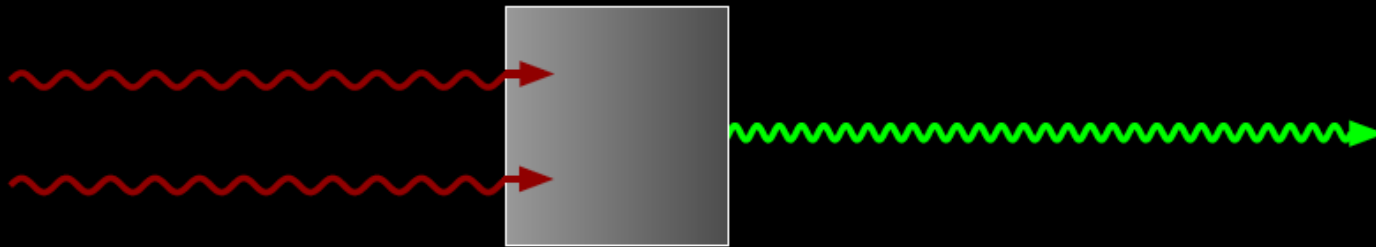


Non-linear optics, $k \cdot p$ perturbation theory, and the Sternheimer equation



David A. Strubbe

Department of Materials Science and Engineering
Massachusetts Institute of Technology, Cambridge, MA

*Formerly Department of Physics, University of California, Berkeley
Materials Sciences Division, Lawrence Berkeley National Laboratory*

Octopus developers meeting, Lyon

22 October 2012

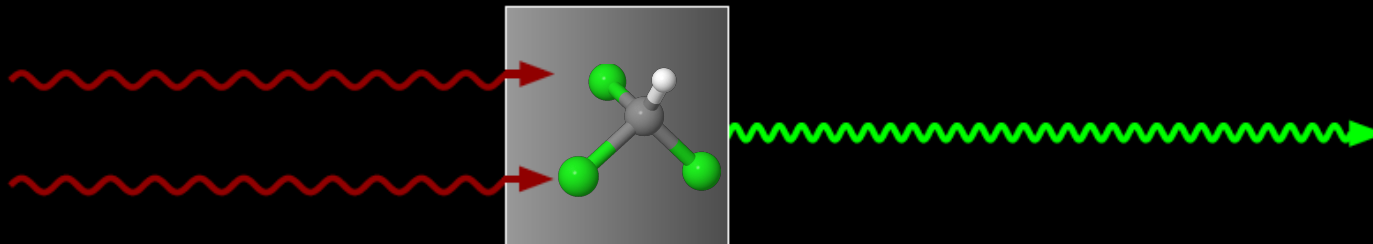
What is non-linear optics?

Polarizability (linear optics) $\alpha(-\omega, \omega)$
absorption, refraction $\text{Im } \alpha, \text{Re } \alpha$

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

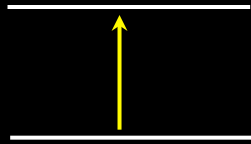
$$\beta(2\omega; -\omega, -\omega)$$

Hyperpolarizability: second-harmonic generation (SHG) etc.



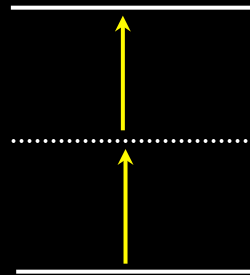
Consider only perturbative processes via Taylor expansion of dipole moment.
Not high-harmonic generation!

Quantized picture of non-linear optics



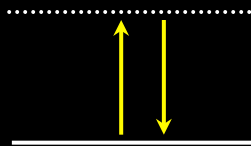
absorption

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

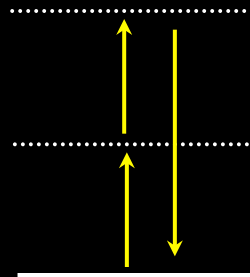


two-photon absorption

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



refraction



second-harmonic generation

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

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.

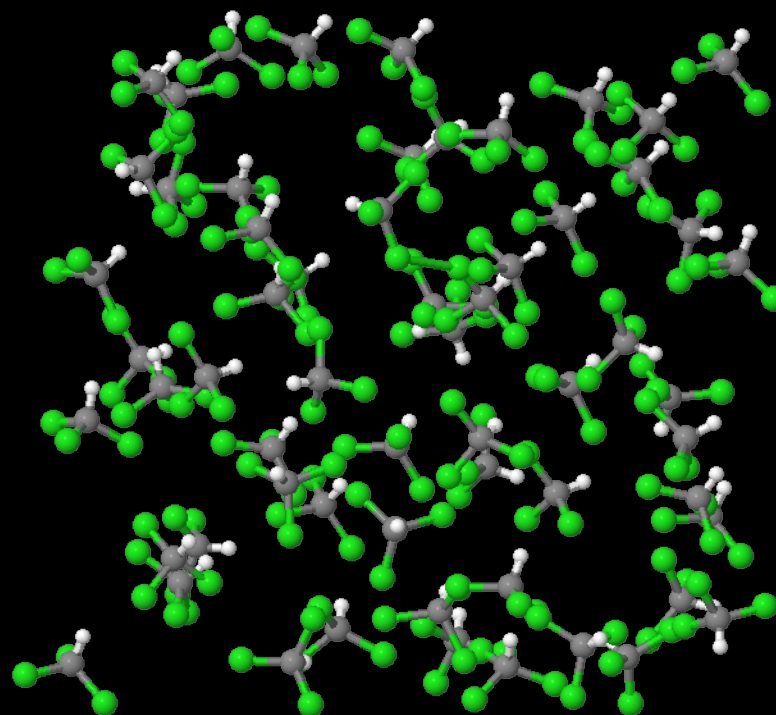
Question: How does the liquid environment affect non-linear optical properties of molecules?

gas-phase EFISH	1.0 ± 4.2	Kaatz <i>et al.</i> , <i>J. Chem. Phys.</i> 108 , 849 (1998)
liquid EFISH	-68 ± 7	Kajzar <i>et al.</i> , <i>Phys. Rev. A</i> 36 , 2210 (1987)

CHCl_3 molecule. Values in atomic units. $\lambda = 1064 \text{ nm}$

Relate experimental measurements in solution to intrinsic molecular properties.

Goal: calculations on snapshots from *ab initio* molecular dynamics, in periodic supercell.



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.

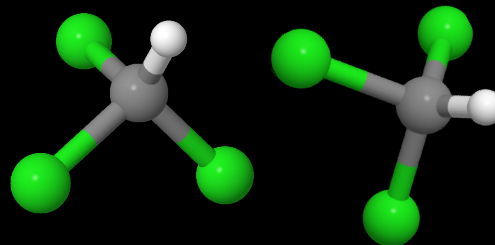
Electric-field-induced second-harmonic generation (EFISH) is coherent third-order process, based on field lining up molecules.

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

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.

$$\beta_{\text{EFISH}}^i = \frac{1}{5} \sum_j (\beta_{ijj} + \beta_{jij} + \beta_{jji})$$

Vertical-vertical and horizontal-vertical polarizations for experiment.

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

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

Convergence is more demanding for nonlinear response

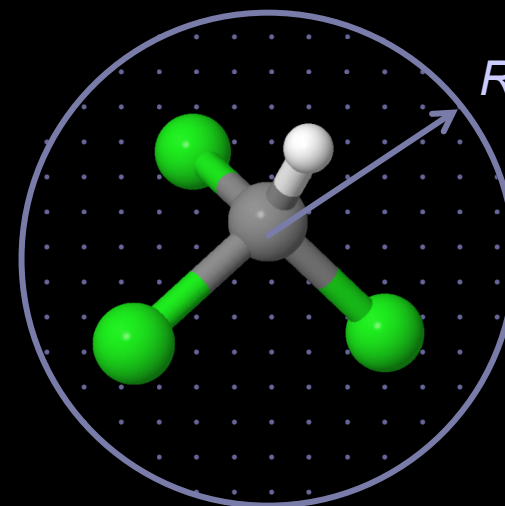
Basis Set	μ_z	α_{yy}	α_{zz}	β_{yyy}	β_{yyz}	β_{zzz}	$\bar{\alpha}$	$\beta_{ }$	$\beta_{\text{HRS}}^{\text{VV}}$
GTO 5Z _{SA} (aug-cc-pV5Z)	0.404	65.70	46.79	27.35	-15.31	22.27	59.40	-5.01	16.90
NBS 5Z4Pe8 (SIESTA)	0.398	65.45	46.28	24.54	-14.90	21.37	59.06	-5.07	15.68
RS 1r (h=0.25, r=22)	0.399	66.02	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)

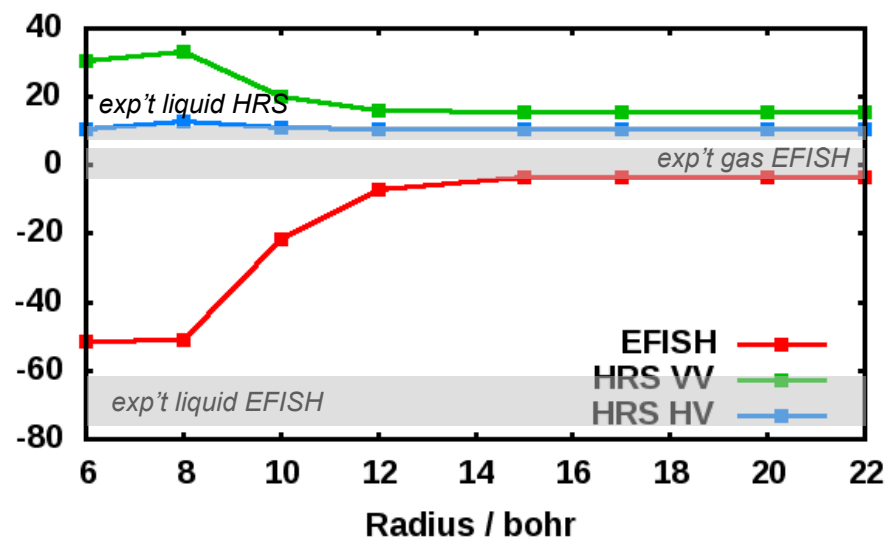
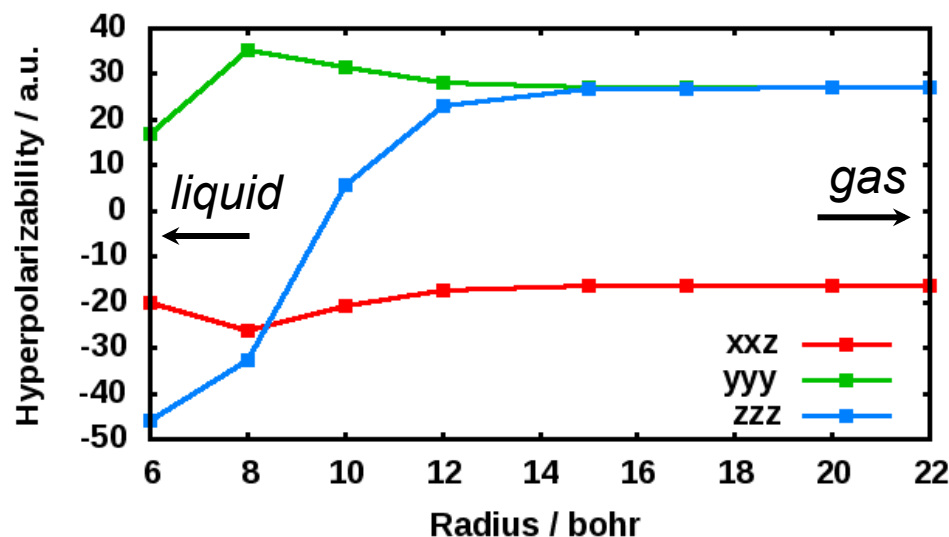
Comparison of Gaussian-type orbitals, SIESTA numerical basis sets, real-space grid: need five-zeta basis sets with diffuse functions, or very long-range real-space grid.

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

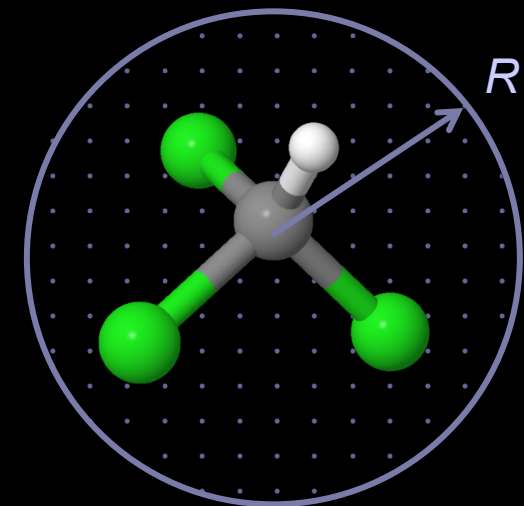
Compare: only $12 a_0$ converges ground state
all atoms contained within $3 a_0$ radius



1. Effect of electronic confinement on molecule



	EFISH (gas)	EFISH (liq)	HRS VV	HRS HV
exp't	1.0 ± 4.2	-68 ± 7	15.7 ± 0.6	9.9 ± 0.4
calc.	-3.47	-51.6	31.0	12.1



Consider sphere with molecular volume of liquid.

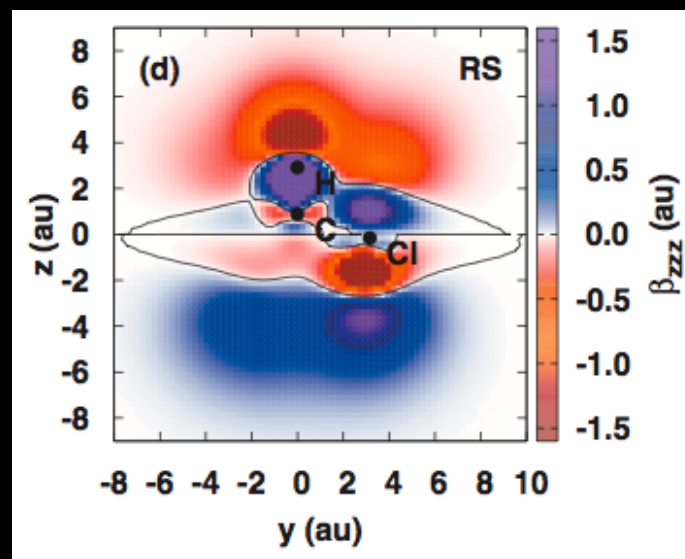
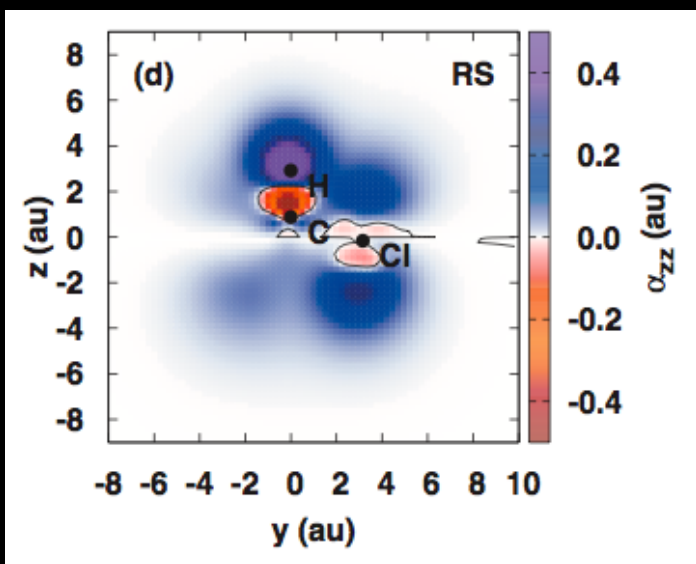
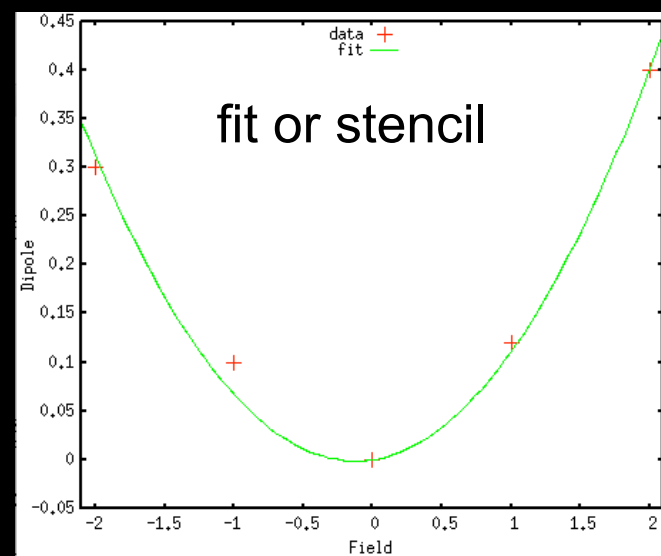
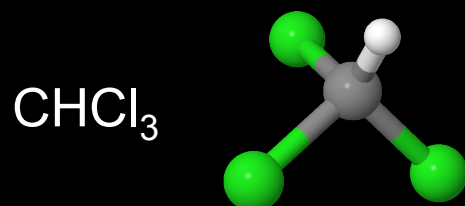
Confinement increases β_{EFISH} magnitude and brings close to liquid values

Theoretical methods for nonlinear response in TDDFT

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!



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

Sternheimer equation

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

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

Calculate variation of occupied wavefunctions in linear response.

One frequency at a time.

$$H = H^{(0)} + H^{(1)} e^{i\omega t}$$

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

$$H_{\alpha\pm}^{(1)} = V_{\alpha\pm}^{(1)} + V_H \left[n_{\alpha\pm}^{(1)} \right] + \int f_{xc} [n] n_{\alpha\pm}^{(1)} (r) d^3r \quad \text{Hartree XC kernel}$$

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

$$P'_n = 1 - \left| \psi_n^{(0)} \right\rangle \left\langle \psi_n^{(0)} \right| \quad \left\langle \psi^{(0)} \right| \psi_{\alpha\pm}^{(1)} \rangle = 0$$

SCF cycle: solve linear equation for each state, update $n^{(1)}$ and $H^{(1)}$.

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

Sternheimer equation: projectors and resonances

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

Project out unperturbed state to enforce standard phase convention.

$$P'_n = 1 - \left| \psi_n^{(0)} \right\rangle \left\langle \psi_n^{(0)} \right| \quad \left\langle \psi^{(0)} \left| \psi_{\alpha\pm}^{(1)} \right\rangle = 0$$

Can also project out occupied states for linear density response.

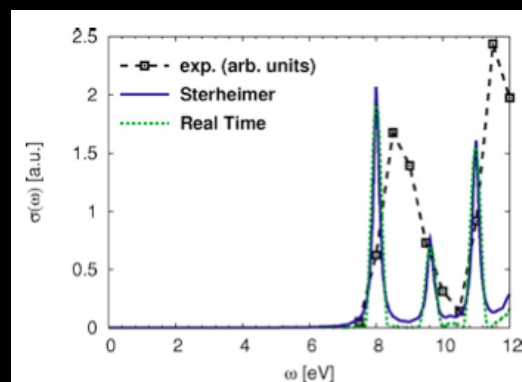
$$n_{\pm}^{(1)} = \sum_n^{\text{occ}} \left(\psi_{n\pm}^{(1)} \left[\psi_n^{(0)} \right]^* + \psi_n^{(0)} \left[\psi_{n\mp}^{(1)} \right]^* \right) = \sum_n^{\text{occ}} \left(P_c \psi_{n\pm}^{(1)} \left[\psi_n^{(0)} \right]^* + \psi_n^{(0)} \left[P_c \psi_{n\mp}^{(1)} \right]^* \right)$$

$$P_c = 1 - \sum_n^{\text{occ}} \left| \psi_n^{(0)} \right\rangle \left\langle \psi_n^{(0)} \right| \quad \text{Larger null space: fewer solver iterations.}$$

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

Experiment is broadened anyway.
Allows us to obtain imaginary part
of response as well.

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



Sternheimer equation: $2n+1$ Theorem

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

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

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

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

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

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).

Perturbations in Sternheimer equation

Electric field in finite system: $V = \mathcal{E} \cdot r \quad \frac{\partial H}{\partial \mathcal{E}} = r$

(Can also study response to magnetic fields, ionic displacements, strain, etc.)

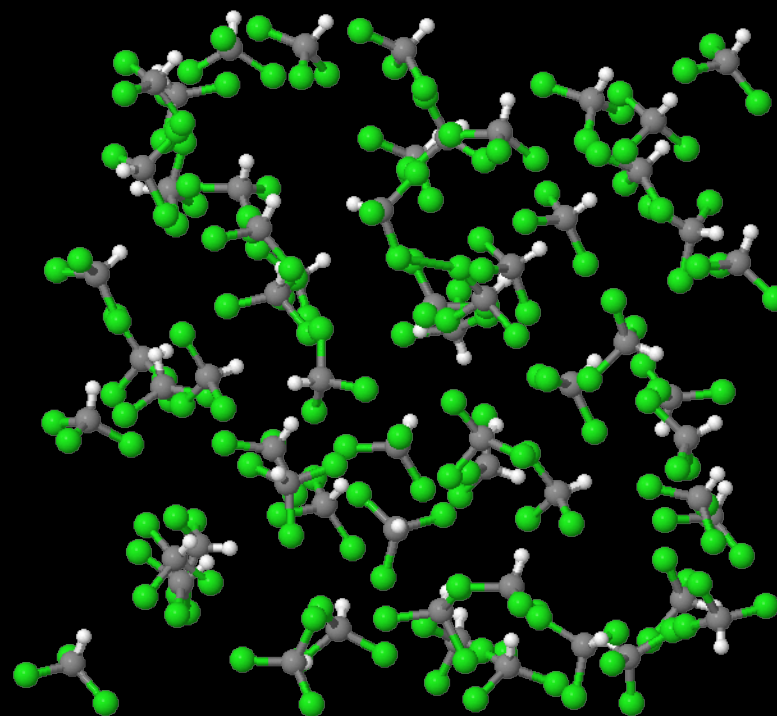
Dipole reformulation with quantum theory of polarization in extended system

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

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

$k \cdot p$ perturbation theory (non-SCF):

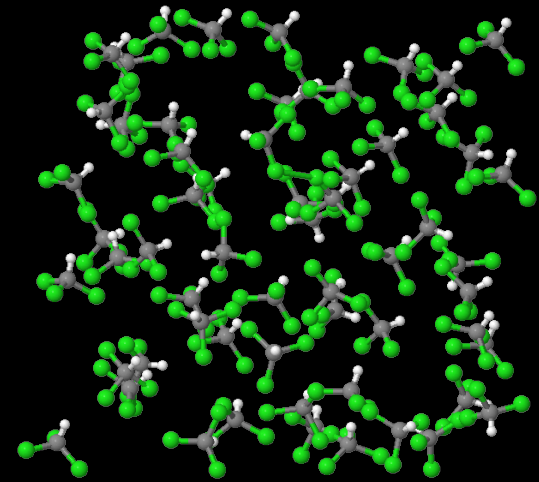
$$\frac{\partial H_k}{\partial k} = -i \nabla + k + [V_{nl}, r]$$



Polarization of a periodic system

Linear response can get derivatives
but not the polarization itself.

$$r \rightarrow -i \frac{\partial}{\partial k}$$



Berry phase with “strings” of k-points:

$$P = -\frac{e}{2\pi} \text{Im} \ln \prod_{ns} \left\{ \left\langle \psi_n(k_s) \left| e^{-2\pi i x/L} \right| \psi_n(k_{s+1}) \right\rangle \right\}$$

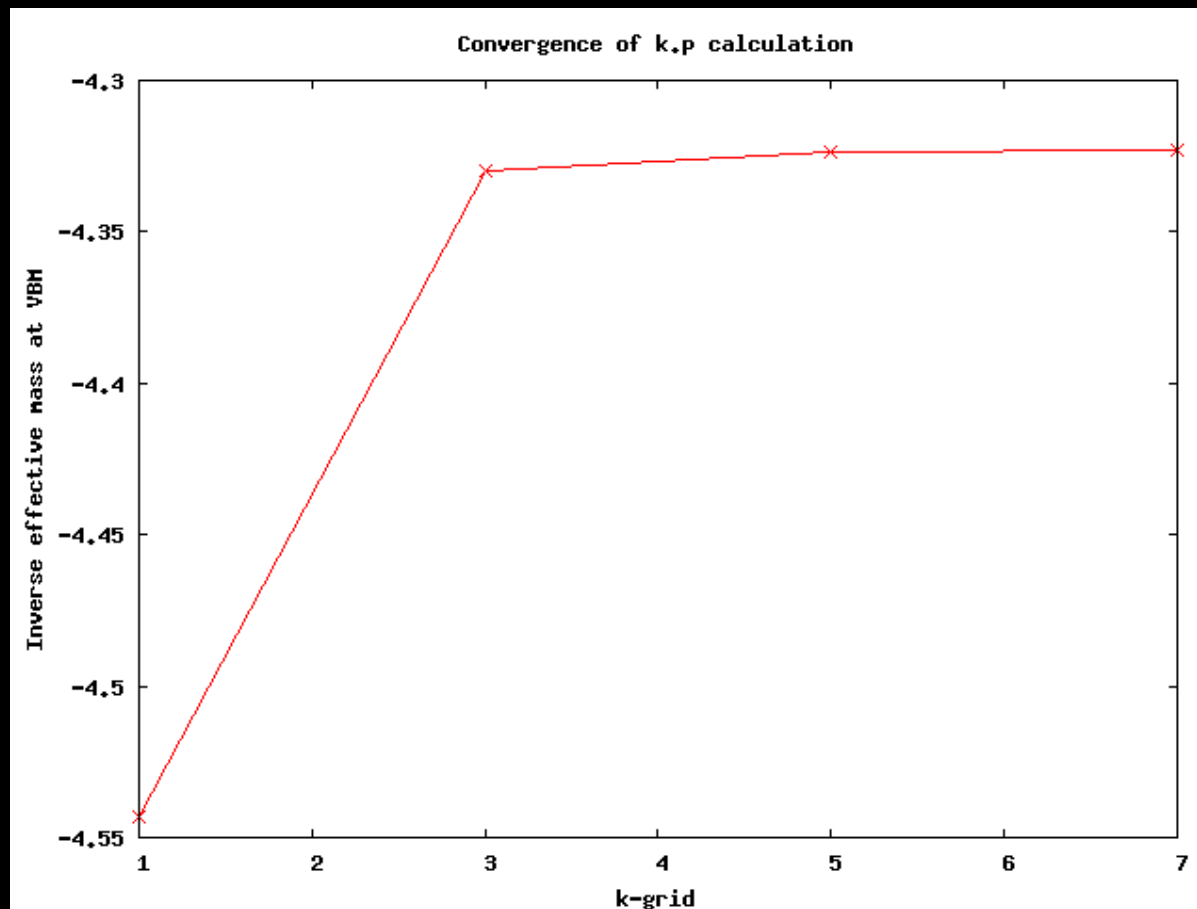
Single-point Berry phase (from just the Γ point)

$$P = -\frac{e}{2\pi} \text{Im} \ln \det \left\{ \left\langle \psi_m \left| e^{-2\pi i x/L} \right| \psi_n \right\rangle \right\}$$

Yaschenko, Fu, Resca, and Resta, PRB 58, 1222 (1998)

Si $k.p$ perturbation

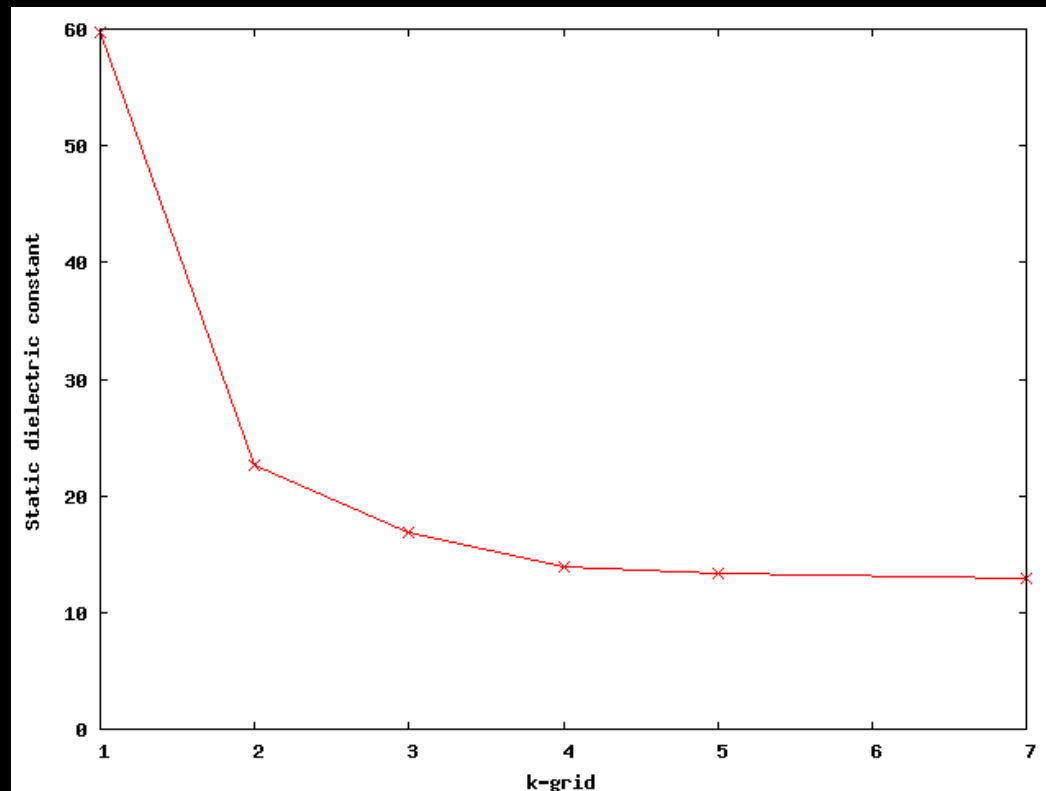
$$\frac{1}{m^*} = \frac{\partial^2 \epsilon_{mk}}{\partial k_i \partial k_j} = \delta_{ij} + 2 \left\langle u_{mk}^{(0)} \left| \frac{\partial H_k}{\partial k_i} \left(-i \frac{\partial}{\partial k_j} \right) u_{mk}^{(0)} \right. \right\rangle$$



Si dielectric constant

$$\alpha_{ij}(\omega) = -e \sum_{m,k}^{\text{occ}} \left[\left(\langle u_{mk}^{(0)} | -i \frac{\partial}{\partial k} \right) | u_{mkj}^{(1)}(\omega) \rangle + \langle u_{mkj}^{(1)}(-\omega) | \left(-i \frac{\partial}{\partial k} | u_{mk}^{(0)} \rangle \right) \right]$$

$$\epsilon_{ij} = \delta_{ij} + 4\pi\alpha_{ij}/V$$



LDA, static: 12.87 vs. 13.1 in literature (“60 special k -points”)

ZH Levine and DC Allan, *Phys Rev Lett* **63**, 1719 (1989)

Vibrational / rotational contributions

Many measurements are at $\lambda = 1064$ nm. For organic molecules, typically:

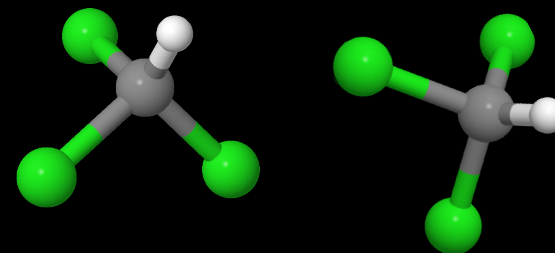
- above vibrational frequencies, so can neglect vibrations
- below electronic resonances so little dispersion

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

Z^* = 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)

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

Calculation of Born effective charges

Standard method: change in polarization for finite atomic displacements. Requires $3N_{\text{atoms}}$ calculations.

$$F_{s\alpha} = \langle \psi | \frac{\partial V_s}{\partial R_\alpha} | \psi \rangle + F_{\text{ion-ion}} + Z_s E$$

$$Z_{s\alpha\beta}^* = \langle \psi'_\beta | \frac{\partial V_s}{\partial R_{s,\alpha}} | \psi \rangle + \text{cc.} + Z_s$$

$$|\psi'_\beta\rangle = \frac{\partial}{\partial \mathcal{E}_\beta} |\psi\rangle \quad Z_{s\alpha\beta}^*(\omega)$$

Example: H₂O molecule

O	-0.47	0.00	0.00	H	0.23	-0.09	0.00	$\Delta = 0.002$
	0.00	-0.32	0.00		-0.07	0.32	0.00	
	0.00	0.00	-0.65		0.00	0.00	0.16	

DFT/GGA, USPP, 22 Ry, 40 a_0 supercell, displacement/polarization method
A Pasquarello and R Resta, *Phys Rev B* **68**, 174302 (2003)

O	-0.51	0.00	0.00	H	0.25	-0.06	0.00	$\Delta = 0.07$
	0.00	-0.34	0.00		-0.07	0.17	0.00	
	0.00	0.00	-0.64		0.00	0.00	0.32	

DFT/GGA, Troullier-Martins PP, 22 Ry, finite system, Octopus

O	-0.53	0.00	0.00	H	0.26	-0.05	0.00	$\Delta = 0.01$
	0.00	-0.36	0.00		-0.07	0.18	0.00	
	0.00	0.00	-0.66		0.00	0.00	0.33	

DFT/GGA, Troullier-Martins PP, 250 Ry, finite system, Octopus

Δ is deviation from acoustic sum rule

Linear solvers

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

Sparse: iteration with only matrix-vector products cheaper than inversion.
General advice: focus on preconditioner, not solver.

$$Ax = y \quad PAx = Py$$

Use smoothing. But effective preconditioners are hard in real space (especially in periodic systems).

Y Saad, *Iterative methods for sparse linear systems* (2000)

Krylov subspace methods

conjugate gradients (CG): Hermitian

biconjugate gradients (BiCG)

biconjugate gradients stabilized (BiCGSTAB)

quasi-minimal residual (QMR)

complex symmetric

general

symmetrized

symmetric: $a_{ij} = a_{ji}$, $A = A^T$

Hermitian: $a_{ij} = a_{ji}^*$, $A = A^\dagger$

$$\longrightarrow A^T Ax = A^T y$$

Linear solvers

$$Ax = y \quad \left(H^{(0)} - \epsilon^{(0)} \pm \omega_\alpha \right) P'_n \psi_{\alpha\pm}^{(1)} = -P'_n H_{\alpha\pm}^{(1)} \psi^{(0)}$$

All have failure conditions where can't make more progress.

QMR > BiCGSTAB > CG > BiCG

Sometimes rectified in next SCF iteration.

Sternheimer matrix: Hermitian if no complex shift

Symmetric only if real (no complex shift AND finite system or periodic Γ -only)

Often assume CG is good enough (as for ground state), but response of CHCl_3 could not be converged by CG. Symmetric QMR was successful.

Hermitian + complex shift can be handled by modifying symmetric QMR with *conjugated* dot product.

$$H^{(0)} - \epsilon^{(0)} + \omega + i\eta \quad \langle u, v \rangle = \sum u_i v_i \rightarrow \sum u_i^* v_i$$

Solver parallelism: over domains in dot products.

Performance on Hermitian system

$k\cdot p$ perturbation for Si 2x2x2 k -sampling (8-atom cubic cell)
no complex shift, so Hermitian. 40 Ry cutoff

Solver	Hamiltonian applications	Elapsed time (min:sec)	States converged?
cg	15k	0:50	most
QMR conj. dot product	11k	0:58	all
QMR symmetrized	138k	17:49	all
QMR general	62k	11:35	all
bicgstab	14k	0:52	none

Performance on non-Hermitian system

electric perturbation for Si 1x1x1 k -sampling
imaginary shift, not Hermitian or symmetric

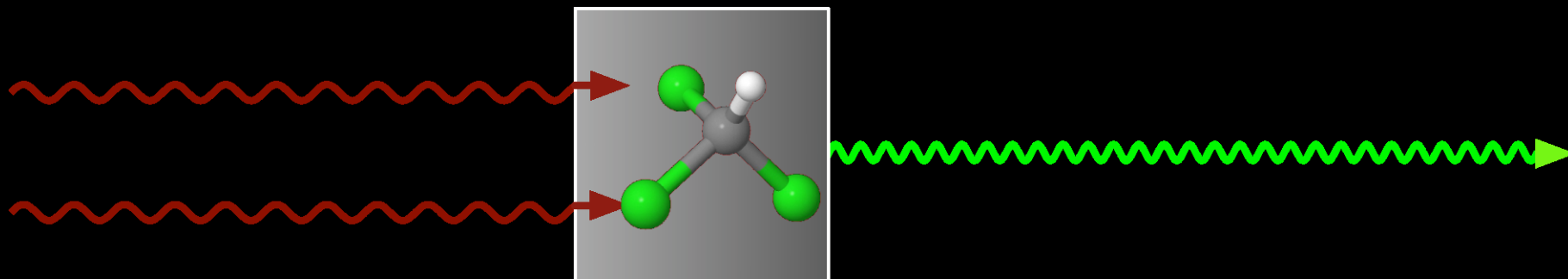
Solver	Hamiltonian applications	Elapsed time (min:sec)	States converged?
QMR conj. dot product	5k	0:40	all
QMR symmetrized	85k	10:57	all
QMR general	-	-	no SCF convergence
bicgstab	5k	0:20	most

The second-order Sternheimer equation

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

$$V_{\mathcal{E}} = -i \frac{\partial}{\partial k} \quad H^{(1)} \left| \psi^{(1)} \right\rangle = \left| \frac{\partial^2 \psi}{\partial k \partial \mathcal{E}} \right\rangle$$

$$\begin{aligned} \left(H^{(0)} - \epsilon^{(0)} \pm \omega_{\alpha} \right) P'_n \psi_{\alpha\pm}^{(1)} &= -P'_n H_{\alpha\pm}^{(1)} \psi^{(0)} \\ \left(H^{(0)} - \epsilon^{(0)} \pm \omega \right) P'_n \psi_{\omega\pm}^{(2)} &= \\ -\frac{1}{2} P'_n \left[\left(H_{\mathcal{E}\pm}^{(1)} - \epsilon_{\mathcal{E}\pm}^{(1)} \right) \psi_k^{(1)} + \left(H_k^{(1)} - \epsilon_k^{(1)} \right) \psi_{\mathcal{E}\pm}^{(1)} \right] &- P'_n H_{\mathcal{E}\pm}^{(2)} \psi^{(0)} \end{aligned}$$



Acknowledgments

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