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INVERSION SPLITTING OF LEVELS IN FREE COMPLEXES OF TRANSITION METALS

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Octahedral complexes of transition metals are considered with a degenerate electron term that leads to several equivalent equilibrium configurations with a large potential barrier between them. The electron oscillation problem for each configuration is solved in an adiabatic approximation, while the interaction between them is taken into account by perturbation theory. The system is then found to possess a number of close stationary levels (inversion splitting). The problem is solved for electron terms of the type E_g and T_{2g} (for tetragonal and trigonal distortions of the octahedron in equilibrium configurations). Parameters of inversion levels are determined, formulas for the absolute value of splitting are obtained, and examples of numerical calculations are given. A quantitative criterion is established for the applicability of the theory.

1. INTRODUCTION

FREE complexes of transition metals with a degenerate electron term have certain singularities which were investigated by several workers. Foremost among them is the Jahn-Teller effect—deviations of the equilibrium configuration from the maximum symmetry (internal asymmetry)—and the presence of several equivalent equilibrium configurations[1,2]. In the case when the potential barrier between the equivalent configurations is low, the specific effect in the complex, connected with the presence of electron degeneracy, reduces to a special kind of interaction between the electron motion and the oscillatory motion[3,4]. If this barrier is sufficiently large, however, each equilibrium configuration can be regarded approximately as a separate entity, and the interaction between them should lead then to an additional level splitting.

The possibility of transitions between equivalent configurations of an octahedral complex was first noted by Van Vleck[5]. However, this problem, as far as we know, has not yet been solved.[1)] On the other hand, an account of the interaction between these configurations discloses additional stationary states with close-lying energy levels, which undoubtedly should be manifest in many optical, magnetic, and thermodynamic properties of the system. In the present communication we present a general solution of this problem for the cases of greatest interest (without account of interaction with the rotations). In the future we plan to use these results for an investigation of the aforementioned physical properties of the systems under consideration.

2. GENERAL THEORY

A. We consider an octahedral complex of the type MX_6, where M is an atom or ion of a transition metal and X is a diamagnetic particle (atom, ion, or molecule) for which the electron term is l-fold degenerate in the configuration of the regular octahedron. In the general case the Hamiltonian of the system has the form

$$H = H_q + H_Q + V(q, Q), \tag{1}$$

where H_q and H_Q are the electron and oscillatory Hamiltonian, and $V(q, Q)$ is the operator of interaction between the electron motion and the oscillatory motion.

We assume for simplicity that the internal closed electron shells of the metal M form together with the nucleus an effective core, and the detailed electron structure of the particle X can be disregarded. Then q denotes the aggregate of the coordinates of the outer d-electrons, and H_Q includes the interaction of the core M with X, approximated with the aid of the force constants (Q denotes the aggregate of the normal coordinates of the regular octahedron). This assumption is

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[1)] In our previous communication[6] we considered the oscillatory interaction between three minima without account of the associated electron states. The results obtained in this manner have, in the light of the present paper, a limited applicability.

not limiting, for in principle we can obtain analogous results also by using the molecular orbital approximation method.

B. The specific singularities of the electron-oscillation problem connected with the presence of the electron degeneracy, manifest themselves in the solution of the electron equation. This is given in several papers, and we refer here to Opick and Pryce [2] and to our earlier paper [7].

We expand the operator V in terms of the normal coordinates Q:

$$V = V(q, 0) + \sum_{\alpha=1}^{p} \left(\frac{\partial V}{\partial Q_\alpha}\right)_0 Q_\alpha + \ldots \quad (2)$$

The l-fold electron degeneracy is obtained with account of the zeroth term of this expansion. We assume the linear term to be a small perturbation.[2)] Then the adiabatic potential can be determined from the solution of the secular equation. Its l roots—multidimensional surfaces—cross at the point $Q_\alpha = 0$ $(\alpha = 1, \ldots, p)$ corresponding to the configuration of the regular octahedron. Outside this point these surfaces diverge, generally speaking, although in some regions some of them may coincide. Usually this splitting of the surfaces of the potential energy is the result of interaction with only a certain definite type of oscillations—tetragonal or trigonal and the equilibrium configuration of the system is a tetragonally or trigonally distorted octahedron (internal asymmetry or the Jahn-Teller effect).

C. Of greatest importance to what follows is the conclusion that there is not one but several (N) such equilibrium configurations (or minima of the adiabatic potential), and that they are all equivalent to one another.

We denote the normal coordinates of the system in the i-th asymmetrical configuration by Q^i. We can then write for the electron wave function near the minimum

$$\left[H_q + V(q, 0) + \sum_\alpha \left(\frac{\partial V}{\partial Q_\alpha^i}\right)_0 Q_\alpha^i\right] \psi_i = W_i(Q_\alpha^i)\, \psi_i, \quad (3)$$

$i = 1, 2, \ldots, N$. In the zeroth approximation ψ_i is a linear combination of the initial d-electron functions and is determined by the secular equation.

D. Proceeding to the solution of the oscillation problem, it is necessary to introduce a definite assumption concerning the size of the interaction between the equilibrium configurations. If this interaction is sufficiently strong, the adiabatic approximation cannot be used, generally speaking, in its ordinary form [8]. An analysis of this case is the subject of the cited papers by Moffitt et al. [3,4] In contrast with these papers, we assume that the interaction between the equivalent configurations is sufficiently small. A quantitative criterion for the fulfillment of this assumption is given below.

Assuming the interaction between the states of the minima to be small, the system is described near each of the minima in the zeroth approximation by the usual form of adiabatic approximation with the aid of the wave function

$$\Phi_{i\varkappa} = \psi_i(q_1, \ldots, q_m;\ Q_1^i, \ldots, Q_p^i) \prod_{\alpha=1}^{p} \chi_{n_\alpha}(Q_\alpha^i). \quad (4)$$

Here m is the number of d-electrons of the transition metal, $\chi(Q)$ is the wave function of the harmonic oscillation, and κ is shorthand for the set of quantum numbers $n_1, \ldots, n_p$ characterizing the oscillating state of the system.

E. As a result of the equivalents of all the minima, the system energy calculated with the aid of (4) is independent of the index i and consequently, in the approximation considered, the system is N-fold degenerate. This degeneracy is lifted by taking account of the interaction between the equilibrium configurations. The regular zeroth-approximation functions have the form

$$\Psi_{k\varkappa} = \sum_{i=1}^{N} c_i^k \Phi_{i\varkappa}, \qquad k = 1, 2, \ldots N. \quad (5)$$

It is appropriate to emphasize here that only $\Psi_{k\kappa}$ (and not $\Phi_{i\kappa}$) describe the stationary states of the free complex.

The form of the perturbation energy, namely the interaction between the equilibrium configurations, can be determined from a more accurate solution of the electron-oscillation problem. For this purpose we substitute the function (5) into the Schrödinger equation for the Hamiltonian (1), multiply it from the left by ψ_i^*, and integrate over the electron coordinates. Taking (3) into account, we can obtain a system of equations for the oscillation functions χ':

$$\sum_{i=1}^{N} c_i^k \left[H_Q + W_i(Q_\alpha^i) + U_{ij} - E_\varkappa\right] S_{ij} \prod_{\alpha=1}^{p} \chi'_{n_\alpha}(Q_\alpha^i) = 0, \quad (6)$$

$j, k = 1, 2, \ldots, N$. Here S_{ij} is the overlap integral of the functions ψ_i and ψ_j, while U_{ij} is the electronic matrix element of the operator

$$U = \sum_\alpha \left(\frac{\partial V}{\partial Q_\alpha}\right)_0 Q_\alpha - \sum_\alpha \left(\frac{\partial V}{\partial Q_\alpha^i}\right) Q_\alpha^i + \hat{A}, \quad (7)$$

where $\hat{A}$ is the nonadiabaticity operator, i.e., the operator containing derivatives of the electronic

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[2)] The quadratic terms of this expansion, combined with the corresponding terms of the core, are contained in H_Q.

function with respect to the nuclear coordinates. In what follows this operator is immaterial, since its matrix elements either vanish or are small compared with the contribution of the other terms in (7).

Putting $U_{ij} = 0$, we find that solutions of the system (6) are the oscillator functions contained in (4) which describe the system without interaction between the equivalent configurations. We can therefore conclude that the operator U describes the interaction between these configurations.

F. Irrespective of the form of the operator (7), we can obtain relatively easily all the qualitative characteristics of the level splitting resulting from the interaction between the minima, on the basis of symmetry considerations. Tables I and II list these characteristics for the cases N = 3 (tetragonal distortions) and N = 4 (trigonal distortions), respectively. We see that when N = 3 two levels are obtained, of which the ground level A_1 is nondegenerate ($U_{12} < 0$, see below), and the excited level E is doubly degenerate. For N = 4 these levels are A_1 and T, of which the latter is triply degenerate.

The splitting pattern for these cases is illustrated in Figs. 1 and 2. In both cases the amount of splitting is determined in first approximation by the matrix element U_{12} of the perturbation (7), calculated with the aid of the functions (4):

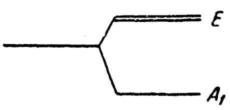

FIG. 1

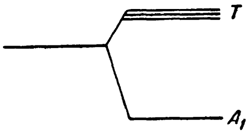

FIG. 2

Table I. Inversion levels in systems with three minima (tetragonal internal asymmetry)

k	Energy	Symmetry	Wave-function coefficients		
			c_1^k	c_2^k	c_3^k
1	$\varepsilon_{1\varkappa} = 2U_{12}^{\varkappa}$	A_1	$1/\sqrt{3}$	$1/\sqrt{3}$	$1/\sqrt{3}$
2	$\varepsilon_{2\varkappa} = -U_{12}^{\varkappa}$	E	$2/\sqrt{6}$	$-1/\sqrt{6}$	$-1/\sqrt{6}$
3	$\varepsilon_{3\varkappa} = -U_{12}^{\varkappa}$		0	$1/\sqrt{2}$	$-1/\sqrt{2}$

Table II. Inversion levels in systems with four minima (trigonal internal asymmetry)

k	Energy	Symmetry	Wave-function coefficients			
			c_1^k	c_2^k	c_3^k	c_4^k
1	$\varepsilon_{1\varkappa} = 3U_{12}^{\varkappa}$	A_1	1/2	1/2	1/2	1/2
2	$\varepsilon_{2\varkappa} = -U_{12}^{\varkappa}$	T	1/2	−1/2	−1/2	1/2
3	$\varepsilon_{3\varkappa} = -U_{12}^{\varkappa}$		1/2	−1/2	1/2	−1/2
4	$\varepsilon_{4\varkappa} = -U_{12}^{\varkappa}$		1/2	1/2	−1/2	−1/2

$$\delta_{\varkappa} = -NU_{12}^{\varkappa}. \tag{8}$$

This value depends naturally on the oscillatory state under consideration.

G. The results obtained enable us to establish a quantitative criterion for the applicability of the theory. The main premise of the theory is that the operator U is a small perturbation. Obviously, for this purpose the condition to be satisfied is

$$U_{12}^{\varkappa} \ll \hbar\omega, \tag{9}$$

where $\hbar\omega$ is an oscillation quantum near one of the minima. We shall show below that for the systems considered here the criterion (9) is well satisfied.

Inasmuch as the considered level splitting clearly corresponds to system transitions from one asymmetrical equilibrium configuration to another equivalent configuration, we have used the designation "inversion" in analogy with the similar phenomenon in ammonia.

3. ELECTRONIC STATE E_g

A. Let us consider the application of the general theory to complexes for which the electron term in the regular-octahedron configuration is the E_g term ($l = 2$) or the T_{2g} term ($l = 3$). These two terms cover practically all the interesting cases of high-spin transition metal complexes with electron configurations d^1 and d^6 (ground state T_{2g}, first excited state E_g) and d^4 and d^9 (ground state E_g, first excited state T_{2g}).[3)]

In all these cases the state of the free atom (or ion) of the metal corresponds to a five-fold degenerate D term, which can be described approximately by five hydrogen-like d-functions φ_1, φ_2, φ_3, φ_4, and φ_5; we choose these functions to be real. The angle parts of these functions correspond in Cartesian coordinates to the factors xy, xz, and yz (T_{2g} symmetry) and $3z^2 - r^2$, $x^2 - y^2$ (E_g symmetry). In the octahedral com-

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[3)] The T_{1g} terms are also important for the electron configurations d^2, d^3, d^7, and d^8, but the internal asymmetry for these terms is so small[9] that the criterion (9) for the applicability of the theory is not satisfied.

plex the D term splits into T_{2g} and E_g, the difference between them amounts to a quantity on the order of several thousand cm^{-1}, so that in most cases in the analysis of one of these terms one can neglect the influence of the second term.

B. Under this assumption, the electron state E_g in the complex is described by the functions φ_4 and φ_5 (in the zeroth approximation). The twofold degeneracy of E_g is lifted only upon interaction with the tetragonal oscillations. This leads to the presence of three equivalent minima of the adiabatic potential, corresponding to equilibrium configurations, in which the octahedron is elongated (prolate) along one of the three tetragonal axes. Along with them, there are also three equivalent equilibrium configurations, corresponding to foreshortened (oblate along one of the diagonals) octahedra. However, the latter are not equivalent to the former[10], since their energy is higher, and will therefore not be considered here.

Near the three minima, the wave functions ψ_i satisfying Eqs. (3) are in the zeroth approximation

$$\psi_1 = \varphi_4, \qquad \psi_2 = -\frac{1}{2}\varphi_4 + \frac{\sqrt{3}}{2}\varphi_5,$$

$$\psi_3 = -\frac{1}{2}\varphi_4 - \frac{\sqrt{3}}{2}\varphi_5 \tag{10}$$

and differ from one another only in their orientation in space.

The oscillating states near each of the minima are characterized by a set of harmonic oscillators, of which those corresponding to the oscillations of Q_2^i and Q_3^i (in the normal-coordinate notation of Van Vleck[1]) have displaced equilibrium positions compared with the analogous oscillations of Q_2 and Q_3 of the regular octahedron:

$$\begin{aligned} Q_2^{(1)} &= Q_2, & Q_3^{(1)} &= Q_3 - Q^0, \\ Q_2^{(2)} &= \frac{1}{2}Q_2 + \frac{\sqrt{3}}{2}Q_3, & Q_3^{(2)} &= -\frac{1}{2}Q_3 + \frac{\sqrt{3}}{2}Q_2 - Q^0, \\ Q_2^{(3)} &= -\frac{1}{2}Q_2 + \frac{\sqrt{3}}{2}Q_3, & Q_3^{(3)} &= -\frac{1}{2}Q_3 - \frac{\sqrt{3}}{2}Q_2 - Q^0. \end{aligned} \tag{11}$$

Here

$$Q^0 = \frac{A}{K_a}, \qquad A = \left(\frac{\partial V_{44}}{\partial Q_2}\right)_0 = -\frac{e}{14\sqrt{3}}[12F_2'(R_0) + 5F_4'(R_0)],$$

$$F_n(R) = \int_0^\infty \frac{r_<^n}{R_>^{n+1}} f^2(r)\, r^2\, dr, \tag{12}$$

where f(r) is the radial part of the hydrogen-like function of the d electron, e is the effective negative charge of the particle X, R_0 is the average distance between M and X, and $K_a = \mu\omega_a^2$ is the forced constant of the normal oscillation of Q_2 or of Q_3 of frequency ω_a, while μ is the mass of the particle X. We note that the parameter A is quite simply related with the quantitative characteristic of the internal asymmetry $\xi = 2|R_{01} - R_{02}|$, (difference between the lengths of the two diagonals of the tetragonally distorted equilibrium octahedron), $A = K_a\xi/\sqrt{3}$, which we introduced earlier[7] and which was approximately calculated in [9].

The difference in the energies of the complex in the regular octahedron configuration and in the equilibrium configuration—the height of the potential barrier between the minima—is

$$\Delta E_a = A^2/2K_a. \tag{13}$$

C. The inversion levels for this case are shown in Table I and in Fig. 1. For the value of the inversion splitting we can obtain from (8) (neglecting the contribution of the nonadiabaticity operator)

$$\delta_\varkappa = -3U_{12}^\varkappa = 3\Delta E_a \gamma_\varkappa, \tag{14}$$

where γ_κ denotes the overlap integral of the oscillatory functions of the two equilibrium configurations in the oscillating state κ:

$$\gamma_\varkappa = \int \prod_{\alpha=1}^{p} \chi_{n_\alpha}(Q_\alpha^{(1)}) \prod_{\alpha=1}^{p} \chi_{n_\alpha}(Q_\alpha^{(2)}) \prod_{\alpha=1}^{p} dQ_\alpha. \tag{15}$$

For the ground state $n_1 = n_2 = \ldots = n_p = 0$ we readily obtain [with account of (11)]

$$\gamma_0 = \exp(-3\Delta E_a/2\hbar\omega_a). \tag{16}$$

The values of γ_κ depend only on the quantum numbers of the displaced (in this case—tetragonal) oscillations. For the excited state corresponding to the excitation of one quantum of the oscillation of Q_2 ($n_2 = 1$, $n_3 = 0$, the remaining n arbitrary), we have

$$\gamma_{1,0} = \gamma_0 (3\Delta E_a/4\hbar\omega_a + 1/2), \tag{17}$$

and for the excited quantum of the oscillation of Q_3 ($n_2 = 0$, $n_3 = 1$)

$$\gamma_{0,1} = \gamma_0 (9\Delta E_a/4\hbar\omega_a - 1/2). \tag{17'}$$

In averaging over the different oscillating states in the substance, the parameter γ_κ is found to depend on the temperature.

Table III lists examples of numerical calculations of the inversion splittings in some complexes in accord with the formulas given. Since the oscillation frequency ω_a is not known exactly, we have made the calculations for the three frequencies closest to the true one.

D. Let us check the fulfillment of the criterion (9) for the applicability of the theory. With the aid of (14) and (13) we can show that condition (9) goes over into

$$\Delta E \gtrsim {}^3/_2 \hbar\omega, \tag{18}$$

which, as can be readily verified with the aid of the data of Table III, is well satisfied in the considered cases.

Table III. Examples of numerical results for the inversion splitting (E_g states)

Complexes	A, atomic units	ω_a, cm^{-1}	δ_0, cm^{-1}	δ_1, cm^{-1}	δ_2, cm^{-1}
$Cu(H_2O)_6^{2+}$	$3.01\cdot10^{-2}$	250	0.006	0.04	0.1
		300	1.5	6.0	17
		350	17	67	158
$Mn(H_2O)_6^{3+}$	$4.13\cdot10^{-2}$	250	$5\cdot10^{-8}$	$6.0\cdot10^{-7}$	$2\cdot10^{-6}$
		300	0.003	0.03	0.06
		350	0.4	2	6

4. ELECTRONIC STATE T_{2g}

In this case asymmetrical configurations of both the tetragonal and trigonal type are possible[2]. We consider each separately.

A. The minima of the adiabatic potential with account of the interaction with the tetragonal oscillations correspond to oblate octahedra. The wave functions of the electronic states near the minima are in the zeroth approximation

$$\psi_1 = \varphi_1, \qquad \psi_2 = \varphi_2, \qquad \psi_3 = \varphi_3. \tag{19}$$

The displacements of the tetragonal normal coordinates are determined by formulas (11), with

$$A = (\partial V_{11}/\partial Q_2)_0 = -(2e/21\sqrt{3})\,[9F_2'(R_0) - 5F_4'(R_0)], \tag{20}$$

and ΔE is determined by (13).

B. The parameters of the inversion levels are given in Table I. However, the absolute value of the splitting vanishes in accordance with (8) and consequently, there is no splitting in the first approximation. The second approximation is obtained by solving the system of oscillation equations (6) in the first approximation in U. Separating the variables in these equations, we obtain for trigonal oscillations of Q_4, Q_5, and Q_6 (which in the zeroth approximation are not displaced) equations of the type

$$[c_1^k H_Q + c_2^k B\gamma_\varkappa Q - E_\varkappa]\,\chi(Q) = 0, \tag{21}$$

$$B = (\partial V_{12}/\partial Q_4)_0 = (e/21R_0)\,[9F_2(R_0) - 5F\;(R_0)], \tag{22}$$

where γ_K is determined as before by formula (15).

Solutions of these equations are also harmonic oscillators displaced by $Q^{(0)} = \pm B\gamma_K/K_b$, where $K = \mu\omega_b^2$, ω_b is the frequency of the trigonal oscillations, and the sign depends on the inversion level k.

Using the first approximation wave functions (for which both the tetragonal and the trigonal oscillations are displaced), we can obtain for the inversion splitting in the second approximation of the perturbation theory:

$$\delta_\varkappa = -3U_{12}^\varkappa = 3B^2\gamma_\varkappa^2/K_b. \tag{23}$$

These formulas contain already two frequencies of the oscillations of the complex—tetragonal ω_a and trigonal ω_b. Unlike the case of E_g, Eq. (23) contains the square of the parameter γ_K. Therefore the condition for the applicability of the theory is even less stringent here than in (18).

C. For trigonal distortions of the complex, four equivalent minima of the adiabatic potentials are possible. Therefore the parameters of the inversion levels are determined by Table II. The zeroth approximation electron wave functions and the displacements of the equilibrium positions of the trigonal oscillations can be found for each of the minima in the cited paper by Opick and Pryce[2]. The height of the potential barrier is

$$\Delta E_b = -2B^2/3K_b, \tag{24}$$

and for the inversion splitting we can obtain

$$\delta_\varkappa = -4U_{12}^\varkappa = {}^8/_3\Delta E_b\gamma_\varkappa, \tag{25}$$

where calculation of γ_K by formula (15) yields for the ground state

$$\gamma_0 = \exp(-4\Delta E_b/3\hbar\omega_b). \tag{26}$$

The criterion for the applicability of the theory does not differ here from (18). Some examples of numerical calculations on inversion splitting, obtained from these formulas, are listed in Table IV. We do not know the exact values of the frequencies ω_a and ω_b, as for the complexes of Table III.

D. It is also of interest to determine, using the data of our calculations, which asymmetrical configurations of free complexes with electronic state T_{2g} are the more stable, tetragonal or trigonal. This can be done by comparing the depths of the minima[2] in these two cases in accord with formulas (24) and (13). It is obvious that the trigonally distorted octahedron is more stable if

$$B^2/A^2 > 3\omega_b^2/4\omega_a^2; \tag{27}$$

in the opposite case the tetragonally distorted octahedron is more stable. As can be seen from Table IV, A and B are of the same order of magnitude. Therefore the solution of this problem is possible only if the frequencies ω_a and ω_b are exactly known. For the frequencies used in Table IV, the trigonal distortions lead to more stable configurations.

Table IV. Examples of numerical results for the inversion splitting (T_{2g} states)

Complexes	A, atomic units	B, atomic units	ω_a, cm^{-1}	ω_b, cm^{-1}	δ_0, cm^{-1}	
					$N=3$	$N=4$
$Ti(H_2O)_6^{3+}$	$1.51 \cdot 10^{-2}$	$0.63 \cdot 10^{-2}$	200	100	0.004	0.03
			250	125	3.0	4.7
			300	150	40	31
$Fe(H_2O)_6^{2+}$	$1.0 \cdot 10^{-2}$	$0.87 \cdot 10^{-2}$	200	100	3.2	1.7
			250	125	36	58
			300	150	104	105

In conclusion I express my gratitude to A. M. Prokhorov for a discussion of some of the aspects of this problem.

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