Petascale Computing to Explore Optical Properties of Materials

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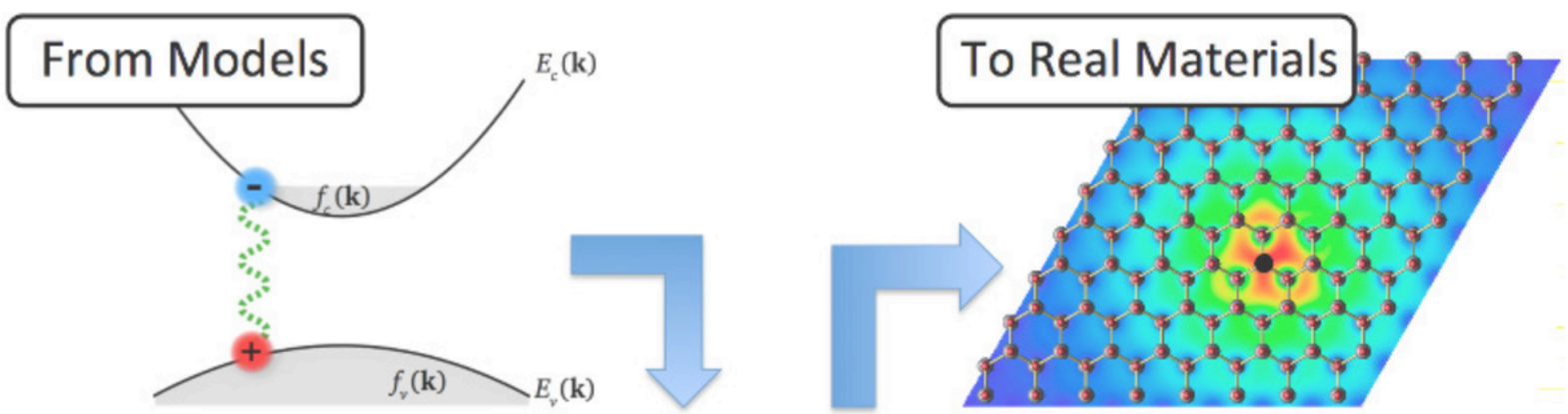
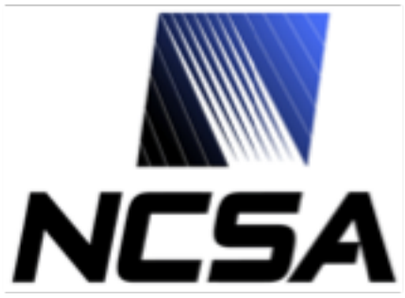


Acknowledgments

- National Science Foundation Research Grant CBET-1437230
- National Center for Supercomputing Applications (NCSA) at University of Illinois
- Blue Waters Supercomputer
- Schleife Research Group



The Schleife Group

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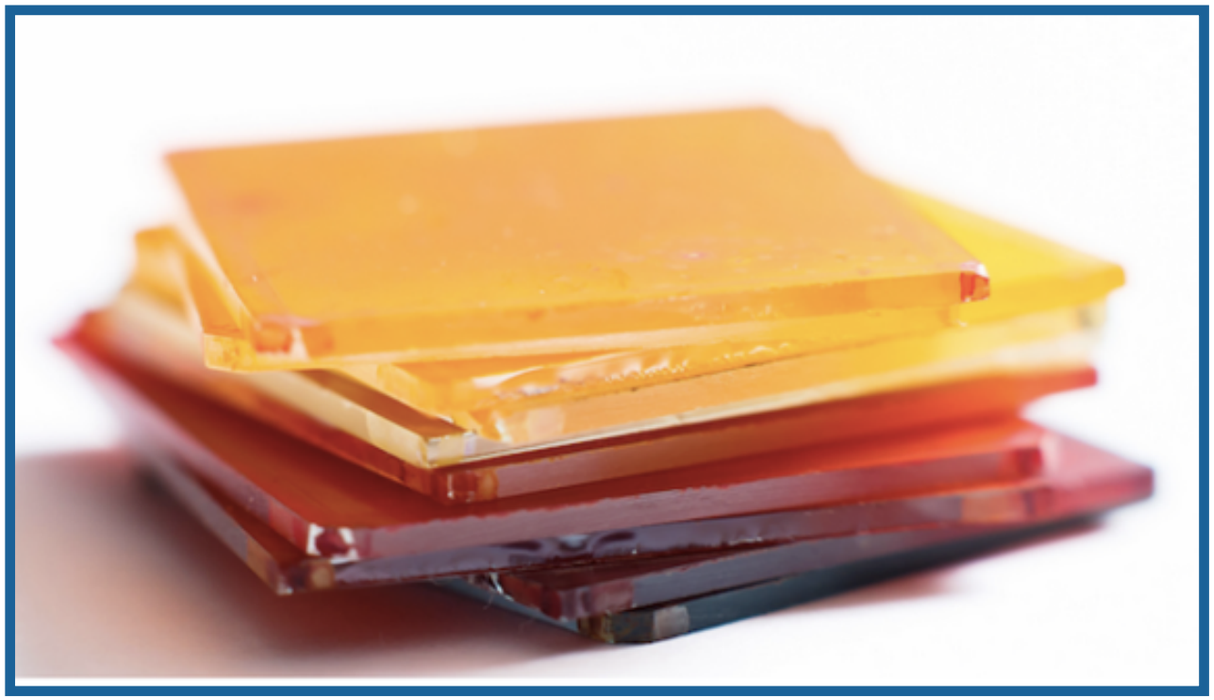
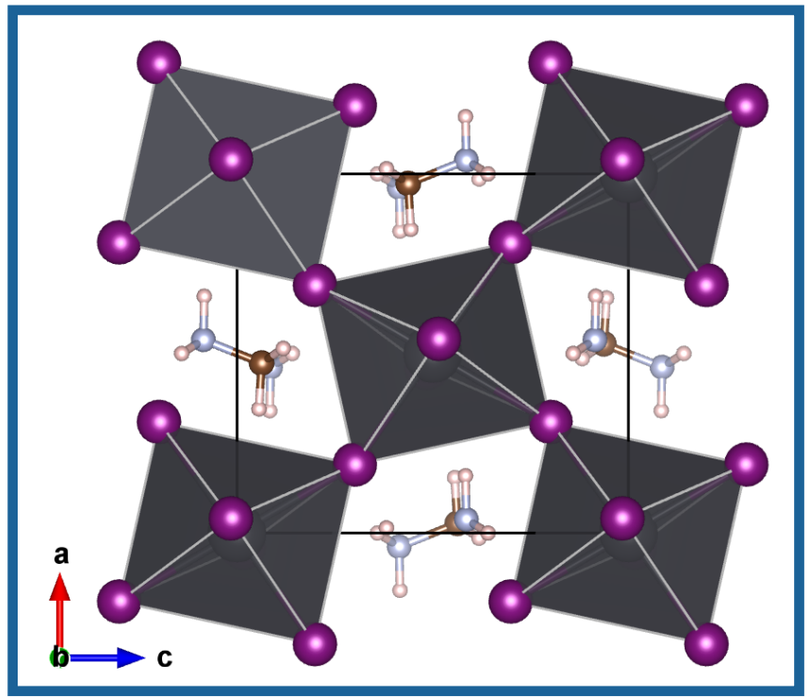
Solar Energy:
A viable form of alternative energy to fuel our growing population needs

The design of photovoltaic materials starts at the atomic level where photon energy is transformed to usable electronic energy

Hybrid Organic Perovskite **Methylammonium Lead-Iodide**





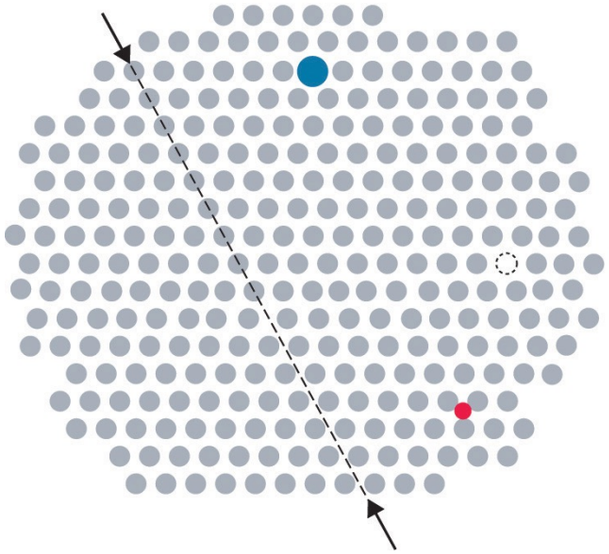
Easy to synthesize - High Opitcla Absorption - Long Carrier Mean-Free-Path

20.1% photo-electrical conversion as a solar cell

Poorly Understood Optical Nature - Contains Poisonous Lead - Unstable!

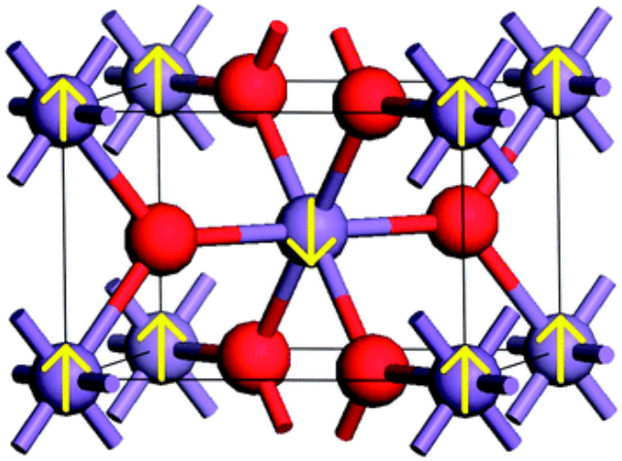
We can address these questions with first-principles calculations

First principles materials science by DFT and beyond

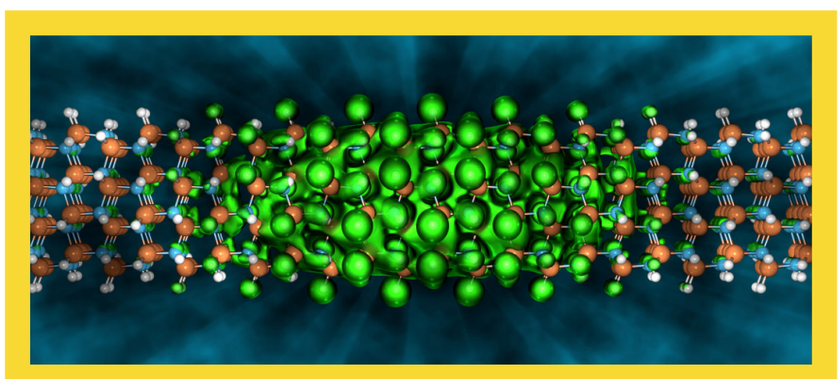


Defects and Crystal Structure

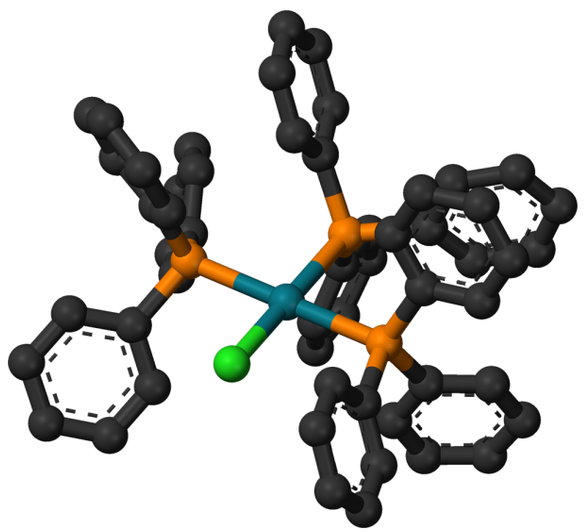
DFT: Density Functional Theory



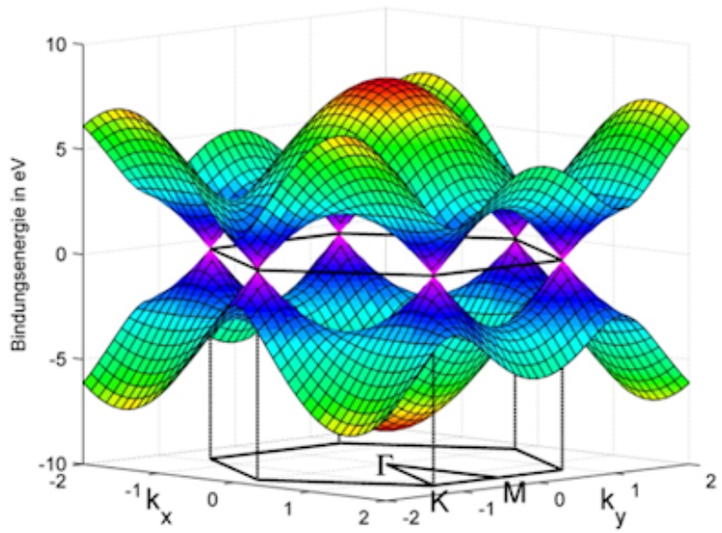
Spin and Magnetism



Optical Response



Catalysts and Reactions



Electronic Nature

http://pubs.rsc.org/en/content/articlehtml/2013/ta/c3ta13559d

http://www.uni-muenster.de/Physik.PI/Zacharias/research/graphene/graphene.html

DFT: Density Functional Theory is an approximation to QM

Quantum Theory

- Exact or numerical theory of atoms and electrons
- Uses **many-body wavefunctions** to calculate materials properties
- Not solvable for many particles
- Requires numerical approaches

Density Functional Theory

- Approximation of electron-electron interaction
- Independent particles
- Uses **electron density** to calculate material properties
- Requires approximation for **correlation** + **exchange**

DFT: Density Functional Theory is an approximation of QM

$$E[\rho] = T[\rho] + \int dr v_{ext}(r)\rho(r) + \frac{e^2}{2}\int dr \int dr' \frac{\rho(r)\rho(r')}{|r - r'|} + E_{xc}[\rho]$$

- Analytic 3D equation for energy
- **Self-consistently** solves for the electronic density and single particle wavefunctions
- Treats electrons as independent particles in a mean field
- Reduced the electron-electron (hole) interaction accuracy

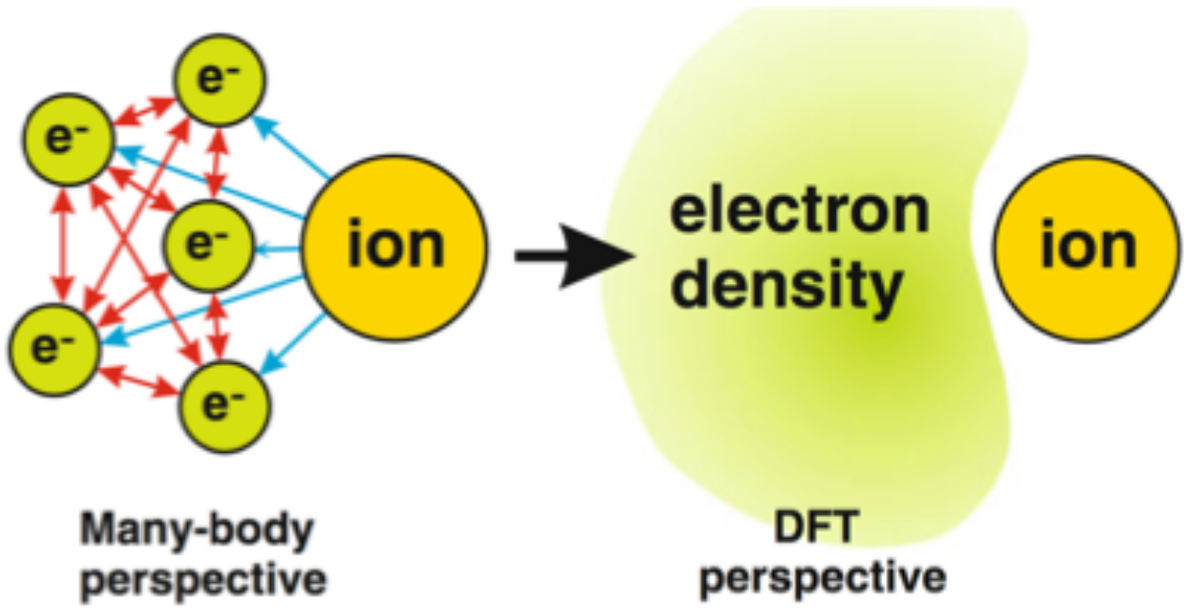
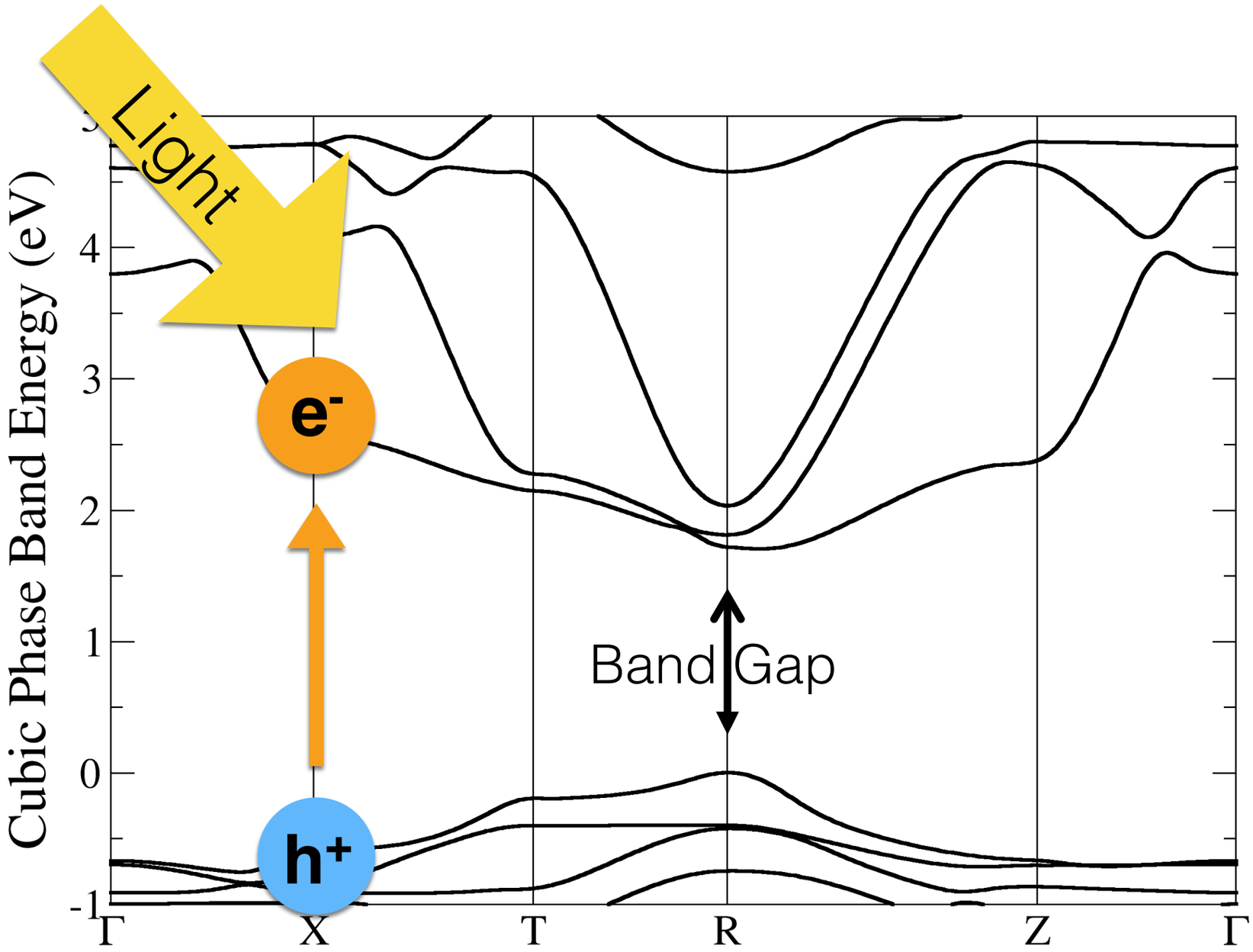


Photo From: F. Bechstedt, Many-Body Approach to Electronic Excitations, Springer, 2015

Electronic structure of $CH_3NH_3PbI_3$ band structure

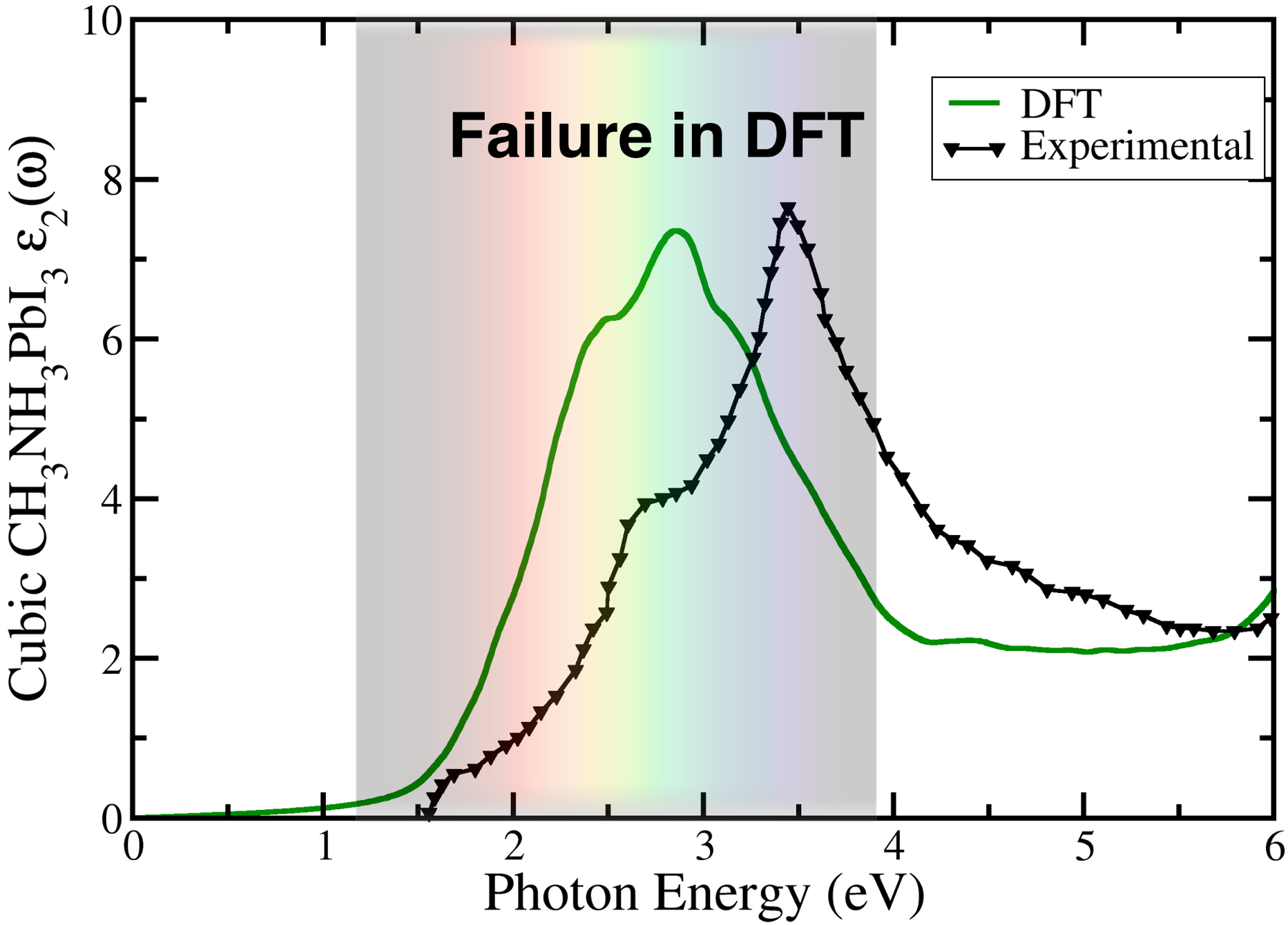


Excited state electrons
Conduction Band

Ground state electrons
Valence Band

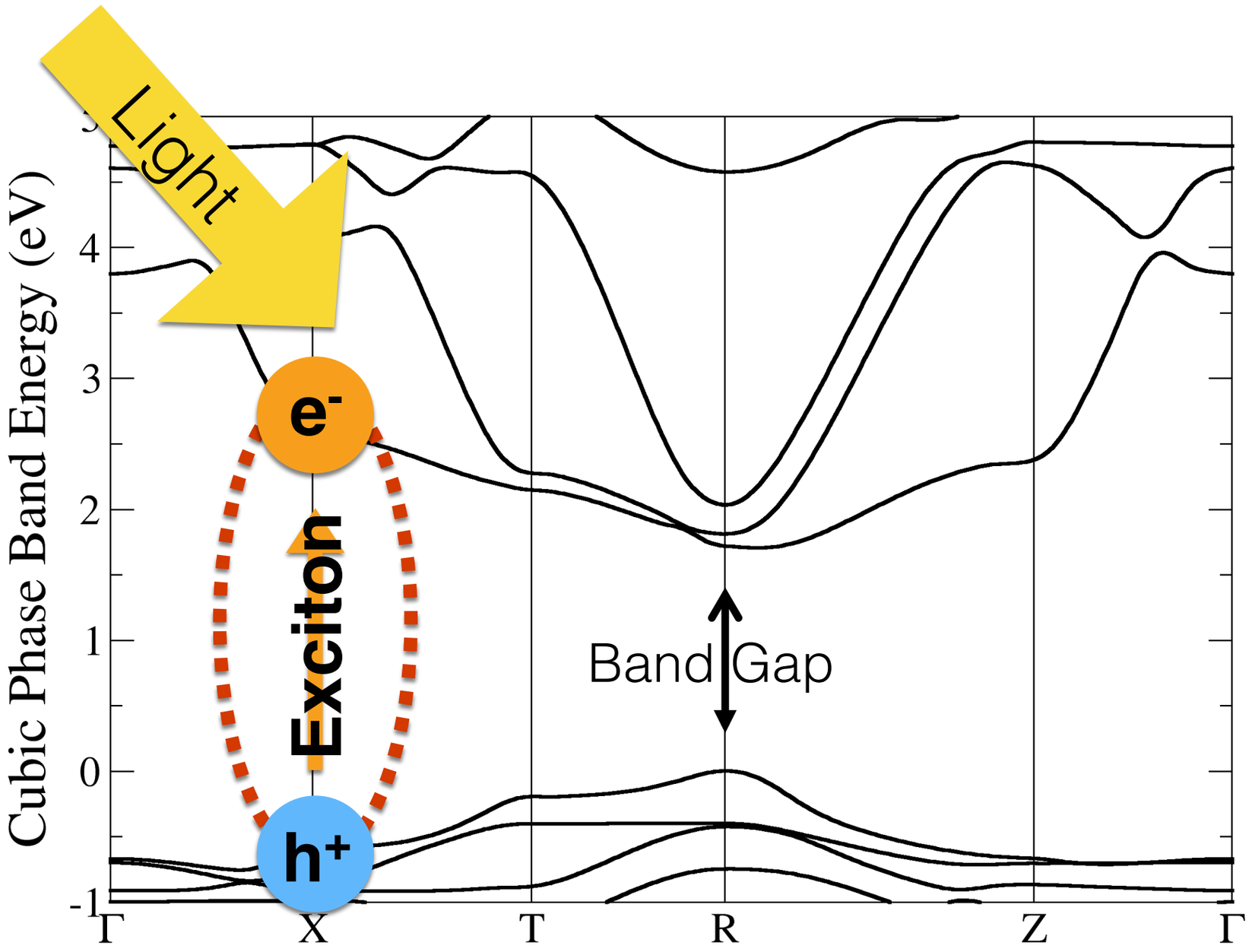
- Electrons in solids occupy energy bands
- Electrons can absorb light and jump from valence to conduction bands

From a band structure, the dielectric function is determined



- The **imaginary dielectric function** determines absorption of photon in material as a function of the photon energy

Optical response - the **Bethe Salpeter Equation (BSE)**



Excited state electrons
Conduction Band

Ground state electrons
Valence Band

- During optical absorption, **electrons leave behind positively charged holes**
- Electrons and holes can bind together to form **Excitons**

Optical response - the **Bethe Salpeter Equation (BSE)**

BSE Hamiltonian Matrix

$$H_{BSE,cvk}^{c'v'k'} = H_{cvk}^{diag} + H_{cvk}^{c'v'k'interaction}$$

Independent particle band structure is on the diagonal of the BSE matrix

Interaction terms between electron and holes are on the off diagonal elements

- ***Very large calculation***
- BSE matrix, for $CH_3NH_3PbI_3$ (tetragonal), is of rank ~ 100,000
- Requires at LEAST ***62 nodes*** for minimum efficiency
- Will require > ***100 nodes for more advanced / accurate calculations***

Optical response - the **Bethe Salpeter Equation (BSE)**

BSE Matrix - Calculated and Processed on Blue Waters

$$\begin{bmatrix} E_{(c-v)_{11}} & (2v-W)_{12} & \cdots \\ (2v-W)_{21} & E_{(c-v)_{22}} & \cdots \\ \vdots & \vdots & \ddots \end{bmatrix}$$

BSE Optical Spectrum

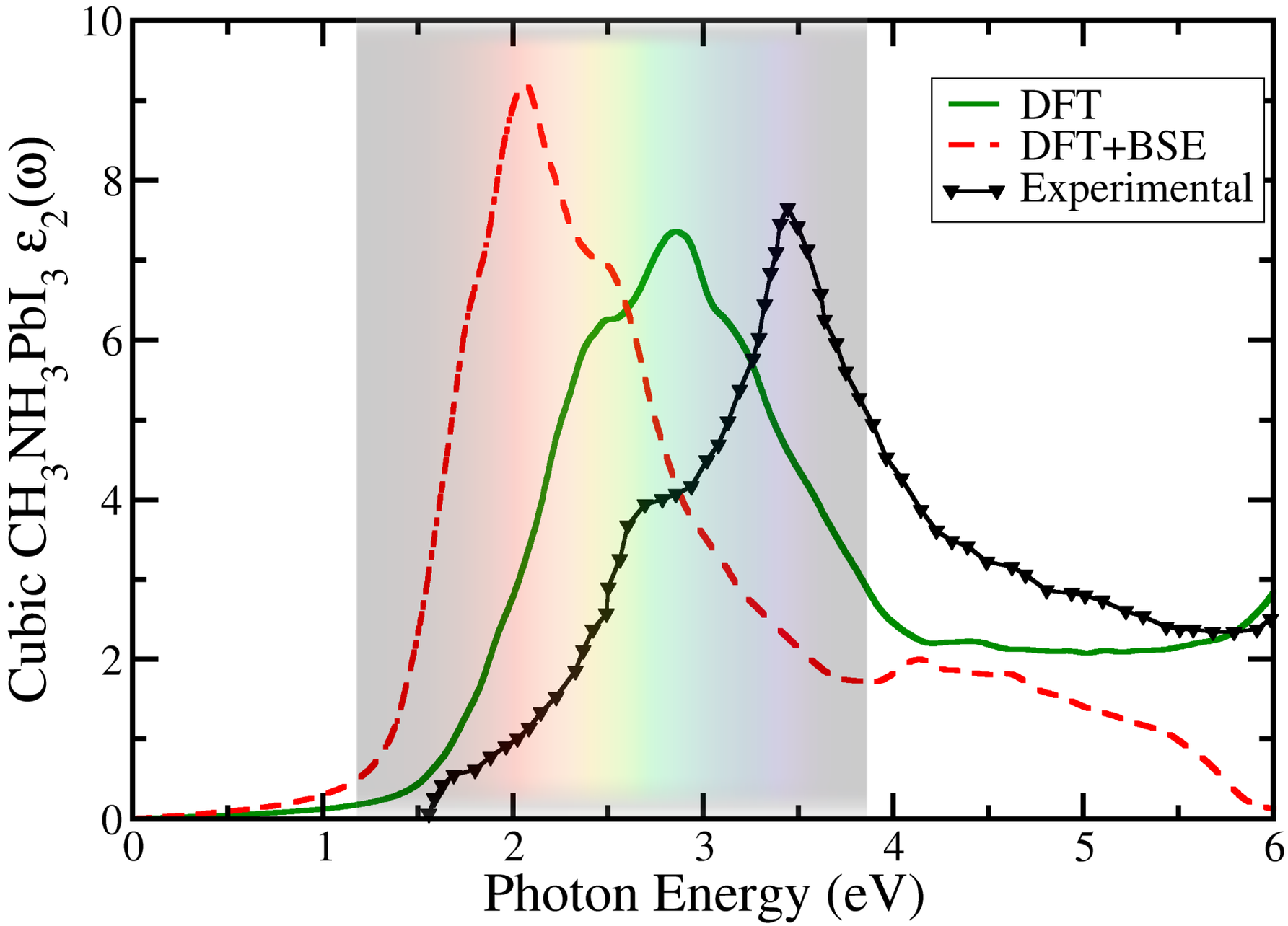
$$\hat{H}|\xi(t_{i+1})\rangle = i\hbar \frac{|\xi(t_{i+2})\rangle - |\xi(t_i)\rangle}{2\Delta t}$$

- Circumvents finding eigenvectors by using a time resolved initial value approach - MPI
  - Requires large amounts of storage for matrix

Exciton Binding Energies

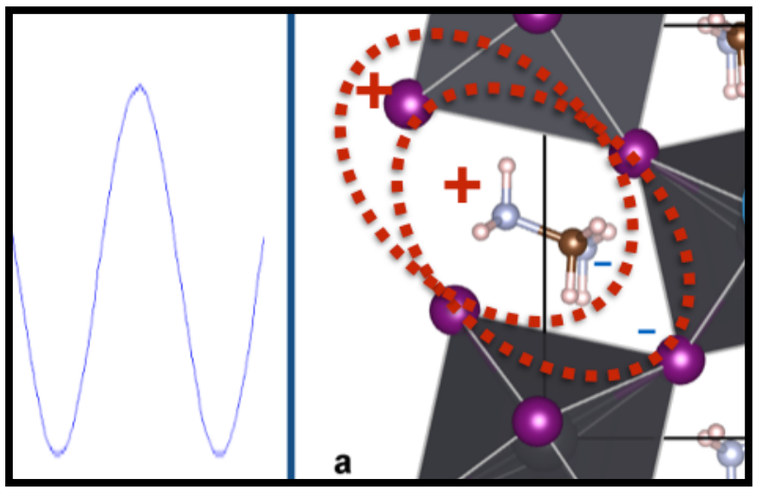
- Matrix eigenvalues by an iterative MPI diagonalization scheme: **Conjugate Gradient Method**
  - Determines strength of bond between electrons and holes

The excitonic effects shifts the absorption edge to lower energies (red shift) which actually worsens our predictions!

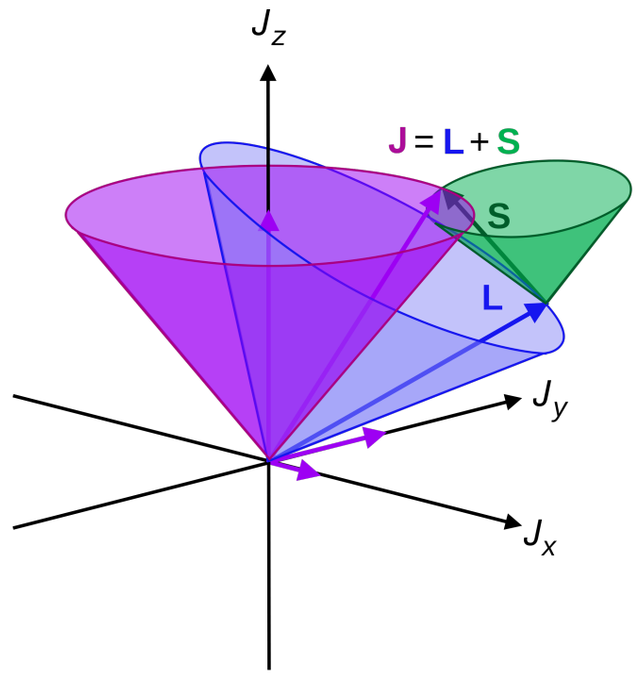


- Even more drastic failure compared to DFT!
- What is our formalism missing?

Optical absorption in $CH_3NH_3PbI_3$ - the mystery at hand



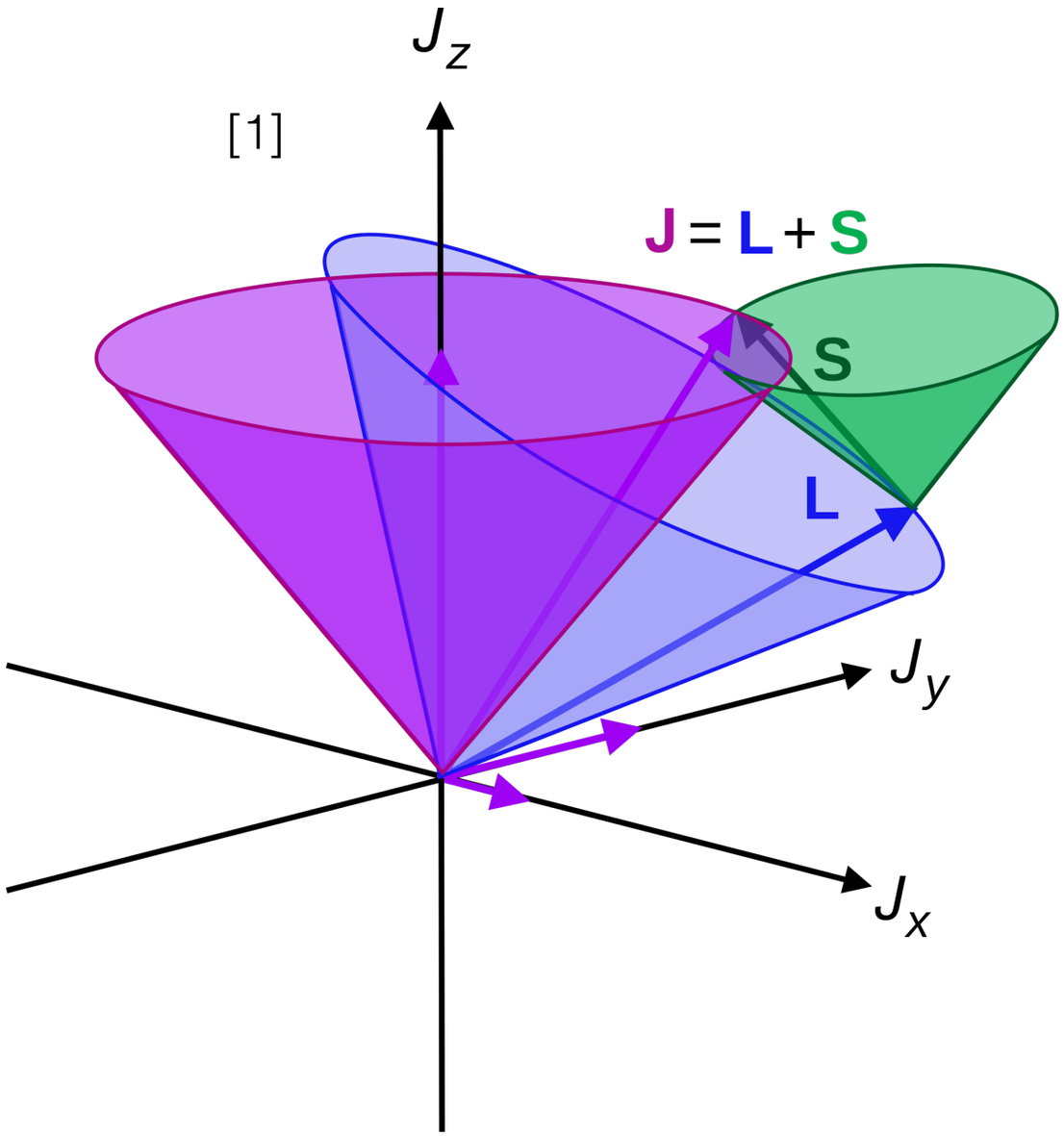
Lattice Screening



SOC for band splitting

- We suggest that capturing the correct optical response of this material requires the inclusion of two more phenomena:
  - Spin-orbit coupling
  - Lattice screening of electron-hole pairs

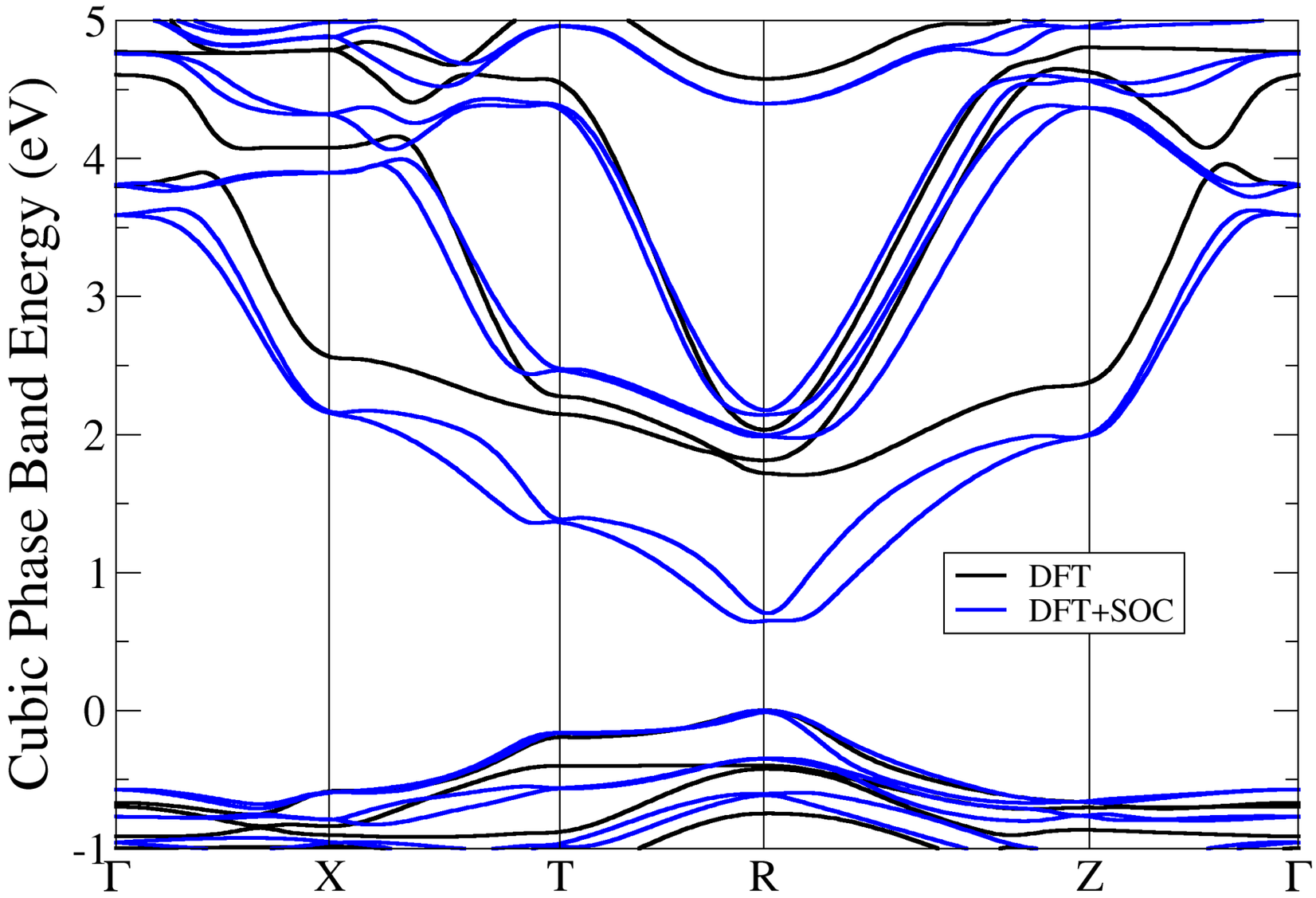
Problem 1: Spin orbit coupling about heavy nuclei



- Spin-Orbit dependence on energy - treats spin explicitly (not done in standard DFT runs)
- Breaks band degeneracy
  - (doubles number of computed states)
- Dramatically shifts band energy
- Quadruples calculation cost

https://en.wikipedia.org/wiki/Angular_momentum_coupling

Problem 1: Spin orbit coupling about heavy nuclei

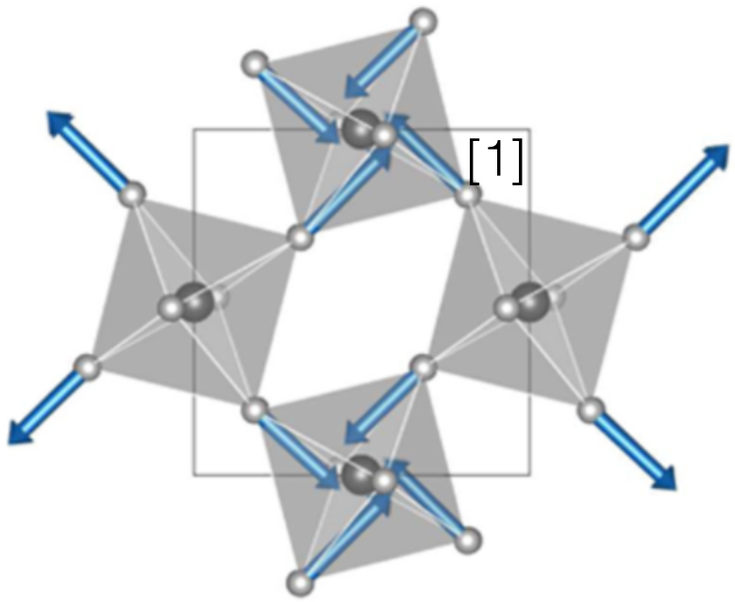


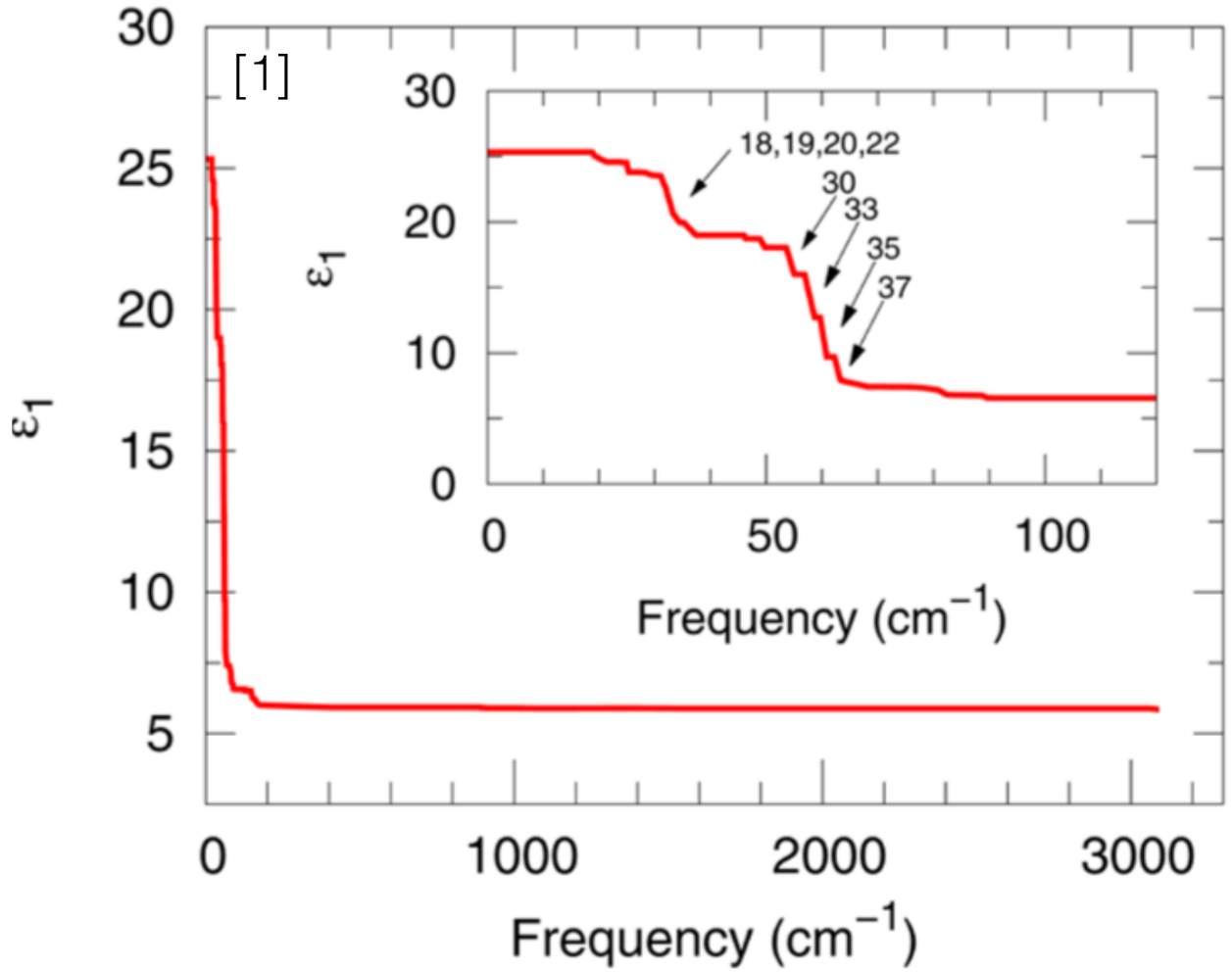
Excited state electrons
Conduction Band

Ground state electrons
Valence Band

- SOC strongly shifts the KS eigenvalues and bands
- A shift in eigenvalues changes the optical peak location

Problem 2: Lattice polarizability and lattice screening

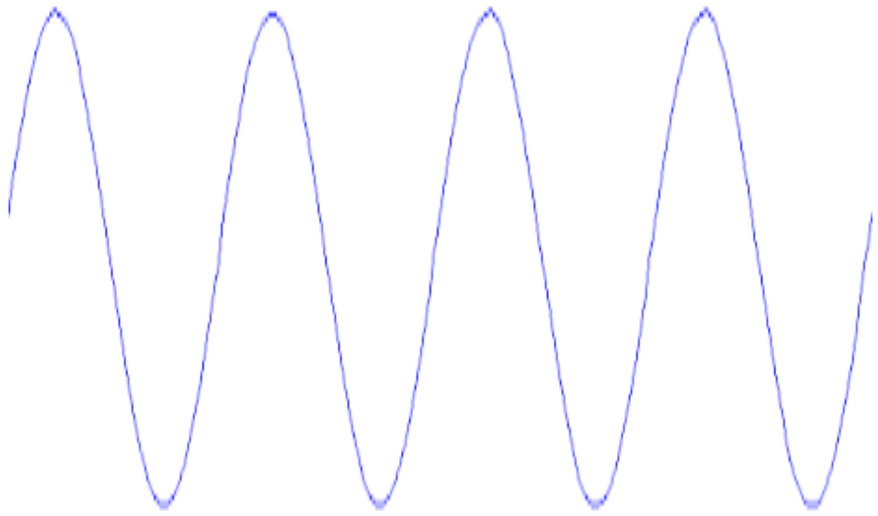


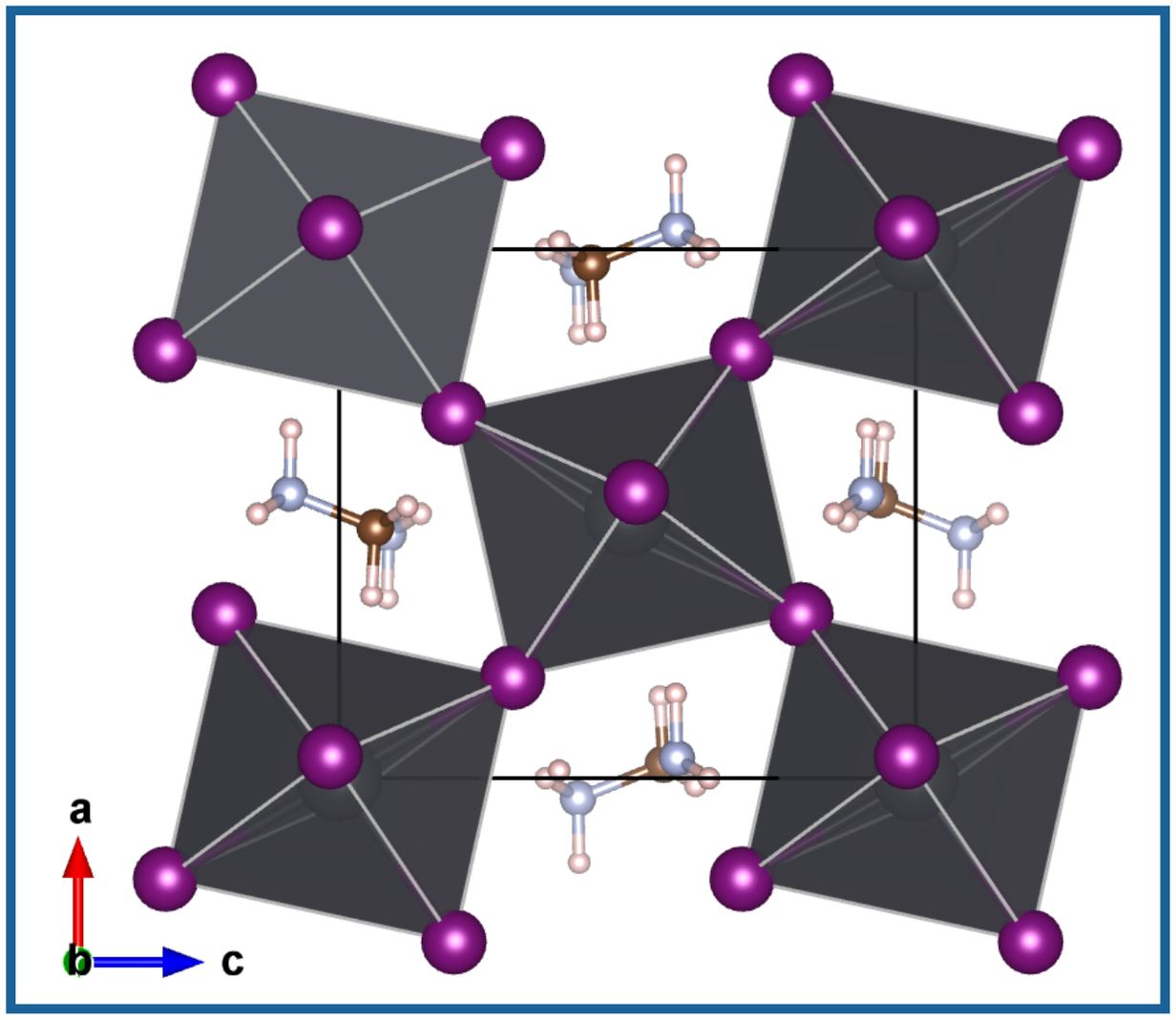


- Experiments and theory have shown that the $CH_3NH_3PbI_3$ lattice is much more polarizable by external electric fields (i.e light) than the electron clouds
- Could result in lattice screening of the electron-hole interaction

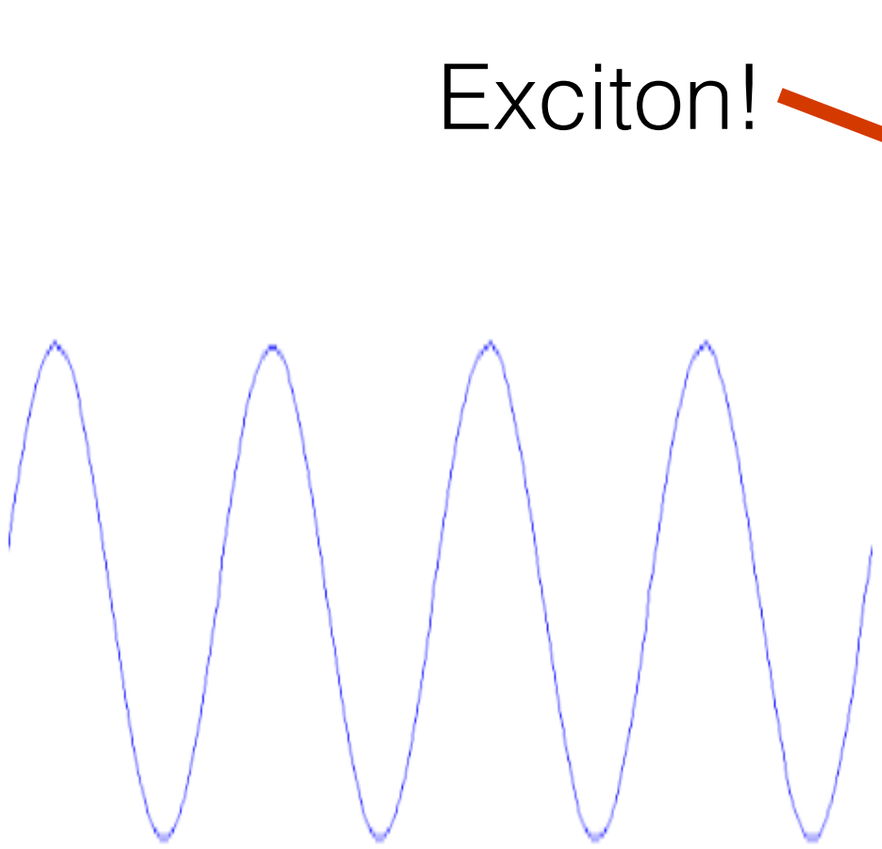
[1] *J. Phys. Chem. C*, **2015**, *119* (46), pp 25703–25718

Lattice screening effects on electron-hole interaction

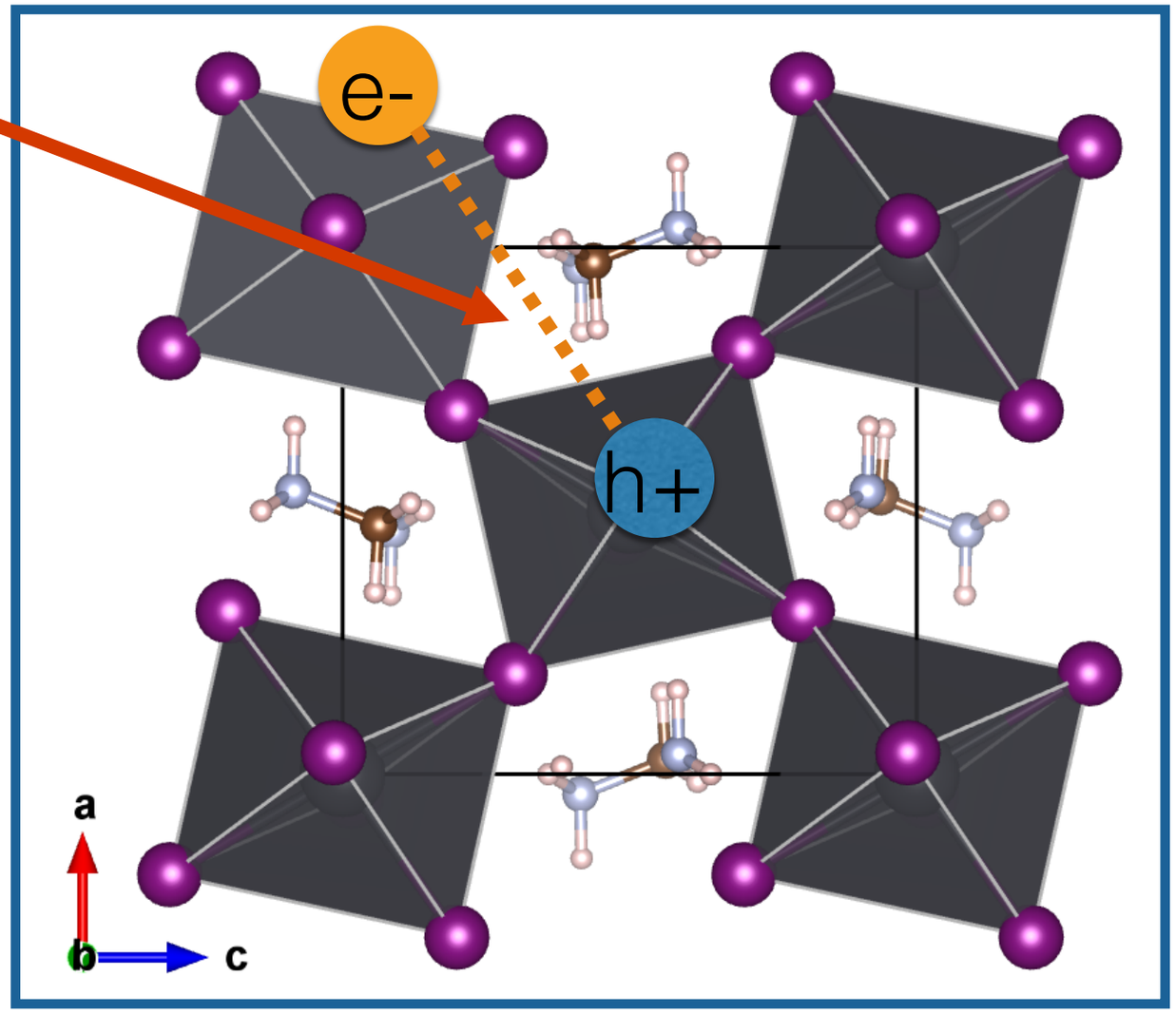




Lattice screening effects on electron-hole interaction

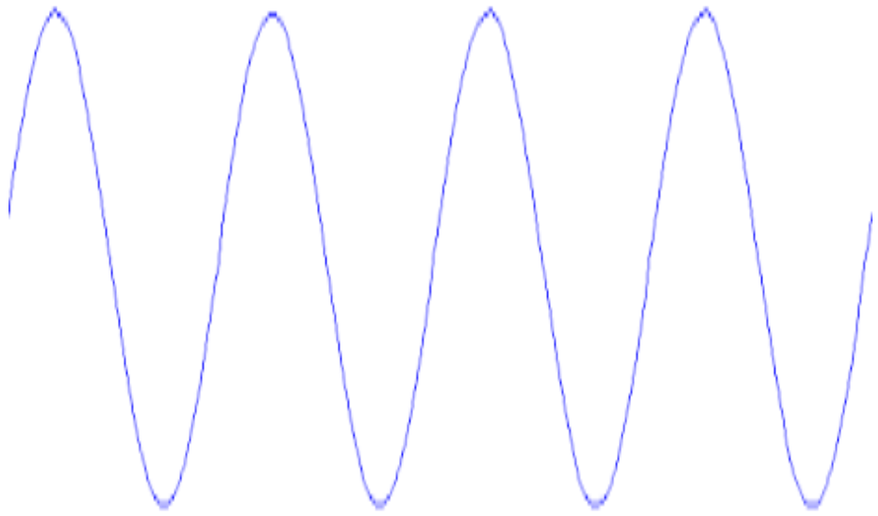


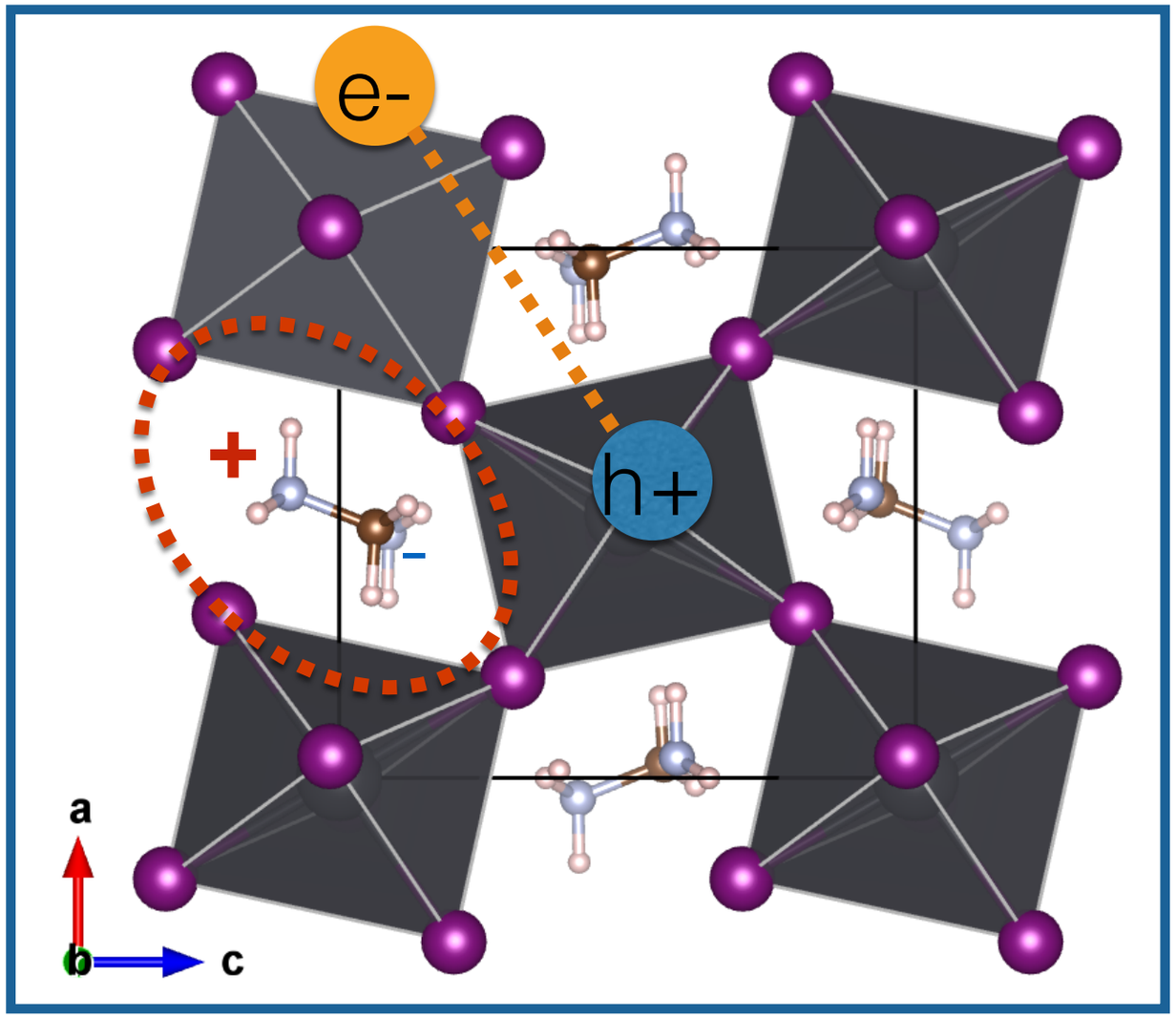
Exciton!



- Under optical illumination, we get **excitons.**

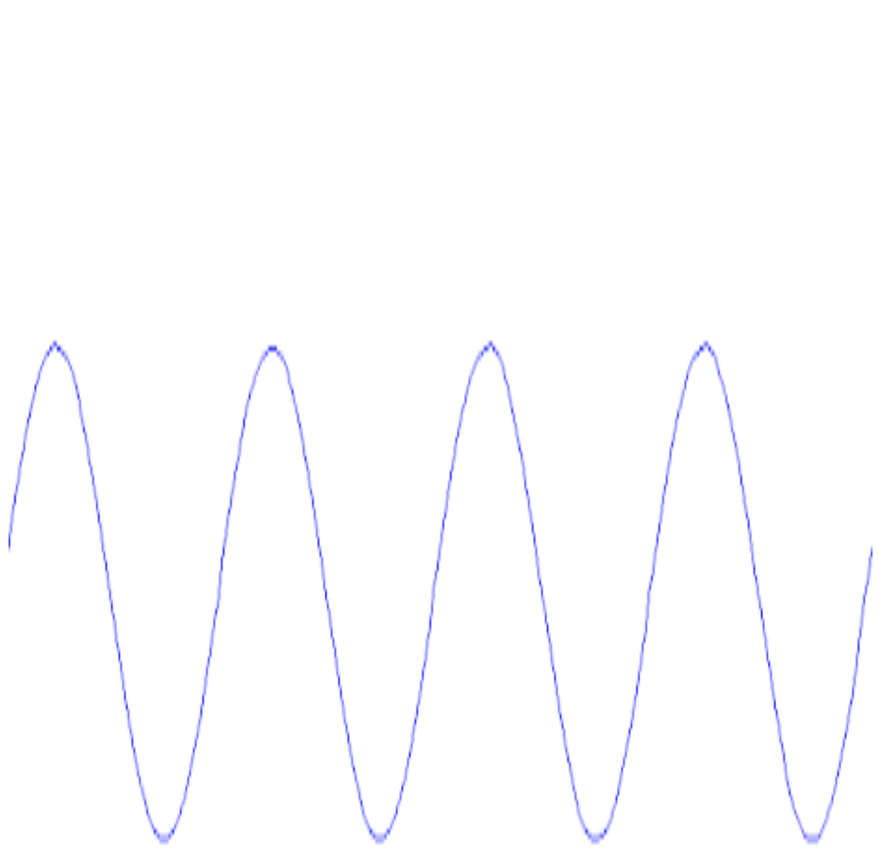
Lattice screening effects on electron-hole interaction

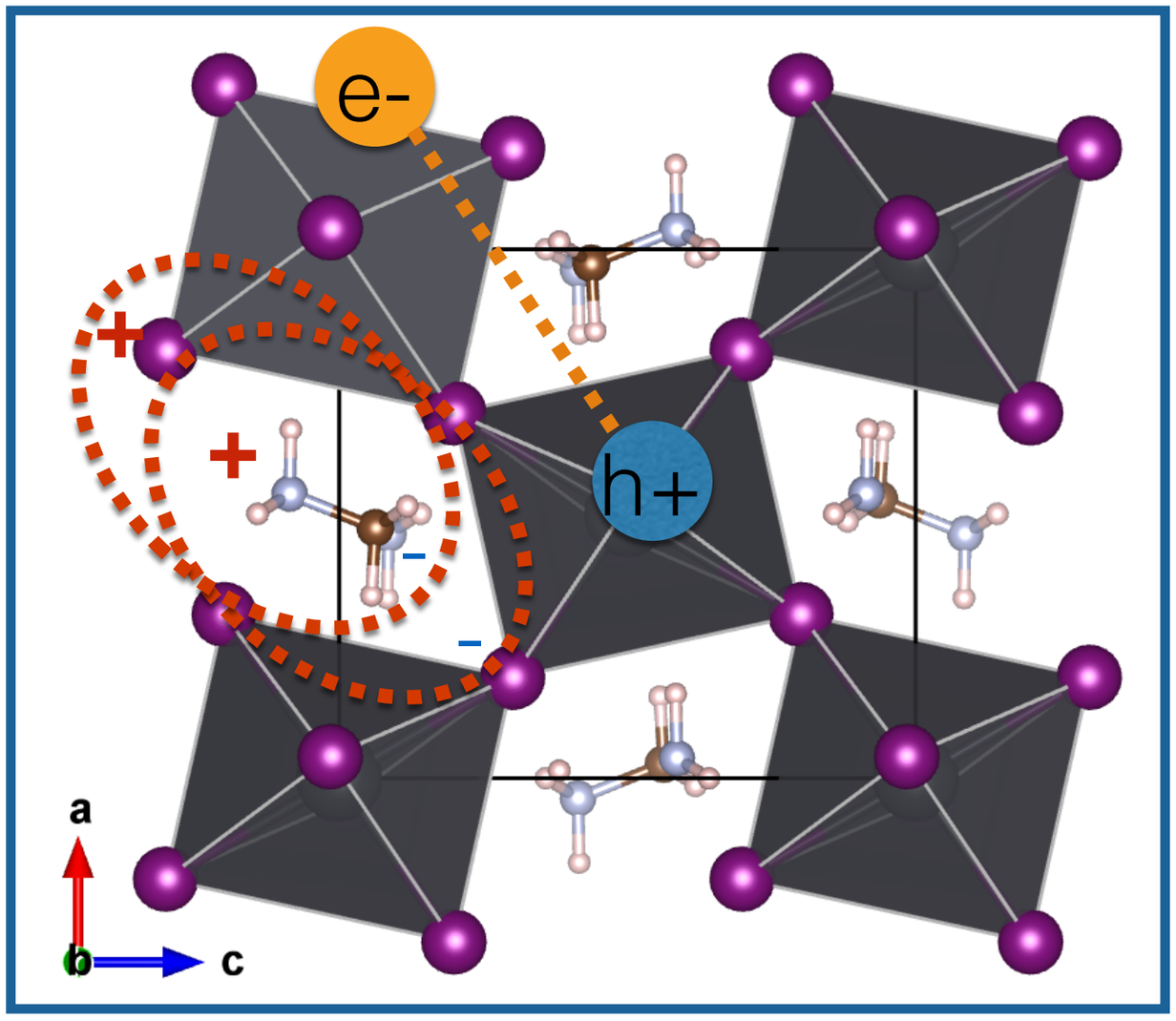




- It is important to remember that **$CH_3NH_3PbI_3$** has a **highly polarizable lattice structure**

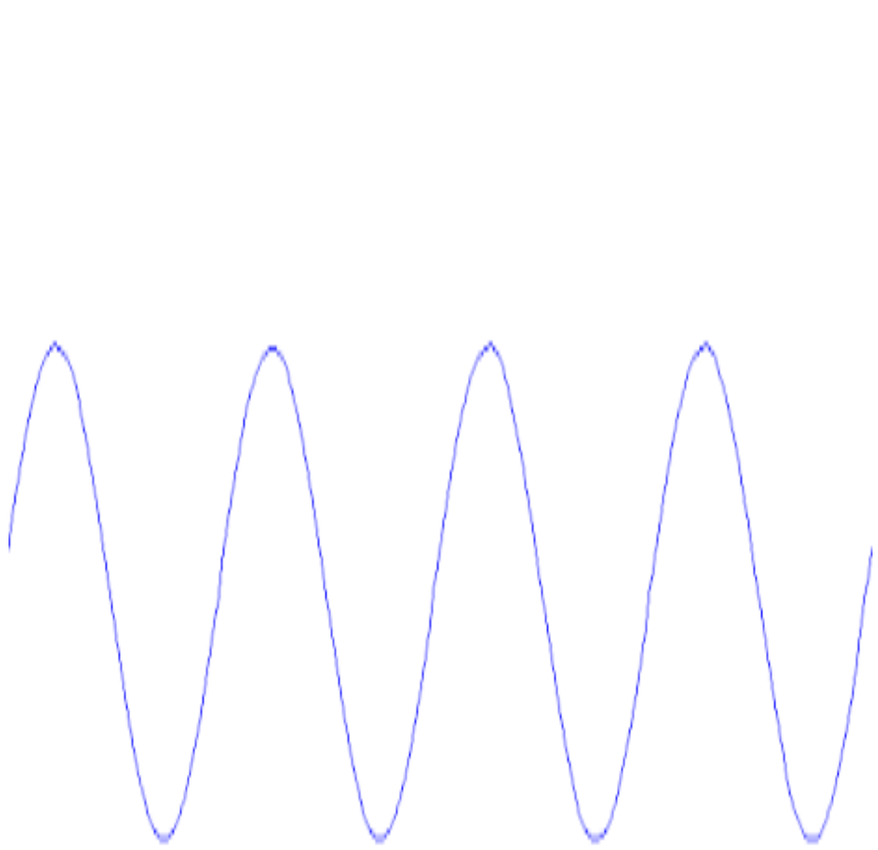
Lattice screening effects on electron-hole interaction

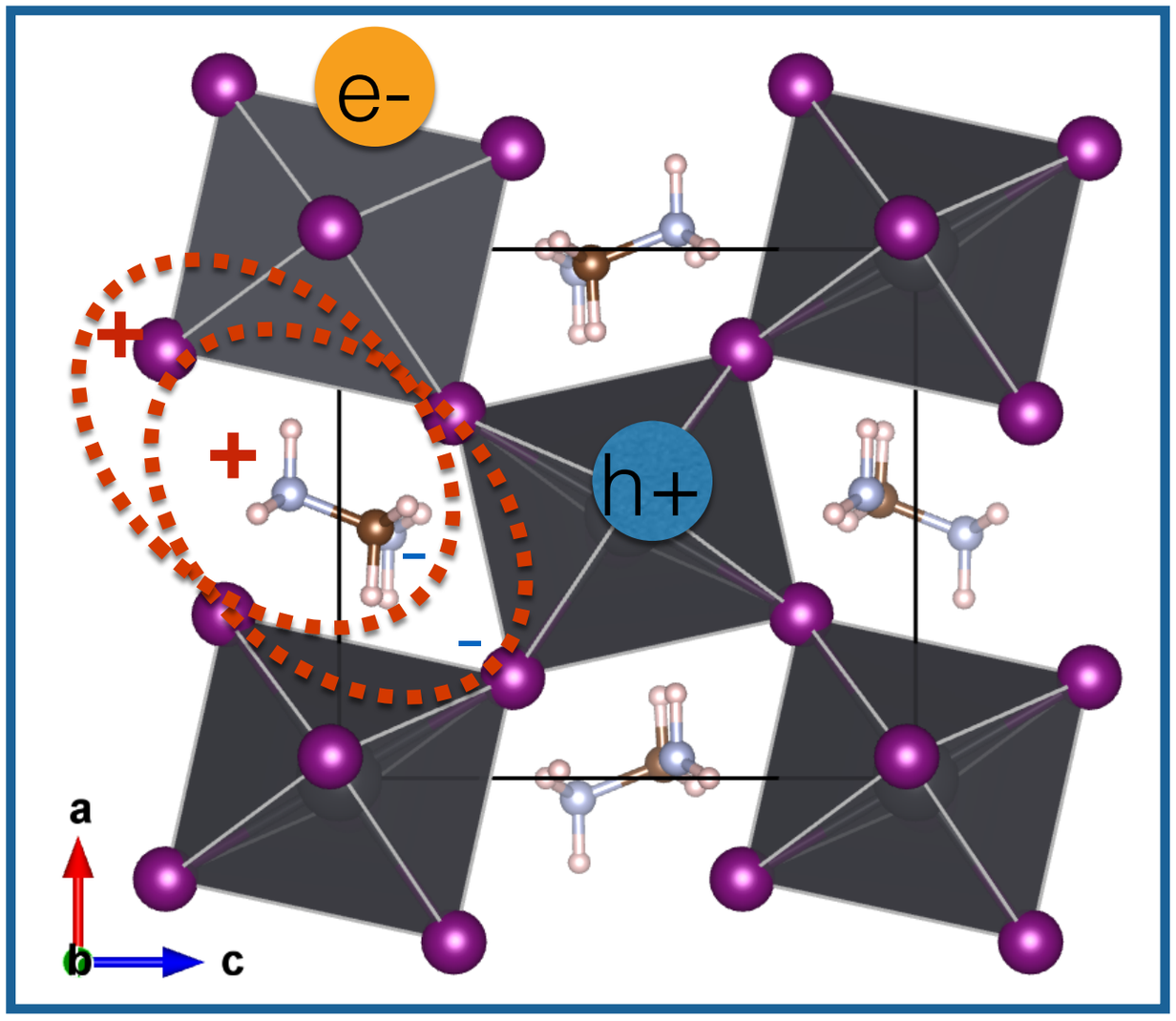




- Under **infrared illumination**, atoms in the l**attice will oscillate**. This **induced local field screens** the electron-hole interaction.

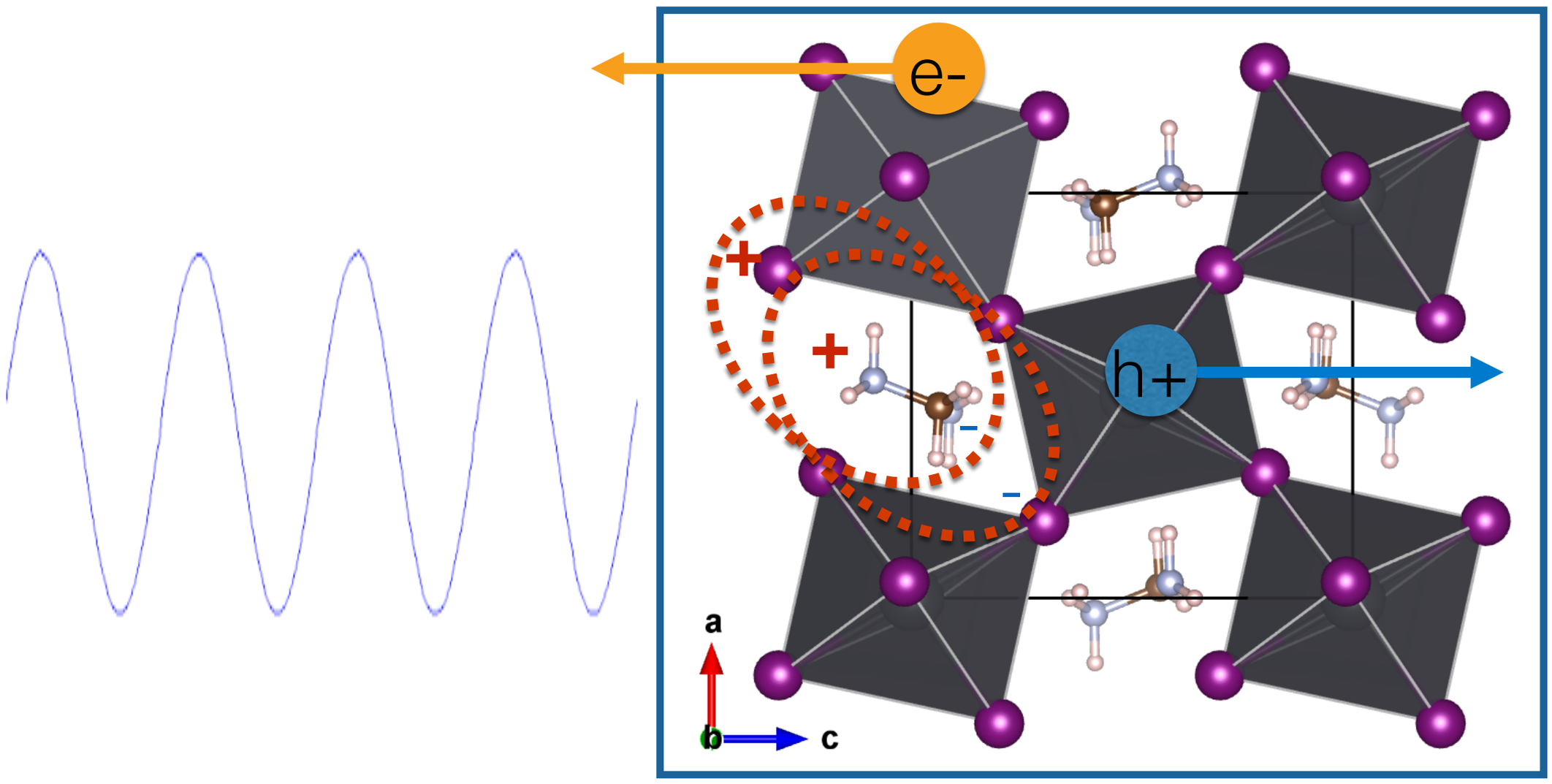
Lattice screening effects on electron-hole interaction





- Thus, the **exciton binding potential** between the electron and hole **is reduced**.
- This is called **Lattice Screening.**

Lattice screening effects on electron-hole interaction



- The electron and hole can **move independently** as **free charges** to carry electrical current.

Introduction of lattice screening to the Bethe-Salpeter Code

- The BSE code typically uses only **electronic screening**
  - Screening from oscillations in the electron cloud
  - Measured by $\boldsymbol{\varepsilon}_\infty$ = high frequency dielectric constant
  - Readily available parameter found in DFT
- We must add **lattice screening**
  - Measured by $\boldsymbol{\varepsilon}_0$ = low-frequency dielectric constant
  - More difficult to find in DFT
  - The wave vector dependence of lattice screening is unclear

Introduction of lattice screening to the Bethe-Salpeter Code

- We will use a model dielectric response to capture the electron interaction for both electronic and lattice screening

$$\varepsilon(q) = 1 + \left(\frac{1}{1-\varepsilon_0} + \alpha \frac{q}{q_{TF}}^2 + \frac{\hbar^2 q^4}{4m^2\omega_p^2} \right)^{-1}$$

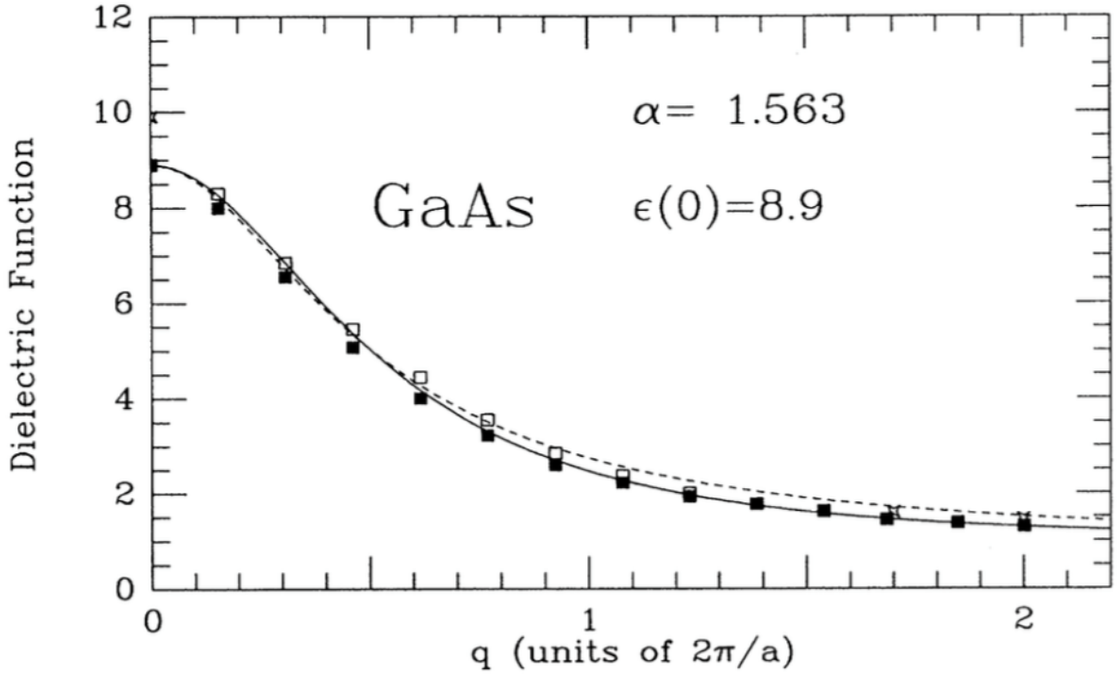


FIG. 3. As in Fig. 1 but referred to GaAs with $\epsilon(0)=\epsilon_0^{RPA}=8.9$. Stars are from Ref. 15.

- ε_∞ = 5.5 from DFT and DFPT, 6.0 from exp.
- ε_0 = 25.0 from DFPT, 32.0 from exp.

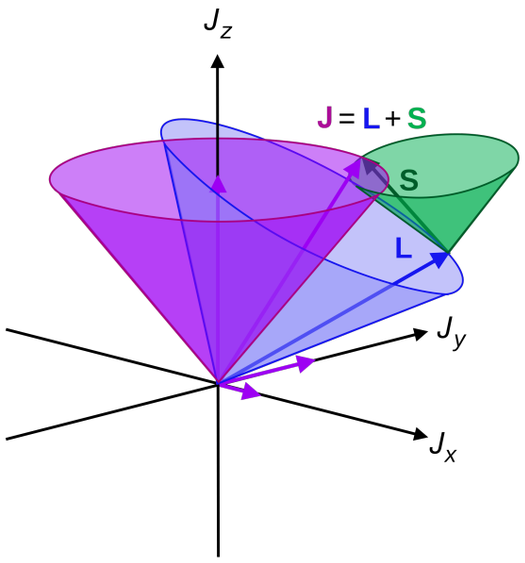
G. Cappellini, R. Del Sole, Lucia Reining, and F. Bechstedt. Phys. Rev. B **47**, 9892

Assembling a more physically accurate model of $CH_3NH_3PbI_3$

Theory

$$H_{BSE,cvk}^{c'v'k'} = H_{cvk}^{diag} + H_{cvk}^{c'v'k'interaction}$$

BSE for Excitonic Effects



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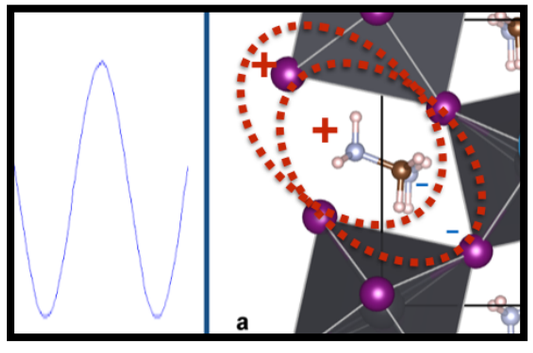
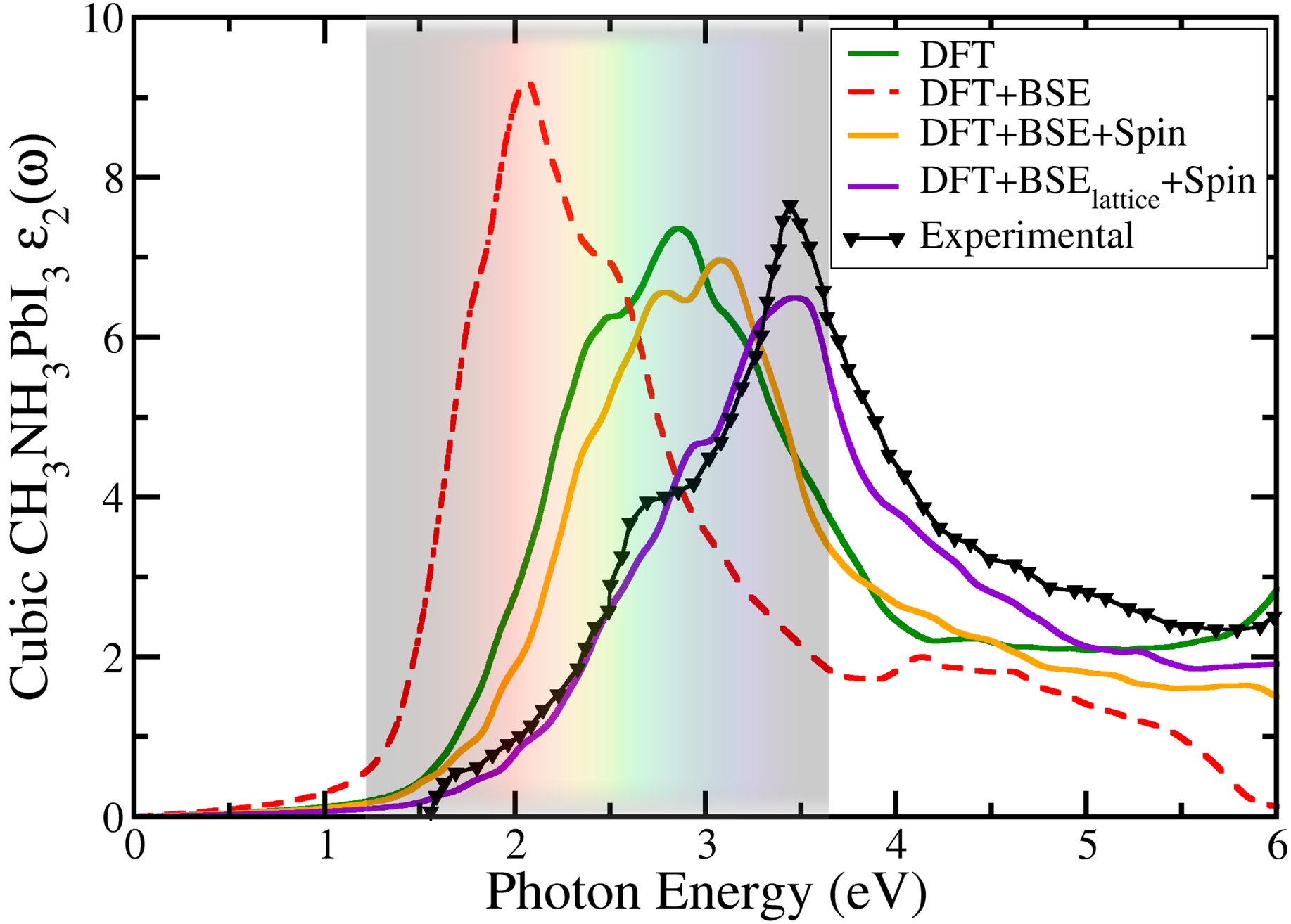


Lattice Screening

Computation

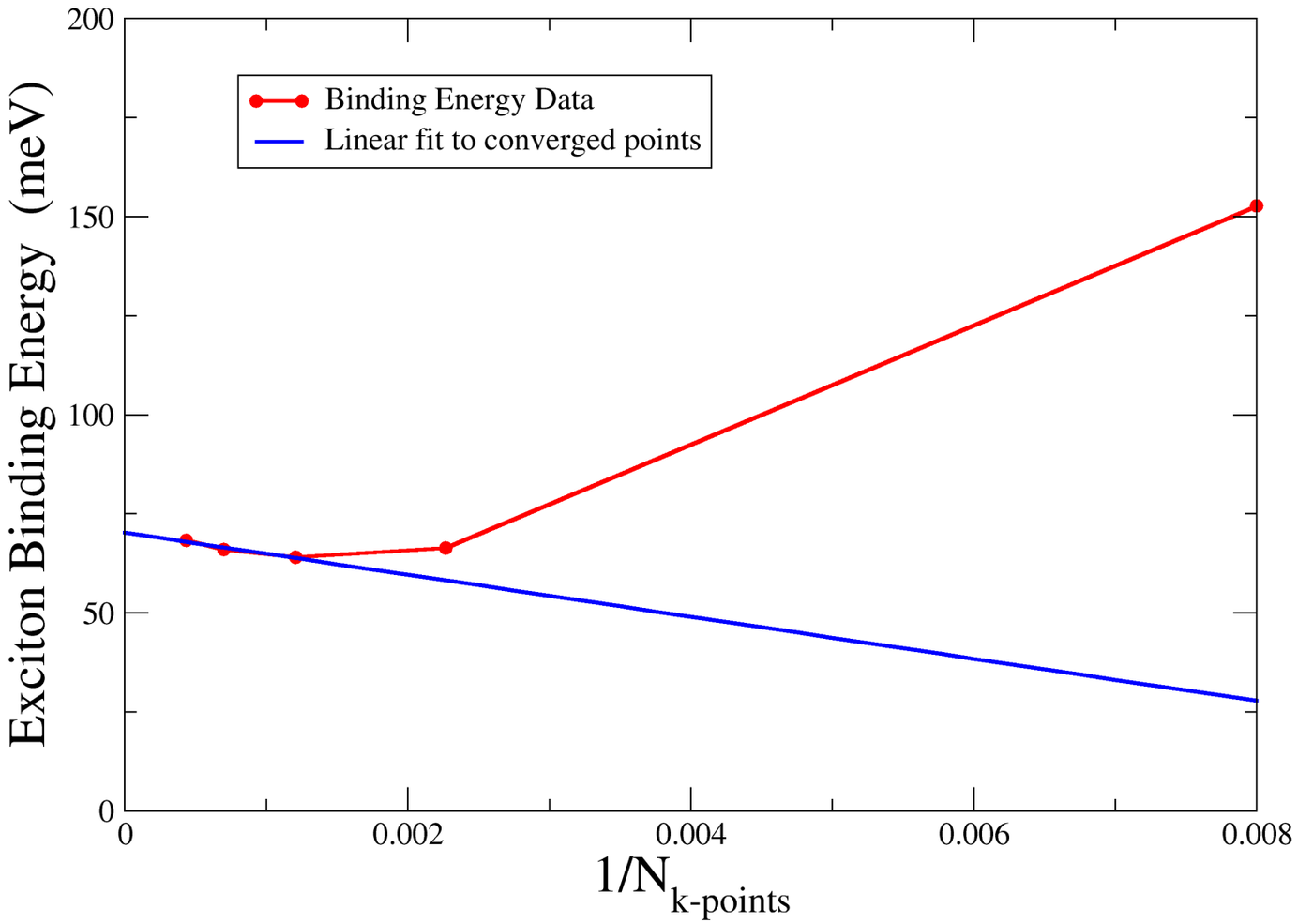
- DFT (small calculations)
  - Wavefunctions, Bands
- BSE runs on 62 nodes
  - Excitonic BSE Matrix
  - Rank 100,000
  - ~100 GB of data
- Spectrum Calculation
  - Calc eigenvalues(vectors)
  - Use them to assemble the dielectric function
  - Exciton binding energies

Final verdict: excellent predictions of experimental spectrum!



- Agrees exceptionally well with experimental results
- Could demonstrate a new method to describe polar semiconductors

Exciton binding energy - a critical computational challenge

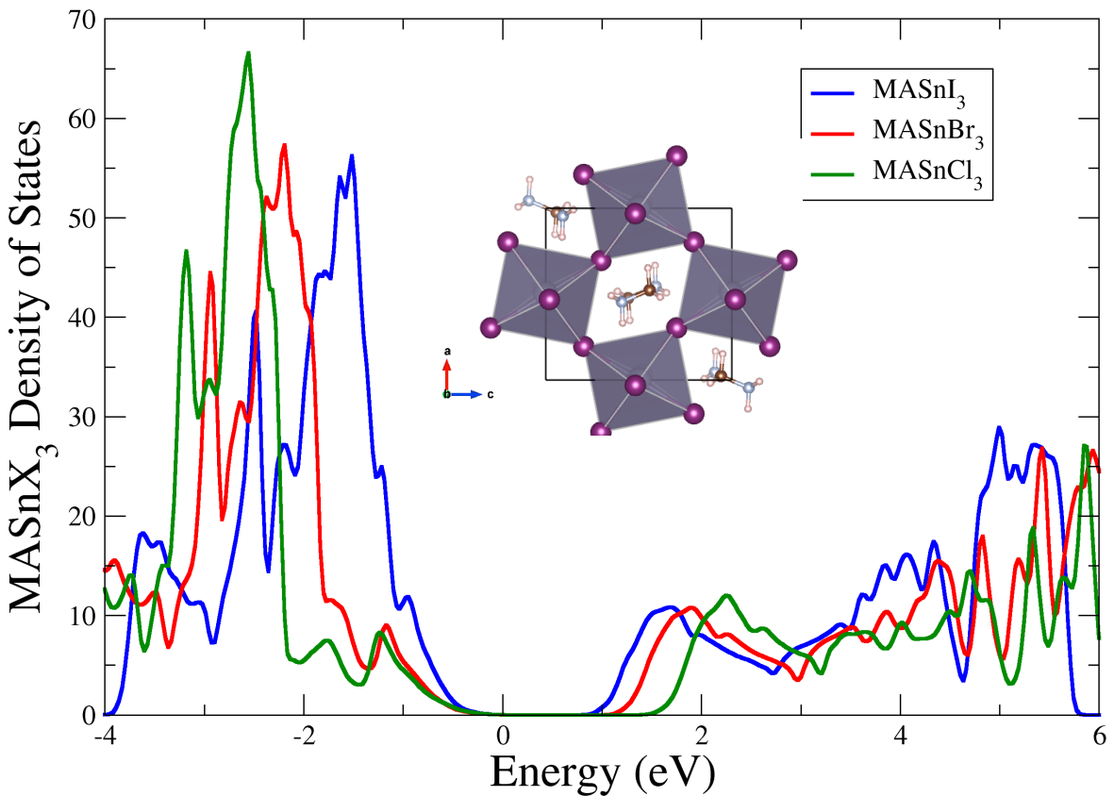


- determines how “bound” electrons and holes are in the materials
- Low binding energies result in more free carriers
- It is very important to be able to predict this value - very costly

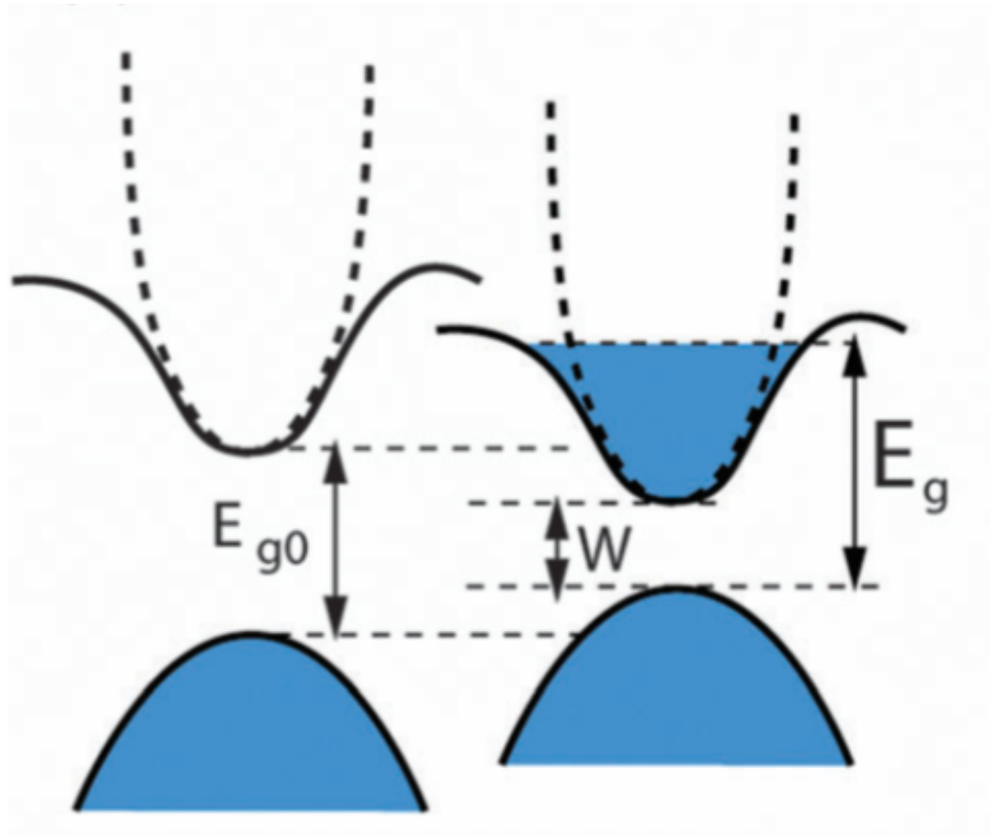
N K-points	$E_{binding}$ (meV)	Rank BSE Matrix	Size BSE Matrix (GB)	Size Wavefunctions (GB)
125	152.6	203	0.0008	0.575
441	66.3	2145	0.034	2.0
827	64.0	4689	0.164	3.8
1429	66.0	8749	0.570	6.5
2295	68.3	14771	1.626	11.0

Future goals: alternative perovskites and free charge carries

- $CH_3NH_3SnX_3$ are a promising alternative to Pb perovskites
- Not as well explored both experimentally and theoretically



- How do free carriers effect the optical properties and spectrum of hybrid perovskite materials



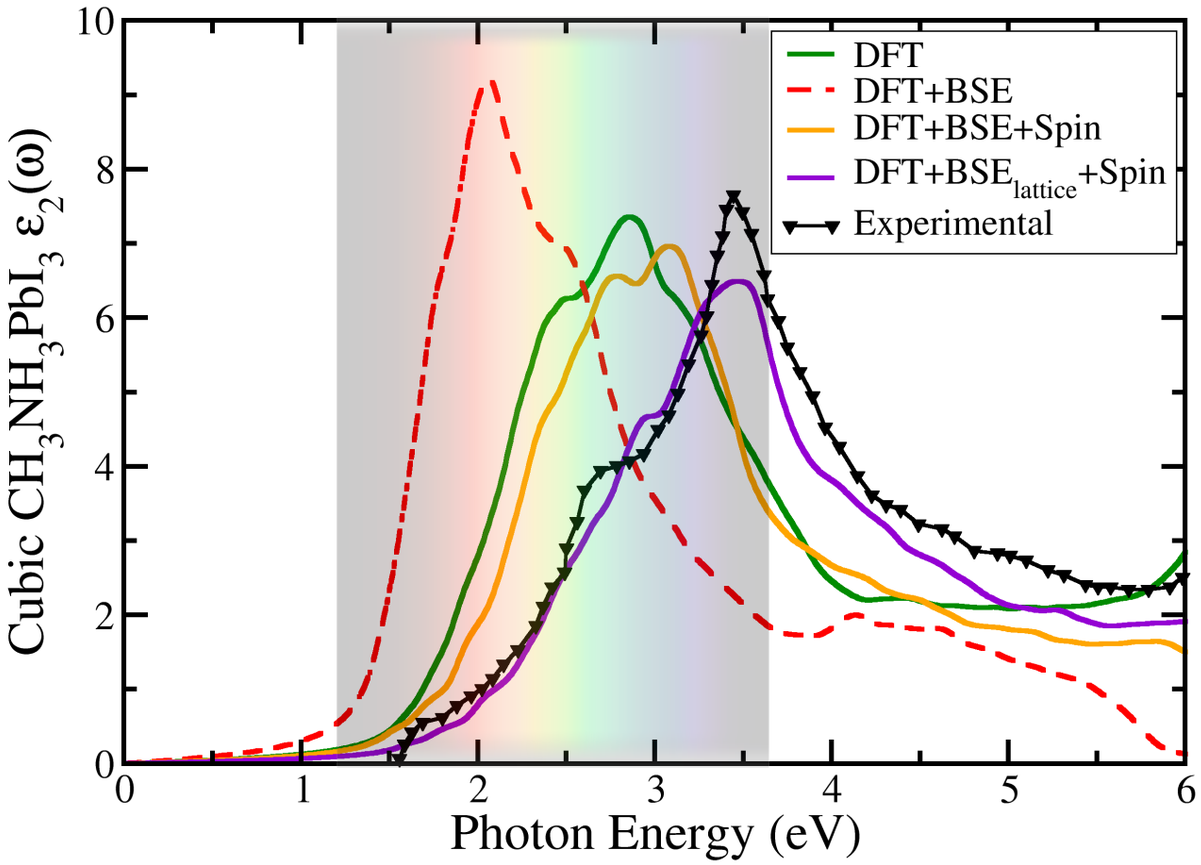
http://pubs.rsc.org/en/content/articlepdf/2014/cs/c3cs60265f?page=search

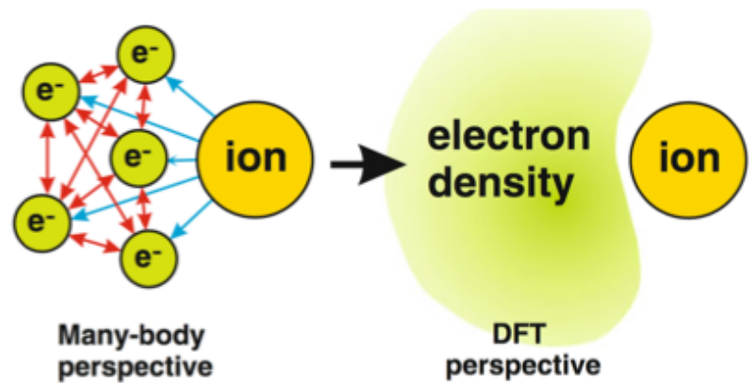
Conclusion

- The inclusion of **excitonic effects, SOC, and lattice screening** are critical to predicting optical properties of perovskite solar cells and other polar semiconductors

- To converge optical calculations, **large data sets must be calculated and stored**

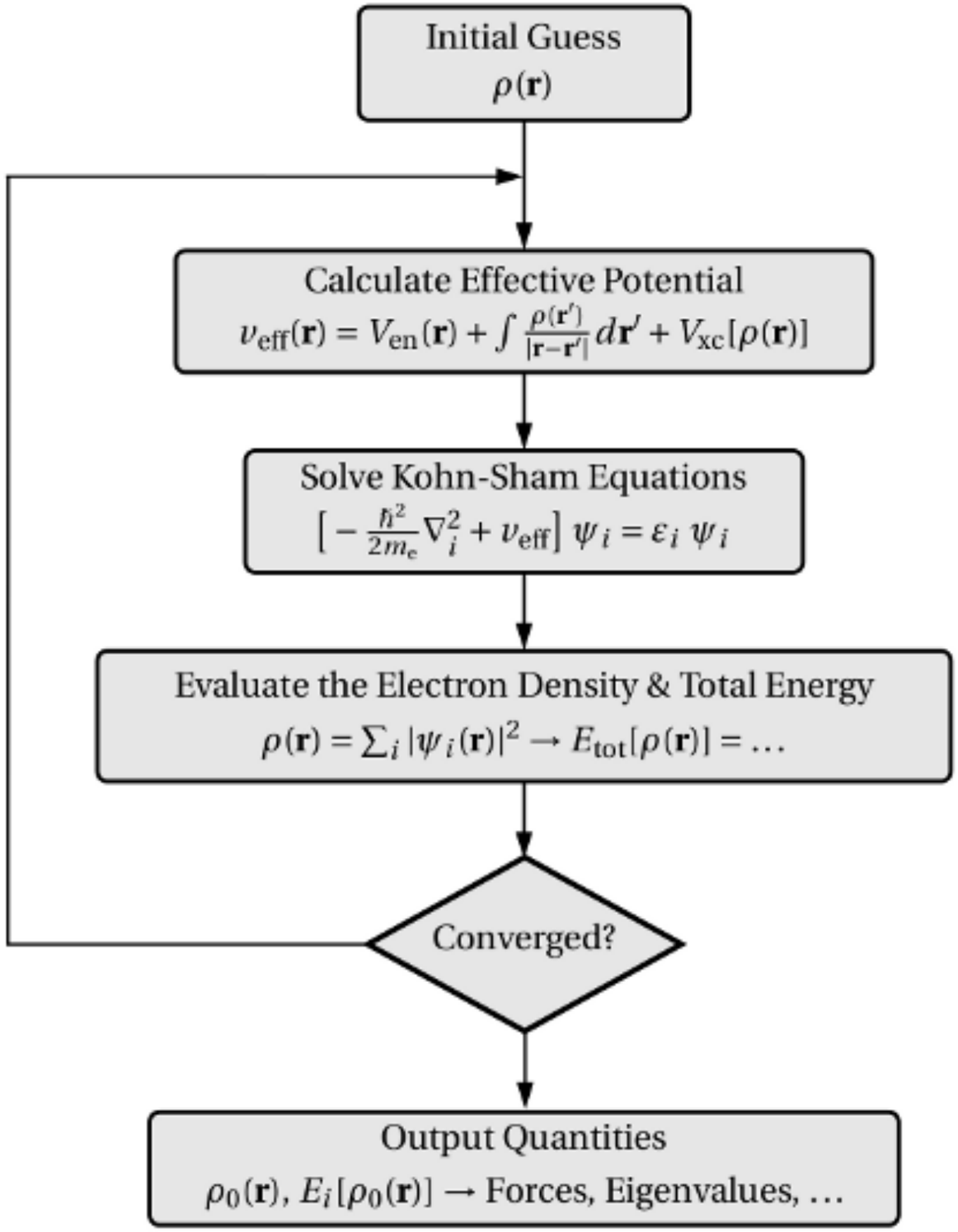
- **Blue Waters Supercomputer and NCSA** have been critical to the success of this project and will be **critical the future higher-accuracy calculations**





$$H_{BSE,cvk}^{c'v'k'} = H_{cvk}^{diag} + H_{cvk}^{c'v'k'interaction}$$

Supplement 1 - DFT Iterative Scheme



http://www.iue.tuwien.ac.at/phd/goes/dissse14.html

Supplement 2 - RPA vs Model Dielectric Function

$$\epsilon_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega) := \delta_{\mathbf{G},\mathbf{G}'} - \frac{4\pi e^2}{|\mathbf{q}+\mathbf{G}||\mathbf{q}+\mathbf{G}'|}\chi^0_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega)$$

- We can calculate dielectric screening by the Random Phase Approximation in DFT. This is extremely expensive for medium to large k-point grids

$$\varepsilon(q) = 1 + \left(\frac{1}{1-\varepsilon_0} + \alpha\frac{q}{q_{TF}}^2 + \frac{\hbar^2 q^4}{4m^2\omega_p^2}\right)^{-1}$$

- Alternatively, we can calculate the dielectric constant in DFT or DFPT then use a model dielectric function that numerically matches RPA results - cheaper and still maintains physical accuracy

https://www.vasp.at/mmars/day2.pdf

G. Cappellini, R. Del Sole, Lucia Reining, and F. Bechstedt. Phys. Rev. B **47**, 9892