Electron–Vibron Interactions in Charged Buckminsterfullerene: Pair Energies and Spectra (Part II)

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Abstract

The ground state energy shifts and excitation spectra of charged buckminsterfullerene $C_{60}^n$, $n = 1, \ldots, 5$ are calculated. The electron–vibron Hamiltonian of Part I is extended to include all $A_g$ and $H_g$ modes with experimentally determined frequencies and theoretically estimated coupling constants. Complex splitting patterns of $H_g$ vibrational levels are found. Our results are relevant to EPR measurements of spin splittings in $C_{60}^{2-}$ and $C_{60}^{3-}$ in solution. Spectroscopic gas-phase experiments will be of interest for further testing of this theory. As

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found in Part I, degeneracies in the electron and vibron Hamiltonians give rise to a dynamical Jahn Teller effect, and to a considerable enhancement of the electronic pairing interaction. This helps to overcome repulsive Coulomb interactions and has important implications for superconductivity in K$_3$C$_{60}$ and the insulating state in K$_4$C$_{60}$.

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1 Introduction

This paper continues the investigations of the electron-vibron interactions within a fullerene molecular anion, C$_{60}^{-}$. In Part I (Ref. [1]) we considered in great detail the idealized case of a single $H_g$ vibron mode coupled to the electronic degenerate $t_{1u}$ orbital for $n=1,..5$ electrons. By solving the problem for strong, intermediate and weak coupling regimes, we have shown the existence of Berry phases for odd $n$, and their importance in determining ground state energies and degeneracies. The Berry phase effects are clearest in strong coupling, where the parity of the pseudorotational orbital angular momentum $L$, is related to the electron filling $n$ by

$$(-1)^{L+n} = 1$$

The effects on the energies however are relatively stronger in weak coupling where quantum corrections enhance pair binding which is a factor $5/2$ larger than the corresponding classical Jahn-Teller (JT) relaxation energy $E^{JT}$. This leads to larger electron-vibron pairing interaction than previously calculated using Migdal-Eliashberg theory. Moreover, this enhancement is of direct importance to C$_{60}^{-}$, where the electron-vibron coupling is weak to intermediate. These encouraging results clearly call for a more realistic study of the full electron-vibron problem of C$_{60}^{-}$. This is the purpose of this paper, where we will address both the vibronic spectrum, and the pairing energies, in quantitative detail.
The full molecular Hamiltonian describes the dynamics of 60 carbon atoms plus 240\(+n\) valence electrons. The problem is substantially simplified by assuming the knowledge of the non interacting spectra for electronic levels [2,3,4] and for molecular vibrations, both from theory [3,4] and experiment [5,6]. For \(n=0\), the electrons form a closed shell. This allows a Born-Oppenheimer decoupling of the vibron and electron systems. For \(n=1,...,5\), however, the extra electrons partly fill the threefold degenerate Lowest Unoccupied Molecular Orbitals (LUMO) states of \(t_{1u}\) symmetry, which give rise to a linearly coupled JT system. Other orbitals, such as the Highest Occupied Molecular Orbitals (HOMO) states of \(h_u\) symmetry, at \(\sim -2\text{eV}\) below the LUMO states, and the \(t_{2g}\) (LUMO+1) states at \(\sim +1\text{eV}\), introduce weaker quadratic electron-vibron couplings which we presently ignore. Further complications may arise from anharmonic effects.

Fortunately, neglect of all these higher order effects is expected to be a very good approximation in \(C_{60}^\sim\), where the \(t_{1u}\) level is very well separated from others, and the C-C bonds are rather stiff and harmonic. Detailed Hartree-Fock calculations have shown, for example, that the energy gain by going from \(I_h\) to \(D_{5d}, D_{3d}, D_{2h}\) symmetries via static JT distortions, are in fact identical to within 1% [7]. Therefore, restricting to the \(t_{1u}\) orbital, to linear JT coupling and harmonic vibrons is very well justified in \(C_{60}^\sim\). Neglecting also Coulomb interactions (they will be discussed separately in Section [8]), the full electronic problem is therefore replaced by a \(3\times3\) matrix linearly coupled to vibrons.

Thus our Hamiltonian is an extension of the single mode mode solved in full in Part I. Here we shall include the eight \(H_g\) vibron modes of real \(C_{60}\), instead of only one. Also we shall include two \(A_g\) vibrons which also couple linearly to the LUMO electrons, even though they do not split its degeneracy. Symmetry prevents all other vibrons different from \(A_g\) and \(H_g\) to interact linearly with the \(t_{1u}\) orbitals. If we further neglect higher order interactions, all other vibrons are decoupled and unaffected by changing the
electronic filling $n$.

Generally speaking, even with these drastic approximations, a realistic description of the dynamical JT state of a C$_{60}^{n-}$ ion is a more complicated affair than the single mode treated in Part I. For a general coupling strength, there is in fact no linear superposition between effects produced by different $H_g$ vibrons coupled to the same $t_{1u}$ orbital. Luckily, however, linear superposition turns out to be valid in the weak coupling perturbative regime, which, in turn, applies, even if only approximately, to fullerene.

In this paper we apply perturbation theory to the full electron-vibron problem of C$_{60}^{n-}$, with $n=1$ to 5 in a $t_{1u}$ orbital, and including all $A_g$ and $H_g$ modes [8]. As in Part I, we make the further approximation of replacing a spherically symmetrical coupling to the true icosahedral hamiltonian on the C$_{60}$ ball. Analytical expressions correct to second order in the electron-vibron coupling strengths are found for ground state and excitation energies, as well as for electron pair binding energies ("effective Hubbard $U$'s"). Using realistic coupling constants from Local Density Approximation calculations, we obtain numerical estimates for these vibron-induced pair energies and find them to be unexpectedly large and negative ($\approx -0.2$eV) for $n=1,3,5$, and even larger but positive ($\approx 0.4$eV) for $n=2,4$. This finding is discussed in qualitative connection with superconductivity in A$_3$C$_{60}$ [9, 10, 11], and with the insulating state of A$_4$C$_{60}$ (A=K,Rb).

The calculated vibron spectrum of C$_{60}^{n-}$ is also presented in detail. Notwithstanding the uncertainty in the physical coupling constants, large splittings of all $H_g$ modes are predicted. These are expected to be observable for example in gas phase C$_{60}$ and C$_{60}^{2-}$ ions. This part is organized as follows: Section 2 defines the multi vibron model. Section 3 describes the perturbative calculation of the spectrum. Section 4 presents the relation of the results to experimental measurements of vibron spectroscopy of C$_{60}^{n-}$ anions. Section 5 discusses the interplay between electron-vibron and Coulomb interactions for the ground state and pair binding energies. We conclude with a short
2 The Hamiltonian

The single electron LUMO states of $C_{60}$ are in a triplet of $t_{1u}$ representation. The important vibrational modes which couple to this electronic shell are of two representations: $A_g$ (one dimensional) and $H_g$ (five dimensional). $A_g$, $t_{1u}$ and $H_g$ are the icosahedral group counterparts of the spherical harmonics $1, \{Y_{1m}\}_{m=-1}^1$, and $\{Y_{2m}\}_{m=-2}^2$ respectively. By replacing the truncated icosahedron (soccer ball) by a sphere, we ignore lattice corrugation effects which are expected to be small for the electron-vibron interactions, since they do not lift the degeneracies of $L = 0, 1, 2$ representations.

The Hamiltonian includes the terms

\[
H = H^0 + H^{e-v} + \cdots
\]

(2)

where electron-electron interactions, anharmonic interactions between phonon modes, and anharmonic coupling terms have been neglected. The non-interacting Hamiltonian is

\[
H^0 = \hbar \sum_k \omega_k \sum_{M=-L_k,L_k} \left( b_{kM}^\dagger b_{kM} + \frac{1}{2} \right) + (\varepsilon - \mu) \sum_{ms} c_{ms}^\dagger c_{ms},
\]

(3)

$b_{kM}^\dagger$ creates a vibron of mode $k$ and energy $\omega_k$ in the spherical harmonic state $Y_{L_kM}$, where $L_k$ denotes the angular momentum of mode $k$, either 0 or 2 according to whether $k$ is an $A_g$ or an $H_g$ representation respectively. $c_{ms}^\dagger$ creates an electron of spin $s$ in an orbital $Y_{1m}$. This Hamiltonian operates on the basis

\[
\prod_{K M} |n_{kM}\rangle_v \prod_{ms} |n_{ms}\rangle_e
\]

(4)

where $|n_{kM}\rangle_v (|n_{ms}\rangle_e)$ is a vibron (electron) Fock state. By setting $\mu \to \varepsilon$ we discard the second term in (3).
The electron–vibron interaction is local and we assume it to be rotationally invariant. The nuclear vibration field of eigenvector $k$ is
\[
    u_k(\hat{\Omega}) = \sum_M \frac{1}{\sqrt{2}} (Y^*_{LM}(\hat{\Omega}) b^\dagger_{L_kM_k} + Y_{LM}(\hat{\Omega}) b_{L_kM_k})
\]
where $\hat{\Omega}$ is a unit vector on the sphere. The interaction between the vibrations and electron density is
\[
    H_{e-v} \propto \sum_k g_k \int d\hat{\Omega} \ u_k(\hat{\Omega}) \sum_s \psi_s^\dagger(\hat{\Omega}) \psi_s(\hat{\Omega})
\]
where the electron field operators are
\[
    \psi_s(\hat{\Omega}) = \sum_{m=-1}^1 Y_{1m}(\hat{\Omega}) c_{ms}
\]
Using the relation
\[
    \int d\hat{\Omega} \ Y_{LM}(\hat{\Omega}) Y_{lm_1}(\hat{\Omega}) Y_{lm_2}(\hat{\Omega}) \propto (-1)^M \langle L, -M | l_{m_1} l_{m_2} \rangle,
\]
where $\langle \cdot | \cdot \rangle$ is a Clebsch-Gordan coefficient \cite{G}, yields the second quantized Hamiltonian
\[
    H_{e-v} = H_{e-v}^A + H_{e-v}^H
\]
\[
    H_{e-v}^A = \sqrt{\frac{3}{2}} \hbar \sum_{k=1}^2 g_k \omega_k \sum_{m} (-1)^m \left( b_{k0}^\dagger + b_{k0} \right)
    \times \langle 0, 0 | 1, -m; 1, m \rangle c_{ms}^\dagger c_{ms}
\]
\[
    H_{e-v}^H = \sqrt{\frac{3}{2}} \hbar \sum_{k=3}^{10} g_k \omega_k \sum_{M=-2}^2 \sum_{m} (-1)^m \left( b_{kM}^\dagger + (-1)^M b_{k-M} \right)
    \times \langle 2, M | 1, -m; 1, m + M \rangle c_{ms}^\dagger c_{ms+M},
\]
where the numerical constants are fixed by the requirement that the classical JT energy gain of a single mode $k$ is $g_k^2/2$ \cite{J}.
The Multi–Mode Spectrum (Weak Coupling)

The perturbation hamiltonian (9) written in the Fock basis (4), connects states whose number of vibrons \( N_v(k) \) of mode \( k \) differs by exactly \( \pm 1 \). Thus, first order corrections to the energies vanish. Second order corrections are obtained by diagonalizing the matrix \[ \Delta^{(2)}_{a,b} = \langle a | H^{e-v} \frac{1}{E_a^{(0)} - H^0} H^{e-v} | b \rangle, \] (10)

where \( |a\rangle \) and \( |b\rangle \) are members of the same degenerate manifold, i.e. they have the same number of vibrons \( N_v(k) \). The sum implied by the inverse operator \((E_a^{(0)} - H^0)^{-1}\) extends just to those states whose \( N_v \)'s differ only by \( \pm 1 \) from that of the multiplet being perturbed. This means that to second order in the coupling constants \( g_k \) there are no direct inter-mode interactions, and the modes can be treated separately. The only second-order inter-mode coupling is a consequence of all the modes having a common ground state \((N_v=0)\). The effect of vibron \( k \) affects this \( N_v=0 \) state either with a pure shift or through both shift and splitting. However all other modes \( k' \), having their ladder built on the same \( N_v=0 \) state, are shifted or split by vibron \( k \), according to the same structure of this \( N_v=0 \) multiplet. This effect takes place through additive contributions proportional to \( g_k^2 \) to the diagonal matrix elements \( \Delta^{(2)}_{a,a} \) relative to the \( k' \) ladder, without involving off-diagonal inter-mode couplings, which would be related to \( g^4 \) and higher order corrections.

A single \( A_g \) mode coupled to a \( t_{1u} \) level is the simple polaron problem, which is exactly soluble [14]: the second order energy is exact. Since the \( A_g \) representation is one-dimensional, it does not split the electronic degeneracy. The only effect is a downward shift of the whole spectrum. The amount of \( A_g \)-related energy shift is found to be \(-E_k^{JT}, -4E_k^{JT} \) and \(-6E_k^{JT} \), for \( n=1,2 \) and 3 respectively (where \( E_k^{JT} \) is the classical JT energy gain \( \equiv g_k^2 \hbar \omega_k / 2 \) of that mode \( A_g(k) \)). Obviously, these results hold for both unpolarized and polarized spin states, since the \( t_{1u} \) levels remain degenerate.
For the $H_g$ modes the situation is more complicated. For $n=1$, the degenerate vibronic $t_{1u}$ ground state is not split by JT coupling, as it conserves its $L=1$ symmetry. For this reason, the only contribution of the vibron $H_g(k)$ to the spectrum of another vibron $H_g(k')$ is just a constant energy shift of $-5/4 g_k^2$, which obviously does not affect energy differences in the spectrum of vibron $k'$. This is perfectly analogous to the effect of a single $A_g$ mode on all the other vibrons.

By contrast, the $n=2,4$ and $n=3$ lowest vibronic multiplets ($N_v=0$) are split (into $1S$, $1D$, $3P$, and $2P$, $2D$, $4S$ levels respectively). Correspondingly, the levels of an interacting vibron $k$ receive different diagonal contributions of order $g_k^2$, from different interacting vibrons $k'$, giving rise to a more intricate pattern of splittings.

For the sake of simplicity, and also since $C_{60}$ seems easiest to obtain in the gas phase [15], we will concentrate on the many-modes spectrum for $n=1$. The perturbative results for all $H_g$ and $A_g$ modes will be presented in Section 4. In principle, the full spectra for $n=2,3,4$, can be determined following the same method.

The spectrum for a single $H_g$ mode is given in Table I for the degenerate multiplets $N_v=0$ and $N_v=1$, and for $n=1$, 2, ($S=0$) and 3 ($S=1/2$) electrons. In Figures (1, 2, 3) we replott on an expanded scale the results of exact diagonalization of Ref [1] for 1, 2 and 3 electrons, along with the straight lines corresponding to present perturbative results for the lowest few states. These figures confirm that perturbative results retain quantitative validity up to $g \approx 0.3$. In the special case $n=1$, moreover, the perturbative results lay within $0.05\hbar\omega$ of the exact value up to $g \leq 0.4$.

We have therefore an approximate analytical estimate of the splittings induced by JT coupling, valid in weak coupling. For example, for $n=1$ the $H_g$ vibron excitation, originally at energy 1 above the ground state, splits into three vibronic levels with relative shifts $-\frac{3}{4} g^2$, $\frac{3}{8} g^2$ and $\frac{9}{8} g^2$ (in units of $\hbar\omega$ of that vibron). Table I contains the complete list of these low lying
excitations energies, accurate to order $g^2$.

Because the effects of all $A_g$ and $H_g$ modes can be linearly superposed, there are two ingredients only, which we need to have in order to transform the analytical shifts of Table I into actual numbers for $C_{60}^{n-}$: the frequencies $\hbar \omega_k$ and the coupling constants $g_k$ of each individual $H_g$ and $A_g$ mode. For the frequencies, there are both calculated and measured values. We can avoid uncertainties by choosing the latter as given, e.g. for neutral C$_{60}$ in Ref. [6]. In doing so, we neglect the well known small systematic frequency shifts associated with bond-length readjustments and other electronic effects going from C$_{60}$ to C$_{60}^{n-}$ [16, 17]. They also depend on the environment of the C$_{60}^{n-}$ ion.

There are several calculated sets of coupling constants $g_k$ [3, 11, 9, 18], but no direct measurement. Since the agreement among the different calculations is far from good, in Section 4 we present the results of several selected sets, which provides an estimate of the relevant uncertainties. We will eventually adopt the most recent values of Antropov et al. [18].

As seen in Table II, almost all of the couplings $g_k$ are weak, $g_k \leq 0.4$. As discussed, in this range the perturbative results are accurate within ten per cent or better for all the low lying states. As the discrepancies among the various estimates of the $g_i$ is much larger, these perturbative formulas are at this stage more than adequate, and particularly good in the $n=1$ case, where the distortion is smallest.

This is fortunate, since exact diagonalization is computationally rather demanding if all $H_g$ modes are included. Better knowledge of frequencies and coupling constants might warrant a calculation of higher orders in $g_k$.

4 Vibron spectroscopy of C$_{60}^{n-}$ anions.

The electron affinity of C$_{60}$ is large (2.7 eV) and experimental evidence has been found that the C$_{60}^{n-}$ [15] and C$_{60}^{2-}$ [19] are stable ions in vacuum. In
solution a wider spectrum of ionization states has been demonstrated electrochemically, up to and including $C_{60}^{5-}$ [20, 21, 22]. As an adsorbate on a metal surface, the electronegative $C_{60}$ molecule naturally picks up electrons [23, 24], and recent evidence has been provided of charge transfer which can be as large as $n=6$ [17]. In the solid state, finally, there are compounds, covering a wide range of charge transfers, from $n=1$, as in TDAE$^+–C_{60}^–$ [25] or Rb$_1$C$_{60}$ [26], $n=3$, as in K$_3$C$_{60}$ or Rb$_2$C$_{60}$ [27], $n=4$ as in K$_4$C$_{60}$ [28], $n=6$ as in Rb$_6$C$_{60}$ [29], or even higher as in Li$_{12}$C$_{60}$ [30, 14].

Among these systems, our calculations so far address concretely only the gas phase case. Unfortunately, to our knowledge no investigation appears to have been made of the vibrational excitations of isolated $C_{60}^–$ and $C_{60}^{2–}$. Our calculated excitation spectrum for $C_{60}^–$ therefore constitutes a prediction which we hope will stimulate new work.

In Table II we report the excitation energies predicted by perturbation theory, applied to the eight modes in the $C_{60}^–$ case. Selection rules are not discussed here for any particular spectroscopy. We simply give the symmetry assignments.

As is seen, the predicted splittings due to dynamical JT coupling are generally quite large, and should be well observed spectroscopically. However, as indicated by comparison between different sets of $g_k$’s, there is a large uncertainty in these predicted splittings of the same order of magnitude as the splittings themselves. As remarked earlier, the same uncertainty does not affect the energetics of the following section, which is on safer grounds. Our calculated spectrum is therefore of qualitative value, and we rather expect it to work backwards. That is, a future precise measurement of the splittings should provide an accurate evaluation of the actual couplings.

As a further caution, we should stress that our spherical representations in the Hamiltonian (8) neglect interactions due to the icosahedral lattice of carbons. For example the vibron multiplet of $L = 3$ decomposes due to the lattice into $T_{2u} \oplus G_u$ [31], etc. In addition to neglecting lattice effects and
anharmonic interactions, we also ignore spin-orbit coupling. As remarked in Part I, it has been shown \cite{32} to yield splittings of the order of 50 cm$^{-1}$ to the $L = 1$ ground state (in Ar matrix), which is not a negligible amount. Thus we estimate that the splittings obtained by our Hamiltonian should dominate the splittings found in the real spectrum.

As pointed out by Bergomi and Jolicoeur \cite{33}, experiments on anions in matrix may be relevant to the vibronic effects. Near infrared and optical spectra of C$_{60}^-$ ions in solution are available \cite{21}. A major $t_{1u} \rightarrow t_{1g}$ optical transition near 1 eV is present for all $n$ values. It is accompanied by additional vibronic shake-up structures, typically near 350, 750, 1400 and 1600 cm$^{-1}$.

This limited information seems as yet insufficient for any relevant comparison with our calculations. Well defined vibrational spectra are instead available for chemisorbed C$_{60}^-$ \cite{17} and for A$_n$C$_{60}$ alkali fullerides \cite{29}. In this case, however, interaction of the electronic $t_{1u}$ level with surface states or with other $t_{1u}$ states of neighbouring balls must turn the level into a broad band, and our treatment as it stands is invalid. One can generally expect rapid electron hopping from a molecule to another to interfere substantially with the dynamical JT process, in a way which is not known at present. The spectra of charged C$_{60}$ adsorbates and solids, in any case, do not present evidence of any dynamic splittings such as those of Table II, but rather of a gradual continuous shift most likely due to a gradual overall change of geometry, as suggested also by LDA calculations \cite{4}.

Summarizing, we are yet unaware of detailed spectroscopic confirmation of the electron-vibron effects. We expect however these effects to be observable in the gas phase of C$_{60}$ and C$_{60}^2$ but not present evidence of any dynamic splittings such as those of Table II, but rather of a gradual continuous shift most likely due to a gradual overall change of geometry, as suggested also by LDA calculations \cite{4}.

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5 Ground state energetics and effective Hubbard $U$’s.

Perturbation theory allows us to write analytic expressions for the energy gain of the ground state at different $n$, and therefore for the pair energy

$$U_n = E_{n+1} + E_{n-1} - 2E_n,$$

as discussed in Ref [1]. Comparison with exact single-mode results shows a systematical perturbative overestimate (Figures 1, 2, 3) of the $H_g$-related ground state energy shift. The error is however relatively small and quite acceptable for the couplings in Table II. The shift is $5/2$ times larger than its classical value, as discussed in Ref. [1]. This factor $5/2$ is important, because it leads in turn to a surprisingly large energetic lowering even for small $g$’s, making JT vibronic coupling a much more important affair than it was understood so far. The physical reason for the large energy gain is that the dynamically JT distorted molecule undergoes a dramatic decrease of vibrational zero-point energy. This adds an extra $-\frac{3}{2}g^2\hbar\omega$ (in the $n=1$ case, say) to the static JT gain $-\frac{1}{2}g^2\hbar\omega$ of each $H_g$ mode. The zero-point energy decreases faster at small $g$ probably because the mexican-hat potential well is more “square-well”-like than the original harmonic potential. We also note that the proliferation of excited states upon coupling $H_g$ with $t_{1u}$ is of fermionic origin, and does not add to the zero-point energy.

Within second order perturbation theory the ground state energy is a sum of all the 2+8 contributions of the $A_g + H_g$ modes:

$$E_{tot}(n) = E_{A_g} + E_{H_g} = a_nE_{A_g}^{JT} + b_nE_{H_g}^{JT} = a_n\sum_{k=1}^{2} E_{k}^{JT} + b_n\sum_{k=3}^{10} E_{k}^{JT},$$

where

$$E_{k}^{JT} = \frac{1}{2}g_k^2\hbar\omega_k,$$
We already discussed in Section 3 the JT ground state energy gains due to an $A_g$ mode, with coefficients $a_n=-1$, -4, and -6, for $n=1$, 2 and 3 respectively. Table I gives the corresponding energies for the $H_g(k)$ modes ($k > 2$). These are given by

$$
\begin{align*}
-\frac{5}{2}E_{2k}^{JT} & \quad n = 1 \\
-10E_{2k}^{JT} & \quad n = 2 \\
-\frac{15}{2}E_{2k}^{JT} & \quad n = 3
\end{align*}
$$

the appropriate coefficients being therefore $b_1=-5/2$, $b_2=-10$, $b_3=-15/2$.

These expressions allow us to compute the individual contribution to the pair energies $U_n$ (Eq. (11)) due to the $A_g$ and $H_g$ modes. We give these formulae in Table III. The corresponding numerical values are reported in Table IV, based on the ground state energy gains as given by the set of coupling constants of Eq. (11).

We consider the unpolarized spin sector. Similar subtractions could easily be done, if needed, for high-spin states, or high- and low-spin, using, for example $E_{tot}(n=2,S=0)$, with $E_{tot}(n=3,S=3/2)$. Although, as we pointed out, the values of the individual $g_s$’s of Ref. [18], [10] and [9] are significantly uncertain, the global $E_{H_g}$ is much less author-dependent, amounting to 102 meV, 84 meV and 78 meV respectively ($n=1$).

As Table II shows, the coupling with the $A_g$ mode pushes $U_1$ further towards negative values, but has the opposite effect on $U_2$ and $U_3$.

The overall enhancement factor $5/2$ in the ground state $H_g$ shift ends up producing a much larger pair energy than expected so far based on classical JT energies [9]. In particular, our calculated JT energy gain of $\approx 0.4$ eV for $n=2$ and $\approx 0.3$ eV for $n=3$ (low-spin) is almost one order of magnitude larger than the currently accepted values! This has important implications, first of all, in determining whether the simple $C_{60}^{-}$ ion, in vacuum, in a matrix or in solution, will choose to be high-spin or low-spin.
In order to discuss this point, we recall the existence of an intra-ball Coulomb repulsion $U$ (not to be confused with the pair energy of Ref [1]), which for a $t_{1u}$ level is a matrix, specified by two main values, $U_\parallel$ (two electrons in the same orbital), and $U_\perp < U_\parallel$ (two electrons in different orbitals). Using the JT energy differences between the high- and low-spin states as

$$E_{S=0}^{(2)} - E_{S=1}^{(2)} = (U_\parallel^{(2)} - 4E_{JT_{Ag}}^{(2)} - 10E_{JT_{Hg}}^{(2)}) - (U_\perp^{(2)} - 4E_{JT_{Ag}}^{(2)} - \frac{5}{2}E_{JT_{Hg}}^{(2)})$$

$$= (U_\parallel^{(2)} - U_\perp^{(2)}) - \frac{15}{2}E_{JT_{Hg}}^{(2)} \approx (U_\parallel^{(2)} - U_\perp^{(2)}) - 0.3eV \quad (15)$$

$$E_{S=\frac{3}{2}}^{(3)} - E_{S=\frac{1}{2}}^{(3)} = (U_\parallel^{(3)} + 2U_\perp^{(3)} - 6E_{JT_{Ag}}^{(3)} - \frac{15}{2}E_{JT_{Hg}}^{(3)}) - (3U_\perp^{(3)} - 6E_{JT_{Ag}}^{(3)})$$

$$= (U_\parallel^{(3)} - U_\perp^{(3)}) - \frac{15}{2}E_{JT_{Hg}}^{(3)} \approx (U_\parallel^{(3)} - U_\perp^{(3)}) - 0.3eV \quad , \quad (16)$$

where we have used the fact that the JT energetics for $n=2, S=1$ is identical to that for $n=1, S=1/2$ [1], while for $n=3, S=3/2$ there is no JT distortion. We have also used the $t_{1u}$ orbital unimodal and bimodal splitting patterns of Part I to identify the filling $(n_1, n_2, n_3)$. In particular the fillings assumed are (0,0,2) for $n=2, S=0$; (1,1,0) for $n=2, S=1$; (0,1,2) for $n=3, S=1/2$; (1,1,1) for $n=3, S=3/2$.

So long as $U^{(n)}$ may be expected to vary slowly with the electron number $n$, then the two energy differences (15) and (16) should be very similar. Moreover, the prevailing of a high- or of a low-spin state is decided by a fine balance between the Coulomb repulsion anisotropy $(U_\parallel - U_\perp)$ and the dynamical JT gain $\frac{15}{2}E_{JT_{Hg}}$. This suggests the possibility that if high-spin is more likely to prevail for $C_{26}^{2-}$ and $C_{60}^{3-}$ in the gas phase, where $U$ is large, the balance might easily reverse in favor of low-spin when in matrix or in solution. Recent EPR data indicate that this is precisely the case. When frozen in a CH$_2$Cl$_2$ glass, $C_{26}^{2-}$ appears to be in a high-spin, $S=1$ state [20]. Hence, in this case $(U_\parallel - U_\perp)$ is larger than 0.3 eV. However, optical and EPR data for $C_{60}^{3-}$ in CH$_2$Cl$_2$ and other matrices favor a low-spin state [21]. Now $U_\parallel^{(3)} - U_\perp^{(3)}$ has therefore become smaller than 0.3 eV. We can conclude that,
even for a single embedded molecule, the balance between intra-ball Coulomb repulsion and dynamical JT energy gains is extremely critical.

Recent photoemission and Auger data \[34\] have shown that the intra $h_u$ HOMO orbital Coulomb $U$ is not as large as it was previously supposed. In particular, a decrease by only 0.23 eV from gas phase $C_{60}$ and the crystalline $C_{60}$ hole-hole Auger shifts, implies $|U| < 1$ eV in the latter. This upper bound is about a factor three smaller than those previously proposed \[35\]. In the light of this observation, it is not at all surprising to find that $U_\parallel - U_\perp$ is in the neighbourhood of 0.3 eV for $C_{60}^n$ in a matrix.

Coming next to the pair binding energies of Ref \[1\], we find large negative dynamical JT-related $U_n$'s for odd $n$. Even if we omit the $A_g$ contribution (which may be irrelevant for superconductivity, due to screening \[18\]), we get $U_3 = -0.2$ eV. This negative value, will cancel at least a good fraction of the Coulomb positive intra-ball pair energy

$$U_{3,Coul} = U_{(2)}^{(2)} + (2U_{(4)}^{(4)} + 4U_{(4)}^{(4)}) - 2(U_{(3)}^{(3)} + 2U_{(3)}^{(3)}) \approx U_\parallel$$

This cancellation implies a severe decrease of the Coulomb pseudopotential $\mu^*$ relative to that calculated when the JT coupling is ignored \[36\]. For a sufficiently strong solid-state screening of the electronic $U_\parallel$ and $U_\perp$, it may well be sufficient to reverse to a negative $\mu^*$, i.e. to an overall negative Hubbard $U$ state.

For $n=2$ and 4, dynamical JT stabilizes the average configuration of $C_{60}^n$, since the pair energy is positive: $U_2 \approx 0.4$ eV. This now acts to reinforce the bare Coulomb pair energy

$$U_{2,Coul}^{(2)} = U_{(3)}^{(3)} - 2U_{(3)}^{(3)} - 2U_{(3)}^{(3)} \approx 2U_\perp - U_\parallel$$

$$U_{4,Coul}^{(5)} = (2U_{(5)}^{(5)} + 8U_{(5)}^{(5)}) + (U_{(3)}^{(3)} + 2U_{(3)}^{(3)}) - 2(2U_{(4)}^{(4)} + 4U_{(4)}^{(4)}) \approx 2U_\perp - U_\parallel$$

where a filling (2,2,1) has been assumed for $n=5$.

For even $n$, the JT coupling stabilizes a correlated insulating state of a lattice of evenly-charged $C_{60}$ molecules. In this type of insulator, fluctuations
about $\langle n_i \rangle = n$ are suppressed, and a gap of order $U_n$ is opened in the electronic spectrum.

This state has an even number of electrons per site, and is non-magnetic, very much like a regular band insulator. However, electron correlations responsible for band narrowing and gap opening are vibronic in origin. We suggest that the (body-centered tetragonal [37]) structure of K$_4$C$_{60}$ and Rb$_4$C$_{60}$ may be a realization of this state where electronic and vibronic interactions play an important role. So far, band calculations [23] and experiments [38] had been in disagreement, the former suggesting a metal, and the latter finding a narrow-gap insulator.

Very recent UPS data on K$_n$C$_{60}$ [40] have shown a decrease of the energy difference between the HOMO and the Fermi level (inside the $t_{1u}$ LUMO) when going from $n=3$ to $n=4$ and finally to $n=6$. This kind of non-rigid band behaviour is in itself not a surprising result. The surprise is that the decrease is very large from $n=3$ to $n=4$ ($\approx 0.4$ eV), and smaller from $n=4$ to $n=6$ ($\approx 0.2$ eV). As pointed out by De Seta and Evangelisti, a positive Coulomb $U$ would predict exactly the opposite. We observe that this behaviour is instead in agreement with our predicted pattern of effective $U_n$ of vibronic origin, which is therefore supported by these data.

Additional experiments which may probe the electron–vibron interactions are short time resolved spectroscopy of excitons in neutral C$_{60}$ [39]. An exciton consists of an electron in the LUMO orbital and a hole in the $H_g$ HOMO levels, which interact with different strengths with the vibrons. The hole-vibron coupling inside the HOMO could be studied along similar lines to those presented above for the $t_{1u}$ LUMO.

As for superconductivity in solids with $n=3$, we expect the enhanced pair binding found here to be crucial for overcoming the on-site Coulomb repulsion and for enhancing $T_c$ over its value in, e.g., graphite intercalates. Broadening of the $t_{1u}$ electron level into a band of non-negligible width makes the present treatment insufficient for quantitative predictions. From the fundamental
point of view however, it is amusing to note that superconductivity can be enhanced by a decrease of lattice zero-point energy. This adds to the usual BCS mechanism of reducing the electron kinetic energy by opening a gap. We hope to pursue this line of thought further in future work.

6 Summary

In conclusion, a full treatment of all the $A_g$ and $H_g$ modes has been given, and shown to yield analytical results with quantitative accuracy for the full dynamical JT problem of $C_{60}^{n-}$. The ground state energetics has been studied, and unexpectedly large energy gains have been found, due to a decrease of zero-point energy. This implies large positive effective $U_n$ for $n=2$ and 4, and a large negative $U_3$, which is very interesting in view of superconductivity in $K_3C_{60}$ and insulating behaviour in $K_4C_{60}$. Detailed vibrational spectra for $C_{60}^{n-}$ are presented, and proposed for spectroscopic investigation, particularly in gas phase.

Related work is also being done by other groups [11].

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| n   | $N_v$ | original degeneracy | $2^{nd}$ order residual degeneracy | excit. energy $E^{(2)} - E_{\text{ground}}^{(2)}$ | $2S+1\Omega$ |
|-----|------|----------------------|----------------------------------|---------------------------------|----------------|
| 1   | 0    | $3(\times 2)$       | -5/4                             | 3                               | 0              | $^2P$          |
| (S = $\frac{1}{2}$) | 1    | $15(\times 2)$      | -2                               | 7                               | $1 - \frac{3}{4} g^2$ | $^2F$          |
|     |      |                      | -7/8                             | 5                               | $1 + \frac{3}{8} g^2$ | $^2D$          |
|     |      |                      | -1/8                             | 3                               | $1 + \frac{9}{8} g^2$ | $^2P$          |
| 2   | 0    | 6                    | -5                               | 1                               | 0              | $^1S$          |
| (S = 0) | 1    | 30                   | -11/4                            | 5                               | $\frac{9}{4} g^2$ | $^1D$          |
|     |      |                      | -5                               | 5                               | 1              | $^1D$          |
|     |      |                      | -17/4                            | 9                               | $1 + \frac{3}{3} g^2$ | $^1G$          |
|     |      |                      | -11/4                            | 7                               | $1 + \frac{9}{8} g^2$ | $^1F$          |
|     |      |                      | -13/8                            | 5                               | $1 + \frac{33}{8} g^2$ | $^1D$          |
|     |      |                      | -7/8                             | 3                               | $1 + \frac{9}{8} g^2$ | $^1P$          |
|     |      |                      | -1/2                             | 1                               | $1 + 9 g^2$    | $^1S$          |
| 2   | 0    | $3(\times 3)$       | -5/4                             | 3                               | 0              | $^3P$          |
| (S = 1) | 1    | $15(\times 3)$      | -2                               | 7                               | $1 - \frac{3}{4} g^2$ | $^3F$          |
|     |      |                      | -7/8                             | 5                               | $1 + \frac{3}{8} g^2$ | $^3D$          |
|     |      |                      | -1/8                             | 3                               | $1 + \frac{9}{8} g^2$ | $^3P$          |
| 3   | 0    | $8(\times 2)$       | -15/4                            | 3                               | 0              | $^2P$          |
| (S = $\frac{1}{2}$) | 1    | 40($\times 2$)      | -9/4                             | 5                               | $\frac{3}{2} g^2$ | $^2D$          |
|     |      |                      | -9/2                             | 7                               | $1 - \frac{3}{4} g^2$ | $^2F$          |
|     |      |                      | -15/4                            | 9                               | 1              | $^2G$          |
|     |      |                      | -15/4                            | 5                               | 1              | $^2D$          |
|     |      |                      | -21/8                            | 3                               | $1 + \frac{9}{8} g^2$ | $^2P$          |
|     |      |                      | -9/4                             | 7                               | $1 + \frac{9}{8} g^2$ | $^2F$          |
|     |      |                      | -9/8                             | 5                               | $1 + \frac{33}{8} g^2$ | $^2D$          |
|     |      |                      | -3/8                             | 3                               | $1 + \frac{9}{8} g^2$ | $^2P$          |
|     |      |                      | 0                                | 1                               | $1 + \frac{9}{8} g^2$ | $^2S$          |
| 3   | 0    | $1(\times 4)$       | 0                                | 1                               | 0              | $^4S$          |
| (S = $\frac{3}{2}$) | 1    | $5(\times 4)$       | 0                                | 5                               | 1              | $^4D$          |
TABLE I. Analytical expressions of energy shifts and excitation energies for the electron-vibron coupling of a single $H_g$ mode, for low-spin and high-spin states, to second order in the coupling constant $g$. 
Table II

| $H_g$ | Exp. Energy (cm$^{-1}$) | coupling $g_k$ | excitation energy $E_{fin} - E_{ground}$ (cm$^{-1}$) | $L_{fin}$ (sym.) |
|-------|------------------------|----------------|------------------------------------------------|----------------|
| 1     | 270.0                  | 0.33 0.33 0.54 | 248 248 212                                      | 3 ($T_{2u} \oplus G_u$) |
|       |                        |                | 281 281 299                                      | 2 ($H_u$) |
|       |                        |                | 303 303 357                                      | 1 ($T_{1u}$) |
| 2     | 430.5                  | 0.37 0.15 0.40 | 387 423 380                                      | 3 ($T_{2u} \oplus G_u$) |
|       |                        |                | 452 434 456                                      | 2 ($H_u$) |
|       |                        |                | 496 441 507                                      | 1 ($T_{1u}$) |
| 3     | 708.5                  | 0.20 0.12 0.23 | 687 701 679                                      | 3 ($T_{2u} \oplus G_u$) |
|       |                        |                | 719 712 723                                      | 2 ($H_u$) |
|       |                        |                | 741 719 752                                      | 1 ($T_{1u}$) |
| 4     | 772.5                  | 0.19 0.00 0.30 | 751 773 722                                      | 3 ($T_{2u} \oplus G_u$) |
|       |                        |                | 783 773 798                                      | 2 ($H_u$) |
|       |                        |                | 805 773 849                                      | 1 ($T_{1u}$) |
| 5     | 1099.0                 | 0.16 0.23 0.09 | 1077 1055 1092                                   | 3 ($T_{2u} \oplus G_u$) |
|       |                        |                | 1110 1121 1103                                   | 2 ($H_u$) |
|       |                        |                | 1132 1164 1110                                   | 1 ($T_{1u}$) |
| 6     | 1248.0                 | 0.25 0.00 0.15 | 1190 1248 1226                                   | 3 ($T_{2u} \oplus G_u$) |
|       |                        |                | 1277 1248 1259                                   | 2 ($H_u$) |
|       |                        |                | 1335 1248 1281                                   | 1 ($T_{1u}$) |
| 7     | 1426.0                 | 0.37 0.48 0.30 | 1281 1179 1332                                   | 3 ($T_{2u} \oplus G_u$) |
|       |                        |                | 1499 1549 1473                                   | 2 ($H_u$) |
|       |                        |                | 1644 1796 1568                                   | 1 ($T_{1u}$) |
| 8     | 1575.0                 | 0.37 0.26 0.24 | 1415 1495 1510                                   | 3 ($T_{2u} \oplus G_u$) |
|       |                        |                | 1655 1615 1608                                   | 2 ($H_u$) |
|       |                        |                | 1815 1695 1673                                   | 1 ($T_{1u}$) |

TABLE II. Vibronic excitation spectrum for the eight $H_g$ modes. Three different sets of coupling constants used in the perturbative expressions of Table I. The relations \[8\] between the coupling strength $g$ and the electron-
phonon coupling $\lambda/N(\epsilon_F)$ (See Ref. [18]) are for $H_g$ modes $g^2 = \frac{6}{5} \lambda/N(\epsilon_F)/\hbar\omega$, and for $A_g$ modes $g^2 = 3\lambda/N(\epsilon_F)/\hbar\omega$. 
### Table III

| mode | $U_1$     | $U_2$     | $U_3$     |
|------|-----------|-----------|-----------|
| $A_g$ | $-2E_{0,k}^{JT}$ | $E_{0,k}^{JT}$ | $4E_{0,k}^{JT}$ |
| $H_g$ | $-5E_{2,k}^{JT}$ | $10E_{2,k}^{JT}$ | $-5E_{2,k}^{JT}$ |

Table III. Analytical expressions for single mode pair energies (low-spin states) to second order in the corresponding coupling constants $g_k$. 

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### Table IV

| Exp. Energy (cm$^{-1}$) | coupling $g_k$ | Ground state energy shift (meV) $n=1$ | $n=2$ | $n=3$ |
|-------------------------|----------------|--------------------------------------|-------|-------|
| $E_{A_g,1}$              | 493.0          | 0.38                                 | -5    | -18   | -27   |
| $E_{A_g,2}$              | 1468.5         | 0.39                                 | -14   | -54   | -81   |
| $E_{H_g,3}$              | 270.0          | 0.33                                 | -5    | -18   | -14   |
| $E_{H_g,4}$              | 430.5          | 0.37                                 | -9    | -36   | -27   |
| $E_{H_g,5}$              | 708.5          | 0.20                                 | -5    | -18   | -14   |
| $E_{H_g,6}$              | 772.5          | 0.19                                 | -5    | -18   | -14   |
| $E_{H_g,7}$              | 1099.0         | 0.16                                 | -5    | -18   | -14   |
| $E_{H_g,8}$              | 1248.0         | 0.25                                 | -12   | -48   | -36   |
| $E_{H_g,9}$              | 1426.0         | 0.37                                 | -30   | -120  | -90   |
| $E_{H_g,10}$             | 1575.0         | 0.37                                 | -33   | -132  | -99   |
| $E_{A_g}$                |               | -18                                  | -72   | -108  |
| $E_{H_g}$                |               | -102                                 | -408  | -306  |
| $E_{\text{tot}}$         |               | -120                                 | -480  | -414  |
| $U_{n,A_g}$              |               | -36                                  | 18    | 72    |
| $U_{n,H_g}$              |               | -204                                 | 408   | -204  |
| $U_{n,\text{tot}}$       |               | -240                                 | 426   | -132  |

**TABLE IV.** Dynamical JT ground state energy shifts due to each mode, their total, and the pair energies $U_n$. Results are accurate to second order in the coupling constants $g_k$. 
Figure 1: Exact (solid line) and perturbative energies (dashed line) for \( n=1 \), one coupled \( H_g \) mode of frequency \( \omega \). The straight lines correspond to second order perturbation theory for the \( N_v=0 \) and \( N_v=1 \) multiplets.

Figure 2: Exact (solid line) and perturbative energies (dashed line) for \( n=2 \), one coupled \( H_g \) mode of frequency \( \omega \). The perturbative lines correspond to the \( N_v=0 \) and the lowest three multiplets of \( N_v=1 \).

Figure 3: Exact (solid line) and perturbative energies (dashed line) for \( n=2 \), one coupled \( H_g \) mode of frequency \( \omega \). The perturbative lines correspond to the \( N_v=0 \) and the lowest three multiplets of \( N_v=1 \). The second order coupling does not split the \( L=4 \) and \( L=2 \) levels in the \( N_v=1 \) multiplet, while the exact theory finds they actually do separate. The next excited level (of species P) is also drawn to show its crossing of the initially lower D level.