
Clemens C. J. Roothaan: $FC = SC\varepsilon^*$

Clemens Carel Johannes Roothaan was born in Nijmegen, the Netherlands, on 29 August 1918. After completing his study at the gymnasium (high school), he enrolled to study electrical engineering at the Technical University of Delft in 1935. During his study at Delft, he was not satisfied with the course curriculum and was inclined towards subjects more focused on physics. To enrich his understanding of various topics in physics, he spent the spring of 1939 at the Technical University of Karlsruhe for auditing classes. He came back to Nijmegen in the summer of 1939. Soon after, World War II was declared, and he was inducted to the Royal Engineers Regiment of the Netherlands army, along with inmates, mostly graduates of the University of Delft. Despite other responsibilities, he could continue with his study there. Later, he along with his brothers were sent to the police lock-up in Hengelo, where he again managed to continue his studies with the resources available from the university library. After three and half months, he was sent to a Nazi concentration camp at Vught. At Vught, he was invited to join the company of the electronic giant N V Philip, who had set up a small manufacturing plant at the camp. Here, he got involved with the Kronig–Penny calculation of Schrödinger equation for a one-dimensional crystal. After the successful completion of the project, he was given a more ambitious project to calculate elastic constants in a classical crystal. This project was formulated in consultation with his professors at Delft. He could again successfully complete the project, and this work was accepted for his Master’s thesis in Delft. Soon after the camp at Vught was evacuated, Roothaan was sent to another Nazi camp at Sachsenhausen. Life at Sachsenhausen was much more difficult than at Vught. Here, he was given the job of a draftsman and later an electrician, and he stayed in the camp until its final evacuation. After that, he was repatriated to the Netherlands, returned to Delft, and officially granted diploma *Ingenieur* (engineer) on 15 October 1945 [1].

Meanwhile, he applied for a postgraduate fellowship in the United States and was admitted to the program of the University of Chicago. He passed the PhD candidacy examination in June 1947 and was accepted to work in the pioneering research laboratory of Robert Mulliken on a Guggenheim Fellowship. Professor Mulliken suggested that he work on the semi-empirical molecular orbital calculations on substituted benzene molecules for his PhD thesis. He started his work along this line but was highly dissatisfied with the semi-empirical molecular orbital (MO) theory developed by Hückel with “alphas and betas”. One of his studies using the Hückel theory was on the structure of ethylene molecule and its excited states. The major problem

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he had was to accept the one-electron Hamiltonian that Hückel proposed in his theory—it was *not defined!* Although he did some calculations and obtained some interesting results, he never accepted their scientific rigor. He was rather fascinated with the self-consistent field (SCF) theory developed by Hartree and Fock (HF) for closed-shell atoms, in which a one-electron Hamiltonian was clearly defined. He did not accept that the MO theory started in the right way and believed that the introduction of the linear combination of atomic orbital (LCAO) approximation developed by Hund, Mulliken, Lennard-Jones, and others into the HF theoretical formulation would provide a better description of the MOs. He proposed this idea to Mulliken, who accepted it and permitted Roothaan to continue working on it for his PhD thesis. It was unknown whether Mulliken was happy or unhappy about it, but he mentioned it in his Nobel lecture [2].

“I tried to induce Roothaan to do his PhD thesis on Hückel type calculations on substituted benzenes. But after carrying out some very good calculations on these, he revolted against the Hückel method, threw his excellent calculations out of the window, and for his thesis developed entirely independently his now well known all-electron LCAO-SCF self-consistent-field method for the calculation of atomic and molecular wave functions, now appropriately referred to, I believe, as the Hartree–Fock–Roothaan method”.

At the same time as his PhD enrollment in the University of Chicago, he got an offer from Professor Karl Herzfeld of the Catholic University of America, Washington, DC. He was invited to join the physics faculty, and he accepted the offer. Since then, he commuted between Chicago and Washington during the period of his PhD work.

To proceed further, the HF–SCF theory needs an introduction. The HF–SCF theory is a single determinant theory in which a set of spin orbitals[†] is calculated variationally by minimizing the energy such that the Slater determinant formed from these spin orbitals gives the best possible approximation to the electronic ground state, $|\Psi_0\rangle$, of a N electron system

$$|\Psi_0\rangle = |\chi_1\chi_2, \dots, \chi_a\chi_b \dots \chi_N\rangle. \quad (1)$$

In Eq. 1, the set of functions $\{\chi\}$ denotes the spin orbitals, each depending on three space variables and one spin variable (collectively say, \mathbf{x}) of the electron occupied in it. The expression in the right-hand side of Eq. 1 is a shorthand notation for the $N \times N$ Slater determinant (representation of many electron antisymmetric wave function) excluding the normalization factor $\frac{1}{\sqrt{N!}}$. In this method spin orbitals are systematically varied retaining their orthonormality, $\langle \chi_a | \chi_b \rangle =$

[†]Spatial orbital is a one-electron wave function which depends on spatial coordinates. Spin orbital is a product of the spatial orbital and the wave function depending on the spin variable.



δ_{ab} (=1 for $a = b$ and 0 for $a \neq b$). In the process, one finally arrives at an equation called the ‘HF integro-differential equation’, that minimizes the energy variationally, $E_0 = \langle \psi_0 | \hat{H} | \Psi_0 \rangle$ (\hat{H} is the Hamiltonian operator of the N electron system), and defines the best possible set of spin orbitals. The HF integro-differential equation is given by

$$\left[h(\mathbf{x}_1) + \sum_{b \neq a} J_b(\mathbf{x}_1) - \sum_{b \neq a} K_b(\mathbf{x}_1) \right] \chi_a(\mathbf{x}_1) = \varepsilon_a \chi_a(\mathbf{x}_1). \quad (2)$$

In the above equation \mathbf{x}_1 represents the coordinates of electron 1, $h(\mathbf{x}_1)$ is the one-electron Hamiltonian operator that includes the electron kinetic energy and its attractive interaction with the nuclei. $J_b(\mathbf{x}_1)$ and $K_b(\mathbf{x}_1)$ are two-electron operators called the Coulomb and exchange operators, respectively. While the Coulomb operator includes the average repulsive interaction of an electron with its $N - 1$ neighboring electrons (the HF approximation) and has a classical origin, the exchange operator originates from the antisymmetry requirement of the N electron wave function (the Pauli exclusion principle) represented by the Slater determinant $|\Psi_0\rangle$ and has a purely quantum mechanical origin. The summations in the above equation run over the occupied orbitals. The action of the Coulomb and exchange operators on the spin orbitals is given by

$$J_b(\mathbf{x}_1)\chi_a(\mathbf{x}_1) = \left[\int d\mathbf{x}_2 \chi_b^*(\mathbf{x}_2) r_{12}^{-1} \chi_b(\mathbf{x}_2) \right] \chi_a(\mathbf{x}_1) \quad (3)$$

$$K_b(\mathbf{x}_1)\chi_a(\mathbf{x}_1) = \left[\int d\mathbf{x}_2 \chi_b^*(\mathbf{x}_2) r_{12}^{-1} \chi_a(\mathbf{x}_2) \right] \chi_b(\mathbf{x}_1). \quad (4)$$

The integrations in the above equations are over the coordinates (three spatial and one spin) of electron 2. The quantity r_{12} is the distance between electron 1 and 2. It can be seen that the action of $K_b(\mathbf{x}_1)$ exchanges electrons between orbitals a and b . The quantity ε_a in Eq. 2 is the energy of the MO χ_a .

The eigenvalue equation given in Eq. 2 is expressed as

$$f(\mathbf{x}_1)\chi_a(\mathbf{x}_1) = \varepsilon_a \chi_a(\mathbf{x}_1), \quad (5)$$

where $f(\mathbf{x}_1)$ defines the one-electron Fock operator. From the expression of the Coulomb and exchange operators (Eqs. 3 and 4) it can be seen that the Fock operator depends on its own eigenfunctions and the HF integro-differential equation (Eq. 2) is non-linear. An analytical solution of this equation is out of the scope and it had to be solved numerically and iteratively. In practice, the integro-differential equation can be numerically solved for atoms exploiting

the high symmetry. For this purpose, one uses a trial and error method—one assumes a trial set of spin orbitals and calculates the Fock operator, and solves Eq. 5 for the N lowest eigenvalues and compares the new set of spin orbitals resulting in the process with the assumed one if they converge within an error limit. Otherwise, the whole procedure is repeated with the new set of spin orbitals obtained in the previous step. In the process what is updated is the average field (as approximated in the HF theory) arising from the two-electron terms of the Fock operator. The iteration is stopped when this field converges and hence the name ‘self consistent field method’. The description presented above is a very brief and conceptual narration of the HF method without much technical details.

For molecules, the solution of the HF equation was out of the scope because of the lack of a central symmetry as in atoms. Roothaan focused on this issue and tried to convert the integro-differential equation of HF to a solvable form for closed-shell (in which all electrons are spin paired) molecules to start with. In this case, the spin can be integrated out from Eq. 5, and it can be converted into its spatial form

$$f(r_1)\psi_a(r_1) = \varepsilon_a\psi_a(r_1). \quad (6)$$

In the above equation r_1 refers to the three spatial variables of electron 1 and $\psi_a(r_1)$ is the spatial part of the molecular spin orbital $\chi_a(x_1)$. Roothaan used all electron LCAO approximation for the molecular orbitals with a set of k number of atomic orbitals. It is given as

$$\psi_a(r_1) = \sum_{\mu=1}^k \phi_{\mu}c_{\mu a}, \quad (7)$$

where ϕ_{μ} 's are the normalized atomic orbitals, ($\int \phi_{\mu}^*\phi_{\mu}dr_1 = 1$), and $c_{\mu a}$'s are the expansion coefficients. The quantity $|c_{\mu a}|^2$ represents the contribution of the atomic orbital ϕ_{μ} in the expansion of MO ψ_a .

In the above equation the set of atomic orbitals $\{\phi_{\mu}\}$ are known and upon introduction of this expansion into Eq. 5 along with variational equation he obtained (after some rigorous algebra) the HF integro-differential equation in the form a set of algebraic equations for the unknown $c_{\mu a}$'s and the orbital energy ε_a . In compact matrix form the equation reads

$$\mathbf{FC} = \mathbf{SC}\varepsilon. \quad (8)$$

In the above equation \mathbf{F} represents the $k \times k$ Fock matrix, elements of which read, $F_{\mu\nu} = \int \phi_{\mu}^*f(r_1)\phi_{\nu}dr_1$, \mathbf{C} is the $k \times k$ coefficient matrix and \mathbf{S} is the $k \times k$ overlap matrix whose



elements are given by, $S_{\mu\nu} = \int \phi_{\mu}^* \phi_{\nu} dr_1$. The quantity ε is a diagonal matrix and its elements define the orbital energy.

Eq. 8 represents a set of k number of linear homogeneous algebraic equations

$$\sum_{\mu=1}^k (F_{\mu\nu} - \varepsilon_a S_{\mu\nu}) c_{\mu a} = 0; \mu = 1, 2, \dots, k. \quad (9)$$

The non-trivial solution of the Eq. 9 is obtained by

$$\det(F_{\mu\nu} - \varepsilon_a S_{\mu\nu}) = 0. \quad (10)$$

The roots of the above equation define the orbital energy ε_a and the k coefficients corresponding to each root when substituted in Eq. 7 yield the corresponding MO. This is the most seminal contribution of Roothaan.

Eq. 9 is solved by an iterative trial and error method. In this case, one assumes a set of $C_{\mu a}$'s and calculates the Fock operator in the basis of atomic orbitals and solves Eq. 9. The new set of $C_{\mu a}$'s obtained in the process is compared with the set from the previous step and the process is repeated until a convergence is reached. While the original HF equation was a complicated mathematical problem for molecules, Roothaan's formulation (vide supra) transformed it to a rather straightforward solution of standard matrix equations. This development was a hallmark in the subject and Roothaan named it as 'LCAO-SCF theory'.

Around the same time as Roothaan's work, there was a parallel and independent development made by G G Hall and J Lennard-Jones in Cambridge, England. The two developments were greatly similar. In those days, scientific results were not published until the PhD was granted, and apparently, the developments in Cambridge and Chicago were not known to each other. The classic papers that appeared from these works [3, 4, 5] represent a milestone in the development of computational quantum chemistry. The formalism is called 'Roothaan–Hall–Hartree–Fock method'. However, Hall's name does not appear in most of the textbooks, and the self-consistent field equations are commonly called Hartree–Fock–Roothaan equations. Later Roothaan extended the LCAO-SCF method to treat open-shell (containing spin unpaired electrons) molecules [6].

Roothaan obtained his PhD degree in June 1950. Soon after, he was invited to join the faculty of physics at the University of Chicago in 1952. During his PhD work, he realized the necessity of developing computational tools to solve LCAO–SCF equations. This involves the computationally intensive calculations of one- and two-electron integrals over the atomic basis functions. It was not possible in those days because of the absence of required computational architecture.



As a faculty of the University of Chicago, he started developing tools to calculate all electron wave function for atoms and molecules in the laboratory for Molecular Structure and Spectra. The major task he undertook was to systemize the calculations of one and two-electron integrals over the atomic basis functions. Klaus Ruedenberg, who came to Chicago from Zürich, joined him in the project. The second major project that he led was the development of computer hardware and software to translate the integrals into computation. It was a daunting task. He was appointed as the Director of the University of Chicago computation center during 1962–1968. During this period, his major focus was on the second project. He developed University's first computer program. In the 1970s and 1980s, he along with his former student John Detrich, worked on the relativistic effects in atoms and molecules [7] and multi-configuration self consistent field theory [8]. After his retirement in 1988, he worked for Hewlett Packard and developed the Itanium chip and co-processors for large-scale computational applications. He breathed his last on 17 June 2019.

In summary, Roothaan's career as a physicist started in an unusual and traumatic environment. However, he stayed firm in his ambitions, and his career remained mostly unaffected with no major external perturbations during World War II. His exemplary and lasting scientific contribution in molecular quantum chemistry is a classic and is a milestone in the development of computational molecular quantum chemistry.

Suggested Reading

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