Improvement of C_{60}'s calculated electron-phonon coupling using hybrid functional

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Reminder : hybrid functional

- In density functional theory (DFT), the energy has the form:

$$E = V_{ion-ion} + T_{el} + V_{el-ion} + U_{Hartree} + E_X[\rho] + E_C[\rho]$$

(A PBE[1] functional is used in this research.)

- Here, we make a hybrid PBE functional :

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

- Popular example of hybrid functional : B3LYP
  - favoured among chemists over LDA & GGA
  - fitted on organic systems
  - contains 20% of exact exchange (α=20%).

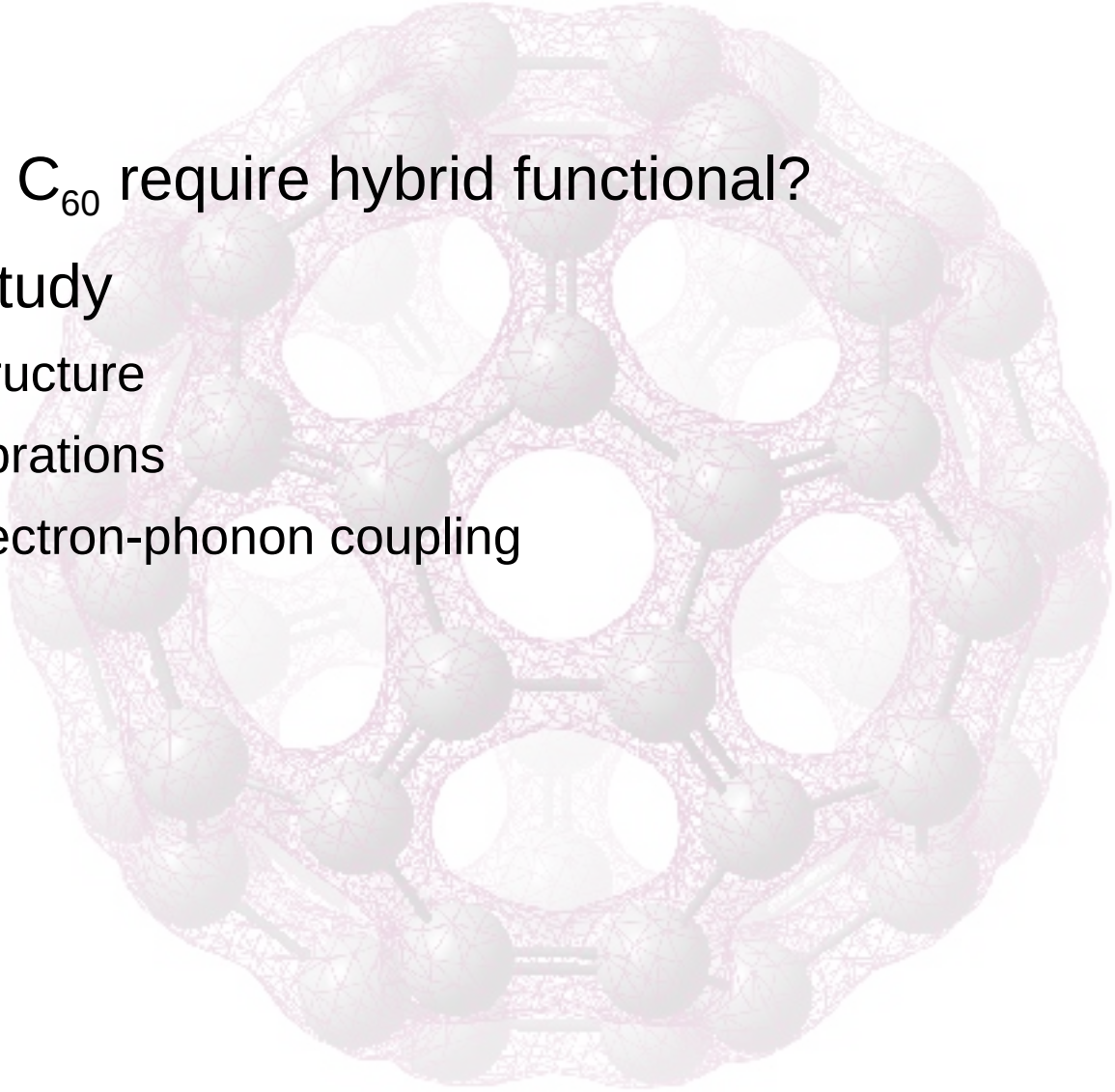
[1] Perdew, Burke and Ernzerhof, *Phys. Rev. Lett.*, **77**, 3865 (1996)

Motivation

- Why assess the problem with hybrid functional?
  - C_{60} is an organic system
  - Its superconducting mechanism is not fully understood
    - Experimental $\lambda/N(\varepsilon_F)$: 83 to 168 meV [2,3]
    - Calculated $\lambda/N(\varepsilon_F)$: 49 to 85 meV [4,5,6]

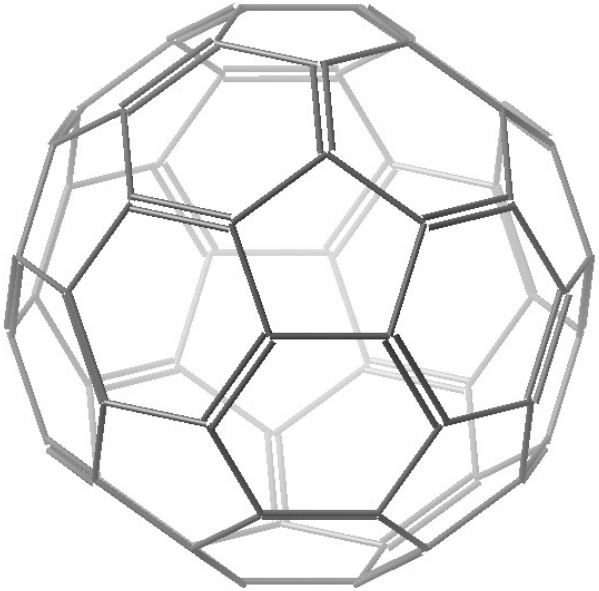
[2] Gunnarsson et al., *Phys. Rev. Lett.* **74**, 1875 (1995).
[3] Aksenov et al., *Phys. Rev. B* **57**, 608 (1998).
[4] Saito, *Phys. Rev. B* **65**, 220508 (2002).
[5] Breda et al., *Chem Phys Lett* **286**, 350 (1998).
[6] Manini et al., *Philos Mag B* **81**, 793 (2001).

The question



- Does C_{60} require hybrid functional?
- We study
  - Structure
  - Vibrations
  - Electron-phonon coupling

Structure



- Is exact-exchange required to get accurate structure?
- Only two independent bonds

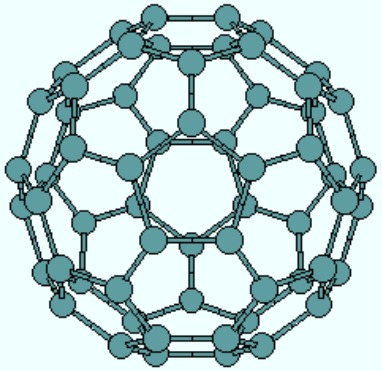
Geometry of C_{60}

Bond length (Å)	Exp.[8]	PBE α=0%	PBE α=30%	B3LYP
Single	1.460	1.454 (-0.4%)	1.444 (-1.1%)	1.452 (-0.6%)
Double	1.381	1.401 (1.5%)	1.386 (0.3%)	1.392 (0.8%)

- PBE accurate
- Exact exchange is not required for C_{60}'s structure

[8] Leclerq et al., *Phys. Rev. B* **48**, 2748 (1993).

Phonon frequencies



Calculated frequencies in cm^{-1}

Mode	Exp.[9]	PBE α=0%	PBE α=30%	B3LYP
$A_g(1)$	496	488 (-2%)	505 (2%)	496 (0%)
$A_g(2)$	1470	1479 (1%)	1549 (5%)	1492 (2%)
$H_g(1)$	273	256 (-6%)	257 (-6%)	265 (-3%)
$H_g(2)$	437	416 (-5%)	407 (-7%)	435 (0%)
$H_g(3)$	710	686 (-3%)	683 (-4%)	721 (2%)
$H_g(4)$	774	770 (-1%)	792 (2%)	785 (1%)
$H_g(5)$	1099	1100 (0%)	1127 (3%)	1123 (2%)
$H_g(6)$	1250	1248 (0%)	1290 (3%)	1265 (1%)
$H_g(7)$	1428	1426 (0%)	1490 (4%)	1442 (1%)
$H_g(8)$	1575	1564 (-1%)	1622 (3%)	1608 (2%)
Δ_{max}		(-6%)	(-7%)	(-3%)

- Slightly better results with B3LYP…
- but overall good agreement (α has small impact on frequencies)
- Only A_g and H_g modes are studied

[9] Bethune et al., *Chem Phys Lett* **179**, 181 (1991).

Electron-phonon coupling : method

- Molecular approximation to $\lambda/N(\varepsilon_F)$:

$$\lambda/N(\epsilon_F) = \sum_{\nu} \frac{1}{M\omega_\nu^2} \frac{1}{3^2} \sum_{i,j=1}^{3} | < i|\vec{\varepsilon}_\nu \cdot \vec{\nabla} V|j > |^2$$

- Computations done using
  - Gaussian 03
  - Basis 6-311g(d) (converged)
  - Frozen phonon method

Electron-phonon coupling : impact of exact exchange (α)

- PBE in line with published calculations (49 to 85 meV)[4,5,6]
- Total coupling strongly affected
- C_{60}^{3-} : same trend (35% increase of $\lambda/N(\varepsilon_F)$)

Calculated $\lambda_\nu / N(\epsilon_F)$ in meV.

Mode	PBE	PBE α=30%	B3LYP
$A_g(1)$	1.3	1.3 (0%)	1.2 (-3%)
$A_g(2)$	7.5	12.0 (59%)	10.9 (45%)
$H_g(1)$	4.7	5.8 (23%)	5.8 (23%)
$H_g(2)$	11.0	13.8 (25%)	10.8 (-2%)
$H_g(3)$	10.4	16.6 (60%)	11.9 (15%)
$H_g(4)$	4.0	4.2 (6%)	5.2 (30%)
$H_g(5)$	4.3	6.3 (49%)	5.0 (17%)
$H_g(6)$	2.6	4.2 (65%)	2.1 (-17%)
$H_g(7)$	15.8	24.6 (56%)	23.0 (46%)
$H_g(8)$	14.2	18.5 (30%)	17.7 (24%)
$\sum H_g$	66.9	94.0 (40%)	81.5 (22%)

[4] Saito, *Phys. Rev. B* **65**, 220508 (2002).
[5] Breda et al., *Chem Phys Lett* **286**, 350 (1998).
[6] Manini et al., *Philos Mag B* **81**, 793 (2001).

Comparison with experiment

- Which functional is most accurate?
- More experiment on λ
  - $N(\varepsilon_F)$=6±2 states/(eV molecule)
  - α=0% → λ=0.3-0.6
  - α=30% → λ=0.4-0.9
  - Exp. → λ=0.7-1.2
- α=30% gives better agreement

Calculated $\lambda_\nu / N(\epsilon_F)$ vs experiment

Mode	PBE		Experiment	
	α=0%	α=30%	Gun.[10]	Han.[11]
$A_g(1)$	1.3	1.3	0	
$A_g(2)$	7.5	12.0	11	
$H_g(1)$	4.7	5.8	19	
$H_g(2)$	11.0	13.8	40	
$H_g(3)$	10.4	16.6	13	
$H_g(4)$	4.0	4.2	18	
$H_g(5)$	4.3	6.3	12	
$H_g(6)$	2.6	4.2	5	
$H_g(7)$	15.8	24.6	17	
$H_g(8)$	14.2	18.5	23	
$\sum H_g$	66.9	94.0	147	97

[10] Gunnarsson et al., *Phys. Rev. Lett.* **74**, 1875 (1995).
[11] Hands et al., *Phys. Rev. B* **77**, 115445 (2008).

Analysis

- How does α enhance $\lambda_\nu/N(\epsilon_F)$?
- $$\lambda_\nu/N(\epsilon_F) = \frac{1}{M\omega^2_{\nu,\alpha_s}} \frac{1}{3^2} \sum_{i,j=1}^{3} | < i_{\alpha_\lambda,\alpha_s} | \vec{\varepsilon}_{\nu,\alpha_s} \cdot \vec{\nabla} \left(\frac{V_{ion,\alpha_s}}{\epsilon_{\alpha_\lambda,\alpha_s}} \right) | j_{\alpha_\lambda,\alpha_s} > |^2$$
  - α_s used for optimisation and frequencies ; small (~ 1%) impact on $\lambda/N(\varepsilon_F)$.
  - α_λ used for frozen phonons ; large (~40%) impact on $\lambda/N(\varepsilon_F)$.
- Effect on ϵ can explain systematic increase of $\lambda_\nu/N(\varepsilon_F)$ with α.
  - HF overestimates gap; LDA/GGA underestimate it.
  - ϵ drops if gap rises.
  - $\lambda_\nu/N(\varepsilon_F) \propto 1/\epsilon^2$
  - Result : $(\alpha \nearrow) \Rightarrow (\lambda_\nu/N(\varepsilon_F) \nearrow)$
- Similar trend in graphene (Lazzeri & al.[12]) :
  increase of coupling (~30%) when LDA replaced by GW
- Shows treatment of screening is critical for accuracy of $\lambda/N(\varepsilon_F)$

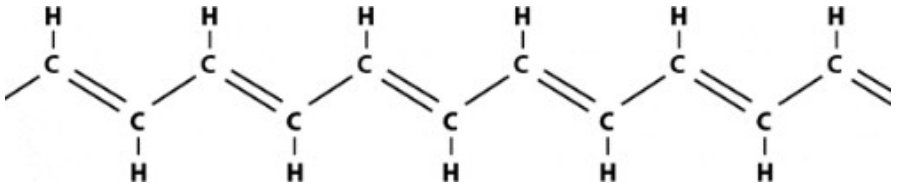
[12] Lazzeri et al., *Phys. Rev. B* **78**, 081406 (2008).

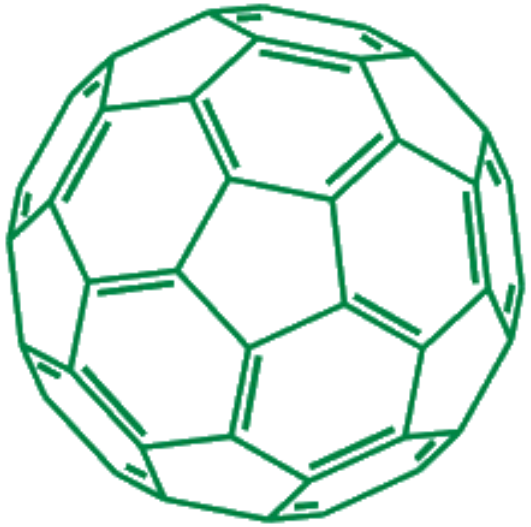
Conclusion

- Effect of exact-exchange on C_{60}^{0} & C_{60}^{3-} :
  - Enhanced accuracy of electron-phonon coupling
  - Description of structure and phonon frequencies remains good
- Suggests that the treatment of screening is critical for accuracy of superconductivity-related properties.

Motivation

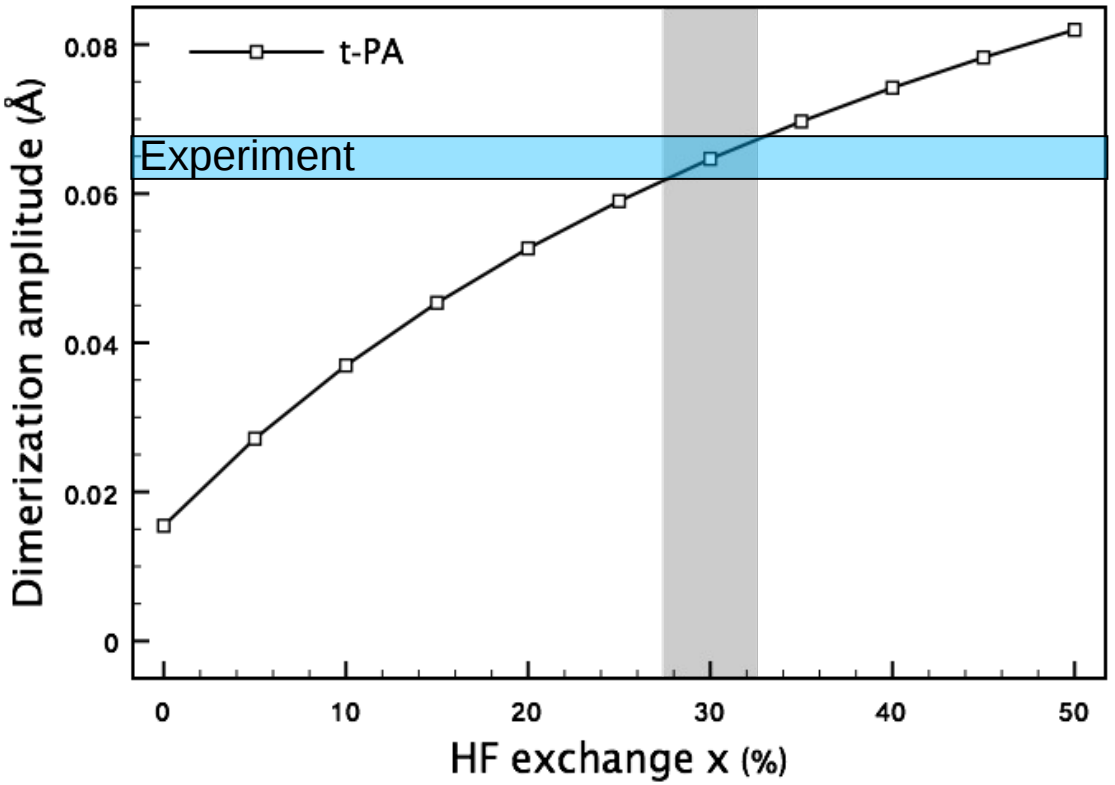
- Why use α=30% in the hybrid PBE functional?
  - Polyacetylene and C_{60} similar…





Motivation

- Polyacetylene dimerization
  - Underestimated by LDA and GGA
  - Exact exchange needed (α=30%)
- Theory supports α~25% for PBE[7]



[7] Perdew, Emzerhof and Burke, *J Chem Phys* **105**, 9982 (1996).

Testing accuracy

- Computations done using
  - Gaussian 03
  - Basis 6-311g(d) (converged)
  - Frozen phonon method
- For PBE, checked with Abinit
  - Plane wave basis
  - linear response method
- Good overall agreement
  - Frequencies agree to 1%
  - Total coupling agree to 6%

Gaussian vs Abinit

Mode	$\lambda_\nu/N(\epsilon_F)$ (meV)		
	Gaussian	Abinit	Δ (meV)
$A_g(1)$	1.3	0.4	-0.9
$A_g(2)$	7.5	7.5	-0.1
$H_g(1)$	4.7	5.1	0.4
$H_g(2)$	11.0	9.3	-1.7
$H_g(3)$	10.4	9.1	-1.3
$H_g(4)$	4.0	4.3	0.3
$H_g(5)$	4.3	4.4	0.2
$H_g(6)$	2.6	2.6	0.0
$H_g(7)$	15.8	14.7	-1.1
$H_g(8)$	14.2	14.2	-0.1
Total	75.8	71.6	-4.2 (-5.5%)