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:

$$E_{HF} = V_{ions\text{-}ions} + T_{electrons} + U_{electrons\text{-}ions} + U_{Hartree} + E_X^{HF}[\psi_i]$$

exact exchange

Hybrid functional

In density functional theory (DFT), the exact exchange is replaced by the exchange-correlation functional (here, PBE[1] variant):

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

exchange functional

In this project, we use a hybrid exchange which mixes PBE's exchange functional with exact exchange:

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

x : mixing parameter

Why use a hybrid functional?

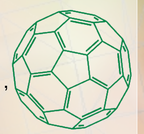
Using such a hybrid functional (with an adjustable parameter x) can enhance the accuracy of calculated properties in organic systems.

A popular example of hybrid functional is B3LYP :

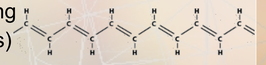
- it is favoured among chemists over LDA & GGA because of it's accuracy,
- it is fitted on carbon systems,
- it contains 20% of exact exchange.

Since hybrid functionals can describe more accurately carbon systems, we study the impact of exact exchange on such systems.

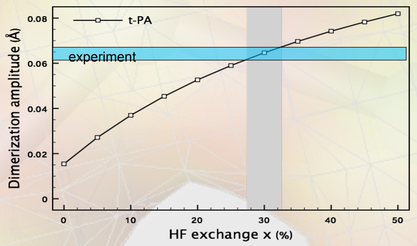
Why C_{60} ?



1. Polyacetylene and C_{60} are similar:
   - they are both made of carbon atoms ,
   - there is dimerization in both. (Dimerization : alternating single and double bonds)



2. Exact exchange is needed to predict accurately trans-polyacetylene's (t-PA's) dimerization[2,3]:
   - traditional functionals (LDA and GGA, including PBE) underestimate dimerization,
   - adding exact-exchange gives better geometry compared to experiment.



Could the amount of exact exchange in a functional have a similar impact on C_{60}? Here we study the impact of this parameter on the following calculated properties:

- structure,
- vibrations,
- electron-phonon coupling.

Structure

- Reminder : C_{60}'s symmetry is such that there is only 2 independent bonds (the single and double 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%)

Difference between theory and experiment

- The pure PBE functional predicts a structure within 1% of experiment.
- With such good results, there is no need of exact exchange to accurately describe C_{60}'s structure.
- Exact-exchange has less impact on C_{60}'s structure than on t-PA's structure.

Phonon frequencies

- We are only interested in the modes that couple with the LUMO electronic states : the Ag and Hg modes.

Phonons frequencies

Mode	Exp.	PBE	PBE 30%	B3LYP
	Frequency (cm^{-1})			
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%)

- Adding exact exchange:
  - raises higher frequencies (shaded in green),
  - has low impact on lower frequencies (blue shade).
- Agreement between theory and experiment:
  - is best with B3LYP (within 3%);
  - is overall good (within 7%).
- Therefore, exact exchange is not needed to accurately describe (within 6%) the phonon frequencies in C_{60}.

Electron-phonon coupling : Method

- Here, we calculate the couplings V_{ep} between the LUMO electronic states and the phonons (Ag and Hg modes) :

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

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

- The computation of electron-phonon couplings was done using :
  - Gaussian 03 code (with 6-31g(d) basis, which is well converged);
  - the frozen phonon method.
- The results obtained with the pure PBE functional were checked against Abinit[4] calculations. Those use:
  - a plane wave basis set,
  - a linear response method (to calculate the couplings).

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%

- The two simulation methods give:
  - phonon frequencies that agree to within 3%,
  - electron-phonon couplings that agree to within 2 meV,
  - total electron-phonon coupling that agree to within 0.5%.
- This overall good agreement give us confidence in the accuracy of the gaussian basis and the frozen phonon method we used.

Results

- With Gaussian, we can assess the effect of the amount of exact exchange in a functional on the electron-phonon couplings.
- The difference between the hybrid and the pure PBE functional is given between parenthesis.

electron-phonon coupling

Mode	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%)

- The results clearly show that exact exchange has an impact on the couplings:
  - strongly coupling modes are highly affected (green shade),
  - weakly coupling modes don't show a clear trend (blue shade).
  - However, since strongly coupling modes form the dominating contribution to the total coupling, it is as well strongly affected by the amount of exact exchange in then functional.
- We see a ~40% increase in total coupling (circled in red) when adding 30% of exact exchange to the functional.

Interpretation

- Why some couplings are strongly affected while others are not?

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

- In particular, why the Ag1-LUMO coupling is the least affected while the Ag2-LUMO coupling is the most affected?
- First, we note that changing a functional affects the way the charge reorganize in a molecule.
  - Since Ag1 shows uniform bond stretching, it doesn't allow for charge reorganization: => a change in functional shouldn't affect Ag1-LUMO coupling.
  - Since Ag2 shows uneven bond stretching, it does allow for charge reorganization: => a change in functional could affect Ag2-LUMO coupling.

Conclusion

- Using a hybrid PBE functional (with exact exchange)
  - doesn't affect significantly C_{60}'s ground state (structure),
  - nor it's phonon frequencies.
- However, the electron-phonon coupling is strongly affected by the amount of exact exchange in the functional:
  - the total coupling is raised by ~40% when 30% of exact exchange is added to a PBE functional.

RQMP

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[1] Perdew, Burke and Ernzerhof, *Phys. Rev. Lett.*, 77, 3865 (1996)
[2] Suhai, Sandor, *Phys. Rev. B*, 51(23), 16553 (1995)
[3] König, G. and Stollhoff, G., *Phys. Rev. Lett.*, 65(10), 1239 (1990)
[4] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman *et al.*, Gaussian 03, Revision C.02, Gaussian, Inc., Wallingford, CT, 2004.