High Throughput Search for New Plasmonic Materials

Ethan Shapera and André Schleife

University of Illinois at Urbana-Champaign

June 4th, 2018

Grants No. CBET-1437230, DMR-1555153

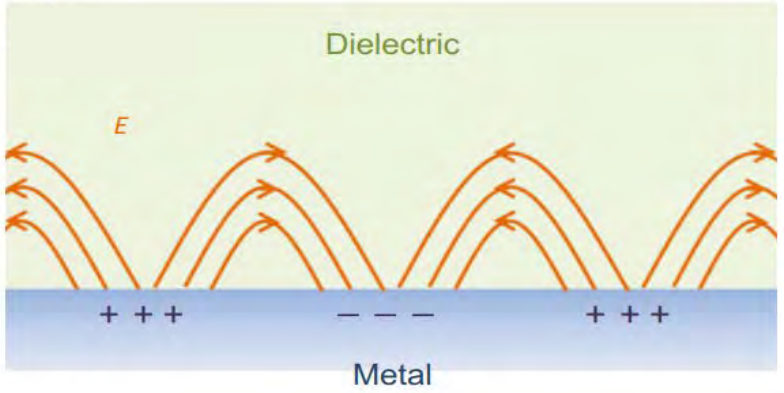
OCI-0725070, ACI-1238993

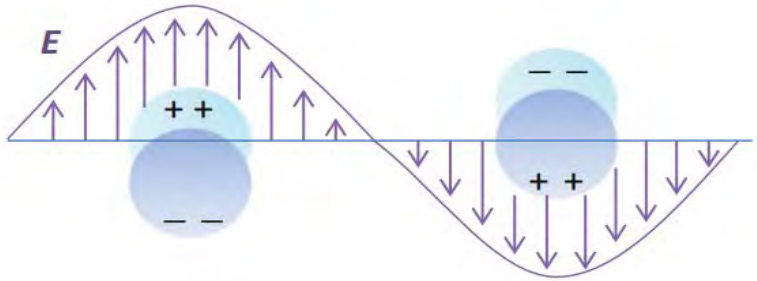
Outline

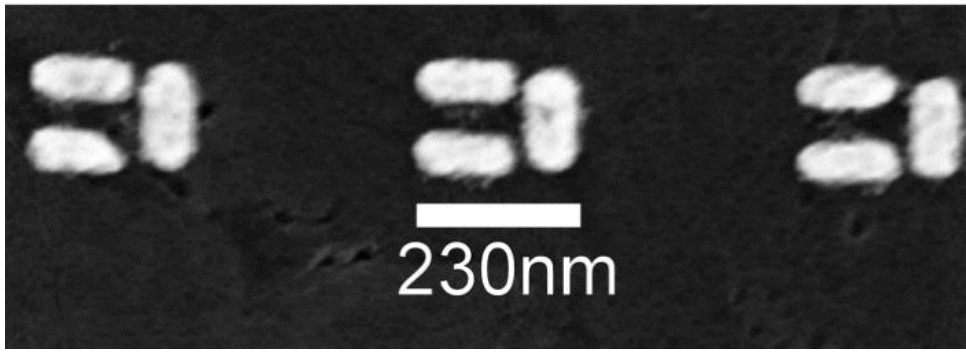
- Introduction
- Theoretical Background
  - Plasmonics
  - Machine Learning
- Methods
  - Density Functional Theory
  - Model Validation
- Preliminary Results
- Future Work

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]





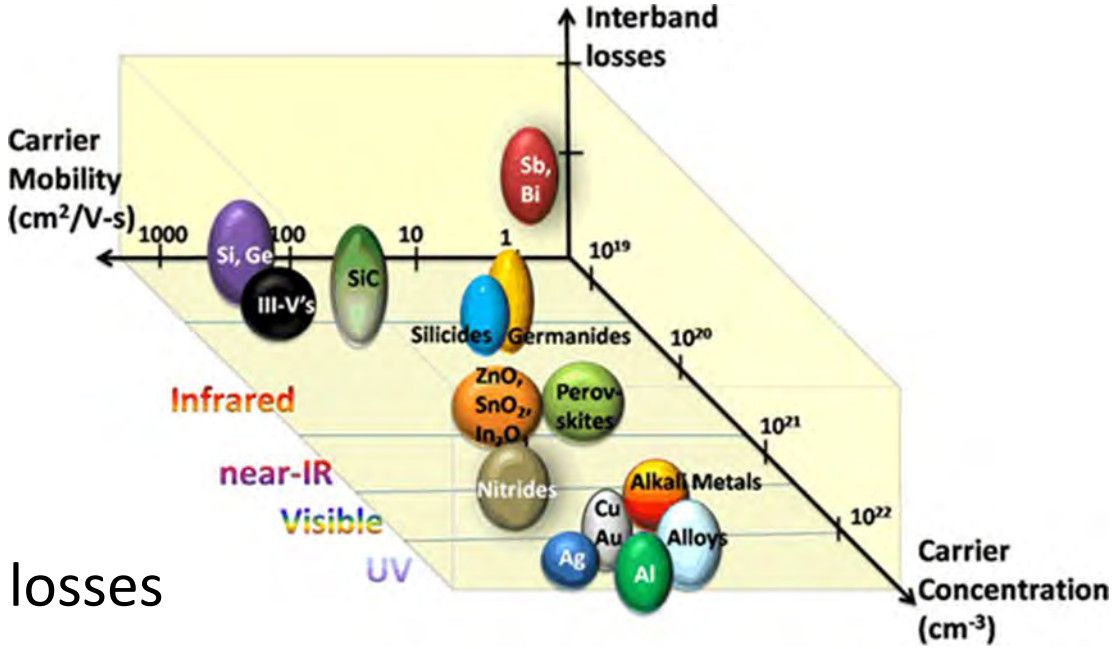


Proposed sensor, Au nanostructures on VO_2 thin film

Images from B. Wu et al., Plasmonic Organic Solar Cells, Nanoscience and Nanotechnology, DOI 10.1007/978-981-10-2021-6_2 (2016), https://doi.org/10.1116/1.4826561 (2013).

Introduction – Material Selection

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



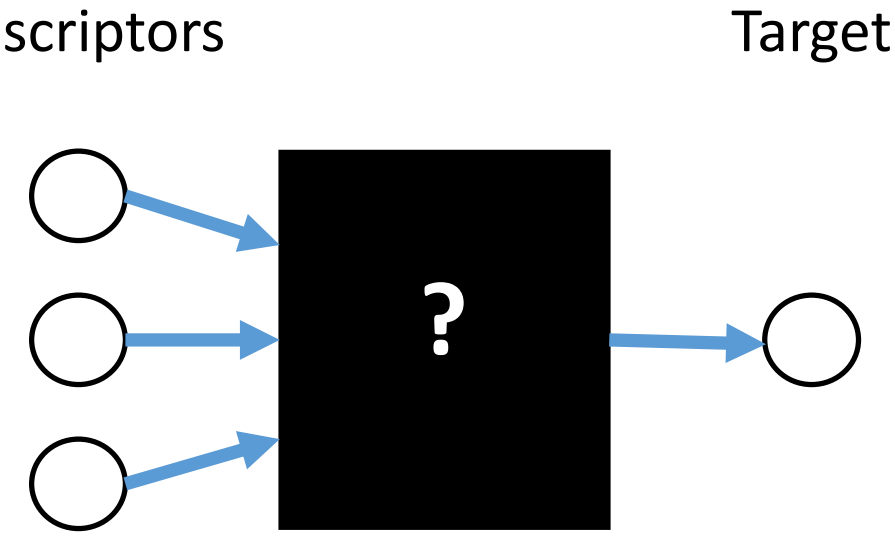
- Current materials [9]:
  - Ag, Au, Cu- high conductivity, large visible losses from interband transitions.
  - Doped semiconductors- tune bandgap to prevent interband transitions, require high doping concentrations.

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

Image from https://doi.org/10.1557/mrs.2012.173 (2012).

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.

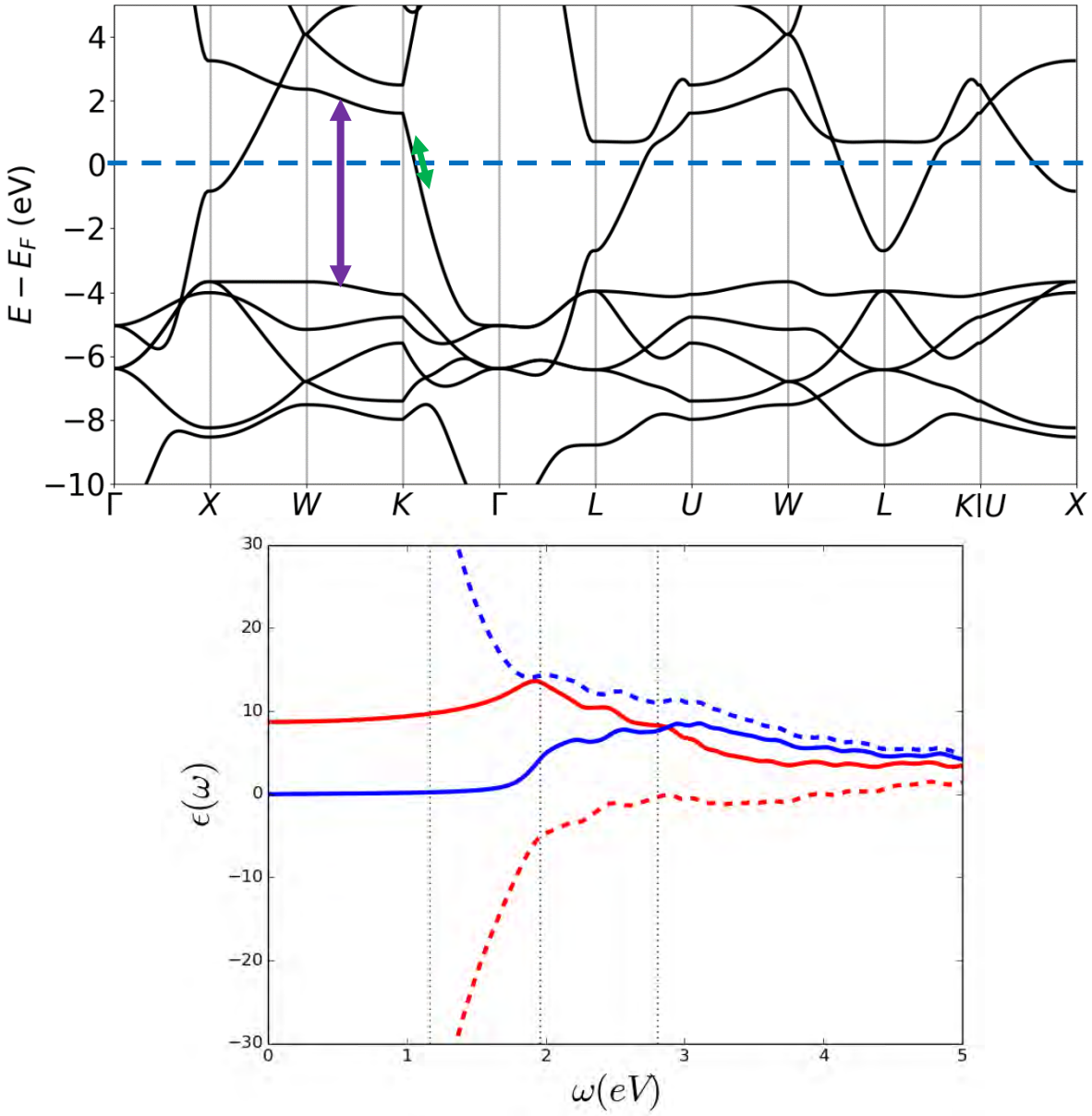


Introduction – The Project

- 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

$$Q = \frac{enhanced|\vec{E}|}{incident|\vec{E}|}$$

- Loss from imaginary part of dielectric function

- From solving Maxwell's equations near the metal-dielectric interface

$$Q_{LSPR}(\omega) = -\frac{\epsilon_1}{\epsilon_2} \qquad Q_{SPP}(\omega) = \frac{\epsilon_1^2}{\epsilon_2}$$

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

Theoretical Background – Machine Learning

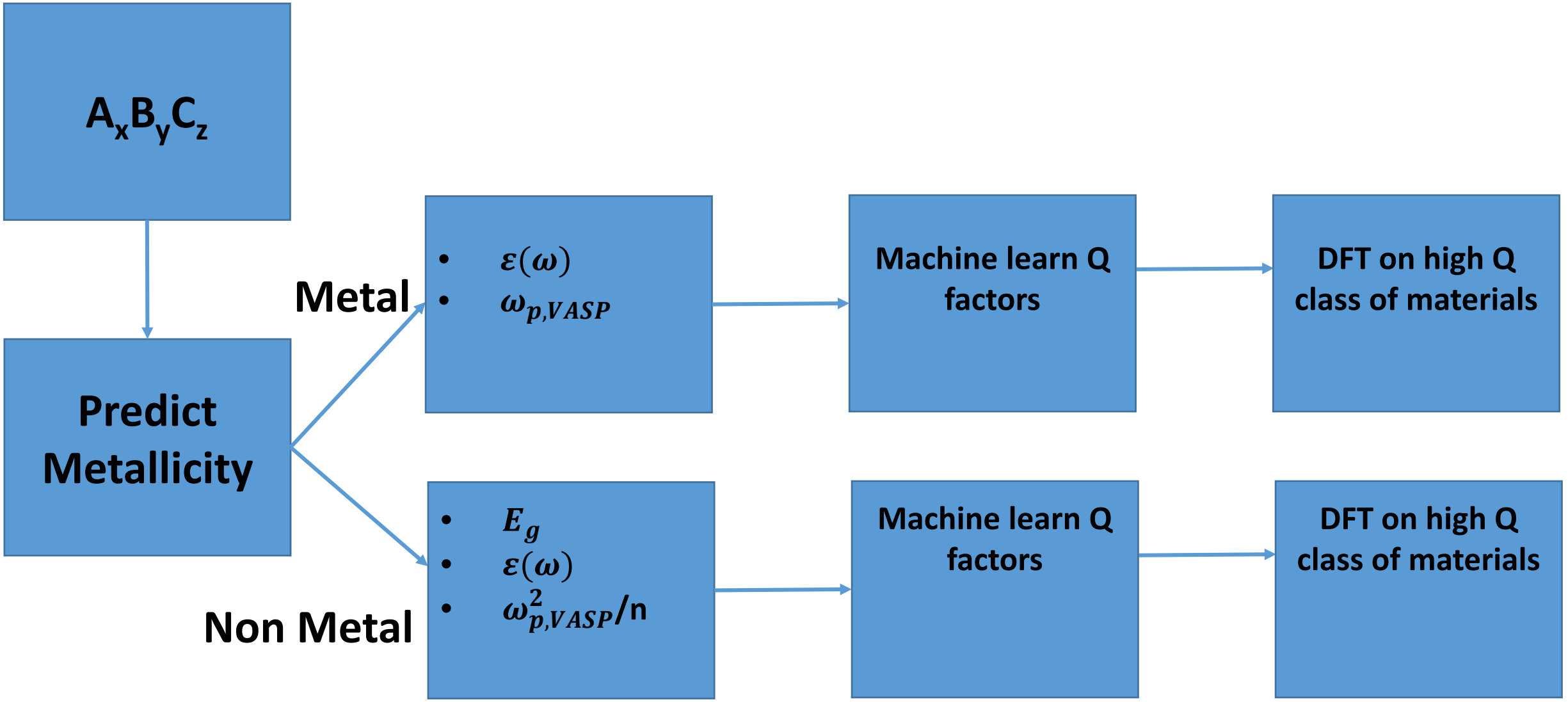
- Purpose is to predict quality factors of materials using descriptors obtainable from chemical formula (e.g. average atomic mass, number of electrons); also gives information about how atomic properties influence bulk.

- 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

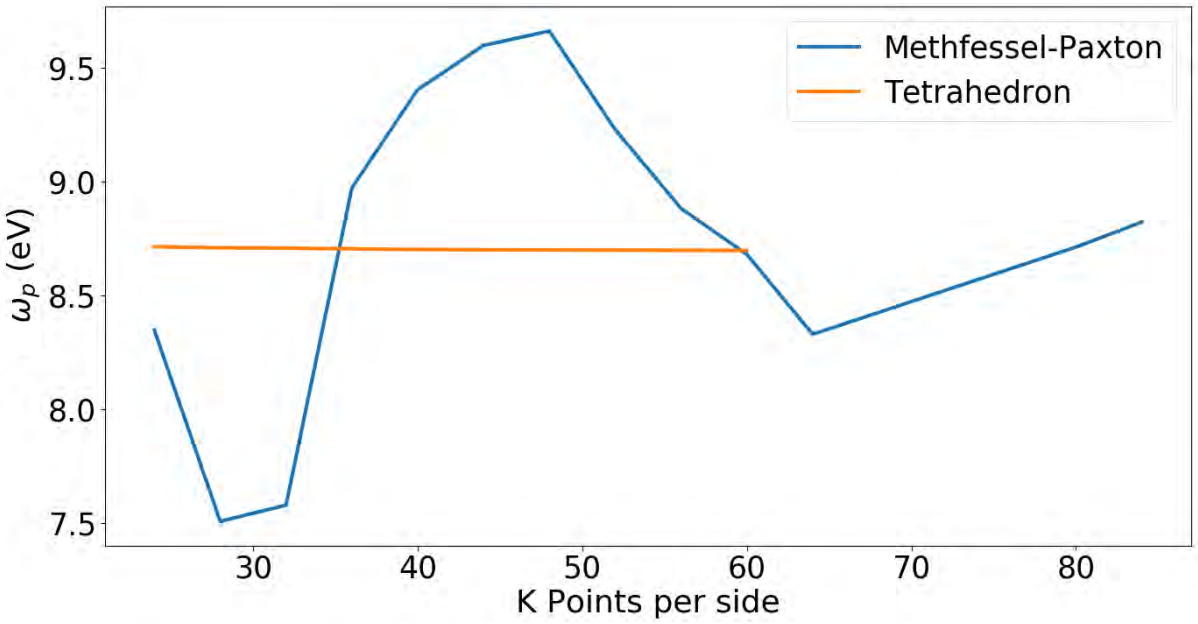


Methods – DFT

- 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

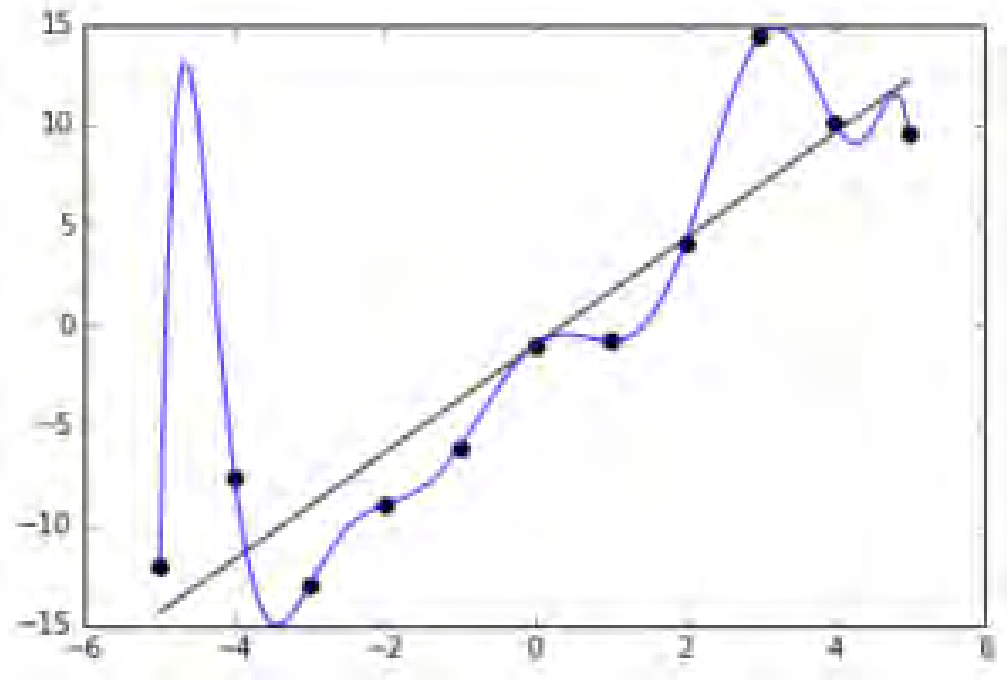
- DFT performed with Vienna Ab-Initio Simulation Package (VASP) on Blue Waters
- Require dense k-point sampling near Fermi surface
- With 25 x 25 x 25 Γ-centered mesh, ω_p is converged within 4%, typically under 1%
- Use 31 x 31 x 31 Γ-centered mesh



Convergence of plasma frequency of Au in VASP.

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.

Image from https://upload.wikimedia.org/wikipedia/commons/thumb/6/68/Overfitted_Data.png/300px-Overfitted_Data.png .

Preliminary Results – Validating DFT results

- Check training set for possible high Q plasmonics

Material	ω_p	$Q_{LSPR,1}$
Au	8.70	0.937
Ag	8.95	1.05
Al	12.4	0.758
Mg	7.58	1.19
Ga	9.76	0.868
Cu_3Au	7.14	1.13
$AgTe_3$	6.80	1.12

Preliminary Results – Validating DFT results

- Check training set for possible high Q plasmonics

Metals already in use

Material	ω_p	$Q_{LSPR,1}$
Au	8.70	0.937
Ag	8.95	1.05
Al	12.4	0.758
Mg	7.58	1.19
Ga	9.76	0.868
Cu_3Au	7.14	1.13
$AgTe_3$	6.80	1.12

Preliminary Results – Validating DFT results

- Check training set for possible high Q plasmonics

Less common metals [11,12]

Material	ω_p	$Q_{LSPR,1}$
Au	8.70	0.937
Ag	8.95	1.05
Al	12.4	0.758
Mg	7.58	1.19
Ga	9.76	0.868
Cu_3Au	7.14	1.13
$AgTe_3$	6.80	1.12

Preliminary Results – Validating DFT results

- Check training set for possible high Q plasmonics

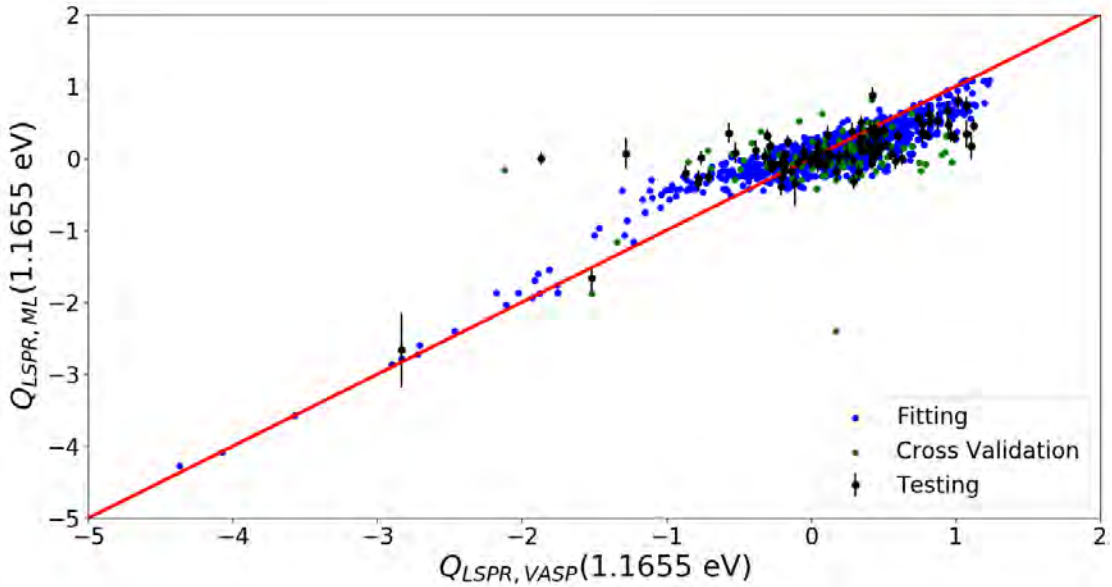
Material	ω_p	$Q_{LSPR,1}$
Au	8.70	0.937
Ag	8.95	1.05
Al	12.4	0.758
Mg	7.58	1.19
Ga	9.76	0.868
Cu_3Au	7.14	1.13
$AgTe_3$	6.80	1.12

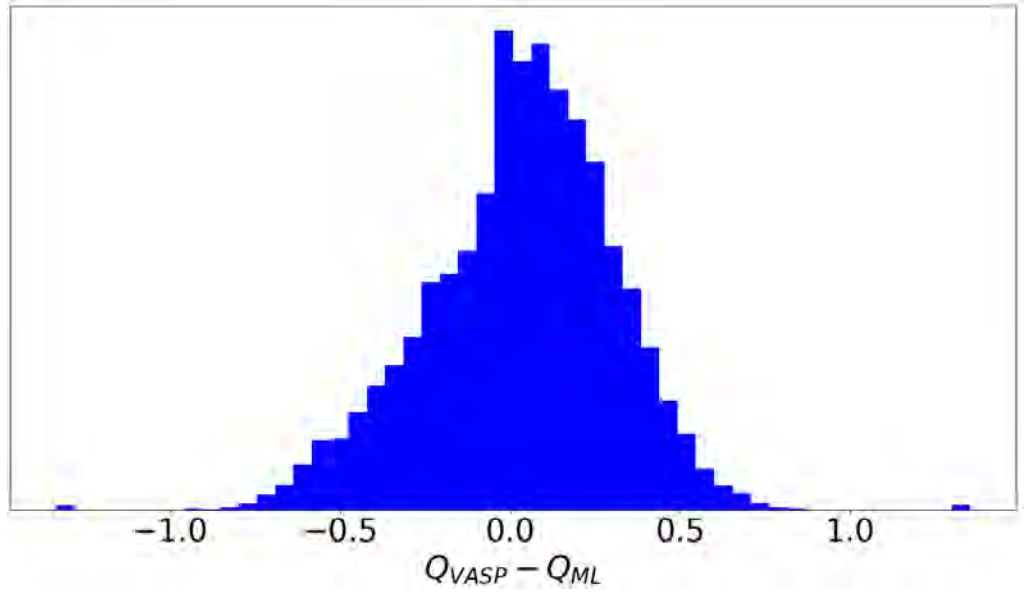
Possible new materials

- 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

Material	$Q_{LSPR,1}$	$Q_{LSPR,2}$	$Q_{LSPR,3}$
$NaLi_3$	0.90±0.10	1.11±0.21	0.74±0.28
Na_3Ca	0.86±0.15	1.17±0.18	0.84±0.21

- 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.

Future Work – Long Term

- 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

[1] Stefan A. Maier, Pieter G. Kik, Harry A. Atwater, Sheer Meltzer, Elad Harel, Bruce E. Koel, and Ari A. G. Requicha. Local detection of electromagnetic energy transport below the diffraction limit in metal nanoparticle plasmon waveguides. 2:229 EP, Mar 2003.

[2] Stefan A. Maier and Harry A. Atwater. Plasmonics: Localization and guiding of electromagnetic energy in metal/dielectric structures. Journal of Applied Physics, 98(1):011101, 2005.

[3] David P. Fromm, Arvind Sundaramurthy, P. James Schuck, Gordon Kino, and W. E. Moerner. Gap-dependent optical coupling of single bowtie nanoantennas resonant in the visible. Nano Letters, 4(5):957-961, 2004.

[4] S. Prayakarao, B. Mendoza, A. Devine, C. Kyaw, R. B. van Dover, V. Liberman, and M. A. Noginov. Tunable vo2/au hyperbolic metamaterial. Applied Physics Letters, 109(6):061105, 2016.

[5] Satoshi Kawata, Atsushi Ono, and Prabhat Verma. Subwavelength colour imaging with a metallic nanolens. Nat Photon, 2(7):438{442, Jul 2008.

[6] Nader Engheta, Alessandro Salandrino, and Andrea Alu. Circuit elements at optical frequencies: Nanoinductors, nanocapacitors, and nanoresistors. Phys. Rev. Lett., 95:095504, Aug 2005.

[7] Nader Engheta. Circuits with light at nanoscales: Optical nanocircuits inspired by metamaterials. Science, 317(5845):1698-1702, 2007.

[8] Tim Stakenborg and Liesbet Lagae. Gold nanoring as a sensitive plasmonic biosensor for on-chip dna detection. Applied Physics Letters, 100(17):173114, 2012.

[9] P. R. West et. al. Searching for better plasmonic materials. Laser & Photonics Reviews, 4(6), 795-808, 2010.

[10] O. Isayev, C. Oses, C. Toher, E. Gossett, S. Curtarolo, and A. Tropsha. Universal Fragment Descriptors

for Predicting Electronic Properties of Inorganic Crystals. ArXiv e-prints, August 2016

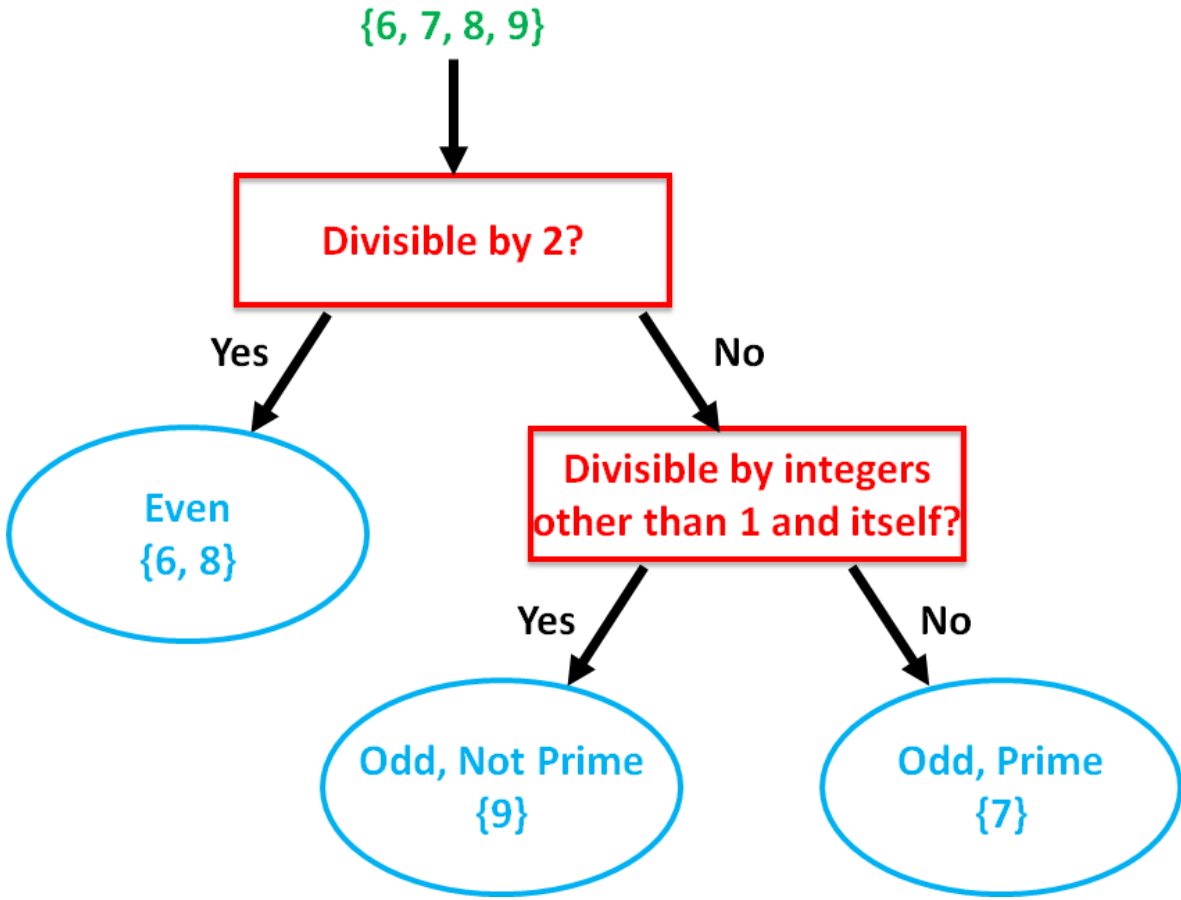
References

[11]Florian Sterl, Nikolai Strohfeldt, Ramon Walter, Ronald Griessen, Andreas Tittl, and Harald Giessen. Magnesium as novel material for active plasmonics in the visible wavelength range. Nano Letters, 15(12):7949-7955, 2015.

[12] Mark W. Knight, Toon Coenen, Yang Yang, Benjamin J. M. Brenny, Maria Losurdo, April S. Brown, Henry O. Everitt, and Albert Polman. Gallium plasmonics: Deep subwavelength spectroscopic imaging of single and interacting gallium nanoparticles. ACS Nano, 9(2):2049-2060, 2015.

Theoretical Background – Decision Trees

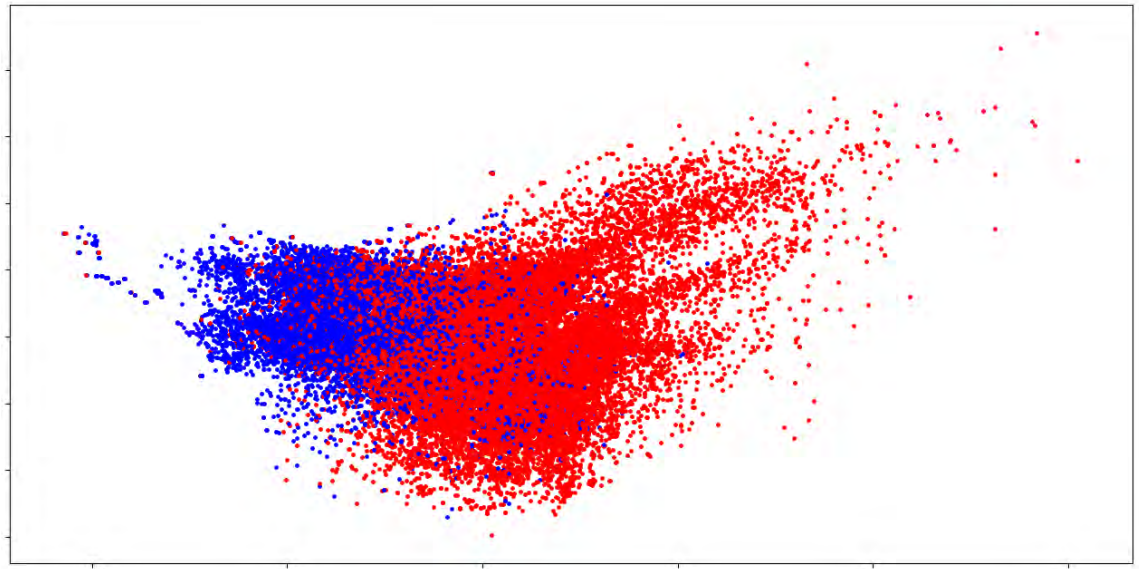
- Learn series of simple decision rules
- Recursively partition fitting set such that data points with similar descriptors are grouped together
- Reduce influence of fitting set using ensembles and adaptive boosting
- Difficult to learn non-linear relations
- Good out of the box choice



Preliminary Results – Metallicity

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

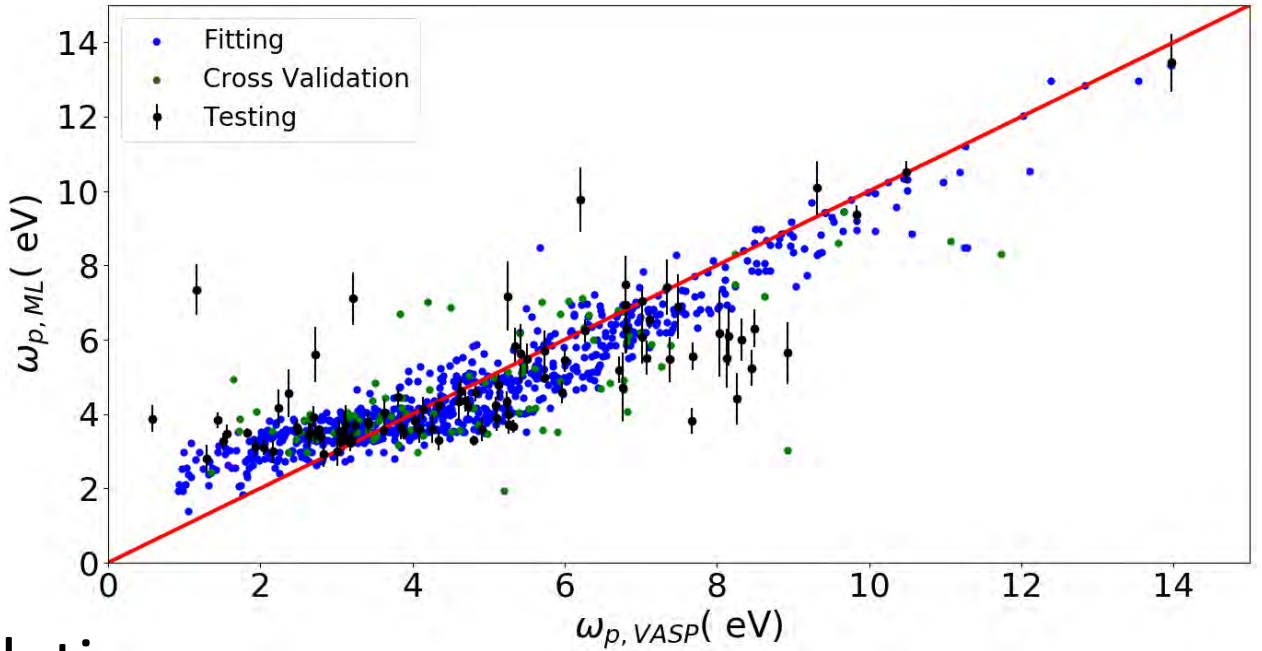
- Atomistic descriptors and crystal symmetry only, Adaboost decision tree.



- 91.9% classification accuracy, 93% accuracy with crystal structure reported in literature [10].

Preliminary Results – Plasma Frequency

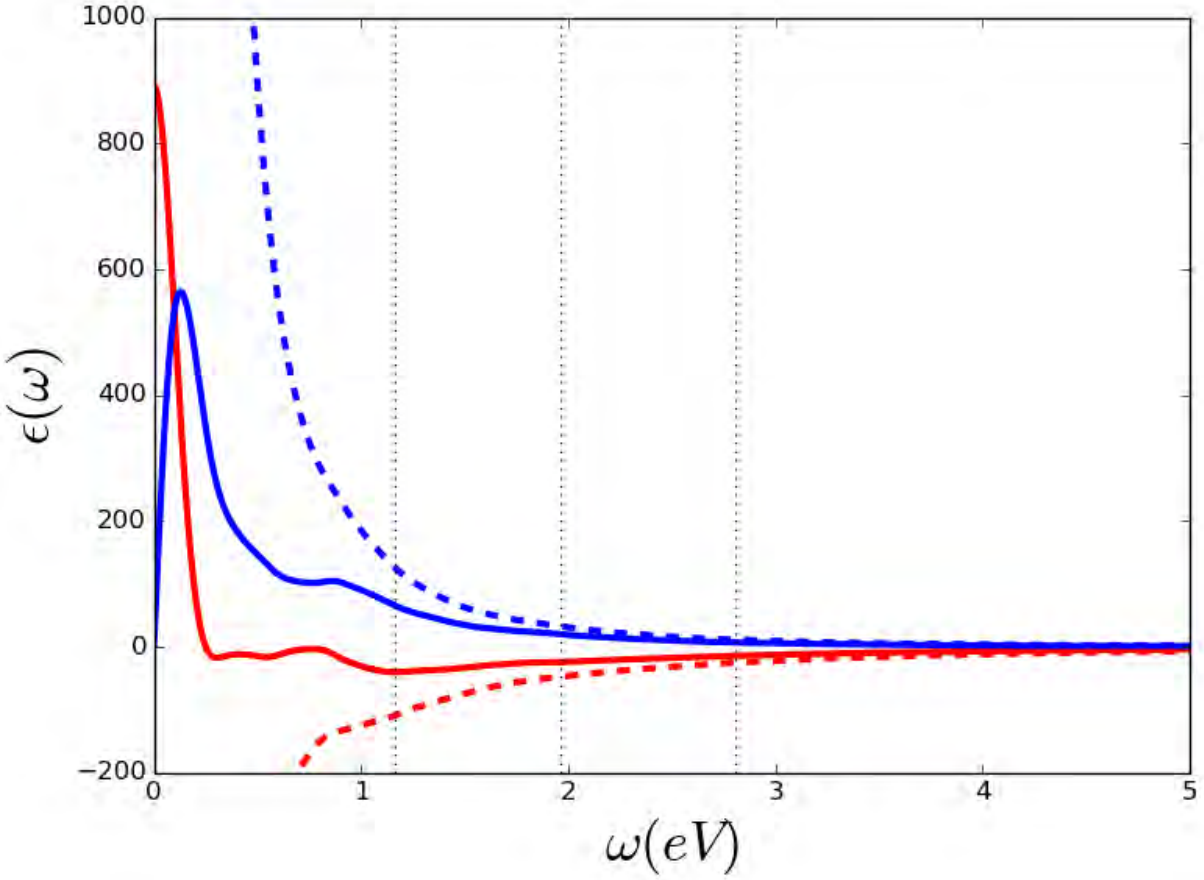
- DFT calculations for 970 metals in materials project.
- AdaBoost decision tree regressor.
- 80-10-10 testing.
- MAEs: 0.63 eV fitting, 1.19 eV validation, 1.05 eV testing .
- Experimental uncertainty ~ 0.25 eV for Au



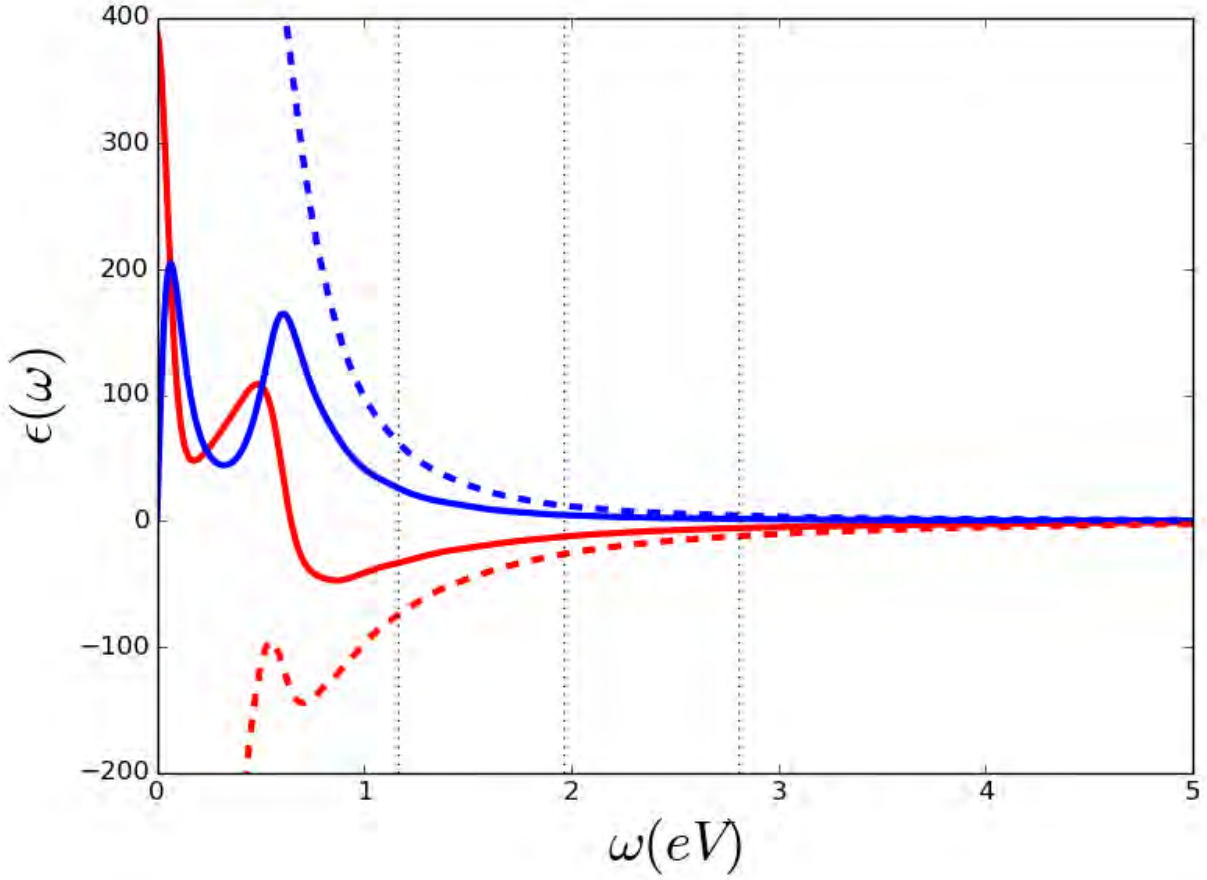
Descriptors

- 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



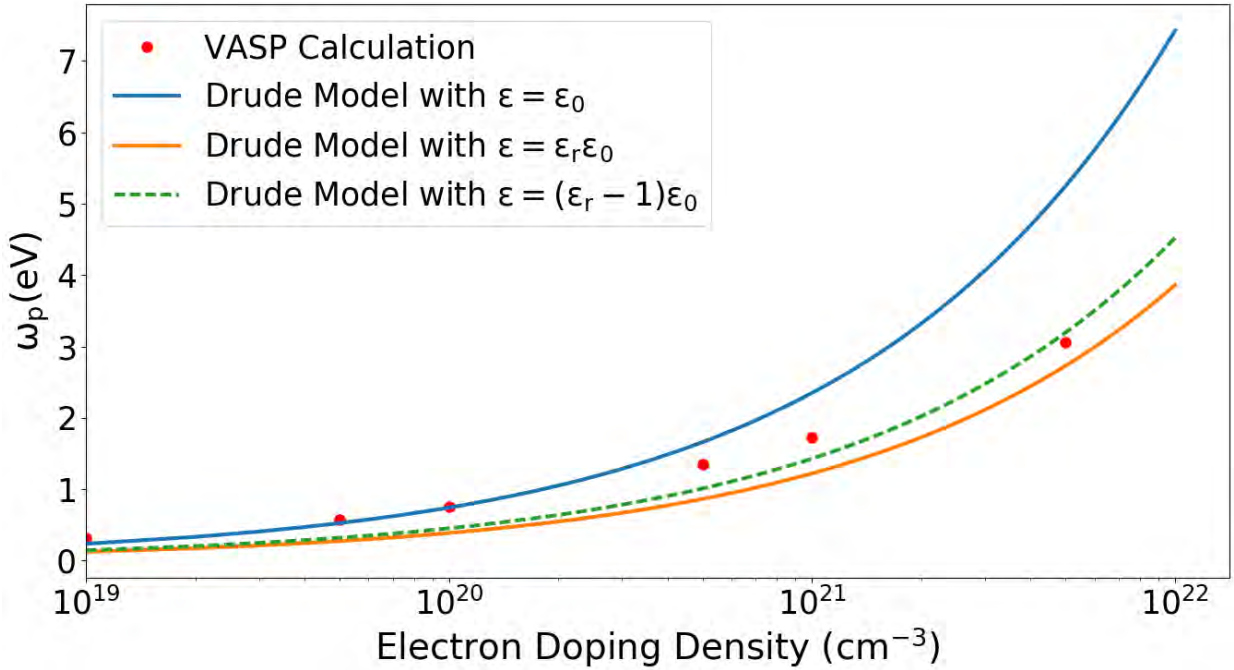
Dielectric Function of Mg

Preliminary Results – Semiconductor Doping

- Plasma frequency depends on doping and lattice dielectric constant in Drude model.

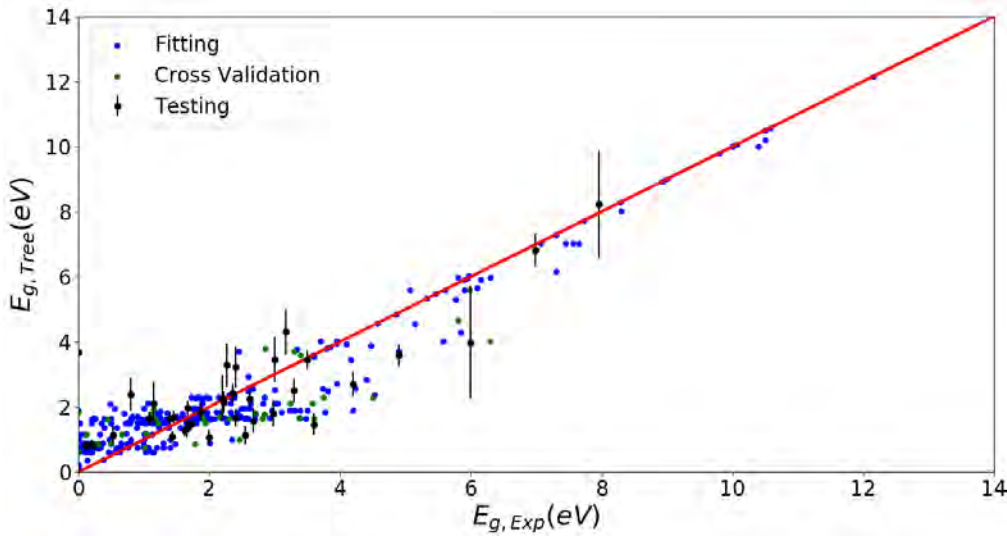
$$\omega_p^2 = \frac{4\pi n e^2}{m\epsilon_{core}} - \frac{1}{\tau^2}$$

- Calculated ω_p consistent with Drude model, but with crossover at high doping



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 .



Source	Method	MAE (eV)
Curtarolo	Linear Correction	0.933 (rms)
Hinuma	PBE	1.06
Hinuma	HSE	0.20
Hinuma	GW_0 PBE	0.15
Hinuma	GW^{TC-TC} HSE	0.16
Hinuma	$GW\Gamma^1$ HSE	0.23
Lee	OLSR, PBE	0.59
Lee	OLSR, mBJ	0.57
Lee	OLSR, PBE+mBJ	0.44
Lee	OLSR, predictor set	0.29
Lee	LASSO, predictor set	0.29
Lee	SVR, predictor set	0.24