Density Functional Theory and Nonlinear Optical Properties

Josep M. Luis

1-5 July 2019, Quito, Current Topics in Theoretical Chemistry Workshop

Institute of Computational Chemistry and Catalysis and Department of Chemistry

University of Girona

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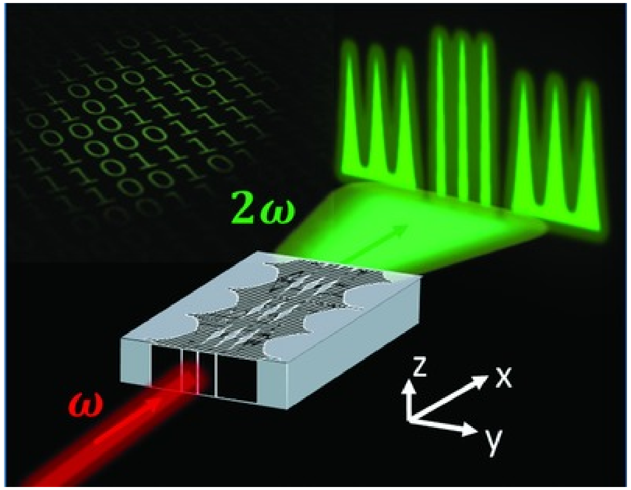
Nonlinear optics

- Interaction of the matter with very high intensity light.
  - Laser light.



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

Nonlinear optical properties

- Taylor series expansion of the molecular dipole moment

$$\mu_a(\omega_\sigma) = \mu_a^{(o)}\,\delta_{\omega_\sigma,0} + \boxed{\alpha_{ab}(-\omega_\sigma;\omega_1)}\,F_b(\omega_1)$$

$$+\frac{1}{2!}K^{(2)}\boxed{\beta_{abc}(-\omega_\sigma;\omega_1,\omega_2)}\,F_b(\omega_1)F_c(\omega_2)$$

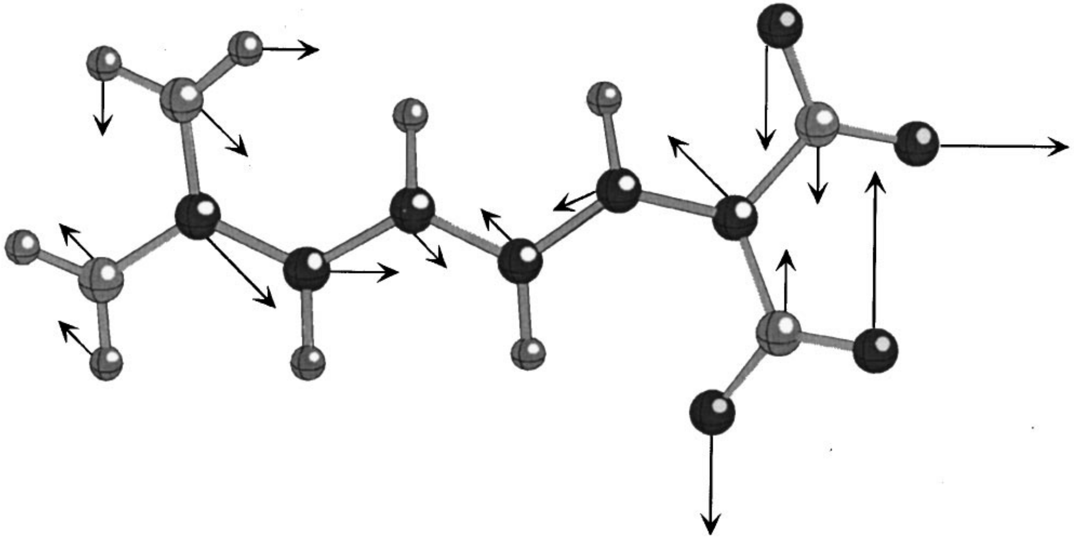
$$+\frac{1}{3!}K^{(3)}\boxed{\gamma_{abcd}(-\omega_\sigma;\omega_1,\omega_2,\omega_3)}\,F_b(\omega_1)F_c(\omega_2)F_d(\omega_3)+\ldots$$

D. P. Shelton, J. E. Rice, Chem. Rev. **1994**, 94, 3.

Nonlinear optical properties

- Within the Born–Oppenheimer approximation:
  - Electronic contribution
  - The vibrational contribution

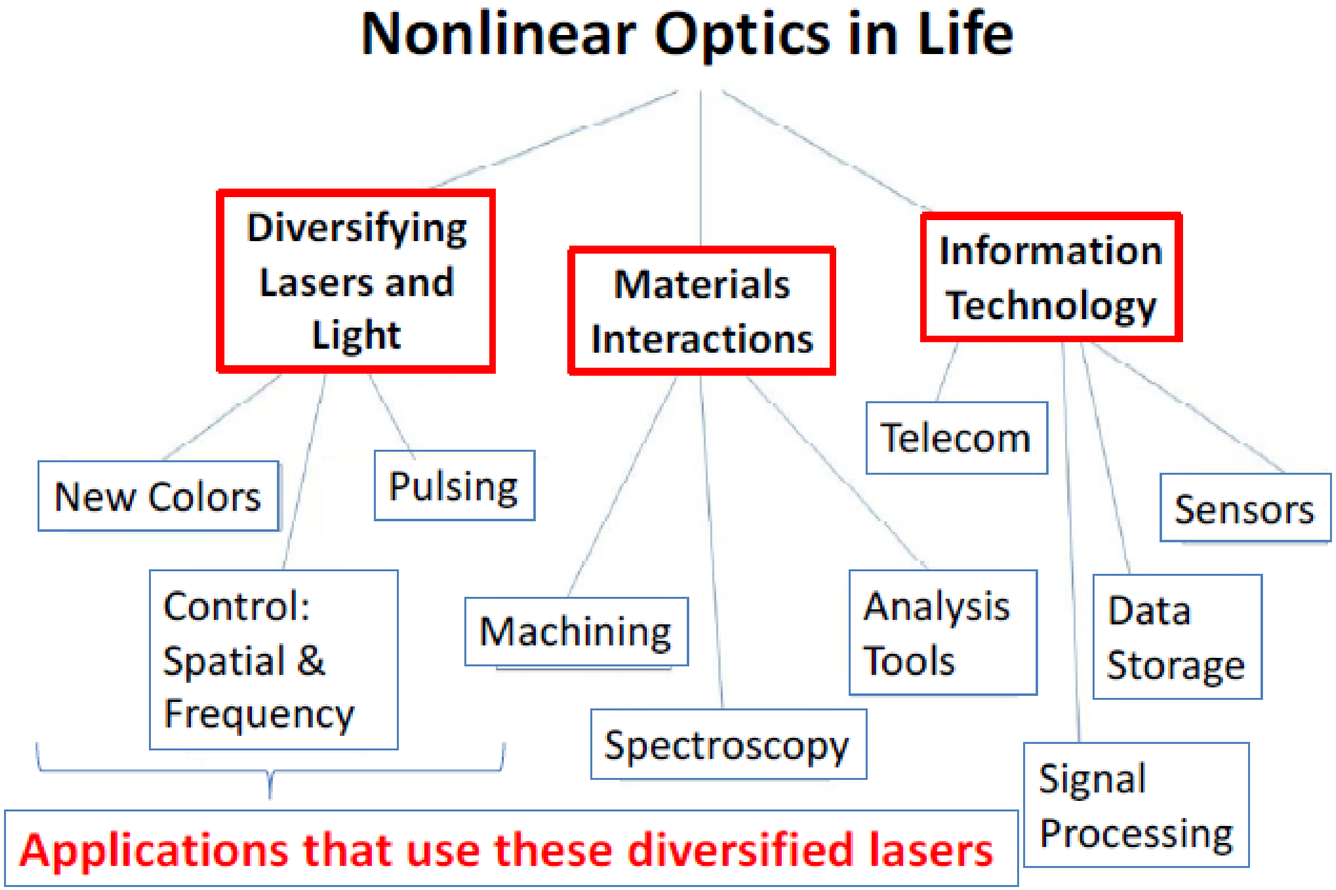
$$P^{tot} = P^{e} + P^{vib}$$



χ_1^L

B. Kirtman, B. Champagne, and J. M. Luis, J. Comput. Chem. **2000,** 21, 1572.

Applications of Nonlinear optics



Nonlinear Optics in Life

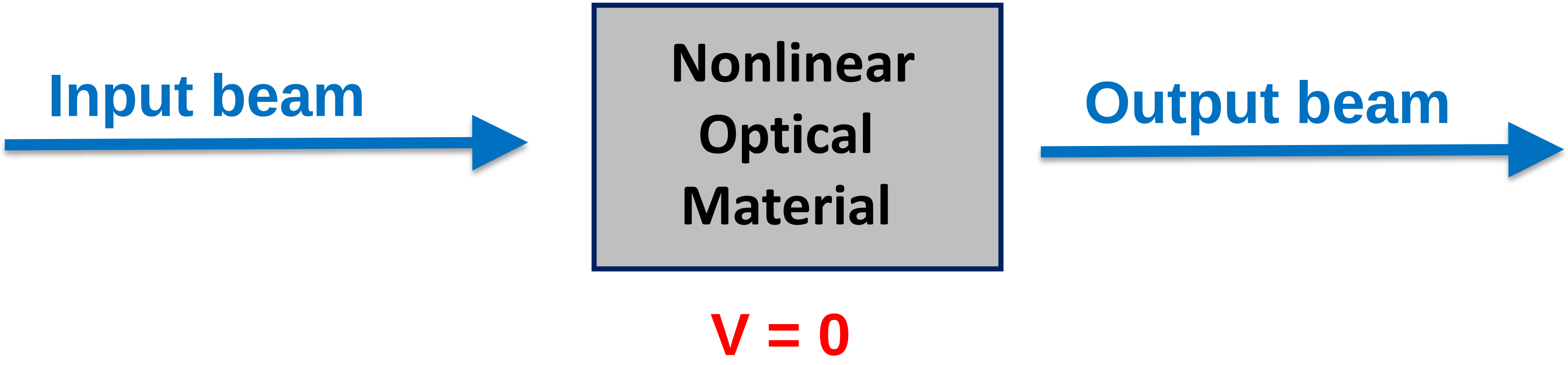
- **Diversifying Lasers and Light**
  - New Colors
  - Control: Spatial & Frequency
  - Pulsing
- **Materials Interactions**
  - Machining
  - Spectroscopy
  - Analysis Tools
- **Information Technology**
  - Telecom
  - Signal Processing
  - Data Storage
  - Sensors

Applications that use these diversified lasers

Elsa Garmire, Optics express, **21**, 30532, 2013.

Applications of Nonlinear optics

- **electro-optical switch**



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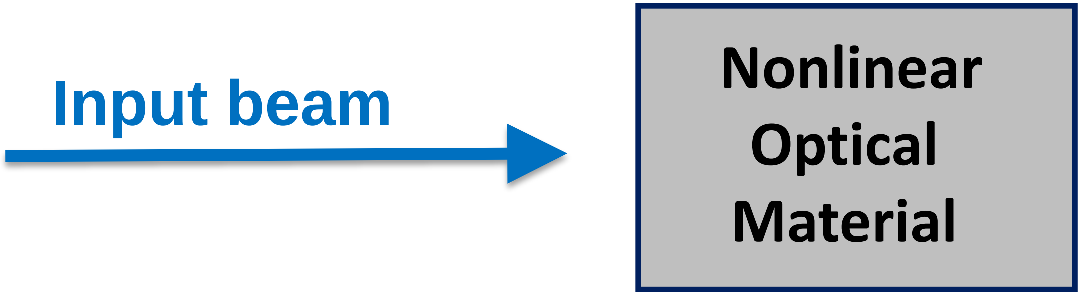
Applications of Nonlinear optics

- **electro-optical switch**

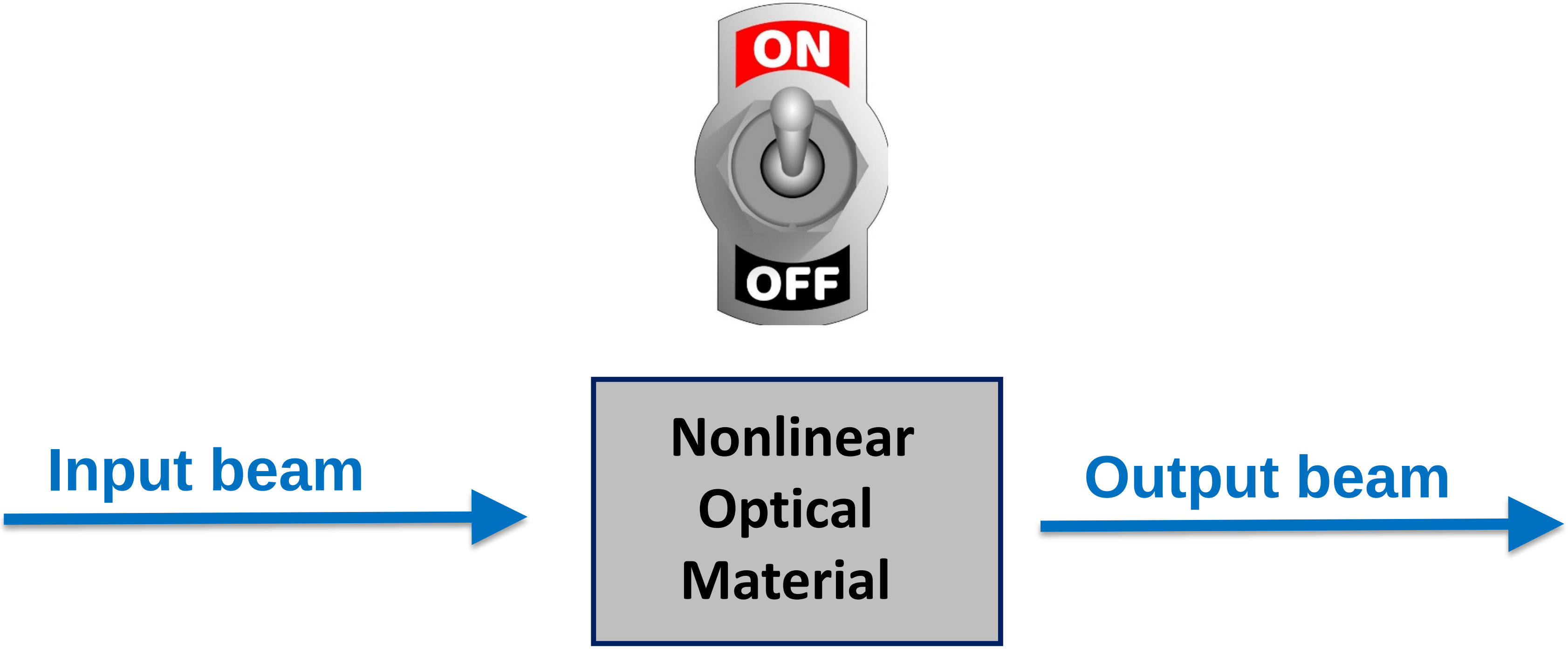


$V = V_{off}$

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

Applications of Nonlinear optics

- **ultrafast all-optical switch**



Input beam

Nonlinear
Optical
Material

Output beam

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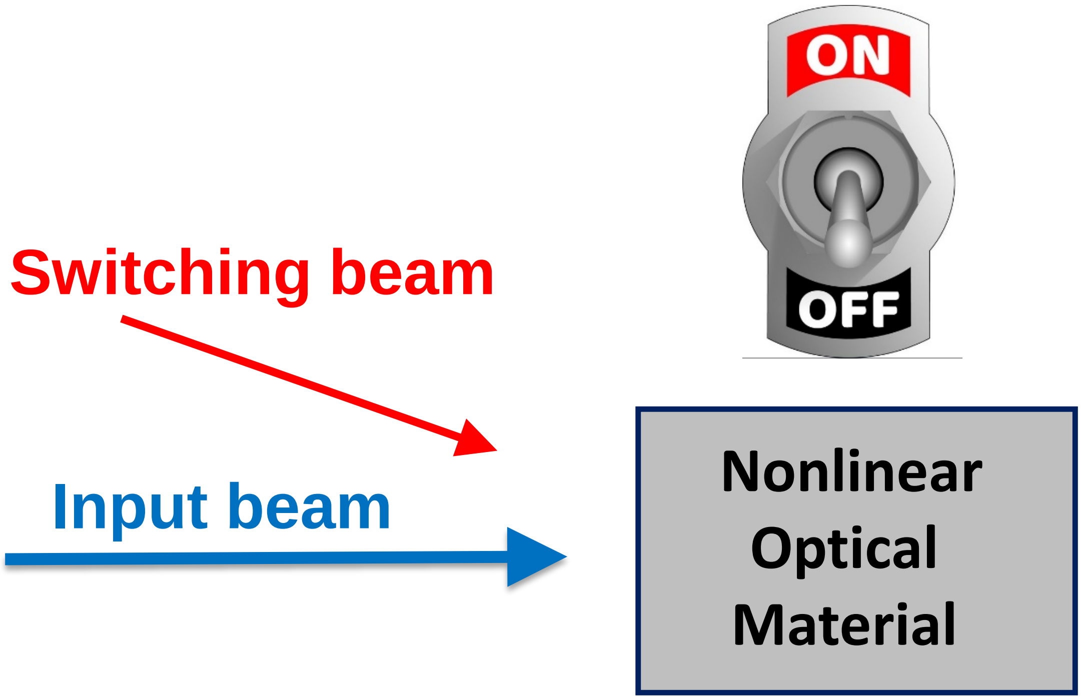
Applications of Nonlinear optics

- **ultrafast all-optical switch**



Switching beam

Input beam

Nonlinear
Optical
Material

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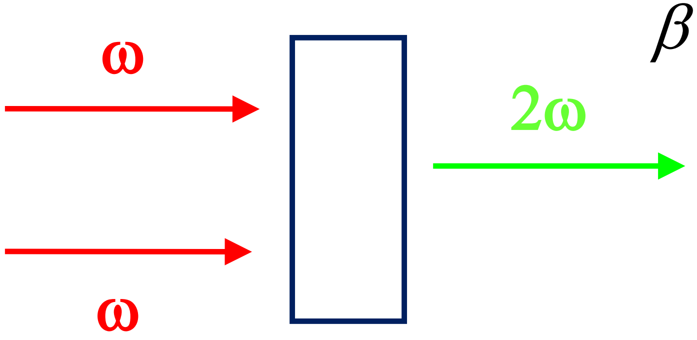
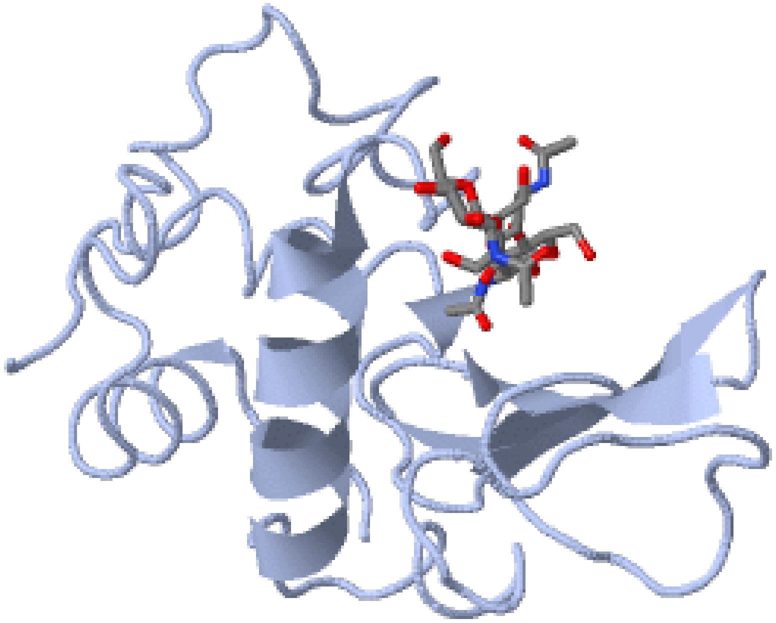
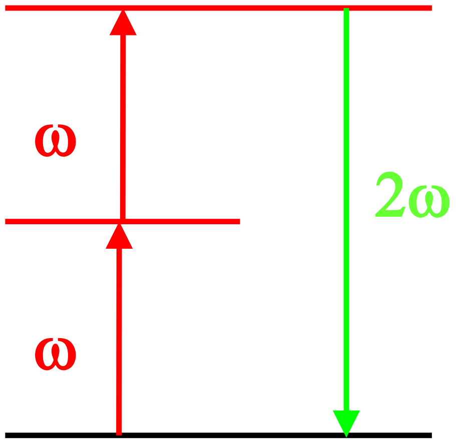
Applications of Nonlinear optics

- **Adsorption of lysozyme on GNPs from second harmonic light scattering**



$$\beta_{abcd}(-2\omega;\omega,\omega)$$

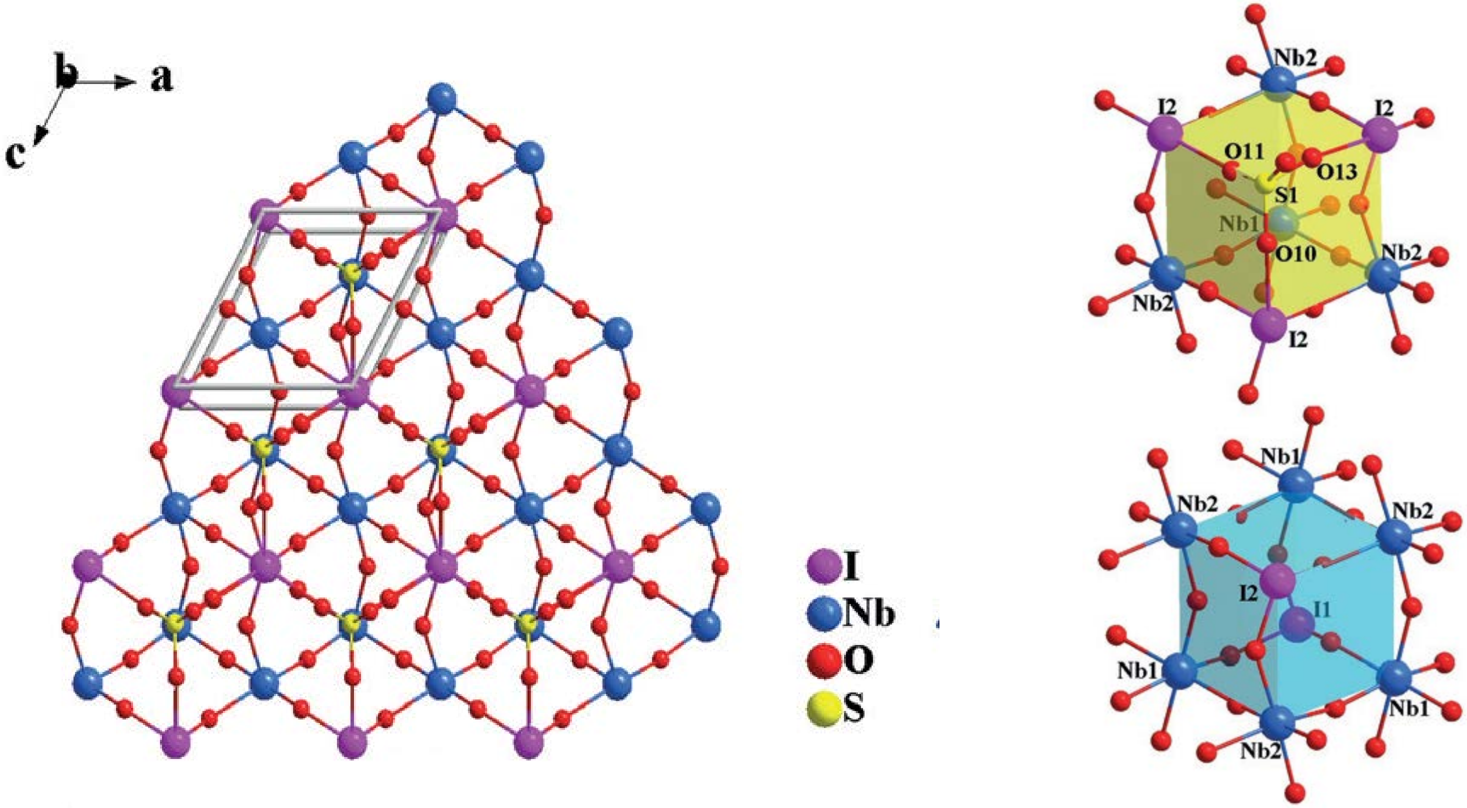




K. Mishra, P. K. Das, Phys. Chem. Chem. Phys., **2019**, 21, 7675.

Materials for Nonlinear optics

- **A Niobium Oxyiodate Sulfate with a Strong SHG Response.**
    - **Rational Multi-Component Design guide by DFT calculations.**



H.-X. Tang, *et al.,* Angew. Chem. Int. Ed. **2019**, 58, 3824.

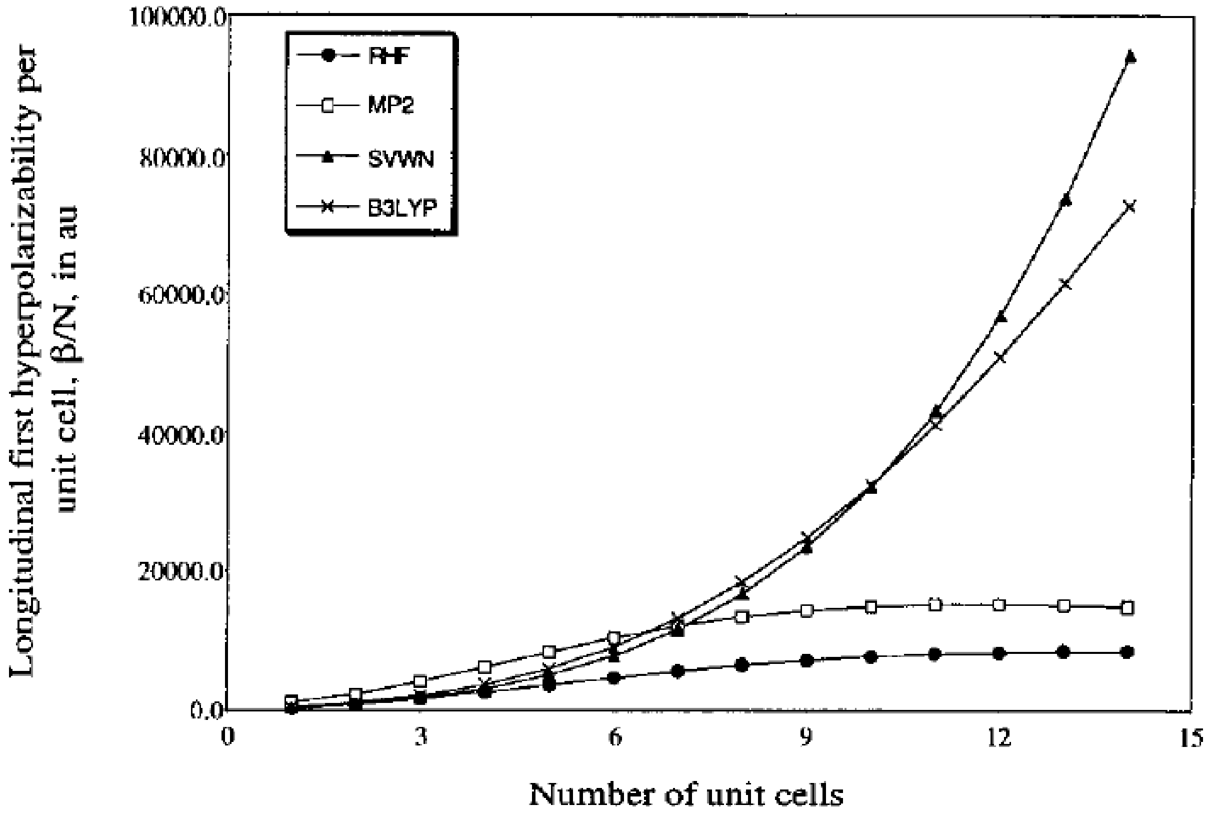
Nonlinear Optical Properties and DFT

- Can **DFA** be trusted for the calculation of **NLOPs**?
  - Conventional GGA XC functionals → unsuitable for NLOP.
  - Increasing PA chain length → **Catastrophic** overestimation.
  - C potential → small role in the error.
  - **Short-sightedness** of the X potential.
    - → Wrong electric field induced charge polarization.

S. J. A. van Gisbergen *et al.* Phys. Rev. Lett. **1999**, 83, 694.
B. Champagne *et* al., J. Phys. Chem. A **2000**, 104, 4755-4763

Nonlinear Optical Properties and DFT

- DFAs with Hartree-Fock exchange.
  - Hybrid functionals → Catastrophic NLOP overestimation.
    - $NH_2(CH=CH)_nNO_2$



B. Champagne *et* al., J. Phys. Chem. A **2000**, 104, 4755-4763

Nonlinear Optical Properties and DFT

- DFAs with Hartree-Fock exchange.
  - Hybrid functionals → Catastrophic NLOP overestimation.

- Long-range corrected DFAs (LC-DFAs).
  - Large amount of long range Hartree-Fock exchange.
  - Improvement in NLOP calculations.
  - Not good enough accuracy.

- DFAs for NLOP?

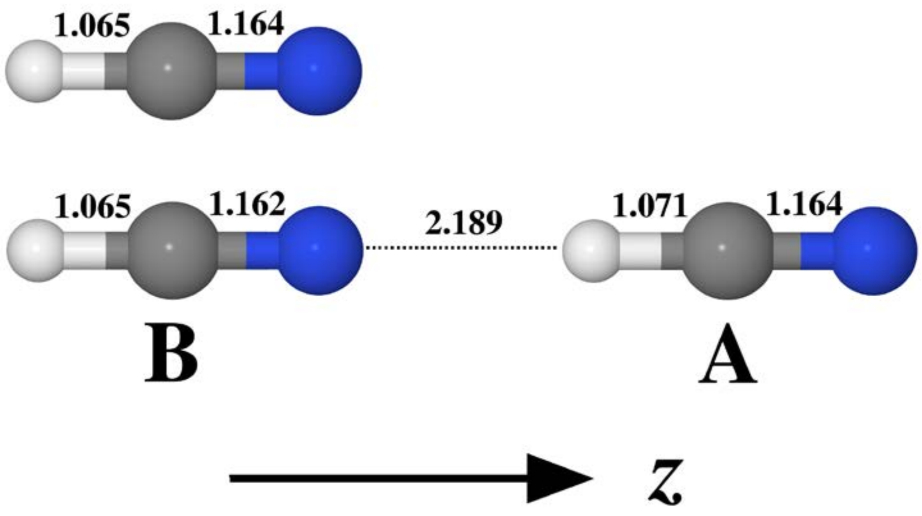
A. Savin, in Recent Developments and Applications of Modern Density Functional Theory, Ed. J. M. Seminario (Elsevier, Amsterdam, 1996), p. 327.
H. Iikura, T. Tsuneda, T. Yanai and K. Hirao, J. Chem. Phys. **2001,** 115, 3540.

Nonlinear Optical Properties and DFT

- Goals:
  - Evaluation of **performance of DFAs** to compute **NLOPs.**
    - **H-bond** dimers.
    - Electronic and **vibrational** contributions.
  - Design of **new LC-DFAs** to compute **NLOPs**.

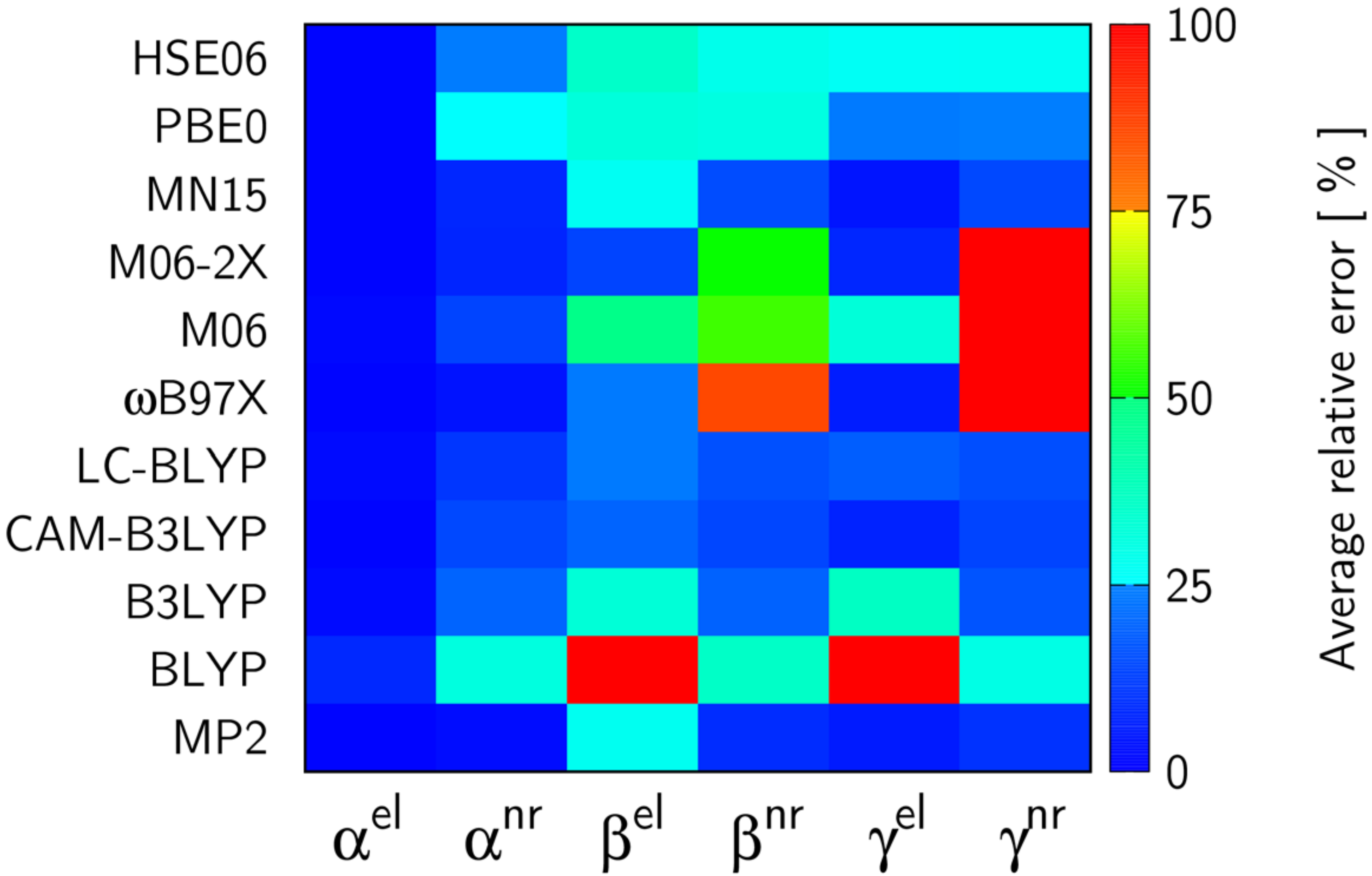
NLOPs of Hydrogen-bonded dimers

- CCSD(T)/aug-cc-pVQZ.
- HCN···HCN, HCN···HNC, HCN···HF, HCN···HCl, HNC···HCN, OC···HF, N_2···HF, FCN···HCCH, FCN···HCCF
- BLYP, B3LYP, CAM-B3LYP, LC-BLYP, wB97X, M06, M06-2X, MN15, PBE0 and HSE06.



R. Zalesny, M. Medved, S. Sitkiewicz, E. Matito, Josep M. Luis, J. Chem. Theory Comput **2019**, 15, 3570.

NLOPs of Hydrogen-bonded dimers



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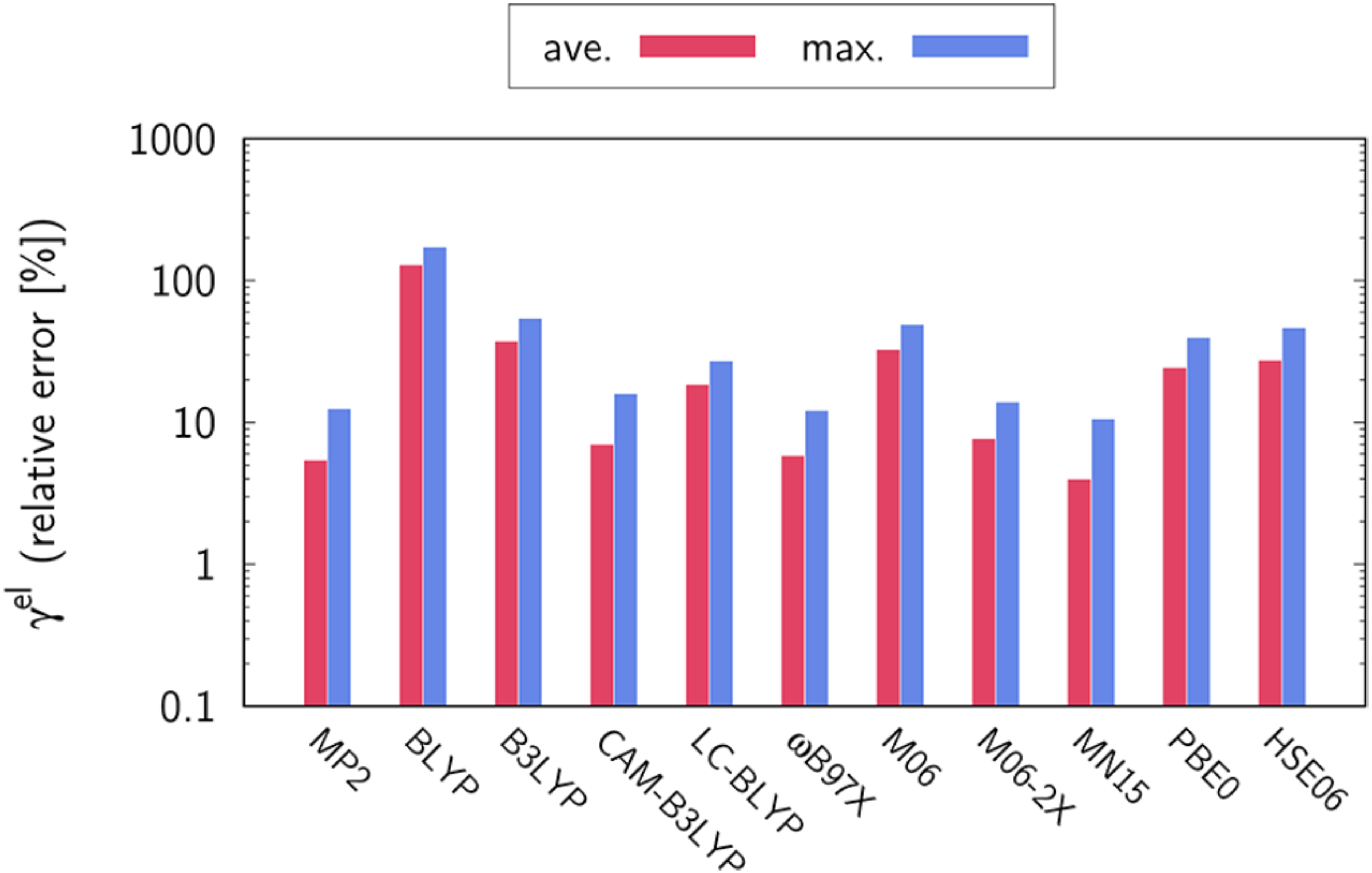

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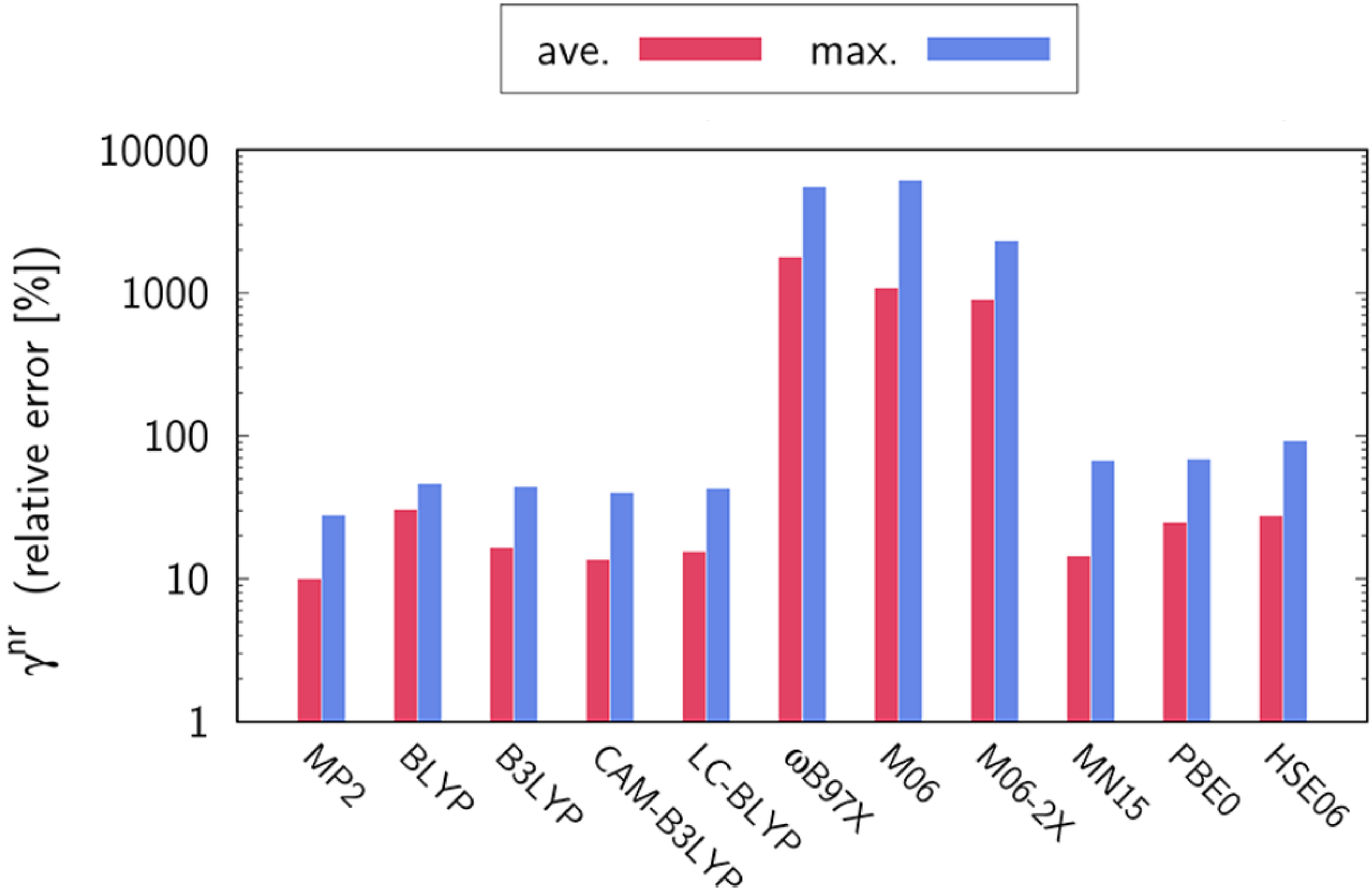

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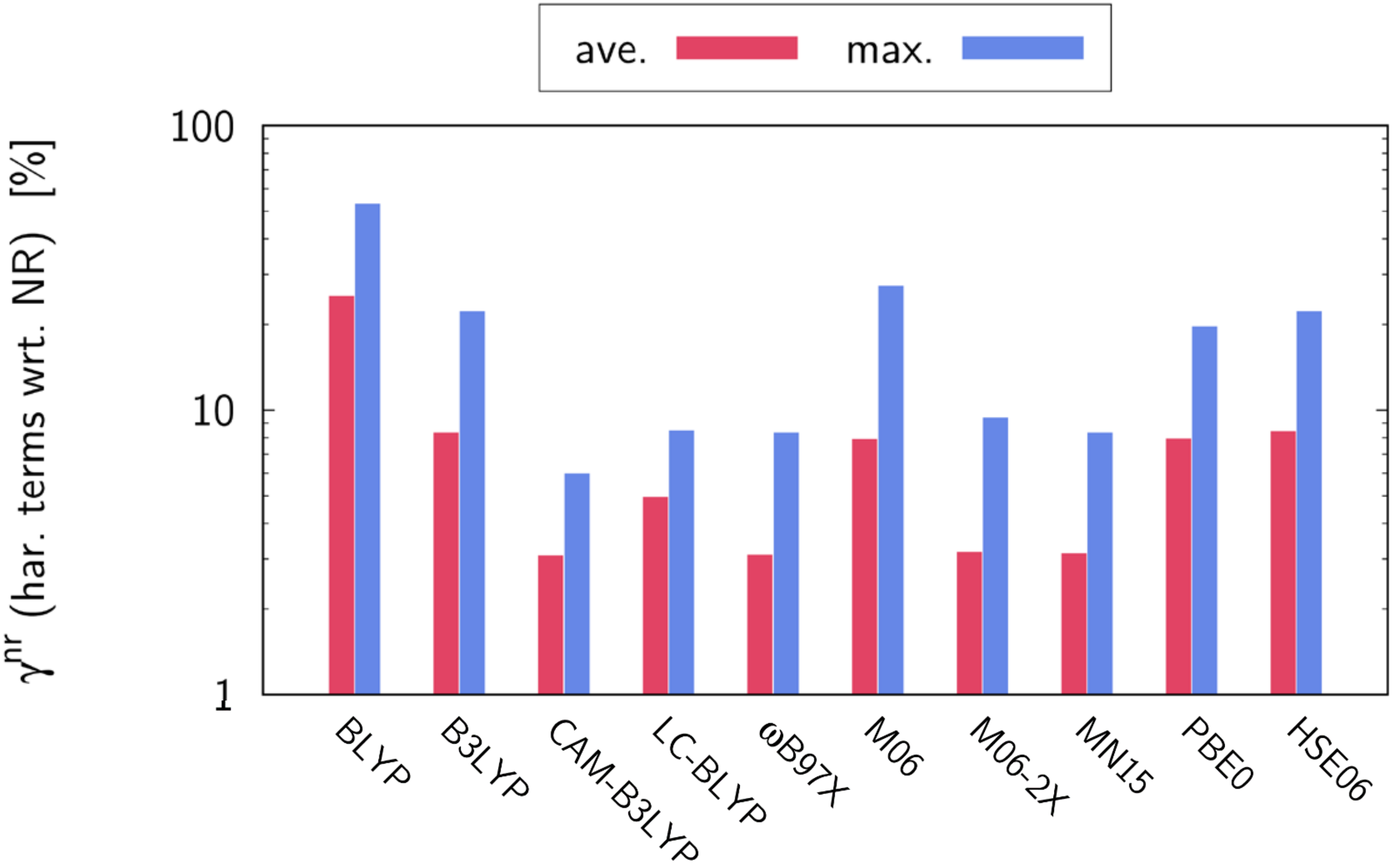

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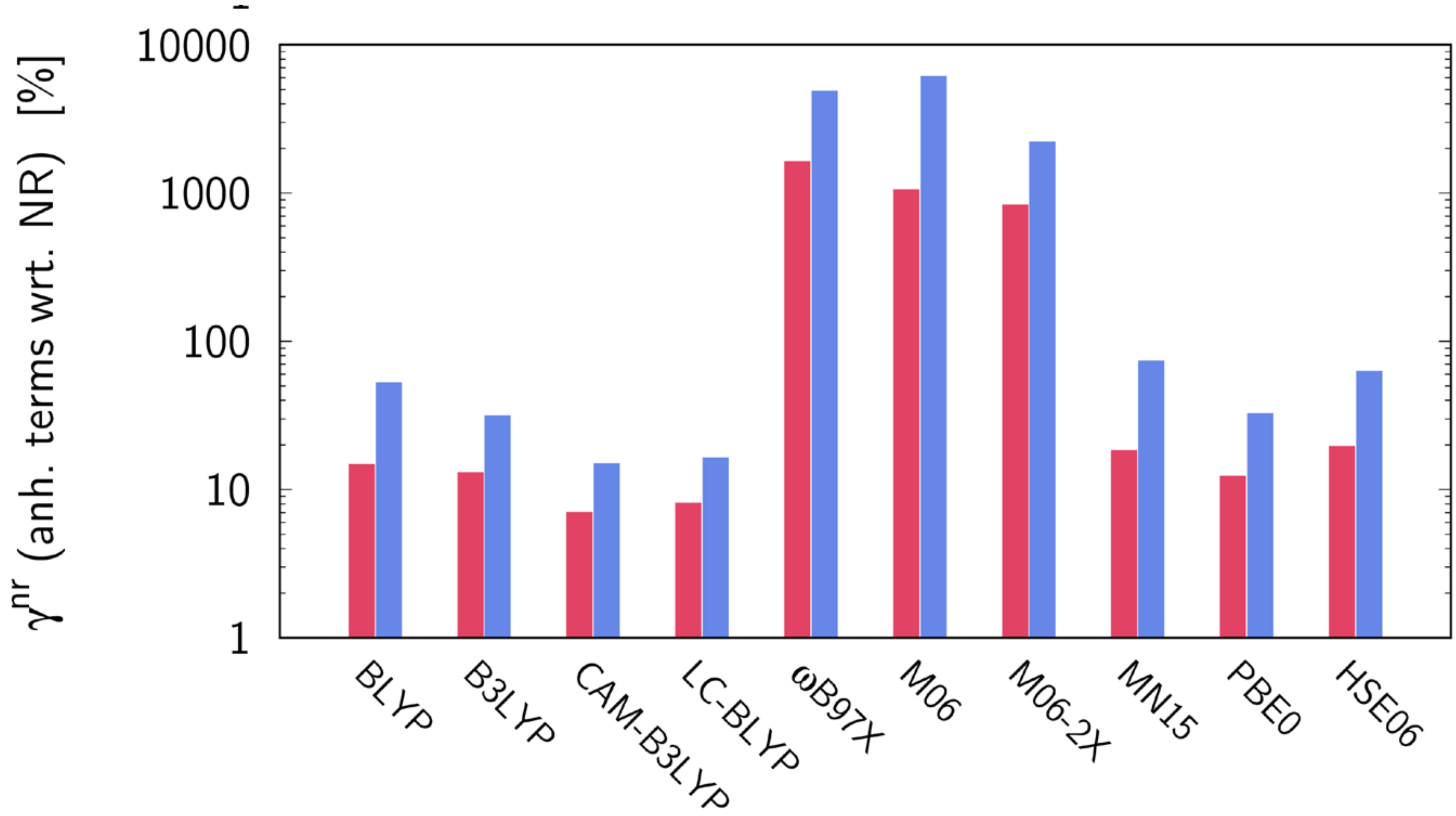
NLOPs of Hydrogen-bonded dimers



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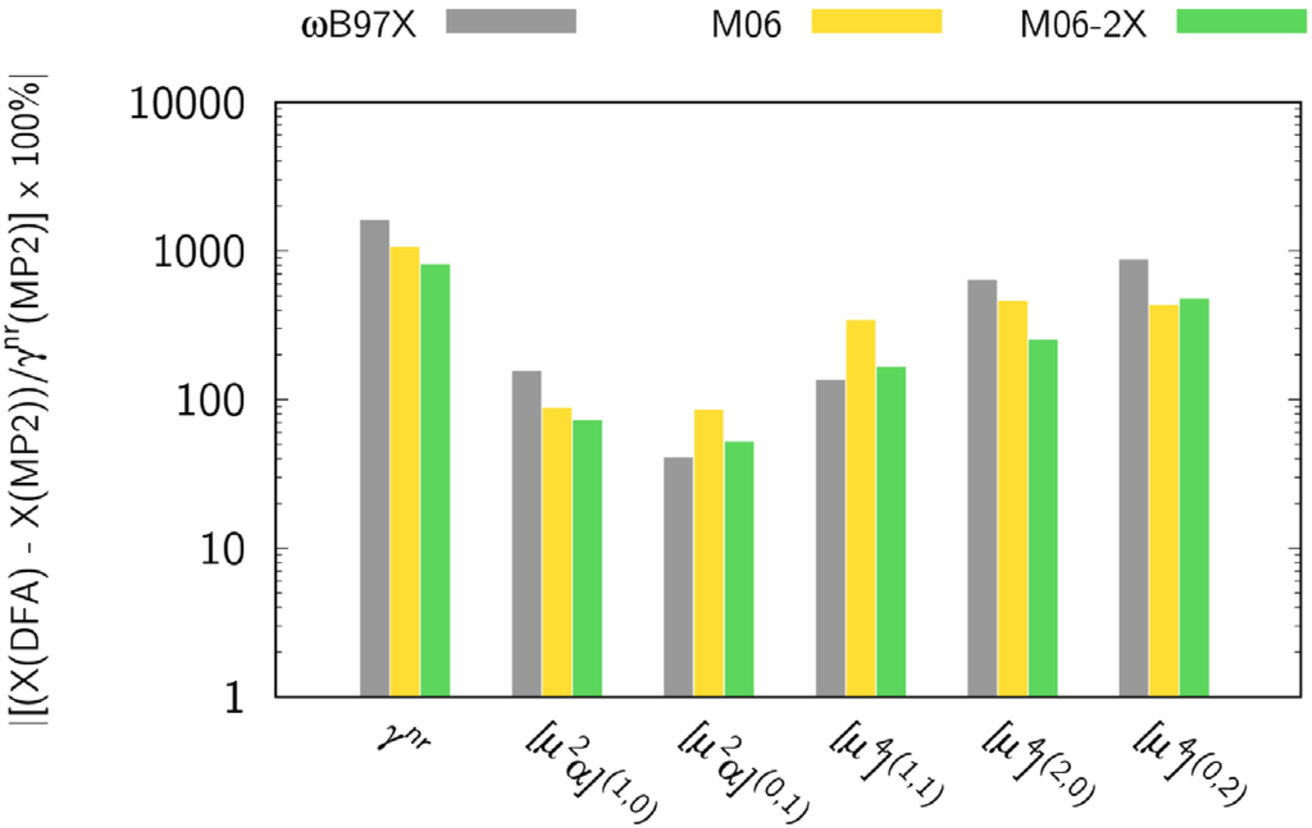
NLOPs of Hydrogen-bonded dimers

- Origin of the error → High order energy derivatives respect to the nuclear coordinates.



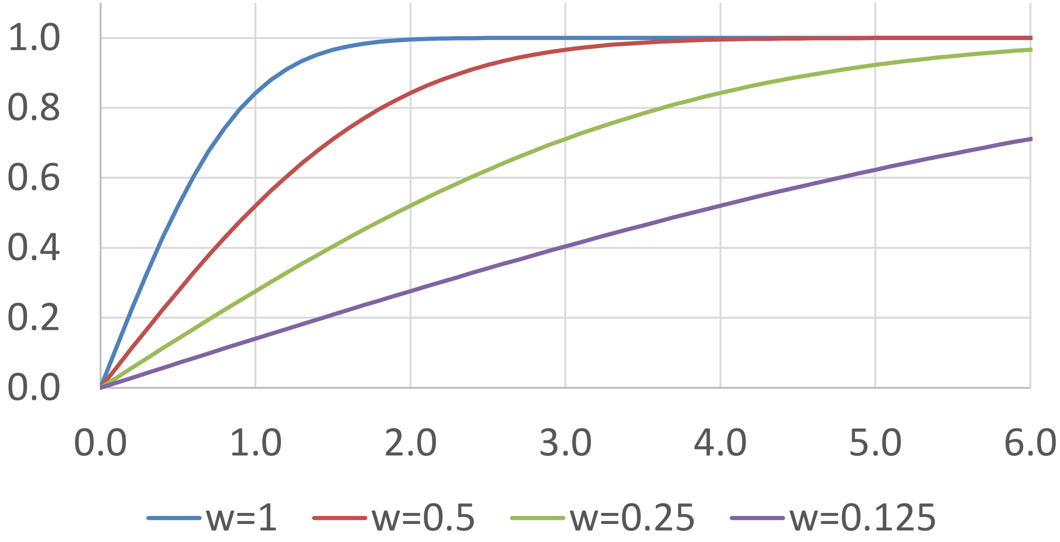
R. Zalesny, M. Medved, S. Sitkiewicz, E. Matito, Josep M. Luis, J. Chem. Theory Comput. **2019**, 15, 3570.

NLOPs and optimally tuned RS-DFTs

- Range-separated functionals (e.g. LC-BLYP) → Best DFA for NLO.
  - Short-range DFT exchange + Long-range HF exchange.

$$\frac{1}{r_{12}} = \frac{1-\left[\alpha + \beta \cdot erf\left(\mu \cdot r_{12}\right)\right]}{r_{12}} + \frac{\left[\alpha + \beta \cdot erf\left(\mu \cdot r_{12}\right)\right]}{r_{12}}$$

  - LC-BLYP ($\mu = 0.47$)



A. Savin, in Recent Developments and Applications of Modern Density Functional Theory, Ed. J. M. Seminario (Elsevier, Amsterdam, 1996), p. 327.
H. Iikura, T. Tsuneda, T. Yanai and K. Hirao, J. Chem. Phys. **2001,** 115, 3540.

NLOPs and optimally tuned RS-DFTs

- OT RS-DFTs → Tune μ for each chemical system

$$J^2(\mu) = \sum_{i=N,N+1} \left[IP_i(\mu) + \varepsilon_i^H(\mu) \right]$$

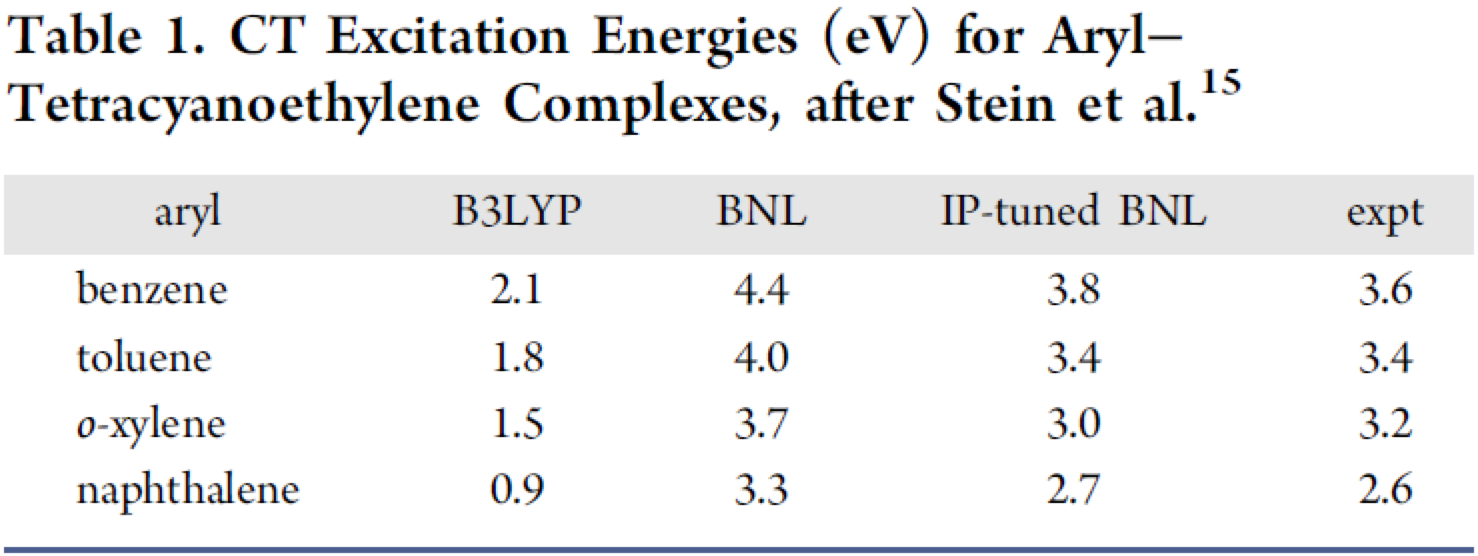
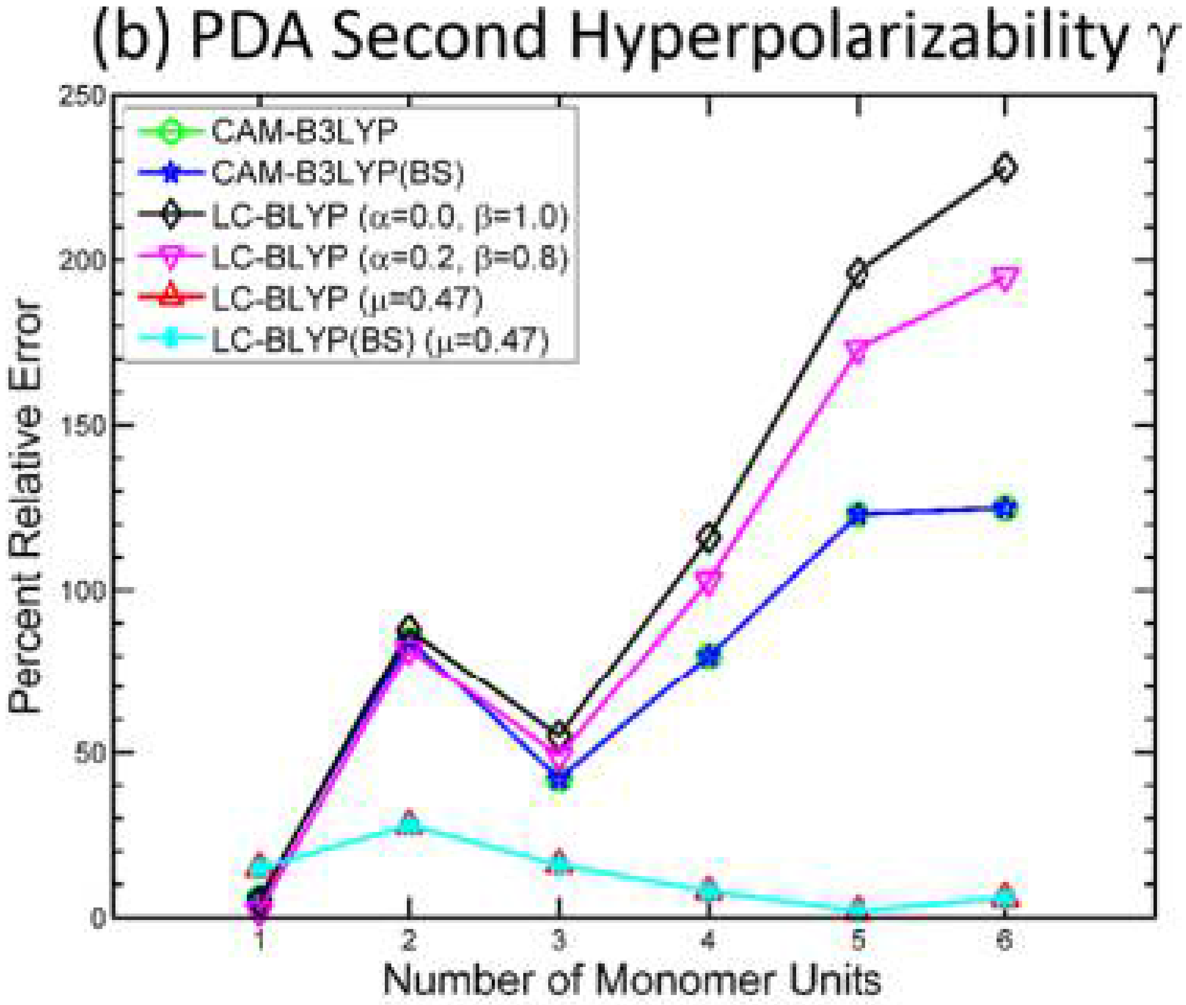


Table 1. CT Excitation Energies (eV) for Aryl–Tetracyanoethylene Complexes, after Stein et al.[15]

aryl	B3LYP	BNL	IP-tuned BNL	expt
benzene	2.1	4.4	3.8	3.6
toluene	1.8	4.0	3.4	3.4
o-xylene	1.5	3.7	3.0	3.2
naphthalene	0.9	3.3	2.7	2.6

R. Baer, E. Livshits, U. Salzner, Theory. Annu. Rev. Phys. Chem. **2010**, 61, 85.
T. Stein, L. Kronik, R. Baer, J. Am. Chem. Soc. **2009**, 131, 2818.

NLOPs and optimally tuned RS-DFTs

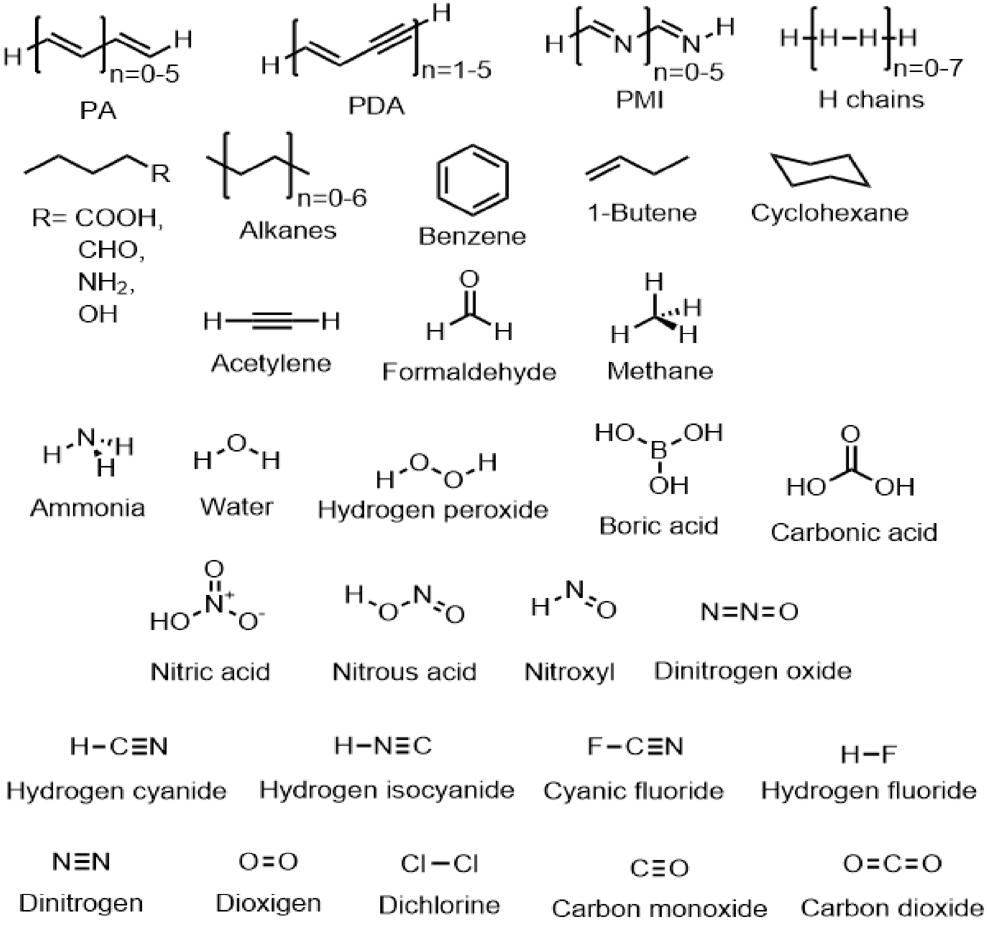


~~NLOP~~

S. Nenon, B. Champagne, M. I. Spassova, Phys. Chem. Chem. Phys. **2014**, 16, 7083.
M. B. Oviedo, N. V. Ilawe, B. M. Wong, J. Chem. Theory Comput. **2016**, 12, 3593.

New NLOP-tailored optimally tuned RS-DFTs

- 60 Chemical systems.



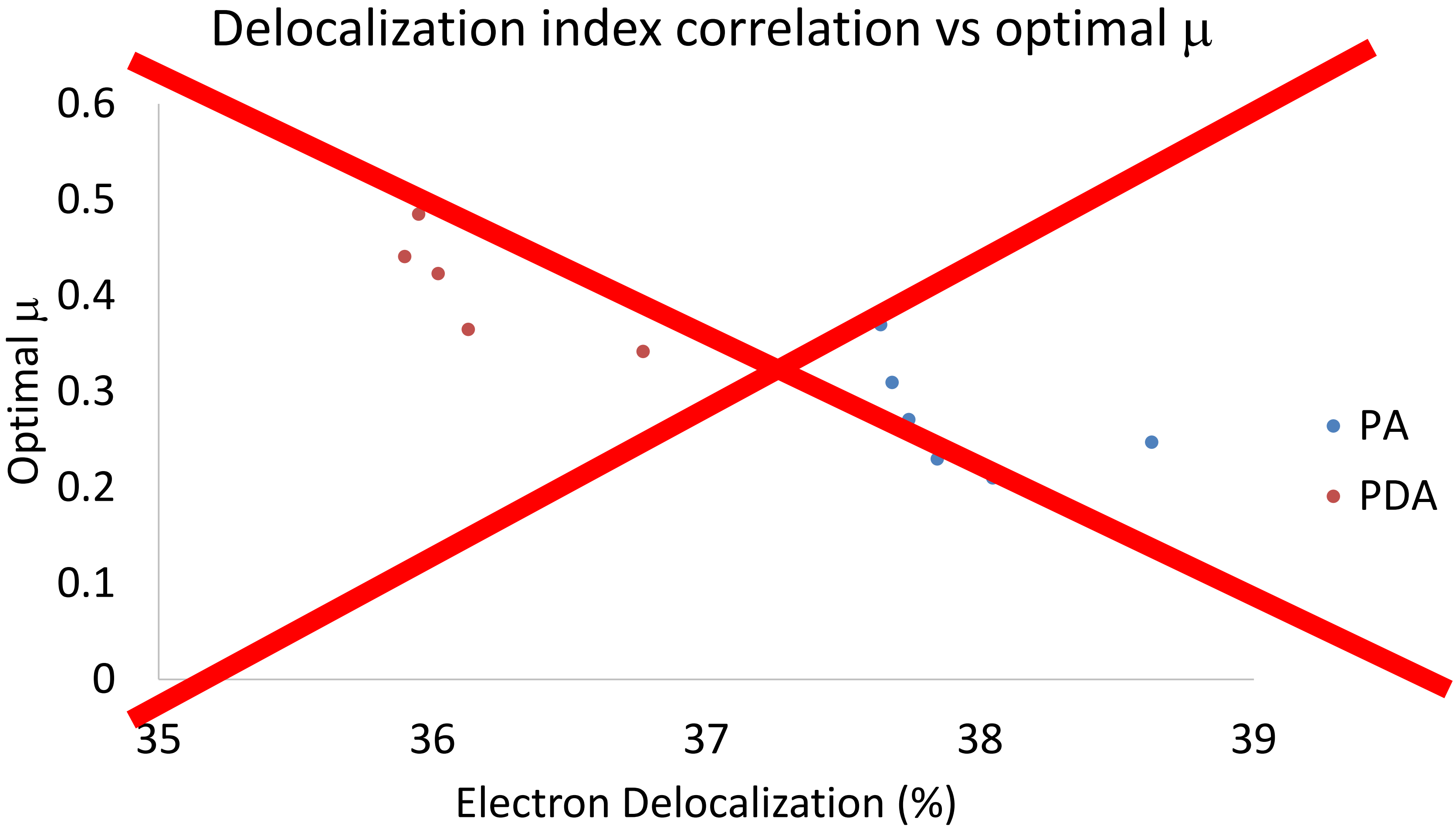
Pau Besalú, Sebastian Sitkiewicz, Pedro Salvador, Eduard Matito, Josep M. Luis, in preparation.

New NLOP-tailored optimally tuned RS-DFTs

- 60 Chemical systems.
  - 33 Small-medium molecules.
  - 27 Oligomers with high NLOP.
- Reference: CCSD(T) NLOPs.
- Starting point: LC-BLYP.
- Optimize μ for each system
  - → Reproduce CCSD(T) NLOPs with tuned LC-BLYP.
- Set of optimal μ → Molecular indicator
  - Prediction of optimal μ to compute the NLOP for each system.

Pau Besalú, Sebastian Sitkiewicz, Pedro Salvador, Eduard Matito, Josep M. Luis, in preparation.

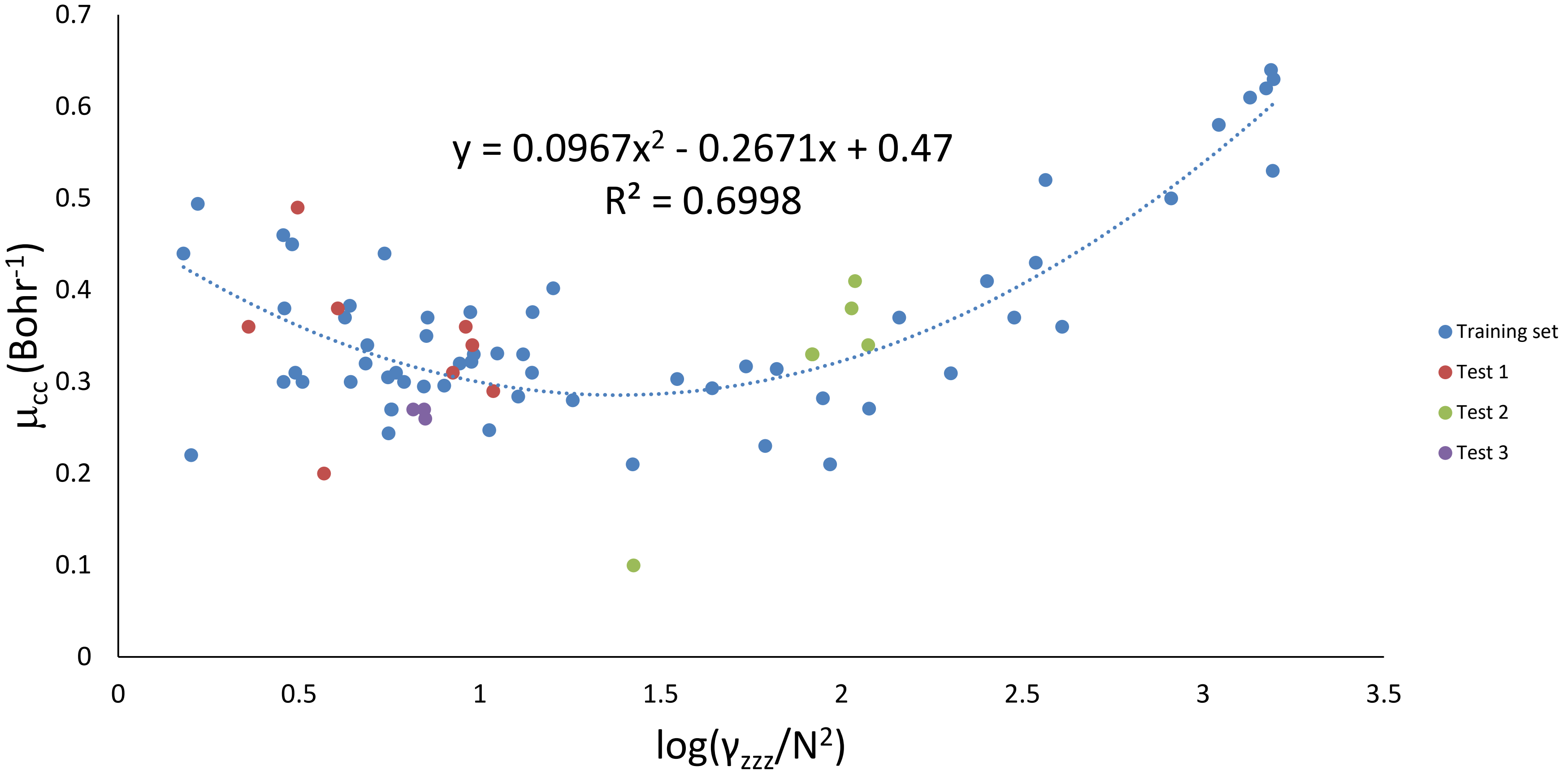
New optimally tuned RS-DFTs



Pau Besalú, Sebastian Sitkiewicz, Pedro Salvador, Eduard Matito, Josep M. Luis, in preparation.

New optimally tuned RS-DFTs

- Indicator: $\log(\gamma^{LC\text{-}BLYP}/N^2)$



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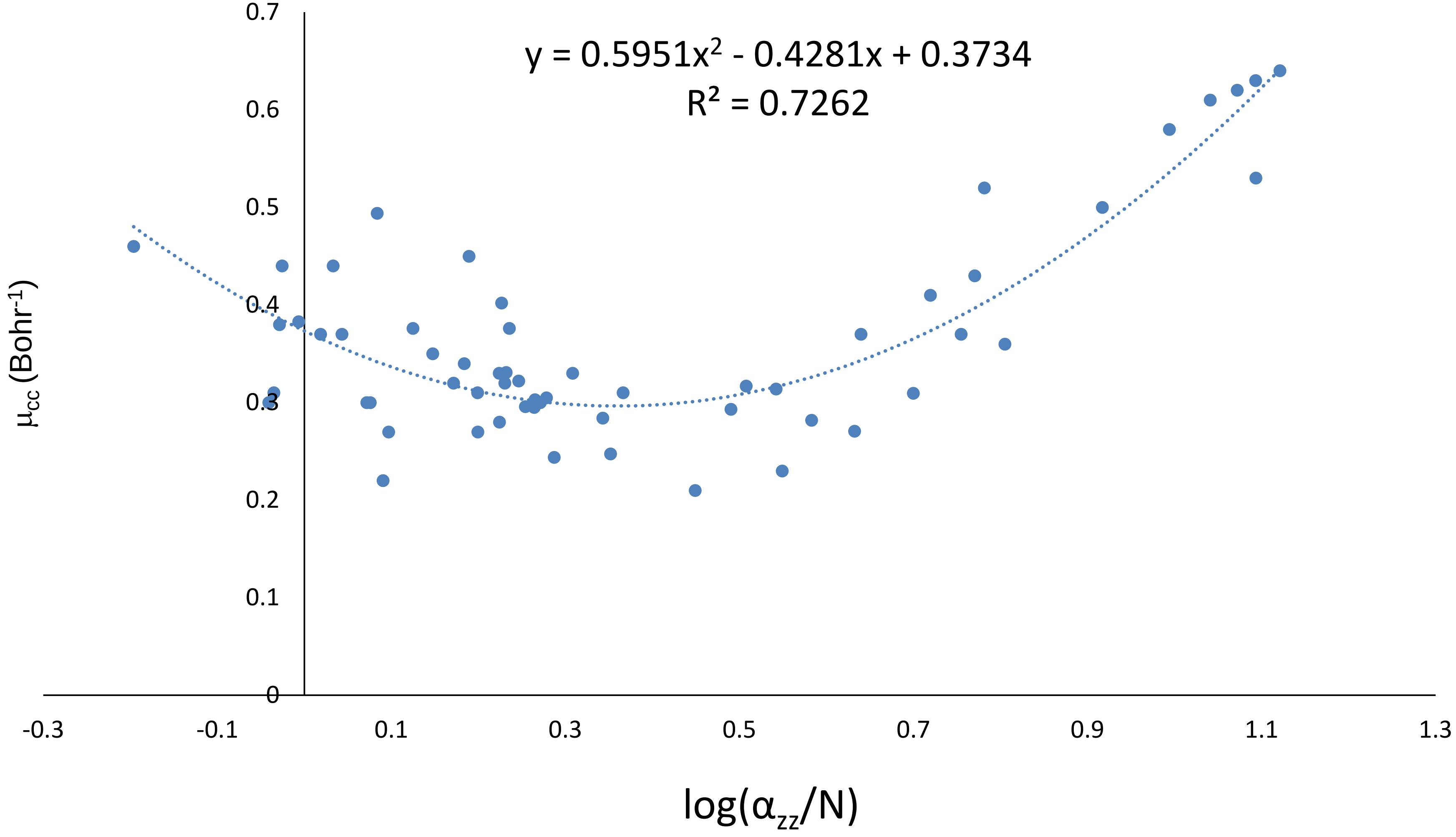
New optimally tuned RS-DFTs

- Indicator: $\log(\alpha^{LC\text{-}BLYP}/N)$.



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New optimally tuned RS-DFTs

- NLOP-tailored OLC-BLYP.

	CAM-B3LYP	LC-BLYP	NLOP OT LC-BLYP
Max Absolute Error	7.7×10^6	2.4×10^6	1.3×10^6
Mean Absolute Error	2.7×10^5	7.4×10^4	3.8×10^4
Max Absolute Relative Error	108.7 %	115.6 %	42.4 %
Mean Absolute Relative Error	22.9 %	20.4 %	8.4%

Pau Besalú, Sebastian Sitkiewicz, Pedro Salvador, Eduard Matito, Josep M. Luis, in preparation.

Summary

- Electronic and vibrational NLOPs of Hydrogen-bonded complexes.
  - CAM-B3LYP → Errors below 20%.
  - LC-BLYP and MN15 → Errors below 30%.
  - wB97x, M06 and M06-2x → Dramatic failure for γ^{NR}.
    - Large errors in high-order energy derivatives respect to nuclear coordinates.
- NLOP-tailored OT LC-BLYP.
  - Optimal tuned μ parameter ↔ log($\alpha^{LC\text{-}BLYP}$/N).
  - More accurate γ than LC-BLYP and CAM-B3LYP.

Acknowledgments

PhD. Students

Steven Roldan
Sergio Fernandez
Sebastian Sitkiewicz
Pau Besalú
Marc Montilla
Liza Petrusevich

Collaborators

Robert Zalesny
Miquel Torrent-Sucarrat
Marc Garcia-Borràs
Heribert Reis
Miquel Solà
Zhi-Ru Li
Miquel Costas
Xavi Ribas
Julio Lloret
Eduard Matito
Pedro Salvador
David Lauvergnat
Miroslav Medved
Bernard Kirtman

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  - Conventional pure XC functionals → unsuitable for NLOP.
  - Increasing PA chain length → **Catastrophic** overestimation.
  - **Short-sightedness** of the X potential → Wrong electric field induced charge polarization.

$$v_{xc}(\boldsymbol{r}) = \int d\boldsymbol{r_1} \frac{\rho(\boldsymbol{r_1})[\bar{g}(\boldsymbol{r},\boldsymbol{r_1}) - 1]}{|\boldsymbol{r} - \boldsymbol{r_1}|} + \frac{1}{2}\int dr_1 \frac{\rho(\boldsymbol{r})\rho(\boldsymbol{r_1})}{|\boldsymbol{r} - \boldsymbol{r_1}|} \frac{\delta\bar{g}(\boldsymbol{r},\boldsymbol{r_1})}{\delta\rho(\boldsymbol{r})}$$

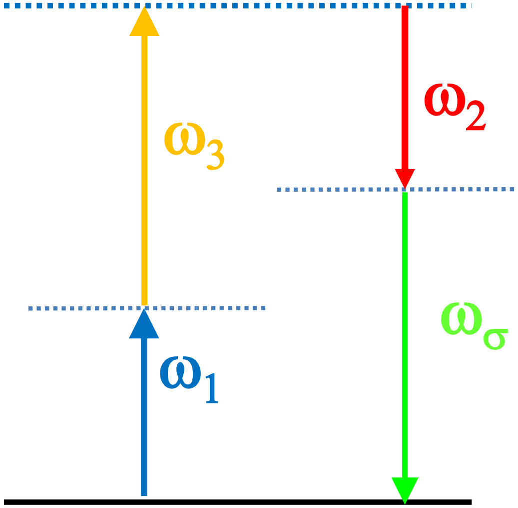
$$= v_{xc}^{hole}(\boldsymbol{r}) + v^{resp}(\boldsymbol{r})$$

S. J. A. van Gisbergen *et al.* Phys. Rev. Lett. **1999**, 83, 694.
B. Champagne *et* al., J. Phys. Chem. A **2000**, 104, 4755-4763

Introduction: Nonlinear optical properties

- **Four wave mixing (FWM) processes.**

$$\gamma_{abcd}(-\omega_\sigma;\omega_1,-\omega_2,\omega_3)$$



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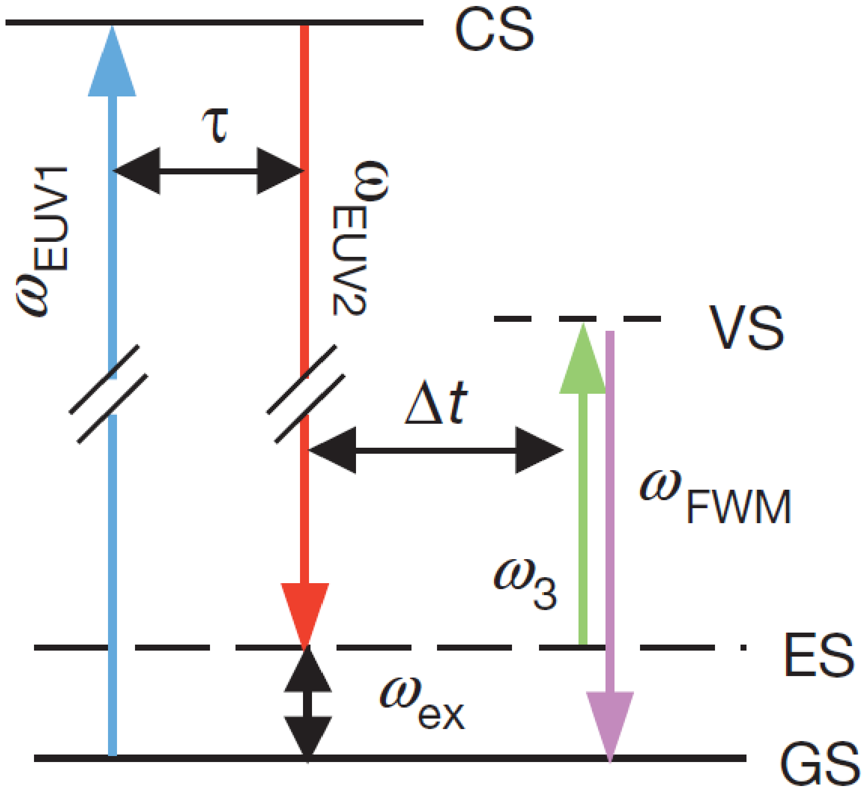
Introduction: Nonlinear optical properties

- **Four wave mixing (FWM) processes**
    - FWM process with extreme-ultraviolet radiation.

$$\gamma_{abcd}(-\omega_{FWM};\omega_{EUV1},-\omega_{EUV2},\omega_3)$$

- Coherent extreme-ultraviolet pulses
- FWM would enable the investigation of **charge-transfer dynamics**



F. Bencivenga *et al.*, Nature **2015**, 520, 205–208,

Introduction: NLOP Decomposition Analysis

- NLOP -> derivatives of the energy

$$\alpha_{ij} = -\left(\frac{\partial^2 E(F)}{\partial F_i \partial F_j}\right) \qquad \beta_{ijk} = -\left(\frac{\partial^3 E(F)}{\partial F_i \partial F_j \partial F_k}\right) \qquad \gamma_{ijkl} = -\left(\frac{\partial^4 E(F)}{\partial F_i \partial F_j \partial F_k \partial F_l}\right)$$

- Differential operator is linear.
  - Derivative of the sum -> sum of derivatives.

$$\mathrm{D(f+g)=(Df)+(Dg)}$$