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A METHOD OF SELF-CONSISTENT CALCULATION OF ELECTRONIC STRUCTURE OF SOLID SURFACES

By

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Abstract

In recent years, band structure calculations of slabs (thin films) of solids have proved successful and useful for elucidating the electronic states at solid surfaces. The present note briefly reviews recent progress in this area, and proposes a new simplified self-consistent LCAO method for calculating the electronic band structure of slabs. The method utilizes the CNDO approximation widely used in quantum chemistry.

§ 1. LCAO Calculations of Slabs

In recent years the electronic structure of solid surfaces has been the subject of a large number of experimental and theoretical studies. It is evident that these studies have been motivated and stimulated by scientists' growing interests in fundamental studies of various surface phenomena including adsorption, surface reactions, and heterogeneous catalysis. A relatively new and promsing method of quantitative calculation of electron states at solid surfaces**) is to consider an n-layer slab (thin film) of the solid in question and to calculate its band structure by means of various well-known techniques that have been developed for band structure calculations of bulk solids.***) Here the number of atomic layers n is, for example, 1,[12,19] 3,[13] 13,[2~4] 16,[6] and 40.[7] The employed techniques are the pseudopotential,[2~5,8,14,15] OPW,[5a] APW,[18] Green's function (KKRZ),[19,19a] LCMTO,[20,21] LCAO (tight-binding),[6~7a,9~13] and density functional[16,17] methods. A slab is bounded by two parallel plane surfaces and is a model suitable for calculations of electronic structure of surfaces.

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**) A concise but informative review of the recent developments in this area has been given by Forstmann (ref. 1).

***) Several examples are listed as ref. 2~ref. 21 at the end of this article. However, this list is far from exhaustive and the above references are to be regarded as arbitrarily chosen examples.

Any of the above-mentioned calculation techniques of band structure has its own merits and demerits. It is therefore very likely that all these methods will survive and coexist in the future.

1 a) LCAO method in band calculations

The sucessful LCAO (tight-binding) calculation of the band structure of lithium by Lafon and Lin[22] in 1966 triggered a revived interest in the use of the LCAO method for band structure calculations. The key to their success was to calculate the matrix elements occurring in the LCAO theory as accurately as possible, which was made possible by the use of modern high-speed computers and some mathematical techniques.[22,23] Since then, much effort has gone into LCAO calculations of band structure, in which attempts have been made to calculate electronic properties of solids from first principles (*ab initio* calculations).[*]

The advantages of the LCAO method are: (i) the matrix equation we have to deal with is relatively small; (ii) band energies can be easily computed at arbitrary points (not limited to symmetry points) in the Brillouin zone; (iii) the effects of the crystalline fields can be included easily; and (iv) the method is particularly suited for band calculations of transition metals, which involve *d*-electrons and is interesting in connection with their catalytic properties.

The necessity of introducing the self-consistency into band calculation has often been pointed out. Recently a considerable number of self-consistent LCAO band calculations have been made.[24] Since a self-consistent solution is obtained after repeated iterative cycles, an efficient computing procedure has to be devised in order to save computing time and to make self-consistent calculations practical.

Also attempts have been made to carry out very precise self-consistent LCAO band calculations which are comparable, in accuracy, to molecular self-consistent LCAO calculations.[25]

1 b) Slab calculations

Suppose that an LCAO calculation of iron starts with a basis set consisting of nine atomic orbitals, namely, the one $4s$ function, three $4p$ functions, and five $3d$ functions of the iron atom. Then the LCAO calculation for bulk iron is performed by constructing and solving a 9×9 matrix equation since the unit cell of bulk iron contains one iron atom. On the other hand, in the case of the LCAO calculation of an n-layer slab of iron, the size of the matrix equation becomes $9n\times9n$ since the unit cell of the slab contains

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[*] Besides *ab initio* LCAO theories, simplified or semi-empirical LCAO theories are being used for discussing band structure (see below).

n iron atoms.*) This difference arises from the fact that a bulk crystal has three-dimensional periodicity whereas a slab is periodic in directions parallel to its surfaces but not in the direction perpendicular to the surfaces, *i. e.*, it has only two-dimensional periodicity. Thus the slab calculation is far more difficult than the corresponding bulk calculation unless the number of layers n is small.

In connection with various problems in surface science, a knowledge of electron distribution at solid surfaces is very important. One of the main purposes of slab calculation is to obtain this distribution with sufficient accuracy. In many occasions it has been pointed out that reliable distribution can only be obtained by means of self-consistent calculations,[3,11,13,16] particularly in the case of transition-metal surfaces.[8,15]**)

The recent LCAO calculation of a copper slab with (001) surfaces by Gay, Smith, and Arilnghaus[13] is remarkable. It is an *ab initio* LCAO calculation of a d-band metal; thus it starts with a basis set consisting of fifteen atomic orbitals, namely, the 1s, 2s, 3s, 4s, 2p, 3p, and 3d functions of copper atom. Furthermore it is a self-consistent calculation. It is to be noted however that this elaboration was only achieved at the expense of the slab thickness; in their calculation the number of layers n was three. One might therefore argue that this slab is too thin to simulate the surface electronic structure of a semi-infinite solid.

1 c) Use of simplified or semi-empirical LCAO theories

Simplified or semi-empirical LCAO theories have been extensively used for discussing band structure of bulk solids. Here LCAO calculations start with considerably simplified expressions for the matrix elements.[26,27] Such simplification is hardly justified from the standpoint of *ab initio* type calculations. It is important however that these simplified LCAO theories are to be used as a "parameterized" LCAO theory or as an "interpolation method" in the sense of Slater and Koster,[23,26,27] and as such they have proved very useful.

So far LCAO calculations of slabs of d-band or transition metals with considerable thickness (say, $n \geq 15$)[6~7a,9,10] have been done by using simplified or semi-empirical LCAO theories. Although these calculations are non-self-consistent, some interesting results have been obtained.

It is interesting to note that in some simplified LCAO calculations[9,10,27]

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*) In the calculation of an iron slab with (100) surfaces by Dempsey, Kleinman, and Caruthers (ref. 7 a), n was taken to be 41; thus the size of the matrix equation is 369×369. However, in this case the central layer of the slab is a reflection plane and the matrix equation can be reduced into a 186×186 equation and a 183×183 equation.

**) Among ref. 2~ref. 15, refs. 3, 8, 11, 13, 14, and 15 are self-consistent calculations.

EHT-like expressions have been used for the matrix elements. Here EHT stands for the extended Hückel theory,[28] which is widely used in the area of quantum chemistry.

In the next section, the use of another well-known approximation method in quantum chemistry, namely, the CNDO (complete-neglect-of-differential-overlap) approximation,[28] for band calculations of bulk solids or slabs will be considered. Its purpose is to provide a new simplified self-consistent LCAO method for calculating the band structure of solids.

§ 2. Simplified Self-Consistent LCAO Calculation of Slabs

The following fundamental equations for the LCAO calculation of band structure are well-known.*)

$$\psi_n(\boldsymbol{k}, \boldsymbol{r}) = \sum_s C_{ns}(\boldsymbol{k})\phi_s(\boldsymbol{k}, \boldsymbol{r}) \tag{1}$$

$$\phi_s(\boldsymbol{k}, \boldsymbol{r}) = N^{-\frac{1}{2}} \sum_p \exp(i\boldsymbol{k}\cdot\boldsymbol{r}_p)\, u_s(\boldsymbol{r}-\boldsymbol{r}_p) \tag{2}$$

$$\sum_s H_{s's}(\boldsymbol{k})C_{ns}(\boldsymbol{k}) = E_n(\boldsymbol{k}) \sum_s S_{s's}(\boldsymbol{k})C_{ns}(\boldsymbol{k}) \tag{3}$$

$$H_{s's}(\boldsymbol{k}) = \int \phi^*_{s'}(\boldsymbol{k}, \boldsymbol{r})\, \hat{H}\, \phi_s(\boldsymbol{k}, \boldsymbol{r})\, d\boldsymbol{r} \tag{4}$$

$$S_{s's}(\boldsymbol{k}) = \int \phi^*_{s'}(\boldsymbol{k}, \boldsymbol{r})\, \phi_s(\boldsymbol{k}, \boldsymbol{r})\, \mathrm{d}\boldsymbol{r} \tag{5}$$

In (1) the one-electron wave function $\psi_n(\boldsymbol{k}, \boldsymbol{r})$ for band n and wave vector $\boldsymbol{k}$ is expressed as a linear combination of the Bloch functions $\phi_s(\boldsymbol{k}, \boldsymbol{r})$, which in turn are constructed as a linear combination of the atomic orbitals $u_s(\boldsymbol{r}-\boldsymbol{r}_p)$ as shown in (2), where N is the number of unit cells in the crystal whose band structure we are calculating. In (1) through (5), each unit cell is assumed to contain only one atom at $\boldsymbol{r}_p$, where the suffix p runs from 1 to N and $\boldsymbol{r}_1$ is taken equal to zero, *i.e.*,

$$\boldsymbol{r}_1 = 0 \tag{6}$$

The coefficients $C_{ns}(\boldsymbol{k})$ in (1) are determined from the matrix equation (3), namely, the Hartree-Fock equation in the LCAO approximation, from which the energy $E_n(\boldsymbol{k})$ of the wave function $\psi_n(\boldsymbol{k}, \boldsymbol{r})$ is also calculated. In (3), the matrix elements $H_{s's}(\boldsymbol{k})$ of the one-electron Hamiltonian operator (Fock operator) $\hat{H}$ and the overlap matrix elements $S_{s's}(\boldsymbol{k})$ are defined by (4) and (5).

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*) See, for example, ref. 23, p. 291 *et seq.*

Since the Hamiltonian $\hat{H}$ for the crystal is supposed to have three-dimensional periodicity (translational invariance), we may write

$$H_{s's}(\boldsymbol{k}) = \sum_{p} \exp(i\boldsymbol{k}\cdot\boldsymbol{r}_p)\, H_{s's}(\boldsymbol{r}_p)\,. \tag{7}$$

Similarly we have

$$S_{s's}(\boldsymbol{k}) = \sum_{p} \exp(i\boldsymbol{k}\cdot\boldsymbol{r}_p)\, S_{s's}(\boldsymbol{r}_p)\,. \tag{8}$$

The matrix elements on the right-hand sides of (7) and (8) are defined by

$$H_{s's}(\boldsymbol{r}_p) = \int u_{s'}^*(\boldsymbol{r})\, \hat{H}\, u_s(\boldsymbol{r}-\boldsymbol{r}_p)\, d\boldsymbol{r} \tag{9}$$

and

$$S_{s's}(\boldsymbol{r}_p) = \int u_{s'}^*(\boldsymbol{r})\, u_s(\boldsymbol{r}-\boldsymbol{r}_p)\, d\boldsymbol{r} \tag{10}$$

Calculating the matrix elements (4) and (9) accurately, and solving the matrix equation (3) self-consistently present several difficult problems, which we have to overcome in order to obtain reliable band structures. These problems have been discussed by many authors and ingenious methods have been devised to get around them.[22~25] As mentioned at the end of the preceding section, a much simplified method of calculating the matrix elements (4) and (9) is presented here; it is a direct application of the CNDO approximation[28] used for discussing the electronic structure of molecules in quantum chemistry. Now that such a rather drastic approximation is introduced, an *ab initio* calculation of band structure is no longer attempted, but instead the set of equations (1) through (5) is used for an interpolative calculation of band structure (see below).

To calculate the matrix element (9) involving the one-electron Hamiltonian $\hat{H}$ we start with the following standard expression:

$$\begin{aligned} H_{s's}(\boldsymbol{r}_p) = &\int u_{s'}^*(\boldsymbol{r}) \left(-\frac{\hbar^2}{2m}\nabla^2 + \sum_{p'} v(\boldsymbol{r}-\boldsymbol{r}_{p'})\right) u_s(\boldsymbol{r}-\boldsymbol{r}_p)\, d\boldsymbol{r} \\ &+ \sum_{n}^{(occ)} \sum_{\boldsymbol{k}} \left(2\big[s'1, sp\,;\, n\boldsymbol{k}, n\boldsymbol{k}\big] - \big[s'1, n\boldsymbol{k}\,;\, n\boldsymbol{k}, sp\big]\right) \end{aligned} \tag{11}$$

On the right-hand side of (11), the first term is a one-electron integral, which involves the kinetic energy part and the electron-core interaction part of the Hamiltonian $\hat{H}$; and the second term is made up of the two-electron integrals of the type,

$$\begin{aligned} \big[s'1, sp\,;\, n\boldsymbol{k}, n\boldsymbol{k}\big] = e^2 &\iint u_{s'}^*(\boldsymbol{r}-\boldsymbol{r}_1)\, u_s(\boldsymbol{r}-\boldsymbol{r}_p) |\boldsymbol{r}-\boldsymbol{r}'|^{-1} \\ &\phi_n^*(\boldsymbol{k}, \boldsymbol{r}')\, \phi_n(\boldsymbol{k}, \boldsymbol{r}')\, d\boldsymbol{r}\, d\boldsymbol{r}' \end{aligned} \tag{12}$$

and of the type,

$$\left[s'1, nk\,; nk\,, sp\right] = e^2 \iint u^*_{s'}(\boldsymbol{r}-\boldsymbol{r}_1)\, \psi_n(\boldsymbol{k}, \boldsymbol{r})\, |\boldsymbol{r}-\boldsymbol{r}'|^{-1} \psi^*_n(\boldsymbol{k}, \boldsymbol{r}')\, u_s(\boldsymbol{r}'-\boldsymbol{r}_p)\, d\boldsymbol{r}\, d\boldsymbol{r}' \tag{13}$$

It must be noted that the double summation over n and $\boldsymbol{k}$ in (11) covers only the occupied (*occ*) one-electron states, *i. e.*, only those states whose energies do not exceed the Fermi energy E_{F}. Defining the density matrix $P(s''p''\,; s'''p''')$ by

$$P(s''p''\,; s'''p''') = \sum_n^{(occ)} \sum_{\boldsymbol{k}} 2N^{-1} C^*_{ns''}(\boldsymbol{k})\, C_{ns'''}(\boldsymbol{k}) \exp\left(\boldsymbol{k}\cdot(-\boldsymbol{r}_{p''}+\boldsymbol{r}_{p'''})\right) \tag{14}$$

and using (1) and (2), we can readily show that the second term on the right-hand side of (11) becomes

$$\sum_{s''}\sum_{p''}\sum_{s'''}\sum_{p'''} P(s''p''\,; s'''p''')\left(\left[s'1, sp\,; s''p'', s'''p'''\right] - \frac{1}{2}\left[s'1, s'''p'''\,; s''p'', sp\right]\right) \tag{15}$$

which consists of two-electron integrals of the type,

$$\left[s'1, sp\,; s''p'', s'''p'''\right] = e^2 \iint u^*_{s'}(\boldsymbol{r}-\boldsymbol{r}_1)\, u_s(\boldsymbol{r}-\boldsymbol{r}_p)\, |\boldsymbol{r}-\boldsymbol{r}'|^{-1} u^*_{s''}(\boldsymbol{r}'-\boldsymbol{r}_{p''})\, u_{s'''}(\boldsymbol{r}'-\boldsymbol{r}_{p'''})\, d\boldsymbol{r}\, d\boldsymbol{r}' \tag{16}$$

and of the type,

$$\left[s'1, s'''p'''\,; s''p'', sp\right] = e^2 \iint u^*_{s'}(\boldsymbol{r}-\boldsymbol{r}_1)\, u_{s'''}(\boldsymbol{r}-\boldsymbol{r}_{p'''})\, |\boldsymbol{r}-\boldsymbol{r}'|^{-1} u^*_{s''}(\boldsymbol{r}'-\boldsymbol{r}_{p''})\, u_s(\boldsymbol{r}'-\boldsymbol{r}_p)\, d\boldsymbol{r}\, d\boldsymbol{r}' \tag{17}$$

In (12), (13), (16), and (17), it is to be remembered that $v(\boldsymbol{r}-\boldsymbol{r}_1)$ and $u^*_{s'}(\boldsymbol{r}-\boldsymbol{r}_1)$ are the same things as $v(\boldsymbol{r})$ and $u^*_{s'}(\boldsymbol{r})$, respectively, because of (6).

Now, Pople and Beveridge[28] have given a good account of the basic rules of the CNDO approximation. When the rule of "complete neglect of differential overlap" is applied to the expression (11) together with (15), the following greatly simplified expressions for the matrix element $H_{s's}(\boldsymbol{r}_p)$ are obtained at once:

$$\begin{aligned} H_{ss}(\boldsymbol{r}_1) = U_{ss} + \sum_{p'}^{p'\neq 1}\left(\int |u_s(\boldsymbol{r})|^2 v(\boldsymbol{r}-\boldsymbol{r}_{p'})\, d\boldsymbol{r} + \sum_{s''} P(s''p'\,; s''p')\left[s1, s1\,; s''p', s''p'\right]\right) \\ + \sum_{s''} P(s''1\,; s''1)\left[s1, s1\,; s''1, s''1\right] - \frac{1}{2} P(s1\,; s1)\left[s1, s1\,; s1, s1\right] \end{aligned} \tag{18}$$

$$H_{s's}(\boldsymbol{r}_1) = -\frac{1}{2} P(s1\,;s'1)\left[s'1, s'1\,; s1, s1\right] \qquad \text{if } s' \neq s \tag{19}$$

$$H_{s's}(\boldsymbol{r}_p) = \beta_{s's}(\boldsymbol{r}_p) - \frac{1}{2} P(sp\,;s'1)\left[s'1, s'1\,; sp, sp\right] \qquad \text{if } p \neq 1 \tag{20}$$

where U_{ss} and $\beta_{s's}(\boldsymbol{r}_p)$ are one-electron integrals defined by

$$U_{ss} = \int u_s^*(\boldsymbol{r})\left(-\frac{\hbar^2}{2m}\nabla^2 + v(\boldsymbol{r})\right)u_s(\boldsymbol{r})\,d\boldsymbol{r} \tag{21}$$

and

$$\beta_{s's}(\boldsymbol{r}_p) = \int u_{s'}^*(\boldsymbol{r})\left(-\frac{\hbar^2}{2m}\nabla^2 + v(\boldsymbol{r}) + v(\boldsymbol{r}-\boldsymbol{r}_p)\right)u_s(\boldsymbol{r}-\boldsymbol{r}_p)\,d\boldsymbol{r} \tag{22}$$

In the CNDO theory, the integrals (21) and (22) are not computed, but instead they are handled in a semi-empirical manner[28] (see below); the two-electron integrals occurring in (18), (19), and (20) are calculated analytically but in a much simplified way.*)

Evidently, the simplified expression for the matrix element $S_{s's}(\boldsymbol{r}_p)$ corresponding to (18) through (20) is

$$S_{s's}(\boldsymbol{r}_p) = \delta_{s's}\delta_{1p} \tag{23}$$

from which we find that the Bloch functions $\phi_s(\boldsymbol{k}, \boldsymbol{r})$ form an orthonormalized system.

So far we have assumed for simplicity that each unit cell of the crystal contains only one atom. However, what we are interested in is the band calculation of n-layer slabs, which have two-dimensional, rather than three-dimensional, periodicity. As was pointed out in the preceding section, each unit cell of an n-layer slab contains several or many atoms, and the number of atoms in a unit cell increases as n increases. The extension of the above equations to such cases is straightforward. For example, the one-electron wave function $\psi_n(\boldsymbol{k}, \boldsymbol{r})$ for a slab is constructed as a linear combination of the Bloch functions,

$$\phi_{s\alpha}(\boldsymbol{k}, \boldsymbol{r}) = N^{-\frac{1}{2}} \sum_p \exp(i\boldsymbol{k}\cdot\boldsymbol{r}_p)\, u_s(\boldsymbol{r}-\boldsymbol{r}_\alpha-\boldsymbol{r}_p) \tag{2'}$$

instead of (2). In (2′) the wave vector $\boldsymbol{k}$ is two-dimensional, and $u_s(\boldsymbol{r}-\boldsymbol{r}_\alpha-\boldsymbol{r}_p)$ is an atomic orbital centered at the α-th atom in the p-th unit cell. (If the number of atoms in the unit cell is m, α runs from 1 to m.**)) As the result, the rest of the equations becomes slightly more complicated notation-wise, and the size of the matrix equation (3) increases. Otherwise there are no essential changes.

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*) All these integrals are evaluated as two-electron Coulomb-type two-electron integrals over s-type Slater atomic orbitals (ref. 28).

**) In eq. (2′) these m atoms are assumed to be of the same kind. Generalization can be made without difficulty.

It is interesting to note that on the right-hand side of the expression (18) for the diagonal matrix element $H_{ss}(\boldsymbol{r}_1)$, the second term,

$$\sum_{p'}^{p'\neq 1}\left(\int |u_s(\boldsymbol{r})|^2 v(\boldsymbol{r}-\boldsymbol{r}_{p'})\,d\boldsymbol{r}+\sum_{s''} P(s''p'\,;s''p')\Big[s1, s1\,; s''p', s''p'\Big]\right)$$

represents the crystalline field effect on the "central" atom, *i. e.*, the atom at $\boldsymbol{r}=\boldsymbol{r}_1=\boldsymbol{0}$. The third term there represents the intraatomic Coulomb repulsion energy within the central atom, and the last term is the exchange energy correction to it. Similar exchange energy terms occur in the expressions (19) and (20) for the off-diagonal matrix elements. In *ab initio* type calculations of band structure, the treatment of the exchange energy terms give rise to difficulty. Very often Slater's $X\alpha$ approximation has been used to calculate them,[23,24] or attempts have been made at calculating them more precisely.[25] In the CNDO approximation, the exchange terms are greatly simplified as shown in (18) through (20), and offer no difficulty.

Now we return to the one-electron integrals (21) and (22). Pople *et al.* have proposed the approximation,[28]

$$\beta_{s's}(\boldsymbol{r}_p) = \beta\int u_{s'}^{*}(\boldsymbol{r})\, u_s(\boldsymbol{r}-\boldsymbol{r}_p)\, d\boldsymbol{r} \tag{24}$$

where β is an empirical parameter and the overlap integral on the right-hand side is calculated analytically.[*] They have also devised a method to assess the value of the integral U_{ss} by using empirical values of atomic ionization potential and electron affinity.

In the present note, it is proposed that U_{ss} in (18) and β in (24) be treated as disposable parameters. Suppose that the simplified LCAO method described above is applied to the band structure calculation of a bulk solid. The values of the above parameters (and, if necessary, those of the orbital exponents in the atomic orbital functions $u_s(\boldsymbol{r})$) are varied to fit the calculated band structure to results of more precise band structure calculations ("interpolation method"[26,27]). It should be a good approximation to use the parameters so determined to calculate the band structure of an n-layer slab of the same solid, which is difficult to obtain by more precise calculation methods.

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*) The "neglect of differential overlap" should not be applied to the calculation of the overlap integral in (24) (ref. 28).

§ 3. Concluding Remarks

Admittedly the argument in the preceding section is of preliminary nature. In this connection a few important questions arise : (i) What is the most appropriate and practical way of determining the disposable parameters? (ii) Does the use of the CNDO approximation make slab calculations really efficient and economical so that a self-consistent calculation can be carried out for a slab consisting of heavy atoms (*e. g.*, Cu, Ni *etc.*) and with considerable thickness, without consuming too much computer time? (iii) Will the results obtained be usable and reliable? These questions together with numerical results obtained for a few interesting systems will be discussed in a subsequent paper.[29]

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