High Throughput Search for New Plasmonic Materials

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Outline

- Introduction
- Theoretical Background
  - Plasmonics
  - Machine Learning
- Methods
  - Density Functional Theory
  - Model Validation
- Preliminary Results
- Future Work
Introduction – Plasmonics

- Control light at subwavelength scale by exciting collective oscillations on metal-dielectric interfaces.

- Oscillations either propagating as Surface Plasmon Polariton (SPP) or localized as Localized Surface Plasmon Resonance (LSPR).

- Would allow numerous applications: subwavelength waveguides, nanoantennas, superlenses, subwavelength imaging, nanocircuitry, biosensors. [1-8]

Introduction – Material Selection

- Response to applied optical field depends on both material selection and geometry.

- Current materials [9]:
  - Ag, Au, Cu- high conductivity, large visible losses from interband transitions.
  - Doped semiconductors- tune bandgap to prevent interband transitions, require high doping concentrations.

- General criteria:
  - Low interband and intraband losses in optical.
  - Negative real part of dielectric function.

Introduction – Machine Learning

- Automate pattern detection in large datasets.
- Have descriptors and some target values. Limited knowledge of how to connect values.
- Want efficient methods for relating descriptors to target.
- Provide large training set, systems for which descriptors and target are known.
- Iteratively search for best statistical relationship.
Introduction – The Project

- Goal to find new materials for plasmonics at optical frequencies.

- Databases of materials contain 10’s-100’s of thousands of materials, not computationally feasible to calculate all dielectric functions.

- Build on existing databases, carry out DFT on a subset to form a training set; machine learn plasmonic figure of merit values, quality factors.

- Apply learned models to find new candidate materials.

- Use as motivation to better understand physics underlying ground and excited state properties.
Theoretical Background – Dielectric Function

- Response of material to applied electric field
- Physics described depends on energy of interest
- Contributions due to intraband and interband transitions
- Drude model for intraband, DFT for interband

Bandstructure and dielectric function of Au.
Theoretical Background – Plasmonics

- Locally enhanced electric field near interface
  \[ Q = \frac{\text{enhanced}|\vec{E}|}{\text{incident}|\vec{E}|} \]

- Loss from imaginary part of dielectric function

- From solving Maxwell’s equations near the metal-dielectric interface
  \[ Q_{LSPR}(\omega) = -\frac{\epsilon_1}{\epsilon_2} \quad Q_{SPP}(\omega) = \frac{\epsilon_1^2}{\epsilon_2} \]

- Evaluate Q at three energies- 1.1655 eV (Nd:YAG), 1.9595 eV (HeNe), 2.8075 eV (HeCd metal vapor)
Theoretical Background – Machine Learning

- Purpose is to predict quality factors of materials using descriptors obtainable from chemical formula (e.g. average atomic mass, number of electrons); also gives information about how atomic properties influence bulk.

- Numerous algorithms available.

- Employ machine learning python library Scikit-learn.

- Work underway to develop automated machine learning system. Will automate process of machine learning for materials properties.
Methods – Workflow

AₓBᵧCₓ

Predict Metallicity

Metal

• ϵ(ω)
• ωₚ,VASP

Non Metal

• E₉
• ϵ(ω)
• ω²ₚ,VASP/n

Machine learn Q factors

DFT on high Q class of materials
Methods – DFT

- Find contribution to dielectric function from interband transitions with DFT.

- Construct training set as ~1000 randomly chosen metals from Materials Project.

- PBE exchange correlation functionals.

- Plane wave cutoff of 550 eV.
**Methods – DFT**

- DFT performed with Vienna Ab-Initio Simulation Package (VASP) on Blue Waters

- Require dense k-point sampling near Fermi surface

- With 25 x 25 x 25 Γ-centered mesh, $\omega_p$ is converged within 4%, typically under 1%

- Use 31 x 31 x 31 Γ-centered mesh

![Convergence of plasma frequency of Au in VASP.](image)
Methods – Model Validation

- Machine learning is susceptible to overfitting.

- Prevent using overfit model with 80-10-10 validation.

- 10%- testing set, fixed.

- 80%- fitting, 10% validation, 20 iterations.

- Balance size of tree or network versus fitting, validation, testing errors.

Preliminary Results – Validating DFT results

- Check training set for possible high Q plasmonics

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<tr>
<th>Material</th>
<th>$\omega_p$</th>
<th>$Q_{LSPR,1}$</th>
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<tbody>
<tr>
<td>Au</td>
<td>8.70</td>
<td>0.937</td>
</tr>
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<td>Ag</td>
<td>8.95</td>
<td>1.05</td>
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Metals already in use
Preliminary Results – Validating DFT results

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Less common metals [11,12]
Preliminary Results – Validating DFT results

➢ Check training set for possible high Q plasmonics

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Possible new materials

➢ Energy above hull < 100 meV, can be stable
Preliminary Results – Learning Q

- Train decision trees for each Q
- MAEs: 0.22 fitting, 0.35 validation, 0.39 testing.
- Reproduces general trend
- Error is same order of magnitude as Q
- No subset produces large outliers
Preliminary Results – Applying model

Apply learned models to all metals in Materials Project

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<th>Q_{LSPR,2}</th>
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</tr>
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<tr>
<td>NaLi$_3$</td>
<td>0.90±0.10</td>
<td>1.11±0.21</td>
<td>0.74±0.28</td>
</tr>
<tr>
<td>Na$_3$Ca</td>
<td>0.86±0.15</td>
<td>1.17±0.18</td>
<td>0.84±0.21</td>
</tr>
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Two possible new materials with low energy above hull

High Q even in near UV, uncommon feature for metals
Future Work – Short Term

- Apply same process to doped semiconductors.

- Require band gap correction to improve estimate of dielectric functions.

- Also consider amount of electron doping - fix at one value.
Choose several high Q metals and doped semiconductors.

Construct several related compounds (e.g. NaLi$_3$ -> KLi$_3$, NaK$_3$).

Apply methods which can better capture correlation and quasiparticle effects, HSE, GW.

Band structure of surfaces.
Future Work – New Physics

- Determining suitability for plasmonic applications requires understanding the physics contributing to absorption and the dielectric function.

- Better capture electron-electron interactions with HSE, include spin orbit coupling.

- Effect of surface vs. bulk on optical properties.
Why Blue Waters?

- Large number of nodes allows submitting many DFT calculations simultaneously, vital for creating training set.

- Accurate description of excited states (hybrid functionals, GW) requires expensive calculations.

- Surface calculations require large supercells up to 100 atoms.

- Powerful compute nodes, large amounts of memory, and efficient parallelization will be necessary for this work.
References


Theoretical Background – Decision Trees

- Learn series of simple decision rules
- Recursively partition fitting set such that data points with similar descriptors are grouped together
- Reduce influence of fitting set using ensembles and adaptive boosting
- Difficult to learn non-linear relations
- Good out of the box choice
Preliminary Results – Metallicity

- 49,077 materials with band structures in Materials Project.

- Atomistic descriptors and crystal symmetry only, Adaboost decision tree.

- 91.9% classification accuracy, 93% accuracy with crystal structure reported in literature [10].
Preliminary Results – Plasma Frequency

- DFT calculations for 970 metals in materials project.
- AdaBoost decision tree regressor.
- 80-10-10 testing.
- MAEs: 0.63 eV fitting, 1.19 eV validation, 1.05 eV testing.
- Experimental uncertainty ~ 0.25 eV for Au
Descriptors

- Number of s-, p-, d-, and f- electrons above the noble gas configuration.
- Reduced mass, average mass, and standard deviation of mass of elements in chemical formula.
- Average, standard deviation, and maximum difference of electronegativities.
- Average, standard deviation, maximum, and minimum characteristic frequency of chemical formula.
- Average and standard deviation of ionic radii.
- Average, standard deviation, and maximum difference of atomic dipole moments.
- Average and maximum difference of azimuthal quantum numbers of highest energy electrons in the elements.
- Total volume of atoms.
- Number of atoms in chemical formula.
Dielectric Functions – Ga and Mg

Dielectric Function of Ga

Dielectric Function of Mg
Plasma frequency depends on doping and lattice dielectric constant in Drude model.

Calculated $\omega_p$ consistent with Drude model, but with crossover at high doping.

$$\omega_p^2 = \frac{4\pi ne^2}{m\varepsilon_{core}} - \frac{1}{\tau^2}$$
Preliminary Results – Bandgap

- DFT has known difficulties calculating bandgaps.

- Use DFT gap and atomistic descriptors and fit to experimental values, 326 semiconductors

- 80-10-10 testing.

- MAEs: 0.50 eV fitting, 0.82 eV validation, 0.88 eV testing.