

# Schroedinger Equation

$$H\psi(\mathbf{r}, t) = (T + V) \psi(\mathbf{r}, t) = \left[ -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right] \psi(\mathbf{r}, t) = i\hbar \frac{\partial \psi}{\partial t}(\mathbf{r}, t)$$

$T = \frac{p^2}{2m}$  is the **kinetic energy operator**,  $m$  is the mass of the particle

$\mathbf{p} = -i\hbar\nabla$  is the momentum **operator**,

$V = V(\mathbf{r})$  is the **potential energy operator**,

$V$  is a real function of the position operator  $\mathbf{r}$

$\nabla$  is the gradient operator, and

$\nabla^2$  is the Laplace operator

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

$$\nabla f(x, y, z) = \left( \frac{\partial f}{\partial x}, \frac{\partial f}{\partial y}, \frac{\partial f}{\partial z} \right)$$

$$\Delta = \nabla^2 = \nabla \cdot \nabla.$$

$$\Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}.$$

$$\square = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} - \frac{1}{c^2} \frac{\partial^2}{\partial t^2}.$$

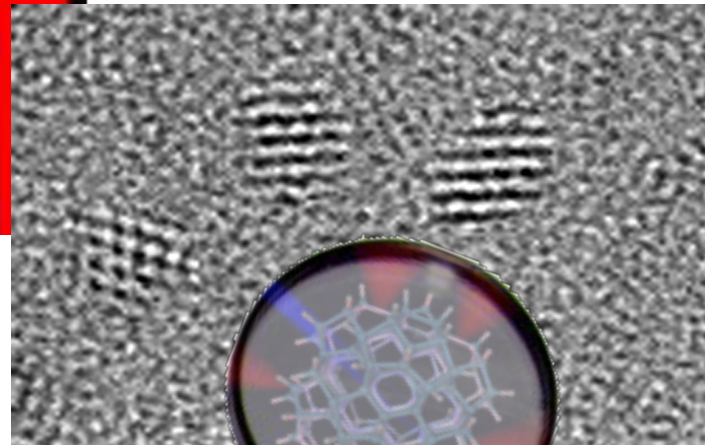
# Basic concepts

---

- Born-Oppenheimer approximation → Schroedinger equation for the electrons in the field of nuclei → SEPARATION OF VARIABLE
- Exact solutions
  - particle in a box
  - hydrogen atoms

# At the microscopic scale

---



Nuclei:  $\{R_I\}_I$   
Electrons:  $\{\psi_i\}_i$

# Born-Oppenheimer Approximation

$$\psi(r, R) = \psi_e(r) \cdot \psi_n(R)$$

$$\text{for } \frac{M_\alpha}{m_e} \gg 1$$

# Electrons and ions in a molecular or condensed system

---

- The non relativistic Hamiltonian of electrons (**e**) and nuclei (**N**) in a molecule or solid is given by:

$$\hat{H} = \hat{T}(\mathbf{R}) + \hat{T}_e(\mathbf{r}) + \hat{V}_{NN}(\mathbf{R}) + \hat{V}_{eN}(\mathbf{r}, \mathbf{R}) + \hat{V}_{ee}(\mathbf{r})$$

$\mathbf{R} = (R_1, R_2, \dots, R_{N_a})$  denotes the set of nuclear (**N**) coordinates

$\mathbf{r} = (r_1, r_2, \dots, r_{N_e})$  denotes the set of electronic (**e**) coordinates

**T** denotes kinetic energy operators and **V** potential energy operators

In the following atomic units are employed:

Length unit: Bohr Radius ( $0.5292 \text{ \AA}$ )

Charge unit: charge of an electron **e**

Mass unit: mass of an electron **m<sub>e</sub>**

# Electrons and ions in a molecular or condensed system

- The non relativistic Hamiltonian of electrons (**e**) and nuclei (**N**) in a molecule or solid is given by:

$$\hat{H} = \hat{T}_N(\mathbf{R}) + \hat{T}_e(\mathbf{r}) + \hat{V}_{NN}(\mathbf{R}) + \hat{V}_{eN}(\mathbf{r}, \mathbf{R}) + \hat{V}_{ee}(\mathbf{r})$$

$\mathbf{R} = (R_1, R_2, \dots, R_{N_a})$  denotes the set of nuclear (**N**) coordinates

$\mathbf{r} = (r_1, r_2, \dots, r_{N_e})$  denotes the set of electronic (**e**) coordinates

**T** denotes kinetic energy operators and **V** potential energy operators

$$\hat{T}_e = \sum_{i=1}^{N_e} \left( -\frac{1}{2} \nabla_i^2 \right)$$

$$\hat{T}_N = \sum_{\alpha=1}^{N_a} \left( -\frac{1}{2M_\alpha} \nabla_\alpha^2 \right)$$

$$\hat{V}_{eN} = - \sum_{\alpha=1}^{N_a} \frac{Z_\alpha}{r_{i\alpha}}$$

$$\hat{V}_{NN} = \sum_{\alpha < \beta}^{N_a} \frac{Z_\alpha Z_\beta}{R_{\alpha\beta}} ; \hat{V}_{ee} = \sum_{i < j}^{N_e} \frac{1}{r_{ij}}$$

# Electrons and ions in a molecular or condensed system

---

- Wavefunctions of electrons and ions in an isolated molecule or solid

$$\hat{H} = \hat{T}_N(R) + \hat{T}_e(r) + \hat{V}_{NN}(R) + \hat{V}_{eN}(r, R) + \hat{V}_{ee}(r)$$

$$\hat{H} \psi(r, R) = E \psi(r, R)$$

In principle, the term:

$$\hat{V}_{eN} = - \sum_{\alpha=1}^N \frac{Z_{\alpha}}{r_{i\alpha}}$$

prevents us from separating the electronic and nuclear coordinates and writing the wavefunction as :

$$\psi(r, R) = \psi_e(r) \cdot \psi_N(R)$$

# The Born-Oppenheimer approximation

---

- The Born-Oppenheimer (BO) approximation consists in assuming that for a broad class of molecular and solid systems, the separation between nuclear and ionic motion is **approximately** correct. The approximation rests on the fact that the **nuclei** (with mass  $M_\alpha$ ) **are much more massive than the electrons** (with mass  $m_e$ ) and thus **in most cases they are nearly fixed with respect to electronic motion**. Hence we can write:

$$\psi(r, R) = \psi_e(r) \cdot \psi_n(R)$$

$$\text{for } \frac{M_\alpha}{m_e} \gg 1$$



# Mathematical details of BO approximation

---

- For a fixed nuclear configuration,  $V_{NN}$  is a constant parameter (it will just shift rigidly the eigenvalues of the total Hamiltonian) and for the purpose of going over the details of the BO approximation, it can be neglected. We write the Hamiltonian of the electrons in the field of nuclei as :

$$\hat{H}_e = \hat{T}_e(r) + \hat{V}_{en}(r) + \hat{V}_{ee}(r) \quad \text{with:}$$

$$\hat{H}_e \psi_e(r, R) = E_e \psi_e(r, R)$$

- We now assume it is approximately correct to write

$$\psi(r, R) \approx \psi_e(r) \cdot \psi_n(R)$$

and we insert this “trial” function in the Schroedinger equation for the coupled nuclei-electron system.

# Mathematical details of the BO approximation

---

- When taking into account that:

$$\hat{T}_e \psi_e \cdot \psi_N = \psi_N \hat{T}_e \psi_e$$

↑ no R dependence

$$\nabla_a^2 \psi_e \psi_N = \psi_e \nabla_a^2 \psi_N + 2 \nabla_a \psi_e \nabla_a \psi_N + \psi_N \nabla_a^2 \psi_e$$

and by definition  $\hat{H}_e \psi_e = E_e \psi_e$

the Schroedinger eq. of the coupled nuclei-electron systems becomes:

$$\begin{aligned} & \psi_e \hat{T}_N \psi_N + \psi_N \cdot \psi_e (E_e + V_{nn}) - \\ & - \frac{1}{2} \left\{ \sum_a \frac{1}{2M_a} (2 \nabla_a \psi_e \nabla_a \psi_N + \psi_N \nabla_a^2 \psi_e) \right\} = \\ & = E_{\text{TOT}} \psi_e \cdot \psi_N \end{aligned}$$

# Mathematical details of the BO approximation

- What is the magnitude of

$$-\frac{1}{2} \left\{ \sum_{\alpha} \frac{1}{2M_{\alpha}} (2 \nabla_{\alpha} \psi_e \nabla_{\alpha} \psi_N + \psi_N \nabla_{\alpha}^2 \psi_e) \right\} ?$$

$$\frac{1}{2M_{\alpha}} \nabla^2 \psi_e \approx \frac{p_e^2}{2M_{\alpha}} \approx \left( \frac{m}{M_{\alpha}} \right) E_e \quad \text{with} \quad \left( \frac{m}{M_{\alpha}} \right) \ll 1$$

$$\nabla_{\alpha} \psi_e \quad \text{same order of: } \nabla_i \psi_e = \psi_e \cdot \hat{p}_e \quad \text{electron momentum}$$

- Since the **ratio between the electronic and ionic masses is in most cases of the order of  $10^{-4}/10^{-5}$** , the terms between curly brackets give negligible contributions to the total energy of the coupled nuclei-electron system and they can be discarded. However there are systems for which the off diagonal non adiabatic terms cannot be neglected (see part on **electron-phonon interaction**).


# “Separating” nuclei and electrons

---

- Neglecting the terms within curly brackets yields:

$$\psi_e \hat{T}_N \psi_N + \psi_N E_e \psi_e + \psi_N \hat{V}_{NN} \psi_e = E_{\text{TOT}} \psi_e \psi_N$$

with  $\left\{ \hat{T}_N + \textcircled{E_e} + \hat{V}_{NN} \right\} \psi_N = E_{\text{TOT}} \psi_N$



The nuclei move in a potential set up by the electrons.

In summary : The large difference between electron and nuclei masses allows us to approximate the total wavefunction as a product of nuclear and electronic wavefunctions. The electronic wave function is obtained by solving the electronic Schrodinger equation for a given set of nuclear coordinates:

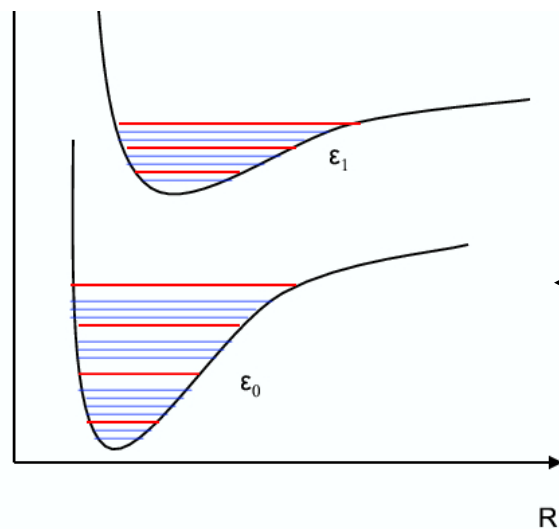
$$\hat{H}_e \psi_e(r, R) = \textcircled{E_e} \psi_e(r, R)$$

and the electronic energy  $E_e$  contributes a potential term to the motion of the nuclei.

# Energy scale separation

Experimentally one finds that molecular energies fall into distinct scales for many systems; for example, using  $\text{cm}^{-1}$ , where  $1\text{eV} = 8066\text{ cm}^{-1}$

	Typical Energies ( $\text{cm}^{-1}$ )	Typical Periods (fs)
Electronic	20,000-80,000	0.5-2
Vibrational	100-4000	10-300
Rotational	0.1-30	1000-300,000



← “well” separated adiabatic potential energy surfaces

# The time independent Schroedinger equation for electrons in the field of nuclei

- We restrict our attention to:

$$\hat{H}_e \psi_e(r, R) = \hat{E}_e \psi_e(r, R)$$

and from now on we drop the suffix  $e$  and treat  $R$  as a parameter  
(drop wavefunction dependence on  $R$ )

$$\hat{H} \psi_0(r) = E_0 \psi_0(r)$$

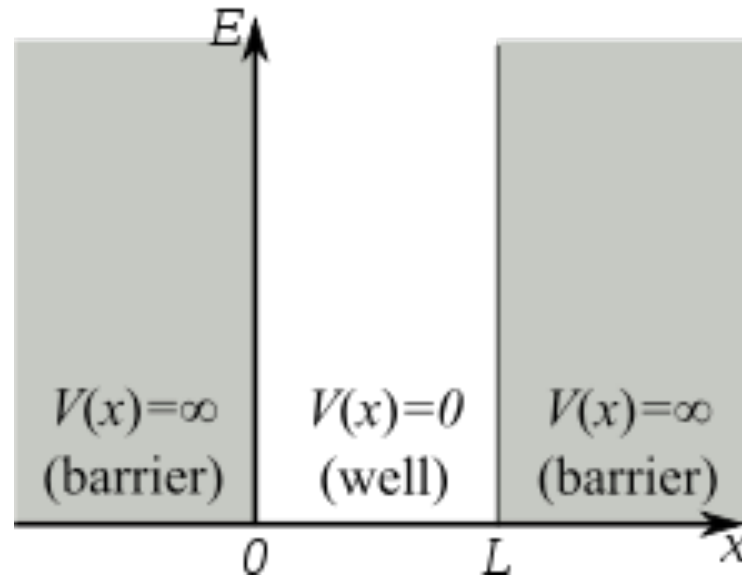
ground state (lowest energy)

$$|\psi(\bar{r}_1, \bar{r}_2, \dots, \bar{r}_{N_e}; s_1, \dots, s_{N_e})|^2 d\mathbf{r}^{N_e} \leftarrow \text{PROBABILITY}$$

$$\int \psi_k^* \psi_l d\mathbf{x}^{N_e} = \langle \psi_k | \psi_l \rangle = \delta_{kl}$$

ORTHONORMAL set of eigenstates of energy  $E_n$

# Exact solutions: particle in a box



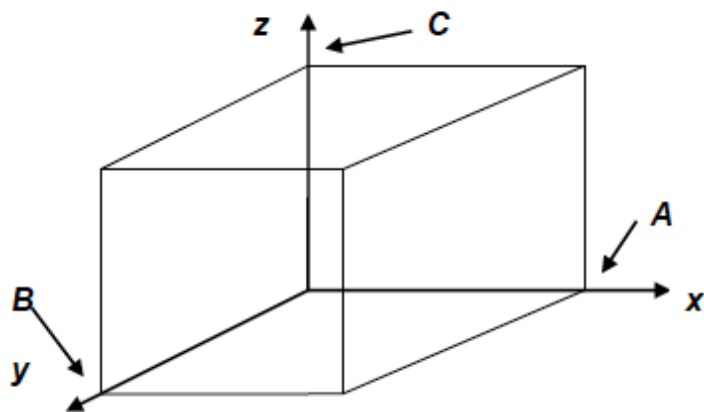
## Schroedinger equation for a free particle in a 3D box

---

Particle (molecule) with mass  $m$  in a 3 dimensional volume of lengths  $A$ ,  $B$  and  $C$  in the  $x$ ,  $y$ ,  $z$  directions.

$$V(x, y, z) = \infty \quad \text{if} \quad \begin{aligned} &x < 0 \text{ or } x > A, \quad y < 0 \text{ or } y > B \\ &z < 0 \text{ or } z > C \end{aligned}$$

$$V(x, y, z) = 0 \quad \text{if} \quad \begin{aligned} &0 \leq x \leq A \text{ or } 0 \leq y \leq B \\ &0 \leq z \leq C \end{aligned}$$





# Schroedinger equation for a free particle in a 3D box

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

Boundary conditions

$$\begin{aligned} 0 &\leq x \leq a \\ 0 &\leq y \leq b \\ 0 &\leq z \leq c \end{aligned}$$

Integers

$$\psi_{n_x, n_y, n_z}(x, y, z)$$
$$= A_x A_y A_z \sin \frac{n_x \pi x}{a} \sin \frac{n_y \pi y}{b} \sin \frac{n_z \pi z}{c}$$

Normalization Constants

How did we  
“guess” this  
type of  
solution? (\*)

$$\int_0^a dx \int_0^b dy \int_0^c dz \psi^*(x, y, z) \psi(x, y, z) = 1$$

(\*)

See appendix 2 of lecture 2 for details on wave equation

## Schroedinger equation for a free particle in a 3D box

---

$$\int_0^a dx \int_0^b dy \int_0^c dz \psi^*(x, y, z) \psi(x, y, z) = 1$$

By substituting the expression of the wavefunction in the normalization integral, we find:

$$\begin{aligned} &\psi_{n_x, n_y, n_z}(x, y, z) \\ &= \left(\frac{8}{abc}\right)^{1/2} \sin \frac{n_x \pi x}{a} \sin \frac{n_y \pi y}{b} \sin \frac{n_z \pi z}{c} \end{aligned}$$

By substituting this result for the wavefunction in the Schroedinger equation, we find an expression for the Energies

$$E_{n_x, n_y, n_z} = \frac{\hbar^2}{8m} \left( \frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right)$$

Non degenerate states only when all the three quantum numbers equal to 1

## Degeneracy → States with equal energy

(1,1,1) 1

(2,1,1) 3

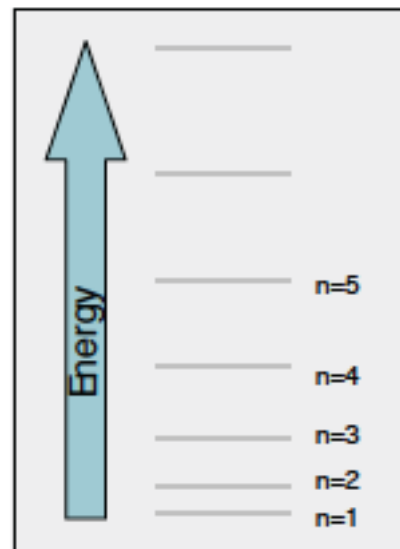
(2,2,1) 3

(3,1,1) 3

(2,2,2) 1

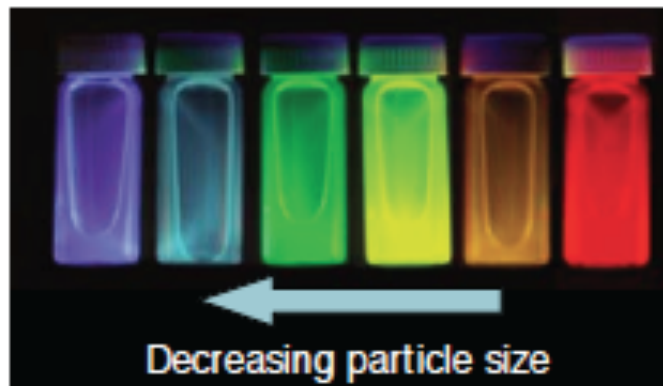
(1,3,2) (1,2,3) (2,1,3) 6

$$E_{n_x, n_y, n_z} = \frac{\hbar^2}{8m} \left( \frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right)$$



# Quantum dot: particle in a 3D box

---



CdSe quantum dots  
dispersed in hexane  
(Bawendi group, MIT)

Color from photon  
absorption

Determined by energy  
level spacing

- Energy level spacing increases  
as particle size decreases.

# Exact solutions: hydrogen atom

## Viewpoint

### A New Look at the Hydrogen Wave Function

Christopher T. L. Smeenk

Joint Attosecond Science Laboratory, University of Ottawa and National Research Council of Canada, Ontario K1A 0R6, Canada

Published May 20, 2013

*A newly-developed “quantum microscope” uses photoionization and an electrostatic magnifying lens to directly observe the electron orbitals of an excited hydrogen atom.*

Subject Areas: **Atomic and Molecular Physics, Quantum Physics**

#### A Viewpoint on:

#### Hydrogen Atoms under Magnification: Direct Observation of the Nodal Structure of Stark States

A. S. Stodolna, A. Rouzée, F. Lépine, S. Cohen, F. Robichaux, A. Gijsbertsen, J. H. Jungmann, C. Bordas, and M. J. J. Vrakking

*Phys. Rev. Lett.* **110**, 213001 (2013) – Published May 20, 2013

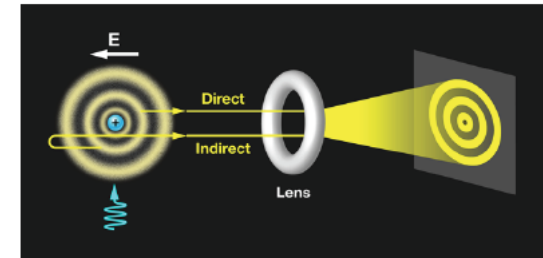


FIG. 1: A photoionization microscope provides direct observation of the electron orbital of a hydrogen atom. The atom is placed in an electric field  $E$  and excited by laser pulses (shown in blue). The ionized electron can escape from the atom along direct and indirect trajectories with respect to the detector (shown on the far right). The phase difference between these trajectories leads to an interference pattern, which is magnified by an electrostatic lens. (APS/Alan Stonebraker)