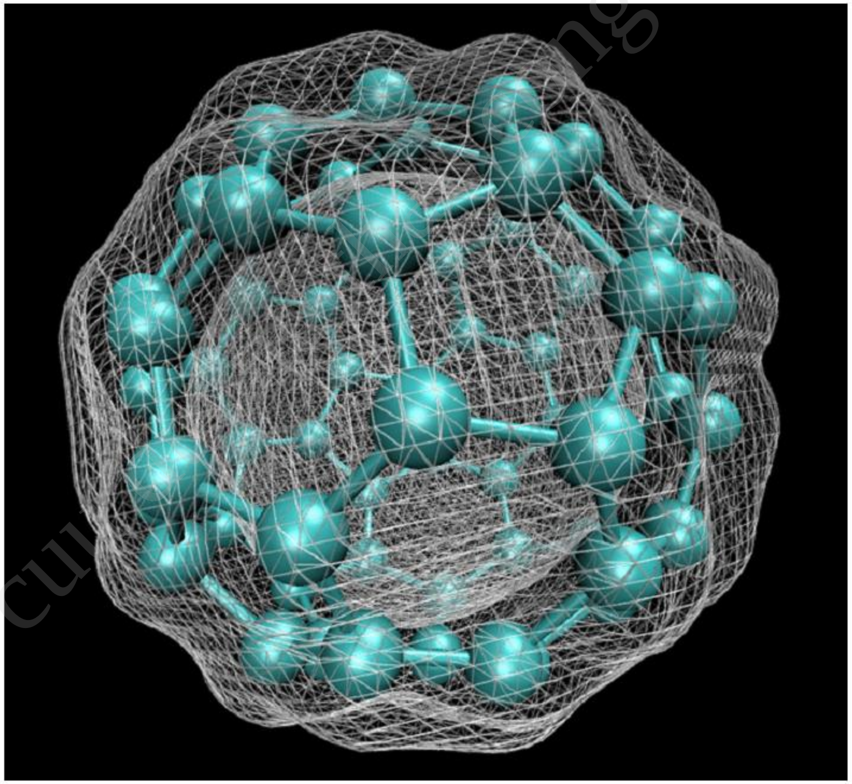
t u nh n

Vũ Hoàng Nam



Chương 1: i u

1.1 Mô nh, p va c tê
1.2 Khả năng của tính toán mô phỏng vật liệu

Chương 2 c nguyên ly cơ n

2.1 Năng ng va c
2.2 Cơ c ng tư
2.2 Phương nh ng c
2.3 Sư ch n
2.4 i n nguyên tư u hydrogen
2.5 Hê đơn nguyên tư

Chương 3 c phương p *ab initio*

3.1 p Hartree-Fock
3.2 c m m va o m a ng
3.3 nh ly Hohenberg-Kohn
3.4 c phương nh Kohn-Sham
3.5 c m m trao i tương quan

Chương 4 Bô cơ sơ va gia thê nguyên tư

4.1 c orbital Slater va Gaussian
4.2 ng ng va hê n n
4.3 Gia thê nguyên tư

Chương 5 ng c c phân tư *ab initio*

5.1 c Hellmann–Feynman
5.2 ng c c phân tư Born-Oppenheimer
5.3 ng c c phân tư Car–Parrinello

Chương 6 Giới thiệu các phần mềm tính toán *ab initio*

6.1 Các phương pháp tính
6.2 Phần mềm Quantum ESPRESSO
6.3 Phần mềm Gaussian

Chương 7 Thực hành trên máy tính

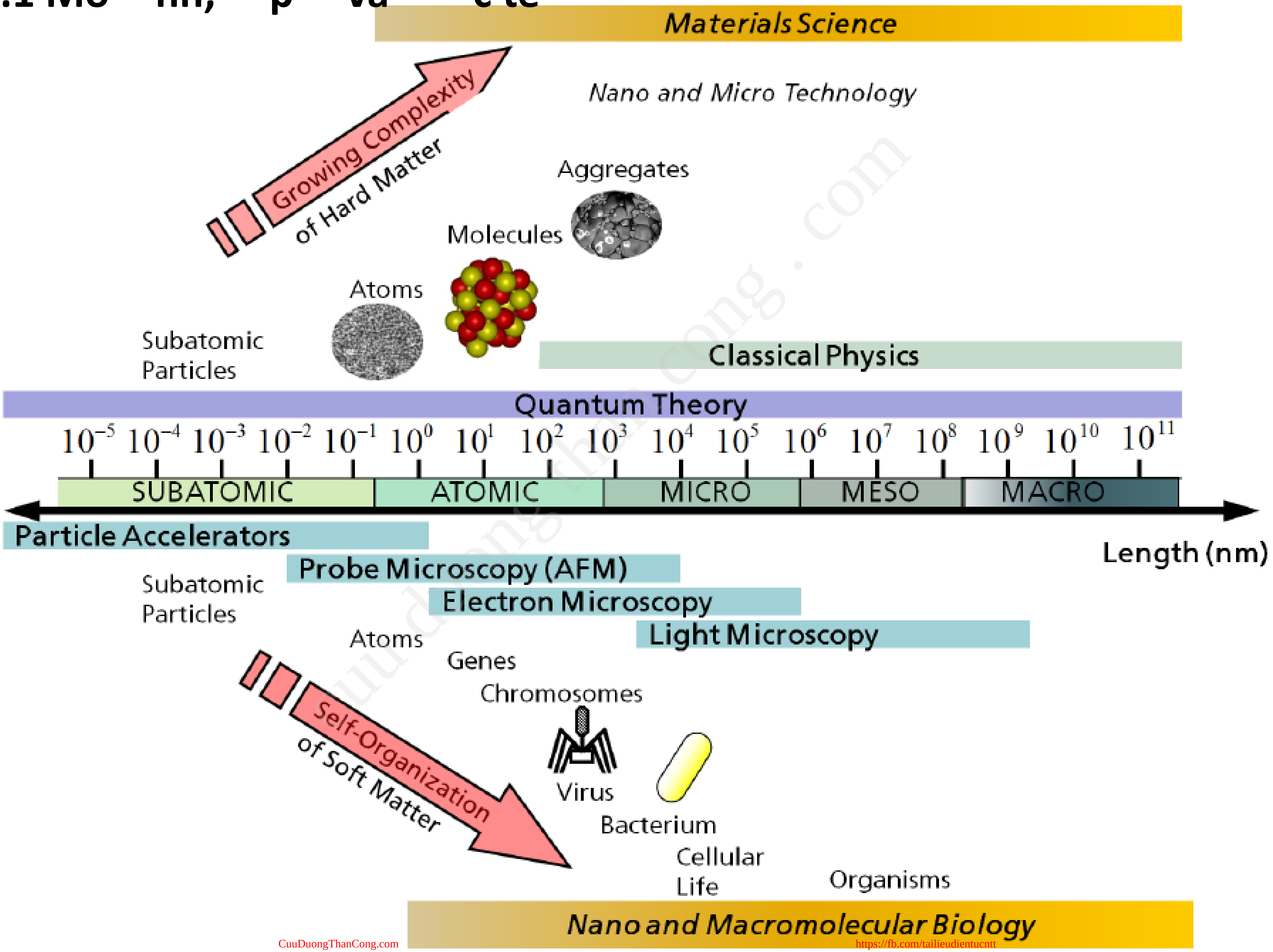
Sinh viên thực hiện mô hình và mô phỏng một số vật liệu cụ thể (ở thể rắn, lỏng hoặc khí).

i u tham o

[1] Valerio Magnasco, *Methods of Molecular Quantum Mechanics An Introduction to Electronic Molecular Structure*, 2009, John Wiley & Sons.
[2] Frank Jensen, *Introduction to Computational Chemistry,* 2007, John Wiley & Sons.
[3] Dominik Marx and Jürg Hutter, *Ab Initio Molecular Dynamics: Basic Theory and Advanced Methods*, 2009, Cambridge University Press.
[4] Jorge Kohanoff, *Electronic Structure Calculations for Solids and Molecules: Theory and Computational Methods*, 2006, Cambridge University Press.
[5] Carlos Fiolhais, Fernando Nogueira, Miguel A.L. Marques (Editor), *A Primer in Density Functional Theory*, 2003, Springer.
[6] David Sholl, Janice A Steckel, *Density Functional Theory: A Practical Introduction*, 2009, Wiley-Interscience.
[7] John M. Wills *et al, Full-Potential Electronic Structure Method: Energy and Force Calculations with Density Functional and Dynamical Mean Field Theory*, 2010, Springer.

Chương 1: i u

1.1 Mô nh, p va c tê



Materials Science

Nano and Micro Technology

Growing Complexity of Hard Matter

Aggregates

Molecules

Atoms

Subatomic Particles

Classical Physics

Quantum Theory

10^{-5} 10^{-4} 10^{-3} 10^{-2} 10^{-1} 10^{0} 10^{1} 10^{2} 10^{3} 10^{4} 10^{5} 10^{6} 10^{7} 10^{8} 10^{9} 10^{10} 10^{11}

SUBATOMIC ATOMIC MICRO MESO MACRO

Length (nm)

Particle Accelerators

Probe Microscopy (AFM)

Electron Microscopy

Light Microscopy

Subatomic Particles

Atoms

Genes

Chromosomes

Self-Organization of Soft Matter

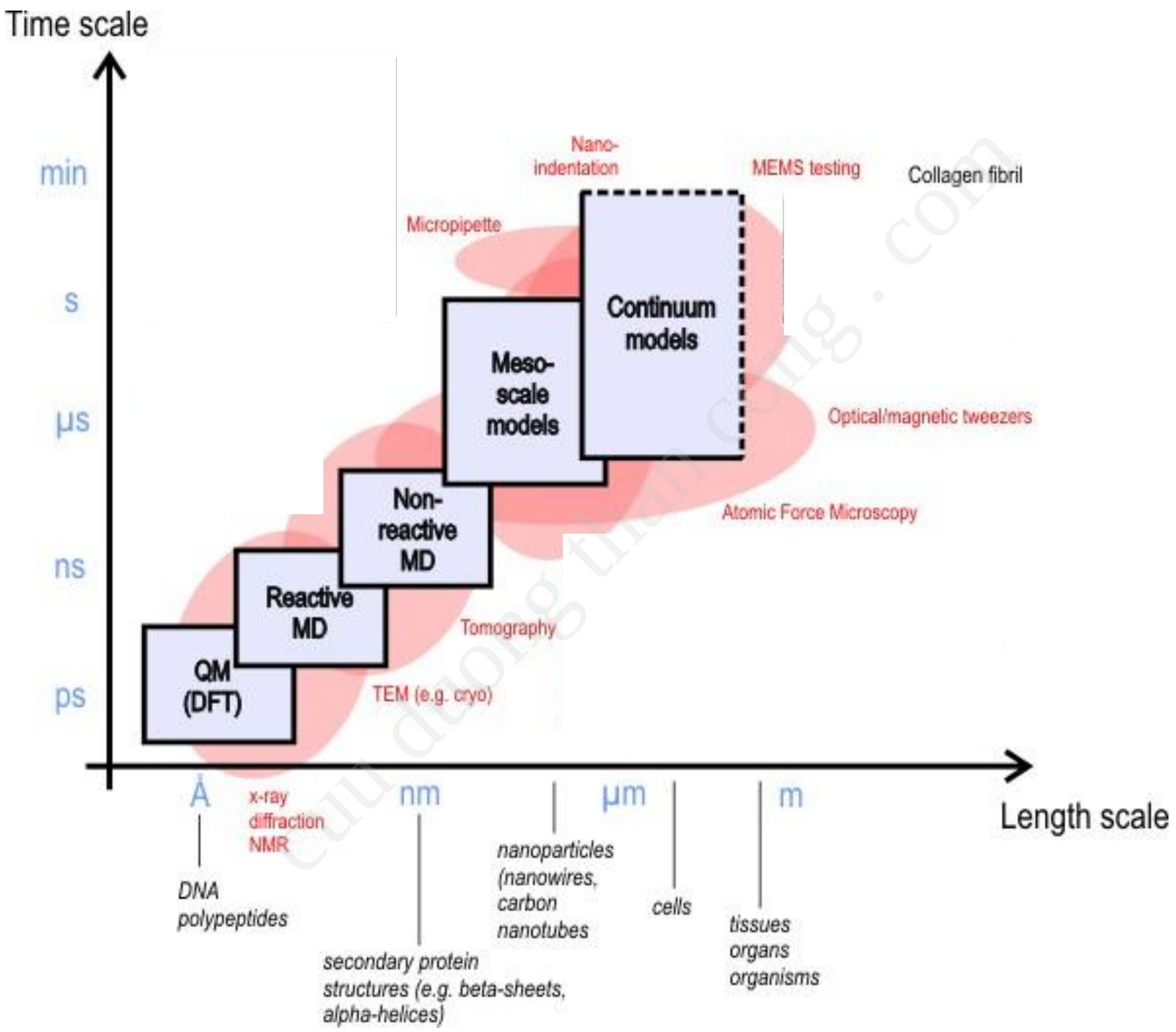
Virus

Bacterium

Cellular Life

Organisms

Nano and Macromolecular Biology


Time scale
min
s
µs
ns
ps
Nano-indentation
MEMS testing
Collagen fibril
Micropipette
Continuum models
Meso-scale models
Optical/magnetic tweezers
Non-reactive MD
Atomic Force Microscopy
Reactive MD
Tomography
QM (DFT)
TEM (e.g. cryo)
Å
x-ray diffraction
NMR
nm
µm
m
Length scale
DNA
polypeptides
secondary protein structures (e.g. beta-sheets, alpha-helices)
nanoparticles (nanowires, carbon nanotubes
cells
tissues
organs
organisms

1.2 Khả năng của tính toán vật liệu

- **Ground-state calculations.**
- **Structural Optimization.**
- **Transition states and minimum energy paths.**
- **Ab-initio molecular dynamics.**
- **Response properties (DFPT).**
- **Spectroscopic properties.**
- **Quantum Transport.**

Chương 2 c nguyên ly cơ n

1. Review of Quantum Mechanics

Schrödinger equation

- Time dependent

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

- Linear partial differential equation ⇒ Superposition principle
- Solution by separation of variables

$$\Psi(\mathbf{r},t) = \varphi(\mathbf{r})\cdot f(t)$$

- Leads to the time-independent Schrödinger equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right]\varphi(\mathbf{r}) = E\,\varphi(\mathbf{r})$$

$$f(t) = \exp\left(-\frac{i\,E\,t}{\hbar}\right)$$

- Eigenvalue equation with solutions: Eigenfunctions $\varphi_n(\mathbf{r})$ and eigenvalues E_n
- Set of eigenvectors form complete orthogonal set
- Solution of time-dependent Schrödinger equation is a superposition of eigenfunctions

$$\Psi(\mathbf{r},t) = \sum_i c_i\,\varphi_i(\mathbf{r})\,\exp\left(-\frac{i\,E_i t}{\hbar}\right)$$

Interpretation of the wave function (Copenhagen interpretation)

- $|\Psi(\mathbf{r},t)|^2\,d^3r$ is the probability of finding an electron in volume d³*r* at *r* rand *t*

$$\mathcal{H}\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

The ultimate goal of most appproaches in solid state physics and quantum chemistry is the solution of the time-independent, non-relativistic Schrödinger equation

$$\hat{H}\Psi_i(\vec{x}_1, \vec{x}_2, ..., \vec{x}_N, \vec{R}_1, \vec{R}_2, ..., \vec{R}_M) = E_i\Psi_i(\vec{x}_1, \vec{x}_2, ..., \vec{x}_N, \vec{R}_1, \vec{R}_2, ..., \vec{R}_M) \tag{1}$$

$\hat{H}$ is the Hamiltonian for a system consisting of M nuclei and N electrons.

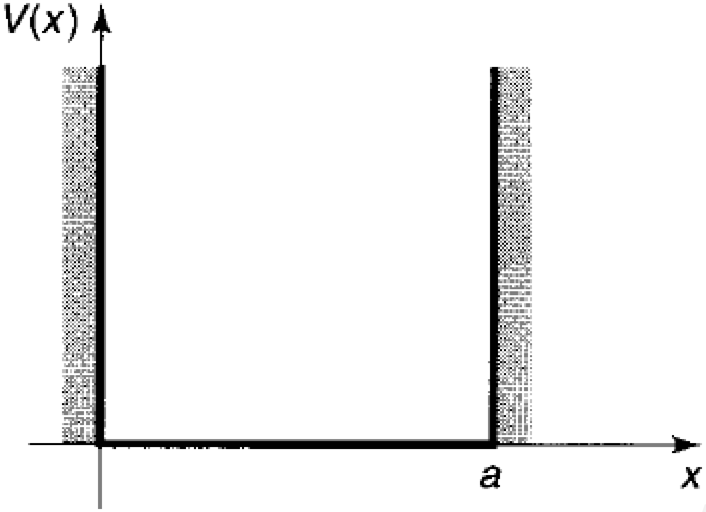
$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \frac{1}{2}\sum_{A=1}^{M}\frac{1}{M_A}\nabla_A^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}} + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{r_{ij}} + \sum_{A=1}^{M}\sum_{B>A}^{M}\frac{Z_A Z_B}{R_{AB}} \tag{2}$$

Here, A and B run over the M nuclei while i and j denote the N electrons in the system.

The first two terms describe the kinetic energy of the electrons and nuclei. The other three terms represent the attractive electrostatic interaction between the nuclei and the electrons and repulsive potential due to the electron-electron and nucleus-nucleus interactions.

Nhắc lại một số bài toán cơ bản

Một vi hạt trong giếng thế sâu vô hạn



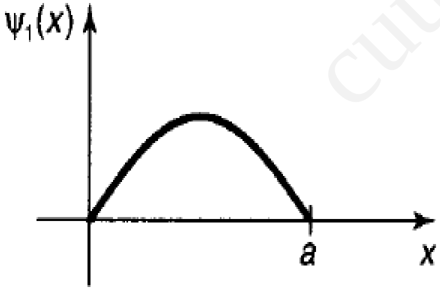
$$V(x) = \begin{cases} 0, & \text{if } 0 \le x \le a, \\ \infty, & \text{otherwise} \end{cases}$$

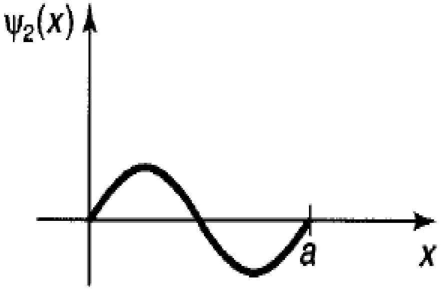
$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi,$$

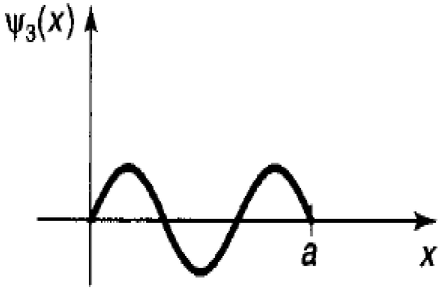
$$\frac{d^2\psi}{dx^2} = -k^2\psi, \quad \text{where } k \equiv \frac{\sqrt{2mE}}{\hbar}.$$

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{n^2\pi^2\hbar^2}{2ma^2}.$$

$$\psi_n(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right).$$







Nguyên tử Hydrogen

Nguyên tử Hydrogen có thế tương tác:

$$V(|\mathbf{r}|) = V(r) = \frac{-Ze^2}{4\pi\epsilon_o r}$$

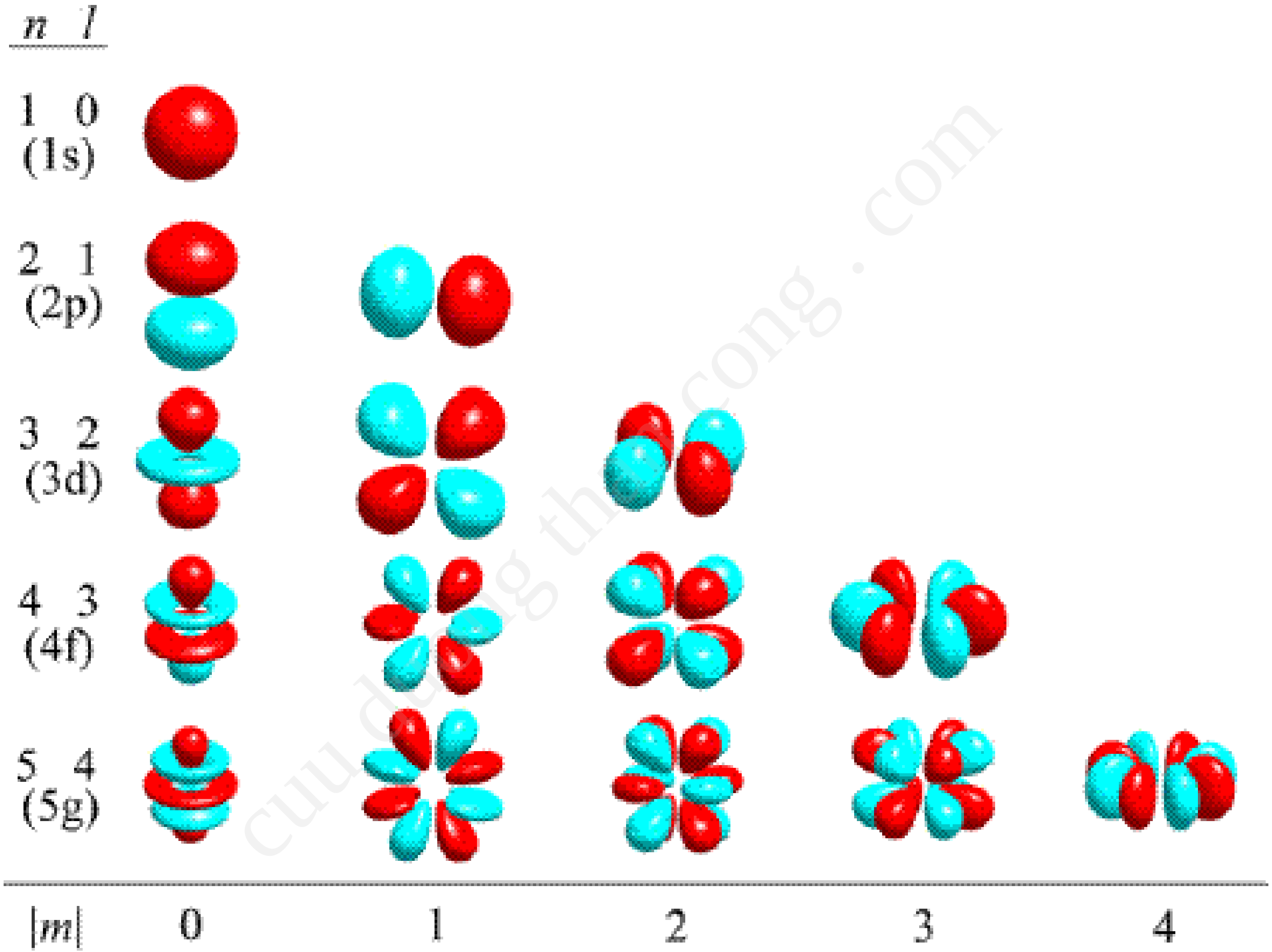
Phương trình Schrödinger cho Hydrogen:

$$\left[-\frac{\hbar^2}{2mr^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{\hbar^2}{2mr^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right) + V(r)\right]\Psi(r,\theta,\phi) = E\Psi(r,\theta,\phi)$$

$$\psi(r,\theta,\phi) = R(r)Y_l^m(\theta,\phi) \qquad \textit{Separation of Variables}$$

$$E_n = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2} = \frac{E_1}{n^2}, \quad n = 1, 2, 3, \ldots .$$

$$\psi_{nlm} = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}}\, e^{-r/na}\left(\frac{2r}{na}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{na}\right)Y_l^m(\theta,\phi).$$


n l
1 0
(1s)
2 1
(2p)
3 2
(3d)
4 3
(4f)
5 4
(5g)
|m|
0
1
2
3
4

Hệ đơn vị nguyên tử

charge, e	$e = 1.602\,176\,462 \times 10^{-19}\ \mathrm{C}$
length, Bohr	$a_0 = 4\pi\varepsilon_0 \dfrac{\hbar^2}{me^2} = 5.291\,772\,087 \times 10^{-11}\ \mathrm{m}$
energy, Hartree	$E_\mathrm{h} = \dfrac{1}{4\pi\varepsilon_0}\dfrac{e^2}{a_0} = 4.359\,743\,802 \times 10^{-18}\ \mathrm{J}$
time	$\tau = \dfrac{\hbar}{E_\mathrm{h}} = 2.418\,884\,331 \times 10^{-17}\ \mathrm{s}$

Hamiltonian in **SI** units : $\hat{H} = -\dfrac{\hbar^2}{2m}\nabla^2 - \dfrac{1}{4\pi\varepsilon_0}\dfrac{Ze^2}{\mathrm{r}}$ The hydrogen-like system

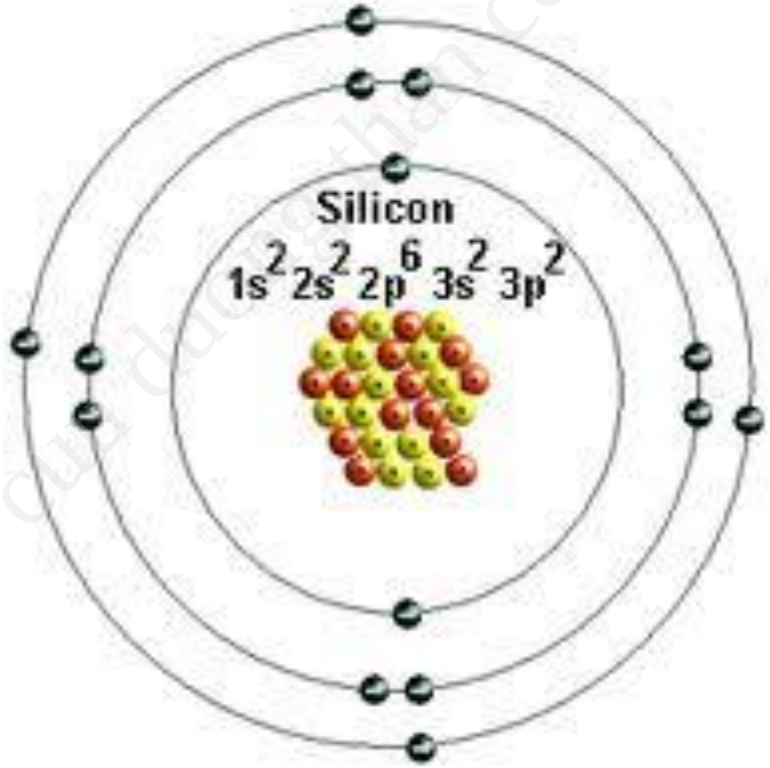
Hamiltonian in ***atomic units (a.u):*** $e = \hbar = m = 4\pi\varepsilon_0 = 1$

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{Z}{r}$$

Many-electron atom

- Many-electron Schrödinger equation

$$\left[-\frac{1}{2}\sum_{i=1}^{n}\nabla_i^2-\sum_{i=1}^{n}\frac{Z}{r_i}+\sum_{i=1}^{n-1}\sum_{j=i+1}^{n}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}\right]\psi(\mathbf{r}_1,\ldots,\mathbf{r}_n)=E\,\psi(\mathbf{r}_1,\ldots,\mathbf{r}_n)$$



Density functional theory (**DFT**) is a computational quantum mechanical modelling method used in physics, chemistry and materials science to investigate the electronic structure (principally the ground state) of many-body systems, in particular atoms, molecules, and the condensed phases