Band Structure Models from Density Functional Theory

01/28/2022
Downfolding school, discussion 1

Plan for the downfolding school

Time: Friday 2pm, once every two weeks

Zoom link: https://illinois.zoom.us/j/9706397652?pwd=eElJOS9CeUVwZmhxekxXZzcrSnRHUT09

(Meeting ID: 970 639 7652
Password: 314678)

Github repo: https://github.com/WagnerGroup/downfolding_school

Plan for the spring semester

Band structure using DFT (01/28)

1. Meaning of KS orbitals and energies, DFT: Kohn-Sham Hamiltonian.
2. The band Hamiltonian
3. Non-self-consistent calculation using the KS Hamiltonian
   Exercise: H chain (H2 with PBC), convergence of non-self-consistent band structure as we use denser kmesh

Localizing wave functions (02/18, 03/04, 03/25)

4. Localization strategies: Wannier. Exercise: in H chain, make localized orbitals
5. Tight-binding models derived from localized representations. Exercise: H chain, obtain t(r).
6. Band interpolation using localized representations (Wannier interpolation).
   Exercise: t convergence with the kmesh -> band structure convergence with kmesh.
7. Transferability. Exercise: obtain the t for H chain and t for a square of H atoms, check if they are equal.

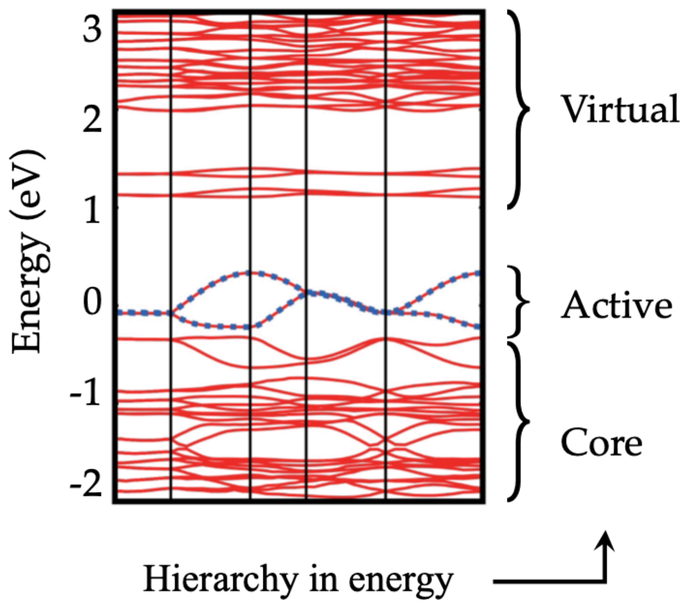
Adding interactions to band structure models (04/08, 04/22, 05/06)

8. Bare interactions
9. RPA
10. cRPA
11. Double-counting problem
12. (optional) *GW*+RPA

We will start the discussions on density-matrix downfolding in the summer.

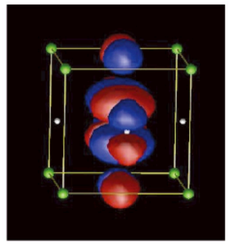
The general procedure for downfolding from DFT

1) Use DFT to identify energy spaces

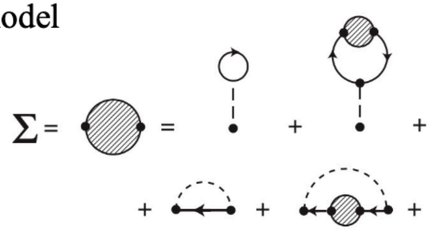


2) Downfold to "active" space

a) Use Wannier functions to parameterize model over the active space

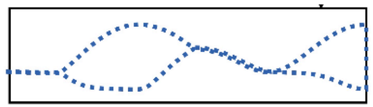


b) Use cRPA+GW to dress low-energy model



3) Solve the model

Solve the resulting effective model using a high-accuracy solver such as DMRG, QMC, DMFT, etc.



Randy Sawaya's PhD dissertation

The general procedure for downfolding from DFT

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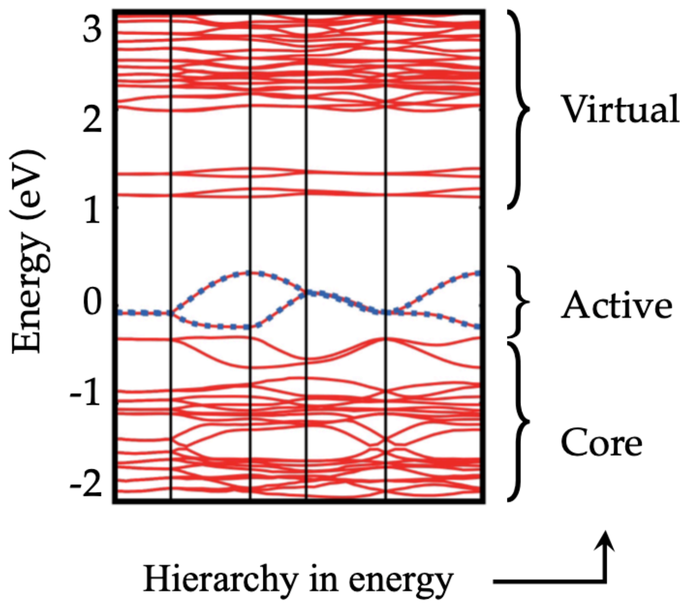

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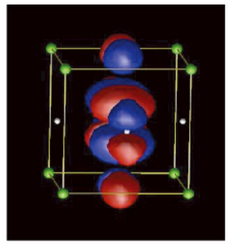

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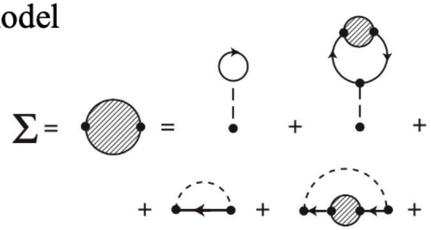

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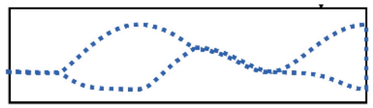


What we are going to focus on today:
Obtain the band structure model from DFT

The many-body Hamiltonian and first-principles

With Born-Oppenheimer approximation:

$$H_{ab} = \underbrace{-\frac{1}{2}\sum_i \nabla_i^2}_{\text{kinetic } \widehat{T}_{\mathrm{e}}} + \underbrace{\frac{1}{2}\sum_{i,j\neq i} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}}_{\text{e-e interaction } \widehat{U}_{\mathrm{ee}}} + \underbrace{\sum_{iI} V_{\mathrm{ext}}\ (\mathbf{r}_i - \mathbf{a}_I)}_{\text{e-i interaction } \widehat{U}_{\mathrm{ei}}}$$

Hartree-Fock

Ansatz:
single Slater determinant of all the occupied orbitals

Hamiltonian:
exact many-body Hamiltonian

Density functional theory

Ansatz:
Exact for non-interacting system.

Hamiltonian:
A fictitious non-interacting system.

Hohenberg-Kohn theorems

$$H_{ab} = \underbrace{-\frac{1}{2}\sum_i \nabla_i^2}_{\text{kinetic } \widehat{T}_{\mathrm{e}}} + \underbrace{\frac{1}{2}\sum_{i,j\neq i}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}}_{\text{e-e interaction } \widehat{U}_{\mathrm{ee}}} + \underbrace{\sum_{iI} V_{\mathrm{ext}}\ (\mathbf{r}_i - \mathbf{a}_I)}_{\text{e-i interaction } \widehat{U}_{\mathrm{ei}}}$$

(Fixed ion positions)

HK Theorem 1:
For any system of interacting particles in an external potential $V_{\mathrm{ext}}(\mathbf{r})$, the potential is determined uniquely, except for a constant, by the ground state particle density $n_0(\mathbf{r})$.

Corollary 1:
All properties (ground and excited state many-body wave functions) of the system are completely determined given only the ground state density.

HK Theorem 2:
A universal functional for the energy $E[n]$ in terms of the density $n(\mathbf{r})$ can be defined, valid for any external potential. For any particular $V_{\mathrm{ext}}(\mathbf{r})$, the exact ground state energy of the system is the global minimum value of this functional, and the corresponding density is the exact ground state density $n_0(\mathbf{r})$.

Corollary 2:
The functional $E[n]$ alone is sufficient to determine the exact ground state energy and density.

The ground state density determines external potential

The ground state density can be found variationally.

$$V_{\mathrm{ext}}(\mathbf{r}) \xleftarrow{\text{HK}} n_0(\mathbf{r})$$

solve SE $\searrow$ $\Psi_i(\{\mathbf{r}\})$ $\nearrow$ get density from the ground state

Formulations of the energy functional

Hohenberg-Kohn functional

$F_{\mathrm{HK}}[n(\mathbf{r})] = \left\langle \Psi_0 \left| \widehat{T} + \widehat{U}_{\mathrm{ee}} \right| \Psi_0 \right\rangle$ since the ground state wave function is a functional of the density.

$$\begin{aligned} E_{\mathrm{HK}}[n] =& T[n] + E_{\mathrm{int}}[n] + \int V_{\mathrm{ext}}(\mathbf{r}) n(\mathbf{r}) \mathrm{d}^3 r \\ =& F_{\mathrm{HK}}[n] + \int V_{\mathrm{ext}}(\mathbf{r}) n(\mathbf{r}) \mathrm{d}^3 r \end{aligned}$$

Levy-Lieb functional

$$F_{\mathrm{LL}}[n] = \min_{\Psi \to n(\mathbf{r})} \left\langle \Psi | \widehat{T} + \widehat{U}_{\mathrm{ee}} | \Psi \right\rangle$$

By minimizing energy for all the wave functions Ψ that have the same density $n(\mathbf{r})$, one can define a unique lowest energy for that density.

A functional can be defined for any density. By minimizing this functional one would find the exact density and energy of the true interacting many-body system.

The Kohn-Sham equations

Replace the original many-body problem by an auxiliary independent particle problem

Assumption:

The ground state density of the original interacting system is equal to that of some chosen non-interacting system.

Kohn-Sham equation:

$$\left\{-\frac{\nabla^2}{2}+v_{\mathrm{eff}}(\mathbf{r})\right\}\varphi_{i,s}(\mathbf{r})=\varepsilon_{i,s}\varphi_{i,s}(\mathbf{r})$$

$$v_{\mathrm{eff}}(\mathbf{r})=v_{\mathrm{ext}}(\mathbf{r})+\frac{1}{2}\int\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}'+v_{\mathrm{XC}}[n]$$

where $v_{\mathrm{XC}}[n]=\dfrac{\delta E_{\mathrm{XC}}[n]}{\delta n}$

The universal density functional:

KE of the non-int system

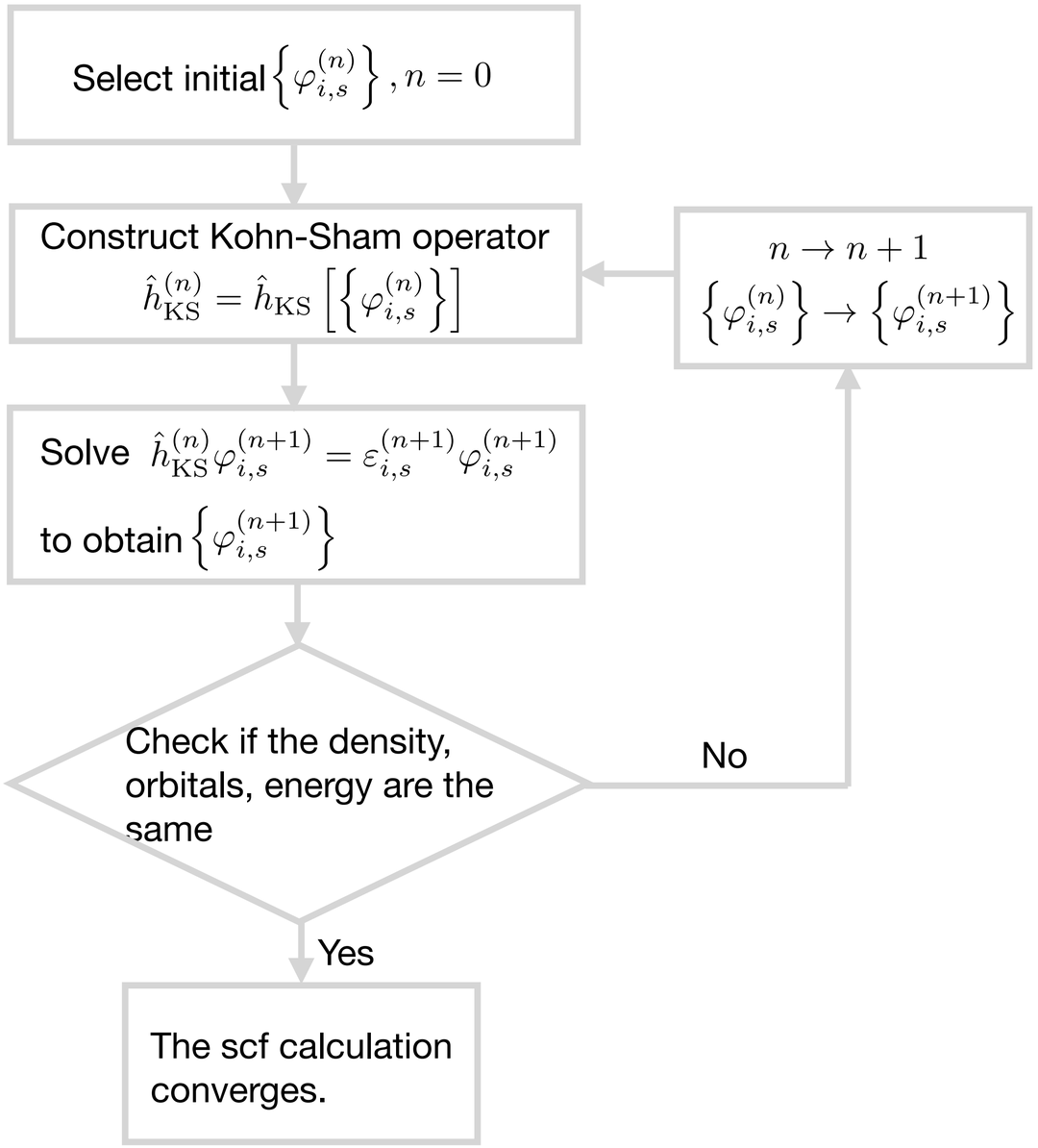
$$E_{\mathrm{KS}}[n]=T_{\mathrm{R}}[n]+\int n(\mathbf{r})v_{\mathrm{ext}}(\mathbf{r})\mathrm{d}\mathbf{r}+\frac{1}{2}\iint\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'+E_{\mathrm{XC}}[n]$$

Hartree term, introduce error by double-counting

The KS orbitals are a mathematical object constructed in order to render the problem more tractable and do not have physical meaning by themselves, but only in terms of the density:

$$n(\mathbf{r})=\sum_{s=1}^{2}\sum_{i=1}^{N_s}|\varphi_{i,s}(\mathbf{r})|^2$$

The self-consistent-field (scf) calculation



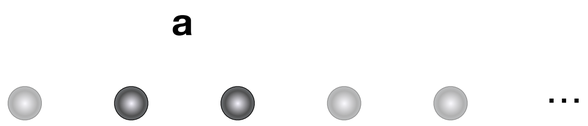
Self-consistent Kohn-Sham equation:

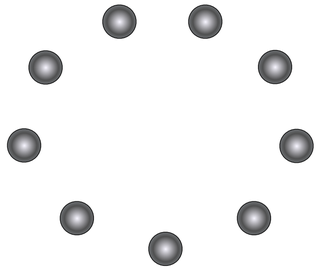
$$\hat{h}_{\mathrm{KS}}\varphi_{i,s}(\mathbf{r}) = \varepsilon_{i,s}\varphi_{i,s}(\mathbf{r})$$

$$\hat{h}_{\mathrm{KS}} = -\frac{\nabla^2}{2} + v_{\mathrm{ext}}(\mathbf{r}) + \frac{1}{2}\int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}' + v_{\mathrm{XC}}[n]$$

For a periodic system

Consider a long one-dimensional chain of equally spaced hydrogen atoms. Imagine wrapping them around to make a circle. When approaching TDL, this should be a good approximation.





Total number of unit cell = N

The periodicity of probability density and the periodic boundary condition enforce:

$$|\psi(\mathbf{r})|^2 = |\psi(\mathbf{r}+n\mathbf{a})|^2$$

$$\psi(\mathbf{r}) = \psi(\mathbf{r}+N\mathbf{a})$$

Thus $\psi(\mathbf{r}+n\mathbf{a}) = C^n(\mathbf{r})\psi(\mathbf{r})$ $\qquad C^N(\mathbf{r}) = 1$

One can show that $C(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}},\ \text{where } \mathbf{k} = \dfrac{2\pi\hat{\mathbf{a}}}{Na}$, and the allowed number of k's = total number of unit cell

For a non-interacting periodic system, we have **the Bloch theorem**:

The eigenvectors with a definite ***k*** can be written as

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{\mathbf{k}}(\mathbf{r})$$

where $u_{\mathbf{k}}(\mathbf{r})$ is periodic.

The Hamiltonian is block-diagonal in terms of ***k***, $\quad H = E_0 + \sum_{i,\sigma,\mathbf{k}} \epsilon^{\sigma}_{n\mathbf{k}} c^{\dagger}_{n\mathbf{k}\sigma} c_{n\mathbf{k}\sigma}$ $\qquad E = E_0 + \sum_{i,\sigma,\mathbf{k}} \epsilon^{\sigma}_{n\mathbf{k}} \left\langle c^{\dagger}_{n\mathbf{k}\sigma} c_{n\mathbf{k}\sigma} \right\rangle$

Example: H chain with PBC

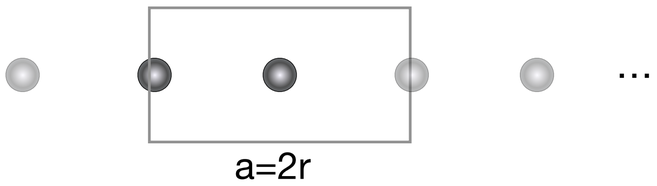
No effective core potential, the e-e interaction is the full Coulomb interaction

Basis for the expansion of wave functions: cc-pVDZ

```
H    S
    13.0100000        0.0196850
     1.9620000        0.1379770
     0.4446000        0.4781480
H    S
     0.1220000        1.0000000
H    P
     0.7270000        1.0000000
```

Total number of functions in the basis: (1+1+3)*2 = 10

Energy functional: PBE

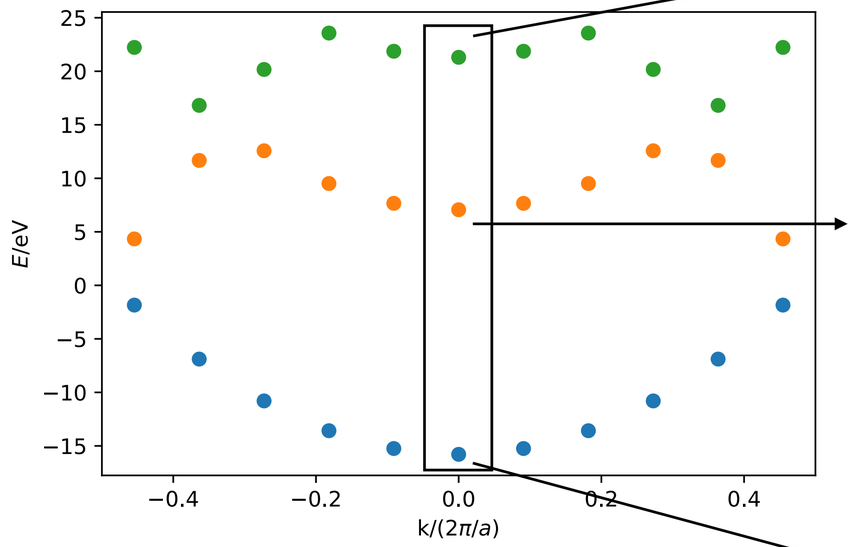


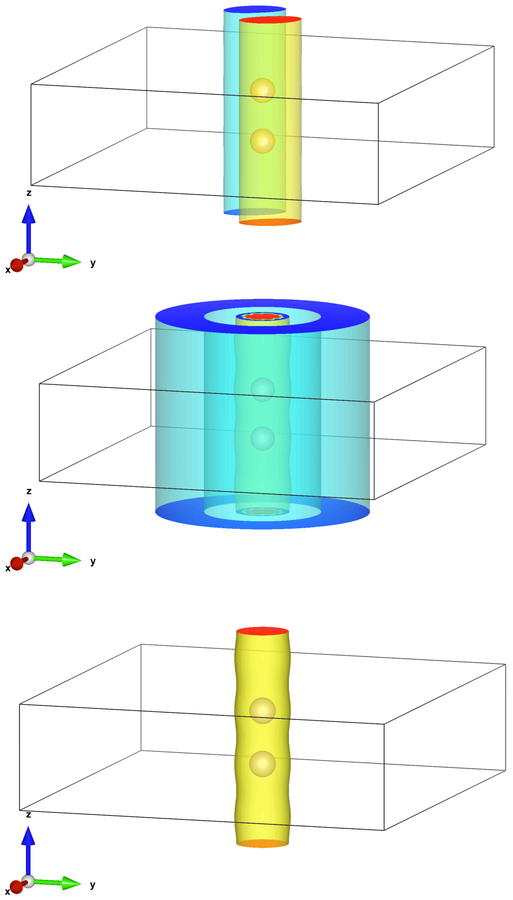
Take r=1.4 and 3.0 for example

KS eigenvectors and eigenvalues

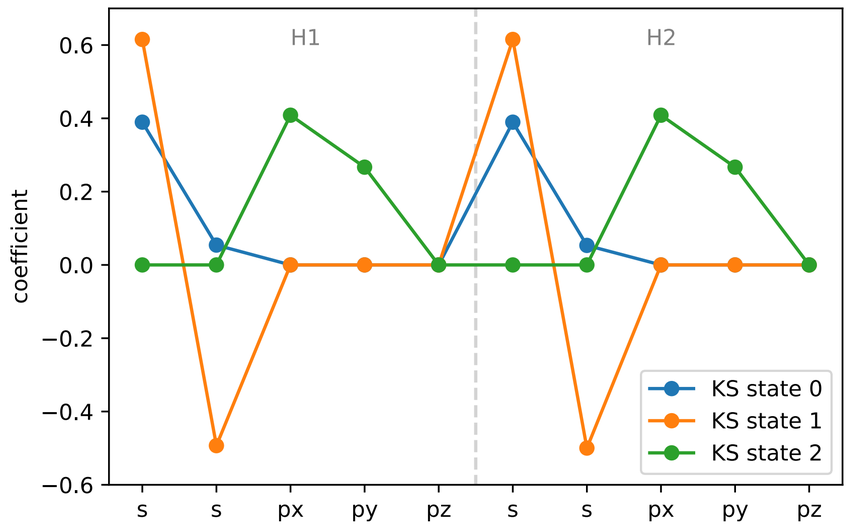
r=1.4

Eigenvalues solved from scf, with 11 kpoints sampled





Eigevectors at k=(0,0,0)

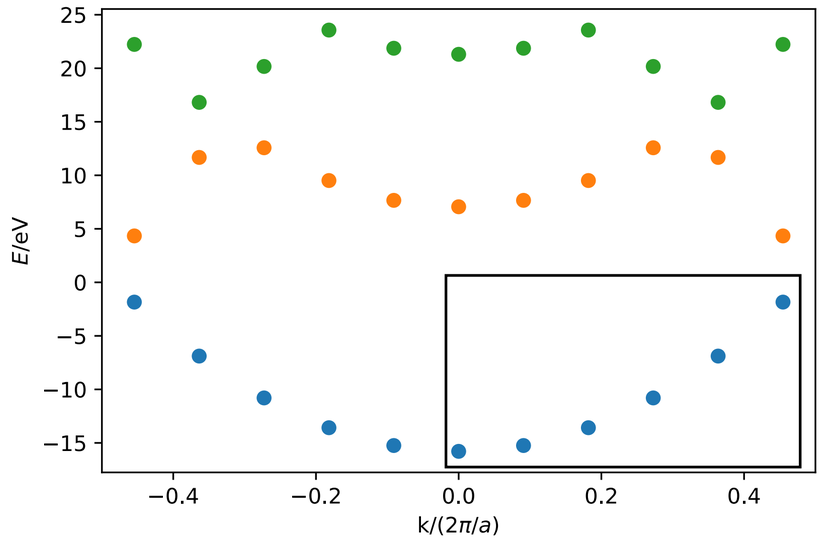


Recall that the kpoints used in scf corresponds to the system size, we really want the properties to be converged with respect to the number of kpoints!

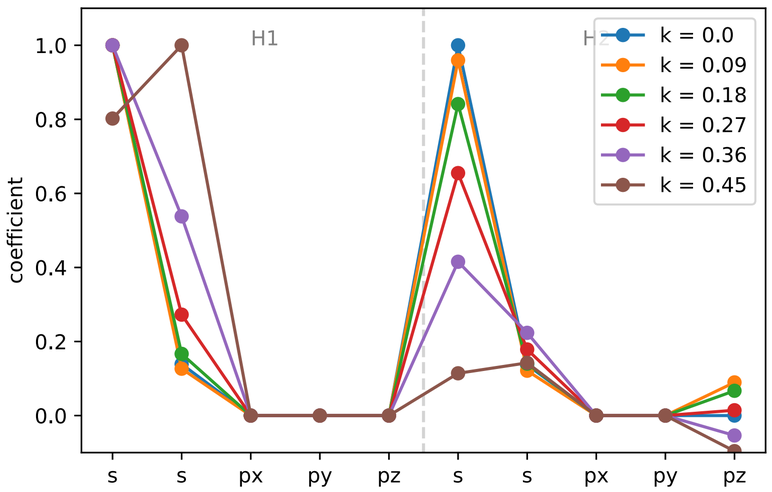
KS eigenvectors and eigenvalues

r=1.4

Eigenvalues solved from scf, with 11 kpoints sampled



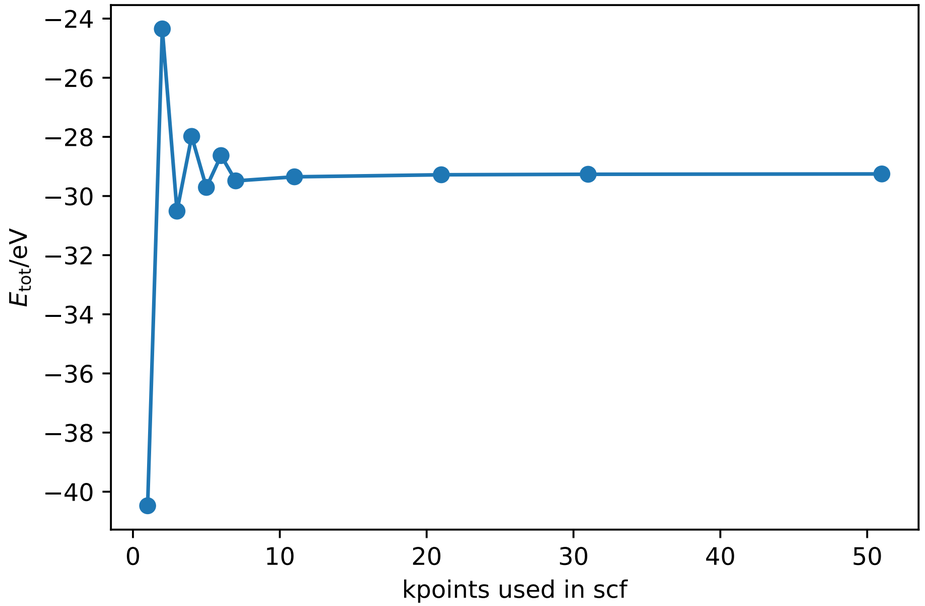
Real part



The convergence of properties with respect to the kmesh

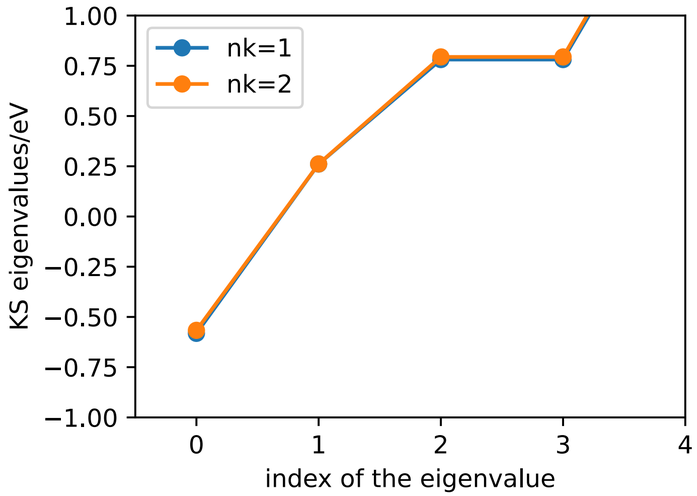
r=1.4

Total energy vs nk

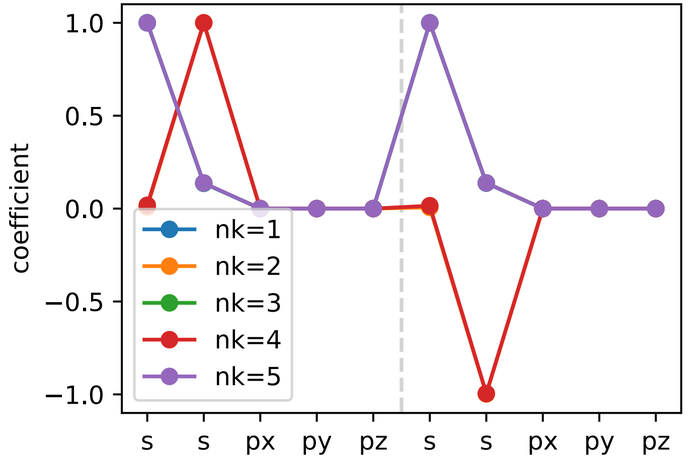


The eigenvalues converge much faster

KS eigenvalues at Gamma vs nk

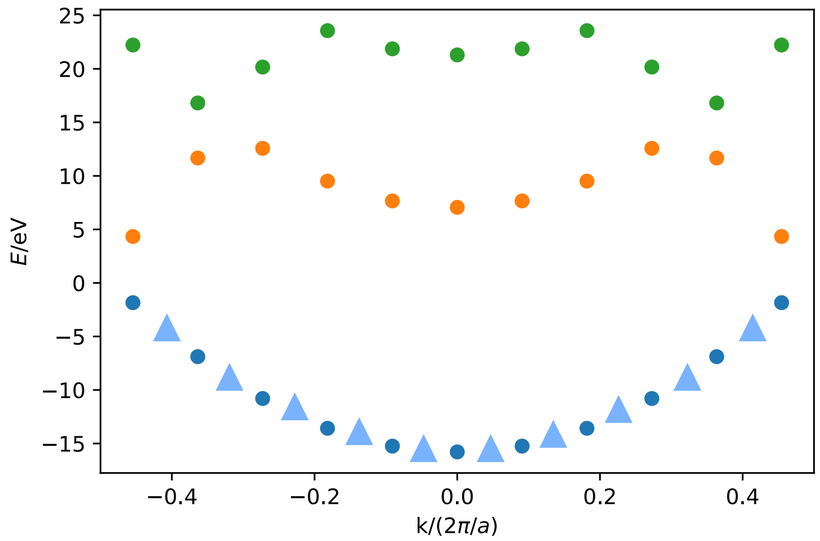


KS orbitals vs nk



Non-self-consistent calculations

To get the eigenvalues and eigenvectors on a denser k mesh, we can do nscf calculation.

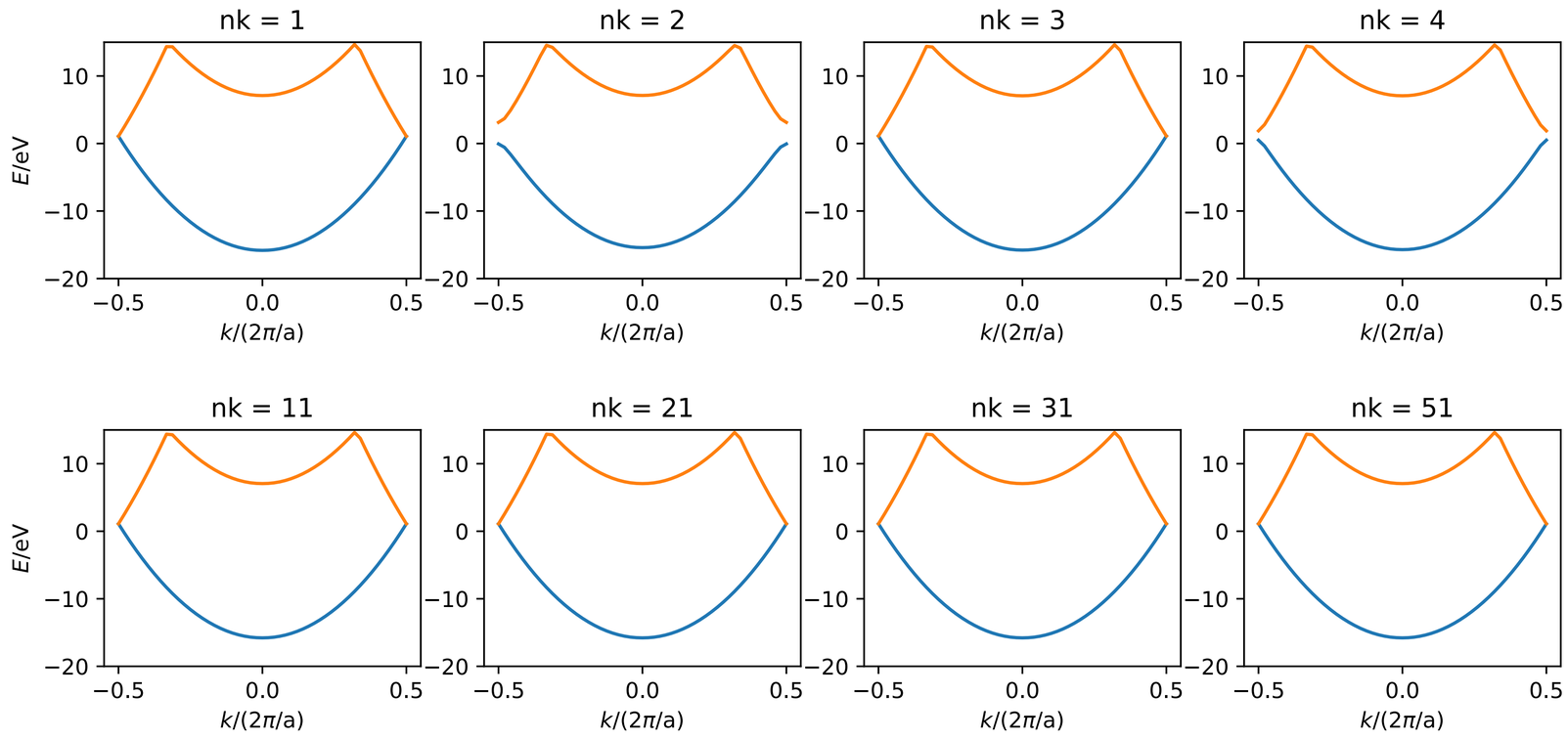


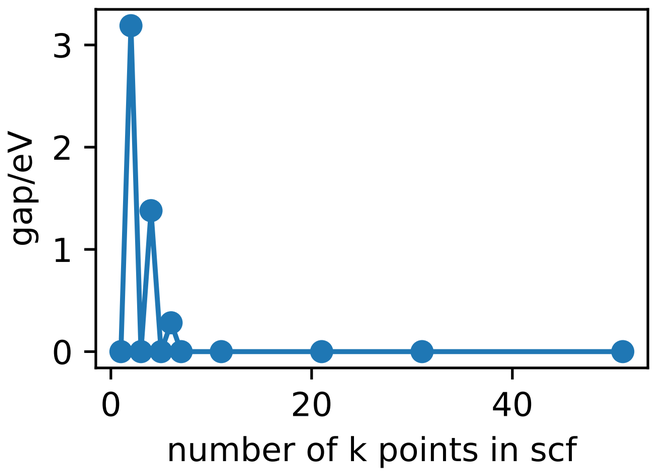
1. One quick way of getting the band structure:
   Interpolate to get the eigenvalues on some unsampled k point.

2. What do we usually do:
   Reconstruct the KS operator on a new k point, then solve the KS equation. Since there is no scf procedure, it is called nscf calculation.

Convergence of the non-self-consistent calculations with respect to the kmesh

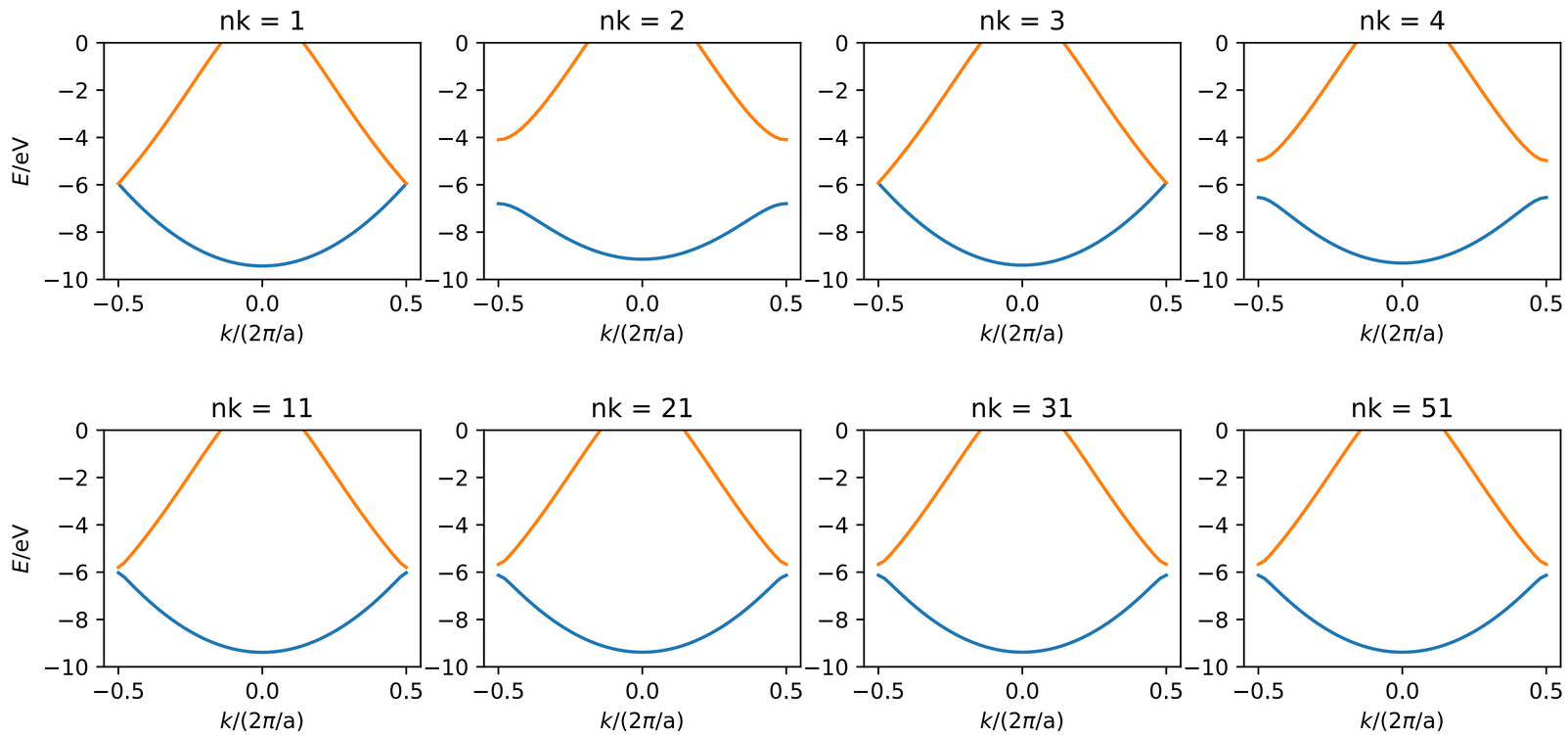
r=1.4, metallic

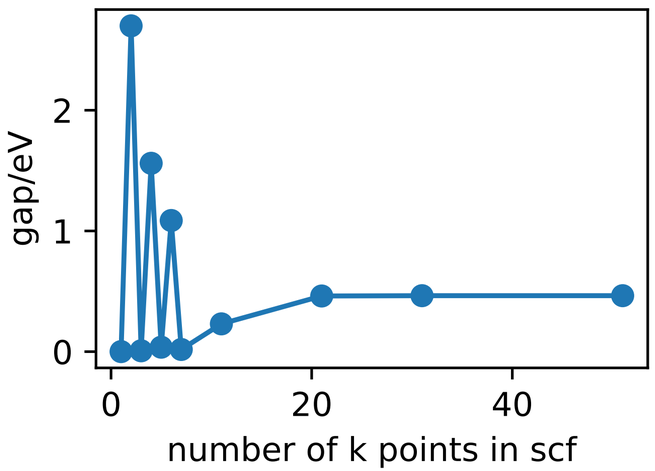




Convergence of the non-self-consistent calculations with respect to the kmesh

r=3.0, insulating





Summary

Band structure using DFT (01/28)

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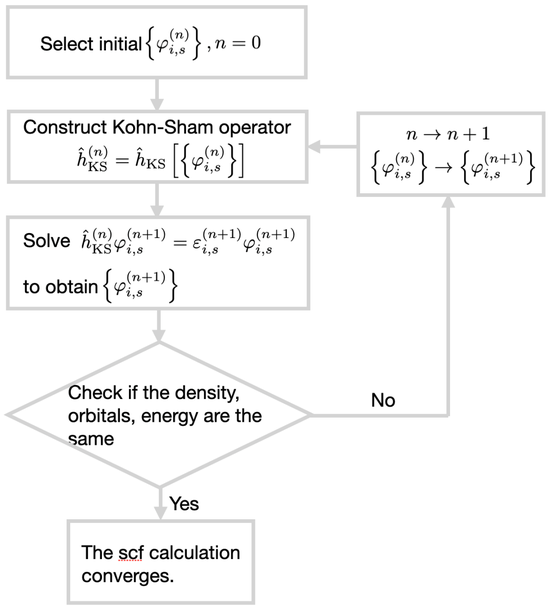
3. Non-self-consistent calculation using the KS Hamiltonian
   Exercise: H chain (H2 with PBC), convergence of non-self-consistent band structure as we use denser kmesh



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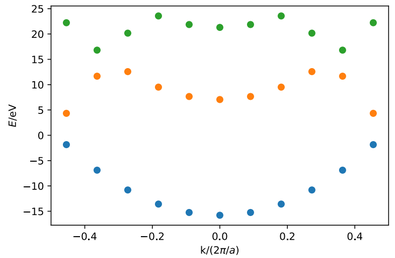
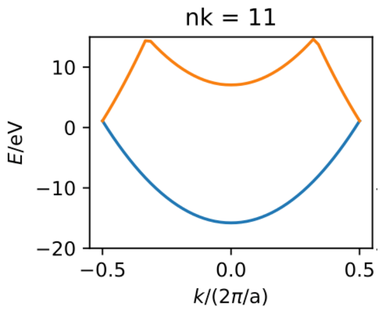
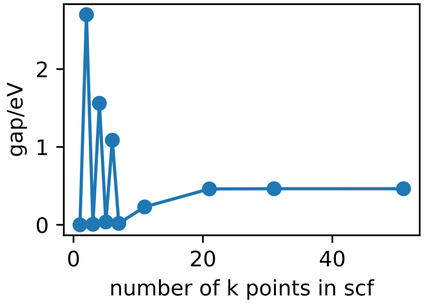
$$H = E_0 + \sum_{i,\sigma,\mathbf{k}} \epsilon_{n\mathbf{k}}^{\sigma} c_{n\mathbf{k}\sigma}^{\dagger} c_{n\mathbf{k}\sigma}$$







Comments on the KS eigenvalues

KS eigenvalues

Generally, the KS eigenvalues differences do not correspond to energy needed to add/remove an electron.

(Exception: The highest eigenvalue in a finite system = minus the ionization energy $-I$)

1. KS eigenvalues and eigenvectors can be taken as input for many-body perturbation approaches (RPA, *GW …*) or QMC.

2. Within KS formalism itself, the eigenvalues have a definite mathematical meaning:
   The Slater-Janak theorem: the eigenvalue is the derivative of the total energy with respect to the occupation of a state

$$\epsilon_i = \frac{\mathrm{d}E_{\mathrm{total}}}{\mathrm{d}n_i} = \int \mathrm{d}^3 r \frac{\mathrm{d}E_{\mathrm{total}}}{\mathrm{d}n(\mathbf{r})} \frac{\mathrm{d}n(\mathbf{r})}{\mathrm{d}n_i}$$

In the term $\frac{\mathrm{d}E_{\mathrm{total}}}{\mathrm{d}n(\mathbf{r})} = V_{\mathrm{XC}}(\mathbf{r}) = \epsilon_{\mathrm{XC}}([n], \mathbf{r}) + n(\mathbf{r}) \frac{\delta \epsilon_{\mathrm{XC}}}{\delta n(\mathbf{r})}$

Vxc can vary discontinuously between states, giving rise to jumps in eigenvalues, leads to the well-know band-gap discontinuity.