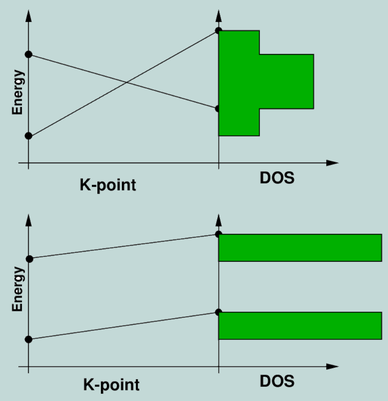
Improving Brillouin zone integration through k.p perturbation theory.

Peter Byrne[1], Phil Hasnip[1], Matt Probert [1]

[1]Department of Physics, University of York, YO10 5DD, UK

Problem

- In periodic systems, we solve a set of coupled Schrodinger equations. One for each sampling point in the Brillouin Zone(BZ)
- Total energy (and derived quantities) depend on the values integrated across the entire BZ. Practically, we sample at some set of points.
- Each evaluation is expensive but we require many to get accurately integrated quantities.
- We often use a regular sampling grid (Monkhurst-Pack) but it is difficult to estimate the uncertainty due to the finite sampling.
- Problems are obvious when attempting to generate bandstructure images:



Piecewise Extrapolation

- Can extrapolate 2nd order polynomials from each sampled k-point.
- First order terms
  - Already accounted for exactly in filled bands
  - Only affects the energy of partially filled bands
  - Modifies the Fermi energy
  - Calculated directly from ground state wavefunction
- Second order terms
  - Gives band curvature
  - Affects energy of all occupied bands.
  - Comes from a sum over states and can be difficult to converge.
- Cannot use interpolation as we do not know the band ordering between k-points.
- Solution is to use extrapolation – mismatch gives an uncertainty on the correction.

k.p Perturbation Theory

Firstly we expand the KS energy of a level as

$$\boldsymbol{E(k+\delta) = E_0 + E_1\delta + \delta E_2 \delta + ...}$$

We start from having solved the HKS equations at a particular k-point which gives us $\boldsymbol{E_0}$ and the ground state wavefunction $\boldsymbol{\Psi_k}$. It can be shown that the first and second order terms are given by,

$$\boldsymbol{P^{\alpha}_{m,n} = \langle \Psi_{k,n} | P^{\alpha} | \Psi_{k,m} \rangle}$$

$$\boldsymbol{E^{\alpha}_{1,m} = iP^{\alpha}_{m,m}}$$

and

$$\boldsymbol{E^{\alpha,\beta}_{2,m} = \left\langle \Psi_{k,m} \middle| [[\hat{H}, r_\alpha], r_\beta] \middle| \Psi_{k,m} \right\rangle - \sum_{m \neq n} \frac{P^{\alpha}_{n,m} P^{\beta}_{m,n} + P^{\beta}_{n,m} P^{\alpha}_{m,n}}{E_n - E_k}}$$

Evaluation of the velocity matrix elements $\boldsymbol{P^{\alpha}_{m,n}}$ is straightforward and the calculation should be small in comparison to solving the HKS equations.

Convergence of the Curvature

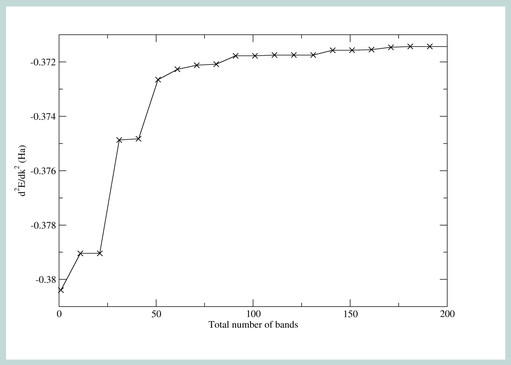


Figure 1: Convergence of the diagonal curvature term for the lowest band in Mg2 with respect to the total number of bands

- Converges slowly with number of bands in the sum
- Requires calculation of many empty bands to converge the highest filled bands
- Alternatively can be done using Sternheimer equation but this limits us to norm-conserving pseudopotentials.

Results

- Results for some materials look mostly reasonable with fine sampling.

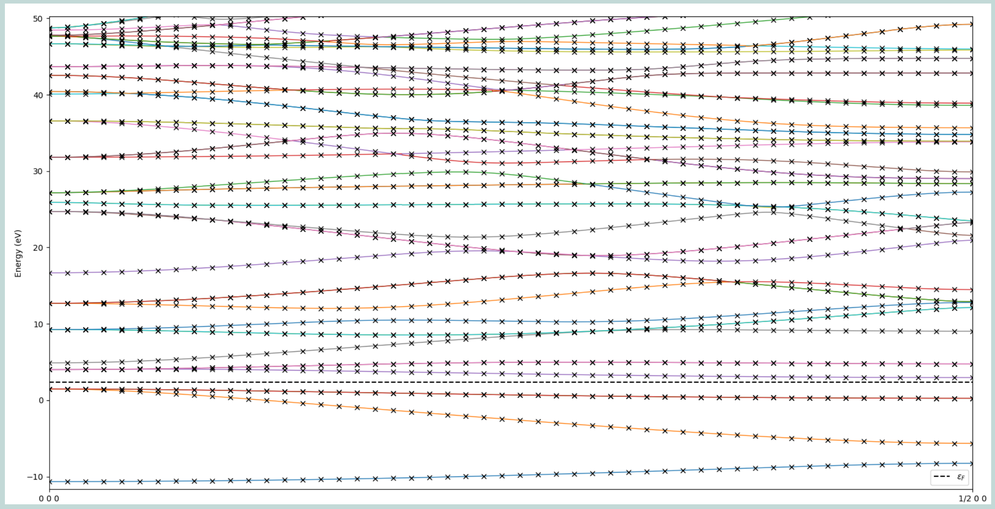


Figure 2: Example extrapolation for Si2 between **Γ** and ***X*** on a fine grid

- Zooming further shows the curvatures being accurately captured.

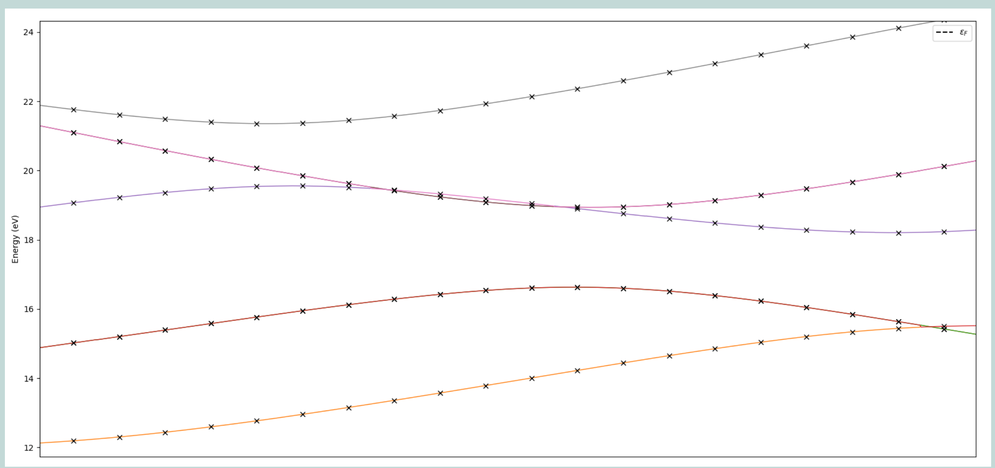


Figure 3: Zoomed in region of extrapolation for Si2 showing curved bands.

- With a finely sampled grid, the curvatures look reasonable and there are no obvious discontinuities.

Issues

- Coarser grids show errors in the curvature (or missing higher order terms) more clearly.

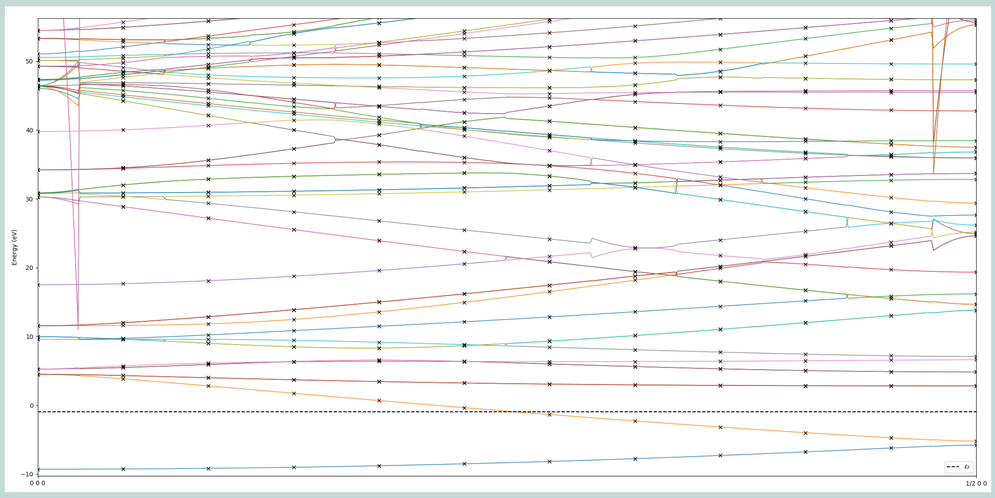


Figure 4: Extrapolation for Mg2 on a coarse grid

- There are problems at degenerate points possibly due to double commutator term. This is calculated via a finite displacement method with respect to pseudopotential projector positions.

Conclusions

- Curvatures require a lot of extra bands ($\approx$ **100**) to converge to within **1%**.
- With high sampling grids, errors in the curvatures are less obvious, as the $\mathbf{k^2}$ term is always small.
- Some materials suffer with problems from degeneracies which may be due to the double commutator being partially calculated by finite displacement.
- Improvements may lie in using the extrapolation to generate the band ordering and then attempting to interpolate with even higher order polynomials.

peter.byrne@york.ac.uk