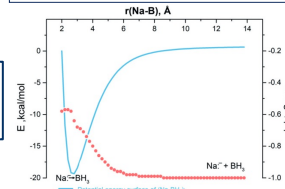
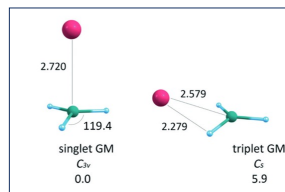


### First realisation of a Lewis adduct with an alkali as Lewis base (DATIVE BOND PICTURE)

- (Na-BH<sub>3</sub>)<sup>-</sup> cluster was generated by laser vaporisation
- The photoelectron spectrum of (Na-BH<sub>3</sub>)<sup>-</sup> suggests the existence of a Na<sup>-</sup> moiety and of a Na-B bond
- Unbiased GM search of 5000 randomly generated structures, on both singlet and triplet PES: CASSCF(8,14)/aug-cc-wCVQZ calculations showed a pronounced multi-reference character
- The singlet GM structure has a Na-B bond
- Computed VDEs confirm that the major species experimentally observed is the singlet GM
- Calculated BDEs (CCSD(T)/aug-cc-pCVQZ with ZPE corrections) show that the heterolytic bond breakage in Na<sup>-</sup> and BH<sub>3</sub> is favoured ⇒ satisfies the IUPAC definition of **DATIVE BOND**:



**“The distinctive feature of dative bonds is that their minimum-energy rupture in the gas phase or inert solvent follows the heterolytic bond cleavage path.”**

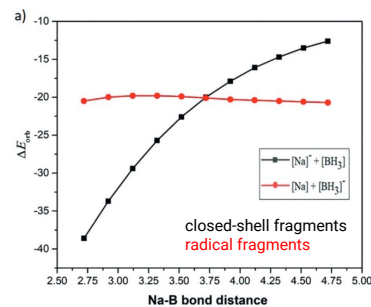
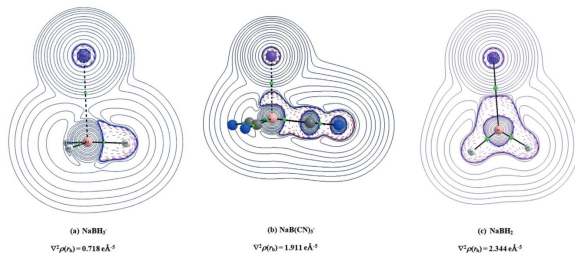
- (Na-BH<sub>3</sub>)<sup>-</sup> can be described as a Na<sup>-</sup>→BH<sub>3</sub> Lewis acid/base adduct
- Analysis of the Mulliken charges on Na, AdNDP and QTAIM confirm the results
- QTAIM: the positive ∇<sup>2</sup>ρ at the Na-B bond indicates closed-shell interactions (dative bond)

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### Comment: NaBH<sub>3</sub><sup>-</sup> has a classic ELECTRON-SHARING COVALENT BOND

- Computed ΔE<sub>orb</sub> via EDA at the DFT level: at equilibrium, the ΔE<sub>orb</sub> value for the electron-sharing interaction is smaller than for the dative bonding
- The Na-B bond is not dative, although the dissociation gives Na<sup>-</sup> and BH<sub>3</sub> as low-lying fragments**
- QTAIM interpretations based on Laplacian values at bond critical points (BCPs) of heavier and more electropositive atoms are not reliable for the nature of a chemical bond
- Mulliken charges are more meaningful but very sensitive to the basis set

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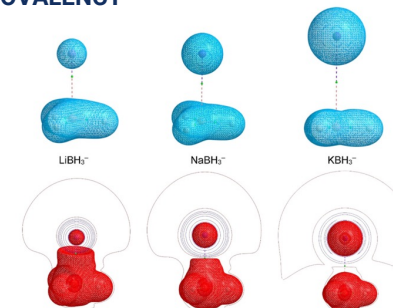
### Answer: DFT-based EDA is not to be trusted

- A dative bond is still electron-sharing
- Given the important multireference character, DFT is not suitable for exploring bonding and dissociation of NaBH<sub>3</sub><sup>-</sup>
- QTAIM results must be dealt with carefully, but they are sustained by AdNDP
- According to the definitions the Na-B is definitely dative, but the real questions are:
  - How do we define a dative bond?
  - Is it time to reconsider the classical definition?
  - Are there theoretical fingerprints that unambiguously distinguish a dative bond?

*Angew. Chem. Int. Ed.* **2020**, 59, 8760.

### The role of electrostatic interactions on delocalization: IONIC-ENFORCED COVALENCY

- Characteristics of the (3, -1) CPs of the M-B bond are inconsistent with covalent bonding
- Electron densities comparable with those of a weak H-bond
- Isosurfaces show interatomic regions that are too electron-deficient to classify these bonds as ordinary or dative covalent bonds
- IQA analysis shows that the xc component of the interaction energy is non-negligible and always attractive, but the variation of interaction energy is mainly controlled by the *Coulombic electrostatic energy* → indicator of IONIC CHARACTER
- The interaction cannot be classified as covalent (neither ordinary or dative)
- However, there's a unique characteristic, unprecedented among known chemical bonds:



**although being entirely controlled by Coulombic electrostatic forces and the electron densities at (3,-1) CPs are extremely low, the magnitude of electron delocalisation between M and B is significantly higher than any other non-covalent interaction**

- Unlike charge-shift bonds, the density at (3,-1) CPs is extremely low (typical of non-covalent interactions)
- The high degree of electron-sharing is possible because of the strong attraction between the two highly charged fragments as metal and boron are kept in close proximity

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### Beyond the classical bond picture: SPIN-POLARISED BOND

- Bonds can suffer spin-polarisation and it can lead to a diradical or diradicaloid species
- Signatures of diradical character are a small singlet-triplet gap and a spin-polarised (broken-symmetry, BS) solution below the closed-shell (CS) one
- EDA doesn't consider spin-polarisation
- Mayer's LSA: <S<sup>2</sup>> decomposed in LOCAL and diatomic spin terms
- Mayer's bond order is 1-p<sup>2</sup>-p<sub>s</sub><sup>2</sup> when BS solution is allowed
- Local spin is <S<sup>2</sup>><sub>A</sub> = 3/4 p<sub>s</sub><sup>2</sup> (1-S<sub>AB</sub><sup>2</sup>)
- So: increase of local spin, decrease of covalent bond order because of spin-polarisation

**Table 1:** Chemical bonding analysis

Chemical Bond	Bond order A-B	Local spin on A and B	EDA A→B vs A←B
Electron-sharing	Large	Small/Null	ΔE <sub>orb</sub> (A* + *B)  <  ΔE <sub>orb</sub> (A + B)
Donor-acceptor	Small	Small/Null	ΔE <sub>orb</sub> (A* + *B)  >  ΔE <sub>orb</sub> (A + B)
Spin-Polarized	Small	Medium/Large	ΔE <sub>orb</sub> (A* + *B)  <  ΔE <sub>orb</sub> (A + B)

- Clearly unnoticed before, the CS description of (Na-BH<sub>3</sub>)<sup>-</sup> is not stable
- Stability analysis reveals an unrestricted BS solution that leads to a lower electronic state
- CASSCF calculations show a non-negligible diradical character (<S<sup>2</sup>>), indicating spin-polarization
- QTAIM for bond orders, local spins and delocalization indexes
- (Na-BH<sub>3</sub>)<sup>-</sup> BS solution shows a small bond order (0.53) but significant local spins on Na and B, suggesting a SPIN-POLARIZED BOND

*Angew. Chem. Int. Ed.* **2021**, 60, 1498.