Research paper

Singlet-triplet interaction in linear triatomic molecules

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ABSTRACT

We present here two-electronic model, which describes singlet–triplet interaction $^1\pi - {}^3\Sigma^+$ in linear tri-atomic molecules. The analysis takes into account spin-orbital coupling terms in electronic Hamiltonian, as well as its symmetry properties. We give the symmetry operators of electronic Hamiltonian including space operators (acting on electronic coordinates) and matrix operators (acting on electronic spin). We consider only deformation π-modes and our resulting 5×5 vibronic matrix describes actual relativistic pseudo-Renner effect $(^1\pi - {}^3\Sigma) \times \pi$. The eigenvalues of vibronic matrix (i.e. potential energy surfaces) have axial symmetry and represented by analytical expressions, include five electrostatic and three spin-orbital parameters.

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1. Introduction

The quality of Born-Oppenheimer adiabatic separation of nuclear and electronic freedom degrees is determined by the Massey parameter [1]

$$\xi = \frac{L\Delta U}{V\hbar},$$

where ΔU is the characteristic adiabatic splitting, L is the coupling-region length, V is the nuclear velocity.

The values $\xi \gg 1$ means adiabatic regime, $\xi \ll 1$ corresponds to essentially non-adiabatic behavior.

The splitting ΔU can be small for several reasons. Two main reasons are: symmetrical configuration of nuclear positions and accidental degeneracy of adiabatic potential energy surfaces. First case causes the famous Jahn-Teller [2] and Renner [3] effects. The references on these subjects include the vast list of publications. Accidental degeneracies are not so wide studied [4].

Present work is devoted to configuration interaction of singlet Renner states $^1\pi$ and triplet states $^3\Sigma^+$, when spin-orbital coupling is taken into account. We mean here, that Massey parameter ξ with $\Delta U = |^3\Sigma^+ - {}^1\pi|$ can be not large for relevant dynamical situations.

At non-relativistic approach, the potential surfaces of electronic states $^1\pi$ and $^3\Sigma^+$ of linear triatomic molecule have different symmetry and multiplicity and can intersect [5]. When spin-orbital coupling is taken into account, the molecular spin and the projection of orbital angular momentum on the molecular axis are not conserved, and electronic states, mentioned above are involved in interaction. Possible resulting intersection of non-relativistic potentials $^1\pi$ and $^3\Sigma^+$, changes to avoided crossing.

In current research, we consider two-electron model of $^1\pi - {}^3\Sigma^+$ interaction, taking into account only deformational π-modes and spin-orbital interactions in electronic Hamiltonian [6].

Since the functional representation of the resulting vibronic matrix is determined only by symmetry properties [7], two-electron model of interaction $^1\pi - {}^3\Sigma^+$ can be applied to many-electron linear triatomic molecules with even number of electrons and three different atoms. Dependence on the number of electrons. concerns only the values of constant parameters of vibronic matrix [8].

The $^1\pi - {}^3\Sigma^+$ interaction reveals essentially, when the electronic states $^1\pi$ and $^3\Sigma^+$ are separated by small energy interval. In this case, $^1\pi - {}^3\Sigma^+$ interaction is the relativistic pseudo-Renner effect of $(^1\pi - {}^3\Sigma) \times \pi$ form.

2. The symmetry of two-electronic Hamiltonian

The basic relativistic effect in Renner systems is the spin-orbital interaction. To consider it, we take the electronic Hamiltonian in the form of sum of two operators: electrostatic Hamiltonian $\hat{H}_{es}$ and spin-orbital interaction $\hat{H}_{so}$:

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$$\hat{H} = \hat{H}_{es} + \hat{H}_{so}. \tag{1}$$

We do not give here the detailed forms for $\hat{H}_{es}$ and $\hat{H}_{so}$, which are well-known and are presented in the publications [6–10].

If the molecule has linear configuration, then electronic Hamiltonian (1) is characterized by the point symmetry group $C_{\infty v}$. The operators of this group, commuting with Hamiltonian $\hat{H}$, have the form:

$$\hat{G}_z^\varepsilon = \hat{C}_1(\varepsilon)\hat{C}_2(\varepsilon)\begin{pmatrix} e^{1\varepsilon/2} & 0 \\ 0 & e^{i\varepsilon/2} \end{pmatrix}_1 \begin{pmatrix} e^{i\varepsilon/2} & 0 \\ 0 & e^{i\varepsilon/2} \end{pmatrix}_2 \tag{2}$$

$$\hat{Z}_\sigma = \hat{\sigma}_{xz}^{(1)}\hat{\sigma}_{xz}^{(2)}\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}_1 \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}_2, \tag{3}$$

where $\hat{C}_i(\varepsilon)$ is the rotation of i electronic coordinates on the angle ε around z and $\hat{\sigma}_{xz}^{(i)}$ is the reflection of i electronic coordinates in the plane xz.

The appearance of matrices in the Eqs. (2) and (3) is caused by the spin operators (the Pauli matrices) in [6].

Space-matrix two-electronic operators $\hat{G}_z^\varepsilon$ and $\hat{Z}_\sigma$ correspond to the rotation ε around the molecular axis $z(\hat{G}_z^\varepsilon)$ and to the reflection in the vertical plane $xz(\hat{Z}_\sigma)$. They do act on the electron coordinates as well as on the electronic spin operators (Pauli matrices) in electronic Hamiltonian $\hat{H}$.

Besides space-matrix symmetry operators, the electronic Hamiltonian $\hat{H}$ is characterized by one more symmetry operator – time-reversal operator $\hat{T}$ [5,11].

$$\hat{T} = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}_1 \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}_2 c.\hat{c}, \tag{4}$$

where $c.\hat{c}$ – is the complex conjugation operator.

The Hamiltonian $\hat{H}$ commutes with operator $\hat{T}$ which is the antiunitary operator [11]. For the model considered with even-numbered electrons

$$\hat{T}^2 = +1 \tag{5}$$

3. Taylor series expansion of electronic Hamiltonian

It is convenient to perform Taylor series expansion of electronic Hamiltonian in terms of π-modes using the irreducible representations of $C_{\infty v}$ symmetry group. In Table, we give the corresponding symmetrized combinations up to second order contributions on π-modes.

Taylor series expansion of electrostatic Hamiltonian has the form:

$$\hat{H}_{es} = \hat{H}_0 + \hat{H}_1 + \hat{H}_2 + \ldots, \tag{6}$$

where $\hat{H}_0$ is nonrelativistic (electrostatic) Hamiltonian of the linear molecule,

$$\hat{H}_1 = \hat{H}_+(\pi_-)q_+ + \hat{H}_-(\pi_+)q_-, \tag{7}$$

$$\hat{H}_2 = \hat{H}_{++}(\delta_-)q_+^2 + \hat{H}_{--}(\delta_+)q_-^2 + \hat{H}_{+-}(\sigma^+)q_+q_-. \tag{8}$$

where $\hat{H}_1$ and $\hat{H}_2$ are the first and the second order contributions in electrostatic Hamiltonian, and $q_\pm$ are the deformation π-modes $(q_\pm = q_x \pm iq_y)$.

In terms of symmetrized combinations from Table, the Taylor series for spin-orbital interaction looks as following:

$$\hat{H}_{so} = \hat{h}_0 + \hat{h}_1 + \hat{h}_2 + \ldots, \tag{9}$$

Where

$$\hat{h}_0 = \sum_{k=1,2}\left[{}^k\hat{h}_+(\pi_-)\hat{\sigma}_+^{(k)} + {}^k\hat{h}_-(\pi_+)\hat{\sigma}_-^{(k)} + {}^k\hat{h}_z(\sigma^-)\hat{\sigma}_z^{(k)} \right], \tag{10}$$

$$\hat{h}_1 = \sum_{k=1,2}\left[{}^k\hat{h}_+^+(\delta_-)q_+\hat{\sigma}_+^{(k)} + {}^k\hat{h}_-^-(\delta_+)q_-\hat{\sigma}_-^{(k)} + {}^k\hat{h}^+(\sigma^+)(q_-\hat{\sigma}_+^{(k)} + q_+\hat{\sigma}_-^{(k)}) \right.$$
$$\left. + {}^k\hat{h}^-(\sigma^-)(q_-\hat{\sigma}_+^{(k)} - q_+\hat{\sigma}_-^{(k)}) + {}^k\hat{h}_z^+(\pi_-)q_+\hat{\sigma}_z^{(k)} - {}^k\hat{h}_z^-(\pi_+)q_-\hat{\sigma}_z^{(k)} \right], \tag{11}$$

$$\hat{h}_2 = \sum_{k=1,2}\left\{ \left[{}^k\hat{h}_+^{++}(\phi_-)q_+^2 + {}^k\hat{h}_+^{--}(\pi_+)q_-^2 + {}^k\hat{h}_+^{+-}(\pi_-)q_+q_- \right]\hat{\sigma}_+^{(k)} \right.$$
$$+ \left[{}^k\hat{h}_-^{++}(\pi_-)q_+^2 + {}^k\hat{h}_-^{--}(\phi_+)q_-^2 + {}^k\hat{h}_-^{+-}(\pi_+)q_+q_- \right]\hat{\sigma}_-^{(k)}$$
$$\left. + \left[{}^k\hat{h}_z^{++}(\delta_-)q_+^2 + {}^k\hat{h}_z^{--}(\delta_+)q_-^2 + {}^k\hat{h}_z^{+-}(\sigma^-)q_+q_- \right]\hat{\sigma}_z^{(k)} \right\} \tag{12}$$

Each operator coefficient in Taylor series (6–12) is transformed by irreducible representation and its row which marked as the argument of the operator. We underline here, that the operator coefficients of Taylor series are transformed by the irreducible representations, which are complex conjugated to the irreducible

Table
Symmetrized combinations of normal modes and Pauli matrices.

Order	#	Symmetry	Type	Symmetrized combinations
1st orb.	1	π	q	$q_+ = q_x + iq_y,\ q_- = q_x - iq_y$
2nd orb.	2	σ^+	qq	q_+q_-
	3	δ	qq	q_+^2, q_-^2
0th spin-orb.	4, 5	σ^-	σ	$\hat{\sigma}_z^{(1)}, \hat{\sigma}_z^{(2)}$
	6	π	σ	$\hat{\sigma}_+^{(1)} = (\hat{\sigma}_y^{(1)} - i\hat{\sigma}_x^{(1)})/2,\ \hat{\sigma}_-^{(1)} = (\hat{\sigma}_y^{(1)} + i\hat{\sigma}_x^{(1)})/2$
	7			$\hat{\sigma}_+^{(2)} = (\hat{\sigma}_y^{(2)} - i\hat{\sigma}_x^{(2)})/2,\ \hat{\sigma}_-^{(2)} = (\hat{\sigma}_y^{(2)} + i\hat{\sigma}_x^{(2)})/2$
1st spin–spin-orb.	8, 9 $k = 1, 2$	σ^+	$q\sigma$	$q_-\hat{\sigma}_+^{(k)} + q_+\hat{\sigma}_-^{(k)}$
	10, 11 $k = 1, 2$	σ^-	$q\sigma$	$q_-\hat{\sigma}_+^{(k)} - q_+\hat{\sigma}_-^{(k)}$
	12, 13 $k = 1, 2$	π	$q\sigma$	$q_+\hat{\sigma}_z^{(k)}, -q_-\hat{\sigma}_z^{(k)}$
	14, 15 $k = 1, 2$	δ	$q\sigma$	$q_+\hat{\sigma}_+^{(k)}, q_-\hat{\sigma}_-^{(k)}$
2nd spin-orb.	16, 17 $k = 1, 2$	σ^-	$q^2\sigma$	$q_+q_-\hat{\sigma}_z^{(k)}$
	18, 19 $k = 1, 2$	π	$q^2\sigma$	$q_+q_-\hat{\sigma}_+^{(k)}, q_+q_-\hat{\sigma}_-^{(k)}$
	20, 21 $k = 1, 2$	π	$q^2\sigma$	$q_+^2\hat{\sigma}_-^{(k)}, q_-^2\hat{\sigma}_+^{(k)}$
	22, 23 $k = 1, 2$	δ	$q^2\sigma$	$q_+^2\hat{\sigma}_z^{(k)}, -q_-^2\hat{\sigma}_z^{(k)}$
	24, 25 $k = 1, 2$	ϕ	$q^2\sigma$	$q_+^2\hat{\sigma}_+^{(k)}, q_-^2\hat{\sigma}_-^{(k)}$