"Electron-phonon coupling in C60 using exact-exchange functional"

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Abstract

The superconductivity in C60 doped crystals is now well understood as a phonon mediated interaction. The strength of the electron-phonon coupling can be deduced by Raman and PES measurments which can then be used to assess the density-functional theory results. Although experimental and computed electron-phonon coupling agree on the total magnitude of the coupling, they do not on the contributions of the individual vibrational modes. Density-functional theory calculations indicate that high frequency modes are responsible for most of the coupling whereas experiments suggest that low frequency modes are the dominating contribution. Up to now, only calculations using the local density approximation (LDA) were performed. In this study, we investigate the effect of exact-exchange functionals, such as B3LYP, on the computed electron-phonon coupling of the different vibrational modes.

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Electron-phonon coupling in C_{60} using exact-exchange functional

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What is exact exchange?

- In Hartree-Fock theory, the energy has the form:

$$E_{HF} = V_{ions\text{-}ions} + T_{electrons} + U_{electrons\text{-}ions} + U_{electrons\text{-}electrons} + E_X^{HF}(\psi_i)$$

  - $E_X^{HF}(\psi_i)$: exact exchange

- In density functional theory (DFT), the exact exchange is replaced by the exchange-correlation functional (here, PBE[4] variant):

$$E_{PBE} = V_{ions\text{-}ions} + T_{el} + U_{el\text{-}ions} + U_{el\text{-}el} + E_X^{PBE}[\rho] + E_C^{PBE}[\rho]$$

[4] Perdew, Burke and Ernzerhof, *Phys. Rev. Lett.*, 77, 3865 (1996)

Hybrid functional

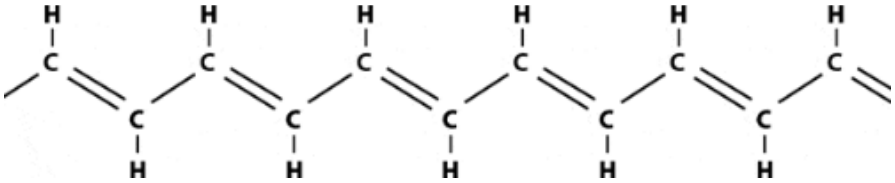
- Here, we hybrid PBE with exact exchange:

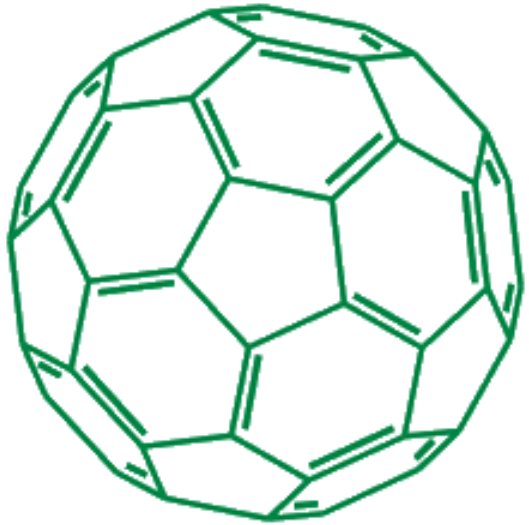
$$E_X^{PBE}[\rho] \rightarrow x\, E_X^{HF}(\psi_i) + (1-x)\, E_X^{PBE}[\rho]$$

- Popular example of hybrid functional : B3LYP
  - favoured among chemists over LDA & GGA
  - fitted on carbon systems
  - contains 20% of exact exchange.
- Since hybrid functionals can describe more accurately carbon systems, we study the impact of exact exchange on such systems.

Motivation

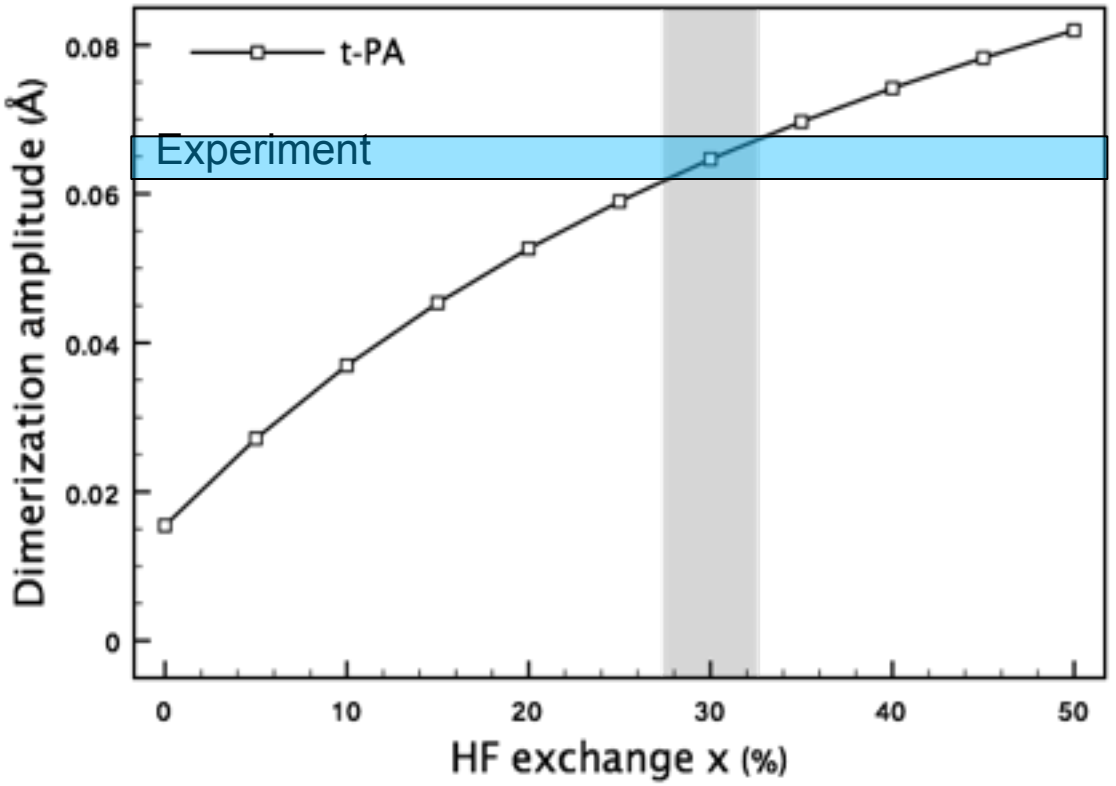
- Polyacetylene and C_{60} similar…
- Dimerization in both
  - Dimerization : alternating single and double bonds





Motivation

- Polyacetylene dimerization
  - Underestimated by traditional functionals (LDA and GGA, including PBE)
  - Exact exchange needed to match experiment



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Why Polyacetylene Dimerizes: Results of *Ab Initio* Computations

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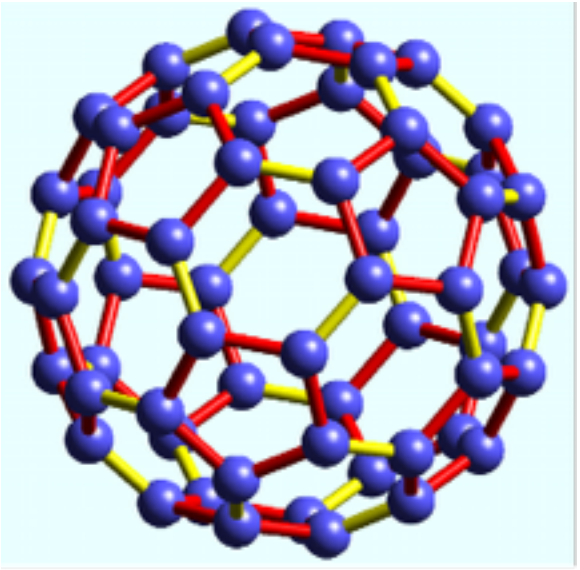
(Received 7 June 1990)

Motivation

- Could the same be true for C_{60}?
  - Structure
  - Vibrations
  - Electron-phonon coupling

Structure



- Is exact-exchange needed to describe C_{60} bond length?
- Only two independent bonds

Structure

Bond (A)	Exp.	PBE	PBE 30%	B3LYP
Single	1.455	1.457 (0.1%)	1.446 (-0.6%)	1.453 (-0.1%)
Double	1.391	1.405 (1.0%)	1.389 (-0.2%)	1.395 (0.3%)

- PBE within 1% (good)
- Exact exchange has less impact on C_{60}'s structure than on t-PA's structure

Phonon frequencies

Phonons frequencies

Mode	Frequency (cm^{-1})					
	Exp.	PBE		PBE 30%		B3LYP	
Ag1	496	488	(-2%)	505	(2%)	497	(0%)
Ag2	1470	1485	(1%)	1560	(6%)	1503	(2%)
Hg1	273	256	(-6%)	256	(-6%)	265	(-3%)
Hg2	437	415	(-5%)	406	(-7%)	433	(-1%)
Hg3	710	683	(-4%)	679	(-4%)	715	(1%)
Hg4	774	771	(-0%)	793	(2%)	786	(2%)
Hg5	1099	1101	(0%)	1130	(3%)	1126	(2%)
Hg6	1250	1256	(0%)	1299	(4%)	1276	(2%)
Hg7	1428	1435	(1%)	1503	(5%)	1454	(2%)
Hg8	1575	1570	(-0%)	1631	(4%)	1617	(3%)
Δ max			(-6%)		(-7%)		(-3%)

- Exact exchange has a small influence on the calculated phonon frequencies
- Slightly better results with B3LYP…
- but overall good agreement

Electron-phonon coupling : method

- Computations done using
  - Gaussian 03
  - Basis 6-31g(d) (complete basis set)
  - Frozen phonon method
- For PBE, checked with Abinit
  - Plane wave basis
  - linear response method
  - FHI pseudo
  - 40Ha cutoff
- Frequencies agree to within 3%
- Coupling have an absolute error of ±1 meV
- Total coupling agree to 0.5%
- Good overall agreement

$$\lambda = N(0)V_{ep}$$

$$V_{ep} = \sum_{\alpha} \frac{1}{M\omega_{\alpha}^2} \frac{1}{g^2} \sum_{i,j=1}^{g} |\langle i|\boldsymbol{\epsilon}_{\alpha} \cdot \nabla V|j\rangle|^2$$

Gaussian vs Abinit

Mode	Frequency (cm-1)			Vep (meV)		
	Gaussian	Abinit	Δ	Gaussian	Abinit	Δ
Ag1	488	484	0.8%	1.2	0.4	0.8
Ag2	1485	1469	1.1%	7.4	7.5	-0.1
Hg1	256	258	-0.7%	4.7	5.1	0.4
Hg2	415	424	-2.1%	11.6	9.3	-2.3
Hg3	683	706	-3.2%	10.4	9.1	-1.2
Hg4	771	766	0.7%	3.7	4.3	0.6
Hg5	1101	1093	0.7%	4.1	4.4	0.4
Hg6	1256	1237	1.5%	2.3	2.6	0.2
Hg7	1435	1414	1.5%	13.7	14.7	1.0
Hg8	1570	1551	1.2%	12.2	14.2	2.0
Total	-	-	-	71.3	71.6	0.5%

Electron-phonon coupling

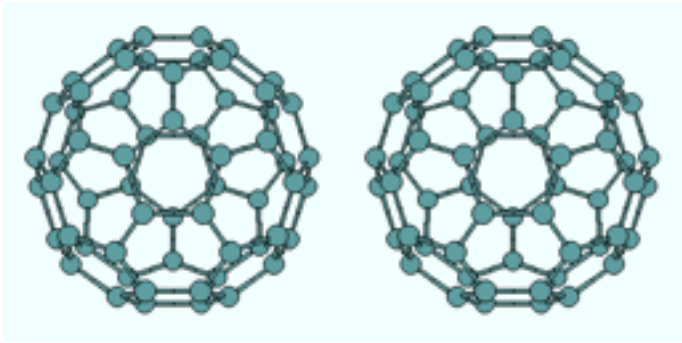
- Influence of the amount of exact exchange
- Quantitative results
  - Strongly coupling modes highly affected
  - Weakly coupling modes don't have a clear trend
  - Total coupling strongly affected

Mode	electron-phonon coupling V_{ep} (meV)				
	PBE	PBE 30%		B3LYP	
Ag1	1.2	1.2	(0%)	1.2	
Ag2	7.4	11.8	(60%)	10.6	
Hg1	4.7	5.1	(8%)	5.8	
Hg2	11.6	14.1	(22%)	11.5	
Hg3	10.4	16.3	(57%)	12.3	
Hg4	3.7	3.8	(3%)	4.7	
Hg5	4.1	5.6	(37%)	4.8	
Hg6	2.3	3.6	(54%)	2.0	
Hg7	13.7	20.3	(49%)	20.0	
Hg8	12.2	16.2	(33%)	14.0	
Total Ag	8.6	13.1	(52%)	11.8	
Total Hg	62.6	85.0	(36%)	75.1	
Total	71.3	98.1	(38%)	87.0	(22%)

Electron-phonon coupling

- Bond stretching uniform in Ag1 and not in Ag2
- Ag2-lumo coupling more affected than Ag1-lumo
- Change in functional affects the way charge reorganize
  - Ag1 show uniform bond stretching:
    don't allow for charge reorganisation
    =>functional shouldn't have a strong impact
  - Ag2 show uneven bond stretching:
    allow for charge reorganisation
    =>functional could have a strong impact

	Ag1	Ag2
PBE	1.2	7.4
PBE 30%	1.2 (0%)	11.8 (60%)



Conclusion

- Hybrid PBE functional (with exact exchange)
  - doesn't affect significantly C_{60} ground state (structure)
  - nor phonon frequencies
- Electron-phonon coupling show large change when exact exchange is added
  - On the order of 40% for 30% of exact exchange

Electron-phonon coupling : experimental data

electron-phonon coupling

Mode	V_{ep} (meV)					
	PBE	PBE 30%		B3LYP	Raman	PES
Ag1	1.2	1.2	(0%)	1.2		
Ag2	7.4	11.8	(60%)	10.6		
Hg1	4.7	5.1	(8%)	5.8	48	19
Hg2	11.6	14.1	(22%)	11.5	20	40
Hg3	10.4	16.3	(57%)	12.3	3	13
Hg4	3.7	3.8	(3%)	4.7	3	18
Hg5	4.1	5.6	(37%)	4.8	1	12
Hg6	2.3	3.6	(54%)	2.0	1	5
Hg7	13.7	20.3	(49%)	20.0	4	17
Hg8	12.2	16.2	(33%)	14.0	3	23
Total Ag	8.6	13.1	(52%)	11.8		
Total Hg	62.6	85.0	(36%)	75.1	83	147
Total	71.3	98.1	(38%)	87.0 (22%)	83	147