OPEN ACCESS

Inorganic Materials COMMENTARY

The Innovation Materials

Interstitial electrons: A real-space electronic dimension for quantum materials

Yin Yang,[1] Pengcheng Ma,[1] and Zhonghao Liu[1,*]

[1]Institute of High-Pressure Physics and School of Physical Science and Technology, Ningbo University, Ningbo 315211, China

*Correspondence: liuzhonghao@nbu.edu.cn

Received: July 10, 2026; Accepted: October 15, 2026; Published Online: October 19, 2026; https://doi.org/10.59717/j.xinn-mater.2026.100249

© 2026 The Author(s). This is an open access article under the CC BY license (https://creativecommons.org/licenses/by/4.0/).

Citation: Yang Y., Ma P. and Liu Z. (2026). Interstitial electrons: A real-space electronic dimension for quantum materials. *The Innovation Materials* **4**:100249.

ELECTRIDES ADD A REAL-SPACE DIMENSION TO ELECTRONIC STRUCTURE

The discovery and design of quantum materials have relied on manipulating electronic degrees of freedom, including charge, spin, orbital, and lattice degrees of freedom (Figure 1A). Through crystal chemistry, dimensionality, pressure, doping, and interface engineering, these variables have enabled diverse emergent phenomena, ranging from unconventional superconductivity and topological states to correlated magnetism. Electronic properties are commonly described in terms of atomic orbitals, chemical bonding, and crystal symmetries that determine the underlying electronic structure.

Electrides provide a complementary real-space perspective of electronic states.[1,2] Unlike conventional solids, electrides host low-energy electronic states within crystal interstices rather than being primarily associated with atomic orbitals or chemical bonds (Figure 1B). The overlap between neighboring interstitial wavefunctions provides a microscopic link between their spatial arrangement and electronic behavior (Figure 1C). These interstitial electrons form crystal-defined real-space electronic architectures, including cavities, channels, and interlayer spaces (Figure 1D). Thus, crystal geometry can define not only the atomic framework but also the spatial distribution and connectivity of interstitial electronic states, providing a distinct route for understanding and designing quantum materials.

This perspective connects modern electride physics with the broader concepts of electron compounds and Hume–Rothery phases, where electron concentration can influence structural stability and phase formation. In these systems, specific electron concentrations can favor particular crystal structures through the electronic-energy benefits associated with bonding states, pseudogaps, and Fermi surface–Brillouin zone interactions near the Fermi level. Electrides extend this broader perspective by showing that electrons can also become spatially organized within crystal voids, making their real-space distribution an important aspect of the electronic structure. This provides a complementary link between crystal architecture and electronic organization, highlighting the spatial arrangement and connectivity of interstitial states as additional dimensions for understanding quantum materials. In this context, interstitial electrons complement rather than replace established electronic concepts, providing an additional real-space dimension for organizing and designing electronic states in quantum materials, where crystal architecture becomes an active parameter in controlling electronic configurations.

FROM ANIONIC ELECTRONS TO INTERSTITIAL ELECTRONIC ARCHITECTURES

Electrides were originally defined as ionic solids in which electrons act as anions.[1] This chemical definition remains useful for identifying and classifying electride materials, but modern studies reveal that interstitial-electron physics extends beyond a simple anionic picture.[2] Advances in first-principles calculations and spectroscopic characterization have enabled increasingly detailed descriptions of electron-rich regions within crystal voids. Real-space analyses such as the electron localization function (ELF) provide a useful complement to band theory, although identifying interstitial electrons requires consideration of both their spatial distribution and their electronic character. Experimentally, high-resolution X-ray diffraction can help resolve charge accumulation in interstitial regions, while scanning tunnelling microscopy and spectroscopy (STM/STS) can probe local electronic states, and angle-resolved photoemission spectroscopy (ARPES) can resolve momentum-dependent spectral features and band dispersions. Combined with first-principles calculations, these complementary approaches can help distinguish interstitial-electron contributions from conventional orbital-derived states, although no single probe provides a universal criterion for identifying all interstitial-electron states. This broader view shifts the focus from whether an electron is formally an anion to how interstitial states are spatially distributed and electronically connected.

Specifically, stronger overlap generally enhances interstitial-state hopping and promotes itinerant behavior, whereas weaker overlap can favor reduced dispersion and greater localization. Their dimensionality, connectivity, and hybridization with atomic states therefore define distinct electronic regimes (Figure 1E), ranging from free-electron-like itinerant states to hybridized and localized states. The conventional electride picture of isolated anionic electrons thus represents one limit of a broader interstitial-electron framework, in which real-space organization and coupling to the atomic framework determine the resulting low-energy electronic states.

INTERSTITIAL ELECTRONS BRIDGE CRYSTAL STRUCTURE AND QUANTUM PHENOMENA

The role of interstitial electronic architectures becomes evident through representative systems hosting distinct interstitial-electron states. Different spatial organizations of interstitial electrons can generate different electronic regimes, including itinerant, weakly dispersive, and hybridized states (Figure 1E), providing diverse pathways toward emergent quantum phenomena.

In layered electrides such as Ca_2N and Y_2C, interstitial electrons form extended quasi-two-dimensional networks between positively charged atomic slabs.[2] Strong connectivity among neighboring interstitial states leads to highly dispersive bands with nearly free-electron-like character. In Y_2C, such itinerant interstitial states have been proposed to contribute to magnetic instabilities associated with enhanced density of states near the Fermi level, representing an itinerant regime where interstitial electrons behave as delocalized carriers while retaining their real-space origin.

A different regime emerges when crystal geometry organizes interstitial electrons into electronic lattices. In Li_5Si, interstitial electrons form kagome-like networks within crystal voids (Figure 1F), generating characteristic features including Dirac cones, van Hove singularities, and flat bands.[3] More recently, YCl was shown to host a dice-lattice interstitial-electron network, demonstrating that electronic lattices can emerge from interstitial-electron distributions rather than conventional atomic arrangements.[4] Such electronically defined lattices provide an alternative route toward engineering flat bands, Dirac dispersions, and related quantum states.

Hybridization with atomic orbitals represents another important regime. The electride superconductor La_3In provides an example in which localized interstitial states within La cages strongly hybridize with La-derived orbitals near the Fermi level.[5] Rather than acting as isolated electron anions, these interstitial states become integrated into the low-energy electronic structure through coupling with the atomic framework. This hybridized regime occurs in a superconducting electride, providing a platform for investigating how interstitial states participate in low-energy electronic processes. Their specific roles in superconductivity and other emergent phenomena remain open questions.

Together, these examples illustrate how crystal geometry, interstitial-electron connectivity, and hybridization can organize electronic states into different regimes, providing a real-space complement to conventional band- and orbital-based descriptions of quantum materials. Interstitial-electron architectures offer opportunities to explore emergent quantum phenomena (Figure 1G) through the interplay between real-space electronic organization and low-energy electronic properties.

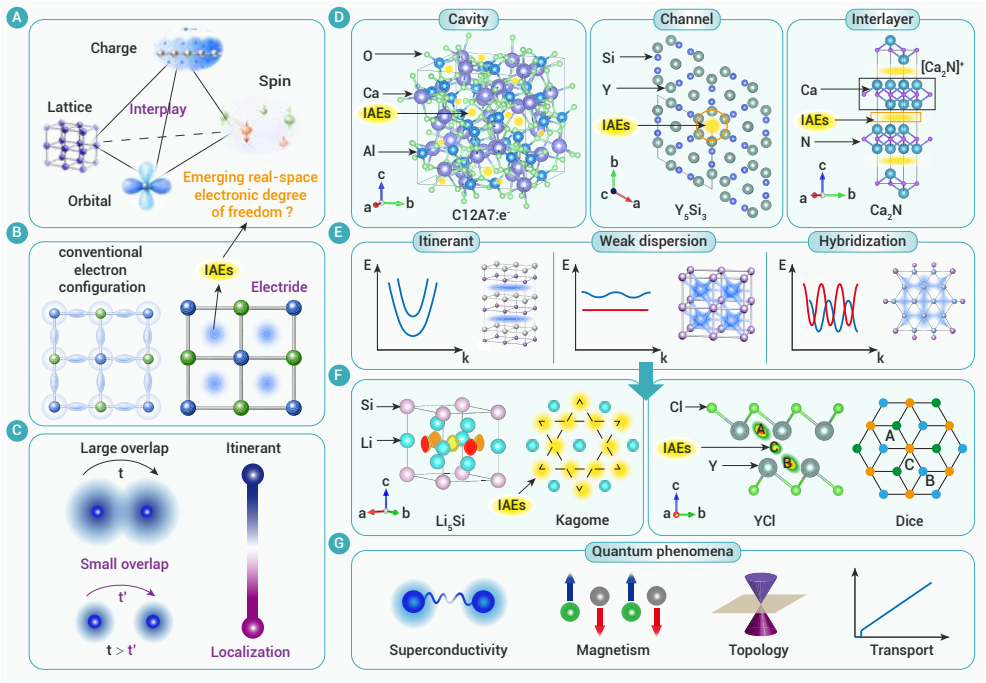


Figure 1. Interstitial anion electrons (IAEs) as a real-space electronic dimension bridging crystal architecture and quantum phenomena (A) Conventional electronic degrees of freedom and the extension toward interstitial electronic states. (B) Conventional electron configurations and electrides with interstitial anionic electrons. (C) Interstitial-electron wavefunction overlap governs hopping and localization. (D) Crystal-defined interstitial electronic architectures, including cavities, channels, and interlayer spaces. (E) Representative interstitial-electron-derived electronic regimes. (F) Emergent kagome and dice electronic lattices formed by interstitial electrons in Li_5Si and YCl. (G) Representative quantum phenomena enabled by interstitial electronic architectures.

OUTLOOK: TOWARD REAL-SPACE ELECTRONIC-STATE ENGINEERING

The significance of interstitial electrons extends beyond identifying new electride compounds. Modern quantum materials are commonly designed through atomic orbitals, electronic bands, and interfaces, whereas interstitial electrons provide a complementary route for engineering low-energy states through their real-space organization. Because interstitial states are characterized by their geometry, connectivity, and hybridization with the atomic framework, they can be tuned through crystal design, chemical modification, strain, and pressure. In particular, high-pressure approaches have emerged as a powerful strategy for accessing interstitial-electron states that are difficult to stabilize under ambient conditions by modifying atomic packing, electron transfer, and bonding configurations. Beyond tuning existing materials, pressure can also enable the formation of new electride phases by driving electron redistribution and unconventional bonding. These high-pressure systems provide a valuable platform for exploring the evolution of interstitial electronic architectures under extreme conditions. Future efforts may therefore move from identifying interstitial electrons toward controlling their spatial architectures and coupling with surrounding electronic states, offering new possibilities for exploring topology, magnetism, superconductivity, and correlated phenomena.

Several challenges remain before interstitial electrons can become a predictive design element for quantum materials. Although computational methods such as ELF analysis are effective for identifying electron-rich regions, experimentally distinguishing interstitial-electron contributions from conventional orbital-derived states remains challenging. Progress will require improved spectroscopic probes, more stable materials synthesis, and quantitative descriptors linking interstitial-electron localization, connectivity, and hybridization to physical properties. Establishing such relationships between crystal architecture, interstitial electronic states, and emergent phenomena will be essential for developing a predictive framework. Rather than replacing established concepts such as orbital and band engineering, interstitial-electron physics provides an additional real-space dimension for designing quantum materials, where crystal structures can be used to organize electronic states and explore new electronic functionalities.

REFERENCES

1. Dye J.L. (2003). Electrides: Ionic salts with electrons as the anions. *Science* **301**:607–608. DOI:10.1126/science.1088105
2. Hosono H. and Kitano M. (2021). Advances in materials and applications of electrides. *Chem. Rev.* **121**:3121–3185. DOI:10.1021/acs.chemrev.0c00732
3. You J.-Y., Lyu P., Wang Y.-M., et al. (2022). Emergent kagome bands in the electride Li_5Si. *J. Am. Chem. Soc.* **144**:5527–5533. DOI:10.1021/jacs.1c12816
4. Geng S., Wang X., Guo R., et al. (2026). Experimental realization of dice-lattice flat band at the Fermi level in layered electride YCl. *Nat. Commun.* **17**:2213. DOI:10.1038/s41467-026-69049-0
5. Liu Z., Wang X., Yang Y., et al. (2026). Free-anionic duality of interstitial electrons drives superconductivity in electrides. *J. Am. Chem. Soc.* **148**:27520–27527. DOI:10.1021/jacs.6c05978

FUNDING AND ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (NSFC, Grant No. 12222413), the Natural Science Foundation of Ningbo (Grant No. 2024J019), the "Innovation Yongjiang 2035" Key R&D Programme-International Sci-tech Cooperation Projects (Grant No. 2025Z224), the funding of Ningbo Yongjiang Talent Program and the Mechanics Interdisciplinary Fund for Outstanding Young Scholars of Ningbo University (Grant No. LJ2024003). The funders had no role in study design, data collection and analysis, decision to publish, or preparation of the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.