Data-Driven Electronic Structure Analysis of Metal-Organic Frameworks

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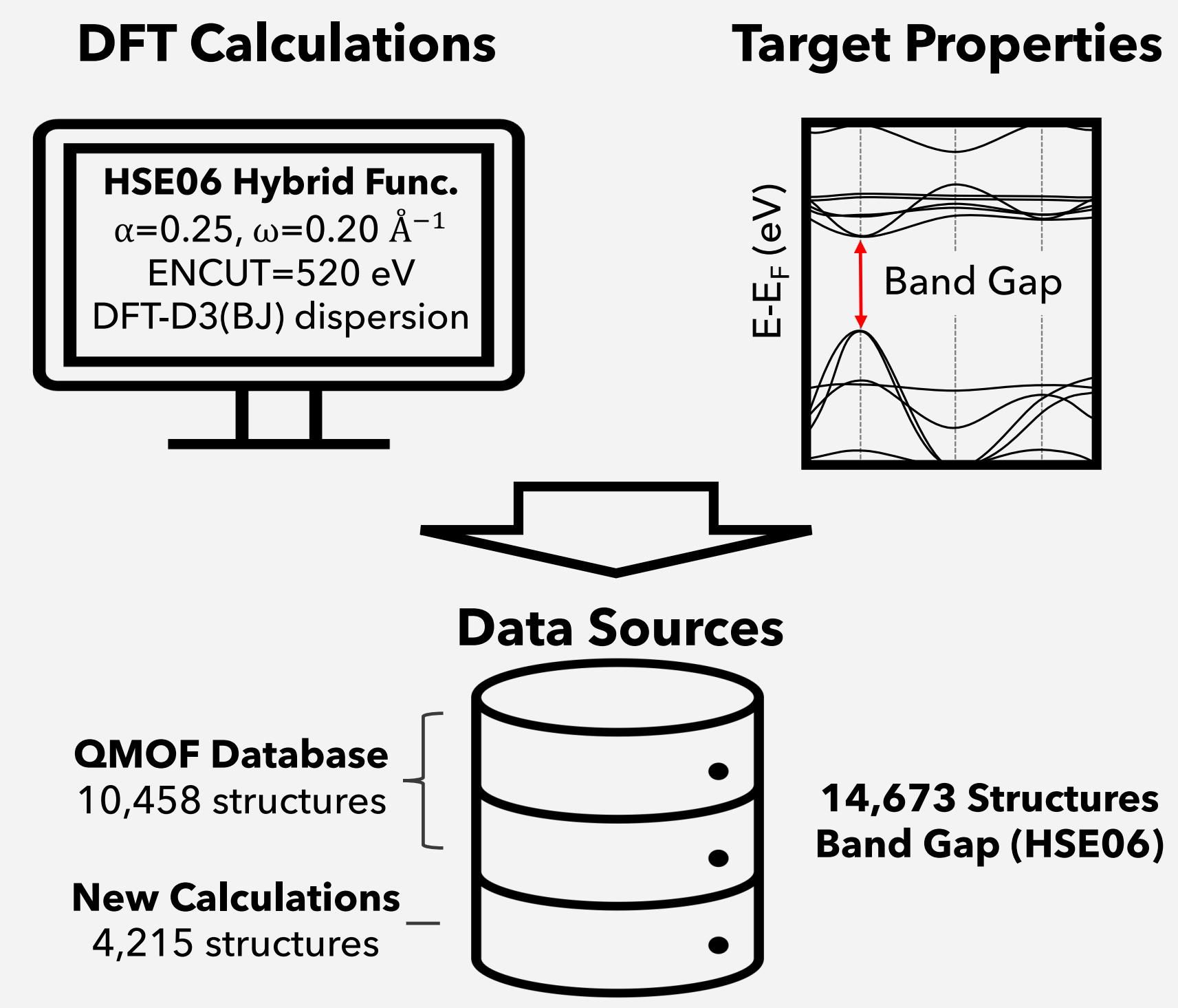
Introduction ...

⊟ Motivation

- **Problem:** Prior MOF band gap ML relies on PBE labels, which systematically underestimate E_g and hinder real-world screening
- **Solution:** We assembled a high-fidelity HSE06 dataset of ~15,000 MOFs
- **Composition:** 10,458 entries sourced from QMOF[1] + 4,215 newly calculated structures
- **Impact:** Provides accurate electronic labels to train fairer models, improving identification of semi-conductive MOFs and reducing PBE-induced bias

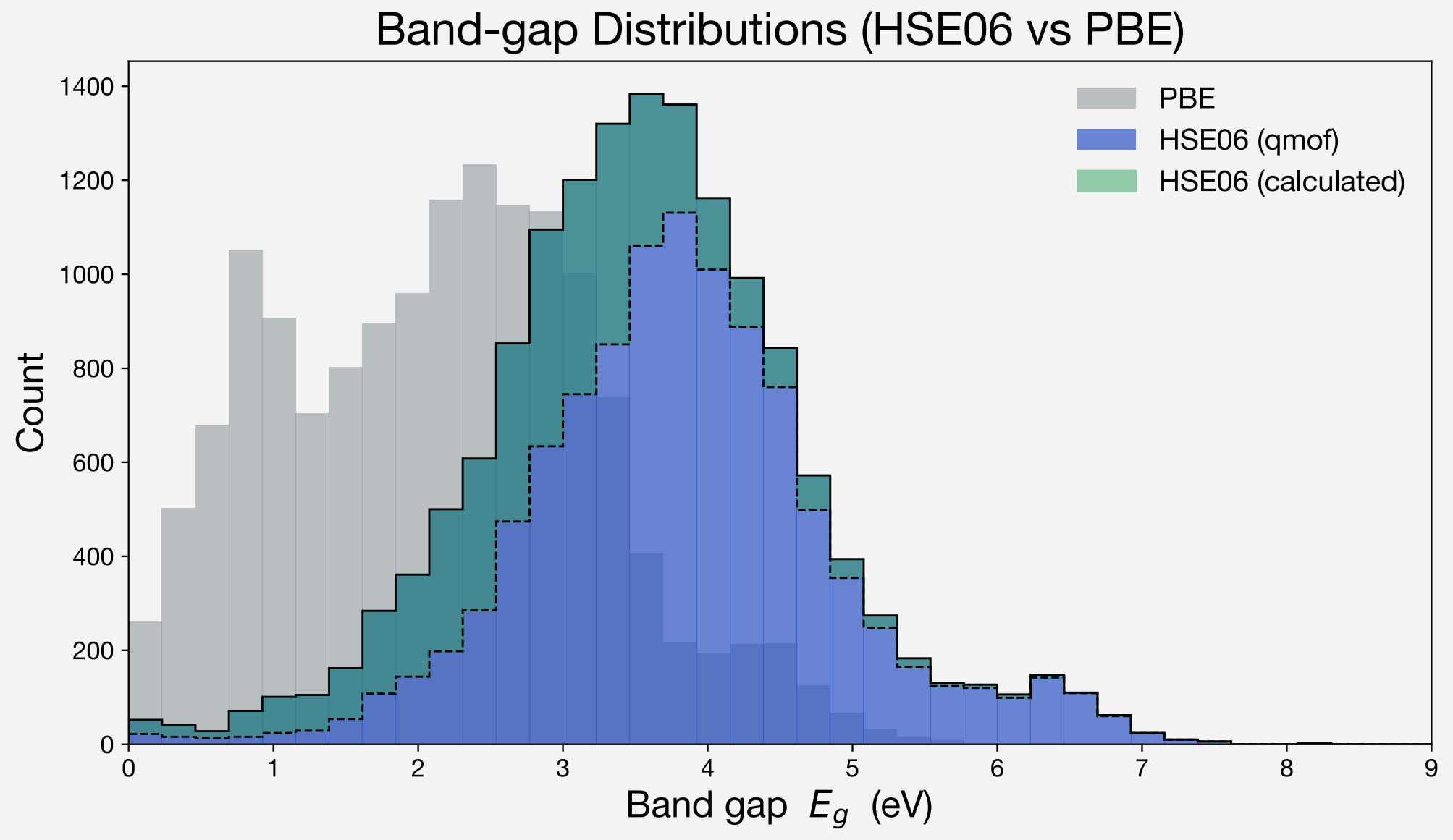


⊟ Dataset Overview

HSE06 vs. PBE Systematic Bias Correction

- **PBE Limitation:** Distribution clearly shows the underestimation of band gaps across entire domain
- **Largest errors:** Low band gap MOFs (E_g < 1.5eV) show 0.5-1.5eV discrepancies
- **HSE06 Solution:** Hybrid functional corrects bias and enables accurate ML training

Band-gap Distributions (HSE06 vs PBE)



Enabling generalizable model training

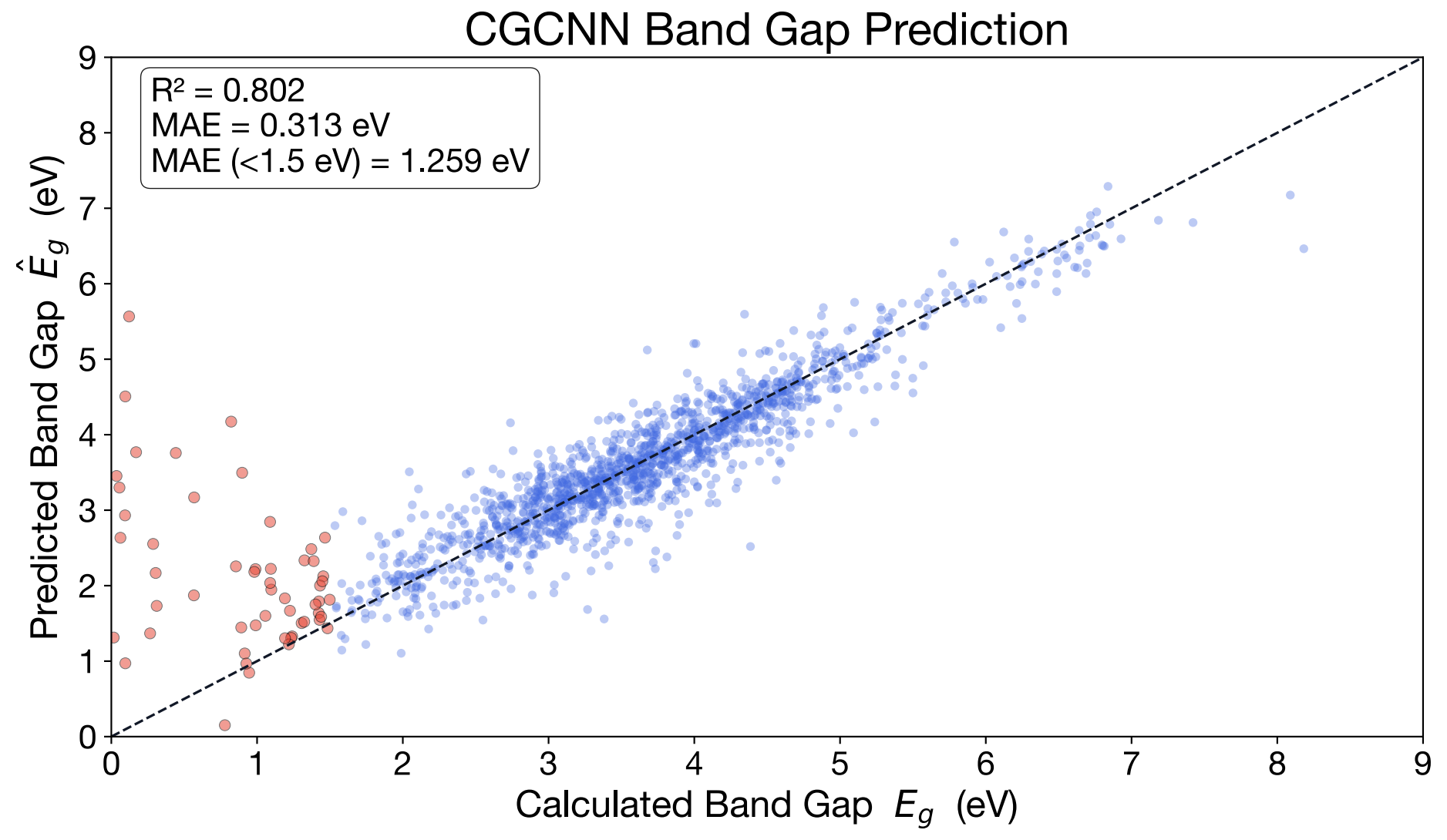
- **Complete spectrum:** 14,673 MOFs spanning 0–8 eV
- **Balanced extremes:**
  - Near-conductive: 472 structures (E_g < 1.5 eV)
  - Insulating: 468 structures (E_g > 6 eV)
- **Peak region:** Majority at 2-4 eV (semiconductors)
- **Why it matters:** Prevents model overfitting to central peak; captures underrepresented low-gap materials

Initial Analysis & Methodology ✕ ...

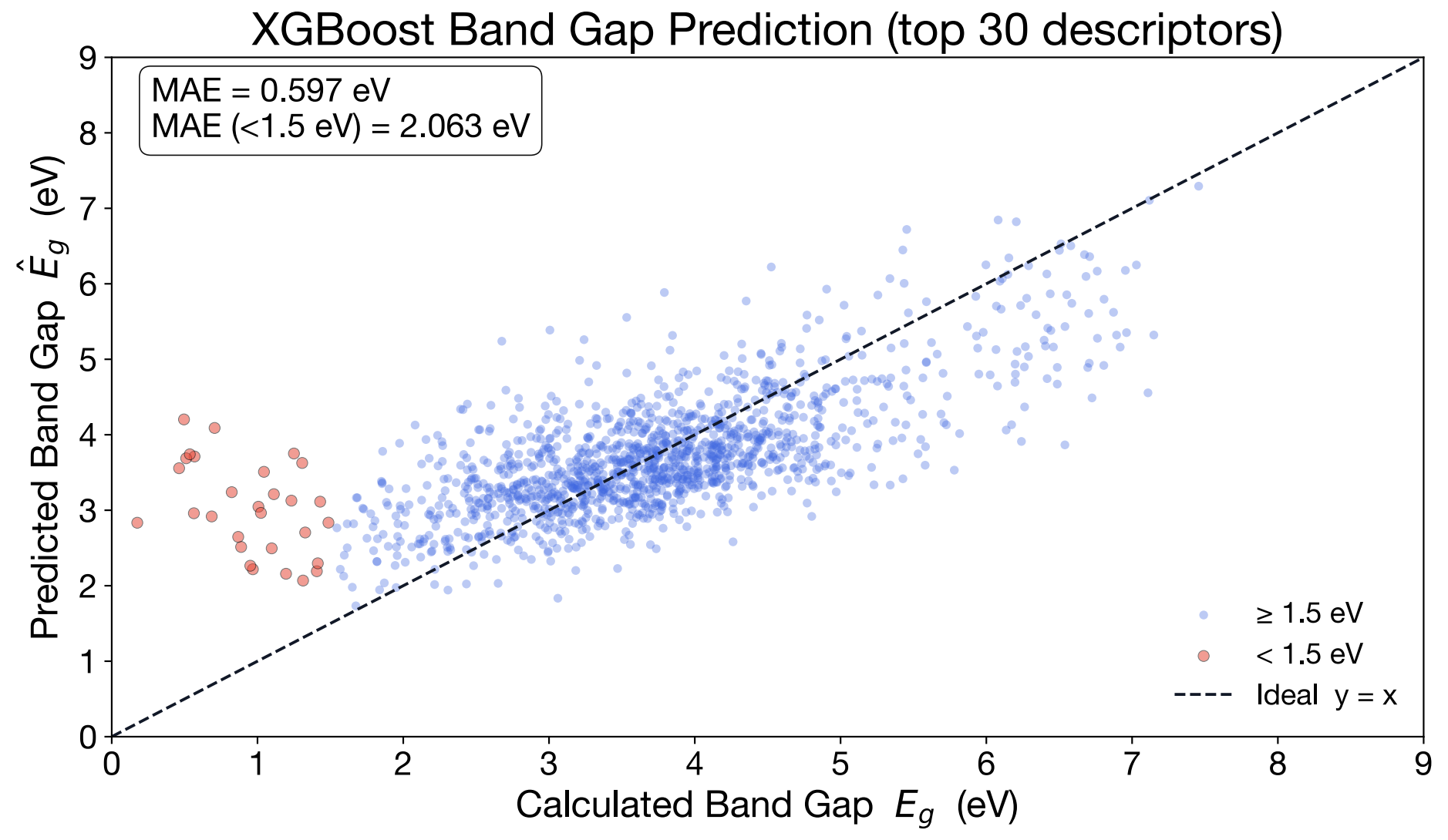
# Initial Analysis of ML Performance

- **GNN baseline:** CGCNN[2], a foundational crystal GNN model, was first evaluated for band gap prediction
- **Systematic limitation:** Despite strong global correlation, CGCNN exhibits consistent overestimation and increased error within the low-band-gap regime (E_g < 1.5 eV)
- **Interpretable approach:** Gradient-boosted decision trees (XGBoost) were employed to elucidate key structural and geometric features
- **Descriptor set:** Feature selection encompassed radial distribution function (RDF) peaks, crystallographic symmetry parameters, pore metrics, bond lengths, and coordination shell statistics
- **Feature contributions:** Short-range RDFs and symmetry descriptors emerged as most important, yet geometry-only features proved insufficient for accurate prediction of low-gap MOFs

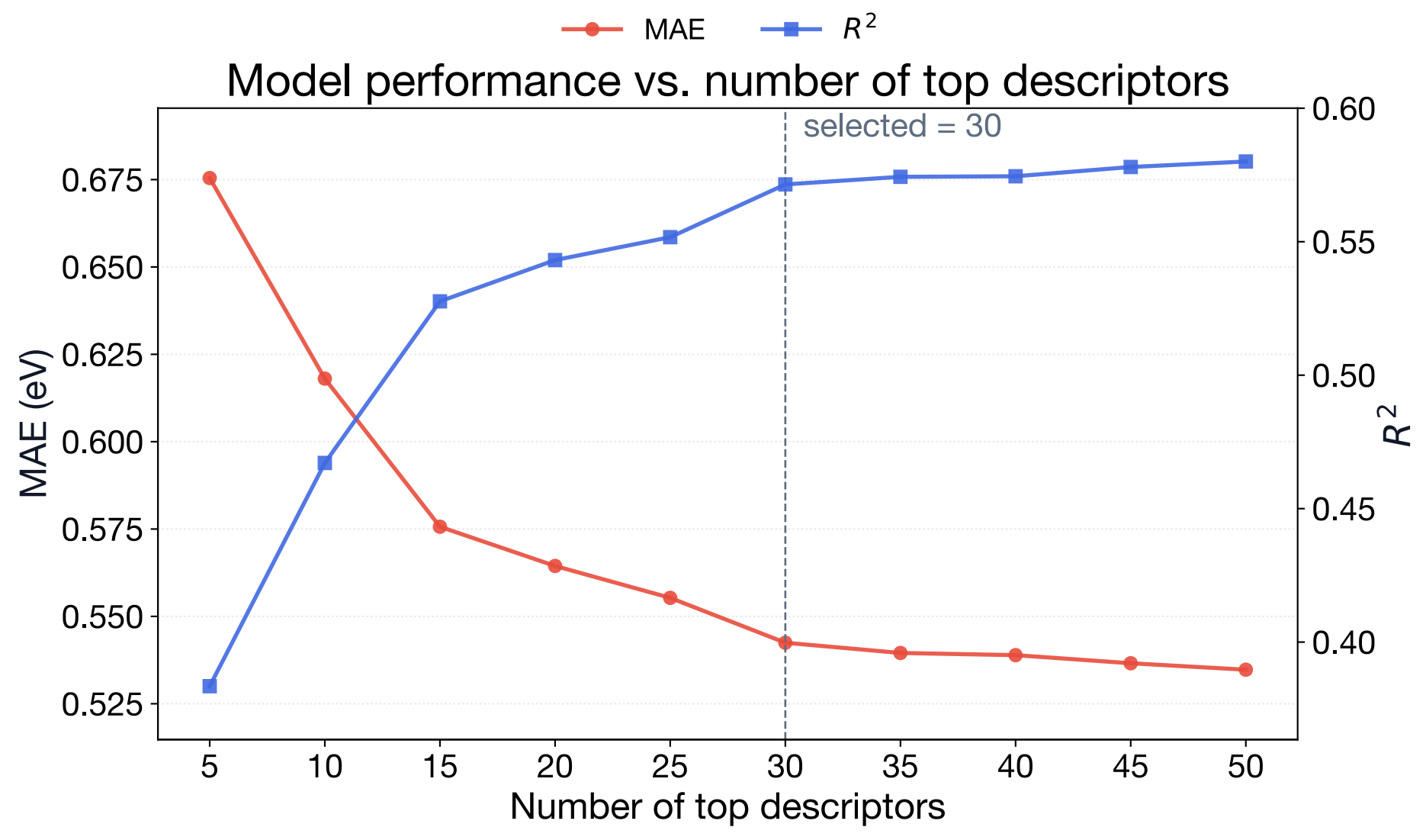
CGCNN Band Gap Prediction



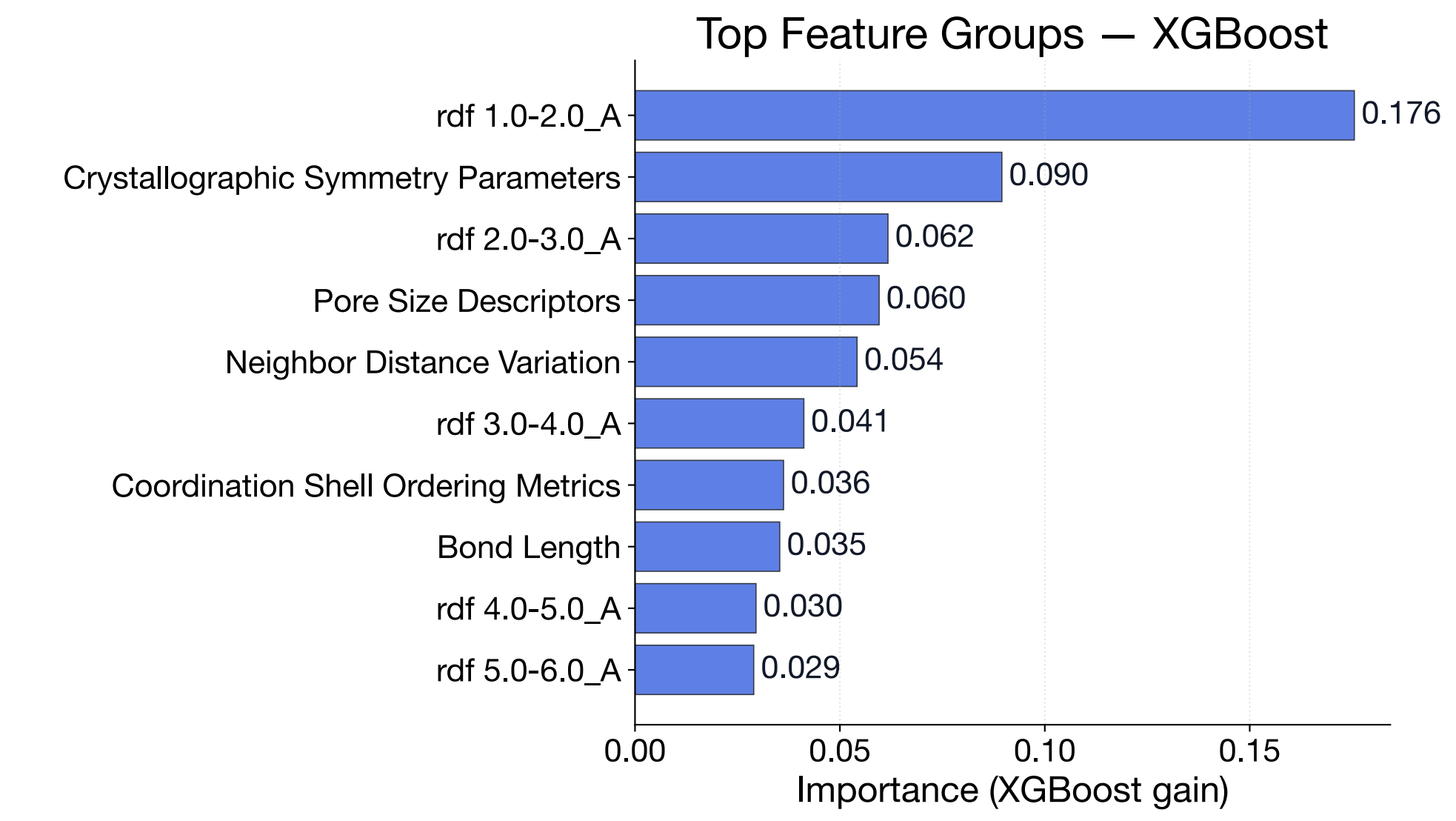
XGBoost Band Gap Prediction (top 30 descriptors)



Model performance vs. number of top descriptors

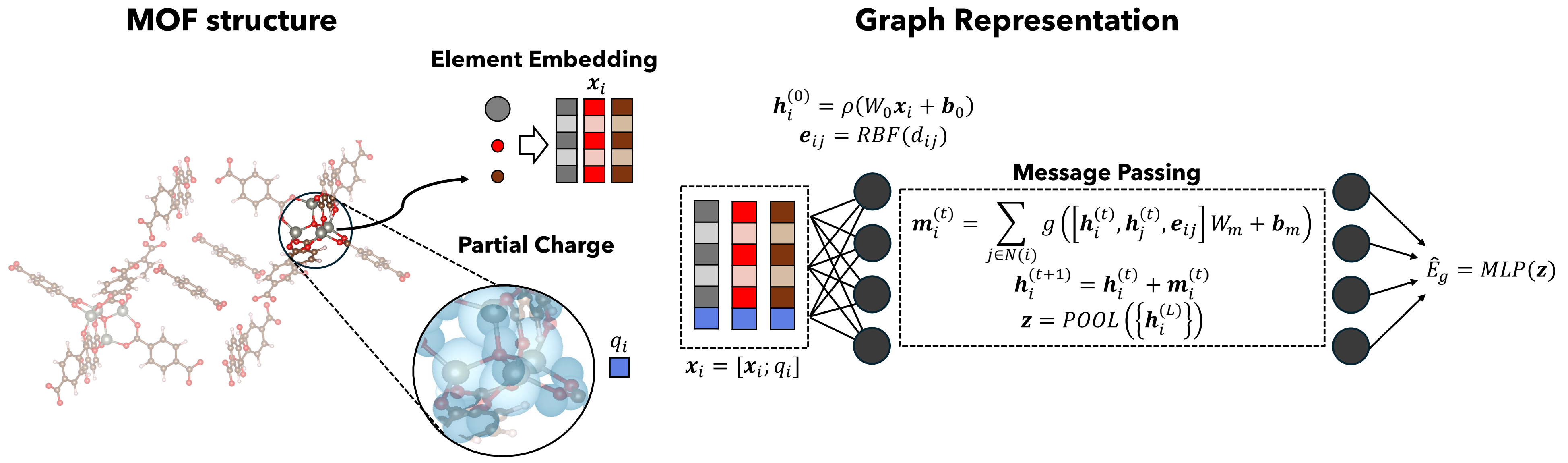


Top Feature Groups — XGBoost



# Model Description

- **Physics-informed node features:** Use per-atom partial charges predicted by PACMAN[3] to encode electrostatics and donor-acceptor character, which can be key for near-conductive MOFs
- **Graph construction:** Each atom's feature vector x_i is extended to $[x_i; q_i]$, directly integrating partial charge information into message passing and global pooling layers
- **Comparative methodology:** Benchmark scalar addition strategies by appending single-valued elemental features in the same fashion as charge, to evaluate the impact of different node augmentations.


MOF structure
Graph Representation
Element Embedding
$\boldsymbol{x}_i$
Partial Charge
q_i
$\boldsymbol{h}_i^{(0)} = \rho(W_0 \boldsymbol{x}_i + \boldsymbol{b}_0)$
$\boldsymbol{e}_{ij} = RBF(d_{ij})$
Message Passing
$\boldsymbol{m}_i^{(t)} = \sum_{j \in N(i)} g\left(\left[\boldsymbol{h}_i^{(t)}, \boldsymbol{h}_j^{(t)}, \boldsymbol{e}_{ij}\right] W_m + \boldsymbol{b}_m\right)$
$\boldsymbol{h}_i^{(t+1)} = \boldsymbol{h}_i^{(t)} + \boldsymbol{m}_i^{(t)}$
$\boldsymbol{z} = POOL\left(\left\{\boldsymbol{h}_i^{(L)}\right\}\right)$
$\boldsymbol{x}_i = [\boldsymbol{x}_i; q_i]$
$\hat{E}_g = MLP(\boldsymbol{z})$

Results & Conclusion ✕ ...

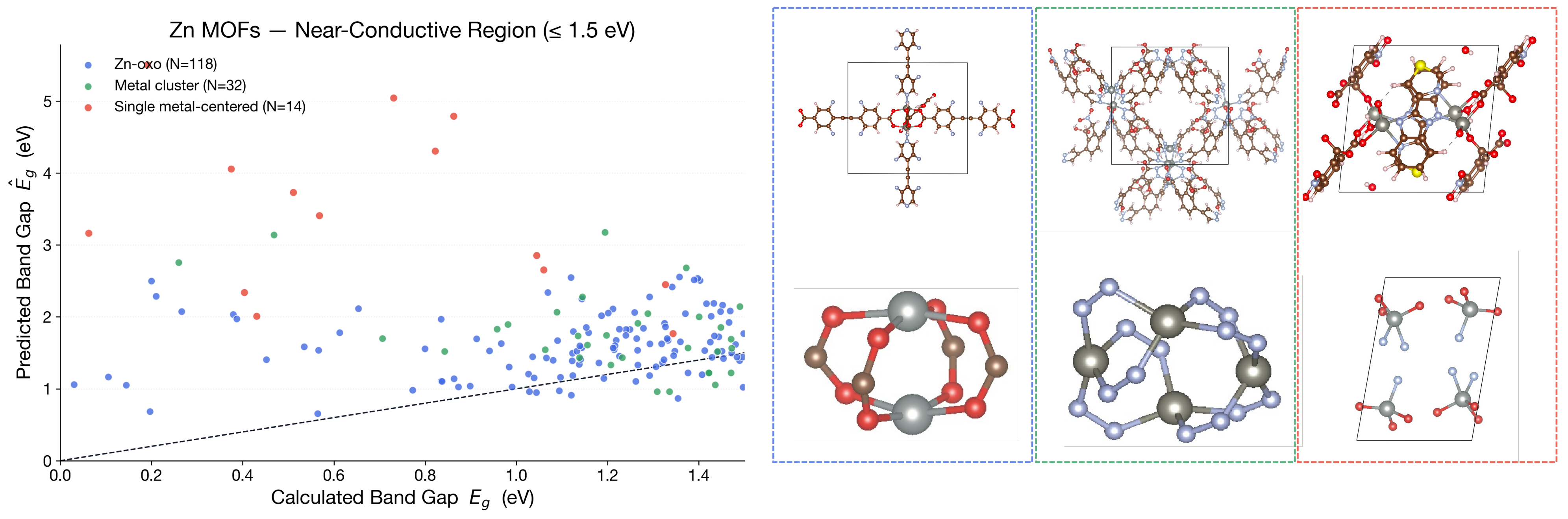
# Results

- **Charge embedding impact:** Incorporation of partial atomic charges produced the highest global accuracy and the lowest mean absolute error (MAE) for low-band-gap MOFs among all tested scalar augmentations, demonstrating that electrostatics-aware representations deliver information beyond geometric descriptors
- **Low-gap challenge remains:** Despite these gains, models continue to systematically overpredict for E_g < 1.5 eV, indicating the need for further integration of physical mechanisms to fully resolve conductive MOF prediction

Embedding Feature	MAE	MAE (E_g<1.5eV)	R^2
Charge	**0.2879 ± 0.0027**	**1.1492 ± 0.1362**	**0.8320 ± 0.0150**
Nf Unfilled	0.3064 ± 0.0088	1.2482 ± 0.0423	0.8161 ± 0.0244
Default	0.3067 ± 0.0058	1.1774 ± 0.1162	0.8198 ± 0.0183
GS Magnetic Moment	0.3077 ± 0.0118	1.2191 ± 0.1284	0.8198 ± 0.0209
GS Band Gap	0.3094 ± 0.0018	1.2319 ± 0.0650	0.8181 ± 0.0114
Np Unfilled	0.3099 ± 0.0073	1.2137 ± 0.0350	0.8189 ± 0.0175
Nd Unfilled	0.3110 ± 0.0077	1.2015 ± 0.0206	0.8178 ± 0.0141
GS Volume per Area	0.3146 ± 0.0110	1.2303 ± 0.1534	0.8086 ± 0.0215
Average	0.3077 ± 0.0099	1.2161 ± 0.0883	0.8179 ± 0.0163

# Case Study: Zn MOFs

- **Dataset focus:** Near-conductive Zn-MOFs (E_g < 1.5 eV) classified into Zn-oxo bridges (~71%), metal clusters (~20%), and single-metal-centered motifs (~9%)
- **Motif-specific results:** Zn-oxo structures yield the tightest residuals, clusters show moderate prediction error, single-metal-centered motifs exhibit the largest dispersion
- **Interpretation:** Predictive difficulty intensifies with increasing frontier orbital localization: Zn-oxo < clusters < single-center, highlighting underrepresented ligand-field and charge transfer effects in isolated centers, motivating further physical model enhancements



# Conclusion

- **Electrostatics-aware GNNs:** Integrating per-atom charge embeddings generally improves band gap prediction for MOFs, outperforming purely geometry-based or elemental scalar augmentation strategies
- **Persistent challenge:** Systematic overestimation remains for highly localized, low-gap cases—especially in isolated metal-center motifs—highlighting the need for further incorporation of ligand-field effects and advanced electronic descriptors
- **Outlook:** Ongoing work will focus on embedding deeper physical priors and environment-dependent features to achieve robust, transferable predictions across diverse MOF chemistries

References

[1] Rosen AS, et al. *npj Comput. Mater.* 8, 112 (2022)
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[3] Zhao G, Chung YG. *J. Chem. Theory Comput.* 20, 5368-5380 (2024)

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Resources https://github.com/kang-minhyuk/mof-electronic-structure

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