Theory of Spontaneous Polarization of Endohedral Fullerenes

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A pseudo-Jahn–Teller model describing central atom distortions is proposed for endohedral fullerenes of the form A@C_{60} where A is either a rare gas or a metal atom. A critical (dimensionless) coupling \( g_c \) is found, below which the symmetric configuration is stable and above which inversion symmetry is broken. Vibronic parameters are given for selected endohedral fullerenes.

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Shortly after it was established that fullerenes are closed-cage structures of carbon, investigators speculated that atoms and clusters might be coaxed to occupy the space inside the cage. The existence of such endohedral fullerenes is now well-established by experiment [1]. Such space inside the cage. The existence of such endohedral fullerenes shows some promise as a technique to modify fullerene properties such as electric polarizability, optical and infrared absorption, and magnetic susceptibility.

Several numerical studies [2–6] have concluded that for the case of metal endohedral dopants, such as Na@C_{60}, Li@C_{60}, and Ca@C_{60}, the metal atom transfers its valence electrons to the C_{60} cage, and establishes an off-center equilibrium position, resulting in a net electric dipole moment for the molecule. For the case of rare gas dopants, however, the central atom sits at the cage center.

A classical model was used by Erwin [7] to explain the two disparate cases; for metal dopants, the charge transferred to the cage occupies a highly delocalized \( t_{1u} \) orbital. Erwin treats the resulting negatively charged cage as a perfectly conducting sphere. The total energy of the metal cation and the conducting sphere is minimized by placing the cation off-center where electrostatic interaction between the cation and the cage can be made more attractive as the charge on the cage is polarized. The distortion is stabilized in Erwin’s model by including a short-ranged repulsive interaction of Lennard-Jones form for the electron overlap between the cation and cage electrons.

Such a classical model would predict that for the case of metal dopants, inversion symmetry is broken as the central atom is stabilized in an off-center equilibrium position; while for closed-shell rare gas atoms, there will be no charge transfer and, consequently, no central atom distortion. However, this classical model suffers from two serious problems. First, for the case of singly-ionized alkali atoms, such a classical model would again predict no charge transfer, as such an atom is isoelectronic to a rare gas atom. Thus, charged metallofullerenes such as Li@C_{60} would have the cation symmetrically positioned according to the classical model. This, however, contradicts electronic structure calculations [2]. Second, for the distortive case of metallofullerenes, the net dipole moment calculated from the classical model is zero, as the contributions from the cation and the polarized cage exactly cancel.

The purpose of this work is two-fold: (1) to remedy the shortcomings of the classical model, and (2) to give insight into the physical mechanisms underlying previous numerical studies. We present here a model for the distortion mechanism where the electronic states are treated quantum mechanically. The propensity of the central atom for distortion can be understood as arising from the pseudo–Jahn–Teller (PJT) effect, where excited electronic states are mixed with highest occupied molecular orbital (HOMO) through a symmetry-breaking distortion. We note that PJT models have been successfully invoked in other contexts to describe, for example, distortions in the case of the F-center and in oxygen and nitrogen impurities in silicon [8].

We give analytical expressions for the magnitude of the distortion in this PJT model, and we find that there is a critical vibronic coupling \( g_c \); for values of \( g > g_c \), the dopant moves off-center, and for \( g \leq g_c \), the dopant sits at the cage center. We also find that for linear coupling the adiabatic potential surface is spherically symmetric, in good agreement with the numerical calculations [2], while the symmetry of the perturbative warping of the adiabatic potential can be explained with the addition of higher order terms.

We detail a model for the PJT coupling that involves a displacement of the central ion in endohedrally doped C_{60}. We start by describing the electronic structure of the C_{60} molecule. The valence electrons that are of interest are the radially-directed \( p \) electrons on the carbon atoms that take part in \( \pi \) bonding. There is one such electron on each carbon atom, the remaining valence electrons taking part in \( \sigma \) bonding and having a much lower energy. From the atomic \( p \) orbitals on each carbon, we construct molecular orbitals consistent with the \( I_h \) symmetry of the C_{60} molecule. However, since C_{60} is nearly spherical [8], it is possible to associate the different manifolds of molecular orbitals with angular mo-
mentum states \( L \). The \( C_{60} \) cage is electrically neutral; hence, the HOMO is the filled \( h_u \) level coming from the \( L = 5 \) molecular orbitals \([1]\). The lowest unoccupied molecular orbital (LUMO) is a \( t_{1u} \) manifold, also coming from \( L = 5 \). Slightly higher in energy however is a \( t_{1g} \) manifold, from \( L = 6 \). It is this excited state that plays a crucial role in our PJT coupling model.

We now consider the Jahn-Teller (JT) interaction involving the displacement of the central ion from its on-center position. For the case of dopants isoelectronic to the rare gases, the HOMO remains the filled \( h_u \) manifold. Such a state is non-degenerate, and consequently there is no pure JT interaction. There is, however, a PJT interaction involving the excited \( t_{1g} \) manifold. The \( t_{1g} \) manifold is the one of interest since the displacement modes of the central ion \( \vec{Q} \) span the irreducible representation \( t_{1u} \), and \( t_{1g} \) is contained in the direct product \( h_u \otimes t_{1u} \).

The Hamiltonian is taken to be

\[
\mathcal{H} = \mathcal{H}_o + \mathcal{H}_{\text{elas}} + \mathcal{H}_{\text{JT}} \tag{1}
\]

\( \mathcal{H}_o \) is the electronic Hamiltonian and gives the electronic energy of the \( h_u \) and \( t_{1g} \) manifolds for the fully symmetric (I\(_h\)) system

\[
\mathcal{H}_o = 0 \langle h_u | h_u \rangle + \Delta | t_{1g} \rangle \langle t_{1g} |,
\]

where \( \Delta \) is the energy difference between the \( t_{1g} \) and \( h_u \) manifolds, \( \Delta = E(t_{1g}) - E(h_u) \). \( \mathcal{H}_{\text{elas}} \) is the elastic Hamiltonian for a classical displacement of the central ion. Assuming the harmonic approximation,

\[
\mathcal{H}_{\text{elas}} = \frac{k}{2} (Q_x^2 + Q_y^2 + Q_z^2) \mathbf{I},
\]

where \( \mathbf{I} \) is the electronic identity operator. Actually, \( \vec{Q} \) includes \( t_{1u} \)-symmetric distortions of the \( C_{60} \) cage as well as a displacement of the central ion. But since the cage is much more massive than the dopant atoms considered (large cage mass approximation), the collective displacement \( \vec{Q} \) is well approximated by dopant displacement alone. Lastly, we have the \( \mathcal{H}_{\text{JT}} \) that describes the PJT coupling between the \( h_u \) and \( t_{1g} \) manifolds resulting from a displacement of the central ion from its on-center position, \( (h_u \otimes t_{1g}) \otimes t_{1u} \) coupling. These matrix elements are determined from the coupling coefficients given by Fowler and Cieuxmans (Table 5 of Ref. \([2]\)) where the coordinate axes are chosen to be coincident with the three orthogonal \( C_2 \) rotation axes. In our eight dimensional electronic space, we have

\[
\mathcal{H}_{\text{JT}} = \begin{pmatrix}
0 & h_{\text{JT}} \\
(\nu_{\text{JT}}) & 0
\end{pmatrix},
\]

where

\[

\begin{pmatrix}
t_{1x} & t_{1y} & t_{1z} & h_{x} & h_{x^2-y^2} & h_{JT} & h_{\eta} & h_{\zeta}
\end{pmatrix} = \begin{pmatrix}
-\sqrt{3} V Q_x & 0 & 2 V Q_z & 0 & 0 & 0 & 0 & 0
\end{pmatrix},
\]

and \( V \) gives the strength of the PJT coupling. We note that \( h_{x} = \sqrt{3/8} h_{\theta} - \sqrt{5/8} h_{\epsilon} \) and \( h_{x^2-y^2} = \sqrt{5/8} h_{\theta} + \sqrt{3/8} h_{\epsilon} \), in which \( h_{\theta} \) and \( h_{\epsilon} \) are the states employed in Ref. \([2]\).

We proceed by diagonalizing the Hamiltonian in Eq. \([1]\). By way of example, we consider the simple case in which \( Q_x = Q_y = 0 \). That is, we consider the particular case in which the central ion displaces along one of the \( C_2 \) symmetry axes. In this instance, the electronic Hamiltonian matrix reduces to three \( 2 \times 2 \) blocks and two \( 1 \times 1 \) blocks. The \( h_{x^2-y^2} \) and the \( h_c \) states are unaffected by this particular distortion; and so, their energies remain unchanged. One \( 2 \times 2 \) block, which mixes the states \( h_{x^2} \) and \( t_{1z} \), has the form

\[
\mathcal{H}^A = \begin{pmatrix}
0 & c V Q \\
c V Q & \Delta
\end{pmatrix},
\]

where \( c = 2 \).

The two remaining \( 2 \times 2 \) blocks, mixing the pairs of states \( \{h_{\eta}, t_{1x}\} \) or \( \{h_{\zeta}, t_{1y}\} \), also have the form given in Eq. \([1]\) with \( c = \sqrt{3} \).

The energy shift for a distortion \( Q \) is found by summing over the ten lowest energy states, including spin degeneracy. Hence, we find

\[
E = 2 E^A + 4 E^B - \frac{k Q^2}{2},
\]

where \( E^A = \frac{\Delta}{\Delta} \left[ (\Delta)^2 + 4 V^2 Q^2 \right]^{1/2} \) and \( E^B = \frac{\Delta}{\Delta} \left[ (\Delta)^2 + 3 V^2 Q^2 \right]^{1/2} \). We then minimize \( E \) with respect to \( Q \). We find that \( Q_0 = 0 \), corresponding to no displacement of the central ion, gives the minimum energy configuration when JT coupling is weak. More precisely, if

\[
g = \frac{V^2}{k \Delta} \leq \frac{1}{40},
\]

there is no displacement of the central ion. On the other hand, if the JT coupling is strong enough, \( g > \frac{1}{40} \), the minimum energy configuration is found for \( Q_0 \neq 0 \). That is, the total energy of the endohedrally doped \( C_{60} \) molecule can be reduced if the central ion displaces from its on-center position. The minimum energy configuration is found when \( Q_0 \equiv V Q_0/\Delta \) satisfies the equation

\[
\frac{2}{(1 + 16 Q_0^2)^{1/2}} + \frac{3}{(1 + 12 Q_0^2)^{1/2}} = \frac{1}{8g}.
\]
We now consider the most general displacement of the central ion. Here, we parametrize $Q_x$, $Q_y$, and $Q_z$ by $Q_x = Q \sin \theta \cos \phi$, $Q_y = Q \sin \theta \sin \phi$, and $Q_z = Q \cos \theta$. We substitute this into the matrix for the full Hamiltonian. The corresponding characteristic equation, whose roots yield the energy eigenvalues, is found to be independent of $\theta$ and $\phi$. Thus, the one-electron energy eigenvalues are independent of the direction of the displacement of the central ion, and the adiabatic energy surface is spherical.

Such an accidental SO(3) symmetry has been known to occur in other Jahn-Teller systems with icosahedral symmetry \cite{13}. The adiabatic potential $E$ as a function of central atom displacement is plotted in Fig. 1 \cite{1} for $g > g_c$. When the kinetic energy associated with the displacement $\vec{Q}$ is included in Eq. 3, low frequency excitations corresponding to a rotation of the distortion about the symmetric configuration are found, together with higher frequency radial excitations. Such excitations have been previously discussed elsewhere \cite{4,6}. It is important to note that there is no geometric phase in this model. Thus, this model establishes the quantization condition for the rotational wavefunctions previously assumed \cite{4,6}.

![FIG. 1. Adiabatic potential $E$ vs. magnitude of $t_{1u}$ distortion $Q$ for $\text{Na}^+@C_{60}$. A second curve (dashed) with reduced vibronic coupling $V$ ($g = 0.02$) is shown where the symmetric configuration is stable.](image)

For the case of metallic dopants, the HOMO becomes the $t_{1u}$ manifold \cite{1}. Here, such a partially filled state is subject to JT distortions. In fact, it has been proposed that such coupling is responsible for superconductivity in the alkali-doped fullerides \cite{13}. However, the JT distortion is of $h_g$ symmetry, and thus does not contribute to a dipole moment. In addition to the $t_{1u} \otimes h_g$ JT coupling, there is PJT coupling between the $t_{1u}$ and $t_{1g}$ electronic states by a $t_{1u}$ distortion, $(t_{1u} \oplus t_{1g}) \otimes t_{1u}$ coupling. We take the PJT coupling to be

$$h_{JT} = t_{1g} \begin{pmatrix} t_{1ux} & t_{1uy} & t_{1uz} \\ t_{1ux} & V Q_z & -V Q_y \\ t_{1uz} & V Q_y & -V Q_z \end{pmatrix}.$$ \hspace{1cm} (10)

Diagonalizing the electronic Hamiltonian yields the following eigenvalues: 0, $\Delta^\prime$, and $E_{\pm} = \frac{\Delta'}{2} \pm \left[ \left( \frac{\Delta'}{2} \right)^2 + V^2 Q^2 \right]^{1/2}$ where $\Delta'$ is the $t_{1u} - t_{1g}$ energy gap. Again, the eigenvalues are invariant under rotations \cite{6}.

For alkali metal endohedral fullerenes with a $t_{1u}$ ground state, we find that the energy shift for a distortion $Q$ is

$$E = \frac{\Delta'}{2} - \left[ \left( \frac{\Delta'}{2} \right)^2 + V^2 Q^2 \right]^{1/2} + \frac{1}{2} k Q^2,$$ \hspace{1cm} (11)

By minimizing the total energy, we conclude that there is no distortion unless $g > \frac{1}{V^2}$. A non-vanishing electric dipole moment results from the PJT distortion. Because of SO(3) invariance, we consider without loss of generality the case of a simple axial distortion ($Q_z \neq 0$) of an endohedral dopant isoelectronic to a rare gas atom. We find that a spontaneous dipole moment is formed for a non-vanishing distortion $Q_z$, in contrast to the classical model of Erwin which assumes perfectly metallic screening. Using the vibronic eigenstates of Eq. 3 together with the Clebsch-Gordan coefficients obtained from Ref. 12, we find an electric dipole moment in the direction of the central atom distortion of the form

$$p = 8 p_0 \left( \frac{\alpha}{1 + \alpha^2} + \frac{\sqrt{3} \beta}{1 + \beta^2} \right)$$ \hspace{1cm} (12)

where $p_0$ is a reduced matrix element, $(t_1||p||h)$, $\alpha = \sqrt{1 + 16 Q_z^2 - 1}{4 Q_z}$, and $\beta = \sqrt{1 + 12 Q_z^2 - 1}{2 \sqrt{3} Q_z}$. That numerical calculations on light rare gas endohedrals find the equilibrium of the rare gas dopant at the cage center indicates that $g$ for these systems is less than $\frac{1}{V^2}$. In the case of positively charged alkali endohedrals such as $\text{Na}^+@C_{60}$ and $\text{Li}^+@C_{60}$, previous calculations 4,6 have found an off-center equilibrium position for the alkali ion, indicating that $g$ for these endohedrals exceeds $\frac{1}{V^2}$.

Parameters for selected endohedrals are given in Table 3. For $\text{Na}^+@C_{60}$, we take $\Delta = 2.8$ eV, $Q_0 = 0.7$ Å, and $E = -0.12$ eV \cite{3}. From Eqs. 3 and 10, we fit the results of Ref. 3 with $V = 0.69$ eV/Å and $k = 5.8$ eV/Å$^2$, giving $g = 0.03$.

Assuming the primary coupling is between $t_{1u}$ and $t_{1g}$, we estimate the relevant parameters for $\text{Na}^+@C_{60}$ on the basis of previous calculations. We take $\Delta = 1.0$ eV, $Q_0 = 1.5$ Å, and $E = -1.4$ eV \cite{3}. We fit the results with $V = 2.47$ eV/Å and $k = 1.63$ eV/Å$^2$, giving $g = 3.73$. 


Ca@C_{60} can be treated within the same framework. For Ca@C_{60}, the electronic ground state for \text{I}_h symmetry is \text{3T}_{1g}. PJT coupling with the \text{3T}_{1u} state gives rise to a distortion that breaks inversion symmetry. The calculations of Ref. \cite{5} can be fit with \( V = 1.65 \text{ eV/Å} \) and \( k = 3.62 \text{ eV/Å}^2 \), giving \( g = 0.58 \).

The SO(3) invariance of the adiabatic potential within the linear PJT coupling will be broken when higher order couplings are taken into account. The amount of the warping of the adiabatic potential has been found \cite{2} to be negligible when the central atom dopant is either a rare gas or a positively charged alkali atom. Thus, the linear PJT model well describes the previous numerical calculations for these cases.

For the case of Ca@C_{60}, it has been found \cite{5} that the molecular symmetry is broken down to \text{C}_5v. While the addition of \text{3T}_{1g} \otimes \text{h}_g linear JT coupling for Ca@C_{60} does not break SO(3) invariance, \text{D}_{5d} warping \cite{17} of the adiabatic potential surface does result from quadratic JT coupling involving distortions of \text{h}_g symmetry \cite{18}, leading to a molecular symmetry of \text{C}_{5v}. The softest modes of C_{60} are of \text{h}_g symmetry; consequently, there is a small energy cost for such distortions. For such a quadratic coupling to the low frequency \text{h}_g vibrations, the directions of three-fold symmetry can contain relative maxima, while the directions of two-fold symmetry contain saddle points. For weak coupling, such a warping will be small compared to the PJT stabilization energy.

We conclude that PJT coupling provides a unifying framework for understanding the spontaneous polarization of endohedral fullerenes. The parameters of our PJT model were obtained by fitting to previous numerical calculations. We find that the structural distortion resulting from endohedral doping is yet another example illustrating the importance of vibronic effects in shaping the properties of fullerene systems.

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### TABLE I. Vibronic parameters for selected endohedrals.

| Dopant | \( \Delta \) or \( \Delta' \) (eV) | \( Q_0 \) (Å) | \( V \) (eV/Å) | \( k \) (eV/Å²) | \( g \) |
|--------|------------------|---------|--------|---------|------|
| Na⁺    | 2.8              | 0.7     | 0.69   | 5.78    | 0.03 |
| Na     | 1.0              | 1.5     | 2.47   | 1.63    | 3.73 |
| Ca     | 1.31             | 0.83    | 1.65   | 3.62    | 0.58 |

\( ^a \) Ref. \cite{4}  \( ^b \) Ref. \cite{3}  \( ^c \) Ref. \cite{19}  \( ^d \) Ref. \cite{17}

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