ELECTRONIC STRUCTURE OF ALKALINE METAL HYDRIDES ACCORDING TO MO LCAO-SCF-CNDO CLUSTER CALCULATIONS

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This paper presents the results of a quantum chemical study of compounds MH (M = Li, Na, K, Rb, and Cs) in a cluster approximation. The calculations were performed by the MO LCAO-SCF-CNDO method (special variation which proved to be effective for studying model systems of high-temperature superconductors). The calculation reproduces the expected electron density distribution on the hydrogen and metal atoms in the hydrides as well as the energy characteristics: M-H and M-M bond energies and the binding energies of compounds. The latter qualitatively correlate with the bond energies in the series of compounds LiH–CsH. The calculated Fermi energies and forbidden gaps at the Fermi level suggest that in the series being investigated a perfect crystal of lithium hydride will have the highest electric resistance. It is established that the quantum chemical characteristics of the electronic structure of MH change nonmonotonically from Li to Cs.

The hydrides of s-elements are of practical value as effective sources and accumulators of hydrogen, selective catalysts, ion conductors of electric current in melts, etc. For theoretical investigations they are of interest as compounds with highly polar chemical bonding, unique effective charge on the hydrogen atom, and significant effects of lattice dislocations on the properties of these compounds. The structure, stability, and reactivity of ordinary and complex hydrides of light elements were investigated at the levels of isolated molecules, ions, and radicals [1-3]. For comparing the calculated data with experiment and predicting the properties of materials based on these hydrides, cluster calculations modeling crystal lattices are required.

This paper reports on a quantum chemical study of the electronic structure of group IA metal hydrides and analyzes the effect of the nature of the metal on the properties of the compounds. Since any real crystal has deviations from the ideal arrangement of atoms in the lattice, several types of lattice defects in lithium hydride and their effects on the properties of this compound are studied.

For electronic structure calculations of the clusters modeling the compounds MH (M = Li, Na, K, Rb, and Cs) and LiHm (n ≤ 1 for m < 1, m = 1, and m > 1), we used a special variation of the MO LCAO-SCF-CNDO method which proved to be effective for investigating model systems of high-temperature superconductors [4, 5]. To improve the self-consistency process and model an infinite extension of the crystal lattice, we employed displacement of the diagonal matrix elements of the Fock matrix of central atoms to the sites of peripheral atoms of the cluster in each iteration. The calculations were performed in a basis set of valence s-orbitals of interacting atoms. The parameters of the orbitals correspond to the state of isolated atoms. (The calculations that include polarization of basis set orbitals [5] did not lead to qualitatively different results.)

The results can significantly vary or be even contradictory for clusters of different size. Therefore, we preliminarily calculated the clusters [M13H14]−, [M19H38]19−, and [M43H38]5+ denoted as C13, C19, and C43, respectively. Figure 1 shows the composition and structure of C43. The geometry of this cluster was chosen based on the data of [6]. It appeared that the size of the cluster affects the magnitude but not the character of variation of the calculated quantities in the series of MH from Li to Cs. For C43, one can note equalization of electron density distribution on the metal atoms located inside (M1, Mm) and on the surface (M5−1, Mm+2) of the crystal. The latter...
may be taken into account when one chooses lattice space to study the defects modeling the real crystal. This, together with moderate computation time, determines the choice of the C43 cluster for investigating the electronic structure of alkaline metal hydrides and modeling various defects of their crystal lattice.

The calculated characteristics of the electronic structure of MH compounds (M = Li, Na, K, Rb, Cs) are shown in Fig. 2. The calculation reproduces the expected electron density distribution in the hydrides: the hydrogen atoms are polarized negatively, and the metal atoms are polarized positively. The absolute values of electrovalence $V_e$ and covalence $V_c$ (calculated in accordance with the results of [4, 7]) and valence $S$ of the hydrogen and metal atoms depend on the positions of these atoms in the model cluster. This is especially true for hydrogen atoms. The Hsurf atoms lying at the lattice sites have the greatest absolute values of covalence and the least values of electrovalence. The Hsurf atoms are characterized by larger values of $V_e$ and smaller values of $V_c$. On the surface of the crystal, the electrovalences of the metal atoms (Msurf, Msurf2) are lower, and the covalences are higher, than those of the metal atoms (Me, Mint) located inside the crystal lattice. This points to a certain sensitivity of the surface of the compounds to interaction with polar reagents. The maximal reactivity of the surface in accordance with the maximal free valence is predicted for rubidium and cesium hydrides. The lowest covalence of lithium in its hydride may indicate that this compound has increased tendency toward lattice deformations compared to other alkaline metal hydrides. Defects will be most probably located inside the crystal. The highest electrovalence and the absolute valence of lithium in LiH probably determine the properties of this compound, for example, the highest thermodynamic stability and the lowest reactivity.

All electron distribution characteristics on the hydrogen and metal atoms in compounds of the series LiH-CsH vary nonmonotonically (Fig. 2). This may be explained by the nonmonotonic variation of electronegativity in the series of group IA metals:

<table>
<thead>
<tr>
<th>Element</th>
<th>Li</th>
<th>Na</th>
<th>K</th>
<th>Rb</th>
<th>Cs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electronegativity (Allred–Rohkov)</td>
<td>0.97</td>
<td>1.01</td>
<td>0.91</td>
<td>0.89</td>
<td>0.86</td>
</tr>
</tbody>
</table>

The calculation also correctly reproduces the variation of the experimental binding energies of MH from Li to Cs. As the number of the metal increases, the energy indices of M–H and M–M bonds decrease in magnitude (Fig. 3), indicating that the strength of these bonds decreases. The quantum chemical characteristics of M–H bond strength qualitatively correlate with the energies of these bonds in the series LiH–CsH calculated from the experimental standard enthalpies of formation of MH(c) and atomization energies of H2(g) and M(c) (Fig. 4). The calculation predicts a decrease in the stability of MH in the Li–Cs series: the binding energies of the compounds decrease in magnitude. The binding energies calculated from the experimental data change in the same way as $E_{\text{bin}}^{\text{theor}}$ (Fig. 5).