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Surprises in the orbital magnetic moment and g factor of the dynamic Jahn-Teller ion C_{60}^{-}

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We calculate the magnetic susceptibility and g factor of the isolated C_{60}^{-} ion at zero temperature, with a proper treatment of the dynamical Jahn-Teller effect, the associated orbital angular momentum, the Ham-reduced gyromagnetic ratio, and the molecular spin-orbit coupling. A number of surprises emerge. First, the predicted molecular spin-orbit splitting is two orders of magnitude smaller than in the bare carbon atom, due to the large radius of curvature of the molecule. Second, this reduced spin-orbit splitting is comparable to Zeeman energies, for instance, in X-band electron paramagnetic resonance at 3.39 kGauss, and a field dependence of the g factor is predicted. Third, the orbital gyromagnetic factor is strongly reduced by vibron coupling, and so therefore are the effective weak-field g factors of all low-lying states. In particular, the ground-state doublet of C_{60}^{-} is predicted to show a negative g factor of ~ -0.1. [S0163-1829(96)02441-1]

I. INTRODUCTION

A neutral, isolated fullerene molecule is an eminently stable and symmetrical system. The fullerene ions (either negative or positive) along with the electronically excited neutral molecule, particularly the long-lived triplet exciton, undergo instead Jahn-Teller (JT) distortions. The negative ion and the triplet exciton, respectively with t_{1u} and t_{1g} symmetry, will distort according to a linear combination of the eight H_g molecular modes. The JT distortion of the positive ion, with h_u symmetry, involves also the six G_g modes in addition to the eight H_g ones. Although accurate numerical values of all couplings are not yet available in all cases, the static JT energy gains are believed to be roughly of the order of 0.1 eV. This value is comparable with the typical vibrational frequency, and the coupling is generally of intermediate strength. Several descriptions of the static JT effect in fullerene ions can be found in the literature.[1–4]

As pointed out more recently, however, a static JT description, where the pseudorotational motion of the carbon nuclei is treated classically and then quantized separately in the Born-Oppenheimer approximation, is, at least in the isolated molecule and at zero temperature, fundamentally inadequate. In other words, the fullerene ions are expected to be genuine *dynamical* Jahn-Teller (DJT) systems, where different but equivalent distorted configurations (forming the usual static JT manifold[5]) are not independent of one another, but are in fact connected by nonzero transition amplitudes.[6] This in turn requires giving up the Born-Oppenheimer approximation and fully quantizing electronic and ionic motions together, which is the essence of DJT systems.

The physical understanding of the DJT effect in C_{60} ions is greatly eased by initially assuming the strong-coupling limit. In this limit, as it turns out, a *modified* Born-Oppenheimer approximation can again be recovered, provided a suitable gauge field, reflecting the electronic *Berry phase*,[7] is added to the nuclear motion. This situation, discussed originally for the triatomic molecule[8] and subsequently for other JT systems,[9] has been recently the object of a close scrutiny in fullerenes, especially in the negative ions[10–12] and, to a lesser degree, in the positive ion.[13] It is found in particular that, if treated in the strong-coupling limit, the odd-charged fullerene ions, in particular the singly charged C_{60}^{-} (Refs. 10,15) and C_{60}^{+} (Refs. 13,14), the Hund's rule *triplet* ground state of doubly charged C_{60}^{2-}, as well as the neutral t_{1g} triplet exciton,[16] must possess this kind of Berry phase. By contrast, the Berry phases cancel out in the *singlet* configuration of even-charged ions, such as C_{60}^{2-} and C_{60}^{2+}. Although, as stated above, the true electron-vibron coupling in C_{60} is in reality only of intermediate strength, the presence or absence of a Berry phase in the strong-coupling limit of the DJT effect implies a number of physical consequences, which persist at realistic couplings and whose importance has been discussed in detail elsewhere. Properties affected include basic ground-state features such as symmetry[17] and energy,[11,15] spectral features (including characteristic splittings of the lowest vibron excitations with skipping of even angular momenta[10,11,15,18]), scattering anomalies such as suppression of ordinary s-wave attachment of low-energy electrons,[19] and the prediction of orbitally related electron pairing phenomena in idealized molecular metal lattices with weak electron hopping between molecules.[20–23]

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For these and other reasons it seems important to understand completely and quantitatively the DJT effect of single fullerene ions, experimentally as well as theoretically. To date, however, and in spite of a large amount of data collected on fullerene and especially on fulleride systems, there is still frustratingly little *direct* evidence that the JT effect in fullerene ions is, to start with, really dynamical, as theory predicts.

In the solid state, for example, Raman data on metallic fullerides such as K_3C_{60} (Ref. 24) fail to show the characteristic vibron splittings expected for the isolated $C_{60}{}^{3-}$ ions.[11,15] This probably means that in true metallic fullerides the molecular JT effect may be profoundly affected and modified by the large crystal fields, as well as by the strong, rather than weak, intermolecular electron hopping. Even in nonmetallic fullerides like K_4C_{60}, where the insulating behavior is almost certainly due to a molecular JT effect,[11,25] it is presently not at all clear whether the quantum dynamical features are present or suppressed. Fullerene ions have also been widely studied in solutions[26] and in solid ionic salts[27] but again no specific DJT signature has been pinpointed, so far.

The main target remains therefore the *gas-phase fullerene*: The DJT signatures should be unmistakable in ions of either sign and in triplet-excited neutral molecules, particularly if in the future Raman excitations could be studied.[15] What is available so far are essentially only gas-phase photoemission spectra of $C_{60}{}^{-}$ (Ref. 18) and of C_{60}.[28] Encouragingly, the former are fit very well indeed by a DJT theory.[18] Nonetheless, this can only be considered as indirect evidence. The positive ions results have not yet been analyzed, although the appropriate DJT theory has been formulated.[13]

We therefore wish to consider here other properties of the fullerene ions, among those crucially affected by the DJT effect, which could at least in principle be accessed either in the gas phase, in ideally inert matrices, or in suitable salts with especially small crystal-field effects. One such quantity is precisely the molecular magnetic moment. The magnetic moment of a *static* JT molecule is strictly the spin moment. The orbital degeneracy is removed, as long as static JT energies are, as in the case of C_{60}, sufficiently large. The magnetic moment in a *dynamic* JT molecule, conversely, is a compound of spin and orbital moments, since here the quantum effects fully restore the original orbital symmetry.[17] The calculation of the magnetic moment and effective g factor of fullerene ions in their DJT ground state is precisely the subject of this work.

Let us consider for a start the orbital magnetic moments of a molecule. Qualitatively speaking, the proportionality factor between magnetic moments and the mechanical angular momentum can be thought as some *effective* Bohr magneton $e\hbar/2m^*$, where m^* is the mass of the orbiting electron (e is the electron charge and SI units are used throughout). In an atom, $m^*=m_e$, the free electron mass. In a DJT molecule, however, orbital electron motion involves nuclear motion as well, since electronic and vibrational modes are entangled. Therefore, we expect $m^*>m_e$, with a corresponding reduction of the orbital magnetic moment. This is a classic example of the so-called ''Ham reduction factor,''[29] well known in DJT systems.[30] The consequence of orbital reduction is that, while the quantum of mechanical angular momentum is of course universal and equal to $\hbar$, that of the magnetic moment for a DJT molecule is *not universal*.

Below, we will calculate quantitatively the orbital magnetic moment for $C_{60}{}^{-}$. Moreover, since the orbital moment is not easily accessible experimentally, while the total magnetic moment is commonly measured, spin-orbit coupling will have to be introduced, to determine the correct composition of the (DJT-reduced) orbital moment, and of the spin moment. The spin-orbit coupling within the t_{1u} orbital of C_{60} is quantitatively unknown. Here we calculate it, and find some surprises. First, the calculated molecular spin-orbit splitting is very small, roughly one-hundredth of that in the bare carbon atom. This is related to the larger radius of curvature of the molecular orbit. Second, this reduced spin-orbit splitting is now wholly comparable to typical Zeeman energies, for instance, in X-band electron paramagnetic resonance (EPR) at 0.339 T. Hence, a field dependence of the low-temperature susceptibility and of apparent g factors is predicted, at least in an idealized gas-phase EPR experiment. Third, we find that the orbital gyromagnetic factor is strongly reduced by vibron coupling, and so therefore are the effective weak-field g factors for all the low-lying states. The ground-state g factor, in particular, is predicted to be slightly *negative*, about -0.1.

II. MODEL

The basic model Hamiltonian we consider has the following standard structure:

$$H=H^0+H^{e\text{-}v}+H^{\mathrm{so}}+H^B. \tag{1}$$

The JT part $H^0+H^{e\text{-}v}$ has been introduced and discussed in previous papers.[10,11,18] We report here the basic version for the coupling to a single H_g vibrational (quadrupolar) mode:

$$H^0=\hbar\omega\sum_{m=-2}^{2}\left(b_m^\dagger b_m+\tfrac{1}{2}\right)+(\epsilon-\mu)\sum_{m=-1}^{1}\sum_{\sigma=\uparrow,\downarrow}c_{m,\sigma}^\dagger c_{m,\sigma},$$

$$\begin{aligned}H^{e\text{-}v}=g\frac{\sqrt{3}}{2}\hbar\omega\sum_{m_1,m_2,\sigma}&(-1)^{m_2}\langle 1,m_1;1,m_2|2,m_1+m_2\rangle\\&\times[b_{m_1+m_2}^\dagger+(-1)^{m_1+m_2}b_{-m_1-m_2}]\\&\times c_{m_1,\sigma}^\dagger c_{-m_2,\sigma}+\cdots.\end{aligned}\tag{2}$$

H^0 describes the free (uncoupled) electrons and the fivefold-degenerate vibration of frequency ω. $H^{e\text{-}v}$ introduces a (rotationally invariant) standard linear coupling between the electronic state and the vibrational mode. The dimensionless linear coupling parameter is indicated as g (not to be confused with the magnetic factors g_L). Here we neglect higher-order terms in the boson operators, indicated by the ellipsis.

Orbital currents are associated with the partly filled t_{1u} level, which is known to derive essentially from a superatomic $L=5$ orbital of C_{60} as a whole.[31,32] These orbital currents give rise to a magnetic moment, which we now wish to calculate.

Electron spin also contributes to the total magnetic moment. Although uninfluenced by JT coupling [the Hamiltonian (2) conserves spin], spin is coupled to the orbital motion via spin-orbit coupling $H^{\mathrm{so}}=\lambda(\vec{L}\cdot\vec{S})$. The general Hamiltonian finally includes Zeeman coupling to an external magnetic field B along the z axis:

$$H^B=-\mu_B B(g_L L_z+g_S S_z), \tag{3}$$

where $\mu_B=e\hbar/2m$. For generic g_L and g_S factors, the appropriate value for the g_J factor of the spin-orbit coupled state ($|L-S|\leqslant J\leqslant|L+S|$) is[33]

$$g_J=\frac{g_L+g_S}{2}+\frac{L(L+1)-S(S+1)}{2J(J+1)}(g_L-g_S). \tag{4}$$

For $\mathrm{C}_{60}{}^{-}$, $L=1$, $S=\frac{1}{2}$, $J=\frac{1}{2}$, $\frac{3}{2}$, and $g_S=2.0023$ as appropriate for a free spin. Thus, in order to obtain the g_J factors of the individual spin-orbit split states $J=\frac{1}{2}$ and $J=\frac{3}{2}$, we only need to calculate the value of g_L.

Two main phenomena should affect the value of the orbital g_L factor: the $\mathcal{D}^{(L=5)}$ parentage of the t_{1u} ($\mathcal{D}^{(L=1)}$) state and the DJT coupling with the vibrons.

A paper by Cohan[34] provides tables with the icosahedral decomposition of spherical states up to $L=15$, as expansion coefficients on an unnormalized and real basis:

$$\widetilde{Y}^{C/S}_{L,|M|}=\left[\frac{4\pi}{2L+1}\,\frac{(L+|M|)!}{(L-|M|)!}\right]^{1/2}\frac{Y_{L,M}\pm Y_{L,-M}}{2(-1)^{3/4\pm 1/4}}. \tag{5}$$

The tabulated wave functions which transform as t_{1u} are

$$\psi_0\propto 2160\widetilde{Y}^{C}_{5,0}+\widetilde{Y}^{C}_{5,5},$$

$$\psi_{C/S}\propto 72\widetilde{Y}^{C/S}_{5,1}\mp\widetilde{Y}^{C/S}_{5,4}, \tag{6}$$

which can be normalized to obtain

$$\psi_0=\mathcal{C}\left[2160Y_{5,0}+\frac{\sqrt{10!}}{2}(Y_{5,5}+Y_{5,-5})\right]$$

$$=\frac{6}{\sqrt{50}}Y_{5,0}+\sqrt{\frac{7}{50}}(Y_{5,5}+Y_{5,-5}),$$

$$\psi_{C/S}=\mathcal{C}\left[72\sqrt{\frac{6!}{4!}}(Y_{5,1}\pm Y_{5,-1})\mp\sqrt{\frac{9!}{1!}}(Y_{5,4}\pm Y_{5,-4})\right]$$

$$=\frac{1}{\sqrt{2}(-1)^{3/4\pm 1/4}}\left[\sqrt{\frac{3}{10}}(Y_{5,1}\pm Y_{5,-1})\right.$$

$$\left.\mp\sqrt{\frac{7}{10}}(Y_{5,4}\pm Y_{5,-4})\right], \tag{7}$$

yielding

$$\psi_{\mp 1}=\frac{\psi_C\pm i\psi_S}{\sqrt{2}}=\sqrt{\frac{3}{10}}Y_{5,\mp 1}-\sqrt{\frac{7}{10}}Y_{5,\pm 4}. \tag{8}$$

On the $\{\psi_M\}_{M=-1,0,1}$ basis of t_{1u}, the orbital Zeeman coupling with the external magnetic field is diagonal:

$$\langle\psi_M|H^B_L|\psi_{M'}\rangle=-g_1\mu_B\left[\frac{3}{10}(-1)+\frac{7}{10}(4)\right]BM\,\delta_{MM'}$$

$$=-\frac{5}{2}g_1\mu_B BM\,\delta_{MM'}. \tag{9}$$

This formula implicitly defines an effective orbital $\widetilde{g}_1$ factor $\frac{5}{2}g_1$ ($\alpha=\frac{5}{2}$, in the language of Ref. 33). It is convenient to define for the t_{1u} orbital an effective angular momentum $\vec{\widetilde{L}}$, whose z component has the values $-1,0,1$ on the $\{\psi_M\}_{M=-1,0,1}$ basis, in terms of which the orbital Zeeman interaction (3) is rewritten

$$H^B_L=-\widetilde{g}_L\mu_B B\widetilde{L}_z=-\alpha g_L\mu_B B\widetilde{L}_z. \tag{10}$$

It is clear that the enhancement is due to the $|M|=4$ component in the the t_{1u} wave function, which is really $L=5$, but is regarded formally as an effective $\widetilde{L}=1$ state. Reference 32 also provides the explicit spherical parentage of the lowest unoccupied molecular orbital (LUMO), now in a solid-state environment. By computing the spectrum of L_z on the basis provided in that work, we obtain a somewhat smaller value for α, namely, 1.86. However, for gas-phase $\mathrm{C}_{60}{}^{-}$ the group-theoretical value for a strictly $L=5$ parentage, $\alpha=2.5$, is probably more accurate.

We now concentrate on the second effect, namely, that of the coupling of the electronic state with the vibrons. For clarity we start considering a single H_g vibron coupled to the t_{1u} level, as in Eq. (1). We represent the L_z operator in second quantization as $\Sigma_\sigma(c^\dagger_{1\sigma}c_{1\sigma}-c^\dagger_{-1\sigma}c_{-1\sigma})$ [same notation as in Eq. (2)] and we measure the magnetic energy $\mu_B B$ in units of the energy scale of the vibron, $\hbar\omega$, and indicate it by $\mathcal{B}\equiv\mu_B B/\hbar\omega$.

As in Ref. 10, it is instructive to treat first the weak-JT-coupling limit. We solve the quantum problem in perturbation theory to second order in the e-v coupling parameter g, this time including H^B (which is diagonal on the basis $|\psi_M\rangle$) in the unperturbed Hamiltonian. Thus we consider $H=(H^0+H^B)+H^{e\text{-}v}$, and apply nondegenerate perturbation theory to second order within the threefold space of the t_{1u} level, Eq. (7). The second-order energy shift caused by $H^{e\text{-}v}$ to level $|\psi_M\rangle$ [$M=-1,0,1$, unperturbed energy $(\frac{5}{2}-\widetilde{g}_1 M\cdot\mathcal{B})\hbar\omega$] is

$$\Delta^{(2)}_M=\langle\psi_M|H^{e\text{-}v}\frac{1}{\left(\frac{5}{2}-\widetilde{g}_1 M\cdot\mathcal{B}\right)\hbar\omega-(H^0+H^B)}H^{e\text{-}v}|\psi_M\rangle, \tag{11}$$

while off diagonal terms $\Delta^{(2)}_{MM'}$ vanish since $H^{e\text{-}v}$ is rotationally invariant. This shift can be rewritten as

$$\Delta^{(2)}_M=-\frac{3}{4}g^2\hbar\omega\sum_{m=-1,0,1}\frac{(\langle 1,m;1,-M|2,m-M\rangle)^2}{1+\widetilde{g}_1\mathcal{B}(M-m)}. \tag{12}$$

By substituting the Clebsch-Gordan coefficients, and carrying out the sum over m, for each fixed value of M, we get

$$\Delta_0^{(2)} = -\frac{3}{4}g^2\hbar\omega\left[\frac{2}{3}+\frac{1}{2}\left(\frac{1}{1-\tilde{g}_1\mathcal{B}}+\frac{1}{1+\tilde{g}_1\mathcal{B}}\right)\right]$$

$$= -\frac{3}{4}g^2\hbar\omega\left[\frac{5}{3}+\mathcal{O}(\mathcal{B}^2)\right],$$

$$\Delta_{\pm 1}^{(2)} = -\frac{3}{4}g^2\hbar\omega\left[\frac{1}{6}+\frac{1}{2}\,\frac{1}{1\pm\tilde{g}_1\mathcal{B}}+\frac{1}{1\pm 2\tilde{g}_1\mathcal{B}}\right]$$

$$= -\frac{3}{4}g^2\hbar\omega\left[\frac{5}{3}\mp\frac{5}{2}\tilde{g}_1\mathcal{B}+\mathcal{O}(\mathcal{B}^2)\right]. \qquad (13)$$

The weak-field $\mathcal{B}$ expansion is done here under the customary assumption that the magnetic energy is the smallest energy scale in the problem (we will return to this point later, however). The final result for the energy to first order in $\mathcal{B}$ of the three t_{1u}-derived levels is finally

$$E_M^{(2)} = \left(\frac{5}{2}-\frac{5}{4}g^2\right)\hbar\omega - M\left(1-\frac{15}{8}g^2\right)\tilde{g}_1\mathcal{B}\hbar\omega. \qquad (14)$$

The result of e-v coupling is a reduction of both zero-point energy $(-\frac{5}{4}g^2\hbar\omega)$ and magnetic moment. By identification we obtain

$$g_1^{\mathrm{eff}} = \left(1-\frac{15}{8}g^2\right)\tilde{g}_1 = \left(1-\frac{15}{8}g^2\right)\frac{5}{2}g_1 = \left(1-\frac{15}{8}g^2\right)\frac{5}{2}, \qquad (15)$$

the desired perturbative result for the reduction of the g_1 factor due to weak coupling to an H_g mode. The factor $\frac{5}{2}$ reflects the $L=5$ parentage and $(1-\frac{15}{8}g^2)$ is the (weak-coupling) Ham reduction factor[33] of this DJT problem, correctly coincident with that obtained for a general vector observable by Bersuker and Polinger.[35] As anticipated, the reduction factor reflects the increased ''effective mass'' of the t_{1u} electron, as it carries along some ionic mass while orbiting.

However, the coupling in C_{60} is not really weak, and perturbation theory is essentially only of qualitative value. For quantitative accuracy, we can instead solve the problem by numerical (Lanczos) diagonalization,[10,18,15] which is feasible up to realistically large coupling strengths. On a basis of states

$$\Psi = \sum \epsilon_{k_1\mu_1,\ldots,k_N\mu_N,M,\sigma} b_{k_1\mu_1}^{\dagger}\cdots b_{k_N\mu_N}^{\dagger} c_{M\sigma}^{\dagger}|0\rangle \qquad (16)$$

(where $|0\rangle$ is the state with no vibrons and no electrons), truncated to include up to some maximum number N of vibrons (N must be larger for larger coupling), we diagonalize the Hamiltonian operator (1), and take the numerical derivative of the ground-state energy with respect to the magnetic field $\mathcal{B}$. Again, we consider here only the orbital part, and ignore spin for the time being. In Fig. 1 we plot the resulting reduction of g_1 factor as a function of g^2 for a single H_g mode. The initial slope at $g=0$ coincides correctly with $-\frac{15}{8}$, while at larger coupling, the behavior is compatible with the expected Huang-Rhys-type decrease, $\sim\exp(-\chi g^2)$.

We now repeat the same diagonalization including all the eight H_g vibrons with their realistic couplings, as extracted by fitting gas-phase photoemission spectra of $C_{60}{}^{-}$.[18] Including, as in our previous calculation of the ground state and excitation energies,[18,15] up to $N=5$ vibrons for an accuracy of better than two decimal figures, we obtain[36] for the orbital factor of the t_{1u} LUMO of C_{60} a final value of 0.17, whence

$$g_1^{\mathrm{eff}} = 0.17\tilde{g}_1 = 0.17\frac{5}{2} \simeq 0.43. \qquad (17)$$

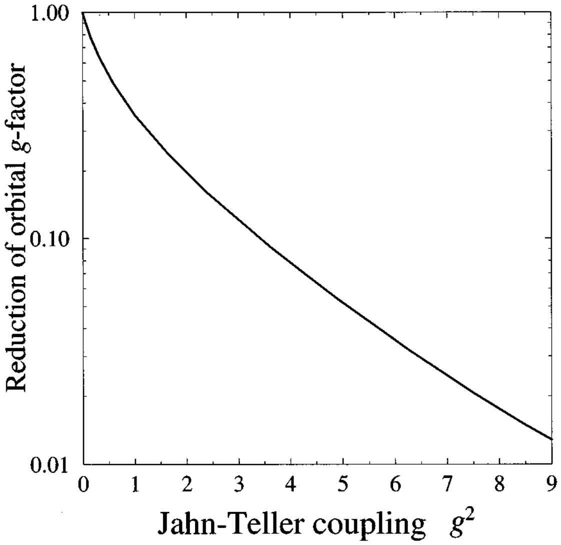

FIG. 1. The reduction factor of the orbital magnetic moment and g factor g_1, due to DJT coupling of the t_{1u} state to a single H_g vibron. The calculation is done by exact diagonalization, the truncated basis set including up to $N=11$ vibrons. Note the fast linear decrease at small g, and also the e^{-g^2} decay as expected at large g. In $C_{60}{}^{-}$, including eight coupled H_g modes instead of one, the overall reduction factor obtained with a similar calculation and realistic couplings is 0.17 (see Sec. III).

With this orbital g_L factor, we can now move on to compute the overall g_J factor in a realistic situation, where, however, spin orbit must be included.

III. SPIN-ORBIT COUPLING IN THE T_{1u} LUMO AND RESULTS

The magnitude of the spin-orbit coupling λ in the t_{1u} state of C_{60} is not known. We estimate it by using straightforward tight binding, as follows. Starting from $2s$ and $2p_x$,$2p_y$,$2p_z$ orbitals for each C atom, and including spin degeneracy, we diagonalize the 480×480 first-neighbor hopping Hamiltonian matrix to obtain all the molecular orbitals. Spin orbit in this scheme is obtained by adding to the hopping Hamiltonian a local coupling on each individual carbon in the form

$$H^{\mathrm{so}} = \lambda_{\mathrm{at}}\sum_i \mathbf{L}_i\cdot\mathbf{S}_i\,. \qquad (18)$$

The level splitting introduced by this term defines the precise value of the spin-orbit coupling for each molecular orbital. We are dealing with π states, which are unaffected by spin orbit in a planar case, such as in graphite. However, in fullerenes, due to curvature, there will be an effect. In particular the splitting between the LUMO states ${}^2t_{1u(1/2)}$ and ${}^2t_{1u(3/2)}$ gives the spin-orbit coupling for the LUMO. Our calculation yields $\lambda = 0.9\times 10^{-2}\lambda_{\rm at}$ for the t_{1u} state of C_{60} when all bonds are assumed to have equal lengths, slightly increasing to

$$\lambda = 1.16\times 10^{-2}\lambda_{\rm at}, \tag{19}$$

when bond alternation is included. Since $\lambda_{\rm at} = \langle 2p_z|\mathbf{L}\cdot\mathbf{S}|2p_x\rangle \simeq 13.5\ \mathrm{cm}^{-1}$,[37] we conclude that the effective spin-orbit splitting of a t_{1u} electron in $C_{60}{}^-$ is of the order of $0.16\ \mathrm{cm}^{-1} = 19\ \mu$eV. This value is exceedingly small, due both to the small value of λ in carbon, a low-Z element, and (mainly) to the large curvature radius of C_{60}. For relatively large radius R, as appropriate to fullerenes and nanotubes, one can expect a small spin-orbit effect in π states, of order $\lambda \sim 1/R^2$, the lowest power of curvature which is independent of its *sign*. The π-electron radius of C_{60}, $R\sim$ 5 Å, is one order of magnitude larger than in the carbon atom, correctly suggesting a reduction of two orders of magnitude from the atom to C_{60}. Larger splittings of 30–50 cm^{-1} observed in luminescence spectra had earlier been attributed to spin orbit.[38] These values are incompatible with our estimate, and we conclude that these splittings must be of different origin, unless an enhancement of two orders of magnitude over the gas phase could somehow arise due to the host matrix.

We can now include this spin-orbit coupling in the calculation of the full g factor. A strong-spin-orbit approach[39] $\lambda \gg E_{\rm JT}$, relevant for JT transition metal impurities, is not useful here, since clearly $\lambda \ll E_{\rm JT} \approx 140$ meV (Refs. 18 and 15) $\sim \hbar\omega$. In this case, the purely orbital description of the Berry phase DJT of Refs. 10 and 11 provides the correct gross features, to which spin orbit adds small splittings. These splittings are controlled by the g_J factors of Eq. (4). In our $t_{1u}\otimes H_g$ case, an effective "$\tilde{L}=1$" ground state is turned, for positive λ, into a "$J=\frac{1}{2}$" ground-state doublet and a "$J=\frac{3}{2}$" excited quartet. If we assume the usual weak-field limit $\mu_B B \ll \lambda$, we can recast Eq. (4) in the form

$$g_{\frac{1}{2}} = -\frac{1}{3}g_S + \frac{4}{3}g_L \simeq -\frac{2}{3} + \frac{4}{3}g_L \tag{20}$$

and

$$g_{\frac{3}{2}} = \frac{1}{3}g_S + \frac{2}{3}g_L \simeq \frac{2}{3} + \frac{2}{3}g_L . \tag{21}$$

According to these linear formulas, the orbital reduction factor g_1 (Fig. 1) is easily deformed on the vertical axis to give g_J. Since g_L decreases from 1 to 0 for increasing JT coupling, we see that while $g_{3/2}$ is always positive, $g_{1/2}$ may instead become *negative* at large JT coupling. For example, if the $L=5$ parentage enhancement is neglected, then $g_{1/2}$ ranges from $\frac{2}{3}$ at zero coupling to $-\frac{2}{3}$ at strong coupling. Including the $\frac{5}{2}$ orbital parentage factor, $g_{1/2}$ finally varies from $\frac{8}{3}$ to $-\frac{2}{3}$.

The physical reason for a possible overall negative g factor for $J=\frac{1}{2}$ at large e-v coupling, where $g_L \sim e^{-g^2}$, is also clear. The $J=\frac{1}{2}$ overall *mechanical* angular momentum is dominated by $L=1$ orbital component. The *magnetic* moment is instead dominated by the spin component, due to the strong reduction of the orbital part. But in the $J=\frac{1}{2}$ state, spin and orbit are coupled (mainly) upside down, whence the sign inversion.

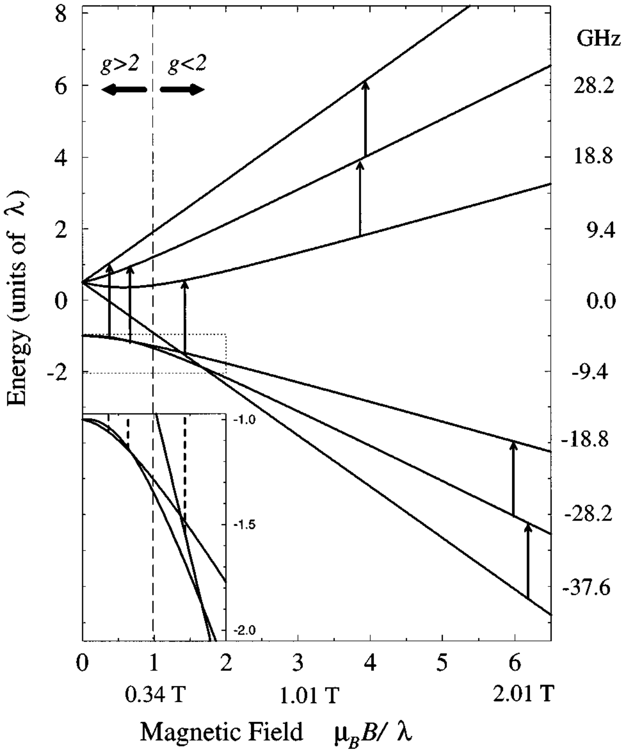

FIG. 2. The low-energy levels of $C_{60}{}^-$ ($g_1^{\rm eff}=0.43$), calculated for increasing magnetic field B. All energies, including $\mu_B B$, are measured in units of the molecular spin-orbit coupling λ, which we estimate to be about 4.7 GHz$\,h$ (Sec. III). The vertical arrows indicate allowed microwave absorption transitions, for a frequency of 9.5 GHz. The apparent g-factor values corresponding to these transitions differ vastly from the free spin value, and are heavily dependent upon the DJT coupling parameters, and the relative value of spin-orbit coupling. The weak-field region shows clearly the $J=\frac{1}{2}$ structure (inset), exhibiting the weak negative g factor. Note also the two ground-state level crossings, corresponding to zero-temperature magnetization jumps of $0.14\mu_B$ and $0.56\mu_B$, for field values of 0.23 T and 0.57 T, respectively.

Inserting the orbital g_L factor (17) in Eqs. (20) and (21), we get the final effective g factor for the ground-state manifold of gas-phase $C_{60}{}^-$:

$$g_{1/2}^{\rm eff} = -0.1, \quad g_{3/2}^{\rm eff} = 0.95. \tag{22}$$

IV. INTERMEDIATE FIELD

We have just obtained in Sec. III a slightly negative value for the g factor of the "$J=\frac{1}{2}$" ground state. This result, valid in the approximation of $\mu_B B \ll \lambda \ll E_{\rm JT}$, becomes unapplicable as soon as $\mu_B B \sim \lambda$. In an ideal EPR-like experiment on gas-phase $C_{60}{}^-$, the resonant quantum $h\nu$ is easily comparable with, or larger than, the spin-orbit frequency scale $\lambda/h = 4.7$ GHz. For example, standard X-band EPR employs a larger frequency of 9.5 GHz, which resonates at $B=0.339$ T, for a free spin.

For ease of comparison in Fig. 2 we report the full spectrum of the Zeeman- and spin-orbit-split low-energy states of C_{60}^-, calculated under the assumption that $\mu_B B \ll E_{\rm JT}$, for increasing magnetic field. Here, arrows indicate the symmetry-allowed microwave absorption transitions, matching an arbitrary excitation frequency 9.5 GHz. EPR-like lines should ideally appear at the corresponding values of the field. Of the seven lines expected, two correspond to (apparent) g factors vastly larger than 2 and five to g factors vastly smaller than 2. These g factors are only apparent, since they depend on the field (since it is not weak), and through it on the frequency chosen. As the figure indicates, the weak-field limit for C_{60}^- should only really be achieved with fields in the order of a few hundred gauss.

V. DISCUSSION AND CONCLUSIONS

Three main predictions result from the present calculation. First, the molecular spin-orbit splitting is very small, a fraction of a degree kelvin. Second, the reduced spin-orbit splitting is now wholly comparable to typical Zeeman energies, for fields of a few kG. Hence, a strong and uncommon field dependence of the g factors is predicted. Third, we find that the orbital gyromagnetic factor is strongly reduced by vibron coupling, and so therefore are the effective weak-field g factors for all the low-lying states. In particular, the isolated C_{60}^- ion in its ''$J=1/2$'' ground state should be essentially nonmagnetic, in fact slightly diamagnetic, if cooled below $T \approx (E_{3/2}-E_{1/2})/k_B \sim 0.2$ K.

For C_{60}^- in solid ionic salts at 77 K and room temperature, Kato *et al.*[27] have found $g^{\rm eff} \simeq 1.999$, with slight anisotropies due to the lattice. Similar $g^{\rm eff}$ values are also obtained for C_{60}^- in molecular sieves,[40] as well as in various solvents and salts[41,42,44,45]. These g factors are relatively close to the bare-spin value, implying that the dynamical orbital effects discussed above are apparently quenched by coupling to the matrix. In the photoexcited triplet state of neutral C_{60}, some evidence has been found for nonthermal jumps between JT valleys,[43] but apparently none for orbital magnetism. In a majority of these systems, all goes as if the extra electron of C_{60}^- or the extra electron-hole triplet pair of C_{60}^- occupied a nondegenerate level, as expected in the static JT case. A detailed discussion of the quenching of quantum orbital effects is beyond the scope of this work. However, we think that coupling to the host matrix, however weak it may be in some cases, must be responsible for the apparent quenching from the DJT to the static JT case. One possibility, for example, is that the extra electron on C_{60}^- acts to strongly polarize the surrounding, which in turn slows down and damps the quantum-mechanical electron tunneling between different JT valleys. Insofar as these couplings seem ubiquitous and fatal to the DJT case, we would provisionally tend to conclude that gas-phase studies may represent the only serious possibility for the observation of orbital moments in fullerene ions.

Stern-Gerlach-like measurements of magnetic moment in gas-phase C_{60}^-, or other similar experiments, are therefore called for to provide a definitive confirmation of the striking quantum orbital effects described in this paper. Since to our knowledge this would be new, we feel that such experiments should be considered, even if very difficult to carry out.

Gas-phase measurements would presumably be easier in the $^3t_{1g}$ triplet exciton state of *neutral* C_{60}. This state has a number of similarities[16] to that of C_{60}^- which we have just described. However, here $S=1$ and $\tilde{L}=1$, leading to a $J=0$ singlet ground state[46] for the triplet exciton with DJT and spin-orbit coupling, and the magnetic anomalies will have to be sought in the lowest excited states.

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[1] F. Negri, G. Orlandi, and F. Zerbetto, Chem. Phys. Lett. **144**, 31 (1988).

[2] C.M. Varma, J. Zaanen, and K. Raghavachari, Science **254**, 989 (1991).

[3] M. Schlüter, M. Lannoo, M. Needels, G.A. Baraff, and D. Tománek, Phys. Rev. Lett. **68**, 526 (1991); J. Phys. Chem. Solids **53**, 1473 (1992).

[4] K.H. Johnson, M.E. McHenry, and D.P. Clougherty, Physica C **183**, 319 (1991).

[5] A. Ceulemans, J. Chem. Phys. **87**, 5374 (1987).

[6] See, e.g., C.L. Wang, W.Z. Wang, Y.L. Liu, Z.B. Su, and L. Yu, Phys. Rev. B **50**, 5676 (1994); W.Z. Wang, C.L. Wang, A.R. Bishop, L. Yu, and Z.B. Su, *ibid.* **51**, 10 209 (1995).

[7] M.V. Berry, Proc. R. Soc. London A **392**, 45 (1984).

[8] G. Delacrétaz, E.R. Grant, R.L. Whetten, L. Wöste, and J.W. Zwanziger, Phys. Rev. Lett. **56**, 2598 (1986).

[9] C.C. Chancey and M.C.M. O'Brien, J. Phys. A **21**, 3347 (1988); J. Phys. C **1**, 47 (1989); M.C.M. O' Brien, J. Phys. A **22**, 1779 (1989); J.P. Cullerne, M.N. Angelova, and M.C.M. O'Brien, J. Phys. C **7**, 3247 (1995).

[10] A. Auerbach, N. Manini, and E. Tosatti, Phys. Rev. B **49**, 12 998 (1994).

[11] N. Manini, E. Tosatti, and A. Auerbach, Phys. Rev. B **49**, 13 008 (1994).

[12] J. Ihm, Phys. Rev. B **49**, 10 726 (1994).

[13] P. De Los Rios, N. Manini, and E. Tosatti, Phys. Rev. B **54**, 7157 (1996).

[14] C.C. Chancey and M.C.M. O'Brien, *Proceedings of the Estonian Academy of Sciences: Physics* [Mathematics **44**, 339 (1995)].

[15] N. Manini and E. Tosatti, in *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*, edited by K.M. Kadish and R.S. Ruoff (The Electrochemical Society, Inc., Pennington, NJ, 1995), Vol. 2.

[16] The $^3t_{2g}$ electronic configuration of the lowest exciton state, from the point of view of orbital symmetry, is analogous to the $^2t_{1u}$ configuration of C_{60}^-. As a consequence, it also undergoes a JT effect associated to coupling with the H_g modes. The $^3t_{2g} \otimes H_g$ DJT problem is also endowed with a Berry phase, similar to the $^2t_{1u} \otimes H_g$.

[17] F.S. Ham, Phys. Rev. Lett. **58**, 725 (1987); J. Phys. Condens. Matter **2**, 1163 (1990).

[18] O. Gunnarsson, H. Handschuh, P.S. Bechthold, B. Kessler, G.

Ganteför, and W. Eberhardt, Phys. Rev. Lett. **74**, 1875 (1995); O. Gunnarsson, Phys. Rev. B **51**, 3493 (1995).

[19] E. Tosatti and N. Manini, Chem. Phys. Lett. **223**, 61 (1994).

[20] N. Manini, E. Tosatti, and S. Doniach, Phys. Rev. B **51**, 3731 (1995).

[21] G. Santoro, M. Airoldi, N. Manini, E. Tosatti, and A. Parola, Phys. Rev. Lett. **74**, 4039 (1995).

[22] G. Santoro, N. Manini, A. Parola, and E. Tosatti, Phys. Rev. B **53**, 828 (1996).

[23] M. Fabrizio, Phys. Rev. B **48**, 15 838 (1993); M. Fabrizio, A. Parola, and E. Tosatti, Phys. Rev. B **46**, 3159 (1992).

[24] P. Zhou, K.A. Wang, P.C. Eklund, G. Dresselhaus, and M.S. Dresselhaus, Phys. Rev. B **48**, 8412 (1993).

[25] R. Kerkoud, P. Auban-Senzier, D. Jerome, S. Brazovskii, I. Luk'yanchuk, N. Kirova, F. Rachdi, and C. Goze, J. Phys. Chem. Solids **57**, 143 (1996).

[26] D. Dubois, K.M. Kadish, S. Flanagan, R.R. Haufler, L.P.F. Chibante, and L.J. Wilson, J. Am. Chem. Soc. **113**, 4364 (1991).

[27] T. Kato, T. Kodama, M. Oyama, S. Okazaki, T. Shida, T. Nakagawa, Y. Matsui, S. Suzuki, H. Shiromaru, K. Yamauchi, and Y. Achiba, Chem. Phys. Lett. **186**, 35 (1991); T. Kato, T. Kodama, and T. Shida, *ibid.* **205**, 405 (1993).

[28] P. Brühwiler (private communication).

[29] F.S. Ham, Phys. Rev. **138**, A1727 (1965).

[30] R. Englman, *The Jahn Teller Effect in Molecules and Crystals* (Wiley, London, 1972).

[31] M.R. Savina, L.L. Lohr, and A.H. Francis, Chem. Phys. Lett. **205**, 200 (1993).

[32] N. Troullier and J.L. Martins, Phys. Rev. B **46**, 1754 (1992).

[33] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Oxford University Press, London, 1970).

[34] N.V. Cohan, Proc. Cambridge Philos. Soc. **54**, 28 (1958).

[35] I.B. Bersuker and V.Z. Polinger, *Vibronic Interactions in Molecules and Crystals* (Springer-Verlag, Berlin, 1989).

[36] The DJT reduction factor is obtained from extrapolation of its finite-cutoff values 0.209 93 $(N=3)$, 0.182 57 $(N=4)$, 0.173 93 $(N=5)$, and 0.171 67 $(N=6)$.

[37] See, e.g., H. Friedrich, *Theoretical Atomic Physics* (Springer, Berlin, 1990), Chap. 2.

[38] Z. Gasyna, L. Andrews, and P.N. Schatz, J. Phys. Chem. **96**, 1525 (1991).

[39] S.E. Apsel, C.C. Chancey, and M.C.M. O'Brien, Phys. Rev. B **45**, 5251 (1992).

[40] P.N. Keizer, J.R. Morton, K.F. Preston, and A.K. Sugden, J. Phys. Chem. **95**, 7117 (1991).

[41] A. Penicaud, J. Hsu, C.A. Reed, A. Koch, K.C. Khemani, P.M. Allemand, and F. Wudl, J. Am. Chem. Soc. **113**, 6698 (1991).

[42] A.J. Schell-Sorokin, F. Mehran, G.R. Eaton, S.S. Eaton, A. Viebeck, T.R. O'Toole, and C.A. Brown, Chem. Phys. Lett. **195**, 225 (1992).

[43] M. Bennati, A. Grupp, M. Mehring, K.P. Dinse, and J. Fink, Chem. Phys. Lett. **200**, 440 (1992); M. Bennati, A. Grupp, P. Bauerle, and M. Mehring, Chem. Phys. **185**, 221 (1994); M. Bennati, A. Grupp, and M. Mehring, J. Chem Phys. **102**, 1234 (1995).

[44] M.M. Khaled, R.T. Carlin, P.C. Trulove, G.R. Eaton, and S.S. Eaton, J. Am. Chem. Soc. **116**, 3465 (1994).

[45] P.D.W. Boyd, P. Bhyrappa, P. Paul, J. Stinchcombe, R.D. Bolskar, Y. Sun, and C.A. Reed, J. Am. Chem. Soc. **117**, 2907 (1995).

[46] This is the order of levels if the sign of the spin-orbit parameter for the $^3t_{2g}$ state is positive. This sign is not obvious. For instance, we also find $\lambda/\lambda_{\rm at}\sim 0.01$ for the h_u highest occupied molecular orbital (HOMO), but $\lambda/\lambda_{\rm at}\sim -0.01$ for the t_{1g} LUMO$+1$. For the $^3t_{2g}$ exciton the spin-orbit sign is probably positive, as for the HOMO and the LUMO parent orbitals.