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NOTE ON

RESOLVENT METHOD FOR QUANTITATIVE CALCULATIONS ON SURFACE STATES AND ADSORPTION

by

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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 :

$$G(E)V\psi = \psi$$  \hspace{1cm} (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 :

$$\det \left| G(E)V - I \right| = 0$$  \hspace{1cm} (2)

Because this is practically impossible for somewhat more complex 
systems, we have invoked an algorithm developed by A. R. Wil­
liams. Equation (1) is multiplied by $V$ and the solutions $E$ are 
found by searching for the zeroes in the eigenvalues of the her­
mitean matrix $V G(E)V - V$. Due to some special properties of 
these 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., 