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Perspective

Perspective on "New developments in molecular orbital theory"

Roothaan CCJ (1951) Rev Mod Phys 23: 69–89

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Abstract. This paper reviews the title article by Clemens Roothaan and the huge impact that his paper has had in modern chemistry. In his paper Roothaan converts the molecular Schödinger equation into a matrix equation by systematically introducing the linear combination of atomic orbitals–molecular orbital approximation and by invoking the variational principle.

Key words: Roothaan equation – Roothaan–Hall – Hartree–Fock – Roothaan self-consistent field

1 Introduction

Quantum chemistry has certainly come of age, and quantum chemical concepts appear in nearly all papers published in the chemical literature today. Actual quantum chemical calculations are now reported in many experimental papers, and computer codes that perform these calculations are now often considered as another piece of chemical apparatus. Various experimental groups now train experts in computational chemistry, along with experts in NMR spectroscopy, mass spectroscopy, and so on. Nearly all molecular electronic structure calculations today start with molecular orbital (MO) calculations, but the history of the development of this methodology is often forgotten. Today's heroes have become the writers of useful computer code, but the basic underpinnings of these codes, the ideas that let these codes develop and become useful and those who developed these ideas, are often forgotten. Who is Roothaan? What did he do that so influenced MO theory? I can make my distinction of theoretical chemist versus computational chemist, should such a distinction be appropriate, on the basis of this answer. This short manuscript reviews the 1951 paper by C.C.J. Roothaan entitled "New developments in molecular orbital theory" [1], hopefully putting this paper in some perspective. When I was a graduate student interested in theoretical chemistry this paper was required reading, and it is interesting to note that this paper is the first reprint in the book by Parr [2] "Quantum theory of molecular electronic structure" published in 1963, which itself had a large impact on the development of quantum chemistry as a useful tool. Slater in his 1963 book "Quantum theory of molecules and solids" [3], which had a similarly strong influence in the physics community, also assigns much of the credit of the "modern" Hartree–Fock MO method to Roothaan's paper. I had a good deal of trouble with this paper, as did my contemporaries, for it is full of the statement infamous to all students "The proof of Eq. X is elementary, and will be omitted here." (Looking back at this paper, the proofs are obvious, but I did not think so at the time!) Regardless, understanding this paper is fundamental to really understanding MO theory.

2 New developments in MO theory, 1951

To put the reader in the proper perspective of the time, I quote below part of the first paragraph of Roothaan's paper:

> "For dealing with the problems of molecular quantum mechanics, two methods of approximation have been developed which are capable of handling many-electron systems. The Heitler–London–Pauling–Slater or valence bond (VB) method [1–3] originated from a chemical point of view. The atoms are considered as the material from which the molecule is built; accordingly, the molecular wave function is constructed from the wave functions of individual atoms. The Hund–Mulliken or molecular orbital (MO), method [4] is an extension of the Bohr theory of electronic configurations from atoms to molecules. Each electron is assigned to a one-electron wave function or molecular orbital, which is the quantum mechanical analog of an electron orbit. Each of the two fundamentally so different approaches has its merits: ..." [4].

This last statement might have been so prior to Roothaan's 1951 paper, but this paper clearly gave the advantage to MO theory. Prior to this work, the extension of VB and MO theory to molecules seemed rather ad hoc. This paper systematized MO theory by converting the many-dimensional molecular Schödinger equation (non-relativistic, time-independent and fixed nuclei)

$$\mathbf{H}\Psi_\mathrm{I} = E_\mathrm{I}\Psi_\mathrm{I} \tag{1}$$

$$\mathbf{H} = -\hbar^2/2m\sum_i \nabla_i^2 - \sum_i\sum_\mathrm{A} Z_\mathrm{A}e^2/R_{\mathrm{A},i} + \sum_i\sum_{j<i} e^2/r_{i,j} \ , \tag{2}$$

in which the symbols take on their usual meanings, a seemingly impossible differential equation, into the now familiar matrix equation, often called the Roothaan equation (or Roothaan–Hall [5] equation)

$$\mathbf{FC} = \mathbf{SC}\varepsilon \tag{3}$$

first by assuming a determinental antisymmetrized product (AP) wave function for the closed shell system [6]

$$\Psi_\mathrm{I} = |\Phi_1(1)\bar{\Phi}_1(2)\Phi_2(3)\bar{\Phi}_2(4)\cdots\Phi_n(N-1)\bar{\Phi}_n(N)| \tag{4}$$

and then, the crucial step, by systematically introducing the linear combination of atomic orbitals $\{\chi_\mu\}$ (LCAO-MO) approximation

$$\Phi_i = \Sigma_\mu \chi_\mu C_{\mu i} \tag{5}$$

The bars over orbitals in equation (4) designate β-spin. By carefully invoking the variational principle for the MO coefficients $C_{\mu i}$ an equation is obtained for the molecular orbitals in terms of the "Fock" operator **f**

$$\mathbf{f}\Phi_i = \varepsilon_i\Phi_i \ , \tag{6}$$

with **f** given in terms of a Coulomb operator $\mathbf{J}_i$ and exchange operator $\mathbf{K}_i$

$$\mathbf{f} = \mathbf{h} + \Sigma_i(2\mathbf{J}_i - \mathbf{K}_i) \tag{7}$$

and few of us have not gone through this same derivation, first as students and then, perhaps, as teachers. In addition, few of us have modified this eloquent derivation. The matrix **F** of Eq. (3) was developed in terms of integrals over the one-electron operators and the two-electron Coulomb and exchange operators. The molecular differential equation was successfully transformed into a matrix equation involving molecular integrals. Although solving matrix equations was, and still is, certainly much more familiar than solving the original differential equations by numerical techniques or other various somewhat awkward procedures, routine use of MO theory by the community of chemists and physicists at large awaited the development of fast methods for diagonalization, the evaluation of integrals from those over exponential atomic functions to those over Gaussian atomic functions, and faster computers; however, the basic framework used today in all MO calculations is that described by Roothaan. Open-shell methods of MO theory were also systematized first by Roothaan in 1960 with his introduction of the vector coupling coefficient [7].

The Roothaan paper contains more than the development of the Roothaan equations. There is the description of the use of molecular symmetry. Three points are developed for the closed-shell ground state:

> "(1) The LCAO AP which minimizes the energy is necessarily a singlet and is totally symmetric with respect to the symmetry point group of the molecule.
>
> (2) The best LCAO MO's can be chosen so that they belong in sets to irreducible representations of the symmetry group of the molecule.
>
> (3) The best LCAO MO's can all be chosen real."

The assumption here is that if the total many-electron Hamiltonian commutes with various symmetry operations of the group $\mathscr{C}$ then the Fock operator that leads to **F** can also be chosen in such a fashion. In such a case each MO will transform as one of the irreducible representations of the group. The ideas presented in the Roothaan paper are very important, and allow factorization of the Roothaan equations into simpler blocks, one for each irreducible representation, but experience has indicated that on occasion there are "Hartree–Fock instabilities" that destroy the symmetry of the resultant MOs. However, the Fock operator can always be constrained to have the symmetry of the nuclei.

It is difficult to imagine the world of chemistry without MO theory, and the possibilities that the Roothaan paper opened up for its future. Of course, it is possible that if Roothaan had not developed this as he did, the time was ripe, and others would have. In fact, as suggested earlier in this perspective, in the paper by Hall [5] similar ideas were developed, but without the same impact.[1] Nevertheless, the Roothaan paper "New developments in molecular orbital theory" is probably the keystone paper that led to the dominance of MO theory over VB theory, and its widespread and easy usage today.

References

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2. Parr RG (1963) Quantum theory of molecular electronic structure. Benjamin, New York
3. Slater JC (1963) Quantum theory of molecules and solids, vol 1. McGraw-Hill, New York, see, in particular, Appendix 7
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5. Hall GG (1951) Proc Roy Soc Lond Scr A 205: 541
6. Slater JC (1929) Phys Rev 34: 1293
7. Roothaan CCJ (1960) Rev Mod Phys 32: 179

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[1] It is difficult to say why this is so. Perhaps the immediate interest of the Chicago group in detailed computation is part of the reason, a development in which the two 1960 papers by Ransil that reported self-consistent-field calculations on diatomic molecules became quite important in pointing toward the future high reliance on computers and their role in quantum chemistry [Ransil B (1960) *Rev Mod Phys* 32: 239; Ransil B (1960) *Rev Mod Phys* 32: 245]