Machine Learning for Molecular Engineering

Problem Set 2 (Perovskites)

Date: February 24, 2023
Due: March 9, 2023 at 11:59pm

Instructions Please submit your solution on Canvas as an IPython (Jupyter) Notebook file, `*.ipynb`. We highly suggest using Google Colab for this course and using this template for this problem set. Your submission should contain *all* of the code that is needed to fully answer the questions in this problem set when executed from top to bottom and should run without errors (unless intentional). Please ensure that your plots are visible in the output file and that you are printing any additional comments or variables as needed.

To get started, open your Google Colab or Jupyter notebook starting from the problem set template file pset2.ipynb (direct Colab link). You will need to use the data files here.

Background

In this problem set you will learn how to use neural networks to predict the properties of crystalline materials of varying composition. The focus will be on **perovskite** materials.

Perovskite materials

Natural perovskite is a mineral composed of calcium titanium oxide ($CaTiO_3$). It was discovered in Russia by Gustav Rose and named after mineralogist L. A. Perovski. More generally, we called any material whose crystalline structure is similar to the perovskite mineral a *perovskite*. You don't *need* to know anything about crystal structure to succeed in this P-Set, but we encourage you to learn about crystal structure if you are not familiar with the topic.

Because their structure can support a large number of combinations of elements, perovskites are one of the most abundant structural families and are found in an enormous number of compounds which have wide-ranging properties, applications, and importance, such as solar cells, piezoelectrics or catalysts.

Structure of perovskites

The general chemical formula for perovskite compounds is ABX_3, where 'A' and 'B' are two cations. Typically A is large (alkali metal, rare earth or even organic cation such as methylammonium in lead-halid perovskites), B is a transition metal, and X is an anion, oxide, fluoride, nitride or a halide that is bound to both cations. The idealized structure of perovskites is cubic (space group $Pm\bar{3}m$), with the B cation in 6-fold coordination and surrounding anions forming an octahedron, and the A cation in 12-fold cuboctahedral coordination. However, this ideal structure is often distorted for real materials and shows reduced symmetry. These distortions, for instance, are responsible for the lack of central symmetry in $BaTiO_3$ and its piezoelectric behavior.

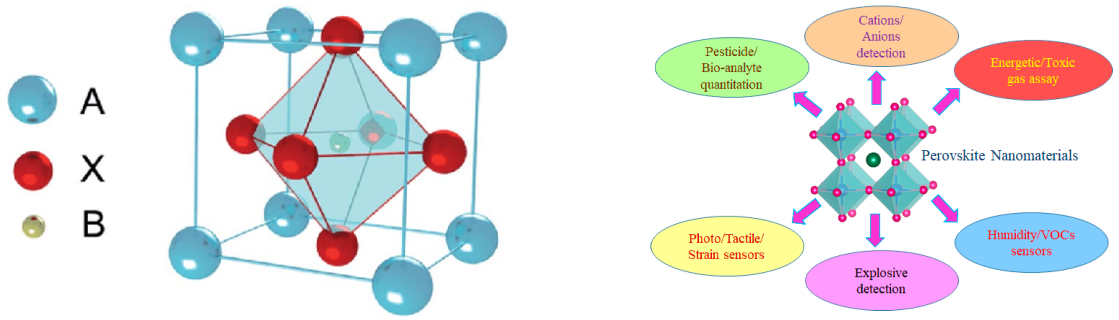
There are many possible A, B, and X elements that can be combined in stable perovskite structures. Furthermore, it is possible to combine different choices of elements for A, B and X, which results in an enormous combinatorial space of possible perovskites that can be made and used based on their properties.

Properties of perovskites

Because their compositions and thus their properties are extremely tunable, pervoskites are exciting materials platforms for many applications.

For example, solar cells based on organic-inorganic halide perovskites (with an organic cation in the A site and lead or a related element in the B site, and Cl, Br or I as X) are the subject of extensive research. Since their discovery about a decade ago, perovskite solar cells have reached efficiency close to that of silicon photovoltaics (around 25%) but are much cheaper to manufacture and can be made into thin films that are flexible and foldable. Although they are a promising platform for widespread affordable photovoltaics, perovskite solar cells suffer from stability issues that prevent mass adoption.

Because of the presence of multiple metal and oxygen sites on their surfaces and the ability of oxygen to participate actively in surface reactions, perovskites are investigated as catalysts that can match the performance of scarce transition metals like ruthenium. Many inorganic perovskites show exciting magnetic and electric phenomena such as photochromic, electrochromic and image storage. Perovskites also have applications for chemical sensing for molecular recognition.


A
X
B
Cations/ Anions detection
Pesticide/ Bio-analyte quantitation
Energetic/Toxic gas assay
Perovskite Nanomaterials
Photo/Tactile/ Strain sensors
Humidity/VOCs sensors
Explosive detection

(a) Perovskite crystal structure

(b) Applications for molecular sensing

Figure 1: Perovskite structure and applications [1]

Data Generation

The data you will be modeling is generated with high-quality Quantum Chemistry calculations using Density Functional Theory (DFT). Each structure takes hundreds of CPU hours to calculate. They are fairly expensive to obtain. Your task is to train predictive models to help theorists to reduce their computational cost.

Python packages required for this exercise

In this problem set, you will asked to use Pandas DataFrames. If you have not used Pandas before, please work through this tutorial.

Part 1: Modeling unalloyed perovskites

In this question, you are asked to predict E_{hull} (Energy above hull). It has the unit of eV/Atom. It describes the thermodynamic stability of the crystal structure. If $E_{hull} = 0.0$, it means the structure is at its most stable form.

Energy Above Hull: The energy of decomposition of this material into the set of most stable materials at this chemical composition, in eV/atom. Stability is tested against all potential chemical combinations that result in the materials composition. For example, a Co_2O_3 structure (cobalt oxide) would be tested for decomposition against other Co_2O_3 structures, against Co and O_2 mixtures, and against CoO and O2 mixtures. E_{hull} is computed as :

$$E_{\mathrm{Co_2O_3}} - \min(2E_{\mathrm{Co}} + \frac{3}{2}E_{\mathrm{O_2}}, 2E_{\mathrm{CoO}} + E_{\mathrm{O_2}}, E_{\mathrm{Co_2O_3}})$$

Unlike pset 1, you will be performing regression tasks. For regression tasks, a metric we can use to evaluate model performance is the coefficient of determination, or the R^2 score. It is defined as:

$$R^2 = 1 - \frac{\sum_i^{N_{\mathrm{data}}}(y_i - \hat{f}(\mathbf{x}_i))^2}{\sum_i^{N_{\mathrm{data}}}(y_i - \mathrm{mean}(y_i))} \tag{1}$$

where i is the index for each sample, y_i is the target value, $\hat{f}$ is the model, and $\mathbf{x}_i$ is the feature vector. The larger the R^2 score the more accurate the prediction is. If your prediction is perfect $R^2 = 1$. Note that metrics like mean absolute error (MAE) or mean squared error (MSE) can provide more meaningful and interpretable measures of performance.

You will first need to load the dataset using the code provided.

Part 1.1 (5 points) Encoding chemical formulae into feature vectors

After loading the pandas dataframe, take a moment to inspect your data by looking at the rows (samples) and columns (features). The important chemical information is stored in columns `[‘A’, ‘B’, ‘X’]` and E_{hull} is stored in the column `e_above_hull`.

First, you will train a model that uses chemical compositions (e.g. $CaTiO_3$) to predict Energy above Hull(E_{hull}) which is a scalar property. How can you map a chemical formula like $CaTiO_3$ to numeric features for training a model? You need to define a dictionary to encode elements into numerical features so that we can apply programs like linear regressions on these input features. One way to do is to use one-hot encoding to transform elements into bit vectors. For example, if we have elements Fe, Ni, and Mn for A and B sites, we can assign bit vectors of size 3 to fully encode this label information. We do not encode the elements for the X site because Oxygen is the only element available in our dataset for X. We present simple examples on how you should encode perovskite chemistries in table 1.

Use `preprocessing.LabelBinarizer()` to transform features [‘A’, ‘B’] into one-hot encoded arrays. We provided the choices of elements for A/B sites in `elements.npy` which can be loaded using the code we provided to you. These elements are the “vocabularies” you need to use to construct your bit vectors. Next, convert the hull energies to another array for use in regression.

Before you start, please read the documentation about `preprocessing.LabelBinarizer()` and understand the example code in the documentation. Your code should output two numpy arrays (`X` and `y`).

A site	B site	bit vector representation
‘Fe’	‘Ni’	$[1, 0, 0, 0, 1, 0]$
‘Mn’	‘Ni’	$[0, 0, 1, 0, 1, 0]$
‘Fe’	‘Mn’	$[1, 0, 0, 0, 0, 1]$
‘Fe’	‘Fe’	$[1, 0, 0, 1, 0, 0]$

Table 1: Example bit vector representation of A/B sites in perovskites

Hint: There are many ways to do it. One way to do it is to loop over rows (perovskites) in your dataframe and encode A and B into bit vectors separately, and then stack the two arrays horizontally using `np.hstack`.

Part 1.2 (5 points) Modeling with ridge regression

After obtaining bit vector representations for the perovskite composition, train a ridge regressor (linear regression with L2 regularization) to predict E_{hull} (column name: `e_above_hull`). Randomly split your data into train/test with an 80%/20% ratio. Report your test score. Plot your prediction using a scatter plot (`matplotlib.pyplot.scatter`) for both train and test data.

Please first read the documentation on `sklearn.linear_model.Ridge` before training the model. We have also provided a code snippet for creating a scatter plot.

Part 1.3 (10 points) Modeling with a multi-layer perceptron

Using the same train/test split, train a model to predict E_{hull} using a multi-layer perceptron with the following parameters in table 2. Visualize your prediction for train and test data with a scatter plot. Calculate the number of parameters used in your MLP given the provided ‘`hidden_layer_sizes`’. Briefly comment on the meaning of (256, 256, 256) which is the input you will use for the `hidden_layers_sizes` option as it pertains to learned intercepts and coefficients. Also comment in one sentence on the difference between hyperparameters and optimized parameters with examples for both.

Please first read the documentation on `sklearn.neural_network.MLPRegressor` and understand the meaning of each hyperparameter before training the model.

`‘hidden_layer_sizes’`	(256, 256, 256)
`‘activation’`	’relu’
`‘alpha’`	0.16
`‘solver’`	’adam’
`‘early_stopping’`	False

Table 2: Hyperparameters to be used in Part 1.3

Part 1.4 (3 points) Chemical transferability of one-hot representations

We have prepared a special holdout set for you to test your model performance. This holdout set contains elements that do not exist in the training set. Load the holdout set using the code provided. Featurize the data with label encoder defined in Part 1.1. Validate your trained ridge regressor and MLP by computing the R^2 score for both of them. Visualize your prediction with a scatter plot for the two models you trained. Briefly describe explain what you observed. Do either of these models generalize well to this new data?

Part 1.5 (5 points) Featurize perovskites with physical descriptors

Now load the data for atomic properties stored in `mendeleev.csv` with the code we provided. Use all the numerical features to construct a new feature set for prediction (please exclude atomic symbols which are strings). You need to split the data into a training (80%) set and a test (20%) set and then scale the data with `preprocessing.StandardScalar` as shown in problem set 1. Train on the training set with a MLP with the same hyperparameters we provided to you in Part 1.3. Visualize your prediction with scatter plots for both train and test data.

Part 1.6 (5 points) Chemical transferability of physical descriptors

Report the R^2 score on your holdout set using the model trained in Part 1.5 and visualize your prediction with a scatter plot like you did before. Has your prediction on the holdout set improved? Briefly explain why.

Part 2: Modeling alloyed (hybrid) perovskites

In this part, you will be asked to model alloyed perovkites with MLPs for both classification and regression tasks. Alloying simply means mixing two or more types of crystal materials together, this sometimes results superior properties of materials. See Figure 2 for a visual understanding. For example, Steel is made by alloying Iron (Fe) with other elements and has superior properties than pure Iron.

As the result of alloying perovskites, the A/B sites will have more than one elements of different fractions. For example, in the dataframe, you will see the element compositions at A/B sites are represented by a dictionary like: `{‘Fe’: 0.15, ‘Mn’: 0.05}` . The keys represent possible elements at the site and the values represent the composition fraction.

Please load a new dataset with the code we provided.

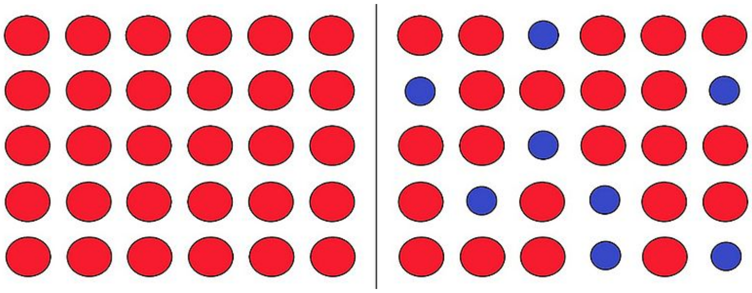


Figure 2: Alloying simply means mixing elements together. By allowing mixed systems, we have more possibilities for different structures which may exhibit more beneficial or tunable properties.

Part 2.1 (5 points) Encoding fractional compositional information

In this question, you will be asked to write code to encode both chemical and composition information for A/B sites. Similar to what you developed in Part 1.1, you can use the composition fraction to encode the chemical information. For example, if both Fe and Mn present at site A with fraction 0.15, and 0.05 respectively, instead of representing its composition with `[1, 0, 1]`, replace 1 with the actual compositions which are provided as values in the dictionary. As a result, you will get `[0.15, 0, 0.05]`. Encode the A and B site separately and concatenate them into one bit vector (table 3).

A site	B site	bit vector representation
`{‘Fe’: 0.15, ‘Ni’: 0.05}`	`{‘Mn’: 0.2}`	$[0.15, 0.05, 0, 0, 0, 0.2]$
`{‘Fe’: 0.15, ‘Mn’: 0.05}`	`{‘Fe’: 0.1, ‘Mn’: 0.1}`	$[0.15, 0, 0.05, 0.1, 0, 0.1]$

Table 3: Example bit vector representation of A/B sites with compositional information

Develop the code to encode all the alloyed perovskites into a new feature set `X_alloy` with compositional information. Split your data into a train (80%) and test (20%) set. Fit an MLP to predict `e_above_hull` on the training data with the hyperparameters listed in table 4. Report your R^2 scores for both train and test data. Visualize your prediction for both train and test data with a scatter plot.

`‘hidden_layer_sizes’`	(50)
`‘activation’`	’tanh’
`‘alpha’`	0.0001
`‘solver’`	’adam’
`‘early_stopping’`	False

Table 4: Hyperparameters to be used in part Part 2.1

Part 2.2 (15 points) Optimize your MLP architecture with HyperOpt

In PSet 1, you used grid search for model hyperparameters. However, grid search in many cases is not tractable due to combinatorial explosion. In practice, there exist more efficient algorithms to improve exploration efficiency. Tree of Parzen Estimators (TPE) is such a more advanced search method based on sequential model-based optimization. The details of TPE algorithm are beyond the scope of this class, but you are encouraged to read more about it in ref. [2]. TPE has been implemented in the `Hyperopt` package. In this part, you will try to use `Hyperopt` to explore the space of hyperparamters for MLP.

We have provided the skeleton code for you with predefined ranges of hyperparameters in the template file, but you will have to write your own `model_eval()` function which should take a suggested hyperparameter set (and `‘early_stopping‘` set to `False`) and return the resulting 5-fold cross-validation (CV) score on the training data you obtained from Part 2.1. Run the program for 40 evaluations. The `hyperopt` program might take a while to run, and you can check the progress bar to monitor the program executions. If it takes longer than a couple of hours, consult with your classmates or the TAs.

Finally, use the optimized hyperparameter set to train a MLP with all the training data again, and report your validation score on the test data you obtained from Part 2.1. Have you seen any improvement?

Caveats What Hyperopt will do is to optimize your hyperparameters given the range you provide and minimize your loss function using `hyperopt.fmin`. Please note that because a higher

R^2 indicate better performance, you should minimize the negative R^2 score with `fmin` (We have implemented this for you). Also, to constrain the complexity of the search space, we have fixed the hidden layer width for all the layers during the search. If you have more than one hidden layer, all layers will have the same width. However, in practice, you could have different hidden layer widths for each hidden layer.

Part 2.3 (5 points) Applying MLPs to classifying electronic properties of alloyed perovskites

In this part, you will be making a multi-category classifier to classify different types of perovskites based on their electronic structures which characterizes their energy levels of electrons in crystals.

Electronic Structure: The electronic band structure (or simply band structure) of a solid describes the range of energy levels that electrons may have within it, as well as the ranges of energy that they may not have (called band gaps or forbidden bands).

These types include *direct bandgap materials*, *indirect bandgap materials*, and *metals*. These three types of materials have different electronic properties. Materials that do not have band gaps are metals and conduct electrons. For materials with band gaps, they can either be insulating or semi-conducting. A band gap is the energy difference between the conduction band and valence band. Whether the minima of the conduction bands and the maxima of the covalent band are aligned affects the process of electronic excitation and its optical properties like absorption. If they are aligned, it is a direct bandgap material; if they do not align, it is a indirect bandgap material. See Figure 3 to have a visual understanding. In general, direct bandgap materials have a wider range of electronic and optical application in industry. You are asked to make a MLP-based classifier to classify the three classes of electronic materials mentioned.

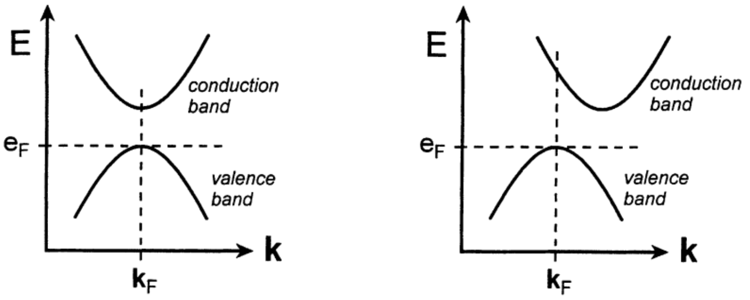


Figure 3: Graphical description for direct/indirect bands (from [3])

The dataset you will use is the same as what you loaded in Part 2.1. Please also use the same encoded features you developed in Part 2.1 and use the same MLP architecture and hyperparameters you obtained from hyperopt in Part 2.2. The class labels are in the "class" column in your loaded dataframe. Randomly split your data into 80% train and 20% test data and train a classifier on your training data.

Please use the `metrics.ConfusionMatrixDisplay` class to visualize the classification result for both train and test data. Unlike the binary classification task from Problem Set 1, there are three classes to predict so your confusion matrix will have a size of 3x3.

Before you start, please read documentations on `sklearn.neural_network.MLPClassifier` to understand the examples.

Part 3: Accelerating neural networks with GPUs

You may have noticed that the neural network as implemented by sklearn was both relatively inflexible and rather slow to train. Sklearn is great for using common algorithms and predefined model types, but cannot be used to build a fully custom model for end-to-end training. PyTorch (and other frameworks like TensorFlow, JAX or CNTK) is built for easily training and implementing deep learning models. The backbone of PyTorch is reverse-mode automatic differentation (AD), which is a programmatic framework to compute the gradients of your model output (a loss function) with respect to model parameters and inputs. Reverse-mode AD provides an easy way for machine learning researchers to construct models without having to think about explicit writing the gradient programs. These gradients are vital for optimizing (*i.e.* fitting) the weights efficiently. PyTorch also allows you to perform your training process on a GPU (Graphical Processing Unit), which will significantly accelerate computation and decrease training time.

In this part, you will re-implement the same neural network as in Part 2.2 using PyTorch's API and using a GPU for training. To speed up training, you should be sure to use a graphical processing unit (GPU) on Colab. PyTorch is pre-installed on Google Colab, so you can import it directly. We've provided some skeleton code in the template file, but you will of course need to fill in the details. After this exercise, we hope you will be comfortable building your own machine learning workflow using PyTorch by adapting this and other example code.

Optional reading The PyTorch Tutorial and Quickstart Guide are great companion resources to the functional PyTorch primer we present in this question. We suggest taking a moment to go through their examples to gain familiarity with basic PyTorch use cases and rely upon these official guides to fill in any details which may be not explicitly stated in this problem and in Problem Set 3, where you'll be training a more complicated neural network using a similar framework. Likewise for debugging we suggest leafing through this guide paying special attention to the advice surrounding size mismatch (when in doubt inspect shapes) and device mismatch. Note tensor operations generally require all tensors to be on the same device (cpu or cuda), you can check the device attribute of tensors as you debug and shuttle data to specific devices with '.to(device)'.

Part 3.1 (2 points) Request a GPU on Google Colab

In Google Colab, find `Notebook Settings` under the `Edit` menu. In the `Hardware accelerator` drop-down, select GPU as your hardware accelerator. Check that you successfully requested a GPU using the code we provided.

Part 3.2 (10 points) Build Datasets and DataLoaders in PyTorch

Code for processing data samples can get messy. From the perspective of good software engineering, it is good to modularize the dataloading procedure. In PyTorch, you will find two data-related classes, `torch.utils.data.Dataset` and `torch.utils.data.DataLoader`, which are used to manage data when training a model.

From Part 2.1, you should already have the data featurized and split into a train and test set. Retrieve 10% of your training data as the validation set to be used to check for training convergence. Because training a deep neural network model takes time, so we won't perform cross validation or hyperparameter optimization as you did in previous psets. However, you might still want to do it in your final project if you decide to use a neural network based model.

Next, you need to construct your dataset and loader, with `torch.utils.data.Dataset` and torch.utils.data.DataLoader. A DataLoader is an object that iterates over your dataset and we provided an example of how to loop over your data. By using DataLoader you can utilize useful features such as memory pinning, multi-processing, and automatic batching when loading your data. You can also customize your data loading procedure to perform any on-the-fly preprocessing calculations.

The central object in Pytorch is torch.Tensor. They are very similar to the np.array objects you are already familiar with. You can easily transform a np.array to torch.Tensor, and send the torch.Tensor to a Nvidia GPU which is very fast at parallelized tensor operations. A nice tutorial can be found here.

We have provided you with a PerovskiteDataset class that implements Dataset for this problem set. Using this, fill in the skeleton code to construct your train, validation and test dataloaders with batch_size=256, using your train, validation and test datasets; remember to set shuffle=True to shuffle the dataset. Ensure your implementation is correct by iterating over your dataloader to retrieve batches of data (using our provided code). What is the shape of each batch? And how many batches are there in your dataset?

Part 3.3 (15 points) Define the MLP in PyTorch

There are many ways to define a neural network in PyTorch. For the purpose of this exercise, we would like you to use the nn.Module class to implement your MLP from Part 2.2. This method is a little bit more complicated than some other approaches but is more generalizable to the more complex architectures we will be discussing later in the course.

The nn.Module class requires two methods: an __init__ method where you initialize any components of the neural network, and a forward class where you define the forward computation associated with the given network, i.e. how to compute a prediction given input data. Fortunately, many standard layers, including the feedforward layer used in the MLP, are already implemented in PyTorch, and you can call them to simplify your code. In particular, you will want an nn.Linear layer for each hidden layer and either the nn.ReLU or nn.Tanh layer for your activation function after each linear layer. You may also use a nn.Sequential module to stack layers; the output of the first layer within a nn.Sequential module will be fed as the input to the second, and so on. Look at our code snippets to understand how all of these layers work; you can use these to help you implement your MLP. Ensure that the layers of your model are attributes of your class, so PyTorch will know to auto-differentiate through the parameters of those layers.

We have provided the skeleton code for implementing your MLP in PyTorch as a nn.Module. Fill in the remainder of the code, remembering to use the optimal hyperparameters you found in Part 2.2.

Part 3.4 (10 points) Implement functions for training and testing

Now that you have defined the model architecture and a DataLoader, you can use them to train the model. First you need to choose an optimizer that takes the gradients computed from backpropagation to update model parameters through a variant of stochastic gradient descent. Depending on the hyperparameter you found as optimal in Part 2.2, you should use either stochastic gradient descent (torch.optim.SGD) or the Adam optimizer (torch.optim.Adam). The optimizer object takes the model parameters which you can retrieve with model.parameters(). You also need to specify a starting learning rate lr, which you should set to 1e-3. Do not implement L2 regularization; don't copy the alpha parameter into PyTorch.

Next, you will want to write a training loop. We have provided the skeleton code of a training loop; this is essentially standard, so you can copy it for virtually any neural network. We use the `DataLoader` to loop over the training data and use the model to predict the binding probabilities for each minibatch. You will now need to compute a loss; in this case, we want the mean-squared error loss implemented as `nn.functional.mse_loss()`; this requires both your model output and the ground-truth data. Once this is done, PyTorch will compute $\nabla_{\boldsymbol{\theta}}\mathcal{L}$ to find the gradient step direction. This is done for you when you call `loss.backward()`. The optimizer receives the gradient and optimize your model by then calling `optimizer.step()`. Always remember to remove the accumulated gradient from a previous calculation (minibatch) by calling `optimizer.zero_grad()` at the beginning of the minibatch processing. Please take a moment to reflect on this procedure: all of the complicated gradient calculation/update is nicely wrapped by these function calls so that you do not need to think about the numerics behind the scenes. Complete the `train()` function following these guidelines. You will next want to complete the `validate()` function which uses the validation `DataLoader` and computes the loss on the validation set; it is otherwise very similar.

Looping over the entire training data set once is called an *epoch*. The `train()` and `validate()` function you will implement is only for one epoch, and should return a train loss and validation loss computed as averages over all the batches. Train and validate your model for 400 epochs.

Record the average train and validation loss for each epoch and plot these on a single graph (the code to do this has already been provided). Finally report your test R^2 of your trained model on the test data. You would need to transform your prediction from `torch.Tensor` to `np.array` to compute the R^2 and use `sklearn.metrics.r2_score`.

Part 4: Conclusion

Part 4.1 (5 points) Feedback survey

You will get 5 points for completing the survey posted on Canvas. This will help us improve future problem sets.

Acknowledgement

We thank Daniel Schawbe-Koda for helping with the data generation for this problem set.

References

[1] Chen, Y., Zhang, L., Zhang, Y., Gao, H. & Yan, H. Large-area perovskite solar cells–a review of recent progress and issues. *RSC advances* **8**, 10489–10508 (2018).

[2] Bergstra, J., Bardenet, R., Bengio, Y. & Kégl, B. Algorithms for hyper-parameter optimization. In *25th annual conference on neural information processing systems (NeurIPS 2011)*, vol. 24 (Neural Information Processing Systems Foundation, 2011).

[3] Abedin, M. I., Islam, A. & Hossain, Q. D. A self-adjusting lin-log active pixel for wide dynamic range cmos image sensor. In *2015 IEEE International Conference on Telecommunications and Photonics (ICTP)*, 1–4 (IEEE, 2015).