Structures of LaH$_{10}$, EuH$_9$, and UH$_8$ superhydrides rationalized by electron counting and Jahn-Teller distortions in a covalent cluster model

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Abstract

The superconducting hydrides LaH$_{10}$, EuH$_9$, and UH$_8$ are studied using chemically intuitive bonding analysis of periodic and molecular models. We find trends in the crystallographic and electronic structures of the materials by focusing on chemically meaningful building blocks in the predicted H sublattices. Atomic charge calculations, using two complementary techniques, allow us to assign oxidation states to the metals and divide the H sublattice into neutral and anionic components. Cubic [H$_8$]$^{q-}$ clusters are an important structural motif, and molecular orbital analysis of this cluster in isolation shows the crystal structures to be consistent with our oxidation state assignments. Crystal orbital Hamilton population analysis confirms the applicability of the cluster model to the periodic electronic structure. A Jahn-Teller distortion predicted by MO analysis rationalises the distortion observed in a prior study of EuH$_9$. The impact of this distortion on superconductivity is determined, and implications for crystal
structure prediction in other metal-hydrogen systems are discussed. Additionally, the performance of electronic structure analysis methods at high pressures are tested and recommendations for future studies are given. These results demonstrate the value of simple bonding models in rationalizing chemical structures under extreme conditions.

Introduction

Activity surrounds high-pressure hydrides due to reports of superconductivity near room temperature.\(^1\) In an effort to realise the prediction that hydrogen would become a room-temperature superconductor under sufficient pressure,\(^2\) a variety of hydrogen-rich binary materials \(\text{AH}_x\) have been predicted and synthesized. Among non-metal elements the sulfur-hydride system has been fruitful, with \(\text{H}_3\text{S}\) predicted and confirmed to be a superconductor with a critical temperature \(T_c\) of 203 K,\(^3,4\) and controversy surrounds reports of room-temperature superconductivity in an indeterminate compound of carbon, sulfur, and hydrogen.\(^5–7\) Metal-hydride systems have produced a number of superhydrides, particularly involving metals near the \(s/d\) border of the periodic table. \(\text{LaH}_{10}\) is perhaps the most recognisable example of this class, predicted and analysed theoretically\(^8\) before experiments confirmed the structure\(^9\) and then superconductivity at 250 K.\(^10,11\) Other examples include \(\text{CaH}_6,\)\(^12,13\) zirconium hydrides including \(\text{ZrH}_3, \text{Zr}_4\text{H}_{15},\) and \(\text{ZrH}_6,\)\(^14–17\) and various hydrides of yttrium.\(^8,18–20\) Some predictions of new hydride superconductors are yet to be realised,\(^21\) which has been attributed to shortcomings in DFT methods or the possibility that the superhydrides are not conventional phonon-mediated superconductors described by BCS theory.\(^22,23\)

The “workhorse” of this field is crystal structure prediction (CSP), an umbrella term for computational methods for determining the crystal structure of a material without any prior information.\(^24–29\) Studies utilizing this method generally identify the most thermodynamically stable phases for a chosen \(\text{AH}_x\) system as a function of pressure by running CSP calculations at various pressures and A:H ratios.\(^8\) Superconducting critical temperatures
can then be estimated for all candidate structures.

Some researchers have worked to understand these materials from a chemical perspective. “Chemical precompression” describes the strategy of ‘alloying’ hydrogen with another metal, so the compound should require less extreme pressures to induce superconductivity than would pure hydrogen. A growing focus of material design is ternary hydrides \( \text{ABH}_x \), where it is hoped that the combination of two metals will stabilize the phase at more accessible pressures due to additional chemical precompression. The combinatorial space of ternary phases is much larger than the binary phases, so chemical insight must be combined with efficient computational procedures to search efficiently for candidate materials. Ion size effects have also been explored, as the reduction in enthalpy arising from dense packing of atoms is a major contributor to thermodynamic stability at high pressures. Some of the highly symmetrical structures predicted for binary hydrides, such as \( \text{CaH}_6 \) and \( \text{LaH}_{10} \), are the densest binary sphere packings (DBSPs) for the appropriate stoichiometry and radius ratio. However, this model does not account for covalency in the anion sublattice, and hard-sphere radii are poorly defined under pressure, particularly for hydrides. Geometrical strain arising from size-cavity mismatch has been studied in a quantum chemical framework by chemical pressure density functional theory (CP-DFT), showing that distortions of symmetrical hydrides can indeed be caused by metal ion size (e.g. hexagonal channel widening in \( \text{SrH}_6 \) compared to \( \text{CaH}_6 \)).

Electron density and electron localization function (ELF)
calculations of compressed metal lattices have shown that the metals act as templates for the hydrogen networks, even though metal-hydrogen covalency is weak.\textsuperscript{35,36} Chemical insight also led to the discovery of Eu$_8$H$_{46}$, a high-pressure hydride isostructural to the “Zintl clathrates” (e.g. Ba$_8$Si$_{46}$), because such large unit cells are too expensive to be included in routine CSP studies.\textsuperscript{37} Electron counting is widely used in solid state chemistry to assign formal oxidation states,\textsuperscript{38} and can be used to rationalise structural trends through models like the Zintl-Klemm concept or the 18-n rule.\textsuperscript{39,40} Solids containing cluster anions are particularly amenable to electron counting analysis - for example, the conductivities of metal hexaborides, MB$_6$, can be predicted from the metal valence state by application of the Wade-Mingos rules.\textsuperscript{41–44}

In this study we focus on covalent sub-units in the H-H networks of LaH$_{10},$\textsuperscript{11} EuH$_9,$\textsuperscript{37} and UH$_8,$\textsuperscript{45,46} all shown in Figure 1, in order to explain structural trends. LaH$_{10}$ is well-studied by theory and experiments, as described above.\textsuperscript{8–11} EuH$_9$ was predicted to exist in two forms, $F\bar{4}3m$ and $P6_3/mmm$, of which we study the pseudo-cubic $F\bar{4}3m$ form, and XRD data collected at 86-130 GPa were consistent with this material. The strong spin polarization of Eu$^{2+}$ is expected to preclude superconductivity, though a calculation neglecting magnetism predicted a superconducting $T_c$ of 27 K.\textsuperscript{37} UH$_8$ was first predicted in a CSP survey of uranium hydrides and a $T_c$ of 23-33 K was calculated, but XRD data were ambiguous over whether a produced phase was UH$_8$ or UH$_9$.\textsuperscript{46} A subsequent synthetic study confirmed that the phase was indeed UH$_8$.\textsuperscript{45}

All three contain cubic H$_8$ clusters in their anion sublattices, as shown in Figure 1, but the cubes are distorted in EuH$_9$, so we wish to explain the stability of this motif and the distortion in an electron counting framework, and find whether it is related to superconductivity. It is important to note that the hydrogen sublattices of all superhydrides are predicted but not confirmed because high-pressure X-ray diffraction can provide information on the symmetry and lattice parameters of a material, and these data must then be compared to theoretical predictions to determine the most likely structure. We analyse charge and bonding pat-
terns in periodic structures, including benchmarking of analytical methods on CaH$_6$, and use these insights to devise cluster models which capture the balance of covalent and ionic behaviour of hydrogen. Crystal orbital Hamilton population (COHP)$^{47,48}$ calculations, an established tool for studying hydride-rich materials,$^8$ validate the cluster models and reveal striking differences between inequivalent hydrogen atoms. Electron counting and molecular orbital theory provide intuitive explanations of structural trends in the superhydrides.

**Methodology**

Periodic Density Functional Theory calculations were performed with VASP,$^49$ version 5.4.4, using the PAW$^{50}$-PBE$^{51}$ method with plane-wave cutoff of 600 eV. k-point grids of 15-15-15 were used for optimizations of CaH$_6$, UH$_8$, and LaH$_{10}$, and a 12-12-12 grid was used for EuH$_9$. All geometries were optimized until the components of the forces on all atoms were less than 0.03 eV/Å. Calculations on CaH$_6$ were performed using a hard H pseudopotential ("H$_h$") and a 700 eV plane-wave cutoff, though subsequent tests found that this did not cause a significant change to the structural optimizations compared to the ordinary H pseudopotential and a 600 eV cut-off (see Figure S1 for details).

Electron densities were analysed with the Quantum Theory of Atoms in Molecules (QTAIM) method.$^{52}$ Calculations were performed with the Bader program.$^{53}$ To ensure accurate results for compressed structures, we tested the effect of the number of points in the fine FFT grid (NG(X,Y,Z)F in VASP) on the computed AIM charges for CaH$_6$. At 210 GPa, 200 points along each vector were required to ensure convergence of the Ca charges to within 0.05 |e|, while at ambient pressure this threshold is reached with the default value of 80. The H charges converged at 80 points at 0 GPa and 140 points at 0 GPa. Full results are available in Figure S2. In summary, in CaH$_6$ the metal charges converge with respect to FFT grid more slowly than the H charges, and pressure significantly increases the required number of grid points. All QTAIM results were collected with 250 grid points.
Local orbital bonding analysis was performed with LOBSTER.\textsuperscript{54} Single-point calculations for LOBSTER analysis used 12-12-12 grids due to memory constraints. LOBSTER analysis requires projection of the plane-wave wavefunction into a local (Slater) orbital basis, and the quality of the results depends on the basis functions chosen for each element. Projection quality is measured by “charge spilling”, which is the percentage of electron density lost by the projection. The dependence of charge spilling on basis set were determined for CaH\textsubscript{6}, UH\textsubscript{8} and LaH\textsubscript{10} by performing LOBSTER projections at various pressures with and without high-lying p orbitals (4p for Ca, 6p for La, 7p for U). For all three compounds, the two bases give similar results at 0 GPa but inclusion of the extra p orbital causes the charge spilling to rise rapidly as pressure increases. In particular, for CaH\textsubscript{6} the larger projection basis gives a superior projection at 0 GPa (1.90\% vs 2.34\%) but much worse results at 210 GPa (10.4\% vs 3.7\%). Full results are available in Figure S3. Important conclusions from these tests:

1. Inclusion of diffuse, high-energy atomic orbitals worsens projection quality for compressed structures

2. Basis sets must be tested on high-pressure structures

Full basis functions used in this study were Ca 3s3p4s, La and Eu 4f5s5p5d6s, U 5f6s6p6d7s, H 1s, with the PBEVaspFit basis set.\textsuperscript{54} All projections for UH\textsubscript{8}, EuH\textsubscript{6} and LaH\textsubscript{10} have charge spillings of less than 3\% except for UH\textsubscript{8} at 210 GPa (3.09\%). 3\% was recommended as a threshold for a good projection in a recent study on high-throughput analysis with LOBSTER.\textsuperscript{55} COHP analysis of LaH\textsubscript{10} and UH\textsubscript{8} was done with structures optimized at 0 GPa to maximise the quality of the projection. Phonon calculations were performed with VASP in the density functional perturbation theory (DFPT) framework, and the results were analysed using phonopy.\textsuperscript{56}

Gas-phase DFT calculations were performed with ORCA,\textsuperscript{57} version 5.0.3, using the PBE functional,\textsuperscript{51} def2-SVP basis functions,\textsuperscript{58} and a CPCM solvent model\textsuperscript{59} with the dielectric constant of water to aid convergence of anions. The cubic H\textsubscript{8} structure was taken from the
150 GPa optimized structure of UH$_8$, and molecular orbitals were calculated by a single-point with a 6- charge. The distorted H$_8$ structure was taken from the 150 GPa optimized structure of EuH$_9$, and molecular orbitals were calculated by a single-point with a 2- charge.

**Results and discussion**

To establish a chemically intuitive picture of the metal hydrides, we optimized the structures of CaH$_6$, UH$_8$, EuH$_9$ and LaH$_{10}$ at 0-210 GPa, in 30 GPa steps, and then calculated atomic charges with the aim of determining oxidation states for the metals. Results for EuH$_9$ could not be collected at 0-30 GPa because the H network optimized to form H$_2$ molecules, while the other phases were prevented from doing this by symmetry. UH$_8$ and LaH$_{10}$ retain cubic symmetry at all pressures, but EuH$_9$ undergoes a small compressive tetragonal distortion ($\frac{b}{a} = 0.993$ at 150 GPa) because the distorted cube contains four parallel edges which are fractionally shorter than the other eight. We will describe this structural distortion in detail later.

For the atomic charge calculations we use QTAIM,\textsuperscript{52} based solely on electron density, and Mulliken analysis,\textsuperscript{60} based on atomic orbitals, as the fundamentally different methods of apportioning electrons to individual atoms provide complementary pictures of the materials. Figure 2 shows the calculated charges of the metals from both methods.

All curves show that the magnitude of the metal charge decreases as pressure increases, because compression increases overlap and reduces charge separation. The AIM charges show small differences between the metals, with charges ranging from 1.4 to 1.8 at 0 GPa and increasing in the order Eu, Ca, La, U. The Mulliken charges have one qualitative difference in that Ca has a far larger charge - almost 2 - than the other three metals. This reflects the strongly ionic nature of Ca, while Eu, La and U all have valence $d$ orbitals which are low enough in energy to bond with the H network covalently. The computed charges are as expected in that Ca and Eu typically form +2 cations, La is typically 3+, and U can have
oxidation states ranging from +3 to +6. Support for the assignment of Eu$^{2+}$ comes from the spin moments of 6.81-6.82, indicative of a $4f^7$ configuration. The similarity between La and U in both methods suggests an assignment of U$^{3+}$, which would match UH$_3$, the ambient-pressure uranium hydride.

In the hydrogen charge calculations, the charges become less negative as pressure increases. For LaH$_{10}$ and EuH$_9$ we can divide the hydrogens into those which form H$_8$ cubes, H$^{\text{cube}}$, and those which form the tetrahedral interstitial sites, H$^{\text{tet}}$. The two types are shown as grey and black atoms respectively in Figure 1. The AIM hydrogen charges for EuH$_9$ and
LaH$_{10}$ are shown in Figure 2, separated into the cube and tetrahedral sites. Mulliken charges were excluded from the figure for clarity and can be found in Figure S8. The H$^{\text{tet}}$ atoms have smaller negative charges than the H$^{\text{cube}}$ atoms, according to both charge analysis methods, and resemble neutral atoms, while the H$_8$ cubes are anionic. For our electron-counting analysis of the H$_8$ cubes, we will therefore assume that the interstitial atoms are neutral and consider only electron transfer from the metal to H$_8$. This assumption allows us to treat UH$_8$, EuH$_9$ and LaH$_{10}$ on an equal basis when rationalizing the symmetric and distorted cube geometries. The left-hand side of Figure 3 shows a molecular orbital (MO) diagram for a free H$_8$ cube, with $O_h$ point symmetry, which is our starting point for studying the structures of UH$_8$, EuH$_9$ and LaH$_{10}$. The shapes and energetic ordering of the orbitals have been computed by DFT (Figure S9), but are shown here in a simplified representation and have not been orthogonalized to maximise the similarity between the cartoon and computed orbitals.

Stable formal oxidation states arise from any configuration which gives completely filled valence shells. The simplest is neutral H$_8$, where the $a_{1g}$ and $t_{1u}$ sets are completely filled and

Figure 3: Walsh diagram showing orbital correlations between the cubic ($O_h$) and distorted ($D_{2d}$) geometries of an H$_8$ cluster.
the $t_{2g}$ and $a_{2u}$ sets are vacant. Completely filling the $t_{2g}$ set gives a closed-shell $H_8^{6-}$ ion, which fits into an extreme ionic counting picture of $UH_8$ since +6 is the highest accessible oxidation state for $U$. The final option is to singly fill each of the $t_{2g}$ orbitals, forming $H_8^{3-}$ which matches with $La^{3+}$ in $LaH_{10}$, supporting the model of neutral tetrahedral $H$ atoms. A free $H_8^{3-}$ ion would have a quartet ground state, having three unpaired electrons, but in a solid the spin information will be lost when the $t_{2g}$ MOs form bands by overlapping with other atoms. The $H-H$ bond lengths in the cubes offer another perspective on the oxidation state of $U$; the optimized cube edge length at 150 GPa in $LaH_{10}$ is 1.231 Å, while in $UH_8$ it is elongated to 1.293 Å, consistent with additional electron donation into the antibonding $t_{2g}$ orbitals. If a $H_8^{3-}$ charge is assigned to $LaH_{10}$ then the bond lengths suggest that $U$ is in an oxidation state higher than +3, i.e. +6. This extreme formal charge separation belies significant covalency between $U$ and $H_8$.

To confirm the applicability of the molecular bonding model to the crystalline materials, we must show that hydrogen-metal interactions and $H-H$ bonds between cube and tetrahedral atoms do not fundamentally change the bonding within the cube. We have therefore calculated crystal orbital Hamilton populations (COHPs) for neighbouring pairs of atoms in $LaH_{10}$, which are shown in Figure 4. This analysis was done for the 0 GPa structure because it has the highest projection quality (lowest charge spilling). To confirm that the 0 GPa optimized structure contains the same essential bonding features as the compressed unit cells, in Figure S13 we plot the PDOS for $La$ and both inequivalent $H$ sites at 0 and 150 GPa, which show that the the distinguishing features of each atom are preserved across the pressure range, and the PDOS for all atoms broadens quite uniformly under pressure. The plots on the left side of Figure 4 show COHPs for a $H^{\text{cube}}-H^{\text{cube}}$ bond and a $H^{\text{cube}}-H^{\text{tet}}$ bond. The principal peaks in the two COHP curves are non-coincident, showing that the two types of $H-H$ bond are composed of distinct electronic states. The $H^{\text{cube}}-H^{\text{tet}}$ COHP shows a single large peak, indicative of a strong bonding interaction, so these interactions are important in determining structure. By comparing to the MOs in Figure 3 we can assign the
peaks in the cube edge COHP. The $a_{1g}$ and $t_{1u}$ peaks are bonding and fully occupied, while the $t_{2g}$ antibonding peak crosses the Fermi level, supporting our molecular model of $[H_8]^3$ with a half-filled $t_{2g}$ manifold. The $a_{2u}$ peak is difficult to assign on the basis of this COHP alone, but the ambiguity can be resolved with other COHPs (see below). Corresponding plots for UH$_8$, in Figure S11, show very similar behaviour for the H-H and U-H COHPs; since UH$_8$ has no tetrahedral interstitial H atoms, the similarity between H-H COHPs in LaH$_{10}$ and UH$_8$ validates the H$_8$ molecule as a structural model for the periodic hydrides. One noticeable difference is that the H-H $t_{2g}$ antibonding peak is largely below $E_F$ in UH$_8$, indicating greater electron transfer to the cube, as suggested above on the basis of H-H bond lengths. The right side of Figure 4 shows La-H COHPs for the cube and tetrahedral H sites.

Figure 4: Crystal orbital Hamilton population (COHP) analysis of LaH$_{10}$. H$^{\text{cube}}$ atoms are shown in grey and H$^{\text{tet}}$ in black. Upper left: H$^{\text{cube}}$−H$^{\text{cube}}$ with annotations showing the assignment of $[H_8]$ molecular orbitals to COHP peaks. Lower left: H$^{\text{cube}}$−H$^{\text{tet}}$. Upper right: La−H$^{\text{cube}}$. Lower right: La−H$^{\text{tet}}$.

The largest bonding peak in the La−H$^{\text{cube}}$ COHP coincides with the $t_{1u}$ H-H band, and the H-H $t_{2g}$ band also coincides with an La-H bonding band that crosses the Fermi level. The interaction between H$_8$ $t_{2g}$ and La 5$d$ orbitals may therefore control the transport properties
of LaH$_{10}$, possibly including superconductivity. The La–H$^{\text{tet}}$ COHP has a single bonding peak coincident with the cube-interstitial H-H bonding peak, and an antibonding peak well above the Fermi level.

Finally, we plotted H-H COHPs for the face and body diagonals of the cube (Figure S12), which allow us to assign the high-energy peak corresponding to the fully antibonding $a_{2u}$ orbital. The peaks appear at the same energies as in the H$^{\text{cube}}$–H$^{\text{cube}}$ COHP (Figure 4) but differ in their sign, i.e. whether they are bonding or antibonding, and the absolute values are much smaller because these are not nearest-neighbour interactions. The face diagonal behaves as expected from the MOs - the $a_{1g}$ and $a_{2u}$ peaks are bonding, while the $t_{1u}$ and $t_{2g}$ peaks are antibonding. However, the body diagonal peaks all have the opposite signs to those expected from the MOs, with $a_{1g}$ and $t_{2g}$ paradoxically antibonding while $t_{1u}$ and $a_{2u}$ are bonding. We believe that this anomaly is due to the H atoms at opposite corners of the cube interacting with their periodic images through a metal atom, which could be comparable in strength to the intra-cube covalency along the body diagonal. This theory is supported by the fact that the $t_{1u}$ peak, which overlaps strongly with the metal, is larger than the $a_{1g}$ peak, and that the same behaviour is observed in LaH$_{10}$ and UH$_8$. In conclusion, the COHP results clearly demonstrate that the H networks of the periodic materials are well represented by a molecular H$_8$ model.

In EuH$_9$ the cubes distort to a $D_{2d}$ geometry in which four parallel edges shorten relative to the other eight (1.183 Å vs 1.214 Å at 150 GPa), as shown in the diagram on the right of Figure 3, and the angles distort so the faces go from square to rhombic.$^{37}$ The Walsh diagram in Figure 3 shows that this is consistent with the assignment of a 2- charge to H$_8$.$^{61}$ As before, the orbital energies and shapes are computed by DFT but shown in a simplified representation here, and the computed results are shown in Figure S10. Placing two electrons in the $t_{2g}$ orbitals renders the structure unstable with respect to a Jahn-Teller distortion which lowers the symmetry to stabilize that pair of electrons. The reduction in symmetry causes the triply degenerate $t_{2g}$ to separate into a $b_2$ orbital and a doubly degenerate $e$ pair. The
occupied $2b_2$ orbital is bonding along the four shorter edges of the cluster and antibonding along the other eight, consistent with the observed distortion. Oxidation state and MO analysis therefore successfully explains the $H_8$ cube distortion observed only in EuH$_9$, and this distortion, which makes the tetrahedral sites inequivalent, may be the reason that a cubic EuH$_{10}$ phase has not been observed.$^{37}$

Predictions for accessible structures of superhydrides can be made on the basis of this analysis. For a ternary hydride, the average oxidation state of the cations must be +3 for a cubic LaH$_{10}$-type structure to be stable. A $H_8$ cube in a superhydride of a 4+ cation, as might be expected for Zr, would also have a Jahn-Teller instability, but it would differ from EuH$_9$ in that the distortion would need to stabilize two pairs of electrons. The cube should therefore shorten eight bonds and elongate four, reversing the ordering of the $2e$ and $2b_2$ orbitals in Figure 3. The consequences of such a distortion for stable stoichiometries are not obvious, but we suspect that Zr would match Eu in forming ZrH$_9$ and not ZrH$_{10}$. To our knowledge, the structures of high-pressure Zr hydrides have only been investigated for compositions up to ZrH$_6$$^{14-17}$ and determining the positions ZrH$_9$ and ZrH$_{10}$ relative to the convex hull for the Zr-H system is outside the scope of this work.

Finally, we wish to investigate the connection between superconductivity and the Jahn-Teller distortion in EuH$_9$. We have done this by calculating the phonon band structure of LaH$_{10}$, identifying the mode which most closely resembles this distortion, and comparing to electron-phonon coupling (EPC) calculations in literature$^8$ to see whether this mode contributes significantly to the EPC constant. Figure 5 shows the phonon band structure of LaH$_{10}$, undistorted and distorted primitive cells of LaH$_{10}$, and the primitive cell of EuH$_9$ for comparison. These calculations were done at 300 GPa to eliminate imaginary frequencies and maximise comparability to literature. By inspection of the computed vibrational modes we find that mode 22 (44.54 THz at $\Gamma$) distorts the $H_8$ cube in LaH$_{10}$ to resemble EuH$_9$ most strongly. This comparison is shown on in Figure 5, and an important structural detail is that this distorted structure has one short and two long H-H bonds in the cube, just like EuH$_9$. 

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Figure 5: L: Phonon band structure of LaH$_{10}$ at 300 GPa. R: Undistorted and distorted primitive unit cells of LaH$_{10}$, where the distortion is over mode 22, and the optimized structure of EuH$_9$. La atoms are shown in green, Eu in pink, and H in grey. Orange and blue bonds denote elongated and compressed H-H bonds respectively.

The distorted structures in Figure 5 show longer bonds in orange and shorter bonds in blue. The phonon band structure is very similar to one previously computed which shows the contribution of each phonon mode to EPC. Comparing the two graphs shows that the Jahn-Teller distortion mode makes no contribution to EPC, so the distortion does not directly explain the difference in predicted critical temperatures between LaH$_{10}$ and EuH$_9$. The difference must therefore be due to other factors such as stoichiometry or metal-hydrogen interactions, the latter of which has been proposed to be an important difference between LaH$_{10}$ and YH$_{10}$. Conversely, if this vibrational mode is not a vital ingredient for superconductivity in LaH$_{10}$ then distorted derivatives featuring 2+ or 4+ cations may yet be viable candidates for high-temperature superconductors.

**Conclusions**

Structural trends in the high-pressure hydrides UH$_8$, EuH$_9$, and LaH$_{10}$ have been rationalised by the intuitive chemical tools of oxidation states and molecular orbital theory. Viewing the predicted hydrogen networks as an assemblage of atoms and clusters, rather than a metal-centered clathrate, allows us to divide the H atoms into chemically meaningful groups and
study their electronic structures. *Ab initio* atomic charge calculations, using the QTAIM and Mulliken formalisms, show that some H atoms are effectively neutral in the lattice, while the H₈ cubes are anionic. Formal oxidation states for the metals were assigned on the basis of charge calculations, so the electronic structures of the hydrides could be discussed in terms of electron transfer from metal atoms to hydrogen clusters. Molecular orbital descriptions of the H₈ clusters, validated by COHP analysis, rationalize the previously predicted crystal structures, including a Jahn-Teller distortion in EuH₉. The distortion is found not to be directly relevant to superconductivity, so these results inform the scope of the search for new high-temperature superconductors. These methods can be easily applied to predictions of composition and structure in the growing family of compressed metal hydrides.

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**Supporting Information Available**

Method testing results and additional electronic structure figures (PDF), and geometries of all optimized structures in VASP POSCAR format (zip archive).

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The superconducting hydrides LaH$_{10}$, EuH$_9$ and UH$_8$ are studied using DFT-based periodic and molecular bonding analysis. Charge calculations allow assignment of formal oxidation states and reveal that some hydrogen environments are anionic while others are neutral. A cluster model of an H$_8$ cube rationalises the symmetric structures of LaH$_{10}$ and UH$_8$, and predicts a Jahn-Teller distortion which is observed in EuH$_9$. This method contributes a new dimension to explorations of high-pressure hydride chemistry.