LCAO-MO-MATRIX METHOD FOR MANY ELECTRON SYSTEMS AND THEIR APPLICATION TO DEFECTS IN IONIC CRYSTALS !

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LCAO-MO-MATRIX METHOD FOR MANY ELECTRON SYSTEMS AND THEIR APPLICATION TO DEFECTS IN IONIC CRYSTALS !

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Résumé. — Une méthode de matrices LCAO-MO est présentée. Elle permet un traitement simultané d'une impureté atomique et de son entourage cristallin. La méthode utilise toutes les informations fournies par les solutions Hartree-Fock des ions libres qui constituent le cristal. Elle a le caractère d'un traitement fondamental (*ab initio*) et ne contient aucun paramètre de rajustement. La méthode est appliquée aux centres d'hydrogène dans KCl. Les résultats sont comparés avec les données expérimentales gagnées par EPR, optique et dommage de radiation.

Abstract. — A LCAO-MO-Matrix method is presented which allows a uniform treatment of a defect atom and its crystal environment. This method utilizes all the information offered by the Hartree-Fock solutions of the free ions forming the crystal. It has the character of an *ab initio* treatment not containing any fitting parameter. This method is applied to hydrogen centres in KCl. The results are briefly compared with the experimental data of EPR, optic, and radiation damage.

The theoretical methods for treating defects in solids make little use of the knowledge we have of the solutions gained through the Hartree-Fock equations of free ions. These are the wave functions and their one-electron energies. For example typical calculations for the ground state, which is measured by EPR, use exclusively the wave functions of free ions, respectively their overlap-integrals. Often methods for calculations for excited states do not even make use of this knowledge.

In this talk I want to introduce to you a method using the complete information gained by Hartree-Fock treatments for free atoms and ions.

As an example I will calculate the interstitial hydrogen center in KCl and compare the results to EPR, absorption, photochemical effects, and emission.

Startingpoint is the Schroedinger equation of the crystal :

$$\mathcal{H}\psi_i = \varepsilon_i^{MO}\,\psi_i$$

where $\mathcal{H}$ is the Hamiltonian composed by the sums of the ionic part, the Madelung part, and others :

$$\mathcal{H} = \sum \mathcal{H}_{ion} + \sum \mathcal{H}_{mad} + \sum \mathcal{H}_{rep} + \sum \mathcal{H}_{pol} + \cdots$$

ψ should be described by ionic wave functions φ

$$\psi_i = \sum_j C_{ij}\,\varphi_j\,.$$

With a simple derivation we can prove that the matrix elements of the Hamiltonian in the system of the ionic functions φ can be written as

$$< \varphi_i\,|\,\mathcal{H}\,|\,\varphi_j > \; = \; - < \varphi_i\,|\,\varphi_j > \sqrt{\varepsilon_i\,\varepsilon_j}$$

with ε

$$\varepsilon = \varepsilon_{orb} + \varepsilon_{mad} + \varepsilon_{rep} + \varepsilon_{pol} + \cdots$$

as sum of the ionic orbital energy plus the Madelung energy, and some other smaller parts like repulsion and polarization energy.

To obtain the proper energies in the crystal we have to diagonalize the Hamiltonian matrix. This technique will provide two results :

1) The Eigenvalues are the energies ε_i^{Mo} of the molecular orbitals, giving us the optical energies of the centre.

2) The Eigenvektors lead to the molecular orbitals ψ_i being automatically orthogonal. They inform us about EPR experiments and transition matrix elements.

As an example, we will treat now a unit cell in a cubic potassium chloride crystal, a cluster with 4 chlorine and 4 potassium ions.

As basic wave functions we use the orbitals tabulated by Clementi [1]. Their Hartree-Fock energies are modified by the Madelung potential. These energies are shown in figure 1, you see there the potassium and the chlorine energies.

Combining these ions according to our matrix method, we get the new energies showing band character even in this simple cluster. For further discussion we'll only need this upper part.

Figure 2 shows the upper part of figure 1.

We will now add a hydrogen atom at the interstitial site in the centre of the cube. Its wave function interacts with some of the band states. The resulting
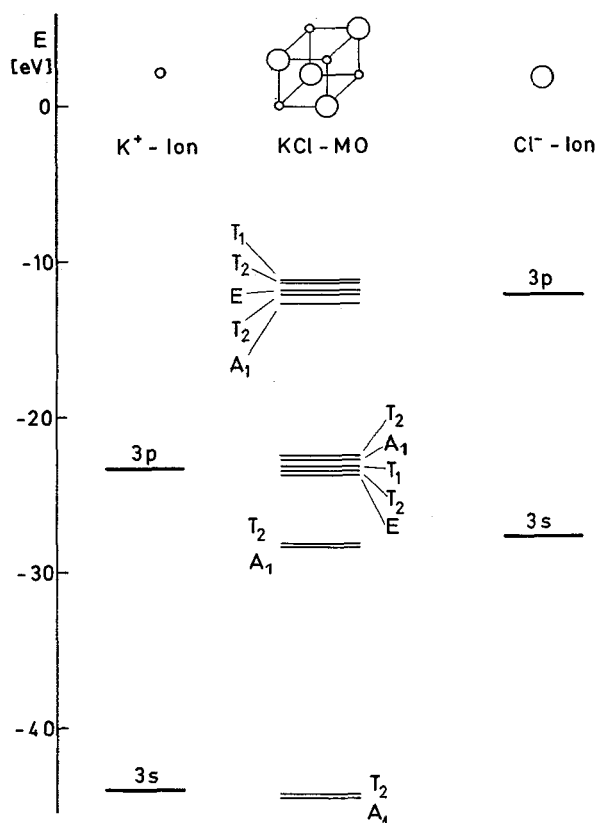
FIG. 1. — Orbital energies of K⁺, Cl⁻ and the KCl cluster.
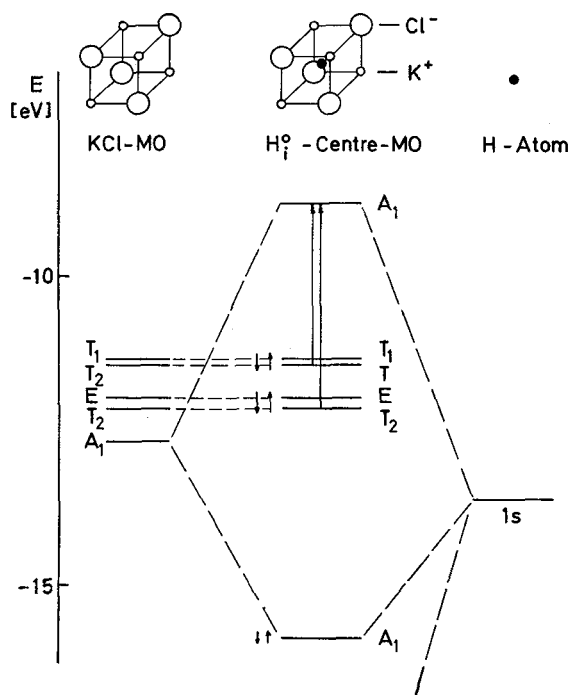
FIG. 2. — Orbital energies of the KCl cluster and the H$_i^0$-centre.

energies are strongly separated from the band (see Fig. 2).

We can now populate the levels, each one with two electrons. We start from the deepest level. Then the

highest level is occupied by only one electron and becomes paramagnetic. In this figure we now have the complete level scheme for the interstitial hydrogen centre.
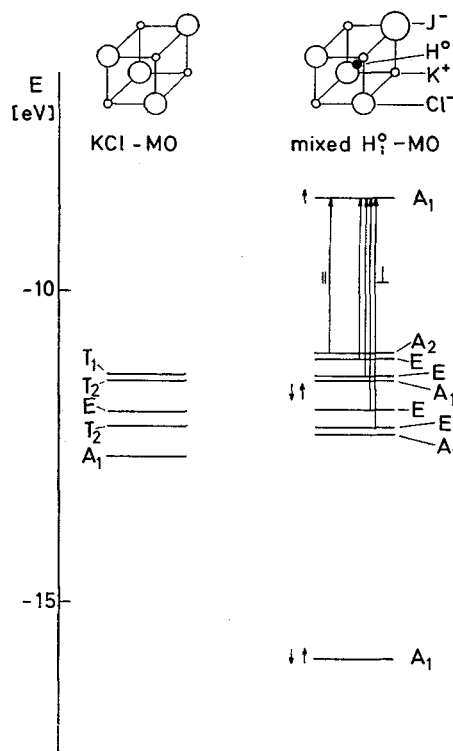
FIG. 3. — Orbital energies of the KCl cluster and the mixed H$_i^0$-centre.

As a quality test we will compare it with the results of various experiments.

From the highest molecular orbital we are able to calculate the spin densities and to compare them with the values measured by EPR. We find better theoretical values than Löwdin and the parameter extended covalency theory give us.

As a next comparison we will take the optical absorption band. It is known that the transition to a 2p level of the hydrogen is energetically too high. So we find from our graph that a transition from the valence band to the highest unpaired level is possible. The valence band states mainly exist of 3p electrons of the chlorine ions. This model therefore agrees with the usual charge-transfer model, in which a common electron of 4 Cl⁻ neighbours is transfered to the hydrogen [2].

If we now calculate the transition probability, we will find only two allowed transitions : the one we can assign to the well-known optical band, the other one is possibly an assumed transition in a higher energetic region [3].

Now we consider this excited state in more detail. The excited electron leaves a hole behind in the chlorine valence band states. If we assume the level scheme to the left of figure 2 to be that of a neighbouring

cluster it should be possible that the hole jumps away forming an H centre in the neighbouring cluster. And indeed this experimental result was presented in Sendai by Reuter and Spaeth [4] following the equation

$$H_i^0 + Cl_s^- \xrightarrow{h\nu} H_i^- + Cl_s^0 \longrightarrow H_s^- + Cl_i^0$$
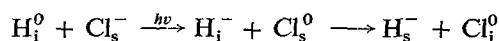
For a final comparison we will have a look on the emission process. In our figure we saw that the moving of the hole competes with emission. So we now will trap the hole by a mixed crystal centre.

For this we will replace one Cl^- neighbour by a larger J^- ion. The molecular orbital levels of the defect cluster will change, the level band becomes broader. Now we expect that the hole will be trapped in this widening of the band and will no longer be able to jump away. Thus the emission should be preferred. Again we find that this experimental result was presented in Sendai [5] by Lohse and Spaeth. They have found emission from interstitial hydrogen centres only in alkali chloride crystals mixed with jodide. Furthermore the model gives the correct answer to questions concerning the polarized emission of those centres.

Now you see that the results of the LCAO-MO matrix method are in good agreement with the experimental results. Our method contains no fitting parameter. Nevertheless we obtain a representation by molecular orbitals from which we learn to understand in the same model such different processes as EPR, absorption, emission, and radiation effects. Time has limited the examples to the interstitial hydrogen centre. But there is no reason not to use this method in any other defect in any other crystal.

References

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DISCUSSION

T. M. WILSON. — The method that you have just described does not appear to allow for changes in the radial extent of the defect wave functions with relaxation of the neighbouring ions. These changes can often be quite large and are extremely important in determining the relative strength of the coupling of the defect to the various modes of relaxation of the neighbouring ions and properties such as the hyperfine interaction of the defect in the ground state, the Stokes shift and spin-orbit splitting.

L. SCHWAN. — It is true that the atomic orbitals are not modified in this approach, but all the observables you have mentioned are obtained from the molecular orbitals (MO) of the cluster. These are determined by the coefficients c_{ik} calculated from the matrix H_{kl}, which depend on all atomic positions on account of both the lattice potential entering the ε_k and the overlap integrals depending even exponentially on the interatomic distances.