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Commentationes

The Ligand Field as a Pseudo-Potential*

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The introduction of a pseudo-potential in crystal field theory is shown to lead to an expression for the orbital splittings which depend upon the squares of the group overlap integrals between the metal and ligand orbitals. A formula is derived whereby the group overlap integral can be directly expressed in terms of the diatomic sigma- and pi-integrals.

Key words: Group overlap integrals – Ligand field as pseudo-potential – Pseudo-Potential, the ligand field as a ~

1. Introduction

In this note we shall consider a transition from a pure crystal field treatment of an inorganic ion or molecule towards a molecular view. The use of pseudo-potentials has been shown [1] to lead to some simple and conceptually appealing models in other contexts. Here we shall attempt to show that it leads to a deeper understanding of the origin of the orbital separation in the ligand field theory. In particular, it will be demonstrated that the dependence of the orbital splittings upon the squares of the overlap integrals provides a supplement to, rather than a replacement [2] of, the usual crystal field effects.

2. Theory

Consider a metal nucleus, M, surrounding by L ligands, which are transformed into each other under the operations of some symmetry group, H, leaving M unaffected. The irreducible representations of this group are $\Gamma_1, \Gamma_2, \ldots, \Gamma_q$, of dimensions $\nu_1, \nu_2, \ldots, \nu_q$ respectively, and we assume that the unitary matrices associated with these representations are defined by the transformation properties of some orthonormal set of functions, viz.

$$f_1^{(1)}, \ldots, f_{\nu_1}^{(1)}; \ldots ; f_1^{(i)}, \ldots, f_{\nu_i}^{(i)}; \ldots ; f_1^{(q)}, \ldots, f_{\nu_q}^{(q)}.$$

We shall then focus our attention on a fixed metal orbital, λ^d, and a normalized, symmetry adapted linear combination

$$\varphi_r^{(j)} = \sum_{i=1}^{L} a_{ir} \lambda_i^\mu \tag{1}$$

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* Dedicated to Professor H. Hartmann on the occasion of his 60th birthday.

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of L equivalent ligand orbitals $\lambda_1^\mu, \ldots, \lambda_L^\mu$. The functions λ^d and $\varphi_r^{(j)}$ are both assumed to transform like $f_r^{(j)}$, and the symmetry involved is understood to be so high, that $\varphi_r^{(j)}$ is uniquely defined.

Let us assume that a given electronic state of the complex consisting of M and the L ligands may be characterized by some effective one-electron molecular Hamiltonian, $\hat{F}$, of the Hartree-Fock type. λ^d and $\varphi_r^{(j)}$ will then mix and produce a bonding molecular orbital, φ_b, and an antibonding molecular orbital, φ_a. Provided that the energy difference $\langle \lambda^d | \hat{F} | \lambda^d \rangle - \langle \varphi_r^{(j)} | \hat{F} | \varphi_r^{(j)} \rangle$ is sufficiently large and positive, one finds to a good approximation, that

$$\varphi_b = \sum_{i=1}^{L} a_{ir} \lambda_i^\mu , \tag{2}$$

and

$$\varphi_a = \sqrt{\frac{1}{1 - G_j^2}} \left(\lambda^d - G_j \sum_{i=1}^{L} a_{ir} \lambda_i^\mu \right), \tag{3}$$

where G_j is the group overlap integral

$$G_j = \left\langle \sum_{i=1}^{L} a_{ir} \lambda_i^\mu | \lambda^d \right\rangle . \tag{4}$$

Notice that the bonding orbital is unaffected by the complex formation, whereas the anti-bonding orbital, φ_a, is Schmidt orthogonalized to φ_b.

We now take φ_a and φ_b to be reasonable approximations to the Hartree-Fock orbitals for the complex. Hence

$$\hat{F} \varphi_a = \varepsilon_a \varphi_a , \tag{5}$$

$$\hat{F} \varphi_b = \varepsilon_b \varphi_b . \tag{6}$$

Substituting (3) into (5) gives

$$\hat{F} \left(\lambda^d - G_j \sum_{i=1}^{L} a_{ir} \lambda_i^\mu \right) = \varepsilon_a \left(\lambda^d - G_j \sum_{i=1}^{L} a_{ir} \lambda_i^\mu \right), \tag{7}$$

and using (2) and (6) yields further

$$\hat{F} \lambda^d + (\varepsilon_a - \varepsilon_b) G_j \sum_{i=1}^{L} a_{ir} \lambda_i^\mu = \varepsilon_a \lambda^d . \tag{8}$$

Equation (8) can be rewritten as

$$(\hat{F} + \hat{U}) \lambda^d = \varepsilon_a \lambda^d , \tag{9}$$

where $\hat{U}$ is a so-called pseudo-potential having the form

$$\hat{U} = (\varepsilon_a - \varepsilon_b) \int dv_2 \sum_{i,s} \varphi_s^{(i)}(2)^* \hat{P}_{12} \varphi_s^{(i)}(2) . \tag{10}$$

The summation in (10) includes all combinations of the type (1), that may be constructed from the orbitals $\lambda_1^\mu, \ldots, \lambda_L^\mu$, and $\hat{P}_{12}$ is an operator interchanging electrons 1 and 2, such that

$$\hat{U}\psi(1) = (\varepsilon_a - \varepsilon_b) \sum_{i,s} \langle \varphi_s^{(i)} | \psi \rangle \varphi_s^{(i)}(1) . \tag{11}$$

The definition of $\hat{U}$ runs parallel to that of the exchange operators appearing in Hartree-Fock theory.

That Eqs. (8) and (9) are, in fact, equivalent is easily established, when it is noticed that all integrals $\langle \varphi_s^{(i)} | \lambda^d \rangle$ vanish due to symmetry, with the exception of $\langle \varphi_r^{(j)} | \lambda^d \rangle$ which is, in turn, equal to G_j.

The operator $\hat{U}$ is a totally symmetric operator, and it plays a similar role to that of the crystal field potential, V, encountered in the usual crystal field theory [3]. When ligand-ligand overlap is neglected we get the still simpler expression

$$\hat{U} = (\varepsilon_a - \varepsilon_b) \int dv_2 \sum_i \lambda_i^\mu(2)^* \hat{P}_{12} \lambda_i^\mu(2) , \tag{12}$$

due to the fact that the coefficients in (1) are the elements of a unitary matrix.

Let us now consider the application of Eq. (8) to an octahedral complex, possessing O_h symmetry. The d-orbitals span a t_{2g} and an e_g representation, in the following denoted just t and e for the sake of simplicity. We get then, assuming that for both sets of orbitals we can set $(\varepsilon_a - \varepsilon_b) \simeq \varepsilon_{ML}^0$, that

$$\varepsilon_a(e) = \langle \lambda^e | \hat{F} | \lambda^e \rangle + \varepsilon_{ML}^0 |G_e|^2 \tag{13}$$

and

$$\varepsilon_a(t) = \langle \lambda^t | \hat{F} | \lambda^t \rangle + \varepsilon_{ML}^0 |G_t|^2 , \tag{14}$$

with λ^e and λ^t being specific metal orbitals associated with the representations e and t, respectively. Hence

$$\varepsilon_a(e) - \varepsilon_a(t) = \langle \lambda^e | V | \lambda^e \rangle - \langle \lambda^t | V | \lambda^t \rangle + \varepsilon_{ML}^0 (|G_e|^2 - |G_t|^2) . \tag{15}$$

Note that for $G_r = G_t = 0$, corresponding to the pure crystal-field model, we get the orbital energy difference which in that theory is called 10 Dq. The inclusion of a more realistic bonding scheme makes the orbital energy difference $\varepsilon_a(e) - \varepsilon_a(t_2)$ also dependent upon the squares of the group overlap integrals. Since (see next section) $G_e^2 = 3S^2(\sigma, d_\sigma)$ and $G_t^2 = 4S^2(\pi, d_\pi)$ where $S(\sigma, d_\sigma)$ and $S(\pi, d_\pi)$ are the usual diatomic sigma- and pi-overlap integrals [4], we get

$$\varepsilon_a(e) - \varepsilon_a(t_2) = \langle \lambda^e | V | \lambda^e \rangle - \langle \lambda^t | V | \lambda^t \rangle + \varepsilon_{ML}^0 (3S^2(\sigma, d_\sigma) - 4S^2(\pi, d_\pi)) . \tag{16}$$

The last parenthesis, like the crystal field term, is likely to be positive for an octahedral complex, since a diatomic sigma overlap is usually larger than a diatomic pi-overlap. The orbital energy difference must, however, not be identified [5] with the crystal field parameter 10 Dq.

We have thus, at the present level of approximation, two co-operating potentials, V and $\hat{U}$. We notice, however, that even though the pure crystal field theory breaks down, the formalism is unaltered. A semi-empirical theory can therefore do no better than to treat the orbital energy differences as adjustable parameters. Quantitative calculations based on $\hat{U}$ alone need certainly not be better than calculations in the pure crystal field theory, and attempts to make them seem so [6] must therefore be viewed with caution.

3. Evaluation of Group Overlap Integrals

The relationship between a group overlap integral G_j and a diatomic overlap $S(l, \mu)$ is given by [4, 7]

$$G_\Gamma = \gamma_\Gamma S(l, \mu)$$

where γ_Γ is a pure number. Consider now the various irreducible representations, Γ_i, spanned by the metal orbitals, $s(\Gamma_i)$, $p(\Gamma_{i'})$, $d(\Gamma_{i''})$ etc. Each of these sets of irreducible representations we shall call a metal set. Similarly, the L σ-orbitals will span a sigma ligand set, $\sigma(\Gamma_j)$, the $2L$ π-orbitals will span a pi ligand set, $\pi(\Gamma_{j'})$, etc. Let us by $\varkappa$ understand the number of representations which a given metal set and a given ligand set have in common. With v_Γ being the dimension of the representation Γ, we shall show the following relation for determining γ_Γ:

$$\Sigma(v_\Gamma \gamma_\Gamma^2) = N\,, \tag{18}$$

where N is the number of orbitals in the ligand set, and the summation includes those $\varkappa$ representations, which are shared between the metal and the ligand set.

For instance, in an octahedral molecule, the sigma ligand set and the d-orbitals, have one common representation, viz. e_g. Hence $\varkappa = 1$ and $2\gamma_e^2 = 6$; $\gamma_e = \sqrt{3}$. The π-ligand set and the d set also have $\varkappa = 1(t_{2g})$. Here $3\gamma_t^2 = 12$ or $\gamma_t = 2$.

In order to prove (18) let $R_l(r) Y_l^m(\theta, \varphi)$ be a metal orbital centered in the xyz-coordinate system and let λ_i^μ $(i = 1, 2 \ldots L)$ be the ligand orbitals, centered at i (Fig. 1). All of the ligand functions transform into each other under suitable rotations of the xyz system, and λ_i^μ has in the $x'y'z'$ system a φ' dependence given by $e^{i\mu\varphi'}$. Without any constraints we can expand λ_i^μ in the $x'y'z'$ coordinate system [8]

$$\lambda_i^\mu = \sum_{l'=0}^{\infty} B_{l'}(r) Y_{l'}^\mu(\theta', \varphi')\,. \tag{19}$$

The Eulerian angles which take (x', y', z') into (x, y, z) are called $(\alpha_i, \beta_i, \gamma_i)$. Transforming (19) into the (x, y, z) system leads to

$$\lambda_i^\mu = \sum_{l'=0}^{\infty} B_{l'}(r) \sum_{m'=-l'}^{l'} Y_{l'}^{m'}(\theta, \varphi) D^{(l')}(\alpha_i \beta_i \gamma_i)_{m'\mu} \tag{20}$$

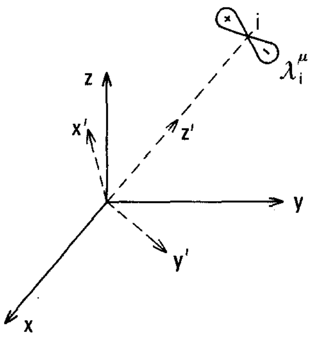

Fig. 1. The Co-ordinate Systems

where $D^{(l')}(\alpha_i\beta_i\gamma_i)$ is a unitary rotation matrix. The overlap integral between $R_l(r)Y_l^m(\theta,\varphi)$ and λ_i^μ is then

$$\begin{aligned}\langle R(r)Y_l^m(\theta,\varphi)|\lambda_i^\mu\rangle &= \sum_{l'=0}^{\infty} \langle R(r)|B_{l'}(r)\rangle \sum_{m'=-l'}^{l'} \langle Y_l^m|Y_{l'}^{m'}\rangle \cdot D^{(l')}(\alpha_i\beta_i\gamma_i)_{m'\mu} \\ &= \langle R(r)|B_l(r)\rangle D^{(l)}(\alpha_i\beta_i\gamma_i)_{m\mu}\,.\end{aligned} \tag{21}$$

The overlap can therefore be written as a product of a quantity $\langle R(r)|B_l(r)\rangle$ depending only upon the shells to which the orbitals belong and a quantity $D^{(l)}(\alpha_i\beta_i\gamma_i)$ depending only upon the position and orientation of the ligand orbitals.

We now define a standard overlap S^μ as the overlap between $R(r)Y_l^\mu(\theta,\varphi)$ and a ligand orbital located on the positive z-axis, such that $x'=x$, $y'=y$ and $z'=z$. Hence

$$S^\mu = \langle R(r)Y_l^\mu(\theta,\varphi)|\sum_{l'=0}^{\infty} B_{l'}(r)Y_{l'}^\mu(\theta,\varphi)\rangle = \langle R(r)|B_l(r)\rangle\,. \tag{22}$$

Using (21) and (22) yields:

$$\langle R(r)Y_l^m(\theta,\varphi)|\lambda_i^\mu\rangle = S^\mu D^{(l)}(\alpha_i\beta_i\gamma_i)_{m\mu}\,, \tag{23}$$

where $S^\mu = S^\sigma, S^\pi, S^\delta, \ldots$.

Utilizing that $D^{(l)}(\alpha_i,\beta_i,\gamma_i)$ is a unitary matrix gives

$$\sum_{m=-l}^{l} |\langle R(r)Y_l^m(\theta,\varphi)|\lambda_i^\mu\rangle|^2 = |S^\mu|^2 \sum_{m=-l}^{l} |D^{(l)}(\alpha_i\beta_i\gamma_i)_{m\mu}|^2 = |S^\mu|^2\,, \tag{24}$$

and an additional summation over i yields

$$\sum_{i=1}^{L}\sum_{m=-l}^{l} |\langle R(r)Y_l^m(\theta,\varphi)|\lambda_i^\mu\rangle|^2 = L|S^\mu|^2\,. \tag{25}$$

We proceed by replacing the orbitals $\lambda_1^\mu, \lambda_2^\mu, \ldots \lambda_L^\mu$ with a set of L linear combinations:

$$\varphi_i = \sum_{j=1}^{L} \lambda_j^\mu a_{ji}\,, \quad (i=1,2,\ldots,L) \tag{26}$$

where a is a unitary matrix. Then

$$\begin{aligned}\sum_{i=1}^{L} |\langle RY_l^m|\varphi_i\rangle|^2 &= \sum_{j=1}^{L}\sum_{k=1}^{L} \langle RY_l^m|\lambda_j^\mu\rangle^*\langle RY_l^m|\lambda_k^\mu\rangle \cdot \sum_{i=1}^{L} a_{ji}^* a_{ki} \\ &= \sum_{j=1}^{L} |\langle RY_l^m|\lambda_j^\mu\rangle|^2\,,\end{aligned} \tag{27}$$

or by comparing (27) with (25)

$$\sum_{i=1}^{L}\sum_{m=-l}^{l} |\langle RY_l^m|\varphi_i\rangle|^2 = L|S^\mu|^2\,. \tag{28}$$

We now suppose that the orbitals λ_i^μ $(i=1,2,\ldots,L)$ span a representation of the molecular point group H. These symmetry orbitals $\varphi_r^{(j)}$ are then of the type (26), and according to (27) and (28) we can write

$$\sum_j \sum_r \sum_{m=-l}^{l} |\langle R(r)\, Y_l^m(\theta,\varphi)|\varphi_r^{(j)}\rangle|^2 = L|S(l,\mu)|^2 , \tag{29}$$

where we have given S^μ one index more; $S^\mu \Rightarrow S(l,\mu)$, l indicating whether we have a $s, p, d \ldots$ set; μ differentiating between $\sigma, \pi, \delta, \ldots$.

The metal orbitals may likewise be characterized according to their irreducible representations. This leads to the orbitals $\psi_{r'}^{(j')}$, and hence (29) is transformed to

$$\sum_{j'} \sum_{r'} \sum_j \sum_r |\langle \psi_{r'}^{(j')}|\varphi_r^{(j)}\rangle|^2 = L|S(l,\mu)|^2 , \tag{30}$$

where the sum over j' takes care of the $\Gamma^{(j)}$ components contained in the $2l+1$ metal orbitals. We have further

$$\langle \psi_{r'}^{(j')}|\varphi_r^{(j)}\rangle = \delta_{jj'}\delta_{rr'} G_j \tag{31}$$

with G_j being the previously defined group overlap integral. Taking the Γ_j representation to be ν_Γ times degenerate, Eq. (30) together with (31) yields

$$\Sigma(\nu_\Gamma G_\Gamma^2) = L|S(l,\mu)|^2 , \tag{32}$$

where the summation extends over the irreducible representations common to the metal- and ligand orbitals. Inserting $G_\Gamma = \gamma_\Gamma S(l,\mu)$ in (32) concludes the proof of (18).

References

1. Weeks, J. D., Hazi, A., Rice, S. A.: Advan. Chem. Phys. **16**, 283 (1969)
2. Schäffer, C. E., Jørgensen, C. K.: Mol. Phys. **9**, 401 (1965)
3. Ballhausen, C. J.: Introduction to ligand field theory. New York: McGraw-Hill 1962
4. Mulliken, R. S., Rieke, C. A., Orloff, D., Orloff, H.: J. Chem. Phys. **17**, 1248 (1949)
5. Dahl, J. P., Ballhausen, C. J.: Advan. Quantum Chem. **4**, 170 (1968)
6. Schäffer, C. E.: Structure and Bonding **5**, 68 (1968)
7. Kettle, S. F. A.: Inorg. Chem. 4, 1821 (1965)
8. Dahl, J. P., Barnett, M. P.: Mol. Phys. **9**, 175 (1965)

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