Linear and non-linear response: phenomenology and calculation with TDDFT

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Linear and non-linear optics

Relation to other topics in school:

Background:
Gross, fundamentals of TDDFT

Applications (mainly linear, could do nonlinear):
Octopus tutorial

More details:
Requist, quantum theory of polarization
Tancogne-Dejean, Microscopic-macroscopic connection
Jornet Somoza, linear response in chemistry
Linear and 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) etc.

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

Absorption

Two-photon absorption

Refraction

Second-harmonic generation

\[ \sigma_{\text{abs}} \propto I \]

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

\[ \sigma_{\text{SHG}} \propto I^2 \]
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
- 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 of non-linear optics

Characterization in surface science and chemistry (very sensitive)

Optical parametric amplifiers
Pockels cells
Laser pointers
Tunable light sources
Optical logic
cohherent 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 susceptibility tensors

Spatial symmetries: e.g. chloroform (CHCl$_3$)

**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>$A_1$</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>$A_2$</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>

$\alpha_{xy} = \frac{\partial^2 E}{\partial x \partial y} \sim xy$

$\mu_i \quad \alpha_{ij}, R_{si,jk} \quad \beta_{ijk}$

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

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

Commonly used units: au, esu

1 au of $\beta$

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

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

Nonlinear optics in solids

Susceptibility tensors for solids

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

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:

\[ \vec{k}_1 + \vec{k}_2 + \vec{k}_3 = 0 \]

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

Adjust angle of incidence to satisfy and get significant conversion.

Molecules vs solids: orders of magnitude.

\[(\text{CH}_3)_2\text{N}^+ \text{ phenyl}^- \text{phenyl}^- \text{NO}_2^- \quad \text{KTiOPO}_4 \quad \chi^{(2)} \sim 10^{-8} \text{ esu} \]

\[ \beta \sim 10000 \text{ au} \quad \text{CHCl}_3 \beta \sim 1 \text{ au}, \chi^{(2)} \sim 10^{-8} \text{ esu} \]
Other perturbations

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


Representation of electric field in finite and periodic systems:

\[ r \rightarrow -i \frac{\partial}{\partial k} \]

\[ V_\mathbf{\varepsilon} = -i \frac{\partial}{\partial k} \]

Quantum theory of polarization


Related to theory of Wannier functions
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.

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

What is measured directly and often reported: \( \mu \beta_{||} \)

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

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

Consider projection along dipole moment.

\[ \beta_{\text{EFISH}}^i = \frac{1}{5} \sum_j (\beta_{ijj} + \beta_{ji} + \beta_{jji}) \]

Vertical-vertical and horizontal-vertical polarizations for experiment.

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

\[ [\beta_{\text{HRS}}^{HV}]^2 = \frac{1}{35} \sum_i \beta_{iii}^2 - \frac{2}{105} \sum_{i \neq j} \beta_{iii} \beta_{ijj} + \frac{11}{105} \sum_{i \neq j} \beta_{ijj}^2 - \frac{2}{105} \sum_{\text{cyclic}} \beta_{ijj} \beta_{jkk} + \frac{8}{35} \beta_{ijj}^2 \]
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).

$$Z^* = \text{Born effective charge}$$

$$F = \mathcal{E} Z^* - kx = 0$$

$$\beta^{\text{vib}} = \frac{Z}{k} \left( 2 \frac{\partial Z}{\partial \mathcal{E}} - \frac{Z}{k} \right)$$

$$\beta^{\text{rot}} = \frac{3\mu}{kT} \alpha$$

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

Local-field factors for solvent

\[ \varepsilon_{\text{screened}} = \varepsilon_{\text{external}} / \varepsilon \]

\[ \varepsilon_{\text{local}} = f \varepsilon_{\text{screened}} \]

Clausius-Mossotti relations, relate bulk to molecular susceptibilities.

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

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     | $\mu_z$ | $\alpha_{yy}$ | $\alpha_{zz}$ | $\beta_{yyy}$ | $\beta_{yyz}$ | $\beta_{zzz}$ | $\bar{\alpha}$ | $\beta_{||}$ | $\beta_{\text{HRS}}$ |
|---------------|---------|---------------|---------------|---------------|---------------|---------------|----------------|-------------|-------------------|
| GTO 5Z$_{sa}$ (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 Ir (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).

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

Explicit time-propagation

Sternheimer equation

aka density-functional perturbation theory (DFPT)
Calculate variation of wavefunctions in linear response.
No need for unoccupied states.
SCF cycle for one frequency at a time

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

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

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

\[
P'_n = 1 - \left| \psi^{(0)}_n \right\rangle \left\langle \psi^{(0)}_n \right|
\]

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.

$$\chi^{(2n)} = \frac{\partial^{(2n+1)} E}{\partial \lambda^{(2n+1)}}$$  \hspace{2cm} F = \frac{\partial E}{\partial R} = \left\langle \psi \left| \frac{\partial H}{\partial R} \right| \psi \right\rangle$$

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

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

$$\beta_{ijk} (-\omega_1; \omega_2, \omega_3) = -4 \sum_{P} \sum_{\zeta = \pm 1} \left[ \sum_{m} \langle \psi^{(1)}_{m \bar{i}} (-\zeta \omega_1) \left| H^{(1)}_j (\zeta \omega_2) \right| \psi^{(1)}_{m \bar{k}} (\zeta \omega_3) \rangle 
- \sum_{mn}^{\text{occ}} \langle \psi^{(0)}_m \left| H^{(1)}_j (\zeta \omega_2) \right| \psi^{(0)}_m \rangle \langle \psi^{(1)}_{m \bar{i}} (-\zeta \omega_1) \left| \psi^{(1)}_{m \bar{k}} (\zeta \omega_3) \right\rangle \right]$$

$$- \frac{2}{3} \int d^3r \int d^3r' \int d^3r'' K_{xc} (r, r', r'') \ n^{(1)}_i (r, \omega_1) \ n^{(1)}_j (r', \omega_2) \ n^{(1)}_k (r'', \omega_3)$$


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.

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

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

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

\[
\begin{align*}
[1 - \chi_0^{(1)}(\omega_1 + \omega_2)f_{\text{uxc}}(\omega_1 + \omega_2)]\chi_{\rho pp}^{(2)}(\omega_1, \omega_2) \\
= \chi_0^{(2)}(\omega_1, \omega_2)[1 + f_{\text{uxc}}(\omega_1)\chi^{(1)}(\omega_1)] \\
\times [1 + f_{\text{uxc}}(\omega_2)\chi^{(1)}(\omega_2)] + \chi_0^{(1)}(\omega_1 + \omega_2)g_{\text{xc}}(\omega_1 + \omega_2) \\
\times \chi^{(1)}(\omega_1)\chi^{(1)}(\omega_2),
\end{align*}
\]

Complicated macroscopic/microscopic relations...


GaAs SHG
**Dyson-like equation**

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

\[ \chi_{0,G,G_1,G_2}^{(2)}(2q,q,q,\omega) = \frac{2}{V} \sum_{n,n',n'',k} \frac{\langle \phi_{n,k}|e^{-i(2q+G)r}|\phi_{n',k+2q}\rangle}{(E_{n,k} - E_{n',k+2q} + 2\omega + 2i\eta)} \left[ (f_{n,k} - f_{n'',k+q}) \frac{\langle \phi_{n',k+2q}|e^{i(q+G_1)r_1}|\phi_{n'',k+q}\rangle \langle \phi_{n'',k+q}|e^{i(q+G_2)r_2}|\phi_{n,k}\rangle}{(E_{n,k} - E_{n'',k+q} + \omega + i\eta)} \right. \\
+ (f_{n,k} - f_{n'',k+q}) \frac{\langle \phi_{n',k+2q}|e^{i(q+G_2)r_2}|\phi_{n'',k+q}\rangle \langle \phi_{n'',k+q}|e^{i(q+G_1)r_1}|\phi_{n,k}\rangle}{(E_{n,k} - E_{n'',k+q} + \omega + i\eta)} \\
+ (f_{n',k+2q} - f_{n'',k+q}) \frac{\langle \phi_{n',k+2q}|e^{i(q+G_2)r_2}|\phi_{n'',k+q}\rangle \langle \phi_{n'',k+q}|e^{i(q+G_1)r_1}|\phi_{n,k}\rangle}{(E_{n'',k+q} - E_{n',k+2q} + \omega + i\eta)} \\
+ (f_{n',k+2q} - f_{n'',k+q}) \frac{\langle \phi_{n',k+2q}|e^{i(q+G_1)r_1}|\phi_{n'',k+q}\rangle \langle \phi_{n'',k+q}|e^{i(q+G_2)r_2}|\phi_{n,k}\rangle}{(E_{n'',k+q} - E_{n',k+2q} + \omega + i\eta)} \left. \right], \quad (38) \]

Magnetic perturbations

Term in Hamiltonian: \( \vec{\mu} \times \vec{B} \)

Perturbation:

\[
\vec{\mu} = \vec{r} \times i\hbar \vec{\nabla}
\]

Quantity of interest (circular dichroism):

\[
\alpha_{\nu\mu,\gamma} = \frac{\partial \alpha_{\nu\mu}}{\partial B_{\gamma}}
\]

Gauge issue with \( A \) and non-local pseudopotentials.

Can use Sternheimer or real-time

**Magnetic perturbations in solids**

\[ \vec{B} = \vec{\nabla} \times \vec{A} \]

Vector potential can be expressed in different gauges.

Separate wavefunction into gauge-dependent and gauge-independent parts.

\[ \vec{E} = \frac{1}{c} \frac{\partial \vec{A}}{\partial t} \]

\[ \vec{\mathcal{E}} = \frac{1}{c} \frac{\partial \vec{A}}{\partial t} \]

E and B fields as in quantum theory of polarization.

Sternheimer equation for response.

Carefully combine parts into gauge-independent quantity.

Raman spectroscopy

Light creates (or destroys) vibrations through excited states

Raman tensor from polarizability derivative with respect to atomic positions

\[ R_i = \frac{\partial \alpha}{\partial r_i} \]

static linear-response calculation of Raman tensors

\[ I \propto \left| \sum_{\alpha i} u_{\alpha i} R_{\alpha i, j k} \right|^2 \]

\[ R_{\alpha i, j k} = 2 \, \text{Tr} \left\{ \frac{\partial v_{\text{ext}}}{\partial u_{i \alpha}} \frac{\partial^2 \rho}{\partial \mathcal{E}_j \partial \mathcal{E}_k} \right\} \]

resonant Raman: need optical method, e.g. TDDFT or Bethe-Salpeter eqn.
non-resonant: can make static approximation
Some references on linear and nonlinear response

