Electron-phonon coupling in the $C_{60}$ fullerene within the many-body GW approach

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We study the electron-phonon coupling in the $C_{60}$ fullerene within the first-principles GW approach, focusing on the lowest unoccupied $t_{1u}$ three-fold electronic state which is relevant for the superconducting transition in electron doped fullerenes. It is shown that the strength of the coupling is significantly enhanced as compared to standard density functional theory calculations with (semi)local functionals, with a 48% increase of the electron-phonon potential $V^{ep}$ with respect to the LDA value. The calculated GW value for the contribution from the $H_g$ modes of 93 meV comes within 4% of the most recent experimental values. The present results call for a re-investigation of previous density functional based calculations of electron-phonon coupling in covalent systems in general.

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I. INTRODUCTION

Electron-phonon coupling in molecular systems is at the heart of several important physical phenomena, including the mobility of carriers in organic electronic devices,\textsuperscript{1,4} the dissociation of excitons at the donor/acceptor interface in organic photovoltaic cells,\textsuperscript{2} or the superconducting transition in molecular solids, from the most famous fulleride case,\textsuperscript{5} to the recent alkali doped picene.\textsuperscript{6} Even though the interplay between phonon-mediating and electronic correlations is still being discussed to better rationalize the superconducting transition all across the fullerenes family,\textsuperscript{10} the magnitude of the electron-phonon coupling (EPC) in $C_{60}$ has been the subject of numerous theoretical and experimental studies since the early 90s in order to evaluate in particular the effective phonon-mediated attractive potential $V^{ep}$ central to the BCS theory.

Of particular relevance for electron-doped fullerenes, the coupling to the lowest unoccupied molecular orbital (LUMO) was explored extensively on the basis of various theoretical approaches\textsuperscript{1,4} from earlier combinations of semi-empirical and density functional theory (DFT) calculations\textsuperscript{11-13} to fully first-principles DFT studies.\textsuperscript{14-21} Concerning the contribution of the $H_g$ vibrational modes, values from 38 meV to 68 meV were calculated within DFT and (semi)local functionals such as the local density approximation (LDA), while the $A_g$ modes were found to provide a much smaller contribution, consistently below about 10 meV. These calculated energies are significantly lower than the available experimental values extracted from photoemission (PES) experiments on isolated fullerenes with $V^{ep}$ found to extend from 96 meV to 147 meV for the $H_g$ modes contribution,\textsuperscript{22,24} and from 107 meV to 158 meV including both $A_g$ and $H_g$ contributions.\textsuperscript{23,24}

In recent work\textsuperscript{25-28} the EPC in $C_{60}$ was revisited using DFT and hybrid functionals. An important outcome of these studies was a significant increase of $V^{ep}$ with increasing percentage of exact exchange within modified B3LYP or PBE functionals. This clearly indicates that in such systems, not only the electronic excitation energies, but also the EPC constants, are very sensitive to the choice of the exchange-correlation functional. Despite the overall better agreement with experiments when hybrid functionals are used, it is unclear which amount of exact exchange should be used for the fullerenes, or any finite or extended system in general. Further, the evaluation of the coupling constant to individual energy levels such as the $t_{1u}$ state in $C_{60}$ relies on the identification of the Kohn-Sham eigenstates and eigenvalues with proper electronic quasiparticle states and excitation energies. From a pragmatic point of view, the amount of exact exchange in e.g. B3LYP is adjusted to reproduce ground-state properties of a set of molecular systems,\textsuperscript{25} but does not guaranty that Kohn-Sham eigenvalues reproduce correctly quasiparticle energies. For example, the $C_{60}$ Kohn-Sham HOMO-LUMO gap is 2.8 eV within the DFT-B3LYP approach.\textsuperscript{26,27} This is better than the 1.6 eV obtained within DFT-PBE,\textsuperscript{28} but still significantly smaller than the 4.9 eV experimental gap in the gas phase.\textsuperscript{29}

In the present work, we study the electron-phonon coupling in the $C_{60}$ fullerene using the first-principles GW approach providing well-defined and accurate quasiparticle energies within a parameter-free many-body perturbation theory framework. We focus on the threefold $t_{1u}$ lowest unoccupied molecular orbital (LUMO) which forms the conducting states in electron-doped fullerenes and thus determines the superconducting properties. We find that the electron-phonon potential $V^{ep}$ is increased by as much as 48% as compared to DFT-LDA calculations, bridging the gap with experimental data. In particular, the contribution from the $H_g$ modes is now found to be within 4% of the two most recent experimental estimates. The present results may invite to reconsider pre-

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vious DFT calculations of the electron-phonon coupling constants involved e.g. in the study of the superconductivity in molecular or extended systems.

II. METHODOLOGY

In the GW quasiparticle formalism\textsuperscript{30-34} for which decades of expertise exist in the case of bulk systems,\textsuperscript{16,19,20} the exchange-correlation potential is described by a non-local energy-dependent self-energy $\Sigma(r, r'u'|E)$ which can be expressed as follows:

\[
\Sigma^{GW}(r, r'|E) = \frac{i}{2\pi} \int d\omega \, G(r, r'|E + \omega)W(r, r'|\omega)
\]

\[
G(r, r'|\omega) = \sum_n \phi_n(r)\phi^*_n(r')/(\omega - \varepsilon_n \pm i\delta)
\]

\[
W(r, r'|\omega) = \int dr'' V^C(r, r''r')\epsilon^{-1}(r'', r'|\omega)
\]

where $G$ is the time-ordered Green’s function\textsuperscript{28} and $W$ the dynamically screened Coulomb potential built from the bare Coulomb potential $V^C$ and the non-local inverse dielectric matrix $\epsilon^{-1}$ at finite frequency. For extended solids, the “starting” ($\varepsilon_n, \phi_n$) eigenstates used to build $G$ and the dielectric response are traditionally obtained from a ground-state DFT calculation with (semi)local functionals such as LDA or PBE.

In the case of isolated molecules, the GW approach was recently thoroughly validated on a large set of small molecules\textsuperscript{27} and larger organic ones such as fullerenes, porphyrins\textsuperscript{38} or DNA/RNA nucleobases.\textsuperscript{39} An excellent agreement with experiment for the ionization energies and electronic affinities were obtained through a simple self-consistency on the eigenvalues with DFT-LDA eigenstates used as the starting point.\textsuperscript{38-40} In this latter approach, labeled GW in what follows, the HOMO-LUMO gap of gas phase C$_{60}$ was calculated to be 4.91 eV,\textsuperscript{38} in much better agreement with experiment than the DFT-B3LYP Kohn-Sham value.

Our calculations are based on a recently developed\textsuperscript{38,41} gaussian-basis implementation of the GW formalism (the FIESTA code) with explicit treatment of dynamical correlations through contour deformation techniques. We start from DFT-LDA eigenstates calculated with the SIESTA package\textsuperscript{32} and a double-zeta plus polarization (DZP) basis\textsuperscript{33} for the description of the valence orbitals combined with standard norm-conserving pseudopotentials.\textsuperscript{34} As shown below, the resulting electron-phonon coupling potentials are very similar to that obtained with all-electron calculations\textsuperscript{16,19,20} at least at the DFT level for which several studies are available. While GW calculations exploiting DFT eigenstates generated with pseudopotentials represent the most common approach,\textsuperscript{32,34} a specific aspect of the present gaussian-basis implementation is that the auxiliary basis described here below has been optimized\textsuperscript{38,39,45} to project onto the products of occupied/unoccupied pseudized eigenstates.

The needed two-point operators such as the dynamical and non-local free-electron susceptibility $\chi_0(r, r'u'|\omega)$, the screened Coulomb potential $W(r, r'u'|\omega)$ and the self-energy operator $\Sigma^{GW}(r, r'u'|\omega)$, are expressed on an auxiliary even-tempered gaussian basis consisting of 4 gaussians per each $(s,p,d)$-channel with localization decay constant $(0.2,0.5,1,2.5,3.2)$ a.u. Such a basis was thoroughly tested in the GW study of a retinal chromophore\textsuperscript{45} of fullerenes, porphyrins or phtalocyanines\textsuperscript{38} and DNA/RNA nucleobases.\textsuperscript{39,46}

For numerical accuracy when calculating the correlation contribution to the self-energy, we first evaluate $\Sigma^{GW}(E)$ on a coarse energy grid to get a first estimate of the quasiparticle energy, and then recalculate $\Sigma(E)$ on a fine energy grid around this energy to refine our calculated correlation contribution. We verify as well that performing the imaginary-axis integration needed in the contour deformation technique (see Ref.\textsuperscript{38}) with 12 gaussian points yields results within 0.1 meV as compared to a calculation using 20 gaussian points.

Following the results of Ref.\textsuperscript{20}, we use the relaxed structure and phonon eigenmodes generated within the DFT-B3LYP approach and a 6-311G(d) basis.\textsuperscript{47} This approach was shown to yield the best eigenfrequencies as compared to Raman experiments.\textsuperscript{38,45} The EPC matrix elements are evaluated using a direct frozen-phonon technique. Namely, we deform the molecule along the $\tilde{c}_i\nu$ vibrational eigenvectors with typical amplitudes of 0.05 Å and compute the slope $\tilde{c}_i\nu \cdot \nabla \tilde{c}_i\nu$ of the variation with respect to the deformation amplitude of the DFT Kohn-Sham eigenvalues, and further of the GW quasiparticle energies. We verify that we remain in the linear regime as confirmed by the small value of the error on the regression coefficient within the fitting procedure. Group theory analysis shows that the $(t_{1u} \otimes t_{1u})$ direct product projects only onto the non-degenerate $A_g$ modes and the five-fold $H_g$ vibrational modes, significantly reducing the number of matrix elements to be calculated. It remains that ten modes can contribute to the coupling, so that a very large number of GW calculations are needed.

To conclude this methodology section, we note that in the present approach based on frozen-phonon techniques where atoms are explicitly displaced, the calculated electron-phonon coupling potentials may be subject to errors related to the use of localized basis ("Pulay errors"). This issue was previously explored at the DFT level by comparing localized-basis and plane-wave calculations showing small differences (see Supplementary Materials, Ref.\textsuperscript{20}). In the present case of GW calculations, we verify here below that increasing both the size of the DFT and auxiliary basis, and taking more diffuse auxiliary orbitals, hardly changes the value of the coupling constants, suggesting again small errors related to the use of finite atom-centered bases.
III. RESULTS

Our results are gathered in Table I where we provide the EPC potential contribution $V^{ep}_{\nu}$ for each of the ten relevant modes, including their degeneracy, namely:

$$V^{ep}_{\nu} = \frac{g_{\nu}}{M\omega_{\nu}^{2}} \sum_{i,j=1}^{3} |<\phi_{i}|(\vec{\varepsilon}_{\nu} \cdot \vec{\nabla})V^{SCF}|\phi_{j}>|^2$$

where $(\vec{\varepsilon}_{\nu} \cdot \vec{\nabla})V^{SCF}$ is the normalized variation of the self-consistent potential under distortion of the molecule along the vibrational mode with index $(\nu)$, degeneracy $g_{\nu}$ and frequency $\omega_{\nu}$. The $(i,j)$ indices run over the $t_{1u}$ manifold with $g_{t_{1u}}=3$ degeneracy. The above formula is the molecular limit of the central definition used in $ab$ initio studies of phonon-mediated superconductivity in extended solids.

In the present frozen-phonon approach, the explicit deformation of the molecule diagonalizes the eigenstates with respect to the perturbation, leaving only the intraband transitions which, thanks to Hellmann-Feynman theorem, can be calculated through the variation of the corresponding energy levels, namely:

$$\sum_{i,j=1}^{3} |<\phi_{i}|(\vec{\varepsilon}_{\nu} \cdot \vec{\nabla})V^{SCF}|\phi_{j}>|^2 = \sum_{i=1}^{3} |(\vec{\varepsilon}_{\nu} \cdot \vec{\nabla})\varepsilon_{i}|^2$$

with derivatives calculated through finite differences. This connects EPC matrix elements and the variation of the electronic energy levels with respect to vibrational displacements. This approach is similar to that of Refs. [16-20] but we use both the GW quasiparticle energies and the DFT Kohn-Sham eigenvalues, allowing direct comparison. As an internal accuracy test, following early group symmetry analysis, the trace of an $H_{g}$ perturbation is zero in the $(t_{1u})$ subspace, namely:

$$\sum_{i=1}^{3} |(\vec{\varepsilon}_{\nu} \cdot \vec{\nabla})\varepsilon_{i}| = 0$$

a condition which is well verified within our DFT and GW calculations.

Our LDA data yield a total 73.4 meV coupling, in good agreement with the 75.8 meV all-electron PBE value of Ref. [20]. Comparing to other calculations, namely extracting the coupling coefficient from the evolution of the DFT-LDA Kohn-Sham eigenvalues under molecular distortion, our 65 meV value for the $H_{g}$ modes contribution is also very close to the 68 meV value by Antropov and coworkers within a full-potential framework, and the 67 meV obtained with an all-electron gaussian basis. Consistently with early Raman analysis, all studies agree on the predominance of the two high energy $H_{g}(8)$ and $H_{g}(7)$ tangential modes, but contributions at lower energy such as from the $H_{g}(2)$ and $H_{g}(3)$ radial modes are found to be important as well.

The central result of the present study is the dramatic 48% increase of the total coupling potential within the GW approach as compared to LDA calculations. $V^{ep}$ is indeed found to increase from 73.4 meV (LDA) to 108.6 meV ($GW$). For the $H_{g}$ modes, the calculated $GW$ value of 92.8 meV agrees well with the two most recent 96.2 meV and 96.5 meV independent experimental estimates of Ref. [21] (Table V) and Ref. [22] respectively. Further, the total $GW$ coupling of 108.6 meV is in close agreement with the latest 106.7 meV experimental value. The present results clearly question the accuracy of the EPC calculated within DFT and (semi)local functionals. In view of the remarkable agreement with experiment obtained with the present parameter-free $GW$ formalism, one can hope that this approach will improve our understanding of phonon-mediated processes in general.

IV. DISCUSSION

We can now comment on the recent studies performed with hybrids functionals. Since both the experimental and GW total coupling potential fall within the rather large [93,111] meV energy range obtained by changing the amount of exact exchange from 20% to 30% in the hybrid DFT approaches, one could certainly build a functional yielding excellent agreement with experiment for this specific $C_{60}$ system. However, clearly, the amount of needed exact exchange may vary from one system to another (see below). It is further instructing to compare mode by mode the various approaches. Considering e.g. the $A_{g}(2)$ and $H_{g}(8)$ modes showing large coupling, it appears that the largest amount of exact exchange tested so far (30%) is not enough to reach the GW results. In contrast, the GW values for the $H_{g}(n=2,3,5,6)$ modes are well within the hybrid functionals range. This suggests that even for a given single molecule, it seems difficult to optimize the amount of exact exchange so as to reproduce the GW results mode by mode. This observation leads to emphasizing the importance of the non-local and dynamical correlation part of the GW self-energy. In our approach where only the energy levels are updated, but not the wavefunctions, the differences between DFT-LDA and GW results can only stem from the replacement of the exchange-correlation functional by the GW self-energy.

An interesting observation is that a non-self-consistent $G_{0}W_{0}$ calculation starting from LDA eigenstates (see column 6 of Table I) leads to a coupling constant which is still significantly larger than the DFT-LDA value, but smaller than the GW one, and very similar to that of the hybrid B3LYP functional. As emphasized in recent work in the case of molecular systems, the significantly too small starting LDA gap leads to a large over-screening in the standard $G_{0}W_{0}$(LDA) approach. In the present $C_{60}$ case, the $G_{0}W_{0}$(LDA) gap is found to be 4.4 eV, much better than the 1.6 eV LDA value, but still smaller than the 4.9 eV experimental and GW values. Qualitatively, this overscreening certainly softens the variations of the ionic and electronic potential seen by the electrons upon lattice distortion.
Recently\(^{51}\), the EPC matrix elements in graphene for the \(\Gamma-E_{2g}\) and \(K-A_{1g}\) phonon modes were studied within a non-self-consistent \(G_0W_0\) (LDA) approach. As compared to DFT-LDA calculations, the square of the deformation potentials, labeled \(\langle D_k^2 \rangle\) and \(\langle D_k^2 \rangle_{LDA}\), were shown to increase by 41\% and 114\% respectively\(^{52}\). This is consistent with our own results, suggesting that EPC matrix elements are significantly affected by the \(GW\) correction in both finite and extended systems. A further important outcome of this study was that, in graphene, the DFT-B3LYP approach yields significantly too large coupling constants as compared to experiment, in contrast with the present case of fullerenes where the DFT-B3LYP calculations underestimate the coupling. This certainly points out to the difficulties in obtaining hybrid functionals which are accurate for both finite and extended systems.

### V. CONCLUSION

In conclusion, we have studied using a first-principles \(GW\) approach the electron-phonon coupling strength in the \(C_{60}\) fullerene, focusing on the \(t_{1u}\) LUMO state of interest to the superconducting transition in the fullerenes. It is found that within \(GW\), the electron-phonon potential \(V^{\text{ep}}\) increases by 48\% as compared to the value calculated within DFT and (semi)local functionals such as LDA or PBE. The calculated 93 meV \(GW\) value for the \(H_g\) modes contribution comes within 4\% of the two most recent experimental estimates. This demonstrates that the present parameter-free approach allows a precise determination of the electron-phonon coupling potential in one of the most studied molecular system. Beyond the important case of the fullerenes, the present results call for a reinvestigation of previous DFT-based calculations of the electron-phonon coupling in organic systems, and possibly as well in “covalent superconducting systems” such as in particular MgB\(_2\) or doped diamond. Similarly, the important phonon-induced renormalization of the electron and hole band width in organic semiconductors may deserve further inspection beyond previous DFT calculations.

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| Mode | \(\omega\) (cm\(^{-1}\)) | Theory | Experiments |
|------|----------------|--------|-------------|
|     |     | LDA | B3LYP | Hybrids | \(G_0W_0\) (LDA) | \(GW\) | Iwahara\(^{a}\) | Hands\(^{b}\) | Gunnarsson\(^{c}\) |
| \(A_g(1)\) | 496 | 0.5 | 1.2 | 1.2 - 1.7 | 1.2 | 1.0 (107\%) | - | 11.3 |
| \(A_g(2)\) | 280 | 0.3 | 0.9 | 1.0 - 1.4 | 1.1 | 0.7 (100\%) | - | 11.3 |
| \(H_g(1)\) | 265 | 0.5 | 1.0 | 1.2 - 1.6 | 1.3 | 1.3 (107\%) | - | 11.3 |
| \(H_g(2)\) | 260 | 0.5 | 1.0 | 1.2 - 1.6 | 1.3 | 1.3 (107\%) | - | 11.3 |
| \(H_g(3)\) | 693 | 2.3 | 4.2 | 5.0 - 5.6 | 5.2 | 5.2 (23\%) | - | 11.3 |
| \(H_g(4)\) | 875 | 2.4 | 4.5 | 5.0 - 5.6 | 5.2 | 5.2 (23\%) | - | 11.3 |
| \(H_g(5)\) | 875 | 2.4 | 4.5 | 5.0 - 5.6 | 5.2 | 5.2 (23\%) | - | 11.3 |
| \(H_g(6)\) | 1265 | 2.1 | 2.1 | 2.0 - 2.4 | 2.3 | 2.3 (9\%) | - | 11.3 |
| \(H_g(7)\) | 550 | 1.3 | 1.7 | 1.0 - 1.5 | 1.3 | 1.3 (107\%) | - | 11.3 |
| \(H_g(8)\) | 550 | 1.3 | 1.7 | 1.0 - 1.5 | 1.3 | 1.3 (107\%) | - | 11.3 |

Total \(A_g\): - 8.2 12.2 12.1 - 14.3 14.8 16.0 (95\%) 10.6 - 11.3
Total \(H_g\): - 65.2 81.5 80.0 - 96.3 78.8 92.6 (42\%) 96.2 96.5 147.0

Total: - 73.4 93.7 93.7 - 110.7 93.6 108.6 (48\%) 106.8 - 158.3

\(^{a}\) Ref. \(^{21}\), Table V.
\(^{b}\) Ref. \(^{22}\)
\(^{c}\) Ref. \(^{24}\)

TABLE I: Calculated electron-phonon coupling contributions to \(V^{\text{ep}}\) for the \(A_g\) and \(H_g\) modes (meV) calculated within LDA, B3LYP (Ref. \(^{20}\), DFT with various hybrid functionals at the same 6-311G(d) level (column Hybrids with data from Refs. \(^{14}\) \(^{21}\)), non-self-consistent \(G_0W_0\) (LDA) and \(GW\). The percentage of increase as compared to LDA is indicated in parenthesis. The experimental data are compiled in the three last columns.

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44. Since the GW formalism is not currently used as a total energy formalism, we adopt the usual strategy of performing such calculations on the best available atomic structures.

45. Vibrational eigenmodes have been obtained with the Gaussian03 code. See: M. J. Frisch et al., GAUSSIAN (03, Revision C02, Gaussian, Inc., Wallingford, CT, 2004).

46. As a convergency test, in the case of the $H_\delta$ mode showing the largest coupling, we verify that with the use of a larger and more diffuse auxiliary basis, containing 5 gaussians with decay constants (0.15,0.32,0.69,1.48,3.2) a.u., the GW coupling potential is found to be 65% larger than the LDA reference, to be compared with the 63% found with the auxiliary basis adopted throughout the present work and in Refs. 35, 39. As a second test, we have expanded the Kohn-Sham basis by adding an additional split
s-orbital. The $GW$ coupling potential is found to be 62% larger than the LDA coupling constant, showing again excellent agreement with the 63% of Table I.

51 M. Lazzeri, C. Attaccalite, L. Wirtz, and F. Mauri, Phys. Rev. B 78, 081406 (2008).

52 Similar results, but with reduced differences between DFT-LDA and $G_0W_0$(LDA) calculations were observed in doped graphene. See: A. Grüneis, C. Attaccalite, A. Rubio, D. V. Vyalikh et al., Phys. Rev. B 79, 205106 (2009).