Perovskite Model Description

December 8, 2016

1 Introduction

non capital p throughout the document

composition

In this project we are interested in finding a Perovskite solution with the highest unsaturated Mayer Bond order (UMBO). We approach this problem with Bayesian Optimization. This documentation provides model descriptions for both single-halide and mixed-halide Perovskite and presents results for the single-halide scenario.

2 Single-halide Model

2.1 Model setup

In a single-halide model, the setup contains one halide, one cation and one solvent. There are 3 choices for halides, 3 for cations and 8 for solvents, hence 72 possible setups in total. Let V_x to denote the UMBO of setup x, $x \in \{1, ..., 72\}$. We use vector Z^x to describe the components of setup x. In particular, $Z_i^x, i \in \{1, 2, 3\}$ is a binary variable that indicate s

each value of i corresponding to a specific element

only

whether a cation is present in setup x. We require that $\sum_{i=1}^{3} Z_i^x = 1, \forall x$, since there is one cation present in each setup. Likewise, $Z_i^x, i \in \{4, 5, 6\}$ is a binary variable that indicate s whether a halide is present in setup x. $Z_7^x \in \{s_1, ..., s_8\}$ indicates which solvent is used in setup x. For example, $Z^x = (1, 0, 0, 0, 1, 0, s_4)$ means that setup x contains the first

type of cation, second type of halide, and the 4^{th} type of solvent. In addition, for future computation, we let s_i be a 2-d vector with the first entry being the Mayer bond order and the second entry being the polarity of the i^{th} solvent, $i \in \{1, ..., 8\}$.

objective value of the composition

We assume the presence of cations and halides contributes linearly to the solubility, and we use α_i to quantify the amount contributed by cation/halide i. To correct for the possible non-linear effect of cations and halides, we introduce β_x for each of the setup x. For solvents, we assume they affect the solubility through an unknown function $f : \mathbb{R}^2 \mapsto \mathbb{R}$ which takes into consideration ~~the Mayer bond order~~ and polarity of a solvent. In addition to just a halide, a cation and a solvent, a perovskite ~~solution~~ also contains a ~~invariant group of ions sitting at the center~~. Hence we use ζ to denote the invariant part of the setup. Hence ~~solubility of~~ setup x can be written in the following way:

central ion, for which we choose lead in all compositions. Denote its contribution to the objective by xxx.

$$V_x = \sum_{i=1}^{6} \alpha_i Z_i^x + \beta_x + \zeta + f(Z_7^x). \tag{1}$$

We place the same prior distribution $N(\mu_\alpha, \sigma_\alpha^2)$ on each of α_i, and $N(0, \sigma_\beta^2)$ on β_x. ζ is assume to follow $N(\mu_\zeta, \sigma_\zeta^2)$ ~~We also w~~ $f(\cdot)$ as a Gaussian process with prior mean function $\mu_0(\cdot)$ and covariance $\Sigma_0(\cdot, \cdot)$. Since ζ already captures the invariant contribution from the central ions, it is reasonable for us to assume $\mu_0(\cdot) = \mathbf{0}$. For $\Sigma_0(\cdot, \cdot)$, we use 5/2 Matern kernel. Let $r = \sqrt{\sum_{i=1}^{d} \ell_i (x_{1,i} - x_{2,i})^2}$ denote the distance between point x_1 and x_2 weighed by each dimension. In our case $d = 2$. The covariance between x_1 and x_2 under a 5/2 Matern kernel is calculated as:

Has an accent

We suppose that two compositions have similar objective value if they differ little in their parts. To formalize this, let...

$$\Sigma_0(x_1, x_2) = \sigma_m^2 \left(1 + \sqrt{5}r + \frac{1}{3}5r^2\right) exp\left(-\sqrt{5}r\right), \tag{2}$$

where σ_m^2, ℓ_i are hyper-parameters. With all the components of V_x being normally distributed, V_x is also normally distributed. Hence we are able to describe the joint distribu-

tion of $(v_1, ..., v_{27})$ with a multivariate normal distribution:

$$\begin{pmatrix} V_1 \\ V_2 \\ \vdots \\ V_{135} \end{pmatrix} \sim N(\mu^0, \Sigma^0), \tag{3}$$

where

$$\begin{aligned} \mu_x^0 &= \mathbb{E}\left[\sum_{i=1}^{6} \alpha_i Z_i^x + \beta_x + \zeta + f(Z_7^x)\right] \\ &= \sum_{i=1}^{6} \mu_\alpha Z_i^x + \mu_\zeta + \sum_{i=1}^{15} \mathbb{1}(Z_7^x = s_i)\mu_{0,i} \\ &= 2\mu_\alpha + \mu_\zeta, \end{aligned}$$

and

$$\begin{aligned} \Sigma_{x,x'}^0 &= COV(V_x, V_{x'}) \\ &= \sum_{i=1}^{6} \sigma_\alpha^2 \mathbb{1}(Z_i^x = 1)\mathbb{1}(Z_i^{x'} = 1) + \Sigma_0(Z_7^x, Z_7^{x'}) + \mathbb{1}(x = x')\sigma_\beta^2 + \sigma_\zeta^2 \end{aligned}$$

2.2 Estimation of Hyper-parameters

We estimate the hyper-parameters by maximum likelihood estimation method. Let $\theta = \{\mu_\alpha, \sigma_\alpha, \sigma_\beta, \mu_\zeta, \sigma_\zeta, \ell_1, \ell_2\}$ be the vector of all the hyper-parameters we want to estimate. Let $V = \{v_{i_1}, ..., v_{i_m}\}$ to be the observations we made for $i_1, ..., i_m$. Then the likelihood of

V given θ is

$$\begin{aligned} L(\theta) &= P(V|\theta) \\ &= (2\pi)^{-m/2} * |\Sigma^0(i_1, ..., i_m)| * \exp\left(-\frac{1}{2} u^0(i_1, ..., i_m)^T \Sigma^0(i_1, ..., i_m) u^0(i_1, ..., i_m)\right), \end{aligned}$$

where $u^0(i_1, ..., i_m) = (u^0_{i_1}, ..., u^0_{i_m})$ is a vertical vector, and $\Sigma^0(i_1, ..., i_m)u^0(i_1, ..., i_m)$ is a $m \times m$ matrix with $\{k, j\}$ entry $= \Sigma^0_{i_k, i_j}$.

The MLE of θ is set to be

$$\hat{\theta} = \underset{\theta}{\text{argmax}}\ log(L(\theta)). \tag{4}$$

A maximizer of (4) can be found via gradient-based optimization algorithms such as BFGS.

2.3 Posterior update

We ~~can~~ update the mean and covariance in (3) after we make an observation. Let μ^n and Σ^n denote the mean and covariance in (3) after n observations are made. It is a well known fact that we can update the posterior distribution in the following way: given μ^n and Σ^n, and a new observation $\hat{y}^{n+1}$ which is made about setup x, the new posterior is:

$$\mu^{n+1} = \mu^n + \frac{\hat{y}^{n+1} - \mu^n_x}{\Sigma^n_{xx}} \Sigma^n \mathbf{e}_x, \tag{5}$$

$$\Sigma^{n+1} = \Sigma^n - \frac{\Sigma^n \mathbf{e}_x \mathbf{e}_x^T \Sigma^n}{\Sigma^n_{xx}} \tag{6}$$

Choosing the next composition to be studied

2.4 ~~Selection of next observation~~

Expected Improvement (EI) is used to determine which setup x the next observation is to be made.

~~2.4.1 expected improvement~~

Let $\hat{y}^* = \max_{1,...,n}\{\hat{y_1}, ..., \hat{y_n}\}$ be the largest observed value so far. Assuming a maximizing problem, the expected improvement (EI) of a setup x is:

$$\begin{aligned} EI(x) &= \mathbb{E}\Big[\max\{V_x - \hat{y}^*, 0\}\Big|\mu^n, \Sigma^n\Big] \\ &= (\mu_x^n - \hat{y}^*)\Phi\left(\frac{\mu_x^n - \hat{y}^*}{(\Sigma_{xx}^n)^{1/2}}\right) + (\Sigma_{xx}^n)^{1/2}\phi\left(\frac{\mu_x^n - \hat{y}^*}{(\Sigma_{xx}^n)^{1/2}}\right), \end{aligned}$$

where $\Phi(\cdot)$ and $\phi(\cdot)$ are standard normal cdf and pdf respectively.

We pick the setup with the largest EI:

$$x^* = \underset{x\in\{1,...,72\}}{\text{argmax}}\ EI(x) \tag{7}$$

2.5 Experiment Result

verify that our model fits the data well.

We first use leave-one-out cross validation to ~~find out if 3 is indeed a good description of the UMBO of the setups~~. 20 samples (~~setups~~ and their UMBO) are selected randomly. Each time one sample is left out and parameters are estimated using the rest 19 samples. We then compare the UMBO of the sample left out to the confidence interval of the UMBO calculated based on the parameters estimated. Figure 2.5 plots the result of the cross validation. It can been seen that most of the observed UMBO lies within the corresponding confidence interval, thus indicating a good fit of the model to the data.

hyperparameters of our model

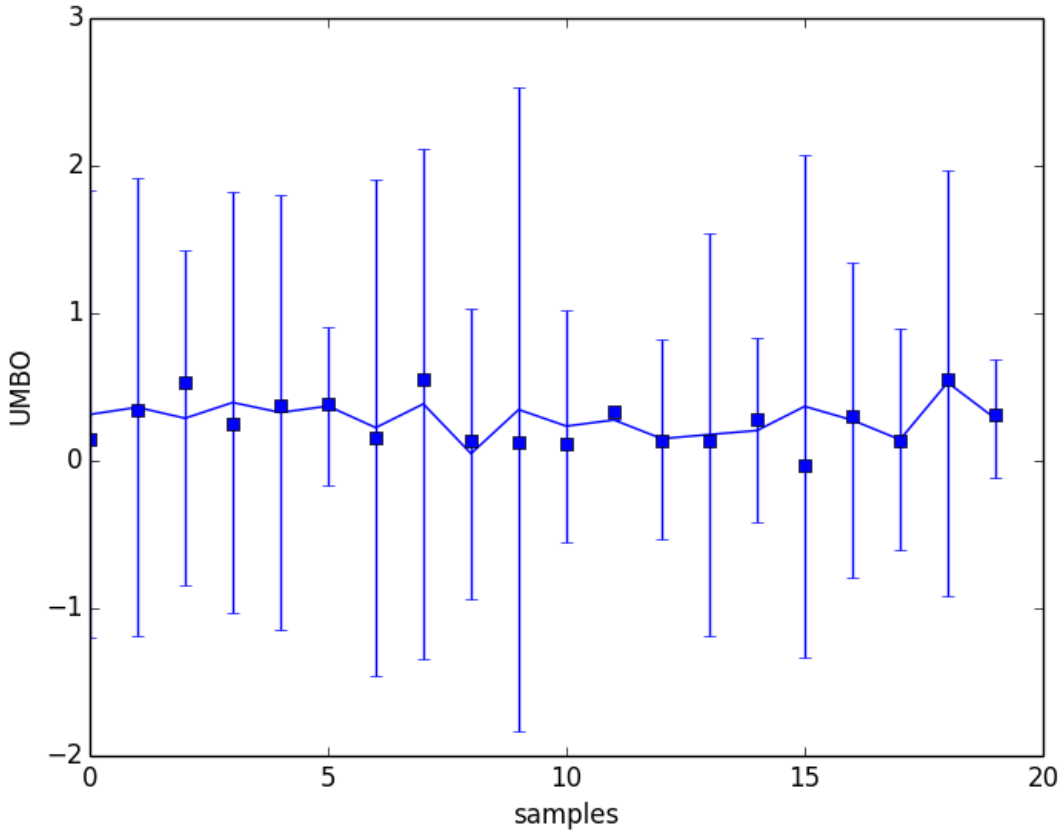

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Figure 2.5 plots the result of the sampling process by using Bayesian optimization method aforementioned. The red line shows the true maximum UMBO among all the possible setups. We can see that it takes 14 iterations for the BO process to converge to the true maximum, which is better than carrying out the sampling randomly.

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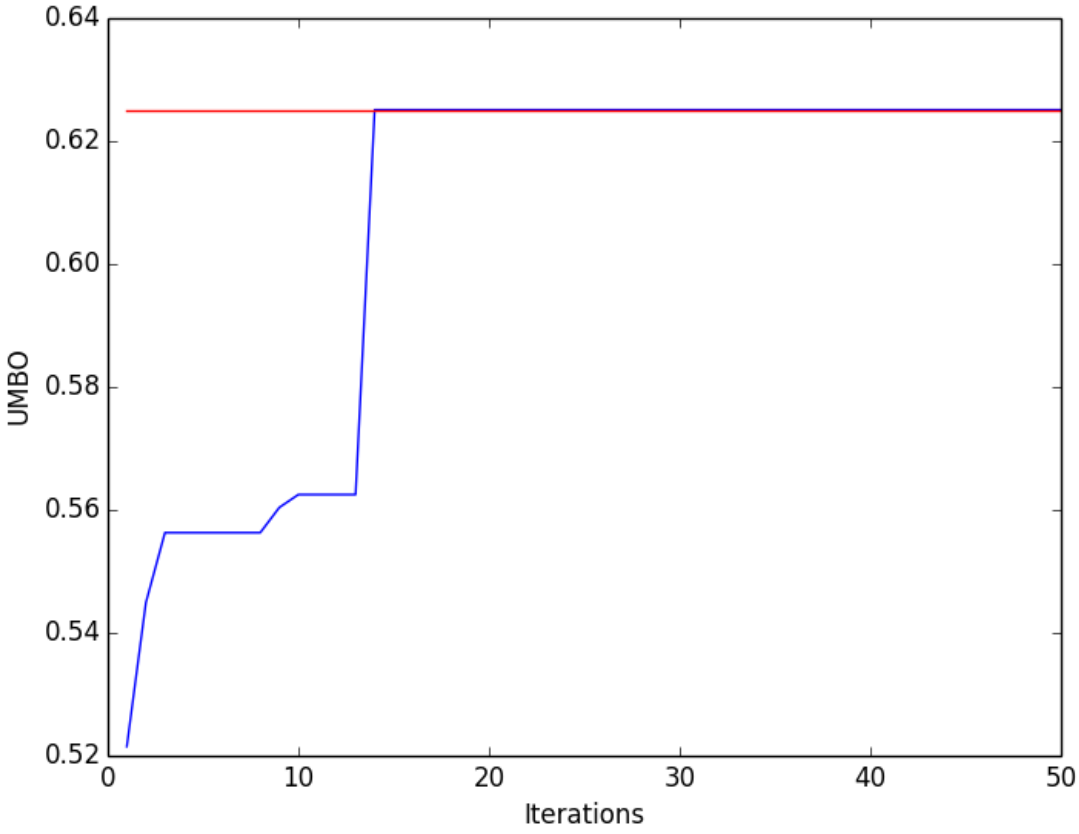
considerably less effort than



3 Mixed-Halide Model

we should omit this for the annual report

3.1 Model setup

Let V_x to denote the UMBO of setup x. For each setup, there are three halides, one cation and a solvent. Since the positioning of the halides matters, there are in total 27*3*8 = 648 possible combinations. (i.e., $x \in \{1, ..., 648\}$). We use vector Z^x to describe the components of setup x. In particular, $Z_i^x, i \in \{1, 2, 3\}$ is a binary variable that indicate which halide is in the 1st position. And We require that $\sum_{i=1}^{3} Z_i^x = 1, \forall x$. For example, $Z_{1,2,3}^x = (0, 0, 1)$

means that iodide is present in the 1st position. Likewise, $Z_i^x, i \in \{4,5,6\}$ is a binary variable that indicates which halide is present in the second position and $Z_i^x, i \in \{7,8,9\}$ in indicates which halide is present in the third position. Z_i^x, $i \in \{10,11,12\}$, indicates which cation is present in the setup. Again it is required that $\sum_{i=10}^{12} Z_i^x = 1, \forall x$. $Z_{13}^x \in \{s_1, ..., s_8\}$ indicates which solvent is used in setup x. In addition, for future computation, we let s_i be a 2-d vector with the first entry being the Mayer bond order and the second entry being the polarity of the i^{th} solvent, $i \in \{1, ..., 8\}$.

We still assume the presence of cations and halides contributes linearly to the UMBO, and we use α_i to quantify the amount contributed by cation/halide i. To correct for the possible non-linear effect of cations and halides, we introduce β_x for each of the setup x. For solvents, we assume they affect the UMBO through an unknown function $f : \mathbb{R}^2 \mapsto \mathbb{R}$ which takes into consideration the Mayer bond order and polarity of a solvent. Moreover, since a perovskite setup contains more than just a cation, a halide and a solvent, we use ζ to denote the invariant part of the setup. Hence UMBO of setup x can be written in the following way:

$$V_x = \sum_{i=1}^{12} \alpha_i Z_i^x + \beta_x + \zeta + f(Z_{13}^x). \tag{8}$$

We place the same distributions on the parameters as in Section 1. We also use the same procedure described in section 1 to place prior, to update posterior and to select the next sample.