Zero-point Renormalization of the Band Gap of Semiconductors and Insulators Using the PAW Method

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Projector-Augmented-Wave (PAW) Method

Imagine that we solve the Kohn-Sham (KS) equations (at least we try). The resulting all-electron (AE) orbitals are represented using plane waves.

**Problem**

The AE orbitals are orthogonal to each other. Therefore, they exhibit rapid oscillations in proximity to the nuclei. An accurate description of this phenomenon requires numerous plane-wave coefficients. This incurs a high computational cost.

**Solution**

We transform the AE orbitals into computationally convenient pseudo (PS) orbitals. The PS orbitals are smoother and require fewer plane-wave coefficients, at the cost of losing their orthogonality.

PAW Transformation → PS KS Equations → PAW Operators

AE information is retained inside augmentation spheres around each nucleus using a radial basis set, the so-called partial waves, \( \{ \psi_n^{(l)} \} \) and \( \{ \Phi_n \} \).

Finally, the wavefunction characters, \( \alpha \) and \( \beta \), are calculated by projecting the PS orbitals onto PAW projectors, \( \{ \alpha \} \) and \( \{ \beta \} \).

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Zero-Point Renormalization (ZPR)

When electrons couple with the vibrations of the crystal lattice (phonons), the Kohn-Sham eigenvalues become renormalized. At zero Kohn, this is called zero-point renormalization. This is particularly important for the band gap. We use perturbation theory at lowest order to calculate the ZPR. In this case, two diagrams contribute:

- Fan-Migdal (FM)
- Debye-Waller (DW)

We use a Fourier-interpolation technique that combines the accurate Bloch states from the unit cell with the electron-phonon potential from a supercell. This way, we can systematically increase the number of states as well as the q-point density.

The DW term can be calculated similarly after employing the so-called rigid-ion approximation.

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Electron-Phonon Matrix Element

The electron-phonon matrix element measures the coupling strength between electrons and phonons. It can be regarded as the probability amplitude associated with this fundamental scattering process:

\[
\delta = \sum_{\vec{q}} \left| \langle \beta | \hat{V}_{\text{el-ph}} | \alpha \rangle \right|^2
\]

Recipe for calculating electron-phonon matrix elements:

- Calculate force constants and derivative of potential in supercell using PW transform.
- Fourier interpolate dynamical matrix to unit cell to obtain phonon modes and frequencies.
- Fourier interpolate electron-phonon potential to unit cell.
- Sandwich electronic bandstructure, as well as other quantities.

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Results (¹)

AE and PS methods yield the same non-adiabatic band-gap ZPR for MgO, AlAs, and ZnS. The AE approach requires significantly more intermediate states to converge.

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Conclusion

We have implemented a state-of-the-art algorithm in VASP for calculating the electron self-energy using finite differences and the PAW method. This provides access to the phonon-induced renormalization of the electronic bandstructure, as well as other quantities.

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Future Developments

- Add more electron-phonon features
  - Transport
  - Phonon self-energy
  - Spin-orbit coupling
- Dynamic quadrupoles in the long-range part
- Compare AE and PS approaches for other observables
- Extend PS formalism beyond electron-phonon renormalization