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# Trattazione completa secondo il modello del campo cristallino della configurazione d$^3$ in un campo non cubico: autofunzioni e matrici di energia

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**Chimica.** — *Trattazione completa secondo il modello del campo cristallino della configurazione* $d^3$ *in un campo non cubico: autofunzioni e matrici di energia* (*). Nota di FRANCO CARIATI, ANTONIO SGAMELLOTTI e VENANZIO VALENTI, presentata (**) dal Socio G. SARTORI.

SUMMARY. — The present paper attempts to extend the application of the crystal field model to transition metal complexes of $MeX_5Y$ type of $d^3$ electronic configuration and non-cubic symmetry. The polyelectronic eigenfunctions have been obtained and classified according to transformation properties of the double group $C_{4v}^*$. Using the strong field scheme, the energy matrices have been calculated taking into account all the perturbations: effect of the crystal field, interelectronic repulsion and spin-orbit coupling. Calculations on the compounds $[ReX_5(PPh_3)]\, PPh_3H$ ($X = Cl, Br$) are in progress.

La teoria del campo cristallino è stata usata con successo per interpretare le proprietà spettroscopiche e magnetiche di complessi di metalli di transizione con configurazione $d^3$ in campi di simmetria ottaedrica [1, 2]. Scopo del presente lavoro è quello di estendere lo studio a composti di coordinazione con configurazioni $d^3$, ma aventi simmetria inferiore a quella cubica. A tal fine sono state calcolate, secondo la teoria del campo cristallino, le autofunzioni e le matrici di energia corrispondenti ad una configurazione $d^3$ in un campo di simmetria $C_{4v}$. Siamo infatti interessati allo studio delle proprietà elettroniche di composti tetragonali del tipo $MeX_5Y$, in cui si può ammettere che i legami Me—X e Me—Y siano diretti in direzioni ottaedriche, ma in cui le forze come leganti di X e Y siano diseguali. In questi calcoli abbiamo tenuto conto non solo delle perturbazioni maggiori già prese in esame da Perumareddi e coll. [3] per lo stesso tipo di simmetria, cioè della repulsione elettrostatica interelettronica di accoppiamento Russel–Saunders (e.r.i.) e dell'effetto di un campo di leganti (c.l.), ma anche della perturbazione minore rappresentata dall'interazione spin–orbita (s.o.). I calcoli sono stati eseguiti secondo il formalismo corrispondente al metodo del campo forte, seguendo lo schema:

$$\psi_{nl} \xrightarrow{\text{c.l.}} A\,(\gamma_i\, m_{\gamma_i}\, m_{s_i} \cdots) \xrightarrow{\text{e.r.i.}} \psi\,(\Gamma_{C_{4v}}\, M_\Gamma\, M_S) \xrightarrow{\text{s.o.}} \psi\,(\Gamma_{C_{4v}}\, M_\Gamma\, M_J)$$

che rende le matrici diagonali rispetto all'operatore della perturbazione dovuta al campo dei leganti.

(*) Lavoro eseguito con il contributo del C.N.R. nell'Istituto di Chimica Generale dell'Università di Milano e nell'Istituto di Chimica Generale ed Inorganica dell'Università di Perugia.

(**) Nella seduta del 19 novembre 1968.

TABELLA I.

*Autofunzioni «nd» monoelettroniche in un campo di leganti di simmetria* $C_{4v}$.

| | |
|---|---|
| $\vartheta \equiv a_1$ | $\vartheta = \|20\rangle \sim \frac{1}{2}(2z^2 - x^2 - y^2)$ |
| $\varepsilon \equiv b_1$ | $\varepsilon = \frac{1}{\sqrt{2}}[\|22\rangle + \|2-2\rangle] \sim \frac{\sqrt{3}}{2}(x^2 - y^2)$ |
| $\xi \equiv e$ | $\xi = \frac{i}{\sqrt{2}}[\|21\rangle + \|2-1\rangle] \sim \sqrt{3}\, yz$ |
| $\eta \equiv e$ | $\eta = -\frac{1}{\sqrt{2}}[\|21\rangle - \|2-1\rangle] \sim \sqrt{3}\, xz$ |
| $\zeta \equiv b_2$ | $\zeta = \frac{1}{i\sqrt{2}}[\|22\rangle - \|2-2\rangle] \sim \sqrt{3}\, xy$ |

Le autofunzioni monoelettroniche classificate secondo le proprietà di simmetria del gruppo $C_{4v}$ sono riportate in Tabella I. La scelta delle fasi nell'impostazione delle autofunzioni di approssimazione zero è stata fatta con i criteri seguiti da Griffith [4] e da Condon e Shortley [5]. Le autofunzioni polielettroniche di tutte le configurazioni possibili, classificate secondo le proprietà di trasformazione del gruppo $C_{4v}^*$ nelle rappresentazioni irriducibili E′ ed E″ sono riportate nelle Tabelle II e III, in cui si è inoltre specificato per ogni autofunzione la sua derivazione dalle rappresentazioni irriducibili del gruppo semplice $C_{4v}$. Con queste autofunzioni si sono calcolati gli elementi di matrice necessari al calcolo dell'energia, espressi in funzione della forza del campo dei leganti ($V_1$, $V_2$, $\cdots$), dei parametri di repulsione interelettronica B e C e della costante di accoppiamento spin–orbita $\zeta$. Le matrici di energia per le rappresentazioni E′ ed E″ del gruppo doppio $C_{4v}^*$ sono riportate rispettivamente in Tabella IV e V. È da notare come alcuni elementi di matrice risultino immaginari pur restando le matrici dei determinati secolari sempre autoaggiunte. Le energie di repulsione interelettronica sono state calcolate utilizzando la Tabella A 26 del Griffith [4], mentre per il calcolo delle energie di accoppiamento spin–orbita si sono utilizzati gli operatori riportati in letteratura [6]. Le espressioni delle energie di campo dei leganti, corrispondenti a tutte le possibili configurazioni, sono riportati in Tabella VI; gli integrali monoelettronici sono stati calcolati secondo le formule di Hartmann e König [7]. In Tabella VI gli integrali monoelettronici di campo dei leganti $G(k)$ ($k = 2,4$) si riferiscono nel caso di una molecola a simmetria $C_{4v}$ del tipo $MeX_5Y$, ai cinque leganti X uguali mentre $G'(k)$ si riferiscono al sesto legante Y, avente forza diversa.

TABELLA II.

*Autofunzioni* E′α′ *di campo forte per la configurazione* $d^3$.

| | |
|---|---|
| $b_1^2 a_1$ | $\psi(^2A_1) = -\overset{+}{\varepsilon}\,\bar{\varepsilon}\,\overset{+}{\vartheta}$ |
| $b_2^2 a_1$ | $\psi(^2A_1) = -\overset{+}{\zeta}\,\bar{\zeta}\,\overset{+}{\vartheta}$ |
| $a_1 b_1 b_2$ | $\psi(^4A_2) = \frac{1}{\sqrt{3}}\left(\overset{+}{\vartheta}\overset{+}{\varepsilon}\bar{\zeta} + \overset{+}{\vartheta}\bar{\varepsilon}\overset{+}{\zeta} + \bar{\vartheta}\overset{+}{\varepsilon}\overset{+}{\zeta}\right)$ |
| | $\psi(^2A_2) = -\frac{1}{\sqrt{2}}\left(\overset{+}{\vartheta}\bar{\varepsilon}\overset{+}{\zeta} - \bar{\vartheta}\overset{+}{\varepsilon}\overset{+}{\zeta}\right)$ |
| | $\psi(^2A_2) = -\frac{1}{\sqrt{6}}\left(2\overset{+}{\vartheta}\overset{+}{\varepsilon}\bar{\zeta} - \overset{+}{\vartheta}\bar{\varepsilon}\overset{+}{\zeta} - \bar{\vartheta}\overset{+}{\varepsilon}\overset{+}{\zeta}\right)$ |
| $a_1^2 e$ | $\psi(^2E) = \frac{-i}{\sqrt{2}}\overset{+}{\vartheta}\bar{\vartheta}\bar{\eta} + \frac{1}{\sqrt{2}}\overset{+}{\vartheta}\bar{\vartheta}\bar{\xi}$ |
| $b_1^2 e$ | $\psi(^2E) = -\frac{i}{\sqrt{2}}\overset{+}{\varepsilon}\bar{\varepsilon}\bar{\eta} + \frac{1}{\sqrt{2}}\overset{+}{\varepsilon}\bar{\varepsilon}\bar{\xi}$ |
| $b_2^2 e$ | $\psi(^2E) = -\frac{i}{\sqrt{2}}\overset{+}{\zeta}\bar{\zeta}\bar{\eta} + \frac{1}{\sqrt{2}}\overset{+}{\zeta}\bar{\zeta}\bar{\xi}$ |
| $a_1 b_2 e$ | $\psi(^4E) = \frac{i}{\sqrt{6}}\left(\bar{\vartheta}\bar{\zeta}\overset{+}{\xi} + \bar{\vartheta}\overset{+}{\zeta}\bar{\xi} + \overset{+}{\vartheta}\bar{\zeta}\bar{\xi}\right) - \frac{1}{\sqrt{6}}\left(\bar{\vartheta}\bar{\zeta}\overset{+}{\eta} + \bar{\vartheta}\overset{+}{\zeta}\bar{\eta} + \overset{+}{\vartheta}\bar{\zeta}\bar{\eta}\right)$ |
| | $\psi(^4E) = \frac{i}{\sqrt{2}}\overset{+}{\vartheta}\overset{+}{\zeta}\overset{+}{\xi} + \frac{1}{\sqrt{2}}\overset{+}{\vartheta}\overset{+}{\zeta}\overset{+}{\eta}$ |
| | $\psi(^2E) = -\frac{i}{2}\left(\overset{+}{\vartheta}\bar{\zeta}\xi - \bar{\vartheta}\overset{+}{\zeta}\bar{\xi}\right) + \frac{1}{2}\left(\overset{+}{\vartheta}\bar{\zeta}\bar{\eta} - \bar{\vartheta}\overset{+}{\zeta}\bar{\eta}\right)$ |
| | $\psi(^2E) = -\frac{i}{2\sqrt{3}}\left(-2\bar{\vartheta}\bar{\zeta}\overset{+}{\xi} + \bar{\vartheta}\overset{+}{\zeta}\bar{\xi} + \overset{+}{\vartheta}\bar{\zeta}\bar{\xi}\right) + \frac{1}{2\sqrt{3}}\left(-2\bar{\vartheta}\bar{\zeta}\overset{+}{\eta} + \bar{\vartheta}\overset{+}{\zeta}\bar{\eta} + \overset{+}{\vartheta}\bar{\zeta}\bar{\eta}\right)$ |
| $a_1 b_1 e$ | $\psi(^4E) = \frac{i}{\sqrt{6}}\left(\bar{\vartheta}\bar{\varepsilon}\overset{+}{\eta} + \bar{\vartheta}\overset{+}{\varepsilon}\bar{\eta} + \overset{+}{\vartheta}\bar{\varepsilon}\bar{\eta}\right) + \frac{1}{\sqrt{6}}\left(\bar{\vartheta}\bar{\varepsilon}\overset{+}{\xi} + \bar{\vartheta}\overset{+}{\varepsilon}\bar{\xi} + \overset{+}{\vartheta}\bar{\varepsilon}\bar{\xi}\right)$ |
| | $\psi(^4E) = \frac{i}{\sqrt{2}}\overset{+}{\vartheta}\overset{+}{\varepsilon}\overset{+}{\eta} - \frac{1}{\sqrt{2}}\overset{+}{\vartheta}\overset{+}{\varepsilon}\overset{+}{\xi}$ |
| | $\psi(^2E) = -\frac{i}{2}\left(\overset{+}{\vartheta}\bar{\varepsilon}\bar{\eta} - \bar{\vartheta}\overset{+}{\varepsilon}\bar{\eta}\right) - \frac{1}{2}\left(\overset{+}{\vartheta}\bar{\varepsilon}\bar{\xi} - \bar{\vartheta}\overset{+}{\varepsilon}\bar{\xi}\right)$ |

*Segue:* TABELLA II.

$a_1 b_1 e$

$$\psi(^2E) = -\frac{i}{2\sqrt{3}}\left(-2\bar{\vartheta}\bar{\varepsilon}\overset{+}{\eta} + \bar{\vartheta}\overset{+}{\varepsilon}\bar{\eta} + \overset{+}{\vartheta}\bar{\varepsilon}\bar{\eta}\right) - \frac{1}{2\sqrt{3}}\left(-2\bar{\vartheta}\bar{\varepsilon}\overset{+}{\xi} + \bar{\vartheta}\overset{+}{\varepsilon}\bar{\xi} + \overset{+}{\vartheta}\bar{\varepsilon}\bar{\xi}\right)$$

$b_1 b_2 e$

$$\psi(^4E) = \frac{i}{\sqrt{6}}\left(\bar{\varepsilon}\bar{\zeta}\overset{+}{\xi} + \bar{\varepsilon}\overset{+}{\zeta}\bar{\xi} + \overset{+}{\varepsilon}\bar{\zeta}\bar{\xi}\right) + \frac{1}{\sqrt{6}}\left(\bar{\varepsilon}\bar{\zeta}\overset{+}{\eta} + \bar{\varepsilon}\overset{+}{\zeta}\bar{\eta} + \overset{+}{\varepsilon}\bar{\zeta}\bar{\eta}\right)$$

$$\psi(^4E) = \frac{i}{\sqrt{2}}\,\overset{+}{\varepsilon}\overset{+}{\zeta}\overset{+}{\xi} - \frac{1}{\sqrt{2}}\,\overset{+}{\varepsilon}\overset{+}{\zeta}\overset{+}{\eta}$$

$$\psi(^2E) = -\frac{i}{2}\left(\overset{+}{\varepsilon}\bar{\zeta}\bar{\xi} - \bar{\varepsilon}\overset{+}{\zeta}\bar{\xi}\right) - \frac{1}{2}\left(\overset{+}{\varepsilon}\bar{\zeta}\bar{\eta} - \bar{\varepsilon}\overset{+}{\zeta}\bar{\eta}\right)$$

$$\psi(^2E) = -\frac{i}{2\sqrt{3}}\left(-2\bar{\varepsilon}\bar{\zeta}\overset{+}{\xi} + \bar{\varepsilon}\overset{+}{\zeta}\bar{\xi} + \overset{+}{\varepsilon}\bar{\zeta}\bar{\xi}\right) - \frac{1}{2\sqrt{3}}\left(-2\bar{\varepsilon}\bar{\zeta}\overset{+}{\eta} + \bar{\varepsilon}\overset{+}{\zeta}\bar{\eta} + \overset{+}{\varepsilon}\bar{\zeta}\bar{\eta}\right)$$

$e^2 a_1$

$$\psi(^4A_2) = \frac{1}{\sqrt{3}}\left(\overset{+}{\eta}\overset{+}{\xi}\bar{\vartheta} + \overset{+}{\eta}\bar{\xi}\overset{+}{\vartheta} + \bar{\eta}\overset{+}{\xi}\overset{+}{\vartheta}\right)$$

$$\psi(^2A_1) = \frac{-1}{\sqrt{2}}\left(\overset{+}{\xi}\bar{\xi}\overset{+}{\vartheta} + \overset{+}{\eta}\bar{\eta}\overset{+}{\vartheta}\right)$$

$$\psi(^2A_2) = -\frac{1}{\sqrt{6}}\left(2\overset{+}{\eta}\overset{+}{\xi}\bar{\vartheta} - \overset{+}{\eta}\bar{\xi}\overset{+}{\vartheta} - \bar{\eta}\overset{+}{\xi}\overset{+}{\vartheta}\right)$$

$e^2 b_1$

$$\psi(^2A_1) = -\frac{1}{\sqrt{2}}\left(\overset{+}{\xi}\bar{\xi}\overset{+}{\varepsilon} - \overset{+}{\eta}\bar{\eta}\overset{+}{\varepsilon}\right)$$

$$\psi(^2A_2) = \frac{1}{\sqrt{2}}\left(\overset{+}{\xi}\bar{\eta}\overset{+}{\varepsilon} - \bar{\xi}\overset{+}{\eta}\overset{+}{\varepsilon}\right)$$

$$\psi(^4B_2) = \bar{\eta}\bar{\xi}\bar{\varepsilon}$$

$e^2 b_2$

$$\psi(^2A_1) = -\frac{1}{\sqrt{2}}\left(\overset{+}{\xi}\bar{\eta}\overset{+}{\zeta} - \bar{\xi}\overset{+}{\eta}\overset{+}{\zeta}\right)$$

$$\psi(^2A_2) = -\frac{1}{\sqrt{2}}\left(\overset{+}{\xi}\bar{\xi}\overset{+}{\zeta} - \overset{+}{\eta}\bar{\eta}\overset{+}{\zeta}\right)$$

$$\psi(^4B_1) = -\bar{\xi}\bar{\eta}\bar{\zeta}$$

$e^3$

$$\psi(^2E) = -\frac{i}{\sqrt{2}}\,\overset{+}{\xi}\bar{\xi}\bar{\eta} + \frac{1}{\sqrt{2}}\,\overset{+}{\eta}\bar{\eta}\bar{\xi}$$

TABELLA III.

*Autofunzioni* $E''\alpha''$ *di campo forte per la configurazione* $d^3$.

| | |
|---|---|
| $a_1^2 b_1$ | $\psi(^2B_1) = -\overset{+}{\vartheta}\bar{\vartheta}\overset{+}{\varepsilon}$ |
| $a_1^2 b_2$ | $\psi(^2B_2) = -\overset{+}{\vartheta}\bar{\vartheta}\overset{+}{\zeta}$ |
| $b_1^2 b_2$ | $\psi(^2B_2) = -\overset{+}{\varepsilon}\bar{\varepsilon}\overset{+}{\zeta}$ |
| $b_2^2 b_1$ | $\psi(^2B_1) = -\overset{+}{\zeta}\bar{\zeta}\overset{+}{\varepsilon}$ |
| $a_1 b_1 b_2$ | $\psi(^4A_2) = \bar{\vartheta}\bar{\varepsilon}\bar{\zeta}$ |
| $a_1^2 e$ | $\psi(^2E) = -\frac{i}{\sqrt{2}}\overset{+}{\vartheta}\bar{\vartheta}\bar{\eta} - \frac{1}{\sqrt{2}}\overset{+}{\vartheta}\bar{\vartheta}\bar{\xi}$ |
| $b_1^2 e$ | $\psi(^2E) = -\frac{i}{\sqrt{2}}\overset{+}{\varepsilon}\bar{\varepsilon}\bar{\eta} - \frac{1}{\sqrt{2}}\overset{+}{\varepsilon}\bar{\varepsilon}\bar{\xi}$ |
| $b_2^2 e$ | $\psi(^2E) = -\frac{i}{\sqrt{2}}\overset{+}{\zeta}\bar{\zeta}\bar{\eta} - \frac{1}{\sqrt{2}}\overset{+}{\zeta}\bar{\zeta}\bar{\xi}$ |
| $a_1 b_2 e$ | $\psi(^4E) = \frac{i}{\sqrt{6}}\left(\bar{\vartheta}\bar{\zeta}\overset{+}{\xi} + \bar{\vartheta}\overset{+}{\zeta}\bar{\xi} + \overset{+}{\vartheta}\bar{\zeta}\bar{\xi}\right) + \frac{1}{\sqrt{6}}\left(\bar{\vartheta}\bar{\zeta}\overset{+}{\eta} + \bar{\vartheta}\overset{+}{\zeta}\bar{\eta} + \overset{+}{\vartheta}\bar{\zeta}\bar{\eta}\right)$ |
| | $\psi(^4E) = -\frac{i}{\sqrt{2}}\overset{+}{\vartheta}\overset{+}{\zeta}\overset{+}{\xi} + \frac{1}{\sqrt{2}}\overset{+}{\vartheta}\overset{+}{\zeta}\overset{+}{\eta}$ |
| | $\psi(^2E) = -\frac{i}{2}\left(\overset{+}{\vartheta}\bar{\zeta}\bar{\xi} - \bar{\vartheta}\overset{+}{\zeta}\bar{\xi}\right) - \frac{1}{2}\left(\overset{+}{\vartheta}\bar{\zeta}\bar{\eta} - \bar{\vartheta}\overset{+}{\zeta}\bar{\eta}\right)$ |
| | $\psi(^2E) = -\frac{i}{2\sqrt{3}}\left(-2\bar{\vartheta}\bar{\zeta}\overset{+}{\xi} + \bar{\vartheta}\overset{+}{\zeta}\bar{\xi} + \overset{+}{\vartheta}\bar{\zeta}\bar{\xi}\right) - \frac{1}{2\sqrt{3}}\left(-2\bar{\vartheta}\bar{\zeta}\overset{+}{\eta} + \bar{\vartheta}\overset{+}{\zeta}\bar{\eta} + \overset{+}{\vartheta}\bar{\zeta}\bar{\eta}\right)$ |
| $a_1 b_1 e$ | $\psi(^4E) = \frac{i}{\sqrt{6}}\left(\bar{\vartheta}\bar{\varepsilon}\overset{+}{\eta} + \bar{\vartheta}\overset{+}{\varepsilon}\bar{\eta} + \overset{+}{\vartheta}\bar{\varepsilon}\bar{\eta}\right) - \frac{1}{\sqrt{6}}\left(\bar{\vartheta}\bar{\varepsilon}\overset{+}{\xi} + \bar{\vartheta}\overset{+}{\varepsilon}\bar{\xi} + \overset{+}{\vartheta}\bar{\varepsilon}\bar{\xi}\right)$ |
| | $\psi(^4E) = -\frac{i}{\sqrt{2}}\overset{+}{\vartheta}\overset{+}{\varepsilon}\overset{+}{\eta} - \frac{1}{\sqrt{2}}\overset{+}{\vartheta}\overset{+}{\varepsilon}\overset{+}{\xi}$ |
| | $\psi(^2E) = -\frac{i}{2}\left(\overset{+}{\vartheta}\bar{\varepsilon}\bar{\eta} - \bar{\vartheta}\overset{+}{\varepsilon}\bar{\eta}\right) + \frac{1}{2}\left(\overset{+}{\vartheta}\bar{\varepsilon}\bar{\xi} - \bar{\vartheta}\overset{+}{\varepsilon}\bar{\xi}\right)$ |

*Segue:* TABELLA III.

| | |
|---|---|
| $a_1 b_1 e$ | $\psi(^2E) = -\frac{i}{2\sqrt{3}}\left(-2\bar{\vartheta}\bar{\varepsilon}\overset{+}{\eta} + \bar{\vartheta}\overset{+}{\varepsilon}\bar{\eta} + \overset{+}{\vartheta}\bar{\varepsilon}\bar{\eta}\right) + \frac{1}{2\sqrt{3}}\left(-2\bar{\vartheta}\bar{\varepsilon}\overset{+}{\xi} + \bar{\vartheta}\overset{+}{\varepsilon}\bar{\xi} + \overset{+}{\vartheta}\bar{\varepsilon}\bar{\xi}\right)$ |
| $b_1 b_2 e$ | $\psi(^4E) = \frac{i}{\sqrt{6}}\left(\bar{\varepsilon}\bar{\zeta}\overset{+}{\xi} + \bar{\varepsilon}\overset{+}{\zeta}\bar{\xi} + \overset{+}{\varepsilon}\bar{\zeta}\bar{\xi}\right) - \frac{1}{\sqrt{6}}\left(\bar{\varepsilon}\bar{\zeta}\overset{+}{\eta} + \bar{\varepsilon}\overset{+}{\zeta}\bar{\eta} + \overset{+}{\varepsilon}\bar{\zeta}\bar{\eta}\right)$ |
| | $\psi(^4E) = -\frac{i}{\sqrt{2}}\,\overset{+}{\varepsilon}\overset{+}{\zeta}\overset{+}{\xi} - \frac{1}{\sqrt{2}}\,\overset{+}{\varepsilon}\overset{+}{\zeta}\overset{+}{\eta}$ |
| | $\psi(^2E) = -\frac{i}{2}\left(\overset{+}{\varepsilon}\bar{\zeta}\bar{\xi} - \bar{\varepsilon}\overset{+}{\zeta}\bar{\xi}\right) + \frac{1}{2}\left(\overset{+}{\varepsilon}\bar{\zeta}\bar{\eta} - \bar{\varepsilon}\overset{+}{\zeta}\bar{\eta}\right)$ |
| | $\psi(^2E) = -\frac{i}{2\sqrt{3}}\left(-2\bar{\varepsilon}\bar{\zeta}\overset{+}{\xi} + \bar{\varepsilon}\overset{+}{\zeta}\bar{\xi} + \overset{+}{\varepsilon}\bar{\zeta}\bar{\xi}\right) + \frac{1}{2\sqrt{3}}\left(-2\bar{\varepsilon}\bar{\zeta}\overset{+}{\eta} + \bar{\varepsilon}\overset{+}{\zeta}\bar{\eta} + \overset{+}{\varepsilon}\bar{\zeta}\bar{\eta}\right)$ |
| $e^2 a_1$ | $\psi(^2B_1) = -\frac{1}{\sqrt{2}}\left(\overset{+}{\xi}\bar{\xi}\overset{+}{\vartheta} - \overset{+}{\eta}\bar{\eta}\overset{+}{\vartheta}\right)$ |
| | $\psi(^4A_2) = \bar{\eta}\bar{\xi}\bar{\vartheta}$ |
| | $\psi(^2B_2) = \frac{1}{\sqrt{2}}\left(\overset{+}{\xi}\bar{\eta}\overset{+}{\vartheta} - \bar{\xi}\overset{+}{\eta}\overset{+}{\vartheta}\right)$ |
| $e^2 b_1$ | $\psi(^2B_1) = -\frac{1}{\sqrt{2}}\left(\overset{+}{\xi}\bar{\xi}\overset{+}{\varepsilon} + \overset{+}{\eta}\bar{\eta}\overset{+}{\varepsilon}\right)$ |
| | $\psi(^2B_2) = -\frac{1}{\sqrt{6}}\left(2\overset{+}{\eta}\overset{+}{\xi}\bar{\varepsilon} - \overset{+}{\eta}\bar{\xi}\overset{+}{\varepsilon} - \bar{\eta}\overset{+}{\xi}\overset{+}{\varepsilon}\right)$ |
| | $\psi(^4B_2) = \frac{1}{\sqrt{3}}\left(\overset{+}{\eta}\overset{+}{\xi}\bar{\varepsilon} + \overset{+}{\eta}\bar{\xi}\overset{+}{\varepsilon} + \bar{\eta}\overset{+}{\xi}\overset{+}{\varepsilon}\right)$ |
| $e^2 b_2$ | $\psi(^2B_1) = -\frac{1}{\sqrt{6}}\left(2\overset{+}{\xi}\overset{+}{\eta}\bar{\zeta} - \overset{+}{\xi}\bar{\eta}\overset{+}{\zeta} - \bar{\xi}\overset{+}{\eta}\overset{+}{\zeta}\right)$ |
| | $\psi(^2B_2) = -\frac{1}{\sqrt{2}}\left(\overset{+}{\xi}\bar{\xi}\overset{+}{\zeta} + \overset{+}{\eta}\bar{\eta}\overset{+}{\zeta}\right)$ |
| | $\psi(^4B_1) = -\frac{1}{\sqrt{3}}\left(\overset{+}{\xi}\overset{+}{\eta}\bar{\zeta} + \overset{+}{\xi}\bar{\eta}\overset{+}{\zeta} + \bar{\xi}\overset{+}{\eta}\overset{+}{\zeta}\right)$ |
| $e^3$ | $\psi(^2E) = -\frac{i}{\sqrt{2}}\,\overset{+}{\xi}\bar{\xi}\bar{\eta} - \frac{1}{\sqrt{2}}\,\overset{+}{\eta}\bar{\eta}\bar{\xi}$ |

TABELLA IV.

*Elementi di matrice di campo di leganti, interazione elettrostatica ed interazione spin–orbita per la configurazione* d³. *Rappresentazione* E′.

| $b_1^2 a_1$ | $a_1 b_1 b_2$ | | | $a_1^2 e$ | $b_1^2 e$ | $a_1 b_1 e$ | | | | $e^2 a_1$ | | | $a_1 b_2 e$ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $^2A_1$ | $^4A_2$ | $^2A_2$ | $^2A_2$ | $^2E$ | $^2E$ | $^4E$ | $^4E$ | $^2E$ | $^2E$ | $^2A_1$ | $^4A_2$ | $^2A_2$ | $^4E$ | $^4E$ | |
| $V_{13}-8B+4C$ | $-\frac{2i}{\sqrt{3}}\zeta$ | $\frac{i}{\sqrt{2}}\zeta$ | $\frac{i}{\sqrt{6}}\zeta$ | $0$ | $-i\sqrt{\frac{3}{2}}\zeta$ | $\frac{i}{\sqrt{6}}\zeta$ | $\frac{i}{\sqrt{2}}\zeta$ | $-\frac{i}{2}\zeta$ | $-\frac{i}{2\sqrt{3}}\zeta$ | $\sqrt{2}(3B+C)$ | $0$ | $0$ | $0$ | $0$ | $^2A_1$ |
| | $V_{12}-12B$ | $0$ | $0$ | $0$ | $0$ | $\frac{\sqrt{2}}{3}\zeta$ | $\frac{1}{\sqrt{6}}\zeta$ | $0$ | $-\frac{1}{3}\zeta$ | $0$ | $6B$ | $0$ | $\frac{\sqrt{2}}{3}\zeta$ | $\frac{1}{\sqrt{6}}\zeta$ | $^4A_2$ |
| | | $V_{12}-2B+3C$ | $2\sqrt{3}B$ | $0$ | $0$ | $0$ | $0$ | $\frac{1}{\sqrt{2}}\zeta$ | $0$ | $0$ | $0$ | $-3\sqrt{3}B$ | $\frac{1}{2\sqrt{3}}\zeta$ | $-\frac{1}{2}\zeta$ | $^2A_2$ |
| | | | $V_{12}-6B+3C$ | $0$ | $0$ | $\frac{1}{3}\zeta$ | $-\frac{1}{\sqrt{3}}\zeta$ | $0$ | $-\frac{1}{3\sqrt{2}}\zeta$ | $0$ | $0$ | $-3B$ | $-\frac{1}{6}\zeta$ | $\frac{1}{2\sqrt{3}}\zeta$ | $^2A_2$ |
| | | | | $V_{11}+7B+4C-\frac{1}{2}\zeta$ | $4B+C$ | $0$ | $0$ | $-\sqrt{\frac{3}{2}}\,5B$ | $-\frac{3}{\sqrt{2}}B$ | $-\frac{i\sqrt{3}}{2}\zeta$ | $\frac{1}{\sqrt{2}}\zeta$ | $\frac{1}{2}\zeta$ | $0$ | $0$ | $^2E$ |
| | | | | | $V_{10}-3B+4C-\frac{1}{2}\zeta$ | $0$ | $0$ | $-\sqrt{\frac{3}{2}}\,5B$ | $\frac{3}{\sqrt{2}}B$ | $0$ | $0$ | $0$ | $0$ | $0$ | $^2E$ |
| | | | | | | $V_9-12B+\frac{1}{6}\zeta$ | $0$ | $0$ | $-\frac{\sqrt{2}}{3}\zeta$ | $-\frac{i}{2\sqrt{3}}\zeta$ | $-\frac{\sqrt{2}}{3}\zeta$ | $\frac{1}{6}\zeta$ | $3B-\frac{1}{3}\zeta$ | $0$ | $^4E$ |
| | | | | | | | $V_9-12B+\frac{1}{2}\zeta$ | $0$ | $0$ | $-\frac{i}{2}\zeta$ | $-\frac{1}{\sqrt{6}}\zeta$ | $-\frac{1}{2\sqrt{3}}\zeta$ | $0$ | $3B-\zeta$ | $^4E$ |
| | | | | | | | | $V_9-2B+3C+\frac{1}{2}\zeta$ | $-\sqrt{3}B$ | $\frac{i}{2\sqrt{2}}\zeta$ | $\frac{1}{2\sqrt{3}}\zeta$ | $\frac{1}{2\sqrt{6}}\zeta$ | $\sqrt{\frac{2}{3}}\zeta$ | $0$ | $^2E$ |
| | | | | | | | | | $V_9-6B+3C-\frac{1}{6}\zeta$ | $\frac{i}{2\sqrt{6}}\zeta$ | $-\frac{1}{6}\zeta$ | $\frac{5}{6\sqrt{2}}\zeta$ | $-\frac{\sqrt{2}}{3}\zeta$ | $0$ | $^2E$ |
| | | | | | | | | | | $V_8+10B+5C$ | $-\sqrt{\frac{2}{3}}\,i\zeta$ | $-\frac{i}{\sqrt{3}}\zeta$ | $\frac{i}{2\sqrt{3}}\zeta$ | $\frac{i}{2}\zeta$ | $^2A_1$ |
| | | | | | | | | | | | $V_8-3B$ | $0$ | $-\frac{\sqrt{2}}{3}\zeta$ | $-\frac{1}{\sqrt{6}}\zeta$ | $^4A_2$ |
| | | | | | | | | | | | | $V_8+3C$ | $\frac{1}{6}\zeta$ | $-\frac{1}{2\sqrt{3}}\zeta$ | $^2A_2$ |
| | | | | | | | | | | | | | $V_7-12B+\frac{1}{6}\zeta$ | $0$ | $^4E$ |
| | | | | | | | | | | | | | | $V_7-12B+\frac{1}{2}\zeta$ | $^4E$ |

*Segue:* TABELLA IV.

| | | $a_1b_2e$ | | $b_2^2a_1$ | $e^2b_1$ | | | $b_1b_2e$ | | | | $e^3$ | $e^2b_2$ | | | $b_2^2e$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $^2E$ | $^2E$ | $^2A_1$ | $^2A_1$ | $^2A_2$ | $^4B_2$ | $^4E$ | $^4E$ | $^2E$ | $^2E$ | $^2E$ | $^2A_1$ | $^2A_2$ | $^4B_1$ | $^2E$ |
| $b_1^2a_1$ | $^2A_1$ | 0 | 0 | $c$ | $\sqrt{6}B$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $a_1b_1b_2$ | $^4A_2$ | 0 | $-\frac{1}{3}\gamma$ | $\frac{2i}{\sqrt{3}}\gamma$ | 0 | 0 | 0 | $-\sqrt{\frac{2}{3}}\gamma$ | $-\frac{1}{\sqrt{2}}\gamma$ | 0 | $\frac{1}{\sqrt{3}}\gamma$ | 0 | 0 | 0 | 0 | 0 |
| | $^2A_2$ | $\frac{1}{2\sqrt{2}}\gamma$ | $-\frac{1}{2\sqrt{6}}\gamma$ | $-\frac{i}{\sqrt{2}}\gamma$ | 0 | $\sqrt{3}B$ | 0 | $\frac{1}{2}\gamma$ | $-\frac{\sqrt{3}}{2}\gamma$ | $\frac{\sqrt{3}}{2\sqrt{2}}\gamma$ | $-\frac{1}{2\sqrt{2}}\gamma$ | 0 | 0 | $-2\sqrt{3}B$ | 0 | 0 |
| | $^2A_2$ | $\frac{\sqrt{3}}{2\sqrt{2}}\gamma$ | $\frac{1}{6\sqrt{2}}\gamma$ | $-\frac{i}{\sqrt{6}}\gamma$ | 0 | $3B$ | 0 | $\frac{1}{2\sqrt{3}}\gamma$ | $-\frac{1}{2}\gamma$ | $-\frac{3}{2\sqrt{2}}\gamma$ | $-\frac{1}{2\sqrt{6}}\gamma$ | 0 | 0 | 0 | 0 | 0 |
| $a_1^2e$ | $^2E$ | $-5\sqrt{\frac{3}{2}}B$ | $-\frac{3}{\sqrt{2}}B$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | $B+C$ | 0 | 0 | 0 | $4B+C$ |
| $b_1^2e$ | $^2E$ | 0 | 0 | 0 | $-\frac{i}{2}\gamma$ | $-\frac{1}{2}\gamma$ | $-\frac{1}{\sqrt{2}}\gamma$ | $-\frac{2}{\sqrt{3}}\gamma$ | 0 | $\frac{3}{\sqrt{2}}B$ | $\sqrt{\frac{2}{3}}\gamma+3\sqrt{\frac{3}{2}}B$ | $3B+C$ | 0 | 0 | 0 | $C$ |
| $a_1b_1e$ | $^4E$ | $\sqrt{\frac{2}{3}}\gamma$ | $-\frac{\sqrt{2}}{3}\gamma$ | 0 | $\frac{i}{2}\gamma$ | $-\frac{1}{2}\gamma$ | $\frac{1}{\sqrt{2}}\gamma$ | $3\sqrt{3}B$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| | $^4E$ | 0 | 0 | 0 | $\frac{i\sqrt{3}}{2}\gamma$ | $\frac{\sqrt{3}}{2}\gamma$ | 0 | 0 | $3\sqrt{3}B$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| | $^2E$ | $\frac{3}{2}B$ | $\frac{3\sqrt{3}}{2}B-\frac{\gamma}{\sqrt{3}}$ | 0 | $\frac{i\sqrt{3}}{2\sqrt{2}}\gamma$ | $-\frac{\sqrt{3}}{2\sqrt{2}}\gamma$ | $-\frac{\sqrt{3}}{2}\gamma$ | 0 | 0 | $-\frac{5\sqrt{3}}{2}B$ | $-\frac{3}{2}B$ | $-\sqrt{6}B$ | 0 | 0 | 0 | 0 |
| | $^2E$ | $\frac{3\sqrt{3}}{2}B-\frac{\gamma}{\sqrt{3}}$ | $-\frac{3}{2}B-\frac{2\gamma}{3}$ | 0 | $-\frac{i}{2\sqrt{2}}\gamma$ | $\frac{1}{2\sqrt{2}}\gamma$ | $-\frac{1}{2}\gamma$ | 0 | 0 | $\frac{3}{2}B$ | $\frac{3\sqrt{3}}{2}B$ | 0 | 0 | 0 | 0 | 0 |
| $e^2a_1$ | $^2A_1$ | $-\frac{i}{2\sqrt{2}}\gamma$ | $-\frac{i}{2\sqrt{6}}\gamma$ | $\sqrt{2}(3B+C)$ | $5\sqrt{3}B$ | 0 | 0 | 0 | 0 | 0 | 0 | $-\frac{i\sqrt{3}}{2}\gamma$ | $-5\sqrt{3}B$ | 0 | 0 | 0 |
| | $^4A_2$ | $\frac{1}{2\sqrt{3}}\gamma$ | $-\frac{1}{6}\gamma$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | $\frac{1}{\sqrt{2}}\gamma$ | 0 | 0 | 0 | 0 |
| | $^2A_2$ | $\frac{1}{2\sqrt{6}}\gamma$ | $\frac{5}{6\sqrt{2}}\gamma$ | 0 | 0 | $-3B$ | 0 | 0 | 0 | 0 | 0 | $\frac{1}{2}\gamma$ | 0 | $3B$ | 0 | 0 |
| $a_1b_2e$ | $^4E$ | 0 | $-\frac{\sqrt{2}}{3}\gamma$ | $-\frac{i}{\sqrt{6}}\gamma$ | 0 | 0 | 0 | $3\sqrt{3}B$ | 0 | 0 | 0 | 0 | $-\frac{i}{2}\gamma$ | $\frac{1}{2}\gamma$ | $-\frac{i}{\sqrt{2}}\gamma$ | 0 |
| | $^4E$ | 0 | 0 | $-\frac{i}{\sqrt{2}}\gamma$ | 0 | 0 | 0 | 0 | $3\sqrt{3}B$ | 0 | 0 | 0 | $-\frac{i\sqrt{3}}{2}\gamma$ | $-\frac{\sqrt{3}}{2}\gamma$ | 0 | 0 |

*Segue:* TABELLA IV.

| $a_1b_2e$ | | $b_2^2a_1$ | $e^2b_1$ | | | $b_1b_2e$ | | | | $e^3$ | $e^2b_2$ | | | $b_2^2e$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $^2E$ | $^2E$ | $^2A_1$ | $^2A_1$ | $^2A_2$ | $^4B_2$ | $^4E$ | $^4E$ | $^2E$ | $^2E$ | $^2E$ | $^2A_1$ | $^2A_2$ | $^4B_1$ | $^2E$ | |
| $V_7-2B+3C+\frac{1}{2}\gamma$ | $-\sqrt{3}B$ | $\frac{i}{2}\gamma$ | 0 | 0 | 0 | 0 | 0 | $\frac{5\sqrt{3}}{2}B$ | $-\frac{3}{2}B$ | $-\sqrt{6}B$ | $-\frac{i\sqrt{3}}{2\sqrt{2}}\gamma$ | $\frac{\sqrt{3}}{2\sqrt{2}}\gamma$ | $\frac{i\sqrt{3}}{2}\gamma$ | $-\frac{5\sqrt{3}}{\sqrt{2}}B$ | $^2E$ |
| | $V_7-6B+3C-\frac{1}{6}\gamma$ | $\frac{i}{2\sqrt{3}}\gamma$ | 0 | 0 | 0 | 0 | 0 | $-\frac{3}{2}B$ | $\frac{3\sqrt{3}}{2}B$ | 0 | $\frac{i}{2\sqrt{2}}\gamma$ | $-\frac{1}{2\sqrt{2}}\gamma$ | $-\frac{i}{2}\gamma$ | $\frac{3}{\sqrt{2}}B$ | $^2E$ |
| | | $V_6-8B+4C$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | $-\sqrt{6}B$ | 0 | 0 | $-\frac{i\sqrt{3}}{\sqrt{2}}\gamma$ | $^2A_1$ |
| | | | $V_5-6B+3C$ | 0 | 0 | $\frac{i}{2\sqrt{3}}\gamma$ | $\frac{i}{2}\gamma$ | $-\frac{i}{2\sqrt{2}}\gamma$ | $-\frac{i}{2\sqrt{6}}\gamma$ | $\frac{i}{2}\gamma$ | $-3B$ | $-i\gamma$ | 0 | 0 | $^2A_1$ |
| | | | | $V_5-6B+3C$ | 0 | $-\frac{1}{2\sqrt{3}}\gamma$ | $\frac{1}{2}\gamma$ | $\frac{1}{2\sqrt{2}}\gamma$ | $\frac{1}{2\sqrt{6}}\gamma$ | $-\frac{1}{2}\gamma$ | $i\gamma$ | $-3B$ | 0 | 0 | $^2A_2$ |
| | | | | | $V_5-15B$ | $-\frac{1}{\sqrt{6}}\gamma$ | 0 | $-\frac{1}{2}\gamma$ | $\frac{1}{2\sqrt{3}}\gamma$ | $-\frac{1}{\sqrt{2}}\gamma$ | 0 | 0 | $i\gamma$ | 0 | $^4B_2$ |
| | | | | | | $V_4-6B-\frac{1}{6}\gamma$ | 0 | 0 | $\frac{\sqrt{2}}{3}\gamma$ | 0 | $\frac{i}{2\sqrt{3}}\gamma$ | $\frac{1}{2\sqrt{3}}\gamma$ | $\frac{i}{\sqrt{6}}\gamma$ | $-\frac{2}{\sqrt{3}}\gamma$ | $^4E$ |
| | | | | | | | $V_4-6B-\frac{1}{2}\gamma$ | 0 | 0 | 0 | $\frac{i}{2}\gamma$ | $-\frac{1}{2}\gamma$ | 0 | 0 | $^4E$ |
| | | | | | | | | $V_4-3B+3C-\frac{1}{2}\gamma$ | 0 | 0 | $\frac{i}{2\sqrt{2}}\gamma$ | $\frac{1}{2\sqrt{2}}\gamma$ | $-\frac{i}{2}\gamma$ | $-\frac{3}{\sqrt{2}}B$ | $^2E$ |
| | | | | | | | | | $V_4+3B+3C+\frac{\gamma}{6}$ | $3\sqrt{6}B$ | $-\frac{i}{2\sqrt{6}}\gamma$ | $-\frac{1}{2\sqrt{6}}\gamma$ | $-\frac{i}{2\sqrt{3}}\gamma$ | $\frac{\sqrt{2}}{\sqrt{3}}\gamma+\frac{3\sqrt{3}}{\sqrt{2}}B$ | $^2E$ |
| | | | | | | | | | | $V_3-3B+4C+\frac{1}{2}\gamma$ | $\frac{i}{2}\gamma$ | $\frac{1}{2}\gamma$ | $\frac{i}{\sqrt{2}}\gamma$ | $3B+C$ | $^2E$ |
| | | | | | | | | | | | $V_2-6B+3C$ | 0 | 0 | $-\frac{i}{2}\gamma$ | $^2A_1$ |
| | | | | | | | | | | | | $V_2-6B+3C$ | 0 | $\frac{1}{2}\gamma$ | $^2A_2$ |
| | | | | | | | | | | | | | $V_2-15B$ | $-\frac{i}{\sqrt{2}}\gamma$ | $^4B_1$ |
| | | | | | | | | | | | | | | $V_1-3B+4C-\frac{1}{2}\gamma$ | $^2E$ |

TABELLA V.

*Elementi di matrice di campo di leganti, interazione elettrostatica ed interazione spin–orbita per la configurazione* d³. *Rappresentazione* E''.

| $a_1^2 b_1$ | $a_1^2 b_2$ | $b_1^2 b_2$ | $a_1 b_1 b_2$ | $a_1^2 e$ | $b_1^2 e$ | $a_1 b_1 e$ | | | | $e^2 a_1$ | | | $a_1 b_2 e$ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $^2B_1$ | $^2B_2$ | $^2B_2$ | $^4A_2$ | $^2E$ | $^2E$ | $^4E$ | $^4E$ | $^2E$ | $^2E$ | $^2B_1$ | $^4A_2$ | $^2B_2$ | $^4E$ | $^4E$ | |
| $V_{17}-8B+4C$ | $-i\zeta$ | 0 | 0 | $\frac{i}{\sqrt{2}}\zeta$ | 0 | $\frac{i}{\sqrt{2}}\zeta$ | $-\frac{i\sqrt{3}}{\sqrt{2}}\zeta$ | $\frac{i\sqrt{3}}{2}\zeta$ | $-\frac{i}{2}\zeta$ | $\sqrt{6}B$ | 0 | 0 | 0 | 0 | $^2B_1$ |
| | $V_{16}-8B+4C$ | $4B+C$ | 0 | $\frac{1}{\sqrt{2}}\zeta$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | $\sqrt{6}B$ | $\frac{1}{\sqrt{2}}\zeta$ | $\frac{\sqrt{3}}{\sqrt{2}}\zeta$ | $^2B_2$ |
| | | $V_{15}+12B+4C$ | 0 | 0 | $\frac{1}{\sqrt{2}}\zeta$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | $^2B_2$ |
| | | | $V_{12}-12B$ | 0 | 0 | $\frac{1}{\sqrt{6}}\zeta$ | 0 | 0 | $\frac{1}{\sqrt{3}}\zeta$ | 0 | $6B$ | 0 | $\frac{1}{\sqrt{6}}\zeta$ | 0 | $^4A_2$ |
| | | | | $V_{11}+7B+4C+\frac{1}{2}\zeta$ | $4B+C$ | 0 | 0 | $-\frac{5\sqrt{3}}{\sqrt{2}}B$ | $-\frac{3}{\sqrt{2}}B$ | $\frac{i\sqrt{3}}{2}\zeta$ | $-\frac{\sqrt{3}}{\sqrt{2}}\zeta$ | $-\frac{\sqrt{3}}{2}\zeta$ | 0 | 0 | $^2E$ |
| | | | | | $V_{10}-3B+4C+\frac{1}{2}\zeta$ | 0 | 0 | $-\frac{5\sqrt{3}}{\sqrt{2}}B$ | $\frac{3}{\sqrt{2}}B$ | 0 | 0 | 0 | 0 | 0 | $^2E$ |
| | | | | | | $V_9-12B-\frac{1}{6}\zeta$ | 0 | 0 | $\frac{\sqrt{2}}{3}\zeta$ | $\frac{i}{2\sqrt{3}}\zeta$ | $-\frac{1}{\sqrt{6}}\zeta$ | $\frac{1}{2\sqrt{3}}\zeta$ | $3B+\frac{1}{3}\zeta$ | 0 | $^4E$ |
| | | | | | | | $V_9-12B-\frac{1}{2}\zeta$ | 0 | 0 | $-\frac{i}{2}\zeta$ | 0 | $\frac{1}{2}\zeta$ | 0 | $3B+\zeta$ | $^4E$ |
| | | | | | | | | $V_9-2B+3C-\frac{1}{2}\zeta$ | $-\sqrt{3}B$ | $-\frac{i}{2\sqrt{2}}\zeta$ | $-\frac{1}{2}\zeta$ | $-\frac{1}{2\sqrt{2}}\zeta$ | $-\frac{\sqrt{2}}{\sqrt{3}}\zeta$ | 0 | $^2E$ |
| | | | | | | | | | $V_9-6B+3C+\frac{1}{6}\zeta$ | $-\frac{i}{2\sqrt{6}}\zeta$ | $\frac{1}{2\sqrt{3}}\zeta$ | $-\frac{1}{2\sqrt{6}}\zeta$ | $\frac{\sqrt{2}}{3}\zeta$ | 0 | $^2E$ |
| | | | | | | | | | | $V_8+4B+3C$ | 0 | 0 | $\frac{i}{2\sqrt{3}}\zeta$ | $-\frac{i}{2}\zeta$ | $^2B_1$ |
| | | | | | | | | | | | $V_8-3B$ | 0 | $-\frac{1}{\sqrt{6}}\zeta$ | 0 | $^4A_2$ |
| | | | | | | | | | | | | $V_8+4B+3C$ | $-\frac{1}{2\sqrt{3}}\zeta$ | $-\frac{1}{2}\zeta$ | $^2B_2$ |
| | | | | | | | | | | | | | $V_7-12B-\frac{1}{6}\zeta$ | 0 | $^4E$ |
| | | | | | | | | | | | | | | $V_7-12B-\frac{1}{2}\zeta$ | $^4E$ |

*Segue:* TABELLA V.

| | | $a_1b_2e$ | | $e^2b_1$ | | | $b_1b_2e$ | | | | $b_2^2b_1$ | $e^3$ | $e^2b_2$ | | | $b_2^2e$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $^2E$ | $^2E$ | $^2B_1$ | $^2B_2$ | $^4B_2$ | $^4E$ | $^4E$ | $^2E$ | $^2E$ | $^2B_1$ | $^2E$ | $^2B_1$ | $^2B_2$ | $^4B_1$ | $^2E$ |
| $a_1^2b_1$ | $^2B_1$ | 0 | 0 | $\sqrt{2}(B+C)$ | 0 | 0 | 0 | 0 | 0 | 0 | $4B+C$ | 0 | 0 | 0 | 0 | 0 |
| $a_1^2b_2$ | $^2B_2$ | $\frac{\sqrt{3}}{2}\gamma$ | $-\frac{1}{2}\gamma$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | $\sqrt{2}(B+C)$ | 0 | 0 |
| $b_1^2b_2$ | $^2B_2$ | 0 | 0 | 0 | $-3\sqrt{6}B$ | 0 | $\frac{1}{\sqrt{6}}\gamma$ | $\frac{1}{\sqrt{2}}\gamma$ | $\frac{1}{2}\gamma$ | $-\frac{1}{2\sqrt{3}}\gamma$ | $-i\gamma$ | 0 | 0 | $\sqrt{2}(3B+C)$ | 0 | 0 |
| $a_1b_1b_2$ | $^4A_2$ | 0 | $\frac{1}{\sqrt{3}}\gamma$ | 0 | 0 | 0 | $-\frac{1}{\sqrt{2}}\gamma$ | 0 | 0 | $-\gamma$ | 0 | 0 | 0 | 0 | 0 | 0 |
| $a_1^2e$ | $^2E$ | $-\frac{5\sqrt{3}}{\sqrt{2}}B$ | $-\frac{3}{\sqrt{2}}B$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | $B+C$ | 0 | 0 | 0 | $4B+C$ |
| $b_1^2e$ | $^2E$ | 0 | 0 | $\frac{i}{2}\gamma$ | $\frac{1}{2\sqrt{3}}\gamma$ | $\frac{1}{\sqrt{6}}\gamma$ | $\frac{2}{\sqrt{3}}\gamma$ | 0 | $\frac{3}{\sqrt{2}}B$ | $\frac{3\sqrt{3}}{\sqrt{2}}B-\frac{\sqrt{2}}{\sqrt{3}}\gamma$ | 0 | $3B+C$ | 0 | 0 | 0 | $C$ |
| $a_1b_1e$ | $^4E$ | $-\frac{\sqrt{2}}{\sqrt{3}}\gamma$ | $\frac{\sqrt{2}}{3}\gamma$ | $-\frac{i}{2}\gamma$ | $-\frac{1}{2\sqrt{3}}\gamma$ | $\frac{\sqrt{2}}{\sqrt{3}}\gamma$ | $3\sqrt{3}B$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| | $^4E$ | 0 | 0 | $\frac{i\sqrt{3}}{2}\gamma$ | $-\frac{1}{2}\gamma$ | $-\frac{1}{\sqrt{2}}\gamma$ | 0 | $3\sqrt{3}B$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| | $^2E$ | $\frac{3}{2}B$ | $\frac{3\sqrt{3}}{2}B+\frac{1}{\sqrt{3}}\gamma$ | $-\frac{i\sqrt{3}}{2\sqrt{2}}\gamma$ | $\frac{1}{2\sqrt{2}}\gamma$ | $\frac{1}{2}\gamma$ | 0 | 0 | $-\frac{5\sqrt{3}}{2}B$ | $-\frac{3}{2}B$ | 0 | $-\sqrt{6}B$ | 0 | 0 | 0 | 0 |
| | $^2E$ | $\frac{3\sqrt{3}}{2}B+\frac{\gamma}{\sqrt{3}}$ | $-\frac{3}{2}B+\frac{2}{3}\gamma$ | $\frac{i}{2\sqrt{2}}\gamma$ | $-\frac{5}{2\sqrt{6}}\gamma$ | $\frac{1}{2\sqrt{3}}\gamma$ | 0 | 0 | $\frac{3}{2}B$ | $\frac{3\sqrt{3}}{2}B$ | 0 | 0 | 0 | 0 | 0 | 0 |
| $e^2a_1$ | $^2B_1$ | $-\frac{i}{2\sqrt{2}}\gamma$ | $-\frac{i}{2\sqrt{6}}\gamma$ | $5\sqrt{3}B$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | $-\frac{i\sqrt{3}}{2}\gamma$ | $-3B$ | 0 | 0 | 0 |
| | $^4A_2$ | $-\frac{1}{2}\gamma$ | $\frac{1}{2\sqrt{3}}\gamma$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | $-\frac{\sqrt{3}}{\sqrt{2}}\gamma$ | 0 | 0 | 0 | 0 |
| | $^2B_2$ | $\frac{1}{2\sqrt{2}}\gamma$ | $\frac{1}{2\sqrt{6}}\gamma$ | 0 | $-3B$ | 0 | 0 | 0 | 0 | 0 | 0 | $-\frac{\sqrt{3}}{2}\gamma$ | 0 | $5\sqrt{3}B$ | 0 | 0 |
| $a_1b_2e$ | $^4E$ | 0 | $\frac{\sqrt{2}}{3}\gamma$ | 0 | 0 | 0 | $3\sqrt{3}B$ | 0 | 0 | 0 | 0 | 0 | $\frac{i}{2\sqrt{3}}\gamma$ | $\frac{1}{2}\gamma$ | $\frac{i\sqrt{2}}{\sqrt{3}}\gamma$ | 0 |
| | $^4E$ | 0 | 0 | 0 | 0 | 0 | 0 | $3\sqrt{3}B$ | 0 | 0 | 0 | 0 | $-\frac{i}{2}\gamma$ | $\frac{\sqrt{3}}{2}\gamma$ | $\frac{i}{\sqrt{2}}\gamma$ | 0 |

*Segue:* TABELLA V.

| $a_1 b_2 e$ | | $e^2 b_1$ | | | $b_1 b_2 e$ | | | | $b_2^2 b_1$ | $e^3$ | $e^2 b_2$ | | | $b_2^2 e$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $^2E$ | $^2E$ | $^2B_1$ | $^2B_2$ | $^4B_2$ | $^4E$ | $^4E$ | $^2E$ | $^2E$ | $^2B_1$ | $^2E$ | $^2B_1$ | $^2B_2$ | $^4B_1$ | $^2E$ | |
| $V_7-2B+3C-\frac{1}{2}\zeta$ | $-\sqrt{3}B$ | 0 | 0 | 0 | 0 | 0 | $\frac{5\sqrt{3}}{2}B$ | $-\frac{3}{2}B$ | 0 | $-\sqrt{6}B$ | $-\frac{i}{2\sqrt{2}}\zeta$ | $\frac{\sqrt{3}}{2\sqrt{2}}\zeta$ | $\frac{i}{2}\zeta$ | $-\frac{5\sqrt{3}}{\sqrt{2}}B$ | $^2E$ |
| | $V_7-6B+3C+\frac{1}{6}\zeta$ | 0 | 0 | 0 | 0 | 0 | $-\frac{3}{2}B$ | $\frac{3\sqrt{3}}{2}B$ | 0 | 0 | $\frac{5i}{2\sqrt{6}}\zeta$ | $-\frac{1}{2\sqrt{2}}\zeta$ | $\frac{i}{2\sqrt{3}}\zeta$ | $\frac{3}{\sqrt{2}}B$ | $^2E$ |
| | | $V_5+5C$ | $-\frac{i}{\sqrt{3}}\zeta$ | $-\frac{i\sqrt{2}}{\sqrt{3}}\zeta$ | $\frac{i}{2\sqrt{3}}\zeta$ | $-\frac{i}{2}\zeta$ | $-\frac{i}{2\sqrt{2}}\zeta$ | $-\frac{i}{2\sqrt{6}}\zeta$ | $\sqrt{2}(3B+C)$ | $\frac{i}{2}\zeta$ | $-3\sqrt{3}B$ | $-i\zeta$ | 0 | 0 | $^2B_1$ |
| | | | $V_5-6B+3C$ | 0 | $\frac{1}{6}\zeta$ | $\frac{1}{2\sqrt{3}}\zeta$ | $\frac{1}{2\sqrt{6}}\zeta$ | $\frac{5}{6\sqrt{2}}\zeta$ | 0 | $\frac{1}{2\sqrt{3}}\zeta$ | $-\frac{i}{3}\zeta$ | $-3\sqrt{3}B$ | $-\frac{i2\sqrt{2}}{3}\zeta$ | 0 | $^2B_2$ |
| | | | | $V_5-15B$ | $-\frac{\sqrt{2}}{3}\zeta$ | $\frac{1}{\sqrt{6}}\zeta$ | $\frac{1}{2\sqrt{3}}\zeta$ | $-\frac{1}{6}\zeta$ | 0 | $\frac{1}{\sqrt{6}}\zeta$ | $\frac{i2\sqrt{2}}{3}\zeta$ | 0 | $-\frac{i}{3}\zeta$ | 0 | $^4B_2$ |
| | | | | | $V_4-6B+\frac{1}{6}\zeta$ | 0 | 0 | $-\frac{\sqrt{2}}{3}\zeta$ | $-\frac{i}{\sqrt{6}}\zeta$ | 0 | $-\frac{i}{6}\zeta$ | $\frac{1}{2\sqrt{3}}\zeta$ | $-\frac{i\sqrt{2}}{3}\zeta$ | $\frac{2}{\sqrt{3}}\zeta$ | $^4E$ |
| | | | | | | $V_4-6B+\frac{1}{2}\zeta$ | 0 | 0 | $\frac{i}{\sqrt{2}}\zeta$ | 0 | $\frac{i}{2\sqrt{3}}\zeta$ | $\frac{1}{2}\zeta$ | $-\frac{i}{\sqrt{6}}\zeta$ | 0 | $^4E$ |
| | | | | | | | $V_4-3B+3C+\frac{1}{2}\zeta$ | 0 | $\frac{i}{2}\zeta$ | 0 | $\frac{i}{2\sqrt{6}}\zeta$ | $\frac{1}{2\sqrt{2}}\zeta$ | $-\frac{i}{2\sqrt{3}}\zeta$ | $-\frac{3}{\sqrt{2}}B$ | $^2E$ |
| | | | | | | | | $V_4+3B+3C-\frac{1}{6}\zeta$ | $\frac{i}{2\sqrt{3}}\zeta$ | $3\sqrt{6}B$ | $-\frac{5i}{6\sqrt{2}}\zeta$ | $-\frac{1}{2\sqrt{6}}\zeta$ | $-\frac{i}{6}\zeta$ | $-\frac{\sqrt{2}}{\sqrt{3}}\zeta+\frac{3\sqrt{3}}{\sqrt{2}}B$ | $^2E$ |
| | | | | | | | | | $V_{14}+12B+4C$ | 0 | $-3\sqrt{6}B$ | 0 | 0 | $\frac{i}{\sqrt{2}}\zeta$ | $^2B_1$ |
| | | | | | | | | | | $V_3-3B+4C-\frac{1}{2}\zeta$ | $-\frac{i}{2\sqrt{3}}\zeta$ | $\frac{1}{2}\zeta$ | $\frac{i}{\sqrt{6}}\zeta$ | $3B+C$ | $^2E$ |
| | | | | | | | | | | | $V_2-6B+3C$ | $-\frac{i}{\sqrt{3}}\zeta$ | 0 | $\frac{i}{2\sqrt{3}}\zeta$ | $^2B_1$ |
| | | | | | | | | | | | | $V_2+5C$ | $-\frac{i\sqrt{2}}{\sqrt{3}}\zeta$ | $-\frac{1}{2}\zeta$ | $^2B_2$ |
| | | | | | | | | | | | | | $V_2-15B$ | $-\frac{i}{\sqrt{6}}\zeta$ | $^4B_1$ |
| | | | | | | | | | | | | | | $V_1-3B+4C+\frac{1}{2}\zeta$ | $^2E$ |

TABELLA VI.

*Energie di campo dei leganti per la configurazione* d$^3$. *Simmetria* $C_{4v}$.

$$V_1 = \frac{3}{7}[G(2) - G'(2)] - \frac{1}{21}[40\,G(4) + 2\,G'(4)]$$

$$V_2 = -\frac{1}{21}[35\,G(4) + 7\,G'(4)]$$

$$V_3 = \frac{3}{7}[G'(2) - G(2)] - \frac{1}{21}[30\,G(4) + 12\,G'(4)]$$

$$V_4 = \frac{3}{7}[G(2) - G'(2)] - \frac{1}{21}[5\,G(4) + 2\,G'(4)]$$

$$V_5 = -\frac{1}{3}\,G'(4)$$

$$V_6 = \frac{2}{7}[G(2) - G'(2)] + \frac{1}{21}[8\,G'(4) - 15\,G(4)]$$

$$V_7 = \frac{1}{7}[G'(2) - G(2)] + \frac{1}{21}[3\,G'(4) - 10\,G(4)]$$

$$V_8 = \frac{4}{7}[G'(2) - G(2)] - \frac{1}{21}[5\,G(4) + 2\,G'(4)]$$

$$V_9 = \frac{1}{7}[G'(2) - G(2)] + \frac{1}{21}[25\,G(4) + 3\,G'(4)]$$

$$V_{10} = \frac{3}{7}[G(2) - G'(2)] + \frac{1}{21}[30\,G(4) - 2\,G'(4)]$$

$$V_{11} = \frac{5}{7}[G'(2) - G(2)] + \frac{1}{21}[20\,G(4) + 8\,G'(4)]$$

$$V_{12} = \frac{2}{7}[G(2) - G'(2)] + \frac{1}{21}[20\,G(4) + 8\,G'(4)]$$

$$V_{13} = \frac{2}{7}[G(2) - G'(2)] + \frac{1}{21}[55\,G(4) + 8\,G'(4)]$$

$$V_{14} = \frac{6}{7}[G(2) - G'(2)] + \frac{1}{21}[3\,G'(4) - 10\,G(4)]$$

$$V_{15} = \frac{6}{7}[G(2) - G'(2)] + \frac{1}{21}[25\,G(4) + 3\,G'(4)]$$

$$V_{16} = \frac{2}{7}[G'(2) - G(2)] + \frac{1}{21}[15\,G(4) + 13\,G'(4)]$$

$$V_{17} = \frac{2}{7}[G'(2) - G(2)] + \frac{1}{21}[50\,G(4) + 13\,G'(4)]$$

Le matrici di energia sono state controllate riproducendo in caso ottaedrico $[G'(5) = G(k)]$ gli autovalori calcolati da Runciman e coll. [2] per una determinata scelta dei valori dei parametri Dq, B, C, $\zeta$. Sono in corso calcoli che utilizzano le matrici di energia, riportate nel presente lavoro, allo scopo di interpretare le proprietà elettroniche dei composti $[ReX_5(PPh_3)]PPh_3H$ con X = Cl, Br.

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