

Vietnam Academy of Science and Technology
Ho Chi Minh City Institute of Physics

QuantumLab-HCMIP

Electronic structure theory for molecules and materials

Lecture 01: Introduction

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Notes

- **Time:** 14h00 – 16h45 (break: 15 mns)
 - Learning: ~60%
 - Practice: ~20%
 - Discussion: ~20%
- **Grade**
 - Homework: ~20%
 - Midterm exam: ~30%
 - Final exam: ~50%

Lecture 01: Introduction

1. Why and what?

- Why we need electronic structure?
- What electronic structure is?

2. Basic concepts

- Born-Oppenheimer (BO) approximation
- Variational principle

1. Why and what?

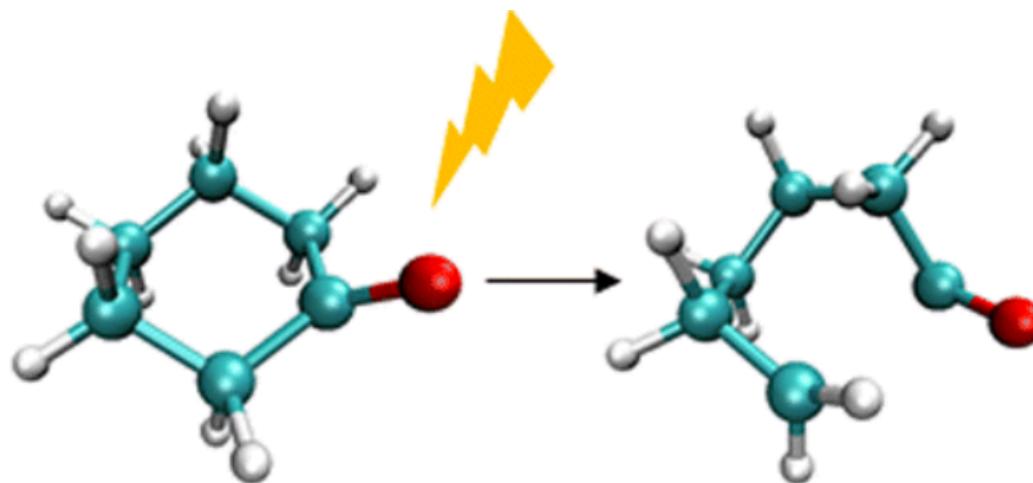
- Why we need it?

Photochemical reaction:

Solar energy conversion

Photocatalysis

Bio-medication



1. Why and what?

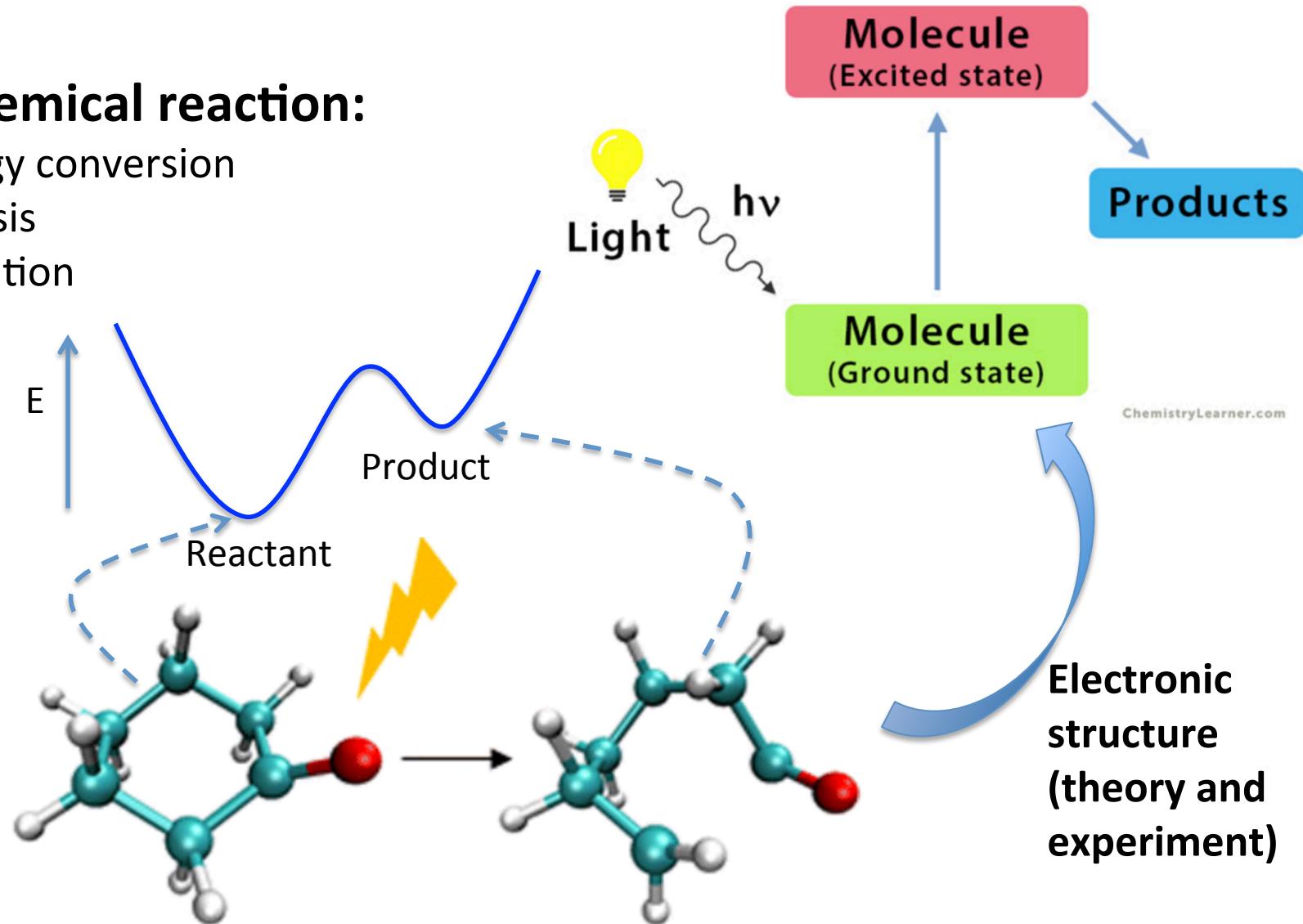
- Why we need it?

Photochemical reaction:

Solar energy conversion

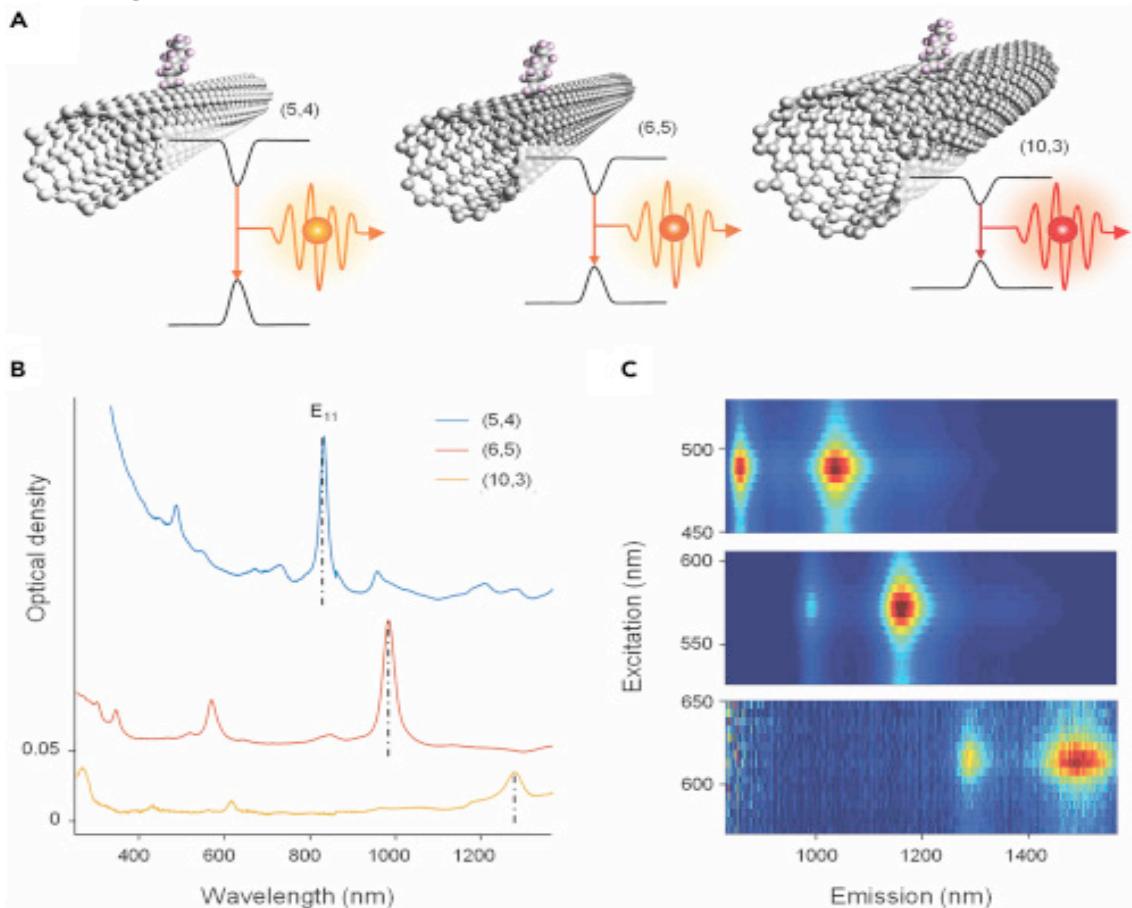
Photocatalysis

Bio-medication



1. Why and what?

- Why we need it?

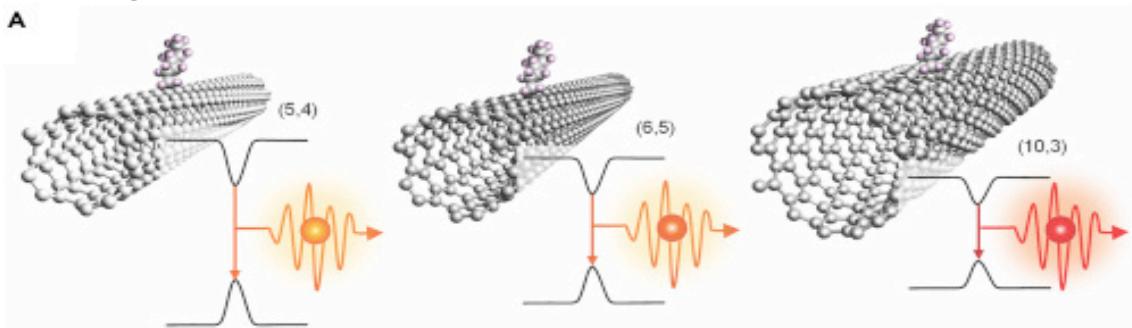


Single photon emission:

- Bioimaging
- Quantum computing
- Photonic devices
- Energy conversion

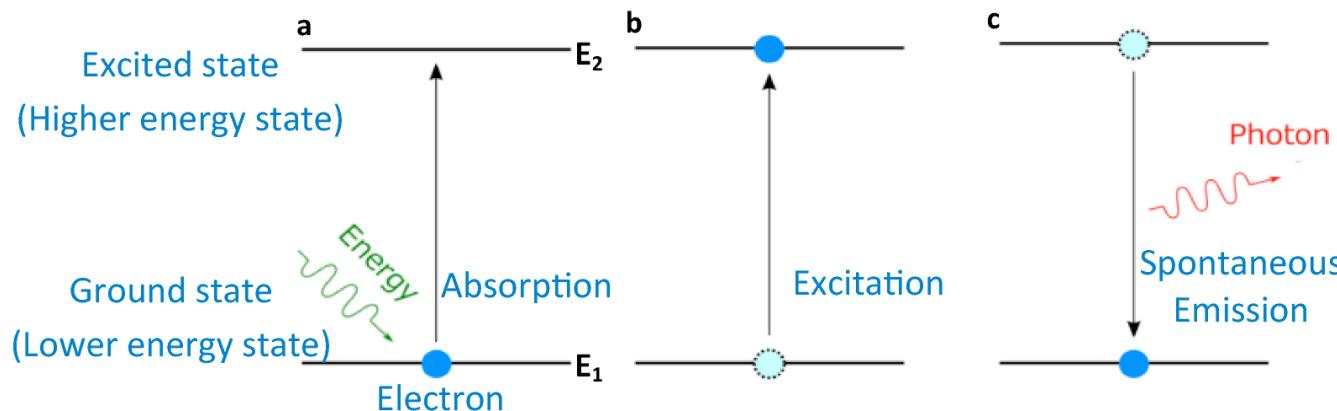
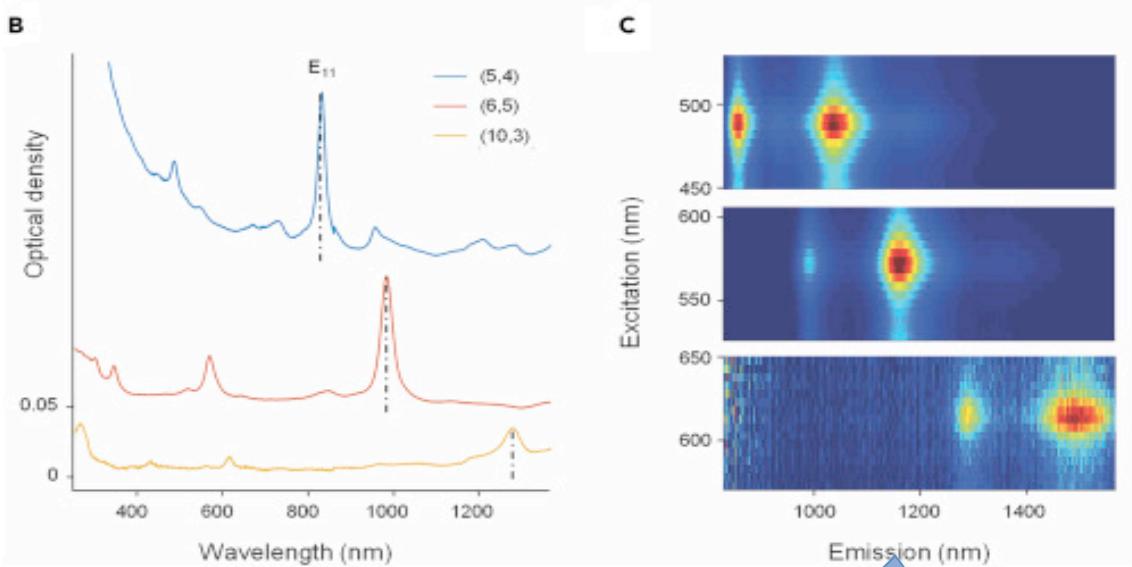
1. Why and what?

- Why we need it?



Single photon emission:

- Bioimaging
- Quantum computing
- Photonic devices
- Energy conversion



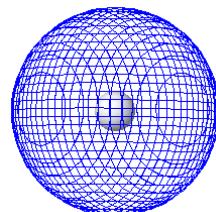
**Electronic
structure
(theory and
experiment)**

1. Why and what?

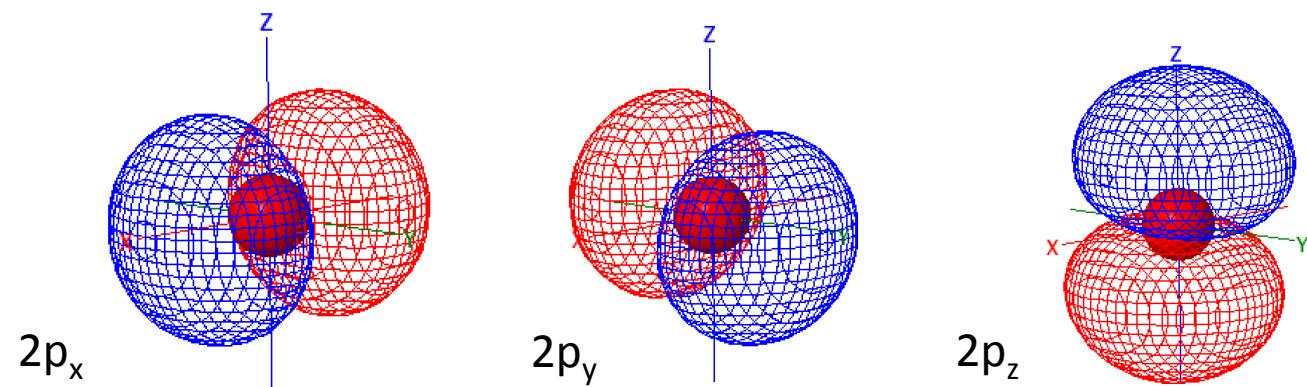
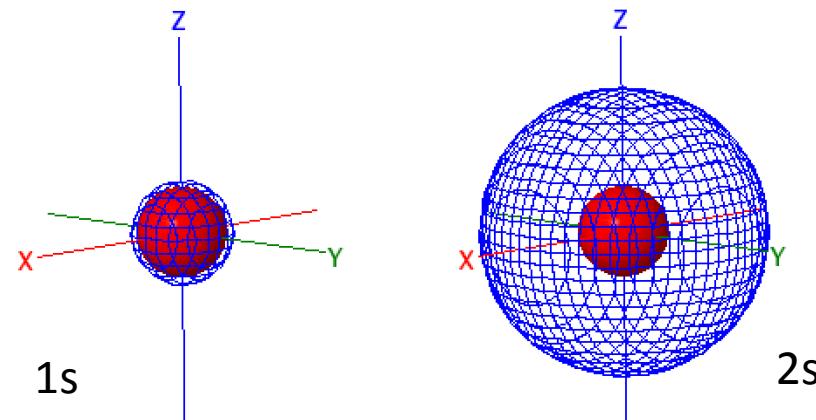
Electronic structure is the state of motion of electrons in an electrostatic field created by stationary nuclei. The term encompass both the wavefunctions of the electrons and the energies associated with them.

Electron configuration in atoms

H: $1s^1$

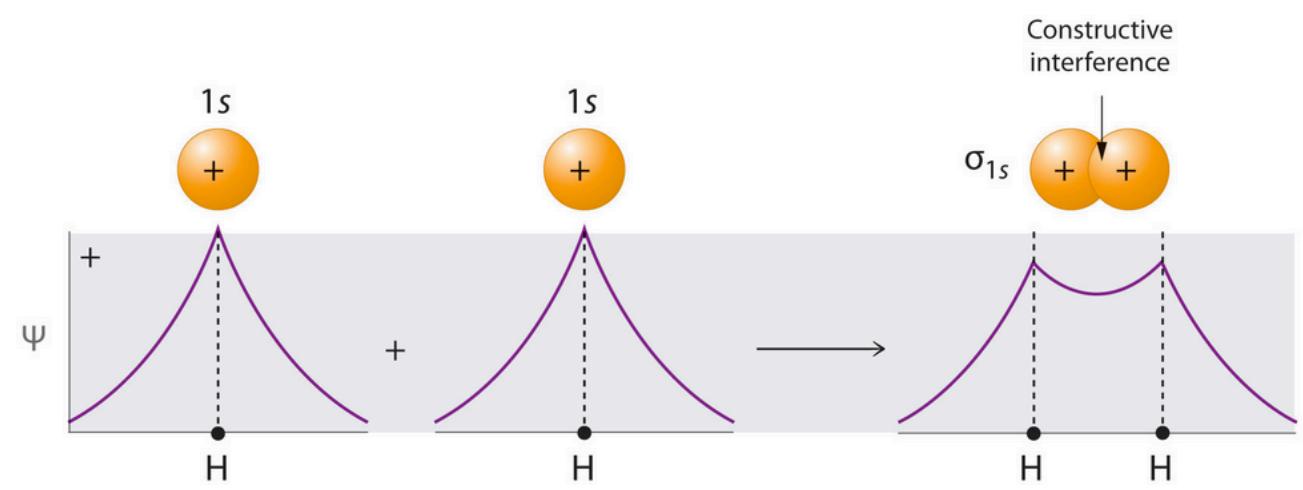
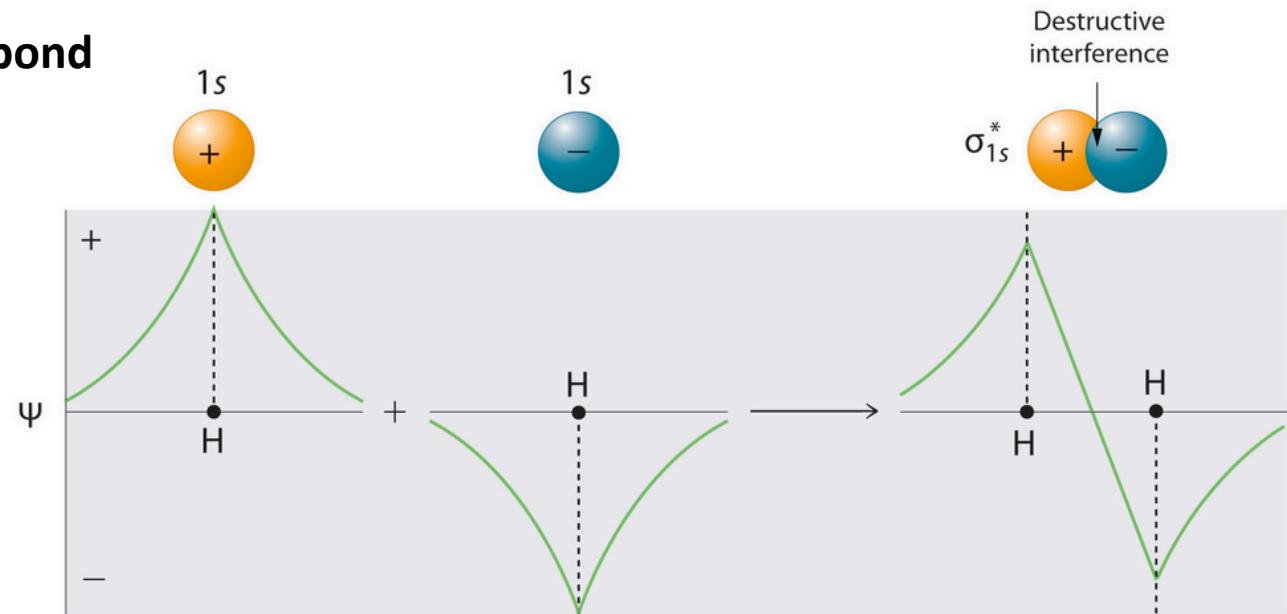
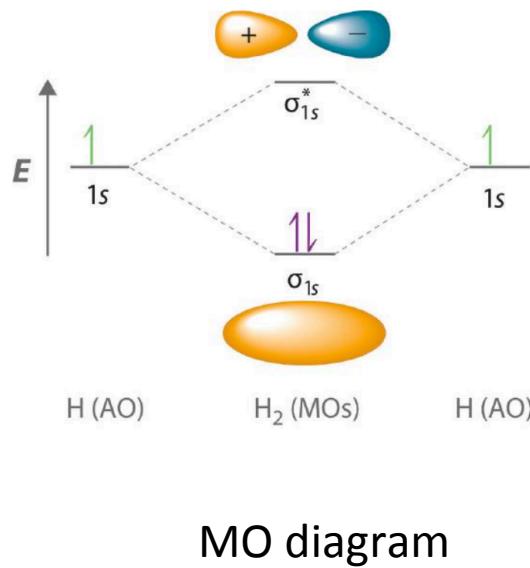


O: $1s^2 2s^2 2p^4$



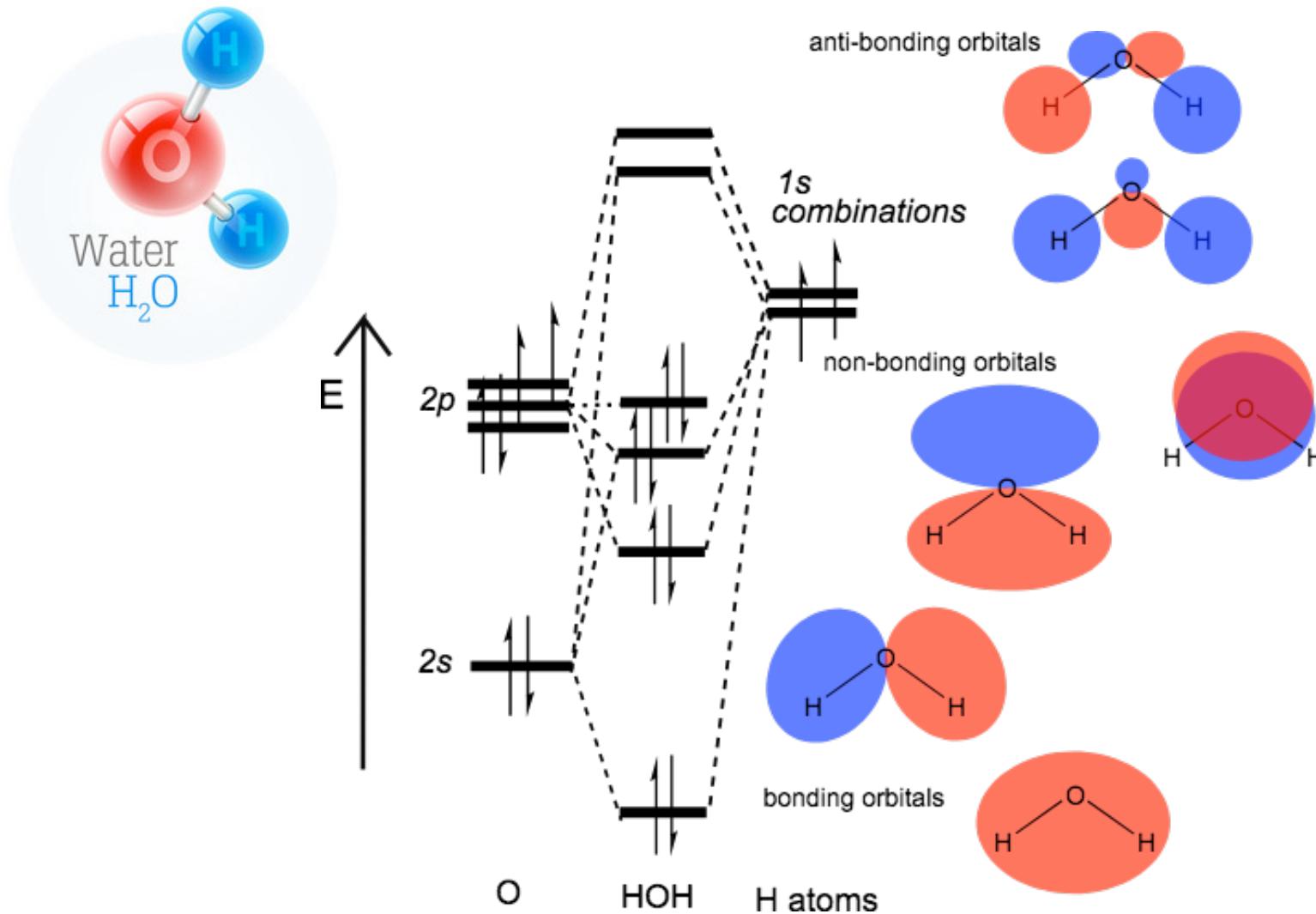
1. Why and what

Molecules? covalent bond



1. Why and what

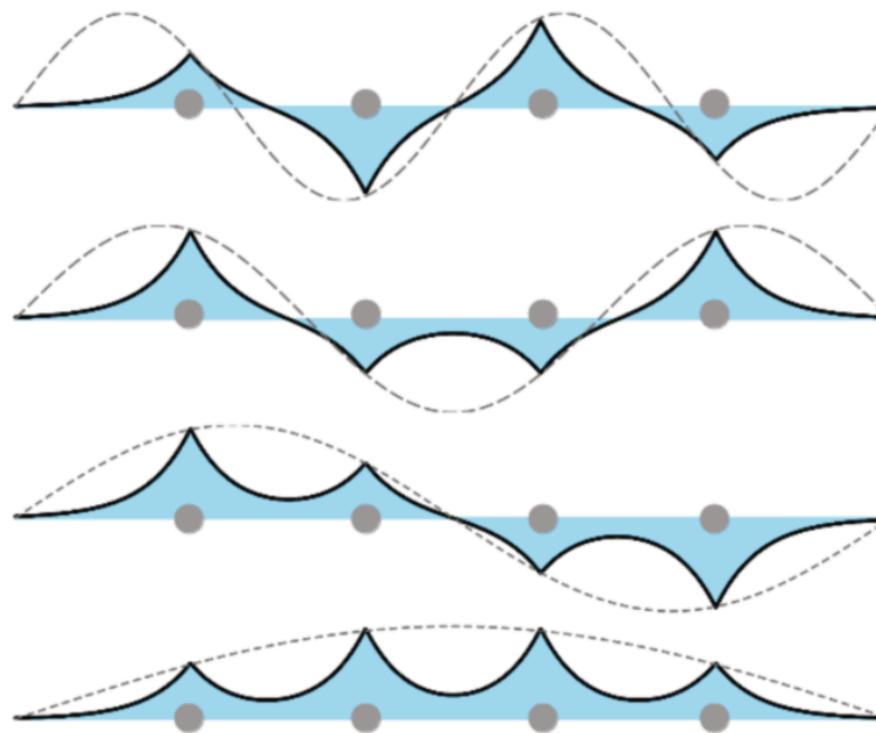
Molecules? covalent bond



1. Why and what

Crystalline solids?

A simple case: 4-atom chain



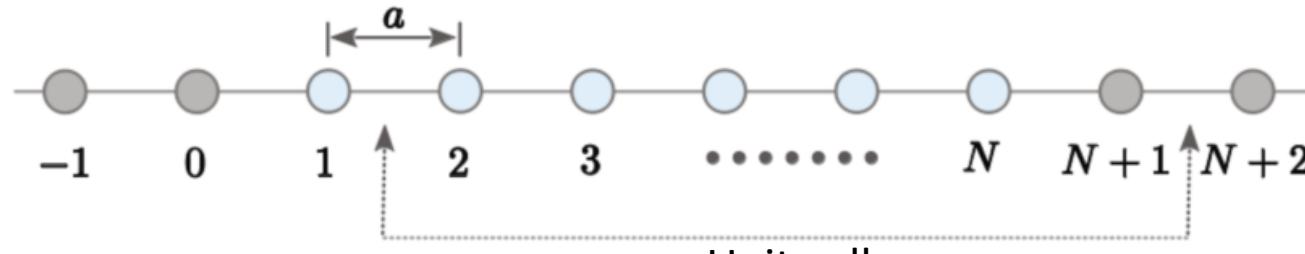
Infinite crystal => **infinite orbitals**



1. Why and what

Crystalline solids?

Infinite 1D



Periodic boundary condition:

$$\psi(\mathbf{r}) = \psi(\mathbf{r} + Na\hat{\mathbf{x}}) .$$

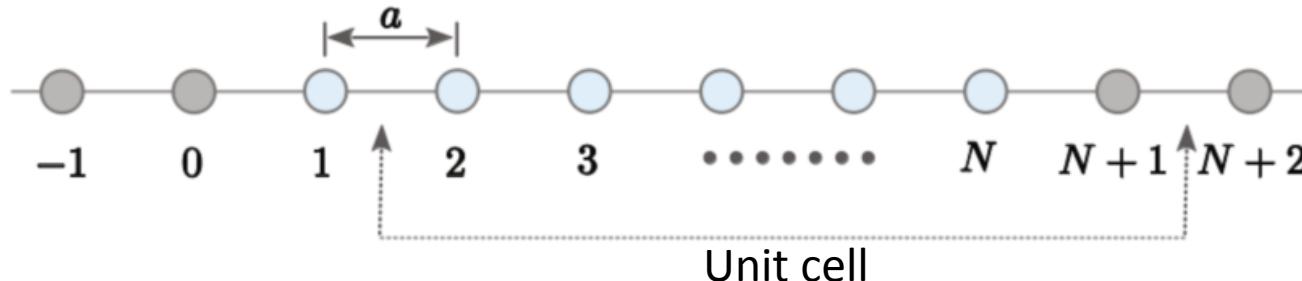
Bloch theorem:

$$\psi(\mathbf{r} + Na\hat{\mathbf{x}}) = e^{i\mathbf{k}\cdot(Na\hat{\mathbf{x}})} \psi(\mathbf{r})$$

$$k = \frac{2\pi}{Na} v, \text{ with } v = 0, 1, \dots, N-1 .$$

1. Why and what

Crystalline solids? **Infinite 1D**



$$\psi(\mathbf{r}) = \sum_{n=1} \sum_{\alpha} \phi_{n,\alpha} \varphi_{\alpha}(\mathbf{r} - \mathbf{R}_n).$$

Atomic basis function, set $\alpha = 1$

$$H\psi(\mathbf{r}) = E\psi(\mathbf{r}) \quad \xrightarrow{\text{Matrix form}} \quad \sum_m H_{n,m} \phi_m = E \phi_n$$

Bloch theorem

$$\phi_n = \phi_0 e^{ikna},$$

(1 atom in unit cell)

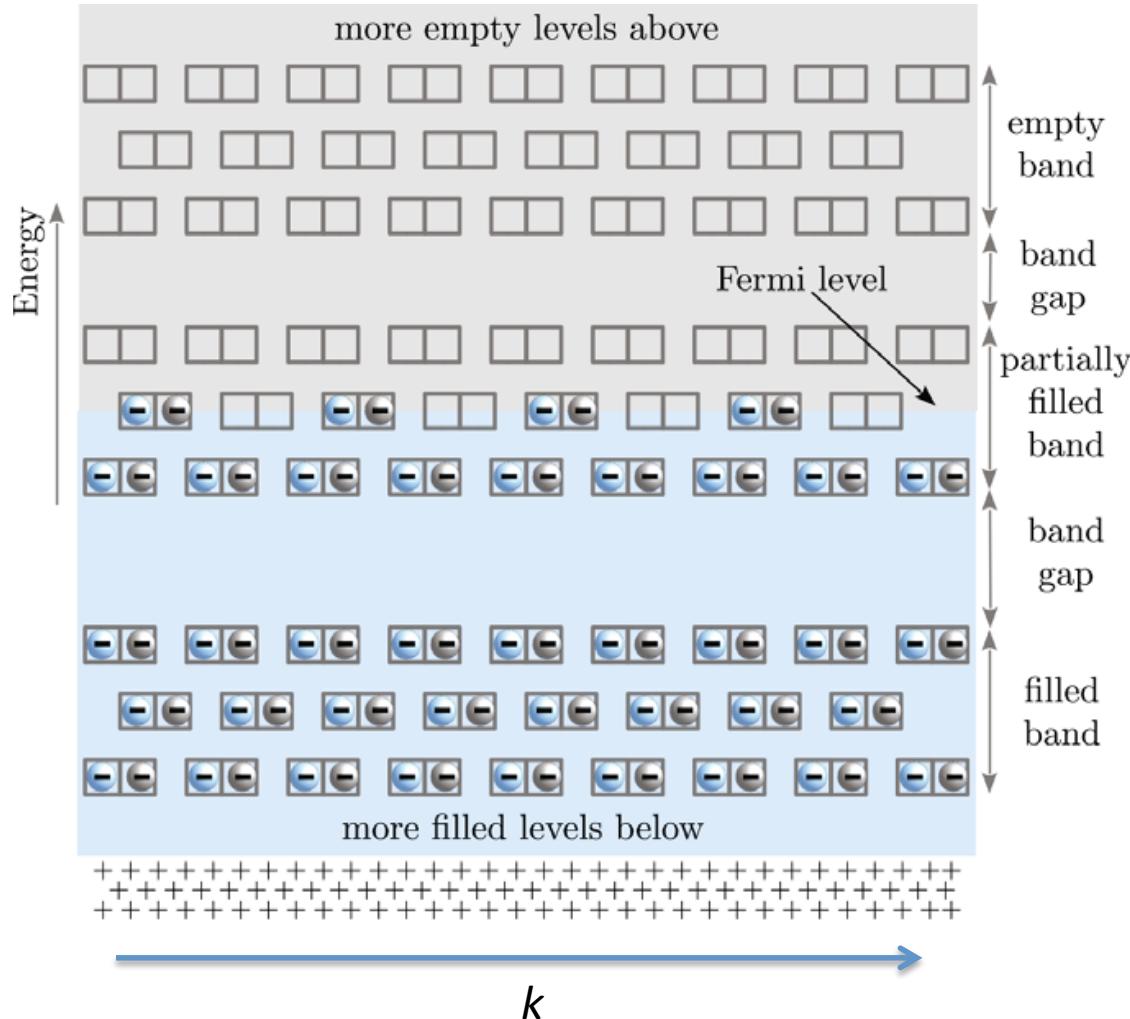
$$\sum_m H_{n,m} \phi_0 e^{ikma} = E \phi_0 e^{ikna},$$

$$E(k) = \sum_m H_{n,m} e^{ik(m-n)a}.$$

1. Why and what

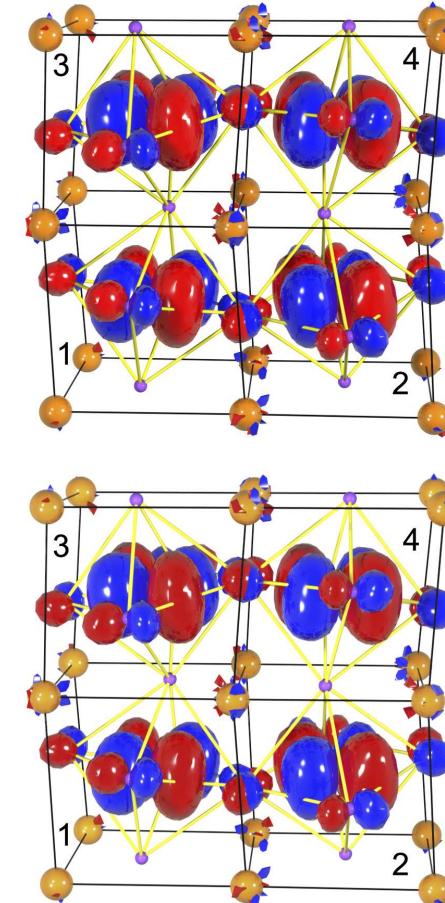
Crystalline solids? **Infinite 3D**

band structure

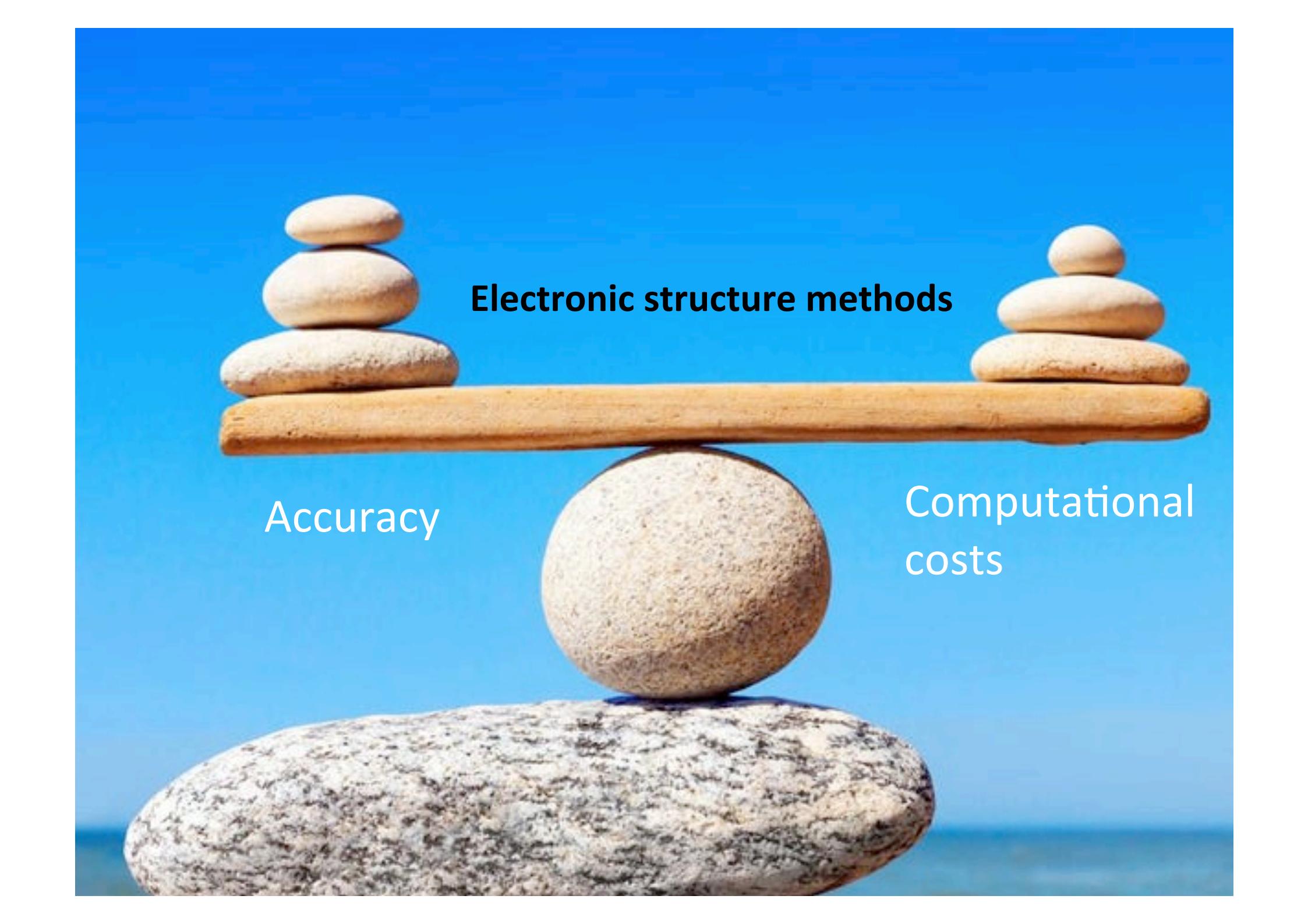


$$\psi(\mathbf{r} + N\hat{\mathbf{a}}) = e^{i\mathbf{k}\cdot(N\hat{\mathbf{a}})} \psi(\mathbf{r})$$

Wannier (localized) orbitals



boxed term



Electronic structure methods

Accuracy

Computational
costs

2. Basic concepts

- Born-Oppenheimer (BO) approximation
- Variational principle

2. Basic concepts

2.1. Born-Oppenheimer approximation

Total Hamiltonians including electronic and nuclear contributions can be written as

$$H = H_e + H_n$$

where

$$H_e = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{I,i} \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2} \sum_{\substack{I,J \\ I \neq J}} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|},$$



 Electron kinetic (electron motion) Electron-electron interaction Electron-nucleus interaction Nucleus-nucleus interaction

$$H_n = - \sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 \xrightarrow{\hspace{2cm}} \text{Nucleus kinetic (Nucleus motion)}$$

2. Basic concepts

2.1. Born-Oppenheimer approximation

Total Hamiltonians

$$H = H_e + H_n$$

Schrodinger equation (SE):

$$H\Psi(\bar{\mathbf{r}}, \mathbf{R}) = E\Psi(\bar{\mathbf{r}}, \mathbf{R}) ,$$

depending on both electrons
and nuclei!

Difficult to solve SE for
electron-nuclear Hamiltonian!

2. Basic concepts

2.1. Born-Oppenheimer approximation

Total Hamiltonians

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Difficult to solve SE for
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Nuclear mass greatly exceed electron
mass => the latter is moving much faster
than the former!

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Factorize the wave-function into
electronic and ionic parts:

$$\Psi(\bar{\mathbf{r}}, \mathbf{R}) = \Phi_n(\bar{\mathbf{r}}, \mathbf{R})\chi_p(\mathbf{R}) ,$$

First, solve for electrons

$$H_e(\bar{\mathbf{r}}, \mathbf{R})\Phi_n(\bar{\mathbf{r}}, \mathbf{R}) = \varepsilon_n(\mathbf{R})\Phi_n(\bar{\mathbf{r}}, \mathbf{R}) .$$

Second, solve for nuclei

$$[H_n + \varepsilon_n(\mathbf{R})]\chi_p(\mathbf{R}) = E\chi_p(\mathbf{R}) .$$

2. Basic concepts

2.1. Born-Oppenheimer approximation

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$$[H_n + \varepsilon_n(\mathbf{R})]\chi_p(\mathbf{R}) = E\chi_p(\mathbf{R}) .$$

Concept

The slowly-varying character that the heavier nuclei positions experience with respect to electronic wavefunctions, results into the possibility of solving the electronic eigenvalue problem with the nuclei positions \mathbf{R} entering just as parameters.

2. Basic concepts

2.1. Born-Oppenheimer approximation



Exercise 1 (15 mns)

Considering the uniform scaling of the electron coordinates

$$\psi(\mathbf{r}_i) \rightarrow \psi(\alpha\mathbf{r}_i) = \alpha^{3N/2} \psi(\alpha\mathbf{r}_i)$$

α is a real scaling factor and N is the number of electrons.

Assuming that $\psi(\mathbf{r})$ is normalized.

Show that:

$$1. \langle \psi_\alpha | \psi_\alpha \rangle = 1; \psi_\alpha = \psi(\alpha\mathbf{r}_i)$$

$$2. \langle \psi_\alpha | T | \psi_\alpha \rangle = \alpha^2 \langle \psi | T | \psi \rangle$$

$$\text{where } T = \frac{1}{2} \sum_i \nabla_i^2$$

$$3. \langle \psi_\alpha | V(\mathbf{R}) | \psi_\alpha \rangle = \alpha \langle \psi | V(\alpha\mathbf{R}) | \psi \rangle$$

where

$$V(\mathbf{R}) = \sum_i \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i \neq j} \frac{Z_i}{|\mathbf{r}_i - \mathbf{R}_j|} + \sum_{i \neq j} \frac{Z_i Z_j}{|\mathbf{R}_i - \mathbf{R}_j|}$$

Exercise 1 (15 mns)

Considering the uniform scaling of the electron coordinates

$$\psi(\mathbf{r}) \rightarrow \psi_{\alpha} = \alpha^{3N/2} \psi(\alpha \mathbf{r}); \quad \mathbf{r} = \{\mathbf{r}_1, \dots, \mathbf{r}_N\}$$

α is a real scaling factor and N is the number of electrons.

Assuming that $\psi(\mathbf{r})$ is normalized.

Show that:

$$1. \langle \psi_{\alpha} | \psi_{\alpha} \rangle = 1 \quad \xrightarrow{\hspace{1cm}}$$

$$\begin{aligned} \langle \psi_{\alpha} | \psi_{\alpha} \rangle &= \alpha^{3N} \int \dots \int |\psi(\alpha \mathbf{r}_i)|^2 d\mathbf{r}_1 \dots d\mathbf{r}_N \\ &= \int \dots \int |\psi(\alpha \mathbf{r}_i)|^2 d(\alpha \mathbf{r}_1) \dots d(\alpha \mathbf{r}_N) \\ &= \int \dots \int |\psi(\mathbf{r}'_i)|^2 d(\mathbf{r}'_1) \dots d(\mathbf{r}'_N) = 1 \end{aligned}$$

$$\text{where } T = \frac{1}{2} \sum_i \nabla_i^2$$

$$2. \langle \psi_{\alpha} | T | \psi_{\alpha} \rangle = \alpha^2 \langle \psi_{\alpha} | T | \psi_{\alpha} \rangle$$

where

$$V(\mathbf{R}) = \sum_i \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i \neq j} \frac{Z_i}{|\mathbf{r}_i - \mathbf{R}_j|} + \sum_{i \neq j} \frac{Z_i Z_j}{|\mathbf{R}_i - \mathbf{R}_j|}$$

Homework!

2. Basic concepts

- Born-Oppenheimer (BO) approximation
- **Variational principle**

2. Basic concepts

2.1. Variational principle

Giving $|0\rangle$ is exact solution of Schrodinger equation (SE):

$$\hat{H}|0\rangle = E_0|0\rangle$$

Giving $|\tilde{0}\rangle$ is an approximation.

Variational principles states that:

$$(1) \quad E_0 \leq E[\tilde{0}] = \frac{\langle \tilde{0} | \hat{H} | \tilde{0} \rangle}{\langle \tilde{0} | \tilde{0} \rangle}$$

2. Basic concepts

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Prove (1):

We can write $|\tilde{0}\rangle = |0\rangle + |\delta\rangle$

$$\frac{1}{1+x} = 1 - x + O(x^2)$$

$$\begin{aligned} E[0 + \delta] &= \frac{\langle 0 | \hat{H} | 0 \rangle + \langle 0 | \hat{H} | \delta \rangle + \langle \delta | \hat{H} | 0 \rangle + \langle \delta | \hat{H} | \delta \rangle}{\langle 0 | 0 \rangle + \langle 0 | \delta \rangle + \langle \delta | 0 \rangle + \langle \delta | \delta \rangle} \\ &= E_0 + \cancel{\langle 0 | \hat{H} - E_0 | \delta \rangle} + \cancel{\langle \delta | \hat{H} - E_0 | 0 \rangle} + O(\delta^2) = E_0 + O(\delta^2) \end{aligned}$$

2. Basic concepts

2.1. Variational principle

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Variational principles states that:

$$(1) \quad E_0 \leq E[\tilde{0}] = \frac{\langle \tilde{0} | \hat{H} | \tilde{0} \rangle}{\langle \tilde{0} | \tilde{0} \rangle}$$

(2) All stationary points of **energy functional** are eigenstates of Schrodinger equation

Prove (2)

Let $|0\rangle$ be a stationary point of $E[\tilde{0}]$

Giving a variation $|\delta\rangle$

$$\langle 0 | \hat{H} - E[0] | \delta \rangle + \langle \delta | \hat{H} - E[0] | 0 \rangle = 0$$

For variation $i|\delta\rangle$

$$\langle 0 | \hat{H} - E[0] | \delta \rangle - \langle \delta | \hat{H} - E[0] | 0 \rangle = 0$$

$$\Rightarrow \langle \delta | \hat{H} - E[0] | 0 \rangle = 0$$

$$\Rightarrow \hat{H}|0\rangle = E[0]|0\rangle$$

Prove (1):

We can write $|\tilde{0}\rangle = |0\rangle + |\delta\rangle$

$$E[0 + \delta] = \frac{\langle 0 | \hat{H} | 0 \rangle + \langle 0 | \hat{H} | \delta \rangle + \langle \delta | \hat{H} | 0 \rangle + \langle \delta | \hat{H} | \delta \rangle}{\langle 0 | 0 \rangle + \langle 0 | \delta \rangle + \langle \delta | 0 \rangle + \langle \delta | \delta \rangle}$$

$$= E_0 + \cancel{\langle 0 | \hat{H} - E_0 | \delta \rangle} + \cancel{\langle \delta | \hat{H} - E_0 | 0 \rangle} + O(\delta^2) = E_0 + O(\delta^2)$$

$$\frac{1}{1+x} = 1 - x + O(x^2)$$

$$\langle 0 | 0 \rangle = 1$$

2. Basic concepts

2.1. Variational principle

- Hellmann-Feynman theorem:**
- (3) If eigenstates are variational, the first-order change in energy due to perturbation may be calculated as expectation value of perturbation operator

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- Hellmann-Feynman theorem:**
- (3) If eigenstates are variational, the first-order change in energy due to perturbation may be calculated as expectation value of perturbation operator

Prove:

Hamiltonian with a perturbation V : $H' = H + \alpha V$

$|\Psi_\alpha\rangle$ is wavefunction associated with H'

$$\frac{dE(\alpha)}{d\alpha} \Big|_{\alpha=0} = \frac{\partial}{\partial \alpha} \frac{\langle \Psi_\alpha | H + \alpha V | \Psi_\alpha \rangle}{\langle \Psi_\alpha | \Psi_\alpha \rangle} \Big|_{\alpha=0}$$

$$\begin{aligned} & |\psi\rangle\langle\psi|H-E|\psi\rangle \\ & \langle\psi|\psi\rangle=1 \\ & \langle\Psi_\alpha|\Psi_\alpha\rangle=1 \end{aligned}$$

$$\begin{aligned} &= 2\text{Re} \left\langle \frac{\partial \Psi_\alpha}{\partial \alpha} \Big|_{\alpha=0} \middle| H - E(0) \right| \Psi \right\rangle + \langle \Psi | V | \Psi \rangle \\ &= \langle \Psi | V | \Psi \rangle \quad (\text{Approximation for small perturbation}) \end{aligned}$$

2. Basic concepts

2.1. Variational principle

Hellmann-Feynman theorem:

- (3) If eigenstates are variational, the first-order change in energy due to perturbation may be calculated as expectation value of perturbation operator

Prove:

Hamiltonian with a perturbation V : $H' = H + \alpha V$

$|\Psi_\alpha\rangle$ is wavefunction associated with H'

More general:

$$\frac{dE(\alpha)}{d\alpha} = \langle \psi_\alpha | V | \psi_\alpha \rangle$$

$$\frac{dE(\alpha)}{d\alpha} \Big|_{\alpha=0} = \frac{\partial}{\partial \alpha} \frac{\langle \Psi_\alpha | H + \alpha V | \Psi_\alpha \rangle}{\langle \Psi_\alpha | \Psi_\alpha \rangle} \Big|_{\alpha=0}$$

$$= 2\text{Re} \left\langle \frac{\partial \Psi_\alpha}{\partial \alpha} \Big|_{\alpha=0} \middle| H - E(0) \right| \Psi \right\rangle + \langle \Psi | V | \Psi \rangle$$

$$= \langle \Psi | V | \Psi \rangle$$

Homework 2

Considering the uniform scaling of the electron coordinates

$$\psi(\mathbf{r}) \rightarrow \psi_{\alpha}(\mathbf{r}) = \alpha^{3N/2} \psi(\alpha \mathbf{r}); \quad \mathbf{r} = \{\mathbf{r}_1, \dots, \mathbf{r}_N\}$$

α is a real scaling factor and N is the number of electrons.

Assuming that $\psi(\mathbf{r})$ is normalized and at a stationary point.

Giving the stationary condition:

$$\frac{\partial}{\partial \alpha} \left\langle \psi_{\alpha} \left| \hat{H}(\mathbf{R}) \right| \psi_{\alpha} \right\rangle \Bigg|_{\alpha=1} = 0$$

Show that :

$$2 \left\langle \psi \left| T \right| \psi \right\rangle + \left\langle \psi \left| V(\mathbf{R}) \right| \psi \right\rangle = - \frac{dE(\alpha \mathbf{R})}{d\alpha} \Bigg|_{\alpha=1}$$

Discussion (~30mns)

- What are other types of chemical/physical bond other than covalent bond?
- Are stationary points of energy functional necessarily ground state? $\nabla E[\psi] = 0$
- Can the variational principle hold true for other states than ground state? (excited variational principle)