

whereas the hole mobility tensor is not. The anisotropy of the electron mobility tensor, however, is much less than what would be expected from the anisotropy of the effective mass tensor on the approximation of isotropic relaxation time, but about what would be expected on the approximation of isotropic mean free path.

For temperatures below 25°K, both resistivity and Hall coefficients show a weak dependence on temperature. This behavior is not easily explicable in terms of Blount and Cohen's model, which would lead to a continued exponential temperature dependence below 25°K. The data suggests another overlap between the conduction and valence bands. However, the dependence of this overlap on concentration would appear to be rather complicated. An alternative source of the low-temperature behavior may possibly be the fuzzing of the band edges C_L , V_L , and V_H on alloying. At this stage it is not possible to decide which, if either, of the two alternatives is correct.

To summarize, the behavior of the resistivity as a function of antimony concentration above 25°K can be explained semiquantitatively in terms of the model proposed by Blount and Cohen. In particular, behavior resembling the semiconductivity predicted by Heine is observed. However, the behavior below 25°K shows that the model is incomplete and additional complications may occur in the band structure of the alloys and possibly also of pure bismuth.

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Hartree-Fock Theory with Nonorthogonal Basis Functions

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Solutions of the Hartree-Fock self-consistent-field equations can be approximated by linear combination of a set of basis functions: the equations then assume a matrix form, as shown by Roothaan. It is possible, however, to obtain the required variational solution of the many-electron problem much more directly by an iterative construction of the density matrix. This method, first developed by the author for expansion in terms of orthogonal basis functions, is extended to the case of a nonorthogonal set.

INTRODUCTION

DURING recent years two modifications of the Hartree-Fock self-consistent-field (SCF) theory have been developed. Numerical integration can be avoided by determining the occupied orbitals as linear combinations of an arbitrary (in principle complete) set of basis functions¹ and the repeated solution of an eigenvalue problem can be avoided by means of a density matrix formulation, followed by direct iterative construction of the density matrix.² This note is concerned with the extension of the iterative process to the case in which the basis functions are nonorthogonal.

Let us represent the n doubly occupied SCF orbitals (A, B, C, \dots) in terms of m nonorthogonal basis functions (a, b, c, \dots), with overlap matrix S , by

$$(A B C \dots) = (a b c \dots) \mathbf{T}, \quad (1)$$

where \mathbf{T} is an $m \times n$ matrix. The density matrices (and hence the energy and the expectation values of all

other dynamical quantities) are then determined by the invariant $\mathbf{R} = \mathbf{T}\mathbf{T}^\dagger$. The (spinless) one-particle density matrix is $\mathbf{P} = 2\mathbf{R}$ and if we assume a Hamiltonian

$$H = \sum_i f(i) + \frac{1}{2} \sum'_{i,j} g(i,j),$$

the energy is given by²

$$E = 2 \operatorname{tr} \mathbf{R} \mathbf{f} + \operatorname{tr} \mathbf{R} \mathbf{G}, \quad (2)$$

where, with a standard notation, the matrix elements are

$$\begin{aligned} f_{ab} &= (a | f | b), \\ G_{ab} &= \sum_{rs} R_{rs} [2(as | g | br) - (as | g | rb)]. \end{aligned} \quad (3)$$

The electron interaction matrix is \mathbf{R} dependent, $\mathbf{G} = \mathbf{G}(\mathbf{R})$, and leads to a nonlinear problem. According to the variation theorem, the best approximate SCF function results when E of (2) is minimized subject to preservation of orthonormality of the occupied orbitals A, B, \dots . In the case of orthonormal basis functions, $\mathbf{S} = \mathbf{1}_m$, and the constraint is simply $\mathbf{T}^\dagger \mathbf{T} = \mathbf{1}_n$. An

¹ C. C. J. Roothaan, *Revs. Modern Phys.* **23**, 61 (1957).

² R. McWeeny, *Proc. Roy. Soc. (London)* **A235**, 496 (1956).

equivalent condition in terms of \mathbf{R} (also necessary and sufficient) is $\mathbf{R}^2 = \mathbf{R}$. With $\mathbf{S} \neq \mathbf{I}_m$ the condition becomes $\mathbf{T}^\dagger \mathbf{S} \mathbf{T} = \mathbf{I}_n$ and the equivalent statement in terms of \mathbf{R} is

$$\boldsymbol{\rho}^2 = \boldsymbol{\rho}, \quad \text{where } \boldsymbol{\rho} = \mathbf{S}^\dagger \mathbf{R} \mathbf{S}^\dagger. \quad (4)$$

E may be minimized, subject to the constraint (4), by an extension of the iterative process already developed.²

THE MODIFIED ITERATIVE METHOD

The extension to the nonorthogonal case depends on the fact that any small change $\delta\boldsymbol{\rho}$, leading from one idempotent matrix to another, may be expressed as an infinite series in an arbitrary (nonsingular) matrix $\boldsymbol{\Delta}$. The proof runs along the lines of a previous paper² and will not be reproduced: up to second order, it yields

$$\delta\boldsymbol{\rho} = (\mathbf{t} + \mathbf{t}^\dagger) + (\mathbf{t}\mathbf{t}^\dagger - \mathbf{t}^\dagger\mathbf{t}) + \dots,$$

where

$$\mathbf{t} = (\mathbf{I} - \boldsymbol{\rho})\boldsymbol{\Delta}\boldsymbol{\rho}. \quad (5)$$

The auxiliary condition (4) is therefore satisfied automatically, for any variation $\boldsymbol{\Delta}$, by putting

$$\delta\mathbf{R} = \mathbf{S}^{-\frac{1}{2}} [(\mathbf{t} + \mathbf{t}^\dagger) + (\mathbf{t}\mathbf{t}^\dagger - \mathbf{t}^\dagger\mathbf{t}) + \dots] \mathbf{S}^{-\frac{1}{2}}. \quad (6)$$

We then consider the systematic reduction of E , starting from an initial \mathbf{R} matrix and making successive changes, $\delta\mathbf{R}$, always choosing $\boldsymbol{\Delta}$ to give the *most rapid* reduction (the method of "steepest descents"). Using the identity $\text{tr } \mathbf{R}\mathbf{G}(\delta\mathbf{R}) = \text{tr } \delta\mathbf{R}\mathbf{G}(\mathbf{R})$, the first order change is found to be

$$\delta E_{(1)} = 2 \text{tr } \delta\mathbf{R}h,$$

where $\mathbf{h} = \mathbf{f} + \mathbf{G}$ is the matrix of the Hartree-Fock Hamiltonian¹; and for a change consistent with orthogonality of the occupied orbitals, (6) gives

$$\delta E_{(1)} = 2 \text{tr} [\boldsymbol{\rho} \mathbf{S}^{-\frac{1}{2}} \mathbf{h} \mathbf{S}^{-\frac{1}{2}} (\mathbf{I} - \boldsymbol{\rho}) + (\mathbf{I} - \boldsymbol{\rho}) \mathbf{S}^{-\frac{1}{2}} \mathbf{h} \mathbf{S}^{-\frac{1}{2}} \boldsymbol{\rho}] \boldsymbol{\Delta}.$$

The steepest descent occurs when $\boldsymbol{\Delta}$ is taken to be a negative multiple of the quantity in square brackets, for this gives the trace its greatest negative value. It then follows from (5) and (6) that, to second order,

$$\delta\mathbf{R} = -\lambda(\mathbf{s} + \mathbf{s}^\dagger) + \lambda^2(\mathbf{s}\mathbf{S}\mathbf{s}^\dagger - \mathbf{s}^\dagger\mathbf{S}\mathbf{s}), \quad (7)$$

where

$$\mathbf{s} = \mathbf{S}^{-\frac{1}{2}} \mathbf{t} \mathbf{S}^{-\frac{1}{2}} = (\mathbf{S}^{-1} - \mathbf{R})\mathbf{h}\mathbf{R}. \quad (8)$$

This may also be written (using the fact that $\mathbf{s}\mathbf{S}\mathbf{s} = \mathbf{s}^\dagger\mathbf{S}\mathbf{s}^\dagger = \mathbf{0}$)

$$\delta\mathbf{R} = -\lambda\mathbf{L} - \lambda^2\mathbf{L}\mathbf{S}\mathbf{M}, \quad (9)$$

where

$$\mathbf{L} = \mathbf{s} + \mathbf{s}^\dagger, \quad \mathbf{M} = \mathbf{s} - \mathbf{s}^\dagger. \quad (10)$$

The analysis of the original paper may now be taken over immediately. The optimum value of λ is given by

$$\lambda_{\text{opt}} = -l/(2m - m'), \quad (11)$$

where

$$l = \text{tr } \mathbf{L}\mathbf{h}, \quad m = \text{tr } \mathbf{L}\mathbf{S}\mathbf{M}\mathbf{h}, \quad m' = \text{tr } \mathbf{L}\mathbf{G}(\mathbf{L}). \quad (12)$$

If $\delta\mathbf{R}^{(k)}$ is the correction computed according to (9), etc., with $\mathbf{R} = \mathbf{R}^{(k)}$, and we define $\mathbf{R}^{(k+1)} = \mathbf{R}^{(k)} + \delta\mathbf{R}^{(k)}$, then the sequence $\mathbf{R}^{(0)}, \mathbf{R}^{(1)}, \mathbf{R}^{(2)}, \dots$, converges to the required solution.

Finally, an initial matrix \mathbf{R} , such that $\mathbf{S}^\dagger\mathbf{R}\mathbf{S}^\dagger$ is accurately idempotent, may be constructed from a trial approximation \mathbf{R}_0 as the limit of the sequence $\mathbf{R}_0, \mathbf{R}_1, \mathbf{R}_2, \dots$, where

$$\mathbf{R}_{k+1} = \mathbf{R}_k \mathbf{S} \mathbf{R}_k (\mathbf{3I} - 2\mathbf{S}\mathbf{R}_k). \quad (13)$$

This result is again a simple generalization of that used in the original work. The process is of second order and usually converges rapidly. It is also useful for restoring idempotency, which may suffer on account of small cumulative errors, at any stage of the SCF process.

CONCLUSION

It appears that the use of nonorthogonal basis orbitals requires little elaboration of the original process, beyond the initial calculation of \mathbf{S}^{-1} . There are two alternative procedures:

(i) initial construction of an orthogonal m -dimensional basis, followed by transformation of all integrals to the new basis [including a transformation of 2-electron integrals, of dimension $\frac{1}{2}m(m+1)$];

(ii) construction of an orthogonal basis, followed by repeated 1-electron transformations between both bases during the iterative process.²

Both alternatives are considerably more cumbersome than the procedure developed in this note. The modified iterative method will shortly be programed for electronic digital computation and used in the determination of approximate SCF functions, for atoms and simple molecules.