2 ; $\ln$; $\sqrt{\ }$; 5
- Operators are usually written as: $\hat{A} = \frac{d^2}{dx^2}$
- Operators are linear if:

$$\hat{A}[c_1 f(x) + c_2 g(x)] = c_1 \hat{A} f(x) + c_2 \hat{A} g(x)$$

Eigenfunction of an operator

- If an operator leaves a function unchanged and simply multiplies it by a constant, we call this function an eigenfunction of the operator
- For example: $\hat{A}f(x) = af(x)$
- Constant a is called the eigenvalue of the operator

Hermitian operator

- An Hermitian operator is also called a self-adjoint operator, such that: $\hat{A} = \hat{A}^* = \hat{A}^\dagger$
- Hermitian operators have real eigenvalues and are symmetric
- This is needed if we want to represent physical observables using operators
- The eigenfunctions of a Hermitian operator are orthogonal (this will be useful later)

How to construct the operator we need?

- Write the classical expression for the observable needed in terms of cartesian coordinates and related momenta

- Exchange classical expressions for the corresponding quantum mechanical operator

$$q \to \hat{q} \qquad p_q \to \hat{p}_q = -i\hbar\frac{\partial}{\partial q} \qquad q = x, y, z$$

- This has to be done in cartesian coordinates but can be changed afterwards

$$\hbar = \frac{h}{2\pi} = 1.05459 \times 10^{-34} \text{ J s}$$

Examples of operators

Observable		Operator	
Name	**Symbol**	**Symbol**	**Operation**
Position	x	$\hat{x}$	multiply by x
Momentum	p_y	$\hat{p}_y$	$-i\hbar\frac{\partial}{\partial y}$
Kinetic energy	K	$\hat{K}$	$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)$
Potential energy	$U(x,y,z)$	$\hat{U}(x,y,z)$	multiply by $U(x,y,z)$

Measurements: Postulate 3

- *"When measuring an observable associated with an operator, the only values that will ever be observed are the eigenvalues of the operator"*

$$\hat{A}\Psi = a\Psi$$

- This means that the measurement of property A can only result in one of its eigenvalues - even if the wave function is not an eigenfunction of $\hat{A}$
- This is very different from what happens in "classical" mechanics!

Total energy operator

- This particular operator is central to quantum mechanics as it defines the allowed energy states of a system
- Starting from the classical total energy, this operator is constructed using the rules established previously:

$$E = K + U(x, y, z) \rightarrow \hat{H} = \hat{K} + \hat{U}(x, y, z)$$

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + \hat{U}(x, y, z)$$

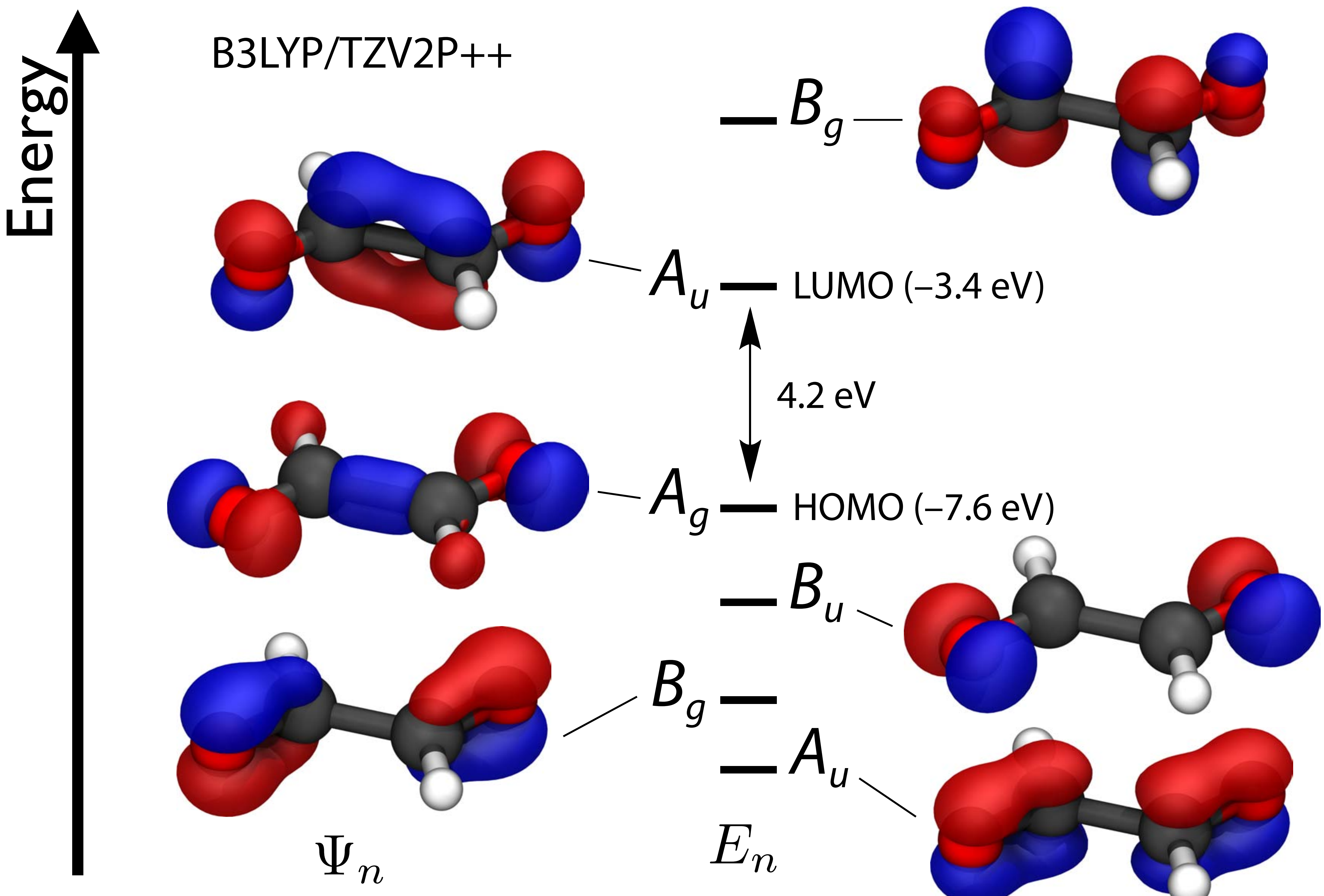
Hamiltonian and solutions

- The eigenvalue equation for the Hamiltonian operator is also known as the time-independent Schrödinger equation

$$\hat{H}\Psi_n = E_n\Psi_n$$

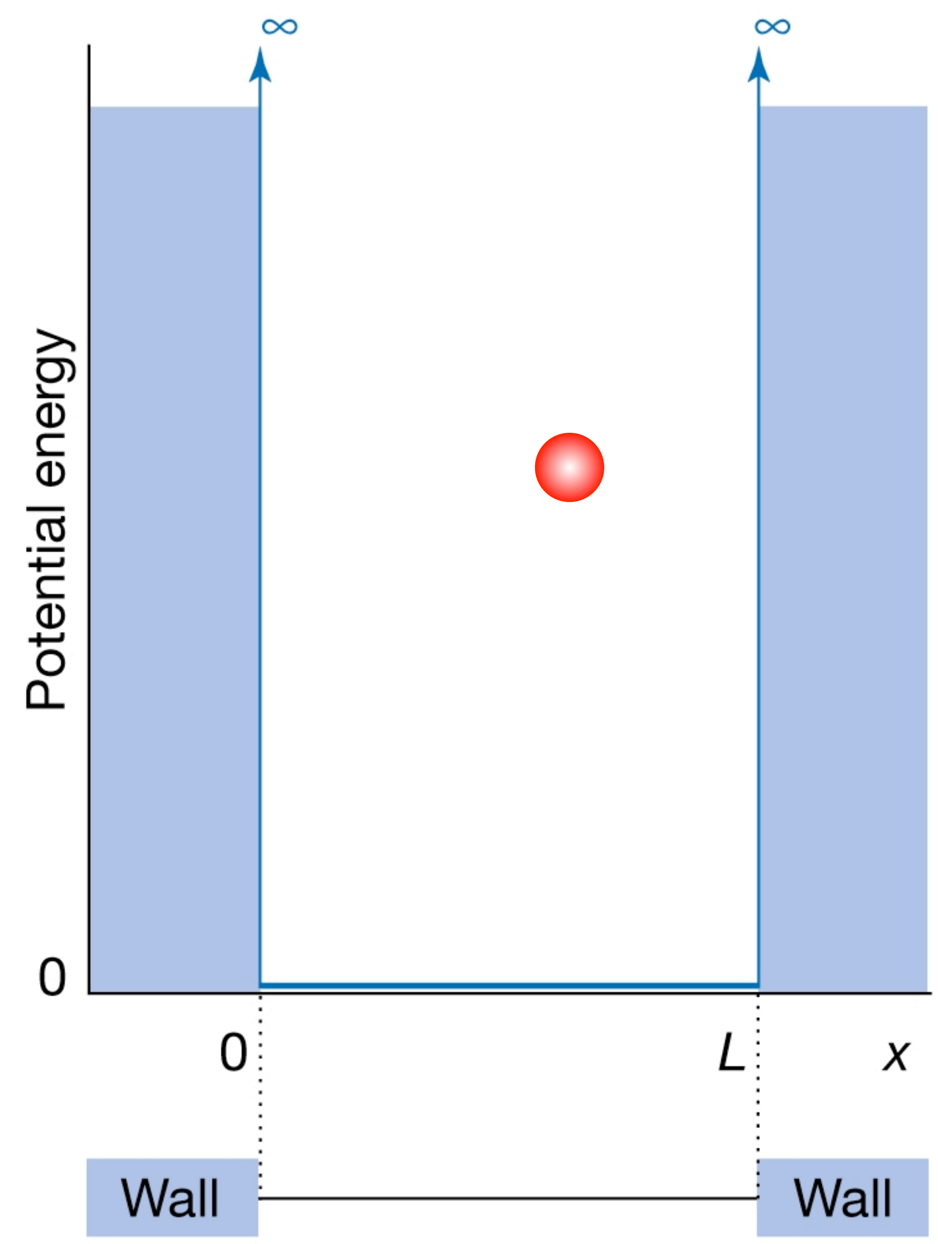
- The allowed energy values, E_n, are the energy levels (energy of molecular orbitals, for example) and the eigenfunctions, Ψ_n, represent the allowed steady-state wave functions for the system

Example of eigenstates

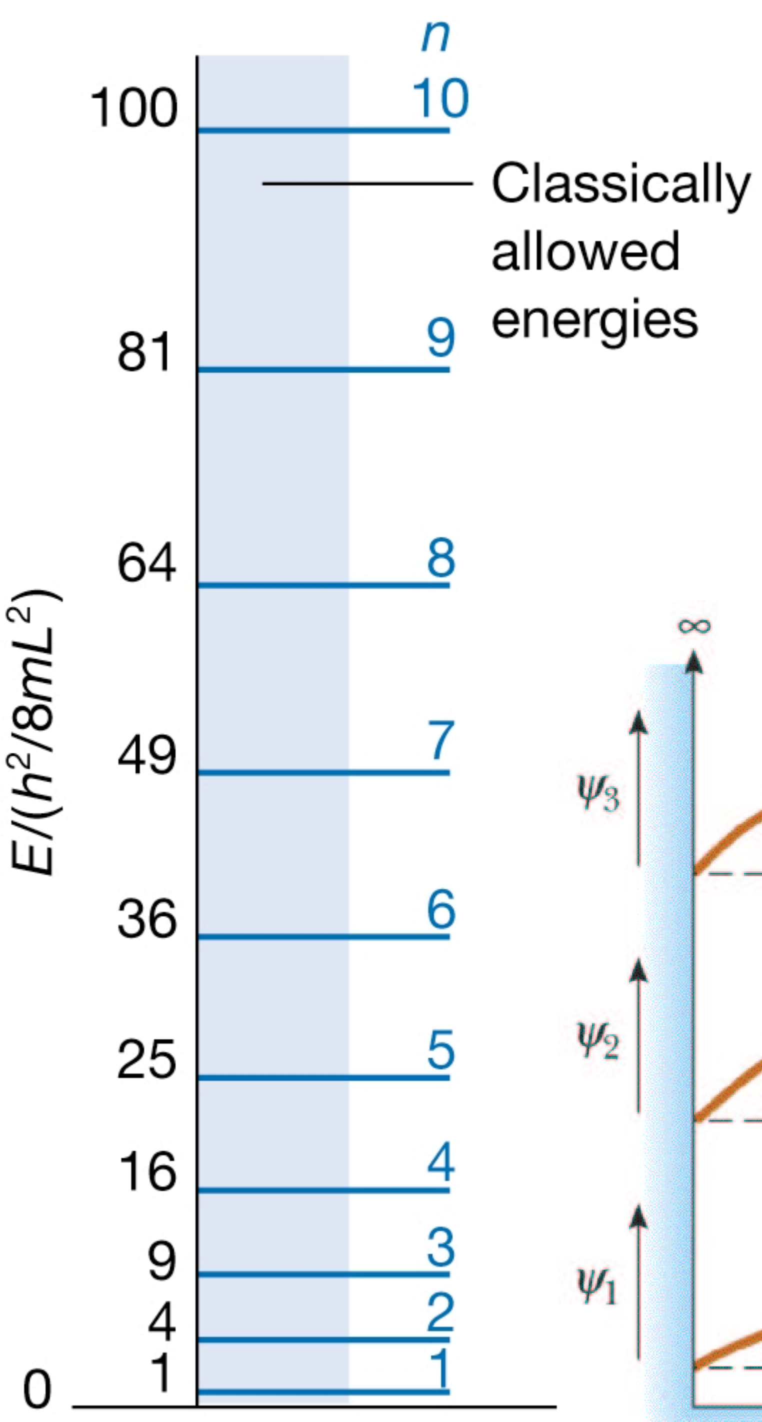


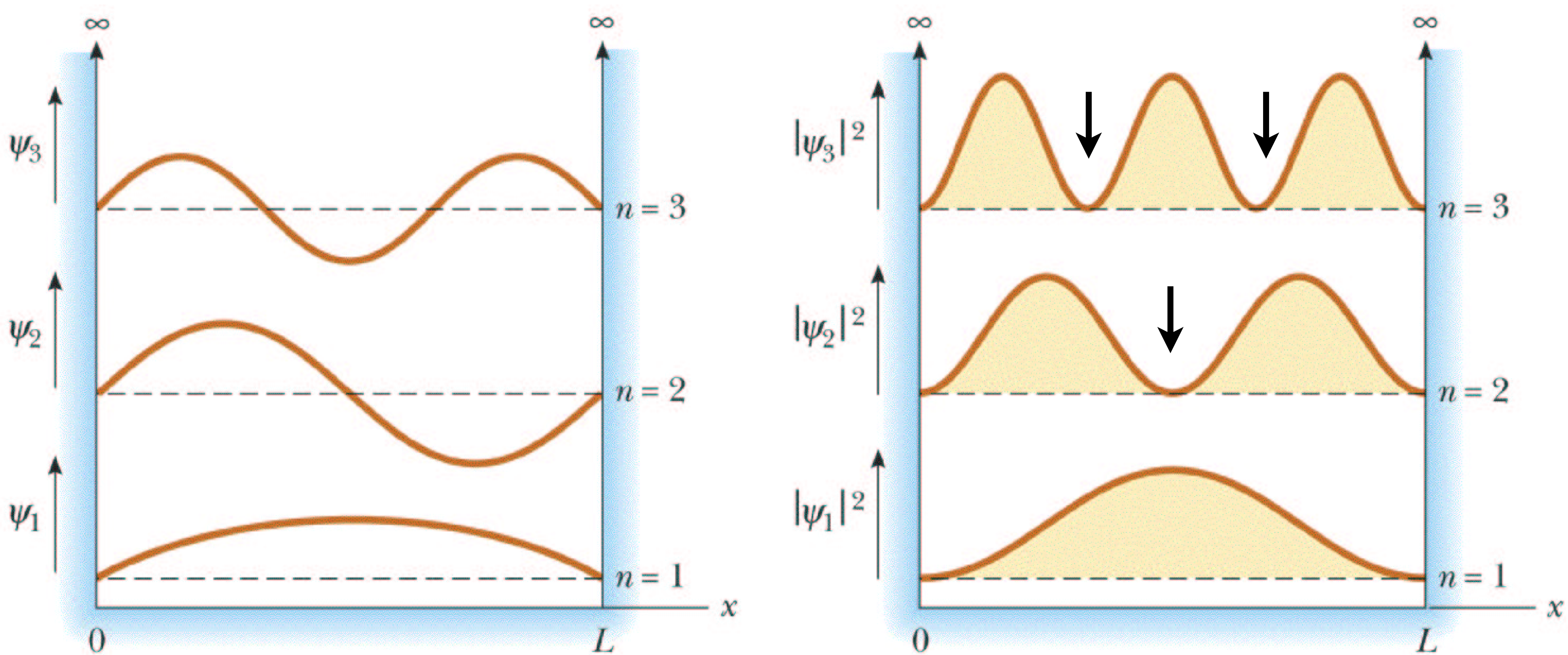
Particle in a box

- Simplest model of a quantum particle
- Quantum model for translational motion
- Useful for UV spectroscopy of conjugated chains

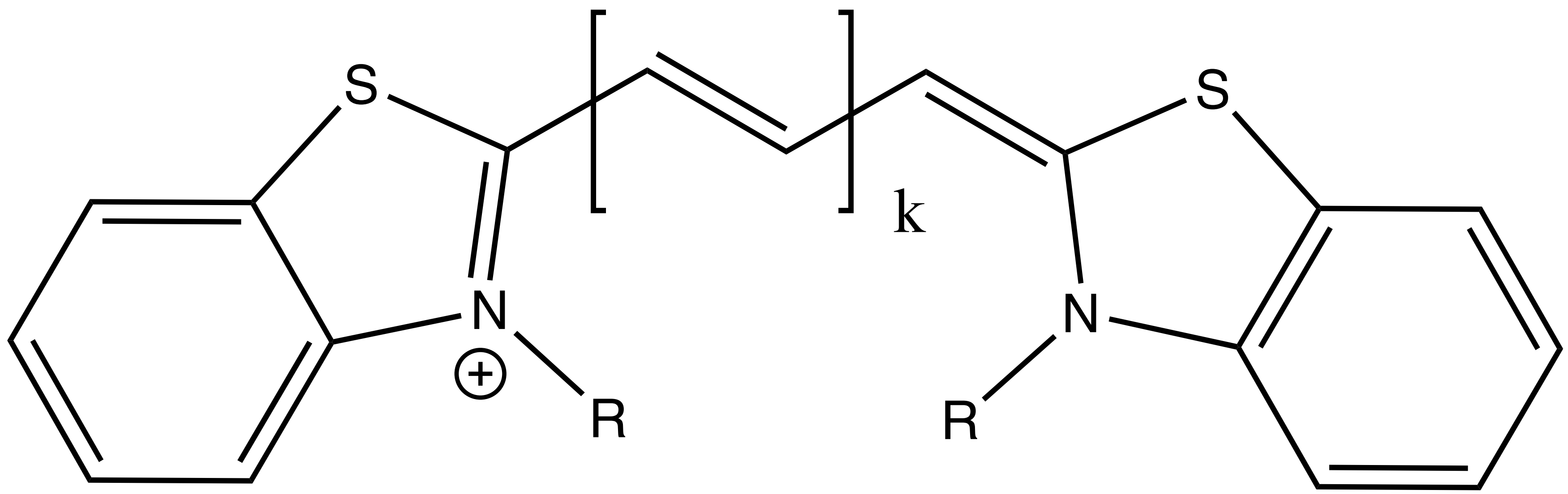


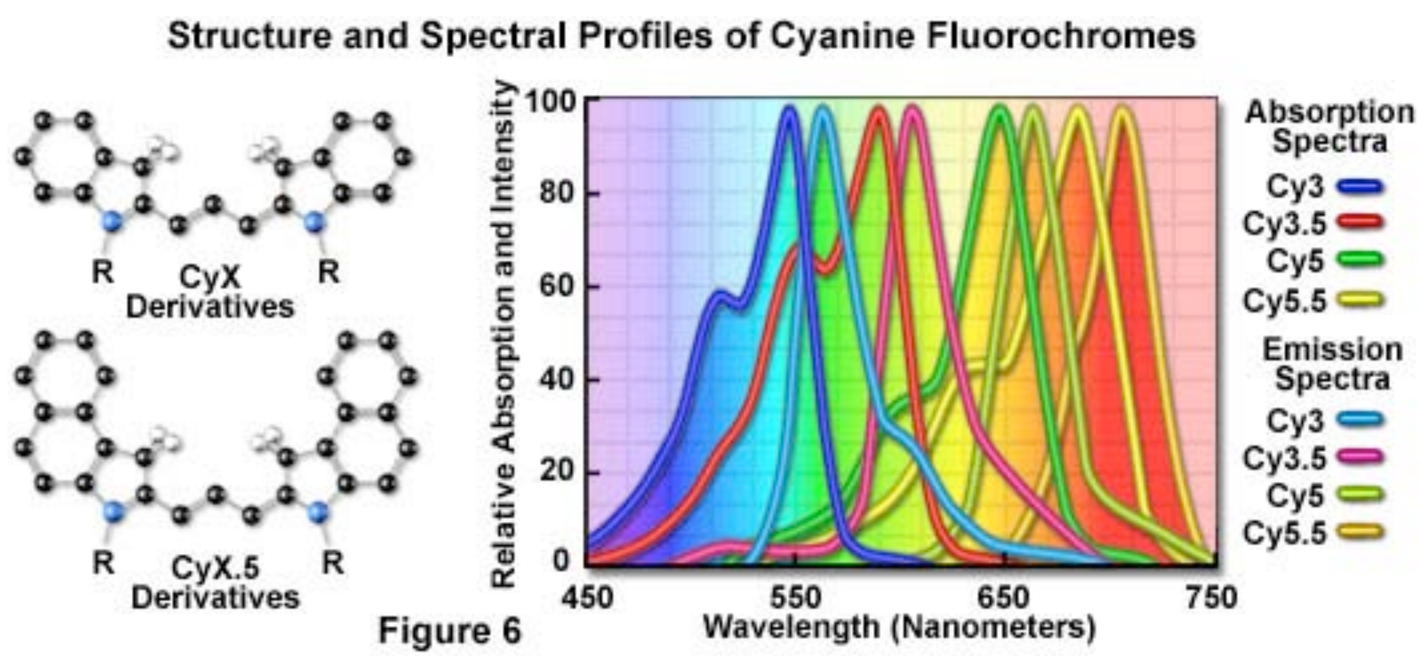
Closer look at the solutions





Cyanine dyes





Quantum dots