(T_{1u} + T_{1g}) \otimes (h_g + \tau_{1u}) \text{ vibronic interaction and superconductivity in } C_{60}^- \text{ fullerides}

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Abstract. The closeness of low-lying T_{1u} and T_{1g} levels of C_{60} could enable their mixing under an odd parity vibration of \tau_{1u} type. In addition, the two levels are susceptible to Jahn-Teller interaction due to five-fold degenerate h_g vibrations. This complex problem of \((T_{1u} + T_{1g}) \otimes (h_g + \tau_{1u})\) vibronic interaction is transformed to a form similar to \((T_{1u} + \tau_{1g}) \otimes (h_g + \tau_{1u})\) vibronic problem of octahedral symmetry. The problem is analysed in an infinite coupling model and compared with the experimental spectroscopic results for the C_{60} radical. The resulting parameters are used to calculate the pair-binding energy and superconducting transition temperature in C_{60}^\text{\textsuperscript{-}} fullerides. Vibronic mixing with the T_{1g} level is found to be responsible for maximising the pair-binding energy at the doping level \(n = 3\). It is also found to be an important source of \(T_c\) enhancement.

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1. Introduction

A number of theories have been proposed to explain the superconductivity in alkali metal doped C_{60} compounds M_3C_{60}. Zhang et al. [1] attribute the behaviour to strong attraction induced by M^+ optical phonon modes, while Chakravarty et al. [2] and Baskaran and Tosatti [3] argue in favour of RVB-type electron-electron exchange and correlation effects on single C_{60} molecules, Varma et al. [4] and a number of other authors [5-7] have emphasised the importance of an intramolecular dynamic Jahn-Teller coupling in accounting for this superconductivity behaviour. A novel idea proposed by Friedberg et al. [8] is that the closeness of the low-lying T_{1u} and T_{1g} levels of an isolated C_{60} (point group symmetry K, icosahedral) may provide a pairing mechanism in C_{60}^- ions. The T_{1u} and T_{1g} levels are triplets of opposite parity. The closeness of these two levels therefore also makes mixing between the two possible under odd parity vibrations, specially of \tau_{1u} type, as explained in the next section. Evidence of mixing between T_{1u} and T_{1g} levels under \tau_{1u} vibrations also comes from infrared reflectivity measurements on doped C_{60} compounds [9, 10]. In addition to this mixing, the two levels are susceptible to Jahn-Teller interaction due to the fivefold degenerate h_g vibrations [4-7]. This paper analyses the \((T_{1u} + T_{1g}) \otimes (\tau_{1u} + h_g)\) vibronic interaction for a C_{60}^\text{\textsuperscript{-}} ion. The relevant vibronic parameters are evaluated by comparison with the experimental spectroscopic results for C_{60} radical. These parameters are used to calculate the pair-binding energy and the contribution of T_{1g} mixing to superconductivity, using the Varma and Lannoo model [4-7].

2. Vibronic Hamiltonian

Since \(T_{1u} \times T_{1g} = A_{1u} + T_{1g} + H_u\), the odd vibrations responsible for mixing between T_{1u} and T_{1g} levels may be of \(A_{1u}, \tau_{1u}\) and \(h_g\) types. Further, since T_{1u} states are derived from the spherical harmonics \(Y_{1u}\), and T_{1g} states from \(Y_{1g}\) [8], a mixing matrix element is non-zero only if the symmetry of the potential and hence of the associated odd vibration belongs to a combination of spherical harmonics \(Y_n^L\) such that \(L = 1, 3, 5, 7, 9, 11\). The \(A_{1u}\) vibration does not satisfy this condition [11]. The \(h_g\) vibrations satisfy the condition only for high values of \(L\), equal to 5 and above, and hence are less important. The \(\tau_{1u}\) vibrations satisfy the condition for \(L = 1\) also and hence are mainly responsible for mixing between the two levels. There are four \(\tau_{1u}\) modes of vibrations [12]. For simplicity, only one \(\tau_{1u}\) mode is considered here, which may be thought of as representative of all four modes. Likewise, only one \(h_g\) mode out of eight [12] is considered. The appropriate vibronic Hamiltonian in the vector space \(|X_u\rangle, |Y_u\rangle, |Z_u\rangle, |X_g\rangle, |Y_g\rangle, |X_s\rangle\) can be written as

\[
H = \sum_{i,i'} [\omega (a_i^\dagger a_i + S/2) + \omega' (a_i^\dagger a_{i'} + 3/2)] I + V \tag{1}
\]

\(i = u, s, \xi, \eta, \zeta; \ i' = x, y, z.\)

Here \(|X_u\rangle, |Y_u\rangle\) and \(|Z_u\rangle\) refer to T_{1u} orbitals, and \(|X_s\rangle, |Y_s\rangle\) and \(|Z_s\rangle\) to T_{1g} orbitals. \(I\) is the unit matrix, \(\omega\) is the...
frequency of the fivefold degenerate $h_\omega$ mode, $\omega'$ is the frequency of the threefold degenerate $\tau_{1u}$ mode, and $a_i^+ (a_i)$ are the phonon creation (destruction) operators. $V$ is given by

$$
V = \begin{pmatrix}
\frac{1}{2} k_u \left( -Q_0 + \sqrt{3} Q_0 \right) & \frac{\sqrt{3}}{2} K_u Q_0 & \frac{\sqrt{3}}{2} K_u Q_x & 0 & \frac{\sqrt{3}}{2} K_u Q_z & K' Q_y \\
\frac{\sqrt{3}}{2} K_u Q_0 & \frac{1}{2} k_u \left( -Q_0 + \sqrt{3} Q_0 \right) & \frac{\sqrt{3}}{2} K_u Q_x & 0 & K' Q_z & 0 \\
\frac{\sqrt{3}}{2} K_u Q_0 & \frac{\sqrt{3}}{2} K_u Q_x & -Q_0 & \frac{\sqrt{3}}{2} K_u Q_z & 0 & K' Q_y \\
0 & K' Q_0 & 0 & \frac{\sqrt{3}}{2} K_u Q_x & \frac{\sqrt{3}}{2} K_u Q_z & K' Q_x \\
K' Q_x & 0 & K' Q_0 & 0 & \frac{\sqrt{3}}{2} K_u Q_x & K' Q_y \\
0 & K' Q_0 & K' Q_x & \frac{\sqrt{3}}{2} K_u Q_z & \frac{\sqrt{3}}{2} K_u Q_x & 0 \\
\end{pmatrix}
$$

Here $\Delta$ is the energy separating the $T_{1u}$ and $T_{1g}$ levels, $Q_i = \sqrt{\frac{3}{2}} (a_i^+ + a_i)$, and $K_u$, $K_g$ and $K'$ are coupling parameters. The Fulton-Gouterman operator $G$ [13-15], given by

$$
G = \exp[\pi i (a_x^+ a_x + a_y^+ a_y + a_z^+ a_z)],
$$

is used to transform to a new vector space $\{ |X_\lambda \rangle, |Y_\lambda \rangle, |Z_\lambda \rangle \}$, where $\lambda = 1$ or $-1$ and

$$|A_\lambda \rangle = \frac{1}{2} (1 + \lambda G) |A_0 \rangle + (1 - \lambda G) |A_g \rangle ,$$

with $A = X, Y$ or $Z$. In the new vector space the six-dimensional Hamiltonian (1) is reduced to two three-dimensional ones given by

$$H_\lambda = \sum_{i=1}^{6} \omega_i (a_i^+ a_i + 5/2) + \omega (a_i^+ a_i + 3/2)$$

$$+ \frac{1}{2} (1 + \lambda G) I + V$$

$$i = e, \theta, \xi, \eta, \zeta; \quad i' = x, y, z; \quad \lambda = 1, -1. \quad (2)$$

3. Variational solution

Let us attempt a unitary transformation with the help of a transformation matrix

$$U = \begin{pmatrix}
\exp \sum_{i} \frac{f_{i+}}{\sqrt{2}} (a_i^+ - a_i) \\
\end{pmatrix} I \quad (4)
$$

where $I$ is the unit matrix and all $f_i$ are variational parameters.

$$UH U^{-1} = H_\lambda^0 + H'_\lambda$$

$$H_\lambda^0 = \begin{pmatrix}
f_0 - \sqrt{3} f_e & -f_e & -f_e & -f_e & f_e - \sqrt{3} f_e & f_e + \sqrt{3} f_e \\
\end{pmatrix}$$

$$V_\lambda = \begin{pmatrix}
f_0 & -\sqrt{3} f_e & f_e & -\sqrt{3} f_e \\
\end{pmatrix}$$

where $f^2 = f_e^2 + f_0^2 + f_x^2$.

$$K_\lambda = (K_+ + K_- e^{-i \gamma}) \quad (7)$$

$$K_\lambda = (K_+ + K_- e^{-i \gamma}) \quad (8)$$

$$\text{and}

\begin{align*}
g_e &= f_e^2 + \frac{2K'}{\sqrt{3} K_\lambda} f_e, \quad g_0 = f_0 + \frac{2K'}{\sqrt{3} K_\lambda} f_e, \quad g_x = f_x + \frac{2K'}{\sqrt{3} K_\lambda} f_e.
\end{align*} \quad (8)$$