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Electron Spin Resonance Spectra of Low-Symmetry High-Spin Cobalt(II) Complexes. 4.[1] Tetragonal-Octahedral Dichlorotetrakis(pyridine)- and Dichlorotetrakis(pyrazole)cobalt(II)

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The ESR spectra of tetragonal-octahedral dichlorotetrakis(pyridine)- and dichlorotetrakis(pyrazole)cobalt(II) have been recorded. The former yields $g_\parallel = 3.33$ and $g_\perp = 4.46$, and the latter yields $g_1 = 2.14$, $g_2 = 4.55$, and $g_3 = 5.83$. The g values of tetragonal-octahedral complexes are related to the bonding abilities of axial and equatorial ligands. Quantitative angular overlap calculations allowed us to reproduce the g values and the energies of the electronic transitions. The e_π values are discussed.

Introduction

The ESR spectra of high-spin cobalt(II) complexes have been shown to be extremely sensitive to low-symmetry components of the ligand field,[1-7] making their interpretation on the basis of the spin-Hamiltonian approach rather vague and uninformative.

We have recently started a program of characterization of the ESR spectra of low-symmetry high-spin cobalt(II) in order to check how they can be interpreted with the use of an angular overlap approach. Tetragonal-octahedral complexes appear to be particularly interesting in this respect, since it has been shown that the magnetic properties depend essentially on the π metal–ligand interactions,[8] which are easily accounted for in the angular overlap formalism.

It appeared interesting for us to study the $Co(py)_4Cl_2$ and $Co(pyz)_4Cl_2$ complexes (py = pyridine; pyz = pyrazole), for which crystal structure determinations are available,[9,10] since recently there has been some debate on the values of the e_π parameters of pyridine ligands with transition-metal ions.[11,12]

Experimental Section

$Co(py)_4Cl_2$ was prepared as previously described[8] and stored under an atmosphere saturated with pyridine. Single crystals were obtained by slow evaporation of acetone solutions containing an excess of pyridine and oriented on a Perspex rod with the aid of a polarizing microscope.

$Co(pyz)_4Cl_2$ was prepared as described for $Ni(pyz)_4Cl_2$[10] by using pyrazole in excess. Single crystals obtained from acetone solution were found to be isomorphous to the nickel ones with the use of a Philips PW 1100 diffractometer with Mo Kα radiation with prominent faces (110), (001), and (1$\bar{1}$0). The cell parameters are $a = 13.69$ Å, $b = 9.31$ Å, $c = 14.81$ Å, and $\beta = 116.6°$.

Single-crystal ESR spectra down to 4.2 K were recorded with the apparatus previously described.[3]

Table I. Principal g Values and Directions for $Co(pyz)_4Cl_2$

		a^*	b	c
g_1	4.55 ± 0.08	0.8684	0.4692	0.1611
g_2	5.83 ± 0.02	−0.2701	0.7196	−0.6397
g_3	2.14 ± 0.03	−0.4161	0.5119	0.7515

Results

The polycrystalline powder spectra of undiluted $Co(py)_4Cl_2$ and $Co(pyz)_4Cl_2$ are shown in Figure 1.

The spectra of $Co(pyz)_4Cl_2$ are clearly axial, with $g_\parallel = 2.3$ and $g_\perp = 4.5$. The spectra of $Co(py)_4Cl_2$ are less readily interpreted. Although every precaution was taken to avoid loss of pyridine when the crystals were ground, by operating in a glovebox under an atmosphere saturated with pyridine, we believe that some decomposition does occur. The single-crystal spectra confirmed that the complex is tetragonal at 4.2 K, yielding $g_\parallel = 3.33$ and $g_\perp = 4.46$. No sign of decomposition of the crystal was observed.

The crystal of $Co(pyz)_4Cl_2$ was rotated along two orthogonal directions, whose direction cosines in the monoclinic cell are

a^*	b	c
0.5990	0.8008	0.0
0.8008	−0.5990	0.0

The angular dependence of the g^2 values in the two planes is shown in Figure 2. The principal g values and directions were obtained by the method suggested by Weil,[13] and they are shown in Table I.

The single-crystal spectra reveal that the g values are actually rhombic. The lowest g value $g_1 = 2.14$ is found to be quite close to the Co–Cl bond direction (see Figure 3), making an angle of ~5° with it, while the in-plane g axes are found to be quite close to the bisectors of the bond angles. In particular the highest g value $g_2 = 5.83$ is found to bisect the bond angles which are smaller than 90°.

The ESR signals for the two complexes are broad (typically ~500 G) and in no case was hyperfine splitting detected. We were not able to obtain crystals doped into suitable isomorphous complexes; therefore only the data relative to the pure complexes are reported.

Discussion

Despite the similarity of the two complexes, both of which are *trans*-dichloro octahedral with four heterocyclic nitrogen donor atoms in the plane, the g values are somewhat different. In particular $g_\parallel$ is distinctly smaller in the pyrazole as compared to the pyridine derivative and $g_\perp$ is appreciably split in the former.

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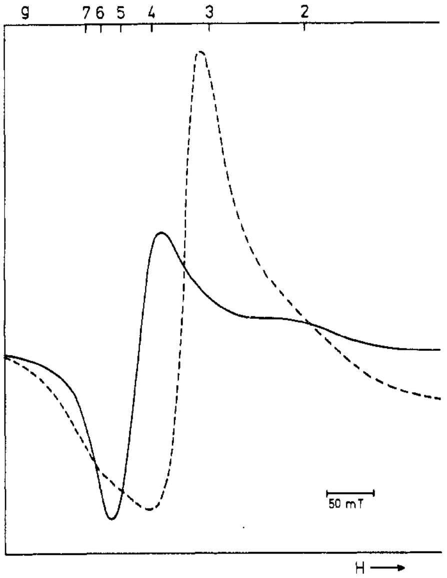

Figure 1. Polycrystalline-powder ESR spectra at 4.2 K of undiluted $Co(pyz)_4Cl_2$ (—) and $Co(py)_4Cl_2$ (- - -).

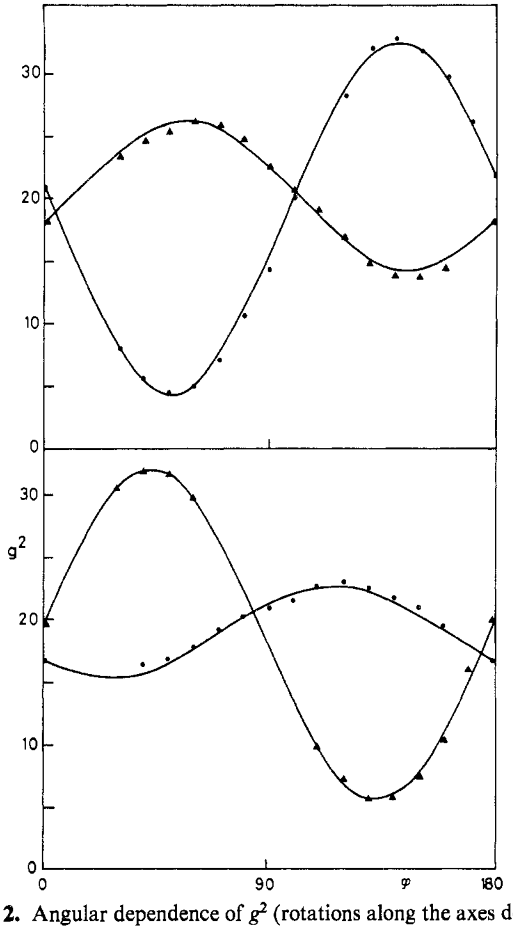

Figure 2. Angular dependence of g^2 (rotations along the axes defined in the text). The curves correspond to the least-squares fit of the experimental points.

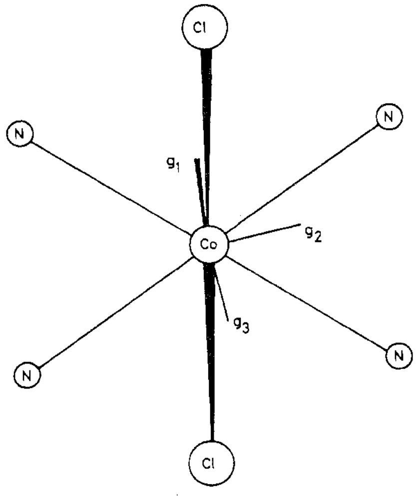

Figure 3. Orientation of principal *g* directions in the molecular frame.

The theory of ESR spectra of tetragonally distorted octahedral high-spin cobalt(II) complexes was established by Abragam and Pryce.[14] They showed that the *g*-value pattern depends essentially on the low-symmetry splitting of the ground $^4T_{1g}$ term of octahedral symmetry. Theory predicts $g_\parallel > g_\perp$ if ^4E_g lies lowest, while the reverse is true if $^4A_{2g}$ has the minimum energy. This approach is substantially correct, but it must be stressed that the splitting of $^4T_{1g}$ cannot be predicted simply on the basis of axial compression or elongation. As a matter of fact, in a first approximation[8]

$$\Delta = E(^4A_{2g}) - E(^4E_g) = E(xy) - E(xz) \qquad (1)$$

In classic ligand field terms, (1) can be expressed as (2),[15]

$$\Delta = 3Ds - 5Dt \qquad (2)$$

which shows that quadratic ligand field terms which enter into the *Ds* parameters are very important in determining the splitting. Since these are not obtained from the electronic spectra of octahedral complexes, the interpretation of Δ in terms of the nature of the ligands remains dubious, since a two-dimensional spectrochemical series should be available.

The angular overlap approach[16] is obtaining large popularity, since it uses parameters which in principle can be estimated on the basis of σ- and π-bonding ability of the ligand.

According to this model Δ can be expressed as eq 3,[8] where

$$\Delta = 4e_{\pi\perp}{}^{eq} - 2e_{\pi\parallel}{}^{eq} - 2e_\pi{}^{ax} \qquad (3)$$

$e_{\pi\perp}{}^{eq}$ and $e_{\pi\parallel}{}^{eq}$ are the parameters relative to π interaction of equatorial ligands in and out of the plane, respectively, and $e_\pi{}^{ax}$ is the axial π-bonding parameter. It has been assumed that the axial ligand is linearly ligating in order to keep tetragonal symmetry.

Relation 3 shows that Δ, and therefore the *g*-value pattern, depends essentially on the π-bonding ability of the axial and equatorial ligands.

For the complexes under study, we learn from the X-ray structure determinations[9,10] that the pyridine planes make an angle of ~45° with the plane of the metal–nitrogen chromophore, while the pyrazole planes are orthogonal to the CoN_4 plane.

Simple geometrical arguments suggest that for pyridine $e_{\pi\parallel}{}^{eq} = e_{\pi\perp}{}^{eq} = {}^1/_2 e_\pi{}^{py}$, while for pyrazole $e_{\pi\parallel}{}^{eq} = 0$ and $e_{\pi\perp}{}^{eq} = e_\pi{}^{pyz}$. Substituting these expressions into (3), one finds eq 4.

$$\Delta_{py} = e_\pi{}^{py} - 2e_\pi{}^{Cl} \qquad \Delta_{pyz} = 4e_\pi{}^{pyz} - 2e_\pi{}^{Cl} \qquad (4)$$

The observed *g* values demand that both Δ_{py} and Δ_{pyz} are negative. Since the expressions of (4) are valid in the hole formalism, $e_\pi{}^{Cl}$ is expected to be negative, corresponding to an antibonding effect on the metal orbitals. Therefore, for Δ_{py} and Δ_{pyz} to be negative, $e_\pi{}^{py}$ and $e_\pi{}^{pyz}$ must both be negative and the following relations must hold:

$$|e_\pi{}^{py}| > 2|e_\pi{}^{Cl}| \qquad |e_\pi{}^{pyz}| > {}^1\!/_2|e_\pi{}^{Cl}| \qquad (5)$$

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If bonding considerations must have any validity, an antibonding π ability for both pyridine and pyrazole with cobalt(II) is thus established.

With these considerations in mind, we attempted a quantitative fit of the g values and the electronic transitions. Octahedral cobalt(II) complexes in general show essentially two bands[17] in the regions around 6000–10 000 cm^{-1} and 20 000 cm^{-1}. Their assignment to the electronic transitions may be ambiguous.

The electronic spectra of Co(pyz)$_4$Cl$_2$ are particularly well resolved for octahedral cobalt(II) and show bands at 6500, 9300, 18 800, and 23 500 cm^{-1}, which we assign to transitions to $^4E_g(^4T_{2g})$, $^4B_{1g}(^4T_{2g})$, $^4E_g(^4T_{1g})$, and $^4A_{2g}(^4T_{1g})$, respectively. Support for this assignment comes from the spectra of the corresponding iron(II) and nickel(II) complexes.[18,19] The spectra were analyzed in the nonadditive ligand field scheme,[20] and the parameters Dq, Ds, Dt, and $\beta = B/B_0$ were obtained.[18,19] The values of the parameters are extremely similar in both the iron and nickel complexes; therefore we believe that they should not vary much in the case of the cobalt complex. As a matter of fact with use of the values reported for nickel and iron, together with the reported matrices,[21] the above-suggested assignment is confirmed. A systematic variation of the parameters showed that the best fit of the transitions could be achieved with the values $Dq = -1100/-1200$, $Ds = 1000/1050$, $Dt = 300/400$, and $B = 800/850$ cm^{-1}. Since only four experimental bands can be compared with the calculated transitions, the range of the parameters is somewhat large, but giving a narrower one would be unrealistic.

It can be shown[22] that the Dq, Ds, and Dt parameters of the nonadditive scheme are related to the angular overlap parameters for a *trans*-MA$_4$X$_2$ complex according to eq 6.

$$\begin{aligned} Dq &= \tfrac{3}{10}e_\sigma^{\text{eq}} - \tfrac{4}{10}e_{\pi\perp}^{\text{eq}} \\ Ds &= \tfrac{2}{7}e_\sigma^{\text{ax}} - \tfrac{2}{7}e_\sigma^{\text{eq}} + \tfrac{2}{7}e_\pi^{\text{ax}} + \tfrac{2}{7}e_{\pi\parallel}^{\text{eq}} - \tfrac{4}{7}e_{\pi\perp}^{\text{eq}} \qquad (6) \\ Dt &= \tfrac{6}{35}e_\sigma^{\text{ax}} - \tfrac{6}{35}e_\sigma^{\text{eq}} - \tfrac{8}{35}e_\pi^{\text{ax}} - \tfrac{8}{35}e_{\pi\parallel}^{\text{eq}} + \tfrac{16}{35}e_{\pi\perp}^{\text{eq}} \end{aligned}$$

In the case of both the pyridine and the pyrazole complexes, the number of e_λ parameters reduces to 4 with the above assumptions, which exceeds the number of the nonadditive parameters. However it is possible to obtain expressions for e_σ^{Cl}, e_σ^{py}, and e_π^{py} on one side and e_σ^{Cl}, e_σ^{pyz}, and e_π^{pyz} on the other, leaving e_π^{Cl} as an adjustable parameter.

The corresponding expressions are shown in eq 7 and 8.

$$\begin{aligned} e_\sigma^{\text{Cl}} &= \tfrac{10}{3}Dq + Ds + \tfrac{25}{6}Dt + \tfrac{2}{3}e_\pi^{\text{Cl}} \\ e_\sigma^{\text{pyz}} &= \tfrac{10}{3}Dq - Ds + \tfrac{5}{3}Dt + \tfrac{2}{3}e_\pi^{\text{Cl}} \qquad (7) \\ e_\pi^{\text{pyz}} &= -\tfrac{3}{4}Ds + \tfrac{5}{4}Dt + \tfrac{1}{2}e_\pi^{\text{Cl}} \end{aligned}$$

$$\begin{aligned} e_\sigma^{\text{Cl}} &= \tfrac{10}{3}Dq + \tfrac{35}{6}Dt + \tfrac{4}{3}e_\pi^{\text{Cl}} \\ e_\sigma^{\text{py}} &= \tfrac{10}{3}Dq - 2Ds + \tfrac{10}{3}Dt + \tfrac{4}{3}e_\pi^{\text{Cl}} \qquad (8) \\ e_\pi^{\text{py}} &= -\tfrac{3}{2}Ds + \tfrac{5}{2}Dt + e_\pi^{\text{Cl}} \end{aligned}$$

With use of (7) and the Dq, Ds, and Dt values obtained from the electronic spectra, the e_λ parameters are

$$\begin{aligned} e_\sigma^{\text{pyz}} &= -4333 \text{ cm}^{-1} + 0.66e_\pi^{\text{Cl}} \\ e_\pi^{\text{pyz}} &= -250 \text{ cm}^{-1} + 0.50e_\pi^{\text{Cl}} \\ e_\sigma^{\text{Cl}} &= -1333 \text{ cm}^{-1} + 0.66e_\pi^{\text{Cl}} \end{aligned}$$

Table II. Best Fit of the Electronic and ESR Transitions of Co(pyz)$_4$Cl$_2$

Energy of Transitions, cm^{-1}

calcd	obsd	calcd	obsd
6934	6500	18 863	18 800
7013		18 949	
9712	9300	19 085	
9770		19 215	
9848		19 296	
9936		19 353	
		23 607	23 500
		23 620	

g Values

	calcd	obsd		calcd	obsd
g_1	5.84	5.83	g_3	2.16	2.14
g_2	4.57	4.55			

Parameters

$e_\sigma^{\text{pyz}} = -4333 \text{ cm}^{-1} + 0.66e_\pi^{\text{Cl}}$ $\quad k = 0.9$

$e_\pi^{\text{pyz}} = -250 \text{ cm}^{-1} + 0.5e_\pi^{\text{Cl}}$ $\quad \zeta = -533 \text{ cm}^{-1}$

$e_\sigma^{\text{Cl}} = -1333 \text{ cm}^{-1} + 0.66e_\pi^{\text{Cl}}$

Table III. Fit of the Electronic and ESR Transitions of Co(py)$_4$Cl$_2$

Energy of Transitions, cm^{-1}

calcd	obsd	calcd	obsd
6265	7000	18 836	17 000
6304		18 770	
9770	8700	19 114	18 800
9824		19 208	
9875		19 268	
9951		19 345	
		22 953	
		22 964	

g Values

	calcd	obsd		calcd	obsd
$g_\parallel$	3.53	3.33 ± 0.03	$g_\perp$	4.49	4.46 ± 0.03

Parameters

$e_\sigma^{\text{py}} = -4333 \text{ cm}^{-1} + 1.33e_\pi^{\text{Cl}}$ $\quad k = 0.9$

$e_\pi^{\text{py}} = e^{\text{py}} = -125 \text{ cm}^{-1} + e_\pi^{\text{Cl}}$ $\quad \zeta = -533 \text{ cm}^{-1}$

$e_\sigma^{\text{Cl}} = -1333 \text{ cm}^{-1} + 1.33e_\pi^{\text{Cl}}$

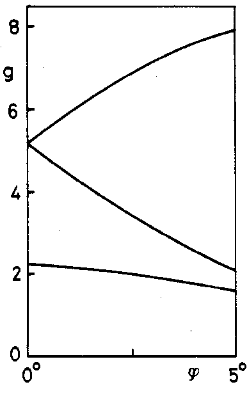

Figure 4. Variations of the g values for Co(pyz)$_4$Cl$_2$ as a function of the deviation, φ, of the in-plane bond angles from 90°. The other parameters are $B = 800$ cm^{-1}, $\zeta = -533$ cm^{-1}, $e_\sigma^{\text{pyz}} = -4333$ cm^{-1}, $e_\pi^{\text{pyz}} = -250$ cm^{-1}, $e_\sigma^{\text{Cl}} = -1333$ cm^{-1}, and $e_\pi^{\text{Cl}} = 0$.

We calculated the g values, with the procedure we described previously.[2] The geometrical parameters used as an input were those of the crystal structure;[10] i.e., the in-plane bond angles are ~92 and 88°. The calculated g values are quite satisfactory, as shown in Table II. Also the principal directions are nicely reproduced.

From the calculations the extreme sensitivity of the g values to angular distortions in the molecular plane is apparent. In

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Figure 4 the effect of varying the in-plane bond angles is shown. For $\varphi = 0°$ the bond angles are 90° and the g values have the required tetragonal symmetry; setting $\varphi = 1°$, i.e., the bond angles to 89 and 91°, can cause a splitting of $g_\perp$ of the order of 1.4.

The calculated g values are independent of the value of e_π^{Cl}, provided that relation 7 is used, since Δ_{pyz} remains constant. When e_π^{Cl} is set to 0, the value of e_σ^{Cl} is rather small, but it is expected to increase if e_π^{Cl} is given negative values. There is one point which is worth being considered. Assuming nonlinear ligation of the equatorial ligands as we have done implies that the usual relations for tetragonal complexes are no longer valid. In particular it is not true that $Dq^{\text{ax}} = Dq - {}^7/_4Dt$. As a matter of fact the Dq of chlorine ($Dq = {}^3/_{10}e_\sigma - {}^4/_{10}e_\pi$) turns out to be extremely small from our calculated values. It is 400 when $e_\pi^{\text{Cl}} = 0$ and becomes smaller as it increases.

If the values of the parameters used for $\text{Co(pyz)}_4\text{Cl}_2$ are used for $\text{Co(py)}_4\text{Cl}_2$, only setting $e_{\pi\parallel}^{\text{py}} = e_{\pi\perp}^{\text{py}} = {}^1/_2 e_\pi^{\text{pyz}}$, a reasonable fit of the g values is found as shown in Table III. The agreement with the electronic transitions can be considered as fair, since they are more poorly resolved than those of $\text{Co(pyz)}_4\text{Cl}_2$. The value of Δ_{py} thus calculated is $-250\ \text{cm}^{-1}$, which compares well with the value reported by Gerloch for the interpretation of the magnetic anisotropy data.[8] He actually used somewhat different values for e_σ^{py} and e_σ^{Cl}. Although they can change the energies of the electronic transitions a little, they do not influence the g values.

The present data do not allow us to obtain absolute values of e_π^{py}, e_π^{pyz}, and e_π^{Cl}; however it seems reasonable to use small values for all of these parameters, in accord with previous findings by Horrocks[6] and Gerloch.[8]

Registry No. $\text{Co(py)}_4\text{Cl}_2$, 14077-25-9; $\text{Co(pyz)}_4\text{Cl}_2$, 72843-09-5.

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Quasi-Relativistic SCF Xα Study of Octahedral 5f^1 Complexes[1]

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Quasi-relativistic SCF Xα calculations have been carried out for the octahedral 5f^1 complexes $\text{Pa}^{\text{IV}}\text{X}_6^{2-}$, $\text{U}^{\text{V}}\text{X}_6^-$ (X = F, Cl, Br, I), and $\text{Np}^{\text{VI}}\text{F}_6$. The 5f → 5f excitation energies calculated by using the transition-state method agree well with the available absorption spectra. Ionic effects appear to dominate the trends observed in the f-orbital ligand field splitting.

Introduction

Although ab initio calculations of ML_N complexes have been carried out extensively for the situation in which M is a transition metal or main-group element,[2a] lanthanide and actinide complexes have been somewhat neglected. Such calculations are computationally difficult for traditional LCAO schemes, although the multiple scattering Xα (MSXα) method is capable of solving such a problem without undue cost, even when relativistic effects are included. The Xα method has been applied to the neutral species UF_5,[2b] UF_6,[2b-6] UCl_6,[7] NpF_6,[4,5] and PuF_6.[4,5] Considerable success was obtained in their agreement with photoelectron and absorption spectra.

In the present study, quasi-relativistic SCF Xα calculations were carried out on a series of 5f^1 complexes: PaX_6^{2-}, UX_6^- (X = F, Cl, Br, I), and NpF_6. The study of such series has aided the interpretation of the electronic structure in terms of parameters commonly used in inorganic chemistry. In this case, the main object of study was the nature of the 5f ligand field splitting relative to the oxidation state of the metal ion and to the halide ion. Previously, only the relative extent of σ- and π-type ligand–f orbital interactions has been discussed, in terms of the semiempirical angular-overlap model.[8]

As a test of the SCF Xα calculations, 5f → 5f excitation energies were determined to compare with available experimental results.[9-11]

Computational Details

The calculations were performed by using a version of the MS Xα routine described by Slater,[12] modified, in the Dirac–Slater framework, to include relativistic effects. The Dirac–Slater MO model has previously been solved for a number of polyatomic systems by using the discrete variational method.[4] The computational effort necessary, however, is substantial but may be reduced considerably by constraining the potential to muffin-tin form. This allows the use of the efficient scattered-wave (SW) formalism either via Green's function technique[13] or by means of the elimination method.[14] The resulting secular equation for the orbital energies ϵ_i is of the same form as in the nonrelativistic SW formalism:[15]

$$\det|G_{pq}(\epsilon) - (\bar{\mu}_p^{-1}(\epsilon))\delta_{pq}| = 0$$

The propagators $G_{pq}(\epsilon)$ describe the scattering of the waves in the region of constant potential from sphere p to sphere q; they only depend

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