NOTE ON

RESOLVENT METHOD
FOR QUANTITATIVE CALCULATIONS
ON SURFACE STATES AND ADSORPTION

by

A. VAN DER AVOIRD, S. P. LIEBMANN, D. J. M. FASSAERT
Institute of Theoretical Chemistry
University of Nijmegen, The Netherlands

SUMMARY

Existing methods for the evaluation of surface and adsorption effects on one-electron states in crystals can be divided into two classes. The first group of methods is based on solid state band theory. They treat semi-infinite crystals by rather approximate, mostly tight-binding schemes and the surface is usually regarded as a perturbation of the infinite periodic crystal. The application of the resolvent method, which is an elegant way of incorporating the effect of this perturbation, requires the infinite crystal to be a very simple one (for instance, only one orbital per unit cell) or, in case of more complex crystals such as transition-metals or semiconductors, it necessitates the use of model hamiltonians depending on a few parameters only. The second class of methods works on finite clusters of atoms, treating those by the more sophisticated MO-LCAO methods commonly applied to molecules. Although the essential effects of the surface and of adsorption are probably quite localized, these clusters must remain so small that results are distorted by undesirable boundary effects.

In this communication a method is described which combines advantages of both approaches. It works on finite crystals and can use any of the more evolved LCAO techniques applied to molecules. On the other hand, by imposing periodic boundary conditions,
using Bloch orbitals and by application of the resolvent method, simplifications are obtained which permit the treatment of larger crystals.

One starts with a finite crystal periodic in three directions, «cleaves» this crystal so that two surfaces are obtained and adsorbs some (periodic) layers of atoms or molecules on those surfaces. The effect of the perturbation $V$ caused by this cleavage, by the surface potential and by adsorption is calculated by the resolvent or Koster-Slater method, the resolvent $G(E)$ being constructed from the solutions of the periodic crystal and some non-interacting adsorbate layers. Since the direct effects of surface formation and adsorption are localized within a few surface layers of the crystal, the Koster-Slater equation:

$$G(E)V\psi = \psi$$ (1)

can be defined in a much smaller basis space than the secular equation over all crystal layer orbitals. This equation (1), which we have actually obtained in matrix form also accounting for non-orthogonality of the basis atomic orbitals, has usually been solved for $E$ by finding the roots of the equation:

$$\det | G(E)V - I | = 0$$ (2)

Because this is practically impossible for somewhat more complex systems, we have invoked an algorithm developed by A. R. Williams. Equation (1) is multiplied by $V$ and the solutions $E$ are found by searching for the zeroes in the eigenvalues of the hermitean matrix $V G(E) V - V$. Due to some special properties of those eigenvalues, which were explained in the lecture, this search can very easily be programmed. The calculation of the one-electron wave functions $\psi$ is then performed by standard procedures. A more detailed description of this method can be found in *Phys. Rev., B* 10 1230 (1974) and *Phys. Rev. B*, Jan. 15 (1975).