Published in final edited form as:

Comput Theor Chem. 2018 February 1; 1125: 128–132. doi:10.1016/j.comptc.2018.01.010.

Visualizing the molecular wave function in σ -coordinated complexes¹

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Abstract

The π -complex theory developed by Michael J. S. Dewar in 1949 has had its most profound impact as part of the Dewar-Chatt-Duncanson model, a seminal and foundational contribution to the field of organometallic chemistry. Over time it has demonstrated its utility in systems far from those originally envisaged, including σ -coordinated metal-complexes. This latter application is notable due to Dewar's original skepticism that his π -complex theory could be extended to σ -bonds. Separately it has previously been demonstrated that a one-electron wave function, can be shown to satisfy an exact one-electron Schrödinger equation describing the motion of the single electron in the average field of the remaining electrons. To celebrate the centenary of his birth this paper seeks to demonstrate that σ -coordinated metal-complexes present a perfect system to exemplify both the utility of the one-electron wave function and the power of the π -complex theory.

Graphical abstract

¹Dedicated to the memory of Michael J. S. Dewar on the centennial of his birth

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Keywords

Michael J. S. Dewar; Dewar-Chatt-Duncanson Theory; sigma-coordinated complexes; single-electron wave function; pi-complex theory

Metal-olefin bonding, as described by Dewar-Chatt-Duncanson theory, is a synergistic combination of forward donation of electron density from the olefin, through overlap of the filled π bonding orbital and an empty metal hybrid orbital, and back donation from the metal, formed by overlap of a filled metal d-orbital and the π^* antibonding orbital. The analogy between π -olefin complexation and σ -bond coordination can be seen in Figure 1, and today there are many such examples of σ -bond coordination. Dihydrogen complexes represent the prototype for such σ -bond coordination, with $\text{W}(\text{CO})_3(\text{PR}_3)_2(\text{H}_2)$ being the first complex synthesized displaying metal coordination of a nearly intact H_2 molecule [1]. The attachment of H_2 to the metal results in a H-H bond stretched about 20% over that in free H_2 , indicating that it is chemically attached and activated towards breaking. Increasing back donation, such as in the *cis*-chloro isomer of $\text{Ir}(\text{Cl}_2)(\text{PMe}_3)_2\text{H}(\text{H}_2)$ [2], leads to an elongated H_2 complex, in this case with a d_{HH} of 1.11 Å. In solution this complex yields a much longer d_{HH} of 1.5 Å due to ligand substitution by the much weaker H_2O σ -donor. The varying degree of H-H bond rupture evident across a wide array of $\text{L}_n\text{M}(\text{H}_2)$ complexes has led to the categorization of these σ -complexes into either true H_2 complexes ($d_{\text{HH}} = 0.8 - 1.0$ Å), elongated H_2 complexes ($d_{\text{HH}} = 1.0 - 1.3$ Å), compressed dihydrides ($d_{\text{HH}} = 1.3 - 1.6$ Å), or dihydrides ($d_{\text{HH}} > 1.6$ Å) [3]. The structures for $[(\text{C}_5\text{Me}_5)\text{OsH}_4(\text{PPh}_3)][\text{BF}_4]$ (Fig 2A), $[(\text{C}_5\text{Me}_5)\text{OsH}_4(\text{AsPh}_3)][\text{BF}_4]$ (Fig 2D) and $[(\text{C}_5\text{Me}_5)\text{OsH}_4(\text{PCy}_3)][\text{BF}_4]$ (Fig 2G) determined by single crystal neutron diffraction [4] are shown in Fig 2. In addition to the lengthening of the H-H bond in going from $\text{L} = \text{PPh}_3$ to $\text{L} = \text{AsPh}_3$ to $\text{L} = \text{PCy}_3$ there is a dramatic change on H-H bond orientation, going from parallel to the L-Os-centroid(C_5Me_5) plane in the $\text{L} = \text{PPh}_3$ and $\text{L} = \text{AsPh}_3$ complexes, to perpendicular in the $\text{L} = \text{PCy}_3$ complex. Based on the structural categories identified above this change in orientation correlates with a change in description of the σ -complex from that of an elongated H_2 complex to that of a compressed dihydride.

Approximate solutions to the Schrödinger equation based on electron density, ρ^e , rather than the wave function, Ψ , as the fundamental variable date back to the origin of the equation itself [5,6]. The development of local one-electron, density-based operators as alternatives to the non-local Hartree-Fock (HF) operator coincided with the introduction of the electronic computer and signified the advent of an approximate density-based calculational method [7]. The first Hohenberg-Kohn theorem [8] subsequently confirmed the plausibility of such approaches by demonstrating that the electron density uniquely determines the Hamiltonian, and thus the properties of the system. While the Hohenberg-Kohn formalism expresses the Schrödinger equation entirely in terms of ρ^e , the Kohn-Sham (KS) formulation [9] utilizes both ρ^e and single particle wave functions, $\Psi_i(x)$, often termed KS orbitals. While density-functional theory (DFT) can be implemented in several ways the most widely used DF calculations today are based on the KS approach, with the electron density and KS orbitals connected as $\sum_{i=1}^N |\Psi_i(x)|^2 = \rho^e(x)$. It is important to note that KS orbitals differ significantly from their HF counterparts and for all practical purposes there is no wave

function *per se* in DFT [10]. Where ρ^e is the experimental density, obtained typically by X-ray or neutron diffraction, a different perspective can be adopted. For a 2-electron system with only one occupied spatial orbital, a knowledge of $\sqrt{\rho^e(x_1)/2}$ allows for either an orbital-free calculation using the Hohenberg-Kohn formulation of DFT, or for the calculation of exact exchange-correlation functionals for use in the KS formalism [11]. For an N-electron system, the wave function, $\Psi(x_1) = \sqrt{\rho^e(x_1)/N}$ can be shown to satisfy an exact one-electron Schrödinger equation, describing the motion of the single electron, x_1 , in the average field of the remaining N-1 electrons, and for a specific nuclear configuration, R (Born-Oppenheimer approximation) [12-14].

Factorization of the N-electron wave function for the Schrödinger equation in (1) yields $\Phi(x_2...x_N/x_1)$, a conditional amplitude describing the system of N-1 electrons with positions $x_1...x_N$, when one electron is known to be in position x_1 [15]. Requiring $\Phi(x_2...x_N/x_1)$ to be normalized yields an expression for $\Psi(x_1)$, the one electron wave function expressed in terms of the electron density, (5):

$$H^N \Psi(x_1...x_N) = E^N \Psi(x_1...x_N) \quad (1)$$

$$\Psi(x_1...x_N) = \Psi(x_1) \Phi(x_1...x_N | x_1) \quad (2)$$

$$\int \Phi^*(x_2...x_N | x_1) \Phi(x_2...x_N | x_1) dx_2...dx_N = 1 \quad (3)$$

$$N \int \Psi^*(x_1...x_N) \Psi(x_1...x_N) dx_2...dx_N = \rho^e(x_1) \quad (4)$$

$$[\Psi(x_1)]^2 = N^{-1} \rho^e(x_1), \text{ so } \Psi(x_1) = \sqrt{\rho^e(x_1)/N} \quad (5)$$

Partitioning the N-electron Hamiltonian in an equivalent manner results in a one-electron Hamiltonian, H^1 , and an N-1 Hamiltonian of the remaining core electrons:

$$H = H^1 + H^{N-1} \text{ where } H^1 = -\frac{1}{2} \nabla(x_1)^2 - \sum_{j=2}^R \frac{Z_R}{r_{1R}} + \sum_{j=2}^N \frac{1}{r_{1i}} \quad (6)$$

Substituting (6) and (2) into (1), multiplying by $\Phi^*(x_2...x_N/x_1)$, and integrating over $dx_2...dx_N$ gives (9):

$$[H^1 + H^{N-1}]\Psi(x_1)\Phi(x_2...x_N|x_1) = E^N\Psi(x_1)\Phi(x_2...x_N|x_1) \quad (7)$$

$$\int \Phi^*(x_2...x_N|x_1)[H^1 + H^{N-1}]\Psi(x_1)\Phi(x_2...x_N|x_1)dx_2...dx_N = \int \Phi^*(x_2...x_N|x_1)E^N\Psi(x_1) \cdot \Phi(x_2...x_N|x_1)dx_2...dx_N$$

(8)

$$[H^1 + \int \Phi^*(x_2...x_N|x_1) \cdot (H^{N-1})\Phi(x_2...x_N|x_1)dx_2...dx_N]\Psi(x_1) = E^N\Psi(x_1) \quad (9)$$

If $\langle E^{N-1} \rangle$ is the mean energy of the frozen core of $\Psi(x_1...x_N)$, (10):

$$\int \Psi^*(x_1...x_N)H^{N-1}\Psi(x_1...x_N)dx_2...dx_N = \langle E^{N-1} \rangle \quad (10)$$

then by substituting (2) into (10) we can see that $\langle E^{N-1} \rangle$ is the solution for the Schrödinger equation in (12):

$$\Psi(x_1) \int \Phi^*(x_2...x_N|x_1)H^{N-1}\Phi(x_2...x_N|x_1)dx_2...dx_N\Psi(x_1) = \langle E^{N-1} \rangle \quad (11)$$

$$H^{N-1}\Phi(x_2...x_N|x_1)\Psi(x_1) = \langle E^{N-1} \rangle \Psi(x_1) \quad (12)$$

Substituting $\langle E^{N-1} \rangle$ into (9) and rearranging gives the Schrödinger equation for the one-electron wave function shown in (14), which describes the motion of the single electron, x_1 , in the average field of the remaining N-1 electrons. It is important to note that (14) is exact save for the Born-Oppenheimer approximation:

$$[H^1 + \langle E^{N-1} \rangle]\Psi(x_1) = E^N\Psi(x_1) \quad (13)$$

$$H^1\Psi(x_1) = (E^N - \langle E^{N-1} \rangle)\Psi(x_1) \quad (14)$$

As noted in reference [14] $\langle E^{N-1} \rangle$ represents the energy of the core after the “sudden” removal of the one electron. Thus, as previously noted, the quantity $(E^N - \langle E^{N-1} \rangle)$ is essentially the ionization potential as defined in Koopmans’ theorem.

Now also from (5) we have:

$$\rho^e(x_1) = N[\Psi(x_1)]^2 \quad (15)$$

Differentiation and division by $\rho^e(x_1)$ gives (17):

$$\nabla \rho^e(x_1) = 2N\Psi(x_1)\nabla\Psi(x_1) \quad (16)$$

$$\frac{\nabla \rho^e(x_1)}{\rho^e(x_1)} = 2 \frac{\nabla\Psi(x_1)}{\Psi(x_1)} \quad (17)$$

Since the topology of a scalar field is revealed by the gradient of that field, a semi-log plot of the experimental electron density gradient, $\nabla \ln(\rho^e(x_1))$, displays the topology of the one-electron wave function [16]. Structures for $[(C_5Me_5)OsH_4(PPh_3)][BF_4]$, $[(C_5Me_5)OsH_4(AsPh_3)][BF_4]$, $[(C_5Me_5)OsH_4(PCy_3)][BF_4]$, and $[FeH_3(PMe_3)_4][BPh_4]$ are available from the Crystallography Open Database (<http://www.crystallography.net/cod/>) as id# 4112042, 4112043, 4112044 and 4116957 respectively. The MoPro program suite [17] was used to generate both the static, ρ^e , and gradient norm, $|\nabla \rho^e|$, electron density maps in a given plane. In Figure 2 $|\nabla \rho^e|/\rho^e$ are plotted as isocontour maps for $[(C_5Me_5)OsH_4(PPh_3)][BF_4]$ (Fig 2B and 2C), $[(C_5Me_5)OsH_4(AsPh_3)][BF_4]$ (Fig 2E and 2F), and $[(C_5Me_5)OsH_4(PCy_3)][BF_4]$ (Fig 2H and 2I).

For all three complexes isocontour plots are displayed for cross-sections in the Os-H₂ plane (Figs 2B, 2E and 2H) as well as in the Os-dihydride plane (Figs 2C and 2F) for L= PPh₃ and L= AsPh₃, and the Os-H₁(hydride)-H_b (H₂) plane for L= PCy₃ (Fig 2I). The change in H-H bond orientation for $[(C_5Me_5)OsH_4(PCy_3)][BF_4]$ is also apparent in the isocontour plot (Fig 2H) where the Osmium and the four hydrogens are seen to be nearly coplanar. And while the topology of the metal-hydride interaction is markedly different from that of the metal-H₂ interaction, the $|\nabla \rho^e|/\rho^e$ contours in the Os-H₂ plane are remarkably similar in all three complexes, despite the significant H-H bond-lengthening observed for L= PCy₃, and in contrast to interaction being classified as a “compressed dihydride” for L= PCy₃. Thus this interpretation derived from electron density offers a perspective markedly different from that based on internuclear separation, namely that the fundamental character of the Os-H₂

interaction persists despite H-H bond lengthening and a dramatic change in orientation relative to the metal center.

The σ -complex $[\text{FeH}_3(\text{PMe}_3)_4][\text{BPh}_4]$ (Fig 3A) highlights how such differing perspectives can yield dramatically different analyses. Selective deuteration has shown that this complex undergoes rapid intramolecular hydrogen exchange in the solid state [18], leading to a characterization of H_1 and H_2 as possibly “retaining a memory of their chemical origin”. This characterization, which the authors self-characterized as “speculative”, is obviously informed by the similarity in Fe-H distances for H_1 and H_2 when compared to the much longer Fe- H_3 distance. This in turn led to a description of H_3 as putatively being a “proton coordinating to a classical hydride-Fe bond” [19]. However the $|\nabla\rho^e|/\rho^e$ plot for $[\text{FeH}_3(\text{PMe}_3)_4][\text{BPh}_4]$ (Fig 3B) clearly characterizes the Fe-H bond as that of a hydride, while the H_2 - H_3 interaction contours most closely resemble those of the dihydrogen in $[(\text{C}_5\text{Me}_5)\text{OsH}_4(\text{PPh}_3)][\text{BF}_4]$ and $[(\text{C}_5\text{Me}_5)\text{OsH}_4(\text{AsPh}_3)][\text{BF}_4]$, albeit marginally distorted by asymmetry. Critical point analysis, using the Laplacian operator $\nabla^2\rho^e$ (Fig 2C) yields another interpretation, one where the Fe- H_2 interaction occurs via a critical point, i.e. a point where $\nabla\rho^e = 0$, through only one of the hydrogens. Fig 3D displays the results for a similar critical point analysis for $[(\text{C}_5\text{Me}_5)\text{OsH}_4(\text{PCy}_3)][\text{BF}_4]$. This analysis reveals critical points between the metal center and all four hydrogens, which in the the Quantum Theory of Atoms in Molecules (QTAIM) formalism [20] denotes the existence of a “bond path” from the Osmium to each of the hydrogens. The result however reveals no equivalent critical point between H_a and H_b , the erstwhile components of the bound H_2 molecule. Thus while perspectives derived from structural analysis can be quite distinct from those based on an electron density perspective, the latter are by no means monolithic, but can greatly depend on the formalism employed. And while the Laplacian operator has found widespread utility, as shown above $|\nabla\rho^e|/\rho^e$ alone mirrors the topology of the one-electron wave function $\Psi(x_1)$.

It has been noted by others that Dewar-Chatt-Duncanson theory has had a “profound effect on the development of organometallic chemistry” [21]. In the case of Michael J. S. Dewar this theoretical framework was an outgrowth of his more general π -complex theory. In a fraught presentation of his framework at a conference in Montpellier in 1950 Dewar was faced with a skeptical, predominantly American audience that included Saul Winstein, who though Canadian was based at the University of California at Los Angeles. In taking issue with the contrast drawn between Winstein’s own triangular dotted description for the interaction of ethylene with a cation, X^+ , and the π -complex model Winstein stated: “*I find troublesome Dewar’s statement that our formulation of the ethylene bromonium ion involves a ring but his doesn’t. All that is meant by a 3-membered ring is a triangular arrangement of three atoms.*” Dewar’s response that “*Equivalent valence bond descriptions of π -complexes can of course be given....[however] this description is unsatisfactory since it does not explain why π -complexes are formed from olefins with acceptors, and not with radicals or anions.*” made, as per the account [22], little impact on Winstein. Given that Dewar’s analysis was electronic while Winstein’s perspective was essentially structural, a more salutary, and definitely more pithy, response would have been “*Well, yes and no.*” As can be seen from Figures 2 and 3 perspective most assuredly matters.

Acknowledgments

The author wishes to acknowledge the Welch Foundation (Grant# BH-0018) for its continuing support of the Chemistry Department at St. Edward's University.

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Highlights

- For an N-electron system, the wave function. $\Psi(x_1)$ has previously been shown to satisfy an exact one-electron Schrödinger equation, $H^1\Psi(x_1) = (E^N + \langle E^{N-1} \rangle)\Psi(x_1)$
- $N\rho^e/\rho^e$ isocontour maps for various Metal-H2 complexes are plotted
- Comparisons with the static ρ^e electron density map the Laplacian operator are given

Figure 1.

A: Metal-olefin bonding with forward donation of electron density from the π bond to an empty metal d-orbital, and back donation from a filled metal d-orbital to the π^* antibonding orbital; **B:** Metal-H₂ bonding with forward donation of electron density from the σ bond to an empty metal hybrid orbital, and back donation from a filled metal d-orbital to the σ^* antibonding orbital.

Figure 2.

A: The structure, **B:** the $|\nabla\rho^e|/\rho^e$ isocontour plot in the Os-H₂ plane, and **C:** the $|\nabla\rho^e|/\rho^e$ isocontour plot in the Os-dihydride plane for [(C₅Me₅)OsH₄(PPh₃)][BF₄]; **D:** The structure, **E:** the $|\nabla\rho^e|/\rho^e$ isocontour plot in the Os-H₂ plane, and **F:** the $|\nabla\rho^e|/\rho^e$ isocontour plot in the Os-dihydride plane for [(C₅Me₅)OsH₄(AsPh₃)][BF₄]; **G:** The structure, **H:** the $|\nabla\rho^e|/\rho^e$ isocontour plot in the Os-H₂ plane, and **I:** the $|\nabla\rho^e|/\rho^e$ isocontour plot in the Os-H₁(hydride)-H_b (H₂) plane for [(C₅Me₅)OsH₄(PCy₃)][BF₄].

Figure 3.

A: The structure, **B:** the $|\nabla\rho^e|/\rho^e$ isocontour plot in the Fe-H₂ plane, **C:** Critical path analysis, using the Laplacian operator $\nabla^2\rho^e$ of [FeH₃(PMe₃)₄][BPh₄], and **D:** Critical path analysis, using the Laplacian operator $\nabla^2\rho^e$ for [(C₅Me₅)OsH₄(PCy₃)][BF₄].