A Coupled Dipole Approach to Electron Energy Gain Spectroscopy

Jacob Busche
Physics, Oregon State University

NNIN REU Site: Washington Nanofabrication Facility & Molecular Analysis Facility, University of Washington, Seattle, WA
NNIN REU Principal Investigator: Dr. David J. Masiello, Department of Chemistry, University of Washington
NNIN REU Mentors: Nichloas W. Bigelow and Steven C. Quillin, Department of Chemistry, University of Washington
Contact: buschej@onid.orst.edu, masiello@u.washington.edu, bigelow@u.washington.edu, quills@u.washington.edu

Abstract:

Electron energy gain spectroscopy (EEGS) is a spectroscopic technique designed to provide high-resolution imaging of metal nanoparticles and their collective electronic oscillations called plasmons. The EEGS procedure involves pumping a plasmon with a continuous or pulsed light source from a laser, passing a high-energy (~ 100 keV) electron beam generated within a scanning transmission electron microscope (STEM) near the nanoparticle, and observing the energy lost or gained by the electron as a result of its interaction with a plasmon. The primary directive of this project is to produce a numerical model of an EEGS experiment to simulate and predict the new spectral and spatial information content contained within it. A plasmon resonance peak was observed during simulations using this technique, suggesting electron energy gain can provide a viable, zero-loss peak independent method for probing the electronic behavior of metal nanoparticles.

Introduction and Procedure:

An EEGS simulation is conducted by using a coupled dipole or discrete dipole approximation (DDA) method that assumes the target nanoparticle is composed of a large number of individual polarizable points that interact with external electric fields. The nanoparticle is then driven by both a laser and a STEM in a numerical simulation, and the induced or scattered electric field of the nanoparticle is calculated as the matrix of dipole moments in the target is allowed to relax into a energy-favorable self-consistent state. The electric field of the laser is approximated by a monochromatic plane-wave, and at the sub-wavelength scale of the nanoparticle target, is taken to be constant.

A second order interaction between the photon field of the laser light and the electron beam from the STEM becomes possible due to the plasmon oscillation coupling with both forms of radiation. A probability of photon energy transfer is generated that is proportional to the product of the electric fields and polarizations due to both the plane-wave and electron beam interactions [1], and a plot can be generated for each target arrangement to determine the normalized loss probability for each photon of energy gained by a passing electron. The numerical experiment can produce energy-gain spectra for particles of varying geometry between ~ 10 nm and ~ 100 nm in length along any given axis, providing a tool for probing interesting nanoparticle arrangements.

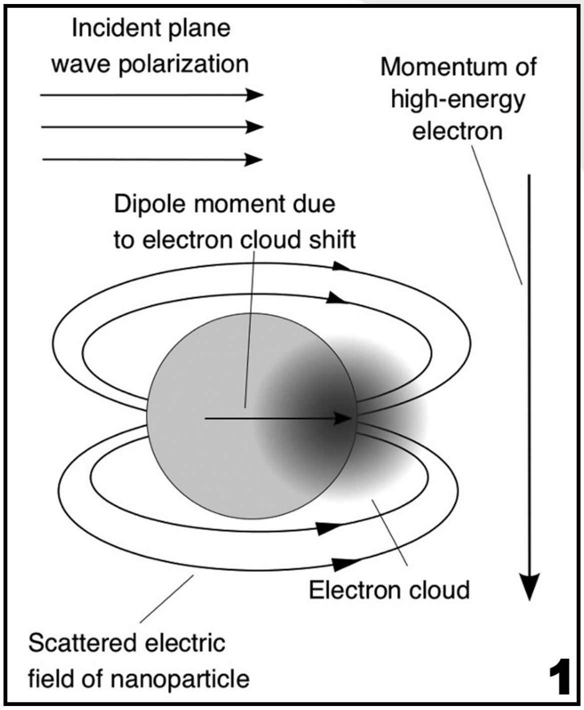
EEGS was developed from; (1) earlier simulations performed by B. T. Draine [2] that used the DDA to determine plasmon resonance peaks under excitation from plane-wave mono-chromatic light only, and (2) electron energy loss spectroscopy (EELS) simulations performed by N. W. Bigelow and A. Vaschillo, which described the energy loss probability of passing electrons to an unexcited target. EEGS is designed to probe the plasmon-electron interaction probabilities at specific energies given by the plane-wave excitation of the system, thus freeing the results from uncertainty derived from the zero-loss-peak of a STEM [3].

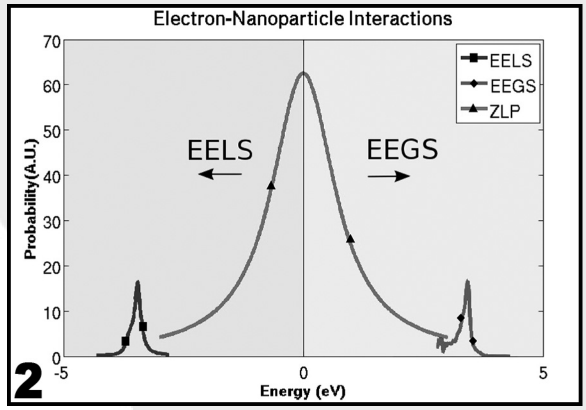
Results:

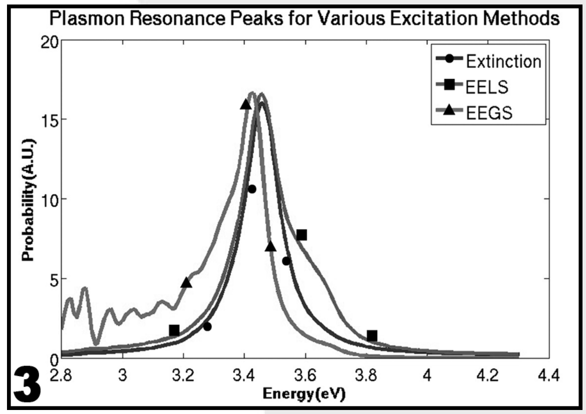
The preliminary numerical experiments performed in this study modeled a spherical silver nanoparticle with a 15 nm diameter and dipole moments spaced at 1 nm. A typical plasmon peak was observed at 3.42 eV, which agreed well with the plasmon resonance spectrum generated by DDA and EELS simulations. The expression determining the gain probability was incomplete at the time of the simulation, although the data shown in the figure are correct up to a scaling factor. However, the large degree of qualitative agreement between the EEGS results and those of DDA and EELS show that electron energy gain spectroscopy can produce accurate and interesting new results in metal nanoparticle systems.

Future Work:

The energy gain probability expression in EEGS will be further refined, and the energy gain spectra from new simulations will be compared with known results from DDA and EELS methods to determine the accuracy of the technique. Numerical experiments on targets of interesting geometry will follow, probing the natural plasmon frequencies of nanoparticle systems that appear in active research.







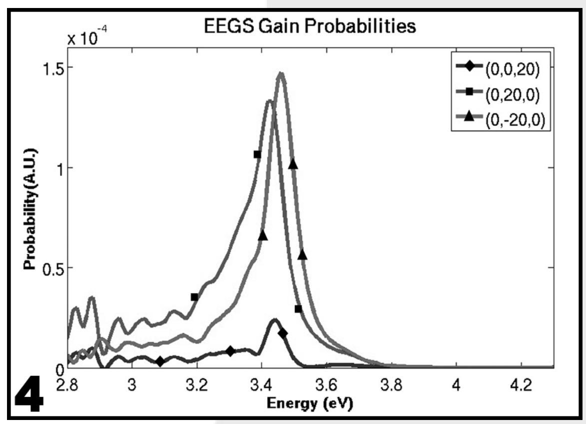


Figure 1, above: Experimental setup used to construct a typical EEGS simulation.

Figure 2, top right: The probability of energy loss or gain of a high energy electron passing a nanoparticle. The central zero-loss peak is described by a Lorentzian distribution.

Figure 3, middle right: Typical plasmon resonance peaks are shown in DDA, EELS, and EEGS spectroscopies computed via the DDA.

Figure 4, bottom right: The energy gain probability at several locations using EEGS. Both electrons and light propagate in the positive x-direction, with light polarized in the positive y-direction.

Acknowledgments:

I would like to thank Dr. David Masiello for welcoming me into his group and teaching me so much in such a short period of time. I would also like to thank Steven Quillin and Nicholas Bigelow for introducing me to their research and mentoring me through the rough patches, Niket Thakkar and Dr. Charles Cherqui for showing me how much fun the pursuit of knowledge can be, Paul Newbert for his instrumental assistance in life outside of research at this program, and the NNIN REU Program and the NSF for their support and funding of this great opportunity.

References:

[1] Arseño-Garcia, A. and García de Abajo, F. J.; "Discrete-dipole approximation for scattering calculations"; New Journal of Physics 15, 103021, 16 pp (2013).

[2] Draine, B. T. and Flatau, P. J.; "Discrete-Dipole Approximation for Scattering Calculations"; Journal of the Optical Society of America A Vol.11, No. 4, 1491-1499 (1994).

[3] Bigelow, N. W.; Vaschillo, A.; Iberi, V.; Camden, J. P.; Masiello, D. J.; "Characterization of the electron-and photon-driven plasmonic excitations of metal nanorods"; ACS Nano Vol.6, No. 8, 7497-7504 (2012).