

Density-Functional Theory for Practitioners - Lecture 5

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~~Revision~~ -> Poster Gallery Walk

1. Create your poster of your topic (see bellow)
2. Mix groups – so new groups has someone from each group – explain the poster you are standing at.
3. Move on to the next poster at the signal.

Topics:

1. ~~Types of Bonds~~
2. Covalent Bonding
3. Ionic Bonding
4. Metallic Bonding
5. Hydrogen and Dispersion Bonding
6. Distortion of Bonds

You can also discuss with us or your group what you like/dislike on the last lecture and tutorial!

Poster Gallery Walk

Thank you all for nice work on the posters:



This lesson

Must know	Should know	Nice to know
Kohn-Sham energies	Ionization energies and electron affinities	Different excitation energies
Surface energies	Surface phase diagrams	Surface structures

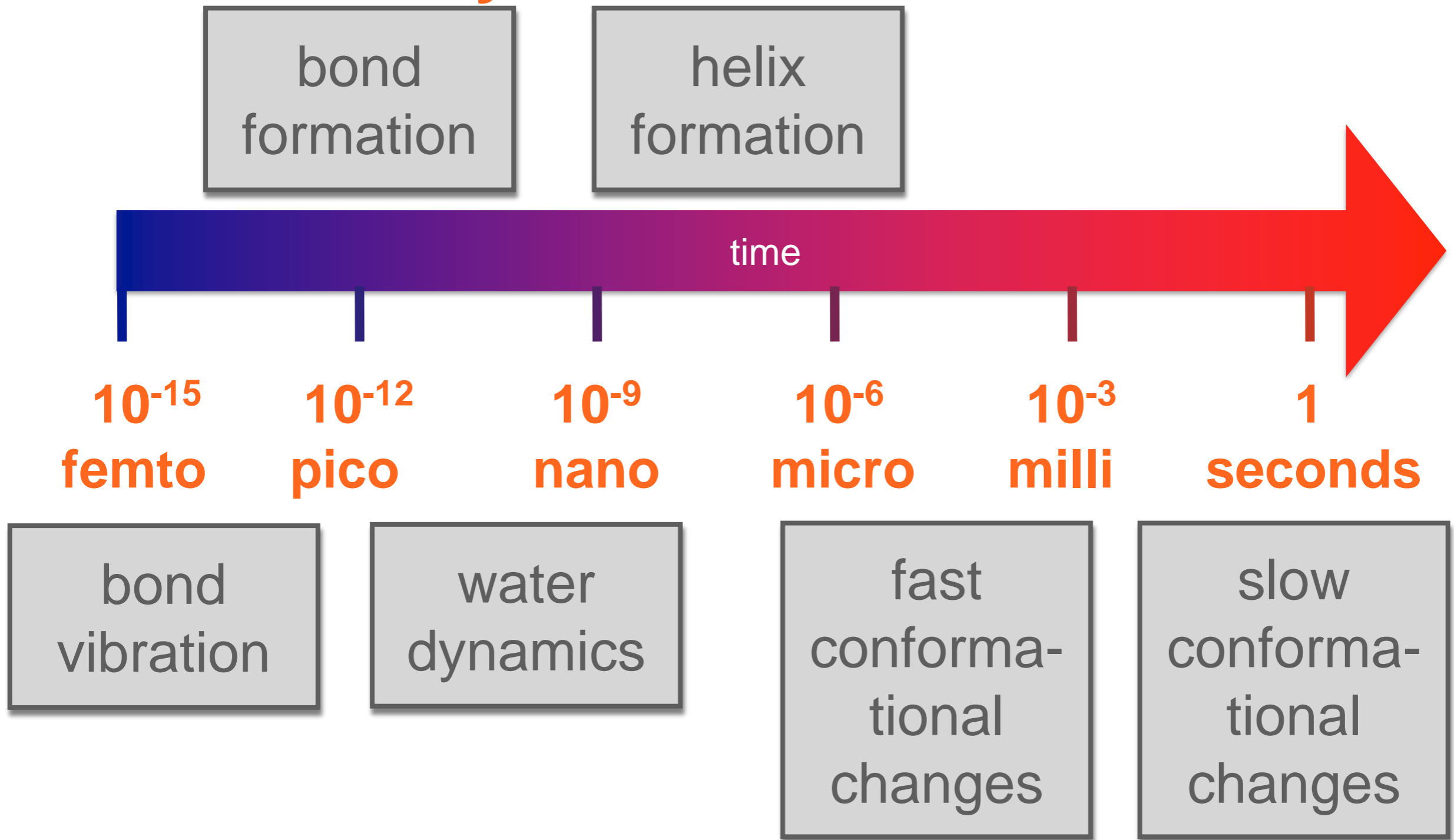
Learning outcomes

After completion of this class you

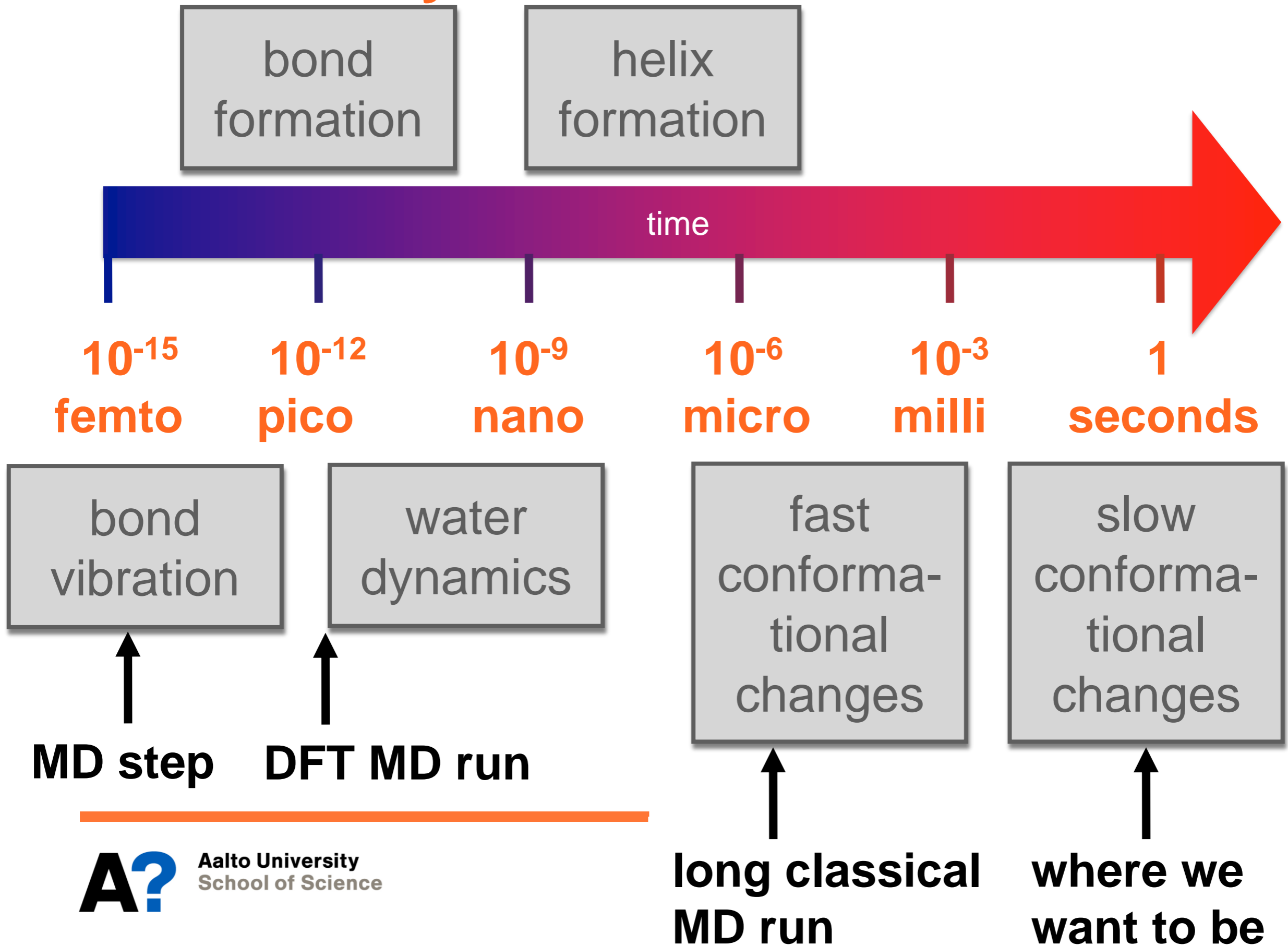
- are familiar with Kohn-Sham energies and their pros and cons.
- ~~have a first understanding of DFT in surface science.~~



Molecular dynamics — time scale



Molecular dynamics — time scale



Recap: Kohn-Sham (KS) equations

$$v_{\text{aux}}[n](\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + v_{\text{Hartree}}[n](\mathbf{r}) + v_{\text{xc}}[n](\mathbf{r})$$

KS potential

KS orbitals/wave functions

$$\left[-\frac{\nabla_{\mathbf{r}}^2}{2} + v_{\text{aux}}[n](\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

$$n(\mathbf{r}) = \sum_i^{N_e} |\phi_i(\mathbf{r})|^2$$

KS eigenvalues

Recap: Kohn-Sham (KS) equations

But what are these eigenvalues ϵ_i ?

$$v_{\text{aux}}[n](\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + v_{\text{Hartree}}[n](\mathbf{r}) + v_{\text{xc}}[n](\mathbf{r})$$

KS potential

KS orbitals/wave functions

$$\left[-\frac{\nabla_{\mathbf{r}}^2}{2} + v_{\text{aux}}[n](\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

$$n(\mathbf{r}) = \sum_i^{N_e} |\phi_i(\mathbf{r})|^2$$

KS eigenvalues



Kohn-Sham energy

$$E_{KS}[n] = T + E_{\text{external}} + E_{\text{Hartree}} + E_{\text{xc}}$$

We want to minimise the energy subject to the constraint that the KS states are orthogonal.

$$\mathcal{L}[n] = E_{KS}[n] - \sum_{i,j}^N \varepsilon_{ij} \int \varphi_i^*(\mathbf{x}) \varphi_j(\mathbf{x}) d\mathbf{x} ; w. \int \varphi_i^*(\mathbf{x}) \varphi_j(\mathbf{x}) d\mathbf{x} = \delta_{ij}$$


$$\frac{\delta \mathcal{L}}{\delta \varphi_i^*} = 0 \quad \forall i$$

Method of Lagrange multipliers

Taking into account that $E_{KS}[n]$ can be diagonalized, so only diagonals $\varepsilon_{ii} = \epsilon_i$; 1 electron energies are important

Lagrange multipliers

$$\frac{\delta \mathcal{L}}{\delta \varphi_i^*} = 0 \quad \forall i$$

$$\left[-\frac{\nabla_{\mathbf{r}}^2}{2} + v_{\text{aux}}[n](\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$


The KS eigenvalues are Lagrange multipliers!

But are they really just a mathematical trick?

Density-functional theory and excitations

In exact DFT, the ionisation potential is given by Kohn-Sham eigenvalue of highest occupied state.

$$I_{\text{KS}} = -\epsilon_N(N)$$

Density-functional theory and excitations

In exact DFT, the ionisation potential is given by Kohn-Sham eigenvalue of highest occupied state.

$$I_{\text{KS}} = -\epsilon_N(N)$$

Otherwise we have Janak's theorem:

$$\frac{\partial E}{\partial n_s} = \epsilon_s$$



Janak's theorem

$$\frac{\partial E}{\partial n_s} = \epsilon_s$$

integrating and making midpoint approximation:

$$E(N + 1, s) - E(N) = \int_0^1 dn \epsilon_s(n) \approx \epsilon_s(0.5)$$

↑
affinity as a total
energy difference

↑
Slater's transition state



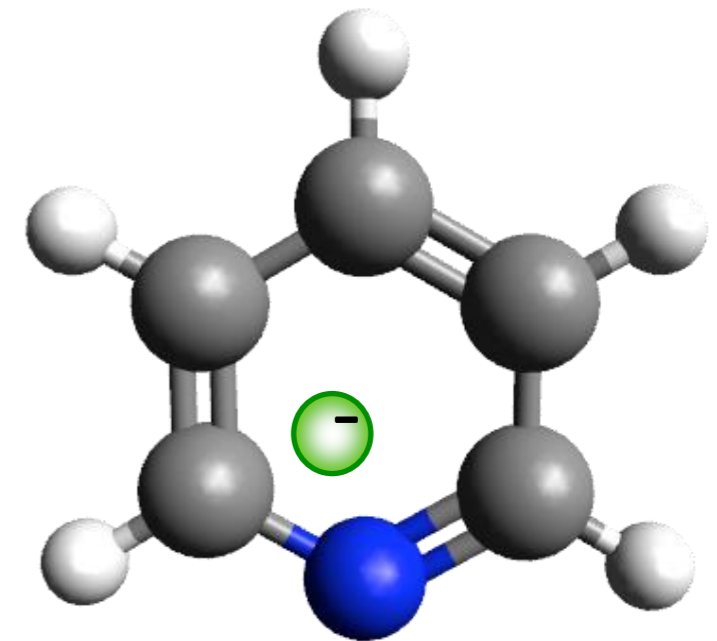
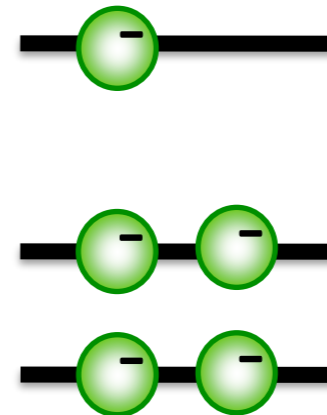
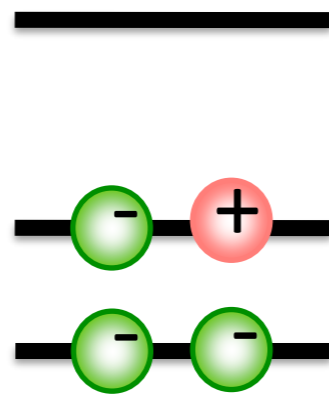
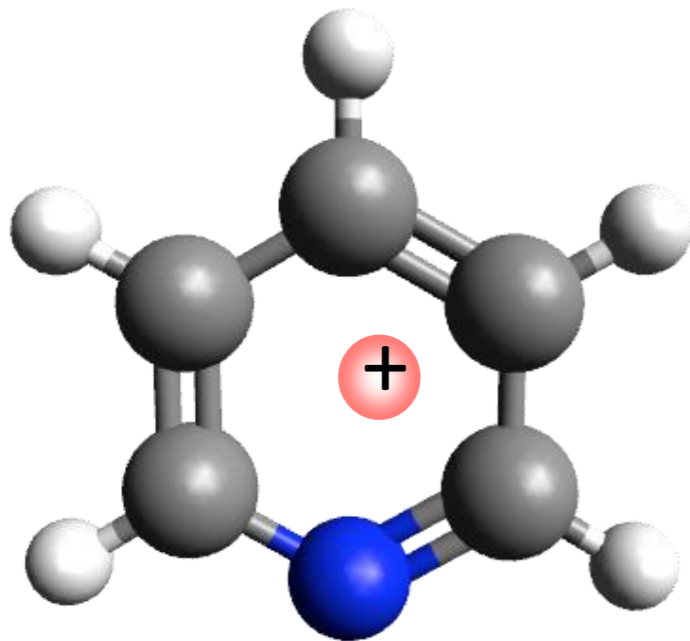
Ionisation Potential, Affinity and (Band) Gaps

Charged excitations:

$$\epsilon_s = E(N \pm 1, s) - E(N)$$

electron removal

electron addition



Ionisation Potential, Affinity and (Band) Gaps

Could use total energy method to compute:
(also known as Δ SCF)

$$\epsilon_s = E(N \pm 1, s) - E(N)$$

Ionisation Potential, Affinity and (Band) Gaps

Could use total energy method to compute:
(also known as Δ SCF)

$$\epsilon_s = E(N \pm 1, s) - E(N)$$

Ionisation potential:

minimal energy to remove an electron

$$I = E(N - 1) - E(N)$$

Ionisation Potential, Affinity and (Band) Gaps

Could use total energy method to compute:
(also known as Δ SCF)

$$\epsilon_s = E(N \pm 1, s) - E(N)$$

Electron affinity:

minimal energy to add an electron

$$A = E(N) - E(N + 1)$$

Ionisation Potential, Affinity and (Band) Gaps

Could use total energy method to compute:
(also known as Δ SCF)

$$\epsilon_s = E(N \pm 1, s) - E(N)$$

Band gap or HOMO-LUMO gap:

HOMO: highest occupied molecular orbital

LUMO: lowest unoccupied molecular orbital

$$E_{gap} = I - A$$



Ionisation Potential, Affinity and (Band) Gaps

Could use total energy method to compute:
(also known as Δ SCF)

$$\epsilon_s = E(N \pm 1, s) - E(N)$$

But!

- only justified for differences of ground states
- difficult to find excited state density
- excited state density is not unique
- separate calculation for every excitation needed

Ionisation Potential, Affinity and (Band) Gaps

Also, we do not have the exact XC-functional!

$$I = E(N - 1) - E(N)$$

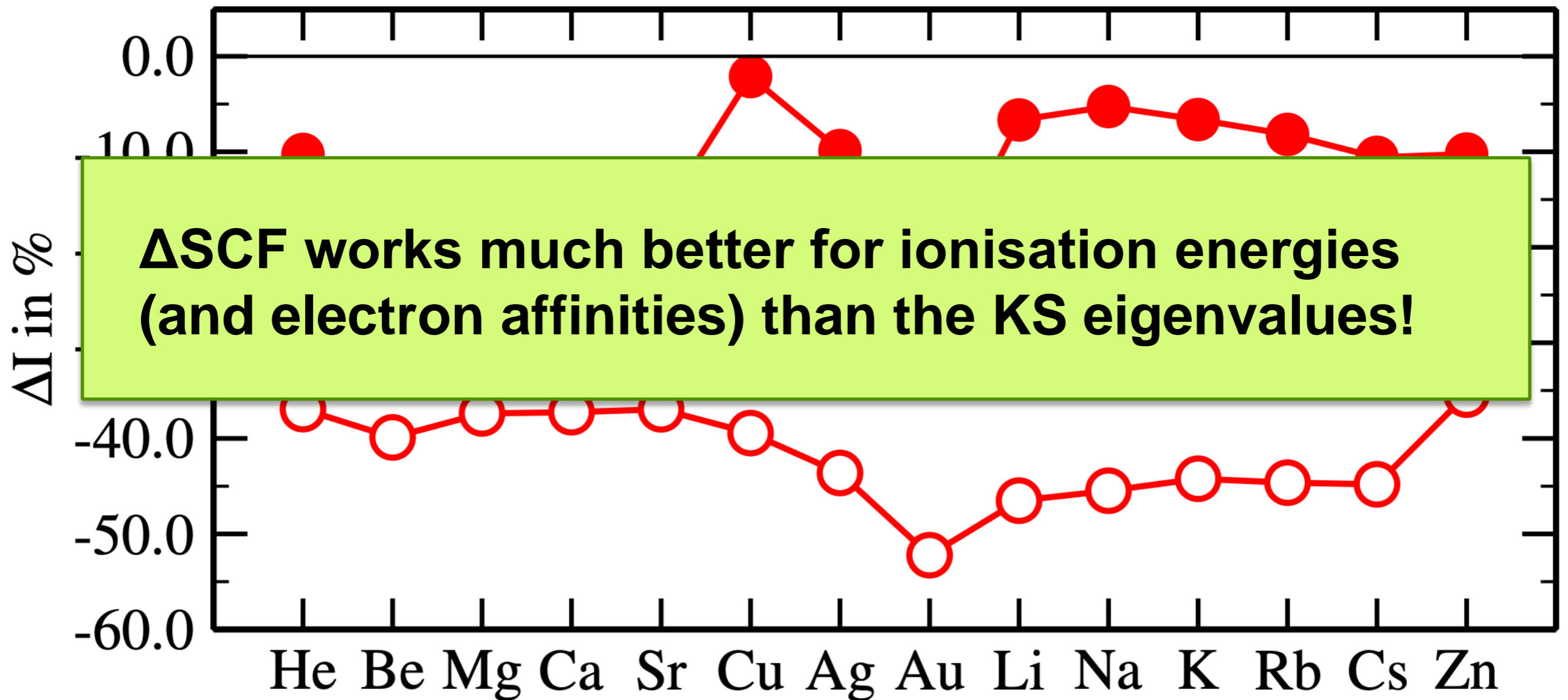
$$I = \epsilon_N(N)$$

eigenvalues are
not exact

total energies are
not exact

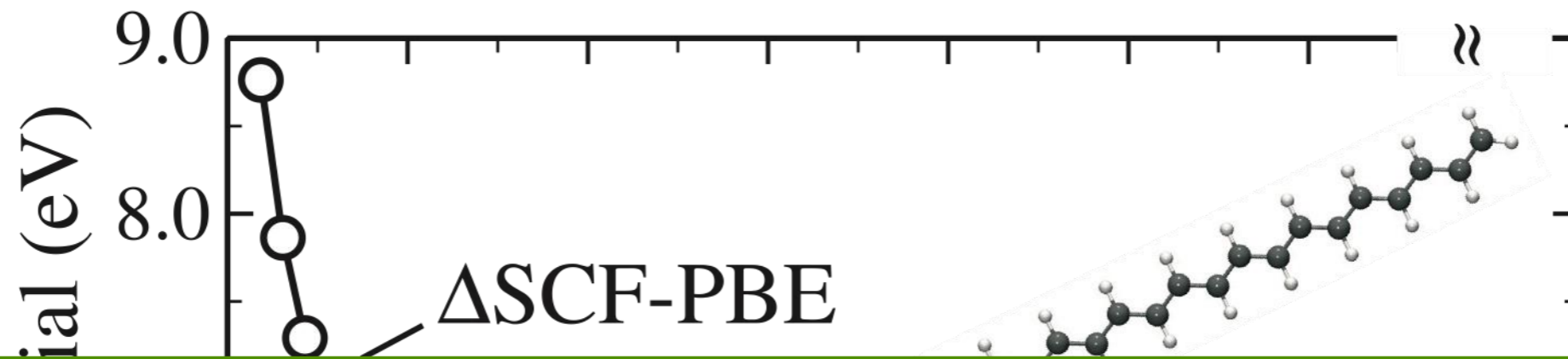
Ionisation Potential, Affinity and (Band) Gaps

Ionisation potential in the LDA

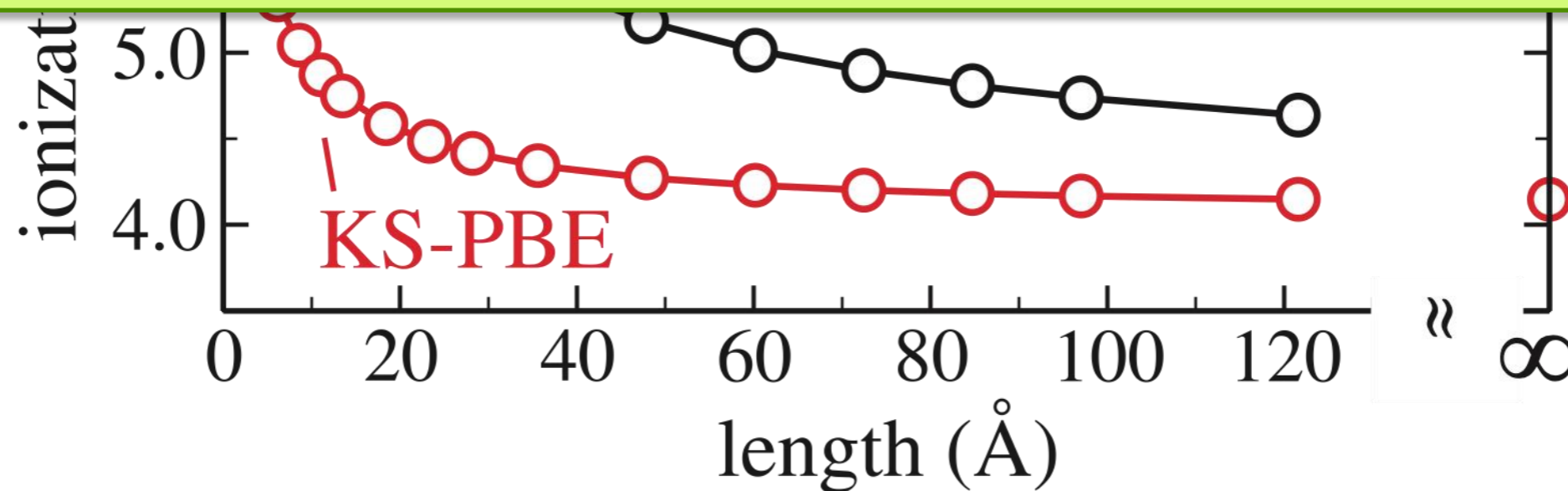


Δ SCF versus eigenvalues for finite systems

oligoacetylenes

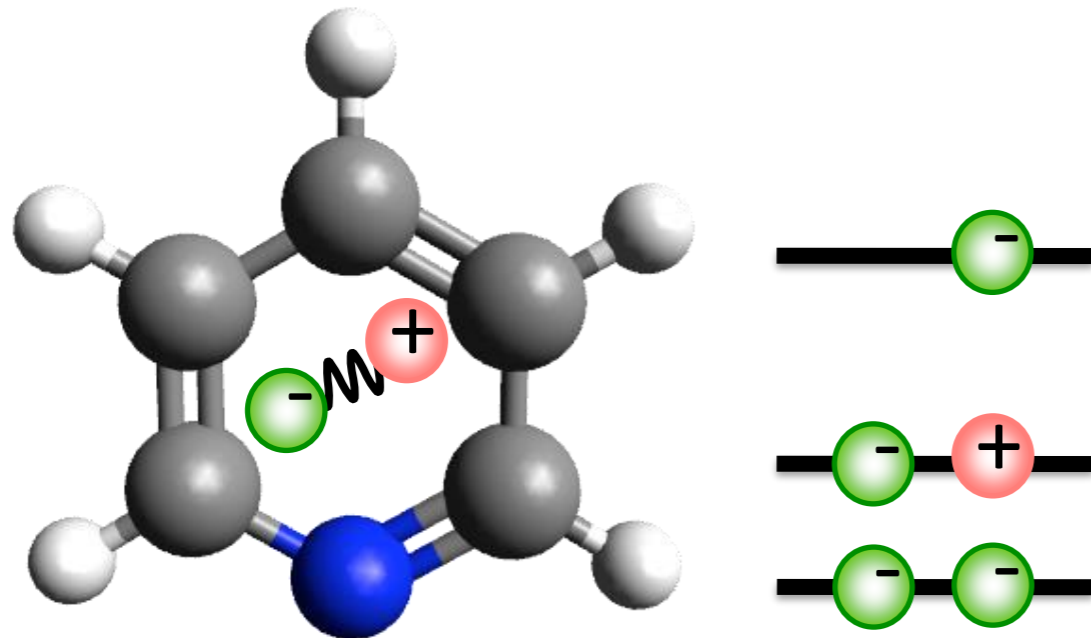


For delocalised states Δ SCF and the KS eigenvalues agree (and are often equally wrong)!



Other excitations

optical (neutral)



exciton
(electron-hole pair)

$$E_{\text{exciton}} = E^*(N) - E(N)$$

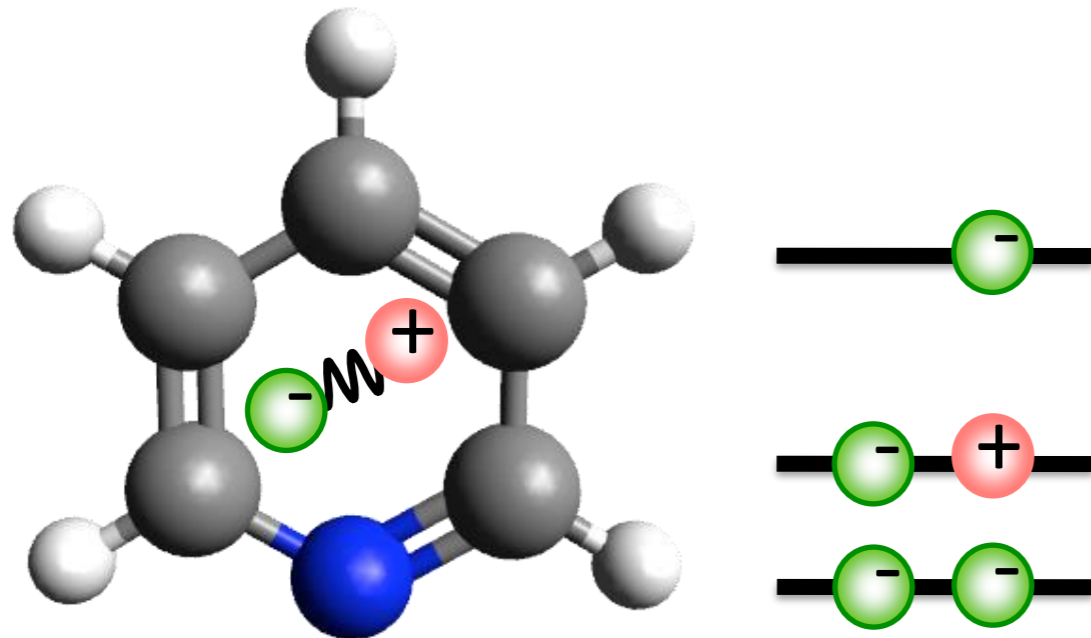


system in the optically
excited state

Can be calculated
with time-dependent
DFT (TDDFT).

Other excitations

optical (neutral)



other excitations:

- Auger excitations
- plasmons
- magnons
- satellites
- ...

exciton (electron-hole pair)

Questions - eigenenergies

$$I_{\text{KS}} = -\epsilon_N(N) \quad \epsilon_s = E(N \pm 1, s) - E(N)$$

$$\frac{\partial E}{\partial n_s} = \epsilon_s \quad E(N + 1, s) - E(N) = \int_0^1 dn \epsilon_s(n) \approx \epsilon_s(0.5)$$

$$I = E(N - 1) - E(N) \quad A = E(N) - E(N + 1)$$

$$E_{\text{gap}} = I - A$$

$$E_{\text{exciton}} = E^*(N) - E(N)$$

