Computer simulation of advanced materials International Summer School

Atom and molecular structure Quantum level of matter

Alexander Nemukhin

Department of Chemistry, M.V. Lomonosov Moscow State University
and
N.M. Emanuel Institute of Biochemical Physics, Russian Academy of Sciences

Computer simulation of advanced materials
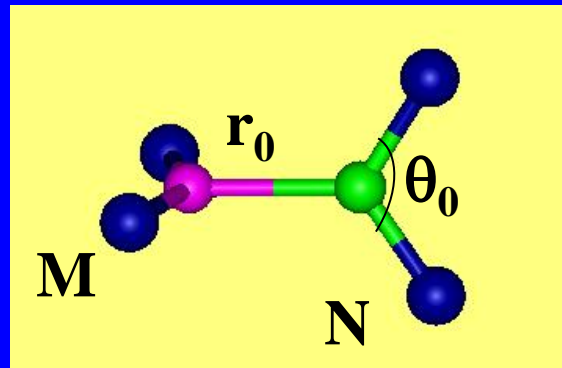
Atom and molecular structure
Quantum level of matter

Textbook materials and illustrations

- **Chemical structure theory is valid (molecules, chemical bonds, …)**
- **Model systems composed of large number of atoms are of interest**
- **Proteins may be considered as advanced materials (at least for biotechnology)**

Molecular mechanical (MM) model
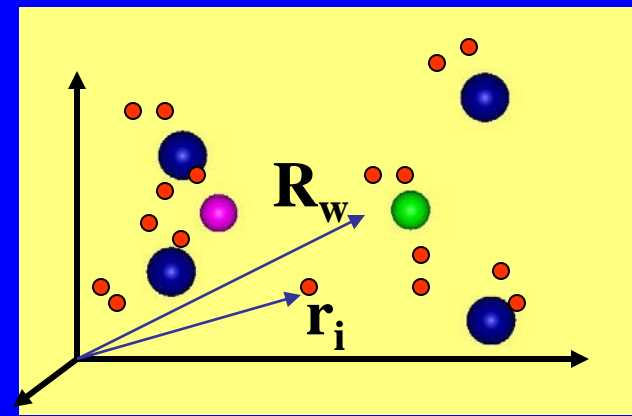## The system is composed of atoms

$$E_{MM} = \sum_{i=stretches} k_i(r_i - r_{i0})^2 + \sum_{j=bends} k_j(\theta_j - \theta_{j0})^2 +$$

$$\sum_{l=torsions} \left[\frac{V_{l,1}}{2}(1 + \cos\phi_l) + \frac{V_{l,2}}{2}(1 + \cos 2\phi_l) + ... \right] +$$

$$\sum_{MN} \frac{q_M q_N}{r_{MN}} + \sum_{MN} 4\varepsilon_{MN} \left[\left(\frac{\sigma_{MN}}{r_{MN}} \right)^{12} - \left(\frac{\sigma_{MN}}{r_{MN}} \right)^{6} \right]$$

$$k_i, r_{i0}, k_j, \theta_{j0}, V_{l,1}, V_{l,2}, q_M, \varepsilon_{MN}, \sigma_{MN} \text{ - parameters}$$

Molecules are stable systems of nuclei and electrons

As such, their structure and dynamics should be governed by Quantum Mechanics

$$\hat{H}\Psi = E_{QM}\Psi$$

$$\hat{H} = \sum_i \left(-\frac{1}{2}\Delta_{r_i} \right) + \sum_w \left(-\frac{1}{2M_w}\Delta_{R_w} \right) + \sum_{i<j} \frac{1}{r_{ij}} + \sum_{w<v} \frac{Z_w Z_v}{R_{wv}} - \sum_{iw} \frac{Z_w}{|R_w - r_i|}$$

Electronic structure models

$$HC = ESC$$

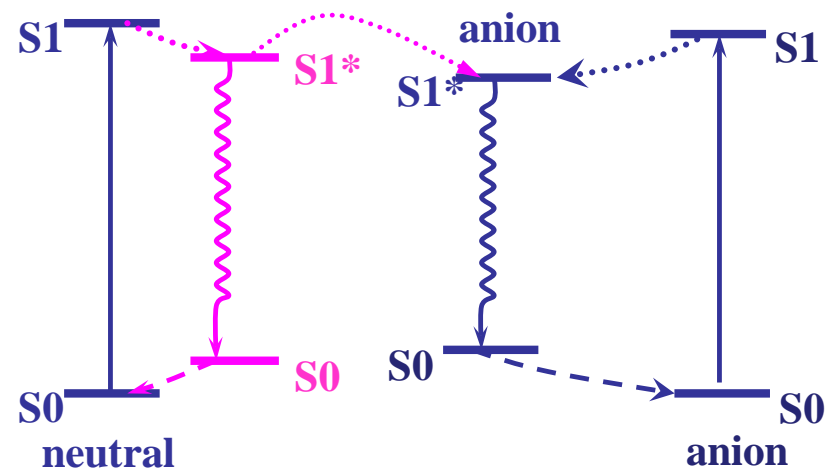**Numerical solution of matrix equations**

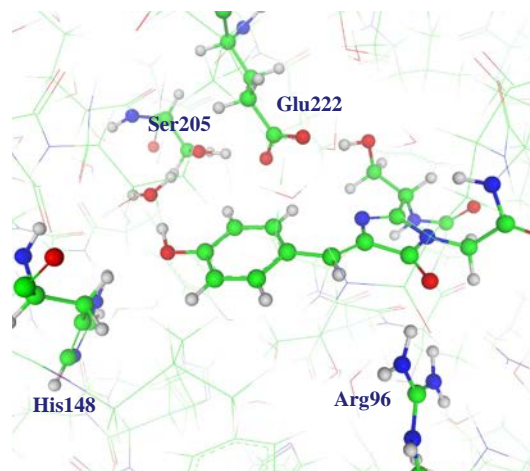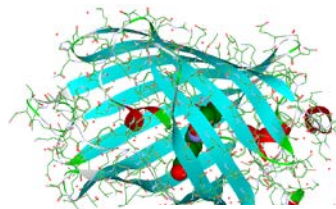# Why do we need quantum mechanics?

Why do we need quantum mechanics?

- Excited electronic states are involved
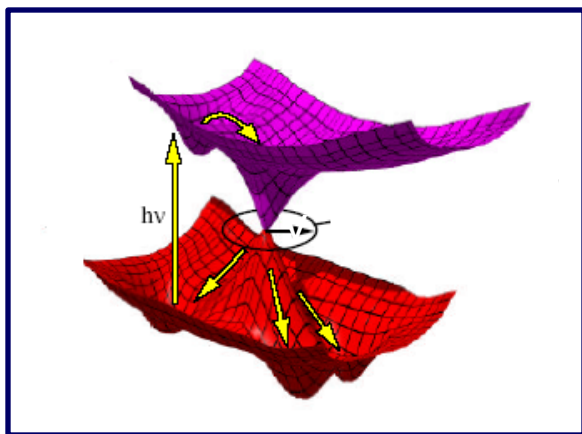
Example: fluorescent proteins

Bravaya K.B., Grigorenko B.L., Nemukhin A.V., Krylov A.I., Acc Chem Res, 45, 265 (2012)

Why do we need quantum mechanics?

- Cleavage and formation of chemical bonds are involved

Example: hydrolysis of adenosine triphosphate (ATP) in motor proteins

Grigorenko B.L., Nemukhin A.V., et al., Proc Natl Acad Sci USA, 104, 7057 (2007)
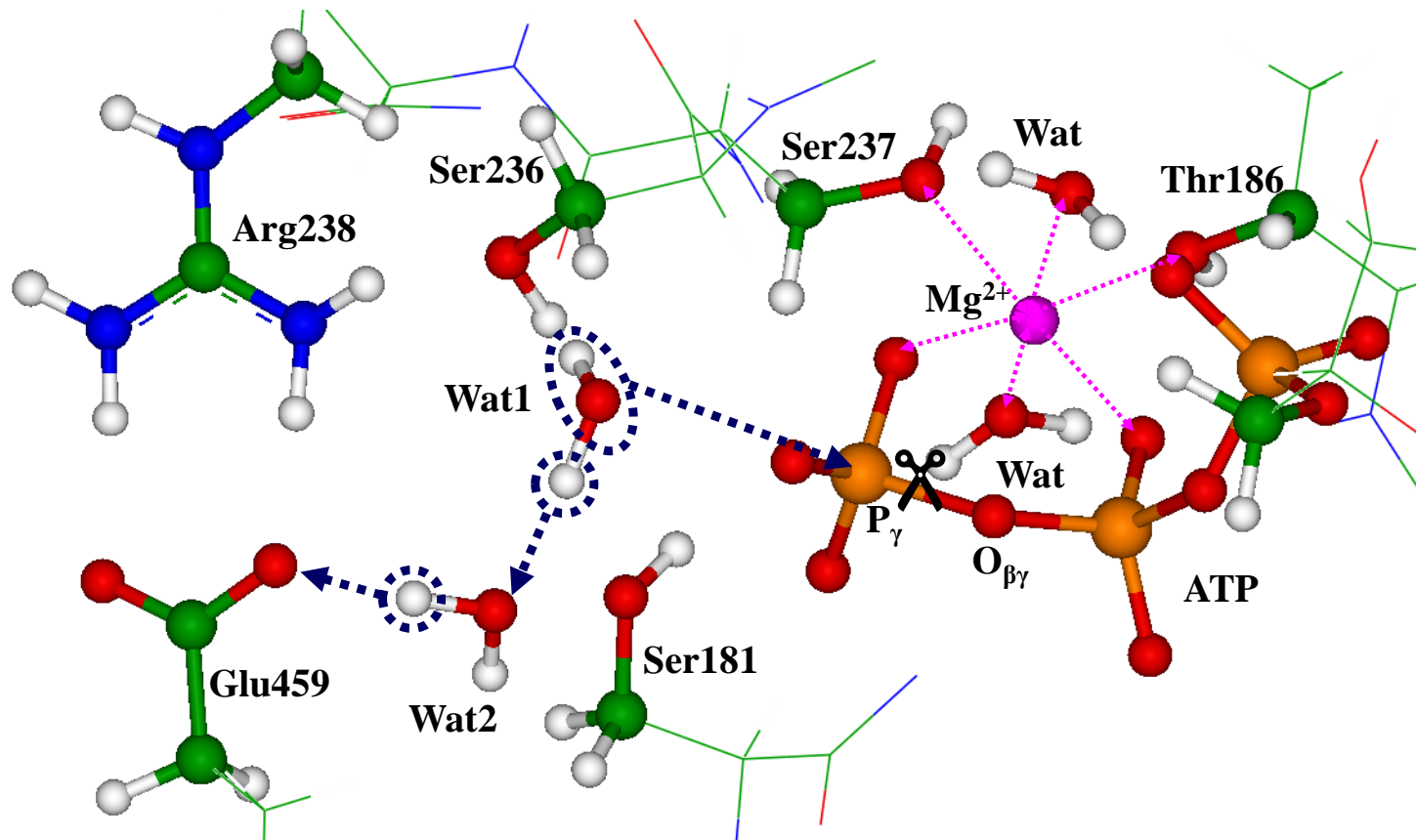
Why do we need quantum mechanics?
- Force field parameters may be not accurate enough
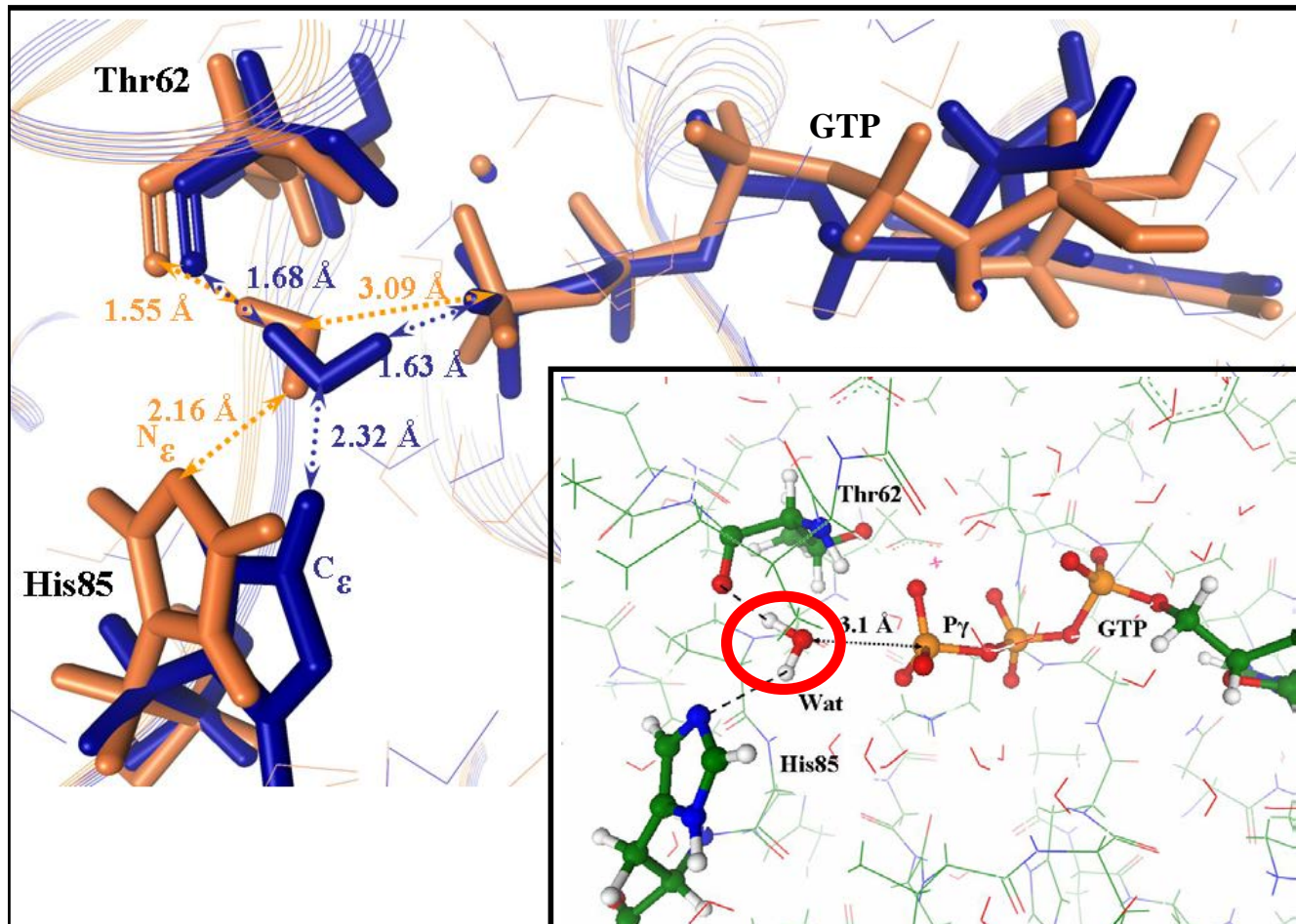
Grigorenko B.L., Shadrina M.S., Nemukhin A.V., et al., Biochim Biophys Acta, 1784, 1908 (2008)

Computer simulation of advanced materials

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Atom and molecular structure
Quantum level of matter

Basics of quantum mechanics

Basics of quantum mechanics

General considerations

Quantum and classical mechanics

Wavefunctions

Observables

Hydrogen atom

Spin

Quantum mechanics is the theory of the behavior of microscopic objects, including electrons and nuclei, for which

$$\text{the \underline{action}} \quad \mathbf{S} \; = \int_{t0}^{t1} L(q_1,...,q_n,t)dt$$

is comparable to the Planck's constant $\hbar \approx 10^{-34}$ J·s

Classical Mechanics

The Lagrangian function ($L=T-V$)

The Euler-Lagrange equations $\qquad \dfrac{d}{dt}\dfrac{\partial L}{\partial \dot{q}_i} - \dfrac{\partial L}{\partial q_i} = 0 \qquad (i=1,...,n)$

The Hamiltonian ($H=T+V$) $\qquad H(q_1,...,q_n,p_1,...,p_n,t)$

The Hamilton's equations $\qquad \dot{p}_i = -\dfrac{\partial H}{\partial q_i} \qquad \dot{q}_i = \dfrac{\partial H}{\partial p_i}$

The Hamilton–Jacobi formulation

$$H(q_1,...,q_n,\frac{\partial S}{\partial q_1},...,\frac{\partial S}{\partial q_n},t)+\frac{\partial S}{\partial t}=0$$

Classical mechanics $\mathbf{S} \gg \hbar$	Correspondence principle	Quantum mechanics $\mathbf{S} \sim \hbar$
<u>System</u> can be characterized by a function of coordinates and time $$S(q_1,...,q_n,t)$$ S defines <u>states</u> of the system	← ⬭ →	<u>System</u> can be characterized by functions of coordinates and time $$\Psi(q_1,...,q_n,t)$$ Each Ψ refers to a <u>state</u> of the system
This <u>function</u> S can be found as a solution of the differential equation $$H(q_1,...,q_n,\frac{\partial S}{\partial q_1},...,\frac{\partial S}{\partial q_n},t)+\frac{\partial S}{\partial t}=0$$		<u>Functions</u> Ψ can be found as solutions of the differential equation $$i\hbar\frac{\partial \Psi}{\partial t}=\hat{H}\Psi$$
Knowing function S one can find trajectories and to compute <u>observables</u>		Knowing functions Ψ one can compute <u>observables</u>

Classical and Quantum Mechanics

Keywords:

System

States … of the system

Wavefunction … of a state

Observables … for a particular state

Quantum Mechanics: Keyword "System"

System $\Longrightarrow$ the Hamiltonian operator $\hat{H}$

As only we select a system for an analysis we can write down an explicit expression for the Hamiltonian operator.

Examples:

A particle of mass m in a one-dimentional potential $V(x)$	$\hat{H} = -\dfrac{\hbar^2}{2m}\dfrac{\partial^2}{\partial x^2} + V(x)$
One-elctron atom: an electron in the field of a nucleus	$\hat{H} = -\dfrac{\hbar^2}{2\mu}\left(\dfrac{\partial^2}{\partial x^2} + \dfrac{\partial^2}{\partial y^2} + \dfrac{\partial^2}{\partial z^2}\right) - \dfrac{Ze^2}{r}$

Quantum Mechanics: Keyword "States of the system"

An essential feature of QM is that certain parameters of the system can take on discrete values varying from one state to another by 'quantum jumps'.
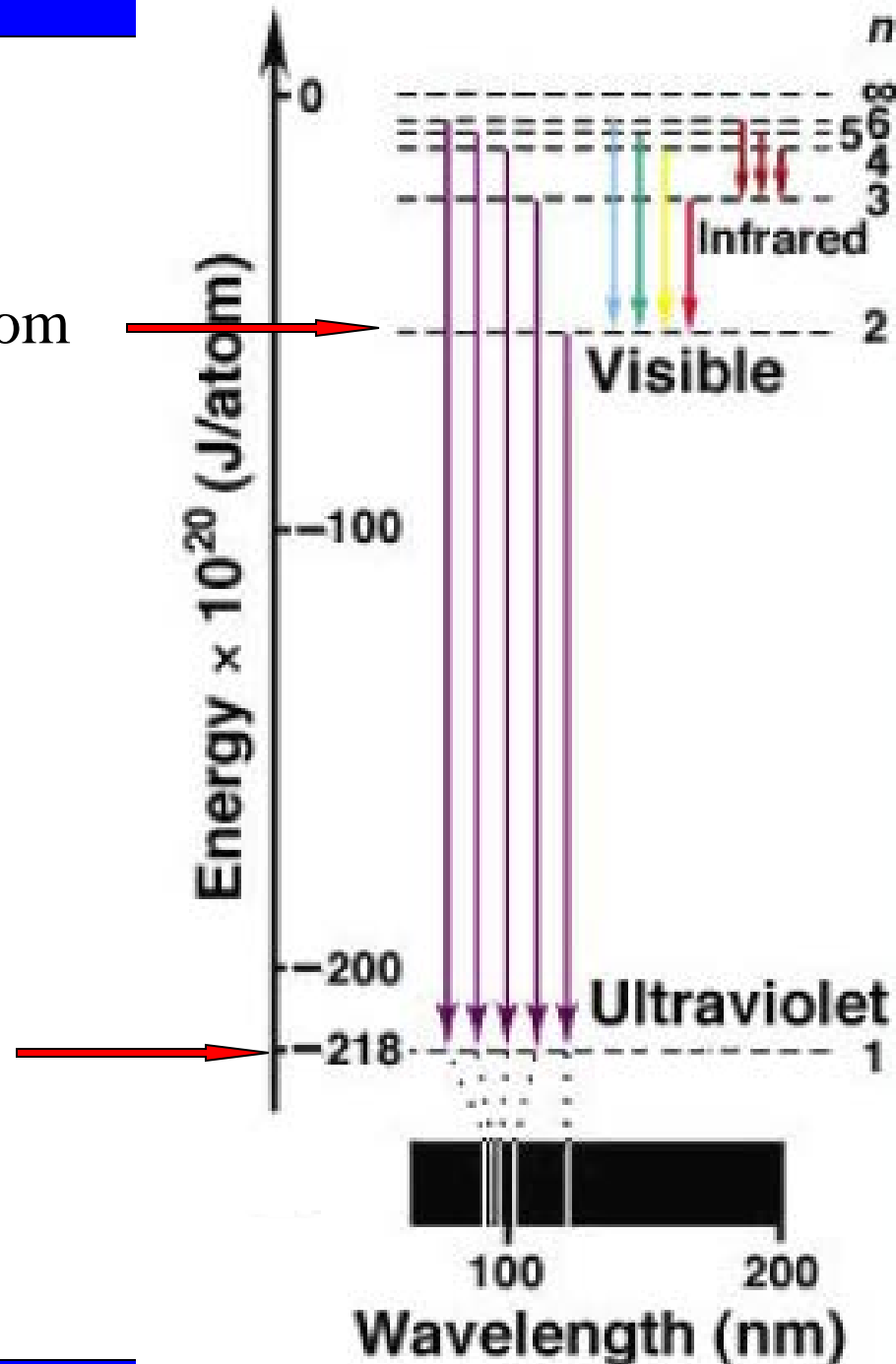
Example: Few states of the hydrogen atom

State	Total energy (10^{20} J/atom)	Electronic angular momentum
1s	-218.6	0
2s	-54.6	0
2p	-54.6	$\sqrt{2}\,\hbar$

These 'jumps' are observed in experimental spectroscopy

States 2s and 2p of the hydrogen atom

Total energy $(10^{20}$ J/atom)
-218.6
-54.6
-54.6

State 1s of the hydrogen atom

Quantum Mechanics

Keywords:

System

States … of the system

Wavefunction … of a state

Observables … for a particular state

Quantum Mechanics: Keyword "Wavefunction"

The state of a system is described by a wavefunction of the coordinates and the time $\Psi(q_1, \ldots, q_n, t)$

The probability:

$$\Psi * (\vec{r}, t)\Psi(\vec{r}, t)dxdydz \qquad \text{The probability that the particle is in the volume element } dxdydz \text{ located at } \vec{r}, \text{ at time } t.$$

Ψ must satisfy mathematical conditions:
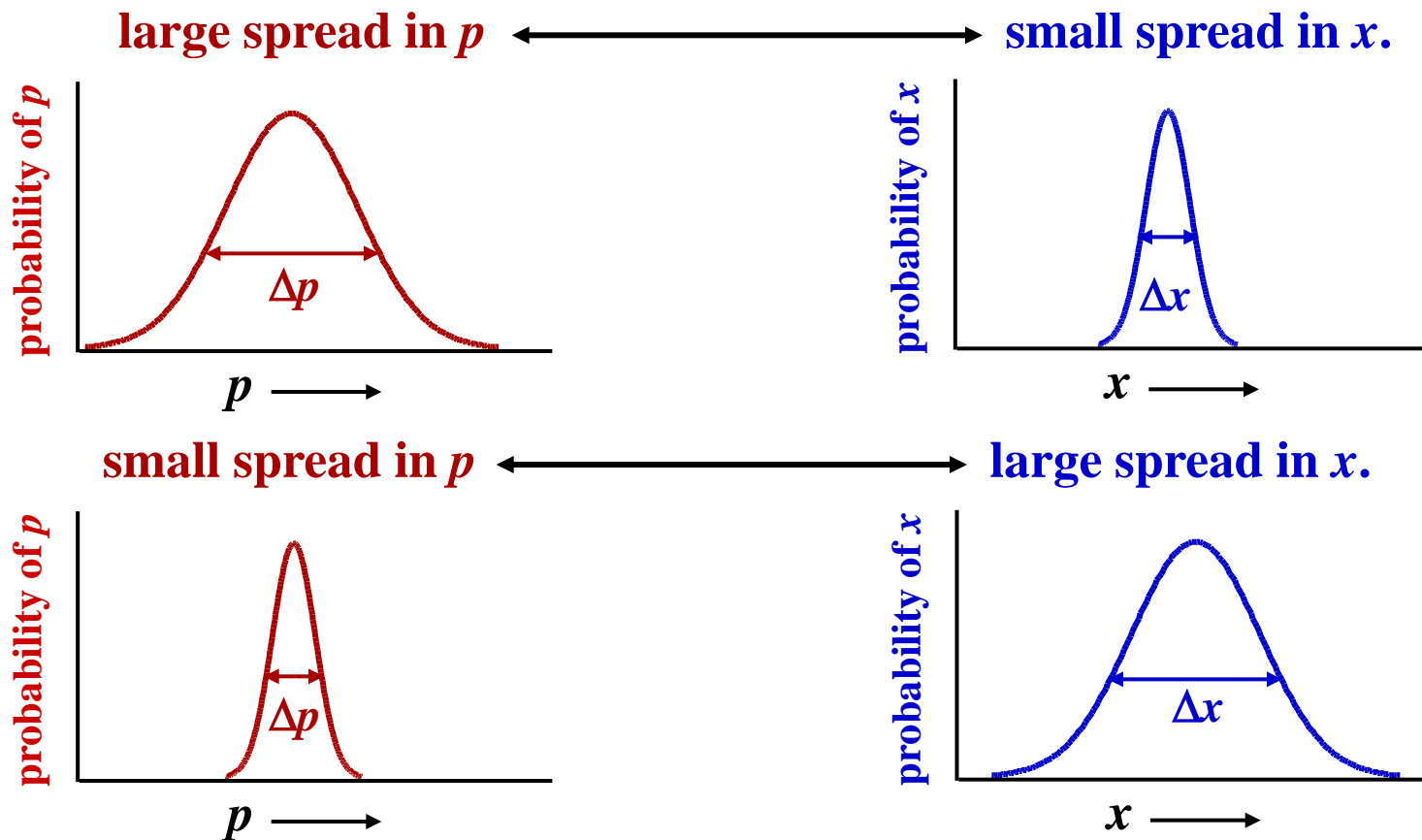- Single-value
- Continuous
- Quadratically integrable

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \Psi * (\vec{r}, t)\Psi(\vec{r}, t)dxdydz = 1$$

Quantum Mechanics: Keyword "Wavefunction"

Why probabilities?
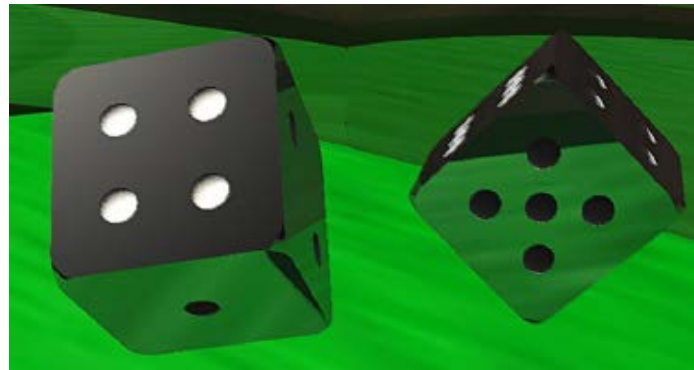
The Heisenberg <u>uncertainty principle</u>: "The more precisely the position is determined, the less precisely the momentum is known in this instant, and vice versa."

large spread in p ⟷ **small spread in x.**

probability of p

Δp

p →

probability of x

Δx

x →

small spread in p ⟷ **large spread in x.**

probability of p

Δp

p →

probability of x

Δx

x →

Quantum particles do not travel along trajectories.

Keyword "Wavefunction": Superposition principle

The "negative content" (Landau, Lifshchitz) of the uncertainty principle is balanced by the "positive content" of
the <u>superposition principle</u>:

If Ψ_1, Ψ_2, …, Ψ_n are the possible states of a system, then the linear combination of these states is also a possible state of the system

Physical consequence: The equations for Ψ must be linear, e.g.,

$$i\hbar\frac{\partial\Psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2} + V(x,t)\Psi(x,t)$$

Either the Schrödinger equation, or the superposition principle should be postulated

Postulates of Quantum Mechanics

1. Probabilities (due to the uncertainty principle):

$$\Psi^*(\vec{r},t)\Psi(\bar{r},t)\,dxdydz$$

The probability that the particle is in the volume element $dxdydz$ located at $\bar{r}$, at time t.

2. The superposition principle:

If $\Psi_1, \Psi_2, \ldots, \Psi_n$ are the possible states of a system, then the linear combination of these states is also a possible state of the system.

and

3. For every observable mechanical quantity of a system, there is a corresponding linear Hermitian operator associated with it.

Quantum Mechanics

Keywords:

System

States … of the system

Wavefunction … of a state

Observables … **for a particular state**

Keyword "Observables"

For every observable mechanical quantity of a system, there is a corresponding linear Hermitian operator associated with it.

To specify this operator, write down the classical expression for the observable in terms of Cartesian coordinates and the corresponding

linear momentum, and then replace each coordinate x by the operator

$\widehat{x}$ and each momentum component p_x by the operator $\quad \widehat{p}_x = -i\hbar\dfrac{\partial}{\partial x}$

Keyword "Observables"

Some mechanical quantities and their operators

Position (x)

$$\widehat{x}$$

Linear momentum (p_x)

$$\widehat{p}_x = -i\hbar \frac{\partial}{\partial x}$$

Angular momentum
($L_z = xp_y - yp_x$)

$$\widehat{L}_z = -i\hbar(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x})$$

Total energy ($T+V$)

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

Keyword "Observables"

If a system is in a state described by a normalized wavefunction Ψ, then the average value of the observable A in this state is given by

$$\overline{A}_{\Psi} = \langle \Psi \mid \widehat{A}\Psi \rangle$$

The Hermitian operator ensures a real number for $\overline{A}$.
We talk on average values by the same reasons as on probabilities (the uncertainty principle).

Keyword "Observables": Eigenfunctions and eigenvalues

Finding eigenfunctions and eigenvalues of operators associated with observables is one of the major goals of QM.

Solution of the time-independent Schrödinger equation $\hat{H}\Psi_i = E_i\Psi_i$ allows one to find the total energies E_i of the system under study.

In particular, for any molecule composed of electrons (e) and nuclei (n)

$$\hat{H} = \widehat{T}_{electrons} + \widehat{T}_{nuclei} + \widehat{V}_{e-e} + \widehat{V}_{n-n} + \widehat{V}_{e-n}$$

The differential equations must be augmented by the boundary conditions for the wavefunctions (single-value, continuous, …) since they describe waves of probabilities.

Eigenfunctions and eigenvalues of the component L_z

$$\hat{L}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) = -i\hbar\frac{\partial}{\partial\varphi}$$
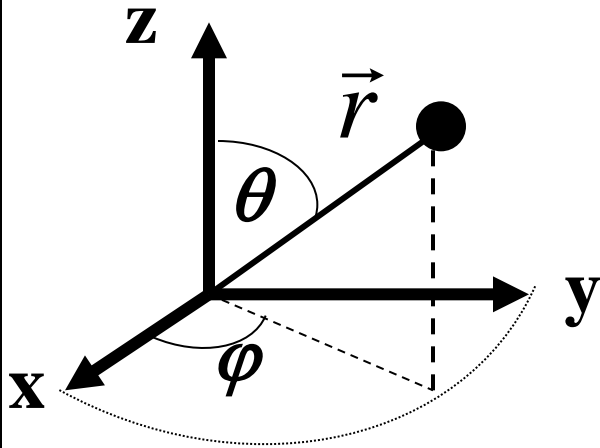
Differential equation:

$$\hat{L}_z\Phi_m(\varphi) = l_z\Phi_m(\varphi)$$

Conditions:

$$\Phi(\varphi + 2\pi) = \Phi(\varphi)$$

$$\langle\Phi|\Phi\rangle = \int_0^{2\pi}\Phi^*(\varphi)\Phi(\varphi)d\varphi = 1$$

Answers:

$$l_z = m\hbar$$

$$\Phi_m(\varphi) = \frac{1}{\sqrt{2\pi}}\exp(im\varphi)$$

$$m = 0, \pm 1, \pm 2, \ldots$$

z

$\vec{r}$

θ

φ

x

y

z

$\cdot$
$\cdot$

$+3\hbar$

$+2\hbar$

$+\hbar$

0

$-\hbar$

$-2\hbar$

$-3\hbar$

$\cdot$
$\cdot$

'quantum jumps'
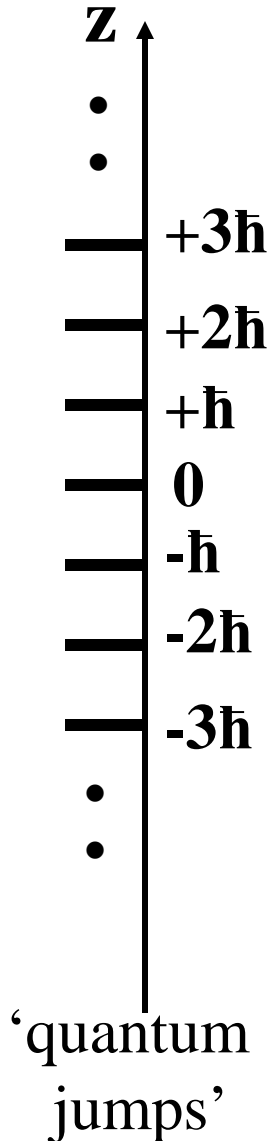
Keyword "Observables": Measurements

Important question of the QM theory: What do we know about A in the state characterized by the wavefunction Ψ?

Answer: If Ψ happens to coincide with one of the eigenfunctions of $\widehat{A}$ then in this particular state we know A precisely, and the only result of the measurement is the corresponding eigenvalue of $\widehat{A}$

If Ψ does not coincide with any of the eigenfunctions of $\widehat{A}$ then we can predict only the averaged value of A:

$$\overline{A}_\Psi = \langle \Psi \mid \widehat{A}\Psi \rangle$$

A probability of measuring a particular value a_k in the state Ψ is

$$w_k = \mid \langle \Phi_k \mid \Psi \rangle \mid^2$$

where Φ_k is the corresponding eigenfunction of $\widehat{A}$.

Another important question of the QM theory:

Can we know two mechanical variables A and B simultaneously and precisely?

Answer: Two observables A and B are principally simultaneously measurable (have the common set of eigenstates) if and only if their corresponding operators commute $\widehat{A}\widehat{B} = \widehat{B}\widehat{A}$.

More specifically: The commuting operators have the same set of eigenfunctions, and **if** the wavefunction of a particular state coincides with one of these eigenfunctions, one may know A and B simultaneously and precisely **in this state**.

When the operators do not commute, one can **never** know A and B simultaneously and precisely in any state.

Keyword "Observables": Back to the uncertainty principle

Quantitative side of the uncertainty principle
The uncertainties ΔA and ΔB of any two observables in any physical state Ψ satisfy the inequality

$$\Delta A \cdot \Delta B \geq \frac{1}{2} \, | \, \langle \Psi \, | \, (\widehat{A}\widehat{B} - \widehat{B}\widehat{A}) \, | \, \Psi \rangle \, |$$

Position and momentum: $\quad \widehat{x}\widehat{p}_x - \widehat{p}_x x = i\hbar$

hence, $\quad \Delta x \cdot \Delta p_x \geq \dfrac{\hbar}{2}$

Angular momentum operators

$$\hat{L}_x = y\hat{p}_z - z\hat{p}_y = -i\hbar(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y})$$

$$\hat{L}_y = z\hat{p}_x - x\hat{p}_z = -i\hbar(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z})$$

$$\hat{L}_z = x\hat{p}_y - y\hat{p}_x = -i\hbar(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x})$$

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

The commutators

$$\hat{L}_x\hat{L}_y - \hat{L}_y\hat{L}_x = i\hbar\hat{L}_z \qquad \hat{L}^2\hat{L}_x - \hat{L}_x\hat{L}^2 = 0$$

$$\hat{L}_z\hat{L}_x - \hat{L}_x\hat{L}_z = i\hbar\hat{L}_y \qquad \hat{L}^2\hat{L}_y - \hat{L}_y\hat{L}^2 = 0$$

$$\hat{L}_y\hat{L}_z - \hat{L}_z\hat{L}_y = i\hbar\hat{L}_x \qquad \hat{L}^2\hat{L}_z - \hat{L}_z\hat{L}^2 = 0$$

All three components of angular momentum cannot be measured simultaneously, which tells us that there does not exist any physical state in which the direction of angular momentum is definite. However, there do exist states in which the magnitude of angular momentum is definite along with one component.
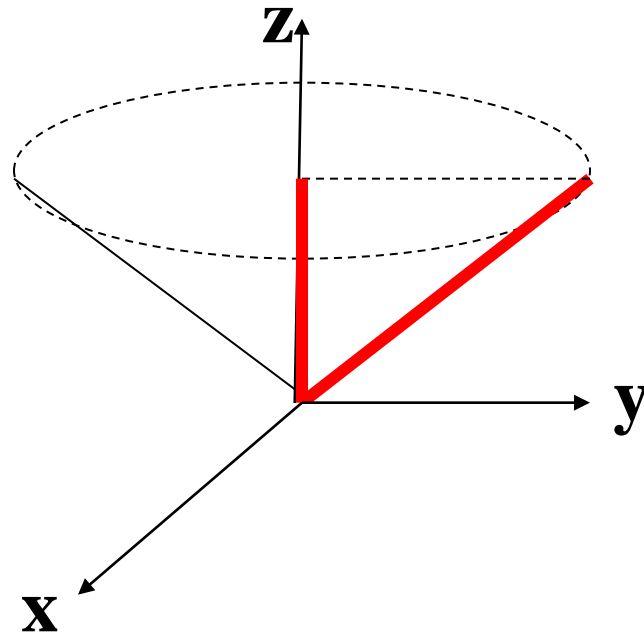
One can know simultaneously and precisely L^2 and L_z while no knowledge on L_x and L_y is allowed. The physical reasons are traced back to the uncertainty principle.

Keyword "Observables": Example of commuting operators

The commuting operators $\widehat{L}^2$ and $\widehat{L}_z$ have a common set of eigenfunctions.

$$\widehat{L}_z = -i\hbar \frac{\partial}{\partial \varphi}$$

$$\widehat{L}^2 = -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\varphi^2} \right]$$

The solutions

$$\widehat{L}_z Y_{lm}(\theta,\varphi) = (\hbar m) Y_{lm}(\theta,\varphi)$$

$$\widehat{L}^2 Y_{lm}(\theta,\varphi) = \hbar^2 l(l+1) Y_{lm}(\theta,\varphi)$$

$$m = 0, \pm 1, \pm 2, ..., \pm l$$

$$l = 0, 1, 2, ...$$

The spherical harmonics

$$
\begin{aligned}
Y_{00} &= \sqrt{\frac{1}{4\pi}} \\
Y_{11} &= -\sqrt{\frac{3}{8\pi}} \sin\theta\, e^{i\phi} \\
Y_{10} &= \sqrt{\frac{3}{4\pi}} \cos\theta \\
Y_{1,-1} &= \sqrt{\frac{3}{8\pi}} \sin\theta\, e^{-i\phi} \\
Y_{22} &= \sqrt{\frac{15}{32\pi}} \sin^2\theta\, e^{2i\phi} \\
Y_{21} &= -\sqrt{\frac{15}{8\pi}} \sin\theta \cos\theta\, e^{i\phi} \\
Y_{20} &= \sqrt{\frac{5}{16\pi}} (3\cos^2\theta - 1) \\
Y_{2,-1} &= \sqrt{\frac{15}{8\pi}} \sin\theta \cos\theta\, e^{-i\phi} \\
Y_{2,-2} &= \sqrt{\frac{15}{32\pi}} \sin^2\theta\, e^{-2i\phi}
\end{aligned}
$$

Hydrogen atom

The one-electron atom: The <u>system</u> - an electron with the charge e and mass μ in the field $V(r) = -\dfrac{Ze^2}{r}$

The Hamiltonian operator

$$\widehat{H} = -\frac{\hbar^2}{2\mu r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{\widehat{L}^2}{2\mu r^2} - \frac{Ze^2}{r}$$
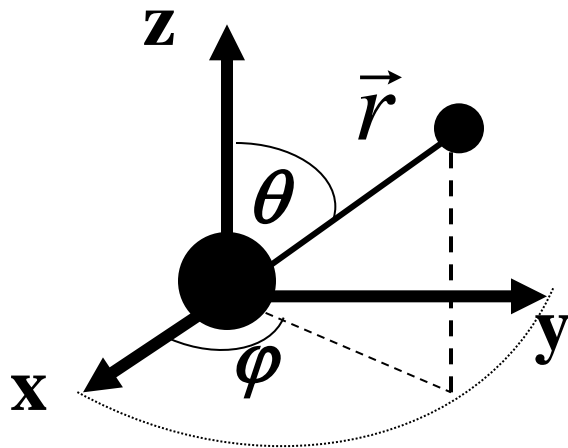
<u>States of the system</u> are described by the solutions of the equation

$$\widehat{H}\Psi(r,\theta,\varphi) = E\Psi(r,\theta,\varphi)$$

Since $\widehat{H}, \widehat{L}^2$ and $\widehat{L}_z$ are the pairwise commuting operators

$$\widehat{H}\widehat{L}^2 - \widehat{L}^2\widehat{H} = 0, \quad \widehat{H}\widehat{L}_z - \widehat{L}_z\widehat{H} = 0, \quad \widehat{L}^2\widehat{L}_z - \widehat{L}_z\widehat{L}^2 = 0$$

there exist states in which the total energy, the magnitude of angular momentum, and the component of angular momentum are definite.

Hydrogen atom

$$\widehat{H}\widehat{L}^2 - \widehat{L}^2\widehat{H} = 0, \quad \widehat{H}\widehat{L}_z - \widehat{L}_z\widehat{H} = 0, \quad \widehat{L}^2\widehat{L}_z - \widehat{L}_z\widehat{L}^2 = 0$$
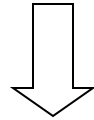
$\Downarrow$

Therefore, the energy eigenstates may also be chosen to be eigenstates of the angular momentum operators

$$\Psi_E(r,\theta,\varphi) = R_{El}(r)Y_{lm}(\theta,\varphi)$$

$$\widehat{L}_z Y_{lm}(\theta,\varphi) = (\hbar m)Y_{lm}(\theta,\varphi)$$
$$\widehat{L}^2 Y_{lm}(\theta,\varphi) = \hbar^2 l(l+1)Y_{lm}(\theta,\varphi)$$
$$m = 0,\pm 1,\pm 2,...,\pm l$$
$$l = 0,1,2,...$$

$$Y_{00} = \sqrt{\frac{1}{4\pi}}$$
$$Y_{11} = -\sqrt{\frac{3}{8\pi}}\sin\theta e^{i\phi}$$
$$Y_{10} = \sqrt{\frac{3}{4\pi}}\cos\theta$$
$$Y_{1,-1} = \sqrt{\frac{3}{8\pi}}\sin\theta e^{-i\phi}$$
$$Y_{22} = \sqrt{\frac{15}{32\pi}}\sin^2\theta e^{2i\phi}$$
$$Y_{21} = -\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{i\phi}$$
$$Y_{20} = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1)$$
$$Y_{2,-1} = \sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{-i\phi}$$
$$Y_{2,-2} = \sqrt{\frac{15}{32\pi}}\sin^2\theta e^{-2i\phi}$$

Hydrogen atom

Therefore, the energy eigenstates may also be chosen to be eigenstates of the angular momentum operators

$$\Psi_E(r,\theta,\varphi) = R_{El}(r)Y_{lm}(\theta,\varphi)$$

Radial eigenfunctions $R_{El}(r)$ and energies E are computed from the ordinary differential equation

$$-\frac{\hbar^2}{2\mu r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left[\frac{\hbar^2 l(l+1)}{2\mu r^2} - \frac{Ze^2}{r} - E\right]R(r) = 0$$

Boundary conditions: $R(r)$ and dR/dr must be continuous, $R(r)$ must be quadratically integrable $\int_0^\infty R^2(r)r^2 dr < \infty$.

The answers: $R_{nl}(r) \propto \text{Pol}_{nl}(r)\exp(-\beta_n r)$

$$E_n = -\frac{Z^2}{2n^2}\frac{\mu e^4}{\hbar^2} \qquad n=1,2,... \qquad l=0,1,...,n-1 \qquad m=-l,\ -l+1,...l$$

Hydrogen atom: States

Quantum Mechanics: Keywords "States of the system"

An essential feature of QM is that certain parameters of the system can take on discrete values varying from one state to another by 'quantum jumps'.

Example: Few states of the hydrogen atom

State	Total energy (10^{20} J/atom)	Electronic angular momentum
1s	-218.6	0
2s	-54.6	0
2p	-54.6	$\sqrt{2}\,\hbar$

$$E_n = -\frac{Z^2}{2n^2}\frac{\mu e^4}{\hbar^2}$$

$$n=1,2,\ldots \qquad l=0,1,\ldots,n-1 \qquad m=-l,\,-l+1,\ldots l$$

1s $n=1, l=0, m=0$

2s $n=2, l=0, m=0$

2p $n=2, l=1, m=-1,0,1$

3s $n=3, l=0, m=0$

...

1s   *n=1, l=0, m=0*

R_{nl}^2

R_{nl}

$R_{nl}^2 r^2$
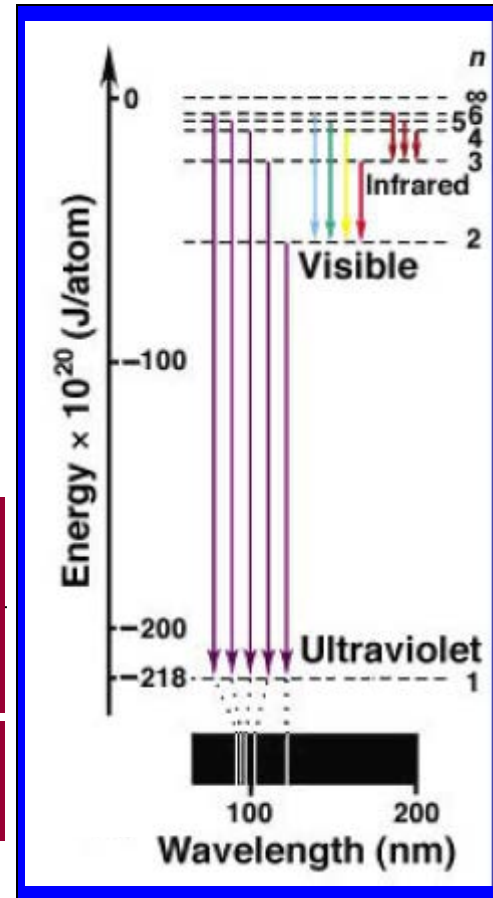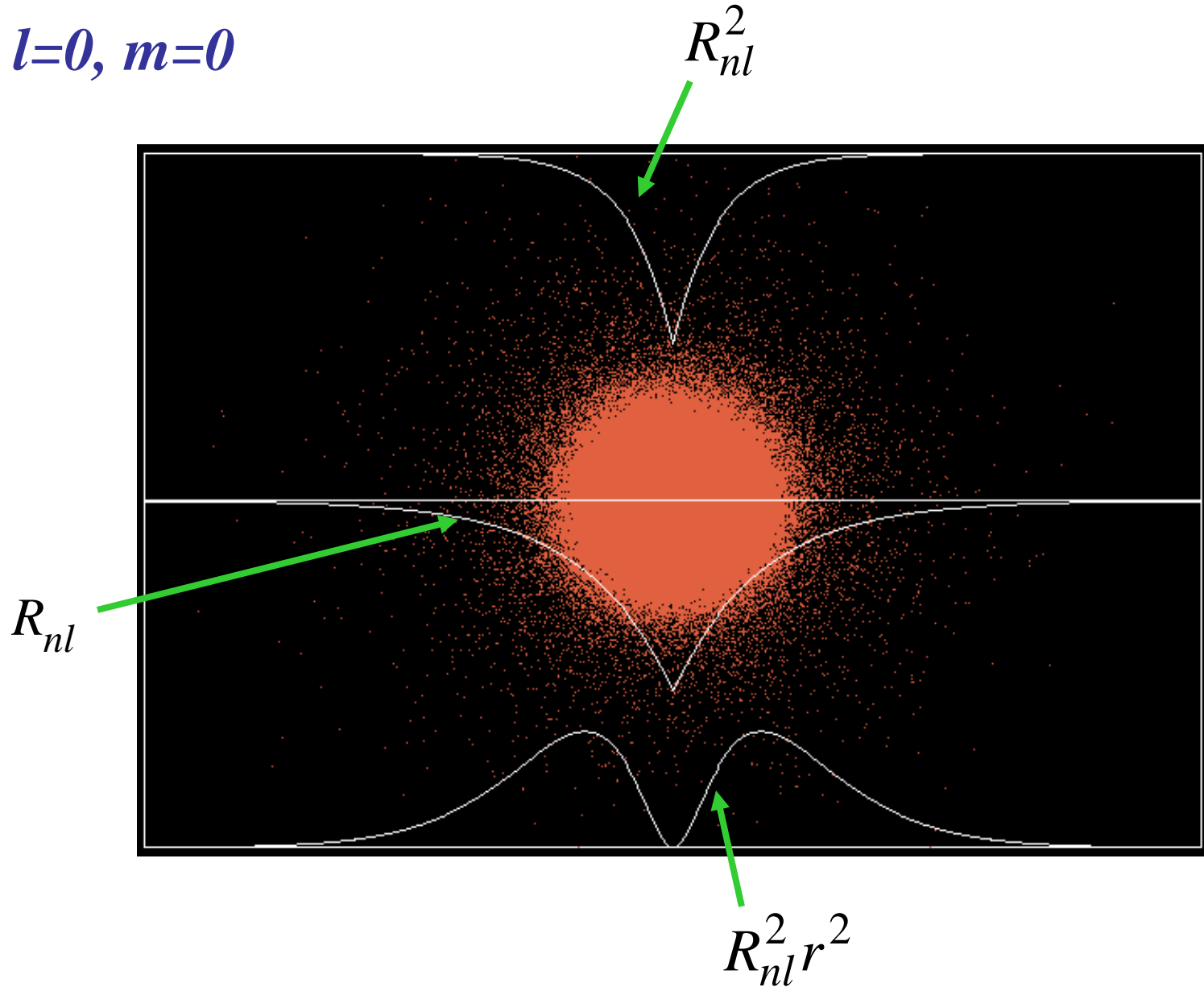
Hydrogen atom: Images of wavefunctions

2s   *n=2, l=0, m=0*

R_{nl}^2

R_{nl}

$R_{nl}^2 r^2$
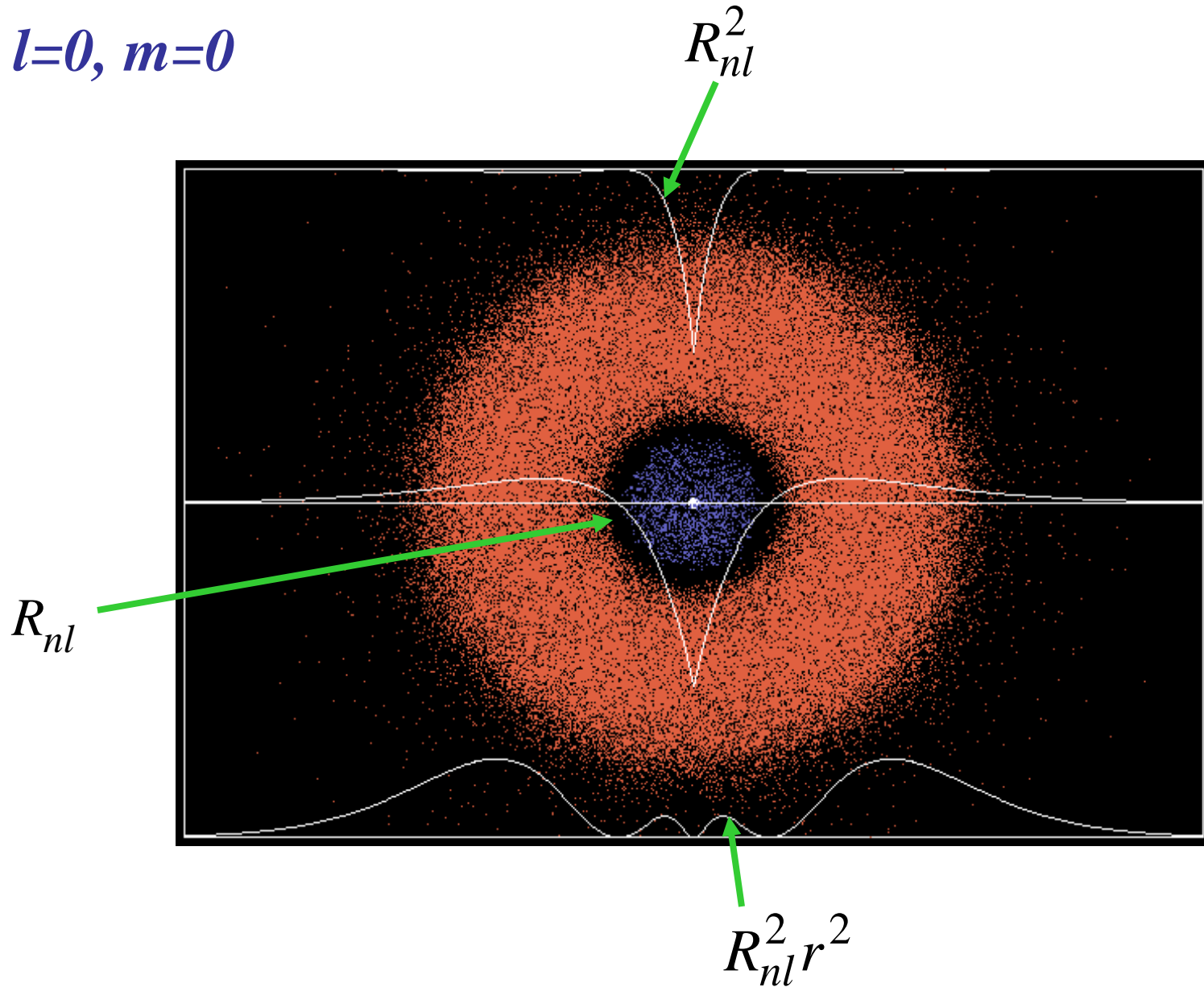
Hydrogen atom: Images of wavefunctions

2p   *n=2, l=1, m=0*
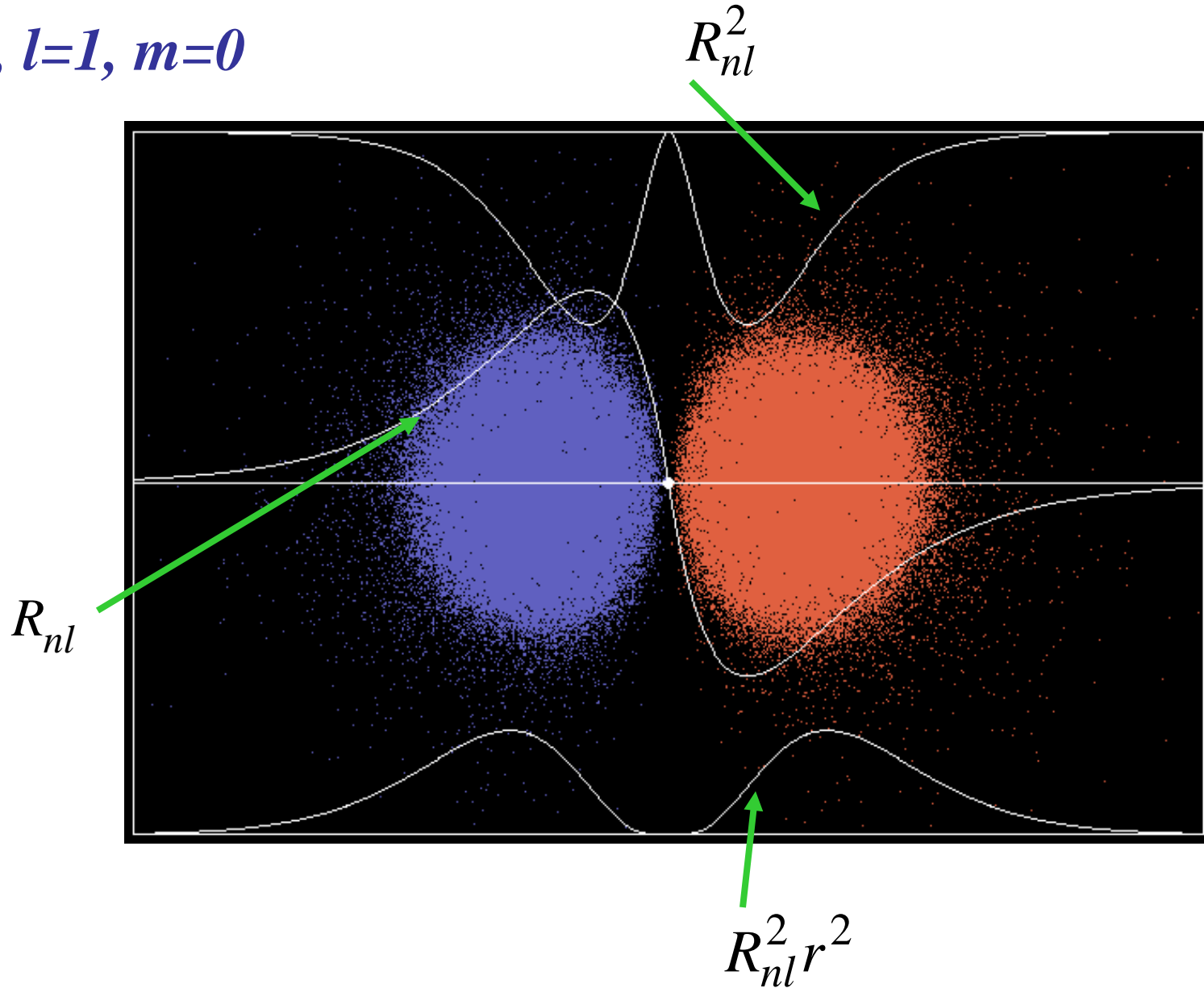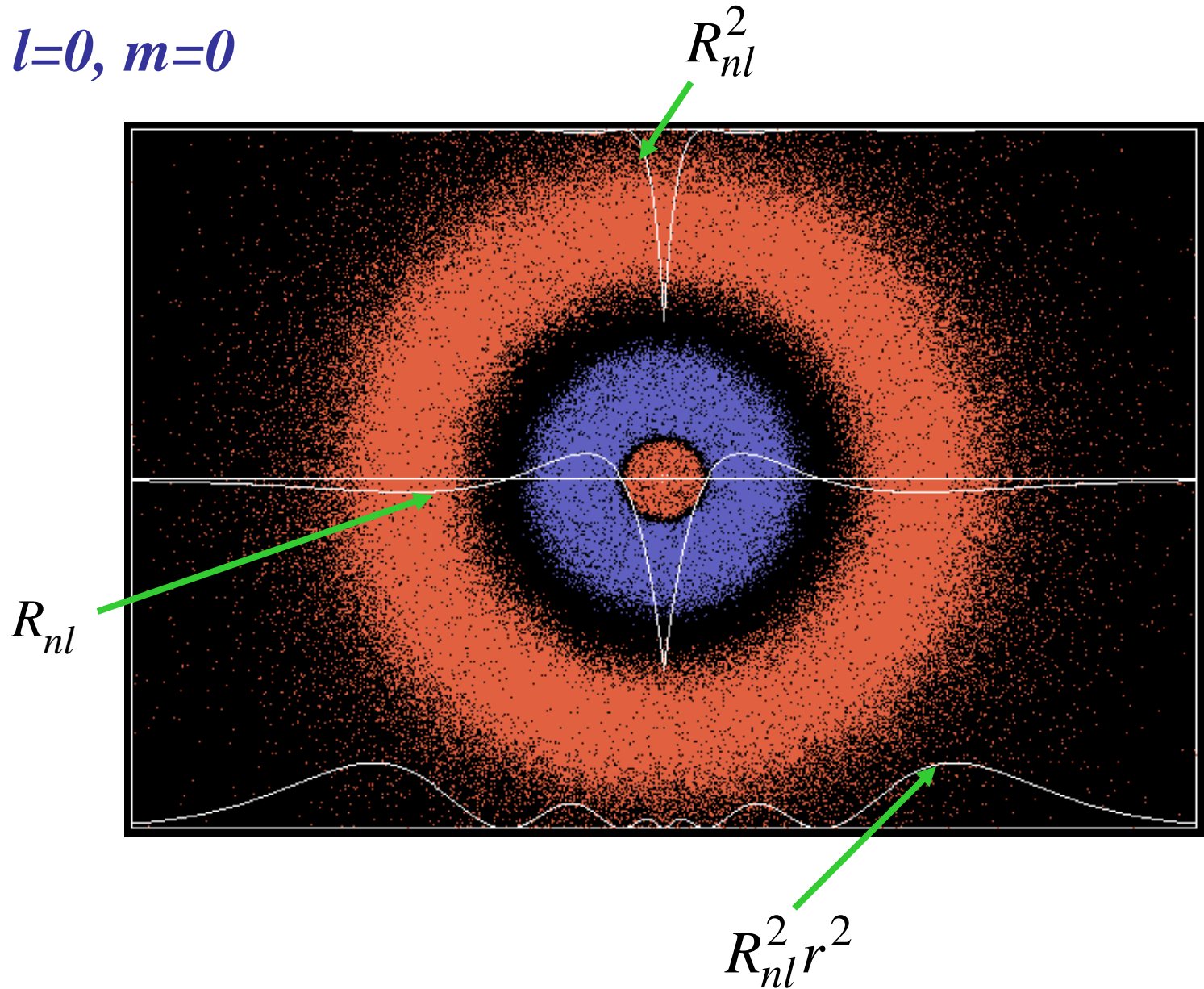
R_{nl}^2

R_{nl}

$R_{nl}^2 r^2$

3s   *n=3, l=0, m=0*

R_{nl}^2

R_{nl}

$R_{nl}^2 r^2$

3p   *n=3, l=1, m=0*

R_{nl}^2

R_{nl}

$R_{nl}^2 r^2$

3d $n=3, l=2, m=0$

R_{nl}^2

R_{nl}

$R_{nl}^2 r^2$
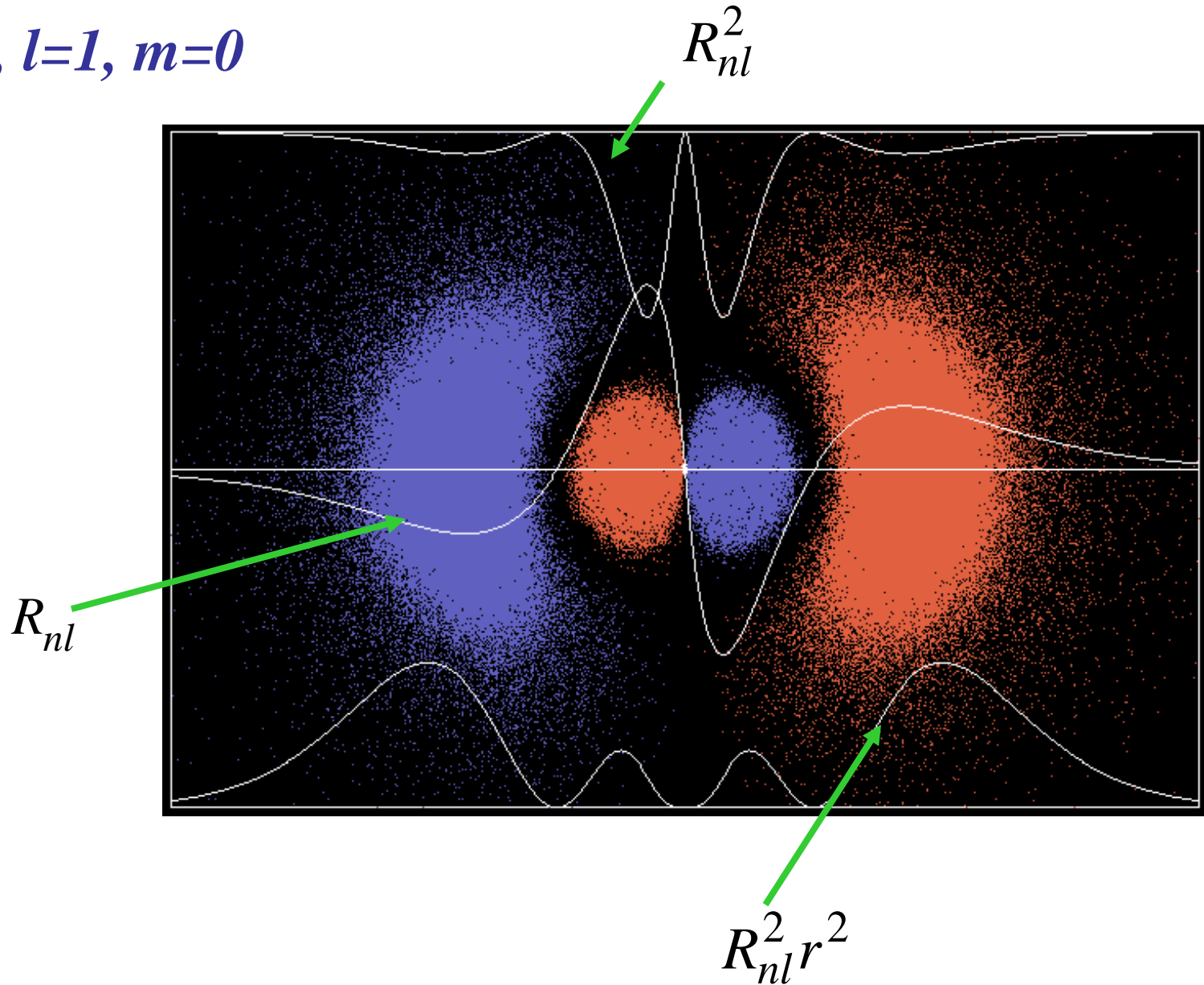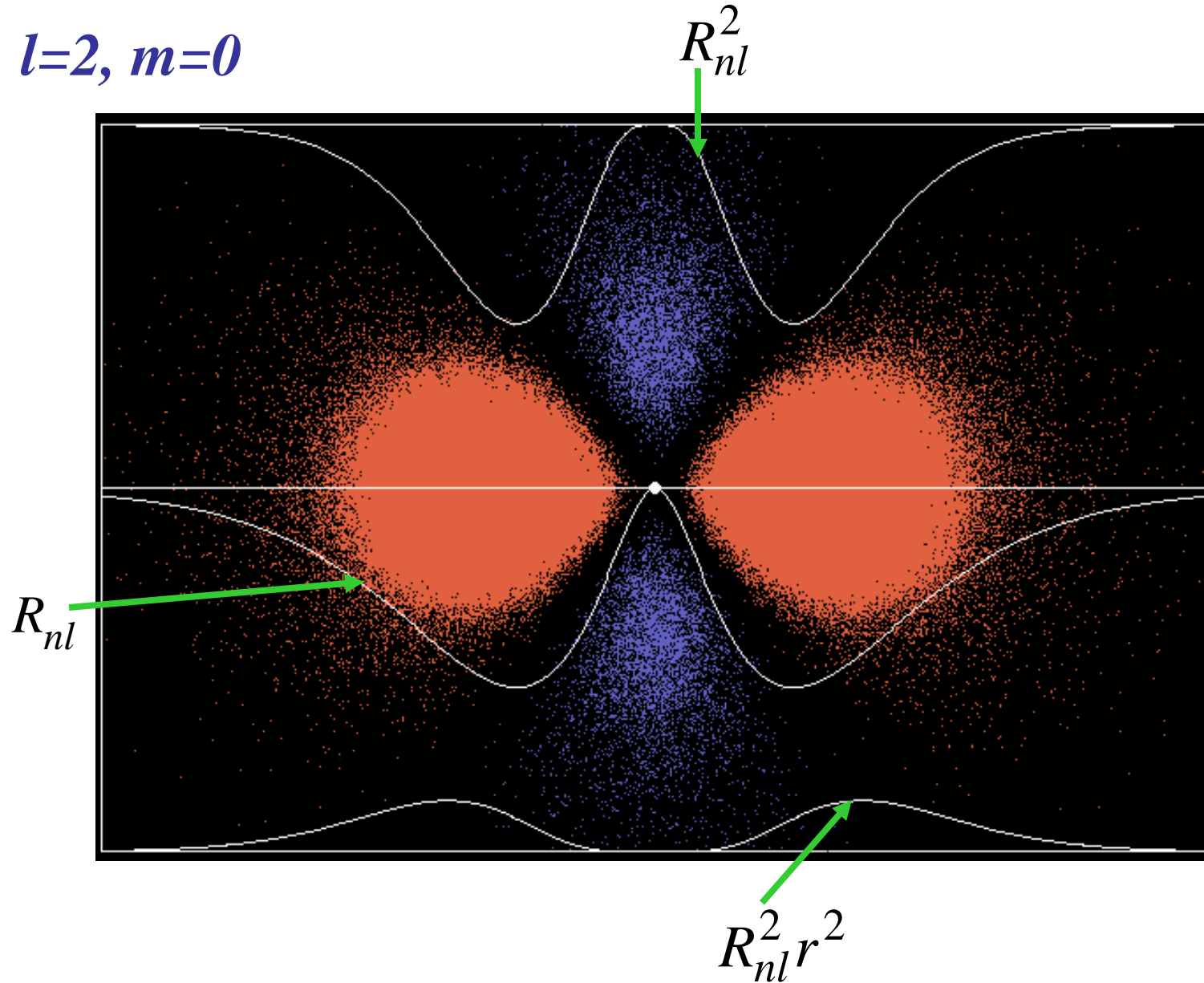
Hydrogen atom: Atomic Orbitals (AOs)
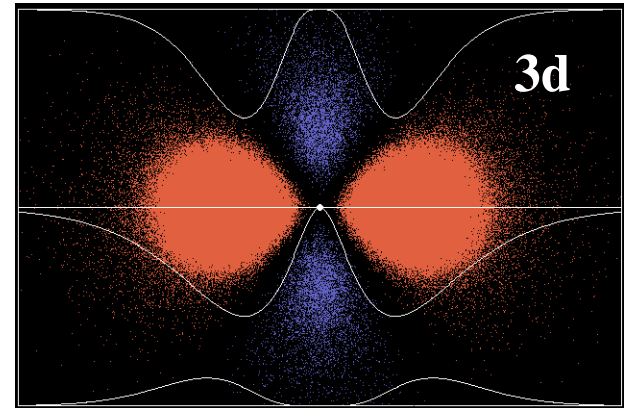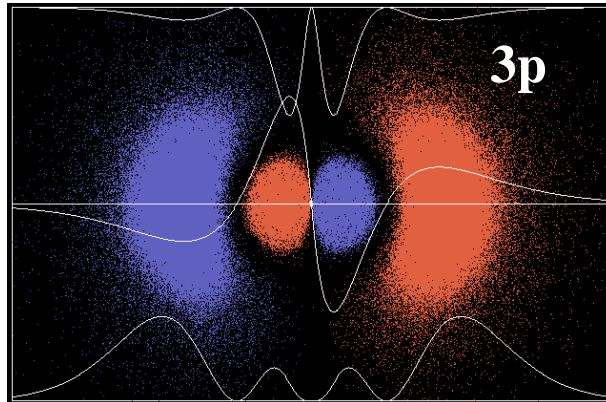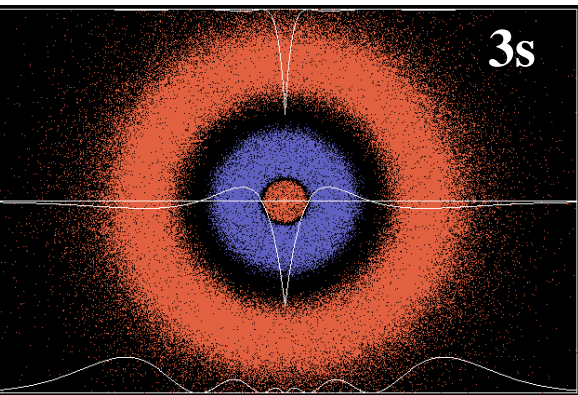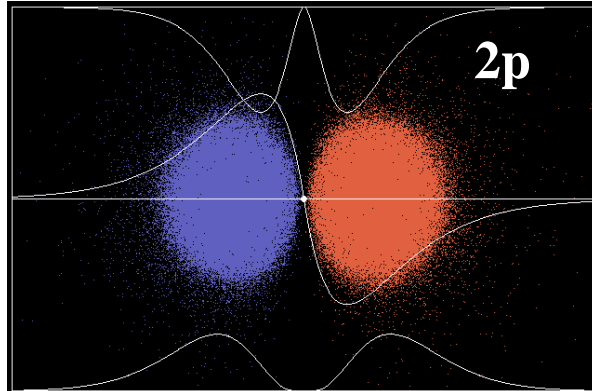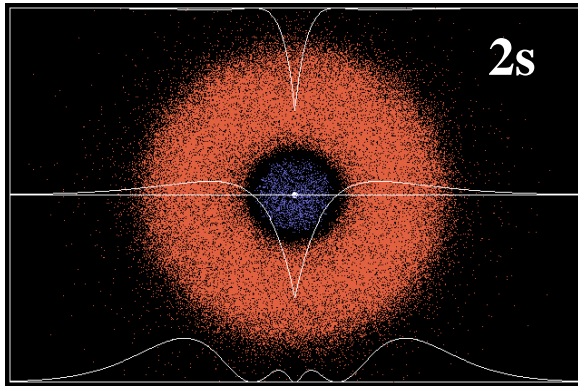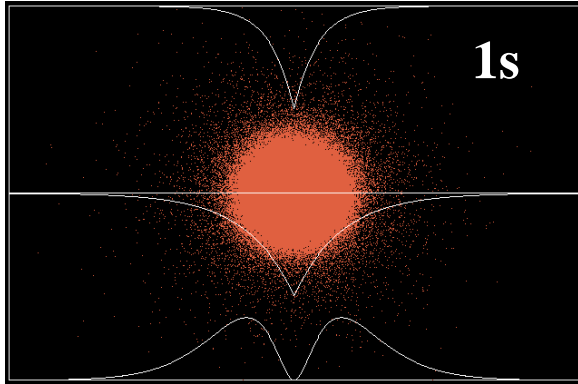
Spin

In the non-relativistic quantum mechanics, we have to assign to every 'elementary' particle an angular momentum which is not related to possible 'orbiting' of the particle. An internal angular momentum, the vector with components s_x, s_y, s_z, is called spin. Unlike orbital angular momentum these components cannot be expressed in terms of Cartesian coordinates and linear momenta.

The square of the spin length is a characteristic feature of a particle: for every electron in all states it has the value

$$s^2 = \hbar^2 s(s+1) \xrightarrow{\;s=1/2\;} \frac{3\hbar^2}{4}$$

Spin

The theory of spin is constructed by analogy with the theory of orbital angular momentum.

Important: the commutator relations

$$\hat{s}_x \hat{s}_y - \hat{s}_y \hat{s}_x = i\hbar \hat{s}_z \qquad \hat{s}^2 \hat{s}_x - \hat{s}_x \hat{s}^2 = 0$$

$$\hat{s}_z \hat{s}_x - \hat{s}_x \hat{s}_z = i\hbar \hat{s}_y \qquad \hat{s}^2 \hat{s}_y - \hat{s}_y \hat{s}^2 = 0$$

$$\hat{s}_y \hat{s}_z - \hat{s}_z \hat{s}_y = i\hbar \hat{s}_x \qquad \hat{s}^2 \hat{s}_z - \hat{s}_z \hat{s}^2 = 0$$

- only two quantities are measurable s^2 and s_z
- $\hat{s}^2$ and $\hat{s}_z$ have a common set of eigenvectors $|s, m_s\rangle$

$$\hat{s}^2 | s, m_s \rangle = \hbar^2 s(s+1) | s, m_s \rangle$$

$$\hat{s}_z | s, m_s \rangle = \hbar m_s | s, m_s \rangle$$

For electrons: $s=\frac{1}{2}$ (always)

$$m_s = -\frac{1}{2}, +\frac{1}{2}$$

Spin

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$$\widehat{s}_z\widehat{s}_x - \widehat{s}_x\widehat{s}_z = i\hbar\widehat{s}_y \qquad\qquad \widehat{s}^{\,2}\widehat{s}_y - \widehat{s}_y\widehat{s}^{\,2} = 0$$

$$\widehat{s}_y\widehat{s}_z - \widehat{s}_z\widehat{s}_y = i\hbar\widehat{s}_x \qquad\qquad \widehat{s}^{\,2}\widehat{s}_z - \widehat{s}_z\widehat{s}^{\,2} = 0$$

- only two quantities are measurable s^2 and s_z
- $\widehat{s}^{\,2}$ and $\widehat{s}_z$ have a common set of eigenvectors $|s, m_s\rangle$

$$\widehat{s}^{\,2}|s, m_s\rangle = \hbar^2 s(s+1)|s, m_s\rangle$$

$$\widehat{s}_z|s, m_s\rangle = \hbar m_s|s, m_s\rangle$$

For electrons: $s=\frac{1}{2}$ (always)

$$m_s = -\tfrac{1}{2}, +\tfrac{1}{2}$$

$$\widehat{L}_z Y_{lm}(\theta, \varphi) = (\hbar m) Y_{lm}(\theta, \varphi)$$

$$\widehat{L}^2 Y_{lm}(\theta, \varphi) = \hbar^2 l(l+1) Y_{lm}(\theta, \varphi)$$

$$m = 0, \pm 1, \pm 2, \ldots, \pm l$$

$$l = 0, 1, 2, \ldots$$

Orbital angular momentum

Spin

Two possible spin states of an electron
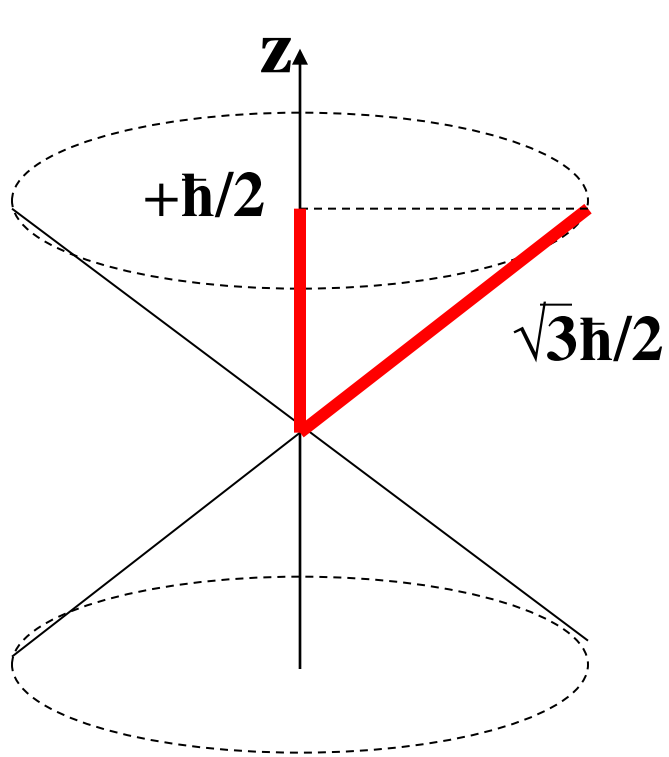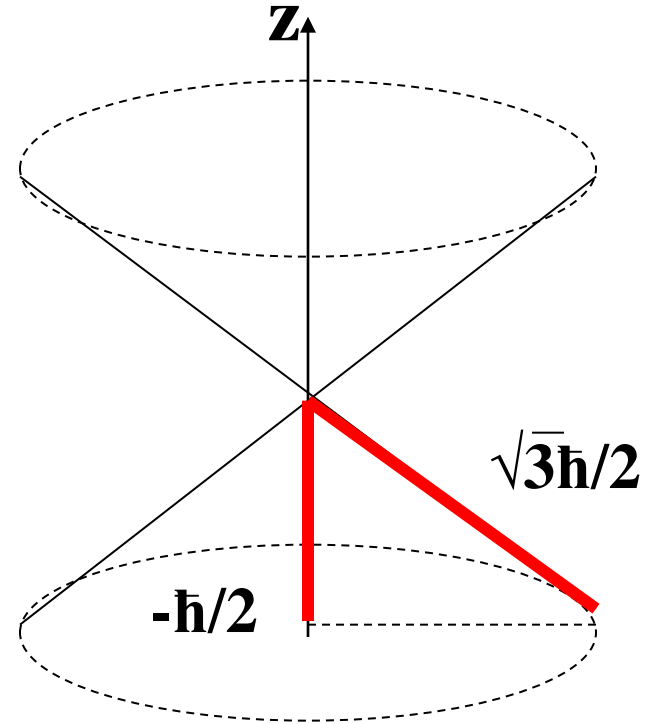
$$|\alpha\rangle = |s = 1/2, m_s = 1/2\rangle$$

$$|\beta\rangle = |s = 1/2, m_s = -1/2\rangle$$

2-electron spin vectors $\qquad (j_1=½, j_2=½)$

The total spin of two electrons may be either |½-½|=0 (singlet states),
or ½+½=1 (triplet states)

Two possible spin states of an electron

$|\alpha\rangle = |s=1/2, m_s=1/2\rangle \qquad |\beta\rangle = |s=1/2, m_s=-1/2\rangle$
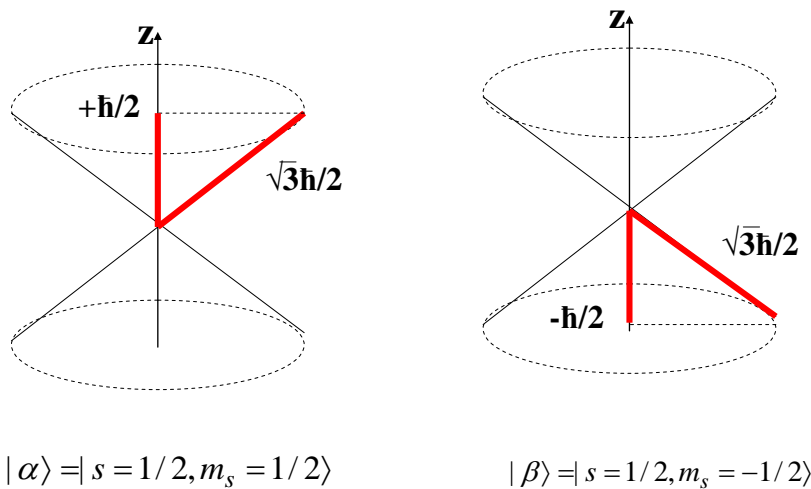
Singlet state 2-electron spin vector

$$|0,0\rangle = \frac{1}{\sqrt{2}}\{|\alpha\rangle_{(1)}|\beta\rangle_{(2)} - |\beta\rangle_{(1)}|\alpha\rangle_{(2)}\}$$

Triplet state 2-electron spin vectors $\begin{cases} |1,1\rangle = |\alpha\rangle_{(1)}|\alpha\rangle_{(2)} \\[2mm] |1,0\rangle = \dfrac{1}{\sqrt{2}}\{|\alpha\rangle_{(1)}|\beta\rangle_{(2)} + |\beta\rangle_{(1)}|\alpha\rangle_{(2)}\} \\[2mm] |1,-1\rangle = |\beta\rangle_{(1)}|\beta\rangle_{(2)} \end{cases}$

Interchange Hypothesis For Identical Particles

Interchanging the positions of two identical particles does not change the physical state.

Identical (elementary) particles have the same parameters – the mass, charge, and magnitude of spin momentum. Positions $\vec{r}$ and spin projections σ are considered as 'coordinates'.

The wavefunctions must be either symmetric or antisymmetric with respect to an interchange of positions and spin projections of any pair of identical particles:

$$\Psi(\vec{r}_1\sigma_1,...,\vec{r}_i\sigma_i,...\vec{r}_j\sigma_j,...,\vec{r}_N\sigma_N) = \pm\Psi(\vec{r}_1\sigma_1,...,\vec{r}_j\sigma_j,...\vec{r}_i\sigma_i,...,\vec{r}_N\sigma_N)$$

The Spin Statistics Theorem

Systems of identical particles with integer spin s = 0; 1; 2;… are described by wavefunctions that are symmetric under the interchange of particle coordinates and spin. Systems of identical particles with half-integer spin s = 1/2; 3/2;… are described by wavefunctions that are antisymmetric under the interchange of particle coordinates and spin.

Particles with integer spin are known as Bosons. Particles with half-integer spin are known as Fermions. Examples include, in particular, electrons, and protons.

Therefore, electronic wavefunctions must satisfy a condition

$$\Psi(\vec{r}_1\sigma_1,...,\vec{r}_i\sigma_i,...\vec{r}_j\sigma_j,...,\vec{r}_N\sigma_N) = -\Psi(\vec{r}_1\sigma_1,...,\vec{r}_j\sigma_j,...\vec{r}_i\sigma_i,...,\vec{r}_N\sigma_N)$$

Quantum Mechanics for the Electronic Structure Theory

System
States of the system

Correspondence principle
Classical mechanics

Wavefunctions
Superposition principle
Hilbert space

Observables
Uncertainty principle

Hydrogen atom
Orbitals

Spin
Spin coupling
Interchange hypothesis

Molecules are stable systems of nuclei and electrons
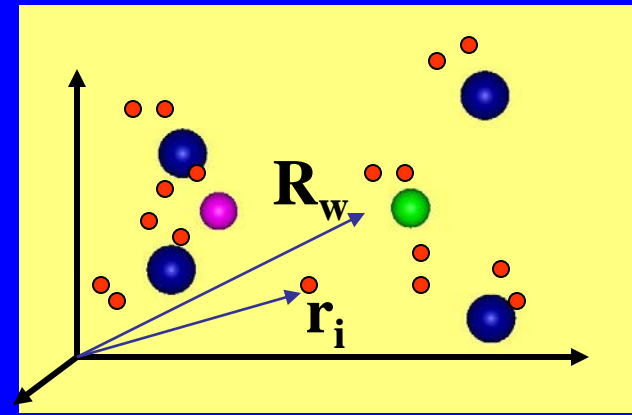
$$\hat{H}\Psi = E_{QM}\Psi$$

$$\hat{H} = \sum_i \left(-\frac{1}{2}\Delta_{r_i} \right) + \sum_w \left(-\frac{1}{2M_w}\Delta_{R_w} \right) + \sum_{i<j} \frac{1}{r_{ij}} + \sum_{w<v} \frac{Z_w Z_v}{R_{wv}} - \sum_{iw} \frac{Z_w}{|R_w - r_i|}$$

Molecules are stable systems of nuclei and electrons

Moving further
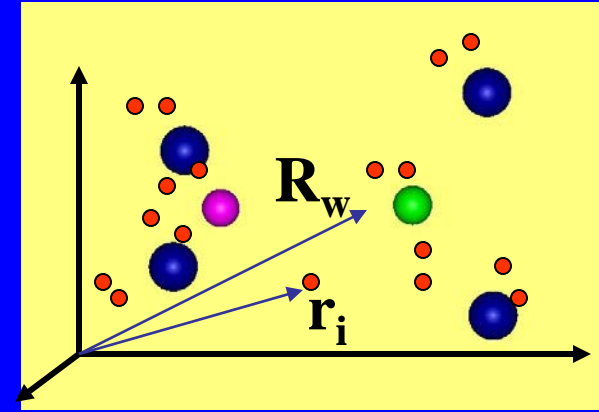
$$\hat{H}\Psi = E_{QM}\Psi$$

$$\hat{H} = \sum_i \left(-\frac{1}{2}\Delta_{r_i} \right) + \sum_w \left(-\frac{1}{2M_w}\Delta_{R_w} \right) + \sum_{i<j} \frac{1}{r_{ij}} + \sum_{w<v} \frac{Z_w Z_v}{R_{wv}} - \sum_{iw} \frac{Z_w}{|R_w - r_i|}$$

The Born-Oppenheimer approximation

To a high degree of accuracy we can separate electron and nuclear motion due to larger masses of nuclei

The Born-Oppenheimer Approximation

$$\hat{H} = \hat{T}_{electrons} + \hat{T}_{nuclei} + \hat{V}_{e-e} + \hat{V}_{n-n} + \hat{V}_{e-n}$$

to the nuclear equation

$$\hat{H}_{el} = \hat{T}_{electrons} + \hat{T}_{nuclei} + \hat{V}_{e-e} + \hat{V}_{n-n} + \hat{V}_{e-n}$$

Electronic equation $\qquad \hat{H}_{el}\psi_{el}(r;R) = E_{el}\psi_{el}(r;R)$

BO approximation leads to the idea of a potential energy surface

$$U(R) = E_{el} + V_{n\text{-}n}$$

Solution of the nuclear quantum equation allow us to determine a large variety of molecular properties.

An example are vibrational spectra.

Example: calculated vibration of the -C=O group in the bacteriochlorophyll of photosynthetic reaction centers
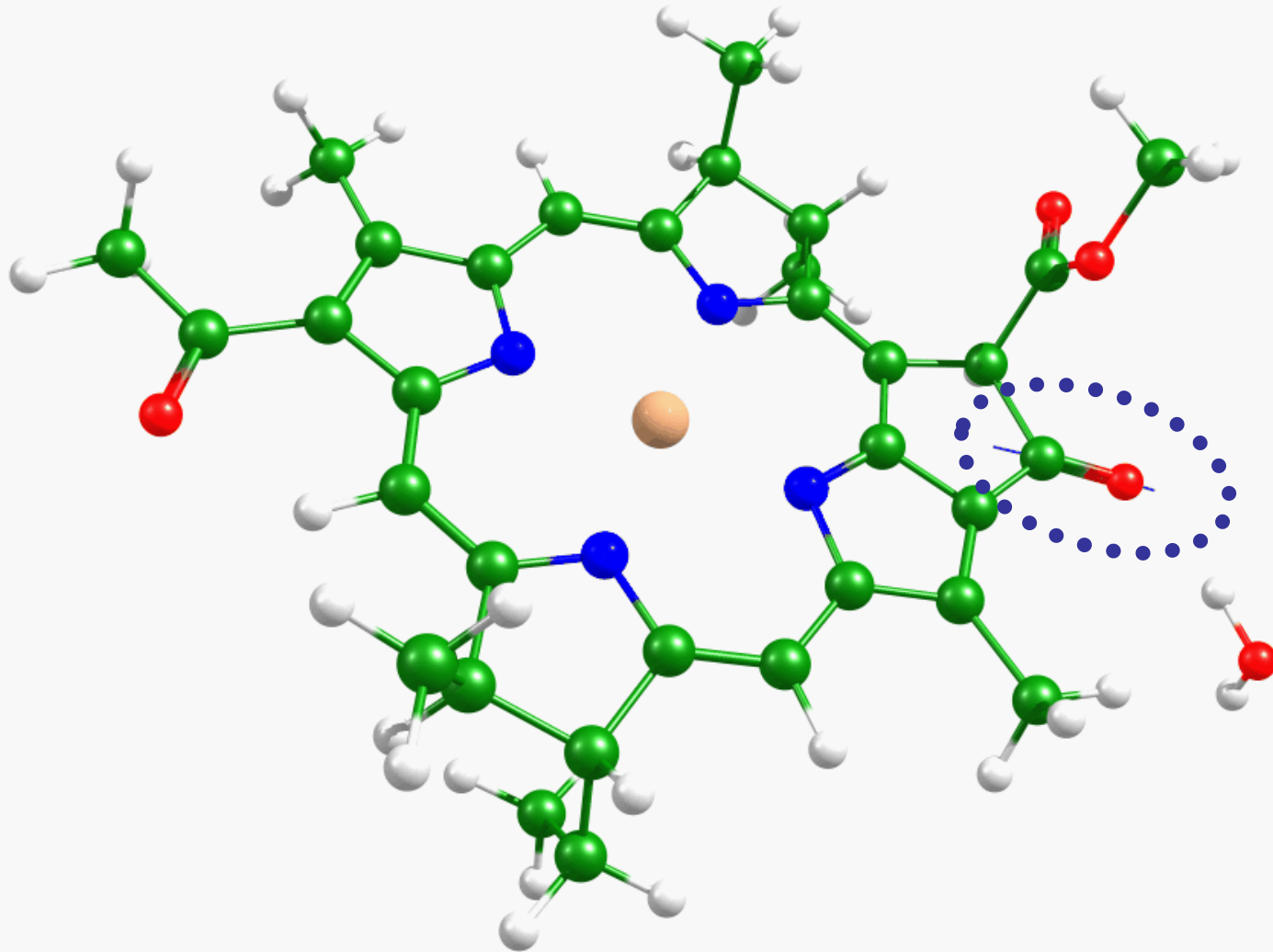
Example: calculated vibration with the imaginary frequency on the route of retinal isomerization in rhodopsin

C_{11}

C_{12}

Bathorhodopsin

Rhodopsin

Khrenova M.G., Bochenkova A.V., Nemukhin A.V., Proteins, 78, 614 (2010)
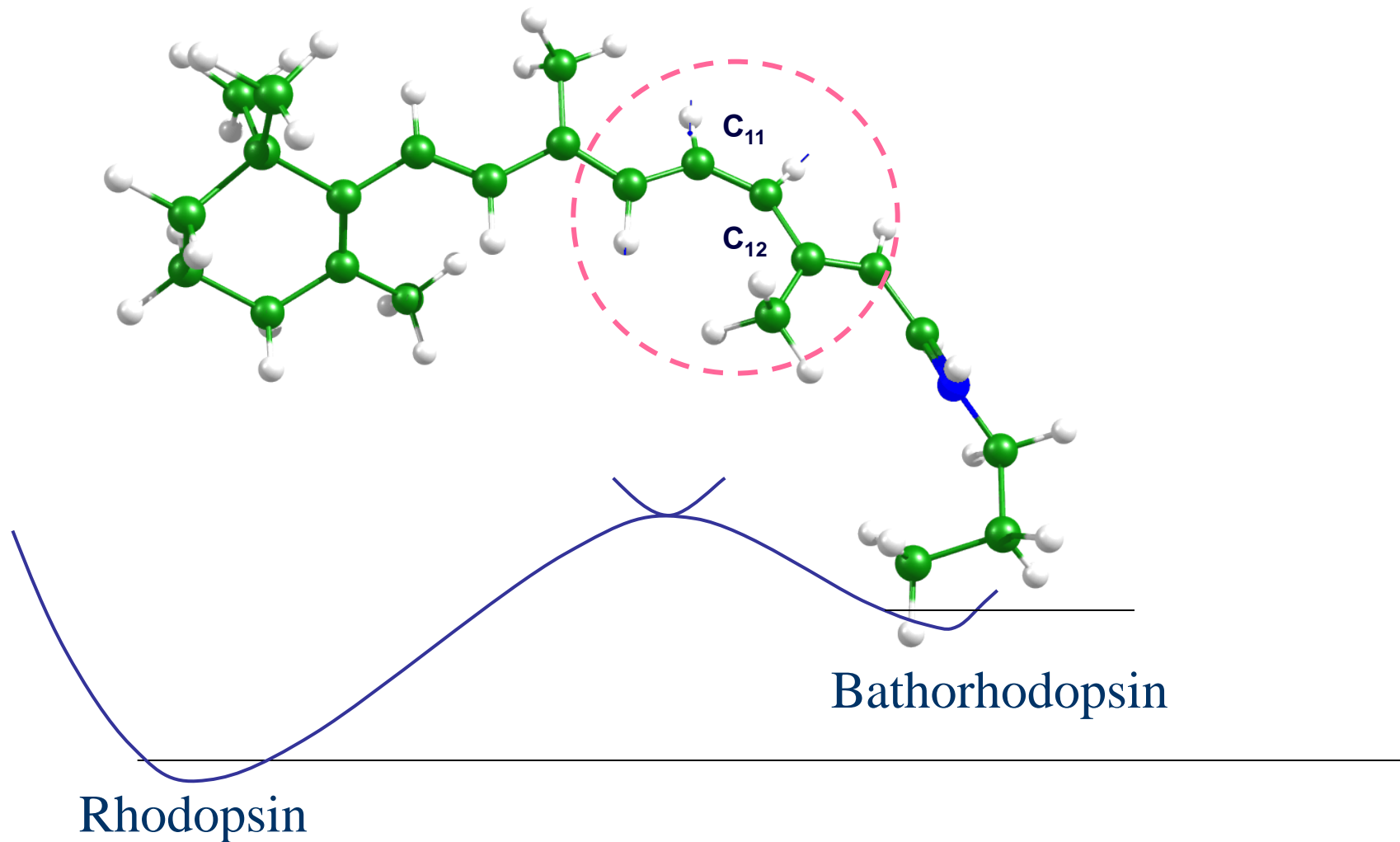
About electronic equation etc

**The lecture by Professor Gian Paolo Brivio
"Ab-initio & DFT"   on July 18**

Concluding examples
How does it work?

Concluding examples
How does it work?

Green Fluorescent Protein
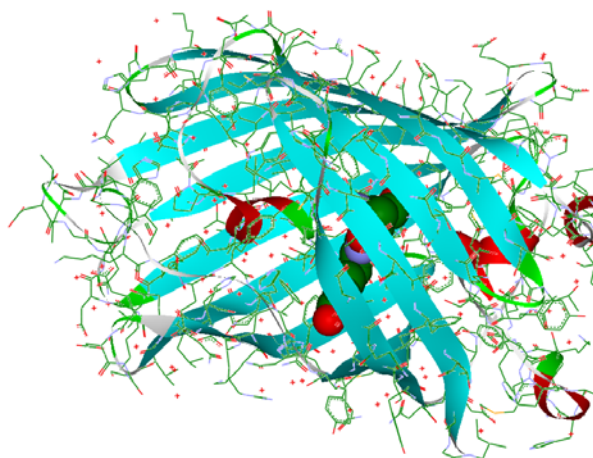
Chromophore
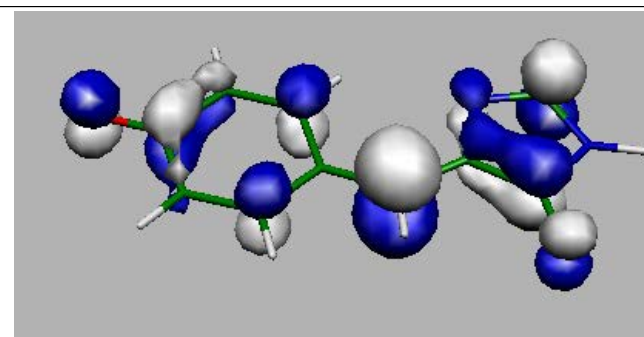
LUMO
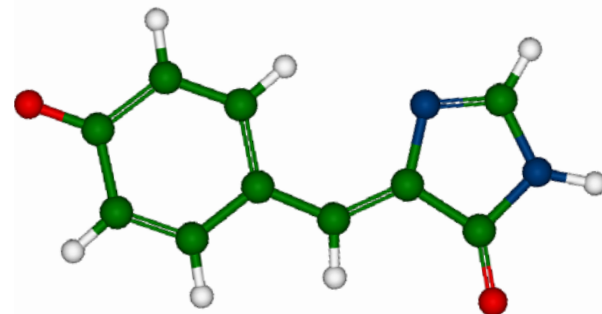
hydroxybenzylidene-imidazoline
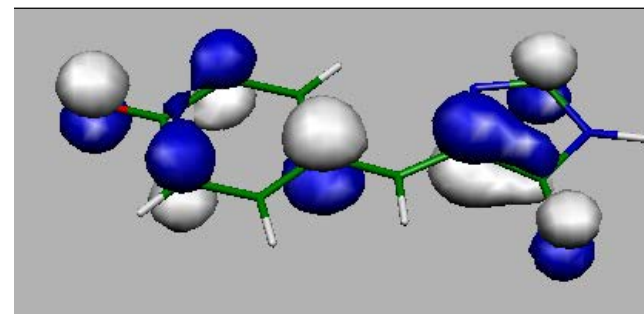
HOMO

Anionic GFP in the gas phase
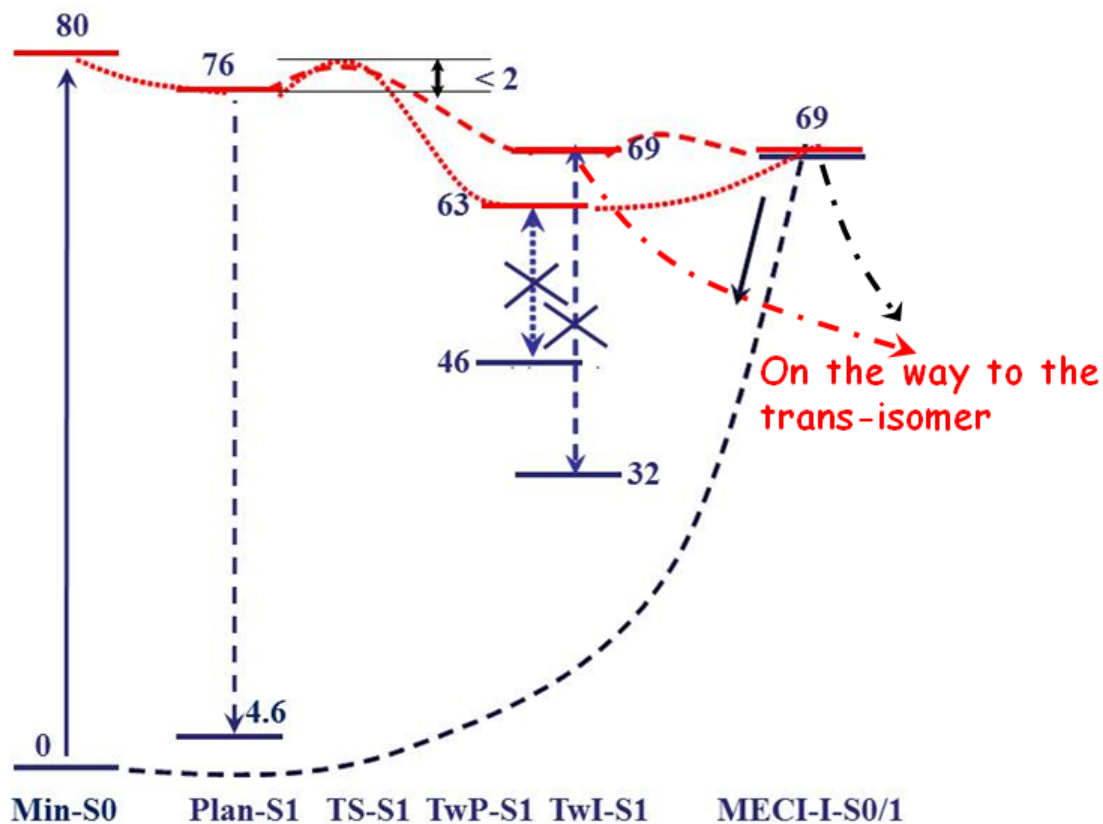
CASSCF(12/11)/cc-pVDZ

On the way to the trans-isomer

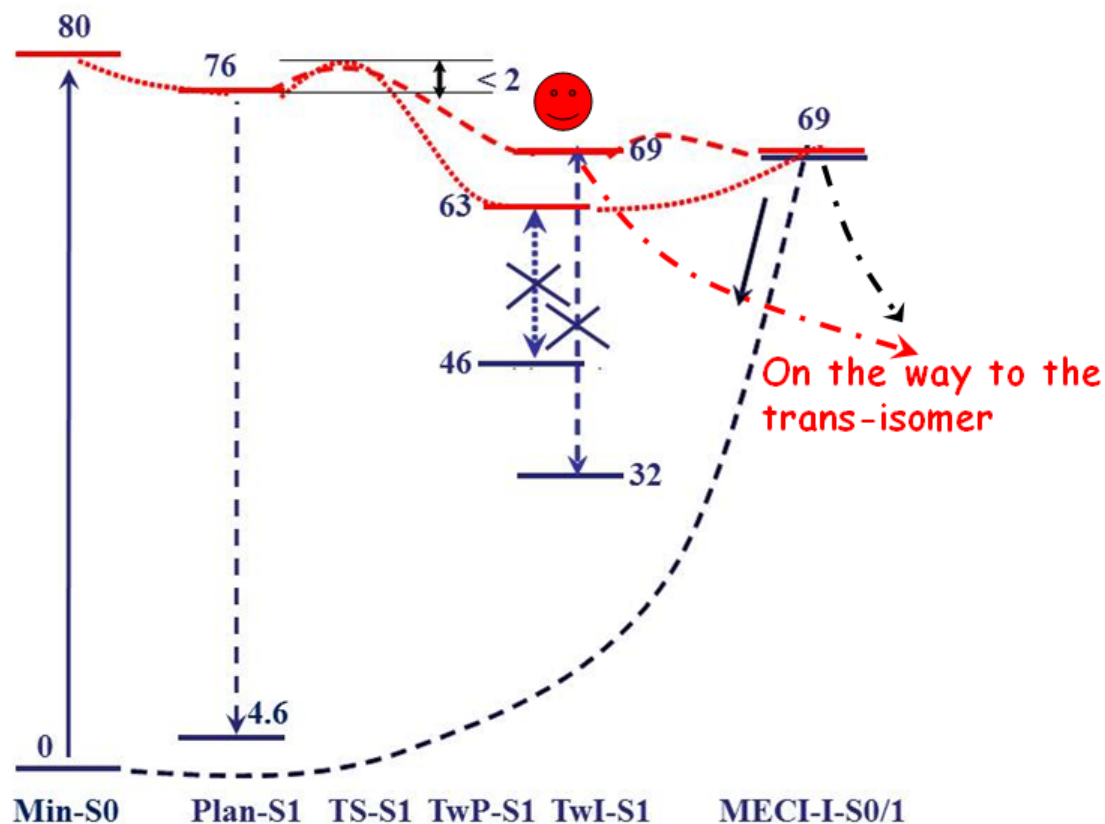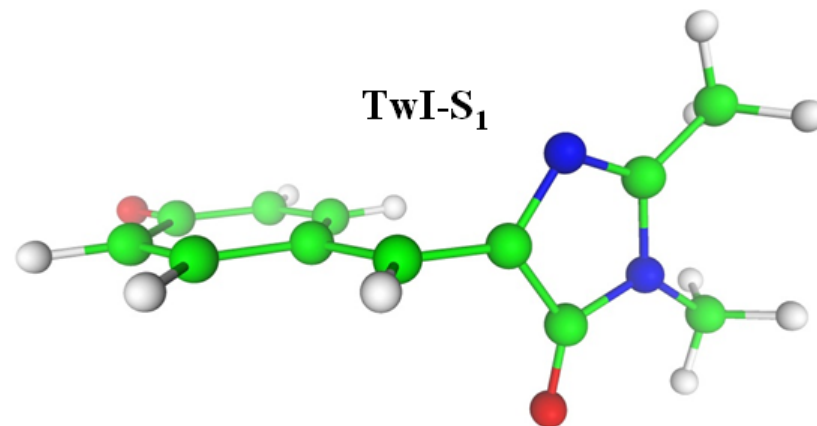Min-S0   Plan-S1   TS-S1   TwP-S1   TwI-S1   MECI-I-S0/1

I. Polyakov, B. Grigorenko, E. Epifanovsky, A. Krylov, A. Nemukhin
// *J. Chem. Theory Comput.* **2010, 6, 2377**

Anionic GFP in the gas phase

CASSCF(12/11)/cc-pVDZ

Min-S$_0$

1.41   1.38

80

76

≤ 2

69   69

63

46

32

On the way to the trans-isomer

0

4.6

Min-S0   **Plan-S1** **TS-S1** **TwP-S1** **TwI-S1**   **MECI-I-S0/1**

I. Polyakov, B. Grigorenko, E. Epifanovsky, A. Krylov, A. Nemukhin
// *J. Chem. Theory Comput. 2010, 6, 2377*

Anionic GFP in the gas phase

CASSCF(12/11)/cc-pVDZ

Plan-S$_1$

1.45   1.42

80

76

≤ 2

69

69

63

46

32

On the way to the trans-isomer

4.6

0

Min-S0   Plan-S1   TS-S1   TwP-S1   TwI-S1   MECI-I-S0/1

I. Polyakov, B. Grigorenko, E. Epifanovsky, A. Krylov, A. Nemukhin
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Anionic GFP in the gas phase

CASSCF(12/11)/cc-pVDZ

TwP-S$_1$

80

76

< 2

69

69

63

46

32

On the way to the
trans-isomer

4.6

0

Min-S0   Plan-S1   TS-S1 TwP-S1 TwI-S1   MECI-I-S0/1

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Anionic GFP in the gas phase

CASSCF(12/11)/cc-pVDZ

TwI-S$_1$

On the way to the trans-isomer

80

76

< 2

69

69

63

46

32

4.6

0

Min-S0   Plan-S1   TS-S1 TwP-S1 TwI-S1   MECI-I-S0/1

I. Polyakov, B. Grigorenko, E. Epifanovsky, A. Krylov, A. Nemukhin
// *J. Chem. Theory Comput. 2010, 6, 2377*

Anionic GFP in the gas phase

CASSCF(12/11)/cc-pVDZ

MECI-S$_{0/1}$

On the way to the trans-isomer

Min-S0   Plan-S1   TS-S1 TwP-S1 TwI-S1   MECI-I-S0/1
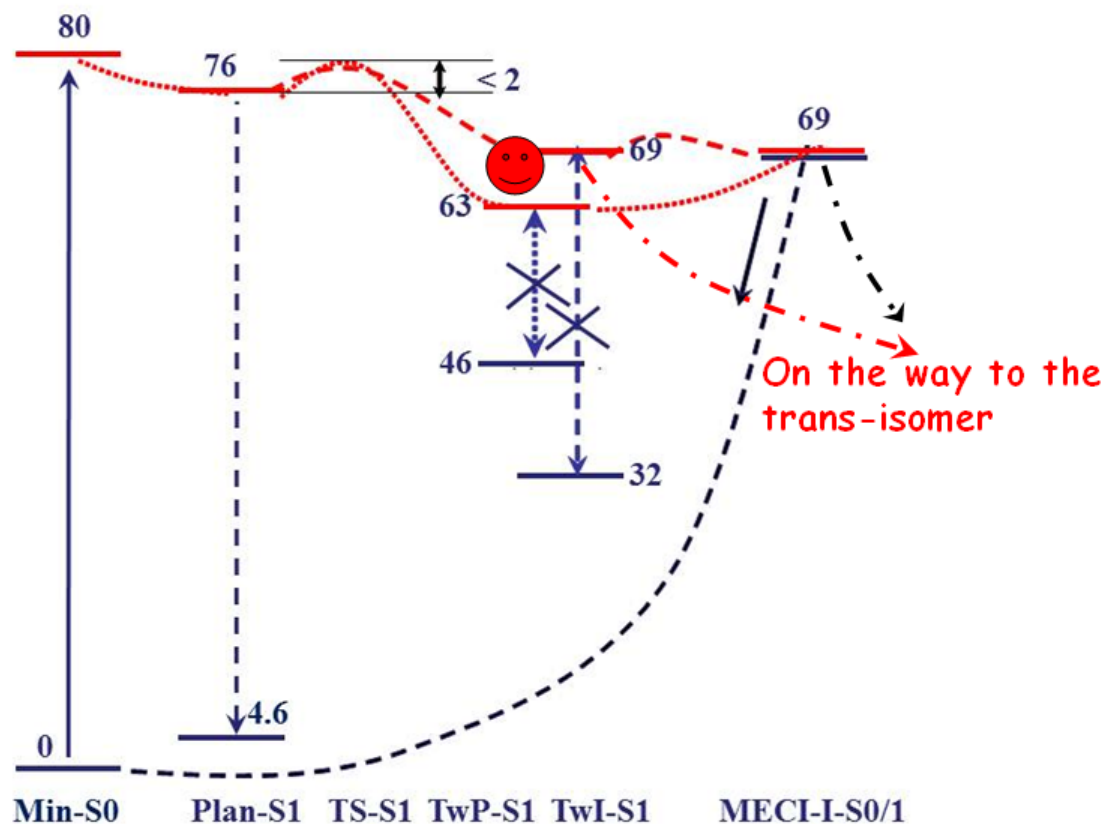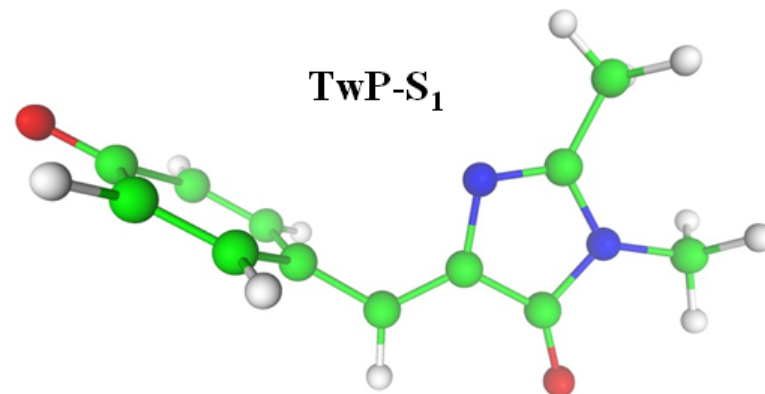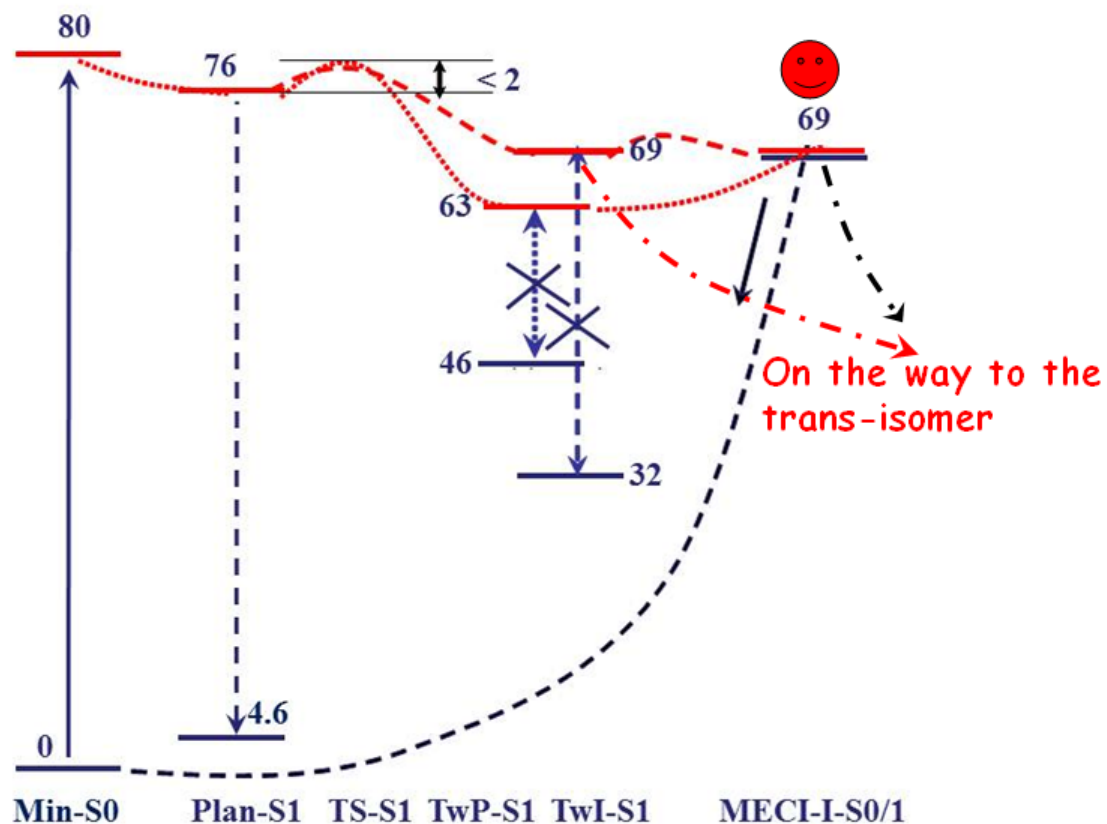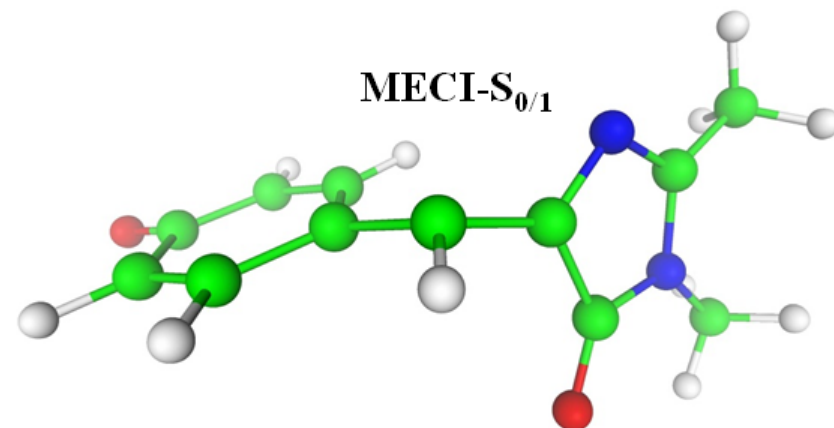
I. Polyakov, B. Grigorenko, E. Epifanovsky, A. Krylov, A. Nemukhin
// *J. Chem. Theory Comput.* 2010, 6, 2377

Concluding examples
How does it work for large systems?

Practically useful tool - Quantum mechanical – molecular mechanical (QM/MM) approach
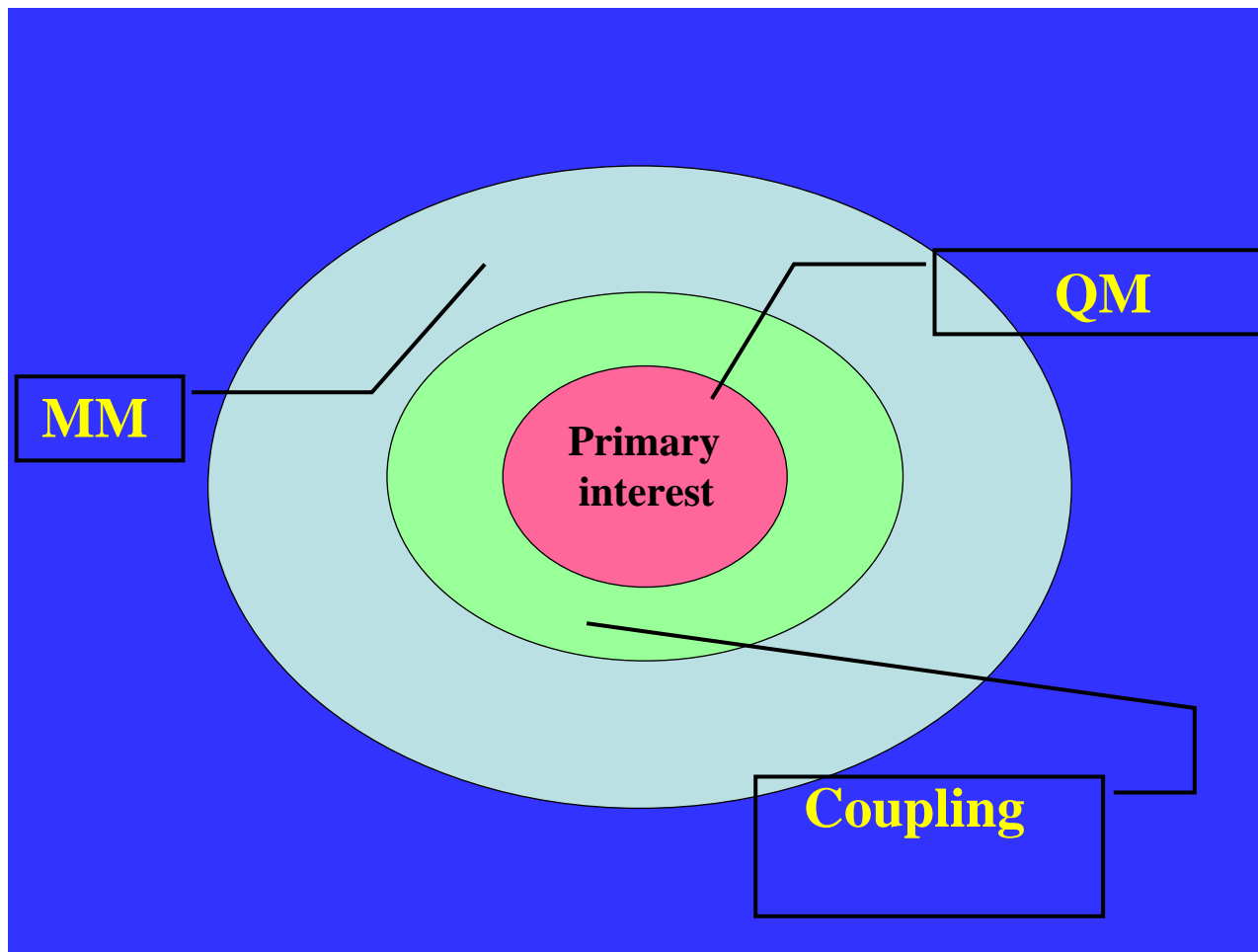
The results of QM/MM simulations: Geometry of the GFP active site

Theory: QM/MM (DFT(PBE0/6-31G*)/Amber)

Experiment (PDB ID - 1GFL):
X-ray diffraction (PH 7, resolution 1.9A)
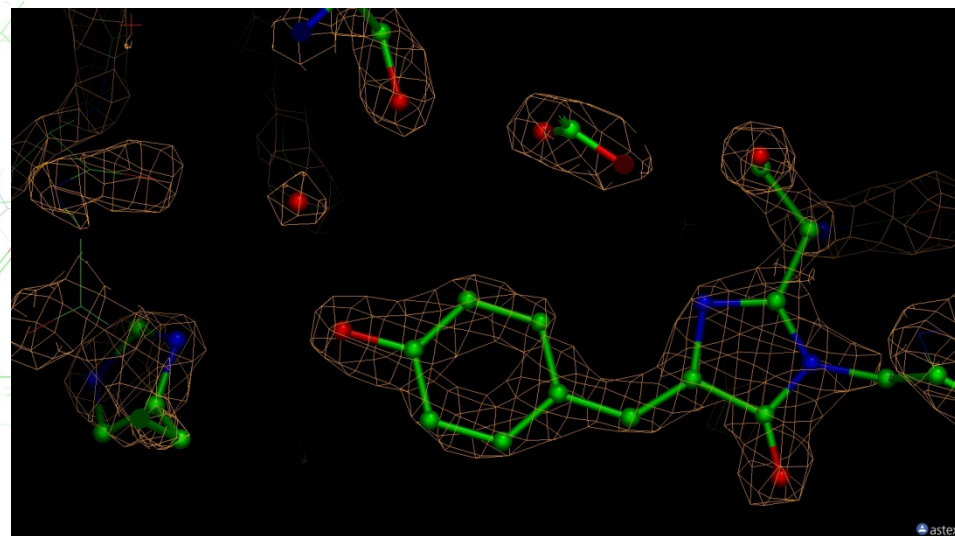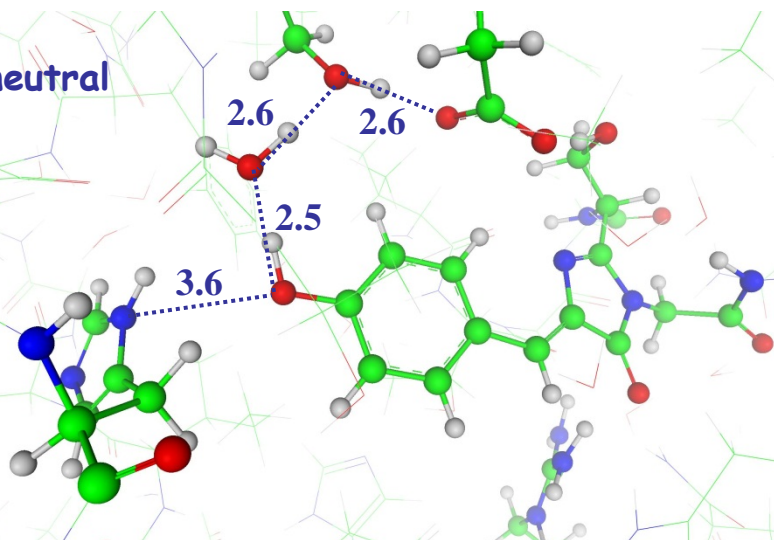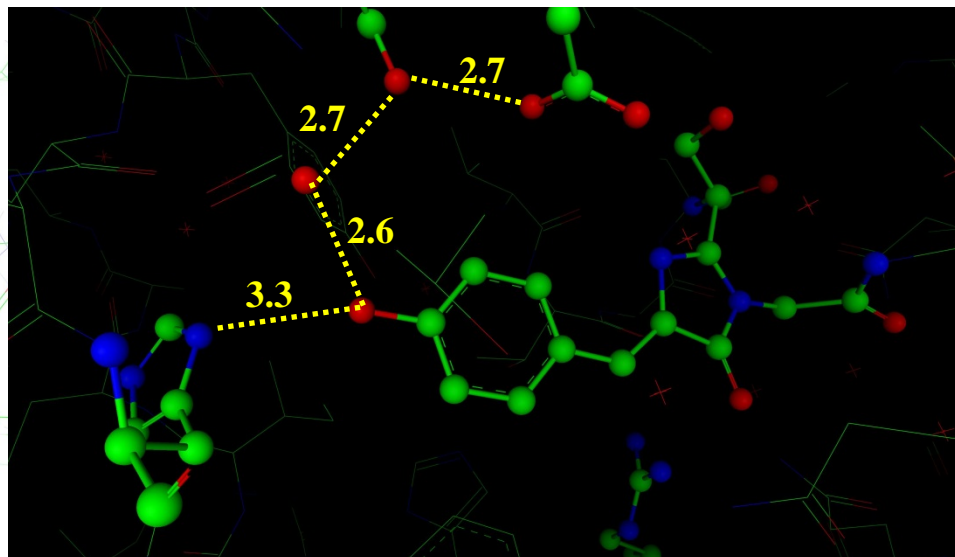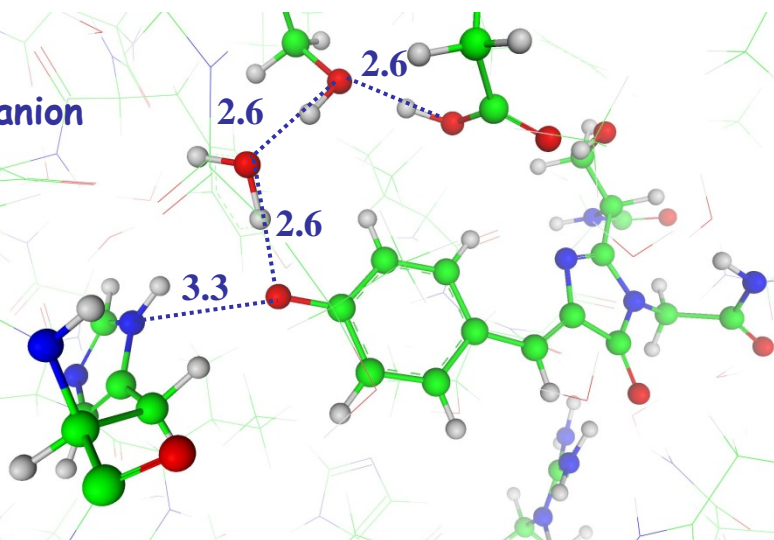
What does happen upon photoexcitation?
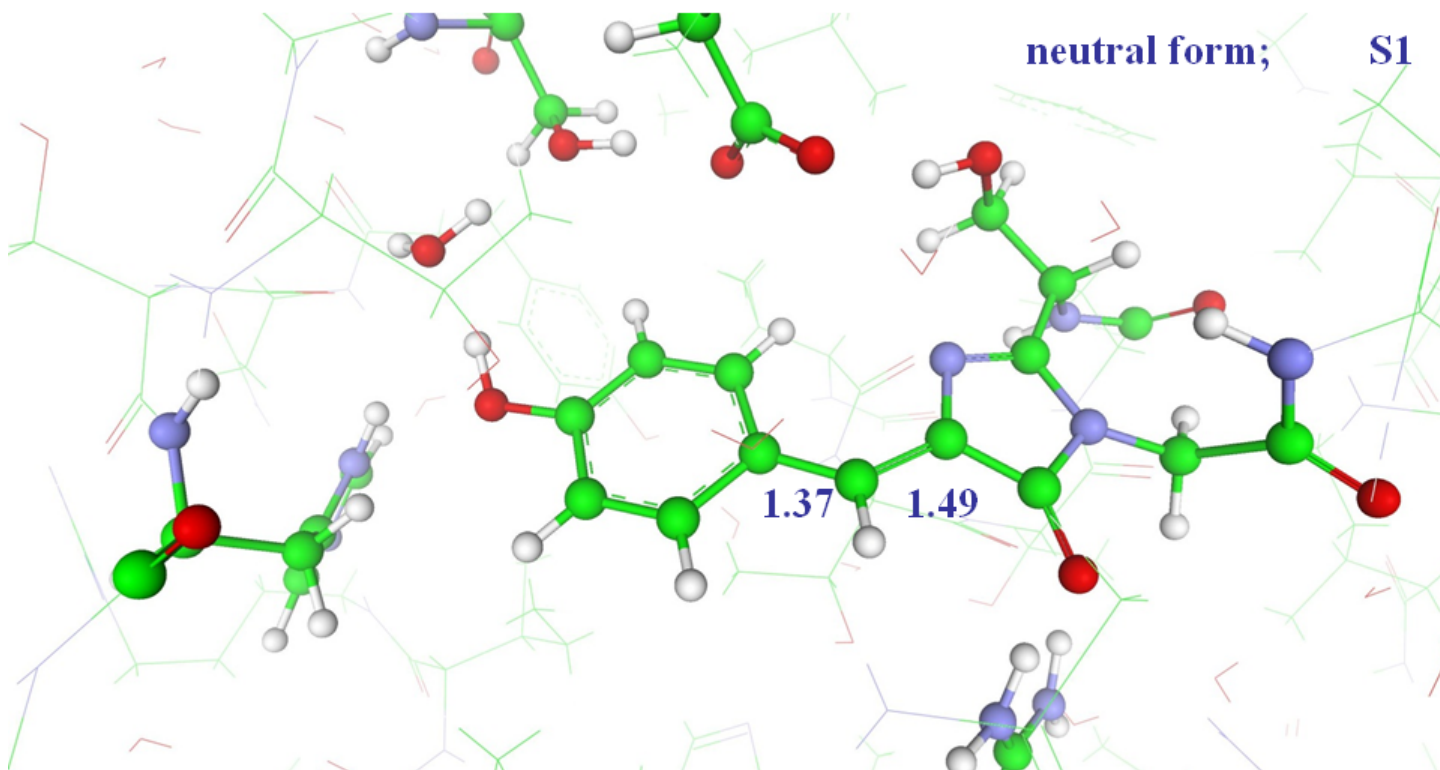## CASSCF(10/9)/6-31G*/AMBER results
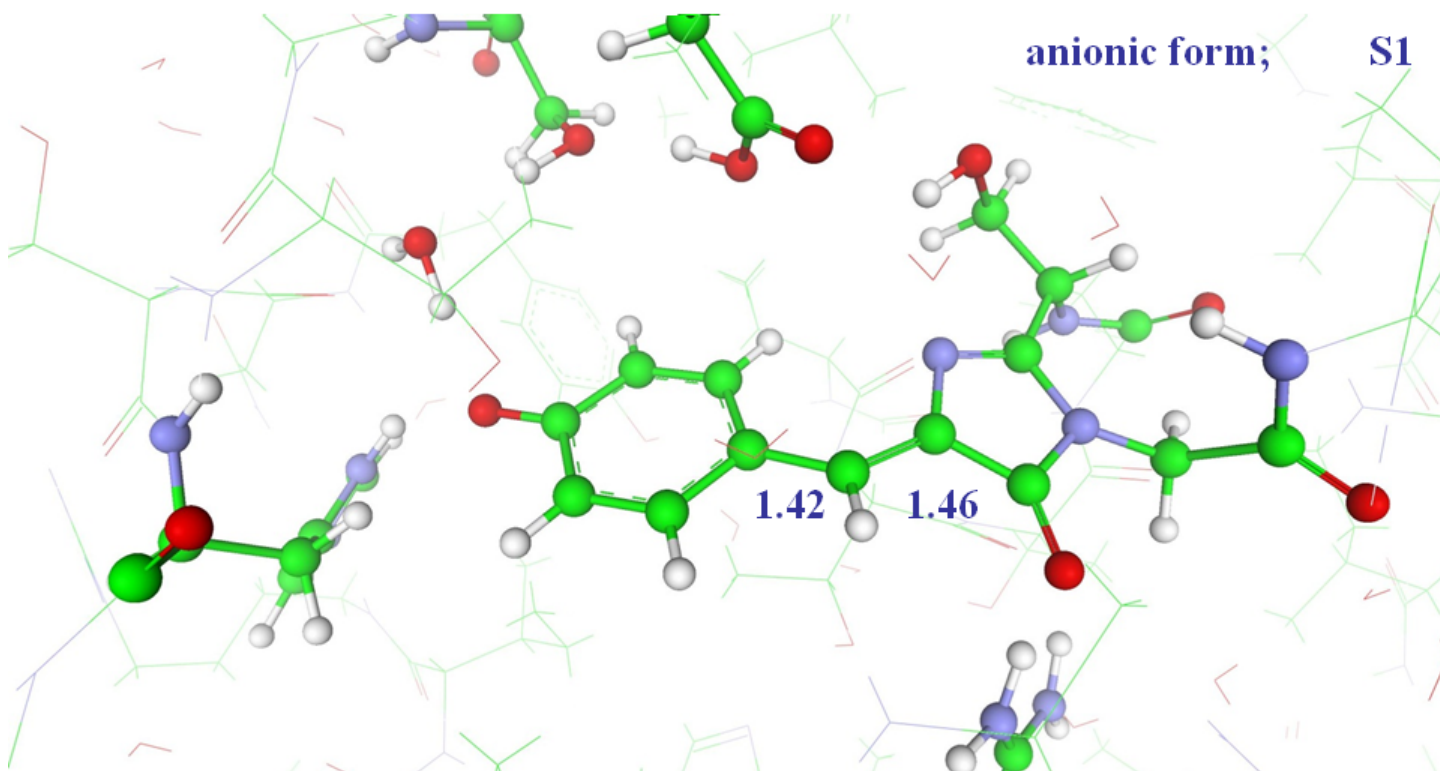

neutral form;   S0

1.44   1.36

What does happen upon photoexcitation?
CASSCF(10/9)/6-31G*/AMBER results

S1

anion

S1

S1*

S1*

S0

S0

S0

S0

neutral

anion

neutral form;   S1

1.37   1.49

What does happen upon photoexcitation?
CASSCF(10/9)/6-31G*/AMBER results

anionic form;   S1

1.42   1.46

What does happen upon photoexcitation?
CASSCF(10/9)/6-31G*/AMBER results

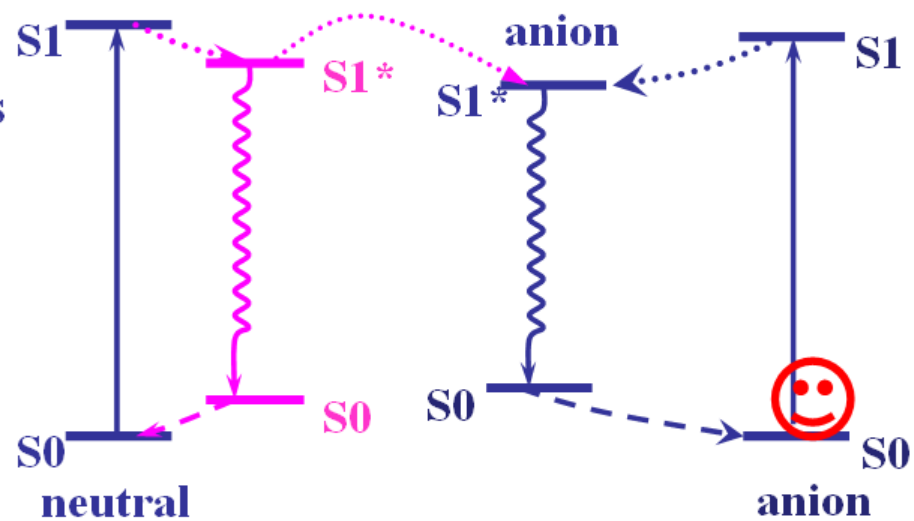anionic form;   S0

1.42   1.37
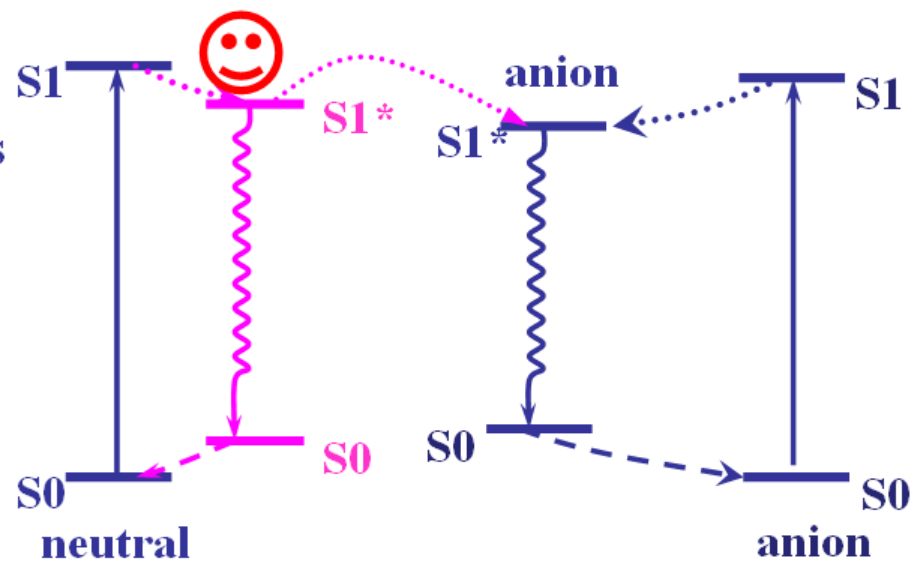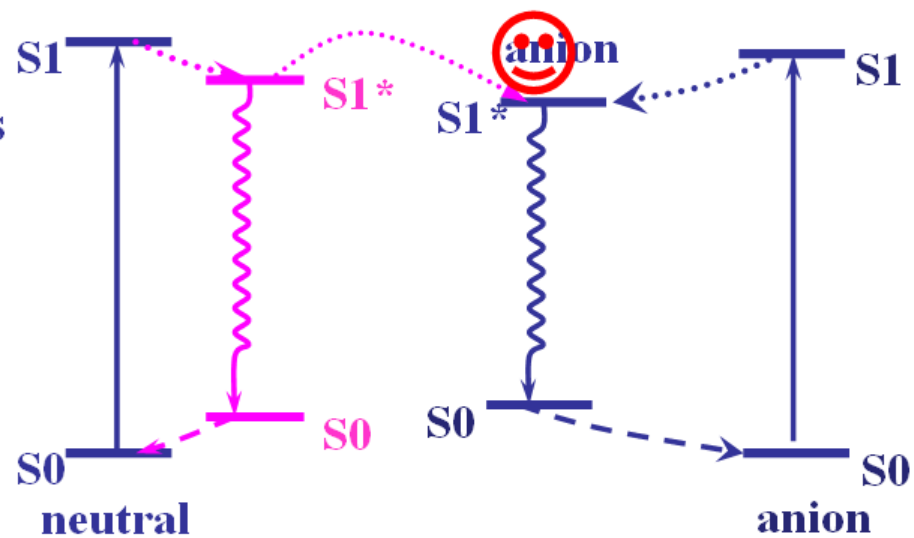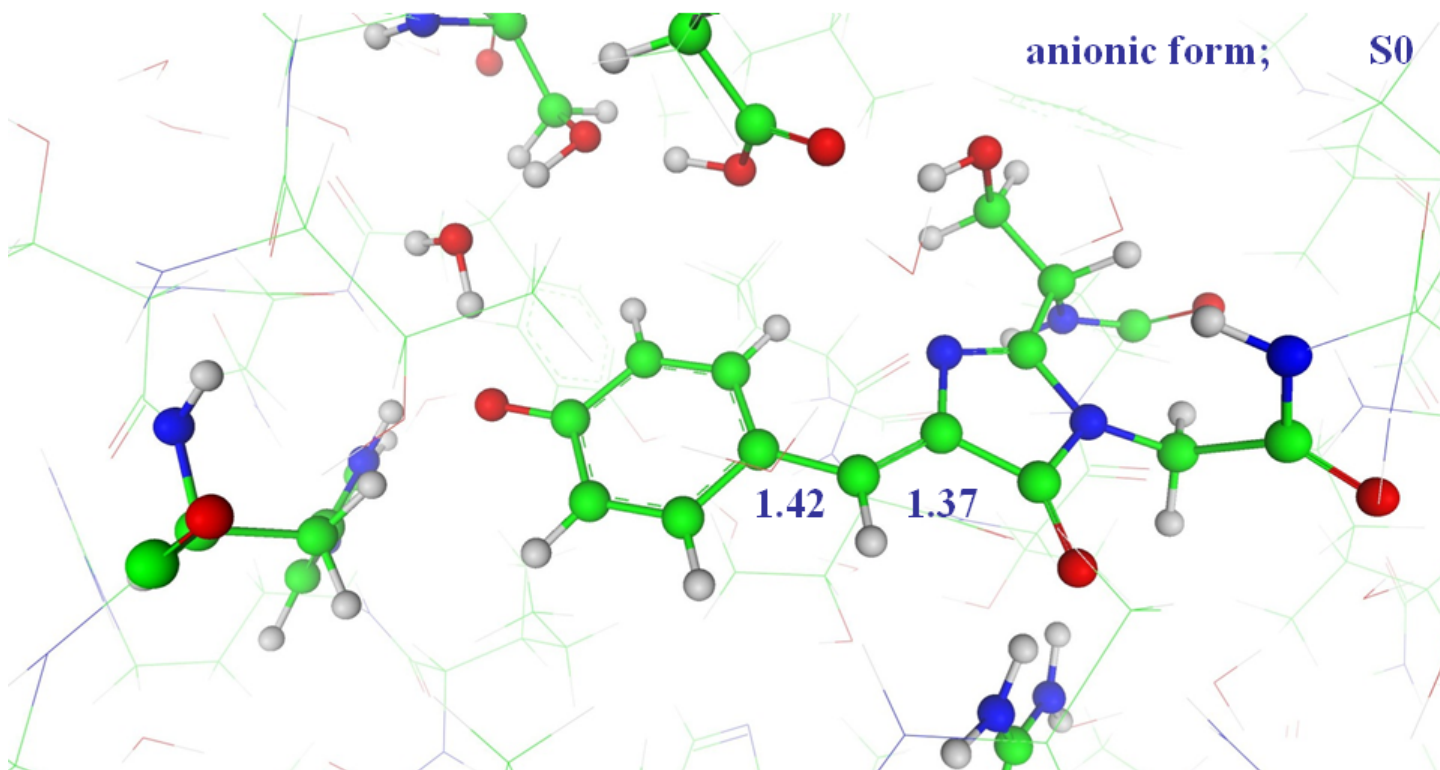
Computer simulation of advanced materials
International Summer School

Atom and molecular structure
Quantum level of matter
*Textbook materials and **illustrations***

Software QM: GAMESS(US), Firefly, NWChem, CP2K
QM/MM: GAMESS(US)-Tinker

Concluding Remarks

- This is a part of the lecture course 'Quantum Mechanics and Molecular Structure' for students of the Chemistry Department of the M.V. Lomonosov Moscow State University

- Part of the tutorial lecture at the workshop "Mathematical and Computational Approaches to Quantum Chemistry (Institute of mathematics and its applications, Minneapolis, 2008)

- Thanks to co-authors of the papers