The Molecular Tensor: Adiabatic Nonlinear Polarizability

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.
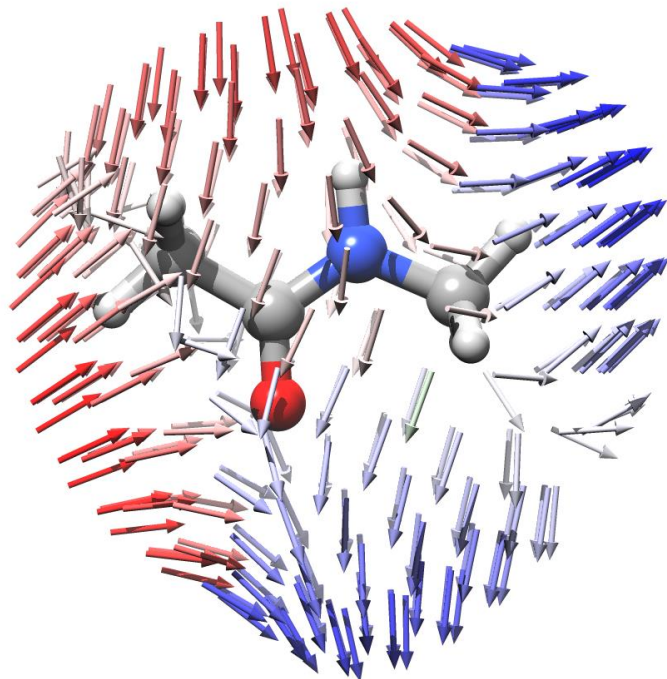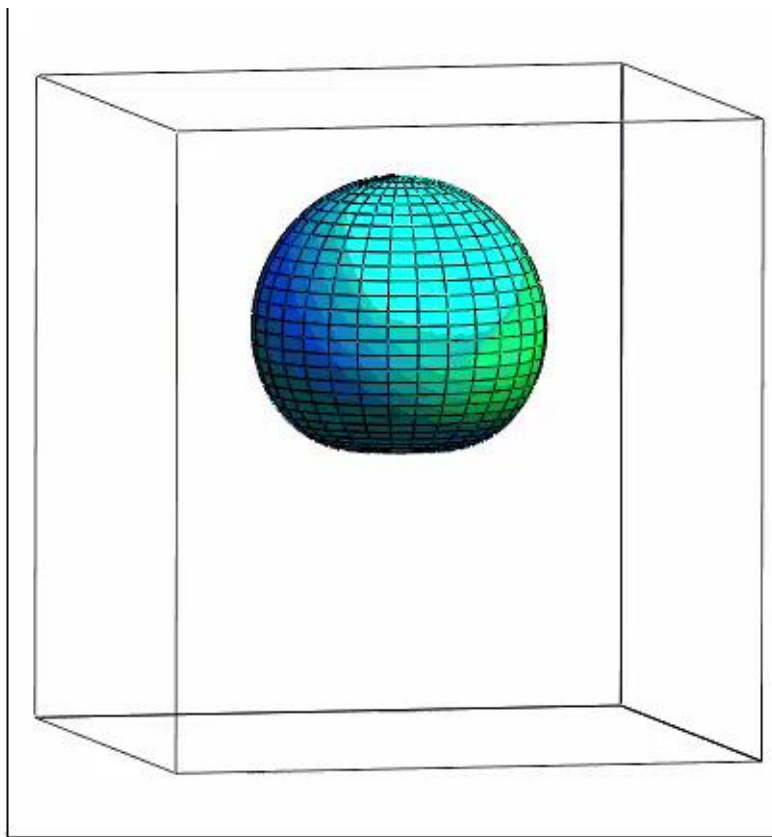
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$(xpos,ypos,zpos),(xneg,yneg,zneg)$

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

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In linear interactions describing reflection, refraction, and light-scattering, the driving field induces a polarization at the same frequency.

Time
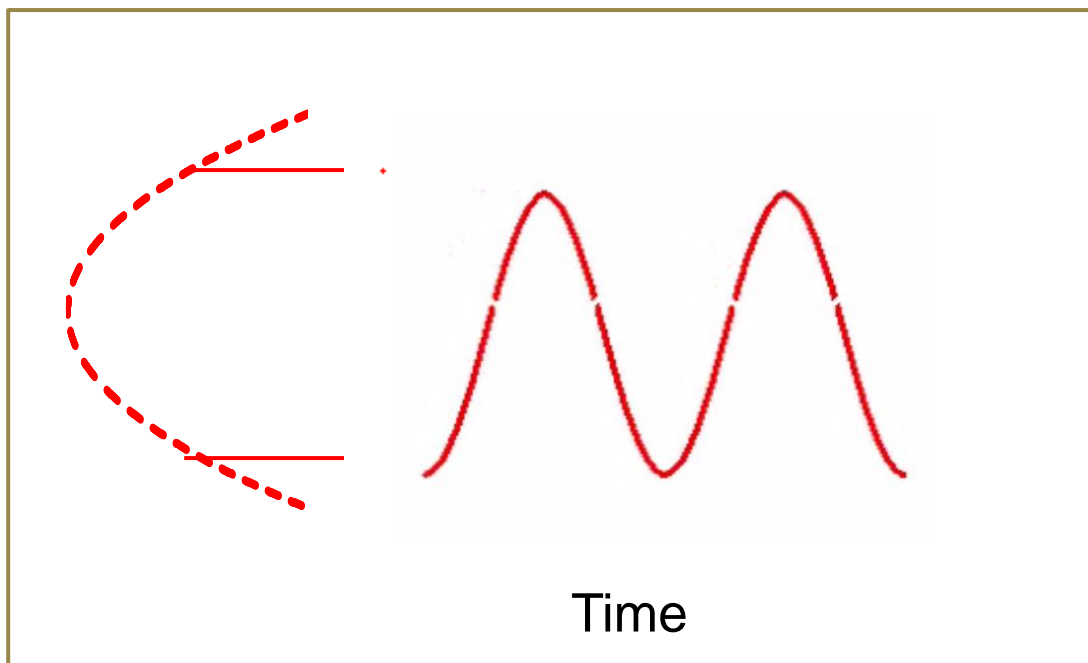
$$\alpha = \frac{\partial^2 H}{\partial E^2}$$

The linear polarizability is given by the curvature of the potential energy surface describing the induced dipole vs. applied field.
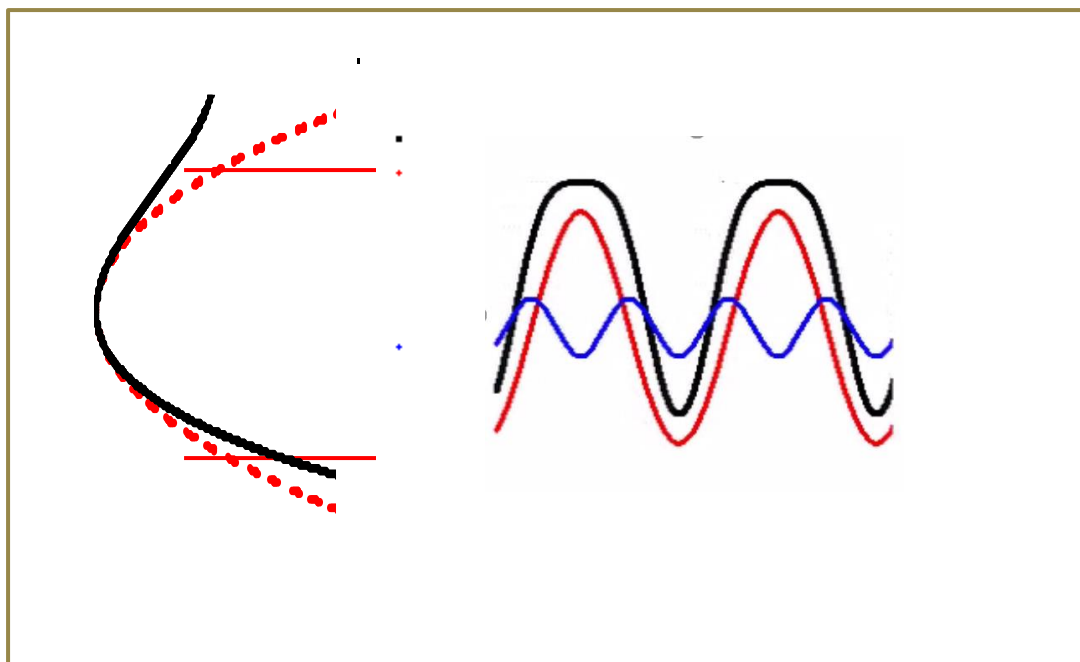
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When the field strength is increased, additional anharmonic contributions become significant, resulting in distortions in the induced polarization.
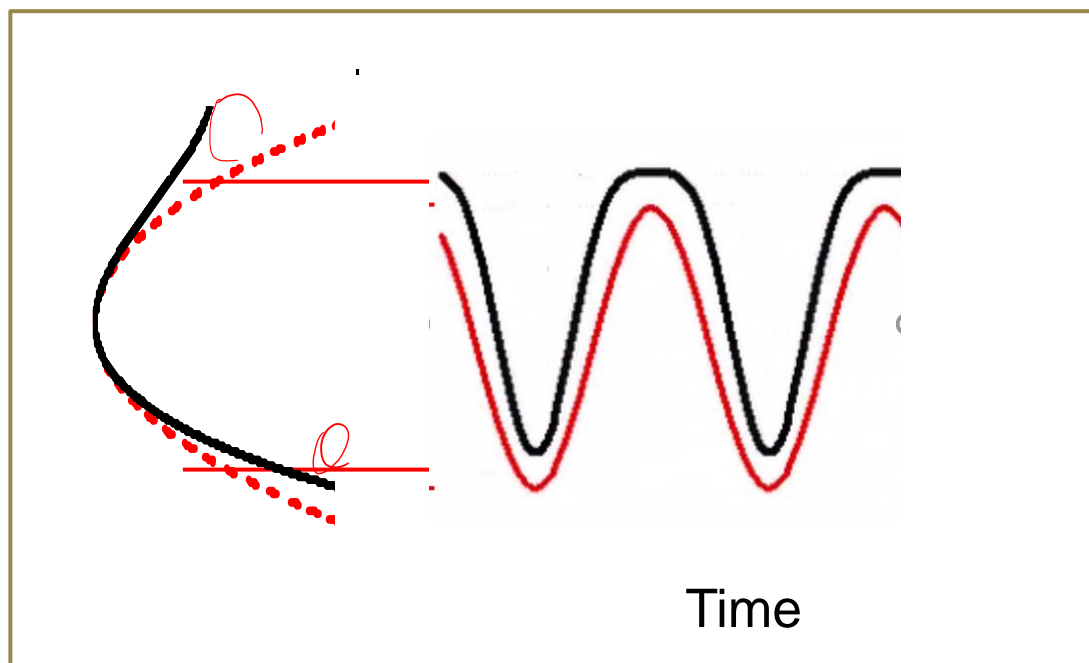

Time

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

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

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These distortions in the time-domain are recovered in the frequency-domain by contributions at the higher harmonics.

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The net polarization at the second harmonic frequency arises from the coherent interference of all "oscillators".
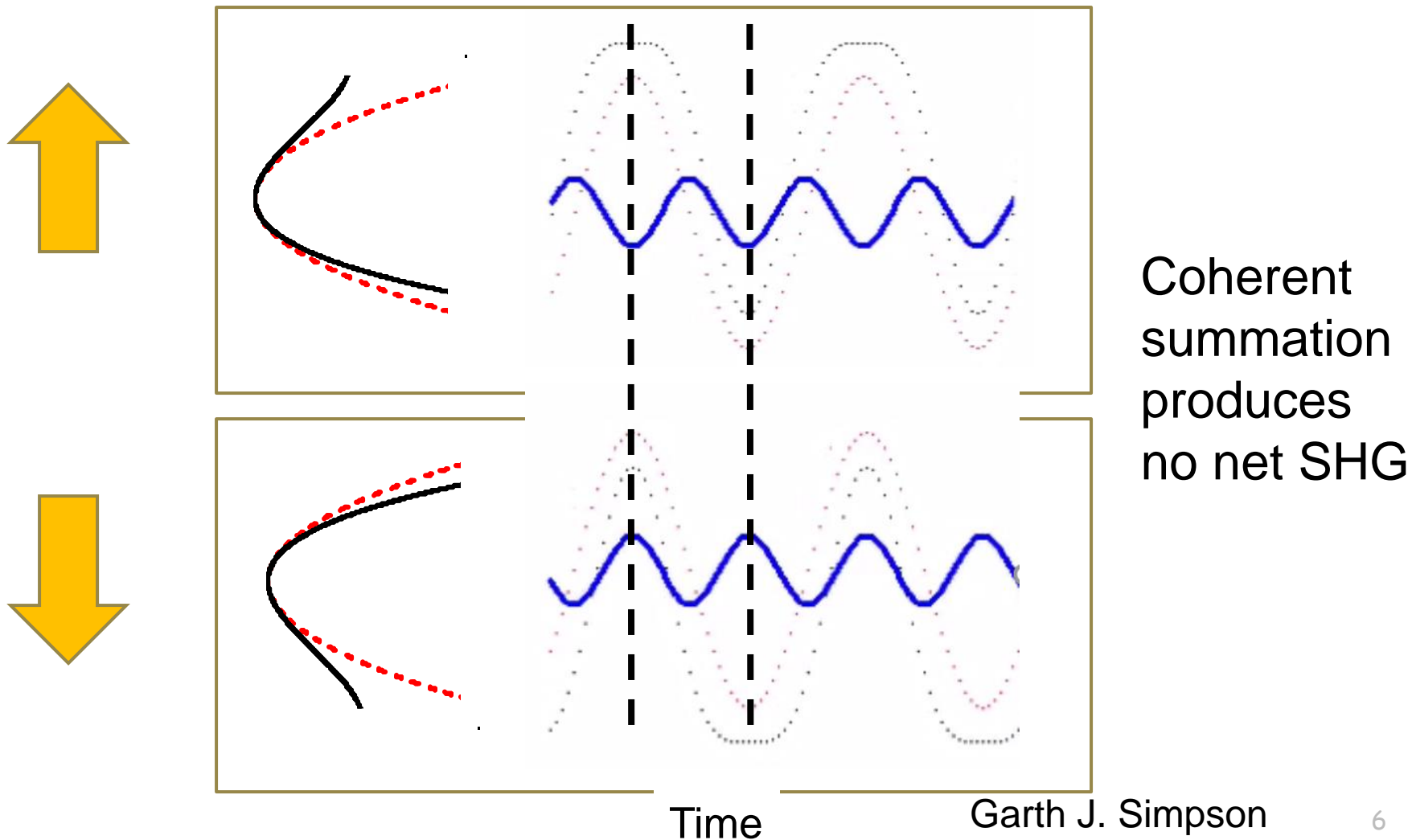
Coherent summation produces no net SHG

Time

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When the field strength is increased, additional anharmonic contributions become significant, resulting in distortions in the induced polarization.
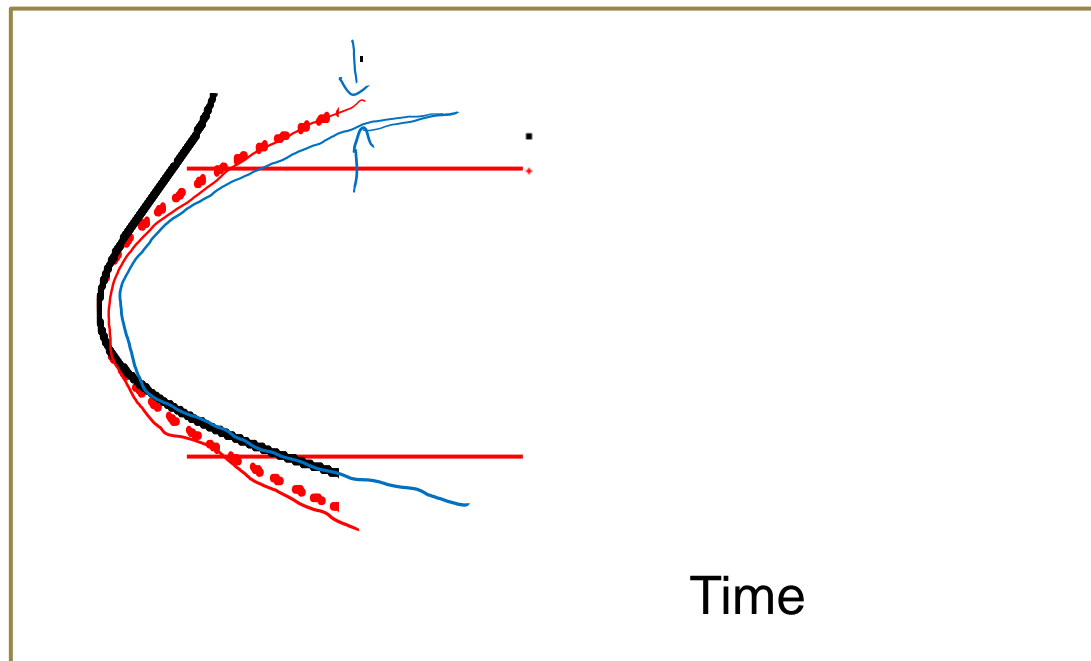
$$\gamma = \frac{\partial^4 H}{\partial E^4}$$

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

Time

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

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

$$\gamma_{ijkl} = \frac{\partial^4 H}{\partial E_i \partial E_j \partial E_k \partial E_l}$$

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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%.

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