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A journey through metallophilic interactions: computational approaches and insights

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Metallophilic interactions, defined as counterintuitive weak attraction between closed-shell metal cations, are essential for stabilizing molecular and solid-state structures, driving supramolecular assemblies or designing functional materials. Despite over half a century of intensive study, the physical origin of metallophilic interactions remains controversial, with competing perspectives arising from the interplay of dispersion, relativistic effects, covalency, or Pauli repulsion concepts. This perspective provides a comprehensive review of computational studies published since 2020, with a focus on both classical and emerging approaches. State-of-the-art computational methods are critically assessed, emphasizing their limitations, inconsistencies, and the implications these challenges pose for accurately describing these interactions. Finally, we highlight open questions and unresolved challenges, underscoring the urgent need for deeper insight into these enigmatic interactions, which continue to captivate both computational and experimental researchers alike.

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1. Introduction

Although Pauli repulsion and electrostatics would predict repulsion between two closed-shell (d^{10} , $d^{10}s^{-2}$) or pseudo-closed-shell (d^8) metal cations,¹ experimental evidence has

revealed that such metals can instead attract, both intra- and intermolecularly,² giving rise to discrete complexes,³ infinite chains,⁴ or clusters.⁵ First recognized in gold(I) compounds and termed *auriphilicity* by Schmidbaur *et al.* in 1988,⁶ this phenomenon was later generalized by Pyykkö as *metallophilicity*,⁷ now established as a class of weak yet structurally decisive interactions.⁸ The initial criterion, based on short M–M distances, shorter than the sum of their van der Waals radii observed in X-ray structures,^{9–11} was originally taken as evi-

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exploring their subsequent experimental properties, such as molecular assemblies and luminescence.

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complexes containing metal–metal interactions, their properties and potential applications associated with them, paying special attention to the analysis of weak interactions that lead to supramolecular structures.

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dence of metal–metal interactions, but is now acknowledged to be insufficient proof of genuine metal–metal attraction.¹²

Far from being innocent, these interactions are pivotal in directing supramolecular assemblies,^{13,14} stabilizing reactive intermediates in catalysis,^{15,16} or enabling applications in sensing and luminescent materials,^{17,18} particularly in organic light-emitting diode (OLED) technologies.¹⁹ Moreover, these interactions can even transmit antiferromagnetic coupling between metal centers through unsupported M...M contacts in the solid state.^{20,21} Experimental and computational studies have revealed homo- and heterometallophilic interactions across a wide range of cations, including d¹⁰ (Au(I), Ag(I), Cu(I), Hg(II)),^{8,22–25} d⁸ (Au(III), Pd(II), Pt(II)),^{26–28} and d¹⁰s² (Pb(II), Tl(I)) species.^{29,30}

While these metal–metal interactions are ubiquitous in fully or partially supported systems,^{31–40} unsupported complexes provide a unique opportunity to probe their intrinsic nature.^{41–47} In supported systems, bridging ligands can artificially bring metals into proximity, and interaction energies are often difficult to quantify, whereas unsupported systems offer a cleaner framework to investigate the fundamental forces governing these contacts.

Moreover, the vast majority of reported metallophilic interactions are observed in the solid state, as these contacts are often too weak to persist in solution.^{48,49} Nonetheless, a few examples in the literature demonstrate the self-association of metal complexes in solution *via* metallophilic interactions.^{50–59} Therefore, the role of solvation must be carefully considered when analyzing these phenomena.

Despite extensive study, the physical origin and nature of metallophilic interactions remain a subject of ongoing debate, challenging fundamental chemical principles. The early work of Hoffmann *et al.* in 1978 and 1985, using the extended Hückel method on Cu(I) and Au(I) complexes, proposed that net stabilization arises from spd orbital hybridization, specifically through the filled nd orbitals of one metal center and the

vacant (n + 1)s/(n + 1)p orbitals of the other (Fig. 1A).^{60,61} Later, Pyykkö and coworkers demonstrated that the potential energy curves (PECs) of aurophilic interactions are repulsive at the Hartree–Fock (HF) level of theory, but become attractive at the Møller–Plesset second-order perturbation (MP2) level of theory,^{62–65} highlighting the crucial role of electron correlation in their stabilization.^{1,66} Furthermore, they proposed that relativistic effects increase this stabilization through expansion of the 5d orbitals and contraction of the 6s/6p orbitals (Fig. 1B).

Two decades later, Grimme and Djukic proposed that the attraction between two Rh(I) metal cations arises predominantly from ligand–ligand (L–L) dispersion effects, whereas the direct metal–metal interaction plays only a minor role (Fig. 1C).⁶⁷ They also emphasized that such oligomers are intrinsically unstable in the gas phase, achieving stability only when solvation effectively screens the electrostatic repulsion through an appropriate ligand arrangement, thereby restoring the correct asymptotic behavior. Building on this, Mata and colleagues further argued, using local correlation methods on Group 11 metal systems, that electron correlation effects originating from the ligands themselves are more determinant than the direct metal–metal interaction in the stabilization (Fig. 1D).⁶⁸ In a complementary perspective, Fonseca-Guerra and coworkers concurred with the dsp orbital hybridization model, acknowledging a covalent contribution to stabilization; however, they proposed that the dominant factor is intermolecular Pauli repulsion, which is counterbalanced by electrostatic, dispersion and weak orbital interactions (Fig. 1E).⁶⁹ Finally, a combination of experimental and computational studies by Cockroft *et al.* and Rulišek *et al.* indicates that metallophilic interactions are weak (from 25 to 30 kJ mol⁻¹) but comparable to hydrogen bonds, with dispersion playing a less significant role than previously assumed (Fig. 1F and G).^{49,70}

While various approaches have been proposed to rationalize these interactions, considerable inconsistencies remain



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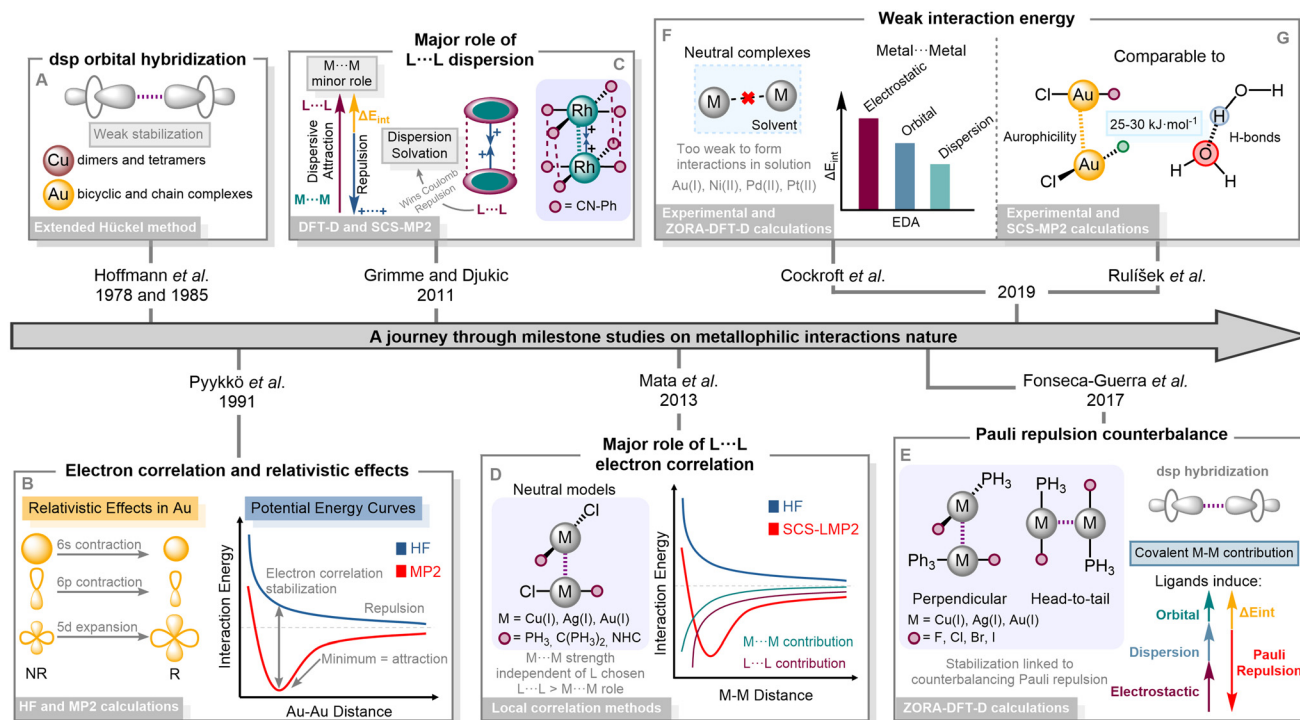


Fig. 1 Key studies in the understanding of the nature of metallophilic interactions: Hoffmann *et al.* in 1978 and 1985 (A), P. Pyykkö *et al.* in 1991 (B), Grimme and Djukic in 2011 (C), Mata *et al.* in 2013 (D), Fonseca-Guerra *et al.* in 2017 (E), Cockroft *et al.* in 2019 (F) and Rulišek *et al.* in 2019 (G).

regarding both their fundamental nature and their quantitative strength. Accordingly, computational studies in this field continue to face several inherent challenges:

(I) The levels of theory typically employed are highly demanding, as electron correlation must be explicitly considered to accurately describe these interactions. Historically, MP2 has been the most widely used method, although it is known to overestimate metallophilic interactions.⁷¹ Spin component-scaled (SCS)-MP2 and coupled cluster single, double and perturbative triple excitation CCSD(T) methods offer a more accurate description but at a substantially higher computational cost.^{72,73} More recently, dispersion-corrected density functional theory (DFT-D) functionals have been applied with reasonable success,⁷⁴ yet the more rigorous correlated methods remain preferable for a detailed characterization of the interaction nature.

(II) Owing to these computational demands, most studies rely on simplified models that mimic the compounds under investigation. While such models are often necessary, they may compromise chemical representativity, and caution is required when interpreting the results. Moreover, studying metallophilic interactions in isolation is particularly challenging, as ligands simultaneously affect the electron density of the metal centers, modulate the metal-metal contacts, and introduce additional interactions, both attractive and repulsive, such as π -stacking or steric hindrance, thereby complicating the computation of accurate interaction energies. Careful selection of model ligands is therefore essential.

(III) Most studies are performed in the gas phase, whereas metallophilicity is primarily observed in the solid state by X-ray diffraction. Consequently, important factors such as counterion influence, packing effects and solvent contributions may be overlooked. More sophisticated approaches, including ONIOM,⁷⁵ QM/MM,⁷⁶ or periodic DFT,⁷⁷ can be employed to account for these factors, albeit with a considerable increase in computational cost and methodological complexity.

Herein, we highlight recent advances and diverse approaches in this field from 2020 to the present, focusing on studies aimed at elucidating the nature of metallophilic interactions, predominantly through computational investigations of unsupported systems. We discuss current perspectives on the origin of this phenomenon and the computational tools employed by experts, while critically examining the challenges and unresolved questions that continue to shape the study of these fascinating interactions.

2. Computational approaches

2.1. Dispersion-driven approach

Traditionally, metallophilic interactions have been interpreted as dispersion-driven phenomena reinforced by the pronounced relativistic effects characteristic of heavy-metal cations, a perspective that remains the most widely employed. Within this context, Miranda-Rojas, Mendizabal, and co-



workers investigated a series of dinuclear bridged gold(I) complexes of the type $[\mu\text{-dpm}(\text{AuR})_2]$, where dpm denotes bis(phosphino)methane and $\text{R} = \text{C}_6\text{H}_5$, C_6F_5 , C_6Cl_5 , and Cl .⁷⁸ To unravel the cooperative nature of the forces governing the interplay between $\text{Au(I)}\cdots\text{Au(I)}$ and aryl π -stacking interactions, they employed a multilevel computational strategy comprising MP2, CCSD(T), and pure DFT-D functionals, such as PBE-D3 (BJ) and TPSS-D3(BJ),^{79–81} combined with the natural bond orbital (NBO),⁸² Wiberg bond index (WBI),⁸³ quantum theory of atoms in molecules (QTAIM),⁸⁴ and noncovalent interaction (NCI) analyses.⁸⁵ NBO analysis revealed that the stabilization of the $\text{Au(I)}\cdots\text{Au(I)}$ interaction arises from donation of a lone pair (LP) orbital of one gold center into an antibonding orbital of the other. The low WBI values between the gold atoms corroborate with its noncovalent nature, while QTAIM and NCI analyses further support the presence of weak yet attractive, noncovalent interactions. Although the metal–metal and aryl–aryl distances fall within the expected range for noncovalent interactions, they display certain discrepancies with respect to the experimental values; consequently, intermolecular models in parallel orientation of type $[\text{PH}_3\text{AuC}_6\text{X}_5]_2$ ($\text{X} = \text{H}$, F , and Cl) were proposed. The computed energy decomposition analysis (EDA)⁸⁶ in them confirmed that dispersion and electron correlation terms are the dominant contributors among weak interactions.

To address the lack of structural evidence for gold(III) aurophilicity, Blasco, Monge, López-de-Luzuriaga and colleagues designed the theoretical model $[\text{Au}(\text{CH}_3)_3(\text{NH}_3)]_2$, based on the well-known bis-orthometalated complexes reported in the literature (Fig. 2A).⁸⁷ Calculations were performed at the RI-MP2 and CCSD(T)/def2-TZVP levels of theory,⁸⁸ yielding Au–Au distances of 3.5–3.6 Å, consistent with the metallophilicity range. The PECs demonstrate the crucial role of electron correlation effects. At the HF level of theory, where this effect is neglected, the curves are purely repulsive, and an overall binding energy ($\Delta E_{\text{int}} < 0$) is obtained due to ionic forces. In contrast, attractive minimum at shorter distances appears at the MP2 and CCSD(T) levels of theory, pointing to dispersion as the major driving force. Moreover, the $\text{Au(III)}\cdots\text{Au(III)}$ stabilizing interaction energy at the CCSD(T) level is 10.5 kJ mol^{-1} , lower than $\text{Au(I)}\cdots\text{Au(I)}$ interactions, as expected. Finally, EDA showed that stabilization arises primarily from dispersion and electrostatic terms, while QTAIM and IRI topological analyses confirm the noncovalent, attractive nature of these interactions.

In a complementary approach within the same study, the $\{[\text{Au}(\text{N}_3)_4]_2\}^{2-}$ ion pair was also investigated at the RI-MP2/def2-TZVP level of theory, reaching a minimum in the PECs at 3.21 Å, although the interaction remained repulsive due to electrostatic forces between the anions (Fig. 2B). Additionally, its optimization at the RI-B3LYP-D3(BJ)/def2-TZVP level of theory led to dissociation.⁸⁹ This model was also examined by Scheiner, Zierkiewicz *et al.*, who focused on the role of the counterion (Fig. 2C).⁹⁰ The authors reported that the minimum observed at the DKH2-MP2/def2TZVP level of theory in gas-phase calculations corresponds to a metastable minimum,⁹¹ as the total energy is higher (less negative) than

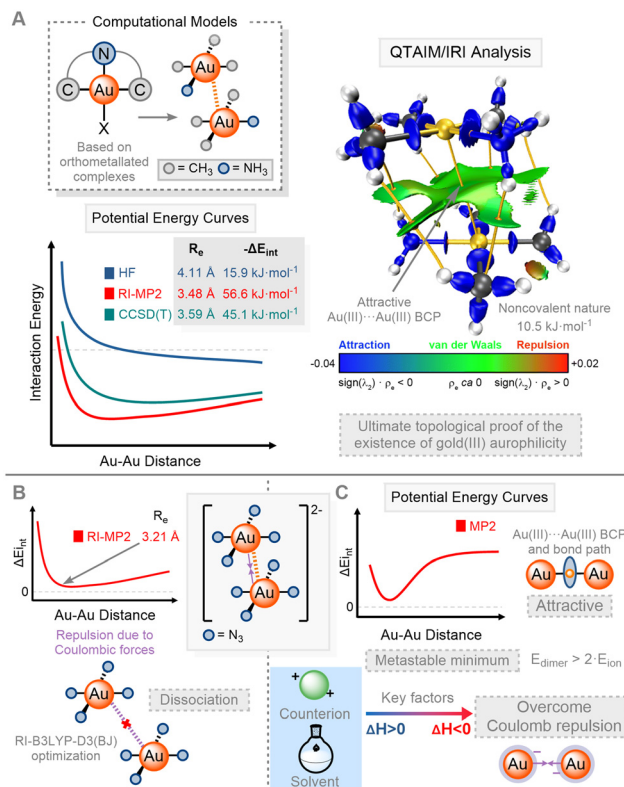


Fig. 2 Summary of the key notes of studies on the neutral $\text{Au(III)}\cdots\text{Au(III)}$ model (A) and anionic models (B and C). Reproduced from ref. 87 with permission from the Royal Society of Chemistry, copyright 2023.

that of the sum of separated ions. QTAIM and NCI topological analyses reveal a bond path between the gold centers, indicating an attractive interaction; nevertheless, it is insufficient to overcome the coulombic repulsion. Inclusion of surrounding counterions (two Me_4N^+ cations) or immersion in a simulated solvent reverses the stabilization, changing the interaction energy from endothermic values of $+209 \text{ kJ mol}^{-1}$ to exothermic values of -13 to -140 kJ mol^{-1} . Therefore, the inclusion of counterions and solvation must be considered for certain systems, such as anion–anion dimers, to overcome coulombic repulsion.

Two extensive studies on the feasibility and strength of unsupported $\text{Au}\cdots\text{M}$ ($\text{M} = \text{d}^8$ cation) interactions in computational models derived from experimentally characterized complexes have been reported by López-de-Luzuriaga, Monge, and co-workers. First, the authors investigated neutral and cationic models featuring $\text{Au(I)}/\text{Au(III)}\cdots\text{Pt(II)}$ interactions at the MP2/def2-TZVP level of theory (Fig. 3A).⁹² PECs obtained at the HF and MP2 levels of theory revealed that electron correlation effects, together with electrostatic contributions, are crucial for stabilization. The metal–metal interaction energies were estimated to be approximately 15 kJ mol^{-1} , whereas relativistic effects were comparatively minor, contributing only 2–10% of the total interaction energy, less significant than in $\text{Au(I)}\cdots\text{Au(I)}$ or $\text{Au(I)}\cdots\text{Hg(II)}$ interactions. Bonding and topological analyses of the electron density indicate that the $\text{Au}\cdots\text{Pt}$ inter-



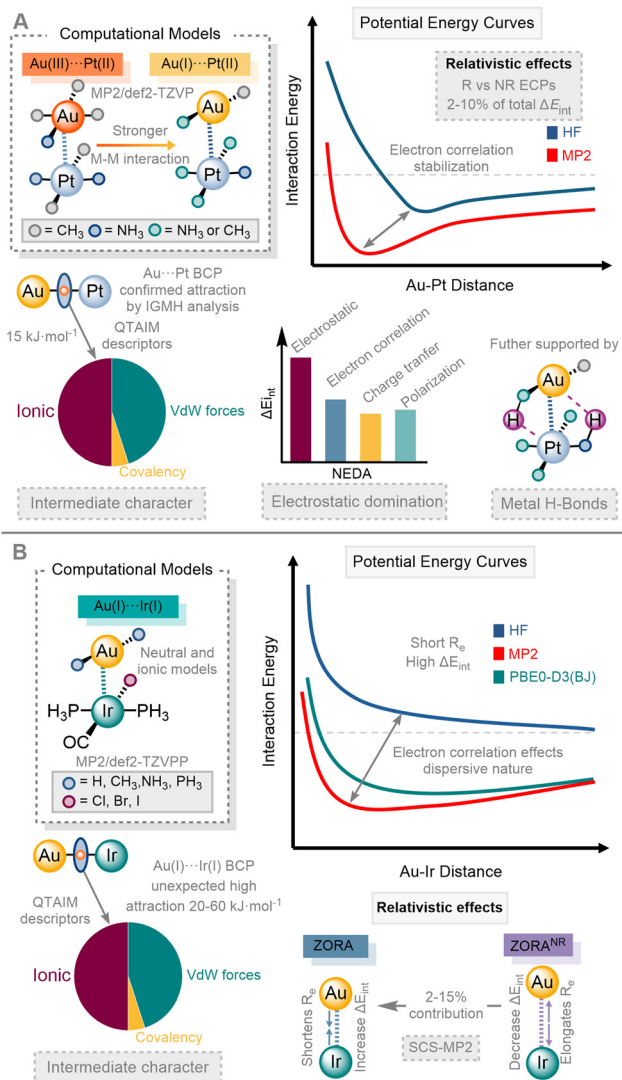


Fig. 3 Overview of the key aspects of studies on Au(I)/Au(III)···Pt(II) (A) and Au(I)···Ir(I) (B) interactions.

actions correspond to regular closed-shell contacts with some degree of electron sharing, exhibiting an intermediate character between ionic, dispersion and weak covalent interactions. Interestingly, ligand–ligand (L–L) interactions, exemplified by metal–hydrogen bonds, contribute equally to, or even surpass, the M–M interactions in stabilizing these models.

The same authors applied a similar methodology to examine unsupported Au(I)···Ir(I) interactions, for which no experimental evidence has yet been reported. Neutral and ionic models of the type $[\text{Ir}(\text{CO})\text{X}(\text{PH}_3)_2][\text{AuR}_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{and I}$; $\text{R} = \text{H}, \text{CH}_3, \text{NH}_3, \text{and PH}_3$) were optimized at the MP2/def2-TZVPP level of theory, all exhibiting a minimum bearing a Au(I)···Ir(I) contact (Fig. 3B).⁹³ The PECs indicate that electron correlation and consequently dispersion are the main driving forces, significantly more pronounced than in Au···Pt systems. The computed Au(I)–Ir(I) distances are remarkably short (2.76–3.11 Å), and the interaction energy values are unusually high (20–60 kJ mol⁻¹), rivalling those of Au(I)···Au(I) contacts.

Bonding and topological analyses confirm that the stabilization of these systems is dominated by attractive Au(I)···Ir(I) interactions, which are noncovalent and predominantly dispersive. Notably, these analyses also reveal a small degree of electron sharing, reflecting a partial covalent character. Finally, ZORA-SCS-MP2 calculations indicate that relativistic effects enhance metallophilic interactions,⁹⁴ although they contribute only 2–15% of the total interaction energy.

Following predictions from theoretical models of metallophilic interactions, Santibañez and Mendizabal investigated six dimeric models featuring unsupported d¹⁰–d¹⁰s² interactions, such as Au(I)···Pb(II) and Au(I)···Bi(III) systems.⁹⁵ Calculations were carried out at various levels of theory, including HF, CCSD (T), MP2, SCS-MP2, and several DFT-D functionals. The results revealed that the proposed metallophilic interactions are adequately captured only when electron correlation effects are explicitly included. The Au–M equilibrium distances (~3.4–4.0 Å) and interaction energies (~10 kJ mol⁻¹) arise primarily from dispersion, consistent with classical metallophilic interactions. These findings reinforce the existence of this type of complex exhibiting these less explored M–M interactions.

Bickelhaupt, Fonseca-Guerra, and co-workers investigated pseudo closed-shell d⁸–d⁸ metallophilic interactions using eclipsed $[\text{M}(\text{CO})_2\text{X}_2]_2$ dimers ($\text{M} = \text{Ni}, \text{Pd}, \text{and Pt}$; $\text{X} = \text{Cl}, \text{Br}, \text{and I}$) to elucidate the underlying bonding mechanism.⁹⁶ The relativistic DFT-D functional ZORA-BLYP-D3(BJ)/TZ2P was employed in combination with PECs, bond analyses, and the EDA method.^{97,98} Their results revealed that the attraction between the dimers is stabilized by electrostatic interactions alongside dispersion interactions promoted by the ligands. The stability of the dimers increases as M varies from Ni to Pt, due to the electron density becoming more diffuse around M and interpenetrating more effectively toward the nucleus of the other monomer (see Fig. 4), resulting in stronger electro-

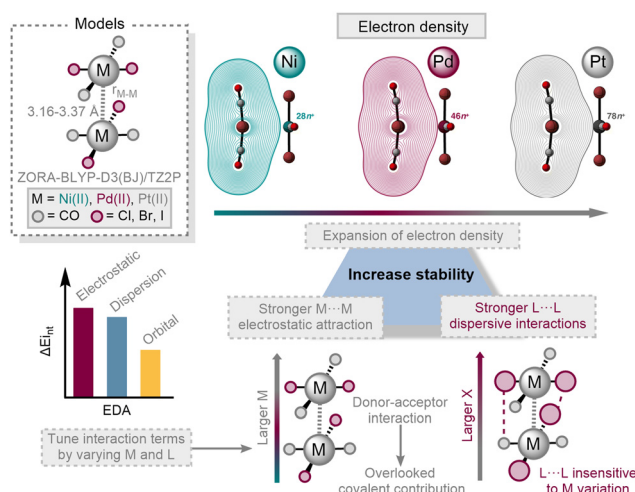


Fig. 4 Summary of the principal factors discussed by Bickelhaupt, Fonseca-Guerra, and co-workers on d⁸–d⁸ metallophilic interactions. Reproduced from ref. 96 with permission from the Royal Society of Chemistry, copyright 2024.



static attraction. Additionally, larger X ligands (*i.e.*, $\text{Cl} < \text{Br} < \text{I}$) generate greater dispersion interactions, further enhancing stability. These interactions are insensitive to variations in the metal center and become dominant only when X is large and M is small. Moreover, they reported that an understudied covalent component arising from L–L and M–M donor–acceptor interactions is present, indicating that the interactions are not purely dispersion-driven. These findings align with previous studies on the bonding relationship in Os–W and Os–Cr unsupported complexes, where dispersion forces constitute the main stabilizing contribution, while donor–acceptor Os–W/Cr interactions provide a minor covalent component rather than a true dative metal–metal bond.⁴⁴

Finally, Xu studied the counterintuitive cation–cation attraction in the experimentally characterized $\{[\text{Ag}(\text{bpy})_2]_2\}^{2+}$ cation pair (bpy = 2,2'-bipyridine) through a purely computational investigation.⁹⁹ Using DFT-D in combination with electrostatic potential (ESP) mapping, NCI analysis, QTAIM, EDA, and symmetry-adapted perturbation theory (SAPT),¹⁰⁰ the author demonstrated that this attraction cannot be explained solely by classical electrostatics. According to Coulomb's law, the observed Ag(I)–Ag(I) distance at 3.22 Å in the optimization should correspond to a repulsion of 103.1 kcal mol⁻¹. This destabilization, however, is mitigated by charge delocalization onto the coordinating ligands and by dispersive L–L interactions, which collectively counterbalance the coulombic repulsion. Quantitative energy analysis revealed that the apparent Ag(I)⋯Ag(I) attraction does not originate from a genuine argentophilic interaction, but instead from the ligands, which diminish Pauli repulsion and provide additional stabilizing contributions.

Taken together, these recent studies slightly depart from the classical perspective; while they confirm the central role of electron correlation effects (*i.e.*, dispersion), they show that M–M interactions are weaker than previously assumed, with a subtle yet significant covalent component that had long been overlooked.

2.2. M–M Pauli repulsion and L–L attraction

In 2021, Wan, Yang, Che *et al.* published a striking study that reignited the debate on the nature of closed-shell M–M interactions.¹⁰¹ Using relativistic DFT-D and post-HF methods, applied to representative X-ray structures of gold and silver coordination complexes, they proposed that such interactions are intrinsically repulsive, predominantly driven by strong Pauli repulsion between the metal centers, which accounts for approximately 51% of the overall Pauli repulsion in the Au(I)–Au(I) model system (Fig. 5A). However, when ligands are included, dispersion and electrostatic contributions outweigh the overall Pauli repulsion, leading to net stabilization. Subsequently, the metal centers undergo dsp orbital hybridization, facilitated by strong relativistic effects, which exerts opposing influences on the M–M interaction: while $(n+1)s$ – nd orbital hybridization promotes M–M Pauli repulsion, $(n+1)p$ – nd orbital hybridization can suppress it, in contrast to the original model proposed by Hoffmann *et al.*^{60,61} Moreover, the linear geometry of these d¹⁰ metal complexes was proposed to suppress L–L Pauli repulsion by twisting the L–M–M–L dihedral angle, while still preserving the strength of attractive interactions between the ligands, highlighting the vital importance of ligands in stabilization. Finally, caution is warranted when evaluating the impact of relativistic effects on metallo-

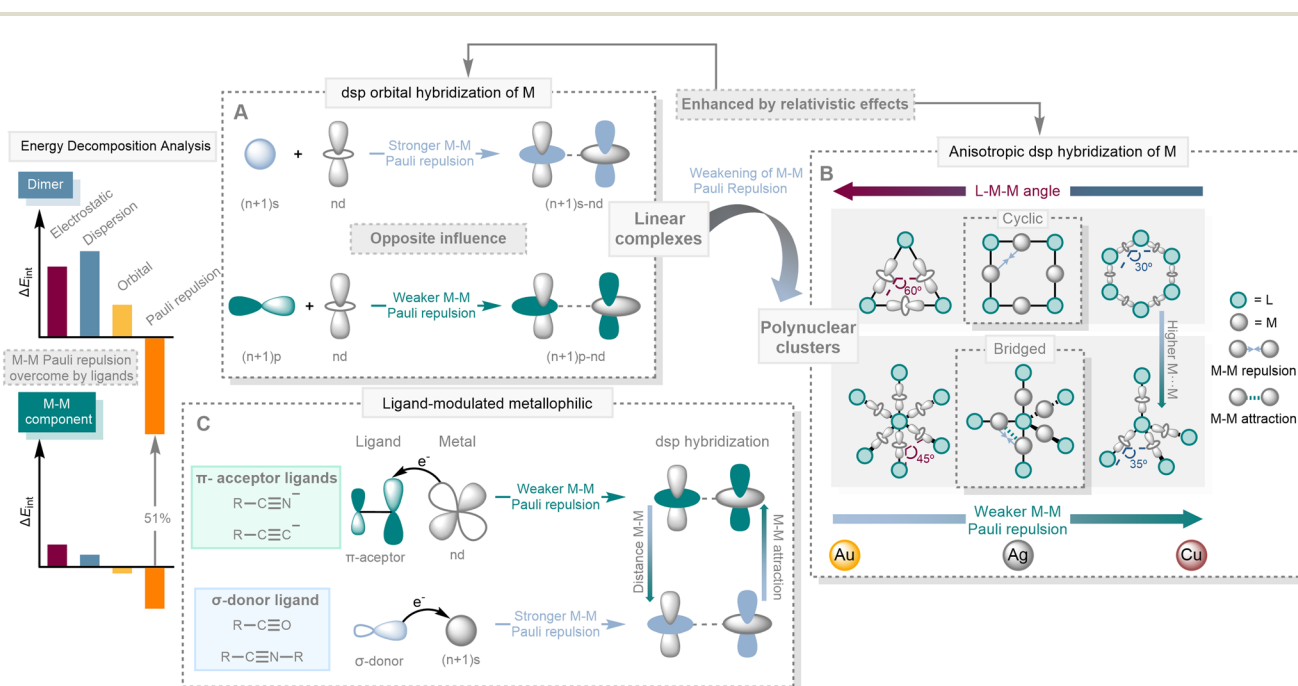


Fig. 5 Outline of the modulation of M–M Pauli repulsion in linear complexes (A), polynuclear clusters (B), and its ligand-dependent variation (C).



philic interactions, as their influence extends not only to orbital hybridization but also to electron correlation effects.

Building on this concept, Wan, Che, and co-workers extended it to polynuclear d^{10} metal clusters.¹⁰² They investigated a series of Cu(I), Ag(I), and Au(I) clusters, comparing their behaviour with corresponding linear coordination analogues employing the ZORA-PBE0-D4/TZ2P level of theory,¹⁰³ EDA and topological calculations (Fig. 5B). In these clusters, the M–M interactions remain repulsive; however, anisotropic $(n + 1)s$ – nd orbital hybridization reduces orbital overlap along the M–M axis compared to linear complexes, resulting in the weakening of the M–M Pauli repulsion from 6% to 52%. Notably, Au(I) clusters exhibit stronger M–M Pauli repulsion than Cu(I) and Ag(I) clusters, resulting from more pronounced $(n + 1)s$ – nd orbital hybridization driven by stronger relativistic effects. When studying clusters with central bridging atoms, a balance emerges between M–M Pauli repulsion and the attractive contributions of M–M bonding interactions. Furthermore, the electronegativity of the ligands modulates this repulsion, with more strongly electron-donating ligands enhancing $(n + 1)s$ – nd orbital hybridization and consequently increasing M–M Pauli repulsion.

As these previous studies suggested that ligands play a decisive role in modulating metallophilic interactions, Wan *et al.* systematically examined how their π -acceptor and σ -donor properties influence the M–M Pauli repulsion in both d^{10} and d^8 metal complexes.¹⁰⁴ Their analysis relies primarily on natural orbital for chemical valence (NOCV) and EDA methods at the PBE0-D3(BJ) level of theory,¹⁰⁵ based on Rh(I), Au(I) and Pt(II) X-ray structures. The evaluation of a series of π -accepting and σ -donor ligands demonstrates that they modulate M–M interactions *via* two principal mechanisms. Electron density delocalization from the metal into the vacant orbitals of π -accepting ligands (*e.g.*, isocyanides and nitriles) mitigates M–M Pauli repulsion, shortening M–M contacts. Conversely, σ -donor ligands (*e.g.*, alkynides and cyanides) transfer electron density from their lone pairs into the vacant $(n + 1)s$ orbital of the metal, enhancing Pauli repulsion and elongating M–M distances (Fig. 5C). Altogether, these findings not only resolve ambiguities in the L–M relationship but also provide a guiding principle for ligand design to deliberately tune metallophilic interactions.

Overall, these works challenge long-standing views, suggesting that metallophilic interactions may, in fact, be inherently repulsive. Crucially, it is the ligands that tip the balance, modulating Pauli repulsion between metals and stabilizing the overall system.

2.3. Covalent approach

A new approach, grounded in Lewis acid–base and covalent bonding concepts, has recently been employed to investigate the nature of metallophilic interactions. Using this framework, Wang, Cheng and co-workers rationalized the exceptional case of closed-shell Au(I)–Au(I) interactions in *trans*-(AuX)₂ compounds (X = F, Cl, Br, I, and NH₂), providing an illustrative example (Fig. 6A).¹⁰⁶ Using the relativistic ZORA-TPSS-D3(BJ)

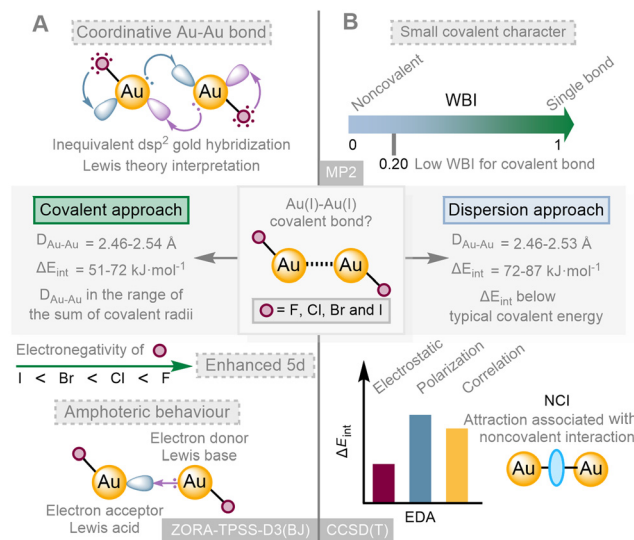


Fig. 6 Summary of the key points of the study on *trans*-(AuX)₂ models from covalent (A) and dispersive (B) approaches.

functional in combination with several analyses, including electron localization function (ELF),¹⁰⁷ NCI, NBO, EDA, and adaptive natural density partitioning (AdNDP) analysis,¹⁰⁸ they attributed the nature of the Au(I)–Au(I) interaction to a coordinative covalent bond. The Au–Au distances (2.46–2.54 Å) are too short for a classical auriphilic interaction, and the interaction energy values (51–72 kJ mol^{−1} at the ZORA-CCSD(T) level of theory) are relatively high, yet they do not fall within the covalent bonding regime (≥ 250 kJ mol^{−1}). This behaviour can be understood in terms of inequivalent dsp hybridization at the gold center, which endows it with an amphoteric character, allowing it to act simultaneously as a Lewis acid and a Lewis base. Consequently, one gold atom functions as the electron donor while the other serves as the electron acceptor, stabilizing dimerization. Moreover, ligands with higher electronegativity favour the activation of the 5d electron of gold, thus reinforcing the covalent character of the bond.

Later, the same *trans*-(AuX)₂ model systems (X = F, Cl, Br, and I) were investigated by Miranda Rojas, Mendizabal and colleagues, who employed a more classical approach to explore the dominant forces governing the Au(I)–Au(I) interaction (Fig. 6B).¹⁰⁹ Geometry optimizations and interaction energies were calculated using several DFT-D functionals (TPSS, PBE, and B3LYP) as well as post-HF methods, such as MP2 and CCSD(T) levels of theory. Their results indicate that the Au(I)–Au(I) distances are short, falling within the covalent bond range (2.46–2.53 Å), whereas the associated interaction energy values (72–87 kJ mol^{−1}) remain considerably lower than those of the typical covalent bonding. WBI and NBO analysis reveal a slight covalent character, but not sufficient to classify the Au(I)–Au(I) contact as a purely covalent bond. Furthermore, EDA and topological analyses confirm that electron correlation and orbital terms are the dominant contributions to the overall stabilization, while the electrostatic term is attractive but not dominant.



Building on Lewis acid–base principles, Cheng, Wang, and co-workers extended their previous studies on the existence of closed-shell metal interactions. In their study, simplified heterobimetallic systems comprising $d^{10}\text{--}d^8$ (Ag(I) , $\text{Au(I)}\text{--}\text{Pd(II)}$) and $d^{10}\text{--}d^{10}$ (Ag(I) , $\text{Au(I)}\text{--}\text{Hg(II)}$) species, derived from experimentally characterized compounds, were examined using long-range corrected (LC)-DFT-D calculations.¹¹⁰ Acidity/basicity descriptors, together with topological and bonding analysis tools such as the interaction region indicator (IRI),¹¹¹ ELF, NBO, AdNDP, and EDA, were employed. Their results support the view that these M–M interactions are essentially dative in nature, consistent with Lewis acid–base rules. The studied interactions arise from dsp hybridized orbitals (see Fig. 7A), with inner d-orbital participation playing a decisive role. The strength of such interactions increases with the relativistic character of the metal center, which enhances d orbital activity. Furthermore, this covalent coordinative bond, and consequently the activity of the d electrons, can be reinforced by electron-donor ligands at the Lewis base (Ag(I) and Au(I) fragments) or by electron-withdrawing ligands at the Lewis acid (Pd(II) and Hg(II) fragments). EDA supports that the metal–metal attraction is dominated by the orbital component rather than by dispersion.

Frontera *et al.* examined the classic $\text{Hg(II)}\cdots d^8\text{M}$ ($\text{M} = \text{Pd(II)}$, Pt(II)) interactions from a molecular orbital perspective, offering an alternative explanation to the conventional view

that attributes them to dispersion reinforced by relativistic effects.¹¹² The authors primarily relied on NBO and EDA analyses at the PBE0-D3/def2-TZVP level of theory, applied to both the X-ray and optimized structures of representative complexes $[\text{Hg}(\text{C}_6\text{F}_5)_2][\text{Pd}(\text{L})]$ ($\text{L} = N,N'$ -disalicylidene-*o*-phenylenediamine) and $[\text{K}_2\text{PtHg}(\text{CN})_6]$ (Fig. 7B). They suggest that these heterometallic interactions are, in fact, donor–acceptor spodium bonds, with Hg(II) acting as a Lewis acid. Charge transfer from the filled $4d_{z^2}$ orbital of Pd(II) or the $5d_{z^2}$ orbital of Pt(II) to the empty $6p_z$ orbital of Hg(II) highlights the nucleophilic role of Pd/Pt (Lewis base) and the electrophilic role of Hg (Lewis acid). Additionally, EDA results indicate that the electrostatic term is the most significant contributor, while dispersion and orbital components contribute comparably, suggesting that this type of interaction cannot be classified as a classical metallophilic interaction.

In summary, these studies stand out by interpreting metallophilic interactions through Lewis and covalent bonding concepts, providing an intuitive, orbital-based framework that accounts for their saturability and directionality. Ligands are key, tuning the Lewis acidity or basicity of the metal centers and shaping their strength and character.

2.4. Estimation of interaction energy by QTAIM parameters

As highlighted in the present work, topological tools are being widely employed in the study of metallophilic interactions and have also been used, for example, to estimate the interaction energy of hydrogen bonds.^{113,114} In this context, Frontera *et al.* developed a method based on QTAIM parameters to estimate the strength of aurophilic and argentophilic interactions.¹¹⁵ They examined a set of 84 model systems, which were validated against selected X-ray crystal structures from the Cambridge Structural Database (CSD), where these interactions play a decisive role in solid-state arrangements. The electron density of these models was computed at the relativistic $x2c\text{-PBE0-D4}$ functional,¹¹⁶ revealing the presence of a bond critical point (BCP) between the metal centers of each model. Based on these results, they derived eqn (1) and (2) to predict $\text{Au(I)}\cdots\text{Au(I)}$ and $\text{Ag(I)}\cdots\text{Ag(I)}$ interactions, respectively, using the electron density (ρ_e) at the metal–metal BCP.

$$E_{\text{int}}(\text{kcal mol}^{-1}) = -688.65 \times \rho_e(\text{a.u.}) + 10.03 \quad (1)$$

$$E_{\text{int}}(\text{kcal mol}^{-1}) = -850.66 \times \rho_e(\text{a.u.}) + 11.17 \quad (2)$$

This method addresses the need for fast and clear estimation of these interactions, making it accessible to a broad range of researchers, while offering valuable insight into their impact on molecular and solid-state properties. The QTAIM approach enables the isolation of metal–metal BCPs, making it possible to separate the energetic impact of these interactions from other contributions, and it can also be applied to intramolecular systems. Nevertheless, high-level methods such as CCSD(T) and SCS-MP2 with counterpoise correction are recommended when rigorous quantification is required.

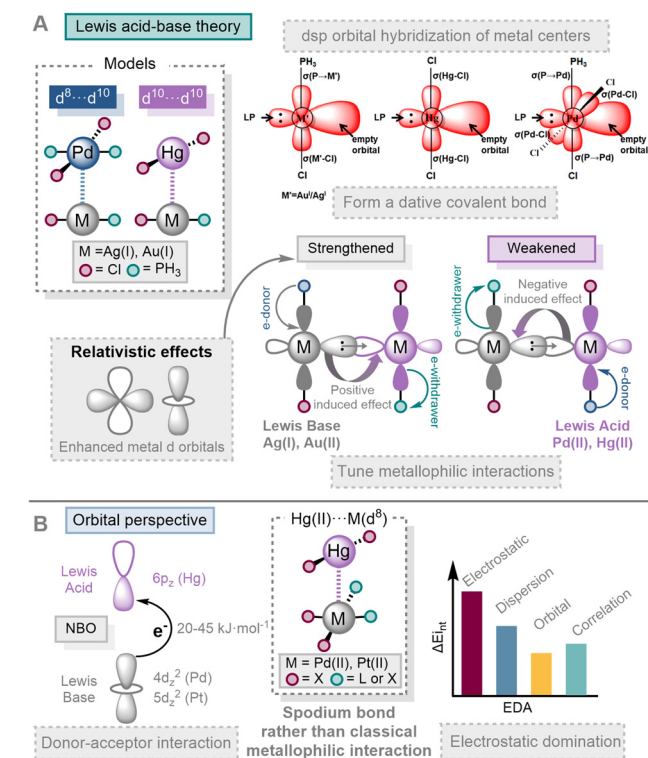


Fig. 7 Overview of the study on $d^8\cdots d^{10}$ and $d^{10}\cdots d^{10}$ interactions based on Lewis theory (A), and of the study on $\text{Hg(II)}\cdots\text{M}(d^8)$ interactions from an orbital perspective (B). Reproduced from ref. 112 with permission from American Chemical Society, copyright 2023.



3. Summary and outlook

As highlighted throughout this comprehensive perspective, metallophilic interactions remain highly topical and continue to fuel significant attention. Researchers are keen to rationalize their origin to deliberately tune these interactions, thereby controlling the processes and properties that arise from them. In the following section, we present the current landscape of computational approaches for studying the nature of metallophilic interactions, highlighting key methods and critically evaluating their respective strengths and limitations.

3.1. Trends in computational studies

In recent years, DFT-based methods have been increasingly adopted to prove both the origin of metallophilic interactions and their influence on chemical behaviour. This is particularly appealing, as DFT offers a balance between accuracy and efficiency, approaching post-HF levels of theory while drastically reducing computational cost. DFT-D functionals, particularly TPSS-D3(BJ) or PBE0-D3(BJ),^{80,81,103} have emerged as the most reliable tools for evaluating these interactions.⁷⁴ Nevertheless, one should be aware that such empirical corrections may fail to properly describe the long-range R^{-6} decay of dispersion interactions.¹¹⁷ Moreover, the use of long-range corrected (LC) and hybrid functionals is advised to mitigate delocalization error (DE),¹¹⁸ which are particularly pronounced in pure functionals and can significantly affect both physical and chemical properties.

In this regard, post-HF methods are recommended, as their explicit treatment of electron correlation effects is essential for accurately capturing the nature of metallophilic interactions. The CCSD(T) approach is generally employed to benchmark noncovalent interactions and is considered the most accurate method; however, its high computational cost restricts its application to relatively small systems. A more widely used alternative, owing to its lower computational cost, is the MP2 level of theory. While MP2 provides a reasonable estimate of metallophilic interactions, it has been shown to overestimate their strength and remains computationally demanding for larger systems.⁷¹ More recently, SCS-MP2 has emerged as a more reliable and balanced approach.¹¹⁹ Further improvements have been achieved through density fitting approximations, such as resolution of identity (RI) and domain-based local pair natural orbital (DLPNO), which accelerate calculations while enhancing accuracy.^{120–122}

It is well established that relativistic effects play a crucial role in the chemical properties of heavy metals and, consequently, significantly influence metallophilic interactions. A common approach to account for these effects is the use of effective core potentials (ECPs),¹²³ in which the inner-core electrons are represented by a single potential that incorporates relativistic contributions. A more rigorous, albeit computationally demanding, approach is the zeroth-order regular approximation (ZORA),⁹⁴ which incorporates relativistic effects at the all-electron level. This formalism is frequently preferred in studies that specifically focus on relativistic contributions of

the M–M interactions. The influence of relativistic effects is typically assessed by comparing relativistic and non-relativistic ECPs, or by performing relativistic ZORA and non-relativistic ZORA Hamiltonian calculations, the latter often using an artificially accelerated speed of light by a factor of 100. Additionally, less commonly employed, yet noteworthy, relativistic approaches include the Douglas–Kroll–Hess (DKH) and exact two-component (x2c) methods.^{91,116}

Metallophilic interactions are considerably weaker than covalent or ionic bonds but stronger than conventional van der Waals forces, with reported interaction energy values spanning a wide range, from negligible values up to those comparable to strong hydrogen bonds (ΔE_{int} 0 to 60 kJ mol⁻¹),^{8,124–126} underscoring inherent inconsistencies. Recent combined experimental and computational studies suggest that metallophilic interactions are generally weaker than those initially suggested using early MP2 calculations, typically falling in the 25–30 kJ mol⁻¹ range.⁷⁰ In this context, careful treatment of basis set superposition error (BSSE) is crucial, as it can spuriously lower interaction energies, leading to an artificially enhanced stabilization. Counterpoise correction is most applied,¹²⁷ while basis set enlargement to complete basis set limit (CBS) provides a less frequent yet effective alternative.

As shown in this perspective, truly isolating metallophilic interactions is anything but simple,¹²⁸ especially in supported systems where counterpoise corrections are not straightforward. In such cases, the QTAIM framework provides a qualitative indicator, allowing the metal–metal BCP to be examined in isolation. Nevertheless, CCSD(T) or SCS-MP2 methods, combined with at least triple- ζ basis sets and often employing density fitting approximations, are recommended for accurate evaluation of interaction energies.

Most computational studies in this topic have been conducted in the gas phase, even though metallophilic interactions primarily manifest in the solid state and, to a lesser extent, in solution. Caution is therefore warranted when interpreting gas-phase results, as crystal packing, counterions, and solvent effects can significantly influence both the strength and nature of these interactions. Incorporating periodic DFT or QM/MM approaches for solid-state systems, and continuum solvent models for solution calculations when appropriate, provides a more realistic and reliable description of their true behavior.

Furthermore, common methods in these studies include decomposing the total interaction energy methods (e.g., EDA, natural energy decomposition analysis (NEDA),¹²⁹ local energy decomposition (LED),¹³⁰ AdNDP, or SAPT), alongside bond indices and topological analyses of the electron density. Widely employed by both experimental and computational researchers, topological methods provide qualitative, visual insights into interactions and enable their classification by type and relative strength.¹³¹ Accordingly, methodologies such as QTAIM, NCI, IRI, ELF and independent gradient model based on Hirshfeld partition (IGMH)¹³² are recurrently applied in the literature.



3.2. Critical assessment of approaches

Over the years, a variety of computational strategies have been developed to rationalize metallophilic interactions. These approaches range from classical perspectives pointing up electron correlation and relativistic effects to more recent frameworks incorporating covalency, Lewis Acid–base theory, and metal–metal Pauli-repulsion counterbalance considerations. These trends have gradually emphasized the previously underappreciated role of ligands in mediating metallophilic attraction, indicating that metal centers may be less influential than initially thought. Nevertheless, notable discrepancies persist concerning the impact of relativistic effects and spd orbital hybridization.¹⁰¹

The classical view, in line with Pyykkö's perspective, posits that metallophilicity arises primarily from electron correlation effects (*i.e.* dispersion-driven) and it is further reinforced by relativistic effects in heavy metal atoms. To demonstrate this, PECs are typically computed using methods that account for electron correlation, such as CCSD(T), MP2, SCS-MP2 or DFT-D functionals, and compared with approaches that neglect correlation, such as the HF level of theory. Including electron correlation markedly stabilizes interaction energies and shortens M–M distances relative to the HF level of theory, underscoring its decisive role. It is important to note that while all dispersion arises from electron correlation, not all electron correlation originates from dispersion.⁷¹ In addition, relativistic effects are widely recognized to enhance metallophilic interactions, yet their role remains debated: while stronger relativistic contributions are expected to correlate with increased interaction strength, high-level methods challenge this trend, showing no systematic increase down group 11.¹³³ Recent studies using QTAIM, NBO, EDA, and bond indices indicate that these interactions also have a covalent component that cannot be ignored.^{92,93,96} However, one may ask whether this covalent component (*i.e.*, orbital overlap) is merely a consequence of the metal–metal attraction driven by electron correlation effects.

A remarkable perspective on metal–metal closed-shell interactions was introduced by Che *et al.*, who suggested that these interactions are intrinsically repulsive in nature. Based on dsp hybridization of the metal orbitals, they showed that M–M Pauli repulsion dominates the interaction, while the ligands modulate and counterbalance this repulsion. Therefore, the $(n - 1)d\text{-}ns$ hybridization orbitals of metals enhance M–M Pauli repulsion, while the $(n - 1)d\text{-}np$ hybridization mitigate it. As a result, σ -donor ligands that supply electron density to the $(n - 1)d\text{-}ns$ orbitals weaken M–M interactions, whereas π -acceptor ligands that withdraw electron density from the $(n - 1)d\text{-}np$ orbitals reinforce them. Strong relativistic effects facilitate dsp metal hybridization, but their impact remains unclear, as they also affect electron correlation effects, complicating the rationale of metallophilic interactions. Thus, this approach focuses on identifying ligands capable of mitigating M–M Pauli repulsion, thereby allowing attractive dispersion and electrostatic forces to dominate and

stabilize the M–M interaction. The methodology relies on the EDA method at DFT-D levels of theory, and on strategic model fragmentation to isolate the M–M contribution. However, two main concerns arise: first, DFT-D is not the most reliable level of theory, and correlated methods such as SCS-MP2 or DLPNO-CCSD(T) would be more suitable; second, this manual fragmentation to extract the M–M component constitutes an approximation; therefore, the resulting values should be regarded as qualitative and interpreted with appropriate caution. Nevertheless, this perspective underscores that ligands play a more significant role than was originally assumed in the early days of the field.

A fresh covalent perspective frames metallophilicity through the lens of Lewis acid–base theory, grounded in molecular orbital analysis and extensively supported by NBO, EDA, and topological tools to characterize it. These studies align with Hoffmann's perspective,^{60,61} in which metallophilic attraction arises from dsp orbital hybridization. Ligands modulate the d orbital activity, allowing the metal center to function as a Lewis base that interacts with a Lewis acid featuring vacant s or p orbitals. Relativistic effects further enhance d orbital participation, amplifying the interaction. This framework also accounts for the saturability and directionality of metallophilic interactions, characteristics typically associated with covalent bonding. However, while offering an intuitive and straightforward explanation for metallophilic interactions, their fundamental origin remains ambiguous, as the M–M distances are relatively long, and the interaction energy values are far too low to qualify as true covalent bonds. If the driving force were purely covalent, the HF method should, in principle, be able to describe the interaction, since it accounts for orbital overlap. Yet, it has been consistently demonstrated that the HF level of theory fails to capture the attractive nature of metallophilic interactions. Furthermore, if these interactions were predominantly driven by spd hybridization, substantial geometric distortions would be expected upon dimerization, whereas their general absence further underscores the uncertainty surrounding their true nature.

Taken together, metallophilic interactions reveal themselves as a rich and multifaceted phenomenon, far more nuanced than previously appreciated. Arising from the interplay of electron correlation, electrostatics, and orbital effects, they defy a single unifying principle. The interpretation of metallophilicity hinges on the chosen definition: considering it as a direct metal–metal interaction *versus* the tendency of metal compounds to form aggregates leads to different conclusions, which are also highly system-dependent. Each metal system exhibits unique subtleties, requiring careful experimental and computational analysis, as identical models can be rationalized through multiple approaches. Fully understanding these interactions is not only key to rationalizing the structure and reactivity, but also essential for harnessing their potential in molecular design, materials science, and supramolecular properties.

Finally, the term “*metallophilic interactions*” may not fully reflect the true physical nature of these metal–metal contacts.



Perhaps it is time to reconsider or even move beyond this historical terminology, one that originated in a crystallography-driven era, where interatomic distances rather than underlying physical forces defined significance. We hope that this perspective inspires and encourages the community to devise a terminology rooted in the fundamental physics of noncovalent interactions, moving beyond a purely descriptive, metallo-centric view and fostering a deeper understanding of their origin and significance.

Author contributions

F. R.: conceptualization, formal analysis, visualization and writing – original draft. M. E. O., J. M. L., and M. M.: funding acquisition, supervision and writing – review & editing. All authors have reviewed and approved the final version of the manuscript.

Conflicts of interest

There are no conflicts of interest.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

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