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Ligand Field Theory for Planar Complexes: First Principles Validation of the Critical Effects from Coordination Voids

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Dedicated to Dr Michael A. Hitchman, 1941-2016

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Abstract: Multi reference CASSCF/NEVPT2 wavefunction calculations on planar *cis*-[MA₂B₂] complexes show that large d_{xz}/d_{yz} splittings are a feature of the symmetry of the ligand field and are not due to the Orgel effect or phase coupled ligation as previously proposed based on the MO version of the angular overlap model. Instead, the splitting can be attributed to the π components of the local ligand fields in the 'void' regions above and below the molecular plane. The potential in these regions is lower than the d orbital barycentre leading to negative parameter values which is fully consistent with the cellular ligand field interpretation of ligand field theory. The wider implications of ligand field effects from coordination voids are considered.

The elegant spectroscopic studies of Cassidy and Hitchman on square planar [CuCl₄]²⁻ established a d-orbital sequence of $d_{z^2} < d_{xz}/d_{yz} < d_{xy} < d_{x^2-y^2}$.^[1] However, this experimental sequence was at odds with the theoretical predictions of the angular overlap model (AOM).^[2] The simplest AOM parameterization has just two adjustable parameters, $e_{\sigma}(\text{Cl})$ and $e_{\pi}(\text{Cl})$ leading to the following d-orbital energy expressions:

$$\begin{aligned} E(d_{x^2-y^2}) &= 3e_{\sigma}(\text{Cl}) \\ E(d_{z^2}) &= e_{\sigma}(\text{Cl}) \\ E(d_{xy}) &= 4e_{\pi}(\text{Cl}) \\ E(d_{xz}) &= E(d_{yz}) = 2e_{\pi}(\text{Cl}) \end{aligned}$$

The two lowest energy transitions at 12500 ($d_{xy} \rightarrow d_{x^2-y^2}$) and 14300 cm^{-1} ($d_{xz}/d_{yz} \rightarrow d_{x^2-y^2}$) give $e_{\sigma}(\text{Cl}) = 5367 \text{ cm}^{-1}$ and $e_{\pi}(\text{Cl}) = 900 \text{ cm}^{-1}$ whereupon the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition is expected at $2 \times 5367 = 10733 \text{ cm}^{-1}$ about 6000 cm^{-1} lower than the actual transition energy of $\sim 17000 \text{ cm}^{-1}$.

The apparently low energy of d_{z^2} in planar systems is a universal feature of planar complexes and ultimately stems from interactions between the d_{z^2} orbital and the metal's valence s orbital. However, there are two very different mechanisms for accounting for this d-s interaction.

One approach is based on simple molecular orbital (MO) theory. In D_{4h} symmetry, both the $3d_{z^2}$ and $4s$ Cu orbitals transform as a_{1g} and may mix together. This d-s mixing configuration interaction can be added to the Schäffer/Jorgensen (SJ) version of the

AOM^[3] via the second-order e_{ds} parameter which alters the energy expression for d_{z^2} to:

$$E(d_{z^2}) = e_{\sigma}(\text{Cl}) - 4e_{ds}$$

Hence, an e_{ds} value of around 1500 cm^{-1} gives the required 6000 cm^{-1} lowering of d_{z^2} .

The alternative approach is based on ligand field theory (LFT) as described by Gerloch and Woolley (GW).^[4] In the GW AOM (which we renamed the cellular ligand field (CLF)^[5] model to distinguish it from the SJ version), the d orbitals are perturbed by local potentials associated with appropriate regions of electron density. As we discussed in the first of our original series of ligand field analyses,^[6] the potential in the 'void' regions above and below the molecular plane has a metal 4s component which is of σ symmetry with respect to the metal $3d_{z^2}$. Since the 4s orbital is higher than $3d_{z^2}$ (or equivalently, the potential in the region is lower than the d electron barycenter), the sign of the parameter is negative. By placing dummy ligands on the +Z and -Z axes and with $e_{\sigma}(\text{void}) = -3000 \text{ cm}^{-1}$ for each, the required lowering of d_{z^2} is achieved.

The idea of a ligand field from a coordination void was controversial. Schäffer even described it as an "unintelligible concept"^[7] but this assertion stems from the MO interpretation of the AOM. In the absence of a ligand, there are no orbitals with which the d functions can overlap. In contrast, once we recognize the true significance of the 'field' in LFT, a negative potential in a coordination void is both straightforward to understand and completely consistent with the CLF formalism.

The basis set for a ligand field calculation is the set of states derived from an atom-like, pure d^n configuration. As soon as there is at least one ligand attached to the metal, there will be a ligand field which surrounds the *entire* metal. As a matter of formal mathematics, it will always be possible to divide this potential field into spherical and aspherical components. The empirically-observed fact that LFT calculations on real complexes (usually with four or more ligands and using the AOM to model the ligand field potential) consistently reproduce the experimental spectroscopic and magnetic properties of Werner-type complexes^[8] suggests that the presumption of an atom-like set of

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d orbitals is largely correct which in turn implies that the ligand field potential is dominated by the spherical component. Hence, both interelectron repulsion and spin orbit coupling can successfully be treated within a central field – i.e. spherical – approximation.

In contrast, the CLF e parameters depend on the interaction between the d electrons and the aspherical components of the local ligand field potential. If the local potential is higher than that for the spherical average – the barycenter – positive e parameters will result. If the local potential is less than the barycenter, the parameters exert a negative effect. In a coordinatively saturated octahedral complex, for example, the potential in the bond regions will be higher than the barycenter and the CLF parameters will be positive (Figure 1, left). It is then easy to imagine that removing the ligands on the Z axis, and bringing those on X and Y closer to compensate, will increase the potential in the bond regions – hence giving larger, positive CLF parameters – whilst reducing the potential in the void region to below the barycenter which then implies negative CLF parameters (Figure 1, right).

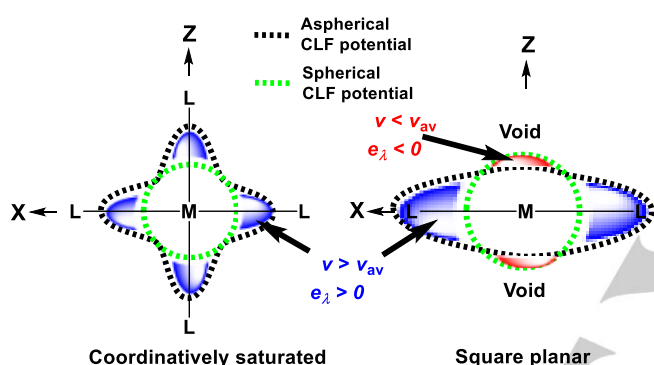


Figure 1. Schematic representation of the cross section of the spherical (green dashed circle) and aspherical (black dashed line) CLF potential for an octahedral (left) and planar (right) complex. Blue indicate regions with a potential higher than the CLF barycentre and red, regions which are at a lower potential than the barycentre. The sizes of the blue and red regions compared to the green spherical average have been enlarged for illustrative purposes..

Our CLF analysis for planar $[\text{CuCl}_4]^{2-}$ yielded a strong σ component from the coordination voids.^[6] While we considered the possibility of a coordination void also providing a π effect, we dismissed the idea at that time since (i) we could reproduce the observed d-d spectra already, (ii) there were insufficient experimental data to support adding extra parameters and (iii) we assumed the effect would be small. However, with the advent of *ab initio* ligand field theory (AI LFT)^[9], we can now generate data from first principles and explicitly test this assumption.

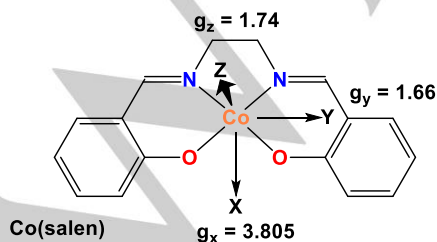


Figure 2. Structural diagram for Co(salen) with axis frame definition and experimental EPR g values (see ref. ^[10] for details).

AI LFT as implemented in the ORCA program suite^[11] is based on multiconfigurational, complete active space SCF (CASSCF) wavefunction theory with an n-electron valence shell perturbation (NEVPT2) treatment of dynamic correlation. The active space comprises the five 'd' orbitals with n electrons corresponding to the formal d^n configuration of the metal center. This generates a one-to-one mapping between the CASSCF configuration state functions and the Russell-Saunders term energies familiar from LFT from which the one-electron d-orbital energies and the two-electron Racah interelectron repulsion parameters can be extracted. The AI LFT d orbital energies can then be used to derive AOM (or CLF) e parameter values.

A major difference between the SJ AOM and the GW CLF approaches occurs for planar Co(II) Schiff's base complexes like Co(salen) (salen = N, N'-ethylenebis(salicylaldiminate), Figure 2). Since the bite angles are close to 90° , both AOM and CLF schemes initially predict (nearly) degenerate d_{xz} and d_{yz} orbitals. For the idealized case of exactly 90° bite angles, the d orbital energy expressions are as given below with d_{xz} and d_{yz} exactly degenerate. (N.B. the ligand field effects from centrosymmetrically-related ligands cannot be separated so only the average of the N and O perturbations is relevant.)

$$\begin{aligned} E(d_{x^2-y^2}) &= 3e_\sigma(N/O) \\ E(d_{z^2}) &= e_\sigma(N/O) - 4e_\delta(\text{AOM}) = e_\sigma(N/O) + 2e_\sigma(\text{void}) \text{ (CLF)} \\ E(d_{xy}) &= 2e_\pi(O) \\ E(d_{xz}) &= E(d_{yz}) = 2e_{\pi\perp}(N/O) \end{aligned}$$

However, based on the experimental EPR g-values, Hitchman suggested a d_{yz}/d_{xz} splitting of $\sim 3000 \text{ cm}^{-1}$.^[12]

Hitchman's analysis of the d-orbital sequence in Co(salen) was informed by considering related Cu(II) complexes. The AOM bonding parameters deduced for Cu(salen) were increased by $\sim 10\%$ for the Co(II) analogue and the estimated d_{xz}/d_{yz} splitting of 3000 cm^{-1} was accounted for by adding the rhombic terms $\langle d_{xz} | V_{LF} | d_{xz} \rangle = -1500 \text{ cm}^{-1}$ and $\langle d_{yz} | V_{LF} | d_{yz} \rangle = +1500 \text{ cm}^{-1}$ to the ligand field potential. The magnitude of these terms was justified 'by comparison with the analogous copper complex' even though in his analyses of these analogues, Hitchman consistently argues for the near degeneracy of d_{xz} and d_{yz} .^[13] The exception appears to be Cu(3-Phacac)₂ (3-Phacac = 3-phenylacetylacetonate) where the observation of four distinct d-d transitions suggests a d_{xz}/d_{yz} splitting of at least 1600 cm^{-1} . However, there is no detailed discussion about the mechanism of the splitting – i.e. whether its origin is electronic, structural or some combination of both. However, notwithstanding how they were arrived at, Hitchman's d-orbital sequences for Cu(salen) and Co(salen) are largely corroborated by AI LFT (Figure 3).

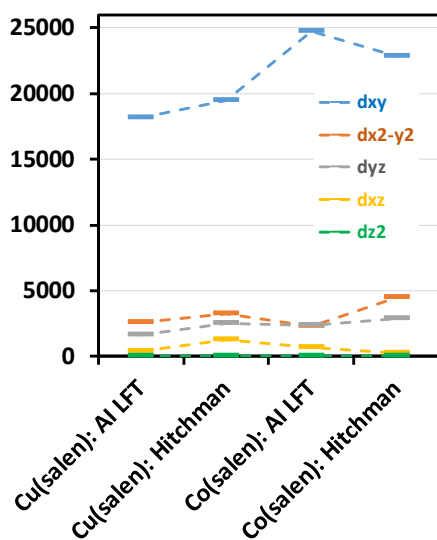


Figure 3. Relative d-orbital energies for Cu(salen) and Co(salen) from AI LFT calculations (see Supporting Information) or derived from Figure 2 of reference [12]. d-orbital labels refer to axis frame definition shown in Figure 2 of this paper.

Hitchman generated a splitting of the d_{xz} and d_{yz} orbitals in Co(salen) by recognizing that the actual C_{2v} symmetry could generate a rhombic ligand field the effect of which he 'added subsequently as a perturbation'.^[12] Subsequently, Ceulemans *et al.*^[14] extended the MO AOM and attributed the splitting to 'phase coupled ligation' (or the Orgel effect)^[14-15] which relates to a ligand where the *cis* donor atoms are connected by a delocalized π system. The phases of the $p\pi$ orbitals on the donor atoms, and perpendicular to the ligand plane, switch from in-phase for the lowest π level to out-of-phase for the next one, to in-phase for the one above that and so on. In-phase combinations (ψ -type in Figure 4) overlap only with d_{xz} and out-of-phase (χ -type in Figure 4) only with d_{yz} . Hence, if one or other π level dominates, the d_{xz}/d_{yz} orbitals will split.

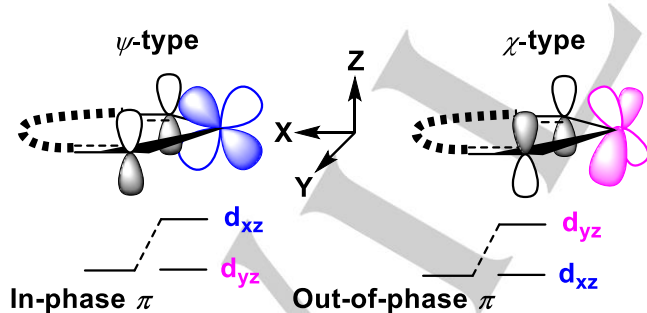


Figure 4. Schematic representation of phase-coupled ligation. Left: the π -type orbitals at the ligand donor atoms are in phase and overlap only with the metal d_{xz} orbital. Right: the π -type orbitals at the ligand donor atoms are out of phase and overlap only with the metal d_{yz} orbital.

In the CLF model, the ligand field potential has no phase information so phase coupling is not possible. In our original analysis of Co(salen)^[10] we were able, after much work, to find a region of parameter space which reproduced the g-values and their directions and kept the d_{xz}/d_{yz} splitting small at ~ 250 cm⁻¹. AI

LFT now shows us that the expectation of near degenerate d_{xz} and d_{yz} orbitals was incorrect and that the large d_{xz}/d_{yz} splitting is real and quite large (~ 1500 cm⁻¹, see Supporting Information). However, some 30 years after our original study, the present analysis finally provides a much simpler and more elegant solution – *asymmetric* π interactions from the coordination voids. This yields new expressions for the d_{xz} and d_{yz} orbital energies which facilitate any desired splitting of d_{xz} and d_{yz} . For Co(salen), all we require for d_{yz} to be 1500 cm⁻¹ higher than d_{xz} is for $e_{\pi x}(\text{void}) - e_{\pi y}(\text{void})$ to be -750 cm⁻¹, a reasonable number given that $e_{\sigma}(\text{void})$ is of the order of -3000 cm⁻¹.

$$E(d_{xz}) = 2e_{\pi\perp}(N/O) + 2e_{\pi x}(\text{void})$$

$$E(d_{yz}) = 2e_{\pi\perp}(N/O) + 2e_{\pi y}(\text{void})$$

A π interaction from the coordination void requires the involvement of the metal's valence p orbitals. The mechanism behind this p-d coupling parallels that for s-d coupling (Figure 5). The e parameters in the CLF formalism depend on the interaction between local d orbitals and the potential in the cell which normally arises from bonding orbitals, χ_{λ} . Critically, the χ_{λ} have contributions from the ligands and the metal valence s and p orbitals. As the ligands on the Z axis are removed to generate a planar species, the ligand parts of χ_{λ} disappear and we are left only with the metal contributions – valence metal s gives $e_{\sigma}(\text{void})$ and valence metal p_x and p_y give respectively $e_{\pi x}(\text{void})$ and $e_{\pi y}(\text{void})$.

We had presumed the metal 4p orbitals would be far away in energy and the associated matrix elements would be negligible. However, until now, we had no independent way to test this assumption. AI LFT provides the necessary, first principles tool and shows that the metal valence p orbitals make an important contribution.

The interesting feature of this p-d coupling is that it is a π effect with respect to the void cell interaction with the metal center but is actually mediated via the in-plane M-L σ -bonding interactions which populate the valence metal p orbitals. Since there are two in-plane p orbitals, p_x and p_y , differences in in-plane σ bonding are manifest as differences in void cell π contributions. Importantly, p-d coupling can thus restore the correct molecular symmetry to the ligand field. Without p-d coupling, the effective ligand field symmetry of Co(salen) is D_{4h} and d_{xz} and d_{yz} are accidentally degenerate. With p-d coupling, the ligand field regains the correct molecular C_{2v} symmetry and d_{xz} and d_{yz} can have substantially different energies.

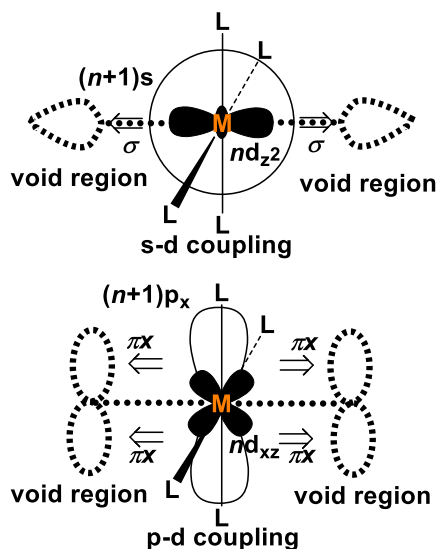


Figure 5. Schematic representation of s-d and p-d coupling from the coordination voids in planar complexes.

Crucially with respect to which version of the AOM/CLF model is correct, the p-d coupling should be a general feature of *cis*-planar complexes while the Orgel effect is restricted to those ligands with a suitable delocalized π system. Hence, the MO version of the AOM predicts degenerate d_{xz}/d_{yz} for a system like *cis*-[NiF₂(CO)₂] where there can be no phase coupling of the Orgel type. AI LFT calculations (Figure 6 and the Supporting Information) give a large d_{xz}/d_{yz} splitting of 1880 cm⁻¹ which demonstrates from *first principles* that the Orgel effect is the wrong mechanism and that the CLF coordination void concept is correct.

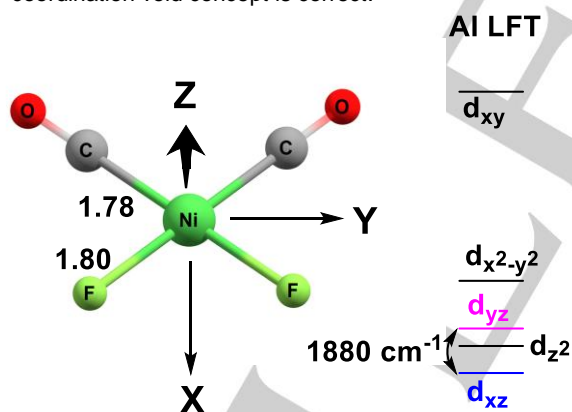


Figure 6. Geometric and electronic structure of model *cis*-NiF₂(CO)₂ complex. All acute L-M-L angles are 90°. Details of the AI LFT calculation are in the Supporting Information.

The ramifications of s-d and p-d coupling are widespread and affect both the MO version of the AOM and the CLF as well as our basic understanding of the ligand fields of metal complexes. The MO AOM can get into difficulties when orbital-overlap arguments from simple MO models are used to interpret ligand field properties which are inherently multi-configurational. The (non-existent) Orgel effect is one such example where simple MO theory suggests a plausible model which turns out to be

inconsistent. There are many others which will be described in detail elsewhere. However, p-d coupling will also require certain CLF analyses to be rethought. Any analysis, whether theoretical or experimental, where the effective ligand field symmetry is higher than the actual molecular symmetry will need re-examining. For example, the spectroscopic study^[16] and the CLF analysis^[17] of *cis*-[PtCl₂(NH₃)₂] both presumed degenerate d_{xz}/d_{yz} orbitals and hence that there were only three possible excited singlet states. AI LFT calculations (Figure 7 and Supporting Information) show this is an erroneous assumption since there is a substantial d_{xz}/d_{yz} splitting of 1637 cm⁻¹ consistent with significant p-d coupling. Hence, all four excited singlets should have been considered.

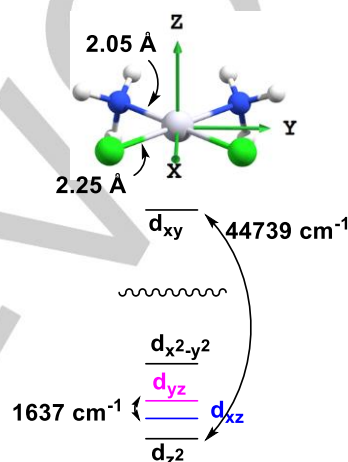


Figure 7. Geometric and electronic structure of model *cis*-[PtCl₂(NH₃)₂]. All acute L-M-L angles are 90°. Details of the AI LFT calculation are in the Supporting Information.

There is also now the significant question of how large does a void cell need to be before s-d and p-d coupling effects are observable? Not all couplings will be obvious. Some will be subsumed within the existing parameters and may easily be missed. The challenge is that p-d coupling adds more parameters which will make it harder to find unique solutions. Nevertheless, after some 30 years, AI LFT appears to have finally vindicated the GW version of ligand field theory.

AI LFT is close to the embodiment of the 'more complete theory' which Orgel and Griffith^[18] named ligand field theory but could not access in 1957. Significantly, it should be noted that these pioneers also considered that crystal field theory and MO theory would only be capable of 'expressing certain aspects' of their more complete model. AI LFT has highlighted some fundamental differences between potential-based ligand field theory as expressed in the CLF model and orbital-overlap-based MO theory as expressed in the SJ AOM. These results suggest that a potential-based picture of the ligand field is the better representation of the special physics of d electrons in Werner complexes.

Acknowledgements

The author acknowledges Professor Frank Neese and Dr Mihail Atanasov for providing a pre-release version of Orca with the AI

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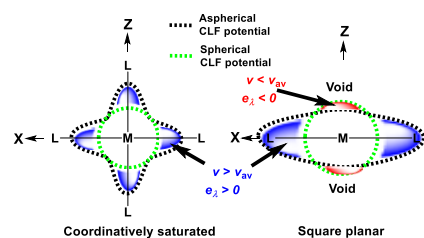
LFT code and Chemical Computing Group for access to the Molecular Operating Environment.

Keywords: cellular ligand field • angular overlap model • ab initio ligand field theory • planar complexes

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Entry for the Table of Contents

Key Topic: Coordination Chemistry



Potential is everything. The local ligand field potential in a cell containing a ligand is higher than the average which leads to positive parameter values and an increase in d orbital energies but it is lower in a 'coordination void' and the parameters are negative. Voids can exert strong σ and π effects. They also illustrate a fundamental difference between ligand field theory as originally envisioned by its pioneers and the simple MO overlap approach which has become the commonly accepted picture.