

## Implementing Gaussian Quadrature in Molecular Plasmonics

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### Abstract:

For certain metals that support localized surface plasmon resonances, the resonant frequency of the material's electrons falls within the realm of visible light. We can use light to collectively and coherently oscillate the surface electrons in nanoparticles made up of these metals, magnifying the light in intensity. Such an environment could potentially be used to catalyze reactions occurring near these particles. Interactions between the molecules and the nanoparticle may alter the molecular electronic landscape into a configuration that is favorable to the reaction. This interaction occurs in part through the image effect. The goal of this project was to develop a computationally feasible process in which to determine the molecule's electronic structure after it has been image-dressed by a nanoparticle of arbitrary shape. In order to make larger molecules more tractable, we implemented Gaussian quadrature instead of the trapezoidal rule to calculate the contour integral describing the electron density of the molecule. This change resulted in the code running approximately 100 times faster than before.

### Introduction:

When a localized surface plasmon resonance (LSPR)-supporting metal nanoparticle is excited with light, its surface electrons oscillate collectively and coherently. When multiple LSPR nanoparticles are brought together, hot spots form, localized regions of high electric field intensity. These hot spots could be used in catalytic applications [1, 2]. Subjecting the molecules to these electric fields will alter the electronic landscape of the molecules into something that is hopefully more favorable for the desired reaction.

The nanoparticle and the molecule interact through the image effect [3, 4]. The electric field from the plasmon pushes the electrons in the molecule, inducing a dipole moment. This dipole gives off its own electric field, pushing the electrons in the nanoparticle into an "image" dipole, thus reducing the net electric field inside the metal to zero. However, rearranging the electrons affects the plasmon, altering the resulting electric field. This altered electric field induces a new dipole in the molecule (see Figure 1). In this way, the nanoparticle and the molecule interact with each other an infinite number of times until the system converges to some configuration.

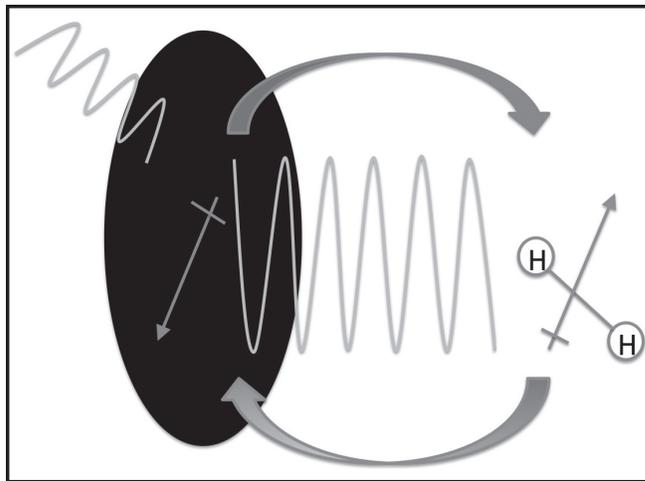


Figure 1: The molecule and nanoparticle repeatedly perturb each other through the image effect.

It was the goal of this project to develop a computationally feasible process to determine the electronic structure of this image-dressed molecule.

### Methodology:

We started by calculating the interacting Green's function,  $\mathcal{G}$ , for a molecule interacting with a nanoparticle [4]. We can use the Dyson expansion to write  $\mathcal{G}$  as an infinite geometric series as shown in Figure 2, where  $G$  is the noninteracting Green's function for the molecule in vacuum and  $\Sigma$  is the self-energy [5].  $\Sigma$  takes into account a single perturbation experienced by the molecule. Thus by calculating this infinite series, we took into account the infinite number of perturbations experienced by the molecule.

$$\mathcal{G} = G + (\Sigma G)G + (\Sigma G)^2G + (\Sigma G)^3G + \dots$$

Figure 2: The Dyson expansion of the interacting Green's function.

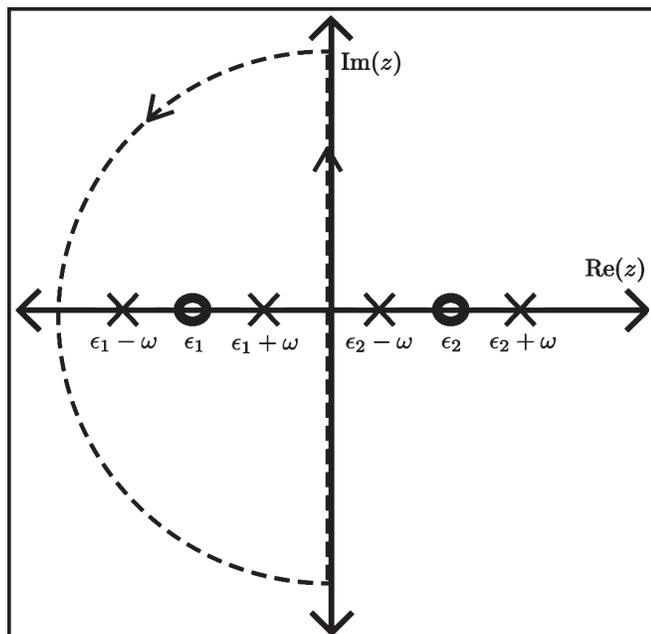


Figure 3:  $\mathcal{G}$  is integrated around singularities associated with occupied orbitals to obtain the interacting one-matrix.

We then took the integral of  $\mathcal{G}$  with respect to  $z$ , the frequency of interaction between the nanoparticle and the molecule. We integrated along a contour that encapsulated all singularities associated with occupied orbitals (see Figure 3). By computing this contour integral, we obtained the interacting one-matrix [6, 7]. Thus we were able to gain information on the electronic structure of the molecule in the form of an electron density.

To increase the speed of the code, Gaussian quadrature was implemented to numerically calculate the contour integral. Gaussian quadrature approximates the function as a  $2n-1$  degree Taylor polynomial, where  $n$  is the number of points taken. It does this by intelligently sampling the function as seen in Figure 4, where the  $x_i$ 's are the locations at which the function is sampled, and the  $w_i$ 's are the corresponding weights. These values are calculated independently from the function by a nonlinear system of  $2n$  equations.

By switching from the trapezoidal rule to Gaussian quadrature, we reduced the number of times we needed to sample the function from 100,000 to 1000. Thus, this change made the

$$\int_{-1}^1 f(x) dx \approx \sum_{i=1}^n w_i f(x_i)$$

Figure 4: Gaussian quadrature intelligently samples the function in order to approximate the integral.

code approximately 100 times faster than before. This made larger molecules, such as azulene, become more tractable as input molecules.

#### Future Work:

In its current state, the code only performs calculations for the alteration of one electron. We hope to further develop this process to consider the configuration of all electrons at the same time. This will allow us to make predictions in experimental spectroscopies as well as begin to model catalytic applications of plasmonics.

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