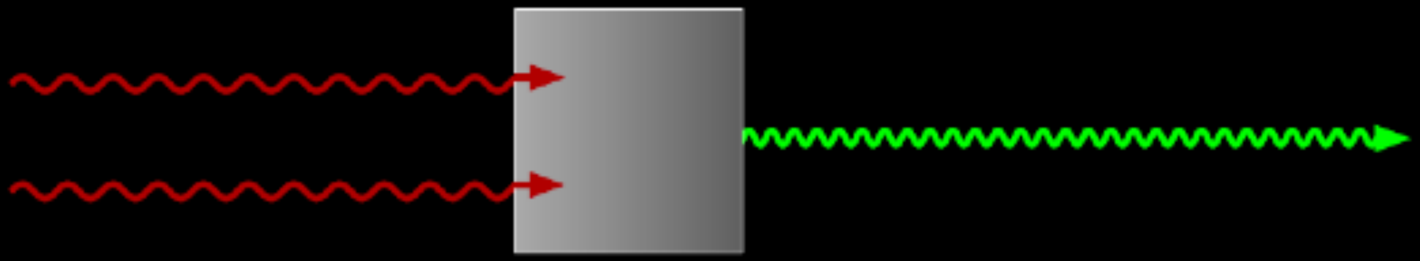
Linear and non-linear response:

phenomenology and calculation with TDDFT



David A. Strubbe

Department of Physics,

University of California, Merced, USA

Benasque, 13 April 2025

Linear and non-linear optics relation to other topics here at Benasque

Background:
Gross, fundamentals of TDDFT

Tutorial:
Sternheimer this afternoon

More details:
Tancogne-Dejean, microscopic-macroscopic connection
Parker, linear response in chemistry

Coming up in conference:

High-order (non-perturbative) nonlinear:
Yabana

Linear and non-linear optics

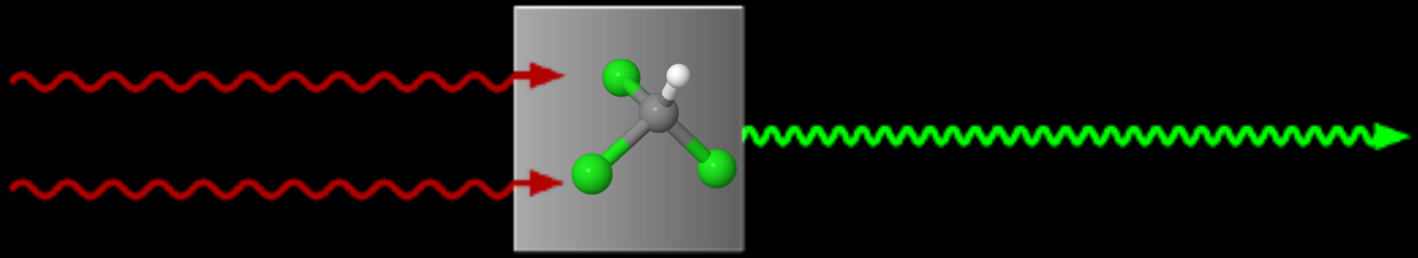
Polarizability (linear optics) $\alpha\left(-\omega,\omega\right)$

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

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

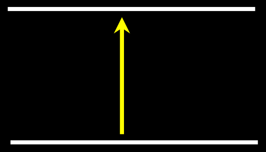
$$\beta(2\omega; -\omega, -\omega)$$

Hyperpolarizability: second-harmonic generation (SHG) *etc*.

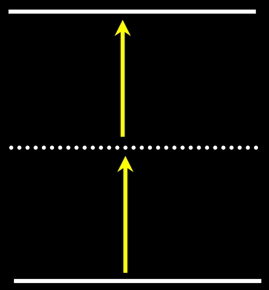


Consider only perturbative processes via Taylor expansion of dipole moment.
Not high-harmonic generation!

Quantized picture

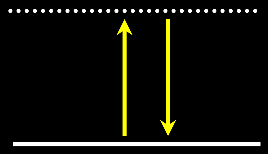


absorption

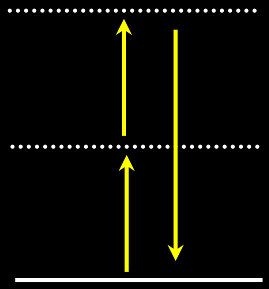


two-photon absorption

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



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 of non-linear optics

Characterization in surface science and chemistry (very sensitive)

Detection of symmetry and orientation of crystals

Optical parametric amplifiers

Pockels cells (tune refractive index)

Laser pointers

Tunable light sources

Optical logic

Coherent anti-Stokes Raman spectroscopy (CARS) (kind of 4-wave mixing)

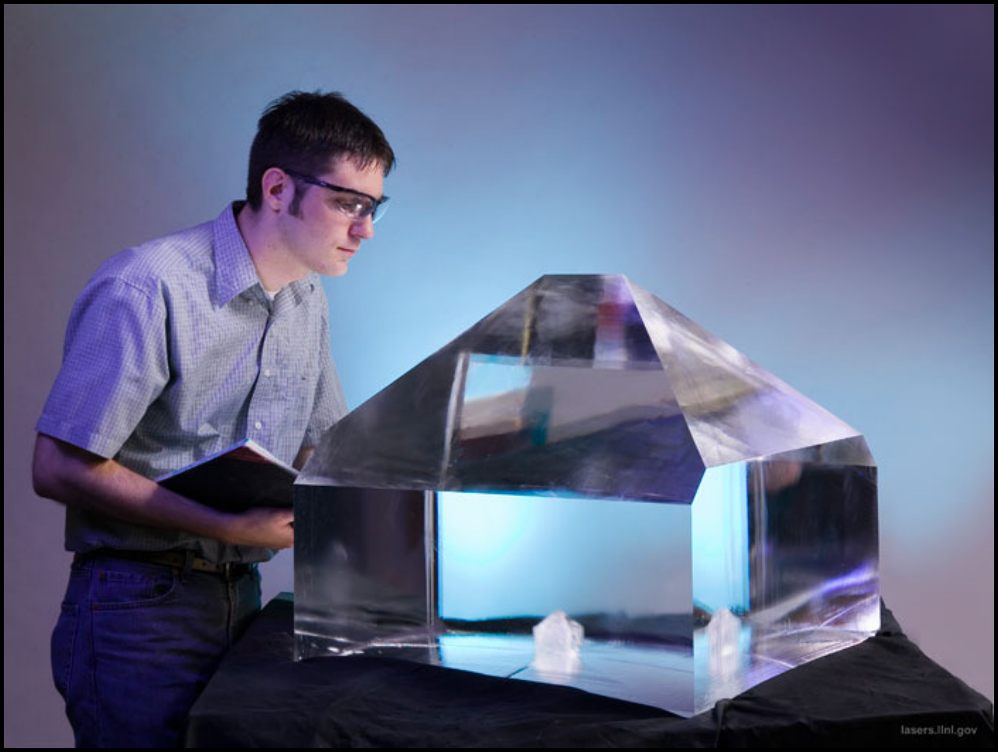
Two-photon fluorescent labels in biology

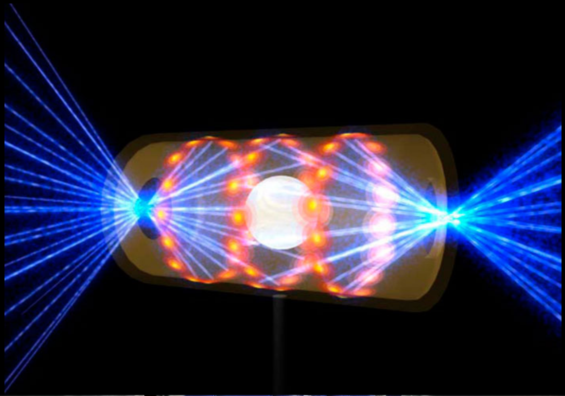
Typically inorganic crystals are used in applications, but organic molecules have the potential to be cheaper and more efficient.

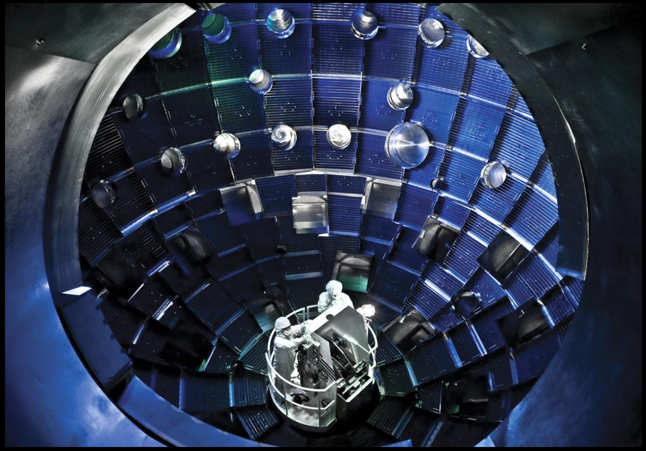
SHG and SFG at the National Ignition Facility (2009)

Lawrence Livermore National Laboratory, Livermore, California

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







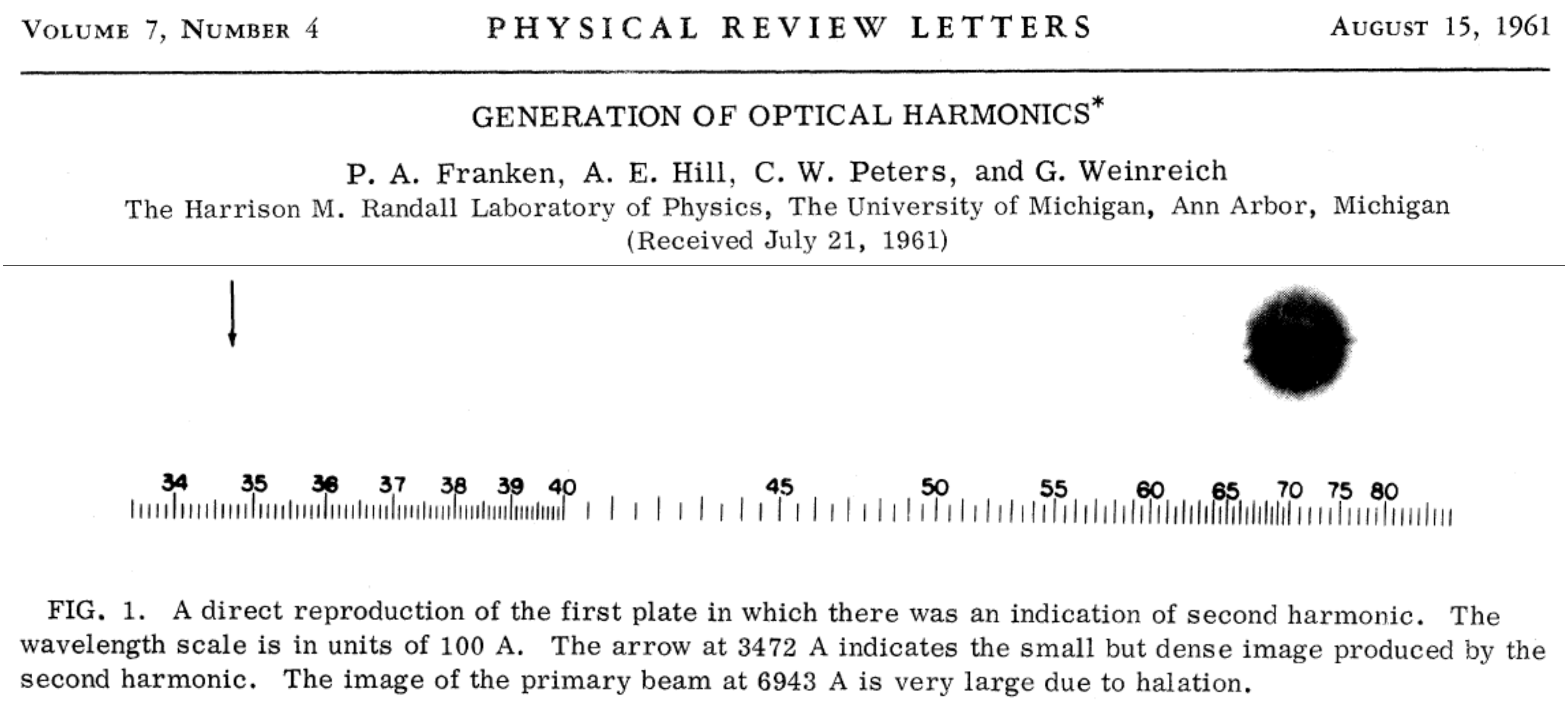
1053 nm
1053 nm
527 nm
1053 nm
351 nm

192 laser beams for inertial confinement fusion, break-even point reached in 2021

Total power = 500 TW

https://lasers.llnl.gov/about/what-is-nif

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!

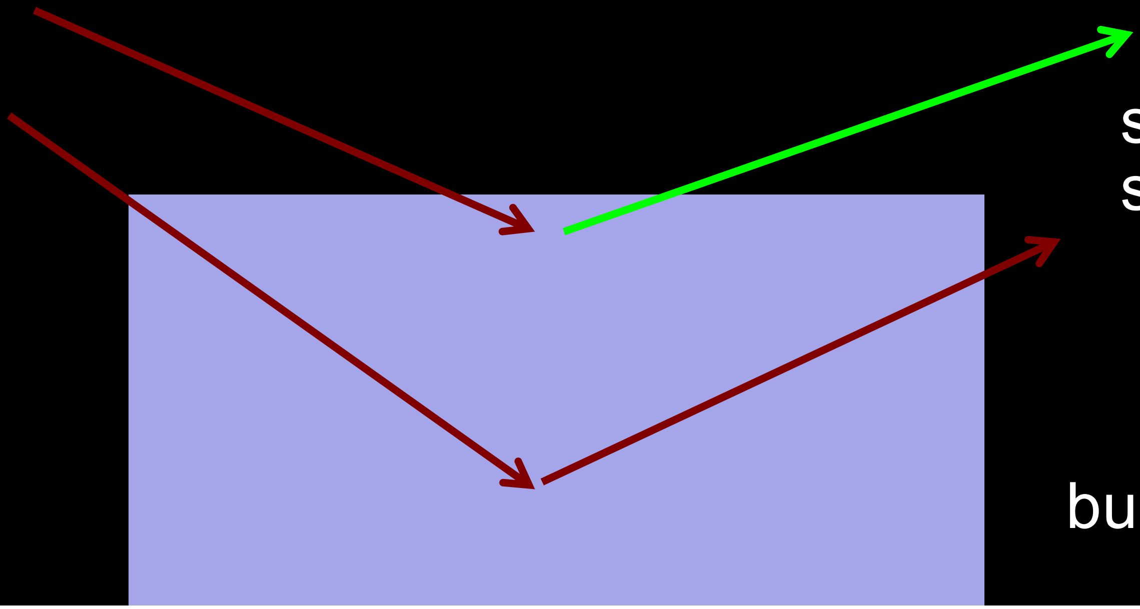
Symmetry properties of nonlinear susceptibility tensors

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 $\beta = 0$



surface: breaks symmetry

e.g. Si crystal

bulk: no SHG

Symmetry properties of nonlinear susceptibility tensors

Permutation symmetry:

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

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

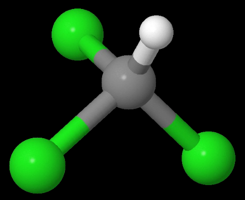
“Kleinman symmetry,” only when off-resonance or $\omega \approx 0$

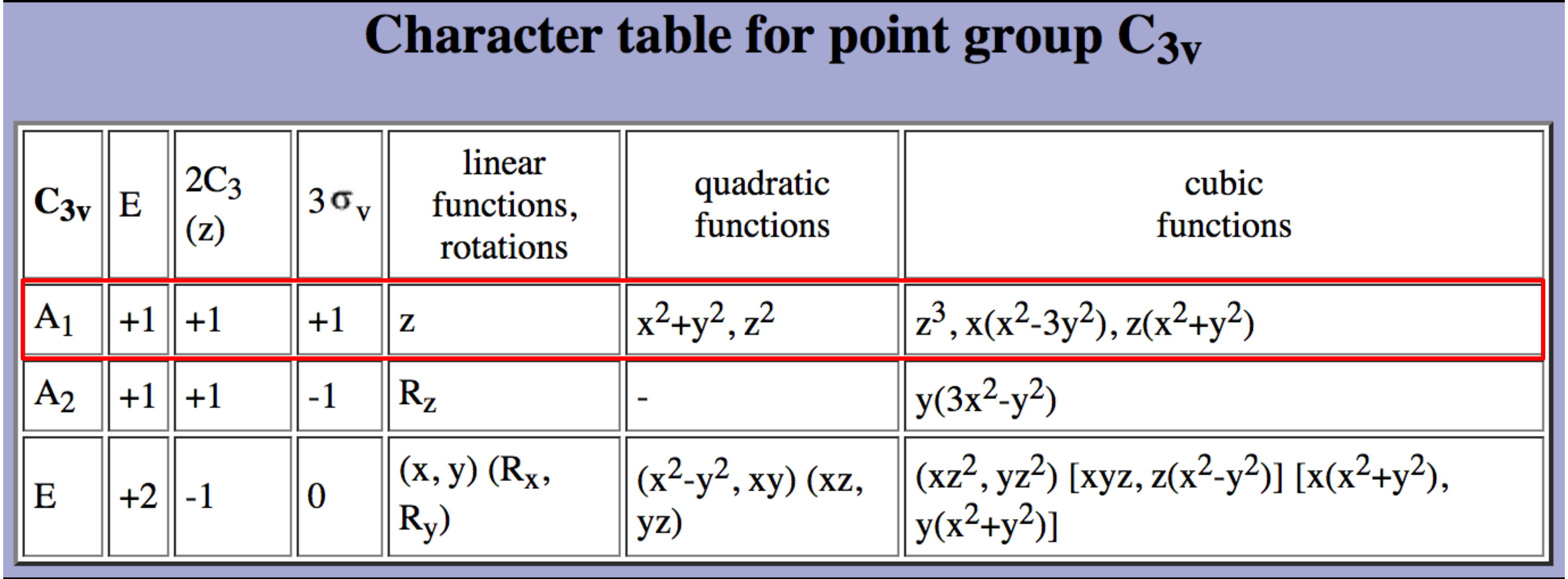
an approximate symmetry

Also Kramers-Kronig relations like for linear optics.

Symmetry properties of 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, $z(x^2-y^2)$] [$x(x^2+y^2)$, $y(x^2+y^2)$]

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

↑ μ_i ↑ $\alpha_{ij}, R_{si,jk}$ ↑ β_{ijk}

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

Nonlinear optics in solids

Susceptibility tensors for solids $\chi^{(1)}_{ij} = \alpha_{ij}/V \quad \chi^{(2)}_{ij} = \beta_{ij}/V$

Now can have *q*-dependence as well. $\chi^{(2)}_{ijk}\left(\vec{q}_1, \vec{q}_2, \vec{q}_3, \omega_1, \omega_2, \omega_3\right)$

Phase-matching condition for constructive interference:

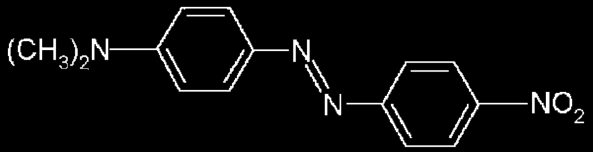
$$\vec{k}_1 + \vec{k}_2 + \vec{k}_3 = 0$$

(NOT momentum conservation; it’s the wavevector in the material)

$$= \frac{n_i(\omega_1)\,\omega_1}{c} + \frac{n_j(\omega_2)\,\omega_2}{c} + \frac{n_k(\omega_3)\,\omega_3}{c}$$

Adjust angle of incidence to satisfy and get significant conversion.

Molecules vs solids: orders of magnitude.



β ~ 10000 au

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

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

renewed interest: some 2D materials are much higher

Other perturbations

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

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

Representation of electric field in finite and periodic systems:

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

Quantum theory
of polarization

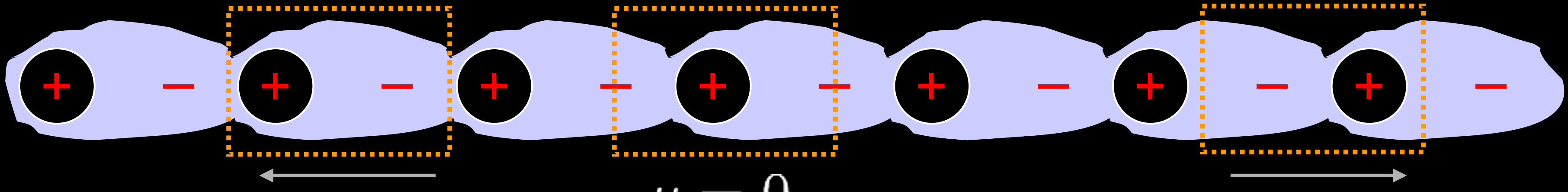
A Dal Corso, F Mauri, and A Rubio, *Phys. Rev. B* **53**, 15638 (1996)

Related to theory of Wannier functions

Quantum theory of polarization

Dipole reformulation with quantum theory of polarization in extended system

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



$$\mu = 0$$

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

k-derivatives from Sternheimer equation (*k*·*p* perturbation theory)

See Octopus tutorial on dielectric constant of silicon from Sternheimer approach

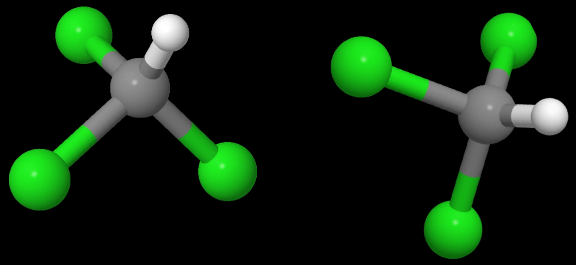
For hyperpolarizability
need also $$\frac{\partial^2 \psi}{\partial \mathcal{E} \partial k}$$ Use second-order Sternheimer equation

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)

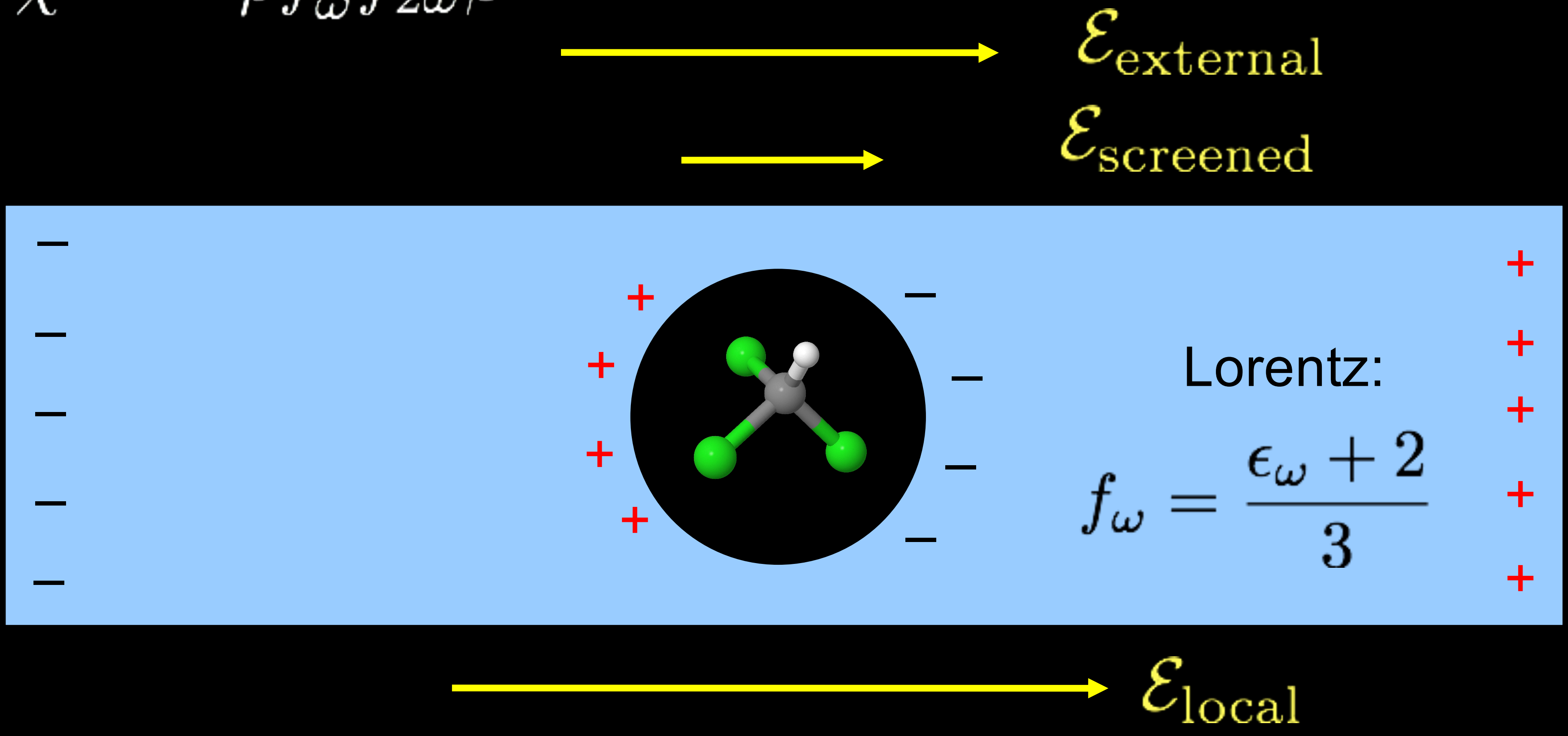
Local-field factors for solvent

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

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

Clausius-Mossotti relations,
relate bulk to molecular susceptibilities.

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



Lorentz:

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

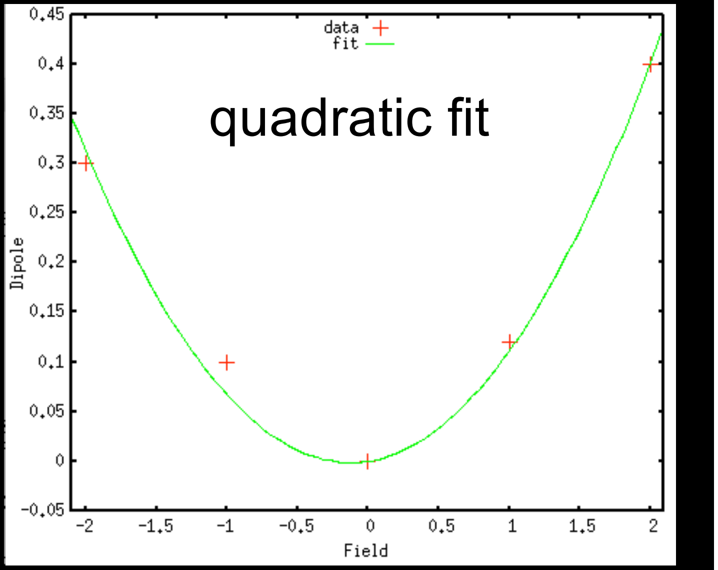
Also generalizations for ellipsoidal cavity, polar solvents.

Theoretical methods for nonlinear response

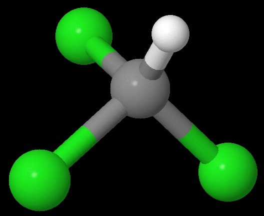
1. Finite differences (static)
2. Explicit time-propagation
3. Sternheimer equation (2*n*+1 Theorem)
4. Sum over states (e.g. Casida equation)
5. Dyson equation
6. Complex polarization propagator
   aka damped response theory

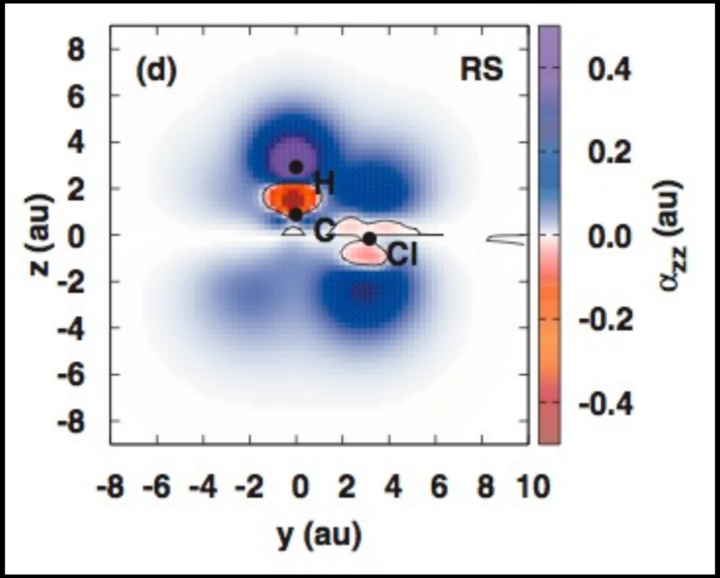
Finite differences

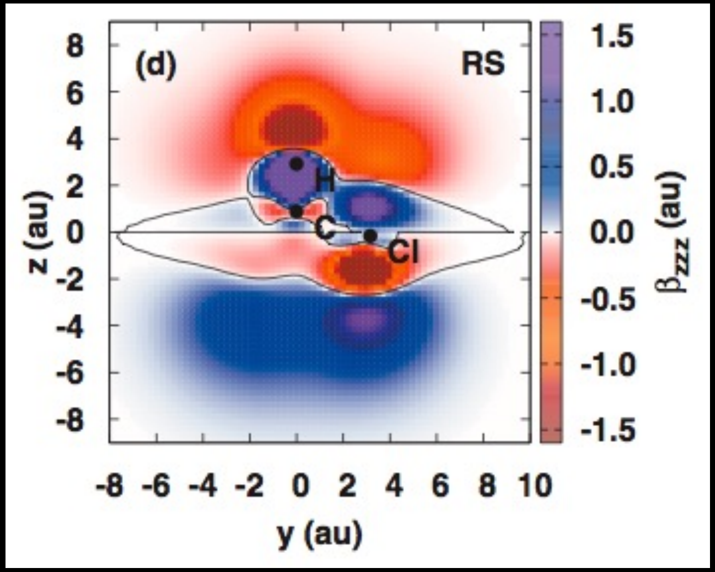
Apply static fields and calculate dipole moment.
No need for special capabilities in code.
Probably most common method used.
Hope static and IR are similar!



$CHCl_3$







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

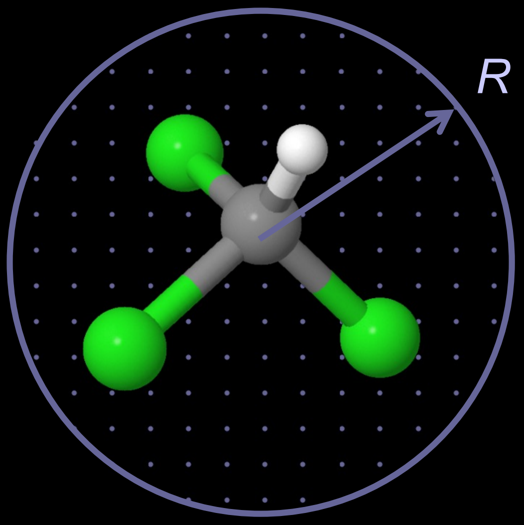
Basis Set	μ_z	α_{yy}	α_{zz}	β_{yyy}	β_{yyz}	β_{zzz}	$\bar{\alpha}$	$\beta_{\|\|}$	β^{VV}_{HRS}
GTO 5Zsa (aug-cc-pV5Z)	0.404	65.70	46.79	27.35	−15.31	22.27	59.40	−5.01	16.90
NBS 5Z4Pe8 (SIESTA)	0.398	65.45	46.28	24.54	−14.90	21.37	59.06	−5.07	15.68
RS lr (h =0.25, r=22)	0.399	66.02	47.00	27.12	−16.36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

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.

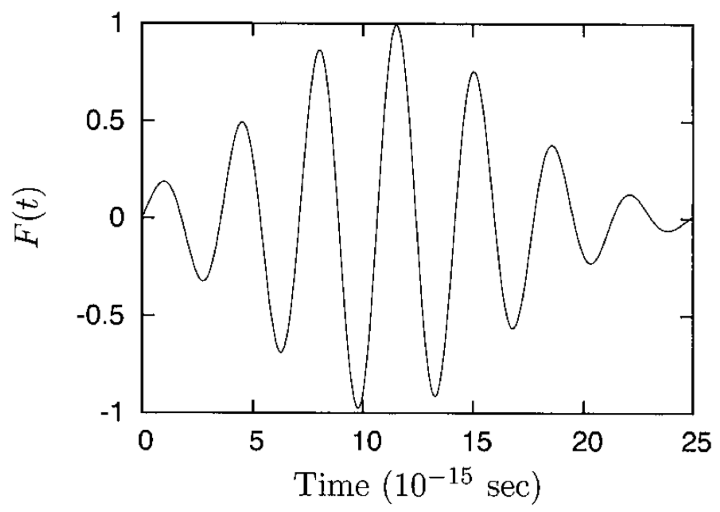
Response extends far from molecule (> 15 a_0)

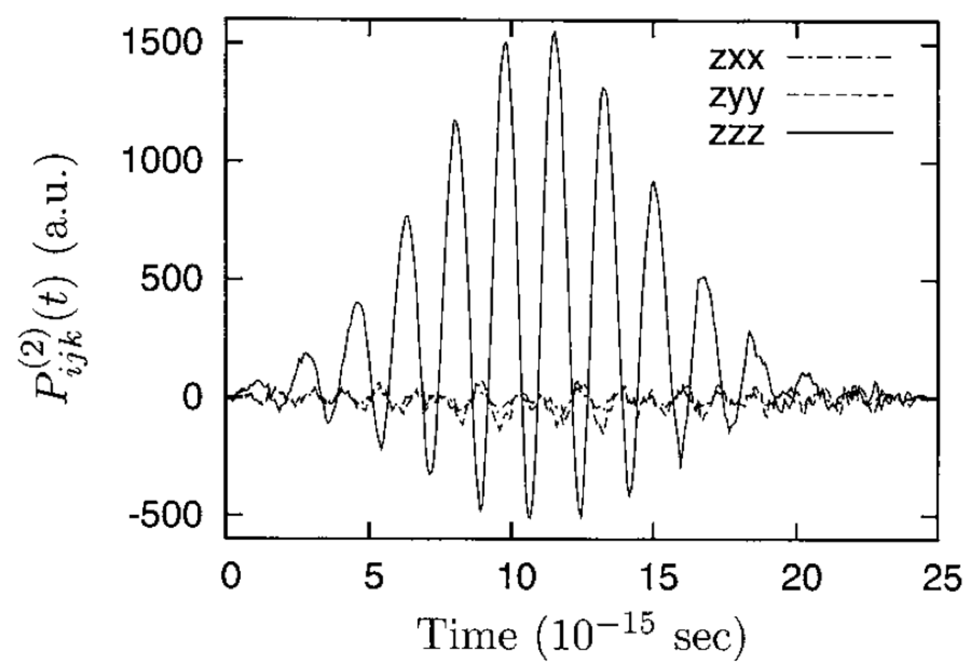
Compare: only 12 a_0 converges ground state
all atoms contained within 3 a_0 radius

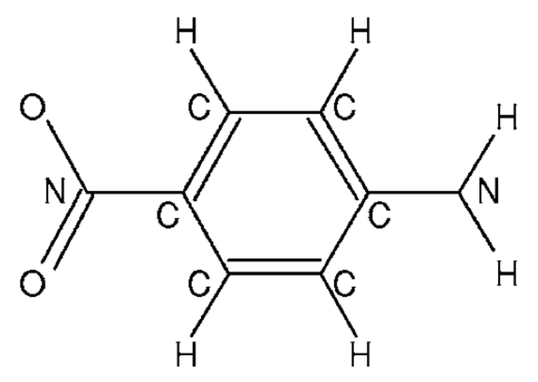


Explicit time-propagation

Cannot use “kick” for all frequencies at once (as for linear optics).
Must calculate separately for each frequency combination.
(though there are some approaches to handle this, by Carlo Rozzi)
Scaling is like one ground-state calculation per time step.
Incident laser pulses (duration ~ imaginary broadening).





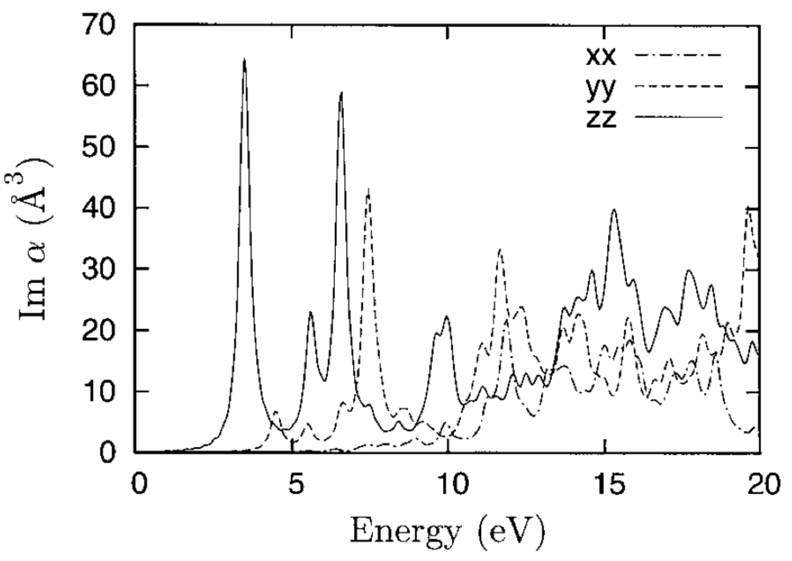


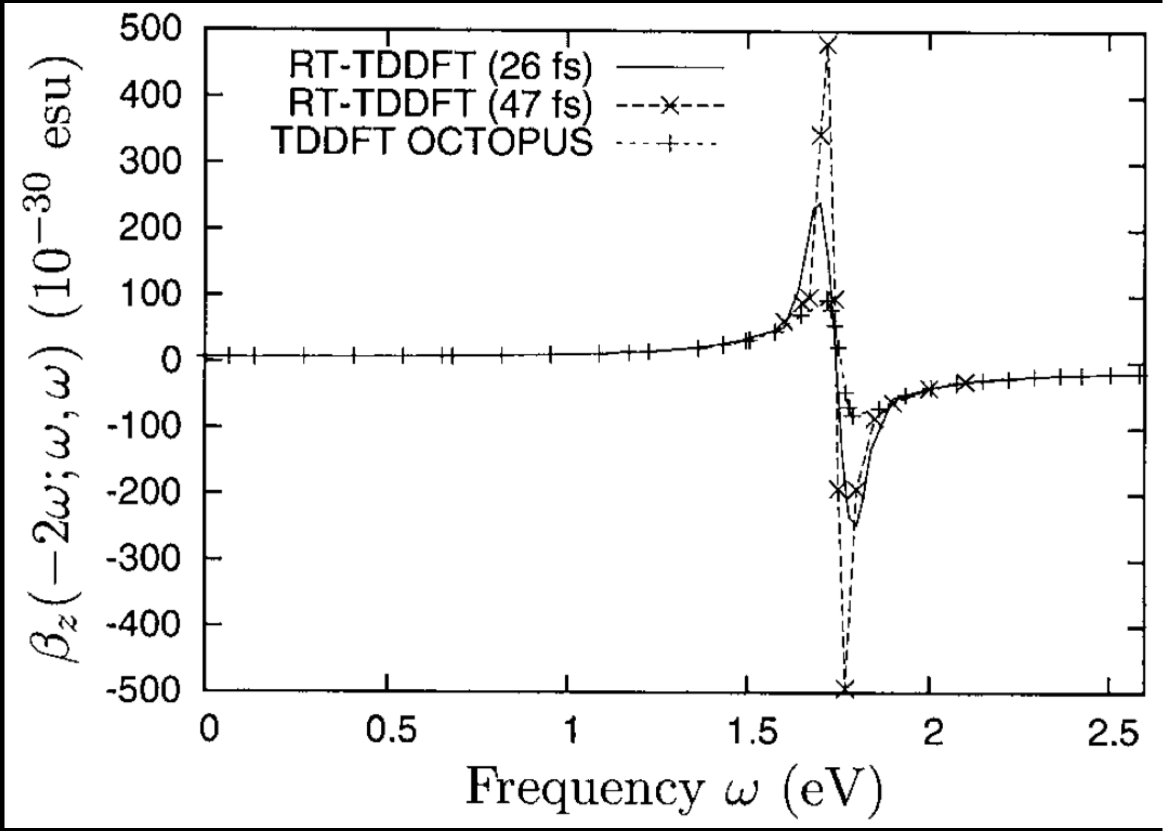
p-nitroaniline

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

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 (DFPT)
Calculate variation of wavefunctions in linear response.
No need for unoccupied states.
SCF cycle for one frequency at a time

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

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

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

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

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.

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

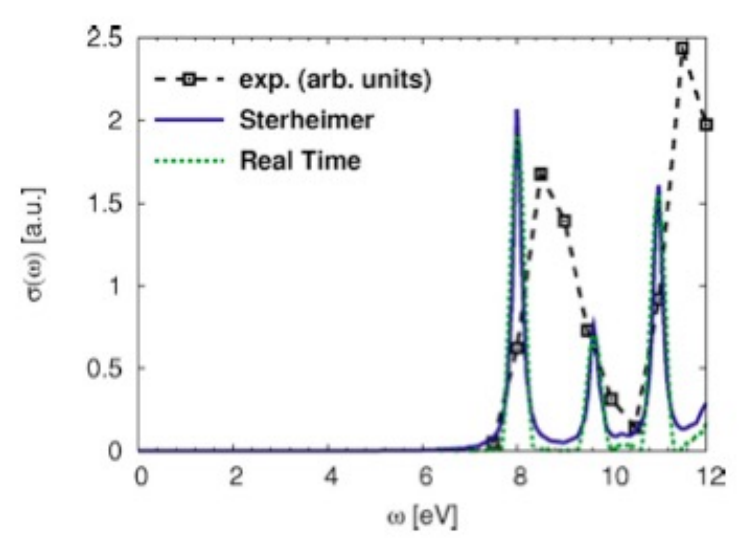
n = 0: Hellman-Feynman Theorem. No wavefunction derivatives at all.
n = 1: Linear variation of wavefunctions gives quadratic response.

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

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

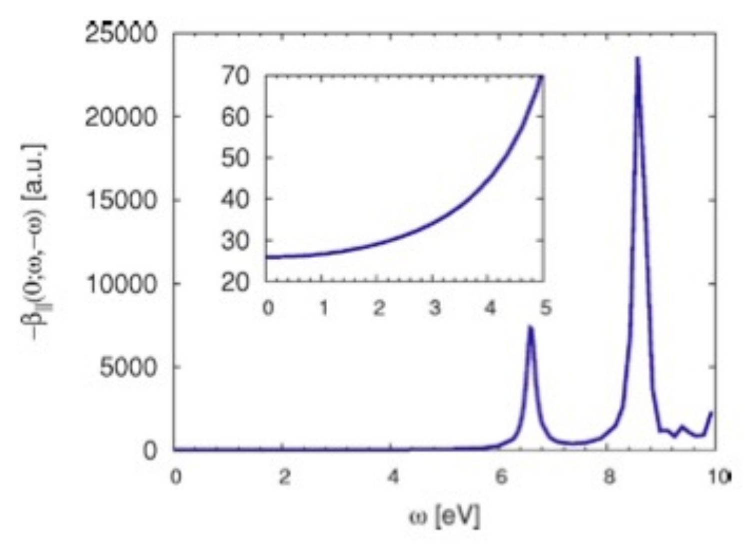
Quantum ESPRESSO and Octopus use equations on previous slide.
ABINIT formulation: find β by minimizing with respect to $\psi^{(1)}$ (variational).

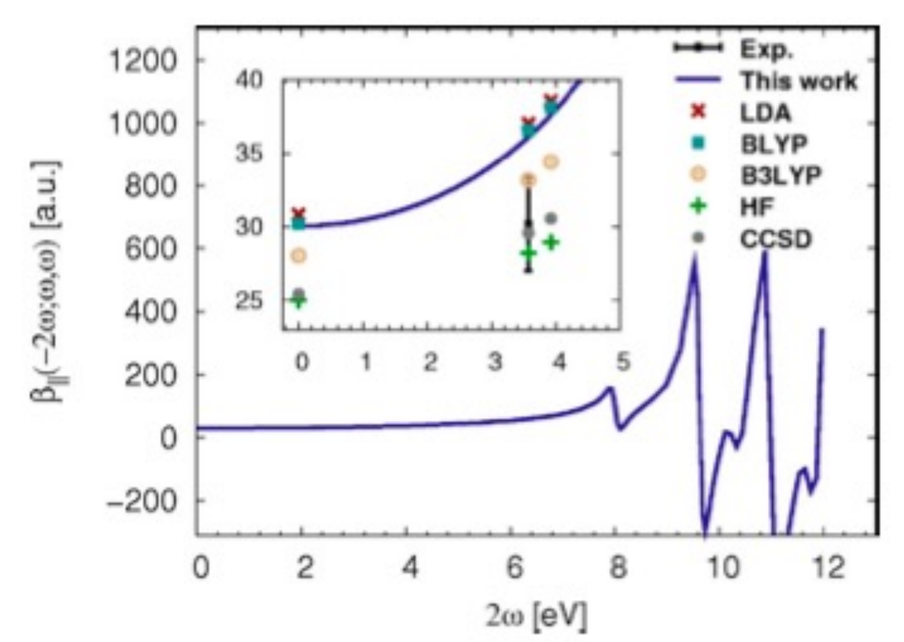
Sternheimer equation: examples from Octopus code



CO linear
spectrum

H_2O optical rectification



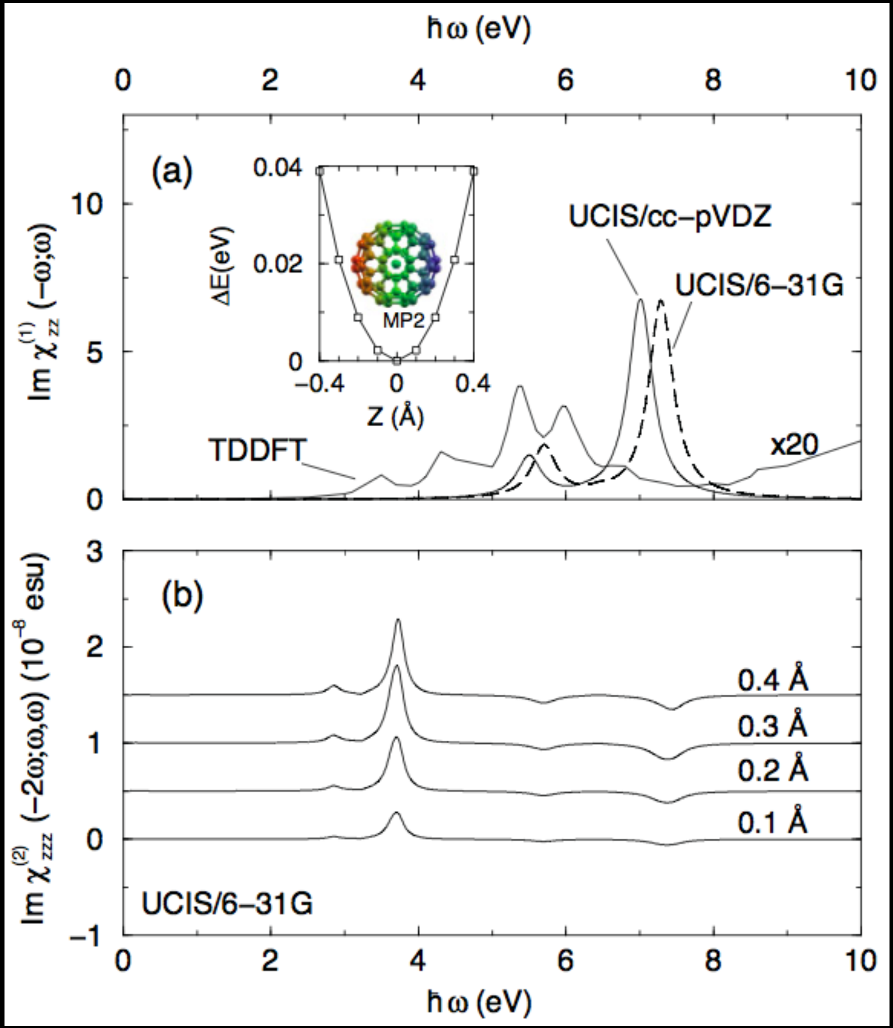


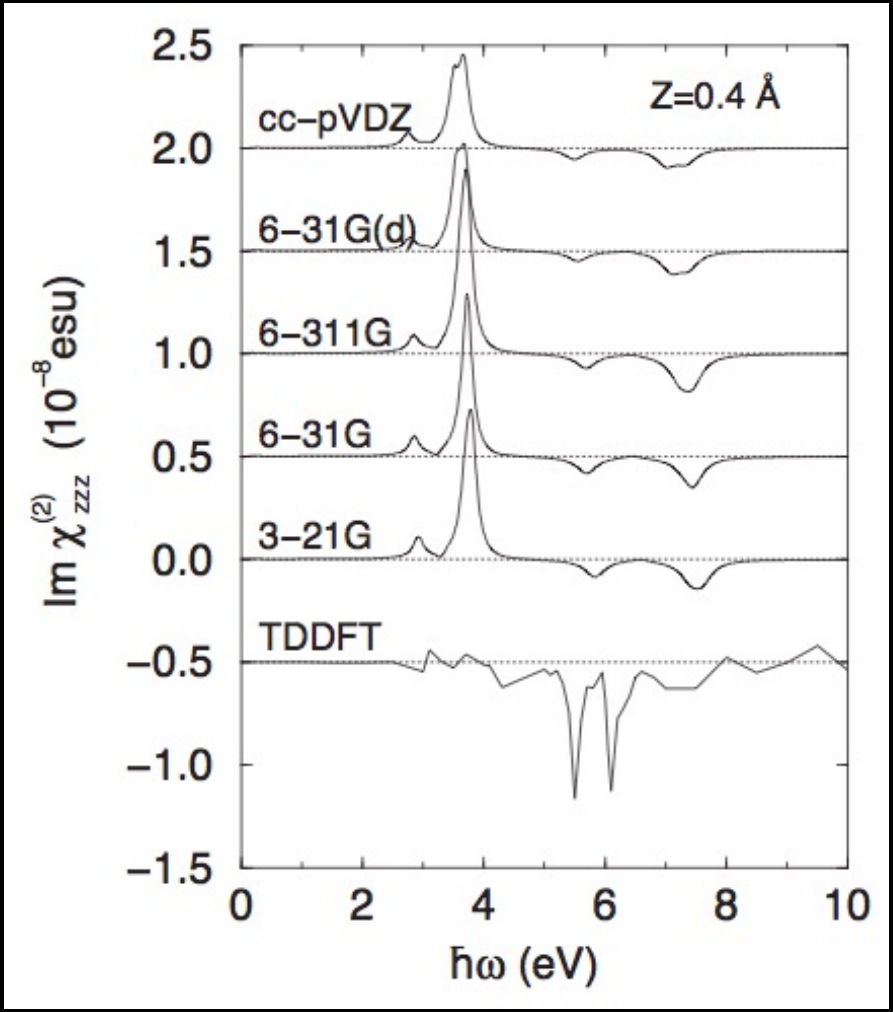
CO SHG

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: same as 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 the so-called “linear response TDDFT,” either as the full non-Hermitian problem, the reduced-size Casida equation if orbitals are real, or the Tamm-Dancoff approximation.

G. Onida, L. Reining, and A. Rubio, *Rev. Mod. Phys.* 74, 601 (2002).
S Hirata and M Head-Gordon, *Chem. Phys. Lett.* 314, 291 (1999).
C Jamorski, ME Casida, and DR Salahub, *J. Chem. Phys.* 104, 5134 (1996) and ME Casida, "Time-dependent density functional response theory for molecules," in *Recent Advances in Density Functional Methods*, edited by DE Chong, vol. 1 of *Recent Advances in Computational Chemistry*, pp. 155-192 (World Scientific, Singapore, 1995).

$$\left[\begin{array}{c|c} A & B \\ \hline -B^* & -A \end{array}\right] \boldsymbol{x} = \omega \boldsymbol{x}$$

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

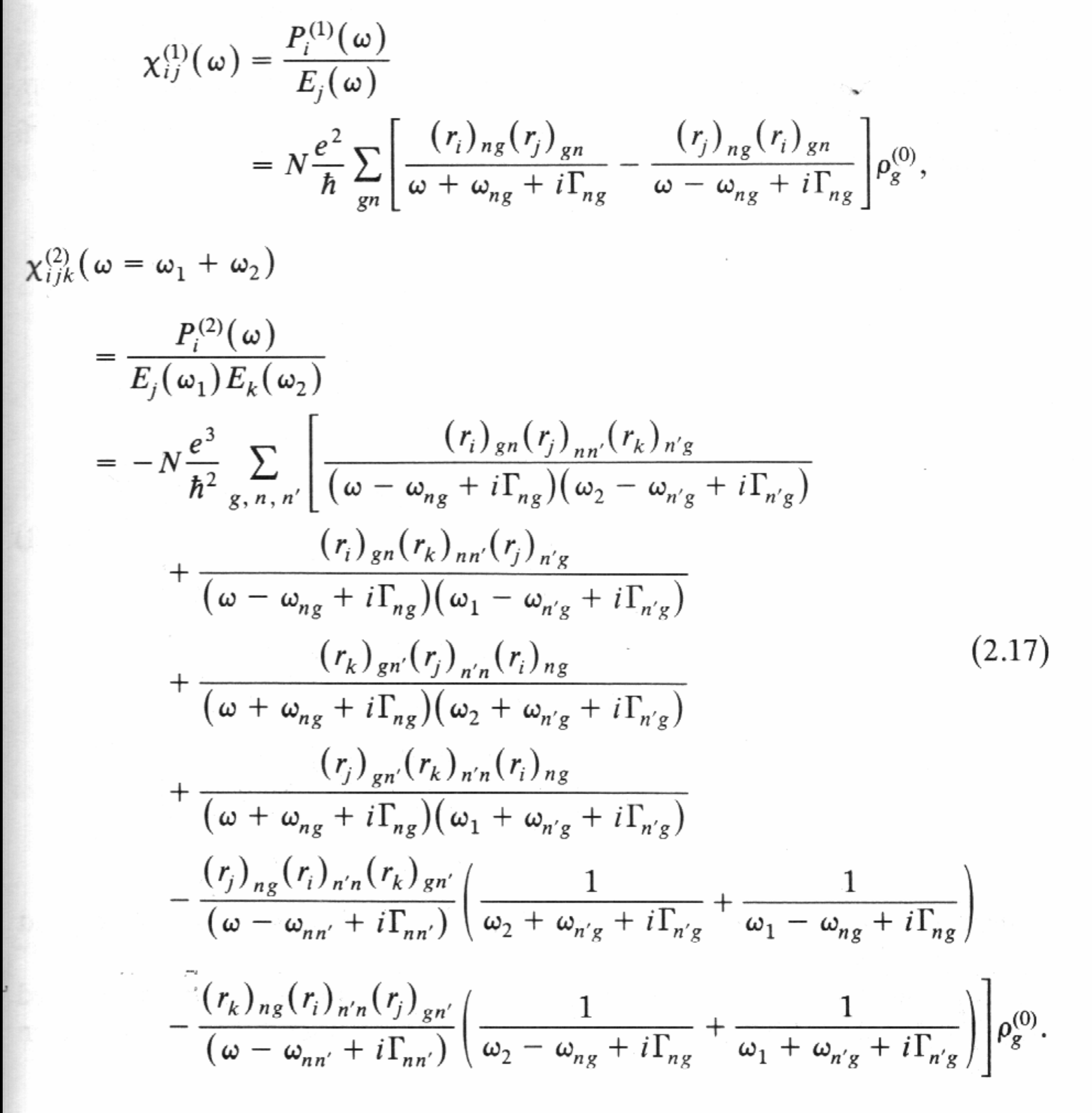
Often used as RPA though: just Kohn-Sham energies and matrix elements.

Sum over states

Arbitrary (or physical but unknown) imaginary broadenings Γ.

Convergence in two sums on states is difficult!

Applied occasionally to two-photon absorption in TDDFT.



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

$$\begin{aligned}
\chi^{(2)}_{ijk}&(\omega=\omega_1+\omega_2)\\
&= \frac{P_i^{(2)}(\omega)}{E_j(\omega_1)E_k(\omega_2)}\\
&= -N\frac{e^3}{\hbar^2}\sum_{g,n,n'}\Bigg[\frac{(r_i)_{gn}(r_j)_{nn'}(r_k)_{n'g}}{(\omega-\omega_{ng}+i\Gamma_{ng})(\omega_2-\omega_{n'g}+i\Gamma_{n'g})}\\
&\quad+\frac{(r_i)_{gn}(r_k)_{nn'}(r_j)_{n'g}}{(\omega-\omega_{ng}+i\Gamma_{ng})(\omega_1-\omega_{n'g}+i\Gamma_{n'g})}\\
&\quad+\frac{(r_k)_{gn'}(r_j)_{n'n}(r_i)_{ng}}{(\omega+\omega_{ng}+i\Gamma_{ng})(\omega_2+\omega_{n'g}+i\Gamma_{n'g})}\\
&\quad+\frac{(r_j)_{gn'}(r_k)_{n'n}(r_i)_{ng}}{(\omega+\omega_{ng}+i\Gamma_{ng})(\omega_1+\omega_{n'g}+i\Gamma_{n'g})}\\
&\quad-\frac{(r_j)_{ng}(r_i)_{n'n}(r_k)_{gn'}}{(\omega-\omega_{nn'}+i\Gamma_{nn'})}\left(\frac{1}{\omega_2+\omega_{n'g}+i\Gamma_{n'g}}+\frac{1}{\omega_1-\omega_{ng}+i\Gamma_{ng}}\right)\\
&\quad-\frac{(r_k)_{ng}(r_i)_{n'n}(r_j)_{gn'}}{(\omega-\omega_{nn'}+i\Gamma_{nn'})}\left(\frac{1}{\omega_2-\omega_{ng}+i\Gamma_{ng}}+\frac{1}{\omega_1+\omega_{n'g}+i\Gamma_{n'g}}\right)\Bigg]\rho_g^{(0)}.
\end{aligned} \tag{2.17}$$

Y-R Shen, *The Principles of Nonlinear Optics*

Dyson-like equation

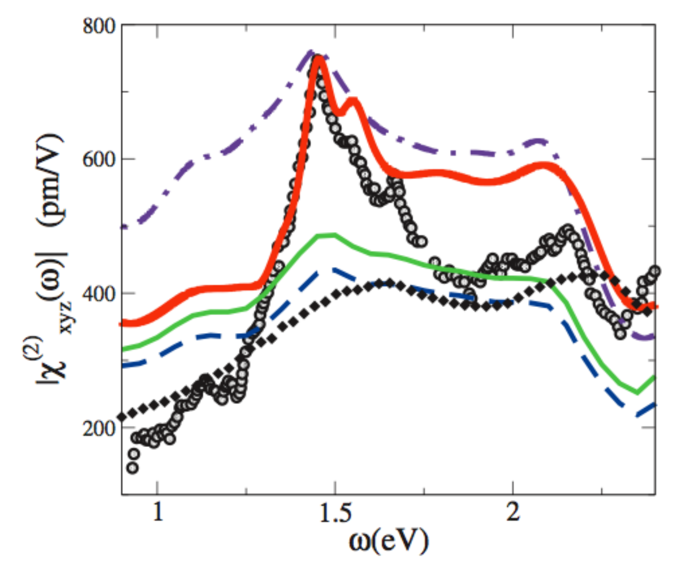
$$\chi = \chi_{\mathrm{KS}} + \chi_{\mathrm{KS}} f_{\mathrm{Hxc}} \chi$$

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

$$\begin{aligned}
&[1-\chi_0^{(1)}(\omega_1+\omega_2)f_{uxc}(\omega_1+\omega_2)]\chi_{\rho\rho\rho}^{(2)}(\omega_1,\omega_2)\\
&\quad=\chi_0^{(2)}(\omega_1,\omega_2)[1+f_{uxc}(\omega_1)\chi^{(1)}(\omega_1)]\\
&\qquad\times[1+f_{uxc}(\omega_2)\chi^{(1)}(\omega_2)]+\chi_0^{(1)}(\omega_1+\omega_2)g_{xc}(\omega_1+\omega_2)\\
&\qquad\times\chi^{(1)}(\omega_1)\chi^{(1)}(\omega_2), \qquad (10)
\end{aligned}$$

GaAs SHG

Complicated macroscopic/microscopic relations…



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.

$$\begin{aligned}\chi^{(2)}_{0,\mathbf{G},\mathbf{G}_1,\mathbf{G}_2}(2\mathbf{q},\mathbf{q},\mathbf{q},\omega) = \frac{2}{V}\sum_{n,n',n'',\mathbf{k}} \frac{\langle\phi_{n,\mathbf{k}}|e^{-i(2\mathbf{q}+\mathbf{G})\mathbf{r}}|\phi_{n',\mathbf{k}+2\mathbf{q}}\rangle}{(E_{n,\mathbf{k}}-E_{n',\mathbf{k}+2\mathbf{q}}+2\omega+2i\eta)}\Bigg[(f_{n,\mathbf{k}}-f_{n'',\mathbf{k}+\mathbf{q}})\frac{\langle\phi_{n',\mathbf{k}+2\mathbf{q}}|e^{i(\mathbf{q}+\mathbf{G}_1)\mathbf{r}_1}|\phi_{n'',\mathbf{k}+\mathbf{q}}\rangle\langle\phi_{n'',\mathbf{k}+\mathbf{q}}|e^{i(\mathbf{q}+\mathbf{G}_2)\mathbf{r}_2}|\phi_{n,\mathbf{k}}\rangle}{(E_{n,\mathbf{k}}-E_{n'',\mathbf{k}+\mathbf{q}}+\omega+i\eta)} \\ +(f_{n,\mathbf{k}}-f_{n'',\mathbf{k}+\mathbf{q}})\frac{\langle\phi_{n',\mathbf{k}+2\mathbf{q}}|e^{i(\mathbf{q}+\mathbf{G}_2)\mathbf{r}_2}|\phi_{n'',\mathbf{k}+\mathbf{q}}\rangle\langle\phi_{n'',\mathbf{k}+\mathbf{q}}|e^{i(\mathbf{q}+\mathbf{G}_1)\mathbf{r}_1}|\phi_{n,\mathbf{k}}\rangle}{(E_{n,\mathbf{k}}-E_{n'',\mathbf{k}+\mathbf{q}}+\omega+i\eta)} \\ +(f_{n',\mathbf{k}+2\mathbf{q}}-f_{n'',\mathbf{k}+\mathbf{q}})\frac{\langle\phi_{n',\mathbf{k}+2\mathbf{q}}|e^{i(\mathbf{q}+\mathbf{G}_2)\mathbf{r}_2}|\phi_{n'',\mathbf{k}+\mathbf{q}}\rangle\langle\phi_{n'',\mathbf{k}+\mathbf{q}}|e^{i(\mathbf{q}+\mathbf{G}_1)\mathbf{r}_1}|\phi_{n,\mathbf{k}}\rangle}{(E_{n'',\mathbf{k}+\mathbf{q}}-E_{n',\mathbf{k}+2\mathbf{q}}+\omega+i\eta)} \\ +(f_{n',\mathbf{k}+2\mathbf{q}}-f_{n'',\mathbf{k}+\mathbf{q}})\frac{\langle\phi_{n',\mathbf{k}+2\mathbf{q}}|e^{i(\mathbf{q}+\mathbf{G}_1)\mathbf{r}_1}|\phi_{n'',\mathbf{k}+\mathbf{q}}\rangle\langle\phi_{n'',\mathbf{k}+\mathbf{q}}|e^{i(\mathbf{q}+\mathbf{G}_2)\mathbf{r}_2}|\phi_{n,\mathbf{k}}\rangle}{(E_{n'',\mathbf{k}+\mathbf{q}}-E_{n',\mathbf{k}+2\mathbf{q}}+\omega+i\eta)}\Bigg], \qquad (38)\end{aligned}$$

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

Complex polarization propagator method

$$\langle\langle P; Q(t)\rangle\rangle^{\mathrm{a}} = \mathrm{i}\Theta(t)\langle \mathbf{0}|[P, Q(t)]|\mathbf{0}\rangle,$$

$$\langle\langle P^{+}; Q\rangle\rangle_{E} = (P\,|\,\tilde{\boldsymbol{h}})(\boldsymbol{h}|E\hat{I} - \hat{H}_{0}|\tilde{\boldsymbol{h}})^{-1}(\boldsymbol{h}\,|\,Q),$$

Like using a Green's function, for perturbation operators *P* and *Q*, expanded in a complete set of states *h*, at a given energy E

J. Oddershede, P. Jørgensen, and D. L. Yeager, *Comput. Phys. Rep.* 2, 33 (1984).

damped response theory for X-ray spectra: expand in basis of occupied and unoccupied, but solve directly for response, not excited states; somehow intermediate between Sternheimer and Casida

$$\left[\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^{*} & \mathbf{A}^{*} \end{pmatrix} - (\omega + i\gamma)\begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix}\right]\begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = -\begin{pmatrix} \mathbf{P} \\ \mathbf{P}^{*} \end{pmatrix},$$

L. Konecny, M. Repisky, K. Ruud, and S. Komorovsky, *J. Chem. Phys.* 151, 194112 (2019)

Magnetic perturbations

Term in Hamiltonian: $\vec{\mu} \times \vec{B}$

Perturbation:

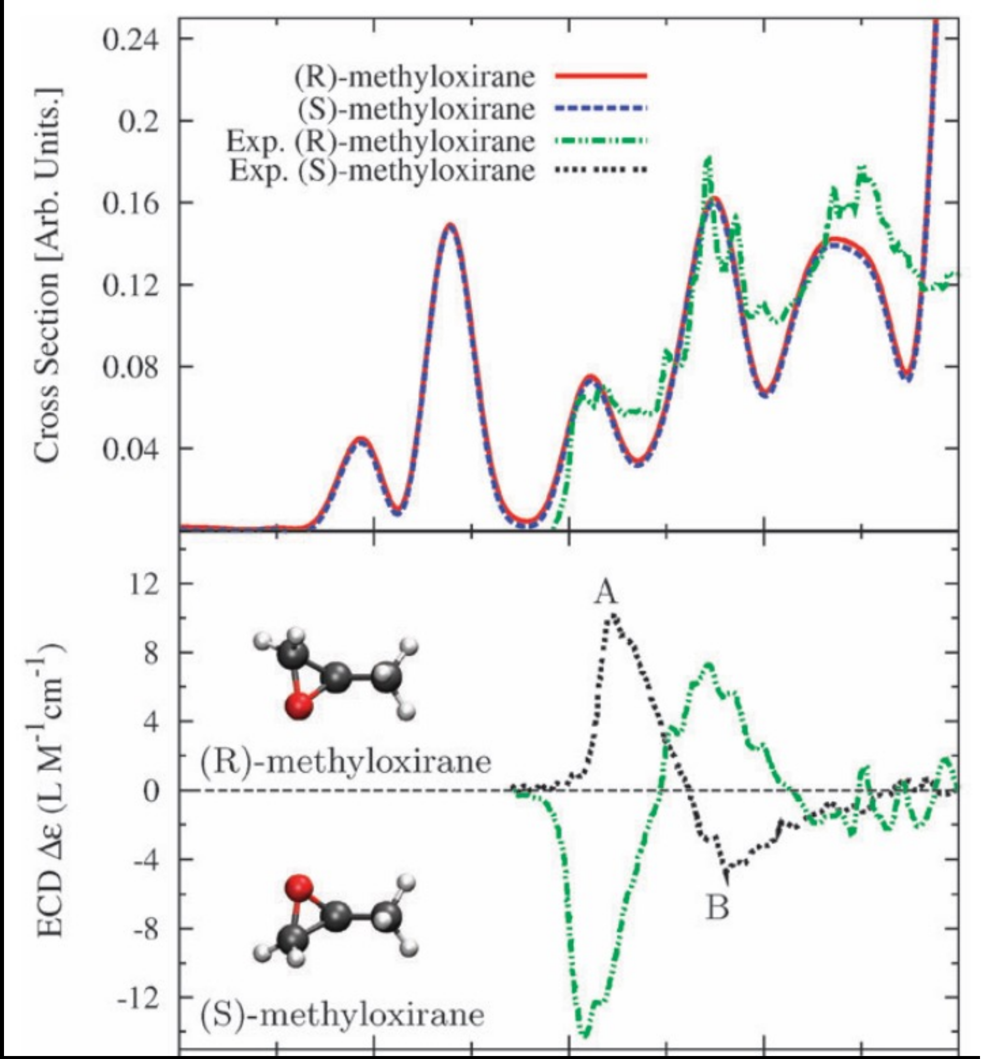
$$\vec{\mu} = \vec{r} \times i\hbar\vec{\nabla}$$

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



Daniele Varsano, Leonardo A. Espinosa-Leal, Xavier Andrade, Miguel A. L. Marques, Rosa di Felice and Angel Rubio, *Phys. Chem. Chem. Phys.* 11, 4481 (2009)

Magnetic perturbations in solids

$$\vec{B} = \vec{\nabla} \times \vec{A}$$

Vector potential can be expressed in different gauges.

$$\vec{\mathcal{E}} = -\frac{1}{c}\frac{\partial \vec{A}}{\partial t}$$

Separate wavefunction into gauge-dependent and gauge-independent parts.
E and *B* fields as in quantum theory of polarization.
First- and second-order Sternheimer equations for response.
Carefully combine parts into gauge-independent quantity.

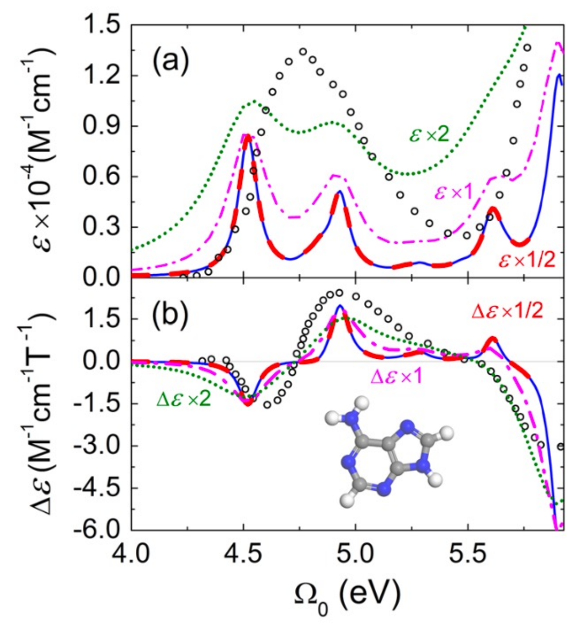
IV Lebedeva, DA Strubbe, IV Tokatly, and A Rubio, *npj Comput. Mater.* 5, 32 (2019)

adenine molecule:

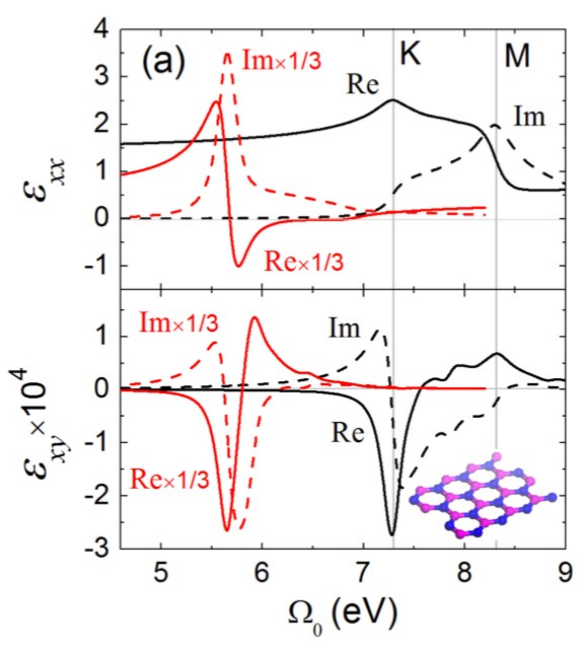
blue, this approach

circles, exp’t

red, magenta, green, finite approach

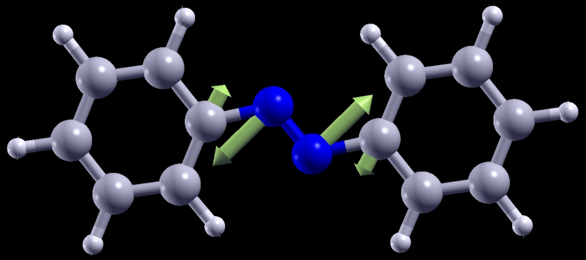


hexagonal BN sheet



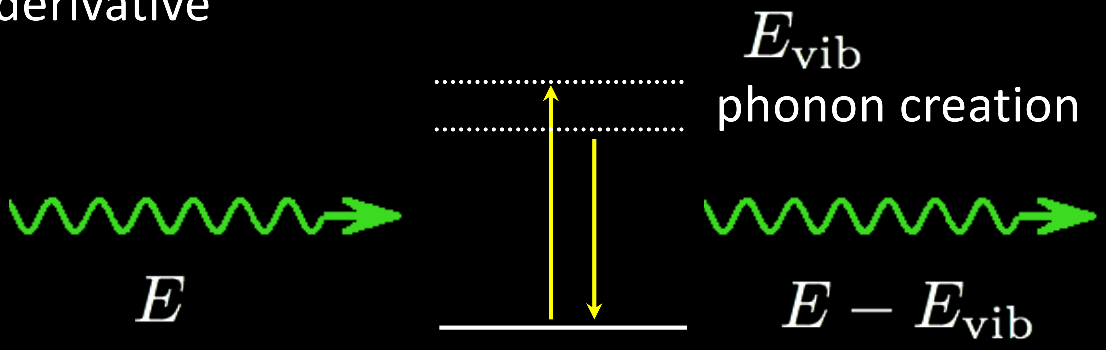
Raman spectroscopy

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
M. Lazzeri and F. Mauri, *Phys. Rev. Lett.* **90**, 036401 (2003)

$$I \propto \left| \sum_{\alpha i} u_{\alpha i} R_{\alpha i, jk} \right|^2$$

$$R_{\alpha i, jk} = 2 \, \mathrm{Tr} \left\{ \frac{\partial v^{\text{ext}}}{\partial u_{i\alpha}} \frac{\partial^2 \rho}{\partial \mathcal{E}_j \partial \mathcal{E}_k} \right\}$$

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

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.

X. Andrade *et al.*, *Phys. Chem. Chem. Phys.* 17, 31371-31396 (2015)

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).

G. Onida, L. Reining, and A. Rubio, *Rev. Mod. Phys.* 74, 601 (2002)