Volume 11, Issue 4, April – 2026 International Journal of Innovative Science and Research Technology
ISSN No: -2456-2165 https://doi.org/10.38124/ijisrt/26apr097

The Electronic Structure of $Be_4N_2Me_2$: A Charge-Shift Perspective

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Publication Date: 2026/04/04

Abstract: The structural, energetic, and topological properties of a tetranuclear beryllium cluster coordinated by methylimide ligands, $Be_4N_2(CH_3)_2$, were investigated using meta-GGA density functional theory and high-level DLPNO-CCSD(T) calculations. The cluster features a distorted diamond-shaped Be_4 core bridged by nitrogen atoms with high thermal stability and no imaginary vibrational frequencies. Local Energy Decomposition (LED) reveals a massive interaction energy between cluster fragments (Δ E = -833.58 kcal/mol), primarily driven by electrostatic attraction and significant non-dispersive correlation. Despite high electron localization between Beryllium atoms, topological analysis of the Laplacian of the electron density ($\nabla^2\rho$) reveals a regime of charge depletion. These results definitively classify the Be–Be and Be–N interactions as possessing substantial charge-shift bond character.

Keywords: *Charge-Shift Bonding, Beryllium Clusters Energy Decomposition Analysis (EDA-NOCV), Local Energy Decomposition (LED), DLPNO-CCSD(T), Topological Electron Density Analysis, Laplacian of Electron Density, LOL, Be–Be Interactions.*

How to Cite: D. K. Jha (2026) The Electronic Structure of Be4N2Me2: A Charge-Shift Perspective. *International Journal of Innovative Science and Research Technology*, 11(4), 13-17. https://doi.org/10.38124/ijisrt/26apr097

I. INTRODUCTION

Beryllium clusters exhibit unique bonding motifs due to the low electronegativity and small atomic radius of the beryllium atom.[1-5] Tetranuclear beryllium complexes are of particular interest for their potential in coordination chemistry and materials science. This study explores the stabilization of a Be_4 core using methylimide (NCH_3^{2-}) ligands, examining the nature of the metal–metal and metal–ligand interactions through a comprehensive suite of electronic structure methods.[6]

II. COMPUTATIONAL METHODS

Geometry optimizations and frequency calculations were performed using the ORCA 6.1 program package.[1] The TPSS meta-GGA functional was employed with the def2-TZVP basis set. Electronic structure and bonding were further refined using high-level DLPNO-CCSD(T) calculations for Local Energy Decomposition (LED) and Energy Decomposition Analysis (EDA).[8] Natural Bond Orbital (NBO) analysis was performed to characterize localized bonding components.[14] Topological analyses, including the Localized Orbital Locator (LOL), Hirshfeld orbital compositions, and the Laplacian of the electron density ($\nabla^2\rho$), were performed via Multiwfn using the converged SCF density.[10]

III. RESULTS AND DISCUSSION

- *Molecular Geometry and Stability*

The optimized structure of $Be_4N_2Me_2$ features a central Be_4 cluster core.

- *Bond Lengths:*

Primary Be–Be bonds are calculated at 2.052 Å, while diagonal distances are approximately 2.151 Å. The bridging Be–N distances are 1.4530 Å.

- *Thermochemistry:*

Vibrational analysis confirmed the structure as a true minimum on the potential energy surface. The total SCF energy was converged to 246.8006 Eh at the Hartree-Fock level and -247.9173 Eh at the CCSD(T) level.

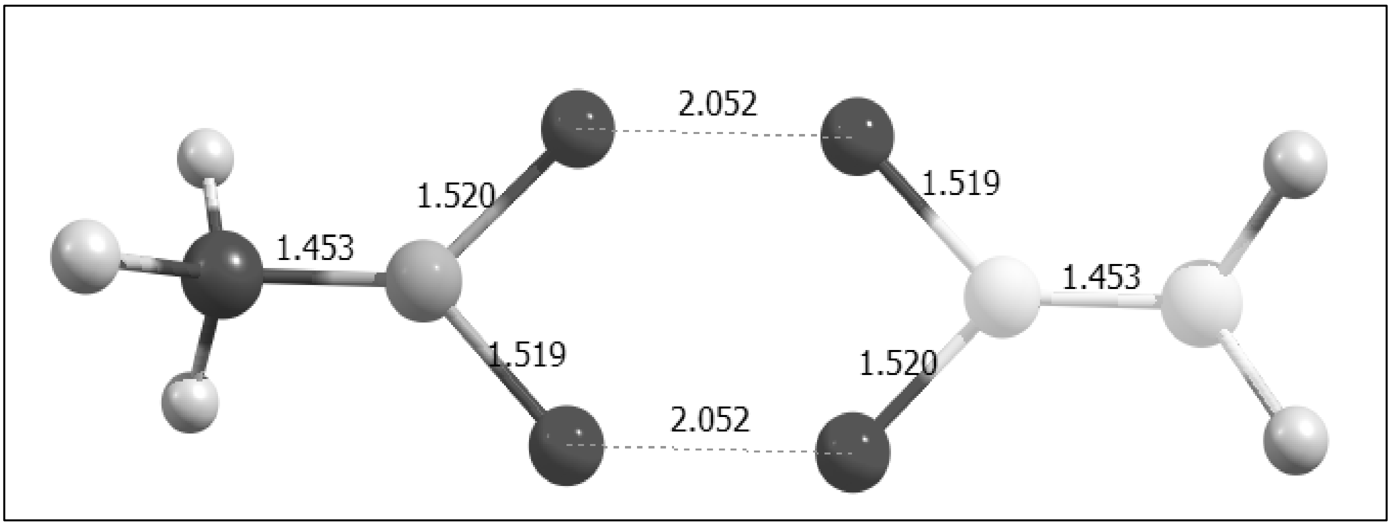

Fig 1 Optimized Molecular Structure of $Be_4N_2Me_2$

➢ *Electronic Structure and Natural Bond Orbital (NBO) Analysis*

The electronic nature of the $Be_4N_2Me_2$ cluster was further elucidated using Natural Bond Orbital (NBO) analysis, providing a detailed description of the charge distribution and bonding motifs within the tetranuclear core.

- *Natural Atomic Charges:*

Natural Population Analysis (NPA) reveals a high degree of charge separation within the molecule. The Beryllium atoms exhibit significant positive charges, calculated at approximately +0.86 e. In contrast, the bridging Nitrogen atoms are highly electronegative with charges of -1.87 e. This substantial polarity suggests that the Be–N interactions possess a predominant ionic/electrostatic character, consistent with the large electrostatic stabilization identified in the LED analysis.

- *Wiberg Bond Index (WBI):*

Despite the high polarity, the Wiberg Bond Indices indicate significant covalent character in the cluster framework. The Be–Be bonds show indices of ~ 0.86$, while the Be–N bonds exhibit indices as high as ~ 1.32, reflecting strong multi-center coordination.

- *Bonding Orbitals:*

The NBO search identified two distinct Be–Be 2-center 2-electron (2c-2e) bonds (e.g., Be1–Be2 and Be3–Be4) with high occupancies of 1.93 e. These bonding orbitals are characterized by nearly pure s-character (~ 91% s, 8% p), indicating the primary utilization of the Beryllium 2s valence orbitals in the formation of the Be_4 core.

- *Donor–Acceptor Interactions:*

Second-order perturbation theory (SOPT) analysis highlights the stabilizing role of the ligands. Significant delocalization is observed from the Nitrogen lone pairs (LP_N) into the empty valence orbitals of the adjacent Beryllium atoms. These donor-acceptor interactions facilitate the covalent-ionic resonance that is characteristic of charge-shift bonding, contributing essentially to the overall stability of the cluster.

➢ *Energy Decomposition Analysis (EDA) and LED*

High-level LED analysis provides a detailed map of the cluster's stability.

- *Fragment Interactions:*

The cluster was partitioned into two equivalent Be_2NMe units. The total interaction energy is -1.3284 Eh (-833.58 kcal/mol).

- *Components:*

Electrostatic attraction (-765.47 kcal/mol) is the dominant stabilizing term. However, the non-dispersive correlation (charge transfer and polarization) contributes a massive -1.065 Eh to the stability. This large non-dispersive term is a hallmark of significant electronic reorganization typical of charge-shift bonding.[12-13]

➢ *Orbital and Topological Analysis*

- *LOL:*

LOL plots show high electron localization in the internuclear regions. Contour maps of the wavefunctions confirm traditional σ-overlap between Beryllium atoms. The degree of electron localisation between N and Be is not as high as in the case of Be1-Be2 and Be3-Be4 bonds, this is a known feature of the "charge-shift bond".[9,12-13]

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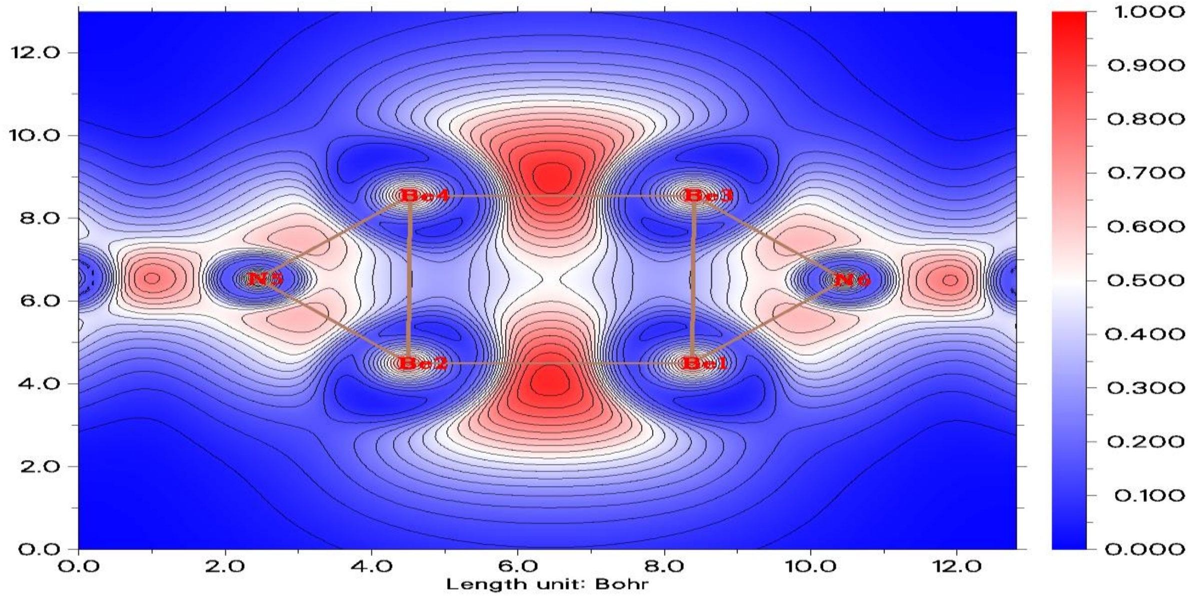

Fig 2 Localized Orbital Locator (LOL) Contour Map showing Electron Localization basins

- *Hirshfeld Compositions:*

Hirshfeld orbital partitioning reveals a highly symmetric electronic distribution across the cluster fragments. Analysis of the frontier region shows distinct orbital characters: Orbital 21 is dominated by the metal core with each Beryllium atom contributing ~21%, whereas Orbital 22 represents the bridging framework with each Nitrogen atom contributing ~24% to the total density.

- *Nature of the Be–Be Bond:*

The electronic structure of the Be_4 core was further elucidated through the visualization of localized orbital wavefunctions. Contour maps of the principal bonding orbitals (Figure 4) reveal a high degree of electron localization along the Be-Be internuclear axes. Despite the visual appearance of traditional σ-bonds, the energetic decomposition suggests a more complex nature. The interaction is characterized by a exceptionally large non-dispersive correlation contribution (-668.25 kcal/mol for strong pairs).

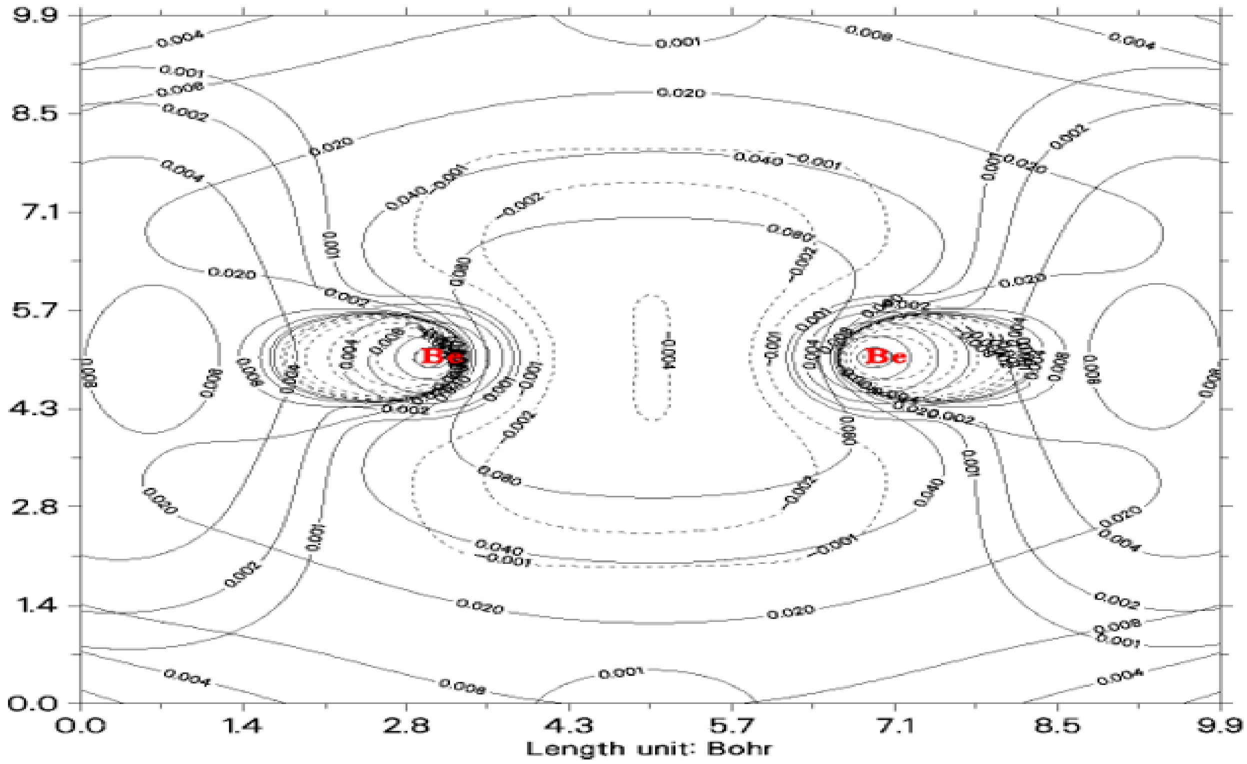

Fig 3 Contour Maps of the Be–Be Bonding Orbital Wavefunctions

- *The Laplacian ($\nabla^2\rho$):*

Definitively, the Laplacian map reveals chage depletion ($\nabla^2\rho > 0$) at the bond critical points within the core. This topological "paradox"—high localization and overlap with charge depletion—is the defining signature of charge-shift bonds (The "Smoking Gun" evidence), when combined with the large non-dispersive correlation from the LED results.

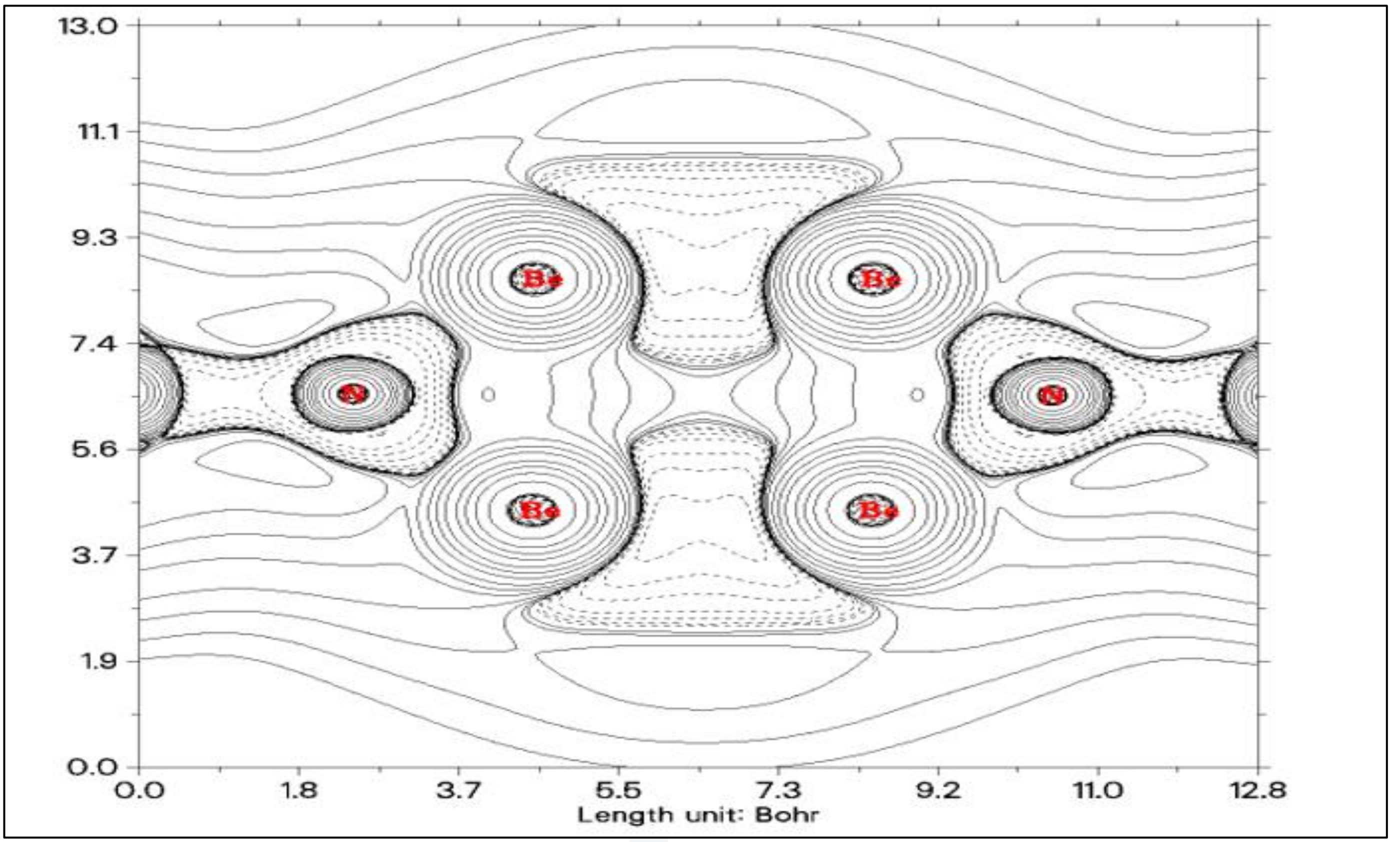

Fig 4 Laplacian of the Electron Density (**$\nabla^2\rho$)** Map highlighting Internuclear Charge Depletion

IV. CONCLUSION

The $Be_4N_2(CH_3)_2$ molecule represents a stable cluster core stabilized by a unique electronic mechanism. While structural and orbital data suggest traditional covalent bonds, the combination of massive non-dispersive correlation energy and a positive Laplacian of the electron density characterizes the core as being held together by charge-shift bonding. The nitrogen bridges play a critical role in providing the electrostatic glue and facilitating the covalent-ionic resonance necessary for the cluster's stability.

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