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Electron-vibron interactions in charged fullerenes. II. Pair energies and spectra

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The ground-state energy shifts and excitation spectra of charged fullerenes $C_{60}{}^{n-}$, $n=1,\ldots,5$ 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 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_3C_{60} and the insulating state in K_4C_{60}.

I. INTRODUCTION

This paper continues the investigations of the electron-vibron interactions within a fullerene molecular anion, $C_{60}{}^{n-}$. 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 $n=1,\ldots,5$ 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

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

The effects on the energies however are relatively stronger in weak coupling, where quantum corrections enhance pair binding, which is a factor $\frac{5}{2}$ *larger* than the corresponding classical Jahn-Teller (JT) relaxation energy $E^{\rm JT}$. This leads to a larger electron-vibron pairing interaction than previously calculated using Migdal-Eliashberg theory. Moreover, this enhancement is of direct importance to $C_{60}{}^{n-}$, 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 $C_{60}{}^{n-}$. 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 knowledge of the noninteracting spectra for electronic levels[2–4] 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 $n=1,\ldots,5$, however, the extra electrons partly fill the threefold-degenerate lowest unoccupied molecular orbitals (LUMO) states of t_{1u} symmetry, which gives rise to a linearly coupled JT system. Other orbitals, such as the highest occupied molecular orbitals (HOMO) states of h_u symmetry, at ~ -2 eV below the LUMO states, and the t_{2g} (LUMO+1) states at $\sim +1$ eV, introduce weaker quadratic electron-vibron couplings which we ignore at present. Further complications may arise from anharmonic effects.

Fortunately, neglect of all these higher-order effects is expected to be a very good approximation in $C_{60}{}^{n-}$, 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 gains 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, restriction to the t_{1u} orbital, to linear JT coupling, and to harmonic vibrons is very well justified in $C_{60}{}^{n-}$. Neglecting also Coulomb interactions (they will be discussed separately in Sec. III), the full electronic problem is therefore replaced by a 3×3 matrix linearly coupled to vibrons.

Thus our Hamiltonian is an extension of the single 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 from interacting 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 $n=1-5$ to a t_{1u} orbital, and including all A_g and H_g modes.[8] As in part I, we make the further approximation of substituting a spherically symmetrical coupling for the true icosahedral Hamiltonian on the C_{60} spheroid. 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 (LDA) calculations, we obtain numerical estimates for these vibron-induced pair energies and find them to be unexpectedly large and negative (≈ -0.2 eV) for $n=1,3,5$, and even larger but positive (≈ 0.4 eV) for $n=2,4$. This finding is discussed in qualitative connection with superconductivity in A_3C_{60},[9–11] and with the insulating state of A_4C_{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 paper is organized as follows: Sec. II defines the multivibron model. Section III describes the perturbative calculation of the spectrum. Section IV presents the relation of the results to experimental measurements of vibron spectroscopy of $C_{60}{}^{n-}$ anions. Section V discusses the interplay between electron-vibron and Coulomb interactions, for the ground-state and pair binding energies. We conclude with a short summary.

II. 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 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

$$H=H^0+H^{e\text{-}v}+\cdots , \tag{2}$$

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

$$H^0=\hbar\sum_k \omega_k \sum_{M=-L_k,L_k} (b^\dagger_{kM}b_{kM}+\tfrac{1}{2})+(\epsilon-\mu)\sum_{ms} c^\dagger_{ms}c_{ms} . \tag{3}$$

Here, $b^\dagger_{kM}$ creates a vibron of mode k and energy ω_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. $c^\dagger_{ms}$ creates an electron of spin s in an orbital Y_{1m}. This Hamiltonian operates on the basis

$$\prod_{KM} |n_{kM}\rangle_v \prod_{ms} |n_{ms}\rangle_e , \tag{4}$$

where $|n_{kM}\rangle_v$ ($|n_{ms}\rangle_e$) is a vibron (electron) Fock state. By setting $\mu \rightarrow \epsilon$ 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

$$u_k(\hat\Omega)=\sum_M \frac{1}{\sqrt{2}}[Y^*_{L_kM}(\hat\Omega)b^\dagger_{L_kMk}+Y_{L_kM}(\hat\Omega)b_{L_kMk}] , \tag{5}$$

where $\hat\Omega$ is a unit vector on the sphere. The interaction between the vibrations and electron density is

$$H^{e\text{-}v}\propto \sum_k g_k \int d\hat\Omega u_k(\hat\Omega)\sum_s \psi^\dagger_s(\hat\Omega)\psi_s(\hat\Omega) , \tag{6}$$

where the electron field operators are

$$\psi_s(\hat\Omega)=\sum_{m=-1}^{1} Y_{1m}(\hat\Omega)c_{ms} . \tag{7}$$

Using the relation

$$\int d\hat\Omega Y_{LM}(\hat\Omega)Y_{lm_1}(\hat\Omega)Y_{lm_2}(\hat\Omega) \propto (-1)^M\langle L,-M|lm_1;lm_2\rangle , \tag{8}$$

where $\langle\cdots\rangle$ is a Clebsch-Gordan coefficient,[12] yields the second quantized Hamiltonian

$$\begin{aligned} H^{e\text{-}v}&=H^{e\text{-}v}_{A_g}+H^{e\text{-}v}_{H_g} , \\ H^{e\text{-}v}_{A_g}&=\sqrt{3/2}\hbar\sum_{k=1}^{2} g_k\omega_k \sum_{ms}(-1)^m(b^\dagger_{k0}+b_{k0})\langle 0,0|1,-m;1,m\rangle c^\dagger_{ms}c_{ms} , \\ H^{e\text{-}v}_{H_g}&=\frac{\sqrt{3}}{2}\hbar\sum_{k=3}^{10} g_k\omega_k \sum_{M=-2}^{2}\sum_{ms}(-1)^m[b^\dagger_{kM}+(-1)^M b_{k-M}]\langle 2,M|1,-m;1,m+M\rangle c^\dagger_{ms}c_{m+Ms} , \end{aligned} \tag{9}$$

where the numerical constants are fixed by the requirement that the classical JT energy gain of a single mode k is $g_k^2/2$.[1]

III. THE MULTIMODE 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 ± 1. Thus, first-order corrections to the energies vanish. Second-order corrections are obtained by diagonalizing the matrix[13]

$$\Delta^{(2)}_{a,b} = \left\langle a \left| H^{e\text{-}v} \frac{1}{E_a^{(0)} - H^0} H^{e\text{-}v} \right| b \right\rangle , \qquad (10)$$

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 ± 1 from that of the multiplet being perturbed. This means that to second order in the coupling constants g_k there are no direct intermode interactions, and the modes can be treated separately. The only second-order intermode coupling is a consequence of all the modes having a common ground state ($N_v = 0$). The vibron k affects this $N_v = 0$ state either by 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 intermode couplings, whose effect would be of order g^4 and higher.

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 $-E_k^{\mathrm{JT}}$, $-4E_k^{\mathrm{JT}}$, and $-6E_k^{\mathrm{JT}}$, 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 $-\frac{5}{4} g_k^2$, 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-mode spectrum for $n = 1$. The perturbative results for all H_g and A_g modes will be presented in Sec. IV. 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 ($S = \frac{1}{2}$) electrons. In Figs. 1, 2, and 3 we replot 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 the 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 lie within $0.05\hbar\omega$ of the exact value up to $g \lesssim 0.4$.

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 (in units of $\hbar\omega$ of that vibron) 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 the same units). Table I contains the complete list of these low-lying excitation energies, accurate to order g^2.

Because the effects of all A_g and H_g modes can be linearly superposed, there are only two ingredients 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,[3,10,9,18] but no direct measurement. Since the agreement among the different calculations is far from good, in Sec. IV 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, Gunnarsson, and Liechtenstein.[18]

As seen in Table II, almost all of the couplings g_k are weak, $g_k \lesssim 0.4$. As discussed, in this range the perturbative results are accurate within 10% 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 more accurate calculation including higher orders in g_k.

IV. 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 $C_{60}{}^{-}$ (Ref. 15) and $C_{60}{}^{2-}$ (Ref. 19) are stable ions in vacuum. In solution a wider spectrum of ionization states has been demonstrated electrochemically, up to and including $C_{60}{}^{5-}$.[20–22] 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 $TDAE^{+}$-$C_{60}{}^{-}$ (Ref. 25) or RbC_{60},[26] $n=3$, as in K_3C_{60} or Rb_3C_{60},[27] $n=4$ as in K_4C_{60},[28] $n=6$ as in Rb_6C_{60},[29] or even higher as in $Li_{12}C_{60}$.[30,16]

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 further 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 ac-

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.

n	N_v	Original degeneracy	Second-order shift $\Delta^{(2)}/g^2\hbar\omega$	Residual degeneracy	Excit. energy $E^{(2)}-E^{(2)}_{\text{ground}}/\hbar\omega$	${}^{2S+1}L$
1	0	3(×2)	$-\frac{5}{4}$	3	0	${}^2P$
($S=\frac{1}{2}$)	1	15(×2)	-2	7	$1-\frac{3}{4}g^2$	${}^2F$
			$-\frac{7}{8}$	5	$1+\frac{3}{8}g^2$	${}^2D$
			$-\frac{1}{8}$	3	$1+\frac{9}{8}g^2$	${}^2P$
2	0	6	-5	1	0	${}^1S$
($S=0$)			$-\frac{11}{4}$	5	$\frac{9}{4}g^2$	${}^1D$
	1	30	-5	5	1	${}^1D$
			$-\frac{17}{4}$	9	$1+\frac{3}{4}g^2$	${}^1G$
			$-\frac{11}{4}$	7	$1+\frac{9}{4}g^2$	${}^1F$
			$-\frac{13}{8}$	5	$1+\frac{27}{8}g^2$	${}^1D$
			$-\frac{7}{8}$	3	$1+\frac{33}{8}g^2$	${}^1P$
			$-\frac{1}{2}$	1	$1+9g^2$	${}^1S$
2	0	3(×3)	$-\frac{5}{4}$	3	0	${}^3P$
($S=1$)	1	15(×3)	-2	7	$1-\frac{3}{4}g^2$	${}^3F$
			$-\frac{7}{8}$	5	$1+\frac{3}{8}g^2$	${}^3D$
			$-\frac{1}{8}$	3	$1+\frac{9}{8}g^2$	${}^3P$
3	0	8(×2)	$-\frac{15}{4}$	3	0	${}^2P$
($S=\frac{1}{2}$)			$-\frac{9}{4}$	5	$\frac{3}{2}g^2$	${}^2D$
	1	40(×2)	$-\frac{9}{2}$	7	$1-\frac{3}{4}g^2$	${}^2F$
			$-\frac{15}{4}$	9	1	${}^2G$
			$-\frac{15}{4}$	5	1	${}^2D$
			$-\frac{21}{8}$	3	$1+\frac{9}{8}g^2$	${}^2P$
			$-\frac{9}{4}$	7	$1+\frac{3}{2}g^2$	${}^2F$
			$-\frac{9}{8}$	5	$1+\frac{11}{8}g^2$	${}^2D$
			$-\frac{3}{8}$	3	$1+\frac{27}{8}g^2$	${}^2P$
			0	1	$1+\frac{15}{4}g^2$	${}^2S$
3	0	1(×4)	0	1	0	${}^4S$
($S=\frac{3}{2}$)	1	5(×4)	0	5	1	${}^4D$

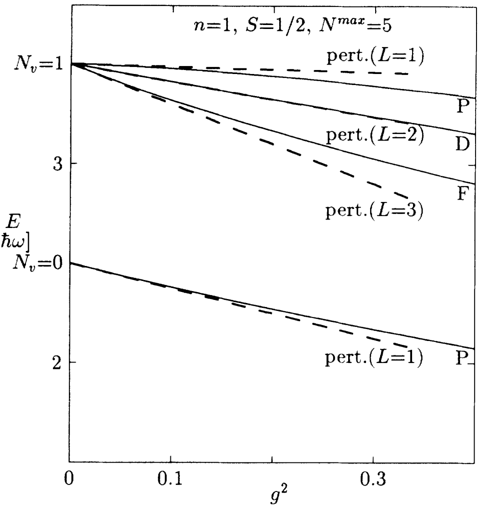

FIG. 1. Exact (solid lines) and perturbative energies (dashed lines) for $n=1$, one coupled H_g mode of frequency ω. The dashed lines correspond to second-order perturbation theory for the $N_v=0$ and $N_v=1$ multiplets.

curate evaluation of the actual couplings.

As a further caution, we should stress that our spherical representations in the Hamiltonian (9) neglect interactions due to the icosahedral lattice of carbon atoms. 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, this has been suggested[32] to yield splittings of the order of 50 cm^{-1} to the $L=1$ ground state (in an 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.

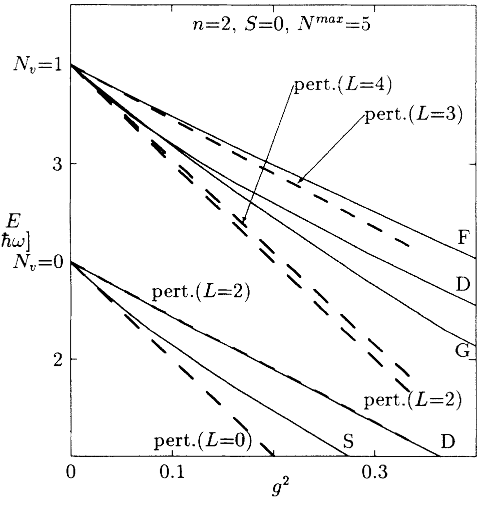

FIG. 2. Exact (solid lines) and perturbative energies (dashed lines) for $n=2$, one coupled H_g mode of frequency ω. The perturbative lines correspond to the $N_v=0$ and the lowest three multiplets of $N_v=1$.

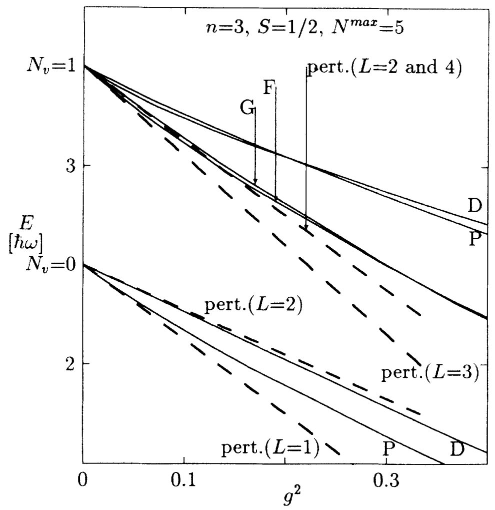

FIG. 3. Exact (solid lines) and perturbative energies (dashed lines) for $n=2$, one coupled H_g mode of frequency ω. The perturbative lines correspond to the $N_v=0$ and the lowest three multiplets of $N_v=1$. The second-order coupling does not split the $L=4$ and $L=2$ levels in the $N_v=1$ multiplet,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

Near-infrared and optical spectra of $C_{60}{}^{n-}$ ions in solution are available.[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 $C_{60}{}^{n-}$,[17] and for A_nC_{60} alkali fullerides.[29] In this case, however, interaction of the electronic t_{1u} level with surface states or with other t_{1u} states of neighboring molecules must turn the level into a broad band, and our treatment as it stands is invalid. One can generally expect rapid electron hopping from one 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.[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 $C_{60}{}^{2-}$. In particular, for $C_{60}{}^{-}$ an observation that each H_g vibron splits into a fourfold multiplet $(T_{2u}+G_u)$ + H_u+T_{1u} (whose two nearly degenerate lowest members correspond to $L=3$) would be an important confirmation of the electron-vibron theory and effects of Berry phases. Raman excitation of this $L=3$ doublet is allowed starting from the T_{1u} ground state.

V. 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

$$U_n = E_{n+1} + E_{n-1} - 2E_n \; , \qquad (11)$$

as discussed in the preceding paper.[1] Comparison with exact single-mode results shows a systematical perturbative overestimate (Figs. 1–3) 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 $\frac{5}{2}$ times larger than its classical value, as discussed in Ref. 1. This factor $\frac{5}{2}$ 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 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 $-\frac{3}{4}g^2\hbar\omega$ (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:

$$E_{\text{tot}}(n) = E_{A_g} + E_{H_g} = a_n E_{A_g}^{\text{JT}} + b_n E_{H_g}^{\text{JT}}$$
$$= a_n \sum_{k=1}^{2} E_k^{\text{JT}} + b_n \sum_{k=3}^{10} E_k^{\text{JT}} \; , \qquad (12)$$

where

$$E_k^{\text{JT}} \equiv \tfrac{1}{2} g_k^2 \hbar\omega_k \; . \qquad (13)$$

We already discussed in Sec. III 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

$$\begin{aligned} &-\tfrac{5}{2}E_{2k}^{\text{JT}} \; , \quad n=1 \; , \\ &-10E_{2k}^{\text{JT}} \; , \quad n=2 \; , \\ &-\tfrac{15}{2}E_{2k}^{\text{JT}} \; , \quad n=3 \; , \end{aligned} \qquad (14)$$

the appropriate coefficients being therefore $b_1 = -\frac{5}{2}$, $b_2 = -10$, and $b_3 = -\frac{15}{2}$.

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 formulas in Table III.

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 (Ref. 9) 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 $g^2 = 3\lambda/N(\epsilon_F)\hbar\omega$.

H_g mode	Expt. energy (cm^{-1}) Ref. 6	Ref. 18	Coupling g_k Ref. 10	Ref. 9	Excitation energy	$E_{\text{fin}} - E_{\text{ground}}$ (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 III. Analytical expressions for single-mode pair energies (low-spin states) to second order in the corresponding coupling constants g_k.

Mode	U_1	U_2	U_3
A_g	$-2E_{0k}^{\mathrm{JT}}$	E_{0k}^{JT}	$4E_{0k}^{\mathrm{JT}}$
H_g	$-5E_{2k}^{\mathrm{JT}}$	$10E_{2k}^{\mathrm{JT}}$	$-5E_{2k}^{\mathrm{JT}}$

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 states, using, for example, $E_{\mathrm{tot}}(n=2,S=0)$ with $E_{\mathrm{tot}}(n=3,S=\frac{3}{2})$. Although, as we pointed out, the values of the individual g_k's of Refs. 18, 10, and 9 are significantly uncertain, the global E_{H_g} is much less author dependent, amounting to 102, 84, and 78 meV, respectively ($n=1$).

As Table II shows, the coupling with the A_g mode pushes U_1 further toward negative values, but has the opposite effect on U_2 and U_3. The overall enhancement factor $\frac{5}{2}$ 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 ≈ 0.4 eV for $n=2$ and ≈ 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 $C_{60}{}^{n-}$ ion, in vacuum, in a matrix, or in solution, will choose to be high spin or low spin.

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.

	Expt. energy (cm^{-1}) Ref. 6	Coupling g_k Ref. 18	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	-17	-108
E_{H_g}			-102	-408	-306
E_{tot}			-120	-480	-414
U_{n,A_g}			-36	18	72
U_{n,H_g}			-204	408	-204
$U_{n,\mathrm{tot}}$			-240	426	-132

In order to discuss this point, we recall the existence of an intramolecular 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). We write the JT energy differences between the high- and low-spin states as

$$\begin{aligned} E_{S=0}^{(2)} - E_{S=1}^{(2)} &= (U_{\parallel}^{(2)} - 4E_{A_g}^{\mathrm{JT}} - 10E_{H_g}^{\mathrm{JT}}) \\ &\quad - (U_{\perp}^{(2)} - 4E_{A_g}^{\mathrm{JT}} - \tfrac{5}{2}E_{H_g}^{\mathrm{JT}}) \\ &= (U_{\parallel}^{(2)} - U_{\perp}^{(2)}) - \tfrac{15}{2}E_{H_g}^{\mathrm{JT}} \\ &\approx (U_{\parallel}^{(2)} - U_{\perp}^{(2)}) - 0.3eV\ , \end{aligned} \tag{15}$$

$$\begin{aligned} E_{S=1/2}^{(3)} - E_{S=3/2}^{(3)} &= (U_{\parallel}^{(3)} + 2U_{\perp}^{(3)} - 6E_{A_g}^{\mathrm{JT}} - \tfrac{15}{2}E_{H_g}^{\mathrm{JT}}) \\ &\quad - (3U_{\perp}^{(3)} - 6E_{A_g}^{\mathrm{JT}}) \\ &= (U_{\parallel}^{(3)} - U_{\perp}^{(3)}) - \tfrac{15}{2}E_{H_g}^{\mathrm{JT}} \\ &\approx (U_{\parallel}^{(3)} - U_{\perp}^{(3)}) - 0.3eV\ , \end{aligned} \tag{16}$$

where we have used the fact that the JT energetics for $n=2$, $S=1$ is identical to that for $n=1$, $S=\frac{1}{2}$,[1] while for $n=3$, $S=\frac{3}{2}$ there is no JT distortion. We have also used the t_{1u} orbital unimodal and bimodal splitting patterns of the preceding paper[1] 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 $n=3$, $S=\frac{1}{2}$; and (1,1,1) for $n=3$, $S=\frac{3}{2}$.

So long as $\mathbf{U}^{(n)}$ can 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 $\frac{15}{2}E_{H_g}^{\mathrm{JT}}$. This suggests the possibility that if high spin is more likely to prevail for $C_{60}{}^{2-}$ 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 electron paramagnetic resonance (EPR) data indicate that this is precisely the case. When frozen in a CH_2Cl_2 glass, $C_{60}{}^{2-}$ 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_2Cl_2 and other matrices favor a low-spin state.[21] Now $U_{\parallel}^{(3)} - U_{\perp}^{(3)}$ has become smaller than 0.3 eV. We can conclude that, even for a single embedded molecule, the *balance between intramolecule Coulomb repulsion and dynamical JT energy gains is extremely critical.*

Recent photoemission and Auger data[33] have shown that the intra-h_u HOMO Coulomb **U** is not as large as 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 $|\mathbf{U}| < 1$ eV in the latter. This upper bound is about a factor of 3 smaller than those previously proposed.[34] In the light of this observation, it is not at all surprising to find that $U_\parallel - U_\perp$ is in the neighborhood of 0.3 eV for $\mathrm{C}_{60}{}^{n-}$ in a matrix.

Coming next to the pair binding energies of the preceding paper,[1] we find large negative dynamical JT-related U_n's for odd n. 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 intramolecule pair energy,

$$U_3^{\mathrm{Coul}} = U_\parallel^{(2)} + (2U_\parallel^{(4)} + 4U_\perp^{(4)}) - 2(U_\parallel^{(3)} + 2U_\perp^{(3)}) \approx U_\parallel \, . \tag{17}$$

This cancellation implies a severe decrease of the Coulomb pseudopotential μ^* relative to that calculated when the JT coupling is ignored.[35] In principle, for a sufficiently strong solid-state screening of the electronic $U_\parallel$ and $U_\perp$, it could even reverse to a negative μ^*, i.e., to an overall negative-Hubbard-U state.

For $n=2$ and 4, the dynamical JT coupling may stabilize the average configuration of $\mathrm{C}_{60}{}^{n-}$, since the pair energy is *positive:* $U_2 \approx 0.4$ eV. This now acts to reinforce the bare Coulomb pair energy

$$\begin{aligned} U_2^{\mathrm{Coul}} &= U_\parallel^{(3)} - 2U_\perp^{(3)} - 2U_\parallel^{(2)} \approx 2U_\perp - U_\parallel \, , \\ U_4^{\mathrm{Coul}} &= (2U_\parallel^{(5)} + 8U_\perp^{(5)}) + (U_\parallel^{(3)} + 2U_\perp^{(3)}) \\ &\quad - 2(2U_\parallel^{(4)} + 4U_\perp^{(4)}) \\ &\approx 2U_\perp - U_\parallel \, , \end{aligned} \tag{18}$$

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

For even n, the JT coupling may stabilize 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 nonmagnetic, 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[36]) structure of $\mathrm{K}_4\mathrm{C}_{60}$ and $\mathrm{Rb}_4\mathrm{C}_{60}$ may be a realization of this state, where electronic and vibronic interactions play an important role. So far, band calculations[23] and experiments[37] had been in disagreement, the former suggesting a metal, and the latter finding a narrow-gap insulator.

Very recent ultraviolet photoemission spectroscopy (UPS) data on $\mathrm{K}_n\mathrm{C}_{60}$[39] 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 behavior is in itself not a surprising result. The surprise is that the decrease is very large from $n=3$ to $n=4$ (≈ 0.4 eV), and smaller from $n=4$ to $n=6$ (≈ 0.2 eV). As pointed out by De Seta and Evangelisti, a (positive) Coulomb U would predict exactly the opposite. We observe that this behavior is instead in agreement with our predicted pattern of an 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}.[38] An exciton consists of an electron in the LUMO 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.

VI. 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 $\mathrm{C}_{60}{}^{n-}$. 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 the superconductivity in $\mathrm{K}_3\mathrm{C}_{60}$ and insulating behavior in $\mathrm{K}_4\mathrm{C}_{60}$. Detailed vibrational spectra for $\mathrm{C}_{60}{}^{n-}$ are presented, and proposed for spectroscopic investigation, particularly in the gas phase. Related work is also being done by other groups.[40,41]

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