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Reply

Reply to Comment on 'Chemical bonding in phase-change chalcogenides'

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Abstract

The above comment on our article (Müller *et al* 2025 *J. Phys.: Condens. Matter* **36** 325706) criticizes our assignment of the chemical bond in phase-change chalcogenides, such as GeTe, as electron-rich ('hypervalent'). The authors claim that these bonds, and all those in $(GeTe)_{1-x}(Sb_2Te_3)_x$ crystals, are electron-deficient and partially multicentre in nature. We show, particularly by focusing on electron-counting rules, that the latter claim is incorrect. It arises from inaccurate counting of electrons in GeTe, in particular, and the mistaken belief that density-based calculations, such as the quantum theory of atoms in molecules (QTAIM) of Bader, suffice to identify the bonding character in molecules or solids.

Keywords: chalcogenide materials, phase-change materials, chemical bonding, electron-rich multicentre ('hypervalent') bonding, density functional calculations, quantum theory of atoms in molecules (QTAIM)

In their comment on our article [1], Gatti and Raty (GR) use techniques based on the electron density and describe the chemical bonding in phase change chalcogenides as 'electron deficient' and partially multicentre. Many of their arguments were presented in an earlier review [2], where GR are two of the authors. We show again here that their analysis is incorrect; the bonding in the chalcogenide materials in question is indeed 'electron-rich' or 'hypervalent'.

The assignments 'electron-deficient' and 'electron-rich' apply to systems that have too few or too many valence electrons, respectively, for all atoms to satisfy the Lewis octet rule (four pairs of bonding electrons, eight valence electrons per atom). B_2H_6 is a textbook example that has at least seven bonds, but it has only 12 electrons and is 'electron-deficient'. The linear molecule XeF_2 has occupied bonding *and* non-bonding ('lone-pair') orbitals. The latter are an essential feature of electron-rich molecules and occur most readily in systems containing the late main-group elements with p-shells that are at least half occupied. Musher [3] considered only molecules containing atoms of groups 15–18 when he introduced the synonym 'hypervalent' for

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electron-rich molecules. Both electron-deficient and electron-rich molecules involve 'half-bonds' (bond order 0.5), despite having different valence-electron counts.

It has been known for nearly 100 years that chemical bonding originates with the interference of the wave functions of the constituent atoms (in the context of density functional theory, the Kohn–Sham orbitals). This interference can be constructive (bonding), destructive (antibonding), or absent (nonbonding), and depends sensitively on the details of the component orbitals, particularly their *signs*. Much information is lost if one considers only the square of the wave function, the electron density. Recovering bonding information from the density requires the use of auxiliary functions, such as the electron delocalization index DI used by GR within the framework of the quantum theory of atoms in molecules (QTAIM) [4].

GR question some details of our method of calculation (LOBSTER), suggesting that unreliable bond indices ICOBI$^{(3)}$ may result from the projection used, our choice of basis functions, or whether the 'overall projection procedure leaves the total electron density invariant locally'. This criticism is misplaced. The plane-wave basis functions are delocalized; energy convergence with increasing kinetic energy cutoff is rapid and can easily be verified [5, figure 1]. The auxiliary local basis functions for projection are all-electron contracted Slater functions that give extremely accurate total energies in Hartree–Fock calculations for atoms. The projection is a *unitary* transformation that changes neither the density nor the energy eigenvalues (band structure). LOBSTER determines the total number of electrons in the plane-wave calculation and the number of electrons after the projection; these numbers are identical in all cases in [1] and in the present work. The same applies to the transformation from atomic orbitals to fragment orbitals.

The Xe–F bond order in electron-rich XeF_2 (known to be 0.5) is reproduced extremely well by the orbital-based program LOBSTER (0.49) [1]; the QTAIM bond order is 0.92, an overestimate of 84%. XeF_2 has 10 p-valence electrons, but similar discrepancies also occur in molecules satisfying the octet rule, such as SCl_2 or $SeBr_2$ (figure 1). The orbital-based bond orders of S–Cl or Se–Br correspond to single bonds, in quantitative agreement with the experimental bond lengths [6, 7], but QTAIM gives extremely poor values. Numerous other examples of the different results arising from using orbital-based and density-based methods are found in the two-dimensional plots ('maps') of electrons shared and transferred during bonding in many materials [1, figure 1]. The view of GR that these maps are 'qualitatively similar' is not supported by detailed examination, particularly for the chalcogenide materials and hypervalent molecules discussed here.

We prefer an orbital-based approach (LOBSTER) to a density-based approach (QTAIM) not because it is 'convenient', but because it retains much information that is lost when orbitals are squared to determine the electron density. We mention just one example showing that density-based results can be chemically or physically unreasonable. If lithium is accommodated in amorphous carbon, QTAIM yields negative charges for certain Li atoms, which conflicts both with the higher electronegativity of carbon and solid state NMR

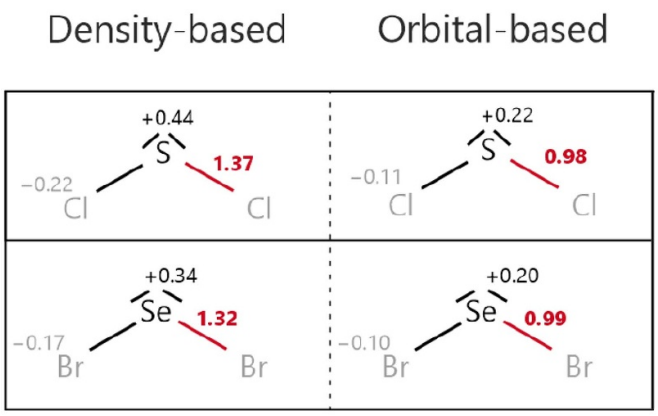

Figure 1. Chemical bonding of octet rule-conforming SCl_2 and $SeBr_2$ molecules calculated from QTAIM (density-based; DI bond orders and Bader charges), and LOBSTER (orbital-based; ICOBI bond orders and Löwdin charges). The experimental bond lengths equal the sum of the respective covalent (single-bond) radii.

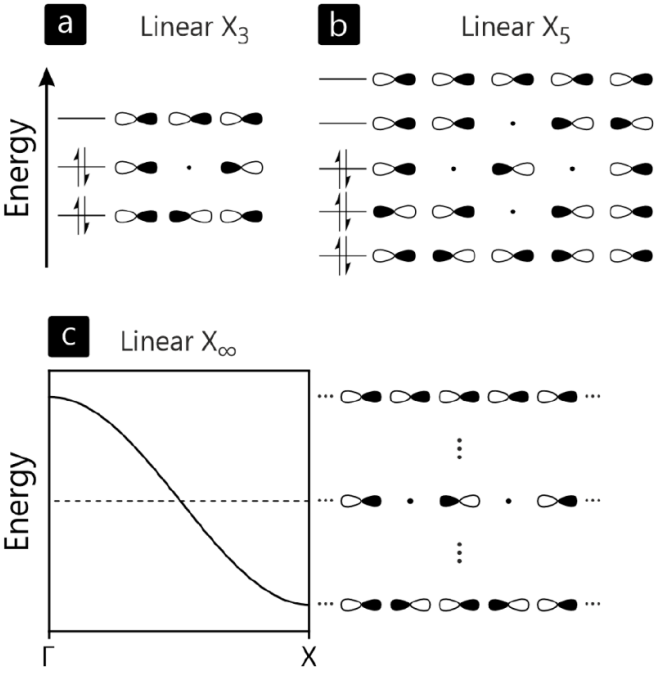

Figure 2. Schematic molecular-orbital diagrams for (a) a hypervalent three-atom molecule, (b) a five-atom molecule, and (c) an infinite chain (with band structure) of atoms with p-electrons.

measurements [8, and references therein]; Löwdin charges are consistent with the absence of anionic Li in amorphous carbon [8]. GR note that the 'maps' mentioned above have been used to identify materials with a favourable 'property portfolio' by noting correlations with bonding mechanisms. We have discussed this matter elsewhere [9] and note here that the same favourable chalcogenide materials are those with the smallest deviation from a rock salt structure. Focusing on the *structure* of a material may be much less controversial than discussing its bonding mechanism [10].

GR focus on the 'true electron count in chalcogenide bonds' in their rationalization of electron-deficient bonding,

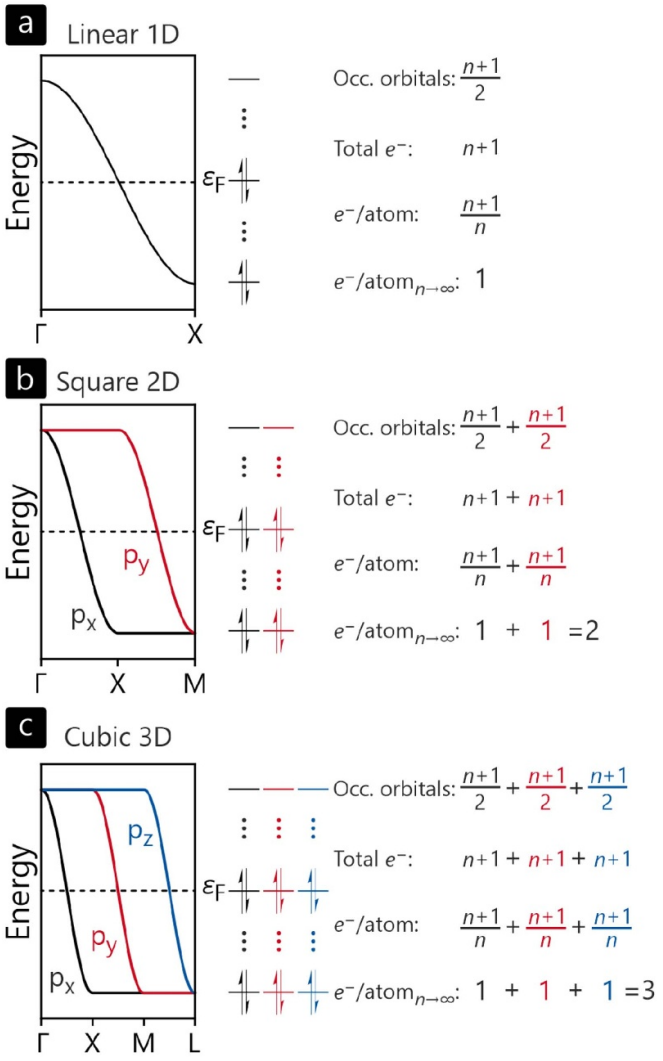

Figure 3. Schematic band structures for hypervalent (a) a linear 1D chain, (b) a 2D square lattice, and (c) a 3D cube with number of occupied orbitals, electrons and electrons per atom involved.

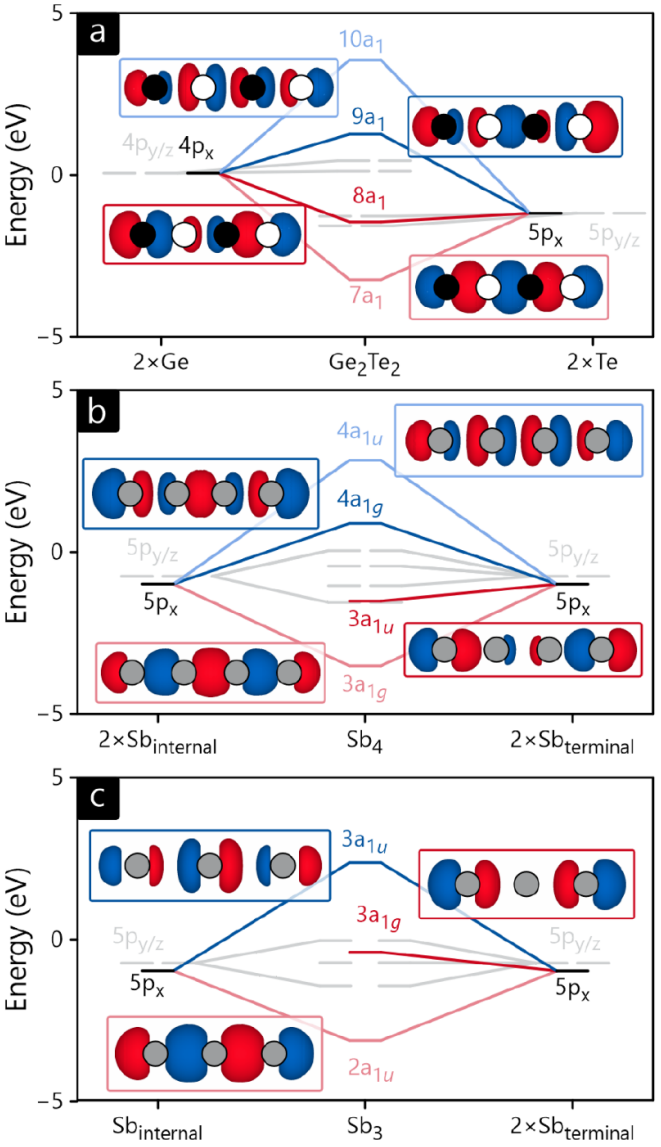

Figure 4. Fragment orbital diagrams of (a) Ge_2Te_2 in cubic GeTe, (b) Sb_4 and (c) Sb_3 in cubic Sb.

but assume incorrectly (as in [2]) that a periodic hypervalent electron-rich multicentre bond is a sequence of three-centre, four-electron (3c-4e) bonds, without providing a quantum-mechanical justification. Papoian and Hoffmann [11], however, showed how to construct such bonds by expanding the Pimentel–Rundle model of a 3c-4e bond involving p-orbitals [12, 13] to n centres (figure 2). There is an occupied, non-bonding orbital at the Fermi energy for all n. If we now apply this model to a linear chain, a square lattice, and a cube, we obtain the electron counts shown in figure 3. For an infinite, 3-dimensional cube, there are 3 p-electrons per atom corresponding to the three perpendicular spatial directions, i.e. p_x, p_y, and p_z, which we assume to be independent. This p-electron configuration is present in β-GeTe (if we average over $4p^2$ and $5p^4$) and cubic Sb ($5p^3$).

GR question our choice of the fragments for which we calculated bond indices. We showed in [1] that the three-centre bond index for the Te–Ge–Te fragment in GeTe is negative, indicating surplus electrons. This is consistent with the valence-electron count of GeTe (10, not 8), with a $4s^2$ surplus electron pair on the divalent Ge atoms. (In Ge–Te–Ge, the central Te atom locally obeys the octet rule.) GR favour studying the fragment Ge_2Te_2, because $GeTe_2$ and Ge_2Te are not repeat units in GeTe. We have noted above, however, that replacing both Ge and Te atoms in β-GeTe by Sb atoms results in simple cubic Sb, which has already been identified as a three-dimensional hypervalent material [11]. The frontier orbitals of Ge_2Te_2, Sb_4, and Sb_3 (figure 4) are strikingly similar, and the three-centre ICOBI$^{(3)}$ for an Sb–Sb–Sb fragment (−0.06) is slightly more than the average of Te–Ge–Te and Ge–Te–Ge, so that our original choice of fragments [1] appears indeed to be 'representative of the real bonding situation in crystalline β-GeTe'.

The shapes of frontier orbitals *and* their occupancies are essential to understand the underlying bonding mechanism, as noted by GR. We provide the Löwdin populations of

Table 1. Numbers of electrons per atom in the frontier orbitals forming hypervalent bonds in cubic GeTe and Sb per $x/y/z$ direction.

Compound	Fragment	Total Löwdin population	Electrons per atom
GeTe	Ge_2Te	2.74	0.91
	$GeTe_2$	3.25	1.08
	Ge_2Te_2	4.03	1.01
Sb	Sb_3	3.01	1.00
	Sb_4	3.99	1.00

the relevant fragment orbitals in table 1, as determined by LOBSTER during the calculation of fragment orbitals. The number of p-electrons per atom (1) conforms precisely to the results calculated for the model of Papoian and Hoffmann [11] for Ge_2Te_2, Sb_3, and Sb_4, as well as the average values for Ge_2Te and $GeTe_2$.

To summarize, GR criticize our classification of the bonding mechanism in phase change chalcogenides as 'electron-rich', as well as other points we make in our article: (1) our use of orbital-based rather than density-based bonding analyses, including property-based 'maps', (2) the counting of electrons in a 3D network of p-orbitals and its consequence for the underlying bonding mechanism, and (3) the choice of fragments of β-GeTe. These criticisms are addressed in this Reply; all are shown to be unfounded. The current interest in phase-change chalcogenides and their bonding mechanisms justifies an in-depth bonding analysis, such as carried out in [1] and the present response. This is much to be preferred over a theory based on unsubstantiated claims that lead to needless dispute.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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