Electron-phonon coupling in C_{60} using hybrid functionals

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The calculations of the electron-phonon coupling in C_{60} molecules are analyzed in the context of hybrid functionals within the density-functional theory (DFT) approach. We find that increasing the contribution of the exchange energy calculated with a Fock operator in a functional from 0 to 30% has little impact on structural properties and phonon frequencies, but it generates a strong increase of the total electron-phonon coupling ($\sim$40%). The resulting electron-phonon couplings for each vibrational mode are in better agreement with experimental data. In particular, the H_g vibrational modes contribution to the total coupling increased from 67 to 94 meV, which compares favorably with the most recent experimental value of 97 meV. With this new result, the deduced electron-phonon coupling parameter λ was increased from a range of 0.3–0.6 to 0.4–0.9, which now overlaps with the distribution of experimental values (0.7–1.2). Thus, the disagreements found in the literature about superconductivity-related properties in fullerides may be in part explained by the great sensitivity of those DFT results to the choice of functional.

Superconductivity in A_3C_{60} was experimentally observed[1] soon after the synthesis of C_{60} crystals. Recently, superconductivity in Cs_3C_{60} was measured at 38K.[2,3] Thus, alkali-doped C_{60} has one of the highest T_c among conventional superconductors. However, our understanding of the superconducting mechanism is still incomplete despite considerable research efforts devoted to this material. For instance, the total electron-phonon coupling is found experimentally to range from 83 to 168 meV,[4–6] while the calculated values range from 49 to 85 meV.[7–13] The published distributions of the coupling among vibrational modes show even stronger disagreement.[4–13] These discrepancies between experimental and theoretical values motivate the need for further investigation.

Trans-polyacetylene (*t*-PA) is another problematic system for density-functional theory (DFT) calculations. Previous DFT studies reported that the Peierls deformation observed in this polymer is strongly underestimated by local-density approximation (LDA) and generalized gradient approximation (GGA) functionals.[14,15] Hybrid functionals, incorporating partial exact exchange, were shown to be required for accurate results.[16] These hybrid schemes have also been shown to have a rigorous formal justification within exact density-functional theory.[17]

A widely used hybrid functional is B3LYP.[18] It is a modification of local-spin-density approximation functional, which incorporates 20% of the exchange energy from the Fock operator. This functional is popular mainly because of its accuracy for organic systems.[19] Since fullerenes are carbon molecules, it is important to investigate how their calculated properties are affected when such hybrid schemes are used, as compared to traditional functionals employed for extended electronic systems. In light of the discrepancies mentioned above, we study in particular the impact of including partly exact exchange on the phonon-related properties of C_{60}. In this study, bond lengths, dimerization amplitude, phonon frequencies, and electron-phonon couplings are

examined. We also investigate the effect of adding charges to the molecule as in alkali-doped C_{60}.

Here we use a custom hybrid functional that incorporates partial exact exchange in a GGA functional designed by Perdew, Burke, and Ernzerhof—the PBE (Ref. 20) functional. We denote the fraction of exchange energy calculated with the Fock operator in this hybrid functional by the parameter α. The present calculations were done both with $\alpha=0\%$, which is the original PBE functional, and $\alpha=30\%$. This last value was found to be optimal for *t*-PA's dimerization.[21] Moreover, it has been shown that a value around $\alpha=1/4$ in such hybrid schemes normally yields optimum accuracy for molecules.[22] Yet, we recognize that the determination of the alpha parameter is currently not completely *ab initio* and further work needs to be done in this direction. The present calculations were also performed with the B3LYP as it is a widely used functional.

The calculations were done using the GAUSSIAN 03 code[23] with a well-converged 6-311g(d) basis set. The electron-phonon couplings to individual phonon modes were calculated using the frozen phonon method.[24] The ground state of the $-3e$ charged molecule was constrained to be fully spin polarized to fix the lowest unoccupied molecular orbital (LUMO) occupation numbers in the frozen phonon approach. Some calculations were also carried out using ABINIT,[25,26] which uses a plane wave basis set and a linear response method to calculate phonon frequencies and electron-phonon couplings. The accuracy of both the 6-311g(d) basis set and the frozen phonon method is demonstrated by the good agreement obtained with these two approaches.[27]

Table I summarizes the calculated C_{60} structural properties for different functionals. Because of the molecule symmetry, I_h, only single and double bond lengths need to be reported. The dimerization amplitude (defined as the difference between the double- and single-bond lengths) and the relative difference with experiment are also given for com-

TABLE I. Comparison of C_{60} structure properties using different functionals. The relative difference with experiment is given in parenthesis.

Bond length (Å)	$C_{60}{}^0$			
	Expt. 28	PBE $\alpha=0\%$	PBE $\alpha=30\%$	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%)
Dimerization	0.078	0.053 (−32%)	0.058 (−26%)	0.059 (−24%)
Bond length (Å)	$C_{60}{}^{3-}$			
	Expt. 29	PBE $\alpha=0\%$	PBE $\alpha=30\%$	B3LYP
Single	1.453	1.453 (0.0%)	1.441 (−0.9%)	1.449 (−0.3%)
Double	1.397	1.417 (1.5%)	1.404 (0.5%)	1.410 (0.9%)
Dimerization	0.056	0.035 (−37%)	0.037 (−34%)	0.038 (−32%)

parison. We observe a slight (~1%) bond contraction and a small (~10%) increase of dimerization upon addition of some exact exchange in the functional. We note that all results are within the accepted accuracy of DFT. Globally, it is obvious that the addition of partial exact exchange does not significantly enhance the agreement between the calculations and experiment for the structural properties. This is in contrast with t-PA's dimerization, where incorporating a certain amount of exact exchange is essential to obtain the correct bond lengths.

We have also obtained results for the charged C_{60} (doped with three electrons) and found a slight single-bond contraction and a small double bond extension. Those trends agree with experimental observations. Since addition of partial exact exchange has the same effect in $C_{60}{}^{3-}$ as in $C_{60}{}^0$, the agreement with experiment remains similar.

We now turn our attention to the vibrational properties. Table II summarizes the frequencies of the modes that couple with the LUMO electronic states since these states form the electronic levels at the Fermi energy in doped fullerene crystals. The phonon modes must have A_g or H_g symmetry to exhibit this coupling.[30]

TABLE II. Calculated frequencies in cm^{-1} for vibrational modes of $C_{60}{}^0$ that couple with LUMO electronic states. The relative difference with experiment (Ref. 31) is given in parenthesis.

Mode	Expt.	PBE $\alpha=0\%$	PBE $\alpha=30\%$	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%)

The experimental results are taken from Raman spectroscopy at room temperature on undoped solid C_{60}.[31] We note that the closest agreement between theory and experiment is obtained with the B3LYP functional. However, all three functionals give results within the accepted accuracy of DFT. Therefore, having a certain amount of exact exchange is not required to calculate accurate phonon frequencies or geometries for C_{60}. Thus, it could be argued that hybrid functionals are not needed for this material.

The electron-phonon coupling parameter is usually extracted from the electron-phonon spectral function.[32] However, the small dispersion of the electronic and phononic bands in fullerenes allows us to approximate the electronic states and vibrational modes of the crystal by those of the molecule.[4,7,8,33] The total electron-phonon coupling $\lambda/N(\epsilon_F)$ can then be obtained using[34]

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

where M is the mass of a carbon atom, ν labels the vibrational mode, ω_ν is the frequency of a given vibrational mode, $\vec{\varepsilon}_\nu$ is the corresponding $3N$ dimensional polarization vector, i and j are the threefold degenerate LUMO electronic states for which we are evaluating the coupling, and V is the screened ionic potential of the whole molecule. The orthonormalization of $\vec{\varepsilon}_\nu$ chosen here requires that we use the density of states per molecule at the Fermi energy, $N(\epsilon_F)$, in our expression for λ.

We use a frozen phonon approach to calculate the matrix elements $\langle i|\vec{\varepsilon}_\nu \cdot \vec{\nabla} V|j\rangle$. In this method, these matrix elements are evaluated as the slope of the LUMO Kohn-Sham eigenvalues with respect to the phonon's normal coordinate. The resulting couplings are given in Table III.

We note that the neutral molecule electron-phonon couplings $\lambda_\nu/N(\epsilon_F)$ for mode ν computed with the PBE ($\alpha=0\%$) and B3LYP functionals, respectively, agree to within 1 meV with the most recent LDA (Ref. 11) and B3LYP (Ref. 13) results, demonstrating their reproducibility. The H_g contribution to the total coupling $\Sigma_{H_g}\lambda_\nu/N(\epsilon_F)$ is found to be 67 meV when $\alpha=0\%$, in line with previous LDA

TABLE III. Calculated electron-phonon couplings to vibrational mode $\lambda_\nu/N(\epsilon_F)$ in meV. For hybrid functionals, the relative difference with PBE results is given in parenthesis. Results obtained from PES and Raman measurements are also presented (Refs. 4–6).

Mode	C_{60}^{0}			C_{60}^{3-}			Experiment			
							PES (C_{60}^{-})		Raman (C_{60}^{3-})	
	PBE	PBE α=30%	B3LYP	PBE	PBE α=30%	B3LYP	Gun (Ref. 4)	Han (Ref. 35)	Win (Ref. 5)	Aks (Ref. 6)
$A_g(1)$	1.3	1.3 (0%)	1.2 (−3%)	6.2	5.6 (−11%)	5.8 (−7%)	0			
$A_g(2)$	7.5	12.0 (59%)	10.9 (45%)	6.6	10.5 (59%)	9.7 (47%)	11			
$H_g(1)$	4.7	5.8 (23%)	5.8 (23%)	3.0	4.1 (36%)	4.1 (36%)	19		48	20
$H_g(2)$	11.0	13.8 (25%)	10.8 (−2%)	9.9	11.6 (16%)	10.2 (2%)	40		20	21
$H_g(3)$	10.4	16.6 (60%)	11.9 (15%)	12.9	16.0 (24%)	14.1 (9%)	13		3	8
$H_g(4)$	4.0	4.2 (6%)	5.2 (30%)	4.6	5.8 (27%)	6.1 (33%)	18		3	10
$H_g(5)$	4.3	6.3 (49%)	5.0 (17%)	4.0	4.7 (17%)	4.6 (15%)	12		1	11
$H_g(6)$	2.6	4.2 (65%)	2.1 (−17%)	3.4	4.1 (21%)	3.6 (7%)	5		1	10
$H_g(7)$	15.8	24.6 (56%)	23.0 (46%)	13.3	21.6 (63%)	20.7 (56%)	17		4	46
$H_g(8)$	14.2	18.5 (30%)	17.7 (24%)	14.8	22.2 (50%)	19.6 (33%)	23		3	42
Total A_g	8.8	13.3 (50%)	12.2 (38%)	12.8	16.1 (25%)	15.5 (21%)	11			
Total H_g	66.9	94.0 (40%)	81.5 (22%)	65.9	90.0 (37%)	82.9 (26%)	147	97	83	168
Total	75.8	107.3 (42%)	93.7 (24%)	78.7	106.1 (35%)	98.5 (25%)	158			

calculations,[8–11] which range from 49 to 68 meV. Thus the PBE results share the trend of previous calculations and underestimate the experimental coupling.

Raising α to 30% systematically increases the couplings. Moreover, the modes with the largest couplings are highly affected. The global effect is a 42% enhancement of the total coupling $\lambda/N(\epsilon_F)$. The C_{60}^{3-} shows the same trend, with a 35% increase in $\lambda/N(\epsilon_F)$ when α is increased to 30%. The amount of exact exchange α substituted in the functional therefore has a significant impact on $\lambda/N(\epsilon_F)$ whether the molecule is charged or not.

Since there are strong variations in the calculated couplings, we may compare them with experimental values to determine which functional gives the best agreement with experiment. Two experiments have been carried out to quantitatively assess the electron-phonon couplings to individual vibration modes: Winter et al.[5] used Raman spectroscopy on single crystal K_3C_{60} while Gunnarsson et al.[4] used photoemission spectra (PES) on a plasma of C_{60}^{-}. Winter analyzed the Raman spectra using Allen's formula.[36] However, Aksenov et al.[6] argued against the validity of this formula for phonons near the center of the Brillouin zone. Therefore, they have reinterpreted the width of Winter's Raman peaks in terms of the center of the zone phonon relaxation rate in the presence of disorder and took into account the finite bandwidth of fullerene crystals.

Since Aksenov's analysis only gives the relative amplitude of the couplings, his results can be rescaled to improve agreement with all our calculated distributions of the coupling, and most results agree to within a factor of 2. This level of agreement cannot be reached with the data of Winter et al.

If we compare our present C_{60}^{0} results with Gunnarsson's analyses of PES data, we find an improvement upon raising α to 30%. Given that this experiment, unlike Raman scattering, gives information on the absolute value of the couplings,

this means that a hybrid PBE functional better describes $\lambda_\nu/N(\epsilon_F)$ than the original PBE. However, many of our α=30% results remain much lower than Gunnarsson's, which means that the discrepancy between the total couplings is significant. Hands et al.[35] argued that Gunnarsson's fit of PES data attributed signal intensity to the H_g modes that should be assigned elsewhere. Thus, they carried out another spectroscopy experiment[35] and found a value of 97 meV for $\Sigma_{H_g}\lambda_\nu/N(\epsilon_F)$ in C_{60}^{-}. Our result of 94 meV for α=30% is much more in line with this value than the value obtained by Gunnarsson of 147 meV.

Since band structure calculations yield $N(\epsilon_F)$ =6–8 states eV^{-1} molecule^{-1} and experimental determinations are in the range of 4–8 states eV^{-1} molecule^{-1},[30] we take $N(\epsilon_F)$=4–8 states eV^{-1} molecule^{-1} and deduce from our results λ=0.3–0.6 for α=0% and λ=0.4–0.9 for α =30%. Since experimental results range from λ=0.7 to λ =1.2,[30,37] the agreement between calculations and experiments is significantly improved if hybrid functionals are used.

Having shown the strong impact of partial inclusion of exact exchange on the electron-phonon coupling, we here analyze qualitatively the dependence of $\lambda_\nu/N(\epsilon_F)$ on α. Further investigations, not presented here, reveal that the increase of coupling is not caused by changes in the geometries, the phonon frequencies, nor their eigenvectors.[27] Hence, the remaining factors that can be affected are the wave functions and the screened potential. Rigorously, in evaluating the electron-phonon coupling, the appropriate quantities in Eq. (1) should be the wave functions and potential (including self-energy effects) of the quasiparticle Dyson equation. It is shown that neither the Hartree-Fock nor the Kohn-Sham potential (within LDA and GGA) describes quasiparticle self-energy effects adequately, leading to errors such as incorrect quasiparticle band gaps.[38] On the other hand, mixing in some exact-exchange energy from the Fock

operator to the exchange-correlation potential, as in the hybrid functionals above, often can mimic the correct quasiparticle potential. Assuming the permittivity ϵ (i.e., screening) is the most affected factor, this suggests a qualitative interpretation explaining the systematic increase of $\lambda_\nu/N(\epsilon_F)$ with α. First, Hartree-Fock is known to overestimate the quasiparticle energy gaps while LDA and GGA have the opposite trend. The addition of a fraction of exact exchange in the PBE functional therefore increases the calculated gap. Since the dielectric constant ϵ decreases as the gap rises, ϵ has an inverse relationship with α. From Eq. (1), $\lambda_\nu/N(\epsilon_F)$ involves the screened potential of the molecule $\vec{\varepsilon}_\nu \cdot \vec{\nabla} V = \Delta V = \epsilon^{-1} \cdot \Delta V_{ion}$ and therefore $\lambda_\nu/N(\epsilon_F) \propto 1/\epsilon^2$. Thus, $\lambda_\nu/N(\epsilon_F)$ should rise with α, as observed here. Since ϵ is a dielectric matrix (which has a complex spatial dependence) and not a dielectric constant, the increase of $\lambda_\nu/N(\epsilon_F)$ with α should depend on the particular mode ν studied, as observed here.

Such an increase of couplings has also recently been observed in graphene and graphite by Lazzeri et al.[39] when LDA/GGA is replaced with the *GW* many-body approach.[38] This demonstrates that the treatment of screening in the method used to compute the electron-phonon coupling can greatly affect the results obtained. The search for the appropriate functionals to calculate the electron-phonon coupling is thus important.

In conclusion, we have studied the hybrid DFT schemes as a possible solution to the reported discrepancies between experimental and theoretical determinations of C_{60}'s electron-phonon coupling data. We find that increasing the contribution of the exchange energy calculated using the Fock operator in the functional from $\alpha=0\%$ to $\alpha=30\%$ has little impact on the structural properties and vibrational frequencies of the coupling modes, but it results in a strong increase of the total electron-phonon coupling ($\sim 40\%$). This improves the agreement with experimental determinations of the electron-phonon coupling data. In particular, it brings the H_g contribution to the total coupling $\Sigma_{Hg} \lambda_\nu/N(\epsilon_F)$ from 67 to 94 meV, in which is much closer to the most recent experimental value of 97 meV. Also, the associated value of λ including uncertainties overlaps that of experiments. This great variability of the electron-phonon coupling with the method used reveals the need for an approach which is more accurate in this domain.

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