Theoretical Calculations of Nonlinear Optical Response

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Introduction

MDITR: Materials & Devices for Information Technology Research

- **Center Goals:**

  - **Developing**, by rational design that exploits recent advances in quantum and statistical mechanics, transformative new electro-optic materials and devices with enhanced properties including bandwidth, drive voltage, optical loss, power consumption, and stability.

  - **Enabling** all-optical information processing by development of new third-order nonlinear optical materials that offer ultra-fast, large nonlinearities and low loss at telecommunication wavelengths.

- <u>Our</u> Goal:

  - **Develop** systematic theoretical approaches for the design or screening of materials with desirable nonlinear optical (NLO) properties.

Outline

- **Density Functional Theory Approach**
    - Definition of the properties of interest
    - Accuracy of the methodology
    - Comparison with other reported results
    - Problems with highly delocalized systems and possible solutions
- **Real Space Green's Function Approach**
    - Brief description of the method
    - Preliminary results

Density Functional Approach

Definition of the Electric Properties

The electric properties were calculated with Finite Field Perturbation Theory (FFPT) using two strengths of electric field (0.0005 and 0.0010 au) for each axis direction, and the resulting dipole moment was fitted to the following equation:

$$\mu_\alpha = \mu_\alpha^0 + \alpha_{\alpha\beta}\mathbf{F}_\beta + \frac{1}{2!}\beta_{\alpha\beta\gamma}\mathbf{F}_\beta\mathbf{F}_\gamma + \frac{1}{3!}\gamma_{\alpha\beta\gamma\delta}\mathbf{F}_\beta\mathbf{F}_\gamma\mathbf{F}_\delta + \cdots$$

α, β and γ = {x,y,z}, the summations are implicit.

μ_α and μ_α^0 are the induced and permanent dipole moments.

$\alpha_{\alpha\beta}$, $\beta_{\alpha\beta\gamma}$ and $\gamma_{\alpha\beta\gamma\delta}$ are the polarizability, first hyperpolarizability and second hyperpolarizability tensors, respectively.

F_α correspond to the components of the electrostatic field.
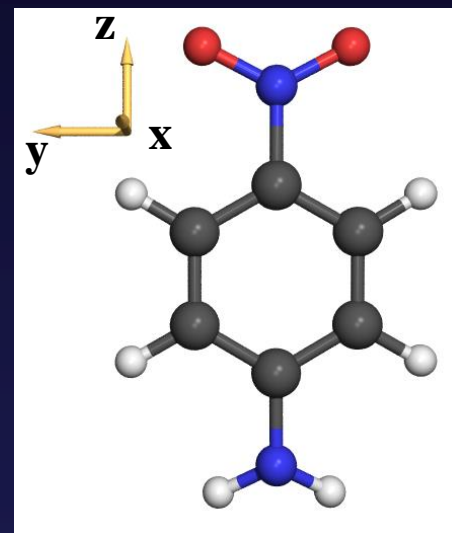
Electric Properties of the p-Nitroaniline

Effect of the Basis Set

Method/Basis Set	$|\mu^0|$ (D)	1/3 Tr(α) (Å^3)	β_{zzz} (10^{-30} esu)
HF/6-31+G(d,p)	7.88	13.69	10.94
HF/aug-cc-pVDZ	7.73	14.54	10.06
HF/aug-cc-pVTZ	7.71	14.58	9.73
HF/HyPol	7.72	14.60	9.77

Effect of the Electron Correlation

| Method/Basis Set	$|\mu^0|$ (D)	α_{zz} (Å^3)	β_{zzz} (10^{-30} esu)
HF/6-31+G(d,p)	7.88	19.58	10.94
MP2/6-31+G(d,p)	7.06	22.00	17.70
B3LYP/6-31+G(d,p)	7.88	23.34	17.25
HF/[3s2p2d/2s1p][a]	7.82	20.76	10.98
MP2/[3s2p2d/2s1p][a]	6.87	23.39	18.22

a) F. Sim, S. Chin, M. Dupuis and J. E. Rice, *J. Phys. Chem.* **97**, 1158 (1993).

Electric Properties of the julolidinyl-n-isoxazolone J(1,n=0-2) Chromophores Calculated at B3LYP level

Dipole Moment (Debye)

	Basis Set	x	y	z	Tot
J(1,0)	6-31+G(d,p)	-9.19	-6.10	1.15	11.09
	aug-cc-pVDZ	-9.07	-5.88	1.11	10.86
J(1,1)	6-31+G(d,p)	-10.78	-6.82	2.53	13.00
	aug-cc-pVDZ	-10.66	-6.59	2.46	12.78
J(1,2)	6-31+G(d,p)	-14.17	-5.80	3.60	15.73
	aug-cc-pVDZ	-14.00	-5.59	3.50	15.48

Polarizability (Å^3)

	Basis Set	xx	yy	zz	$\overline{\alpha}$
J(1,0)	6-31+G(d,p)	76.6	46.2	25.5	49.5
	aug-cc-pVDZ	78.3	47.6	26.5	50.8
J(1,1)	6-31+G(d,p)	105.7	49.8	30.2	61.9
	aug-cc-pVDZ	107.8	51.2	31.3	63.4
J(1,2)	6-31+G(d,p)	145.9	52.9	33.6	77.5
	aug-cc-pVDZ	148.2	54.5	34.9	79.2

J(1,0)

J(1,1)

J(1,2)
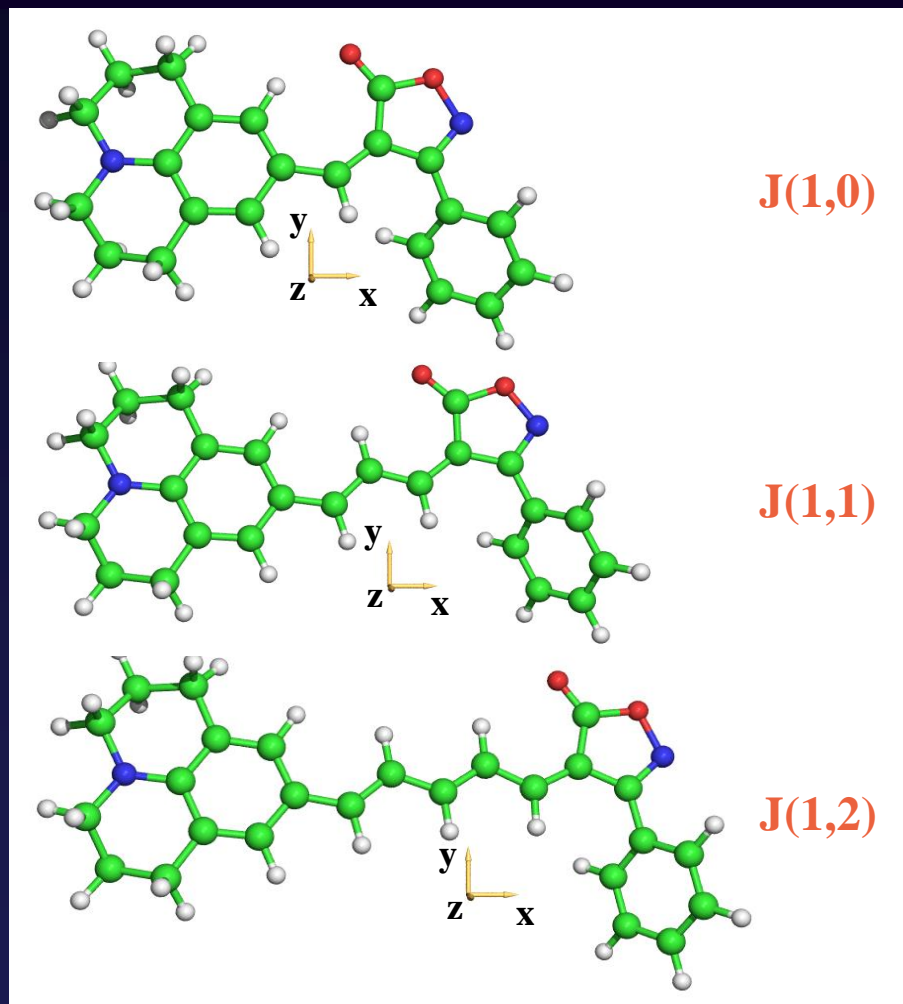
Comparison of the Electric Properties of the J(1,n=0-2) Chromophores Predicted in this Work with Other Available Values

Method	$|\mu^0|$ (D)			$1/3\,Tr(\alpha)$ ($\mathring{A}^3$)			β_{zzz} (10^{-30} esu)		
	J(1,0)	J(1,1)	J(1,2)	J(1,0)	J(1,1)	J(1,2)	J(1,0)	J(1,1)	J(1,2)
INDO-SOS[a]	10.70	11.40	13.20	28.00	36.00	45.00			
HF/6-31G[b]	10.71	12.47	15.49						
HF/cc-pVDZ[c]	9.09	9.61	10.36						
B3LYP/cc-pVDZ[c]	9.00	9.92	11.07						
MP2/6-31G*[c]	8.43	8.77	9.33						
PBE[a]	11.20	13.30	16.20	48.40	61.20	77.90	15.40	43.00	96.90
B3LYP/6-31+G(d,p)	11.09	13.00	15.73	49.50	61.90	77.50	14.20	38.80	80.60

a) B. Eichinger, private comm. b) D. Q. Lu, B. Marten, Y. X. Cao, M. N. Ringnalda, R. A. Friesner and W. A. Goddard, *Chem. Phys. Lett.* **242**, 543 (1995). c) O. V. Prezhdo, *Adv. Mat.* **14**, 597 (2002).

Electric Properties of H_n as a Function of Chain Length

n	Polarizability (10^3 au)			Second Hyperpolarizability (10^6 au)		
	HF	MP2	B3LYP	HF	MP2	B3LYP
22	1.40	1.39	1.56	11.63	13.51	4.14
32	3.32	3.37	3.96	112.02	122.72	31.00
42	6.13	6.44	7.89	577.89	671.10	145.19

Dipole Moment of Model "Push-Pull" Polymers as a Function of Chain Length
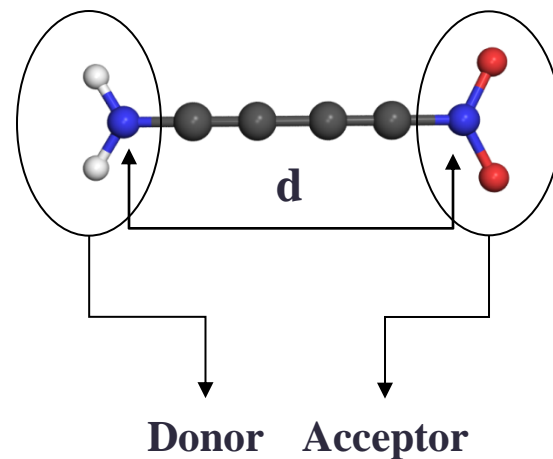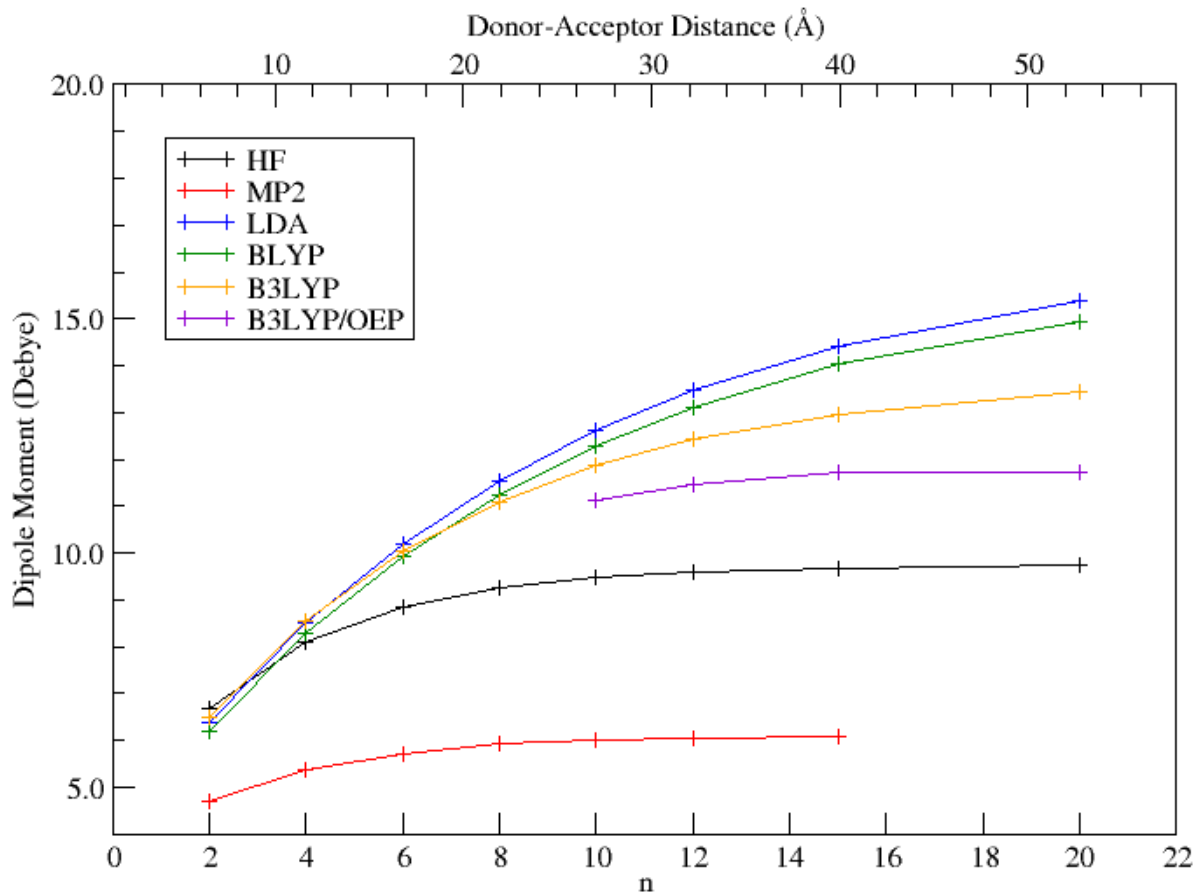
Real-Space Green's Function Approach

The single particle Green's function is defined as:

$$G^{\pm}(\mathbf{r}, \mathbf{r}', E) = \langle \mathbf{r} | \frac{1}{E - \hat{H} \pm i\gamma} | \mathbf{r}' \rangle = \sum_j \frac{\psi_j(\mathbf{r}) \psi_j^*(\mathbf{r}')}{E - E_j \pm i\gamma}$$

The linear response function[a] is constructed from G^+ :

$$\chi_0(\mathbf{r}, \mathbf{r}', \omega = 0) = -\frac{2}{\pi} \text{Im} \int_{-\infty}^{E_F} dE \, G^+(\mathbf{r}, \mathbf{r}', E) G^+(\mathbf{r}', \mathbf{r}, E)$$

The polarizability can be calculated from the first-order density perturbation as shown:

$$
\begin{aligned}
\rho_\mu^{(1)}(\mathbf{r}) &= \int d\mathbf{r}' \chi_0(\mathbf{r}, \mathbf{r}') \times h_\mu(\mathbf{r}') \\
h_\mu(\mathbf{r}) &= \int d\mathbf{r}' \left\{ \frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{xc}(\mathbf{r}, \mathbf{r}') \right\} \times \rho_\mu^{(1)}(\mathbf{r}') + v_\mu^{ext}(\mathbf{r}). \\
\alpha_{\mu\nu} &= -\int d\mathbf{r} \, r_\mu \rho_\nu^{(1)}(\mathbf{r}).
\end{aligned}
$$

a) M.J. Stott and E. Zaremba, *Phys. Rev. A* **21**, 12 (1980).

Some Preliminary Results

Dipole Polarizabilities of Rare-Gas Atoms (in au)

Methods	He	Ne	Ar	Kr	Xe
FEFF	1.56	2.96	10.71	15.41	23.95
SVWN5	1.64	2.88	11.88	17.86	
HF	1.32	2.33	10.71	16.39	
MP2	1.36	2.62	11.11	16.74	
Exp.[a]	1.39	2.67	11.09	16.75	27.32

Dipole Polarizabilities of Some Molecular Systems (in au)

Methods	CCl_4	C_{60}
FEFF	82.42	519
SVWN5	74.03	
MP2	69.97	
BLYP[b]		545
Exp.	69.3	596[c]

a) R. R. Teachout and R. T. Pack, *At. Data* **3**, 195 (1971).

b) J. I. Iwata, K. Yabana, and G.F. Bertsch, *J. Chem. Phys.* **115**, 8773 (2001).

c) J. S. Meth, H. Vanherzeele, and Y. Wang, *Chem. Phys. Lett.* **197**, 26 (1992).

Conclusions

- **Density Functional Theory Approach**

    Pros: Applicable to small and medium-sized systems.

    Accurate prediction of linear and nonlinear properties in most molecular systems.

    Cons: Large systems are still challenging.

    Nonlinear properties of highly delocalized systems do not saturate properly with bridge length.

    Probably not adequate for the screening of hundreds of candidate systems.

- **Real Space Green's Function Approach**

    Pros: Applicable to very large systems (hundreds of heavy atoms).

    Solvent effect could be included explicitly.

    Easily extended to frequency-dependent properties.

    Can be improved systematically.

    Cons: Requires some theoretical development and programming.

    Potentials not yet suited to molecular systems.