Gold Susceptibility

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1 Motivation and Theoretical formulas

The third-order susceptibility χ^3 already can be calculated well for semiconductors (Si, C) with the TDDFT method in OCTOPUS code. So I want to extend the method to metal, for example, gold.
The basic idea is to incident the gold bulk with the monochromatic laser pulse with different intensities. The incident external laser pulse has a simple cosine shape and $\hat{e_x}$ polarization within velocity gauge regime,

$$A_{ext}(t) = A_0 \cdot cos(\omega t + \frac{\pi}{2})\hat{e_x} \tag{1}$$

the $\pi/2$ phase is to make sure the field start from zero. The electric field $E_{ext}(t)$ can be related with gauge field $A_{ext}(t)$ with Eq.2,

$$\vec{E}_{ext} = \frac{-1}{c}\frac{d\vec{A}_{ext}}{dt} \tag{2}$$

here c is the light speed. The response is recorded as induced field $\vec{A}_{ind}$. The total field $\vec{A}_{tot}$ is the summation of external field and induced field.

$$\vec{A}_{tot} = \vec{A}_{ext} + \vec{A}_{ind} \tag{3}$$

The dielectric function $\epsilon(\omega)$ is the ratio of the Fourier components of the external and the total fields.

$$\begin{aligned} \frac{1}{\epsilon(\omega)} &= \frac{FT\{A_{tot}\}}{FT\{A_{ext}\}} = \frac{FT\{A_{ext} + A_{ind}\}}{FT\{A_{ext}\}} \\ &= 1 + \frac{\int_{0_+}^{T} e^{i\omega t - \eta t}\frac{-dAind(t)}{dt}dt}{\int_{0_+}^{T} e^{i\omega t - \eta t}\frac{-dA_{ext}(t)}{dt}dt} \end{aligned} \tag{4}$$

Here $\eta = 0.2eV$ is a small quantity to establish the imaginary part of the response. The refractive index $N(\omega)$ can be connected with dielectric function $\epsilon(\omega)$ by splitting the real part and imaginary part.

$$N(\omega) = n(\omega) + i\kappa(\omega) \qquad \epsilon(\omega) = \epsilon_1 + i\epsilon_2 \tag{5}$$

$$n^2(\omega) = \frac{\epsilon_1}{2}[sgn(\epsilon_1)\sqrt{1 + (\epsilon_2/\epsilon_1)^2} + 1] \tag{6}$$

$$\kappa^2(\omega) = \frac{\epsilon_1}{2}[sgn(\epsilon_1)\sqrt{1 + (\epsilon_2/\epsilon_1)^2} - 1] \tag{7}$$

If the system showing a not negligible absorption, such as in our metal system, the third order susceptibility χ^3 can be extracted from the relation between refractive index and intensity as Eq.8 $\sim$ 12 [1].

$$n = n_0 + \Delta n = n_0 + n_2 I \tag{8}$$

$$\kappa = \kappa_0 + \Delta\kappa = \kappa_0 + \kappa_2 I \tag{9}$$

$$\chi_R^{(3)} = (4n_0\epsilon_0 c/3)(n_0 n_2 - k_0 k_2) \tag{10}$$

$$\chi_I^{(3)} = (4n_0\epsilon_0 c/3)(n_0 k_2 + k_0 n_2) \tag{11}$$

$$I = 2n_0\epsilon_0 c|E|^2 \tag{12}$$

2 Results and Analysis

2.1 Parameters setting of TDDFT

mesh spacing: s = 0.2 Bohr
k-points sampling grid: $20 \times 20 \times 20$
Incident photon energy $1.968eV$, wavelength $\lambda = 630nm$.
TDPropagator : aetrs
TDTimeStep : 0.05 $[\hbar/Ha]$ = 0.00121 [fs]
TDExponentialMethod :16th-Lanczos
TDPropagationTime : 300 [a.u.] = 7.257 [fs]

2.2 Incident laser field

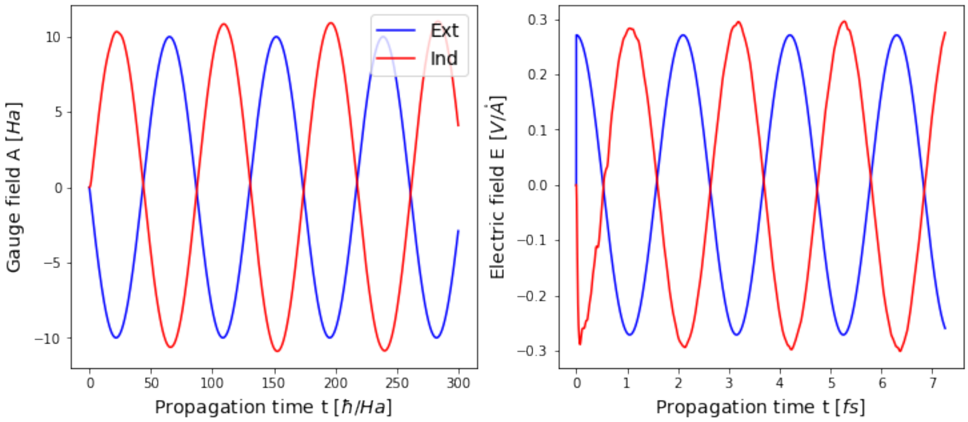

Figure 1: The incident laser field $A_{ext}(t) = A_0 \cdot cos(\omega t + \frac{\pi}{2})\hat{e_x}$. (Left) is represented with gauge field A[Ha] and atom unit time[$\hbar/Ha$], (Right) used the electric field $E[V/\mathring{A}]$ and femtosecond time unit [fs]. Blue curve is the external laser field, and red curve is the induced field.

2.3 N-I relation

I use laser fields with different intensities to incident the gold bulk, and get the relation between κ-I and n-I in Fig.2, in right subfigure, the real part of refractive index n-I curve shows a perfect linear relation $n = n_0 + n_2 I$. So we can extract the $n_0 = 3.18$ and $n_2 = 5.53 \times 10^{-18} m^2/W$.
For left subfigure, I use the polynomial fitting to extract the fitting coefficient κ_0 and κ_2. For example, the n-th order polynomial fitting likes Eq.13.

$$\kappa = \kappa_0 + \kappa_2 I + \kappa_3 I^2 + ... + \kappa_n I^{n-1} \tag{13}$$

The polynomial fitting order will effect the fitting coefficients, but it also shows a convergence trend for higher order, which shown in Fig.3, the value of κ_0 and κ_2 are all converged after 12-th polynomial fitting.

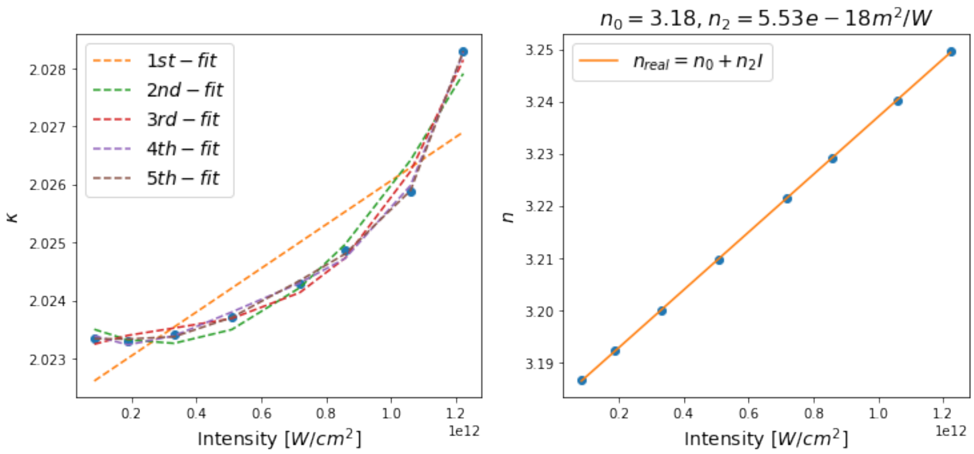

Figure 2: Relation between κ-I and n-I.

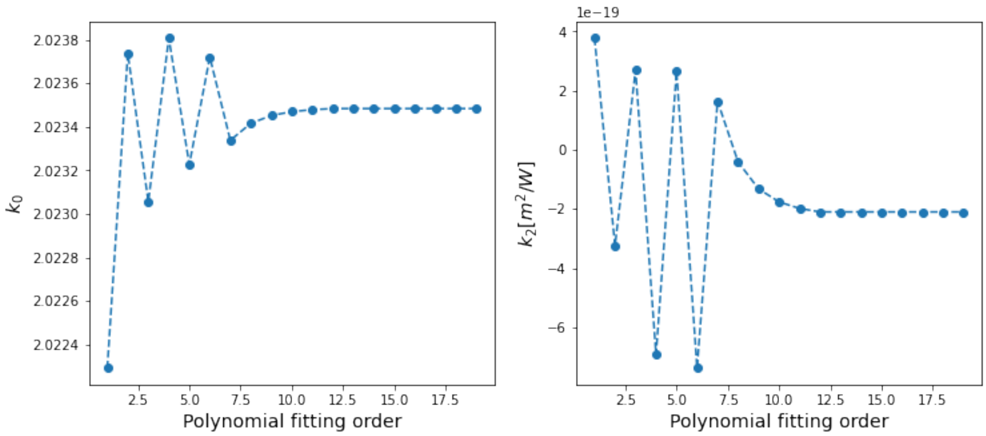

Figure 3: The convergence of κ_0 and κ_2 for different polynomial fitting order.

Then I compare my simulation results with the reference experimental data in Fig.4 and 5. [2], the experiment data also use $630nm$ external laser pump with z-scan technique. It shows the value of χ^3 will change for different pulse duration, I compare them with different propagation time and different polynomial fitting order.
It shows a nearly linear relation between $|\chi^3|$ and pulse duration in double log coordinate system. It seems the two separated parts are in the same linear line, I am doing a longer calculation and expect the two parts will coincide for 100 fs $(10^{-13}s)$ scale.
The calculation of Iridium is also possible and in my plan.

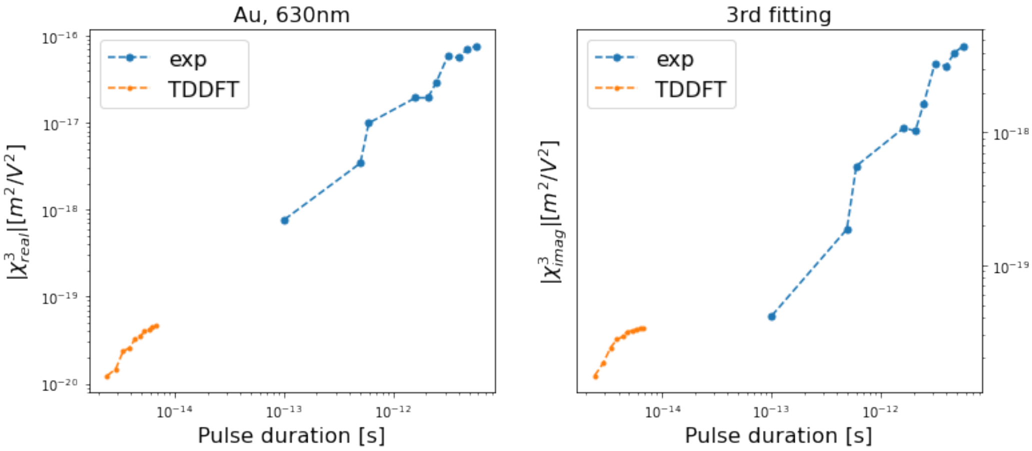

Figure 4: χ^3 comparison for TDDFT and experimental data. 3rd fitting for χ^3_{imag}.

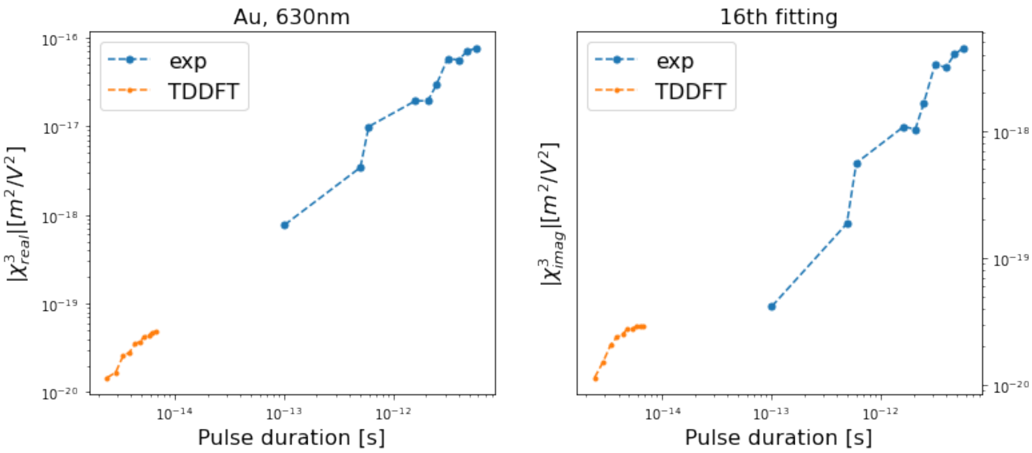

Figure 5: χ^3 comparison for TDDFT and experimental data. 16th fitting for χ^3_{imag}.

References

[1] Raúl del Coso and Javier Solis. Relation between nonlinear refractive index and third-order susceptibility in absorbing media. *J. Opt. Soc. Am. B*, 21(3):640–644, Mar 2004.

[2] Robert W. Boyd, Zhimin Shi, and Israel De Leon. The third-order nonlinear optical susceptibility of gold. *Optics Communications*, 326:74–79, 2014.