An SCF Study of Spin Density in the CoCl$_2^-$ Ion

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SCF calculations on the free CoCl$_2^-$ ion are reported, some of the results of which have already been discussed in the literature in connection with polarised neutron scattering experiments. The effect of basis sets is studied in some detail. Spin densities and deformation charge densities are also given. A set of thermally averaged structure factors is calculated directly from the molecular wavefunction and compared with a set of experimental structure factors.

Neutron scattering by crystals arises by interaction with atomic nuclei and by the magnetisation density originating from unpaired electron spin-density. Consequently the distribution of unpaired electrons in open shell molecules can be probed using neutrons. If the neutron beam is polarised it is easier to extract the intensity of scattering caused by unpaired spin-density. In a typical experiment a paramagnetic substance is placed in a magnetic field and the scattering of a beam of neutrons first polarised parallel and then antiparallel to the magnetic field is then measured. As a result the flipping ratio, which is the ratio of intensities of scattered neutrons with spin parallel to the field, to those with spin antiparallel, can be obtained. It can be expressed as

$$R = \frac{(F_N + F_M)^2}{(F_N - F_M)^2}$$

(1)

where $F_N$ is the nuclear structure factor for the unit cell and $F_M$ is the magnetic structure factor. Providing $F_N$ is known from an unpolarised neutron experiment, $F_M$, the structure factor contribution arising from unpaired spin density alone, can be obtained. $F_M$ itself is the Fourier transform of the time average of the magnetisation density, $\langle \rho_M(r) \rangle$

$$F_M(S) = \int \langle \rho_M(r) \rangle \exp(iS \cdot r) \, dr$$

(2)

and is a function of $s$, the scattering vector. The magnetisation density $\rho_M(r)$ differs from the spin density by the orbital contribution to the magnetisation. This increases the spherical component of the structure factors by a factor $\frac{3}{2}g$ as well as a small extra correction, which in the case of the CoCl$_2^-$ may be estimated using the dipole approximation. In other systems where the orbital component is much larger, better approximations than this must be employed. Thus, subject to the uncertainties arising from extinction, multiple scattering and the orbital component to the magnetisation density, the magnetic structure factor is directly related through a Fourier transform to the electron spin-density [eqn (2)]. In practice the extraction of a spin-density distribution requires modelling procedures. Two models have been used to analyse polarised neutron data. In the first model, based on techniques developed for X-ray diffraction, the static electron density is expressed as a sum of pseudoatom densities

$$\rho(r) = \sum_k \rho_k(r_k)$$

(3)

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with $\rho_k(r_k)$ being the density centred around each atom $k$. $\rho_k$ are themselves developed as a multipole expansion:

$$\rho_k(r_k) = \sum_l \sum_{m=0}^l \rho_{klm} r_k^{-l} Y_{lm}^*(\theta_k, \phi_k).$$  \hspace{1cm} (4)

An alternative model begins with a simple molecular-orbital model and generates the atomic densities in terms of products of these orbitals. This method allows 'chemical intuition' to be used in the development of the model and the results can be expressed in familiar chemical terms. In its most recent form this model is made equivalent to a complete multipole expansion to some chosen order.  

This technique is in its infancy. Among the few systems examined for unpaired spin densities are CoCl$_2^-$, CrF$_6^-$ and Ni(NH$_3$)$_4$(NO$_2$)$_2$. Parallel theoretical studies of these systems have been made and comparisons of the theory and experiment have been given in previous publications.  

The details of the calculations for CoCl$_2^-$ are presented in this paper. This is part of a continuing study of transition-metal complexes which have been examined by polarised neutron scattering. The general purpose is to investigate which level of calculation is needed to obtain concordance between theoretical and experimental spin-densities. We have already published detailed comparisons of the spin densities from $\textit{ab initio}$ Hartree-Fock (HF) calculations and those from experiment.  

It is the purpose of this paper to present details of these calculations, to examine the spin- and charge-densities associated with the resulting wavefunctions and to extend the comparison with experiment to include structure factors. 

It is not surprising that CoCl$_2^-$ has been included among the first molecules to be examined with polarised neutrons; it is comparatively simple and a considerable amount of accurate structural, spectral and magnetic data exist for this ion. Most theoretical work has been semi-empirical, using the ligand-field model, but two previous $\textit{ab initio}$ studies have been performed, one by Hillier et al. and the other by Barber et al. The former employed the restricted Hartree-Fock method with near a double-zeta quality basis and the latter used both the Xα and the unrestricted Hartree-Fock method with a rather small Co basis set.

**Electronic Structure and Ionic Geometry**

CoCl$_2^-$ has an $e^4t_{2g}^4A_2$ ground-state. Because our main interest is in spin-density distributions, the majority of our calculations employed the unrestricted Hartree-Fock (UHF) method, which enables areas of excess $\alpha$- as well as $\beta$-spin to be determined, and hence spin polarisation can be observed. We use it in this paper to calculate the spin and charge densities, bond lengths and structure factors for the CoCl$_2^-$ ion. In all cases the expectation value $\langle S^2 \rangle$ differed from the expected value of 3.75 by at most 0.2%, indicating that the spin contamination introduced by the use of the UHF method is small.

**Selection of Basis Sets**

A weakness in many previous $\textit{ab initio}$ investigations of transition-metal systems has been the use of rather restricted basis sets. There have only been a few careful basis-set studies on such molecules, in contrast to the extensive basis-set information which has been built up for earlier elements in the periodic table. Even the investigations which have been carried out have not examined the use of ionic bases, as opposed to atomically optimised sets, although many transition-metal compounds are appreciably ionic. Justification for this is to be found in the remark of Bagus and Schaefer to the effect that any basis which adequately describes neutral Mn should do a fair job of...
Initial molecular calculations were performed with the (9s5p3d) basis of Roos et al.\textsuperscript{11} contracted to a single-zeta set. Because of the importance of a diffuse set of \textit{d}-functions in reproducing the energy difference between the \textit{s}^2\textit{d}^\textit{**}, \textit{sd}^\textit{**} and \textit{s}\textit{d}^\textit{**2} configurations of the first transition series, this basis was supplemented by a diffuse \textit{d}-function. To complement this set the single-zeta basis of McLean and Chandler\textsuperscript{12} was employed. All other calculations used their double-zeta chlorine basis. The first double-zeta (DZ) basis adopted for Co was that of Wachters, contracted as in the original paper,\textsuperscript{10} [table 1, entry (2)]. While a very large basis should be flexible enough to account for bonding involving Co, Co\textsuperscript{+} or Co\textsuperscript{2+}, it is doubtful whether the basis in entry (2) is large enough to accomplish this task. Trial calculations on the atom and ions were misleading on this point. Whereas there is a lowering of 0.011 hartree on optimising the basis for Co\textsuperscript{+} a lowering of only 0.007 hartree is obtained for Co\textsuperscript{2+}, indicating that perhaps the Co basis is adequate for an ion in which the Co formal charge is +2. However, while the energy improvement for Co\textsuperscript{2+} is negligible there is nevertheless a considerable change in the outer orbital exponents, and in the molecular calculations of table 1, entry (3), it is seen that changing to the Co\textsuperscript{2+} basis is important, leading to an energy improvement of 0.020 hartree. This basis\textsuperscript{1} was used to optimise the Co—Cl bondlength while maintaining the tetrahedral geometry, giving the Co—Cl length of 249.3 pm. Further basis-set improvements were made on this geometry. One of the known deficiencies of the Wachters basis is the lack of functions to describe the \textit{p} orbital, which is important in covalent interactions with transition metals. This deficiency is rectified in entry (5) where a set of more-diffuse \textit{p}-functions have been added. Their exponent was chosen using the even-tempered criterion of Ruedenberg et al.\textsuperscript{13} It is seen that this extension of the basis lowers the total CoCl\textsubscript{2} energy significantly, by 0.02 hartree. Further improvement can be made by optimisation of the \textit{p}-exponent as in entry (6), but the small lowering in energy (0.003 hartree) hardly makes this worthwhile. As discussed above, Roos et al.\textsuperscript{11} have indicated that a more-diffuse set of \textit{d}-functions is important. This extension is made in entry (7) with a \textit{d}-exponent optimised for the \textit{3d}^\textit{**} configuration of the atom by Hay.\textsuperscript{14} A further gain of 0.014 hartree is obtained from this change. Consideration of the work of Hood et al.\textsuperscript{15} on TiH\textsubscript{4} suggests the basis set of entry (8). In this basis the most important changes are the

\textsuperscript{1}The 14s9p5d Co\textsuperscript{2+} basis set in the contraction 6211111/5112/32 follows in the form exponent (atomic): \textit{s}—functions: 301.343 (0.000 604) 44 785.1 (0.004 443) 10 269.1 (0.022 827) 2910.59 (0.093 012) 935.54 (0.292 175) 353.762 (0.673 995) 140.083 (0.669 443) 57.9851 (0.362 013) 20.5790 (1.0) 8.5278 (1.0) 2373.21 (10) 0.953 365 (1.0) 0.124 281 (1.0) 0.044 172 (1.0); \textit{p}—functions: 1835.93 (0.003 283) 432.998 (0.027 748) 59724 (0.126 637) 53.1708 (0.364 489) 22.1839 (0.598 187) 9.75387 (1.0) 4.083 96 (1.0) 1.696 024 (0.713 562) 635 275 (3.343 175); \textit{d}—functions: 48.6164 (0.026 248) 13.576 106 (0.159 776) 4.550 46 (0.429 594) 1.533 179 (0.094 243) 0.468 179 (1.0).
<table>
<thead>
<tr>
<th>entry</th>
<th>cobalt basis</th>
<th>Co/Co$^{2+}$</th>
<th>chlorine basis</th>
<th>$R_{Co-Cl}$/pm</th>
<th>remarks</th>
<th>energy /hartree</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9s5p4d/3s2p2d</td>
<td>Co$^{2+}$</td>
<td>12s5p/4s2p</td>
<td>226.3</td>
<td>Roos et al.$^{13}$ Co$^{2+}$, with added diffuse d-function ($\alpha = 0.2$), McLean and Chandler$^{12b}$ Cl</td>
<td>-3213.45529</td>
</tr>
<tr>
<td>2</td>
<td>14s9p5d/8s4p2d</td>
<td>Co</td>
<td>12s5p/6s4p</td>
<td></td>
<td>original Wachters$^{10}$ basis set, McLean and Chandler$^{12b}$ Cl</td>
<td>-3219.51124</td>
</tr>
<tr>
<td>3</td>
<td>14s9p5d/8s4p2d</td>
<td>Co$^{2+}$</td>
<td>12s5p/6s4p</td>
<td></td>
<td>primitive set optimised for Co$^{2+}$, with Wachters' contraction</td>
<td>-3219.53087</td>
</tr>
<tr>
<td>4</td>
<td>14s9p5d/8s4p2d</td>
<td>Co$^{2+}$</td>
<td>12s5p/6s4p</td>
<td>249.3</td>
<td>bond-length optimised using basis (3)</td>
<td>-3219.56188</td>
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<tr>
<td>5</td>
<td>14s10p5d/8s5p2d</td>
<td>Co$^{2+}$</td>
<td>12s5p/6s4p</td>
<td></td>
<td>add a p-function ($\alpha = 0.28$) to basis (4)</td>
<td>-3219.58146</td>
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<tr>
<td>6</td>
<td>14s10p5d/8s5p2d</td>
<td>Co$^{2+}$</td>
<td>12s5p/6s4p</td>
<td></td>
<td>diffuse p-function in basis (5) optimised to ($\alpha = 0.19$)</td>
<td>-3219.58462</td>
</tr>
<tr>
<td>7</td>
<td>14s10p6d/8s5p3d</td>
<td>Co$^{2+}$</td>
<td>12s5p/6s4p</td>
<td></td>
<td>diffuse d-function ($\alpha = 0.1219$) added to basis 5</td>
<td>-3219.59537</td>
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<tr>
<td>8</td>
<td>14s11p6d/10s8p3d</td>
<td>Co</td>
<td>12s5p/6s4p</td>
<td>226.3</td>
<td>Wachters' basis$^{10}$ contracted to 10s6p2d with 2p-functions ($\alpha = 0.2458, 0.0967$) and a single d-function ($\alpha = 0.1219$) added</td>
<td>-3219.62791</td>
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<tr>
<td>9</td>
<td>14s9p5d/8s4p2d</td>
<td>Co$^{2+}$</td>
<td>12s5p/6s4p</td>
<td>226.3</td>
<td>RHF calculation with basis 3</td>
<td>-3219.50241</td>
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Table 2. Energies of the outer orbitals in CoCl$_2^-$

<table>
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<tr>
<th>m.o.</th>
<th>calculation $^8$α</th>
<th>calculation $^8$β</th>
<th>RHF</th>
<th>calculation $^b$</th>
<th>RHF</th>
<th>calculation $^c$α</th>
<th>calculation $^c$β</th>
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<tr>
<td>10t$_2$</td>
<td>-0.0838</td>
<td>0.1059</td>
<td>0.1019</td>
<td></td>
<td>-0.1196</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2t$_1$</td>
<td>-0.0890</td>
<td>-0.0862</td>
<td>-0.1174</td>
<td>-0.0862</td>
<td>-0.1193</td>
<td>-0.1157</td>
<td></td>
</tr>
<tr>
<td>3e</td>
<td>-0.1027</td>
<td>-0.0911</td>
<td>-0.1244</td>
<td>-0.0984</td>
<td>-0.1363</td>
<td>-0.1293</td>
<td></td>
</tr>
<tr>
<td>9t$_2$</td>
<td>-0.1347</td>
<td>-0.1061</td>
<td>-0.1318</td>
<td>-0.1123</td>
<td>-0.1619</td>
<td>-0.1386</td>
<td></td>
</tr>
<tr>
<td>8a$_1$</td>
<td>-0.3483</td>
<td>-0.2418</td>
<td>-0.2675</td>
<td>-0.3505</td>
<td>-0.4392</td>
<td>-0.3448</td>
<td></td>
</tr>
<tr>
<td>2e</td>
<td>-0.3965</td>
<td>-0.1355</td>
<td>-0.1616</td>
<td>-0.1409</td>
<td>-0.4822</td>
<td>-0.1624</td>
<td></td>
</tr>
</tbody>
</table>

$^α$ Calculation numbers refer to the entries in table 1. $^b$ From ref. (7). $^c$ From ref. (8).

Flexible contractions of the $s$- and $p$-functions. From ref. (15) it would appear that the increased flexibility of the $s$-functions nets the greatest lowering in energy. The resulting basis is probably flexible enough to accommodate changes in the Co charge without requiring further optimisation. However, the calculations of entry (8) were not made at the optimised bondlength, but at the experimental bondlength, hence there is no entry which can be compared directly with (8) to give the energy lowering resulting from this increased flexibility. If the energy change on going from the experimental to the optimum bondlength [the energy of entry (4) minus that of entry (3)] is taken to be constant (0.03 hartree) over basis sets, then the energies in entries (7) and (8) can be used to give an estimate of this lowering, of 0.06 hartree. This is less than half of the energy change wrought by increasing the $s$-flexibility alone, in Ti.$^{15}$

**Orbital Energies**

UHF orbital energies for basis set (8) and restricted Hartree–Fock (RHF) energies for basis set (3) are given along with results from Hillier et al.$^7$ and Barber et al.$^8$ in table 2. Basis set (8) is much larger than that of Barber et al.$^8$ but the relative ordering of levels remains unchanged, with the raising of the 8t$_2$ $β$-orbital above the 8a$_1$ and 2e orbitals. Also, both calculations show a large gap between the 8a$_1$ and 2e and 8t$_2$ α-orbitals. This gap was remarked upon by Barber et al.$^8$ as being inconsistent with ESCA data. They attributed the discrepancy in part to an inadequate basis set. The present basis is large enough on Co to be approaching the Hartree–Fock limit, but is still deficient in that the chlorines have no $d$-polarisation functions. Nevertheless a sizeable gap still exists and inclusion of $d$-functions would not be expected to close that markedly even though the nearest overlying orbitals are predominantly chlorine in character. Notice also that there is a considerable gap between the 2e and 8t$_2$ α- and $β$-orbitals; it being the $β$-orbitals which lie closest to the RHF orbitals.

**Spin and Charge Densities**

The axis system and cube containing the CoCl$_2^-$ unit for the discussion of spin and charge densities is shown in fig. 1.

Not all aspects of the density arising from filled or half-filled $t_2$ and $e$ sets of orbitals in the $T_d$ point group are immediately obvious. It is clear that the $e$ orbitals result in density being concentrated along the three Cartesian axes. From this it might be expected that the maximum density from the $t_2$ orbitals should lie along the bisector between pairs of Cartesian axes and hence pass through the mid-point of each cube edge in.
Spin Density in the CoCl$_2^-$ Ion

Fig. 1. Coordinate system for CoCl$_2^-$.

Fig. 2. Planes for which density plots are given, $\sigma_v =$ plane 1 and $\sigma_d =$ plane 2 in the text.

Fig. 3. \( \alpha \)-spin contours.

Fig. 4. \( \beta \)-spin contours.

Fig. 5. A superposition of both spin components.

Fig. 6. A contour plot of the total spin density.

In fact, although there is significant density along each cube edge, the maximum density passes through the corners of the cube, because of overlap between the three $d_{z^2}$-functions.

Spin-density plots are shown for the two planes illustrated in fig. 2. They are a plane containing Co and two chlorines and a plane containing the mid-point of three faces.

The spin density arising from calculations with basis set (7) will be analysed in detail and used as a reference to compare densities from other bases. Fig. (3)-(5) show, respectively, the densities in plane 1 as a contour plot, then as a three-dimensional diagram and a contour plot in plane 2. The lowest contours are assigned the value 0.000244 e.a.u.$^{-3}$ ( = 1/4096 e.a.u.$^{-3}$). Subsequent contours are each increased by a factor of 2 to an upper limit of 0.5 e.a.u.$^{-3}$. The $\alpha$-spin contours are solid lines and $\beta$-spin contours are given by dashed lines.

The largest features are close to the Co nucleus. As ligand-field theory predicts that all the spin density should lie in the $t_2$-orbitals it is expected that the density near Co should resemble that of a $d_{z^2}$-orbital. Comparison of fig. 3, showing the total spin...
Fig. 3. Spin density of CoCl$_2^-$ from table 1 [entry (7)] in plane 1 of fig. 2. Full lines represent $\alpha$-spin density, long broken lines (---) $\beta$-spin density and short broken lines (---) zero contours. The same representation is used in fig. 5-12.

Fig. 4. 3D-plot of the spin density of CoCl$_2^-$ from table 1 [entry (7)] in plane 1 of fig. 2.
Spin Density in the CoCl$_2^-$ Ion

Fig. 5. Spin density of CoCl$_2^-$ from Table 1 [entry (7)] in plane 2 of fig. 2.

Fig. 6. Density of the $\alpha$-spin $8t_2$-orbital, $\rho_{8t_2}^\alpha$.

density, with fig. 6, showing the density in the same plane from occupation of the $8t_2$-orbital, which is composed mostly of metal $d$-orbitals, bears this out. Obvious differences in the two densities occur as the distance from the nucleus increases.

Along the north–south direction in fig. 3 and centred on the Co, are two regions of negative spin-density. Four similar regions occur in fig. 5, the six of them forming an octahedral arrangement of $\beta$-spin about the Co. This almost certainly arises from spin polarisation in the filled $e$-orbitals. The 3D diagram, fig. 4, reveals more detail near the
Fig. 7. Spin density from the remaining $t_2$ valence orbitals, $\rho_{t_2}^{\text{spin}} = \rho_{s_{t_2}} + \rho_{p_{t_2}} - (\rho_{s_{t_2}} + \rho_{p_{t_2}})$.

Co nucleus showing that the double peaks there are not precisely of the same height and also revealing a sharp spike of negative density at the nucleus. Since only $s$-functions can have density at the nucleus this is attributed to spin polarisation of the $s$-orbitals.

Around the chlorine there is a sharp peak at the nucleus, a smaller, more diffuse peak 0.15 a.u. towards the Co, and a very low banana-shaped region centred about the Co–Cl bond. The peak at the nucleus implies that some spin is transferred to an $s$-orbital on the chlorine. It is more evident from the 3D surface that the spin density in the chlorine is very small. Spin away from the chlorine has its maxima on the bond axis, implying a $\sigma$-bonding framework, as expected from ligand-field theory for a tetrahedral molecule.

Some useful insights into the origin of the asymmetry in the spin density about the Co and about some of the other spin features can be gained by examining individual spin-orbitals. The orbital which carries most of the spin density about the Co is the $t_2$-orbital, which consists mainly of metal $d$-functions and is plotted in fig. 6. There is no comparable occupied $\beta$-spin orbital. Density about the Co from the $8t_2$ m.o. shows the expected mirror symmetry and the asymmetry seen in fig. 3 comes mainly from the smaller contributions from the 10$e$, 9$e$, and 8$e$ $\beta$-orbitals. These orbitals have mainly ligand $p$ character. However, it is not clear either from the m.o. coefficients or the orbital densities which $\alpha$- and $\beta$-orbitals have similar character and hence which two should be paired together to give a residual spin-density plot. Consequently the remaining outer $t_2$-orbitals have been combined to obtain the residual spin, as $\rho_{t_2}^{\text{spin}} = \rho_{s_{t_2}} + \rho_{p_{t_2}} - (\rho_{s_{t_2}} + \rho_{p_{t_2}})$, which is plotted in fig. 7. Around the Co there is a complex pattern of spin density. Most importantly it contains the elements to explain the asymmetry seen in the full spin-density plot in fig. 3. Along the north–west direction from the Co the spin in turn is positive, negative and finally farthest from the nucleus it is positive again and this positive density will add significantly to the outer regions of the $8t_2^*$-orbital density. Conversely, along the south–west direction the spin is negative,
Spin Density in the CoCl$_{4}^-$ Ion

Fig. 8. The spin density of the 2e-orbitals in CoCl$_{4}^-$.  

positive and finally negative again so that this last region again significantly affects the $t_2^6$ density. This means that in the total density the $t_2^6$ density is drawn in towards the Co along the south-west direction and expanded outwards along the north-west direction. This arises from admixture of metal $p$- and $d$-orbitals to give a product of octopole ($f$-orbital) symmetry in the density. Also the low $\beta$-spin peak along the Co–Cl bond has its origin in this same diffuse $\beta$ density along the bond in fig. 7. For the region around Cl, it is clear from fig. 6 and 7 that the density gets roughly equal contributions from $\rho_{\alpha}^*\alpha$ and $\rho_{\beta}^*\beta$.

The remaining major features in fig. 3 come from the 2e-orbitals. Fig. 8 shows a plot of $\rho_{2e}^\alpha - \rho_{2e}^\beta$, which illustrates the difference in radial extent of the $\alpha$ and $\beta$ spin-orbitals.

Spin polarisation in cobalt $s$-orbitals causes the sharp negative spin peak at the Co nucleus, but this polarisation is not solely confined to one of the $a_1$-orbitals. Three orbitals $8a_1$, $6a_1$ and $3a_1$ are found to contribute and these contain contributions from the $4s$, $3s$ and $2s$-orbitals of Co, respectively. The last two being predominantly Co $3s$ and $2s$ in character. Two of the orbitals $8a_1$ and $6a_1$, and hence the $4s$ and $3s$ orbitals, show positive spin densities at the nucleus while the third, $3a_1$, containing the $2s$-orbital shows negative spin-density and makes the predominant contribution at the nucleus. Because of the limitations inherent in Gaussian orbitals, quantitative estimates of this spin density at the nucleus are not given here, but these results are in qualitative agreement with numerical Hartree–Fock results of Watson and Freeman$^{16}$ who found spin densities at the nucleus for the $2s$- and $3s$-orbitals of Mn$^{2+}$ of $-7.15$ a.u. and $3.22$ a.u., respectively.

The interesting thing about the calculated spin density of CoCl$_{4}^-$ is that it is very stable to change in the basis. The cobalt bases range from single-zeta to triple-zeta in the valence region, and yet there are no radical differences in the spin-density plots. Fig. 9–12 show plots obtained using several of the basis sets from table 1. These densities
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Fig. 9. The spin density of $\text{CoCl}_4^{2-}$ from the basis shown in table 1 [entry (1)].

Fig. 10. The spin density of $\text{CoCl}_4^{2-}$ from table 1 [entry (3)].
Spin Density in the CoCl$_4^{2-}$ Ion

Fig. 11. The spin density of CoCl$_4^{2-}$ from table 1 [entry (4)], i.e. with the bondlength optimised.

Fig. 12. The spin density of CoCl$_4^{2-}$ from table 1 [entry (8)].
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Fig. 13. The spin density of \( \text{CoCl}_2^- \) from a RHF calculation [table 1, entry (9)].

Fig. 14. The deformation density of \( \text{CoCl}_2^- \) from table 1 [entry (7)], in plane 1 of fig. 2. Full lines represent positive contours, long broken lines (-----) represent negative contours, and short broken lines (---) zero contours. The same representation is used in fig. 15 and 16.
Spin Density in the CoCl$_4^{2-}$ Ion

are best discussed by comparing them with the spin density analysed at length above and shown in fig. 3. Compared with this reference, it can be seen that the single-zeta calculation (fig. 9) has a reduced polarisation contribution from the e-orbitals. In addition, the peak of positive spin density centred on Co is slightly contracted compared with the reference. The spin on the chlorine is also higher, but as previously pointed out the amount of spin on the chlorine is very small so this does not constitute a significant change. With the double-zeta basis [entry (3) of table 1] (fig. 10) the spin polarised e-orbital density has risen to be similar to the reference, the peak around Co has expanded slightly and the extremely low peak behind the chlorine has been reduced, but the excess size of the almost insignificant rise in $\beta$ spin-density along the Co–Cl bond direction has persisted. Further minor changes, which are most evident around the chlorine, occur when the bond length is optimised (fig. 11), but it must be emphasised that while these changes are easy to see on the contour plots they are nevertheless very minor changes. With the lengthening of the bond on optimisation the main Co feature becomes less distorted. Addition of a diffuse p-function again only makes minor changes. Finally, even with the largest of the basis sets (fig. 12), there are only minor changes when compared to the reference; the spin is spread more broadly around the chlorine and the $\beta$-spin rise along the bond is larger.

For comparison, fig. 13 contains a spin-contour plot from an RHF calculation. It should be compared to fig. 10, which was obtained from the same basis. The RHF spin-density comes from the sum of the densities of the three half-occupied $t_2$ m.o. The positive features of the two plots are very similar, but of course the RHF calculation cannot give any of the $\beta$-spin arising from spin polarisation. It is interesting to note that the positive features of the RHF density come from just the 10$t^2$-orbitals whereas in the UHF density, the 8$t^2$, 9$t^2$ and 10$t^2$-orbitals are required to obtain the same approximate features.

Deformation Density

The deformation density is defined as

$$
\rho_d(r) = \rho_{mol}(r) - \sum_{\text{atoms}} \rho_a(r)
$$

where $\rho_{mol}(r)$ is the molecular density-distribution-function and $\rho_a(r)$ is the spherically averaged atomic density calculated in the same basis as used in the ion. In cases where polarisation functions are added to the molecular wavefunction they are not included in the atomic density.

The deformation density is examined for three of the calculations reported here. First the double-zeta plus polarisation (DZP) calculation from entry (7) of table 1 is discussed (fig. 14 and 15) and secondly the deformation densities of UHF and RHF calculation with the same basis [entries (9) and (3) of table 1] are compared.

The DZP density in fig. 14 shows a negative region on Co which, in the same way as in the spin plots, loses the symmetry of the $d_{yz}$-orbitals, by the admixture of p-orbitals into the wavefunction. Also seen are positive regions with the symmetry of e-orbitals which have slightly more density than the negative regions. The apparent anisotropy of the metal d-orbitals is caused by two effects. The major one is just a consequence of the definition of the deformation density in that spherical ions are subtracted. Because of spherical averaging each of the d-orbitals of the metal ion has an occupation of 1.4, whereas in the molecule the configuration is ca. $d_{3z^2-r^2}$,$d_{yz}$,$d_{xy}$,$d_{x^2-y^2}$,$d_{x^2}$. Consequently the difference density will show a build-up of charge in the e-orbitals and a deficiency in the $t_2$-orbitals. The second effect comes from the delocalisation of charge from the ligands on bonding. The small positive region near the mid-point of the bond indicates a build-up of bonding density from $\sigma$-donation to the metal 4s, 4p- and 3d-orbitals.
Table 1 [entry (7)] in plane 2 of fig. 2.

Fig. 15. The deformation density of CoCl$_4^{2-}$ from table 1 [entry (7)] in plane 2 of fig. 2.

Fig. 16. Difference density $\rho^{\text{UHF}} - \rho^{\text{RHF}}$ [entries (3) and (9) of table 1]: (a) contour plot; (b) 3D-plot.

Fig. 15 shows the deformation of fig. 14 in plane 2 of fig. 2. There are four positive regions of $e$-type symmetry of the same height as in fig. 14. Between these, there are four negative regions of $t_2$ symmetry† which have less density than in fig. 14. At large distances from the nucleus (ca. 3 a.u.) there is a low circular region of density. This is attributed to the effect of polarisation functions, mostly diffuse $s$-functions. The ionic orbitals used here contains two $4s$-functions, but they contribute little to the ionic wavefunction. In the molecular wavefunction, however, the $4s$-functions have larger coefficients, leading to the low positive circular region from the Co.

The deformation density from the UHF and RHF calculations of entries (3) and (9) of table 1 are almost identical. To show the small difference fig. 16 contains a plot of $\rho^{\text{UHF}} - \rho^{\text{RHF}}$. The largest feature is the negative peak at the Co nucleus seen in

† $t_2$-Orbitals have density along the edges of a cube, with the maximum at the corners.
Spin Density in the CoCl$_2^-$ Ion

The 3D plot, indicating a loss of electrons from near the nucleus. The other cobalt features are a distorted double peak in the same region as the peaks from the $t_2$ d-orbitals, and a negative region along the north-south axis. All features can be rationalised in terms of spin-polarisation effects. The peak at the nucleus arises from the same polarisation of the s-orbitals seen in fig. 4. The positive regions arise from a migration of $\alpha$-spin density into the $t_2$-region. This leaves behind an excess of $\beta$-spin density seen along the north-south axis.

Spin Structure Factors

A more direct comparison can be made with experiment through the spin structure factors

$$F_{\text{spin}}(S) = \sum_{j=1}^{M} f_j^{\text{spin}}(S) \exp (iS \cdot r_j)$$

(6)

where there are $M$ molecules in the unit cell. A neutron diffraction study of the Cs$_2$CoCl$_4$ crystal$^{17}$ showed the space group to be 14/mcm with the Co atoms at special positions $b$; the chlorines of each CoCl$_2^-$ unit are at positions $l$, on a mirror plane and each unit cell contains four asymmetric units. The importance of the unit-cell information is that it establishes that the structure factor can simply be written as

$$F_{\text{spin}}(S) = 4f_j^{\text{spin}}(S)$$

(7)

where $f_j^{\text{spin}}(S)$ is the molecular spin scattering factor. Here $f_j^{\text{spin}}$ can be expanded as

$$f_j^{\text{spin}}(S) = f_j^\alpha(S) - f_j^\beta(S)$$

(8)

where the superscripts $\alpha$ and $\beta$ refer to $\alpha$- and $\beta$-spins. The molecular spin scattering factors can be written as

$$f_j^\alpha(S) = \int \rho_j^\alpha(r) \exp (iS \cdot r) \, dr.$$  

(9)

In the LCAO method the $\alpha$-spin density function is, where the $j$ subscript has been omitted for convenience,

$$\rho_j^\alpha(r) = \sum_{rs} P_{rs}^\alpha \chi_j^r(r) \chi_j^s(r)$$

(10)

where $P_{rs}^\alpha$ is the $\alpha$-spin density matrix, and $\chi_j^r$ and $\chi_j^s$ are contracted Gaussian functions. Substituting into eqn (9) yields

$$f_j^\alpha(S) = \sum_{rs} P_{rs}^\alpha \int \chi_j^r(r) \chi_j^s(r) \exp (iS \cdot r) \, dr = \sum_{rs} P_{rs}^\alpha X_{rs}(S)$$

(11)

where $X_{rs}(S)$ are the generalised scattering factors of Stewart.$^{18}$ In the case where the generalised scattering factors are constructed from Gaussian orbitals, the integrals involved can be performed analytically.$^{19}$ Consequently the evaluation of molecular spin scattering factors from wavefunctions built from Gaussian functions can be programmed in a straightforward manner.$^{20}$

The experiment, however, measures thermally averaged structure factors and hence in the practical situation eqn (6) has to contain a temperature factor. By analogy with the usual treatment of thermal motion in structural studies, where each atom is considered to move independently, each generalised scattering factor in eqn (6) is multiplied by its own temperature factor, so that

$$f_{\text{dyn}}(S) = \sum_{rs} P_{rs} X_{rs}(S) T_{rs}(S)$$

(12)
is the dynamic, molecular scattering factor. Here the temperature factor, $T_n$, associated with each pair of orbitals $\chi_r$ and $\chi_s$, is approximated by the anisotropic Debye-Waller model. When $\chi_r$ and $\chi_s$ are both on the same centre the spin density is assumed to move in the same way as the nucleus. Hence, the atomic thermal parameters are applied to each one-centre density.

The behaviour of two-centre terms in the density function under thermal motion is not so clear, although it can be approximated in terms of the motions of the two nuclei. Four such approximations were tested, three of which average the motion over the two nuclei, while the fourth neglects entirely the thermal motion of the two-centre terms.

The temperature factor for the orbital product $\chi_r \chi_s$ can be expressed as

$$T_n(S) = \exp \left( -\frac{1}{2} \mathbf{S}^\dagger \mathbf{U}_n \mathbf{S} \right)$$

(13)

where $\mathbf{U}_n$ is the mean-square displacement matrix of the orbital product. Stewart has used two approximations to $T_n$. The procedure followed was to use the probability distribution-function for each atom to form a probability distribution-function for the mid-point of the bond. The average probability distribution-function was then Fourier transformed to obtain the two-centre temperature factor in terms of an average mean-square displacement matrix,$^{18}$

$$T_n(S) = \exp \left[ -\frac{1}{2} \mathbf{S}^\dagger g (\mathbf{U}_A + \mathbf{U}_B) \mathbf{S} \right],$$

(14)

where $\mathbf{U}_A$ and $\mathbf{U}_B$ are the displacement matrices of atoms A and B, respectively. When the motions of atoms A and B are uncorrelated, i.e. they move independently and the factor $g$ is $\frac{1}{2}$. When the motions are correlated, in a rigid rod translation, $g$ is $\frac{1}{2}$. These two cases will be referred to as models 1 and 2, respectively. Coppens et al.$^{22}$ have used a different approach. They approximate the temperature factor of the mid-point of the bond by the average of the temperature factors of each atom, rather than by the average of the distribution functions. This leads to the expression

$$T_n(S) = \frac{1}{2} \left[ \exp \left( -\frac{1}{2} \mathbf{S}^\dagger \mathbf{U}_A \mathbf{S} \right) + \exp \left( -\frac{1}{2} \mathbf{S}^\dagger \mathbf{U}_B \mathbf{S} \right) \right]$$

(15)

which will be referred to as model 3. In the fourth model, $T_n$ is assumed to be zero if $\chi_r$ and $\chi_s$ are on different centres. Thus the thermally smeared theoretical spin structure-factor can be expanded in terms of the thermally smeared scattering factors, $f_{\text{syn}}$

$$F_{\text{syn}}(S) = \sum_{j=1}^{M} f_{\text{syn}}(j) \exp \left( iS \cdot \mathbf{r}_j \right).$$

(16)

The effect of each of these models was checked using the double-zeta wavefunction derived from entry (4) of table 1. The set of 66 even structure-factors, which are also available from experiment,$^{23}$ were calculated. All the structure factors are decreased by the effect of thermal motion, as they must be, but the important question is whether there is any significant difference between the different models for treating the two-centre terms in the density. A simple method of comparison is to use the residual index, or $R$ factor

$$R = \frac{\sum |F_e| - |F_o|}{\sum |F_o|}$$

(17)

with $F_e$ being the static structure-factor, $F_o$ the calculated dynamic structure-factor and the summation being over all 66 reflections. The $R$ factors for each model are collected in table 3. The effect of thermal motion is comparatively small because the low temperature at which the thermal factors were obtained (4.2 K) and because of the high atomic weight of the atoms involved. Quite evidently each model produces essentially identical results for these low thermal factors. Consequently model 1 was chosen for more extended structure factor investigations.
An extended set of structure factors was calculated using the large basis of Hood et al.\textsuperscript{13} [table 1, entry (8)]. 423 structure factors were calculated for most allowed values of \( h, k \) and \( l \) up to \( \sin \theta / \lambda = 0.72 \text{Å}^{-1} \). The series is complete in \( h \) and \( k \), but for reasons of computational cost \( l \) has a maximum of 12. There are three reasons for making these calculations. First, such a large data set as this is not experimentally available, so the calculated structure factors, coming as they do from a completely defined spin density, can be used to test the applicability of pseudooatom models in the least-squares fitting process. The results of this investigation have been reported elsewhere.\textsuperscript{4} Secondly, it is possible, in principle, to obtain the spin density by taking the inverse Fourier-transform of the structure factors. However, such attempts must be hampered by truncation errors. Having available a set of theoretical structure-factors which can, at least in principle, be extended as far as desired enables an investigation of these truncation effects. The results of such an investigation using the 423 structure factors from above have been communicated already.\textsuperscript{4} Unfortunately, the symmetry of the Cs\textsubscript{2}CoCl\textsubscript{4} crystal is low enough for the number of reflections to increase rapidly as the radius of the Ewald sphere increases. As a result, a thorough investigation of truncation effects is prohibitively expensive for CoCl\textsubscript{2}-. Employing a higher symmetry crystal such as K\textsubscript{2}NaCrF\textsubscript{6} allows a more complete study to be made.\textsuperscript{24}

The third reason for generating the structure factors from the best HF basis-set was to enable a more direct comparison with the experimental data. This bypasses the use of a model in interpreting the data to get them into a form for comparison with theory. Use of the model always allows for a bias to produce what is expected chemically, to be unconsciously included. In the present case the chemical expectations must be influenced by what is known from ligand-field and Hartree-Fock m.o. theory, and so any bias is likely to tend toward agreement with HF theory.

Even at the spin structure-factor level there is still not direct comparison with experiment because the scattering samples the magnetisation density, not the spin density as calculated here. The effects of spin–orbit coupling should be included in the wavefunction to obtain a magnetisation density, but this has not yet been achieved for large molecules. In practice the experimental magnetic structure factors, \( F_{\text{mag}} \), are scaled by the experimental \( g \) factor so that they can be expressed in units of electrons. Other factors which are taken account of are multiple reflections, extinction and the spin alignment factor, \( A \), which measures the fraction of spins which are aligned by the magnetic field. So a magnetic structure factor \( F_{\text{mag}} \) corrected for multiple reflections and extinction is scaled by \( g \) and \( A \) to give a scaled structure factor:

\[
F_{\text{mag}}^{\text{scale}} = \frac{2}{g} F_{\text{mag}} \frac{1}{A}.
\]

A set of 66 structure factors treated as in eqn (18) was taken from Figgis et al.\textsuperscript{23} and is compared with thermally averaged theoretical spin structure-factors in fig. 17, where the structure factors are plotted against \( \sin \theta / \lambda \). The concordance between the two sets of data was measured by the \( R \)-factor [eqn (17)], which has a value of 8.68%. It can be seen from fig. 17 that the theoretical spin structure-factors are not closely related to the experimental values. There is a large difference between the theoretical and experimental spin structure-factors. At low \( \sin \theta / \lambda \) the experimental values are substantially smaller than the theoretical ones. At high \( \sin \theta / \lambda \) the reverse is true. For a small region...
Fig. 17. Experimental and theoretical spin structure factors for CoCl$_4^{2-}$: (×) experimental; (+) theoretical.

around $\sin \theta / \lambda = 0.4$ there is close agreement between the experimental data and theory. Consequently, it can be concluded that theory has shifted density from near the nucleus and put it into regions more distant from the nucleus.

**Concluding Remarks**

The present study of the tetrachlorocobaltate ion is intended to provide data with which to test models currently used in the analysis of polarised neutron scattering experiments and at the same time to test the performance of HF calculations against the experimental findings. At the qualitative level there is good agreement between the theoretical and experimental spin-density plots. Somewhat surprisingly it was found that the spin density is very stable to basis-set change.

However, at the more quantitative level, as shown by the comparison of calculated and experimental spin structure-factors, it is seen that there is considerable disagreement. These are undoubtedly due to inadequacies in the theoretical treatment. The major deficiencies in order of their probable importance for CoCl$_4^{2-}$ are: (1) neglect of the effect of neighbouring ions in the crystal lattice; (2) neglect of correlation effects; and (3) an inadequate compensation for spin–orbit coupling. We are currently continuing our investigations by examining each of these possibilities.
References


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