Surfing plane waves with LOBSTER: Mulliken and Löwdin charges

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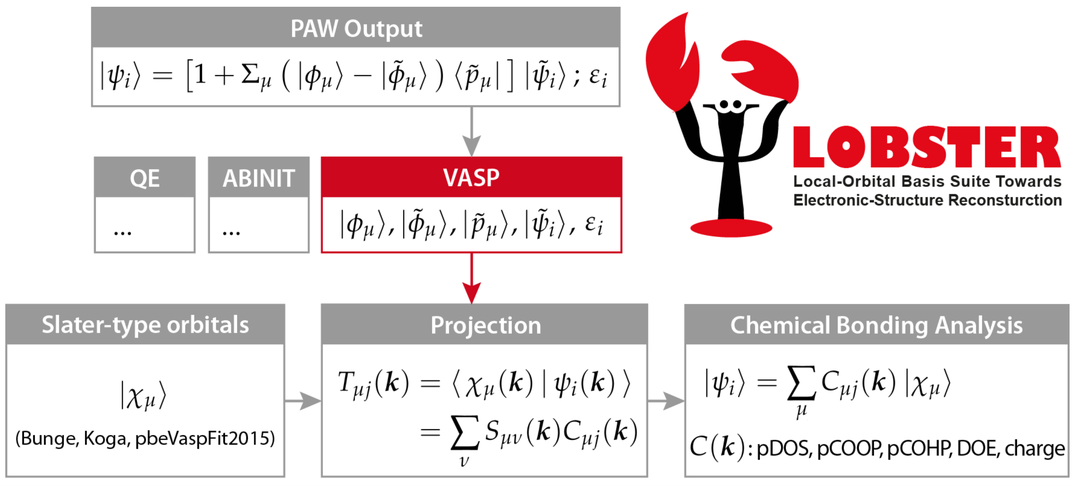
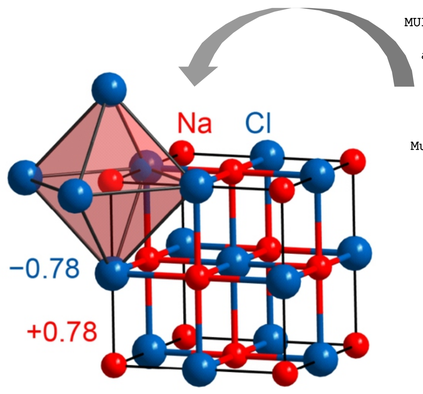
Introduction

Plane-wave DFT calculations have become a well-known practice within the computational solid-state physics, chemistry and materials science community. Understanding of the chemical and physical nature of a given material will facilitate designing materials with desired properties. LOBSTER[1] (Local-Orbital Basis Suite Towards Electronic-Structure Reconstruction) provides the tools for analyzing the underlying electronic structure in terms of local orbitals and their interactions to give new insight for chemical understanding.
LOBSTER can be downloaded for free from http://www.cohp.de/.



Methods

Traditionally, it was impossible to directly calculate charges from plane waves, so that resource-consuming real-space density-based techniques have become well-established methods. LOBSTER automatically performs reciprocal-space wavefunction-based Mulliken and Löwdin population and charge analyses that tackle the problems of the common methods in terms of resources and chemical reasonableness[2,3].



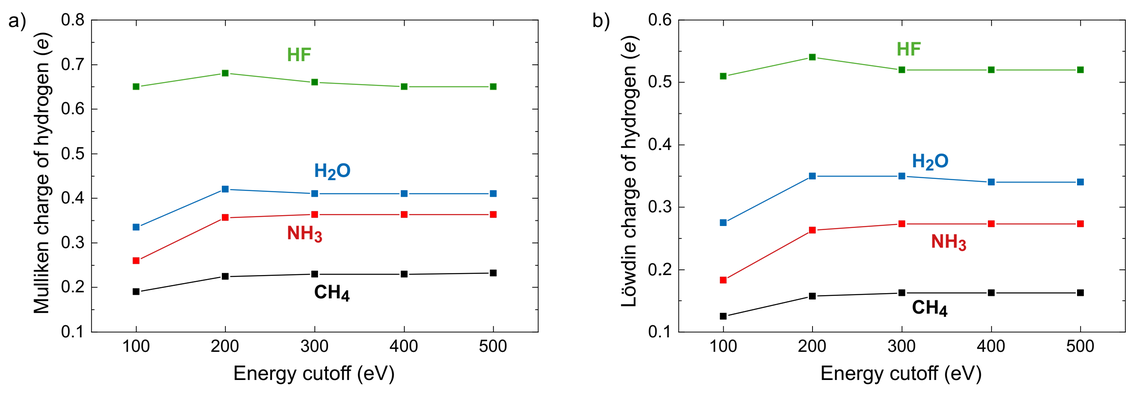
MULLIKEN and LOEWDIN POPULATION ANALYSIS

atom#	atom	Mulliken charge	Loewdin charge
1	Na	0.78	0.67
5	Cl	-0.78	-0.67
	total	0.00	0.00

Mulliken and Loewdin gross orbital population

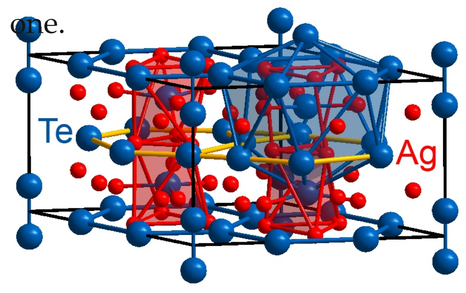
atom#	atom	basisfunction	Mulliken GP	Loewdin GP
1	Na	3s	0.22	0.33
		2p_y	2.00	2.00
		2p_z	2.00	2.00
		2p_x	2.00	2.00
		total	6.22	6.33
5	Cl	3s	1.95	1.87
		3p_y	1.95	1.93
		3p_z	1.95	1.93
		3p_x	1.95	1.93
		total	7.78	7.67

The Mulliken and Löwdin population analyses, as implemented in LOBSTER, do not suffer from what is called “basis set dependency” because they combine the advantages of using plane waves and local basis sets.

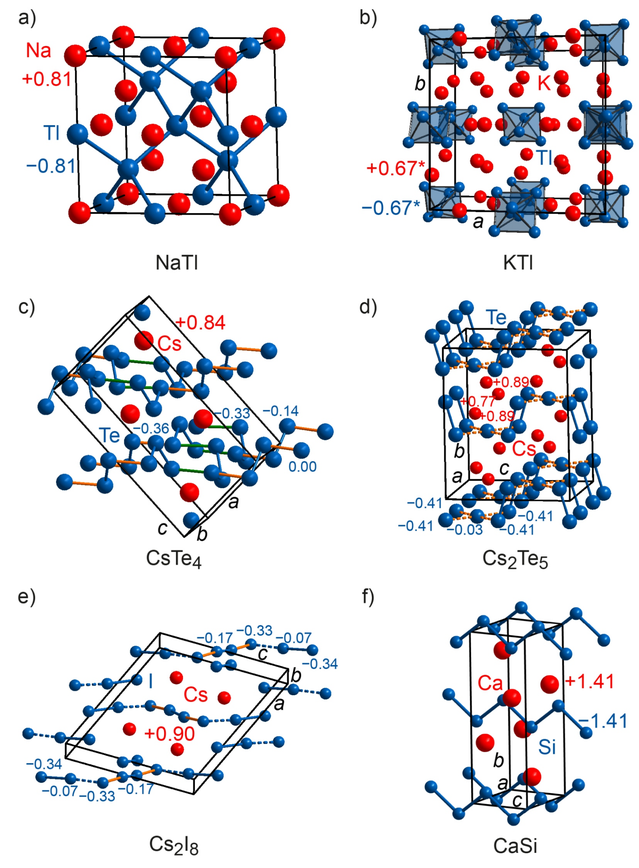


Zintl phases and polar intermetallics

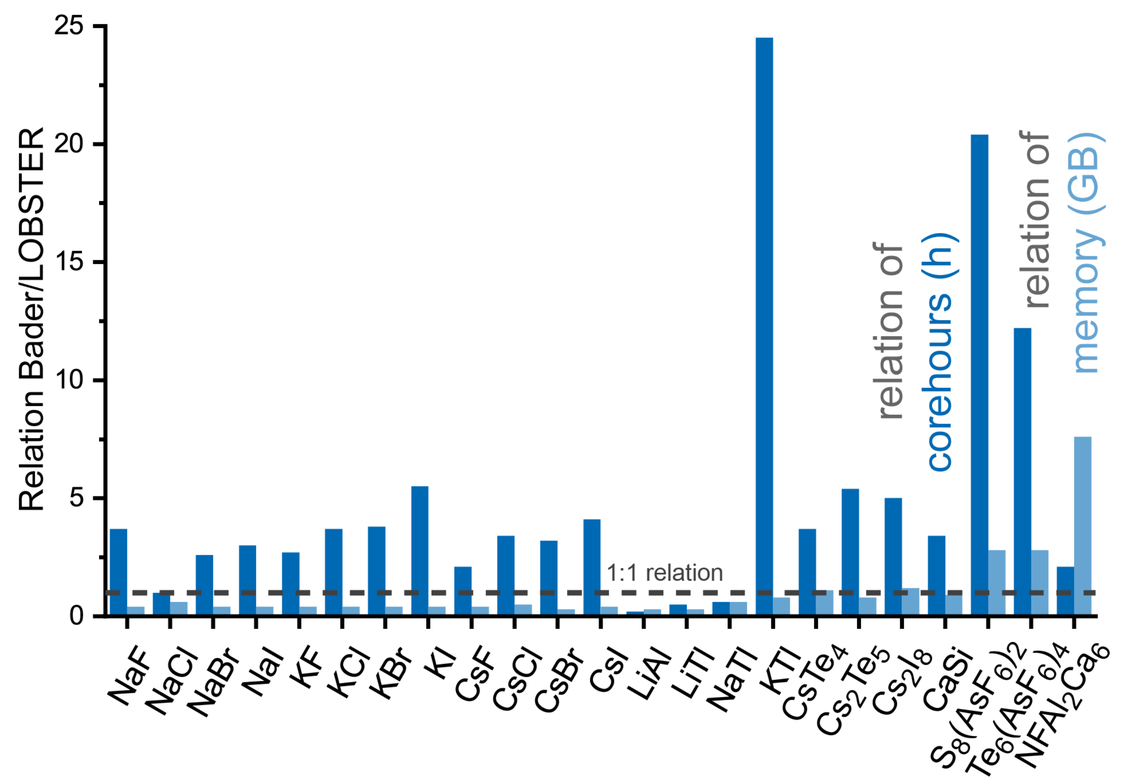
A closer look on the mineral stützite[2,4] $Ag_{5-x}Te_3$ in three compositions, i.e. “$Ag_{32}Te_{21}$”, “$Ag_{34}Te_{21}$” and “$Ag_{36}Te_{21}$”, revealed the limits of the Zintl–Klemm concept; however, applying the Mulliken and Löwdin population analysis tool allowed directly calculating the charges from the plane-wave-based computation. By using Madelung energies based on Mulliken charges, the electron-precise composition “$Ag_{34}Te_{21}$” was identified to be the most stable one.



$Ag_{5-x}Te_3$



The Mulliken and Löwdin population analyses in LOBSTER have evidenced to be competitive approaches in comparison to density-based methods, e.g. Bader’s charge analysis[5], regarding the consumption of resources. On average, the Bader charge analyses consumed about 5.1× more corehours and 1.1× more memory than the respective LOBSTER calculations in our test cases. In addition to the massively improved performance, we retain the level of data quality.



Acknowledgements

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Learn more:

[1] a) S. Maintz, V. L. Deringer, A. L. Tchougréeff and R. Dronskowski, *J. Comput. Chem.* , 2013, **34**, 2557–2567, b) S. Maintz, V. L. Deringer, A. L. Tchougréeff and R. Dronskowski, *J. Comput. Chem.* , 2016, **37**, 1030–1035.
[2] C. Ertural, S. Steinberg and R. Dronskowski, *RSC Adv., 2019*, **9**, 29821–29830.
[3] a) V. L. Deringer, C. Merlet, Y. Hu, T. H. Lee, J. A. Kattirtzi, O. Pecher, G. Csanyi, S. R. Elliott and C. P. Grey, *Chem. Commun.* , 2018, **54**, 5988–5991, b) J.-X. Huang, G. Csányi, J.-B. Zhao, J. Cheng and V. L. Deringer, *J. Mater. Chem. A*, 2019, **7**, 19070–19080.
[4] K. C. Göbgen , F. C. Gladisch and S. Steinberg , *Inorg. Chem.*, 2018, **57** , 412 —421
[5] R. F. W. Bader, *Atoms in Molecules: A Quantum Theory*, Oxford University Press, Oxford, 1994.