MODELING THE ELECTRONIC STRUCTURE OF GRAPHITE INTERCALATION COMPOUNDS WITH LITHIUM BY METAL COMPLEXES WITH POLYBENZENE SYSTEMS


The electronic structure of intercalation compounds obtained by inclusion of an alkali metal in graphite is considered using molecular complexes \( C_6H_6Li_2 \), \( (C_6H_6)_2Li \), and \( (C_6H_6)_3Li \) in the lowest energy states as examples. Modeling the electron distributions of the intercalates requires inclusion of metal d-orbitals in the basis set of AOs and rejection of purely ionic models. It was found that exclusion of the lithium d-AO from the basis set significantly increases the ionic character of the distributions.

INTRODUCTION

Studies of the intercalation compounds of alkali metals in graphite (intercalates) is of great interest due to their extremely unusual physical and chemical properties. Intercalates are defined by the formula \( C_nM \), where \( M \) is an alkali metal, \( n \geq 2 \) in the case of lithium, and \( n \geq 3, 4 \) in the case of heavier alkali metals. Graphite intercalation compounds (GIC) are synthesized at high pressures, but retain many of their properties in normal conditions [1-3]. At atmospheric pressure, the density of the metal in the intercalate may exceed that in the free metal (fourfold for \( C_4Cs \) and tenfold for \( C_2Li \)). Moreover, the nature of the valent state of an atom lying between the graphite layers in saturated metal GIC is also of considerable interest, since one can expect that even inner electron shells would be deformed in the intercalate.

The \textit{ab initio} studies of the electronic structure of intercalates by the \( X \alpha \) and density functional methods [4-7] indicate that the alkali metal is ionized due to the transition of the valence electron to the vacant \( \pi \)-orbital band of graphite (the metal s-band lies above the Fermi level by more than 1 eV). However, this currently widespread ionic model suggesting complete transfer of an electron from metal to graphite for saturated intercalates has some important disadvantages. For example, it does not explain the high density nor the stability of the metal in the intercalate.

In this work, we attempt to estimate the electron distribution in lithium intercalates using simple molecular models, i.e., finite systems that are analogous to fragments of an intercalate lattice. Without drawing global conclusions or evaluating the properties of intercalates, which is impossible in the framework of the approximations used, we would like to trace the changes in the valent state of the lithium atom due to variations of its environment. This approach to modeling intercalation compounds was earlier used by us in [8], which describes some molecular complexes of lithium with benzene and naphthalene. It is reported in [8] that neglect of the contributions of lithium d-orbitals can significantly alter the charge distribution between the metal and the aromatic hydrocarbon that models graphite. In particular, the deviations from the purely ionic structure were attributed to the population of lithium d-orbitals, which becomes significant for systems with \( D_{6h} \) symmetry. Below we discuss the calculations of some lithium complexes with benzene systems, \( C_6H_6Li_2 \), \( (C_6H_6)_2Li \), and \( (C_6H_6)_3Li \); these compounds have geometrical configurations of \( D_{6h} \) symmetry, i.e., the symmetry occurring in GIC. These structures model very simple fragments of intercalates, which allows one to judge the behavior of metal atoms in the vicinity of the surface of the graphite lattice, the state of the lithium atom in
The cell, and the interaction between metal atoms from different "layers" separated by the graphite lattice. Hydrogen atoms are introduced in these models to exclude the effects of unsaturated $\sigma$-bonds. The results of comparisons between complexes with benzene, naphthalene, and anthracene show that this is an adequate model.

The following section describes the parameters of the calculation scheme and the choice of model complexes for the calculation; Section 2 (A, B, C) reports on the results of calculations for the C$_6$H$_6$Li$_2$, (C$_6$H$_6$)$_2$Li, and (C$_6$H$_6$)$_3$Li$_2$ systems. The last section summarizes the chief tendencies found for the highly symmetric metal complexes with benzenes.

1. CHOICE OF MODELS AND THE CALCULATION PROCEDURE

The general principle for constructing molecular complexes and details of the calculation scheme are treated in [8]. Figure 1 schematically shows the structures of C$_6$H$_6$Li$_2$, (C$_6$H$_6$)$_2$Li, and (C$_6$H$_6$)$_3$Li$_2$. The $D$ parameter, which is comparable to interlayer distances in intercalates, was taken to be 3.5 au; the C--C and C--H bond lengths are 2.684 and 2.046 au, respectively. This geometrical configuration, which corresponds to the lattice structure of the C$_2$Li intercalate, is called standard. The (C$_6$H$_6$)$_2$ and (C$_6$H$_6$)$_3$ fragments consisting of parallel aromatic rings will be termed di- and tribenzene.

The main calculations were carried out by the restricted Hartree-Fock method for closed and open shells using the GAMESS program [10]. In some cases, the two-configuration SCF approximation according to the combined valence bond (CVB) procedure was used; it allows one to take into consideration part of the correlation energy. The calculations were performed in the minimal STO-3G and double-zeta 3-21G basis sets as well as in the 3-21G basis set complemented by two d-functions (exponents are 0.4 and 0.09) on the Li atoms. The atomic charges were estimated using the natural bond orbital (NBO) procedure [11], substantially annihilating the basis set superposition errors. The calculated parameters of polybenzene complexes are compared with the similar characteristics of the simple C$_6$H$_6$Li$_2$ system.

2. RESULTS AND DISCUSSION

A. C$_6$H$_6$Li$_2$. The lowest electronic states of the complex and effective charges of lithium atoms in these states were calculated using the standard 3-21G basis set. The results of calculations are given in Table 1. The lowest electronic states of the complex differ in the two-electron occupancies of the $a_{1g}$ and $a_{2u}$ MOs, which correlate with the 2s-states of the lithium atom, and of $e_{2u}$, which corresponds to the lowest virtual MO of the benzene molecule. While correlating with AOs, these MOs consist of AOs of only one subsystem ($a_{1g}$ and $a_{2u}$ are subsystems of the alkali metal, and $e_{2u}$ is the subsystem of benzene); therefore, the charge distribution between the subsystems is strictly specified by the electronic configuration of the state.

The lowest electronic states correspond to the absence of an effective charge on the lithium atoms. Since the $a_{1g}$ and $a_{2u}$ MOs, resembling the bonding and antibonding orbitals of the free Li$_2$ molecule, as well as the $^1A_{1g}$ and $^3A_{2u}$ states of the whole complex are close in energies, we estimated the energies of the totally symmetric state by the CVB method in the two-configuration approximation. It was found that the energies of the $^1A_{1g}$ and $^3A_{2u}$ states virtually coincide, and the weights of the $...a_{1g}^2$ and $...a_{2u}^2$ configurations are almost equal in absolute value (0.75 and 0.67). This suggests the great role of the pair electron correlation in this state and allows us to interpret the result based on the

![Fig. 1. Fragments of intercalate structures. Complexes with standard geometry: a) C$_6$H$_6$Li$_2$; b) (C$_6$H$_6$)$_2$Li; c) (C$_6$H$_6$)$_3$Li$_2$.](image-url)