Ab-initio Crystal Orbital Treatment of a Disordered System

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A crystal orbital treatment of a substitutional disordered linear chain of Li atoms is described. The dependence of the energy bands and charge distributions on the number of substituents is discussed.

A considerable interest over the last years has been devoted to the electronic properties of substitutional disordered systems[1]. The idea behind the approach we present in this note is very simple. A crystal orbital calculation has to be done on a unit cell with a large number of atoms to obtain the electronic structure of the unperturbed system. The substituents are than put into the unit cell and if the unit cell is large enough this represents than an approximation to the real perturbed system. This means that the periodic condition on the large unit cell does not influence the results to any large extent. Due to the computational restrictions normaly the unit cell is not large enough, and to preserve the meaning of the method the number of the substituents has to be small.

As a first step in further exploring this method we treated a linear chain of Li atoms substituted by H atoms. An ab initio crystal orbital treatment was done as described previously[2]. The basis set was a minimal STO-3G as prescribed by Pople et al.[3]. The unit cell contains 9 Li atoms and the interatomic distances of the linear chain were varied to obtain equilibrium geometry with interatomic distances of 2.797 Å. Since the primitive unit cell consists of only one Li atoms, our approach includes the interactions between nine neighbours.

The disordered systems were obtained by replacing Li atoms with H atoms without geometry relaxations. The numbers of substituents were one, two and four. The places of H atoms were determined by a random number generator program. The energy bands of unsubstituted and three disordered systems are given in Figures 1 and 2. The unperturbed Li system has metallic character since the number of electrons in the unit cell, or in the primitive unit cell, is even. The substituents with even number of electrons do not change the metallic character though all bands become splitted at the edge of the zone at $k=\pi/a$. This is to be expected since the symmetry of the primitive unit cell is not conserved. Before discussing the results we should stress that we did not do the statistics on the disordered systems. This means that only one calculation has been done for one given arrangement of substituents. To make statistics one should do calculations for different arrangements of substituents and avarange then all results. Such an attempt needs a tremendous amount of computer time and on the ab initio level can not be done at the present status of computing. The fact that calculations do not include statistics also means that all relevant results are more pronounced and not masked by the influence of the different impurity arrangements.

The changes caused by substituents are quite substantial. The energy bands of the Li chain from -2.37350 a.u. to -2.37290 a.u. are composed by 1s orbitals of the Li atoms. The substituents change this drasticaly. No one band of disordered systems falls in this region. All bands are displaced below and above the previously mentioned numbers. The displacement is increasing with the number of substituents. This fact can be rationalized by the simple idea that in the unsubstituted system there is a certain degree of interaction between the 1s orbitals of Li atoms but involving the substituents these are diminished.

Concerning the energy bands attributed to the bonding between 2s and 2p orbitals of Li atoms the situation is quite different. Some energy bands in disordered systems are composed almost exclusively from Li 2s orbitals but others can be described as energy bands corresponding to Li–H bonds (σ). The numbers of such bands are: one, two and five for one, two and four substituents respectively. In

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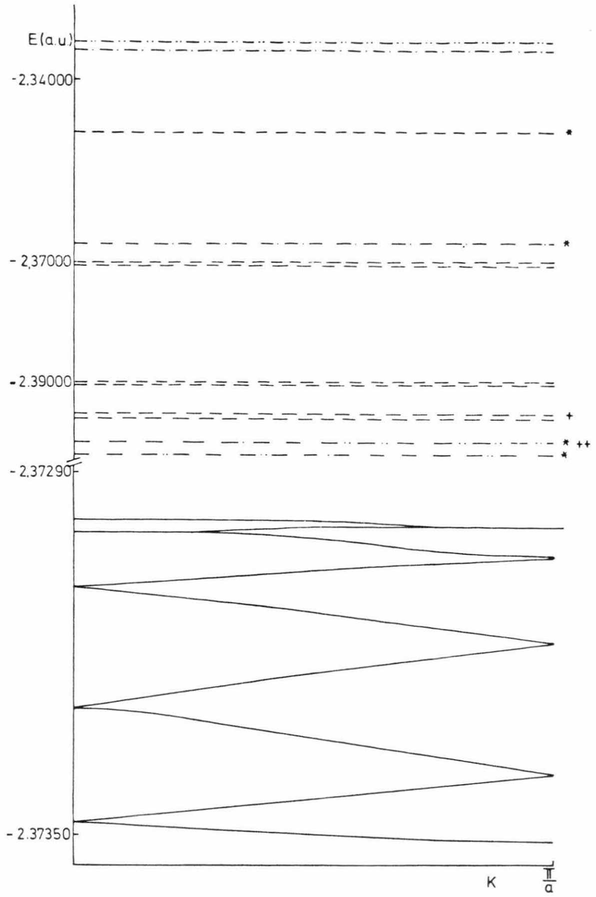

Fig. 1. Energy bands of chains of Li atoms (———), Li atoms with 1H atom (— — —), 2H atoms (— · — · —) and 4H atoms (— · · — · · —). * Almost degenerate bands, + (+ +) energy bands of systems with one (two) and two (four) impurities coincide. Note the changes in scale.

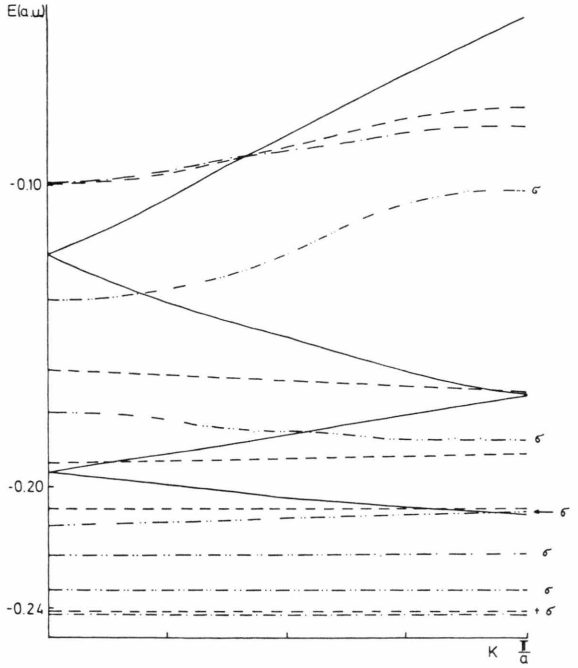

Fig. 2. Energy bands (continuation of Figure 1). Fermi levels are at $k = \pi/2\,a$.

Table 1. Charges with one H substituent on the 6 position.

Li	Li	Li	Li	Li	H	Li	Li	Li
3.013	3.013	2.942	3.089	2.909	1.093	2.909	3.089	2.940

the system with four substituents the last half occupied band is the bonding between Li and H atoms. Increasing the number of substituents the energy of the Fermi level is decreasing with a lowest value of − 0.12442 a. u.

Some insight into the nature of the disordered system can also be obtained from the charge distributions. In the case of one H substituent the H atom gains electrons. Its charge is 1.093 e. The nearest Li atoms loose charges (2.909 e) but the next nearest Li atoms gain them (3.089 e). The Li atoms further apart remain almost neutral (3.012 e, Table 1). In the system with two H atoms both H atoms gain charges to even larger extent than previously (1.096 e). The nearest Li atoms lose charges (2.916 e and 2.891 e). One Li atom between H atoms gains charge to high extent (3.133 e), but again Li atoms further apart from H atoms are almost neutral (3.020 e). In the case with four H substituents the picture is drasticaly changed. H atoms remain almost neutral (1 e and 0.995 e). That Li atom which is between H atoms gains charge (3.131 e) while the Li atoms which have H atoms only on one side loose it (2.985 e). Li atoms further apart from H atoms have charges 2.954 e. The calculations on the disordered systems show that oscillations of charge appear. To be sure that the oscillation is not an artificial effect of the basis set we did a calculation with the basis set[3] STO-4G and with the Slater exponent for hydrogen equal to one. The results of the system with four H substituents show that the charges are slightly different (the largest difference is 0.02) but the magnitudes of charge oscillations are just the same as with the basis set STO-3G.

Many years ago Friedel[4] has pointed out that in the vicinity of the impurity the electron density oscilates with a sinusoidal function of distance r and falls of as r^{-3}. Oscillations of charges as determined from the system with one impurity roughly obey the equation derived by Friedel. Any detailed discussion is of course impossible because of the limited size of the treated system.

The energy bands description and the discussion of the charges show that there are no bands that can be described as localized bands composed only of the orbitals of the substituents. But in all treated systems the bands assigned as σ are spread only over substituents and their nearest neighbours.

Acknowledgements

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