Objectives:

1. Develop a simple conceptual 1D model for NLO effects based on classical mechanics.

2. Extend to 3D and relate to computational chemical calculations of adiabatic NLO polarizabilities.

Note: Citations to the contents of these slides should reference the following textbook:
The linear polarizability is given by the curvature of the potential energy surface describing the induced dipole per applied field.
In linear interactions describing reflection, refraction, and light-scattering, the driving field induces a polarization at the same frequency.

\[ \alpha = \frac{\partial^2 H}{\partial E^2} \]

The linear polarizability is given by the curvature of the potential energy surface describing the induced dipole vs. applied field.

Garth J. Simpson
When the field strength is increased, additional anharmonic contributions become significant, resulting in distortions in the induced polarization.

\[ \beta = -\frac{\partial^3 H}{\partial E^3} \]

The adiabatic hyperpolarizability is given by the asymmetric anharmonicity in the potential energy surface.

Garth J. Simpson
These distortions in the time-domain are recovered in the frequency-domain by contributions at the higher harmonics.
The net polarization at the second harmonic frequency arises from the coherent interference of all “oscillators”.

Coherent summation produces no net SHG
When the field strength is increased, additional anharmonic contributions become significant, resulting in distortions in the induced polarization.

\[ \gamma = \frac{\partial^4 H}{\partial E^4} \]

The adiabatic second hyperpolarizability is given by the symmetric distortion away from a quadratic potential energy surface.

Garth J. Simpson
Extension of the adiabatic polarizability to 3D

\[ \alpha_{ij} = \frac{\partial^2 H}{\partial E_i \partial E_j} \]

\[ \beta_{ijk} = \frac{\partial^3 H}{\partial E_i \partial E_j \partial E_k} \]

\[ \gamma_{ijkl} = \frac{\partial^4 H}{\partial E_i \partial E_j \partial E_k \partial E_l} \]
The adiabatic approximation implicitly assumes that all resonances are sufficiently high in energy that the lineshape functions $S$ are constant, such that the energy weighting is similar for generating each virtual state.

As such, the adiabatic polarizability clearly cannot be used to describe spectroscopic measurements and resonance-enhanced measurements. Even in nonresonant SHG, the energy gap between the two virtual states is 100%.