Materials Modeling using first principles calculation

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Theoretical Model of Materials

Capture both *material-specific* and *universal* properties:

**Goals:**
- Identify microscopic mechanism
- Complement experimental probes
- Predict new novel materials or structure

**Ingredients:**
- **Electrons:** Need Quantum Mechanics
  - Interacting many-body problem (an outstanding problem)
  - Need computational method (with physically acceptable approximations)
  - Evaluate concerned properties
  - May Not-be-so-good for strongly correlated electron systems

- **Nuclei:** Needs the inter-atomic potential

Electrons and nuclei interact via Electromagnetic fields
P. A. M. Dirac (1929)

“The underlying physical laws necessary for a large part of physics and the whole of chemistry are completely known, the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble”.

Computational Modeling (Density Functional Theory)

\[ i\hbar \frac{d\Psi(\{\vec{r}_i\}, t)}{dt} = \hat{H}\Psi(\{\vec{r}_i\}, t) \]

\[ H = \sum_{i=1}^{N_e} \nabla_i^2 + \sum_{i=1}^{N_e} V_{Nuc}(r_i) + \sum_{i=1}^{N_e} V_{Effec}(r_i) \]

DFT is a method to solve the electronic structure and energetics of arbitrary materials starting from **first principles**

In theory, it is **exact** for the ground state. In practice, accuracy depends on many factors, including the type of material, the property to be studied, and whether the simulated crystal is a good approximation of reality.

DFT resulted in the **1999 Nobel Prize** for chemistry (W. Kohn). It is responsible for 2 of the top 10 cited papers of ALL time, across all sciences.
For spintronics, dilute magnetic semiconductors (DMS) and half metallic materials plays an important role. One of the drawback is low $T_c$.

Spin Gapless Semiconductors (SGS) are new class of materials. It involves finite band gap in one spin channel and zero gap for other.

Advantages of SGS:
1) High $T_c$
2) Almost no energy required to excite an electron from valence to conduction band $\Rightarrow$ hence easy to tune
3) High spin polarization
Thermoelectric Materials
Antifluorite \( \text{Mg}_2\text{X} \) (X=Si, Ge, Sn) is a promising thermoelectric material due to its high figure of merit (\( ZT > 1 \)).

Well known fact: \( \text{Mg}_2\text{X} \) severely suffer from intrinsic defects such as vacancies, interstitial and anti-site defects ➔ Not much studied!!

Goal: Investigate the effect of magnetic doping and defect mediated changes in the behavior of electronic and thermal excitation ➔ sensitive to the thermoelectric properties.
Fe-based Superconductors

- Planar structure
  Staggered As\(^{3-}\) above and below Fe\(^{2+}\) square plane

- Anti-ferromagnetic (AFM) Ground states
  Antiparallel along ‘a’ and ‘c’. Aligned along ‘b’ axes (b<a)
Superconductivity can occur with doping (x) on any site.

Competing magnetic, structural and superconducting phases

Low-T magnetic phases are more complicated e.g. Spin Density Wave (SDW).

Possibilities of new interesting materials

\[(\text{Ba}_{1-x}\text{A}_x)\text{Fe}_2\text{As}_2\]
\[\text{Ba}(\text{Fe}_{1-x}\text{T}_x)_2\text{As}_2\]
\[\text{BaFe}_2(\text{As}_{1-x}\text{R}_x)_2\]

□ **A** \{Na, K, Cs\}

□ **T** \{Cr, Mn, Co, Ni, Cu\}

□ **R** \{P, F, Se\}


Solar Energy Harvesting

Sunlight to electricity

Sunlight to gas

- SUN is the ultimate source of ALL energy.
- Several energy conversion technologies exist: sunlight to electricity (photovoltaic cells), sunlight to chemical energy (photocatalytic water splitting) fuel cells etc.
- ALL of these technologies rely on specific materials with certain properties, which needs to be found from materials research.
CH$_3$NH$_3$PbI$_3$ : Advantages and Limitations

- **Efficiency**: from 3.8% in 2009 to 22.1% in 2016.
- **Advantages**: i) High absorption coefficient (~10$^4$-10$^5$ cm$^{-1}$), open-circuit voltage, ii) Long carrier diffusion length, iii) Flexible synthesis techniques and device architecture.
- **Limitations**: i) Stability in the external environment, ii) Toxicity of Lead (Pb).
- **Solution**: improving the quality of the film, encapsulation, Altering the organic cation, mixing different halides: No significant improvement.
- **What else**, Cationic transmutation 2Pb$^{+2} \rightarrow$ B$^{+1} +$ B$'^{+3}$.
Double Perovskite (A$_2$BB’X$_6$) structure

- Cubic Fm-3m space group (#225).
- A,B has +1 charge state (8c & 4a wyckoff sites). B’ has +3 charge state (4b site). X are halides (Cl, Br, I) with -1 charge state (24e)
Status of A\textsubscript{2}BB’X\textsubscript{6} as photovoltaic: till now

- Long carrier lifetime & band gap in visible range: Cs\textsubscript{2}AgBiX\textsubscript{6}.
- Shows both direct \([\text{Cs}_2(\text{Cu, Ag, Au})^{+1}\text{(Al, Ga, In, Tl)}^{+3}X_6]\) and indirect \([\text{Cs}_2(\text{Cu, Ag, Au})^{+1}\text{(Sb, Bi)}^{+3}X_6]\) band gap for different constituent combinations.

- **Two problems:**
  
  i) For indirect band gap:
  Weak absorption & high recombination loss \(\Rightarrow\) Less efficiency.

  ii) For direct band gap:
  First direct VBM to CBM transition is *optically forbidden* \(\Rightarrow\) results in higher band gap thus low short circuit current \(\Rightarrow\) Less efficiency.
A$_2$BB’X$_6$ : Pb$^{+2}$ Substitution (Our proposal)

- We propose bivalent D(=Pb) substitution at both B and B’ sites of indirect band gap double perovskite Cs$_2$AgBiX$_6$ (X=Cl, Br, I)
- Cs$_2$(Pb$_{0.5}$Ag$_{0.75}$Bi$_{0.75}$)X$_6$.
  1 out of 4 Ag$^{+1}$ & Bi$^{+3}$ has been substituted with Pb$^{+2}$ in a 40 atom conventional unit cell
Electronic Structure: Cs$_2$AgBiBr$_6$ and Cs$_2$(Pb$_{0.25}$Ag$_{0.75}$Bi$_{0.75}$)Br$_6$

- Indirect → direct band gap transition, Band gap well in the visible region, VBM → CBM transition optically allowed.
Absorption coefficient comparable to state of the art material $\text{CH}_3\text{NH}_3\text{PbI}_3$. Simulated efficiency (SLME) even exceeds that of the best material.

$\text{Cs}_2(\text{Pb},\text{Ag},\text{Bi})\text{Br}_6$ is successfully prepared and characterized by our experimental collaborators.
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