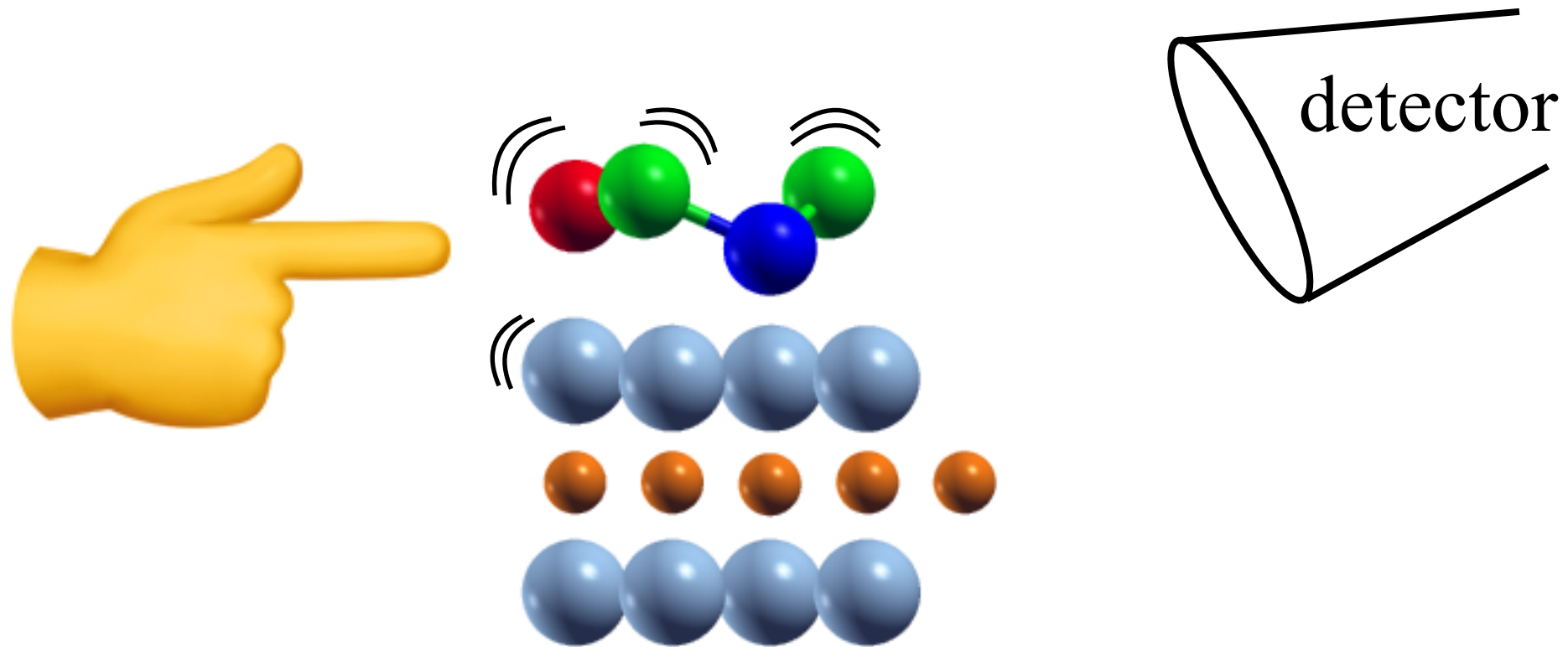


Combining LCAO basis functions with plane waves in OpenMX codes for excitation calculations



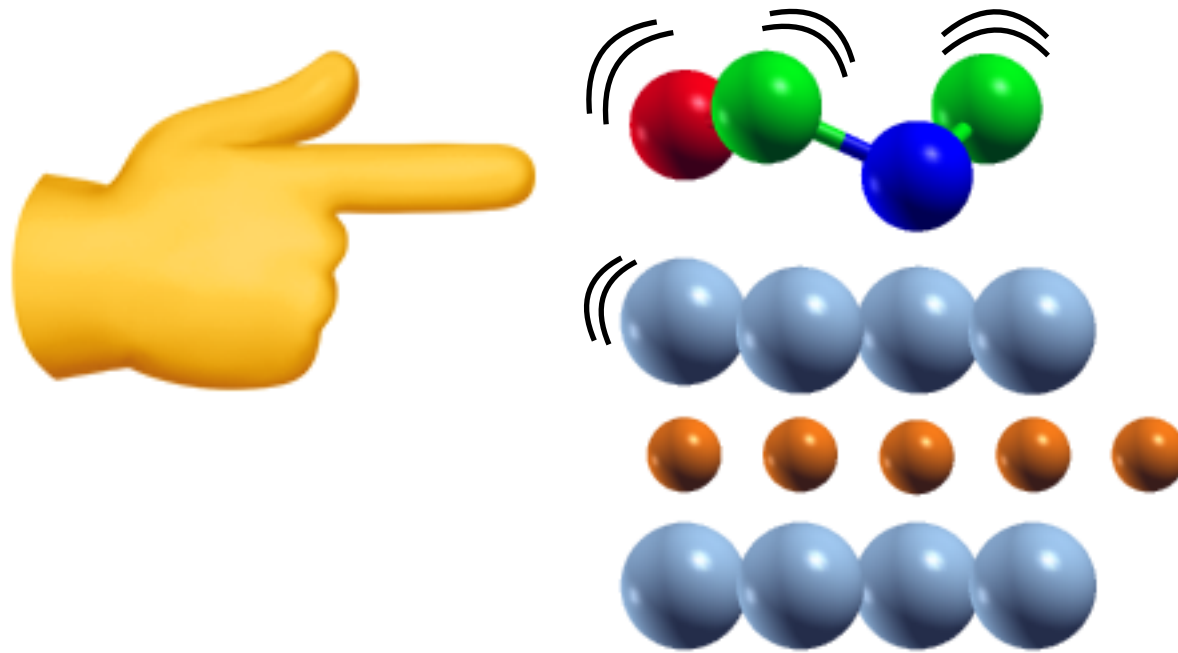
Chi-Cheng Lee

Institute for Solid State Physics, The University of Tokyo, Japan

Developer's meeting, Nov. 24-25, 2016

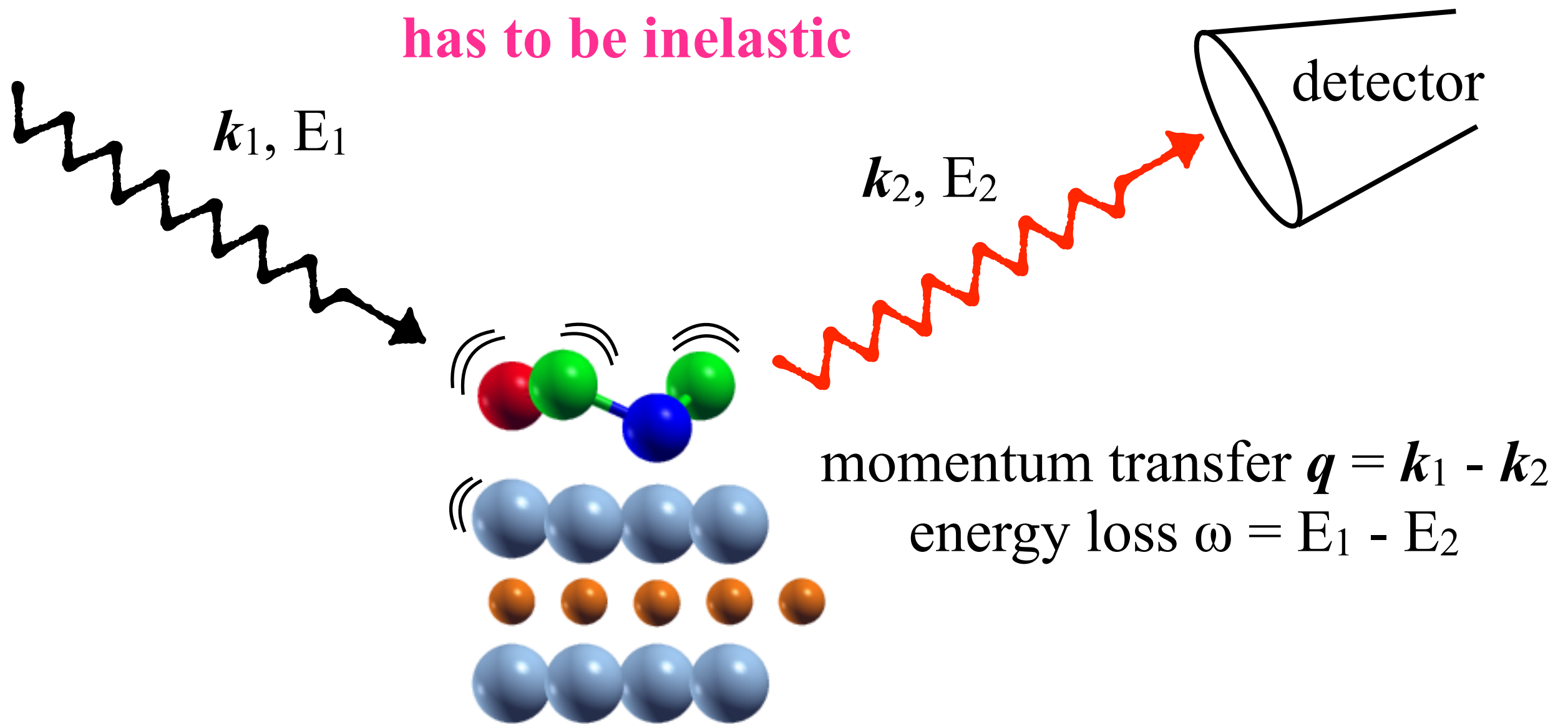
Motivation

Why do we want to study excitations?



- By perturbing the system, one can excite the system from ground state to the excited states.
- Many interesting collective excitations can happen in the system, for example, phonons, plasmons, excitons, and magnons.
- Experiments can measure the physical quantities corresponding to the differences between the ground state and excited states.

Photon, electron, and neutron scattering



- By measure the momentum transfer and the energy loss of the photon, electron, or neutron, we can learn the physical property of the system since the momentum and energy are both conserved.

Kohn-Sham response function

$$\delta n(\mathbf{r}, t) = \int_{-\infty}^t dt' \int d\mathbf{r}' \chi(\mathbf{r}, \mathbf{r}', t-t') V_{\text{ext}}(\mathbf{r}', t') \quad (\text{or spin channel})$$

$$\chi(\mathbf{r}, \mathbf{r}', \omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} \chi(\mathbf{r}, \mathbf{r}', t)$$

$$= \sum_n \frac{\langle \Phi_0 | \hat{n}(\mathbf{r}) | \Phi_n \rangle \langle \Phi_n | \hat{n}(\mathbf{r}') | \Phi_0 \rangle}{\hbar\omega + i\eta - (E_n - E_0)} - \frac{\langle \Phi_0 | \hat{n}(\mathbf{r}') | \Phi_n \rangle \langle \Phi_n | \hat{n}(\mathbf{r}) | \Phi_0 \rangle}{\hbar\omega + i\eta + (E_n - E_0)}$$

$$\chi_0(\mathbf{r}, \mathbf{r}', \omega) = \sum_{i \in \text{occ.}} \sum_{m \in \text{unocc.}} \left\{ \frac{\phi_i(\mathbf{r}) \phi_m^*(\mathbf{r}) \phi_m(\mathbf{r}') \phi_i^*(\mathbf{r}')}{\varepsilon_i - \varepsilon_m - \hbar\omega - i\eta} + \frac{\phi_i^*(\mathbf{r}) \phi_m(\mathbf{r}) \phi_m^*(\mathbf{r}') \phi_i(\mathbf{r}')}{\varepsilon_i - \varepsilon_m + \hbar\omega + i\eta} \right\}$$

K. Yabana *et al.*, Phys. Stat. Sol. (b) **243**, 1121 (2006).

- One can see in the density response function we have the information of the energy difference between the ground state and the excited states together with the probability strength of each oscillator.
- The response function is directly coupled to the scattering experiments described by quantum mechanics and can also be further connected to dielectric functions for studying optical properties.

Completeness of unoccupied bands

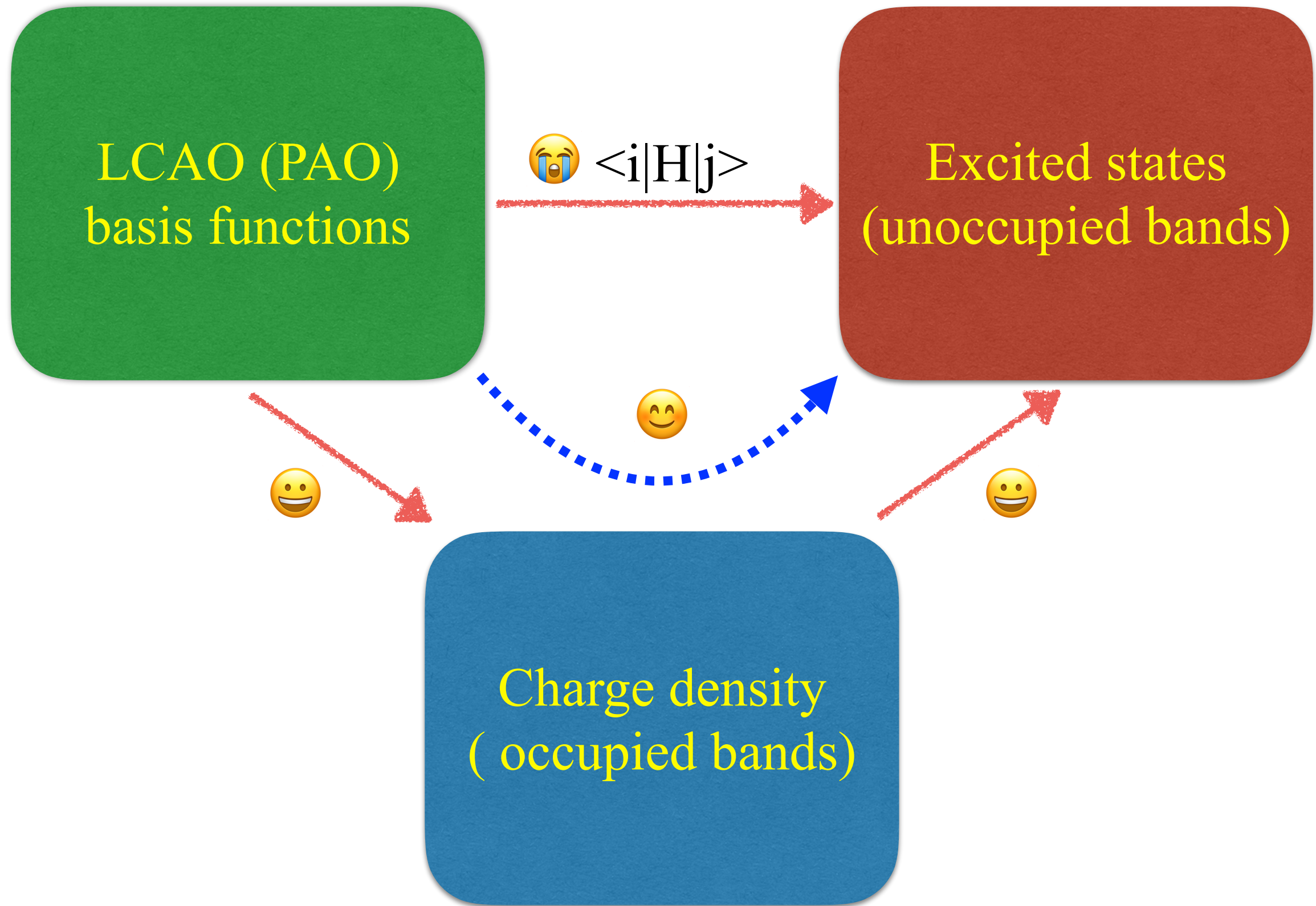
- It is not surprising that we need information of unoccupied bands to study the excitation properties of systems. (In some cases, we don't need the information explicitly via some smart treatment.)
- The completeness of unoccupied states becomes important if we want to calculate the KS response function directly:

$$\chi_0(\mathbf{r}, \mathbf{r}', \omega) = \sum_{i \in \text{occ.}} \sum_{m \in \text{unocc.}} \left\{ \frac{\phi_i(\mathbf{r}) \phi_m^*(\mathbf{r}) \phi_m(\mathbf{r}') \phi_i^*(\mathbf{r}')}{\varepsilon_i - \varepsilon_m - \hbar\omega - i\eta} + \frac{\phi_i^*(\mathbf{r}) \phi_m(\mathbf{r}) \phi_m^*(\mathbf{r}') \phi_i(\mathbf{r}')}{\varepsilon_i - \varepsilon_m + \hbar\omega + i\eta} \right\}$$

- OpenMX codes adopt pseudo atomic orbitals as the basis functions, where the number of bands we usually have is a small number because they are sufficient to describe the ground state.
- Before we go further to calculate susceptibility, we should expand the Hilbert space of the Hamiltonian spanned by the LCAO basis. How?

Combining LCAO basis functions with plane waves

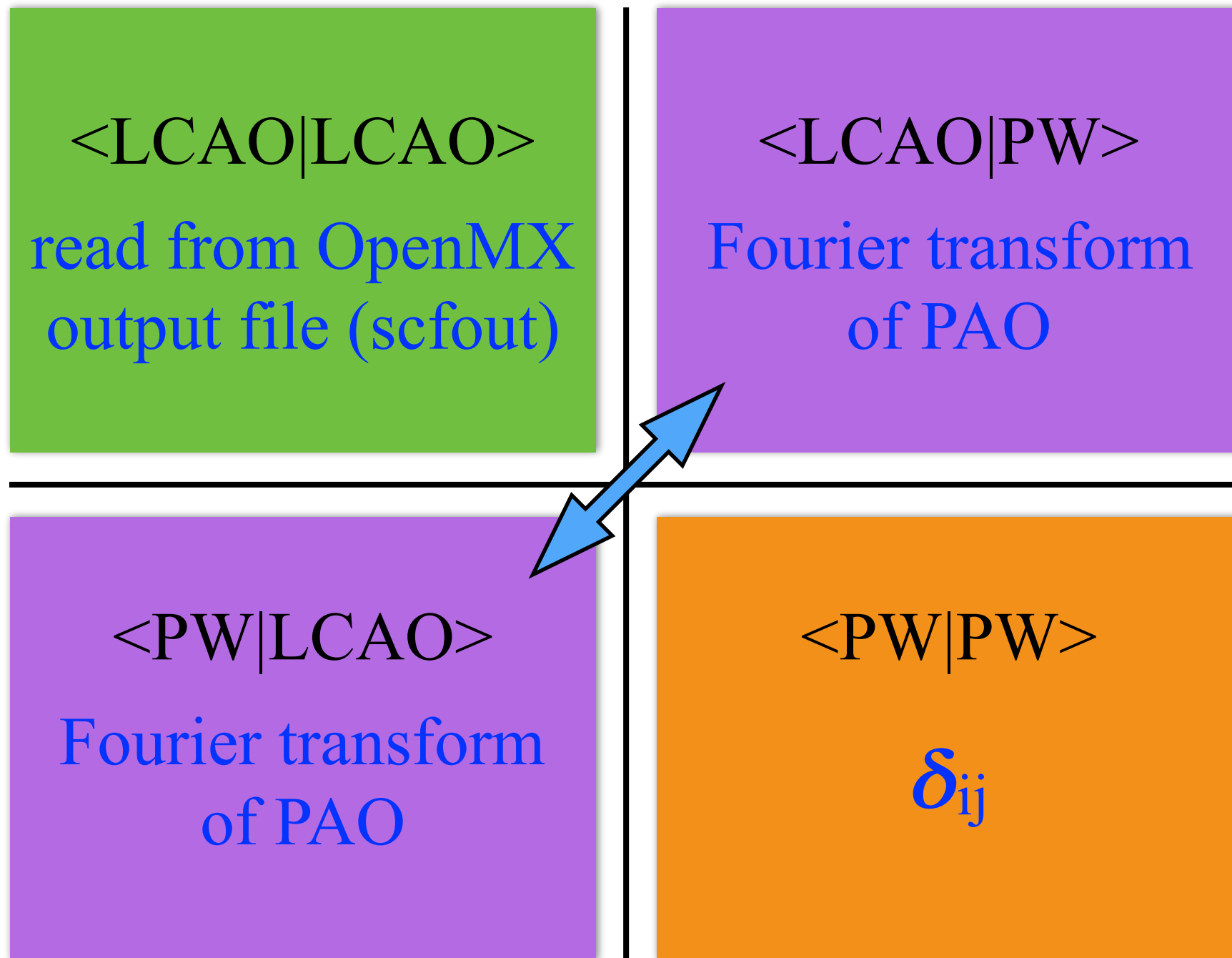
Charge density



Charge density

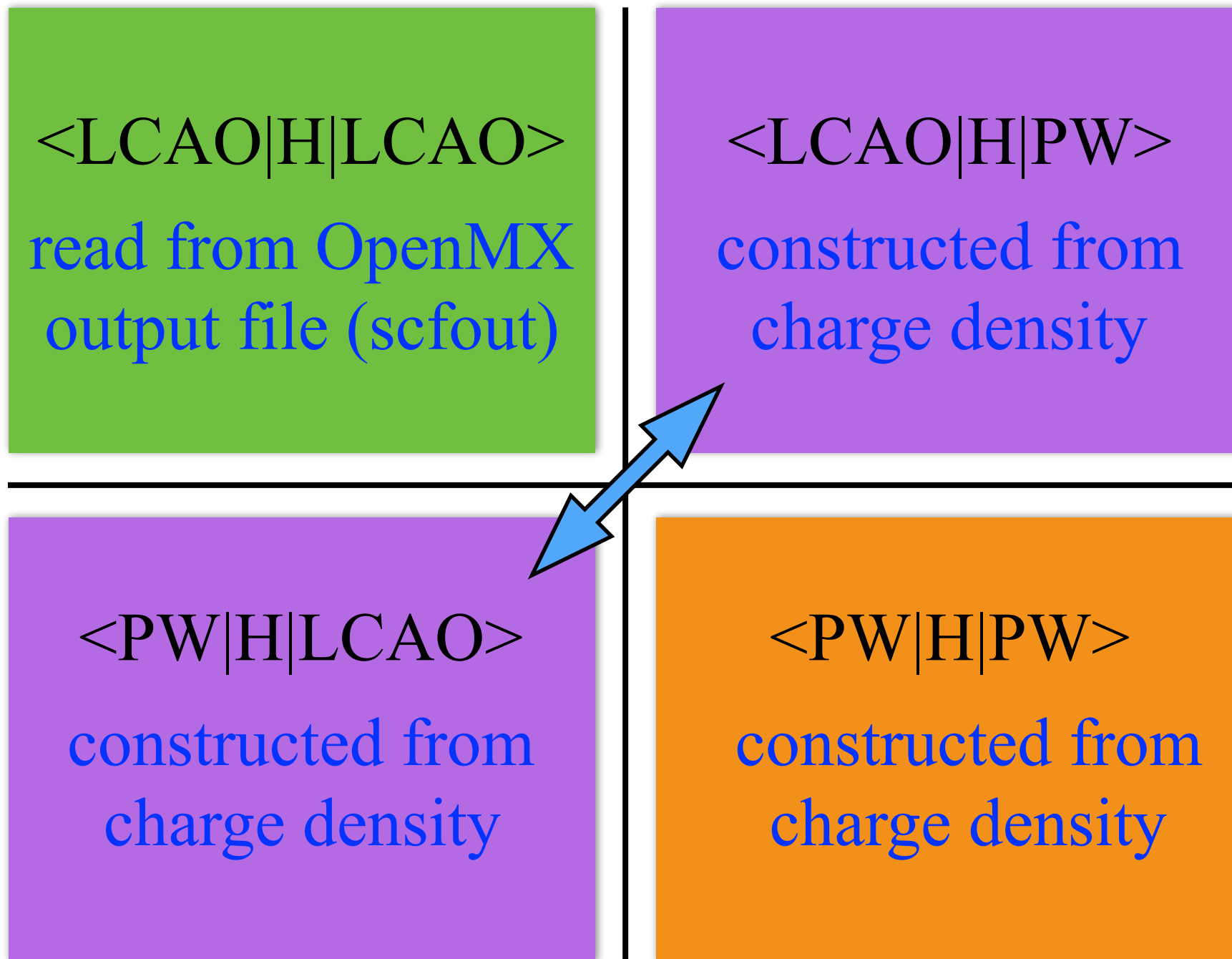


Overlap matrix elements of dual basis sets



- The two sets of basis are not orthogonal to each other

Hamiltonian represented by dual basis sets



- What is the best way to combine two basis sets in terms of the matrix size of each block?

Hamiltonian represented by dual basis sets

$\langle \text{LCAO} | H | \text{LCAO} \rangle$

read from OpenMX
output file (scfout)

- Since we have spent some effort in testing good enough LCAO basis functions to get the well-converged ground state for a studied system, it is better not to change the number of LCAO basis functions.

Hamiltonian represented by dual basis sets

$$\langle \text{LCAO} | H | \text{PW} \rangle$$

constructed from
charge density

- The size of this block is determined by the block size of PWs. We should consider the computational time for constructing this block since we need to calculate the Kohn-Sham Hamiltonian in both the plane-wave and LCAO basis sets.

Hamiltonian represented by dual basis sets

$$\langle \text{PW} | H | \text{PW} \rangle$$

constructed from
charge density

- Unoccupied states are more plane-wave-like compared to the occupied ones. If we want more unoccupied bands, we should increase the number of plane waves corresponding to a large cut-off kinetic energy. We just need to diagonalize the new Hamiltonian with dual basis sets once, like performing band structure calculations.
- In principles, we can also choose PW-only basis set. This might be fine for systems without semicore/core states. For pseudopotentials having those states, we need a lot of PW but just for improving the core-like states, which is inefficient.

Formula for $H(\mathbf{k})$ in collinear calculations

Overlap matrix elements

<LCAO|PW>

$$\langle \vec{k}m | \vec{k} + \vec{G} \rangle = \frac{1}{\sqrt{v}} e^{i(\vec{k} + \vec{G}) \cdot \vec{r}_{0m}} \int_V d\vec{r} \langle 0m | \vec{r} \rangle e^{i(\vec{k} + \vec{G}) \cdot \vec{r}}$$

The $\vec{r}$ means the origin is at the center of the LCAO orbital $|0m\rangle$

$$\int_V d\vec{r} \langle 0m | \vec{r} \rangle e^{i(\vec{k} + \vec{G}) \cdot \vec{r}} = 4\pi i^l Y_{lm}^*(\vec{k} + \vec{G}) \int_0^\infty d\tilde{r} j_l(|\vec{k} + \vec{G}| \tilde{r}) R_{nl}^*(\tilde{r}) \tilde{r}^2$$

- The Fourier components of PAO basis functions can be obtained by utilizing the spherical Bessel functions.

Hamiltonian combining LCAO and PW basis sets

<LCAO|H(k)|PW>

$$\langle \vec{k}m | \hat{H} | \vec{k} + \vec{G} \rangle = \langle \vec{k}m | -\frac{1}{2}\nabla^2 + V_{loc}(\vec{r}) + V_{NL} | \vec{k} + \vec{G} \rangle$$

$$\langle \vec{k}m | -\frac{1}{2}\nabla^2 | \vec{k} + \vec{G} \rangle = \frac{1}{2}|\vec{k} + \vec{G}|^2 \langle \vec{k}m | \vec{k} + \vec{G} \rangle$$

$$\langle \vec{k}m | V_{loc}(\vec{r}) | \vec{k} + \vec{G} \rangle = \frac{1}{\sqrt{v}} \int_V d\vec{r} \langle 0m | \vec{r} \rangle V_{loc}(\vec{r}) e^{i(\vec{k} + \vec{G}) \cdot \vec{r}}$$

$$\sum_{\vec{R},a} \langle \vec{k}m | V_{\vec{R},a} \rangle \langle V_{\vec{R},a} | \vec{k} + \vec{G} \rangle = \frac{1}{\sqrt{V}} \sum_a e^{i(\vec{k} + \vec{G}) \cdot \vec{r}_{0a}} \int_V d\vec{r} \langle V_{0a} | \vec{r} \rangle e^{i(\vec{k} + \vec{G}) \cdot \vec{r}} \sum_{\vec{R}} e^{i\vec{k} \cdot \vec{R}} \langle \vec{k}m | V_{\vec{R},a} \rangle$$

$$= \frac{1}{\sqrt{V}} \sum_a A_a \sum_{\vec{R}} e^{i\vec{k} \cdot \vec{R}} \langle \vec{k}m | V_{\vec{R},a} \rangle$$

$$= \frac{1}{\sqrt{v}} \sum_{\vec{R},a} A_a e^{-i\vec{k} \cdot \vec{R}} \int_V d\vec{r} \langle 0m | \vec{r} \rangle \langle \vec{r} + \vec{R} | V_{0a} \rangle$$

$$A_a = e^{i(\vec{k} + \vec{G}) \cdot \vec{r}_{0a}} \int_V d\vec{r} \langle V_{0a} | \vec{r} \rangle e^{i(\vec{k} + \vec{G}) \cdot \vec{r}}$$

Hamiltonian in PW-only basis

$$\langle \text{PW} | \mathbf{H}(\mathbf{k}) | \text{PW} \rangle$$

$$\langle \vec{k} + \vec{G} | \hat{H} | \vec{k} + \vec{G}' \rangle \xrightarrow{1} T = \frac{1}{2} |\vec{k} + \vec{G}|^2 \delta_{\vec{G}\vec{G}'}$$

cut off energy can be set here

$$\langle \vec{k} + \vec{G} | \hat{V}_{loc} | \vec{k} + \vec{G}' \rangle = \frac{1}{\#grids} \sum_i e^{-i(\vec{G}-\vec{G}') \cdot \vec{r}_i} V_{loc}(\vec{r}_i)$$

This is the potential coming from ground-state charge density so that it can be obtained from the LCAO calculation using OpenMX code. After reading the local potential from the output cube file, we just need to perform the fast Fourier transformation.

$V_{non-local}$

Since we will focus on the collinear calculations first, the $j=l\pm 1/2$ can be averaged. The detail will be discussed on next slide.

Hamiltonian in PW-only basis

$$\langle \text{PW} | \mathbf{H}(\mathbf{k}) | \text{PW} \rangle$$

$$\langle \vec{k} + \vec{G} | \hat{V}_{non-local} | \vec{k} + \vec{G}' \rangle = \sum_{l,m} \langle \vec{k} + \vec{G} | Y_{lm} \bar{V}_{NL}^l(\vec{r}) \rangle \text{sign}(l) \langle Y_{lm} \bar{V}_{NL}^l(\vec{r}) | \vec{k} + \vec{G}' \rangle$$

$$\bar{V}_{NL}^l(r) = \frac{1}{2l+1} (l V_{l,l-\frac{1}{2}}(r) + (l+1) V_{l,l+\frac{1}{2}}(r))$$

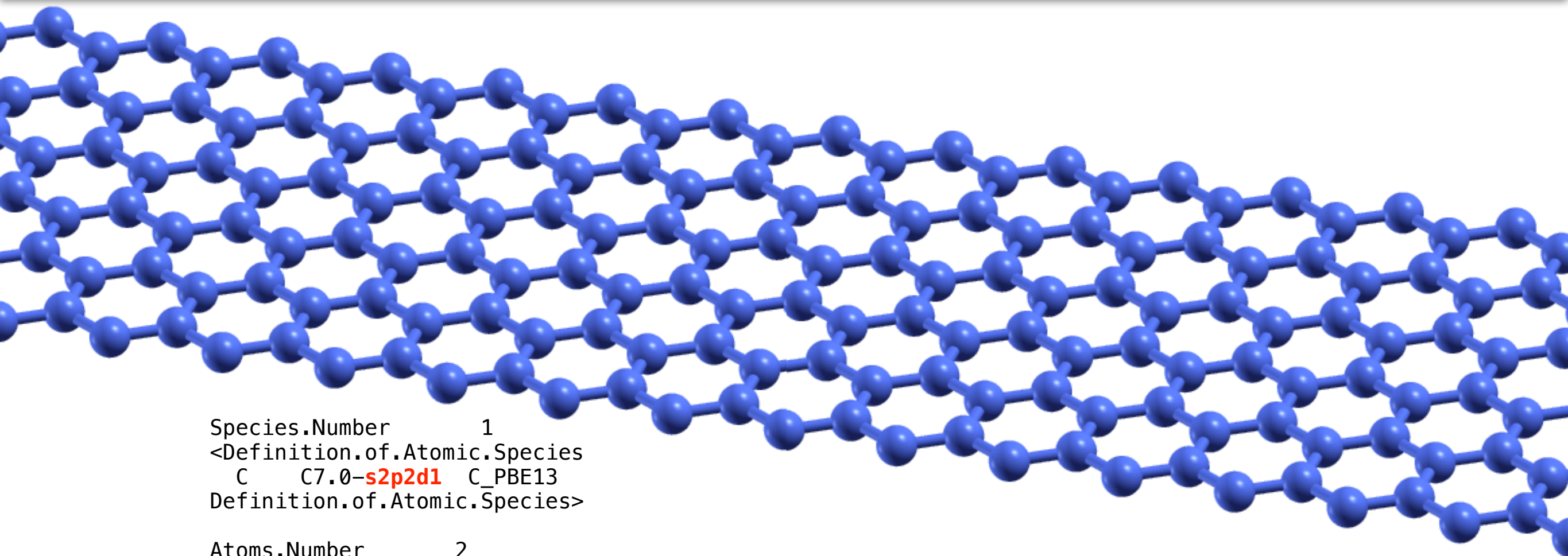
$$\langle \vec{k} + \vec{G} | \hat{V}_{non-local}^{Ion} | \vec{k} + \vec{G}' \rangle = \frac{(4\pi)^2}{v}$$

$$\sum_l \int dr r^2 (-i)^l j_l(|\vec{k} + \vec{G}|r) \bar{V}_{NL}^l(\tilde{r}) \int dr' r'^2 (i)^l j_l(|\vec{k} + \vec{G}'|r') \bar{V}_{NL}^l(\tilde{r}') \sum_{m=-l}^l Y_{lm}(\vec{k} + \vec{G}) Y_{lm}^*(\vec{k} + \vec{G}')$$

$$\langle \vec{k} + \vec{G} | \hat{V}_{non-local} | \vec{k} + \vec{G}' \rangle = \sum_{Ion} e^{-i(\vec{G}-\vec{G}') \cdot \vec{r}_{Ion}} \langle \vec{k} + \vec{G} | \hat{V}_{non-local}^{Ion} | \vec{k} + \vec{G}' \rangle$$

Example of PW-only case

Graphene



```
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  C      C7.0-s2p2d1  C_PBE13
Definition.of.Atomic.Species>
```

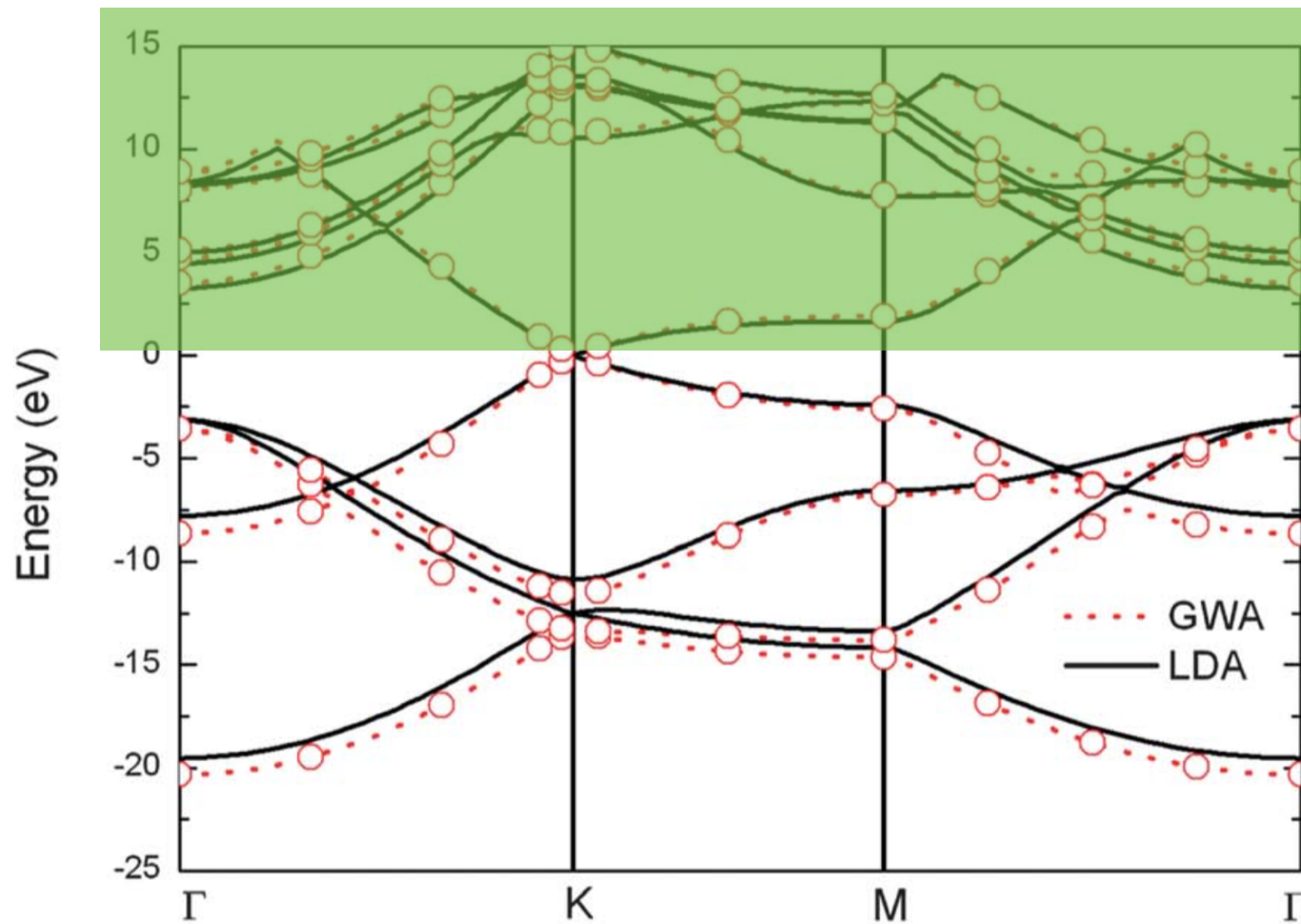
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Atoms.SpeciesAndCoordinates>
```

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Atoms.UnitVectors.Unit  AU
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  0.000000000000000      0.000000000000000      18.897259885789232
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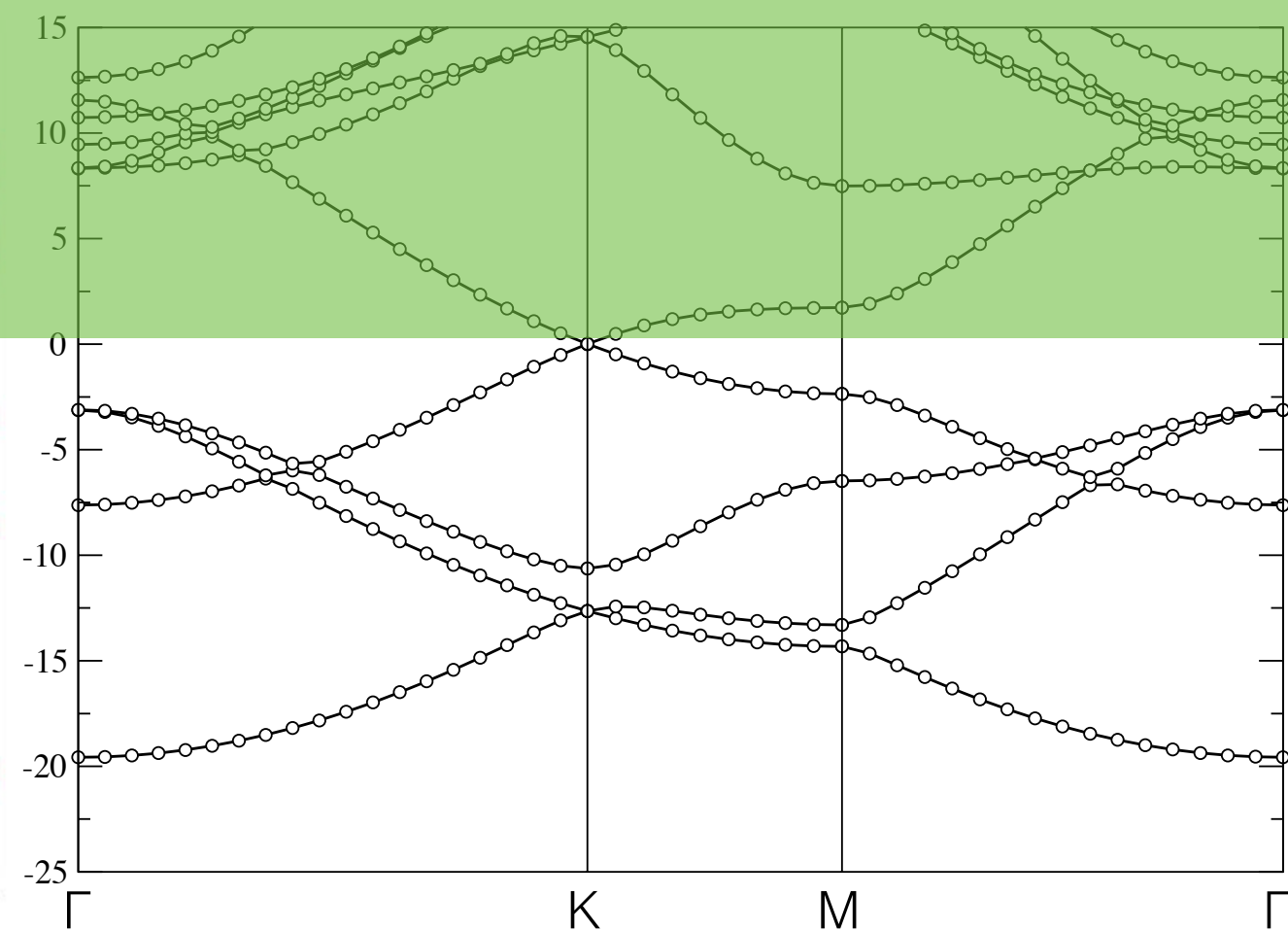
```
scf.XcType          GGA-PBE          # LDA|LSDA-CA|LSDA-PW|GGA-PBE
scf.SpinPolarization Off             # On|Off
scf.energycutoff     200.0            # default=150 (Ry)
scf.Kgrid            12 12 1         # means n1 x n2 x n3
scf.ProExpn.VNA      Off
```


Graphene

PW basis using ABINIT



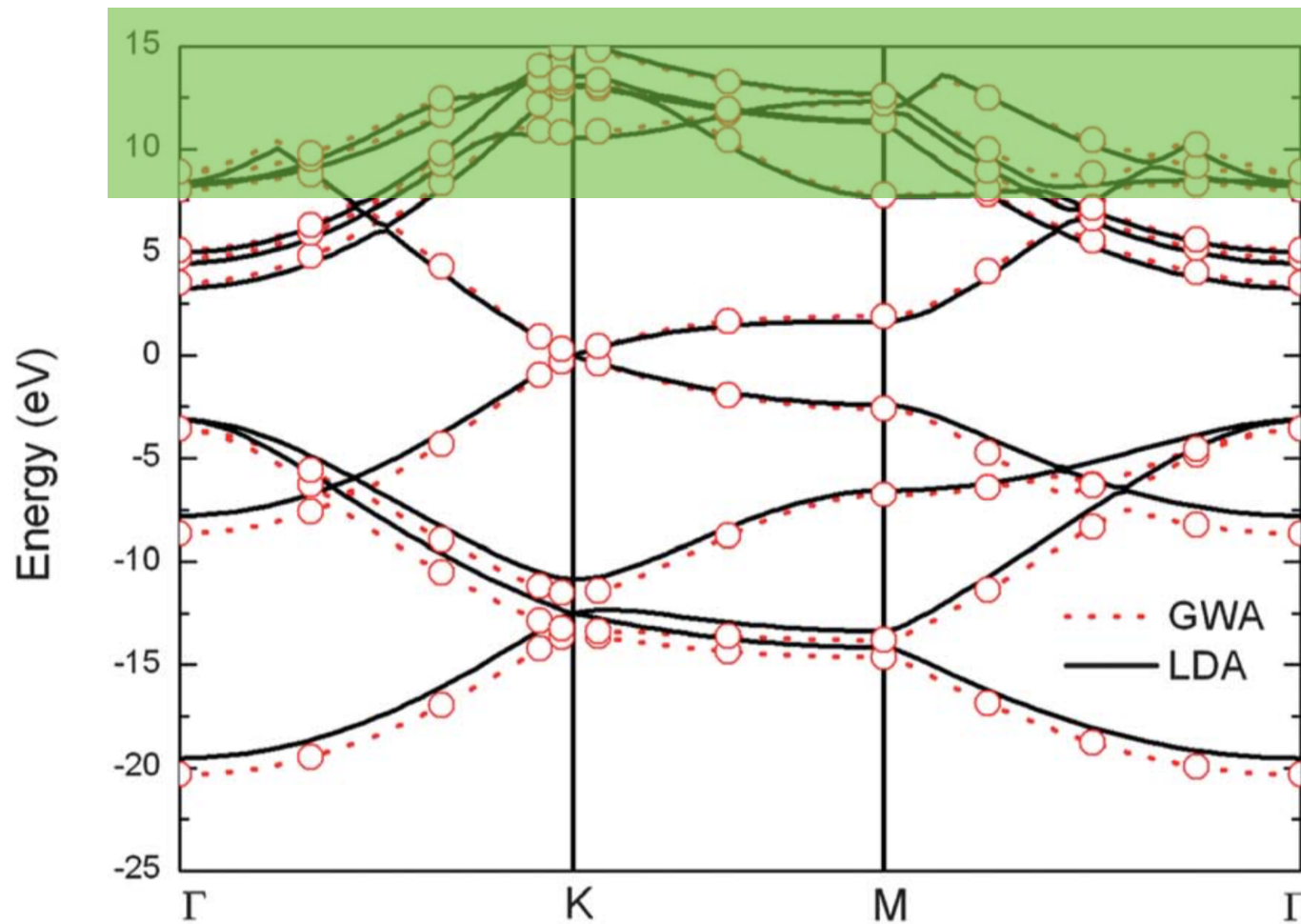
LCAO basis using OpenMX
C7.0-s2p2d1 GGA-PBE



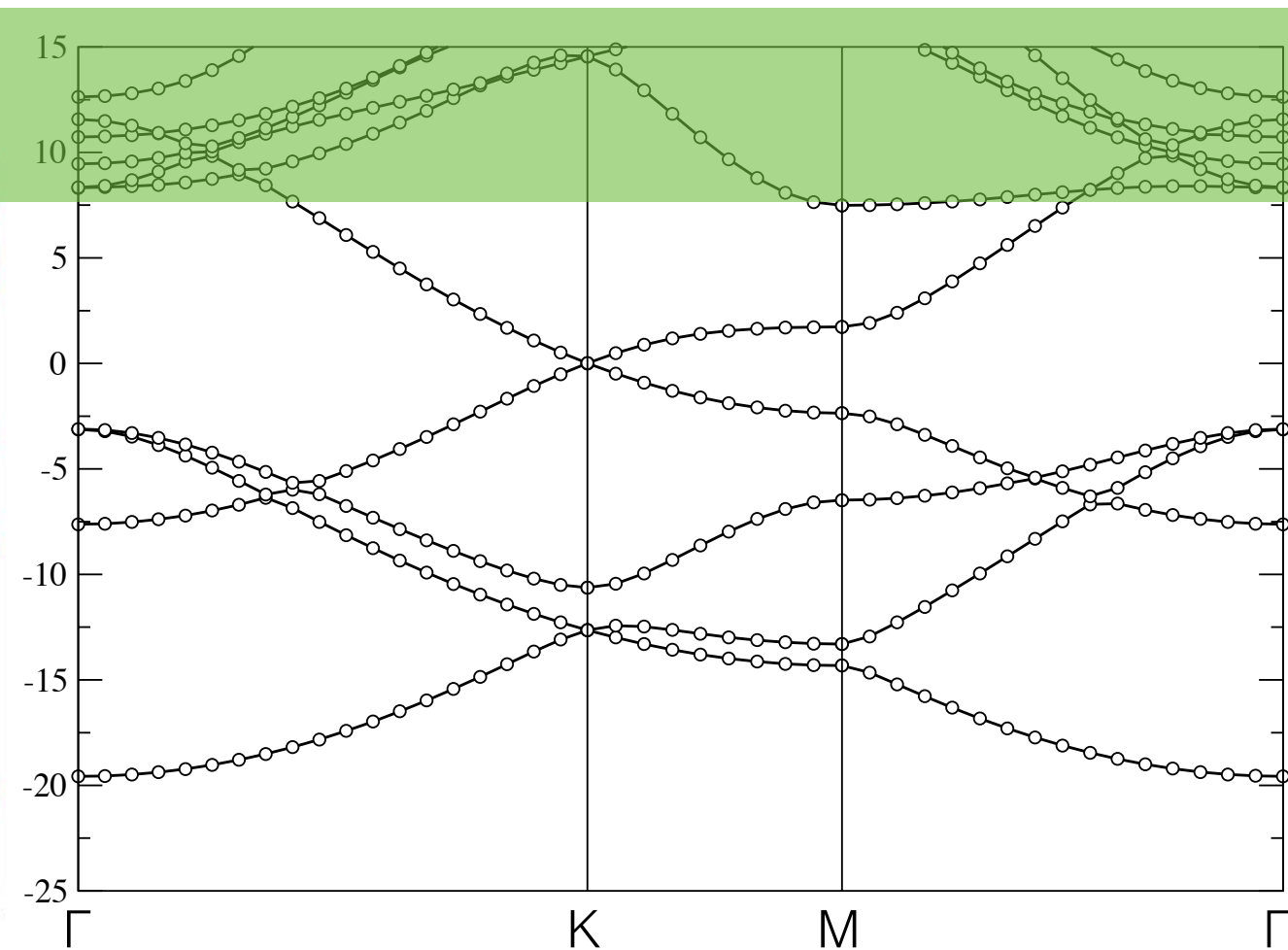
Tie-Yu Lü *et al.*, J. Mater. Chem. **22**, 10062 (2012).

Graphene

PW basis using ABINIT



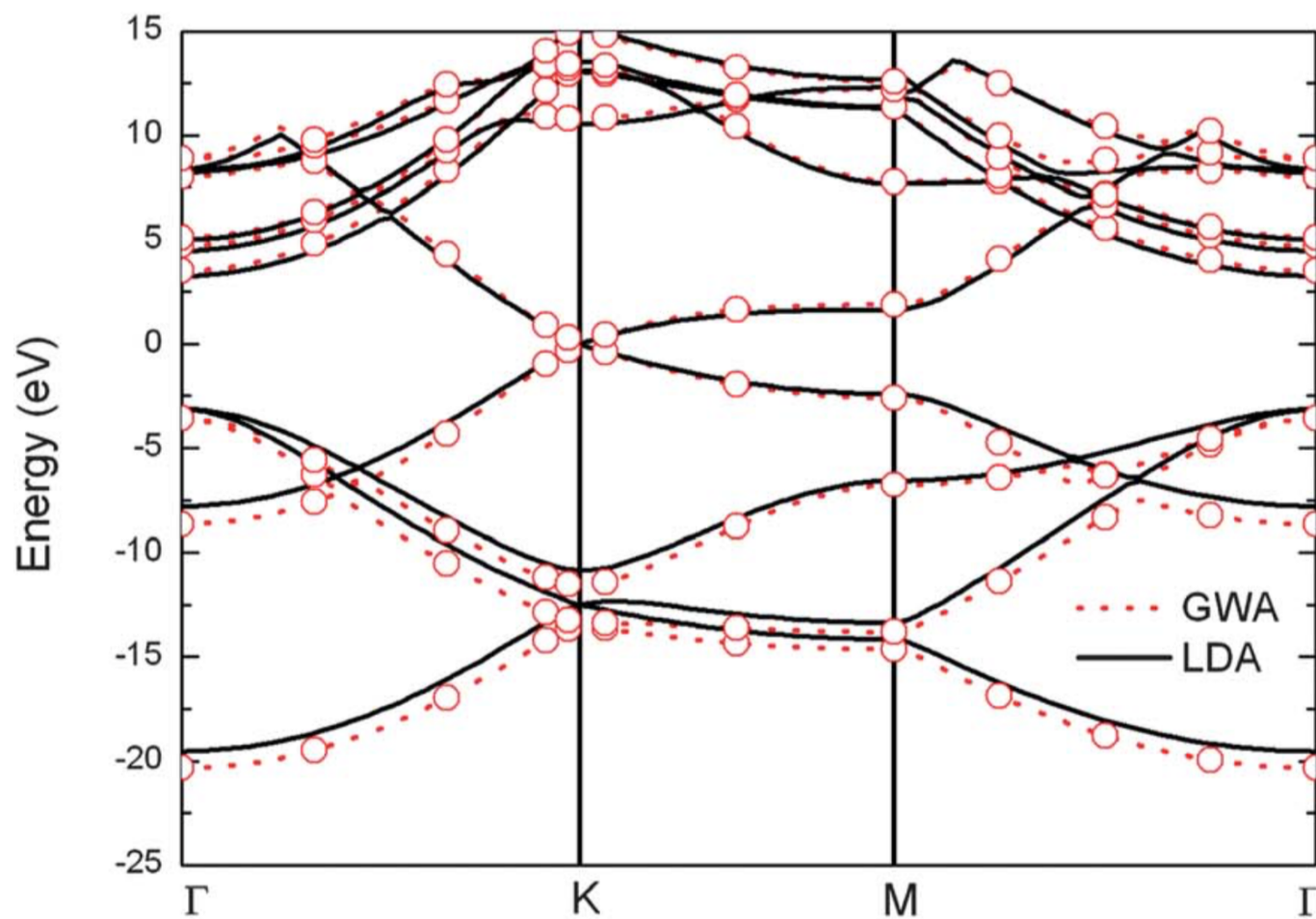
LCAO basis using OpenMX
C7.0-s2p2d1 GGA-PBE



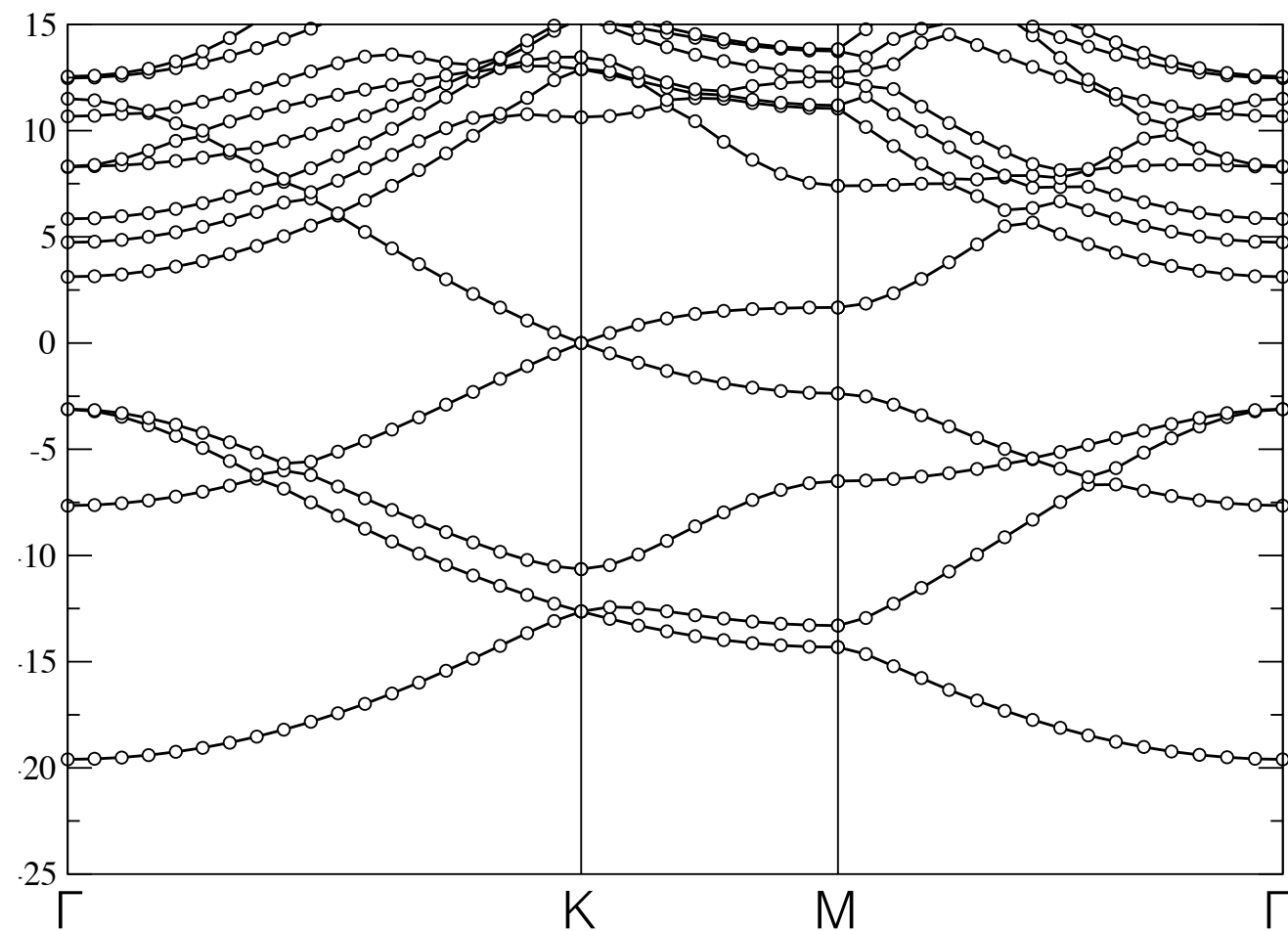
Tie-Yu Lü *et al.*, J. Mater. Chem. **22**, 10062 (2012).

Graphene

PW basis using ABINIT



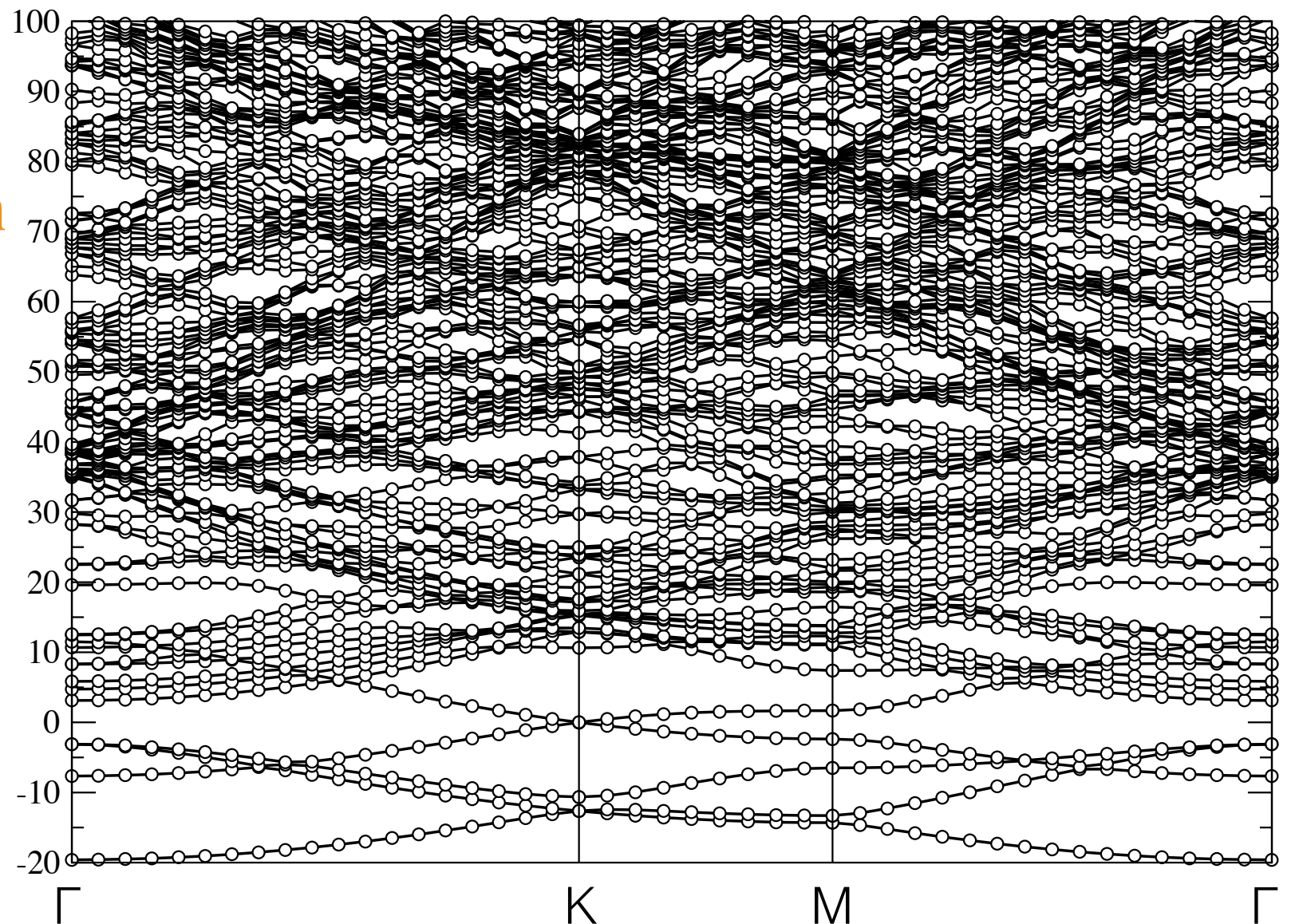
OpenMX
C7.0-s2p2d1 GGA-PBE



- The band structure is re-calculated using PW basis with cut-off energy of 30 Ha.

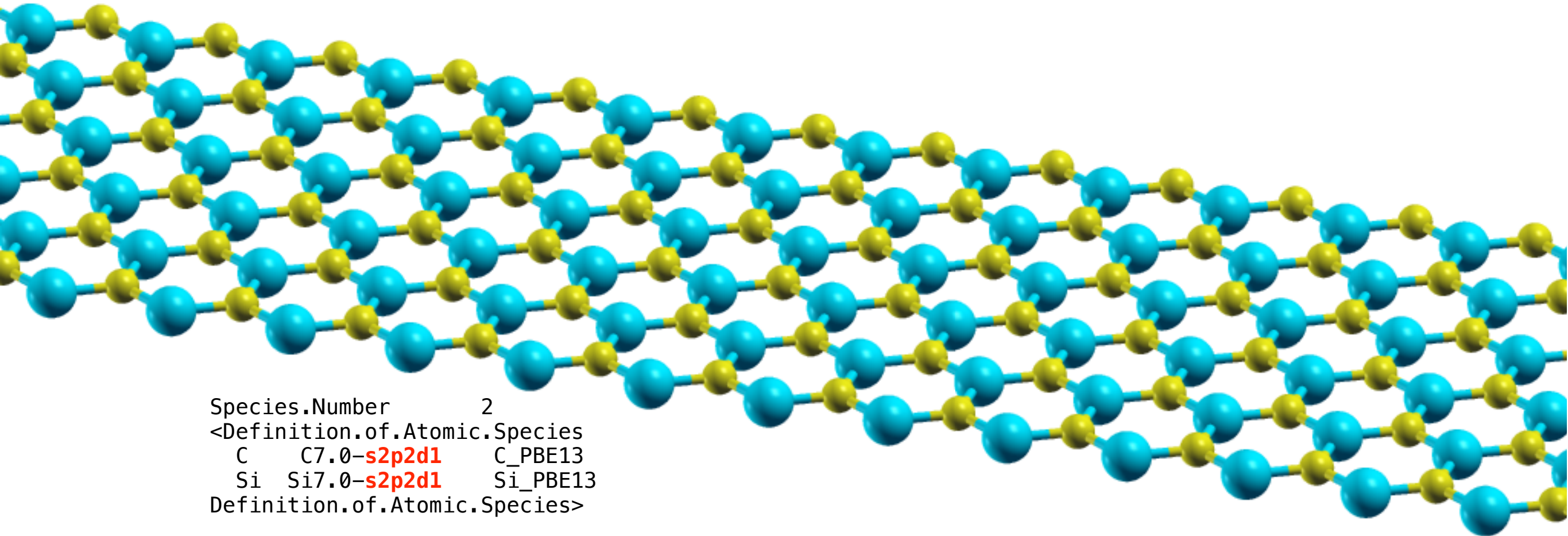
Graphene

Band structure using PW basis constructed from LCAO charge density with C7.0-s2p2d1 and the PW cut-off energy is 30 Ha.



- In principle, we can reproduce complete bands for a wide energy window using large enough cut-off energy as long as the ground-state charge density described by the LCAO basis is good enough.

SiC



```
Species.Number      2
<Definition.of.Atomic.Species
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  Si   Si7.0-s2p2d1    Si_PBE13
Definition.of.Atomic.Species>
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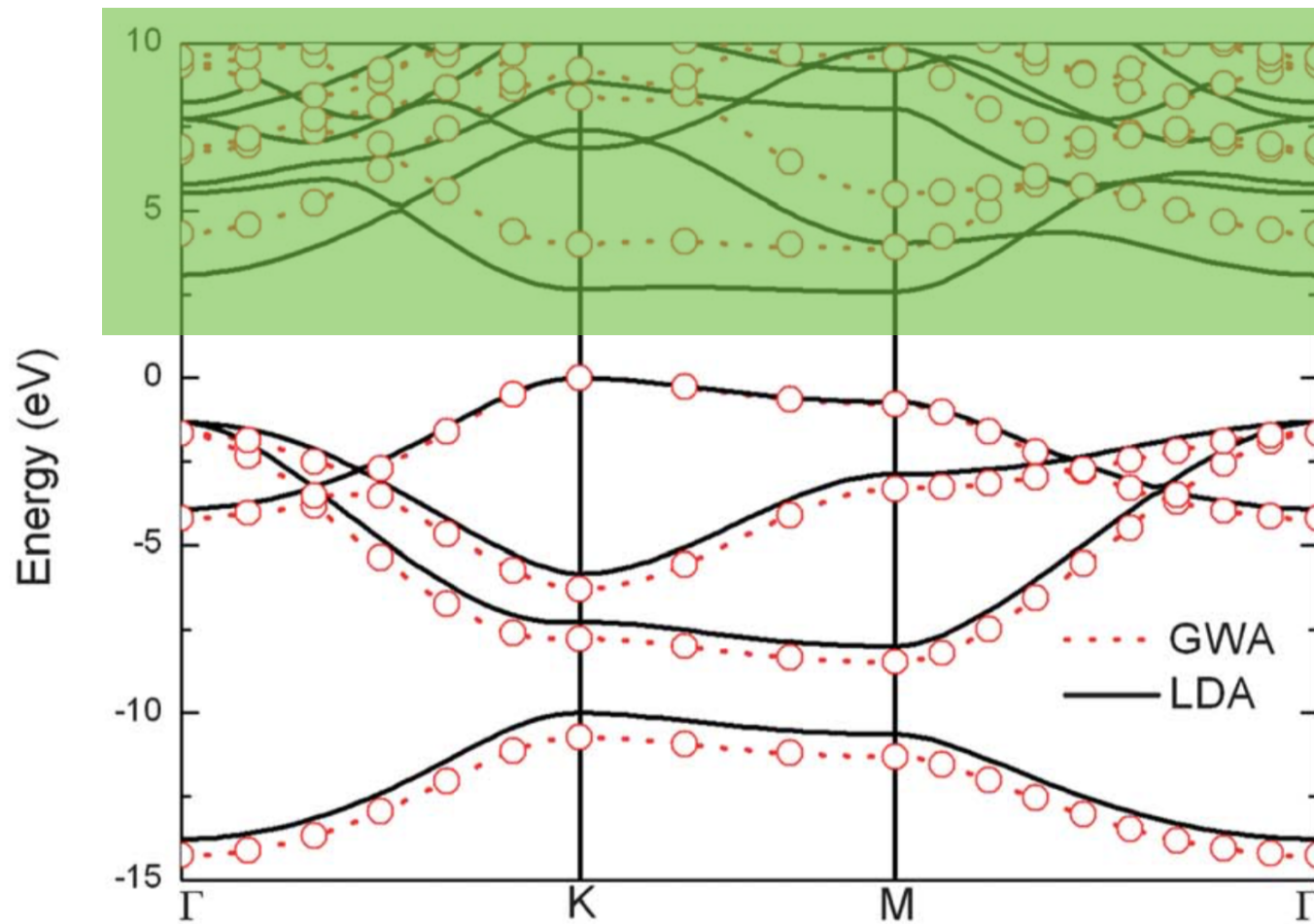
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Atoms.SpeciesAndCoordinates.Unit  FRAC # Ang|AU
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  1 C    0.33333333  0.66666666  0.50000000  2 2
  2 Si   0.66666666  0.33333333  0.50000000  2 2
Atoms.SpeciesAndCoordinates>
```

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Atoms.UnitVectors.Unit  AU
<Atoms.UnitVectors
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 -2.899784529474358  5.022574135835534  0.0000000000000000
  0.0000000000000000  0.0000000000000000  18.897259885789232
Atoms.UnitVectors>
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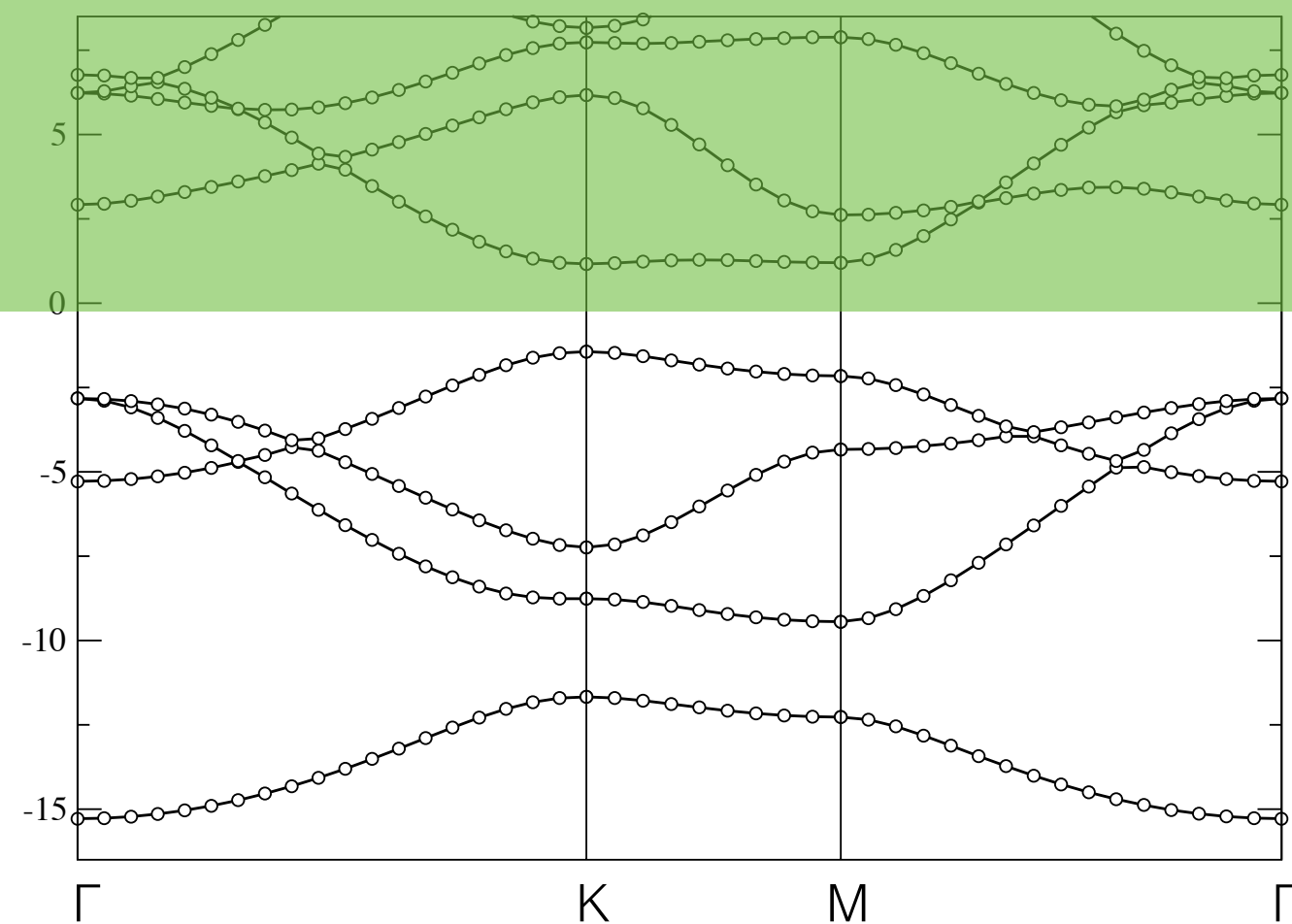
```
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scf.SpinPolarization Off             # On|Off
scf.energycutoff     200.0            # default=150 (Ry)
scf.Kgrid            12 12 1         # means n1 x n2 x n3
scf.ProExpn.VNA      Off
```

SiC

PW basis using ABINIT



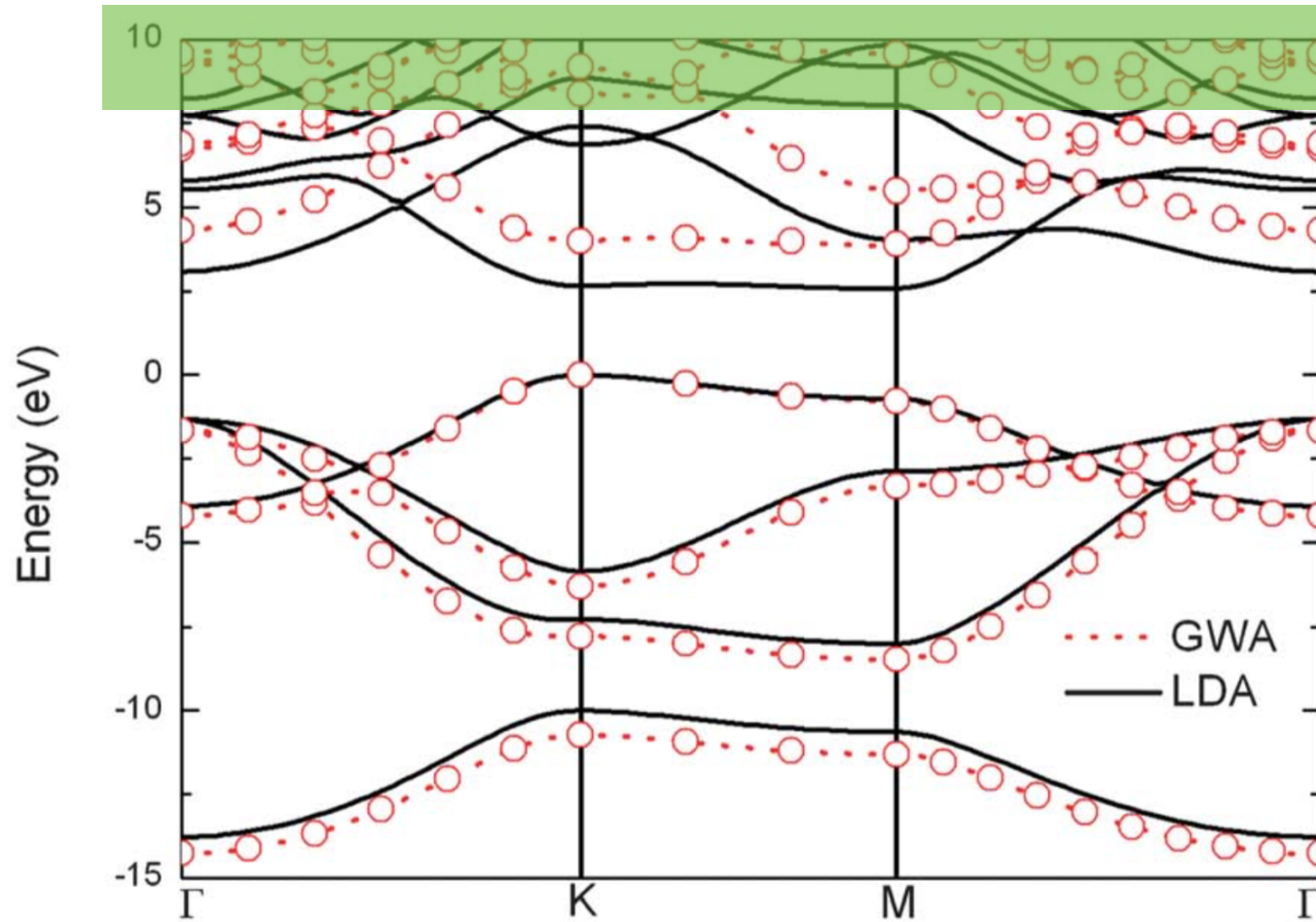
LCAO basis using OpenMX Si(C)7.0-s2p2d1 GGA-PBE



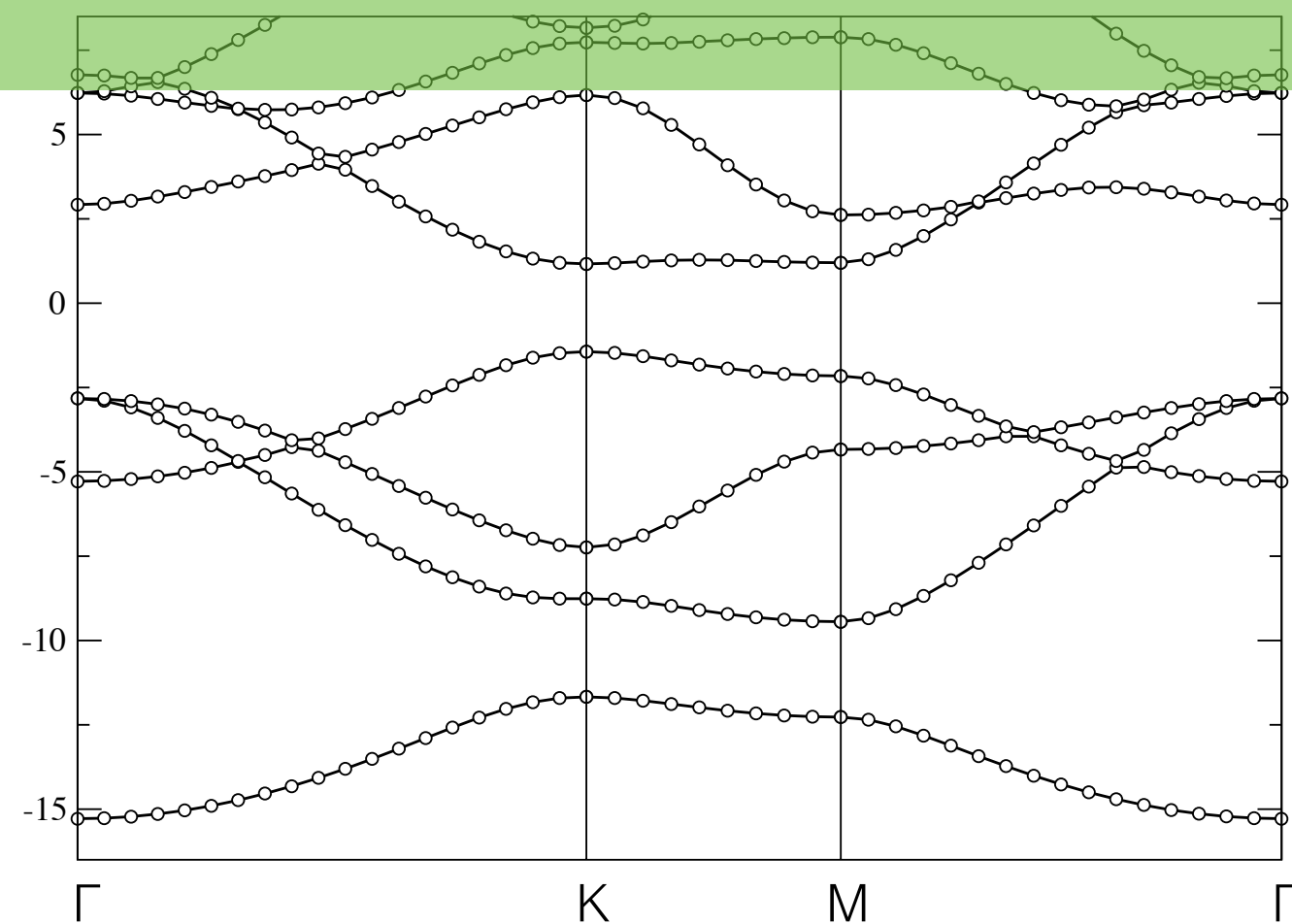
Tie-Yu Lü *et al.*, J. Mater. Chem. **22**, 10062 (2012).

SiC

PW basis using ABINIT



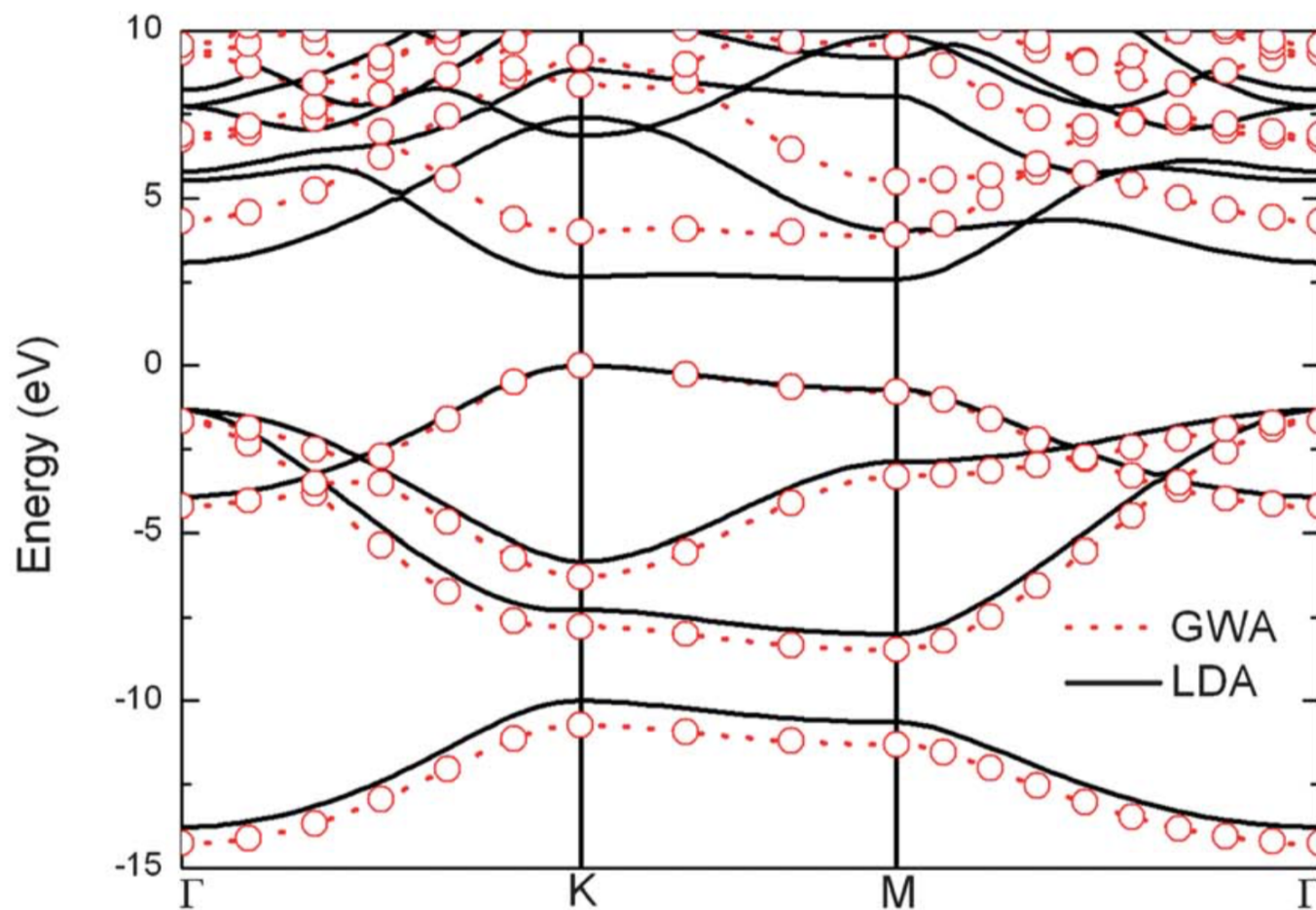
LCAO basis using OpenMX
Si(C)7.0-s2p2d1 GGA-PBE



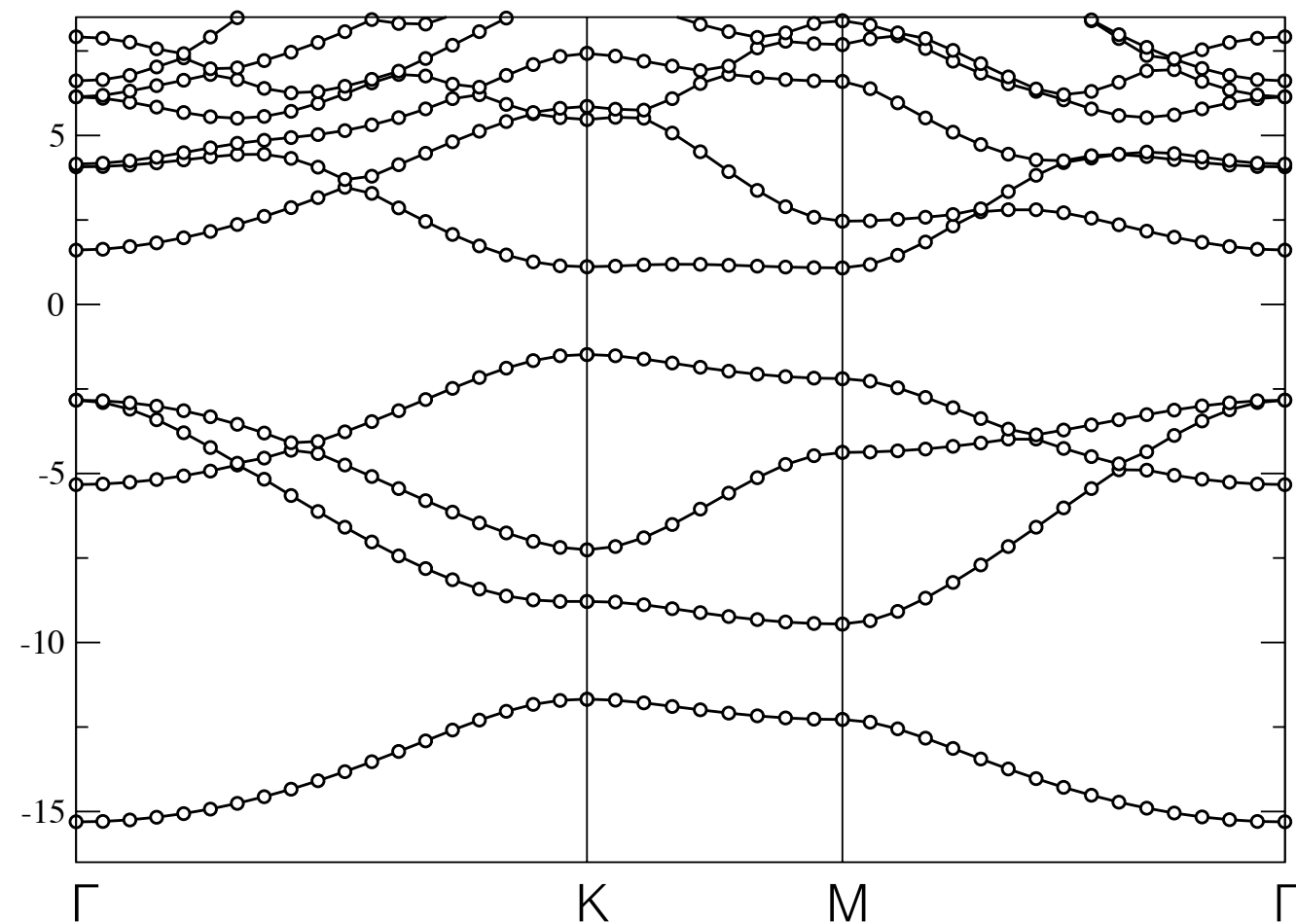
Tie-Yu Lü *et al.*, J. Mater. Chem. **22**, 10062 (2012).

Graphene

PW basis using ABINIT



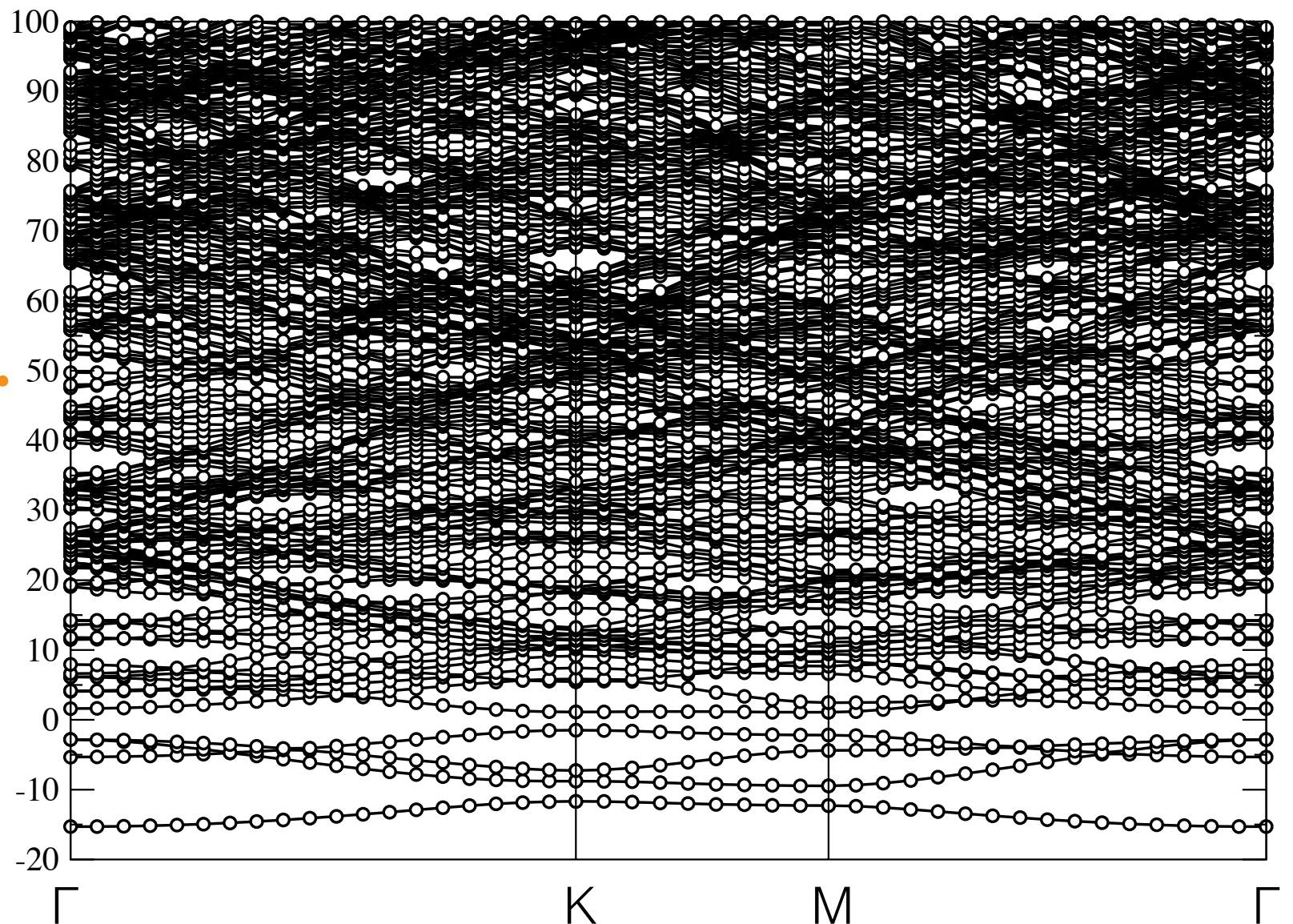
OpenMX Si(C)7.0-s2p2d1 GGA-PBE



- The band structure is re-calculated using PW basis with cut-off energy of 30 Ha.

SiC

Band structure using PW basis constructed from LCAO charge density with Si(C)7.0-s2p2d1 and the PW cut-off energy is 30 Ha.



- In principle, we can reproduce complete bands for a wide energy window using large enough cut-off energy as long as the ground-state charge density described by the LCAO basis is good enough.

Summary

- To study excited-state properties, which can be probed and measured by experiments, we need to expand the Hilbert space of the Hamiltonian represented by the LCAO (PAO) basis.
- Without updating ground-state charge density, changing basis from LCAOs to PWs can directly reproduce the (unoccupied) PW bands that are usually obtained by performing self-consistent calculations in the PW basis from beginning. We can get unoccupied band efficiently via a short cut, that is, using charge density!
- Next step is to code the $\langle \text{LCAO} | H | \text{PW} \rangle$. In that case, probably we only need less number of PWs. Then we will move on to code response functions and to work on the non-collinear case.
- For PW-only case, one can already follow all existing formulae to study excitations.