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Linear Expansion of the Eigenvalues of a Hermitian Matrix and Its Application to the Analysis of the Electronic Spectra of 3*d* Ions in Crystals

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It is shown that the eigenvalues E_i of a Hermitian matrix **H** with matrix elements $H_{ij} = \Sigma_k A_{ij}^k a_k$, where A_{ij}^k are known numbers and a_k a set of parameters, can be exactly expanded as $E_i = \Sigma_k(\partial E_i/\partial a_k)a_k$. This property is applied to the analysis of the optical spectra of transition metal ions in crystals proposed by L. Pueyo, M. Bermejo, and J. W. Richardson (*J. Solid State Chem.* **31**, 217, 1980), and it is shown that this method represents the best fit of the Hamiltonian eigenvalues to the observed (or calculated) spectrum. Further advantages of using this property, in connection with the spectral analysis, are the minimization of the errors associated with the numerical approximations and a reduction in computer time. In the molecular orbital calculation of the optical or uv spectra of these systems, this linear expansion of the eigenvalues give a detailed interpretation of the improvements produced by refined calculations, such as those including configuration interaction. In particular, the changes in one-electron energy and in open-shell repulsion interactions associated with the refinement can be clearly and easily formulated. As examples, the computed spectra of CrF_6^{4-} and CrF_6^{3-} are discussed. © 1985 Academic Press, Inc.

1. Introduction

In this paper we derive an interesting property of the Hermitian matrices **H** whose elements are linear combinations of a given set of parameters a_k: $H_{ij} = \Sigma_k A_{ij}^k a_k$, where A_{ij}^k are known numbers. This sort of matrix is often found in quantum mechanical calculations where a successive perturbation approach is followed. Crystal-field theory is a familiar example. We will show that the eigenvalues E_i of these Hermitian matrices can be exactly expanded as $E_i = \Sigma_k(\partial E_i/\partial a_k)a_k$. The partial derivatives of the eigenvalues with respect to the parameters are implicit functions of all a_k. These derivatives can be analytically and very quickly found in terms of the unitary matrix that diagonalizes **H**.

We have applied this property to a variety of spectroscopic calculations of the optical spectra of transition metal ions in ionic lattices. We will present here two types of applications, one in the context of the empirical analysis of the optical spectra and the other one related to the nonempirical calculation of the transition energies.

The first application is the incorporation of the property into the systematic matrix linearization procedure recently described (*1*, *2*). In these procedures, the Hamiltonian matrix **H** has to be diagonalized NPAR

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+ 1 times at each iteration (NPAR is the number of independent parameters in the problem) in order to compute numerically the first derivatives of the eigenvalues with respect to all the parameters. Using the formulation of this paper, all these derivatives are computed analytically at each iteration by means of a simple matrix multiplication. The computer time is significantly reduced, since one has to diagonalize **H** only once at each iteration. This represents a noticeable improvement of the linearization process, with larger economies in computer time increasing with the number of independent parameters and the rank of **H**. Furthermore, using this relationship between the eigenvalues and the parameters, it is immediately shown that the iterative linearization procedure is a *general* method for a least-squares fitting of the eigenvalues of a matrix to a given set of numbers.

The second application has to do with the calculation of the electronic transition energies in terms of molecular orbital theory. Once the wavefunction of a given electronic state is obtained, one can compute, within the frozen-orbital approximation, the first-order transition energies among different states. A better description of these energies is generally found (*3*) if some amount of configuration interaction (CI) is included in the calculation. A still better representation can be obtained if one considers the empirical correlation energy correction (CEC) that propagates into the molecular system the atomic corrections required to have an exact description of the multiplet energies (*4*). In these refined spectroscopic calculations different Hermitian matrices (the CI matrix, the CI + CEC matrix, etc.) are used, and the transition energies are obtained as differences between eigenvalues. As a consequence, the evaluation of the contributions of different interactions to the final value of the transition energy is not as immediate as it is in the first-order calculation. In this way, one obtains a better transition energy from the refined calculation but the detailed differences between the first-order and the refined description are not generally clear. The application of the method described here represents a simple operation that gives an interesting insight on the changes that the methodological refinements produce in one- and two-electron interactions. Thus, with very little calculation one can appreciate the degree of electronic delocalization among orbitals of different symmetries, and the corresponding changes in open-shell electronic repulsion, accompanying the process of refinement. In particular, our calculation makes straightforward the possibility of expressing the d-d electronic transitions, in a CI or CI + CEC calculation, as linear functions of the 10 independent repulsion integrals (*5*). The advantages of using such integrals instead of the familiar B and C Racah parameters are well-known and have been recently discussed by Sharma *et al.* (*6*).

In Section 2 we give the proof of the linear expansion of the eigenvalues of a Hermitian matrix. In Section 3 we show how this property can be connected with the iterative linearization procedures. The application of the linear expansion to the molecular orbital calculations is presented in Section 4 and the last section contains some selected examples which illustrate the applications.

2. Linear Expansion of the Eigenvalues of *H*

Let us consider the Hermitian matrix:

$$\mathbf{H} = \Sigma_k \mathbf{A}^k a_k, \qquad (1)$$

where the $\mathbf{A}^k$'s are known matrices determined by the symmetry of the problem and the a_k's are parameters.

In this section we will show that the eigenvalues of **H**, E_i, can be expressed as

$$E_i = \Sigma_k(\partial E_i/\partial a_k)a_k = \Sigma_k \alpha_{ik} a_k. \qquad (2)$$

We will also present a simple, analytical method for obtaining the expansion coefficients α_{ik}. These are implicit functions of all the a_k's.

Since $\mathbf{H}$ is Hermitian, we can reduce it to diagonal form by means of a similarity transformation

$$\mathbf{E} = \mathbf{U}^\dagger\mathbf{H}\mathbf{U} = \sum_k \mathbf{U}^\dagger\mathbf{A}^k\mathbf{U}a_k \qquad (3)$$

with

$$\mathbf{U}^\dagger\mathbf{U} = \mathbf{U}\mathbf{U}^\dagger = \mathbf{1}. \qquad (4)$$

We now define the matrices $\boldsymbol{\alpha}^k$:

$$(\boldsymbol{\alpha}^k)_{ij} = (\partial E_{ij}/\partial a_k). \qquad (5)$$

These matrices are diagonal because $\mathbf{E}$ is diagonal and their nonvanishing elements are

$$(\boldsymbol{\alpha}^k)_{ii} = (\partial E_i/\partial a_k). \qquad (6)$$

Inserting Eq. (3) in Eq. (5) and defining $\mathbf{U}^k$ as $(\mathbf{U}^k)_{ij} = (\partial U_{ij}/\partial a_k)$ we have

$$\boldsymbol{\alpha}^k = (\mathbf{U}^k)^\dagger\mathbf{H}\mathbf{U} + \mathbf{U}^\dagger\mathbf{A}^k\mathbf{U} + \mathbf{U}^\dagger\mathbf{H}\mathbf{U}^k. \qquad (7)$$

From Eqs. (3) and (4) we have $\mathbf{HU} = \mathbf{UE}$ and $\mathbf{U}^\dagger\mathbf{H} = \mathbf{E}\mathbf{U}^\dagger$. These results transform Eq. (7) into

$$\boldsymbol{\alpha}^k = (\mathbf{U}^k)^\dagger\mathbf{U}\mathbf{E} + \mathbf{U}^\dagger\mathbf{A}^k\mathbf{U} + \mathbf{E}\mathbf{U}^\dagger\mathbf{U}^k. \qquad (8)$$

Since $\mathbf{E}$ is diagonal we readily find that

$$((\mathbf{U}^k)^\dagger\mathbf{U}\mathbf{E})_{ii} = (\mathbf{E}(\mathbf{U}^k)^\dagger\mathbf{U})_{ii}$$

and, therefore, the diagonal elements of α^k become

$$(\boldsymbol{\alpha}^k)_{ii} = (\mathbf{U}^\dagger\mathbf{A}^k\mathbf{U})_{ii} + (\mathbf{E}\{(\mathbf{U}^k)^\dagger\mathbf{U} + \mathbf{U}^\dagger\mathbf{U}^k\})_{ii} = (\mathbf{U}^\dagger\mathbf{A}^k\mathbf{U})_{ii} \qquad (9)$$

because the term in braces is zero, due to Eq. (4).

Using Eq. (9), we can write, from Eq. (3):

$$\mathbf{E} = \sum_k \boldsymbol{\alpha}^k a_k. \qquad (10)$$

If we define the matrix $\boldsymbol{\alpha}$ as $\alpha_{ik} = (\boldsymbol{\alpha}^k)_{ii}$ we have

$$E_i = \sum_k \alpha_{ik}a_k. \qquad (2)$$

The matrix elements α_{ik} are obtained through a similarity transformation of the matrix $\mathbf{A}^k$ (Eq. (9)), in terms of the matrix $\mathbf{U}$ that diagonalizes $\mathbf{H}$.

3. Application to Iterative Linearization Procedures

In the method of systematic linearization of the electrostatic matrices (1) and (2), it is *assumed* that the eigenvalues of the Hamiltonian matrix satisfy Eq. (2). The best approximations to α_{ik} and a_k are obtained by an iterative calculation in which some initial values of the a_k's are used to estimate the α_{ik}'s by numerical calculation of the first derivatives:

$$\alpha_{ik} = \{E_i(a_i, \ldots, a_k + \delta a_k, \ldots) - E_i(a_1 \ldots a_k \ldots)\}/\delta a_k \simeq (\partial E_i/\partial a_k)_{a_{j\neq k}}. \qquad (11)$$

These α_{ik}'s give a new set of a_k's through a least-squares fitting of Eq. (2) to a set of known eigenvalues E_i°. The procedure is iterated until convergence in a_k and α_{ik} is reached.

The results of Section 2 show that Eq. (9) is a better and faster procedure for obtaining the α_{ik}'s. In the linearization method one has to perform, at each iteration, NPAR + 1 diagonalizations of $\mathbf{H}$ (NPAR = number of independent parameters, a_k) to compute the approximate derivatives through Eq. (11). The computer time will be greatly reduced if we diagonalize $\mathbf{H}$ only once at each iteration, obtain $\mathbf{U}$ and compute all the α_{ik}'s accurately via Eq. (9). Naturally, the advantages of this alternative calculation will increase with the number of parameters and with the rank of $\mathbf{H}$.

Now suppose we were interested in obtaining the values of the parameters a_k's that better reproduce a set of known eigenvalues E_i° of a Hermitian matrix $\mathbf{H}$. Since we know that Eq. (2) holds, we would like to use it for our purpose. We should have to minimize the root mean square deviation between our computed E_i and the E_i° and, therefore, the following linear least-squares equations should be solved:

$$\Sigma_i \Sigma_l \alpha_{ik} \alpha_{il} a_l = \Sigma_i E_i^\circ \alpha_{ik}. \quad (12)$$

However, the coefficients α_{ik} are very involved functions of the a_k's and an iterative procedure is possibly the best solution, namely: (i) selection of some initial values of a_k, (ii) calculation of **H**, via Eq. (1), (iii) obtaining of **U** by diagonalization of **H**, Eq. (3), (iv) calculation of α_{ik}, Eq. (9), and (v) calculation of the new a_k, Eq. (12). But this is exactly the improved version of the linearization procedure proposed in this work. We conclude, then, that the linearization calculation of Ref. (*1*) represents a general method for fitting the eigenvalues of a Hermitian matrix to a set of known values E_i°.

4. Application to Molecular Orbital Calculation of the Electronic Spectra

Although the arguments below can be applied to any electronic transition, we will discuss the *d–d* transitions in particular.

Following the methodology of Richardson *et al.* (*3*), we can write the *i*th *d–d* transition as

$$\Delta E(i; \text{dia}) = n(i; \text{dia})\, \Delta H' + \Sigma_k b(i, k; \text{dia}) I_k, \quad (13)$$

where the term dia holds for the first-order or diagonal calculation, $n(i)$ is the number of *d* electrons involved in the transition, $\Delta H'$ the increment in effective one-electron energy, I_k the independent two-electron integrals chosen to describe the open-shell repulsion energy of the multielectronic states, and $b(i, k)$ are numerical constants.

When we improve the diagonal description with some amount of CI, the influence of the I_k's into the refined value of the transition is very hard to ascertain, due to the appearance of linear contributions of these repulsion integrals in the off-diagonal elements of the CI matrix. Application of Eq. (2), however, allows us to write

$$\Delta E(i; \text{CI}) = n(i; \text{CI})\, \Delta H' + \Sigma_k b(i, k; \text{CI}) I_k, \quad (14)$$

where the term CI indicates the inclusion of this refinement, and the coefficients $n(i; \text{CI})$ and $b(i, k; \text{CI})$ are computed through Eq. (9). Equation (14) gives interesting information on the degree of electronic delocalization (through $n(i; \text{CI})$) arising from the inclusion of CI. Also, the $b(i, k; \text{CI})$ coefficients show the contribution of the I_k's to ΔE.

It is clear that the same can be said about the effects of other refinements introduced as additive matrices to the unrefined Hamiltonian. The spin–orbit interaction, the Racah–Trees correction (*7*), and the empirical correlation energy correction, CEC (*4*), are examples of this type of refinement. The CEC matrix elements do not contain parameters but it is useful to consider them as products:

$$(\text{CEC})_{ij} = (\text{CEC})_{ij}\, \zeta(\text{CEC}), \quad (15)$$

where $\zeta(\text{CEC})$ is a "CEC parameter" with value unity. Then, the CI + CEC calculation gives the linear expression:

$$\Delta E(i; \text{CI} + \text{CEC}) = n(i; \text{CI} + \text{CEC})\, \Delta H' + \Sigma_k b(i, k; \text{CI} + \text{CEC}) I_k + c(i; \text{CI} + \text{CEC})\, \zeta(\text{CEC}). \quad (16)$$

It is convenient to note that the parameters $\Delta H'$ and I_k maintain their values in going from Eq. (13) to Eqs. (14) and (16). These values are obtained from a given SCF calculation and yield different estimations of $\Delta E(i)$ because the linear coefficients $n(i)$ and $b(i, k)$, computed with Eq. (9), are different in each case. This situation contrasts with the one found in the linearization scheme, where different linearizations (such as those with and without CI) pro-

TABLE I

LINEAR COEFFICIENTS AND PARAMETERS FOR SOME ELECTRONIC TRANSITIONS OF CrF_6^{4-} COMPUTED AT R(Cr–F) = 3.59 a.u. (1.90 Å)

Repulsive interactions:		t_{2g}–t_{2g}			t_{2g}–e_g					e_g–e_g		
Parameters I^k:[a]	$\Delta H'$	$\bar{J}(tt)$	$\bar{K}(tt)$	$K(t\zeta, t\zeta)$	$\bar{J}(te)$	$\bar{K}(te)$	$J(t\zeta e\theta)$	$K(t\zeta e\theta)$	i	$\bar{J}(ee)$	$K(ee)$	ζ(CEC)
Coefficients	n_i	b_{i1}	b_{i2}	b_{i3}	b_{i4}	b_{i5}	b_{i6}	b_{i7}	b_{i8}	b_{i9}	b_{i10}	$c_{i\mathrm{CEC}}$
Transition ^5E_g												
→ a^3E_g	0.	0.	0.	0.	0.	4.	0.	0.	0.	0.	0.	—
	0.016	−0.073	0.121	1.084	0.016	4.733	0.	−1.914	−0.382	0.032	−0.032	—
	0.006	−0.028	0.046	1.094	0.006	4.792	0.	−1.923	−0.234	0.012	−0.012	−5.01
	0.009	−0.038	0.064	1.093	0.009	4.776	0.	−1.921	−0.276	0.017	−0.017	−3.66
→ b^3T_{1g}	0.	−1.5	4.5	−2.	0.	1.5	0.	−0.5	0.	0.	0.	—
	0.007	−1.498	4.468	−1.542	−1.411	1.890	1.408	−0.905	−0.316	0.011	0.011	—
	0.007	−1.510	4.489	−1.582	−1.374	1.981	1.381	−0.981	−0.272	0.006	0.002	−5.89
	0.007	−1.509	4.487	−1.575	−1.382	1.950	1.388	−0.957	−0.283	0.007	0.003	−4.32
→ a^3T_{2g}	0.	−1.5	4.5	−2.	0.	0.5	0.	0.5	0.	0.	0.	—
	0.026	−1.538	4.471	−1.462	−1.448	1.358	1.467	−0.432	−0.437	0.033	−0.009	—
	0.011	−1.516	4.487	−1.496	−1.465	1.402	1.474	−0.442	−0.309	0.012	−0.002	−6.33
	0.014	−1.520	4.484	−1.486	−1.465	1.388	1.476	−0.440	−0.341	0.016	−0.003	−4.62
→ a^3A_{2g}	0.	0.	0.	3.	0.	0.	0.	1.	0.	0.	0.	—
	0.097	−0.439	0.731	2.708	0.097	0.097	0.	0.903	−4.109	0.195	−0.195	—
	0.073	−0.330	0.550	2.780	0.073	0.073	0.	0.927	−3.612	0.147	−0.147	−7.11
	0.078	−0.352	0.586	2.766	0.078	0.078	0.	0.922	−3.719	0.156	−0.156	−5.19
Parameters/10^3 (cm^{-1})	9.60	165.65	62.79	6.81	165.21	5.86	161.04	7.91	1.77	171.57	93.86	1

Note. The four rows associated with each transition correspond to the diagonal, CI, CI + CEC, and CI + CECd calculations, respectively.

[a] Defined in Ref. (*3*).

duce different values of the parameters and linear coefficients.

5. Two Examples: The Optical Spectra of CrF_6^{4-} and CrF_6^{3-}

In this section we discuss the application of Eqs. (13), (14), and (16) to the theoretical spectrum of two complex ions whose electronic structures were computed with the methodology of Richardson *et al.* (*3*). The basic Hartree–Fock calculations and the theoretical transition energies were given before (*8, 9*). These theoretical spectra were related to the optimum values of the crystal-field parameters B and C (*1, 8, 9*). Here we will present their linear expansion in terms of $\Delta H'$ and the 10 independent repulsion integrals defined by Richardson *et al.* (*3*).

In Table I we present the SCF parameters and the linear coefficients for the lower quintet–triplet *d–d* transitions of CrF_6^{4-} computed at first-order, with CI limited to the d^4 configuration, with CI + CEC and with CI + CEDd. The CECd is the delocalized CEC and it incorporates, in part, the effects of the metal–ligand mixing (*4*).

These spin-forbidden transitions belong to the configuration of the ground state, which explains the small value of the number of electrons, $n(i)$, involved in these transitions. This number, which is exactly zero in the first-order calculation, increases to 0.01–0.1 by the action of configurational mixing. CEC does not produce a significant effect on $n(i)$.

The effects of the refinements on the nature of these transitions are particularly clear. For instance, the $^5E_g \rightarrow {}^3E_g$ transition is due, according to the first order calculation, to a pure change in the t_{2g}–e_g open-shell repulsion. The CI description shows the significant contributions of the t_{2g}–t_{2g}

TABLE II

EFFECTIVE MONOELECTRONIC, BIELECTRONIC, AND CEC CONTRIBUTIONS (IN UNITS OF 10^3 cm^{-1}) TO THE ENERGIES OF THE TRANSITIONS IN TABLE I

Transition	Effective one-electron	Two-electron energy			One- + two-electron		
t^3e–^5E_g	energy	*t–t*	*t–e*	*e–e*	energy	CEC	Total
→ a^3E_g	0.	0.	23.44	0.	23.44	—	23.44
	0.15	2.95	14.58	2.51	20.19	—	20.19
	0.06	5.75	13.48	0.96	20.25	−5.01	15.24
	0.08	5.10	13.71	1.32	20.21	−3.66	16.55
→ b^3T_{1g}	0.	20.46	4.84	0.	25.30	—	25.30
	0.06	21.94	−3.02	1.98	20.96	—	20.96
	0.07	20.90	−1.27	1.24	20.94	−5.89	15.05
	0.07	20.96	−1.43	1.36	20.96	−4.32	16.64
→ a^3T_{2g}	0.	20.46	6.89	0.	27.35	—	27.35
	0.24	15.94	0.87	4.81	21.86	—	21.86
	0.10	20.42	−0.49	1.94	21.97	−6.33	15.64
	0.13	19.56	−0.31	2.55	21.93	−4.62	17.31
→ a^3A_{2g}	0.	20.43	7.91	0.	28.34	—	28.34
	0.94	−8.31	16.53	15.15	24.31	—	24.31
	0.70	−1.20	13.48	11.40	24.38	−7.11	17.27
	0.75	−2.62	14.09	12.15	24.37	−5.19	19.18

Note. The four rows have the same meaning as in Table I.

and e_g–e_g interactions to this transition. Moreover, integrals that have no effect in the diagonal description, as like $\bar{J}(tt)$ in the →$^3A_{2g}$ transition, become very important after CI.

In Table II we have collected the different contributions to the transition energy in CrF$_6^{4-}$. We observe that the change in effective one-electron energy (one-electron energy plus the interaction with the closed shells (*3*)) makes an insignificant contribution to the final value of these transitions. The partition into t_{2g}–t_{2g}, t_{2g}–e_g, and e_g–e_g contributions is very different after CI. From the numbers in Table II we can have a quantitative insight on the effects of the configurational mixing (within the $3d^4$ configurations).

The fifth column in Table II shows that no matter how the open-shell repulsion is distributed among the different interactions, the contribution of the total repulsion to the transition energies decreases after CI. This is a much more important effect than the increase in the one-electron energy contribution and illustrates that in *these* lower transitions configurational mixing amounts to a redistribution of the electronic charge in the direction of minimizing the repulsion. This ought to be so because (a) the ground state of CrF$_6^{4-}$ is unaffected by the CI considered here (*8*) and (b) this refinement reduces the repulsion energy of the lower-energy states involved in the CI matrices.

The effects of the CEC are also of interest. This correction has a double action on the transition energy. First, it alters the mixing coefficients of the configurational states. Second, it incorporates a new term in the Hamiltonian. The changes in the wavefunction are already included in the fifth column of Table II. The second factor is presented in column six. It is clear from

TABLE III

EFFECTIVE MONOELECTRONIC, BIELECTRONIC, AND CEC CONTRIBUTIONS (IN UNITS OF 10^3 cm^{-1}) TO SOME TRANSITION ENERGIES OF CrF_6^{3-} *in Vacuo* AND IN K_2NaCrF_6

Transition	Effective	Two-electron energy			One- +		
t^3–$^4A_{2g}$	one-electron energy	t–t	t–e	e–e	two-electron energy	CEC	Total
→ t^3–$^2T_{1g}$	0.	20.11	0.	0.	20.11	—	20.11
	0.79	9.38	8.28	0.76	19.21	—	19.21
	0.57	12.73	5.10	0.85	19.25	−3.13	16.12
	0.	20.05	0.	0.	20.05	—	20.05
	0.77	10.13	7.60	0.69	19.19	—	19.19
	0.55	13.28	4.63	0.78	19.24	−3.14	16.10
→ t^3–^2E_g	0.	20.11	0.	0.	20.11	—	20.11
	0.89	8.34	8.55	0.50	18.28	—	18.28
	0.71	10.79	6.53	0.29	18.32	−3.22	15.10
	0.	20.05	0.	0.	20.05	—	20.05
	0.90	8.82	8.11	0.43	18.26	—	18.26
	0.71	11.21	6.14	0.25	18.31	−3.23	15.08
→ t^2e–$^4T_{1g}$	22.03	−309.2	317.7	0.	30.53	—	30.53
	26.05	−337.4	312.0	27.04	27.74	—	27.74
	24.30	−325.1	313.5	15.27	27.94	−1.72	26.22
	23.30	−308.5	316.6	0.	31.35	—	31.35
	27.14	−333.9	311.2	24.32	28.74	—	28.74
	25.43	−322.7	312.6	13.53	28.93	−1.78	27.15
→ t^2e–$^4T_{2g}$[a]	22.03	−309.2	305.7	0.	18.51	—	18.51
	23.30	−308.5	304.6	0.	19.38	—	19.38

Note. For each transition, rows 1, 2, and 3 correspond to the diagonal, CI, and CI + CEC calculations on CrF_6^{3-} *in vacuo*. Rows 4, 5, and 6 have the same meaning for CrF_6^{3-} in K_2NaCrF_6.

[a] This state does not suffer CI within the d^3 configurations; first row is the diagonal, *in vacuo* calculation, and second row the diagonal calculation for CrF_6^{3-} : K_2NaCrF_6.

these numbers that the perturbation of the CEC on the wavefunction is a rather minor effect, the correction to the Hamiltonian being the essential feature. In the free-ion the last correction is, by definition, the full CEC effect. From Table II we learn that this is almost the case in the complex ion.

As a second example, we present in Table II the information corresponding to CrF_6^{3-}. We include results from calculations on CrF_6^{3-} *in vacuo* and in the lattice of K_2NaCrF_6 (*10*). In this cluster the intraconfigurational transitions $^4A_{2g} \rightarrow {}^2E_g$, $^2T_{1g}$ suffer, by the action of CI, an increment in the one-electron energy larger than that seen in CrF_6^{4-}. As in the last cluster, however, the repulsion energy is the main contribution to ΔE. CI reduced this repulsion by several units of 10^3 cm^{-1}. The effects of the lattice potential on these transitions are uniformly small.

It is interesting to observe the differences between an intraconfigurational transition, as that to ^2E_g, and an interconfigurational one, as that to $^4T_{1g}$ or $^4T_{2g}$. In the second type of transition the one-electron energy is a *very* significant portion of the transition and the increment due to the CI is quite substantial, too. The changes in repulsion energy are very large due to the change in population, but the t_{2g}–t_{2g} and t_{2g}–e_g terms almost cancel out, giving rise to a total contribution of the two electron energy smaller than that from $\Delta H'$. In these transitions the effects of the external lattice are also more appreciable.

Finally, we would like to remark that the information collected in Tables I, II, and III is considerably more detailed than that deducible from the values of the B and C parameters. We have now a deeper physical insight on the nature of the transition energy. Such information is immediately accessible once the SCF calculation has been carried out. Furthermore, if the number of observed electronic transitions is adequate, all this information can be obtained through a systematic linearization in terms of the 10 independent repulsion integrals, since the appropriate matrix elements are available (*6*).

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