

Supplementary Information to: Higher-Order Equivariant Neural Networks for Charge Density Prediction in Materials

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Supplementary Notes

1 Additional training details

For training the invDeepDFT and equiDeepDFT models on the MP dataset, we use the same training and model configurations as the original work, training for 10^6 steps. For NMC and QM9 datasets, we use the authors released models, which are reported to have been trained for 5×10^6 and 6.5×10^6 steps respectively. We note that this is comparable to the number of steps Charge3Net is trained for on these datasets, as shown in Supplementary Table 2.

2 Heat capacity and thermal conductivity of faujasite

Computing thermal properties of materials require knowing the phonon modes of the material. A typical approach to finding phonon modes and their corresponding vibrational frequencies is to first compute the Hessian of the total energy with respect to the atomic positions, yielding a second-order (harmonic) approximation to the potential energy surface. The Hessian can be found via finite differences, and the number of displacements required scales with the size of the system under study. These computationally intensive calculations may be made cheaper with accurate charge density estimates from Charge3Net, and we show that the charge density predictions are robust to small perturbations of atomic positions (see Supplementary Fig. 11). Below, we further show that even non-self-consistent calculations of thermal properties with these estimates yield near-perfect agreement with self-consistent calculations of the same.

We evaluate two variants of faujasite zeolite, one that is purely composed of Si and O (USY) [1], and another where a portion of the Si sites are exchanged with Al charge-balanced by Na ions (NaX). The structures of these are shown in Supplementary Fig. 26. Understanding the thermal properties of porous materials such as these via data-driven predictive models could aid high-throughput

screening of gas adsorbents for industrially relevant separation processes such as carbon capture [2, 3, 4]. We note that while the elemental compositions of USY and NaX (Si-O and Na-Al-Si-O, respectively) exist in the Materials Project dataset, porous zeolites are not found in the dataset. Despite this, we show that the constant-volume heat capacity (C_v) obtained via the harmonic approximation from non-self-consistent calculations on ChargeE3Net’s predicted charge densities closely resemble the C_v obtained by self-consistent DFT (see Supplementary Fig. 27). Charge density predictions of USY and NaX had an average ε_{mae} of 0.16% and 0.58%, respectively. This demonstrates ChargeE3Net’s ability to obtain accurate macroscopic properties of unseen structures by predicting local perturbations to the charge density

3 Electronic bandstructure of Si surface

DFT calculations on material surfaces are highly important for understanding catalytic reactions, material interfaces, and corrosion [5]. Because surfaces are not part of the training set, obtaining accurate charge densities from ChargeE3Net shows one example of the model’s ability to generalize to unseen atomic environments.

Pandey shows through tight-binding calculations that the Si(111)-(2x1) surface, the structure of which is plotted in Supplementary Fig. 28, is characterized by pairs of Si sites that undergo significant bond rearrangement to form zig-zag patterns of raised Si atoms. These pairs form chains of π -bonds across the surface. While multiple polymorphs of Si, both experimentally-observed and hypothesized, are catalogued in the Materials Project and part of the training set, ChargeE3Net was not trained on any Si surface charge densities. We obtain the structure of the surface model from [6], and in Supplementary Fig. 29, we show that a non-self-consistent (NSC) calculation using the charge density output by ChargeE3Net reproduces almost exactly the electronic bandstructure of a self-consistent (SC) DFT calculation. Interestingly, even the bands corresponding to the surface Si sites at the valence band maximum and conduction band minimum are accurately reproduced, indicating the model is capable of extrapolating the charge density grid in a physically meaningful way despite new atomic environments such as 3-coordinate surface Si sites. The ε_{mae} of the predicted charge density is approximately 0.83%, and the distribution of charge density prediction error is shown in Supplementary Fig. 28.

Supplementary Tables

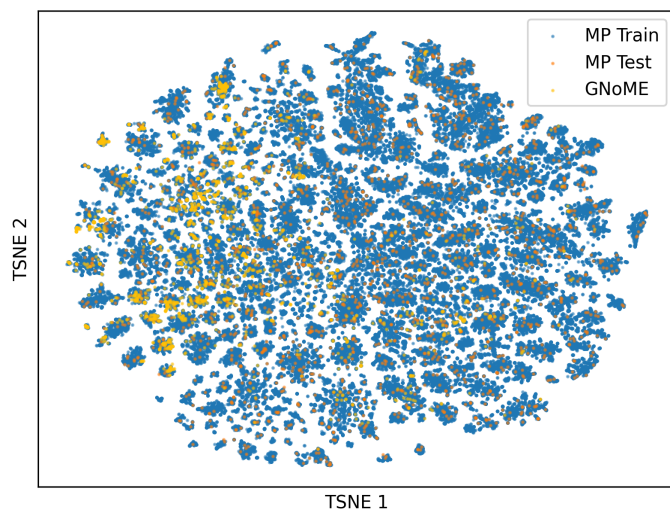
Supplementary Table 1: Training setup

Dataset	Learning Rate	Decay β	L	Batch Size	N_{points}	Steps
NMC	0.01	10^4	4	8	200	$7.5 * 10^5$
QM9	0.01	10^4	4	8	200	10^6
MP	0.005	$3 * 10^3$	4	16	200	10^6

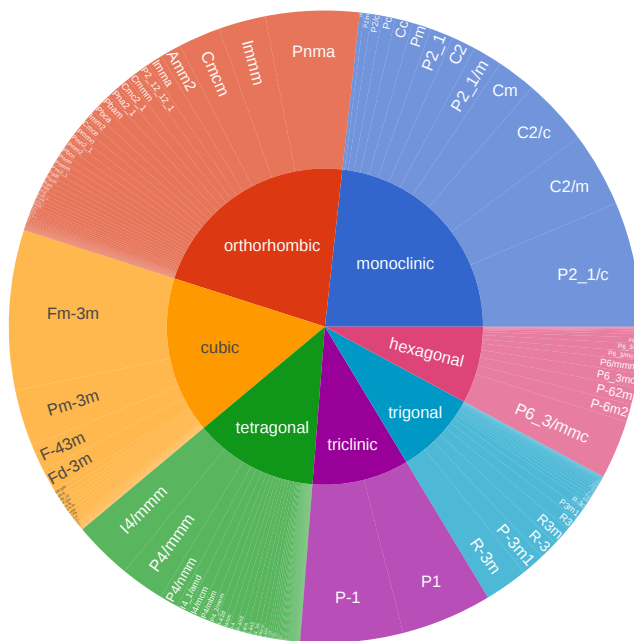
Supplementary Table 2: Loss function ablation, reported in average ε_{mae} (%), $\pm$ one standard error.

Loss Function	MP	QM9	NMC
MSE	0.722 ± 0.011	0.268 ± 0.001	0.076 ± 0.001
L1	0.523 ± 0.010	0.196 ± 0.001	0.060 ± 0.001

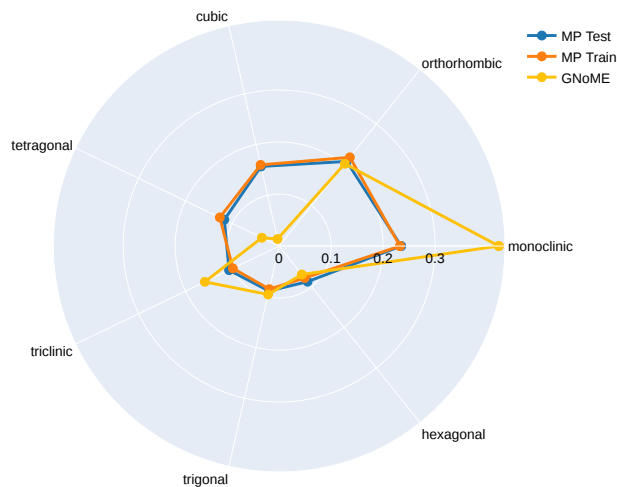
Supplementary Figures



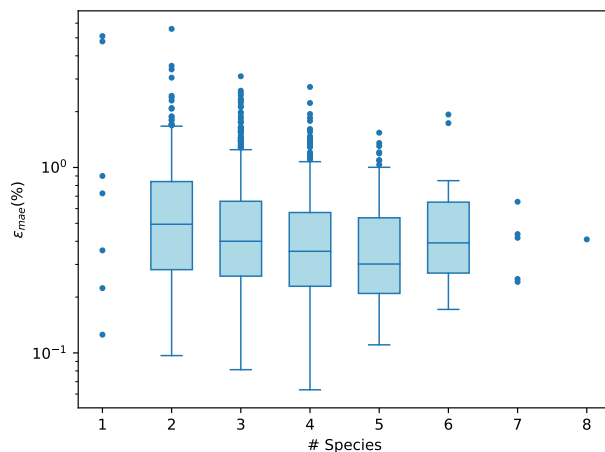
Supplementary Figure 1: t-SNE visualization of Smooth Overlap of Atomic Positions (SOAP) descriptors of the MP train and test subsets, along the GNoME subset used for evaluation. Descriptors are computed using DScibe [7] with a cutoff radius of 4 Å and compressed [8] with $\mu = 1, \nu = 1$.



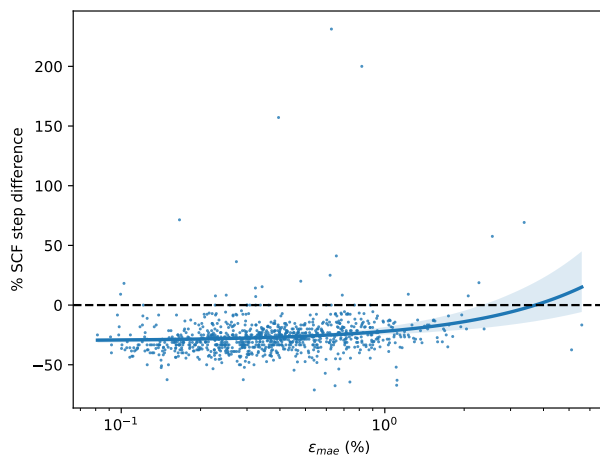
Supplementary Figure 2: Sunburst plot showing the Materials Project training split crystal systems and space groups. Created using PyMatViz [9]



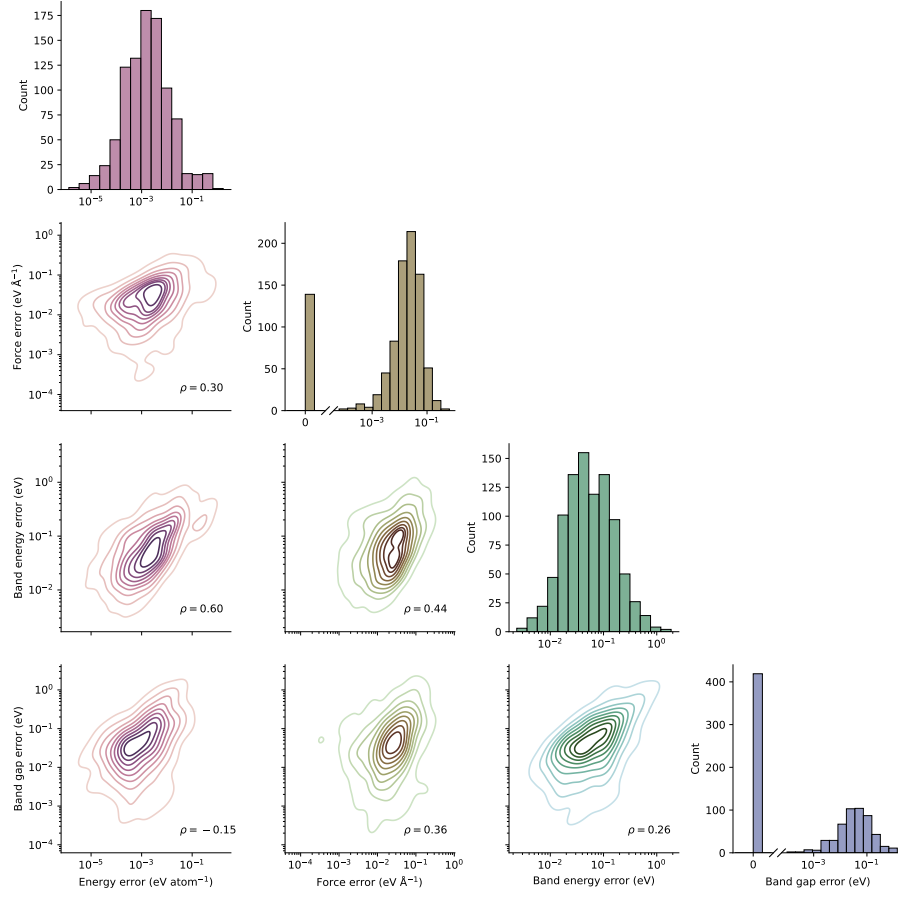
Supplementary Figure 3: Radarplot showing crystal system distribution in Materials Project and GNoME subset. The GNoME subset is made up of materials with five or more unique atomic species. Markers indicate the fraction of each subset which has a particular crystal system structure.



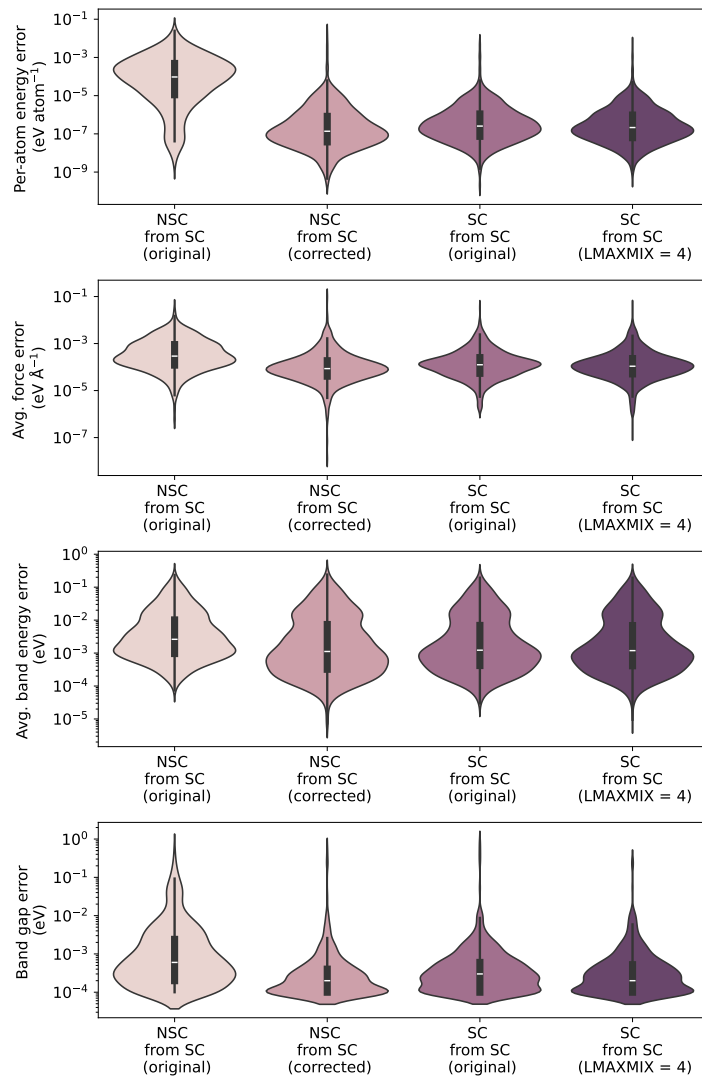
Supplementary Figure 4: Box-plot showing ϵ_{mae} vs. number of species (unique elements) in Materials Project test set materials. Boxes shown for levels with at least 10 materials in the test set. Box-plots show median as center line, upper and lower quartiles as box limits, 1.5x interquartile range as whiskers, and outliers as points.



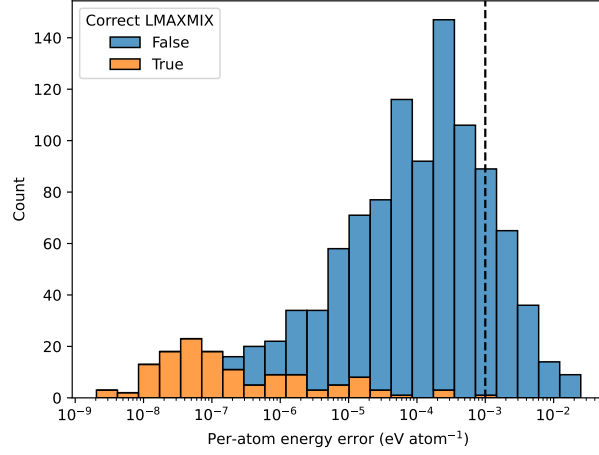
Supplementary Figure 5: ϵ_{mae} plotted against the percent improvement in the number of SCF steps needed to reach self-consistency. Pearson $r \approx 0.19$ for the correlation between ϵ_{mae} and % SCF step difference. Regression line is shown with 95% CI shaded



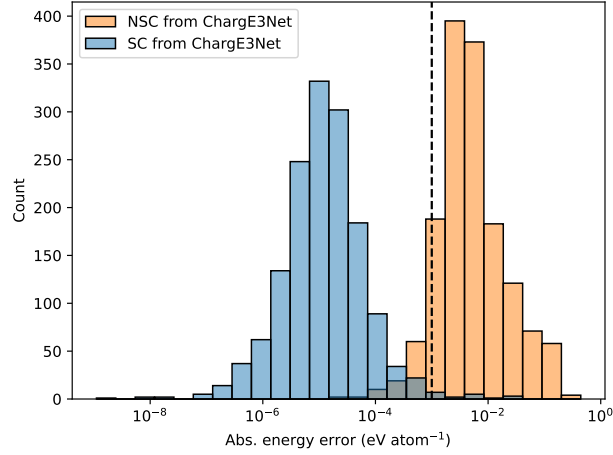
Supplementary Figure 6: (diagonal) Distribution of property errors computed from a non-self-consistent calculation with a ChargeE3Net charge density initialization, and (off-diagonal) density of correlations between property errors. ρ denotes Spearman's correlation coefficients for each off-diagonal plot.



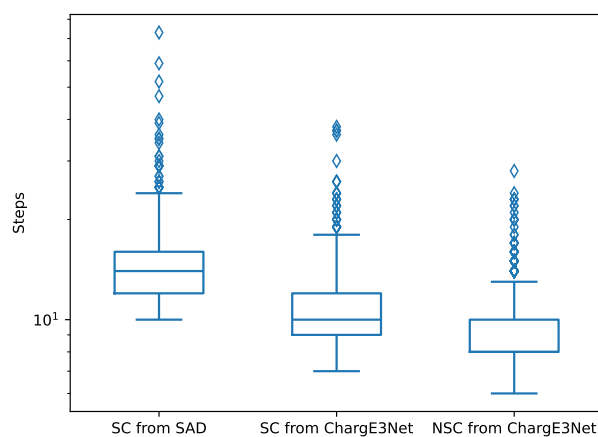
Supplementary Figure 7: Charge densities of the Materials Project test set were computed self-consistently, then computed non-self-consistently (NSC) and self-consistently (SC). (original) denotes the LMAXMIX parameter originally used by Materials Project. (corrected) sets the LMAXMIX parameter to 4 for d-elements and 6 for f-elements. Errors of each property are calculated with respect to the initial self-consistent calculation initialized from SAD. Interior of violin-plots shows median as center line, upper and lower quartiles as box limits, and 1.5x interquartile range as whiskers



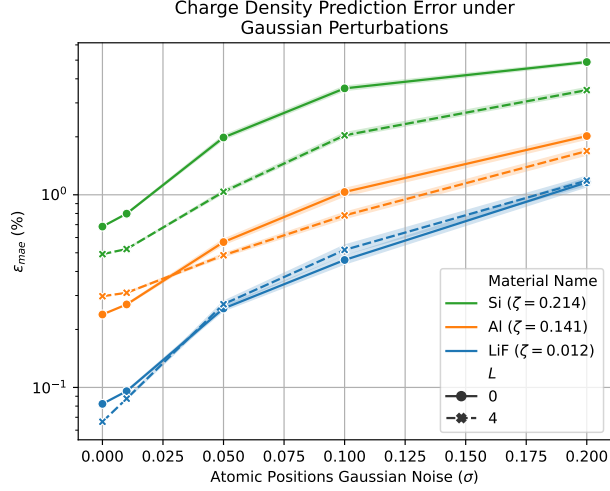
Supplementary Figure 8: Per-atom energy error of non-self-consistent calculations done with self-consistent charge densities using inputs provided by the Materials Project for the test set used in this study. The Materials Project inputs have the LMAXMIX parameter correctly set for only DFT+U calculations (LMAXMIX = 4 for d-elements and = 6 for f-elements).



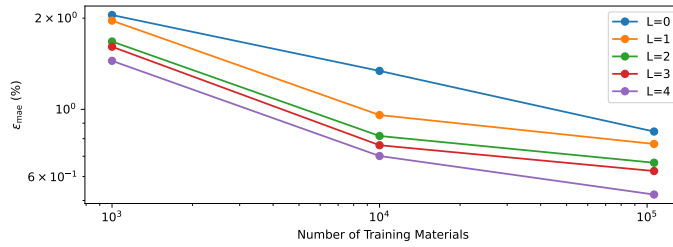
Supplementary Figure 9: Per-atom total energy error of self-consistent (SC, blue) and non-self-consistent (NSC, orange) calculations initialized with ChargeE3Net on a subset of GNoME materials. Dashed vertical line denotes chemical accuracy at 1 meV/atom.



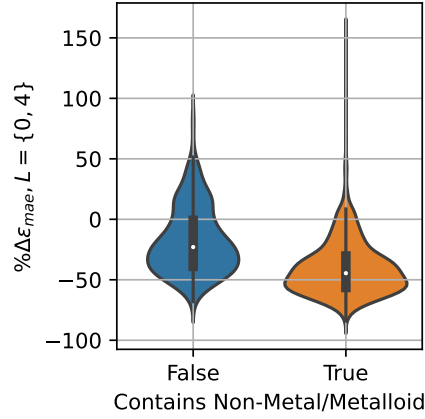
Supplementary Figure 10: Distributions of SCF steps required for convergence of a subset of GNoME materials. Box-plots show median as center line, upper and lower quartiles as box limits, 1.5x interquartile range as whiskers, and outliers as points. The median for NSC from ChargeE3Net is 8 and overlaid on the 25th percentile mark.



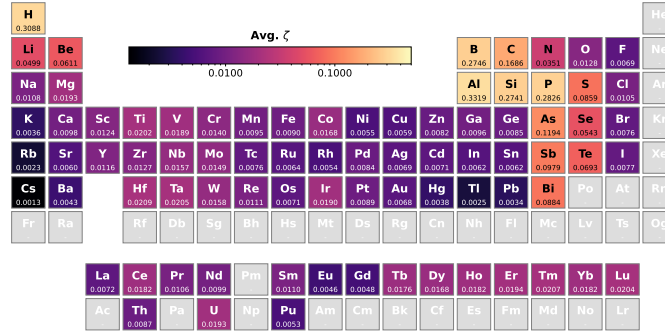
Supplementary Figure 11: ε_{mae} as a function of perturbations of atomic positions for LiF (mp-1138, blue), Al (mp-134, orange), and Si (mp-149, green). Solid lines represent the $L = 0$ variant of ChargeE3Net, while dashed lines represent the $L = 4$ variant of ChargeE3Net. We compute self-consistent DFT calculations with atomic positions $r' = r + \delta$, where r is the original position of the atoms from the Materials Project and $\delta \sim \mathcal{N}(0, \sigma)$. These are used as the ground truth charge densities which we use to compare with ChargeE3Net’s predictions. ζ values are computed for the unperturbed structure charge density. Shaded regions depict 95% CI.



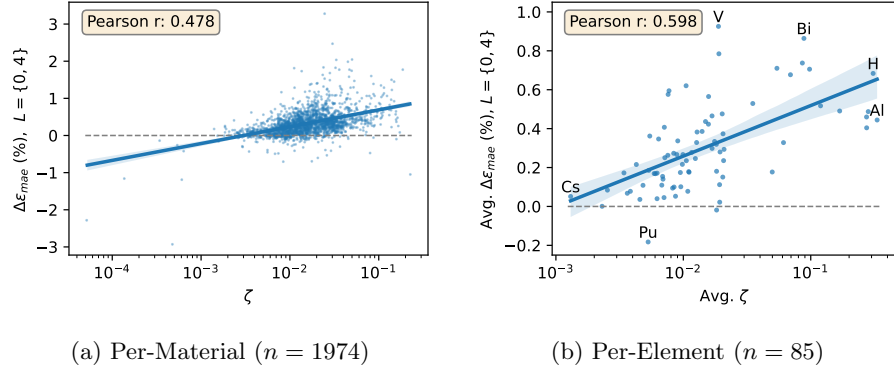
Supplementary Figure 12: Log-log plot of training set size vs performance, measured in average ε_{mae} (%) on the Materials Project test set. We show models train with maximum rotation order $L \in 0, 1, 2, 3, 4$.



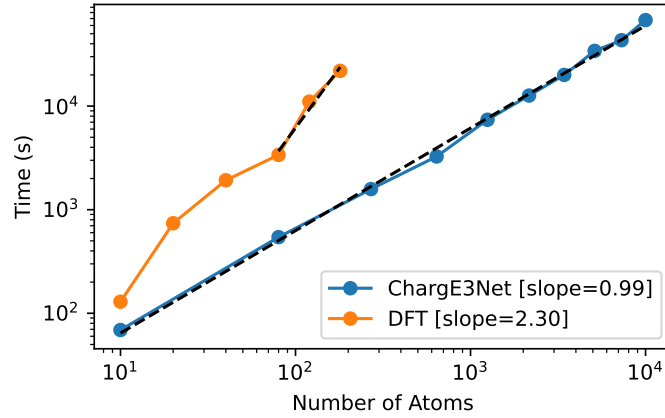
Supplementary Figure 13: Violin plot of the percent change in $\varepsilon_{\text{mae}}(\%)$ from the $L = 0$ to $L = 4$ model for test set materials. 1648 materials contain either a non-metal or a metalloid (orange), while 346 materials are composed of only metals (blue). Interior of violin-plots shows median as center line, upper and lower quartiles as box limits, and 1.5x interquartile range as whiskers



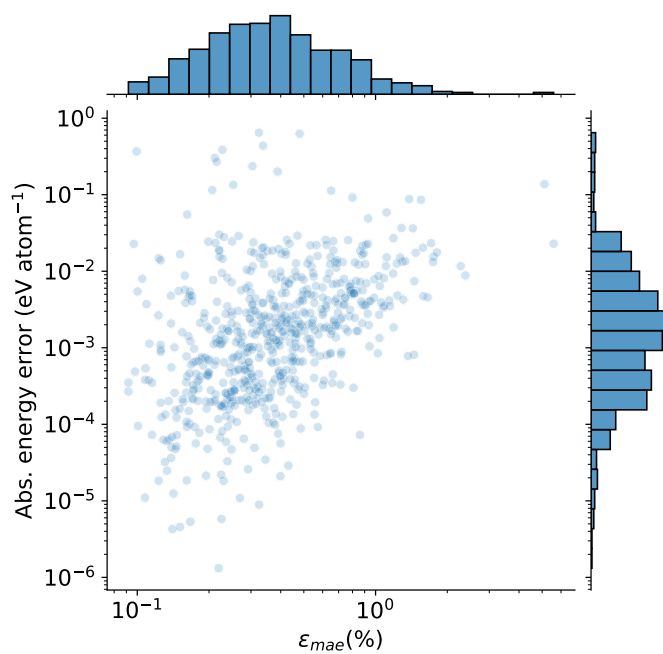
Supplementary Figure 14: Average ζ , computed on DFT-computed charge density at probe points $G_{\text{local},i}$ for each element. Only elements contained in at least 10 test set materials shown.



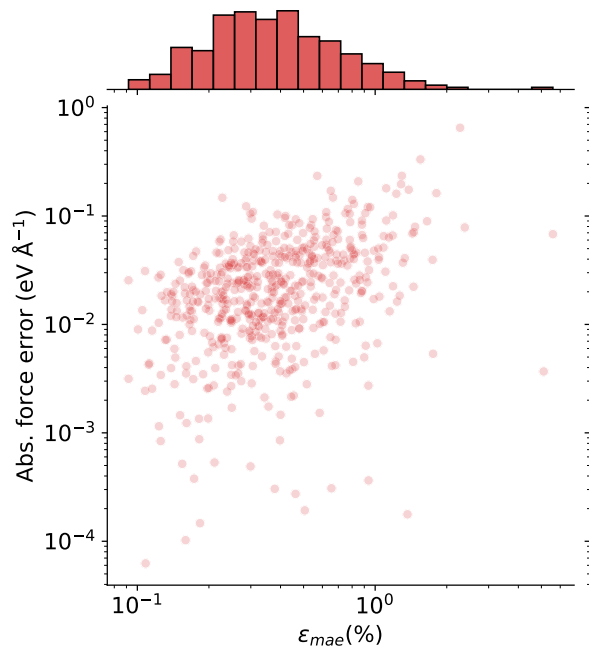
Supplementary Figure 15: $\Delta\epsilon_{\text{mae}}$ (improvement from $L = 0$ to $L = 4$) vs. ζ , on a per-material (left) and per-element (right) basis. For per-element results, the ϵ_{mae} and ζ values are computed over the set of grid points G_{local} , and averaged across all materials containing that element. Only those elements in at least 10 test set materials are shown. Regression line is shown with 95% CI shaded region for both charts.



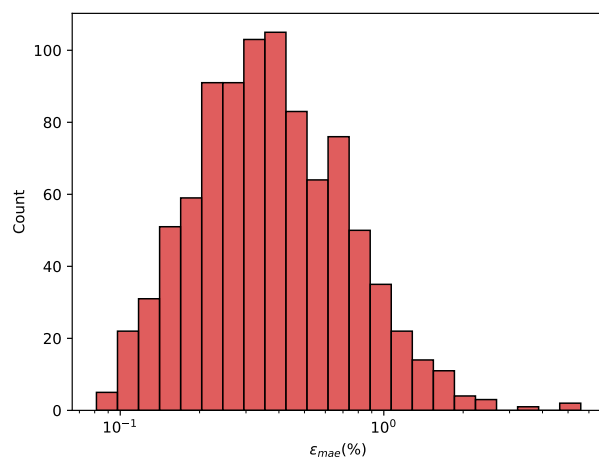
Supplementary Figure 16: Runtime comparison of DFT and our ChargeE3Net model with respect to number of atoms in the evaluated system. DFT is using a 48-core Intel Xeon CPU, while ChargeE3Net uses a single NVIDIA V100 GPU.



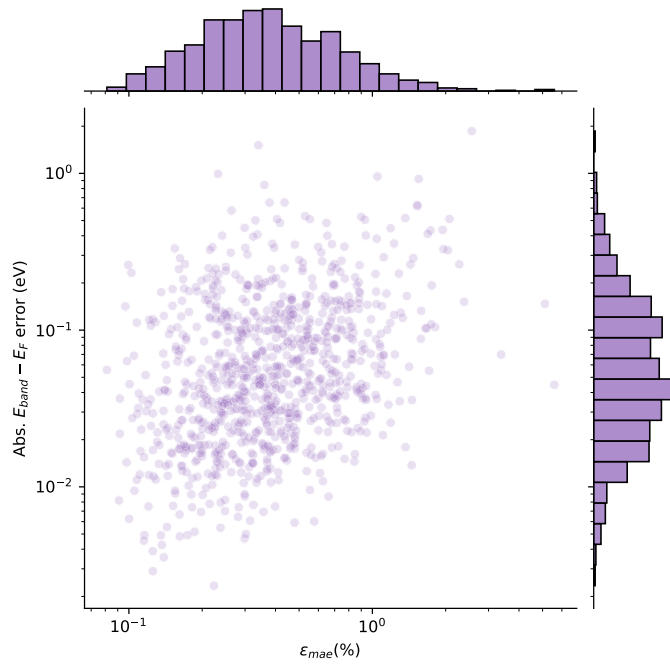
Supplementary Figure 17: Per-atom energy absolute error between non-self-consistent calculations on ChargeE3Net’s charge density predictions and self-consistent calculations plotted against ε_{mae} of the test set. The distributions of the per-atom energy error and ε_{mae} are on the right and top of the plot, respectively. Pearson $r \approx 0.44$ for $\log \varepsilon_{\text{mae}}$ vs. $\log$ energy error.



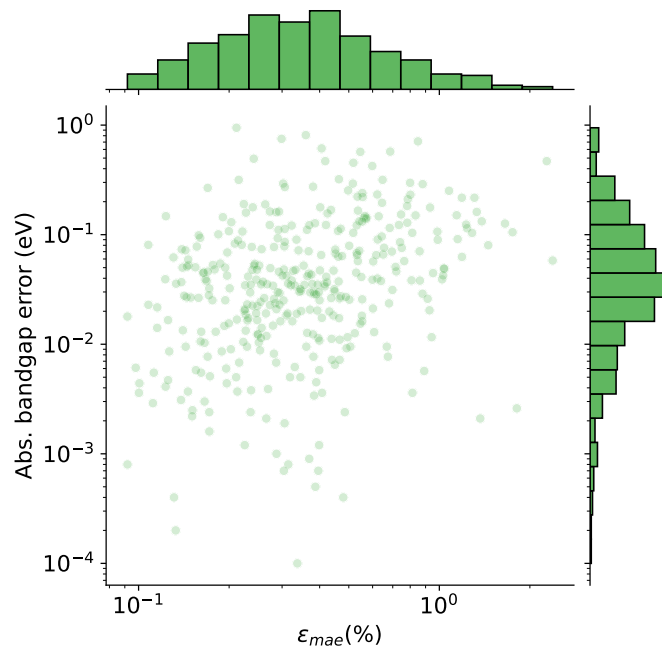
Supplementary Figure 18: Average force absolute error between non-self-consistent calculations on ChargeE3Net’s charge density predictions and self-consistent calculations plotted against ε_{mae} of the test set. The distributions of the force error and ε_{mae} are on the right and top of the plot, respectively. 15% of structures achieved perfect agreement with the ground-truth self-consistent calculation, which are not shown in this plot. See 19 for the distribution of ε_{mae} of these structures. Pearson $r \approx 0.35$ for $\log \varepsilon_{\text{mae}}$ vs. $\log$ force error.



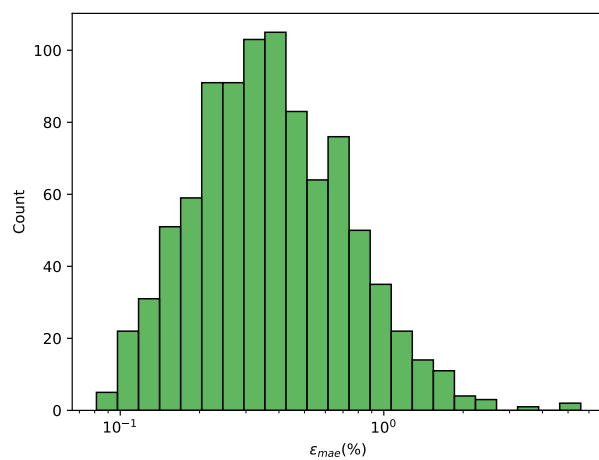
Supplementary Figure 19: Distribution of ϵ_{mae} where each structure has a perfect agreement in forces between a non-self-consistent calculation initialized with ChargeE3Net's prediction and a self-consistent calculation.



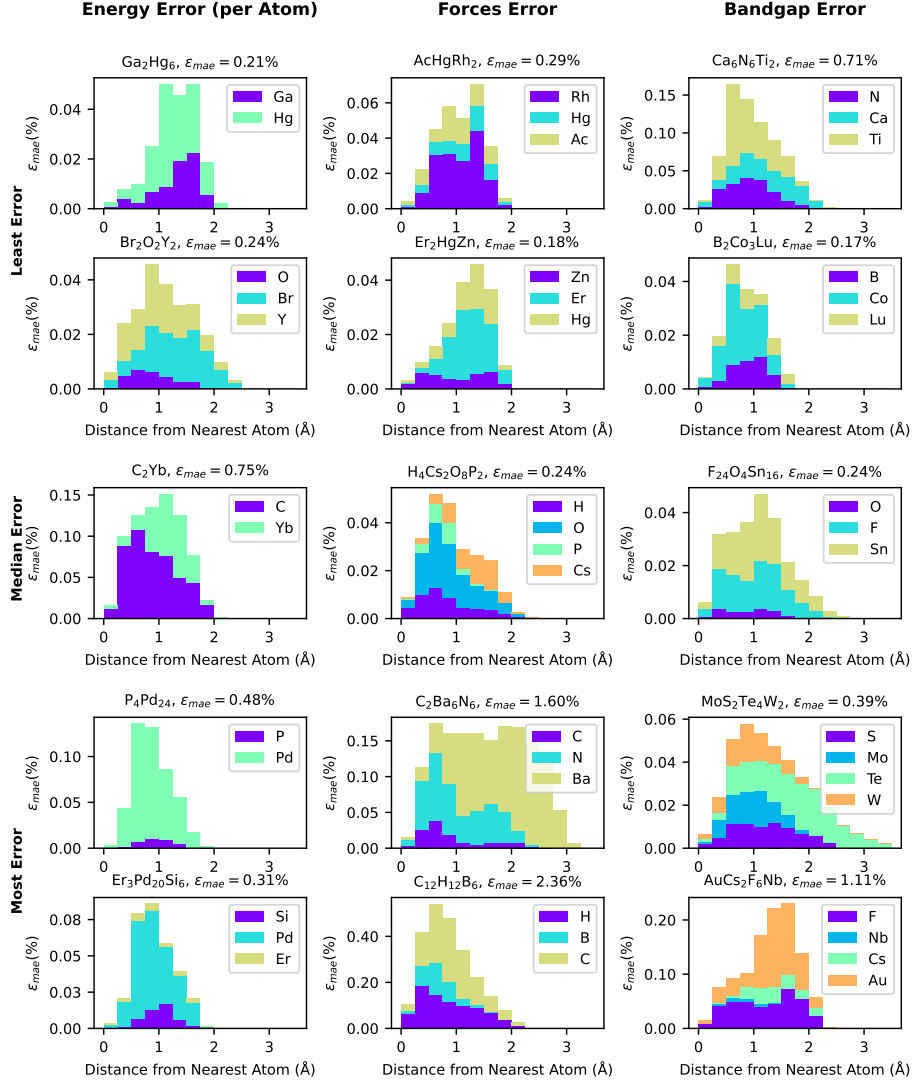
Supplementary Figure 20: Band energy (eigenvalue) absolute error between non-self-consistent calculations on ChargeE3Net’s charge density predictions and self-consistent calculations plotted against ε_{mae} of the test set. The distributions of the band energy error and ε_{mae} are on the right and top of the plot, respectively. Pearson $r \approx 0.35$ for $\log \varepsilon_{\text{mae}}$ vs. $\log$ band energy error.



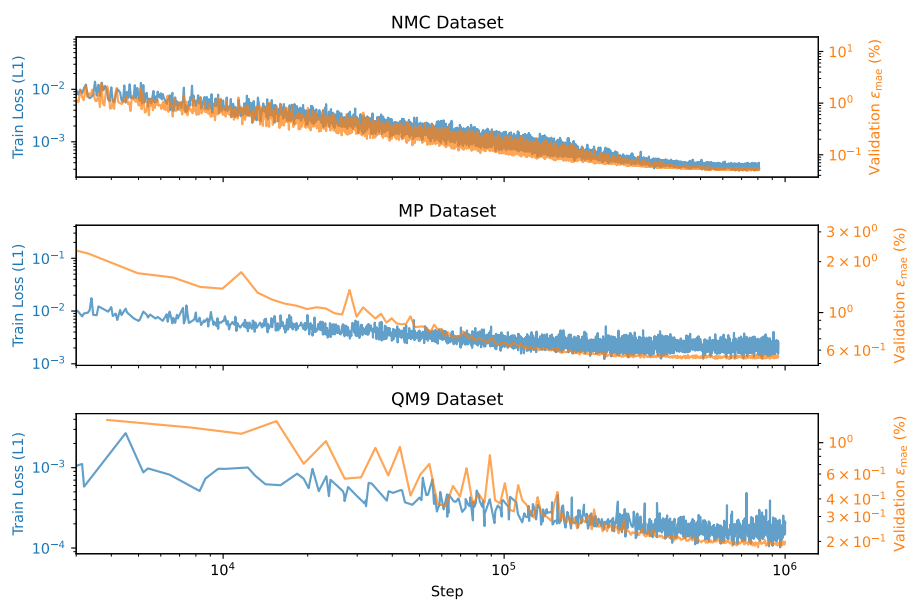
Supplementary Figure 21: Band gap absolute error between non-self-consistent calculations on ChargeE3Net’s charge density predictions and self-consistent calculations plotted against ε_{mae} of the test set. The distributions of the band gap error and ε_{mae} are on the right and top of the plot, respectively. About 43% of structures achieve perfect band gap agreement with self-consistent calculations, which are not shown in this plot, and the distribution of their ε_{mae} is plotted in 22. Pearson $r \approx 0.29$ for $\log \varepsilon_{\text{mae}}$ vs. $\log$ band gap error.



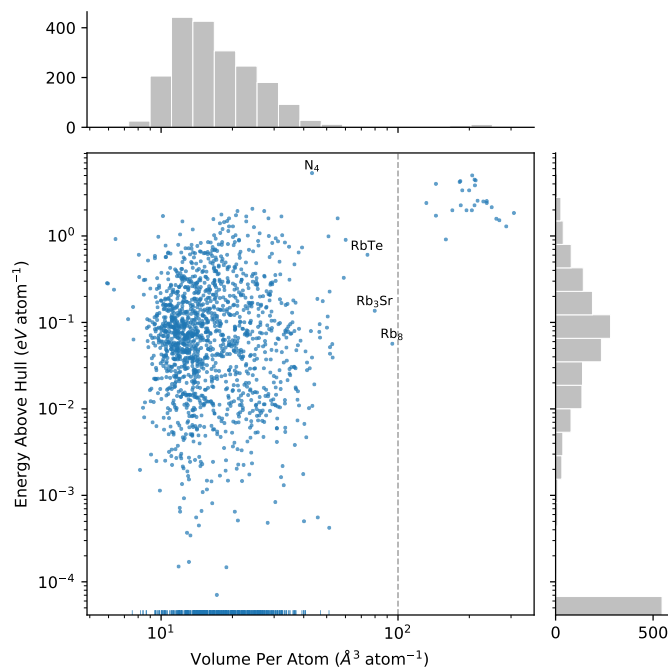
Supplementary Figure 22: Distribution of ϵ_{mae} where each structure has a perfect band gap agreement between a non-self-consistent calculation initialized with Charge3Net's prediction and a self-consistent calculation.



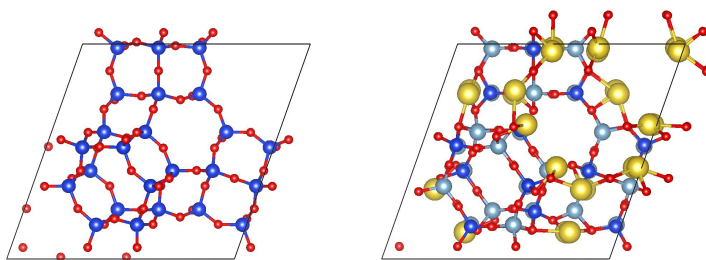
Supplementary Figure 23: Stacked histograms showing ϵ_{mae} , binned by range from nearest atom, for a selection of materials. ϵ_{mae} contributions from individual voxels on G are summed in range bins and according to nearest atom species (stacked colors for each bin). Materials with the two least, median, and two most errors on each of three downstream NSC-from-ChargeE3Net computed properties are shown in rows from top to bottom.



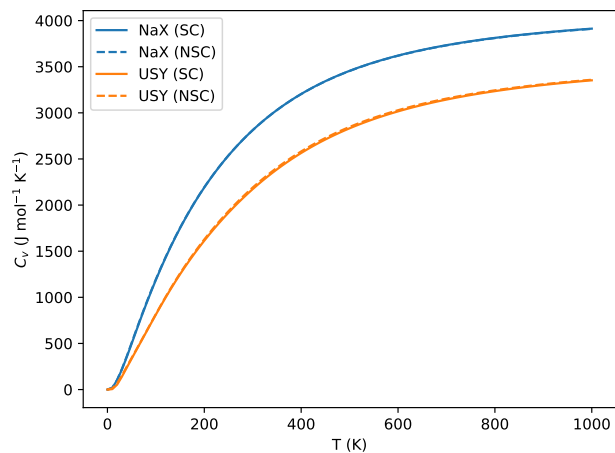
Supplementary Figure 24: Log-log plot of training loss and validation ϵ_{mae} during training of the ChargeE3Net for each of the studied datasets.



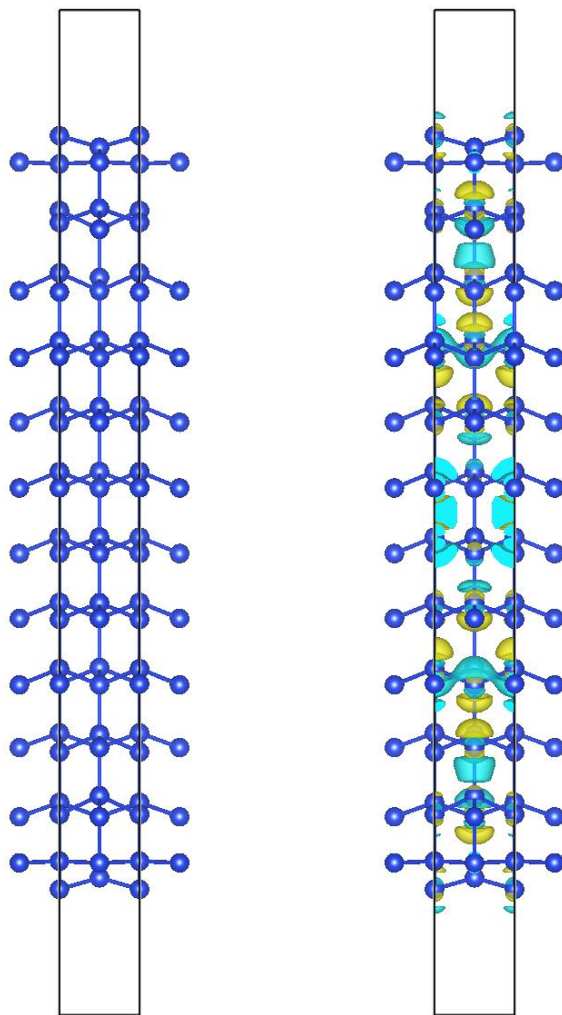
Supplementary Figure 25: Scatterplot of test set Energy Above Hull vs Volume Per Atom ($n = 2000$). 26 materials in excess of $100 \text{ \AA}^3 \text{ atom}^{-1}$ (dashed line) were removed from the test set for other calculations. Of those removed, 25 are in space group *Immm* and one is in *Cmmm*. Thermodynamically stable materials (0.0 eV atom^{-1}) are plotted along the x axis.



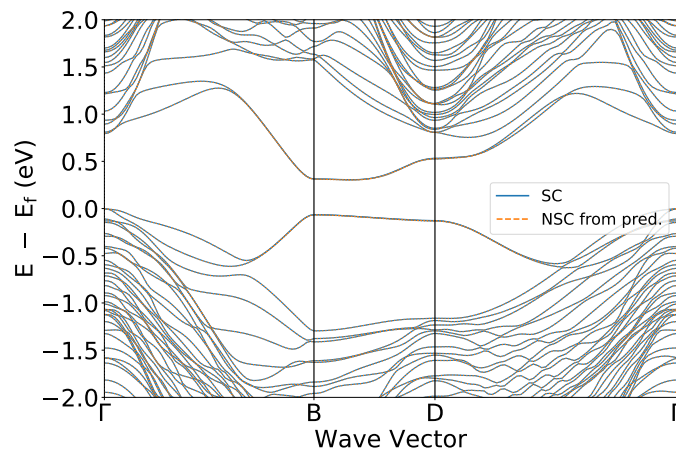
Supplementary Figure 26: Structural models of (right) USY and (left) NaX zeolites, two types of faujasite zeolites. Blue = Si, red = O, grey = Al, yellow = Na.



Supplementary Figure 27: Constant-volume heat capacity as a function of temperature as computed from self-consistent DFT calculations and non-self-consistent calculations on the predicted charge densities. Blue curves are for NaX and orange curves are for USY. Solid curves are computed via self-consistent DFT calculations of atomic displacements, while dashed curves are computed via non-self-consistent DFT calculations using ChargeE3Net’s predicted charge densities of the same.



Supplementary Figure 28: (right) Structural model of a Si(111)-(2x1) surface, and (left) an isosurface of the charge density error overlaid on the structural model. Yellow denotes overestimation while teal denotes underestimation. The isosurface level used here is approximately $1.6 \times 10^{-6} \text{ e}^- \text{ \AA}^{-3}$.



Supplementary Figure 29: Electronic bandstructure of Si(111)-(2x1) surface. Blue represents a self-consistent (SC) DFT calculation with the PBE exchange-correlation functional, and orange represents a non-self-consistent (NSC) calculation using the charge density predicted by ChargeE3Net with the same functional.

Supplementary References

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