Effect of crystal field on the spin density at the copper nucleus in copper complexes

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Abstract. The role of lower symmetry component of the crystal field in causing a mixing of excited $3d^{x-1}4s$ with the ground $3d^x$ configuration and leading to spin density at the nucleus for iron group ions was suggested by Griffith and Orgel. This mechanism has been examined in detail for the two low-symmetry copper complexes, one square planar (D_{4h} symmetry) and the other distorted tetrahedron (D_{2d} symmetry) and the calculation has been performed using the powerful Racah method and tensor operator technique. It is found that for the two types of copper complexes, copper pthalocyanin (square planar, D_{4h} symmetry) and cesium copper chloride (distorted tetrahedron, D_{2d} symmetry) the contribution from this mechanism to the spin density at the nucleus vanishes identically.

1. Introduction

The problem dealt with in the present work is the result of a program which we initiated for studying the effect of configuration interaction on the various physical properties of iron group such as crystal field splittings [1–5], intensity of crystal field spectra [6, 7], reduction of orbital moment and s-o coupling [8] and finally on the spin density at the nuclear site of the ion. The configuration interaction in which we are interested in the said program concerns the mixing of the ground configuration $3d^x$ with the excited configurations $3d^{x-1}4l(4l \equiv 4s, 4p, 4d$ and $4f)$ in which a 3d electron is promoted to the $4s, 4p, 4d$ or $4f$ orbit.

For the explanation of spin density at the nulcear site of iron group ions Abragam *et al* [9] proposed a mechanism where the ground configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^x$ gets admixed via interelectronic repulsion with the excited configuration $1s^2 2s^2 2p^6 3s 3p^6 3d^x Rs$ where Rs is a generalized higher s-orbital orthogonal to all the s-orbitals. The method of evaluating Rs using variational Hartree–Fock calculation has been illustrated by Abragam *et al* [9]. However, this mechanism yielded a result for the spin density equal to -0.3 a.u. instead of the experimental value -3 a.u. approximately in the case of Mn^{2+}. Griffith and Orgel [10, 11] suggested a mechanism which is dependent on crystal field having a symmetry lower than the cubic and causing an admixture of the excited configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{x-1}4s$ with the ground configuration. To our knowledge the size of the contribution from this mechanism to the spin density, although, suggested long ago, was not quantitatively calculated and reported in the

literature. Another mechanism known as core polarization or spin polarization which is now considered to be the most plausible and successful mechanism gave excellent agreement with the experiment. This mechanism is based on the idea of magnetic polarization of an atomic or ionic core of closed shells by an unfilled external shell having a total spin S. The radial functions of s-orbitals of a subshell with spin up and down are considered to be different because of their different coupling with the magnetic d-electrons and the density at the origin will be different for the two cases. Some details of the calculation can be found in the review articles [12,13]. The calculation of spin density involves quantities which are sensitive to the precise form of electron wavefunctions. Further development involving various forms of Hartree–Fock calculation and other rigorous techniques including correlation and relativistic correction may be found in excellent reviews [14,15]. Recent works [16–20] with the highly sophisticated methods such as large multi-configuration H–F technique, multireference configuration interaction technique, many-body perturbation technique etc. are confined within the relatively light atoms. The complexity of these sophisticated calculations seems to indicate conti-nued reliance on the more straightforward spin-polarized H–F technique for heavier atoms or ions.

We would like to stress that the present paper does not aim at explaining the spin density of the two copper complexes, Cu-pthalocyanin (CuPc) and $Cs_2 CuCl_4$ but to see the size of the contribution from the crystal field dependent mechanism suggested by Griffith and Orgel as a part of our program of studying the effect of configuration interaction on the various physical properties of iron group ions as stated earlier. We choose the above two particular ions since the deviation from pure cubic symmetry is large in these cases, a condition necessary for Griffith and Orgel mechanism to have any significance. The first is a covalent square planar complex (D_{4h} symmetry) [21] having a large deviation from cubic symmetry. In $Cs_2 CuCl_4$, the Cu^{2+} ion deviates from pure T_d as observed from X-ray [22,23] and it is best described by D_{2d} symmetry [24]. The epr hyperfine structures from which the experimental values of spin density may be extracted are also available for these two copper complexes [21,25]. To our surprise we found that the contribution to the spin density from Griffith and Orgel mechanism vanishes identically in these two particular cases even though the symmetry deviates appreciably from pure cubic, a result considered to be worth reporting. The null result is evidently due to the particular symmetry of the copper ion. This, of course, does not mean that in the case of other symmetries of the copper complex, the contribution from Griffith and Orgel mechanism will also vanish.

The central density χ of the unpaired spin is calculated from the following expres-sion [9]

$$\chi = \frac{4\pi}{S} \langle \psi | \sum \delta(\mathbf{r}_t) s_{tz} | \psi \rangle_{S_z = S} \qquad (1)$$

where S is the total spin of the ion in its ground configuration, the state ψ is the lowest state of the ground configuration $3d^x$ in a crystal field admixed with the states of excited configuration $3d^{x-1}4s$ via both crystal field and interelectronic repulsion considered together as the perturbation.

2. Method of calculation

The lowest state of the ground configuration $3d^9$ of Cu^{2+} ion in D_{2d} and D_{4h} symmetry is given by [24, 21]

$$\psi_g(3d^9) = (1/2)^{1/2}[|3d^{9\,2}D\,1/2\,2\rangle \mp |3d^{9\,2}D\,1/2\,-2\rangle]$$

$$= (1/2)^{1/2}[|\psi_1\rangle \mp |\psi_2\rangle] \quad \text{(say)}. \tag{2}$$

The upper and lower signs correspond to $D_{2d}(Cs_2CuCl_4)$ and $D_{4h}(CuPc)$ systems respectively. We consider the mixing of this lowest state as given by (2) with the various states of the excited configuration $3d^8 4s$ via the combined action of interelectronic repulsion and crystal field interaction i.e. through the operator

$$\sum_{i<j}(e^2/r_{ij}) + H_c \tag{3}$$

where $H_c = \Sigma_i - |e|V(i)$, and $V(i)$ is the crystal field potential of the ith electron and the summation extends over all the electrons of the unfilled shell. For $Cs_2CuCl_4(D_{2d}$ symmetry)

$$V(i) = a_{20}V_0^{(2)}(i) + a_{40}V_0^{(4)}(i) + a_{44}[V_4^{(4)}(i) + V_{-4}^{(4)}(i)]$$

$$+ a_{32}[V_2^{(3)}(i) - V_{-2}^{(3)}(i)] + a_{52}[V_2^{(5)}(i) - V_{-2}^{(5)}(i)] \tag{4}$$

For CuPc (D_{4h} symmetry)

$$V(i) = a_{20}V_0^{(2)}(i) + a_{40}V_0^{(4)}(i) + a_{44}[V_4^{(4)}(i) + V_{-4}^{(4)}(i)] \tag{5}$$

In (4) and (5) a_{kq}'s are crystal field coefficients and $V_q^{(k)} = r^k Y_k^q$, Y_k^q being a spherical harmonic of order k and component q. In the present calculation we need only to consider the term $a_{20}V_0^{(2)}$ of the crystal field potential, for other terms of the potential the matrix elements of H_c between the states of $3d^9$ and $3d^8 4s$ vanish. The configurationally mixed lowest state becomes

$$\psi = \psi_g(3d^9) - (1/\Delta E)\sum_{\psi_e}\langle\psi_e(3d^8 4s)| \left[\sum(e^2/r_{ij}) + \sum - |e|a_{20}V_0^{(2)}(i)\right]$$

$$\times |\psi_g(3d^9)\rangle|\psi_e(3d^8 4s)\rangle \tag{6}$$

where the general form of the states of the excited configuration $3d^8 4s$ is written as $\psi_e = |3d^8(S_1 L_1)\,4s\,S'L'M'_S M'_L\rangle$ and ΔE is the energy separation of the excited configuration $3d^8 4s$ from the ground $3d^9$ configuration. For the matrix elements of $\Sigma(e^2/r_{ij})$ in (6) we need to calculate only

$$\langle 3d^{9\,2}D|\sum e^2/r_{ij}|3d^8(^1D)4s\,^2D\rangle$$

since the matrix of $\Sigma e^2/r_{ij}$ is diagonal in L, S. Here M_S and M_L values are omitted in the state symbol as the matrix element does not depend on them. Racah [26] has already given a very convenient formula for the evaluation of such matrix element which

reduces to the following (using eq. (79) of Racah [26])

$$\langle 3d^{9}{}^{2}D|\sum e^{2}/r_{ij}|3d^{8}({}^{1}D)4s\,{}^{2}D\rangle$$

$$= (9/14)^{1/2}[\langle d^{9}{}^{2}D||U^{(2)}||d^{9}{}^{2}D\rangle\langle d^{9}{}^{2}D\{|d^{8}({}^{1}D)d^{2}D\rangle 5^{1/2}$$

$$+ \langle d^{9}{}^{2}D\{|d^{8}({}^{1}S)d^{2}D\rangle\langle d^{8}{}^{1}S||U^{(2)}||d^{8}{}^{1}D\rangle 5^{1/2}$$

$$+ \langle d^{9}{}^{2}D\{|d^{8}({}^{1}D)d^{2}D\rangle\langle d^{8}{}^{1}D||U^{(2)}||d^{8}{}^{1}D\rangle 5^{1/2}$$

$$+ \langle d^{9}{}^{2}D\{|d^{8}({}^{1}G)d^{2}D\rangle\langle d^{8}{}^{1}G||U^{(2)}||d^{8}{}^{1}D\rangle 5^{1/2}]R^{(2)}(3d\,3d,\,3d\,4s)$$

$$(7)$$

where the various symbols and quantities have been explained in Racah's papers [26, 27]. Using eq. (74) of Racah [27]

$$\langle d^{9}{}^{2}D||U^{(2)}||d^{9}{}^{2}D\rangle = -\langle d||u^{(2)}||d\rangle = -1 \tag{8}$$

and

$$\langle d^{8}(S_{1}L_{1})||U^{(2)}||d^{8}(S_{1}L'_{1})\rangle = -\langle d^{2}(S_{1}L_{1})||U^{(2)}||d^{2}(S_{1}L'_{1})\rangle \tag{9}$$

The r.h.s. of (9) has been tabulated by Racah [27], eq. (103b).

Carrying out the calculation involved in (7) we finally get

$$\langle 3d^{9}{}^{2}D|\sum e^{2}/r_{ij}|d^{8}({}^{1}D)4s\,{}^{2}D\rangle = -(2/35)^{1/2}R^{(2)}(3d\,3d,\,3d\,4s)$$

where $R^{(2)}(3d\,3d,\,3d\,4s)$ is the interelectronic repulsion integral defined by Condon and Shortley [28]. The matrix element of $\sum V_{0}^{(2)}(i)$ that occurs in (6) is of the form

$$\langle 3d^{9}{}^{2}D\,1/2\,M_{L}|\sum V_{0}^{(2)}|d^{8}(S_{1}L_{1})4s\,{}^{2}L_{1}\,1/2\,M_{L_{1}}\rangle = A \quad (\text{say}) \tag{10}$$

which may be written as (using tensor operator formula [29])

$$A = 9^{1/2}\langle d^{9}{}^{2}D\{|d^{8}(S_{1}L_{1})d^{2}D\rangle(-1)^{L_{1}-M_{L}}[5(2L_{1}+1)]^{1/2}$$

$$\begin{Bmatrix} 2 & 2 & L_{1} \\ 0 & L_{1} & 2 \end{Bmatrix}\langle 3d||V^{(2)}||4s\rangle\begin{pmatrix} 2 & 2 & L_{1} \\ -M_{L} & 0 & M_{L_{1}} \end{pmatrix}. \tag{11}$$

Thus the admixed state ψ in (6) reduces to

$$\psi = (1/2)^{1/2}[|\psi_{1}\rangle \mp |\psi_{2}\rangle] - (\Delta E)^{-1}[-(1/35)^{1/2}R^{(2)}(3d\,3d,\,3d\,4s)$$

$$\times (|\phi_{1}\rangle \mp |\phi_{2}\rangle) + v_{20}\{(1/35)^{1/2}(|\phi_{1}\rangle \mp |\phi_{2}\rangle) - (3/20)^{1/2}(|\phi_{3}\rangle \pm |\phi_{4}\rangle)$$

$$+ (3/140)^{1/2}(|\phi_{5}\rangle \mp |\phi_{6}\rangle)\}] \tag{12}$$

where

$$v_{20} = |e|a_{20}\langle 3d||V^{(2)}||4s\rangle$$

$$= |e|a_{20}(5/4\pi)^{1/2}\begin{pmatrix} 0 & 2 & 2 \\ 0 & 0 & 0 \end{pmatrix}\int R_{3d}^{*}r^{2}R_{4s}r^{2}\,dr$$

$$|\phi_{1}\rangle = |3d^{8}({}^{1}D)4s\,{}^{2}D\,1/2\,2\rangle, \quad |\phi_{2}\rangle = |3d^{8}({}^{1}D)4s\,{}^{2}D\,1/2\,-2\rangle$$

$$|\phi_{3}\rangle = |3d^{8}({}^{3}F)4s\,{}^{2}F\,1/2\,2\rangle, \quad |\phi_{4}\rangle = |3d^{8}({}^{3}F)4s\,{}^{2}F\,1/2\,-2\rangle$$

$$|\phi_{5}\rangle = |3d^{8}({}^{1}G)4s\,{}^{2}G\,1/2\,2\rangle, \quad |\phi_{6}\rangle = |3d^{8}({}^{1}G)4s\,{}^{2}G\,1/2\,-2\rangle$$

and the upper sign in (12) corresponds to $Cs_{2}CuCl_{4}$ and the lower sign to CuPc. The

spin density χ at the nucleus of Cu^{2+} ion can now be easily calculated from (1). Expanding ψ according to (12) χ ultimately comes out to be

$$\chi = \chi_C + \chi_R + \chi_{CR} \tag{13}$$

where

$$\chi_C = [(1/35)(\langle\phi_1|Q|\phi_1\rangle + \langle\phi_2|Q|\phi_2\rangle) + (3/20)(\langle\phi_3|Q|\phi_3\rangle$$
$$+ \langle\phi_4|Q|\phi_4\rangle) + (3/140)(\langle\phi_5|Q|\phi_5\rangle + \langle\phi_6|Q|\phi_6\rangle)](4\pi/S)(v_{20}/\Delta E)^2$$

$$\chi_R = (4\pi/S)(1/35)[(1/\Delta E)R^{(2)}(3d\,3d,\,3d\,4s)]^2[\langle\phi_1|Q|\phi_1\rangle + \langle\phi_2|Q|\phi_2\rangle]$$

$$\chi_{CR} = (4\pi/S)(1/\Delta E)^2[-(1/35)^{1/2}v_{20}R^{(2)}(3d\,3d,\,3d\,4s)]$$
$$\times [\langle\phi_1|Q|\phi_1\rangle + \langle\phi_2|Q|\phi_2\rangle]$$

in which $Q = \Sigma\delta(r_t)s_{tz}$; χ_C represents the contributions to the spin density at the nucleus arising through the admixture of ground $3d^9$ and excited $3d^8 4s$ configurations via crystal field alone as was suggested by Griffith and Orgel [10], χ_R stands for the contribution arising through the admixture of the two configurations via interelectronic repulsion alone and the contribution χ_{CR} arises from the cross terms like

$$\langle\phi_i|\sum e^2/r_{ij}|\psi_g(3d^9)\rangle \quad \langle\psi_g(3d^9)|H_C|\phi_i\rangle \quad \langle\phi_i|Q|\phi_i\rangle.$$

The type of matrix element $\langle\phi_i|Q|\phi_i\rangle$ that we now need is

$$\langle d^8(S_1 L_1)s^2 L_1\,1/2\,M_{L_1}|\sum\delta(r_t)s_{tz}|d^8(S_1 L_1)s^2 L_1\,1/2\,M_{L_1}\rangle = \mathbf{B} \quad \text{(say)}$$

where $M_{L_1} = 2$ or -2. Using (22) and (26) of Racah [26]

$$\mathbf{B} = \langle d^8(S_1 L_1)s_t\,^2 L_1\,1/2\,M_{L_1}|\delta(r_t)s_{tz}|d^8(S_1 L_1)s_t\,^2 L_1\,1/2\,M_{L_1}\rangle$$

$$= \begin{pmatrix} 1/2 & 1 & 1/2 \\ -1/2 & 0 & 1/2 \end{pmatrix}\langle S_1 4s\,1/2||\delta(r)s_0^{(1)}||S_1 4s\,1/2\rangle$$

$$= (-1)^s \cdot 6^{1/2}\begin{Bmatrix} 1/2 & 1 & 1/2 \\ 1/2 & S_1 & 1/2 \end{Bmatrix}|\psi_{4s}(0)|^2$$

where $\psi_{4s}(0)$ is the wave function of 4s electron at $r = 0$ (origin).

3. Results

Calculation yields

$$\chi_C = (4\pi/S)[v_{20}/\Delta E]^2(1/4\pi)\{(1/35)|\psi_{4s}(0)|^2$$
$$- (1/20)|\psi_{4s}(0)|^2 + (3/140)|\psi_{4s}(0)|^2\}$$
$$= 0$$

$$\chi_R = (\Delta E)^{-2}(1/35S)[R^{(2)}(3d\,3d,\,3d\,4s)]^2|\psi_{4s}(0)|^2$$

$$\chi_{CR} = -(\Delta E)^{-2}S^{-1}(1/35)^{1/2}R^{(2)}(3d\,3d,\,3d\,4s)v_{20}|\psi_{4s}(0)|^2$$

Thus χ_C is found to vanish identically in the present case showing that the crystal field through the mechanism suggested by Griffith and Orgel has no contribution to the spin

density at the nuclear site of the copper ion. However the crystal field indirectly gives a non-zero contribution χ_{CR} which involves the crystal field parameter through v_{20}. An estimate of χ_{CR} may be made from the knowledge of a correct radial wave function in the crystal which is difficult to obtain. However, a rough estimate may be made by considering Richardson's wave functions [30, 31].

The energy separation ΔE of the excited configuration $3d^8 4s$ from the ground $3d^9$ configuration for Cu^{2+} ion is obtained from Moore's table [32]

$$\Delta E = 0.74 \times 10^5 \, \text{cm}^{-1} = 3.371688 \times 10^{-1} \, \text{a.u.}$$

Using Richardson's radial functions we have

$$|\psi_{4s}(0)|^2 = 36.2232 \, \text{a.u.}$$

$$R^{(2)}(3d \, 3d, \, 3d \, 4s) = 0.006833 \, \text{a.u.}$$

$$\int R_{3d}^* r^2 R_{4s} r^2 dr = 1.3743 \, \text{a.u.} \tag{14}$$

As in our previous work [5] the value of v_{20} in the case of $Cs_2 CuCl_4$ can be calculated from the knowledge of metal-ligand distance [22, 23], ligand charge ($= -|e|$) and the radial integral given in (14). The value is $v_{20} = 0.0133 \, \text{a.u.}$ for $Cs_2 CuCl_4$.

The value of v_{20} is difficult to estimate in the case of Cu-pthalocyanin. A rough estimate in this case will be made considering v_{20} for the covalent compound CuPc larger than that for $Cs_2 CuCl_4$ by a maximum of one order in magnitude. Thus using the above numerical values and the total spin $S = 1/2$ for Cu^{2+} ion we arrive at the following results

$$\chi_C = 0$$

$$\chi_R = 0.85 \times 10^{-3} \, \text{a.u.}$$

$$\chi_{CR} = -0.165 \times 10^{-2} \, \text{a.u.} \quad \text{(for } Cs_2 CuCl_4)$$

$$= -1.65 \times 10^{-2} \, \text{a.u.} \quad \text{(for CuPc assuming that } v_{20} \text{ has a value 10 times}$$
$$\text{that in the case of } Cs_2 CuCl_4)$$

4. Discussion

The above calculation shows that χ_C, the contribution arising from the mechanism of Griffith and Orgel identically vanishes in the present case. Further, it is clear that χ_{CR} is of very little significance when compared with the experiment which gives a total value of about $-3.2 \, \text{a.u.}$ in Cu(Pc) [21] and $-2.7 \, \text{a.u.}$ in $Cs_2 CuCl_4$ [25] for the spin density at the copper nucleus as derived from the epr hyperfine spectral data of these two copper complexes. Incidentally, we note that the magnitude of χ_R is even smaller than that of χ_{CR}. We conclude that the role of crystal field in contributing to the spin density at the site of copper nucleus in the case of copper pthalocyanin and cesium copper chloride is of very little importance although the symmetry of the copper ion largely deviates from cubic.

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