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The Inversion Eigenvalues of Non-Σ States of Diatomic Molecules, Expressed in Terms of Quantum Numbers

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By adopting the phase convention of Condon and Shortley for spherical harmonics, it is shown how to determine in a standard way phases for electronic wave functions of a diatomic molecule. The method proposed is compared with the united atom method. On the basis of the phase convention introduced, the inversion eigenvalue of a non-Σ state in a diatomic molecule is expressed in terms of quantum numbers characterizing the state in question. The inversion eigenvalue expressions are used to give an extended definition of Mulliken's *c* and *d* notation.

Mit der Phasenkonvention von Condon u. Shortley für die Kugelfunktionen als Grundlage wird eine Standardmethode angegeben, um die Phasenfaktoren der elektronischen Wellenfunktion eines zweiatomigen Moleküls zu bestimmen. Diese Methode wird mit der Methode des vereinigten Atoms verglichen. Auf der Basis der eingeführten Phasenkonvention wird der Inversionswert eines Zustandes in einem zweiatomigen Molekül, der nicht vom Σ-Typ ist, durch die Quantenzahlen ausgedrückt, die den vorliegenden Zustand charakterisieren. Die Ausdrücke für die Inversionseigenwerte werden benutzt, um eine erweiterte Definition von Mullikens *c*- und *d*-Bezeichnungen zu geben.

En adoptant la convention de phase de Condon et Shortley pour les harmoniques sphériques, on montre comment déterminer d'une manière standard les phases des fonctions d'onde électroniques d'une molécule diatomique. Sur la base de la convention de phase ainsi introduite la valeur propre d'inversion d'un état non Σ dans une molécule diatomique est exprimée en termes des nombres quantiques caractérisant l'état en question. Les expressions des valeurs propres d'inversion sont utilisées pour donner une définition étendue des notations *c* et *d* de Mulliken.

1. Introduction

The state functions of a diatomic molecule, like those of any system of particles, may be characterized by their behaviour under inversion, i.e. a change in sign of the laboratory fixed coordinates of all the electrons and nuclei. Hence, all the energy levels of the molecule can be classified as negative or positive, depending on whether the corresponding wave function changes sign or not on inversion. It is well known that the inversion eigenvalues are given by the factors $(-1)^N$ and $(-1)^{N+1}$ for Σ^+- and Σ^--terms, respectively. Following the usual convention, N is the quantum number associated with the total angular momentum exclusive of spin of the molecule. The derivation leading to the factors above, is found in most textbooks dealing with molecular physics, for example Ref. [1]. As for non-Σ-states, it can be shown that given wave functions which differ only in the direction of the angular momenta along the internuclear axis, one can always find a linear combination of these which is invariant under inversion, and one which reverses sign under inversion. However, the question of which of the eigenvalues $+1$ and -1 belongs to a definite linear combination has not yet been answered satisfactorily.

The main purpose of this paper is to show how the phases for electronic wave functions may be determined in a standard way, and accordingly how the inversion eigenvalue of the total wave function may be expressed in terms of quantum numbers characterizing the function. The result will be applied to give an extended definition of the *c*- and *d*-designation of rotational levels introduced by Mulliken.

2. General Considerations

In order to describe our molecular system we introduce two right-handed cartesian systems of axes, both with their origin at the center of mass. The axes in one of the frames, (X, Y, Z), are chosen with fixed directions in the laboratory, and these axes will be referred to as the laboratory-fixed axis system, or more briefly as the laboratory system. The other system, the molecular frame, is rigidly connected to the nuclei and rotates with them. The z-axis coincides with the axis of the molecule from (say) nucleus 1 to nucleus 2. We shall allow the choice of the x-and y-axes to be quite arbitrary. The orientation of the rotating frame may be specified by means of eulerian angles (α, β, γ) as defined by Edmonds [2].

The treatment will be restricted to two types of molecular states. When the electronic spin functions are quantized with respect to their projection upon the molecular axis, we shall deal with eigenfunctions corresponding to Hund's case (a). If, on the other hand, the spin functions are quantized with respect to the spacefixed Z-axis, we shall consider eigenfunctions corresponding to Hund's case (b). However, our conclusion may be easily extended to any coupling situation in the molecule, since the wave functions can be expressed as linear combinations of either case (a) or case (b) functions.

Hund's case (a) functions may be written in symbolic vector notation as

$$\left|\begin{matrix} S\,J \\ qv\Lambda\Sigma\,\Omega \\ M\end{matrix}\right\rangle = \left|\begin{matrix} S \\ q\Lambda\Sigma \\ \end{matrix}\right\rangle |v\rangle \left|\begin{matrix} J \\ \Omega \\ M\end{matrix}\right\rangle , \tag{1}$$

where the decomposition of the function into a product of an electronic, vibrational, and rotational part is a consequence of the Born-Oppenheimer approximation. The electronic functions are characterized by the eigenvalues $S(S+1)\hbar^2$, $\Sigma\hbar$, and $\Lambda\hbar$ of the commuting angular momentum operators $\boldsymbol{S}^2, \boldsymbol{S}_z, \boldsymbol{L}_z$. As usual $\boldsymbol{S}$ and $\boldsymbol{L}$ denote the electronic spin and orbital angular momentum operators, respectively. The letter q in the state symbol represents the other quantum numbers necessary to specify the electronic state.

Since the vibrational part of the wave function $|v\rangle$, is invariant under inversion, it will for simplicity be omitted in the further treatment.

The rotational part of the wave function, $|J\Omega M\rangle$, is common eigenfunction of the three commuting angular momentum operators $\boldsymbol{J}^2$, $\boldsymbol{J}_Z$, and $\boldsymbol{J}_z$ with eigenvalues $J(J+1)\hbar^2$, $M\hbar$, and $\Omega\hbar$, respectively. In agreement with conventional notation, the total angular momentum exclusive of nuclear spin, is denoted by $\boldsymbol{J}$. According to Edmonds [2], p. 65, the rotational function $|J\Omega M\rangle$ can be represented as a function of the eulerian angles (α, β, γ).

Hund's case (b) functions may in the uncoupled representation be written as

$$\left| \begin{matrix} & S & N \\ q\Lambda & & \Lambda \\ & M_S & M_N \end{matrix} \right\rangle = \left| \begin{matrix} & S \\ q\Lambda & \\ & M_S \end{matrix} \right\rangle \left| \begin{matrix} N \\ \Lambda \\ M_N \end{matrix} \right\rangle , \qquad (2)$$

where we have omitted the vibrational part of the wave function. The spin function is quantized with respect to S^2 and S_Z. The rotational function $|N\Lambda M_N\rangle$ is the common eigenfunction of the commuting operators N^2, N_z, and M_Z. The total angular momentum exclusive of spin is in this paper denoted by $\boldsymbol{N}$. The eigenvalues of the last three operators considered, are $N(N+1)\hbar^2$, $\Lambda\hbar$, and $M_N\hbar$. The eigenfunctions $|N\Lambda M_N\rangle$ may be expressed in terms of the eulerian angles [2].

In the coupled representation we form eigenfunctions of the operators $\boldsymbol{J}^2$ and $\boldsymbol{J}_Z$. The coupled eigenfunctions may be written as a linear combination of the uncoupled functions as follows:

$$\left| \begin{matrix} & (SN) & J \\ q\Lambda & \Lambda & \\ & & M \end{matrix} \right\rangle = \sum_{M_S, M_N} \left| \begin{matrix} & S \\ q\Lambda & \\ & M_S \end{matrix} \right\rangle \left| \begin{matrix} N \\ \Lambda \\ N_M \end{matrix} \right\rangle \langle S M_S N M_N | S N J M \rangle . \qquad (3)$$

The expansion coefficients in Eq. (3) are the ordinary Wigner or Clebsch-Gordon coefficients.

By forming the symmetric and antisymmetric linear combinations

$$|\Omega_{S,A}, J\rangle = \frac{1}{\sqrt{2}} \left\{ \left| \begin{matrix} & S & J \\ q\Lambda & \Sigma & \Omega \\ & & M \end{matrix} \right\rangle \pm \left| \begin{matrix} & S & J \\ q - \Lambda & - \Sigma & - \Omega \\ & & M \end{matrix} \right\rangle \right\} , \qquad (4)$$

$$|\Lambda_{S,A}, J\rangle = \frac{1}{\sqrt{2}} \left\{ \left| \begin{matrix} & (SN) & J \\ q\Lambda & \Lambda & \\ & & M \end{matrix} \right\rangle \pm \left| \begin{matrix} & (SN) & J \\ q - \Lambda & - \Lambda & \\ & & M \end{matrix} \right\rangle \right\} \qquad (5)$$

we get eigenfunctions of the inversion operator. In Eqs. (4) and (5) the indices S and A correspond to the plus and minus sign, respectively, and it is supposed that at least one quantum number associated with an angular momentum operator quantized along the molecular axis, is different from zero. The problem in question now, is to express the inversion eigenvalues of the wave functions defined by Eqs. (4) and (5) by means of quantum numbers.

3. The Inversion Operator Applied to the Total Wave Function

As can be shown by simple geometrical considerations, the inversion of the coordinates in the laboratory system is equivalent to a reflection of the molecular fixed electronic coordinates followed by a rotation of the molecular frame through an angle Π about an axis through the origin and perpendicular to the plane of reflection. The rotation may be expressed by means of eulerian angles. If we choose the xz-plane as the reflection plane, then the eulerian angles α, β, and γ in the rotational wave function have to be replaced by $\pi+\alpha$, $\pi-\beta$, and $\pi-\gamma$, respectively. Denoting the reflection operator by $\boldsymbol{\sigma}_{xz}$, and the rotation of the molecular frame by $\boldsymbol{Q}$, the effect of applying the inversion operator $\boldsymbol{I}$ to the functions given by Eqs. (1) and (2), may be written

$$\boldsymbol{I}\left|\begin{array}{ccc} & S & J \\ q\Lambda & \Sigma & \Omega \\ & & M \end{array}\right\rangle = \boldsymbol{\sigma}_{xz}\left|\begin{array}{cc} & S \\ q\Lambda & \Sigma \end{array}\right\rangle \boldsymbol{Q}\,|J\Omega M\rangle \tag{6}$$

and

$$\boldsymbol{I}\left|\begin{array}{ccc} & S & N \\ q\Lambda & & \Lambda \\ & M_S & M_N \end{array}\right\rangle = \boldsymbol{\sigma}_{xz}\left|\begin{array}{cc} & S \\ q\Lambda & \\ & M_S \end{array}\right\rangle \boldsymbol{Q}\,|N\Lambda M_N\rangle\,. \tag{7}$$

The effects of the operators $\boldsymbol{\sigma}_{xz}$ and $\boldsymbol{Q}$ will be discussed separately.

3.1. *The Operator $\boldsymbol{Q}$ Applied to the Rotational Wave Function*

According to Edmonds [2] the rotational wave functions $|N\Lambda M_N\rangle$ are, apart from a normalization factor, identical with the D-functions, $D^N_{\Lambda M_N}(\alpha,\beta,\gamma)$, which define the irreducible representation of the rotation group R_3. As pointed out previously, the operator $\boldsymbol{Q}$ implies that the eulerian angles α, β, and γ should be replaced by $\pi+\alpha$, $\pi-\beta$, and $\pi-\gamma$. Utilizing the symmetry properties of the D-functions, expressed by Eqs. (4.2.4) and (4.2.6) of Ref. [2], we arrive at the following result

$$\boldsymbol{Q}\,|N\Lambda M_N\rangle = (-1)^{N-\Lambda}\,|N,-\Lambda,M_N\rangle\,. \tag{8}$$

Since the matrix elements $D^J_{\Omega M}(\alpha,\beta,\gamma)$ may be regarded as a representation of the eigenvectors $|J\Omega M\rangle$, [2] p. 65, the equation

$$\boldsymbol{Q}\,|J\Omega M\rangle = (-1)^{J-\Omega}\,|J,-\Omega,M\rangle \tag{9}$$

must also hold.

3.2. *The Operator $\boldsymbol{\sigma}_{xz}$ Applied to the Electronic Functions*

In this section we shall consider the effect of the reflection operator $\boldsymbol{\sigma}_{xz}$ applied to the electronic wave functions

$$\left|\begin{array}{cc} & S \\ q\Lambda & \Sigma \end{array}\right\rangle \quad\text{and}\quad \left|\begin{array}{cc} & S \\ q\Lambda & \\ & M_S \end{array}\right\rangle.$$

In recent years this problem has been dealt with by Mustelin [3] and Hougen [4]. Mustelin's treatment is restricted to singlet states. Hougen's treatment seems to be based on the assumption that the electronic function may be written as a product of an orbital function $|\Lambda\rangle$ and a spin function $|S\Sigma\rangle$. Taking into account the antisymmetric character of the electronic function with respect to interchange of any pair of electrons, this assumption is only valid for molecules with two electrons.

In both of the mentioned works the electronic functions are built up of atomic configurations of the "united atom". When applying the reflection operator $\boldsymbol{\sigma}_{xz}$ to the electronic function, this leads to an ambiguity in the sign of a phase factor, i.e. the phase factor δ in the equation

$$\boldsymbol{\sigma}_{xz}\left|q\Lambda\,\begin{matrix}S\\ \Sigma\end{matrix}\right\rangle = \delta\left|q-\Lambda-\begin{matrix}S\\ \Sigma\end{matrix}\right\rangle \tag{10}$$

can not be determined since it depends on the orbital quantum number L. However, L is not a good quantum number in a diatomic molecule, so no particular value of L suggests itself for use in the expression for δ.

In our approach to the problem in question, we shall build up the electronic functions from molecular orbitals. The molecular orbitals are supposed to be linear combinations of atomic orbitals centered on the various nuclei. Such LCAO MO's may be written as

$$|q\lambda\rangle = \sum_{k,l} |kl\lambda\rangle \langle kl\lambda | q\lambda\rangle . \tag{11}$$

The quantum number l and λ define the eigenvalues of the electronic angular momentum operators $\mathbf{l}^2$ and $\mathbf{l}_z$. The quantum number k is a label to distinguish between AO's which can no longer be distinguished by symmetry characteristics. The angular part of the AO's is supposed to be spherical harmonics $Y_\lambda^l(\theta, \varphi)$. Adopting the phase convention of Condon and Shortley [5] for the spherical harmonics, the result of applying the operator $\boldsymbol{\sigma}_{xz}$ to an atomic orbital is given by the equation

$$\boldsymbol{\sigma}_{xz}|kl\lambda\rangle = (-1)^\lambda |kl, -\lambda\rangle . \tag{12}$$

Hence,

$$\boldsymbol{\sigma}_{xz}|q\lambda\rangle = (-1)^\lambda |q, -\lambda\rangle \tag{13}$$

since the expansion coefficients $\langle kl\lambda | q\lambda\rangle$ and $\langle kl, -\lambda | q, -\lambda\rangle$ are equal.

The effect of the reflection upon the molecule – fixed spin functions which are quantized with respect to a component along the molecular axis, is readily shown to be

$$\boldsymbol{\sigma}_{xz}\phi_\sigma^{\frac{1}{2}} = (-1)^{\frac{1}{2}-\sigma}\phi_{-\sigma}^{\frac{1}{2}}, \qquad \sigma = \pm\tfrac{1}{2}, \tag{14}$$

when the intrinsic parity of the spin functions is taken to be even (Trinkham [6], p. 140).

Space-fixed spin functions are not effected by the operator $\boldsymbol{\sigma}_{xz}$ since they are defined in the laboratory system, and they are invariant under an inversion of the space-fixed axes.

In constructing the electronic functions from the molecular spin orbitals, $|q_i\lambda_i\rangle\phi_{\sigma_i}^{\frac{1}{2}}$, we shall follow the account given by Petrashen and Trifonov [7]. A short description of the construction is also to be found in Ref. [1].

The complete antisymmetric wave function of a molecule with n electrons, which is at the same time a common eigenfunction of the angular momentum operators $\boldsymbol{L}_z$, $\boldsymbol{S}^2$, and $\boldsymbol{S}_z$, is expressed by the equation

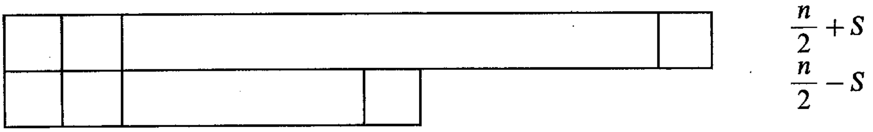
$$\left|\begin{matrix} S \\ qA\,\Sigma \end{matrix}\right\rangle = \sum_{p\in S_n} C(-1)^{\varepsilon(p)}\, p\, |qA(\boldsymbol{r}_1,\dots,\boldsymbol{r}_n)\rangle\, |S\Sigma(\sigma_1,\dots,\sigma_n)\rangle\,. \tag{15}$$

The permutation $p=\begin{pmatrix} i \\ p_i \end{pmatrix}$, which denotes an arbitrary element of the symmetric group S_n, should be applied to the arguments of the functions in Eq. (15). $\varepsilon(p)$ is the number of binary permutations in p and C is a normalization factor.

The spin functions

$$|S\Sigma(\sigma_1,\dots,\sigma_n)\rangle$$

transform in accordance with an irreducible representation of the permutation group, characterized by the following Young diagram:



The diagram consists of two rows of length $\mu_1=\frac{n}{2}+S$ and $\mu_2=\frac{n}{2}-S$, respectively.

Applying the Young operator

$$\hat{\boldsymbol{\Omega}}_{\{\mu\}}=\sum_q \hat{\boldsymbol{Q}} \sum_p (-1)^{\varepsilon(p)} \hat{\boldsymbol{P}} \tag{16}$$

to the spin function

$$\begin{aligned} &\Phi(\sigma_1,\dots,\sigma_n) \\ &\quad=\phi^{\frac{1}{2}}_{\sigma_1=\frac{1}{2}}(1)\dots\phi^{\frac{1}{2}}_{\sigma_{\mu_2}=\frac{1}{2}}(\mu_2)\,\phi^{\frac{1}{2}}_{\sigma_{\mu_2}+1}(\mu_2+1)\dots\phi^{\frac{1}{2}}_{\sigma_{\mu_1}}(\mu_1)\,\phi^{\frac{1}{2}}_{\sigma_{\mu_1}+1=-\frac{1}{2}}(\mu_1+1)\dots\phi^{\frac{1}{2}}_{\sigma_n=-\frac{1}{2}}(n) \end{aligned} \tag{17}$$

we get the desired eigenfunction of $\boldsymbol{S}^2$ and $\boldsymbol{S}_z$, i.e.

$$|S\Sigma(\sigma_1,\dots,\sigma_n)\rangle=\hat{\boldsymbol{\Omega}}_{\{\mu\}}\,\Phi(\sigma_1,\dots,\sigma_n)\,. \tag{18}$$

The effect of the operator $\hat{\boldsymbol{\Omega}}_{\{\mu\}}$ is to first perform antisymmetrization with respect to the spin functions whose arguments lie in the columns of the normal Young tableaux and then to perform symmetrization with respect to the functions in each row.

It is obvious that the constructed function

$$\hat{\boldsymbol{\Omega}}_{\{\mu\}}\,\Phi(\sigma_1,\dots,\sigma_n)$$

is an eigenfunction of $\boldsymbol{S}_z$ with eigenvalue

$$\Sigma\hbar=(\sigma_1+\sigma_2+\dots+\sigma_n)\hbar\,. \tag{19}$$

It can also be shown that the function in question is also an eigenfunction of $\boldsymbol{S}^2$ with eigenvalue $S(S+1)\hbar^2$ [7, 8].

The electronic orbital functions

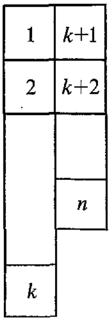
$$|qA(\mathbf{r}_{p_1}, \ldots, \mathbf{r}_{p_n})\rangle$$

transform in accordance with an irreducible representation of the permutation group for which the Young diagram consists of two columns. This Young diagram is the transposed of the corresponding diagram associated with the spin functions $|S\Sigma\rangle$, i.e. the length of its columns is $\frac{n}{2}+S$ and $\frac{n}{2}-S$, respectively. In the normal Young tableaux to the left we have put $k=\frac{n}{2}+S$. Applying the Young operator

$$\hat{\Omega}_{\{\bar{\mu}\}} = \sum_q \hat{Q} \sum_p (-1)^{\varepsilon(p)} \hat{P} \tag{20}$$

to the product function

$$|q_1\lambda_1(\mathbf{r}_1)\rangle\, |q_2\lambda_2(\mathbf{r}_2)\rangle \cdots |q_n\lambda_n(\mathbf{r}_n)\rangle$$



we get the orbital function which is to be combined with the spin function $|S\Sigma\rangle$ in Eq. (15). The operator $\hat{Q}_{\{\bar{\mu}\}}$ implies antisymmetrization with respect to orbitals whose numbers lie in the columns of the normal Young tableaux and thereafter symmetrization with respect to orbital indices lying in each row. Antisymmetrization applied to the columns of the tableaux yields

$$\begin{aligned} &\sum_p (-1)^{\varepsilon(p)} \hat{P} |q_1\lambda_1(\mathbf{r}_1)\rangle \cdots |q_n\lambda_n(\mathbf{r}_n)\rangle \\ &\qquad = \det\{|q_1\lambda_1(\mathbf{r}_1)\rangle \cdots |q_k\lambda_k(\mathbf{r}_k)\rangle\} \\ &\qquad \cdot \det\{|q_{k+1}\lambda_{k+1}(\mathbf{r}_{k+1})\rangle \cdots |q_n\lambda_n(\mathbf{r}_n)\rangle\}\,. \end{aligned} \tag{21}$$

The resulting product of two determinants must them be symmetrized with respect to pairs of functions whose numbers lie in the rows of the Young tableaux. Eq. (21) shows that equal orbitals have to be put into different columns of the Young tableaux if a nonzero result is to be produced.

It can readily be shown that the function

$$|qA\rangle = \hat{\Omega}_{\{\bar{\mu}\}} |q_1\lambda_1(\mathbf{r}_1)\rangle \cdots |q_n\lambda_n(\mathbf{r}_n)\rangle \tag{22}$$

is an eigenfunction of the operator $\mathbf{L}_z$ with eigenvalue

$$A\hbar = (\lambda_1 + \lambda_2 + \cdots + \lambda_n)\hbar\,. \tag{23}$$

Let us now apply the reflection operator $\boldsymbol{\sigma}_{xz}$ to the function given by Eq. (15). Since $\boldsymbol{\sigma}_{xz}$ commutes with the permutation operators, we must have

$$\boldsymbol{\sigma}_{xz}\left|\begin{matrix} & S \\ q\Lambda & \Sigma \end{matrix}\right\rangle = \sum_{p\in S_n} C(-1)^{\varepsilon(p)}\, p\,\boldsymbol{\sigma}_{xz}|q\Lambda(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_n)\rangle\,|S\Sigma(\sigma_1,\ldots,\sigma_n)\rangle\,. \tag{24}$$

When $\Lambda \neq 0$, Eqs. (13) and (22) imply

$$\begin{aligned}\boldsymbol{\sigma}_{xz}|q\Lambda\rangle &= \hat{\boldsymbol{\Omega}}_{\{\tilde{\mu}\}}\,\boldsymbol{\sigma}_{xz}\{|q_1\lambda_1(\boldsymbol{r}_1)\rangle\cdots|q_n\lambda_n(\boldsymbol{r}_n)\rangle\}\\ &= (-1)^{\Lambda}\hat{\boldsymbol{\Omega}}_{\{\tilde{\mu}\}}|q_1,-\lambda_1(\boldsymbol{r}_1)\rangle\cdots|q_n,-\lambda_n(\boldsymbol{r}_n)\rangle\\ &= (-1)^{\Lambda}|q,-\Lambda\rangle\,.\end{aligned} \tag{25}$$

Hence,

$$\boldsymbol{\sigma}_{xz}|q\Lambda\rangle = s_q|q,-\Lambda\rangle \tag{26}$$

when Σ-states are included. The quantity s_q is equal to $(-1)^{\Lambda}$, $+1$, and -1 for non-Σ-states, Σ^+ states, and Σ^- states, respectively.

The reflection operator applied to the spin function gives

$$\boldsymbol{\sigma}_{xz}|S\Sigma\rangle = (-1)_{S-\Sigma}|S,-\Sigma\rangle\,. \tag{27}$$

In the derivation of Eq. (27) we have made use of Eqs. (14), (17), and (18).

By substituting the results of Eqs. (26) and (27) into Eq. (24), one obtains

$$\boldsymbol{\sigma}_{xz}\left|\begin{matrix} & S \\ q\Lambda & \Sigma \end{matrix}\right\rangle = s_q(-1)_{S-\Sigma}\left|\begin{matrix} & S \\ q-\Lambda & -\Sigma \end{matrix}\right\rangle. \tag{28}$$

The construction of the functions

$$\left|\begin{matrix} & S \\ q\Lambda & \\ & M_S \end{matrix}\right\rangle$$

is quite analogous to the one given for electronic functions with spin quantized with respect to the internuclear axis. Remembering that the reflection operator has no effect on the space fixed spin functions, we arrive at the result

$$\boldsymbol{\sigma}_{xz}\left|\begin{matrix} & S \\ q\Lambda & \\ & M_S \end{matrix}\right\rangle = s_q\left|\begin{matrix} & S \\ q-\Lambda & \\ & M_S \end{matrix}\right\rangle, \tag{29}$$

where s_q is defined in connection with Eq. (26).

Let us now consider the united atom model. The state vectors in question may be expanded in eigenvectors of the united atom.

$$\begin{aligned}\left|\begin{matrix} & S \\ q\Lambda & \Sigma \end{matrix}\right\rangle &= \sum_{aL}\left|\begin{matrix} & L & S \\ a & \Lambda & \Sigma \end{matrix}\right\rangle\left\langle\begin{matrix} & L & S \\ a & \Lambda & \Sigma \end{matrix}\right|\left.\begin{matrix} & S \\ q\Lambda & \Sigma \end{matrix}\right\rangle\\ \left|\begin{matrix} & S \\ q-\Lambda & -\Sigma \end{matrix}\right\rangle &= \sum_{aL}\left|\begin{matrix} & L & S \\ a & -\Lambda & -\Sigma \end{matrix}\right\rangle\left\langle\begin{matrix} & L & S \\ a & -\Lambda & -\Sigma \end{matrix}\right|\left.\begin{matrix} & S \\ q-\Lambda & -\Sigma \end{matrix}\right\rangle,\end{aligned} \tag{30}$$

where

$$\left|\begin{matrix} L\,S \\ a\,\Lambda\,\Sigma \end{matrix}\right\rangle$$

is an eigenvector of L^2, the total electronic orbital angular momentum. It may be given as the antisymmetric part of the product vector $|aL\Lambda\rangle\,|S\Sigma\rangle$ (if this vector has an antisymmetric part), i.e.

$$\left|\begin{matrix} L\,S \\ a\,\Lambda\,\Sigma \end{matrix}\right\rangle = \hat{\Omega}_{\mathrm{An}}|aL\Lambda\rangle\,|S\Sigma\rangle\,, \tag{31}$$

where the projection operator is defined as

$$\hat{\Omega}_{\mathrm{An}} = \frac{1}{n!}\sum_{p\in S_n}(-1)^{\varepsilon(p)}\mathrm{p}\,. \tag{32}$$

Following Mustelin [3], the eigenvectors $|aL\Lambda\rangle$ shall be considered as a linear combination of the completely uncoupled eigenvectors

$$|a_1 l_1 \lambda_1\rangle\,|a_2 l_2 \lambda_2\rangle \cdots |a_n l_n \lambda_n\rangle$$

by means of successive Wigner transformations.

$$\begin{aligned} |aL\Lambda\rangle = \sum_{\lambda_1\lambda_2\Lambda_{12}\lambda_3\cdots} & |a_1 l_1 \lambda_1\rangle\,|a_2 l_2 \lambda_2\rangle \cdots |a_n l_n \lambda_n\rangle \\ & \cdot\langle l_1\lambda_1 l_2\lambda_2|l_1 l_2 L_{12}\Lambda_{12}\rangle\,\langle L_{12}\Lambda_{12} l_3\lambda_3|L_{12} l_3 L_{1\ldots 3}\Lambda_{1\ldots 3}\rangle \\ & \cdots\cdots\cdots\cdots\cdots\cdots \\ & \cdot\langle L_{1\ldots,n-2}\Lambda_{1\ldots,n-2} l_{n-1}\lambda_{n-1}|L_{1\ldots,n-2} l_{n-1} L_{1\ldots,n-1}\Lambda_{1\ldots,n-1}\rangle \\ & \cdot\langle L_{1\ldots,n-1}\Lambda_{1\ldots,n-1} l_n\lambda_n|L_{1\ldots,n-1} l_n L\Lambda\rangle\,. \end{aligned} \tag{33}$$

By making use of Eq. (12) and the following property of the Wigner coefficients

$$\langle j_1 m_1 j_2 m_2|j_1 j_2 j m\rangle = (-1)^{j_1+j_2-j}\langle j_1 -m_1 j_2 -m_2|j_1 j_2 j -m\rangle \tag{34}$$

one easily obtains

$$\sigma_{xz}|aL\Lambda\rangle = (-1)^{\sum_i l_i - L + \Lambda}|aL-\Lambda\rangle\,. \tag{35}$$

Since σ_{xz} commutes with the permutation operators, and taking into account Eq. (27), the equation

$$\sigma_{xz}\left|\begin{matrix} L\,S \\ a\,\Lambda\,\Sigma \end{matrix}\right\rangle = w_a(-1)^{-L+\Lambda+S-\Sigma}\left|\begin{matrix} L\quad S \\ a-\Lambda-\Sigma \end{matrix}\right\rangle \tag{36}$$

must hold. In Eq. (36) the parity w_a of the united atom state is introduced.

$$w_a = (-1)^{\sum_i l_i}\,. \tag{37}$$

Let us now return to Eqs. (30). In order to determine the phase factor in the equation

$$\sigma_{xz}\left|\begin{matrix} S \\ q\Lambda\,\Sigma \end{matrix}\right\rangle = \delta\left|\begin{matrix} S \\ q-\Lambda-\Sigma \end{matrix}\right\rangle \tag{38}$$

it is necessary to know those of the state vectors in the considered expansion which are the correct ones in the united atom limit. However, it is very difficult to determine these particular united atomic states if energy calculations are not performed for decreasing values of the internuclear distance.

The results of the preceding paragraph show that a consistent choice of phasis for electronic wave functions can rarely be found on the basis of the united atom model. On the other hand, the sketched MO method may be a standard way of determining phases for electronic wave functions even if the detailed configuration is not known.

4. The Inversion Eigenvalues Expressed in Terms of Quantum Numbers

By combining the results obtained in Sect. 3.1 and 3.2, it is possible to express the eigenvalues of the functions given in Eqs. (4) and (5) in terms of quantum numbers.

From Eqs. (9) and (28) it follows

$$\begin{aligned} I\,|\Omega_S, J\rangle &= s_q(-1)^{\Lambda+J-S}\,|\Omega_S, J\rangle \\ I\,|\Omega_A, J\rangle &= s_q(-1)^{\Lambda+J-S+1}\,|\Omega_A, J\rangle\,. \end{aligned} \tag{39}$$

Application of Eqs. (8) and (29) yields

$$\begin{aligned} I|\Lambda_S, NJ\rangle &= s_q(-1)^{N-\Lambda}\,|\Lambda_S, NJ\rangle \\ I\,|\Lambda_A, NJ\rangle &= s_q(-1)^{N-\Lambda+1}\,|\Lambda_A, NJ\rangle\,. \end{aligned} \tag{40}$$

In the singlet case, we obviously have the equations

$$\begin{aligned} I\,|\Lambda_S, J\rangle &= s_q(-1)^{J-\Lambda}\,|\Lambda_S, J\rangle \\ I\,|\Lambda_A, J\rangle &= s_q\,(-1)^{J-\Lambda+1}\,|\Lambda_A, J\rangle\,. \end{aligned} \tag{41}$$

If $\Lambda \neq 0$, then $s_q = (-1)^{\Lambda}$. By substituting this result in Eqs. (40), it is clearly seen that the states $|\Lambda_S, NJ\rangle$ and $|\Lambda_A, NJ\rangle$ behave under inversion in the same way as Σ^+- and Σ^--states, respectively.

5. Application to Mulliken's *c* und *d* Notation

The results of the preceding section can be applied to the classification of states, particularly to the *c*- and *d*- designation of rotational levels. Mulliken [9] defines the *c*- and *d*-series as follows. For singlet and case (b) he calls the series *c* or *d* depending on whether the lowest level is positive or negative. The definitions of *c*- and *d*-levels in case (a) are made by considering the adiabatic correlation of cases (a) and (b). For regular and inverted triplet states and inverted doublet states the definitions are analogous to the singlet case. For regular case (a) doublet states the *c* and *d* are changed compared to the singlet case. It should be noted that Mulliken's definitions are based on the inversion character of the lowest rotational level. However, which state it is that corresponds to a definite *c*- or *d*-level is not determined. Hence, Mulliken's *c*- and *d*-designation can not serve as good quantum numbers.

For singlet states Herzberg [10] has redefined Mulliken's *c*- and *d*-designation. According to Herzberg's definitions a series of rotational levels in which the even levels are positive and the odd negative, is designated as *c*-levels, and a series in which the even levels are negative and the odd positive, is designated as *d*-levels. A comparison with Eq. (41) shows that the states $|\Lambda_S, J\rangle$ and $|\Lambda_A, J\rangle$ correspond to *c*- and *d*-levels, respectively. In the case of intermediate coupling (multiplet states) Herzberg's designation cannot be adapted since states with different values of N are mixed.

On the basis of this work it is possible to give an extended definition of the *c*- and *d*-levels which will cover the intermediate coupling case, and the redefined *c* and *d* quantities may serve as almost good quantum numbers.

Using Hund's case (b) functions as basis-functions, we propose that a *c*-level should correspond to a state function which can be written as a linear combination of functions from the set

$$\begin{aligned}&\{|\Lambda_S, N=J-S, J\rangle,\ |\Lambda_S, N=J-S+2, J\rangle, \ldots\\ &|\Lambda_A, N=J-S+1, J\rangle,\ |\Lambda_A, N=J-S+3, J\rangle, \ldots\\ &|\Sigma^+, N=J-S, J\rangle,\ |\Sigma^+, N=J-S+2, J\rangle, \ldots\\ &|\Sigma^-, N=J-S+1, J\rangle,\ |\Sigma^-, N=J-S+3, J\rangle, \ldots\}\,.\end{aligned}$$

A *d*-level should correspond to a state function that is an element of the subspace generated by the following set of basis functions:

$$\begin{aligned}&\{|\Lambda_S, N=J-S+1, J\rangle,\ |\Lambda_S, N=J-S+3, J\rangle, \ldots\\ &|\Lambda_A, N=J-S, J\rangle,\ |\Lambda_A, N=J-S+2, J\rangle, \ldots\\ &|\Sigma^-, N=J-S, J\rangle,\ |\Sigma^-, N=J-S+2, J\rangle, \ldots\\ &|\Sigma^+, N=J-S+1, J\rangle,\ |\Sigma^+, N=J-S+3, J\rangle, \ldots\}\,.\end{aligned}$$

The number of functions in the sets considered, depends on the multiplicity. Eq. (40) shows that the inversion eigenvalue of the functions in the first set, is given by the expression $(-1)^{J-S}$, and $(-1)^{J-S+1}$ is the eigenvalue associated with the second set of functions.

If Hund's case (a) functions are used as basis functions, the *c*- and *d*-designation may be introduced in the following way: For non-Σ-states, the *c*(*d*)-designation should be used for levels that correspond to state functions which can be expressed as a linear combination of symmetric (antisymmetric) case (a)-functions. As for the Σ-states, the symmetric (antisymmetric) combination of a Σ^+-state and the antisymmetric (symmetric) combination of a Σ^--state should correspond to a *c*(*d*)-level. These definitions imply, as can readily be seen from Eq. (39), that the inversion eigenvalues of states corresponding to *c*- and *d*-levels are $(-1)^{J-S}$ and $(-1)^{J-S+1}$, respectively.

As a conclusion to these extended definitions of *c*- and *d*-levels, we may point out that a *c*-state (*c*-level) can never perturb a *d*-state (*d*-level) and vice versa, when state functions of the same multiplicity are considered.

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