Vibrations and Berry Phases of Charged Buckminsterfullerene

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(Received 3 June 1994)

A simple model of electron-vibron interactions in buckminsterfullerene ions is solved semiclassically. Electronic degeneracies of $C_{60}{}^{n-}$ induce dynamical Jahn-Teller distortions, which are unimodal for $n \neq 3$ and bimodal for $n = 3$. The quantization of motion along the Jahn-Teller manifold leads to a symmetric-top rotator Hamiltonian. I find molecular Aharonov-Bohm effects where electronic Berry phases determine the vibrational spectra, zero point fluctuations, and electrons' pair binding energies. The latter are relevant to superconductivity in alkali fullerenes.

PACS numbers: 71.38.+i, 33.10.Lb, 74.20.−z

For polyatomic molecules, the adiabatic approximation is often used to eliminate fast electrons in favor of an effective potential for the slow nuclei. This approximation requires special care when the positions of the nuclear coordinates are near points of electronic degeneracy. If the electron-ion interaction is linear in the ionic displacements (a generic case for symmetric, noncollinear molecules [1]) the classical Jahn-Teller (JT) theory [2] predicts that the molecule distorts and some (or all) of the electronic degeneracy is lifted. The classical JT theory is controlled by the largeness of $S = |E^{\rm JT}|/\hbar\omega$, where ω is the characteristic vibrational frequency, and $E^{\rm JT}$ is the relaxed energy of the distortion. For $S = \infty$ (i.e., "strong coupling" or "classical" limit), the zero point motion of the ions is ignored.

At finite S, however, quantum corrections can be quantitatively and qualitatively important. For example, while the JT distortion may break the Hamiltonian symmetry, quantum fluctuations along the degenerate manifold or tunneling between JT minima can restore the ground state symmetry [3]. This is often called the "dynamical Jahn Teller" effect. In addition, ion coordinates may be subject to quantum interference effects. Longuet-Higgins has found that a vibrational orbit which surrounds a point of twofold electronic degeneracy, can acquire a negative sign from the transport of the electron's wave function [3]. This effect, often dubbed as the "molecular Aharonov-Bohm (MAB) effect," produces in triangular molecules half-odd integer quantum numbers. This has been recently confirmed spectroscopically in Na_3 [4]. The MAB effect is a simple example of the geometrical Berry phase, which appears in a wide host of quantum phenomena [5].

The soccerball shaped molecule C_{60} (buckminsterfullerene) and its various crystalline compounds have ignited enormous interest in the chemistry and physics community in past two years [6]. Since the discovery of superconductivity in A_3C_{60} (A=K,Cs,Rb), with relatively high transition temperatures ($T_c \approx$ 20–30 K), much attention has been given to the electronic properties of charged $C_{60}{}^{n-}$ ions. C_{60} a highly symmetrical molecule (a truncated icosahedron), and its electronic lowest unoccupied molecular orbitals (LUMO) are threefold degenerate. Thus the $C_{60}{}^{n-}$ ions are natural candidates for manifestations of dynamical JT effects and MAB effects discussed above. Several groups have identified the fivefold degenerate H_g (d-wave like) vibrational modes that couple strongly to the LUMO orbitals [7–9]. Varma, Zaanen, and Raghavachari (VZR) [7] proposed that these modes undergo a dynamical JT distortion and calculated the JT induced pair binding energies at several fillings. These results were used to explain the large T_c's of fullerenes relative to doped graphite superconductors. VZR used the classical approximation, and restricted their calculation to unimodal distortions (defined later).

Density functional and deformation potential calculations for $C_{60}{}^{-}$ [7,8], estimate $E^{\rm JT} \approx 40$ meV. The important vibrations are in the range of $\hbar\omega \approx 0.1$–0.2 eV. Thus, the classical parameter is in fact quite small: $S \simeq 0.2$–0.4. This indicates that the ions' quantum fluctuations cannot be justifiably neglected.

In this paper the vibrations about dynamically distorted buckminsterfullerine ions are quantized semiclassically. I extend previous work of O'Brien, who has solved the $n = 1$ case both exactly and semiclassically [10,11]. First, the unrestricted classical JT distortions are determined. For $C_{60}{}^{n-}$, $n \neq 3$, the JT distortions are *unimodal*, i.e., involve one quadrupolar mode in the principle axes frame. For $C_{60}{}^{3-}$, the JT distortion is found to be *bimodal*, i.e., two modes are distorted simultaneously. Subsequently, the quantum dynamics parallel and perpendicular to the JT manifold are determined. The excitation spectra and pair binding energies for $n = 1, \ldots, 5$ are determined up to second order in S^{-1}. I will show that Berry phases give rise to selection rules for the pseudorotational quantum numbers. These *kinematical* restrictions effect the pairing interaction between electrons, and, therefore, also the superconducting transition temperature.

This discussion is restricted to the simplest electron-vibron interaction model of C_{60}, which captures the symmetries and degeneracies of this system. Electron-electron interactions are presently ignored. The wave

0031-9007/94/72(18)/2931(4)$06.00

functions of the LUMO t_{1u} states are represented by the $L = 1$ triplet $|x\rangle, |y\rangle, |z\rangle$. A single vibronic H_g multiplet is represented by five real coefficients [7,10],

$$q_m = \sqrt{\pi/5} \sum_{\mu=-2}^{2} M_{m\mu} a_{2\mu},$$
$$M_{m\neq 0,\mu}, = [2\ \mathrm{sgn}(m)]^{-\frac{1}{2}} [\delta_{m,\mu} + \ \mathrm{sgn}(m)\delta_{m,-\mu}], \quad (1)$$
$$M_{0,\mu} = \delta_{\mu,0},$$

where $m, \mu = -2, -1, \ldots, 2$, and a_{lm} are the coefficients of the spherical harmonics Y_{lm} [12]. The Hamiltonian is $H = H^{\mathrm{el}} + H^{\mathrm{vib}}$, where

$$H^{\mathrm{el}} = g\frac{\hbar\omega}{2} \begin{pmatrix} q_0 - \sqrt{3}q_2 & -\sqrt{3}q_{-2} & -\sqrt{3}q_1 \\ -\sqrt{3}q_{-2} & q_0 + \sqrt{3}q_2 & -\sqrt{3}q_{-1} \\ -\sqrt{3}q_1 & -\sqrt{3}q_{-1} & -2q_0 \end{pmatrix}.$$
$$H^{\mathrm{vib}} = \frac{\hbar\omega}{2} \sum_{\mu} (-\partial_\mu^2 + q_\mu^2), \quad (2)$$

where g is the dimensionless electron phonon coupling constant. H^{vib} is invariant under rotations of $\mathbf{q}$ in R^5 and by construction, the eigenvalues of H are invariant under O(3) rotations of the molecule's reference frame. H^{el} is diagonalized by [11]

$$H^{\mathrm{el}} = g\frac{\hbar\omega}{2} T^{-1}(\varpi) \begin{pmatrix} z - \sqrt{3}r & 0 & 0 \\ 0 & z + \sqrt{3}r & 0 \\ 0 & 0 & -2z \end{pmatrix} T(\varpi),$$
$$T = \begin{pmatrix} \cos\psi & \sin\psi & 0 \\ -\sin\psi & \cos\psi & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \cos\theta & 0 & \sin\theta \\ 0 & 1 & 0 \\ \sin\theta & 0 & \cos\theta \end{pmatrix} \begin{pmatrix} \cos\phi & \sin\phi & 0 \\ -\sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad (3)$$

where the Euler angles $\varpi = (\phi, \theta, \psi)$ define the O(3) rotation which diagonalizes H^{el}. In the diagonal basis, the only nonzero vibrational components which couple to the electrons are $\mathbf{q}^{(0)} = (r, 0, z, 0, 0)$.

Since $|\mathbf{q}|^2$ is invariant under O(3) rotations, the total adiabatic potential is

$$V(z,r) = \frac{\hbar\omega}{2}(z^2 + r^2) + \frac{\hbar\omega g}{2} \left[n_1(z - \sqrt{3}r) + n_2(z + \sqrt{3}r) - n_3 2z \right]. \quad (4)$$

n_i are the occupations of the orbitals $|i\rangle$, $i = 1, 2, 3$ (ordered from top to bottom in H^{el}), and $\sum_i n_i = n$. V is minimized by the JT configurations $(\bar{z}, \bar{r}, \bar{n}_i)$, which yield the classical energies $E_n^{\mathrm{cl}} = V(\bar{z}_n, \bar{r}_n)$. The distortions are shown in Table I. We choose $S = \frac{1}{2}g^2$ as our semiclassical parameter.

By (1), if we define axis 3 to be at $\tilde{\theta} = 0$, the z mode is described by $\bar{z}\frac{1}{2}(3\cos^2\tilde{\theta} = 1)$, and the r mode by $\bar{r}\frac{\sqrt{3}}{2}\sin^2\tilde{\theta}\cos(2\tilde{\phi})$. Thus by Table I, $n = 1, 2, 4, 5$ have unimodal distortions which are symmetric about the 3 axis, and $n = 3$ has a bimodal distortion, about the 3 and 1 axes.

In order to quantize the vibrations, it is useful to express the kinetic energy in terms of small fluctuations about the JT distortion. To that end, we parametrize the JT degenerate manifold, $\{\bar{q}_\mu\}$, in terms of the Euler angles ϖ of Eq. (3):

$$\bar{q}_\mu(\varpi) = \sum_{m,m'.\mu'=-2}^{2} M_{\mu,m} D^{(2)}_{m,m'}(\varpi) M^{-1}_{m'\mu'} \bar{q}^{(0)}_{\mu'}. \quad (5)$$

$D^{(L)}$ is the irreducible rotational matrix of angular momentum L [12]. The classical kinetic energy can be derived from (5) by the chain rule for differentiation. After some cumbersome, but straightforward, algebra we ob-

TABLE I. Semiclassical results for the ground states of buckminsterfullerenes [Eq. (2)] of charge n. $(\bar{z}_n, \bar{r}_n)$ are the unimodal (uni) or bimodal (bi) Jahn-Teller parameters; $(\bar{n}_1, \bar{n}_2, \bar{n}_3)$ are electron occupations of adiabatic states. E_n are ground state energies [Eqs. (7),(9)] and U_n are pair binding energies.

n	$(\bar{z}_n, \bar{r}_n)$	$(\bar{n}_1, \bar{n}_2, \bar{n}_3)$	$E_n/(\hbar\omega)$	$U_n/(\hbar\omega)$
0	(0,0)	(0,0,0)	$\frac{5}{2}$	
1	$(g,0)$ (uni)	(0,0,1)	$-S + \frac{3}{2} + \frac{1}{6}S^{-1}$	$-2S + 1 - \frac{1}{3}S^{-1}$
2	$(2g,0)$ (uni)	(0,0,2)	$-4S + \frac{3}{2}$	
3	$(\frac{3}{2}g, \frac{\sqrt{3}}{2}g)$ (bi)	(1,0,2)	$-3S + 1 + \frac{1}{6}S^{-1}$	$-2S + 1 - \frac{1}{3}S^{-1}$
4	$(-2g,0)$ (uni)	(2,2,0)	$-4S + \frac{3}{2}$	
5	$(-g,0)$ (uni)	(1,2,2)	$-S + \frac{3}{2} + \frac{1}{6}S^{-1}$	$-2S + 1 - \frac{1}{3}S^{-1}$
6	(0,0)	(2,2,2)	$\frac{5}{2}$	

tain the compact expression:

$$\begin{aligned}\frac{1}{2}|\dot{\mathbf{q}}|^2 &= \frac{1}{2}\left(\dot{z}^2+\dot{r}^2+\sum_{i=1,3} I_i\omega_i^2\right),\\ \omega_1 &= -\sin\psi\dot{\theta}+\cos\psi\sin\theta\dot{\phi},\\ \omega_2 &= \cos\psi\dot{\theta}+\sin\psi\sin\theta\dot{\phi},\\ \omega_3 &= \dot{\psi}+\cos\theta\dot{\phi},\\ (I_1,I_2,I_3) &= ((\sqrt{3}z+r)^2,(\sqrt{3}z-r)^2,4r^2).\end{aligned} \tag{6}$$

For finite JT distortions, we can identify $I_i(\bar{z},\bar{r})$ as moments of inertia in the principle axes frame [12]. Thus, the Euler angles dynamics follow those of a *rigid rotator* [13].

The unimodal and bimodal cases will be discussed separately. For the unimodal cases, $\bar{r}=0$ and $I_i = \bar{z}^2(3,3,0)$ on the JT manifold. The coordinate ψ decouples from the rotational kinetic, which becomes that of a point particle on the sphere. The quantization of the rotational part is therefore simply $(2I_1)^{-1}\mathbf{L}^2$ [13]. The remaining coordinates are three harmonic oscillators $r_\gamma = (r\cos(2\psi), r\sin(2\psi), z-\bar{z})$. Including the quadratic potential terms in $V(z,r)$, we arrive at the vibrational eigenenergies:

$$E_n^{\text{uni}}[L,n_\gamma] = \hbar\omega\left(\frac{1}{6\bar{z}_n^2}L(L+1)+\sum_{\gamma=1}^{3}(n_\gamma+\tfrac{1}{2})\right). \tag{7}$$

The rotational parts of the eigenfunctions are

$$\Psi_{Lm}^{\text{uni}}(\bar{q}) = Y_{Lm}(\theta,\phi)\prod_{is}|n_{is}\rangle', \tag{8}$$

where $|n_{is}\rangle'$ is an electron Fock state in the principle axes basis. The overlap of this Fock state with a Fock state of the stationary basis is a determinant that contains n factors of $Y_{1\nu_{is}}$. Under reflection, $Y_{Lm}(\pi-\theta,\phi+\pi)\to(-1)^L Y_{Lm}(\theta,\phi)$. Therefore the electronic wave function yields a Berry phase factor of $(-1)^n$ for rotations between inverted points on the sphere which correspond to closed orbits of $\bar{q}$. Because of the invariance under reflection of $\bar{q}$ [and thus the left hand side of (8)], a selection rule is obtained: $(-1)^{L+n}=1$. Thus, the ground state for $n=1,5$ has pseudo-angular-momentum $L=1$ that contributes to the zero point energy.

The analysis of the bimodal case of $n=3$ proceeds along similar lines. From Eq. (6) and Table I, we see that $(I_1,I_2,I_3) = 3g^2(4,1,1)$. Thus, the kinetic energy includes the rotation of a rigid body with two equal moments of inertia. The quantization of this system is the quantum symmetric top Hamiltonian. Fortunately, its solution is a well-known textbook problem (see, e.g., Refs. [1,12]). In addition to the rotator, there are two harmonic oscillators $r_\gamma = (z-\bar{z}, r-\bar{r})$. The eigenvalues of the bimodal $C_{60}{}^{3-}$ molecule are thus given by

$$E^{bi} = \hbar\omega\left(\frac{1}{6g^2}L(L+1)-\frac{1}{8g^2}k^2+\sum_{\gamma=1}^{2}(n_\gamma+\tfrac{1}{2})\right), \tag{9}$$

where L and k are quantum numbers of $|\mathbf{L}|^2$ and L_1, respectively, and $k\le L$. The rotational part of the eigenfunctions are

$$\Psi_{Lmk}^{\text{bi}}[\bar{q}] = D_{mk}^{(L)}(\varpi)\prod_{is}|n_{is}\rangle'. \tag{10}$$

m is the eigenvalue of L_z, where z is a stationary axis. In distinction to the unimodal case, there is no single reflection which fully classifies the symmetry of the wave function. However, one can obtain negative signs by transporting the electronic ground state in certain orbits. We define the rotation of π about principle axis L_i as C_i. The Berry phases associated with these rotations can be read directly from Eq. (3). For example, for $\psi\to\psi+\pi$ (C_3), the states $|1\rangle$ and $|2\rangle$ get multiplied by (-1). Since $D_{m,k}^{(L)}$ transform as Y_{Lk} under C_i, it is easy to determine their sign factors. The results are given below:

$$\begin{aligned} &C_1: |1,0,2\rangle' \to |1,0,2\rangle', && C_1: D_{m,k}^{(L)} \to (-1)^k D_{m,k}^{(L)},\\ &C_2: |1,0,2\rangle' \to -|1,0,2\rangle', && C_2: D_{m,k}^{(L)} \to (-1)^{L+k} D_{m,-k}^{(L)},\\ &C_3: |1,0,2\rangle' \to -|1,0,2\rangle', && C_3: D_{m,k}^{(L)} \to (-1)^{L} D_{m,-k}^{(L)}. \end{aligned} \tag{11}$$

Clearly, $\bar{q}$, being coefficients of quadrupole distortions, is invariant under C_1, C_2, C_3. Thus, C_i describe closed orbits in R^5. In order to satisfy (10) and using the degeneracy of E^{bi} for $k\to -k$, we find that *L must be odd and k must be even.* In particular, the ground state of (9) is given by $L=1$, and $k=0$.

A relevant quantity for superconductivity is the "pair binding" energy [7,14] for odd fillings $n=1,3,5$:

$$U_n = E_{n+1}+E_{n-1}-2E_n\ , \tag{12}$$

where E_n are the total ground state energies. The calculation above finds that all odd fillings have the same semiclassical pair binding energy $U = -2S+1-\frac{1}{3}S^{-1}$. The characteristic Jahn-Teller relaxation frequency is ω, which is of the same order of, or perhaps larger than, the intermolecular hopping rate. Therefore it is a reasonable approximation to model the intramolecular interactions for the conduction electrons of A_3C_{60} by a negative instantaneous interaction given by a Hubbard interaction $-|U|\sum_i n_{i\uparrow}n_{i\downarrow}$, where n_{is} is the density of conduction electrons with spin s on molecule i. Since important perturbations have not been considered here (e.g., intermolecular hopping and electron-electron interactions [14]), I refrain from inferring quantitative predictions for the superconducting transition temperatures.

In Table I we summarize the results for the vibrational contributions to the ground state energies and pair binding energies of $C_{60}{}^{n-}$. The semiclassical results contain three leading terms in the $1/S$ expansion. However, one may rightfully worry about higher order corrections since for C_{60} the experimental estimate is $S=0.2$–0.4. From Fig. 1, we see that at least for the one electron case,

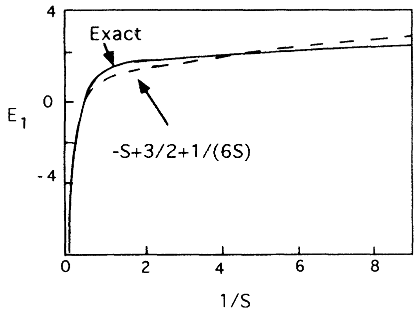

FIG. 1. Ground state energy (in units of $\hbar\omega$) for one electron. Dashed line: semiclassical result, Table I. Solid line: exact results of O'Brien, Ref. [11].

the semiclassical approximation for the ground state energy works reasonably well for $S \geq 0.25$. In Ref. [15], the quantum model (2) is solved exactly in a truncated vibron Fock space. There it is found that the qualitative features of the spectrum (level degeneracies and ordering) are well reproduced by the semiclassical pseudorotator Hamiltonians (7) and (9) down to $S \geq 0.5$. In the quantum regime, the pseudorotational contributions are expected to dominate. If we extrapolate the semiclassical results to small S, we expect a significant enhancement of the magnitude of pair binding energies U_n. Indeed, Refs. [15,16] find at small S that $U_1 \sim -5S + \mathcal{O}(S^2)$ which is a factor of 5/2 larger than the classical Jahn-Teller value $-2S$. From the weak coupling point of view, this enhancement is due to *local* molecular degeneracies. *It is therefore missed in the standard (single band) Migdal-Eliashberg diagrams.* Further details including the effects of multiple vibron modes on the experimental spectra are described in Ref. [15].

In summary, buckminsterfullerene is a correlated quantum electron-vibron system. Semiclassically, the dynamical Jahn-Teller distortions in ${C_{60}}^{n-}$ are quantized as pseudorotators subject to Berry phases. For $n = 1, 2, 4, 5$ there are unimodal distortions which give rise to pseudo-angular momenta spectra, plus three harmonic oscillators. For $n = 3$, there is a bimodal distortion, which generates a spectrum of a symmetric top rotator, plus two harmonic oscillators. The Berry phases of the electronic wave functions have been calculated and their selection rules for the pseudo-angular-momenta quantum numbers have been determined. The pseudorotator energies enhance pair binding, and thus superconductivity, relative to, e.g., doped graphite. It would be exciting to observe the details of the electron-vibron correlations experimentally.

I am indebted to Seb Doniach and Yossi Avron for valuable discussions. This paper was supported in part by grants from the U.S.-Israel Binational Science Foundation, the Fund for Promotion of Research at the Technion, and U.S. Department of Energy No. DE-FG02-91ER45441.

Note added.—After submittal of this Letter, I was made aware of previous work by Erio Tosatti on the connection between Berry phases and superconductivity [17].

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