Non-linear response properties: phenomenology and calculation with TDDFT

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What is non-linear optics?

Polarizability (linear optics) \( \alpha (-\omega, \omega) \)

absorption, refraction \( \text{Im } \alpha, \text{Re } \alpha \)

\[
\mu_i(\mathcal{E}) = \mu_{i0} + \alpha_{ij} \mathcal{E}_j + \frac{1}{2} \beta_{ijk} \mathcal{E}_j \mathcal{E}_k + \ldots
\]

\( \beta(2\omega; -\omega, -\omega) \)

Hyperpolarizability: second-harmonic generation (SHG) \textit{etc.}

Consider only perturbative processes via Taylor expansion of dipole moment. Not high-harmonic generation!
Quantized picture of non-linear optics

 absorption

 two-photon absorption

 refraction

 second-harmonic generation

\[ \sigma_{\text{TPA}} \propto I^2 \]

\[ \sigma_{\text{SHG}} \propto I^2 \]

\[ \sigma_{\text{abs}} \propto I \]
A zoo of nonlinear optical processes

- sum-frequency generation (SFG) \( \beta (\omega_1, \omega_2, -(\omega_1 + \omega_2)) \)
- difference-frequency generation (DFG) \( \beta (\omega_1, \omega_2, -(\omega_1 - \omega_2)) \)
- second-harmonic generation (SHG) \( \beta (\omega, \omega, -2\omega) \)
- optical rectification \( \beta (\omega, -\omega, 0) \)
- Pockels (electrooptic) effect \( \beta (\omega, 0, -\omega) \)
- third-harmonic generation (THG) \( \gamma (\omega, \omega, \omega, -3\omega) \)
- two-photon absorption \( \text{Im} \, \gamma (\omega, \omega, -\omega, -\omega) \)
- four-wave mixing \( \gamma (\omega_1, \omega_2, \omega_3, -(\omega_1 + \omega_2 + \omega_3)) \)

Energy conservation requires frequency arguments to sum to zero.
Applications

Characterization in surface science and chemistry (very sensitive)

Optical parametric amplifiers
Pockels cells
Laser pointers
Tunable light sources
Optical logic
coherent anti-Stokes Raman spectroscopy (CARS) (kind of 4-wave mixing)
Two-photon fluorescent labels in biology

Typically inorganic crystals are used in applications, but organic molecules have the potential to be cheaper and more efficient.
SHG and SFG at the National Ignition Facility

Lawrence Livermore National Laboratory, Livermore, California

600 KH$_2$PO$_4$ crystals of 400 kg each, ultrapure to avoid absorption.

192 laser beams for inertial confinement fusion

Total power = 500 TW
The challenges of nonlinear optics: a cautionary tale

Volume 7, Number 4

PHYSICAL REVIEW LETTERS

August 15, 1961

GENERATION OF OPTICAL HARMONICS*

P. A. Franken, A. E. Hill, C. W. Peters, and G. Weinreich
The Harrison M. Randall Laboratory of Physics, The University of Michigan, Ann Arbor, Michigan
(Received July 21, 1961)

FIG. 1. A direct reproduction of the first plate in which there was an indication of second harmonic. The wavelength scale is in units of 100 A. The arrow at 3472 A indicates the small but dense image produced by the second harmonic. The image of the primary beam at 6943 A is very large due to halation.

The original experimental report of SHG (quartz, 694 nm)

Lesson: check your proofs!
Symmetry properties of nonlinear susceptibility tensors

Inversion symmetry: even orders are zero ($\mu$, $\beta$, $\delta$, etc.).

$$\mu^{(2)} = \frac{1}{2} \beta \mathcal{E}^2$$

Apply inversion: $$-\mu^{(2)} = \frac{1}{2} \beta (-\mathcal{E})^2 = \frac{1}{2} \beta \mathcal{E}^2 = \mu^{(2)}$$

Therefore $\beta = 0$

e.g. Si crystal

surface: breaks symmetry

bulk: no SHG
Symmetry properties of nonlinear susceptibility tensors

Permutation symmetry:

\[ \beta_{ijk}(\omega_1, \omega_2, \omega_3) = \frac{\partial^3 E}{\partial \varepsilon_{i,\omega_1} \partial \varepsilon_{j,\omega_2} \partial \varepsilon_{k,\omega_3}} = \beta_{jik}(\omega_2, \omega_1, \omega_3) \]

\[ \beta_{ijk}(\omega_1, \omega_2, \omega_3) \neq \beta_{jik}(\omega_1, \omega_2, \omega_3) \]

“Kleinman symmetry,” only when off-resonance or \( \omega \approx 0 \)

Also Kramers-Kronig relations.
Symmetry properties of nonlinear susceptibility tensors

Spatial symmetries: e.g. chloroform (CHCl₃)

Character table for point group $C_{3v}$

<table>
<thead>
<tr>
<th>$C_{3v}$</th>
<th>E</th>
<th>$2C_3$ (z)</th>
<th>3$\sigma_v$</th>
<th>linear functions, rotations</th>
<th>quadratic functions</th>
<th>cubic functions</th>
</tr>
</thead>
<tbody>
<tr>
<td>A₁</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
<td>$z$</td>
<td>$x^2+y^2, z^2$</td>
<td>$z^3, x(x^2-3y^2), z(x^2+y^2)$</td>
</tr>
<tr>
<td>A₂</td>
<td>+1</td>
<td>+1</td>
<td>-1</td>
<td>$R_z$</td>
<td>-</td>
<td>$y(3x^2-y^2)$</td>
</tr>
<tr>
<td>E</td>
<td>+2</td>
<td>-1</td>
<td>0</td>
<td>$(x, y) (R_x, R_y)$</td>
<td>$(x^2-y^2, xy) (xz, yz)$</td>
<td>$(xz^2, yz^2) [xyz, z(x^2-y^2)] [x(x^2+y^2), y(x^2+y^2)]$</td>
</tr>
</tbody>
</table>

$\alpha_{xy} = \frac{\partial^2 E}{\partial x \partial y} \sim xy$  \quad $\mu_i$  \quad $\alpha_{ij}$  \quad $\beta_{ijk}$

Zincblende structure (e.g. GaAs) has only $\chi^{(2)}_{xyz} \neq 0$
Conventions and units

Many conventions for pre-factors! Multiple papers on just conventions...

Commonly used units: au, esu

1 au of $\beta$

$= 3.206361 \times 10^{-53} \text{ C}^3 \text{ m}^3/\text{J}^2 \text{ (SI)}$

$= 8.6392 \times 10^{-33} \text{ cm}^4 \text{ statvolt}^{-1} \text{ (esu of } \beta)$

Nonlinear optics in solids

Susceptibility tensors for solids

\[ \chi_{ij}^{(1)} = \frac{\alpha_{ij}}{V} \quad \chi_{ij}^{(2)} = \frac{\beta_{ij}}{V} \]

Now can have \( q \)-dependence as well.

\[ \chi_{ijk}^{(2)} (\vec{q}_1, \vec{q}_2, \vec{q}_3, \omega_1, \omega_2, \omega_3) \]

Phase-matching condition for constructive interference:

\[ \vec{k}_1 + \vec{k}_2 + \vec{k}_3 = 0 \quad \text{(NOT momentum conservation)} \]

\[ = \frac{n_i (\omega_1) \omega_1}{c} + \frac{n_j (\omega_2) \omega_2}{c} + \frac{n_k (\omega_3) \omega_3}{c} \]

Adjust angle of incidence to satisfy and get significant conversion.

Molecules vs solids: orders of magnitude.

\[ \beta \sim 10000 \text{ au} \quad \text{KTiOPO}_4 \quad \chi^{(2)} \sim 10^{-8} \text{ esu} \]

\[ \text{CHCl}_3 \beta \sim 1 \text{ au}, \chi^{(2)} \sim 10^{-8} \text{ esu} \]
Other perturbations

Ionic displacement and strain (Raman tensors, Grüneisen parameters, phonon anharmonicity, pyroelectric tensor, piezoelectric tensor, second-order elastic coefficients, …)

S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Gianozzi, Rev. Mod. Phys. 73, 515 (2001)

Magnetic contributions to nonlinear optical processes.

But usually electric-dipole approximation is sufficient

Representation of electric field in finite and periodic systems:

\[ r \rightarrow -i \frac{\partial}{\partial k} \quad \text{and} \quad V \mathbf{\varepsilon} = -i \frac{\partial}{\partial k} \]

Quantum theory of polarization

Solution measurements of hyperpolarizability

Measurements are usually in solution for molecules. Solvent effects can be strong and complicate comparison between experiment and theory. (In theory, handle via polarizable continuum models or explicit solvent in small clusters or periodic system.)

(Time-averaged) inversion symmetry of solution makes ordinary measurement give zero.

Electric-field-induced second-harmonic generation (EFISH) is coherent third-order process, based on field lining up molecules.

\[ \chi^{(3)} (-2\omega; \omega, \omega, 0) = n \left[ \gamma (-2\omega; \omega, \omega, 0) + \frac{\mu}{3kT} \beta_\parallel (-2\omega; \omega, \omega) \right] \]

What is measured directly and often reported: \( \mu \beta_\parallel \)

Hyper-Rayleigh scattering (HRS) is incoherent second-order process, based on orientational fluctuations.

\[ I_{\text{HRS}} \propto \left\langle \beta_{xyz} \beta_{uvw} \right\rangle \]
Solution measurements of hyperpolarizability

Consider projection along dipole moment.

\[
\beta^i_{\text{EFISH}} = \frac{1}{5} \sum_j (\beta_{ijj} + \beta_{jij} + \beta_{jji})
\]

Vertical-vertical and horizontal-vertical polarizations for experiment.

\[
[\beta_{\text{VV}}^{\text{HRS}}]^2 = \frac{1}{7} \sum_i \beta^2_{iii} + \frac{6}{35} \sum_{i \neq j} \beta_{iii} \beta_{ijj} + \frac{9}{35} \sum_{i \neq j} \beta^2_{ijj} + \frac{6}{35} \sum_{\text{cyclic}} \beta_{ijj} \beta_{jkk} + \frac{12}{35} \beta^2_{ijk}
\]

\[
[\beta_{\text{HV}}^{\text{HRS}}]^2 = \frac{1}{35} \sum_i \beta^2_{iii} - \frac{2}{105} \sum_{i \neq j} \beta_{iii} \beta_{ijj} + \frac{11}{105} \sum_{i \neq j} \beta^2_{ijj} - \frac{2}{105} \sum_{\text{cyclic}} \beta_{ijj} \beta_{jkk} + \frac{8}{35} \beta^2_{ijk}
\]
Vibrational / rotational contributions

Many measurements are at $\lambda = 1064$ nm. For organic molecules, typically:
- above vibrational frequencies, so can neglect vibrations
- below electronic resonances so little dispersion

Rotational and vibrational contributions can be estimated from simple harmonic models, for low-frequency response (e.g. THz).

\[ Z^* = \text{Born effective charge} \]

\[ F = \varepsilon Z^* - kx = 0 \]

\[ \beta_{\text{vib}} = \frac{Z}{k} \left( 2 \frac{\partial Z}{\partial \varepsilon} - \frac{Z}{k} \right) \]

\[ \beta_{\text{rot}} = \frac{3\mu}{kT} \alpha \]

D. Bishop, Rev. Mod. Phys. 62, 343 (1990)

Local-field factors for solvent

Clausius-Mossotti relations, relate bulk to molecular susceptibilities.

\[ \chi^{(2)} = \rho f_\omega^2 f_{2\omega} \beta \]

\[ \mathcal{E}_{\text{screened}} = \mathcal{E}_{\text{external}}/\epsilon \]

\[ \mathcal{E}_{\text{local}} = f \mathcal{E}_{\text{screened}} \]

Lorentz:

\[ f_\omega = \frac{\epsilon_\omega + 2}{3} \]

Also generalizations for ellipsoidal cavity, polar solvents.
Theoretical methods for nonlinear response

1. Finite differences (static)
2. Explicit time-propagation
3. Sternheimer equation (2n+1 Theorem)
4. Sum over states (Casida equation)
5. Dyson equation
Finite differences

Apply static fields and calculate dipole moment. No need for special capabilities in code. Probably most common method used. Hope static and IR are similar!

\[ \text{CHCl}_3 \]

Convergence is more demanding for nonlinear response

| Basis Set                | $\mu_z$  | $\alpha_{yy}$ | $\alpha_{zz}$ | $\beta_{yyy}$ | $\beta_{yyz}$ | $\beta_{zzz}$ | $\bar{\alpha}$ | $\beta_{||}$ | $\beta_{^I^V_{\text{HRS}}}$ |
|-------------------------|----------|---------------|---------------|---------------|---------------|---------------|----------------|-------------|---------------------------|
| GTO 5Zsa (aug-cc-pV5Z)  | 0.404    | 65.70         | 46.79         | 27.35         | -15.31        | 22.27         | 59.40          | -5.01       | 16.90                     |
| NBS 5Z4Pe8 (SIESTA)     | 0.398    | 65.45         | 46.28         | 24.54         | -14.90        | 21.37         | 59.06          | -5.07       | 15.68                     |
| RS lr (h=0.25, r=22)    | 0.399    | 66.02         | 47.00         | 27.12         | -16.36        | 26.94         | 59.68          | -3.47       | 17.44                     |
| RS fd                   | "        | 66.46         | 47.07         | 24.22         | -15.66        | 25.50         | 60.00          | -3.52       | 16.14                     |
| RS 1064 nm              | "        | 66.69         | 47.34         | 30.35         | -18.95        | 31.56         | 60.24          | -4.01       | 19.91                     |
| Expt.                   | 0.409±0.008 | 61±5         | 45±3          |               |               |               | 56±4           | 1±4         |                           |


Comparison of Gaussian-type orbitals, SIESTA numerical basis sets, real-space grid: need five-zeta basis sets with diffuse functions, or very long-range real-space grid.

Response extends far from molecule (> 15 $a_0$)

Compare: only 12 $a_0$ converges ground state all atoms contained within 3 $a_0$ radius
Explicit time-propagation

Cannot use “kick” for all frequencies at once (as for linear optics). Must calculate separately for each frequency combination. Scaling is like one ground-state calculation per time step. Incident laser pulses (duration ~ imaginary broadening).

\[ p\text{-nitroaniline} \]

\[
P^{(2)}_{ijk}(\omega) = \frac{D^{(2)}}{2\pi} \chi^{(2)}_{ijk}(-\omega; \omega_1, \omega_2) F_{\omega_1} F_{\omega_2}
\]

Explicit time-propagation

Sternheimer equation

aka density-functional perturbation theory or coupled perturbed Kohn-Sham
Calculate variation of wavefunctions in linear response.
No need for unoccupied states.
SCF cycle for one frequency at a time

\[
\left( H^{(0)} - \epsilon^{(0)} \pm \omega_{\alpha} \right) P_n' \psi^{(1)}_{\alpha\pm} = -P_n' H^{(1)}_{\alpha\pm} \psi^{(0)}
\]

\[
H^{(1)}_{\alpha\pm} = V^{(1)}_{\alpha\pm} + V_H \left[ n^{(1)}_{\alpha\pm} \right] + \int f_{xc} \left[ n \right] n^{(1)}_{\alpha\pm} (r) \, d^3 r
\]

\[
n^{(1)}_{\pm} = \sum_{n}^{occ} \left( \psi^{(1)}_{n\pm} \left[ \psi^{(0)}_n \right]^* + \psi^{(0)}_n \left[ \psi^{(1)}_{n\mp} \right]^* \right)
\]

\[
P_n' = 1 - \left| \psi^{(0)}_n \right> \left< \psi^{(0)}_n \right|
\]

Need small imaginary broadening \( i\eta \) near resonances for numerical stability.
Sternheimer equation: 2n+1 Theorem

Solving $n$th-order perturbation theory gives $2n+1$ derivative of total energy.

$$\chi^{(2n)} = \frac{\partial^{(2n+1)} E}{\partial \lambda^{(2n+1)}}$$

$$F = \frac{\partial E}{\partial R} = \left\langle \psi \left| \frac{\partial H}{\partial R} \right| \psi \right\rangle$$

$n = 0$: Hellman-Feyman Theorem. No wavefunction derivatives at all.

$n = 1$: Linear variation of wavefunctions gives quadratic response.

$$\beta_{ijk} (-\omega_1; \omega_2, \omega_3) = -4 \sum_P \sum_{\zeta = \pm 1} \left[ \sum_m^{occ} \left\langle \psi_{mi}^{(1)} (-\zeta \omega_1) \left| H_j^{(1)} (\zeta \omega_2) \right| \psi_{mk}^{(1)} (\zeta \omega_3) \right\rangle 
- \sum_m^{occ} \left\langle \psi_m^{(0)} \left| H_j^{(1)} (\zeta \omega_2) \right| \psi_m^{(0)} \right\rangle \left\langle \psi_{mi}^{(1)} (-\zeta \omega_1) \left| \psi_{mk}^{(1)} (\zeta \omega_3) \right\rangle \right.$$ 

$$\left. - \frac{2}{3} \int d^3r \int d^3r' \int d^3r'' K_{xc} (r, r', r'') n_i^{(1)} (r, \omega_1) n_j^{(1)} (r', \omega_2) n_k^{(1)} (r'', \omega_3) \right]$$


Quantum ESPRESSO and Octopus use equations on previous slide.

ABINIT formulation: find $\beta$ by minimizing with respect to $\psi^{(1)}$ (variational).
Sternheimer equation: examples from Octopus code

H$_2$O optical rectification

CO linear spectrum

CO SHG

Sternheimer equation: examples from Octopus code

Efficient scaling with system size: same as ground state. e.g. comparison of TDLDA vs. CIS with Gaussian basis for vibrating N@C$_{60}$

**Sum over states**

Applicable to any method giving excited-state energies and matrix elements, in particular Casida equation for TDDFT.

(Also other theories such as configuration interaction, coupled cluster, Bethe-Salpeter equation, etc.)

Most commonly used as RPA though: just use Kohn-Sham energies and matrix elements.
Sum over states

Arbitrary (or physical but unknown) imaginary broadenings $\Gamma$.

Convergence in two sums on states is difficult!

Applied occasionally to two-photon absorption in TDDFT.

\[
\chi_{ij}^{(1)}(\omega) = \frac{P_i^{(1)}(\omega)}{E_j(\omega)} = N e^2 \sum_{gn} \frac{(r_i)_{ng} (r_j)_{gn}}{\Im} \left[ \frac{(r_j)_{ng} (r_i)_{gn}}{\omega + \omega_{ng} + i\Gamma_{ng}} - \frac{(r_j)_{ng} (r_i)_{gn}}{\omega - \omega_{ng} + i\Gamma_{ng}} \right] \rho_g^{(0)},
\]

\[
\chi_{ijk}^{(2)}(\omega = \omega_1 + \omega_2) = \frac{P_i^{(2)}(\omega)}{E_j(\omega_1) E_k(\omega_2)} = -N e^3 \sum_{g, n, n'} \frac{(r_i)_{gn} (r_j)_{nn'} (r_k)_{n'g}}{\omega - \omega_{ng} + i\Gamma_{ng}} \left[ \frac{(r_j)_{gn} (r_k)_{nn'} (r_i)_{n'g}}{\omega_2 - \omega_{n'g} + i\Gamma_{n'g}} + \frac{(r_k)_{gn'} (r_j)_{nn'} (r_i)_{ng}}{\omega_1 - \omega_{n'g} + i\Gamma_{n'g}} \right] \rho_g^{(0)} \right. \right. \]

Y-R Shen, *The Principles of Nonlinear Optics*
Dyson-like equation

\[ \chi = \chi_{KS} + \chi_{KS} f_{Hxc} \chi \]

Efficient scheme for solids (for linear and non-linear optics): \( k \)-points. Need \( q \rightarrow 0 \) limit, equivalent to \( k.p \) perturbation theory.

\[ [1 - \chi_0^{(1)}(\omega_1 + \omega_2) f_{uxc}(\omega_1 + \omega_2)] \chi^{(2)}_{ppp}(\omega_1, \omega_2) \]
\[ = \chi_0^{(2)}(\omega_1, \omega_2)[1 + f_{uxc}(\omega_1) \chi^{(1)}(\omega_1)] \]
\[ \times [1 + f_{uxc}(\omega_2) \chi^{(1)}(\omega_2)] + \chi_0^{(1)}(\omega_1 + \omega_2) g_{xc}(\omega_1 + \omega_2) \]
\[ \times \chi^{(1)}(\omega_1) \chi^{(1)}(\omega_2), \] (10)

Complicated macroscopic/microscopic relations...

Dyson-like equation

Must converge with respect to unoccupied states in a triple sum.

\[
\chi^{(2)}_{0,G,G_1,G_2}(2q,q,q,\omega) = \frac{2}{V} \sum_{n,n',n''} \frac{\langle \phi_{n,k} e^{-i (2q+G) r} \phi_{n',k+2q} \rangle}{(E_{n,k} - E_{n',k+2q} + 2\omega + 2i\eta)} \left[ (f_{n,k} - f_{n'',k+q}) \frac{\langle \phi_{n',k+2q} e^{i (q+G_1) r_1} \phi_{n'',k+q} \rangle}{(E_{n,k} - E_{n'',k+q} + \omega + i\eta)} \phi_{n,k} \right. \\
+ (f_{n,k} - f_{n'',k+q}) \frac{\langle \phi_{n',k+2q} e^{i (q+G_2) r_2} \phi_{n'',k+q} \rangle}{(E_{n,k} - E_{n'',k+q} + \omega + i\eta)} \phi_{n,k} \\
+ (f_{n',k+2q} - f_{n'',k+q}) \frac{\langle \phi_{n',k+2q} e^{i (q+G_2) r_2} \phi_{n'',k+q} \rangle}{(E_{n'',k+q} - E_{n',k+2q} + \omega + i\eta)} \phi_{n,k} \\
+ (f_{n',k+2q} - f_{n'',k+q}) \frac{\langle \phi_{n',k+2q} e^{i (q+G_1) r_1} \phi_{n'',k+q} \rangle}{(E_{n'',k+q} - E_{n',k+2q} + \omega + i\eta)} \phi_{n,k} \\
\left. \right] 
\]

Some references on nonlinear response

