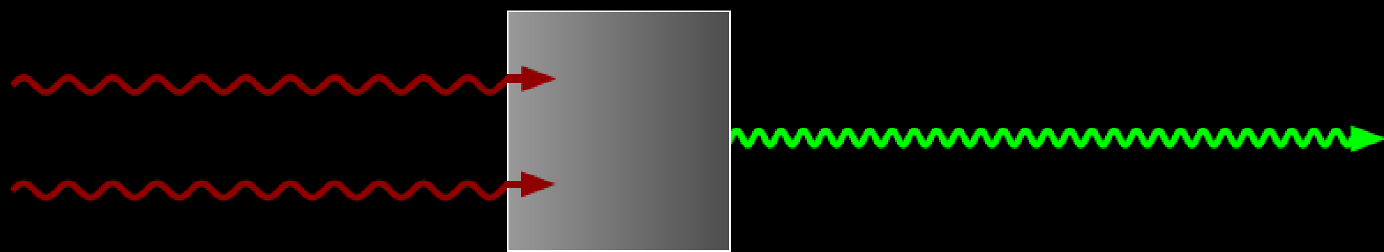
Non-linear response properties:
phenomenology and calculation with TDDFT



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Benasque, 10 January 2012

What is non-linear optics?

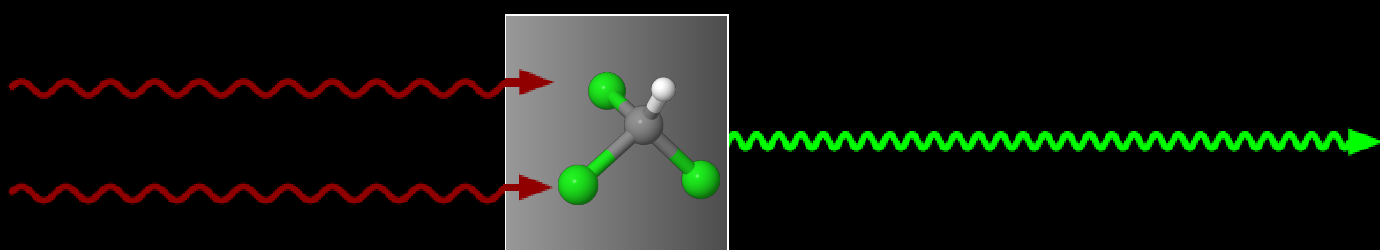
Polarizability (linear optics) $\alpha\left(-\omega,\omega\right)$

absorption, refraction $\mathrm{Im}\ \alpha, \mathrm{Re}\ \alpha$

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

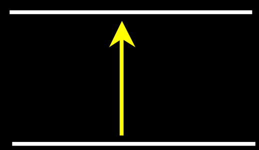
$$\beta(2\omega; -\omega, -\omega)$$

Hyperpolarizability: second-harmonic generation (SHG) etc.

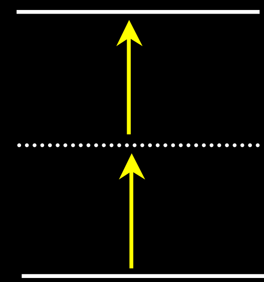


Consider only perturbative processes via Taylor expansion of dipole moment.
Not high-harmonic generation!

Quantized picture of non-linear optics

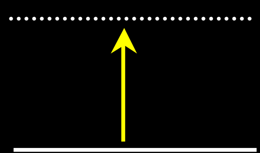


absorption

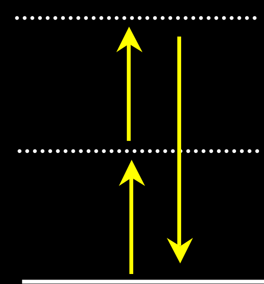


two-photon absorption

$$\sigma_{\mathrm{TPA}} \propto I^2$$



refraction



second-harmonic generation

$$\sigma_{\mathrm{SHG}} \propto I^2$$

$$\sigma_{\mathrm{abs}} \propto I$$

A zoo of nonlinear optical processes

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

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)

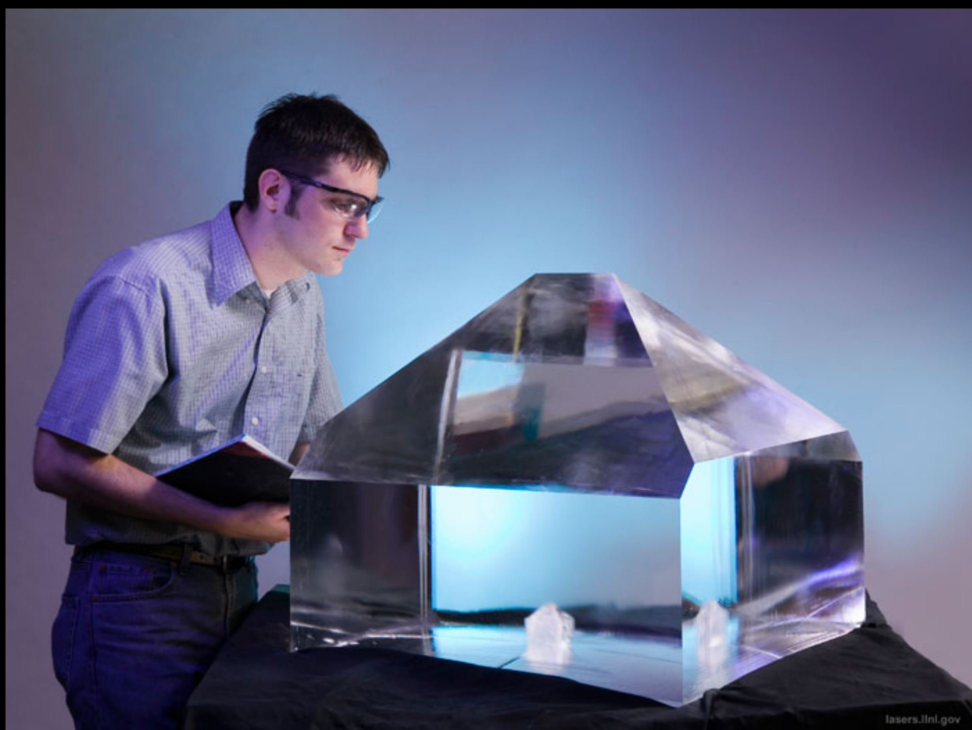
Two-photon fluorescencing labels in biology

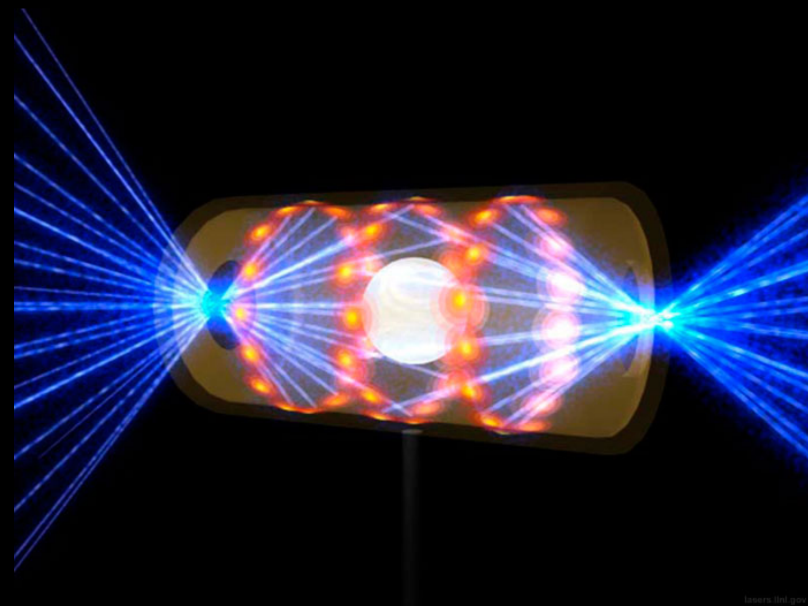
Typically inorganic crystals are used in applications, but organic molecules have the potential to be cheaper and more efficient.

SHG and SFG at the National Ignition Facility

Lawrence Livermore National Laboratory, Livermore, California

600 KH_2PO_4 crystals of 400 kg each, ultrapure to avoid absorption.





192 laser beams for inertial confinement fusion

Total power = 500 TW

1053 nm + 1053 nm → 527 nm

527 nm + 1053 nm → 351 nm

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)

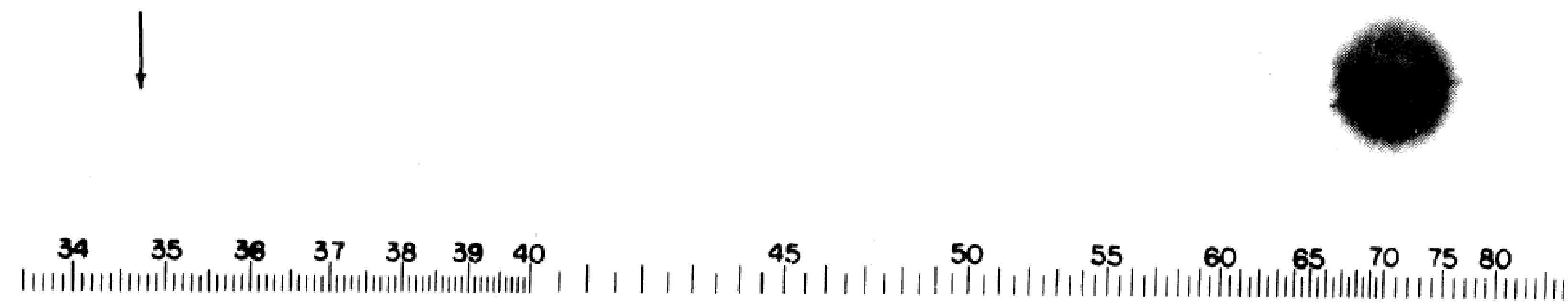


FIG. 1. A direct reproduction of the first plate in which there was an indication of second harmonic. The wavelength scale is in units of 100 A. The arrow at 3472 A indicates the small but dense image produced by the second harmonic. The image of the primary beam at 6943 A is very large due to halation.

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 (μ, β, δ, 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 $\beta = 0$

Hence surface-sensitive if bulk is centrosymmetric.

Permutation symmetry:

$$\beta_{ijk}(\omega_1, \omega_2, \omega_3) = \frac{\partial^3 E}{\partial\mathcal{E}_{i,\omega_1}\partial\mathcal{E}_{j,\omega_2}\partial\mathcal{E}_{k,\omega_3}} = \beta_{jik}(\omega_2, \omega_1, \omega_3)$$

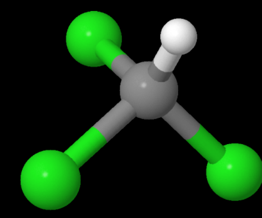
$$\beta_{ijk}(\omega_1, \omega_2, \omega_3) \neq \beta_{jik}(\omega_1, \omega_2, \omega_3)$$

"Kleinman symmetry,"
Only for $\omega \approx 0$

Also Kramers-Kronig relations.

Symmetry properties of nonlinear susceptibility tensors

Spatial symmetries: *e.g.* chloroform ($CHCl_3$)



Character table for point group C_{3v}

C_{3v}	E	$2C_3$ (z)	$3\sigma_v$	linear functions, rotations	quadratic functions	cubic functions
A_1	+1	+1	+1	z	x^2+y^2, z^2	z^3, $x(x^2-3y^2)$, $z(x^2+y^2)$
A_2	+1	+1	-1	R_z	-	$y(3x^2-y^2)$
E	+2	-1	0	(x, y) (R_x, R_y)	(x^2-y^2, xy) (xz, yz)	(xz^2, yz^2) [xyz, $z(x^2-y^2)$] [$x(x^2+y^2)$, $y(x^2+y^2)$]

↑ μ_i ↑ α_{ij} ↑ β_{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…

TABLE I. Expressions for the total dipole moment measured in a dc-electric field induced second harmonic generation experiment

Label	Convention	$[\mu_{\mathrm{Ind}}(2\omega)]/(F_0 F_\omega^2 \cos 2\omega t)$	Zero freq. convergence[a] $\to\beta_0$	$\to\gamma_0$
$AB\equiv T$	Taylor series	$\frac{1}{4}\left[\bar{\gamma}^{T}(-2\omega;\omega,\omega,0)+\frac{\mu\beta_z^{T}(-2\omega;\omega,\omega)}{5kT}\right]$	+	+
B	Perturbation series	$\frac{3}{2}\left[\bar{\gamma}^{B}(-2\omega;\omega,\omega,0)+\frac{\mu\beta_z^{B}(-2\omega;\omega,\omega)}{15kT}\right]$	+	+
B^*	EFISH only	$\frac{3}{2}\left[\bar{\gamma}^{B^*}(-2\omega;\omega,\omega,0)+\frac{\mu\beta_z^{B^*}(-2\omega;\omega,\omega)}{5kT}\right]$	−	+
A	Not used	$\frac{1}{6}\left[\bar{\gamma}^{A}(-2\omega;\omega,\omega,0)+\frac{3\mu\beta_z^{A}(-2\omega;\omega,\omega)}{5kT}\right]$	−	−
X	Phenomenological	$\left[\bar{\gamma}^{X}(-2\omega;\omega,\omega,0)+\frac{\mu\beta_z^{X}(-2\omega;\omega,\omega)}{5kT}\right]$	−	−

[a] Columns three and four indicate whether the convention does (+) or does not (−) converge to β_0 or γ_0 as $\omega\to 0$.

Commonly used units: au, esu

1 au of β
= 3.206361×10^{-53} C^3 m^3/J^2 (SI)
= 8.6392×10^{-33} cm^4 $statvolt^{-1}$ (esu of β)

A. Willetts, J. E. Rice, D. M. Burland, and D. P. Shelton, *J. Chem. Phys.* **97**, 7590 (1992)

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:

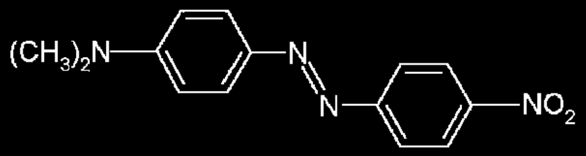
$$\vec{k}_1 + \vec{k}_2 + \vec{k}_3 = 0$$

(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.



β ~ 10000 au

$KTiOPO_4$ $\chi^{(2)} \sim 10^{-8}$ esu

$CHCl_3$ β ~ 1 au, $\chi^{(2)} \sim 10^{-8}$ 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:

$$r \rightarrow -i\frac{\partial}{\partial k} \qquad V_{\mathcal{E}} = -i\frac{\partial}{\partial k}$$

Quantum theory of polarization

A Dal Corso, F Mauri, and A Rubio, *Phys. Rev. B* **53**, 15638 (1996)

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.

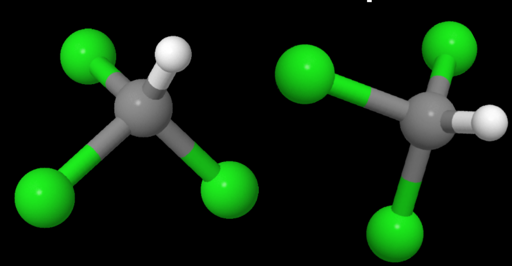
Electric-field-induced second-harmonic generation (EFISH) is coherent third-order process, based on field lining up molecules.

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

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

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

$$I_{\mathrm{HRS}} \propto \langle \beta_{xyz}\beta_{uvw} \rangle$$



Solution measurements of hyperpolarizability

Consider projection along dipole moment.

$$\beta^{i}_{\mathrm{EFISH}} = \frac{1}{5}\sum_{j}\left(\beta_{ijj} + \beta_{jij} + \beta_{jji}\right)$$

Vertical-vertical and horizontal-vertical polarizations for experiment.

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

$$\left[\beta^{\mathrm{HV}}_{\mathrm{HRS}}\right]^2 = \frac{1}{35}\sum_{i}\beta^2_{iii} - \frac{2}{105}\sum_{i\neq j}\beta_{iii}\beta_{ijj} + \frac{11}{105}\sum_{i\neq j}\beta^2_{ijj} - \frac{2}{105}\sum_{\mathrm{cyclic}}\beta_{iij}\beta_{jkk} + \frac{8}{35}\beta^2_{ijk}$$

Vibrational / rotational contributions

Many measurements are at λ = 1064 nm. For organic molecules, typically:

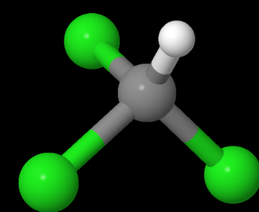
- above vibrational frequencies, so can neglect vibrations
- below electronic resonances so little dispersion

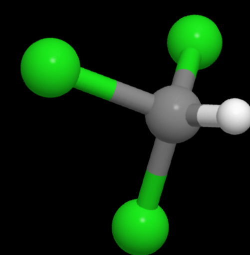
Rotational and vibrational contributions can be estimated from simple harmonic models, for low-frequency response (*e.g.* THz).

Z* = Born effective charge

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

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





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

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

E. Roman, J. R. Yates, M. Veithen, D. Vanderbilt, and I. Souza, *Phys. Rev. B* **74**, 245204 (2006)

Local-field factors for solvent

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

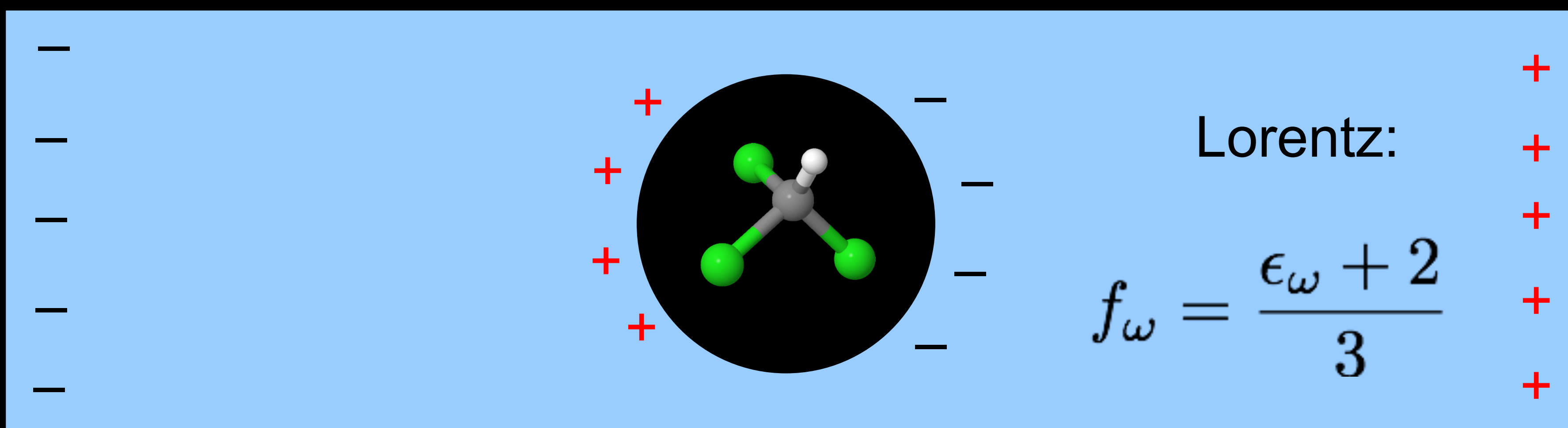
$$\mathcal{E}_{\text{local}} = f\,\mathcal{E}_{\text{screened}}$$

Clausius-Mossotti relations,
relate bulk to molecular susceptibilities.

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

$\mathcal{E}_{\text{external}}$

$\mathcal{E}_{\text{screened}}$



$$f_{\omega} = \frac{\epsilon_{\omega} + 2}{3}$$

$\mathcal{E}_{\text{local}}$

Also generalizations for ellipsoidal cavity, polar solvents.

Theoretical methods for nonlinear response

1. Finite differences (static)

2. Explicit time-propagation

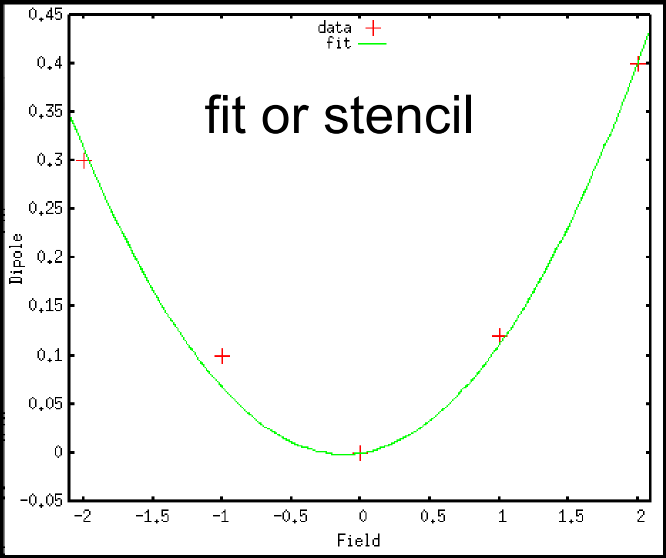
3. Sternheimer equation (2*n*+1 Theorem)

4. Sum over states (Casida equation)

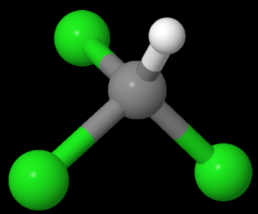
5. Dyson equation

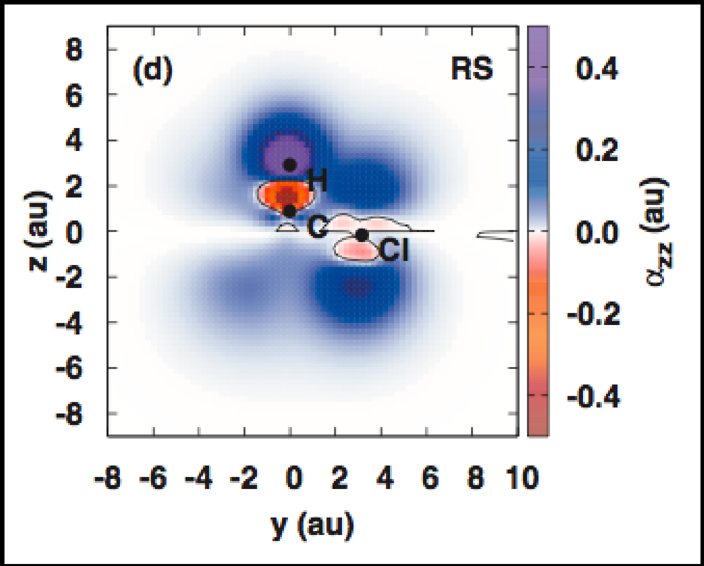
Finite differences

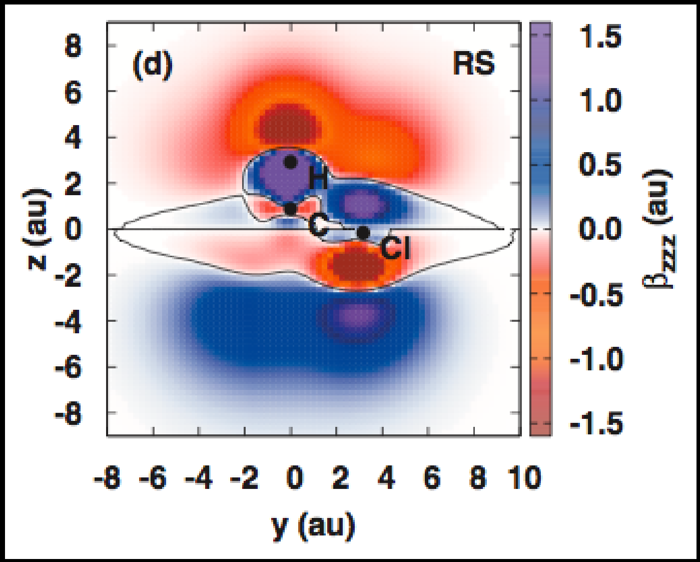
Apply static fields and calculate dipole moment.
No need for special capabilities in code.
Probably most common method used.
Hope static and IR are similar!



$CHCl_3$







F. Vila, D.A. Strubbe, Y. Takimoto, X. Andrade, A. Rubio, S. G. Louie, and J. J. Rehr,
J. Chem. Phys. **133**, 034111 (2010)

Convergence is more demanding for nonlinear response

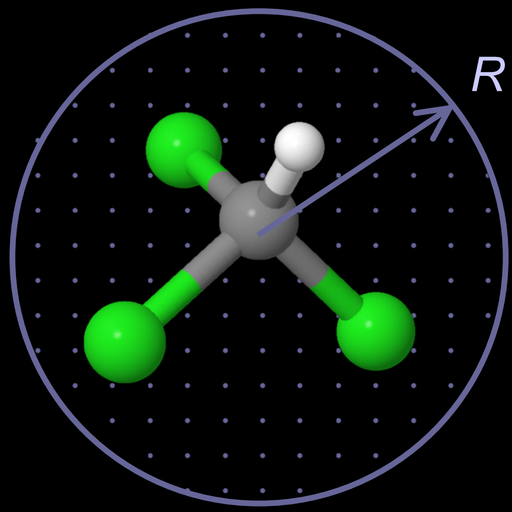
Basis Set	μ_z	α_{yy}	α_{zz}	β_{yyy}	β_{yyz}	β_{zzz}	$\bar{\alpha}$	$\beta_{\|\|}$	β_{HRS}^{VV}
GTO 5Zsa (aug-cc-pV5Z)	0.404	65.70	46.79	27.35	−15.31	22.27	59.40	−5.01	16.90
NBS 5Z4Pe8 (SIESTA)	0.398	65.45	46.28	24.54	−14.90	21.37	59.06	−5.07	15.68
RS lr (h =0.25, r=22)	0.399	66.02	47.00	27.12	−16.36	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	

F. Vila, D.A. Strubbe, Y. Takimoto, X. Andrade, A. Rubio, S. G. Louie, and J. J. Rehr, *J. Chem. Phys.* **133**, 034111 (2010)

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)

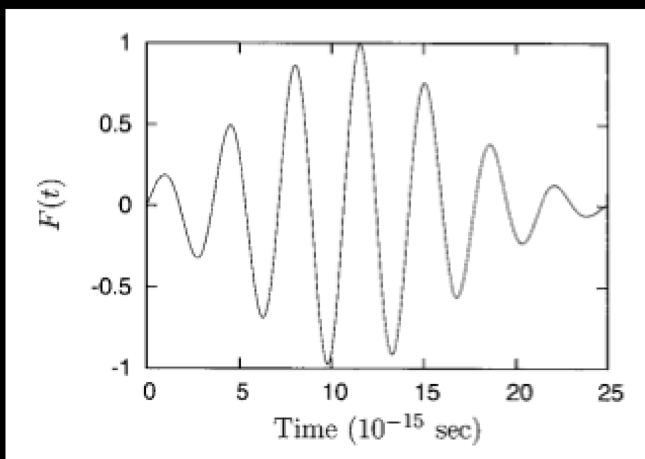
Compare: only 12 a_0 converges ground state
all atoms contained within 3 a_0 radius

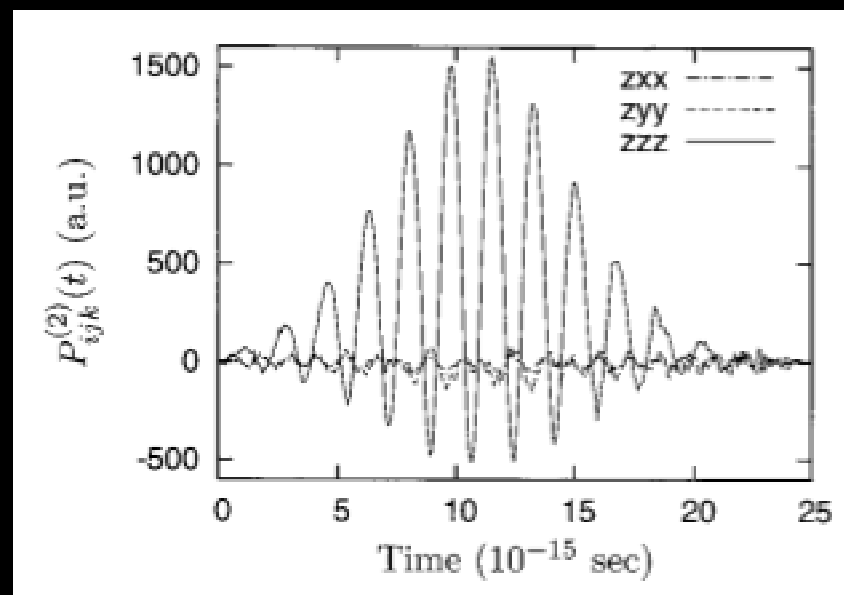


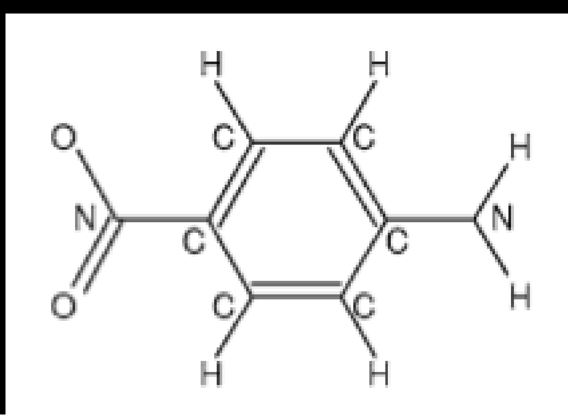
Explicit time-propagation

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).





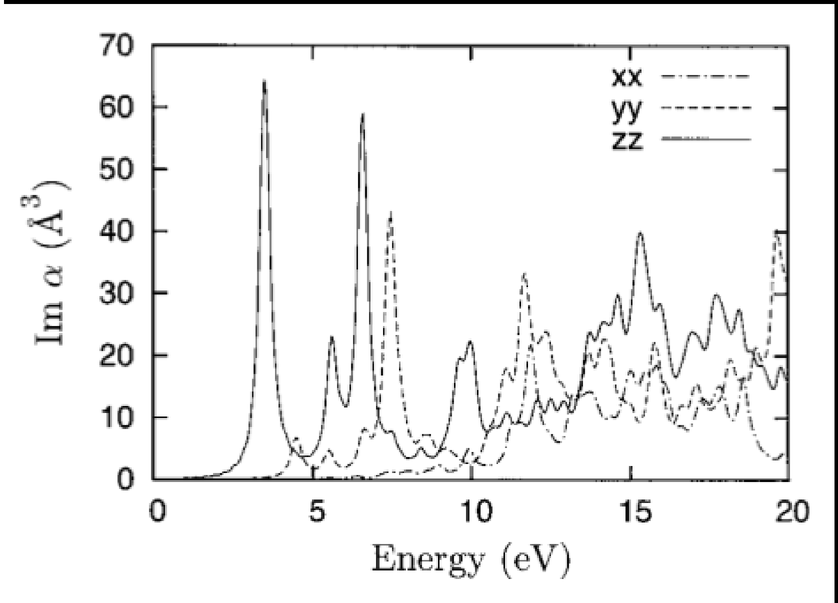


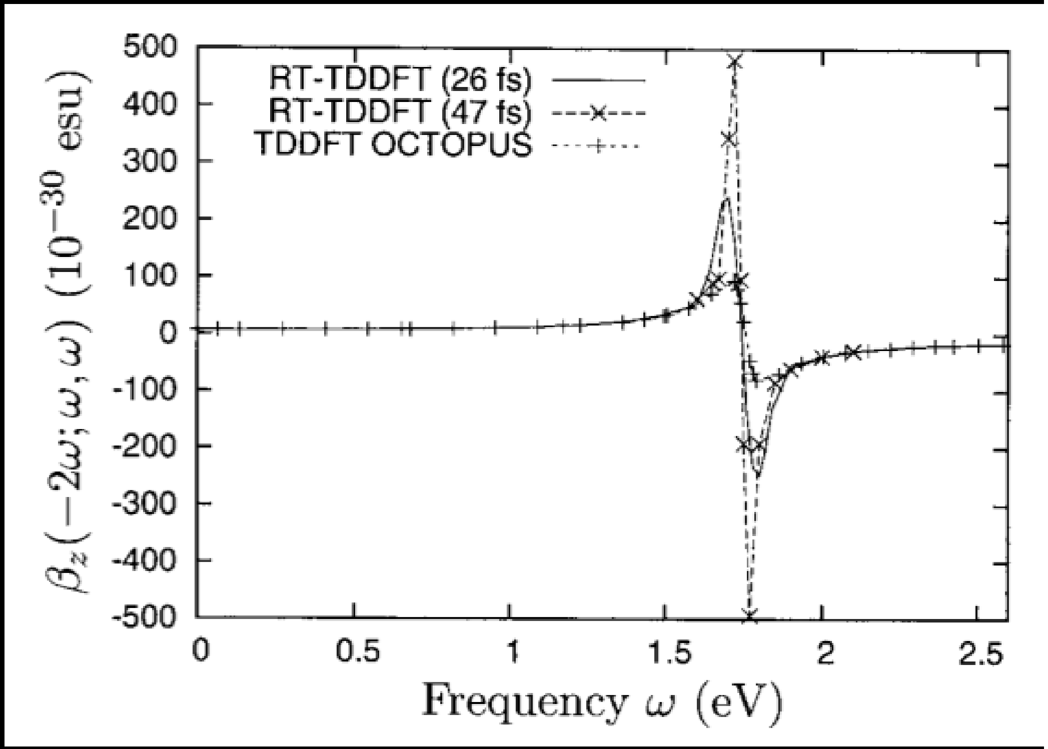
p-nitroaniline

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

Takimoto, Vila, and Rehr, *J. Chem. Phys.* 127, 154114 (2007)

Explicit time-propagation





Takimoto, Vila, and Rehr, *J. Chem. Phys.* 127, 154114 (2007)

Sternheimer equation

aka density-functional perturbation theory or coupled perturbed Kohn-Sham

Calculate variation of wavefunctions in linear response.
No need for unoccupied states.
One frequency at a time (but can use previous freq as starting point).

$$\left(H^{(0)} - \epsilon^{(0)} \pm \omega_\alpha\right) P_n' \psi_{\alpha\pm}^{(1)} = -P_n' H_{\alpha\pm}^{(1)} \psi^{(0)}$$

$$H_{\alpha\pm}^{(1)} = V_{\alpha\pm}^{(1)} + V_{\mathrm{H}}\left[n_{\alpha\pm}^{(1)}\right] + \int f_{\mathrm{xc}}\left[n\right] n_{\alpha\pm}^{(1)}\left(r\right) \mathrm{d}^3 r$$

SCF cycle

$$n_{\pm}^{(1)} = \sum_n^{\mathrm{occ}} \left(\psi_{n\pm}^{(1)} \left[\psi_n^{(0)}\right]^* + \psi_n^{(0)} \left[\psi_{n\mp}^{(1)}\right]^*\right)$$

$$P_n' = 1 - \left|\psi_n^{(0)}\right\rangle \left\langle \psi_n^{(0)}\right|$$

$$\left\langle \psi^{(0)} \middle| \psi_{\alpha\pm}^{(1)} \right\rangle = 0$$

Need small imaginary broadening $i\eta$ near resonances for numerical stability.

Sternheimer equation: 2*n*+1 Theorem

Solving n^{th}-order perturbation theory gives 2*n*+1 derivative of total energy.

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

n = 0: Hellman-Feyman Theorem. No wavefunction derivatives at all.
n = 1: Linear variation of wavefunctions gives quadratic response.

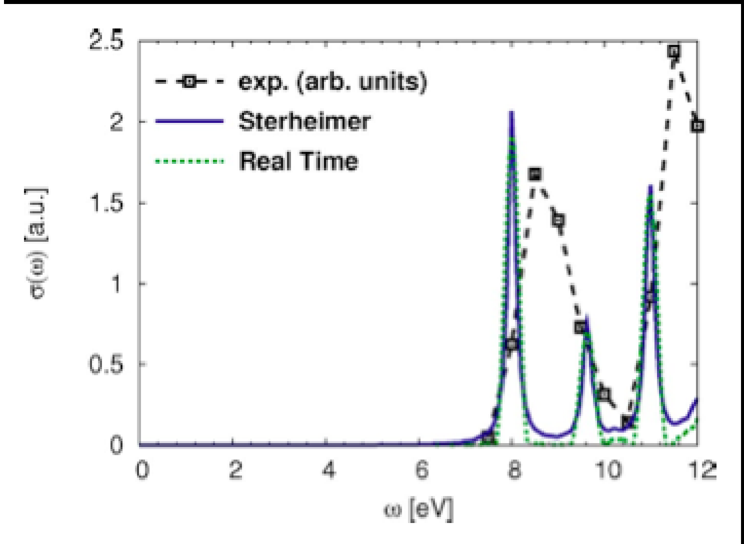
$$\begin{aligned}\beta_{ijk}(-\omega_1;\omega_2,\omega_3) = -4 \sum_P \sum_{\zeta=\pm 1} \Bigg[& \sum_m^{\mathrm{occ}} \left\langle \psi_{mi}^{(1)}(-\zeta\omega_1) \middle| H_j^{(1)}(\zeta\omega_2) \middle| \psi_{mk}^{(1)}(\zeta\omega_3) \right\rangle \\ & - \sum_{mn}^{\mathrm{occ}} \left\langle \psi_m^{(0)} \middle| H_j^{(1)}(\zeta\omega_2) \middle| \psi_m^{(0)} \right\rangle \left\langle \psi_{mi}^{(1)}(-\zeta\omega_1) \middle| \psi_{mk}^{(1)}(\zeta\omega_3) \right\rangle \\ & - \frac{2}{3} \int \mathrm{d}^3 r \int \mathrm{d}^3 r' \int \mathrm{d}^3 r'' K_{\mathrm{xc}}(r, r', r'') \, n_i^{(1)}(r,\omega_1) \, n_j^{(1)}(r',\omega_2) \, n_k^{(1)}(r'',\omega_3) \Bigg]\end{aligned}$$

X. Gonze and J.-P. Vigneron, *Phys. Rev. B* **39**, 13120 (1989)

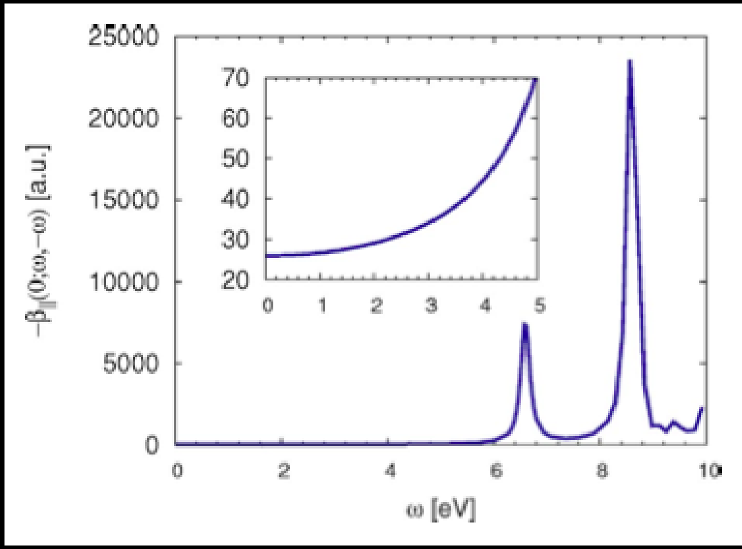
Quantum ESPRESSO and Octopus use equations on previous slide.
ABINIT formulation: find β by minimizing with respect to $\psi^{(1)}$ (variational).

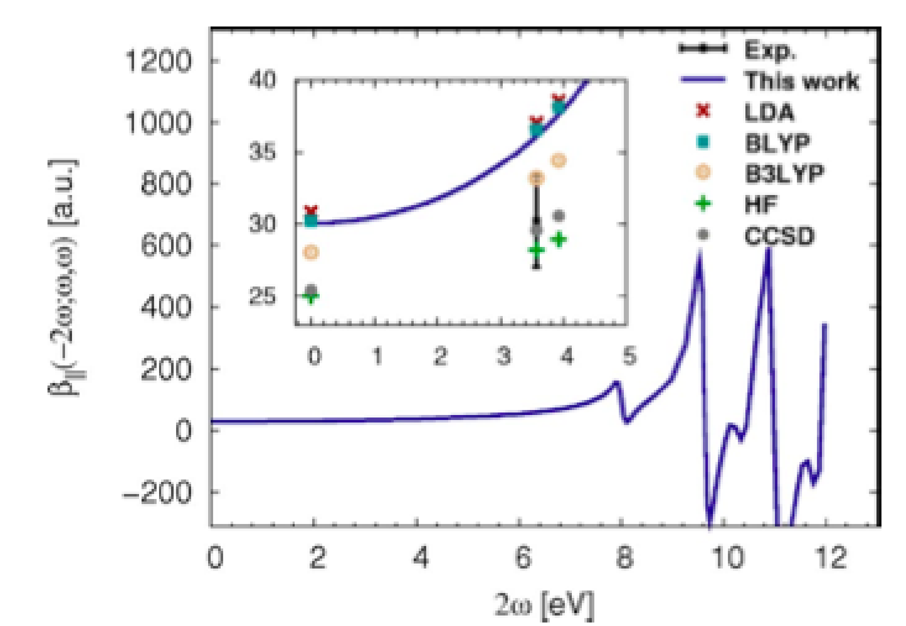
Sternheimer equation: examples from Octopus code

H_2O optical rectification



CO linear spectrum



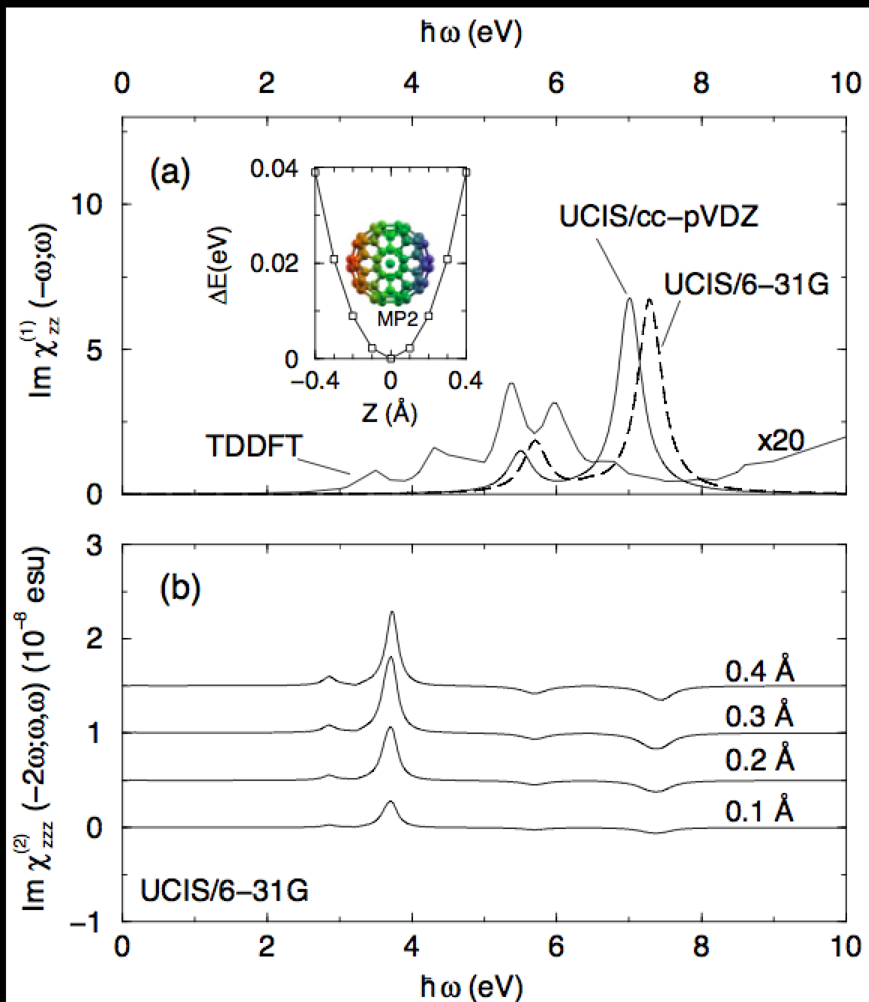


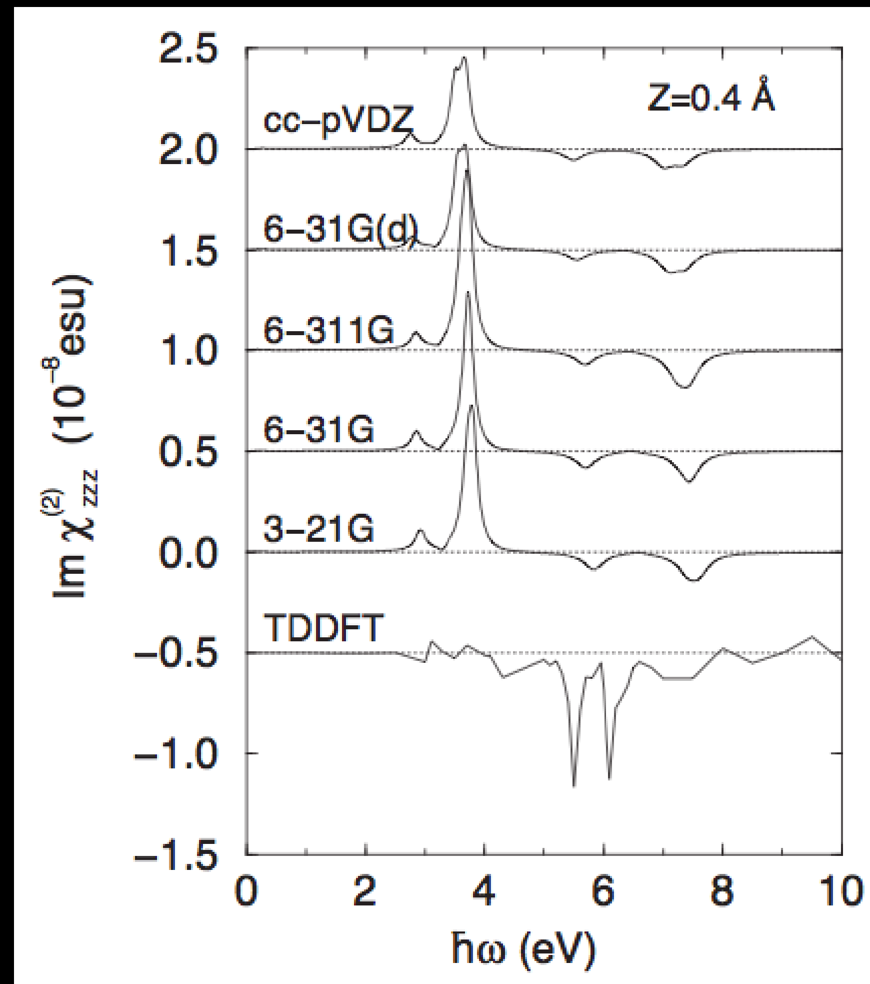
CO SHG

X Andrade, S Botti, MAL Marques, and A Rubio, *J. Chem. Phys.* **126**, 184106 (2007)

Sternheimer equation: examples from Octopus code

Efficient scaling with system size: O(N^2), cheaper than ground state.
e.g. comparison of TDLDA *vs.* CIS with Gaussian basis for vibrating N@C_{60}





G. P. Zhang, D.A. Strubbe, S. G. Louie, and T. F. George, *Phys. Rev. A* **84**, 023837 (2011)

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 [illegible] use Kohn-Sham energies and matrix elements.

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

$$\chi_{ijk}^{(2)}(\omega = \omega_1 + \omega_2)$$

$$= \frac{P_i^{(2)}(\omega)}{E_j(\omega_1)E_k(\omega_2)}$$

$$= -N\frac{e^3}{\hbar^2}\sum_{g,n,n'}\left[\frac{(r_i)_{gn}(r_j)_{nn'}(r_k)_{n'g}}{(\omega - \omega_{ng} + i\Gamma_{ng})(\omega_2 - \omega_{n'g} + i\Gamma_{n'g})}\right.$$

$$+ \frac{(r_i)_{gn}(r_k)_{nn'}(r_j)_{n'g}}{(\omega - \omega_{ng} + i\Gamma_{ng})(\omega_1 - \omega_{n'g} + i\Gamma_{n'g})}$$

$$+ \frac{(r_k)_{gn'}(r_j)_{n'n}(r_i)_{ng}}{(\omega + \omega_{ng} + i\Gamma_{ng})(\omega_2 + \omega_{n'g} + i\Gamma_{n'g})} \qquad (2.17)$$

$$+ \frac{(r_j)_{gn'}(r_k)_{n'n}(r_i)_{ng}}{(\omega + \omega_{ng} + i\Gamma_{ng})(\omega_1 + \omega_{n'g} + i\Gamma_{n'g})}$$

$$- \frac{(r_j)_{ng}(r_i)_{n'n}(r_k)_{gn'}}{(\omega - \omega_{nn'} + i\Gamma_{nn'})}\left(\frac{1}{\omega_2 + \omega_{n'g} + i\Gamma_{n'g}} + \frac{1}{\omega_1 - \omega_{ng} + i\Gamma_{ng}}\right)$$

$$\left.- \frac{(r_k)_{ng}(r_i)_{n'n}(r_j)_{gn'}}{(\omega - \omega_{nn'} + i\Gamma_{nn'})}\left(\frac{1}{\omega_2 - \omega_{ng} + i\Gamma_{ng}} + \frac{1}{\omega_1 + \omega_{n'g} + i\Gamma_{n'g}}\right)\right]\rho_g^{(0)}.$$

Arbitrary (or physical but unknown) imaginary broadenings Γ.

Convergence in two sums on states is difficult!

Applied occasionally to two-photon absorption in TDDFT.

Dyson-like equation

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

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

Complicated macroscopic/microscopic relations…

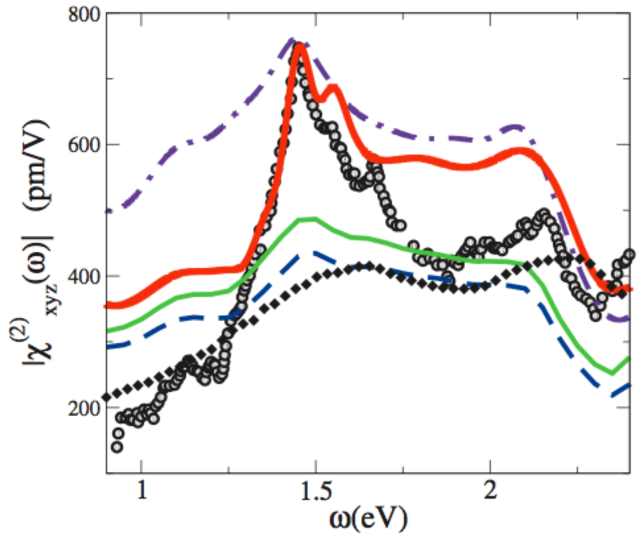


FIG. 1. Experimental spectrum of GaAs from Bergfeld and Daum (Ref. 23) (circles). Calculated $|\chi^{(2)}_{xyz}|$: IPA (solid line); including crystal local-field effects (dashed line); including excitonic effects through the long-range kernel with theoretical (dotted-dashed line) and experimental (Ref. 36) (thick solid line) ϵ_M^{LL}; theoretical calculation from Leitsmann *et al.* (Ref. 17) where the excitons are included within BSE framework (diamond). It should be noted that no scaling or fitting has been done for any of the curves.

G. Senatore and K. R. Subbaswamy, *Phys. Rev. A* **35**, 2440 (1987)
E. Luppi, H. Hübener, and V. Véniard, *J. Chem. Phys.* **132**, 241104 (2010)

Dyson-like equation

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

$$\chi^{(2)}_{0,\mathbf{G},\mathbf{G}_1,\mathbf{G}_2}(2\mathbf{q},\mathbf{q},\mathbf{q},\omega) = \frac{2}{V}\sum_{n,n',n'',\mathbf{k}} \frac{\langle \phi_{n,\mathbf{k}} | e^{-i(2\mathbf{q}+\mathbf{G})\mathbf{r}} | \phi_{n',\mathbf{k}+2\mathbf{q}} \rangle}{(E_{n,\mathbf{k}} - E_{n',\mathbf{k}+2\mathbf{q}} + 2\omega + 2i\eta)} \Bigg[(f_{n,\mathbf{k}} - f_{n'',\mathbf{k}+\mathbf{q}}) \frac{\langle \phi_{n',\mathbf{k}+2\mathbf{q}} | e^{i(\mathbf{q}+\mathbf{G}_1)\mathbf{r}_1} | \phi_{n'',\mathbf{k}+\mathbf{q}} \rangle \langle \phi_{n'',\mathbf{k}+\mathbf{q}} | e^{i(\mathbf{q}+\mathbf{G}_2)\mathbf{r}_2} | \phi_{n,\mathbf{k}} \rangle}{(E_{n,\mathbf{k}} - E_{n'',\mathbf{k}+\mathbf{q}} + \omega + i\eta)}$$

$$+ (f_{n,\mathbf{k}} - f_{n'',\mathbf{k}+\mathbf{q}}) \frac{\langle \phi_{n',\mathbf{k}+2\mathbf{q}} | e^{i(\mathbf{q}+\mathbf{G}_2)\mathbf{r}_2} | \phi_{n'',\mathbf{k}+\mathbf{q}} \rangle \langle \phi_{n'',\mathbf{k}+\mathbf{q}} | e^{i(\mathbf{q}+\mathbf{G}_1)\mathbf{r}_1} | \phi_{n,\mathbf{k}} \rangle}{(E_{n,\mathbf{k}} - E_{n'',\mathbf{k}+\mathbf{q}} + \omega + i\eta)}$$

$$+ (f_{n',\mathbf{k}+2\mathbf{q}} - f_{n'',\mathbf{k}+\mathbf{q}}) \frac{\langle \phi_{n',\mathbf{k}+2\mathbf{q}} | e^{i(\mathbf{q}+\mathbf{G}_2)\mathbf{r}_2} | \phi_{n'',\mathbf{k}+\mathbf{q}} \rangle \langle \phi_{n'',\mathbf{k}+\mathbf{q}} | e^{i(\mathbf{q}+\mathbf{G}_1)\mathbf{r}_1} | \phi_{n,\mathbf{k}} \rangle}{(E_{n'',\mathbf{k}+\mathbf{q}} - E_{n',\mathbf{k}+2\mathbf{q}} + \omega + i\eta)}$$

$$+ (f_{n',\mathbf{k}+2\mathbf{q}} - f_{n'',\mathbf{k}+\mathbf{q}}) \frac{\langle \phi_{n',\mathbf{k}+2\mathbf{q}} | e^{i(\mathbf{q}+\mathbf{G}_1)\mathbf{r}_1} | \phi_{n'',\mathbf{k}+\mathbf{q}} \rangle \langle \phi_{n'',\mathbf{k}+\mathbf{q}} | e^{i(\mathbf{q}+\mathbf{G}_2)\mathbf{r}_2} | \phi_{n,\mathbf{k}} \rangle}{(E_{n'',\mathbf{k}+\mathbf{q}} - E_{n',\mathbf{k}+2\mathbf{q}} + \omega + i\eta)} \Bigg], \tag{38}$$

E. Luppi, H. Hübener, and V. Véniard, *Phys. Rev. B* **82**, 235201 (2010)

Some references on nonlinear response

DA Strubbe, L Lehtovaara, A Rubio, MAL Marques, and SG Louie, “Response functions in TDDFT: concepts and implementation,” in *Fundamentals of Time-dependent density-functional theory* (ch. 7) and references therein.

Yuen-Ron Shen, *The Principles of Nonlinear Optics* (Wiley 1984 / 2002).

P. N. Butcher and D. Cotter, *The Elements of Nonlinear Optics* (Cambridge University Press, 1990).