Applications and Investigations into Complex Band Structure

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Abstract and Introduction

The band structure of a material can provide many details into the properties of perfect crystalline systems, such as electrical conductivity, which has led to many real world applications, two examples are “next generation” photovoltaics and battery electrodes. However, by allowing the wavevector to be complex, we can analyze non-pristine materials where conventional band structure cannot be applied. In this study we simulate complex band structure of systems with interesting chemical properties to better understand the fundamentals of complex band structure. Through these simulations we have found interesting qualitative data that show quantum interference, asymmetric and vertical bands. Using these results can help contribute to advancements in material science and the material genome initiative by providing the mathematical language to describe these model systems.

- At the core of conventional band structure we assume translational symmetry, to which we can evoke Bloch’s theorem: (1)

Wave vector

Wavefunction

$$\psi_{n,\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{n,\vec{k}}(\vec{r})$$

Periodic function (lattice)

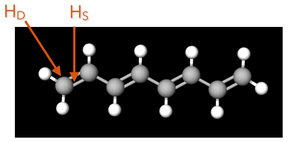
- Physically this assumes there is infinite symmetry in all directions and the wavefunction decays exponentially as we travel from cell to cell (when outside of a band).

Current layer

Coupling to next layer

$$\mathbf{H} = \begin{bmatrix} \mathbf{H_D} & \mathbf{H_S^\dagger} & \mathbf{0} & \mathbf{0} & \cdots \\ \mathbf{H_S} & \mathbf{H_D} & \mathbf{H_S^\dagger} & \mathbf{0} & \cdots \\ \mathbf{0} & \mathbf{H_S} & \mathbf{H_D} & \mathbf{H_S^\dagger} & \cdots \\ \mathbf{0} & \mathbf{0} & \mathbf{H_S} & \mathbf{H_D} & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{bmatrix}.$$

H_D H_S



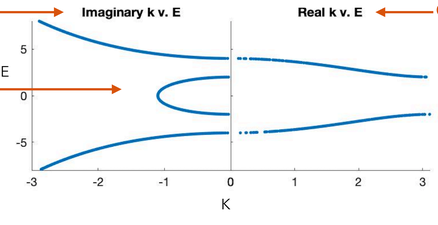
- The coupling between cells and the cells themselves becomes identical, represented as a hermitian and block tridiagonal matrix.
- Mathematically, these are easier to work with
- When we break translational symmetry, such as considering a finite version, the matrix is no longer infinitely long and we are interested in the physical effects of this.

A Simple Example (Su-Schrieffer-Heeger Model) (4)

Complex Band Structure

Conventional Band Structure

Symmetric ellipse



Simulation and Methods

We can analyze the band structure of a material by making use of the transfer matrix. (1)

$$\mathbf{T} = \begin{bmatrix} \mathbf{H_S}^{-\dagger}(E\mathbf{I} - \mathbf{H_D}) & -\mathbf{H_S}^{\dagger}\mathbf{H_S} \\ \mathbf{I} & \mathbf{0} \end{bmatrix}$$

- T(E) connects wavefunctions from one layer to the next.
- The complex band structure comes from the eigenvalues, or in the non symmetric case, the spectra, of this T(E).

Key Questions
1. Can CBS provide additional insight into observed physical phenomena?
2. How does $\| T(E)^k \|$ evolve with k?

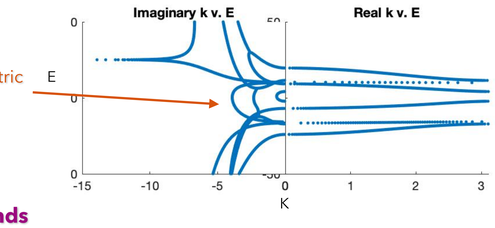
- We can simplify the problem greatly if we note that the diagonal matrix **Hs** represents the coupling to the other cells.
  - Taking the rank(Hs) we can delete all the eigenvalues that do not effect this structure.

Characterizing Behaviors

Asymmetric Complex Bands

- More sophisticated computational studies have reported asymmetric complex bands
- A tight binding model of siloxane motivated by (2) shows asymmetric bands.
- Preliminary hypothesis: Need higher rank **Hs** matrices

Non-Symmetric ellipse



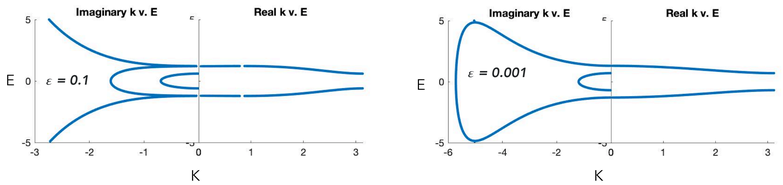
Vertical Bands

Vertical complex bands (5) are a computational artifact and are not physical.

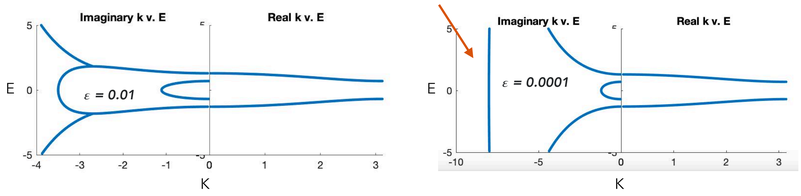
Vary this smaller and smaller

$$\mathbf{Hs} = \begin{bmatrix} 0 & \beta_2 \\ \varepsilon & 0 \end{bmatrix}$$

Watch this grow outwards to vertical



Vertical!

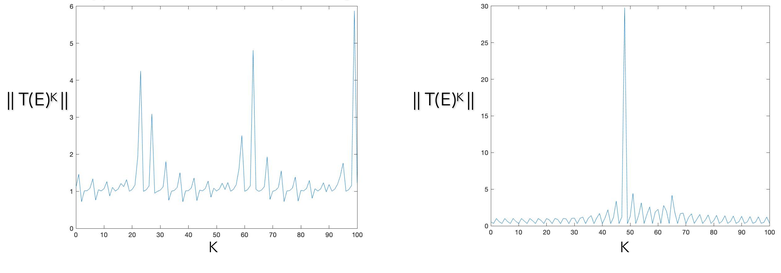


- Conclusion: We see the vertical band becoming more and more separate and apparent as we make ϵ smaller. ϵ=0 is the true answer, the others are approximations.
- Here we found that they arise from having a singular matrix **Hs**

Characterizing Observed Phenomena

Transient Effects

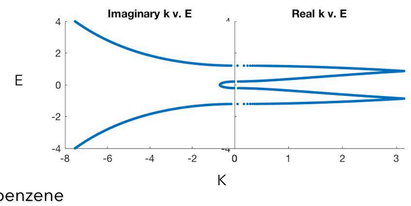
- Conventional analyses expect the wavefunction to decay exponentially between layers of the crystallized structure when outside the band
- This is not always true as observed in the electrical conductance of various polymeric molecules, which display transient effects
- Hypothesis: The unexpected increase in conductance is not caused by spurious changes in the molecular geometry, but are a fundamental consequence of the molecules' band structures.
- Prototypical results with unexpected growth rates:



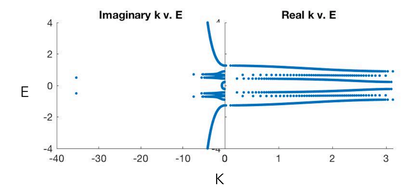
Destructive Quantum Interference

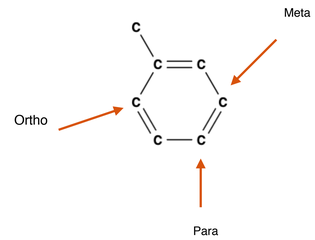
- Destructive Quantum Interference suppresses connections in the wavefunction from one layer to another. How does it manifest in the CBS?

Para-benzene (3)

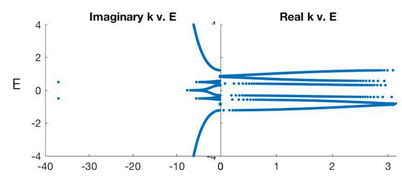


Ortho-benzene





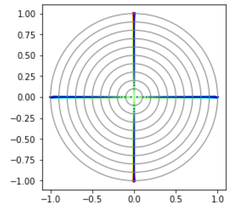
Meta-benzene

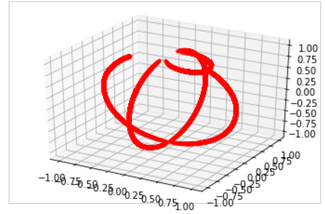


- Conclusion: Destructive Quantum Interference corresponds to infinite wavevectors, k = ∞

Steriographic Projections

- Another way of looking at destructive quantum interference is using stereographic projections.
- Project the complex data onto a Riemann sphere allows us to physically see when k crosses infinity
- Here is the Ortho-benzene molecule again:





Conclusions

- Complex band structure allows us to describe transient effects and destructive quantum interference among other important visual behaviors
- We were able to describe numerical artifacts such as vertical bands
- Furthermore a future study could be to actually visualize our results in a laboratory setting to test whether transient effects could be seen in these chemical compounds

References & Acknowledgments

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