INFORMATION TO USERS

The most advanced technology has been used to photograph and reproduce this manuscript from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

U·M·I

University Microfilms International
A Bell & Howell Information Company
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
313/761-4700 800/521-0600

Order Number 9108177

Quantum crystallography: Density matrix-density functional theory and the x-ray diffraction experiment

Soirat, Arnaud J. A., Ph.D.

City University of New York, 1990

U·M·I
300 N. Zeeb Rd.
Ann Arbor, MI 48106

QUANTUM CRYSTALLOGRAPHY:

DENSITY MATRIX-DENSITY FUNCTIONAL THEORY AND THE X-RAY DIFFRACTION EXPERIMENT

by

ARNAUD J. A. SOIRAT

A dissertation submitted to the Graduate Faculty in
Chemistry in partial fulfillment of the requirements
for the degree of Doctor of Philosophy, The City
University of New York.

1990

This manuscript has been read and accepted for the Graduate Faculty in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

9/21/90 L Massa

Date Chair of Examining Committee

9/24/90

Date Executive Officer

L Massa

Mark Hillery

Supervisory Committee

The City University Of New York

Abstract

QUANTUM CRYSTALLOGRAPHY:

DENSITY MATRIX-DENSITY FUNCTIONAL THEORY AND THE X-RAY DIFFRACTION EXPERIMENT

by

Arnaud J. A. Soirat

Adviser: Professor Lou Massa

Density Matrix Theory is a Quantum Mechanical formalism in which the wavefunction is eliminated and its role taken over by reduced density matrices. The interest of this is that, it allows one, in principle, to calculate any electronic property of a physical system, without having to solve the Schrödinger equation, using only two entities much simpler than an N-body wavefunction: first and second-order reduced density matrices. In practice, though, this very promising possibility faces the tremendous theoretical problem of N-representability, which has been solved for the former, but, until now, voids any hope of theoretically determining the latter.

However, it has been shown that single determinant reduced density matrices of any order may be recovered from coherent X-ray diffraction data, if one provides a proper Quantum Mechanical description of the Crystallography experiment.

A deeper investigation of this method is the purpose of this work, where we, first, further study the calculation of X-ray reduced density matrices N-representable by a single

Slater determinant. In this context, we independently derive necessary and sufficient conditions for the uniqueness of the method.

We then show how to account for electron correlation in this model. For the first time, indeed, we derive highly accurate, yet practical, density matrices approximately N-representable by correlated-determinant wavefunctions. The interest of such a result lies in the Quantum Mechanical validity of these density matrices, their property of being entirely obtainable from X-ray coherent diffraction data, their very high accuracy conferred by this known property of the N-representing wavefunction, as well as their definition as explicit functionals of the density.

All of these properties are finally used in both a theoretical and a numerical application: in the former, we show that these density matrices may be used in the context of Density Functional Theory to highly accurately determine the unknown HK functional, associated with the theorem of Hohenberg and Kohn. The latter is provided by the calculation of helium correlation energy, where we test approximating the second-order density function by the leading term of its McLaurin's series expansion.

To my Parents,
Jacques and Evelyne

To the Memory of my Grandmother,
Gisèle

Acknowledgments

I would like to warmly thank Lou Massa, Professor of Physics and Chemistry at Hunter College and the Graduate School of the City University of New York for sharing with me his enthusiasm for fundamental research in Quantum Mechanics. As a mentor, Professor Lou Massa gave me considerable advice, assistance and encouragement throughout my work, which helped my progress immeasurably.

I wish to express my appreciation to the members of my dissertation committee for their interest in my work: Marc Hillery, Professor of Physics and Gary Quigley, Professor of Chemistry and Biochemistry, both at Hunter College and the Graduate School of the City University of New York, whose comments and suggestions greatly stimulated my research.

As part of my work was devoted to teaching Chemistry, I would also like to thank Ms Irène Whiteman, Chemistry Laboratory Technician at Brookdale Campus, Hunter College, whose wisdom, patience and support helped me so much, and made my two assistantship years a truly pleasant and rewarding experience.

To John Gounarides, Rue He and Lulu Huang, Ph.D. students in Chemistry at Hunter College, I owe the friendliest thanks for numberless captivating discussions.

Table of Contents

Appendix

List of Tables

List of Figures

Chapter I

Introduction:

Density Matrix and
Density Functional Theory
Applied to X-ray Crystallography

I. *Quantum Mechanics Formalism in Different Representations.*

The purpose of any physical law is to predict and explain the behavior of a physical system.

To this end, Quantum Mechanics has been developed for the very purpose of describing atomic or subatomic systems which do not obey the usual laws of Newtonian Classical Mechanics. The goal of Quantum Mechanics is, then, to calculate any properties of microscopic systems from the mass and charge of their constituting particles.
Quantum Mechanics provides the striking result that some physical quantities (such as the energy of the system) may take only some values, not all values, as experiment indicated. These allowed values, called eigenvalues, may be mathematically found by solving the eigenvalue equation, which for a physical quantity q is cast in the following form:[1]

$$\mathbf{Q}\, f = q\, f \qquad (1)$$

where to each physical observable q, corresponds an operator **Q** applying on eigenfunctions f.
The job of Quantum Mechanics is then to tell us how to form these operators, some abstract mathematical objects, corresponding to the physical quantity q which we wish to measure.

Historically, Quantum Mechanics grew up from two different points of view, which, in fact, represent two analogous mathematical formulations of the eigenvalue problem, as it later turned out to be shown.[2-4]

The year 1925 saw, indeed, the birth of modern Quantum Mechanics marked by the two almost simultaneous papers of Heisenberg[5] —in 1925— and Schrödinger[6] —in 1926. The first of these two papers essentially elaborated the formalism of Matrix Mechanics, while the second one set the fundamental basis of Wave Mechanics:

- In Heisenberg's approach, operators are represented by matrices, and apply on a vector (column matrix), called eigenvector. The solution of the eigenvalue equation relies then on Algebra.
- Whereas, in Schrödinger's formalism, the differential operators apply on a function, and the eigenfunctions are found by solving a differential equation, based on Calculus methods.

These apparently different mathematical and physical approaches to Quantum Mechanical problems are actually deeply interrelated; indeed, both theories can be embraced in a more general formalism of Quantum Mechanics, which was first suggested by Dirac[7] and von Newman[8] —in 1930 and 1932, respectively. A mathematical rigorous development of this general formalism of Quantum Mechanics may then be achieved by describing it in a Hilbert space, as we shall soon see.

In any of the three representations, however, the regular Quantum Mechanics formalism is articulated around the same mathematical object: the state vector Ψ, which is considered to contain the maximum available information about the system. Conveniently, this state vector can be indifferently described in any of the three previously mentioned representations —as well as in others—, i.e.

- the ket representation (in the spirit of Dirac's language),
- the function representation (Schrödinger's language),

- and the matrix representation (Heisenberg's language).

which are all in one-to-one relationship. In this work, we shall constantly be dealing with these three ones.

However, since the Hilbert space formulation is a nice generalization of any representation, its mathematics is an essential tool for a deep comprehension of the Quantum Mechanics formalism, and, as a consequence, we shall first briefly review some important theorems on Hilbert space. For an extensive survey of Hilbert space structures, the reader is referred to references 2-4, for the generalities, as well as 7-15 for a more advanced treatment of the subject.

I.1. Separable Hilbert Spaces.

I.1.1. Fundamental Definitions and Theorems.

It is a well-known fact in Mathematics that in a Hilbert space —as well as in any other inner product structures— the leading role belongs to the scalar —or inner— product. Indeed, this fundamental form defines, not only the notion of distance in the given space, but also another metric concept, namely this of angle.[16-17] In the study of the latter, we shall restrict ourselves throughout the rest of this chapter to the concept of right angle, i.e. orthogonality. The following definitions, axioms and theorems are essentially extracted from references 9 and 12, except otherwise noted.

Definition: A Hilbert space is a complete normed space —or Banach space— which has a norm coming from an inner product.

In other words, a Hilbert space is a complete (in the sense of the norm) vector space, provided with an inner product.

A Hilbert space is then:

1. A linear vector space $\mathfrak{H}$ over a field F. Here we shall only consider the case in which F is the field of complex numbers C.

2. $\mathfrak{H}$ is provided with a definite-positive hermitian bilinear form, i.e. a mapping defined on $\mathfrak{H}\times\mathfrak{H} \longrightarrow C$, denoted by $<\varphi|\chi>$ and satisfying the following axioms: $\forall\ \varphi$, $\varphi_1, \varphi_2, \chi, \chi_1$ and $\chi_2 \in \mathfrak{H}$, $\forall\ (a,b) \in C\times C$,

$$\begin{aligned} &\mathfrak{a}.\ <\varphi|a\chi_1+b\chi_2>=a<\varphi|\chi_1> + b<\varphi|\chi_2>; \\ &\mathfrak{b}.\ <a\varphi_1+b\varphi_2|\chi>= a^*<\varphi_1|\chi> + b^*<\varphi_2|\chi>; \qquad (2) \\ &\mathfrak{c}.\ <\varphi|\chi>=<\chi|\varphi>^* \\ &\mathfrak{d}.\ <\varphi|\varphi>\geq 0, \text{ where } = 0 \text{ applies only if } \varphi = 0. \end{aligned}$$

where the axioms have the following meaning: **a** expresses the property of linearity with respect to the right-hand member, whereas **b** the antilinearity with respect to the left-hand member; **c** and **d** ensures the bilinear form to be, respectively, hermitian and definite-positive.

Furthermore, in Quantum Mechanics, we deal at present almost exclusively with a special class of Hilbert spaces, which are called separable. We shall therefore only consider complex Hilbert spaces which satisfy the axiom of separability.

Definition: The Hilbert space $\mathfrak{H}$ is called separable, if there is a countable everywhere dense subset of vectors of $\mathfrak{H}$.

That is to say, if $\mathfrak{H}$ is separable, there exist denumerable linear bases —which are defined as being any subset of $\mathfrak{H}$ having its span dense in $\mathfrak{H}$.

The following consequent theorem will be of particular interest later on.

Theorem: Every subspace of a separable Hilbert space is a separable Hilbert space.

Hence, according to this axiom of separability, the smallest cardinality of a linear basis of $\mathfrak{H}$, called the (linear) dimension of $\mathfrak{H}$, can be only either finite or denumerable. In the former case, the basis will span a separable Hilbert space of finite dimension.

We shall agree that in the future, whenever we refer to a space as a Hilbert space, we mean a complex separable Hilbert space $\mathfrak{H}$ of finite dimension, unless otherwise specified.

In Quantum Mechanics, two important examples of such Hilbert spaces are the essential mathematical structures on which the Schrödinger's and the Heisenberg's formulation of Quantum Mechanics are based. We shall briefly outline the essence of these formulations in the coming section.

I.1.2. Quantum Mechanical Examples of Separable Hilbert Spaces.

* $\mathfrak{L}^2$ space: Schrödinger's formulation

The set of all complex functions Φ (1) for which

$$\int \Phi(1)\,\Phi^*(1)\,d1 < +\infty \tag{3}$$

is a separable Hilbert space, denoted by $\mathfrak{L}^2$, if the inner product is defined by

$$\langle \Phi \mid \psi \rangle = \int \psi(1)\,\Phi^*(1)\,d1 \tag{4}$$

* $\mathfrak{L}_{\mathfrak{m}}{}^2$ space: Heisenberg's formulation

The set of all one-column complex matrices $\underset{\sim}{\Phi}$ with a countable number of elements

$$\underset{\sim}{\phi}(1) = \begin{pmatrix} \phi_1(1) \\ \phi_2(1) \\ \vdots \end{pmatrix} \tag{5}$$

becomes a separable Hilbert space, denoted by $\mathfrak{L}_{\mathfrak{m}}^{2}$, if the inner product is defined by

$$<\Phi|\psi> = \sum_{k} \psi_k(1)\, \Phi_k^{*}(1) \tag{6}$$

Now that we have briefly reviewed the mathematical structures essential to the description of Quantum Mechanics, we shall study the expression of its formalism in these three different representations.

I.2. Exact Description of the State Vector Ψ.

The maximum available information about a system is contained, according to Quantum Mechanics formalism, in the state vector Ψ, which may be written in any of the three previously mentioned languages. We shall, thus, now examine how these three representations are interrelated.

Following Dirac's formalism of Quantum Mechanics[7], the state of a given system is completely specified by the direction of its ket vector $|\Psi>$ in Hilbert Space —its length being physically meaningless and thus arbitrarily taken to be unity (normalized state vector).

Now suppose the system is made up of N particles, and we want to describe it in terms of the states of its component parts. Then, according to the Sudbery's description of the principle of superposition[2], the state $|\Psi>$ can always be written as a linear combination of products of the type $|\Phi_1>|\Phi_2>...|\Phi_N>$, with $|\Phi_i>$ being an element of the state space S_i. $|\Psi>$ is then an element of the state space S, defined as the tensor product of the N state spaces $S_1 \otimes S_2 \otimes ..... \otimes S_N$, in which the products $|\Phi_1>|\Phi_2>...|\Phi_N>$ form a complete set. It is therefore always possible to write down $|\Psi>$, in a unique way, as a linear combination of these products $|\Phi_1>|\Phi_2>...|\Phi_N>$.

$$|\Psi> = \sum_{\text{sets}(12...N)} a(12...N) \; |\Phi_1>|\Phi_2>...|\Phi_N> \qquad (7)$$

This last equation is simply analogous to the decomposition of a vector in a specific vector basis, procedure we are familiar with in the three dimensional euclidean space; the only difference here, in the context of Quantum Mechanics, is that the space of vectors is a Hilbert space, and consequently, the vector basis is of infinite dimension.

Moreover, if one is concerned with the Quantum Mechanical description of a system of N particles moving in space, it is, in fact, highly convenient to describe Ψ in Schrödinger's language, in which the space state consists of the space of all square-integrable functions $\Psi(q)$, called wavefunctions, where $\Psi(q) = < q | \Psi >$ and q stands for the set of spin-position variables (q_1, q_2....., q_N), further abbreviated (1,2,...N).

In such a continuous representation,[18,19] the time evolution of the system with wavefunction ξ (q,t) is described by the Schrödinger equation

$$H \; \xi(q,t) = -\frac{h}{2\pi i} \; \frac{\delta}{\delta t} \xi(q,t) \qquad (8)$$

which has solutions of the form

$$\xi\,(q,t) = \Psi(q)\,\chi(t) \qquad (9)$$

where $$\chi(t) = \exp\,(-\,2\pi i\,E\,t\,/\,h) \qquad (10)$$

provided that $\Psi(q)$ satisfies the time-independent wave equation

$$\mathbf{H}\;\Psi(1,2,\ldots N) = E\;\Psi(1,2,\ldots N) \qquad (11)$$

where **H** is the N-body non-relativistic Hamiltonian operator of the N-particle system. $\Psi(q)$ describes then a stationary state, i.e. a state with constant energy.

For an N-electron system (Fermi-Dirac statistics case), the wavefunction solution to 11 must satisfy the usual properties of "well-behavior", i.e. Ψ must be continuous, quadratically integrable, normalized, with all first derivatives continuous and with single-valued $\Psi\Psi^*$.[20] Moreover, Ψ must satisfy the Pauli principle, which states that $\Psi(1,2,\ldots N)$ must be antisymmetric with respect to the exchange of two electron coordinates. In the position-space of $\Psi(1,2,\ldots N)$, this requirement gives an N-electron wavefunction of the form of a linear combination of Slater determinants :

$$\Psi\,(1,2,\ldots N) = \sum_i d_i\;\Psi_{\det i}\,(1,2,\ldots N) \qquad (12)$$

where $$\Psi_{\det,\,i}\,(1,2,\ldots N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \Phi_a(1) & \ldots & \Phi_p(1) \\ \vdots & \vdots & \vdots \\ \Phi_a(N) & \ldots & \Phi_p(N) \end{vmatrix} \qquad (13)$$

and where $\Phi_a \dots \Phi_p \dots$ are solutions to the one-electron Schrödinger equation

$$H(1)\ \Phi_k(1) = E_k\ \Phi_k(1) \tag{14}$$

In a very general way, the eigenfunctions $\Phi_k(1)$'s, solutions to this last equation, can be exactly written in a basis $\{\psi_j(1)\}$ of infinite dimensions, as:

$$\Phi_k(1) = \sum_j c_{kj}\ \psi_j(1) \tag{15}$$

Depending on the kind of N-electron system being studied, this relation may be physically understood as follows:

- for a molecular system of N electrons, the N Φ's represent the molecular orbitals which are then written as linear combination of atomic orbitals ψ_j, in accordance with the usual LCAO formalism.

- whereas, in the N-electron atomic case, Φ's are atomic orbitals and ψ_j 's monoelectronic basis spin-functions, such as of Slater type.

In both cases, though, the Φ's are orthogonal to each other, chosen to be normalized, and form a complete set. The products of N Φ's therefore also form a complete set, and so do the Ψ_{det} (1,2,...N)'s.

It is thus fully legitimate to write down the exact N-body wavefunction $\Psi(1,2,\dots N)$ as a linear combination of Slater determinants, provided that the summation is made over a complete set —i.e. infinite in number. This is the so-called configuration-interaction formalism.

As a summary, it is clear, then, that the state of an N-electron system is completely specified in the one-electron basis $\{\psi_j(1)\}$ by both:

- the sets of $\{c_{kj}\}$ associated with each Φ_k (where $c_{kj} = <\psi_j | \Phi_k> =$ orthogonal projection of Φ_k along ψ_j), —equation 15.

- the set $\{d_i\}$ associated with the description of $\Psi(1,2,...N)$ in the configuration-interaction formalism, —equation 12.

I.3. Approximate Description of the State Vector Ψ.

For an exact configuration-interaction description of $\Psi(1,2,...N)$, according to equations 12 and 13, we have seen that the summation must be carried over the complete set of Slater determinants, and is therefore infinite in number.

In practice however, this is not feasible for the summation must, of course, be truncated.

For a complete shell N-electron system, the approximation is carried even further where a single Slater determinant is considered to be sufficient. This is the case we shall be dealing with, throughout the rest of this work.

In such a case, we are then looking for the approximation of $\Psi_{exact}(1,2,...N)$ by a single Slater determinant of the form,

$$\Psi_{\text{exact}}(1,2,...N) \equiv \Psi_{\text{det}}(1,2,...N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \Phi_1(1) & \dots & \Phi_N(1) \\ \vdots & \vdots & \vdots \\ \Phi_1(N) & \dots & \Phi_N(N) \end{vmatrix} \qquad (16)$$

where $\Phi_1, ..., \Phi_N$ retain their previous meaning.

The basis $\{\Psi_j(1)\}$ in which the Φ's are expressed, must also be chosen finite, say of M dimensions, and one may, then, describe the linear expansion of the Φ_k's in any of the three representations previously mentioned as:

$$(\forall\ k= 1,...,N) \qquad (17)$$

$$|\phi_k\rangle = \sum_j c_{kj} |\psi_j\rangle \quad \longleftrightarrow \quad \underset{\sim}{\phi}(1) = \underset{\sim}{C}\, \underset{\sim}{\psi}(1) \quad \longleftrightarrow \quad \phi_k(q) = \sum_j c_{kj}\, \psi_j(q)$$

where the vector-column (an (N×1) matrix) is written as,

$$\underset{\sim}{\phi}(1) = \begin{pmatrix} \phi_1(1) \\ \phi_2(1) \\ \cdot \\ \cdot \\ \phi_N(1) \end{pmatrix} \qquad (18)$$

$\underset{\sim}{\psi}(1)$ stands for the vector-column of monoelectronic basis functions, and $\underset{\sim}{C}$ for the coefficient matrix , in which the k$^{\text{th}}$ row is made of the collection of the coefficients of $\phi_k(1)$ in the $\{\Psi_j(1)\}$ basis:

$$\underset{\sim}{\phi}(1) = \begin{pmatrix} c_{11} & \cdots\cdots & c_{1M} \\ c_{21} & \cdots\cdots & c_{2M} \\ \cdot & \cdots\cdots & \cdot \\ \cdot & \cdots\cdots & \cdot \\ c_{N1} & \cdots\cdots & c_{NM} \end{pmatrix} \begin{pmatrix} \psi_1(1) \\ \psi_2(1) \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ \psi_M(1) \end{pmatrix} = \underset{\sim}{C}\,\underset{\sim}{\psi}(1) \qquad (19)$$

II. Drawbacks of the Schrödinger Equation Resolution.

According to the Schrödinger's representation of Quantum Mechanics, the electronic structure and other related properties may be obtained by solving the Schrödinger equation,

$$\mathbf{H}\ \Psi(1,2,...N) = E\ \Psi(1,2,...N) \qquad (11)$$

The Hamiltonian operator **H** for a many-electron system can be cast into a sum of one and two-body operators,[18,19]

$$\mathbf{H} \equiv \sum_{i=1}^{N} \mathbf{h}\,(i) + \sum_{i<j}^{N} \mathbf{g}\ (i,j) \qquad (20)$$

where, on one hand, h (i), the Hamiltonian operator of electron i, consists of (in atomic units)

$$\mathbf{h}\,(i) \equiv -\frac{1}{2}\,\nabla^2(i) + \mathbf{V}\,(i) \qquad (21)$$

the terms being respectively, the kinetic energy operator and the potential of attraction of the electron i by the nuclei.

On the other hand, the two-body operator, written as

$$g\,(i,j) \equiv \frac{1}{r_{ij}} \tag{22}$$

represents the electrostatic potential of repulsion between electrons i and j.

For a one-electron system, only $h(1)$, of course, is left in the Hamiltonian operator, and the eigenvalue equation is then exactly solvable.

Unfortunately, things are not so easy for a many-electron system where, because of the very existence of the interelectronic repulsion operator, no exact solution to the Schrödinger equation is to be obtained. It is then necessary to follow approximation methods, among which some of them will be now briefly reviewed.[18, 20-22]

II.1. Approximation Methods for Solving the Schrödinger Equation.

II.1.1. The Independent Particle Model.

To start with, the simplest, and by so the crudest, approximation that one may think of in this context is provided by considering the many-electron system as made of non-interacting particles (Independent Particle Model). This simply results in neglecting $g\,(i,j)$

in the Hamiltonian and yields an eigenvalue equation exactly solvable by the method of separation of variables. The solution will be, then, of the form of a product of monoelectronic wavefunctions,

$$\Psi(1,2,...N) = \Phi_1(1)\,\Phi_2(1)\,.....\,\Phi_N(N) \qquad (23)$$

where $\Phi_i(i)$ is one out of the infinite number of solutions to the one-electron eigenvalue equation as described in equation 14.

The most important problem with such an N-body solution is that it provides a specification of the orbitals Φ_1, Φ_2 ... to which the electrons are assigned, which is surely a fallacy since the electrons are truly indistinguishable. As a consequence, such an approximation of $\Psi(1,2,...N)$ does nothing less than violating the Pauli principle.

Different other methods have been developed for solving approximately the many-electron Schrödinger equation, using different level of sophistication.[18, 20-22] One of them, the variation method, will be later used in our research and it seems therefore appropriate to briefly review now the main idea of this theory. This is what we shall deal with in the next paragraph.

II.1.2. The Variation Method.

The variation method allows one to obtain an approximation to the ground-state energy of a many-electron system, as well as some of the exited levels, without solving the

Schrödinger equation. This is based on the following variation theorem which states that:[20]

"Given a system with the Hamiltonian operator H, any well-behaved function φ that satisfies the boundary conditions of the problem, will verify the inequality

$$\frac{\langle \varphi \mid H \mid \varphi \rangle}{\langle \varphi \mid \varphi \rangle} \geq E_0 \qquad (24)$$

where E_0 stands for the true value of the lowest energy eigenvalue of H".

Based on this theorem which shows that the variation method allows us to calculate an upper bound for the energy of the system, many variational methods have been developed.[18, 20-22] Table 1 regroups some of the most commonly used methods. However, no matter what, they all proceed through the same path, which could be roughly sketched as follows:

1. Start by choosing any suitable trial function in which some variable parameters have been incorporated.

2. Then, minimize the variational integral of equation 24 by varying the parameters and solving some approximate equation.

Method:	**Start with the trial function**	**minimize W by varying**	**& solve**
Linear Variational	$\Psi = \Sigma c_i f_i$ where f_i = spin-orbital	c_i's	Secular equations (i=1, N) $\sum_k (H_{ik} - S_{ik}W) c_k = 0$
Hartree	$\Psi = \Pi f_i$ where $f_i = h_i (r_i) Y_i (\theta_i, \phi_i)$	f_i's	Hartree equations: $G f_i = W_i f_i$
Hartree-Fock	$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} f_1(1) & \dots & f_N(1) \\ & & \\ f_1(N) & \dots & f_N(N) \end{vmatrix}$	f_i's	Hartree-Fock equations: $F f_i = W_i f_i$

Table 1. Comparison of the Main Variational Methods.

The set of solutions $\{W_1 \geq E_1$, $W_2 \geq E_2$,......., $W_N \geq E_N\}$ so obtained for the first N^{th} energy levels will be the "best" ones that one could get with the chosen form of the trial function, i.e. out of the family of chosen functions. It is clear, thus, that the energy is a functional of the trial function, and consequently its calculated values will critically depend on the choice of the starting function.

As an illustration to this last remark, the alert reader will have noticed that the Hartree method, as described in Table 1, uses an improper trial function of the form of the one previously described in the Independent Particle Model (equation 23). Historically, Fock first realized that this wavefunction was not antisymmetric, and as so, violated the Pauli principle. Moreover, he noticed that it does not take care, either, of the electron spin in the electronic variables. The best way to take account of these two constraints on the trial function, is to write it as a Slater determinant —according to equation 16. This is what gave birth to one of the most widely used approximation method: the Hartree-Fock method.

II.2. Drawbacks of this Approach.

To summarize, the Schrödinger equation allows one to determine —in principle— eigenfunctions and eigenvalues of a linear hermitian operator corresponding to a physical observable. But, for a system of several interacting particles, only approximate solutions may be obtained, based for example on a variational calculation.

However, an important drawback of such an approach of Quantum Mechanics is due to the very nature of the wavefunction.

Indeed, no physical meaning can be given to the wavefunction itself. In front of the increasing complexity of wavefunctions, as computational facilities improve, one is therefore not to expect having a clear understanding of the electronic properties of the system , just by examining the wavefunction.

On the contrary, one must try to extract in some way the essential information contained within the wavefunction, that is to say, the electron density, which is of paramount consequence to the electronic properties of the system.

In a sense, therefore, it appears that the wavefunction, with its N-electron spin-coordinates, carries too much information, overshadowing the essential features of the electron distribution.

The reader would be reinforced in this last idea, if he were to examine more closely the variational methods previously described; in doing so, he would realize that the calculations involved in minimizing the variational integral

$$\frac{\langle \varphi | H | \varphi \rangle}{\langle \varphi | \varphi \rangle}$$

where $$\langle \varphi | H | \varphi \rangle = \int \varphi^*(1,2,...N)\ H\ \varphi(1,2,...N)\ d12...N, \qquad (25)$$

carry out an N-body wavefunction φ.

However, equation 20 showed that the Hamiltonian of an N-body system is, in fact, truly made of a sum of one and two-body operators. It is clear, therefore, that there is no need for such an N-body wavefunction, which induces laborious computer calculations.

It is therefore a matter of interest to develop new methods —bypassing the Schrödinger equation— for calculating the molecular properties of a physical system.

To this end, the Density Matrix and Density Functional Theory have been developed and have proved to be very promising, although they face the tremendous theoretical problem of N-representability that we shall later encounter.

III. *Foundations of Density Matrix and Density Functional Theory.*

The purpose of Density Matrix Theory is to eradicate wavefunctions from Quantum Mechanics formalism in profit of reduced density matrices, further used with the density itself —in Density Functional Theory— to calculate any physical property of the system.

There are several known approaches to introduce the density matrix formalism.[18,19,24-38] We shall, first, essentially follow McWeeny's treatment of the subject,[18] which is by far the clearest one, to set the basis of the theory; then, a new formalism of Quantum Mechanics will be developed, based on the statistical thermodynamical notion of ensemble, in the spirit of Fano's[38], Tolman's[30] or ter Haar's[29] presentations.

To understand the foundations, and the underlying considerable interest, of Density Matrix Theory, our introductory approach will, then, be the following:

- first, from wavefunctions, we shall attach ourselves to show how to elaborate electron density functions;
- then, we shall generalize the latter to form reduced density matrices, which make the true core of the whole theory.

For each step, we shall examine both the one-electron and the many-electron case, as it is suggested by the following flowchart, which also shows the notations used throughout the rest of this work:

WF ⟹ e^- Density Functions ⟹ Reduced Density Matrices

One e^- case

$$\text{WF} \Longrightarrow \rho\,(1) \Longrightarrow \rho\,(1;1')$$

Many e^- case

$$\text{WF} \Longrightarrow \rho_1\,(1) \;\&\; \rho_2\,(1,2) \Longrightarrow \rho_1\,(1;1') \;\&\; \rho_2\,(1,2;1',2')$$

Figure 1. From Wavefunctions to Electron Density Functions and Reduced Density Matrices.

III.1. From Wavefunction to Density Functions.

III.1.1. One-Electron Case: from WF to ρ (1)

For the sake of clarity, we shall first consider a system made of a single electron in an orbital ϕ with spin $+\frac{1}{2}$.

The stationary state of such a system is then described by the wavefunction $\Psi(1) = \phi\ (r,\theta,\phi)\ \alpha\ (s)$, where the symbol (1) retains its earlier meaning of spin-space coordinate.

As previously mentioned, and even for such a simple case, there is no physical meaning to be found in the wavefunction alone, although it contains, in a very hidden way, all information we can possibly know about the system.
For example, one might be interested in measuring the position of the particle, and consequently might wonder what information the wavefunction gives about the result of such a measurement.
According to the Heisenberg's uncertainty principle, one cannot expect Ψ to involve the definite specification of position, as the state of a classical mechanical system would, and in fact, the correct answer to the above question was first provided by Born, shortly after Schrödinger discovered its wave eigenvalue equation.
Born suggested, indeed, that the physical interpretation is provided by a statistical approach to Quantum Mechanics, in which one could not predict with certainty the result of a measurement, but only the probability of various possible results. He then postulated that

$$\Psi(1)\,\Psi^{*}(1)\,d1 \qquad (26)$$

is the probability of finding the only electron of the system in the space-spin volume element d1, that is to say (in spherical coordinate system), at the tip of a vector $\vec{r}$ in a volume element $d\vec{r}$, with spin between s and s+ds.
By so, Quantum Mechanics is fundamentally statistical in nature.

In general, the wavefunction is complex, but the quantity which is experimentally observable, being the product of a complex number with its complex conjugate, is real. If one divides the probability by its volume element, one generates the so-called probability density, defined as,

$$\Psi(1)\,\Psi^{*}(1) \equiv \rho\,(1) \qquad (27)$$

Following McWeeny's nomenclature, ρ (1) bears also the name of density function.

Furthermore, if one is not interested in spin but only in where the electron may be, one can sum over all spin possibilities (i.e. integrate over spin) to get

$$P(\vec{r})\,d\vec{r} = d\vec{r}\int \rho(1)\,ds_1 = |\Psi(1)|^2\; d\vec{r} \qquad (28)$$

which is then, the probability of finding the electron in the volume element $d\vec{r}$, centered at the vector position $\vec{r}$, with any spin.

III.1.2. Many-Electron Case: from WF to ρ_1 (1) & ρ_2 (1,2)

We now generalize to the many electron case, where the stationary state is completely specified by the knowledge of its wavefunction of the form $\Psi(1,2,...N)$, which has the physical interpretation that

$$\Psi(1,2,...N)\ \Psi^*(1,2,...N)\ \ d123...N \qquad (29)$$

is the probability of simultaneously finding electron 1 in d1, electron 2 in d2, ... , electron N in dN.

The probability of finding electron 1 in d1, other electrons anywhere, is then obtained by integrating over all but one variable, as follows:

$$[\int \Psi(1,2,...N)\, \Psi^*(1,2,...N)\ \ d23...N\ ]\ d1 \qquad (30)$$

Since integration is made over dummy variables, the same expression would be valid for the electron i, where 1 would be substituted by i; that is to say, each electron has the same probability of being found in a given volume element, which is in plain accordance with the electron indistinguishability notion.

The probability of finding any electron in the volume element d1 is thus,

$$[\,N \int \Psi(1,2,...N)\, \Psi^*(1,2,...N)\ \ d23...N\ ]\ d1\ \equiv\ \rho_1\,(1)\ d1 \qquad (31)$$

where (1) refers to "point 1" at which the probability is evaluated and not to "electron 1".

By analogy to the one-electron case, ρ_1 (1) is also called the density function.

Again, if no reference to the spin of the electron, in the given volume element, is to be made, one can integrate over the spin variable, and get

$$P_1(\vec{r}_1) = \int \rho_1(1)\, ds_1 \qquad (32)$$

which is the probability per unit volume of finding any electron in $d\vec{r}_1$ at point $\vec{r}_1$, regardless of spin.

The alert reader will have recognize in $P_1(\vec{r}_1)$, the ordinary electron density function measured by X-ray crystallographers.

So far, we have seen how to generate a one-body electron density function from knowing the state wavefunction of the system. The generalization to a two-body density function, that we shall see now, is pretty straightforward.

By analogy, one may construct a "cluster" density of any number of particles. Following this logic,

$$\rho_2(1,2) \equiv N(N-1) \int \Psi(1,2,\ldots N)\, \Psi^*(1,2,\ldots N)\; d3\ldots N \qquad (33)$$

determines the probability of any two electrons being found simultaneously at points 1 and 2 (spin included), while

$$P_2(\vec{r}_1,\vec{r}_2) = \int \rho_2\,(1,2)\; ds_1\, ds_2 \qquad (34)$$

is the probability of finding them at $\vec{r}_1$ and $\vec{r}_2$ with any combination of spins (↑↑; ↓↓; ↑↓).

The physical interpretation of $P_1(\vec{r}_1)$ and $P_2(\vec{r}_1,\vec{r}_2)$ is pretty straightforward: $P_1(\vec{r}_1)$ is called the electron density (although strictly it is a probability density). As McWeeny remarks, the justification of this name lies in the fact that for purposes of calculation, the electrons may often be regarded as actually "smeared out" with a density P_1; the two-body density function $P_2(\vec{r}_1,\vec{r}_2)$, called also the pair function, gives us information on how the motions of two electrons are correlated.

After completing such an elaboration of the one and two-body density functions, we shall proceed to the generalization of density functions into reduced density matrices. The interest of the latter, which are nevertheless more abstract objects than the former, laies in their essential ability to extremely simplify Quantum Mechanics formalism, and by there, to allow the essential beauty of this theory, as we shall soon discover.

III.2. From Wavefunction to Reduced Density Matrices.

III.2.1. One-Electron Case: from WF to ρ (1;1')

As before, the only electron of the system is considered to be in the spin-orbital $\Psi(1)$ to which is associated the fundamental physical interpretation that

$$\Psi(1)\,\Psi^*(1) \equiv \rho\,(1) \tag{27}$$

is the probability density per unit volume.

To see the interest in generalizing ρ (1), we are now examining the calculation of the expectation value of an operator **O**, in the state $\Psi(1)$, defined as

$$<\mathbf{O}> \equiv <\Psi|\mathbf{O}|\Psi> \equiv \int \Psi^*(1)\,\mathbf{O}\,\Psi(1)\,d1 \tag{35}$$

Only two different cases are encountered while calculating such an expectation value:

1. If **O** is a mere multiplier (for example some function of coordinates), then

$$\begin{aligned} <\mathbf{O}> &\equiv \int \mathbf{O}\,\Psi^*(1)\,\Psi(1)\,d1 \\ &\equiv \int \mathbf{O}\,\rho\,(1)\,d1 \end{aligned} \tag{36}$$

The interest of such a formulation is to write the expectation value of an operator as a function of the electron density, so that $< \mathbf{O} >$ is then obtained by simply averaging $\mathbf{O}(1)$ over the electron density $\rho\,(1)$.

2. If $\mathbf{O}$ is an operator involving differentiation or integration, then it is, of course, not possible to use the same formulation and the rules for evaluating the expectation value of such an operator are then the following:

$*$ {1. Apply $\mathbf{O}$ on $\Psi(1)$};

$*$ {2. × by $\Psi^*(1)$};

$*$ {3. Integrate}.

However, it appears that $\mathbf{O}$ works on $\Psi(1)$ **only**, and, in order to express everything in terms of the fundamental density function, one may then use an artifice of calculation: first, change the variable name in Ψ^* from 1 to 1' to prevent $\mathbf{O}$ from operating on $\Psi^*(1)$, and then permute the terms in the integral as follows:

$$\begin{aligned} <\mathbf{O}> &\equiv \int \Psi^*(1)\,\mathbf{O}\,\Psi(1)\,d1 \\ &\equiv \int [\,\mathbf{O}\,\Psi(1)\,\Psi^*(1')\,]_{1'\to 1}\ d1 \\ &\equiv \int [\,\mathbf{O}\,\rho\,(1;1')\,]_{1'\to 1}\ d1 \end{aligned} \qquad (37)$$

In doing so, one has then defined a function which is exactly the same as the previous density function, except for a prime in the complex conjugate wavefunction, i.e.

$$\rho\,(1;1') \equiv \Psi(1)\,\Psi^*(1') \qquad (38)$$

which is called the reduced density matrix.

The rules for calculating the expectation value in such a formulation of equation 37 are then,

$$\langle \mathbf{O} \rangle \equiv \int [\, \mathbf{O}\ \rho\ (1;1')\,]_{1'\to 1}\ d1 \qquad (37)$$

- {1. Operate **O** on $\Psi(1)$};
- {2. Set 1'=1 in $\Psi^{*}(1')$};
- {3. Integrate}.

Again, if one is not interested in getting any information about the spin of the electron, the spinless density matrix is used and defined as

$$P(\vec{r}_1, \vec{r}_1{}') = \int \rho\ (1;1')\ ds_1\ ds_1{}' \qquad (39)$$

The reduced density matrix is a more abstract object than the density function for the simple reason that, unlike $P(\vec{r}_1)$, $P(\vec{r}_1, \vec{r}_1{}')$ has no direct physical interpretation. Its physical meaning is actually provided by setting 1'=1, where

$$[\, P(\vec{r}_1, \vec{r}_1{}')\,]_{1'\to 1} \equiv P(\vec{r}_1, \vec{r}_1) \equiv P(\vec{r}_1) \qquad (40)$$

The reader may now better understand the appearance of the term "matrix" to characterize $\rho\ (1;1')$, which seems somewhat unfortunate since $\rho\ (1;1')$ or its spinless equivalent is no matrix at all.

It arises because $\rho\ (1;1')$ is analogous to an off-diagonal matrix element in which the discrete indices have been replaced by continuous variables 1 and 1'; $\rho\ (1)$ would then be considered as the equivalent to a diagonal matrix element.

Finally, the same artifice may be used in the many-electron case to generate reduced density matrices.

III.2.2. Many-Electron Case: from WF to $\rho_1\ (1;1')$ & $\rho_2\ (1,2;1',2')$

From the N-body wavefunction characterizing the many-electron system under interest, we defined earlier one and two-body density functions, symbolized respectively by $\rho_1(1)$ and $\rho_2(1,2)$.

By analogy to the one-electron case, we may now generalize these functions into one and two-body reduced density matrices, as follows:

$$\begin{aligned} \rho_1\ (1;1') &\equiv N \int \Psi(1,2,\ldots N)\ \Psi^*(1',2,\ldots N)\ d2\ldots N \\ \rho_2\ (1,2;1',2') &\equiv N(N-1) \int \Psi(1,2,\ldots N)\ \Psi^*(1',2',3,\ldots N)\ d3\ldots N \end{aligned} \tag{41}$$

where we carefully put necessary primes in Ψ^*.

Now that the general definitions of the mathematical objects essential to the density matrix theory are defined, it would be perfectly legitimate for the reader to wonder why scientists have been bothering so much, for a few decades, with elaborating such a whole new theory, in which primes were merely set to places where they were not before. To answering this question, we shall devote ourselves in the coming section.

III.3. Elaboration of a New Quantum Mechanics Formalism.

III.3.1. Exact Description of the Ensemble State.

The reduced density matrices $\rho_1(1;1')$ and $\rho_2(1,2;1',2')$, defined by equation 41, are the essential mathematical objects on which a new formulation of Quantum Mechanics will be elaborated. That is to say, Density Matrix Theory provides a new formalism in which the previous leading role of wavefunction is taken over in favor of density matrices.

However, for the sake of obtaining the most global picture of this theory —in the hope of grasping essential concepts and not merely notation artifices— it is important to realize that $\rho_1(1;1')$ and $\rho_2(1,2;1',2')$ are only one way of expressing density operators, which, as we shall soon understand, make actually the true core of the theory.

Indeed, $\rho_1(1;1')$ and $\rho_2(1,2;1',2')$ are, in fact, the representatives of the density operator in the continuous Schrödinger's language. Following the same spirit as in section I.1. of this chapter, we shall, therefore, try to develop the Density Matrix formalism in any of the three previously mentioned representations. However, only highlights of this formalism will be given here; for a more complete description in the three representations, the reader is referred to appendix A.

In the Hilbert space formulation of Density Matrix Theory, instead of representing the physical states Ψ_k by Dirac's ket vectors $|\Psi_k\rangle$, one represents them by the density operator—also called projection operator— given by[19,29,30,38]

$$\hat{\rho}^{kk} \equiv \frac{|\Psi_k\rangle\langle\Psi_k|}{\langle\Psi_k|\Psi_k\rangle} \tag{42}$$

where the denominator is set to 1 for normalized Ψ_k's. In this case, the system is said to be in the pure state k.

Now suppose that the system may be found, not in only one, but in several different states Ψ_a, Ψ_b ... Ψ_k; then, two possibilities could occur, depending on the extent of our knowledge of the system:

- 1. On one hand, we may have only an incomplete knowledge of the dynamical system, where only the probabilities of finding the system in the states Ψ_a, Ψ_b ... Ψ_k are known to be w_a, w_b, ... w_k.

This situation is described by the notion —borrowed from Statistical Thermodynamics[19,29,30] — of ensemble of identical systems of which a fraction w_k are definitely in state k. The system is then said to be a mixed ensemble, and its state is described by the density operator,

$$\hat{\rho} \equiv \sum_k w_k \hat{\rho}^{kk} \equiv \sum_k w_k |\Psi_k\rangle\langle\Psi_k| \tag{43}$$

where, because of their definition of being statistical ensemble weights, w_k are subject to two constraints, namely

$$0 \leq w_k \leq 1, \text{ and } \quad \sum_k w_k = 1 \tag{44}$$

This being done, one has then constructed a tool to describe the system, tool on which the original formulation of Quantum Mechanics may be extended to admit incompletely specified states and ensemble averaging. We shall not, though, more develop this aspect of Density Matrix Theory, for only the other possibility in the extent of the knowledge of the system will be more investigated in our research.

- 2. On the other hand, we may have a complete knowledge of the ensemble —i.e. $w_i = \delta_{ki}$ — and the system, called pure ensemble, being found in its k^{th} state, is then described by $\hat{\rho}^{kk}$ as in equation 42.

It is also useful to consider ensembles in which the states Ψ_k are one-particle energy eigenstates, written, following our previous definitions, Φ_k. For example, if one is to consider an N-electron system, the state of such a system is stationary when the N electrons occupy N of the one-particle eigenstates. The state is then described by the density operator in the one-particle Hilbert space,[19] as

$$\hat{\rho} \equiv \sum_{k=1}^{N} \hat{\rho}^{kk} \equiv \sum_{k=1}^{N} |\Phi_k\rangle\langle\Phi_k| \qquad (45)$$

It should be noted that this density operator describes the state in the one-particle Hilbert space, whereas its corresponding operator in the N-particle Hilbert space is given by

$$\hat{\rho}\,' \equiv |\Psi\rangle\langle\Psi| \qquad (46)$$

where $|\Psi\rangle$ symbolizes the N-particle state vector.

As already mentioned, the analog to $\hat{\rho}$ in the Schrödinger's continuous representation is the kernel of the integral operator, previously called density matrix, and noted $\rho_1(1;1')$:

$$\hat{\rho} \equiv \sum_{k=1}^{N} |\Phi_k\rangle\langle\Phi_k| \quad \text{<-->} \quad \rho_1(1,1') \equiv \sum_{k=1}^{N} \Phi_k(1)\,\Phi_k{}^*(1') \qquad (47)$$

the two representations being linked together by

$$\langle 1 | \Phi_k \rangle \langle \Phi_k | 1' \rangle = \Phi_k(1)\,\Phi_k{}^*(1')$$

(48)

and

$$\hat{\rho}\,\chi(1) = \int \rho_1(1;1')\,\chi(1')\;d1'$$

In such a formulation then, the time dependent Schrödinger equation takes the form of the Quantum Mechanical analog to the classical Poisson's formula, describing the time evolution of the density operator as

$$i\hbar \frac{d\hat{\rho}}{dt} = [\mathbf{H}, \hat{\rho}] \qquad (49)$$

Stationary states (equivalent to $\frac{d\hat{\rho}}{dt} = 0$) can then occur if and only if $\hat{\rho}$ and $\mathbf{H}$ commute. In such a case, they have a common complete set of eigenfunctions, as expressed by

$$\begin{cases} \mathbf{H}\,(1)\ \Phi_k(1) = \varepsilon_k\ \Phi_k(1) \\ \hat{\rho}\,(1)\ \Phi_k(1) = \Phi_k(1) \end{cases} \qquad (50)$$

Again, in a general way, the eigenfunctions solution to these equations can be exactly written in a basis $\{\psi_j(1)\}$ of infinite dimensions, as:

$$\Phi_k(1) = \sum_j c_{kj}\ \psi_j(1) \qquad (15)$$

III.3.2. Approximate Description of the Pure Ensemble State.

Since only finite dimensional basis may be used in practice, the last equation is to be truncated to describe $\Phi_k(1)$ in a basis of, say, M dimensions.

The one-particle density operator $\hat{\rho}$ may, as well, be represented in any of the three languages by (please, refer to appendix A for ampler precisions),

$$\hat{\rho} \equiv \sum_{k=1}^{N} |\Phi_k\rangle\langle\Phi_k| \;\; <\!\!-\!\!-\!\!> \;\; \rho_1(1;1') \equiv \sum_{k=1}^{N} \Phi_k(1)\,\Phi_k{}^*(1') \;\; <\!\!-\!\!-\!\!> \;\; \underset{\sim}{\rho} \equiv (\rho_{ij}) \qquad (51)$$

and substituting for the expression of Φ_k in the $\{\psi_j(1)\}$ basis, one obtains

$$\hat{\rho} = \sum_{i\,j=1}^{M} \rho_{ij}\, |\psi_i\rangle\langle\psi_j| \longleftrightarrow \rho_1(1;1') = \sum_{i\,j=1}^{M} \rho_{ij}\, \psi_j(1)\, \psi_i^*(1') \longleftrightarrow \underset{\sim}{\rho} = (\rho_{ij}) \quad (52)$$

where
$$\rho_{ij} = \sum_{k=1}^{N} c_{ki}^{\,*}\, c_{kj} \quad (53)$$

and therefore,
$$\underset{\sim}{\rho} = \underset{\sim}{C}^{+}\, \underset{\sim}{C} = \underset{\sim}{P} \quad (54)$$

where $\underset{\sim}{C}$ is the (N×M) matrix defined in equation 19, whereas $\underset{\sim}{P}$ is an (M×M) matrix, usually called population matrix.

Finally, the last expression of $\rho_1(1;1')$ allows one to link the function representation to the matrix one in the Density Matrix Theory in an expression that we shall later on make good use of:

$$\rho_1(1;1') = \mathrm{Tr}\ \underset{\sim}{P}\ \underset{\sim}{\psi}(1)\ \underset{\sim}{\psi}^{+}(1') \quad (55)$$

III.4. The Electron Density $\rho(1)$ as a Fundamental Quantity.

III.4.1. The Hohenberg & Kohn Theorem.

At the heart of Density Matrix Theory formalism, lay the reduced density matrices, and ultimately, the electron density. The particular importance of such an observation, which may now somewhat sound trivial, becomes clearer when one realizes the true fundamental importance of the electron density: this is, indeed, the electronic structure of the microscopic system which determines all electronic properties of the system.[24,39-41] This instinctive notion has been made rigorous by the fundamental theory of Hohenberg and Kohn,[42] from now on referred to as HK theorem, which set the basis of Density Functional Theory.[42-46]

According to the HK theorem, the electron density may be viewed as the basic carrier of all information concerning the electronic state of a physical system, which may be sketched as follows:

$$\rho \Longrightarrow V[\rho] \Longrightarrow H[\rho] \Longrightarrow \Psi[\rho] \Longrightarrow O[\rho] \qquad (56)$$

that is to say, the density fixes the external potential, the Hamiltonian operator, the wavefunction of the ground state and any arbitrary operator expectation value.

This theorem is therefore of crucial importance since it asserts that all electronic properties of the system are functionals of the electron density.

However, although it proves it is theoretically possible to recover any electronic property from the electron density, this theorem does not clarify one simple thing: it lacks to tell us how to do so in practice. Particularly, the total energy of the system is still an unknown functional of the density, and this unsolved problem is one of the most important in present day Quantum Mechanics research, as testifies the voluminous relevant literature (see for example references 42 to 46 for a brief list of some fundamental papers; this list is of course far from being exhaustive. Influencing books in this field are given in references 106 and 107). Later in this work, we shall suggest a way to calculate, in practice, an accurate approximation of this unknown HK functional.

In theory, it is however possible to calculate any expectation values and this is provided by the very Density Functional Theory. The reader might be glad to know, at this point, that the efforts he made earlier in understanding the foundations of Density Matrix Theory will be now rewarding, for we shall make a good use of such a background in elucidating the way to calculate any electronic property from two simple mathematical objects: the one and two-body reduced density matrices.

III.4.2. The Density Matrix and Density Functional Theory.

It is a fact in Quantum Mechanics that, to any physical observable corresponds either a one-electron or a two-electron operator, respectively written $\mathbf{O}$ (1) and $\mathbf{O}$ (1,2).[18]

Furthermore, as seen earlier, the expectation value of any of these two operators may be calculated from, respectively, $\rho_1(1;1')$ and $\rho_2(1,2;1',2')$, the one and two-body reduced density matrices, according to

$$
\begin{aligned}
<O(1)> &\equiv \int \Psi^*(12...N)\, O(1)\, \Psi(12...N)\, d1 \equiv \int [\, O(1)\, \rho_1(1;1')\,]_{1'\to 1} d1 \\
<O(1,2)> &\equiv \int \Psi^*(12...N)\, O(1,2)\, \Psi(12...N)\, d1d2 \\
&\equiv \int [\, O(1,2)\, \rho_2(1,2;1',2')\,]_{1'\to 1;\, 2'\to 2}\, d1d2
\end{aligned}
\tag{57}
$$

where the method for proceeding is the same as the one given in equation (37).

As a partial conclusion, one might say that it is clear now that if one could dream of a way to determine the two reduced density matrices of primordial importance, one would have a tool with Density Matrix Theory, to calculate any expectation value, that is to say any physical property of the system, without having to solve the Schrödinger equation. This is in this idea of bypassing the Schrödinger equation, for which no exact solution is to be found for a system of two or more particles, that the paramount interest of Density Matrix Theory lies. If, moreover, one could find a way to relate the determination of density matrices to the density itself, one would then link the Density Matrix theory to the Density Functional theory.

To have a complete picture of the whole theory, the reader now realizes that only one question remains unanswered so far, which is:

how do we get $\rho_1(1;1')$ and $\rho_2(1,2;1',2')$?

The answer to this apparently simple question will show, in the next section, how this theory faces the tremendous theoretical problem of N-representability, which is one of the most important intellectual challenge in the development of this new Quantum Mechanics formalism.

III.4.3. The Quest of N-Representability Conditions.

Direct evaluation methods of the first and the second-order reduced density matrices are not fully possible, for they are challenged by the problem of N-representability, which has had a long history in the literature of Quantum Mechanics.[19,23,34,37]

As seen before, expectation values may be calculated, using the Density Functional formalism, from $\rho_1(1;1')$ and $\rho_2(1,2;1',2')$. However, physically meaningful results will be obtained, only if the density matrices are quantum mechanically valid; that is to say, only if they are related to some proper antisymmetric N-body wavefunction, according to

$$\begin{aligned}\rho_1(1;1') &\equiv N\int \Psi(1,2,\ldots N)\,\Psi^*(1',2,\ldots N)\ d2\ldots N\\ \rho_2(1,2;1',2') &\equiv N(N-1)\int \Psi(1,2,\ldots N)\,\Psi^*(1',2',3,\ldots N)\ d3\ldots N\end{aligned} \tag{41}$$

In such a case then, the density matrices are obtainable by square-integrating the antisymmetric N-body wavefunction $\Psi(1,2,...N)$, and by so, inherit the name of being N-representable.

The very problem of N-representability is, therefore, the problem of finding intrinsic criteria by which to recognize when a density matrix can be related to such a wavefunction. Then, and only then, first and second-order reduced density matrices will deliver quantum mechanically meaningful expectation values.

A clear picture account was provided by Massa,[47] who sketched the essence of the mapping problem associated with N-body wavefunction representability of density matrices by the following figure:

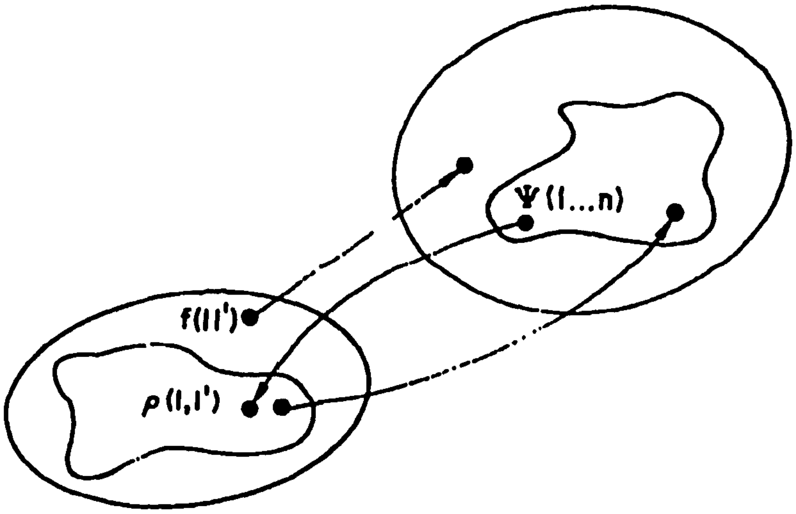


Figure 2. Mapping Problem Associated with Wavefunction N-Representability of Density Matrices.

First, consider the set of all antisymmetric well-behaved N-body wavefunctions $\{\Psi(1,2,...N)\}$.

From this set, determine the set of all valid first-order reduced density matrices by using the fundamental definition of $\rho_1(1;1')$ as mentioned in equation 41, that is to say, by integrating the product of the N-body wavefunction with its complex conjugate over all spin-space coordinate but the spatial coordinates of one particle. Now, we have then constructed the set of all N-representable first-order reduced density matrices.

However, if we consider the set of all one-body functions f(1;1'), this set is larger than that of $\rho_1(1;1')$.[48,49] Hence, if we consider a given one-body function, two possibilities arise in terms of where to find it in this diagram: either it falls inside the set of all N-representable one-body functions, or it falls outside. The former case is what we shall like, for in the latter case it will be impossible to map f(1;1') back to any N-body wavefunction, and thus, to associate any quantum mechanical meaning to the one-body function.

Fortunately enough for the future of Density Matrix Theory, the necessary and sufficient conditions for N-representability of $\rho_1(1;1')$ are known.[19,23,34,37] However, one can't claim the same of $\rho_2(1,2;1',2')$, and for more than twenty years now, quantum scientists have been engaged in the "unbearable" quest of N-representability conditions of the second-order reduced density matrix.

The necessary and sufficient conditions of N-representability of a pure state — described by a density operator in accordance with equations 45 and 47— are, thus, known. Different conventions exist and, in this work, we shall always follow McWeeny's way of expressing the N-representability conditions.[19] Their expression in the three most commonly used representations are the following (see appendix A): a density matrix is N-representable if and only if

$$\begin{array}{llllll} \textbf{1.} & \hat{\rho}^{2}=\hat{\rho} & \longleftrightarrow & \underset{\sim}{P}^{2}=\underset{\sim}{P} & \longleftrightarrow & \int \rho_1(1;1'')\,\rho_1(1'';1')\,d1''=\rho_1(1;1') \\ \textbf{2.} & \hat{\rho}^{+}=\hat{\rho} & \longleftrightarrow & \underset{\sim}{P}^{+}=\underset{\sim}{P} & \longleftrightarrow & \rho_1(1;1')^{*}=\rho_1(1;1') \\ \textbf{3.} & <\hat{\rho}>=\sum_{k=1}^{N}1=N & \longleftrightarrow & \mathrm{Tr}\,\underset{\sim}{P}=N & \longleftrightarrow & \int \rho_1(1;1'')\,d1'=N \end{array} \qquad (58)$$

1. The first condition is equivalent to requiring the density operator to be idempotent. In this case, the operator also bears the name of projector or projection operator, in the sense that if one operates $\hat{\rho}^{kk}$ onto any ket-vector $|\chi>$ of the Hilbert space, one will get the component of this vector along $|\Phi_k>$, according to

$$\begin{aligned} \hat{\rho}^{kk}\,|\chi> &= (|\Phi_k><\Phi_k|)\,|\chi> \\ &= <\Phi_k|\chi>\,|\Phi_k> \end{aligned} \qquad (59)$$

where $<\Phi_k|\chi>$ is the magnitude of the projected vector along $|\Phi_k>$.

This condition ensures, then, the ensemble state to be a pure ensemble state, in the sense of section **III.3.1.**

2. The second condition, by requiring the hermiticity character of the operator, ensures the eigenvalues —i.e. the measurements of any physical property— to be real.

3. Finally, the last constraint ensures the system to be properly normalized to N electrons.

These three conditions, leading to the search of a normalized, hermitian projector, will not only guarantee N-representability of the density matrix, but also imply that the wavefunction, from which it is derived, is a single Slater determinant, a property that we shall deeply investigate later on.

Since necessary and sufficient conditions of N-representability of $\rho_2(1,2;1',2')$ are still unknown, no direct evaluation of a quantum mechanically meaningful second-order reduced density matrix is possible.

It is therefore of tremendous interest to find other ways, if not mathematical, to generate N-representable second-order reduced density matrix. To this end is this research devoted, and it will be shown how to obtain such reduced density matrices from experimental data of X-ray Crystallography.

III.5. Calculation of N-Representable X-ray Density Matrices.

The physical interpretation of the spinless first-order reduced density matrix is provided, according to section III.2.1., by the diagonal element

$$P_1(\vec{r}_1) \equiv P_1(\vec{r}_1, \vec{r}_1) \equiv [P_1(\vec{r}_1, \vec{r}_1')]_{\vec{r}_1' \to \vec{r}_1} \qquad (60)$$

where $P_1(\vec{r_1}, \vec{r_1}')$ is obtained by the usual integration of $\rho_1(1;1')$ over the spin —equation 39— and $\vec{r_1}$ retains its previous meaning of symbolizing the vector-position of any single electron. Indeed, $P_1(\vec{r_1})$ is the regular electron density representing the amplitude of probability of finding one electron at the position $\vec{r_1}$.

III.5.1. Experimental Considerations.

From the experimental point of view, the electron density, for now on written $P(\vec{r})$, may be recovered from the X-ray diffraction experiment, which delivers a set of structure factors $F(\vec{k})$, Fourier transformed of the density.[39]

Indeed, since their wavelengths are comparable to the spacing of atoms in crystals (~ 1 Å), X-rays are diffracted by crystal lattices. The classic coherent X-ray experiment consists, then, in measuring, at discrete value of the scattering vector $\vec{k}$, the intensity $I(\vec{k})$ of the scattered wave. This latter is the square of the wave amplitude, and by so, is given by

$$I(\vec{k}) = |F(\vec{k})|^2 \qquad (61)$$

The value of $F(\vec{k})$ depends on the atoms present in the unit cell and their locations. The structure factors are, therefore, essential data which contain all informations about the structure of the unit cell and provide a way of drawing up a described picture of the location of the atoms in the crystal.

It is important to realize that the experimental intensities differ from the ideal ones by a number of small but significant effects such as polarization, extinction, absorption and truncation.[50] In particular, not the least important of all is the temperature effect associated with the thermal motion of the atomic nuclei, motion which will smear the static electron distribution in a time average manner. However, we shall assume for the rest of this work, that all this experimental effects can be adequately treated so as to arrive at a set of structure factors within small magnitude errors, which would deliver the electron density characteristic of the unit cell.[51]

III.5.2. Theoretical Considerations.

From the theoretical point of view, the Crystallography experiment may be thought of as the sequence sketched by Massa et al.:[47]

$$\{\Phi\} \Rightarrow P(\vec{r}) \Rightarrow F(\vec{k}) \tag{62}$$

where $\{\Phi\}$ is a set of orbitals characteristic of the crystal, which give rise to the electron density $P(\vec{r})$, the source of X-ray scattering which results in measured structure factors $F(\vec{k})$.

Importantly, the above sequence may be reversed:

$$F(\vec{k}) \Rightarrow P(\vec{r}) \Rightarrow \{\Phi\} \tag{63}$$

i.e. given the set of measured structure factors, it is possible to recover the electron density and the companion orbitals, provided that the Crystallography experiment is described within the formalism of Quantum Mechanics.

1. $F(\vec{k}) \Rightarrow P(\vec{r})$:

Choosing a suitable model for $P(\vec{r})$, one can use structure factors to determine the electron density of the crystal, according to the fundamental relationship,

$$F(\vec{k}) = \int P(\vec{r})\ e^{i\vec{k}.\vec{r}}\ d\vec{r} \tag{64}$$

$F(\vec{k})$ and $P(\vec{r})$, as Fourier transforms of one another, are information equivalents.

By recovering $P(\vec{r})$, Crystallography helps to elucidate, not only the structure of crystals, but also its electronic properties. Indeed, as mentioned earlier, the HK theorem[42] asserts that the electron density carries all information concerning the electronic state, and Crystallography provides an experimental image of the electron density.

2. $F(\vec{k}) \Rightarrow P(\vec{r}) \Rightarrow \{\Phi\}$:

The connection between Crystallography and Quantum Mechanics is achieved by ensuring the scattering factors come from an electron density that is consistent with the restrictions of Quantum Mechanics.

With this in mind, it has been suggested by several people, including McWeeny,[52,53] Kurki-Suonio[54] and Stewart,[55] to recover from the experimental crystallographic data , a density with an explicit connection to a set of Quantum Mechanics molecule (or crystal) orbitals. The ultimate goal of such an approach is to provide a more realistic model of the electron density.

Indeed, the traditional approach, which has served Crystallography well, is to express the electron density as a sum of isolated, spherical atoms. However, a more realistic model should describe the bonding that occurs upon formation of the crystal.[24] To obtain information about these non-spherical features of the molecular density, Stewart introduced an LCAO-type formalism for interpreting the X-ray scattering. A set of spatial molecular orbitals $\phi_k(1)$ is described in a monoelectronic atomic basis $\{\psi j(1)\}$ according to

$$(\forall\ k= 1,\ldots,N)\quad |\phi_k> = \sum_j c_{kj}\,|\psi_j> \quad <\!\!-\!\!\!-\!\!> \quad \underset{\sim}{\phi}(1) = \underset{\sim}{C}\ \underset{\sim}{\psi}(1) \qquad (65)$$

where c_{kj} are the usual LCAO coefficients. For an even number of electrons described by N doubly occupied orbitals, the density —according to the Density Matrix formalism previously described— may then be written as

$$P(\vec{r}) \equiv 2\sum_{k=1}^{N} \Phi_k(\vec{r})\,\Phi_k{}^*(\vec{r}) \equiv 2\ \mathrm{Tr}\ \underset{\sim}{P}\ \underset{\sim}{\psi}(\vec{r})\,\underset{\sim}{\psi}^{+}(\vec{r}) \qquad (66)$$

or in its Fourier-equivalent relationship

$$F(\vec{k}) \equiv 2\,\mathrm{Tr}\ \underset{\sim}{P}\ \underset{\sim}{f}(\vec{k}) \qquad (67)$$

where the matrix $\underset{\sim}{f}(\vec{k})$ contains as elements Fourier transforms of basis orbital products, i.e.

$$f_{ij}(\vec{k}) \equiv \int \psi_i(\vec{r})\, \psi_j^*(\vec{r})\; e^{\,i\vec{k}.\vec{r}}\, d\vec{r} \qquad (68)$$

The matrix elements of $\underset{\sim}{P}$ defined above, are treated as least-squares parameters adjusted to fit experimental X-ray structure factors.

However, a simple fit to experimental data will generally lead to a density matrix which is Crystallographically consistent, but Quantum Mechanically inconsistent.[47] This is actually the very problem of N-representability previously described, which is less well-known in this context of Crystallography. That is to say, simple fits to experimental data do not allow one to recover an N-representable density. On the contrary, these restrictions of Quantum Mechanics must be additionally imposed to the fitting procedures. This is only by doing so that Quantum Mechanically valid expectations values will be ultimately recovered from the Density Matrix and Density Functional Theory.

The reader may now plainly evaluate the importance of the contribution, to this field, of Clinton and Massa, who first solved this problem.[56] They suggested to constrain the $\underset{\sim}{P}$ matrix, solution to the best least-squares fitting to experimental data, to be a normalized, hermitian projector (according to equation 58). This is realized by solving the following iterative equation

$$\underset{\sim}{P}_{n+1} = 3\,\underset{\sim}{P}_n^{\;2} - 2\,\underset{\sim}{P}_n^{\;3} + \lambda_k\,\underset{\sim}{f}(\vec{k}) + \lambda_N\,\underset{\sim}{I} \qquad (69)$$

where the first two terms on the right-hand side ensures the purification of an hermitian, near idempotent matrix into an idempotent one —following McWeeny's formalism[19] — and the remaining imposes X-ray data fitting and normalization constraints by the method of the Lagrangian undetermined multipliers.

Such a formalism not only guarantees N-representability of the first-order reduced density matrix but also, implies that the wavefunction from which it is derived is a single Slater determinant. This is the one case in which knowledge of $P_1 (\vec{r}_1, \vec{r}_1')$ is sufficient to determine the full N-body wavefunction and therefore any property of the system. An important literature develops all the details of this method.[47,50,51,56-65]

III.5.3. Partial Conclusion.

Although a single Slater determinant describes an N-body wavefunction where there is no correlation of the particles except that imposed by the antisymmetry, Gilbert[66] and Harriman[67] have shown that there are determinants which nonetheless can describe exactly a given electron density.

In practice, one obtains this single Slater determinant by describing the Crystallography experiment within the context of Quantum Mechanics. To this end, describe the electron density according to the Density Matrix Theory, and best fit the $\underset{\sim}{P}$ matrix elements to X-ray diffraction data, while constraining the solution $\underset{\sim}{P}$ to be a normalized, hermitian projection matrix, as described by the following set of equations:

$$P(\vec{r},\vec{r}') \equiv 2 \ \mathrm{Tr} \ \underset{\sim}{P} \ \underset{\sim}{\psi}(\vec{r}) \ \underset{\sim}{\psi}^{+}(\vec{r}') \tag{70}$$

where
$$\underset{\sim}{P}^{2} = \underset{\sim}{P} \ ; \quad \underset{\sim}{P}^{+} = \underset{\sim}{P} \ ; \quad \mathrm{Tr} \ \underset{\sim}{P} = N \tag{71}$$

These equations are solvable and yield a first-order reduced density matrix N-representable by a single Slater determinant, as

$$\rho_1(1;1') \equiv N \int \Psi_{det}(1,2,...N) \ \Psi_{det}^{*}(1',2,...N) \ d2...N \tag{72}$$

where
$$\Psi_{det}(1,2,...N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \Phi_1(1) & \ldots & \Phi_N(1) \\ \vdots & \vdots & \vdots \\ \Phi_1(N) & \ldots & \Phi_N(N) \end{vmatrix}$$

This solution is, then, used to calculate any higher-order reduced density matrix. The true interest in this method lies in the Quantum Mechanical validity of these density matrices. Indeed, although necessary and sufficient conditions of N-representability are not known for second and higher-order reduced density matrices (which consequently voids any hope of their direct evaluation), any of these density matrices obtained from an N-representable one are also N-representable.

Being Quantum Mechanically meaningful, they are ultimately used within the formalism of Density Matrix and Density Functional Theory to calculate any property of the system regardless of the number of particles involved in the interaction.

The true interest of this method, however, critically depends on the uniqueness, for a given system, of the N-body single Slater determinant so obtained. The uniqueness of this formalism implies the uniqueness of the physical properties later on calculated, and therefore their intrinsic values.

Massa et al. have been aware of the potential problem of a non-unique solution since the early days of the development of this formalism, when they wrote "the single Slater determinant obtained by our procedure may not be unique (...), although we have had no difficulty with multiple solutions"[68]. Since then, Harriman[49] and Levy et al.[69] have studied this question, but no definitive answer, based on a clear argument, has been found until now.

It is our hope, therefore, that the reader will agree with us it is quite a matter of interest to start our deeper investigation of the formalism by first answering the uniqueness question.

Chapter II

Uniqueness of the X-ray Single Slater Determinant

To recover a single Slater determinant from X-ray diffraction data, one has, first, to calculate the $\underset{\sim}{P}$ matrix, representative of the projection (or density) operator in the matrix language. To do so, one has to impose a certain number of experimental conditions of the type of equation 70, over and above the constraints of N-representability, described by equation 71. Such a number is, in fact by definition equal to the number of independent parameters in the $\underset{\sim}{P}$ matrix, and will be, from now on, referred to as the letter K.

A general formula of K was first published in the literature —to the extent of our knowledge— by Clinton and Massa, in 1969.[68] Interestingly enough, since then, several papers have been published on K, claiming results apparently contradictory.[69,70] Because the use of the adequate number of experimental conditions is crucial to the validity of this method, it is of considerable interest to further investigate this problem in the hope of elucidating the apparent contradictions. Our goal will be so, in the coming section.

I. *Number of Independent Parameters in the P Matrix.*

I.1. Projection Concept in X-ray Density Matrix Formalism.

Our goal here is to more deeply understand the concept of projection in a complex separable Hilbert space $\mathfrak{H}$, in the context of Crystallography, based on our previous introductory chapter. For a mathematical study of the projection properties, the reader is referred to references 14, 15, 17 as well as 71 to 89; particularly, we would like to point out the outstanding book recently written by Istratescu[17] on the fundamental inner product structures, which should answer any conceptual question on the subject, and, as so, may be an endless source of inspiration for theoretical scientists for many years. A more applied description of the projection in the context of Quantum Mechanics may be found in references 3, 7, 8, 9, 12 and 13.

Now, suppose one wants to describe in the Hilbert space $\mathfrak{H}$, a system being in the stationary state which is made of N occupied eigenstates Φ_k, described by the ket vectors $|\Phi_k>$'s.

Then, one has to choose a basis spanning the space $\mathfrak{H}$, with, of course, a cardinality equal to the number of dimensions of $\mathfrak{H}$, say M, and to describe the Φ_k's as

$$\forall\, k = 1...N, \qquad |\Phi_k> = \sum_{j=1}^{M} c_{kj}\, |\Psi_j> \tag{73}$$

In the "old" formalism of Quantum Mechanics, one would have, then, to find the set of c_{kj} coefficients in order to completely describe the state of the system. In Density Matrix Theory, however, one tries to recover the projection operator

$$\hat{\rho} \equiv \sum_{k=1}^{N} |\Phi_k\rangle\langle\Phi_k| \tag{74}$$

or any of its equivalent representation.

This is actually our goal in the formalism developed in this work, where the set of data provided by the X-ray diffraction experiment is properly used to generate $\underset{\sim}{P}$, the matrix representative of $\hat{\rho}$.

The concept of projection may be, then, better understood, with the following argument: in a general way, if $\mathfrak{H}$ is defined as the complex separable Hilbert space of M dimensions, spanned by the $\{|\psi_j\rangle\}$ basis, one may realize its hermitian decomposition into a family $(\hat{\rho}_a$, where $a \in \mathfrak{I})$ of hermitian projectors having the property of being orthogonal to each others —i.e. $\hat{\rho}_a \cdot \hat{\rho}_b = 0, \ \forall\, a \neq b$. The extent of the splitting following $(\hat{\rho}_a, a \in \mathfrak{I})$, is the smallest closed linear subspace containing all $\hat{\rho}_a \mathfrak{H}$.[17]

Particularly, one may reduce this decomposition of the space $\mathfrak{H}$ into only two subspaces: $\mathfrak{S}$ and $\mathfrak{S}^{\perp}$, two closed linear subspaces chosen so that

$$\mathfrak{S} \cap \mathfrak{S}^{\perp} = \{0\}, \text{and} \quad \mathfrak{H} = \mathfrak{S} \oplus \mathfrak{S}^{\perp} = \{\, s + s' : s \in \mathfrak{S}\, , s' \in \mathfrak{S}^{\perp}\}$$

where $\mathfrak{S}^{\perp}$ is called the orthogonal complement of $\mathfrak{S}$. Doing so, one has then realized the so-called orthogonal decomposition of $\mathfrak{H}$.

It may then be shown[17] that to each of these subspaces is associated a projector, and there is a one-to-one correspondence between projections and closed subspaces of $\mathfrak{H}$. As a consequence, let $\hat{\rho}$ be the projection operator onto the subspace $\mathfrak{S}$, and $\underset{\sim}{P}$ its matrix representative. Then, $(\underset{\sim}{1} - \underset{\sim}{P})$ projects on $\mathfrak{S}^{\perp}$, and the reader may easily verify that it is true that

$$\underset{\sim}{P}\,(\underset{\sim}{1} - \underset{\sim}{P}) = 0 \tag{75}$$

In the context of Quantum Mechanics, the subspace $\mathfrak{S}$ is considered to be spanned by the N occupied eigenstates $|\Phi_k\rangle$'s, written $\{|\Phi_{k(\text{occupied})}\rangle\}$, whereas the remaining unoccupied ones form a basis $\{|\Phi_{k(\text{unoccupied})}\rangle\}$ which spans $\mathfrak{S}^{\perp}$.

As a conclusion, $\underset{\sim}{P}$ projects onto the occupied subspace, and by so, carries all the information necessary for the very description of the occupied eigenstates, recovered from the McWeeny's factorization property of $\underset{\sim}{P}$ into $\underset{\sim}{P} = \underset{\sim}{C}^{+}\underset{\sim}{C}$,[19] as we shall later on see.

The $\underset{\sim}{P}$ matrix may be recovered from crystallographic data, if one provides a proper Quantum Mechanical model of the X-ray diffraction experiment, which would ensure the N-representability of $\underset{\sim}{P}$, as previously mentioned. The necessary number of experimental conditions to be imposed is then equal to the number K of free parameters in the $\underset{\sim}{P}$ matrix.

We shall now examine the different papers published on K.

I.2. Comparison of Previous Results of K.

Imposing the idempotency on a properly normalized, hermitian density matrix ensures its N-representability by a single Slater determinant. In addition, it vastly decreases the number of independent elements in the $\underset{\sim}{P}$ matrix. Such a number K is a function of both N —the number of occupied orbitals Φ_k— and M—the number of basis functions ψ_j, as we shall soon understand.

Several papers have been published on the evaluation of K, but yield apparent contradictions, as previously said. Historically, Fano[38] published an expression of K in the case where N=1 (case of a projection onto a single pure eigenstate), derivation later further developed by Roman[90] and Blum.[26] The first derivation in the general case, corresponding to a projection operator from a space of M dimensions onto a subspace of N dimensions is due to Clinton and Massa.[68] Later on, Pecora[69] as well as Levy and Goldstein[70] published respectively contradictory result and different derivation.

To correctly compare the different results, it is, first, necessary to clarify the possible cases in which they apply and, possibly, their relationships.
The (M×M) $\underset{\sim}{P}$ matrix may, indeed, be constituted of either complex or real numbers. In the former case, K may then be expressed as the number of independent complex parameters in $\underset{\sim}{P}$ or of real ones.

Table 2 summarizes the different possible cases.

	Case #		
	1	2	3
$\underset{\sim}{P}$	Complex	Complex	Real
K	Complex	Real	Real

Table 2. Number K of Independent Parameters in a Projector: Different Possible Cases of Counting.

Their relationships is, however, more ambiguous.

Indeed, one would usually think that $K_1 = K_3$, since both formulae refer to a case where the counting of conditions on the $\underset{\sim}{P}$ matrix elements is of the same type as the elements themselves (respectively complex-complex and real-real); furthermore, a complex number being completely specified by the knowledge of two real numbers —its real and its imaginary part— one would then assume that $K_2 = 2\,K_1$. However, both relations are in general not valid in the evaluation of K, as we shall soon prove it.

For now, it appears, thus, safer not to assume any relationship between K_1, K_2 and K_3, and calculate each of them separately, when needed.

Our approach in this work will be, first, based on a complex $\underset{\sim}{P}$ matrix and real independent parameters K. Later, the result will be further extended to the two other cases.

Table 3 summarizes the formulae obtained for K, in any of the three cases —when available— by different authors.

Authors	Projection	K_1	K_2	K_3
Fano	M dim -> 1 dim	N.A.	2M-2	N.A.
Roman	M -> 1	N.A.	2M-2	N.A.
Blum	M -> 1	N.A.	2M-2	N.A.
Clinton et al	M-> N	N(M-N)	N.A.	N.A.
Pecora	M-> N	NM-N(N+1)/2	2NM-N(N+1)	NM-N(N+1)/2
Levy et al.	M-> N	N.A.	N.A.	N(M-N)

N.A.= Not Available

Table 3. Number K of Independent Parameters in a Projector: Comparison of Different Published Formulae.

Interestingly, a brief examination of the references listed in the above Table shows the following points:

1. Although Pecora's and Clinton-Massa's formulae disagree in the N-dimensional case, they both properly reduce to the one-dimensional case formula.

2. Levy and Goldstein found the same result as Clinton and Massa did but, based on Pecora's derivation, argued that their derivation was wrong, although the result was right. They then implied that Pecora's result was wrong, without proving why it was so.

To clarify this problem that the reader may, rightly, consider somewhat nebulous, our approach will be the following: in a first time, we shall devote ourselves to finding a formula for K, **independently** of any of the three existing derivations made for the most general N-dimensional case; then we shall compare our answer to the previous published results and, ultimately, suggest an answer to this question.

Since the one-dimensional case formula of K is definitely correct, our approach will be to generalize Fano-Roman's[38,90] derivation to the N-dimensional case.

I.3. Generalization of Fano-Roman's Derivation to the N-Dimensional Case.

We first adapt here Fano-Roman's derivation to our notations.

Our complex $\underset{\sim}{P}$ matrix is of (M×M) dimensions, and consequently, is made of M^2 complex elements, that is to say, $2M^2$ real parameters. According to Roman,[90] who further developed Fano's derivation, "the hermiticity condition [$\underset{\sim}{P}^+ = \underset{\sim}{P}$] reduces this number [of real parameters] to M^2; the normalization condition [$\mathrm{Tr}\underset{\sim}{P} = 1$] provides a further relationship among the elements"; and finally, the pure-state condition $\underset{\sim}{P}^2 = \underset{\sim}{P}$ is equivalent to requiring that "all eigenvalues of [the $\underset{\sim}{P}$ matrix] are 0 and 1, the latter occurring only once." This leads to the "additional condition on [the $\underset{\sim}{P}$ matrix] that its determinant and all minors vanish". K is, then, correctly found to be

$$K = 2M^2 - M^2 - 1 - (M-1)^2 = 2M - 2 \qquad (76)$$

The last condition, i.e. $\underset{\sim}{P}$ representing a pure state, is actually, mathematically equivalent to requiring that the rank of $\underset{\sim}{P}$ is 1. Fano-Roman's derivation implies, then —although not explicitly said so—, that the N-representability constraints on $\underset{\sim}{P}$, in the one-dimensional case, are equivalent to the system of equations

$$\begin{cases} \underset{\sim}{P}^+ = \underset{\sim}{P} \\ \mathrm{Rank}\,\underset{\sim}{P} = 1 \\ \mathrm{Tr}\,\underset{\sim}{P} = 1 \end{cases} \qquad (77)$$

Although it is far from being trivial that the rank condition leads to $(M-1)^2$ real conditions, we shall not examine any further the reason why, for we shall do so while generalizing to the N-dimensional case. In such a case, the normalization condition is understood to be $\mathrm{Tr}\,\underset{\sim}{P} = N$.

I.3.1. Hermiticity Constraint.

The $\underset{\sim}{P}$ matrix, being made of complex p_{ij}'s elements, may, of course, always be written as

$$\underset{\sim}{P} \equiv (p_{ij}) \equiv (Re_{ij} + i\ Im_{ij}) \qquad (78)$$

In order to properly count the number of real conditions arising from the hermiticity constraint $\underset{\sim}{P}^{+} = \underset{\sim}{P}$, it is first necessary to determine the number of diagonal and off-diagonal elements in this matrix. This is pretty straightforward and yields to the following conclusions: the $\underset{\sim}{P}$ matrix being of M^2 dimensions, there are M diagonal complex elements, and consequently a total of $(M^2 - M)$ off-diagonal complex elements —or $M(M-1)/2$ complex elements in each off-diagonal triangle.

The hermiticity constraint may, then, be transcribed into the following equivalent conditions on the $\underset{\sim}{P}$ matrix elements:

* ***diagonal elements:***

$$\forall\, i = 1 \ldots M, \quad p_{ii}^{*} = p_{ii} \iff Im_{ii} = 0 \qquad (79)$$

$\Longrightarrow$ M real conditions.

- ***off-diagonal elements:***

$$\forall i \neq j, \quad p_{ij}^{*} = p_{ji} \iff \begin{cases} \mathrm{Re}_{ij} = \mathrm{Re}_{ji} \\ \mathrm{Im}_{ij} = -\mathrm{Im}_{ji} \end{cases} \tag{80}$$

$$\Longrightarrow 2\,\frac{M(M-1)}{2} \text{ real conditions.}$$

and therefore leads to a total of $(M + M(M-1) =)$ M^2 **real conditions.**

The reader may have noticed that this result is in plain accordance with Fano-Roman's one, which is rather comforting, for the hermiticity constraint is the same, no matter what the dimension of the subspace is.

I.3.2. Rank Constraint: Rank $\underset{\sim}{P} = N$.

According to a recent mathematical article[92], the rank of any $(M \times N)$ matrix $\underset{\sim}{A} = (a_{ij})$, for which $a_{11} \neq 0$, may be computed using the following algorithm:

$$\text{Rank } \underset{\sim}{A} = 1 + \text{Rank } \underset{\sim}{D} \tag{81}$$

where, $\underset{\sim}{D}$ is an $((M-1)\times(N-1))$ matrix of the form

$$\underset{\sim}{D} = \begin{pmatrix} d_{22} & \cdots\cdots & d_{2N} \\ d_{32} & \cdots\cdots & d_{3N} \\ . & \cdots\cdots & . \\ . & \cdots\cdots & . \\ d_{M2} & \cdots\cdots & d_{MN} \end{pmatrix} \tag{82}$$

whose elements are the (2x2) subdeterminants

$$d_{ij} = \begin{vmatrix} a_{11} & a_{1j} \\ a_{i1} & a_{ij} \end{vmatrix} \tag{83}$$

Before using this algorithm, we shall prove the following theorem which has never been mentioned in the literature, and which will provide the key to our argumentation.

* **Theorem:** Let $\underset{\sim}{A}$ be an hermitian matrix.

Then, the algorithm for calculating the rank of a matrix as

$$\textbf{Rank } \underset{\sim}{A} = 1 + \textbf{Rank } \underset{\sim}{D}$$

where the $\underset{\sim}{D}$ elements retain their previous meaning, preserves the hermiticity.

The proof to this theorem is pretty straightforward, as it follows.

* **Proof:** Suppose $\underset{\sim}{A}$ hermitian, then $\begin{cases} a_{ii}^{*} = a_{ii} \\ a_{ij}^{*} = a_{ji} \end{cases}$ (84)

Hence, $\forall (i,j) \;\; a_{ii} \in \Re, \; (a_{ij} \, . \, a_{ji}) \in \Re.$ (85)

The $\underset{\sim}{D}$ elements have, then, the following properties:

- *diagonal elements:*

$$\forall i, \qquad d_{ii} = \begin{vmatrix} a_{11} & a_{1i} \\ a_{i1} & a_{ii} \end{vmatrix} = a_{11}\, a_{ii} - a_{1i}\, a_{i1} \tag{86}$$

But since $\underset{\sim}{A}$ is hermitian, $d_{ii} \in \Re$

$$\Longrightarrow d_{ii} = d_{ii}^{*} \tag{87}$$

- *off-diagonal elements:*

$$\forall (i,j) \qquad d_{ij} = \begin{vmatrix} a_{11} & a_{1j} \\ a_{i1} & a_{ij} \end{vmatrix} = a_{11}\, a_{ij} - a_{1j}\, a_{i1} \tag{88}$$

Again, using the hermicity property of $\underset{\sim}{A}$,

$$d_{ij} = a_{11}\, a_{ji}^{*} - a_{j1}^{*}\, a_{1i}^{*} = (a_{11}\, a_{ji} - a_{j1}\, a_{1i})^{*} \tag{89}$$

$$\Longrightarrow d_{ij} = d_{ji}^{*} \tag{90}$$

Therefore $\underset{\sim}{D}$ is hermitian and the conclusion follows.

This theorem is essential to the proper counting of the number of conditions arising from the constraint Rank $\underset{\sim}{P} = N$, as we shall now see.

In order to use the above algorithm for computing the rank of $\underset{\sim}{P}$, p_{11} must be different from 0. However, this is not a constraint, since it is always possible to reach this condition for a non-zero matrix by using an appropriate elementary row operation (if necessary), transformation which always leaves the rank of the matrix unchanged. We can therefore assume, without any loss of generality, that the condition $p_{11} \neq 0$ is always satisfied.

The $\underset{\sim}{P}$ matrix being of (M×M) dimensions, the computation of its rank following this algorithm will yield the relation

$$\text{Rank } \underset{\sim}{P} = 1 + \text{Rank } \underset{\sim}{D} \tag{91}$$

where $\underset{\sim}{D}$ retains its previous meaning, except for its dimensions which are here ((M-1)×(M-1)).

The same procedure can be used iteratively, and after the N$^{\text{th}}$ iteration, one obtains

$$\text{Rank } \underset{\sim}{P} = N + \text{Rank } \underset{\sim}{X} \tag{92}$$

where $\underset{\sim}{X}$ is an ((M-N)×(M-N)) matrix.

The constraint **Rank** $\underset{\sim}{P} = N$ is then equivalent to

$$\text{Rank } \underset{\sim}{P} = N \iff N + \text{Rank } \underset{\sim}{X} = N \iff \text{Rank } \underset{\sim}{X} = 0 \tag{93}$$

However, the rank of any matrix other than a zero matrix cannot be 0, while the rank of a zero matrix is defined to be 0.[93] The following equivalence is, thus, obtained:

$$\text{Rank } \underset{\sim}{P} = N \iff \underset{\sim}{X} = \underset{\sim}{0} \tag{94}$$

We shall now use the theorem we further derived: since the hermiticity of $\underset{\sim}{P}$ is preserved during this rank computation, $\underset{\sim}{D}$ is hermitian and so is $\underset{\sim}{X}$. The above constraint on $\underset{\sim}{X}$, along with its hermiticity property, leads to the following number of conditions on its elements, and therefore ultimately on the $\underset{\sim}{P}$ elements:

* ***diagonal elements:***

$$\forall\, i = 1 \ldots (M-N), \quad x_{ii} = 0 \tag{95}$$

$\Longrightarrow$ (M-N) real conditions.

* ***off-diagonal elements:***

$$\forall\, i \neq j, \quad x_{ij} = 0 \tag{96}$$

But $x_{ji} = x_{ij}{}^{*}$, and, thus, only the constraints on, say, the upper off-diagonal triangle of $\underset{\sim}{X}$ is to be counted.

$$\Longrightarrow \; 2\,\frac{(M-N)(M-N-1)}{2} \text{ real conditions.}$$

As a conclusion, the constraint Rank $\underset{\sim}{P} = N$ yields a total number of:

$$((M-N) + (M-N)(M-N-1) =) \quad (M-N)^{2} \text{ real conditions.}$$

The reader may have noticed that this last formula properly reduces to the $(M-1)^2$ real conditions found by Roman in the N=1 case.

I.3.3. Diagonal Element Constraint.

Since $\underset{\sim}{P}$ has been already constrained to be hermitian, it is legitimate to assume, without any loss of generality, that $\underset{\sim}{P}$ is always diagonalizable into, say, $\underset{\sim}{P}'$, by a unitary transformation of the basis elements.[91] The diagonal elements of $\underset{\sim}{P}'$, then called its eigenvalues, are real.

The rank constraint on $\underset{\sim}{P}$ (which is basis independent) further reduces the number of non-zero eigenvalues to N. Let λ_i, (i=1..N), be these non-zero eigenvalues.

The first two constraints already studied (i.e. $\underset{\sim}{P}^{+} = \underset{\sim}{P}$ and Rank $\underset{\sim}{P} = N$) may be then summarized as follows: constraining $\underset{\sim}{P}$ to be hermitian and of rank N is equivalent to saying that it is always possible to find a unitary transformation into a basis in which the matrix is diagonal, and can be written as

$$\underset{\sim}{P}' = \begin{pmatrix} \lambda_1 & \cdot & \cdot & \cdots 0 \\ & \cdot & & \\ & & \lambda_N & 0 \\ 0 & & \cdot & \end{pmatrix} \qquad (97)$$

where $\lambda_i \in \Re^*, \forall\, i = 1 \ldots N$.

It is clear, therefore, that, in order for $\underset{\sim}{P}$ to satisfy the hermiticity, normalization and idempotency conditions, one has to finally make some requirements on the above non-zero eigenvalues.

In the one-dimensional case, as Fano and Roman remarked, the condition Tr $\underset{\sim}{P}$ = Tr $\underset{\sim}{P}'$ = 1 properly generates the diagonal matrix of a normalized hermitian projector, since all its eigenvalues are constrained to be 0, but one, guaranteed to be 1 by the normalization condition.

However, one must pay particular attention when generalizing to the N-dimensional case, for Tr $\underset{\sim}{P}$ = N is **not** a sufficient condition to yield a projector.

Indeed, the condition $\sum_{i=1}^{N} \lambda_i = N$ does not guarantee the N non-zero eigenvalues to be all 1, necessary and sufficient condition for a projector (since $\underset{\sim}{P}'^2 = \underset{\sim}{P}' \iff \lambda_i^2 = \lambda_i$, $\lambda_i \neq 0$). The Fano-Roman conditions, thus, —although valid for the one-dimensional case— are not the most general ones and must be substituted by stronger conditions on the eigenvalues, which are

$$\lambda_1 = \lambda_2 = \ldots\ldots = \lambda_N = 1 \qquad \Longrightarrow \text{ N real conditions.} \tag{98}$$

The reader may note that this constraint is different from Fano-Roman's one, but properly reduces to theirs in the N=1 case.

Furthermore, this derivation is in accordance with a well-known theorem on projectors, which states the following:[80]

* **Theorem**: Let $\underset{\sim}{P}$ be an (M×M) hermitian matrix of rank N, then a necessary and sufficient condition that $\underset{\sim}{P}$ is idempotent is that each of N of the characteristic roots of $\underset{\sim}{P}$ is equal to unity, and the remaining (M-N) characteristic roots are equal to 0.

The physical interpretation of such a $\underset{\sim}{P}$ matrix is provided by our previous argument, and may be summarized as follows: $\underset{\sim}{P}$ is always diagonalizable into $\underset{\sim}{P}'$ in its eigenfunction basis —i.e. in $\{\Phi_k\}$. The diagonal elements of the latter—called eigenvalues— have the physical meaning of being occupation numbers of the eigenstates Φ_k, in accordance with Statistical Thermodynamics. Since N of them are equal to 1, there are N occupied eigenstates in the system ground-state, and $\underset{\sim}{P}$ is, as a consequence, the matrix representative of the projection operator $\hat{\rho}$ expressed as $\sum_{k=1}^{N} |\Phi_k\rangle\langle\Phi_k|$.

As a conclusion to this part, we found that the number of independent real parameters in a complex (M×M) $\underset{\sim}{P}$ matrix subject to the system of constraints

$$\left\{ \begin{array}{c} \underset{\sim}{P}^{+} = \underset{\sim}{P} \\ \text{Rank } \underset{\sim}{P} = N \\ \lambda_i = 1 \quad \forall \ i = 1 \ldots N \end{array} \right. \tag{99}$$

—where λ_i 's refer to the eigenvalues— is equal to:

$$2M^2 - (M^2 + (M-N)^2 + N) \ \boxed{= 2MN - N(N+1)}$$

I.4. Mathematical and Physical Interpretation of the Result.

A comparison to Table 3 shows that this result is in accordance with Pecora's formula. At first sight, it may then seem that this is such a formula that one should use to fix the number of independent real experimental conditions on $\underset{\sim}{\boldsymbol{P}}$, say of the form of equation 70.

However, it is, so far, not completely clear that it is so for the following reason: as Levy et al. pointed out, this result does not seem to be correct since it does not properly reduce to 0 when M=N, but to (N^2- N).
This argument seems reasonable, since when M=N, the projection operation is done from the space to itself and is, thus, the identity transformation. $\underset{\sim}{\boldsymbol{P}}$ is then the unit matrix, and, as a consequence, no information is needed to determine it, leading to K=0 in such a case. Based on this argument, Levy et al. implied —in his footnote #7— that Pecora's formula was wrong, although they did not prove where the fallacy in his derivation might have been. Here we point out the interpretation under which this formula is correct.

To do so, we shall compare the case where the projection is realized from an M-dimensional space to an N-dimensional subspace (N≠M), to the one where N=M.

- N≠M case:

The normalized, hermitian projector $\underset{\sim}{P}$ can always be diagonalized, according to the following procedure:[91]

$$\underset{\sim}{P} = \underset{\sim}{U}^{+} \underset{\sim}{P}' \underset{\sim}{U} \tag{100}$$

where
$$\underset{\sim}{U}^{+} \underset{\sim}{U} = \underset{\sim}{U} \; \underset{\sim}{U}^{+} = \underset{\sim}{1}_{M} \tag{101}$$

and
$$\underset{\sim}{P}' = \begin{pmatrix} \underset{\sim}{1}_{N} & \underset{\sim}{0} \\ \underset{\sim}{0} & \underset{\sim}{0} \end{pmatrix} \tag{102}$$

Hence, as McWeeny[19] first showed, $\underset{\sim}{P}$ can always be factorized into

$$\underset{\sim}{P} = \underset{\sim}{C}^{+} \underset{\sim}{C} \tag{103}$$

where the (N×M) $\underset{\sim}{C}$ matrix is made of the first N rows of the unitary matrix $\underset{\sim}{U}$, while $\underset{\sim}{C}^{+}$ of the first N columns of $\underset{\sim}{U}^{+}$.

Based on the orthonormalization requirement $\underset{\sim}{C}\,\underset{\sim}{C}^{+} = \underset{\sim}{1}_{N}$ on the $\underset{\sim}{P}$ matrix factorized as in equation 103, Clinton and Massa claimed that the number of real experimental conditions necessary to uniquely determine a complex $\underset{\sim}{P}$ matrix is $K_p = 2\,N(M-N)$. However, the decomposition of $\underset{\sim}{P}$ into $\underset{\sim}{C}^{+}\underset{\sim}{C}$ is not unique, since, as Pecora wrote, any $\underset{\sim}{C}' = \underset{\sim}{V}\;\underset{\sim}{C}$ (where $\underset{\sim}{V}$ is understood to be an (N×N) unitary matrix) will generate the same $\underset{\sim}{P}$ matrix, which "is just a basic fact of Quantum Mechanics or, more generally, linear eigenvalue theory restated in population matrix language". Hence, the only way one might speak of the uniqueness of $\underset{\sim}{C}$ is **within** a unitary transformation.

To summarize, according to Clinton and Massa, 2 N(M-N) appears to be the number of real independent experimental conditions necessary to uniquely determine $\underset{\sim}{P}$, the matrix representative of a projection transformation from the space of M dimensions to a subspace of N dimensions, **but not** $\underset{\sim}{C}$. The $\underset{\sim}{C}$ matrix is unique only within a unitary transformation in the N-dimensional subspace.

* N=M case:

As previously mentioned, Clinton-Massa's formula properly reduces to $K_P=0$ when M=N.

We shall now examine the decomposition of $\underset{\sim}{P}$ into $\underset{\sim}{C}^{+}\underset{\sim}{C}$ in such a case. From the definition of $\underset{\sim}{C}$, it is clear that the rectangular $\underset{\sim}{C}$ matrix of the previous case becomes now the square $\underset{\sim}{U}$ matrix, so that $\underset{\sim}{P}$ can always be written, when M=N, as

$$\underset{\sim}{P} = \underset{\sim}{U}^{+}\underset{\sim}{U} \quad \text{where} \quad \underset{\sim}{U}^{+}\underset{\sim}{U} = \underset{\sim}{U}\,\underset{\sim}{U}^{+} = \underset{\sim}{1}_{M} \tag{104}$$

Of course, there is also an infinity of unitary transformations in the space we are dealing with, which satisfies this equation.

Now suppose that we are looking for determining one particular $\underset{\sim}{U}$ matrix out of the infinity. Hamermesh[91] showed that the number of real independent conditions necessary to uniquely determine an (N×N) complex unitary matrix is $K_u = N^2$. However, though mathematically correct, this result is physically incorrect in our particular Quantum Mechanical case, where the k^{th} row of the $\underset{\sim}{U}$ matrix is made of the collection of the coefficients of Φ_k in the basis $\{\psi_j\}$. Indeed, it is a well-known fact in Quantum Mechanics that the phase of the state representative Φ_k is physically meaningless and can therefore be arbitrarily chosen.[7,38] This last property has for effect to decrease the number of essential parameters in our $\underset{\sim}{U}$ matrix by the same amount as the number of arbitrarily set phases. The number of real independent conditions to uniquely determine $\underset{\sim}{U}$, apart from the phases of each of the N eigenstates Φ_k, is thus: $K_u = N^2 - N$.

If one realizes that this last number K_u is precisely the difference between Pecora's and Clinton-Massa formulae of K_p,

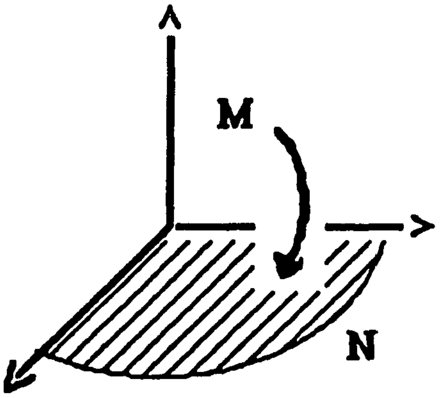
$$2\,MN - N^2 - N = 2\,N\,(M-N) + (N^2 - N) \tag{105}$$

one may interpret Pecora's formula as follows:

$2\,MN - N^2 - N$ is the number of independent real conditions to uniquely determine the projection transformation from the M-dimensional space onto the N-dimensional subspace (2 N (M-N) conditions), as well as the N basis vectors of the subspace, apart from their phases, arbitrarily chosen (additional $(N^2 - N)$ conditions). That is to say, such a K_p allows one to uniquely decompose $\underset{\sim}{P}$ into $\underset{\sim}{C}^+\underset{\sim}{C}$.

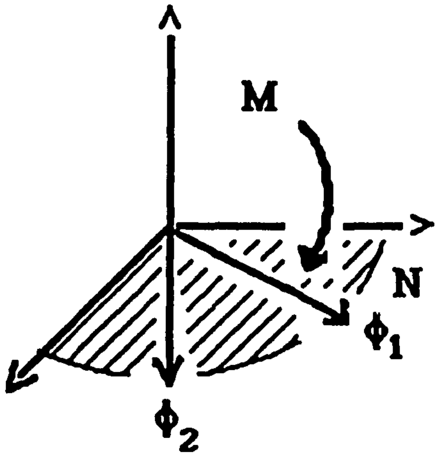
Figure 3 summarizes this interpretation, in the geometrically representable case of a projection from an M=3 dimensional space onto an N=2 dimensional subspace.

<u>Projection from an M-Dim Space</u>
<u>Onto an N-Dim Subspace</u>



$K_p = 2N(M-N)$

<u>Projection from an M-Dim Space</u>
<u>Onto an N-Dim Subspace Spanned</u>
<u>by N Particular Vectors Φ_k</u>



$K = K_p + K_u = 2MN - N(N+1)$

Bridge:

In the N-dimensional subspace, determine a particular basis,

i.e. fix $\{\Phi_k\}$ apart from their phase

$\Rightarrow$ an additional $(N^2 - N)$ real parameters to be fixed

Figure 3. Number K of Independent Parameters in a Projector: Geometrical Interpretation of Pecora vs Clinton-Massa formulae.

The credits one might give to this interpretation is that it clarifies the relationship between Clinton-Massa's formula and Pecora's one, as well as several other points:

1. Pecora noticed that "the phase information of $\underset{\sim}{C}$ is lost in the original constraints" [i.e. $\underset{\sim}{P}^2 = \underset{\sim}{P}$; $\mathrm{Tr}\,\underset{\sim}{P} = N$], but found it "not at all clear".

Here, we showed in which way one might take into account the loss of the phase information in $\underset{\sim}{C}$: there is no effect of it in calculating the number of real independent conditions to uniquely determine $\underset{\sim}{P}$, since this should be basis independent, but only when calculating the number of conditions to uniquely determine $\underset{\sim}{C}$.

2. It clarifies also why the two formulae obtained for K_p by Clinton-Massa and Pecora, both properly reduce to the case where N=1. Indeed, this is because, in such a case, there is only one possible orientation of the basis vector in the one-dimensional subspace (the subspace being fixed), if its phase is meaningless.

If 2 N(M-N) is to be the number of real conditions to uniquely determine the projector, but not its decomposition, it is now interesting to understand why, in our extension of the Fano-Roman's derivation to the N-dimensional case, we obtained Pecora's formula and not Clinton-Massa's formula.

When substituting the original system of conditions on $\underset{\sim}{P}$, namely

$$S(I) = \begin{cases} \underset{\sim}{P}^{+} = \underset{\sim}{P} \\ \underset{\sim}{P}^{2} = \underset{\sim}{P} \\ \mathrm{Tr}\,\underset{\sim}{P} = N \end{cases} \tag{106}$$

—from now on called S(I)— by the system S(II)

$$S(II) = \begin{cases} \underset{\sim}{P}^{+} = \underset{\sim}{P} \\ \text{Rank}\,\underset{\sim}{P} = N \\ \lambda_i = 1 \quad \forall\ i = 1 \ldots N \end{cases}$$

$$(\lambda_i\text{'s} = \text{eigenvalues}) \qquad (107)$$

we imposed some constraints not only on $\underset{\sim}{P}$, but also on $\underset{\sim}{P}'$ —the diagonalized form of the $\underset{\sim}{P}$ matrix— by the bias of the last equation in S(II). Hence, over and above imposing the normalization, hermiticity, and idempotency conditions on $\underset{\sim}{P}$, we also implicitly imposed some conditions on determining the basis in which $\underset{\sim}{P}'$ is found to be

$$\underset{\sim}{P}' = \begin{pmatrix} \underset{\sim}{1}_N & \underset{\sim}{0} \\ \underset{\sim}{0} & \underset{\sim}{0} \end{pmatrix} \qquad (102)$$

Such a basis is made of the collection of occupied and unoccupied eigenstates Φ_k, i.e. $\{\Phi_{k(\text{occupied})}, \Phi_{k(\text{unoccupied})}\}$. Ultimately, the very process of projection allows one to select the N occupied ones, and one does not have to bother anymore with the unoccupied ones (at least for the ground-state description of the system).

Therefore, our formula obtained for K gives the number of real pieces of information required to fix the projection from an M-dimensional space to an N-dimensional subspace spanned, not by any basis of the subspace, but by a particular one: the $\{\Phi_{k(\text{occupied})}\}$ basis.

The whole system S(II) determines, thus, the number of real conditions necessary to, not only uniquely recover $\underset{\sim}{P}$, but also to uniquely fix the decomposition of $\underset{\sim}{P}$ into $\underset{\sim}{C}^{+}\underset{\sim}{C}$

so that the $\underset{\sim}{C}$ matrix yields an N-dimensional basis (by $\underset{\sim}{\phi} = \underset{\sim}{C}\ \underset{\sim}{\psi}$) in which $\underset{\sim}{\phi}$ is the column matrix made of the collection of $\Phi_{k(\mathrm{occupied})}$. This may be the reason why our K is in accordance with Pecora's formula.

The reader may note that, again, in the one-dimensional case, such a problem does not arise for the very reason that only one eigenstate is recovered.

The key point of our argumentation now follows: in Density Matrix formalism, one is not interested in specifically recovering the Φ 's, which are known to contain too much information, but the $\underset{\sim}{P}$ matrix. It is then sufficient to determine $\underset{\sim}{P}$ uniquely, and not $\underset{\sim}{C}$. Any $\underset{\sim}{C}$ matrix yielding the proper $\underset{\sim}{P}$ matrix by $\underset{\sim}{C}^{+}\underset{\sim}{C} = \underset{\sim}{P}$ will then be fine.
In other words, it is not necessary to provide data to fix one matrix $\underset{\sim}{C}$ out of the infinity yielding $\underset{\sim}{P}$, but only to uniquely determine $\underset{\sim}{P}$.
The number of real independent conditions to uniquely determine $\underset{\sim}{P}$ is then

$$\boxed{\boxed{K_p = 2\ N\ (M-N)}} \qquad (108)$$

Although both Clinton-Massa and Levy et al. claim the same result, Levy et al., based on Pecora's derivation, argued that Clinton-Massa's derivation was wrong. The reader may then agree with us that it is interesting to further investigate each derivation and try to clarify their relationship.

I.5. Further Investigations of Previous Derivations of K.

I.5.1. Fano's Derivation.

Fano's K formula refers to the case of a projection of an M-dimensional space onto a one-dimensional subspace.

If one is willing to write the most general formula of the matrix representative $\underset{\sim}{P}$ of a hermitian, normalized projector in the case where M=2, one may refer to Clinton et al.'s paper,[58] which states that $\underset{\sim}{P}$ may always be written as

$$\underset{\sim}{P} = \begin{pmatrix} 1\text{-}p & q \\ q & p \end{pmatrix} \tag{109}$$

where p and q are real numbers, p being positive and $q = \pm\ p^{1/2}\,(1\text{-}p)^{1/2}$.

It appears, thus, that one needs K=2 real conditions to uniquely determine this $\underset{\sim}{P}$ matrix, apart from the sign of q. This is in accordance with Fano's formula, namely 2M-2.

I.5.2. Pecora's Derivation.

Following Clinton-Massa's approach based on McWeeny's decomposition of $\underset{\sim}{P}$ into $\underset{\sim}{C}^{+}\underset{\sim}{C}$ —according to equation 103— Pecora arrived at results different from Clinton-Massa's ones.

After such a factorization of the $\underset{\sim}{P}$ matrix, Pecora considers that "the constraints are summarized by the equation $\underset{\sim}{C}\,\underset{\sim}{C}^{+} = \underset{\sim}{1}_N$, and $\underset{\sim}{P}$ is completely determined by $\underset{\sim}{C}$ ". His analysis is based on counting the number of complex conditions on the complex elements of $\underset{\sim}{C}$. Although this last remark seems quite unimportant at first sight, we shall soon realize the interest of it.

The key step in his derivation, which differs from Clinton-Massa's analysis, is the following: in the system of equations resulting from the constraint $\underset{\sim}{C}\,\underset{\sim}{C}^{+} = \underset{\sim}{1}_N$, Pecora considers that "N(N-1) of [them] are simply complex conjugates of each other", yielding a total number of complex conditions equal to $\frac{N(N+1)}{2}$. This is, in fact, equivalent to considering the $\underset{\sim}{C}\underset{\sim}{C}^{+}$ matrix as hermitian, based on the argument that

$$(\underset{\sim}{C}\,\underset{\sim}{C}^{+})^{+} = \underset{\sim}{C}\,\underset{\sim}{C}^{+} \qquad (110)$$

More fundamentally, what Pecora assumed —although he never explicitly said so— is the following property: since the condition $\underset{\sim}{C}\,\underset{\sim}{C}^{+} = \underset{\sim}{1}_N$ is actually the orthonormalization constraint on the ϕ_k 's since $\underset{\sim}{C}\,\underset{\sim}{C}^{+} = (\langle\Phi_k|\Phi_m\rangle)$, he supposed that the scalar product between any two wavefunctions ϕ_k is hermitian. That is to say, he assumed that the subspace the projection is made onto is a Hilbert subspace.

Pecora then generalized his result to finding the number of real conditions to uniquely determine $\underset{\sim}{P}$, as

$$K_{real} = 2\,NM - N(N+1) = 2\,K_{complex} \tag{111}$$

We shall now see why we warned the reader to use great caution when generalizing a result derived in a particular case.

Indeed, if we exactly follow Pecora's assumptions about the scalar product being hermitian, we get quite a different result than Pecora's one when counting the number of real conditions on the complex $\underset{\sim}{P}$ matrix, arising from the constraint $\underset{\sim}{C}\,\underset{\sim}{C}^{+} = \underset{\sim}{1}_N$. Appendix B shows that, in fact, when the $\underset{\sim}{C}\underset{\sim}{C}^{+}$ is considered to be hermitian, the normalization condition on the N complex diagonal elements of $\underset{\sim}{C}\underset{\sim}{C}^{+}$ yields N real conditions and **not** 2N as Pecora tacitly supposed. This is due to the fact that the diagonal elements are already known to be real since $\underset{\sim}{C}\underset{\sim}{C}^{+}$ is hermitian by hypothesis, and hence, Im_{ii} is not a constraint.

The orthogonalization condition on the off-diagonal elements correctly yields 2 {N(N-1)/2} real conditions (please refer to appendix B).

As a consequence, Pecora's derivation is not consistent in the $K_{(real)}$ case of a complex $\underset{\sim}{P}$ matrix. Following his assumption of the hermiticity property of the scalar product in the subspace of N dimensions, one finds finally, $K_{(real)} = 2\,NM - N^2$ in the case of a complex $\underset{\sim}{P}$, and not $2K_{complex}$, as Pecora claims.

To summarize, assuming the hermiticity of the scalar product in the subspace, $2\,NM - N^2$ is the number of real conditions nécessary to uniquely fix $\underset{\sim}{\boldsymbol{C}}$, which consequently uniquely determines the complex $\underset{\sim}{\boldsymbol{P}}$ matrix.

However, if one minds completely determining $\underset{\sim}{\boldsymbol{C}}$, and therefore the accompanying ϕ's, one has to do so apart from their phases which are known to be physically meaningless, as previously said. This further decreases the number of conditions to uniquely determine $\underset{\sim}{\boldsymbol{C}}$, apart from the Φ's phases, by a number N and yields:

$$K_{(real)} = 2\,NM - N^2 - N = K_{(real)} = 2\,NM - N(N+1) \qquad (112)$$

The reader will note that this is in accordance with our own derivation of K.

Interestingly enough, this turns out to be the very result that Pecora claims, for the following reason: The overcounting in the number of real conditions on the diagonal elements of the assumed hermitian $\underset{\sim}{\boldsymbol{C}}\underset{\sim}{\boldsymbol{C}}^{+}$ matrix (N in number) exactly compensates the oversight of the conditions relative to the arbitrary phase of each ϕ.

I.5.3. Clinton-Massa's Derivation.

The approach followed by Pecora was first elaborated by Clinton and Massa, who found a different result.

In counting the number of orthonormalization conditions on $\underset{\sim}{\boldsymbol{C}}$, Clinton and Massa did not assume the hermiticity of the scalar product in the subspace, but rather chose to impose it. This leads, then, to N^2 complex constraints, and consequently K is found to be

$$K_{(complex)} = NM - N^2 \qquad (113)$$

The reader may easily check that the generalization of this result to $K_{(real)}$ leads, in this case, to $K_{(real)} = 2\,K_{(complex)}$. This is because of their choice to impose on the diagonal elements of $\underset{\sim}{C}\underset{\sim}{C}^{+}$, the condition Im= 0.

More fundamentally, what Clinton and Massa tacitly assumed, is that one has to impose the hermiticity of the scalar product defined in the subspace to ensure the subspace to be a Hilbert subspace.

To decide whether or not this is a legitimate assumption, we shall now use both the introduction made on separable Hilbert space structure and the examination of the concept of projection in Hilbert space, to study the space structure; only this being achieved, shall we move to the understanding of the subspace properties. One will then try to decide which derivation, out of Pecora's and Clinton-Massa's, is the correct one by answering the following questions:

1. Is our space spanned by $\{\psi_j\}$ a Hilbert space?

2. If yes, does the projection process preserve or not the hermiticity character of the scalar product?

For the convenience of the argumentation, we are from now on using the function representation of our formalism, which restrains the generality of the results only in the sense that the $\mathfrak{L}^2$ space is a particular example of separable Hilbert space; the generalization to any separable Hilbert space is, however, straightforward.

In the most general formulation of our formalism expressed in the function representation, we first make the choice of a basis $\{\psi_j(1)\}$ which spans our M-dimensional space. This basis can be any set of M linearly independent complex functions, normalized or not, as long as it satisfies one single condition: since we are dealing with the description of the state of the system by Quantum Mechanics, $\psi_j(1)$'s must be well-behaved functions and therefore must be chosen among the elements of the $\mathfrak{L}^2$ space. Any choice of a basis not satisfying this latter condition would violate the Quantum Mechanics formalism — described in the continuous representation. The basis functions being elements of the $\mathfrak{L}^2$ space, our space is by consequence an M-dimensional complex separable Hilbert space, written $\mathfrak{H}$, and therefore possesses by definition an inner product structure satisfying the axioms of equation 2. Particularly, the inner product is hermitian, i.e. for any choice of basis as a linearly independent subset of $\mathfrak{L}^2$, it is always true that

$$\begin{aligned} &< \psi_i \,|\, \psi_j > = < \psi_j \,|\, \psi_i >^* \\ \Longleftrightarrow\ &\int \psi_i^*(1)\, \psi_j(1)\ d1 \ = \ \left(\int \psi_j^*(1)\, \psi_i(1)\ d1 \right)^* \end{aligned} \tag{114}$$

Now we have answered the first question, we shall examine the second one, which may be resolved in different ways.

1. Our first way of answering the last question will be based on the fundamental theorems on Hilbert space. Indeed, the theorem on separability tells us that any subspace

of $\mathfrak{H}$ is also a separable Hilbert space. As a consequence, the inner product defined on, say, the occupied subspace is hermitian irrespectively of the choice of the basis $\{\psi_j(1)\}$, as long as this latter satisfies the fundamental requirements of Quantum Mechanics. One should therefore not have to impose this property as a constraint when counting the number of conditions arising from the constraint $\underset{\sim}{C}\,\underset{\sim}{C}^{+}=\underset{\sim}{1}_N$ but, on the contrary, can take it for granted.

2. A second way of resolving this question is provided by examining the constraint itself. Indeed, the condition $\underset{\sim}{C}\,\underset{\sim}{C}^{+}=\underset{\sim}{1}_N$ is equivalent to requiring the orthonormalization of the basis functions $\Phi_k(1)$ of the occupied subspace. That is to say, $\Phi_k(1)$'s must satisfy

$$\int \Phi_k^*(1)\,\Phi_m(1)\;d1 \;=\; \delta_{km} \qquad (115)$$

However, since $\Phi_k(1)$ is described in the space basis by

$$\Phi_k(1)=\sum_{j=1}^{M} c_{kj}\,\psi_j(1), \qquad (116)$$

one can rewrite the orthonormalization condition as

$$\sum_{j\,n=1}^{M} c_{kj}^*\,c_{mn}\int \psi_j^*(1)\,\psi_n(1)\;d1 \;=\; \delta_{km} \qquad (117)$$

and it is obvious that the hermiticity property of the inner product of the space is conferred to the subspace. This is in fact nothing more than the above answer restated in terms of the exact expression of the inner product.

3. Finally, one may suggest a third way of solving this problem by further investigating the McWenny's theorem of decomposition.

Consider first a general matrix $\underset{\sim}{P}$ of M^2 dimensions. If this $\underset{\sim}{P}$ matrix is of rank r, $r \leq M$, it is then always decomposable into a product of two rectangular matrices of respective shapes, $(M \times r)$ and $(r \times M)$.

Now consider each of the three constraints on $\underset{\sim}{P}$:

a. $\underset{\sim}{P}^{+}=\underset{\sim}{P}$:

then it is always possible to find a unitary transformation so that
$\underset{\sim}{P}=\underset{\sim}{U}^{+}\underset{\sim}{P}'\underset{\sim}{U}$;

$\underset{\sim}{P}=\underset{\sim}{C}^{+}\underset{\sim}{C}$ if and only if $\underset{\sim}{P}^{2}=\underset{\sim}{P}$, since then $\underset{\sim}{P}'=\begin{pmatrix} \underset{\sim}{1} & \underset{\sim}{0} \\ \underset{\sim}{0} & \underset{\sim}{0} \end{pmatrix}$

However, so far, $\underset{\sim}{C}$ is a rectangular matrix of dimensions $(r \times M)$ where r is the rank of $\underset{\sim}{P}$.

b. Rank $\underset{\sim}{P} = \mathrm{N}$:

then $\underset{\sim}{P}' = \begin{pmatrix} \underset{\sim}{1}_N & \underset{\sim}{0} \\ \underset{\sim}{0} & \underset{\sim}{0} \end{pmatrix}$, and $\underset{\sim}{C}$ becomes an (N × M) matrix.

c. $\underset{\sim}{P}^{\,2} = \underset{\sim}{P}$:

$$\Longleftrightarrow (\underset{\sim}{C}^{+}\underset{\sim}{C})\,(\underset{\sim}{C}^{+}\underset{\sim}{C}) = \underset{\sim}{C}^{+}\underset{\sim}{C}$$

$$\Longleftrightarrow \underset{\sim}{C}^{+}(\underset{\sim}{C}\,\underset{\sim}{C}^{+})\,\underset{\sim}{C} = \underset{\sim}{C}^{+}\underset{\sim}{C} \quad \Longleftrightarrow \quad \underset{\sim}{C}\,\underset{\sim}{C}^{+} = \underset{\sim}{1}_N \qquad (118)$$

Therefore, it is clear that one may rewrite the $\underset{\sim}{P}$ constraints as

if $\underset{\sim}{P}^{+} = \underset{\sim}{P}$ then $\underset{\sim}{P} = \underset{\sim}{C}^{+}\underset{\sim}{C}$, where $\underset{\sim}{C}$ is (N × M)

if and only if $\underset{\sim}{C}\,\underset{\sim}{C}^{+} = \underset{\sim}{1}_N$

i.e. **if and only if** $\underset{\sim}{P}^{\,2} = \underset{\sim}{P}$ and Rank $\underset{\sim}{P} = \mathrm{N}$.

It appears thus, that writing $\underset{\sim}{P}$ as $\underset{\sim}{C}^{+}\underset{\sim}{C}$ where $\underset{\sim}{C}\,\underset{\sim}{C}^{+} = \underset{\sim}{1}_N$ is already taking account of the first constraint of hermiticity of $\underset{\sim}{P}$, and further imposing the two remaining ones: $\underset{\sim}{P}^{\,2} = \underset{\sim}{P}$ and Rank $\underset{\sim}{P} = \mathrm{N}$. That is to say, the hermiticity constraint is implicitly taken into account as soon as one decomposes $\underset{\sim}{P}$ as $\underset{\sim}{C}^{+}\underset{\sim}{C}$, the two other constraints being completely summarized by $\underset{\sim}{C}\,\underset{\sim}{C}^{+} = \underset{\sim}{1}_N$. It seems therefore not necessary to superimpose the hermiticity constraint on $\underset{\sim}{C}\,\underset{\sim}{C}^{+} = \underset{\sim}{1}_N$, for it has already been done.

As a conclusion to this part, when counting the number of conditions arising from $\underset{\sim}{C}\,\underset{\sim}{C}^{+} = \underset{\sim}{1}_N$, one does not have to impose the inner product to be hermitian but can take it for granted. The reader may find then quite interesting to understand why Clinton-Massa's derivation obtain the right answer to K.

First, Clinton and Massa do not address the right way of counting the number of independent parameters in $\underset{\sim}{P}$, for there derivation is based on $\underset{\sim}{C}$. Indeed, as was shown for Pecora's derivation, subtracting the number of orthonormalization conditions —arising from $\underset{\sim}{C}\,\underset{\sim}{C}^{+} = \underset{\sim}{1}_N$ — from the total number of $\underset{\sim}{C}$ elements counts the number of independent parameters in $\underset{\sim}{C}$, but not in $\underset{\sim}{P}$.

Doing so, they overcounted one of the off-diagonal triangle (2 $(N^2\text{-}N)/2$ real parameters) by choosing to impose the hermiticity of the inner product in the occupied subspace. Furthermore, since the counting is based on the $\underset{\sim}{C}$ matrix, one has to correct for the fact that less information is required to uniquely determine the $\underset{\sim}{P}$ matrix, for any $\underset{\sim}{C}$ matrix yielding the correct $\underset{\sim}{P}$ is fine. That is to say, one has to subtract the number of conditions necessary to fix a unitary transformation apart from the arbitrarily chosen phases of the basis elements. They should have done, therefore, the following correction:

$$K_{\text{real}}\,(\text{for } \underset{\sim}{P}) = K_{\text{real}}\,(\text{for } \underset{\sim}{C}) \;-\; (N^2\text{-}N) \qquad (119)$$

Surprisingly enough, the oversight of this last correction exactly compensates the previous overcounting.

I.5.4. Levy et al.'s Derivation.

Levy et al. chose to tackle the problem in a different way. They based their reasoning on the orthogonal decomposition of the space spanned by $\{|\psi_j>\}$, into $\mathfrak{S}$ and $\mathfrak{S}^{\perp}$, respectively the occupied and unoccupied subspaces.

As was shown in section **I.1.** of this chapter, there is a one-to-one correspondence between each subspace and there accompanying projection. It is clear, then, that the projection is completely defined by the knowledge of the corresponding subspace.

Based on this notions, Levy et al. then tried to recover a formula for the real number of pieces of information necessary to fix uniquely $\Psi_{det}(1,2,...N)$ described in a real function basis. They wrote, then: "the number of independent parameters in Ψ_{det} is equal to the number of equations required to fix the Φ subspace. We now assert that this number is N(M-N) because there are N(M-N) orthogonality relations between the Φ and the $\Phi^{\perp}$ orbitals:

$$< \Phi_i \,|\, \Phi_j^{\perp} > = 0, \quad i=1,2 ...N; j=1,2...(M-N). \text{"} \qquad (120)$$

Although it is clear that there are N(M-N) orthogonality relations between the Φ 's and the $\Phi^{\perp}$'s, it is not as clear why this is exactly equal to K, unless one has a previous knowledge of Φ 's and the $\Phi^{\perp}$'s.

Indeed, one may give the following counter-argument to Levy et al.'s assumption: for the sake of commodity, take the case of a projection from a three-dimensional space (M=3) onto a two-dimensional subspace (N=2). $\mathfrak{S}^{\perp}$ is then a one-dimensional subspace, and any $\Phi^{\perp} \in \mathfrak{S}^{\perp}$ spans the subspace and therefore completely specifies it. The following figure somewhat clarifies our hypotheses.

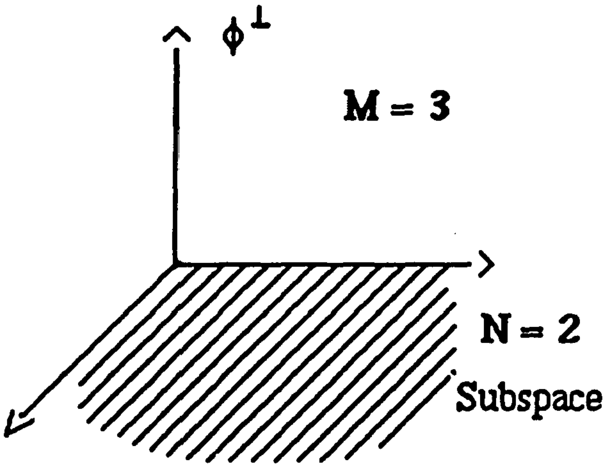


Figure 4. Orthogonal Decomposition of a 3-Dimensional Hilbert Space: Geometrical Representation of the Two Orthogonal Subspaces.

According to Levy et al., the $\mathfrak{S}$ subspace is then completely specified by the N(M-N) = 2 orthogonality relations between the Φ 's and the $\Phi^{\perp}$. Let Φ_1 and Φ_2 be the two elements of $\mathfrak{S}$. One has then the following relations:

$$\Phi^{\perp} \perp \Phi_1 \; ; \; \Phi^{\perp} \perp \Phi_2$$

However, Φ_1 and Φ_2 could be such that $\Phi_1 = k\,\Phi_2$, as described by the following figure,

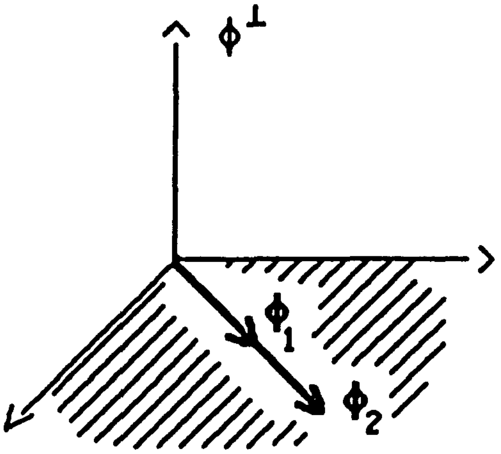


Figure 5. Orthogonal Decomposition of a 3-Dimensional Hilbert Space: Case of two Colinear Vectors in the 2-Dimensional Subspace.

In such a case, the two vectors being colinear, do not form a basis of the $\mathfrak{S}$ subspace, and consequently, do not entirely define the subspace they belong to.

In the case where M=4 and N=3, one could have the following situation:

$$\Phi^{\perp} \perp \Phi_1 \, ; \;\; \Phi^{\perp} \perp \Phi_2 \, ; \;\; \Phi^{\perp} \perp \Phi_3$$

but where $\Phi_3 = \Phi_1 + \Phi_2$. Here again, the set $\{ \Phi_1, \Phi_2, \Phi_3 \}$ does not span the $\mathfrak{S}$ subspace.

As a consequence, these examples show that the orthogonality relations alone do not fix the $\mathfrak{S}$ subspace. To do so, one would need some previous additional information on the basis which span $\mathfrak{S}$ and $\mathfrak{S}^{\perp}$, that is to say, one would need to constrain the set of recovered Φ 's to form a basis of the occupied subspace. This would then make additional constraints to take into account in the search for a K formula.

I.6. Partial Conclusion.

To test whether or not our interpretations are consistent, we may look for obtaining a general picture of the problem, based on the strengths and weaknesses of each derivation.

To this end, first choose a basis $\{\psi j\}$ which spans an M-dimensional complex separable Hilbert space $\mathfrak{H}$, as

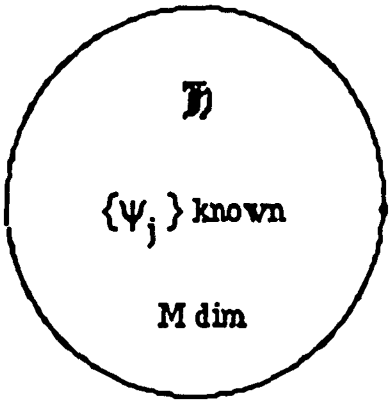


Figure 6. Orthogonal Decomposition of an M-Dimensional Hilbert Space: Sketch of the Space Spanned by a Known Basis.

Then, divide the space into two subspaces $\mathfrak{S}_1$ and $\mathfrak{S}_2$ of respective dimensions N and (M-N). To each of these subspaces is associated a projection which is completely specified by the knowledge of the subspace.

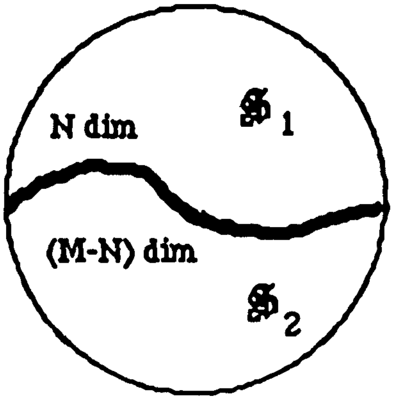


Figure 7. Orthogonal Decomposition of an M-Dimensional Hilbert Space: Sketch of the Two Supplementary Subspaces.

Suppose for now that we do not have any further information about the relationship between $\mathfrak{S}_1$ and $\mathfrak{S}_2$, and that we consider them apart from each other:

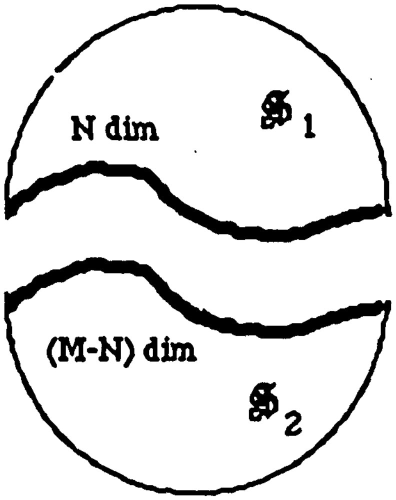


Figure 8. Orthogonal Decomposition of an M-Dimensional Hilbert Space: Sketch of the Subspaces Apart from Each Other.

One may then ask the following question:

1. How many pieces of information do we need to completely specify $\mathfrak{S}_1$?

Let $\{\Phi_i^{(1)}\}$ be a basis of $\mathfrak{S}_1$. $\mathfrak{S}_1$ is completely specified by the knowledge of the coefficients of its basis elements $\Phi_i^{(1)}$'s in the basis $\{\psi_j\}$, following

$$\Phi_i^{(1)} = \sum_{j=1}^{M} c_{ij}\, \psi_j^{(1)} \tag{121}$$

where the c's are supposed to be complex numbers.

Then, according to our interpretation of K, to completely specify the 2NM real parameters from the c's, subject to N^2 real orthonormalization constraints of the $\Phi_i^{(1)}$'s, and apart from their N phases, one would need a **total of $2NM - N^2 - N$ real conditions.**

This last expression is, in fact, equal to $2N(M-N) + (N^2-N)$, which are respectively the number K for determining the projection $\underset{\sim}{P}_1$ onto $\mathfrak{S}_1$—written as $K(\underset{\sim}{P}_1)$, and K for uniquely fixing the decomposition of $\underset{\sim}{P}_1$ into $\underset{\sim}{C}_1{}^{+}\underset{\sim}{C}_1$ apart from the $\Phi_i^{(1)}$ phases —from now on written $K(\underset{\sim}{C}_1)$.

Now suppose that one asks the following question:

2. How many pieces of information do we need to completely specify $\mathfrak{S}_2$, apart from $\mathfrak{S}_1$?

One can then use the same logic for $\mathfrak{S}_2$ as the one previously used for $\mathfrak{S}_1$: to completely specify the 2(M-N)M coefficients of $\Phi_i^{(2)}$ in the basis $\{\psi_j\}$, subject to $(M-N)^2$ real orthonormalization constraints of the 's, and apart from their (M-N) phases, we need a total of $2(M-N)M - (M-N)^2 - (M-N)$ real conditions.

The reader may check that this last expression is in fact equal to

$$K(\underset{\sim}{P}_2) + K(\underset{\sim}{C}_2) = 2N(M-N) + ((M-N)^2 - (M-N)) \qquad (122)$$

counting done in accordance with our previous interpretations.

Therefore, to completely specified both $\mathfrak{S}_1$ and $\mathfrak{S}_2$, apart from each other, one needs a total number of real conditions of $2\,NM - 2\,N^2 + M^2 - M$

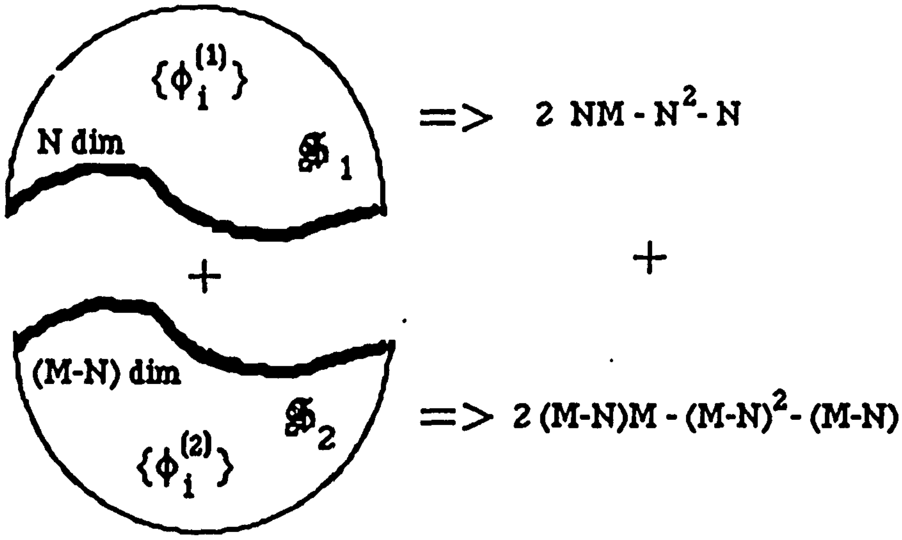


Figure 9. Orthogonal Decomposition of an M-Dimensional Hilbert Space: Total Number of Conditions to Completely Specify the Separated Subspaces Apart from Each Other.

However, we do have an additional information on $\mathfrak{S}_1$ and $\mathfrak{S}_2$, namely their orthogonal complementarity written as

$$\mathfrak{H} = \mathfrak{S}_1 \oplus \mathfrak{S}_2, \text{ where } \mathfrak{S}_2 = \mathfrak{S}_1^{\perp}$$

and sketched as

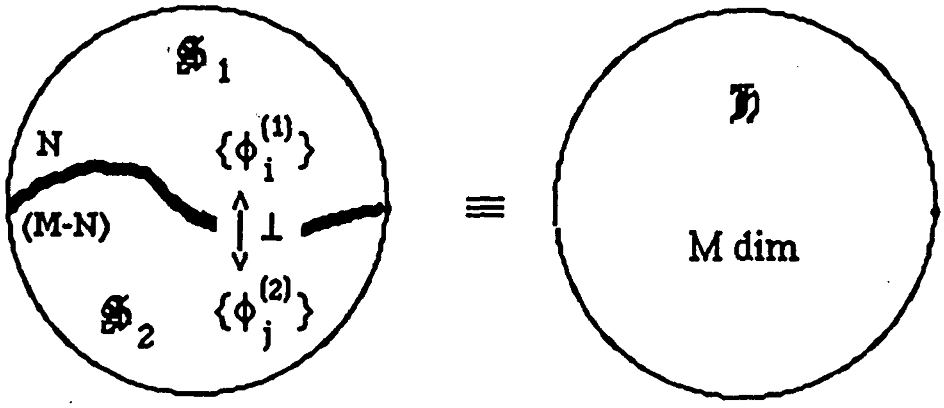


Figure 10. Orthogonal Decomposition of an M-Dimensional Hilbert Space: Union of the Two Orthogonal Subspaces Previously Separated.

These orthogonality relations lead to an additional real number of conditions 2N(M-N).

As a conclusion, one may now finally proceed to the counting of the total number of real conditions answering the question

3. How many pieces of information do we need to completely specify both $\mathfrak{S}_1$ and $\mathfrak{S}_2$, when $\mathfrak{H} = \mathfrak{S}_1 \oplus \mathfrak{S}_2$ and $\mathfrak{S}_2 = \mathfrak{S}_1^{\perp}$?

whose answer is provided by K(total). The reader may check that one finds

$$K(\text{total}) = M^2 - M \tag{123}$$

Moreover, the bases $\{\Phi_i^{(1)}\}$ and $\{\Phi_j^{(2)}\}$ span respectively the subspaces $\mathfrak{S}_1$ and $\mathfrak{S}_2$ of $\mathfrak{H}$. These elements belong therefore to the space $\mathfrak{H}$.

By consequence, if one decides to build the set of cardinality M made by concatenation of the two bases, such as $\{\Phi_i^{(1)},\Phi_j^{(2)}\}$, one has simply created a new basis in the space $\mathfrak{H}$. One may then ask the following question

4. How many pieces of information do we need to uniquely define a new basis $\{\Phi_i^{(1)},\Phi_j^{(2)}\}$ from the old $\{\psi_j\}$ one, apart from their phases?

This is equal to the number of real parameters necessary to uniquely determine the unitary transformation operated on the known old basis, defined as

$$U: \{\psi_j\} \longrightarrow \{\Phi_i^{(1)},\Phi_j^{(2)}\}$$

apart from their phases. This number is given by the Hamermesh formula corrected of the arbitrary phases, and turns out to be exactly what we found via the first route, i.e.

$$K(U) = M^2 - M \tag{124}$$

Our way of counting the conditions is therefore consistent.

A summary of this final conclusion is provided by the following simple sketch.

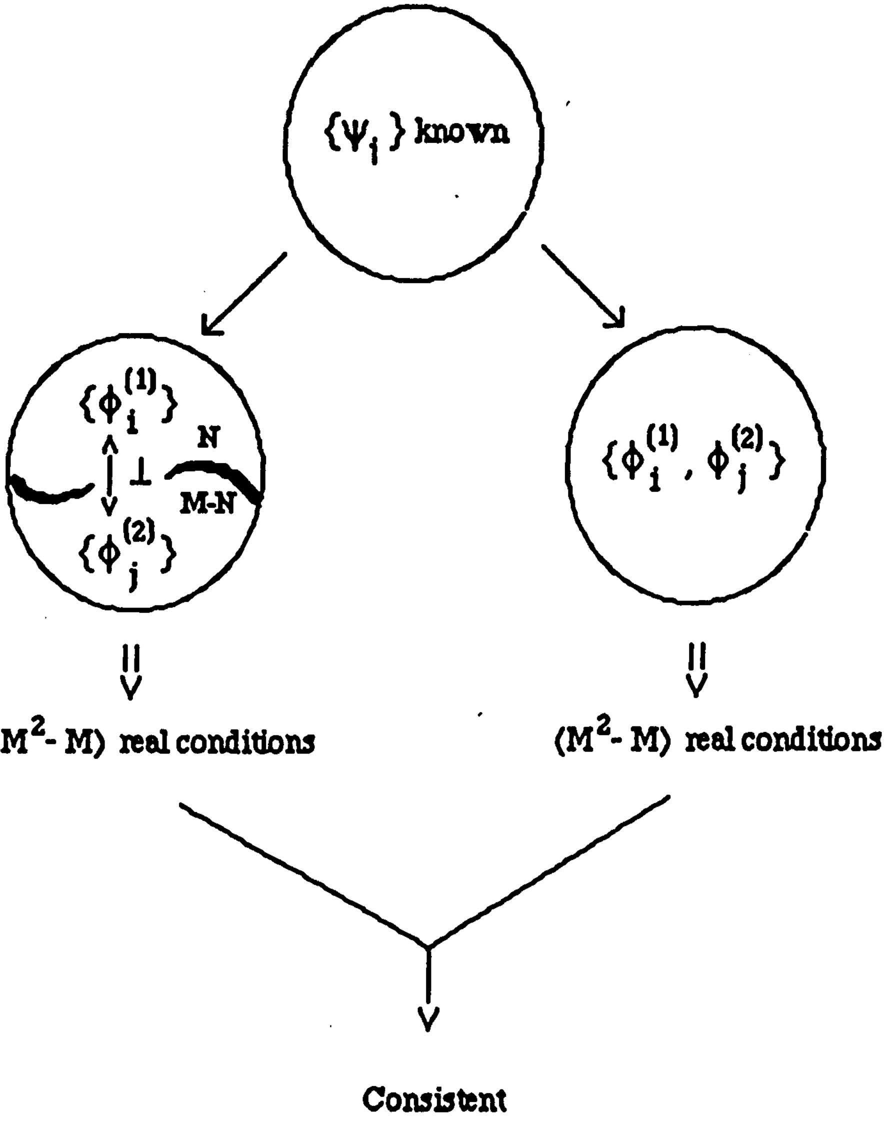


Figure 11. Orthogonal Decomposition of an M-Dimensional Hilbert Space: Summarizing Sketch Showing the Consistence of the Derivation.

Now that we have found a formula giving the total number of X-ray data necessary to determine the $\underset{\sim}{P}$ matrix as

$$\boxed{K_{real} = 2\ N(M-N)} \qquad (125)$$

and suggested an interpretation of other previously published formulae, we shall move on to the study of the uniqueness of our method. This shall be our goal in the next section.

II. Uniqueness of the P Matrix.

To recover a single Slater determinant from X-ray diffraction data, one may follow Clinton-Massa's algorithm[72] which may be sketched as on the following page; procedure which finally yields a first-order reduced density matrix N-representable by a single Slater determinant, as

$$P_1(\vec{r}_1, \vec{r}_{1'}) = N \int \Psi_{det}(1,2,\ldots N)\ \Psi_{det}^{*}(1',2,\ldots N)\ ds_{1\,1'..N}\ d2\ldots N \qquad (126)$$

The uniqueness problem may then be understood as follows: for a given system, if one can prove that the recovered $\underset{\sim}{P}$ matrix is unique in the chosen $\underset{\sim}{\psi}\ (\vec{r})$ basis, then the single Slater determinant will be unique within a unitary transformation.

$$\begin{tikzcd}
\left.\begin{array}{l} P(\vec{r}) \\ \underset{\sim}{\psi}(\vec{r}) \end{array}\right\} \arrow[rr, Rightarrow] & {} \arrow[d, Rightarrow] & \underset{\sim}{P} \arrow[rr, Rightarrow] & {} \arrow[dd, Rightarrow] & \underset{\sim}{C} \arrow[rr, Rightarrow] & {} \arrow[ddd, Rightarrow] & \underset{\sim}{\phi}(\vec{r}) \arrow[rr, Rightarrow] & {} \arrow[dddd, Rightarrow] & \Psi_{\mathrm{det}}\,(1,2,\ldots N) \\
& \begin{array}{c} P(\vec{r}) = P_1(\vec{r}_1;\vec{r}_1{}')_{\vec{r}_1{}'\to\vec{r}_1} = \mathrm{Tr}\,\underset{\sim}{P}\;\underset{\sim}{\psi}(\vec{r})\;\underset{\sim}{\psi}^{+}(\vec{r}) \\ \text{where } \underset{\sim}{P}^{2} = \underset{\sim}{P}\,,\ \underset{\sim}{P}^{+} = \underset{\sim}{P}\,,\ \mathrm{Tr}\,\underset{\sim}{P} = N \end{array} & & & & & & & \\
& & & \underset{\sim}{P} = \underset{\sim}{C}^{+}\underset{\sim}{C} & & & & & \\
& & & & & \underset{\sim}{\phi}(\vec{r}) = \underset{\sim}{C}\,\underset{\sim}{\psi}(\vec{r}) & & & \\
& & & & & & & \Psi_{\mathrm{det}}\,(1,2,\ldots N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \Phi_1(1) & \ldots & \Phi_N(1) \\ \cdot\cdot & \cdot\cdot & \cdot\cdot \\ & \cdot\cdot & \cdot\cdot \\ \Phi_1(N) & \ldots & \Phi_N(N) \end{vmatrix} &
\end{tikzcd}$$

Figure 12. Clinton-Massa's Algorithm to Generate an X-ray Determinant.

However, fixing the proper number of X-ray data in any $\underset{\sim}{\psi}(\vec{r})$ basis —chosen among the sets of M linearly independent functions belonging to the $\mathcal{L}^2$ space— does not necessarily mean that the $\underset{\sim}{P}$ matrix recovered by our method is unique.

Indeed, as Harriman[49] first showed, there is a many-to-one relationship between the (spinless) N-representable first-order reduced density matrices $P_1(\vec{r}_1, \vec{r}_1')$ and the (spinless) density function $P(\vec{r})$, related by

$$P_1(\vec{r}_1, \vec{r}_1')_{\vec{r}_1' \to \vec{r}_1} = P(\vec{r}) \tag{127}$$

To each of these density matrices, there would correspond a $\underset{\sim}{P}$ matrix, and it seems therefore legitimate to suppose, at first sight, the non-uniqueness of our method. The coming section shall, however, prove the contrary by deriving **necessary and sufficient conditions** for the uniqueness of the $\underset{\sim}{P}$ matrix.

According to our previous derivation, there are 2 N(M-N) independent real parameters to be determined in a complex, normalized, hermitian projection matrix $\underset{\sim}{P}$, by the X-ray experimental conditions of the form

$$\begin{aligned} P(\vec{r}) &= \mathrm{Tr}\ \underset{\sim}{P}\ \underset{\sim}{\psi}(\vec{r})\ \underset{\sim}{\psi}^{+}(\vec{r}) \\ &= \sum_{i=1}^{M} \sum_{j=1}^{M} p_{ij}\, \psi_j(\vec{r})\, \psi_i^*(\vec{r}) \end{aligned} \tag{128}$$

Now assume that there is a total of d experimental data obtained from the X-ray experiment —d being large but finite. Then, the experimental constraints described by the above equation form a system of d linear equations, where p_{ij}'s are the unknowns to be determined and $\psi_j(\vec{r})\psi_i^*(\vec{r})$ their corresponding coefficients. If one expands each of these equations, first over i then over j, one may symbolize the whole system of equations by

$$\underset{\sim}{\Gamma}\,\underset{\sim}{\mathfrak{P}} = \underset{\sim}{\mathfrak{X}} \tag{129}$$

where $\underset{\sim}{\Gamma}$ is the $(d \times M^2)$ matrix made of the collection of the p_{ij}'s coefficients, i.e.

$$\underset{\sim}{\Gamma} = (\gamma_{mn}) = (\psi_j(\vec{r}_m)\,\psi_i^*(\vec{r}_m)) \quad \text{where } n = M(i-1) + j, \tag{130}$$

$\underset{\sim}{\mathfrak{P}}$ the $(M^2 \times 1)$ column-vector of the p_{ij}'s unknowns, i.e.

$$\underset{\sim}{\mathfrak{P}} = (\mathfrak{p}_{n1}) = (p_{ij}) \quad \text{where n retains its previous meaning,} \tag{131}$$

and $\underset{\sim}{\mathfrak{X}}$ the $(d \times 1)$ column-vector made of the collection of the X-ray experimental data constituting the right-hand side of the system, i.e.

$$\underset{\sim}{\mathfrak{X}} = (\mathfrak{x}_{m1}) = (P(\vec{r}_m)) \tag{132}$$

Let's examine more closely the $\underset{\sim}{\Gamma}$ matrix: according to equation 130, it is of the form

$$\underset{\sim}{\Gamma} = \begin{pmatrix} \psi_1\psi_1^*(\vec{r}_1) & \cdots\cdots & \psi_M\psi_M^*(\vec{r}_1) \\ \vdots & \vdots & \vdots \\ \psi_1\psi_1^*(\vec{r}_d) & \cdots\cdots & \psi_M\psi_M^*(\vec{r}_d) \end{pmatrix} \tag{133}$$

and may then further be considered as the juxtaposition of M^2 column-vectors $\underset{\sim}{\Gamma}_n$ ($n=1...M^2$), for which each coordinate corresponds to the value of $\psi j \psi i^*$ at the point $(\vec{r}\,1)$, i.e.

$$\underset{\sim}{\Gamma} = (\underset{\sim}{\Gamma}_1 \, \underset{\sim}{\Gamma}_2 \quad \underset{\sim}{\Gamma}_{M^2}) \tag{134}$$

where

$$\underset{\sim}{\Gamma}_n = \begin{pmatrix} \psi j \psi i^*(\vec{r}\,1) \\ \vdots \\ \psi j \psi i^*(\vec{r}\,d) \end{pmatrix} \text{ and } n = M\,(i-1) + j. \tag{135}$$

From these definitions, one may finally construct the $[d \times (M^2+1)]$ matrix made by juxtaposing the column-vector $\underset{\sim}{\mathfrak{X}}$ of experimental data to the $\underset{\sim}{\Gamma}$ matrix, as

$$(\underset{\sim}{\Gamma} : \underset{\sim}{\mathfrak{X}}) = (\underset{\sim}{\Gamma}_1 \, \underset{\sim}{\Gamma}_2 \quad \underset{\sim}{\Gamma}_{M^2} \, \underset{\sim}{\mathfrak{X}}) \tag{136}$$

called the complete matrix of the system.

By doing so, one has now translated the X-ray experimental conditions into a matrix form which carries an inherent simplicity, for the resolution of such a system of linear equations is described by the well-known Krönecker conditions:[16]

1. If Rank $(\underset{\sim}{\Gamma}) \neq$ Rank $(\underset{\sim}{\Gamma} : \underset{\sim}{\mathfrak{X}})$

   then no solution to the system is to be found.

2. If Rank $(\underset{\sim}{\Gamma})$ = Rank $(\underset{\sim}{\Gamma}:\underset{\sim}{\mathfrak{X}})$

   and Rank = number K of independent unknowns

   then there is a unique solution to the system.

3. If Rank $(\underset{\sim}{\Gamma})$ = Rank $(\underset{\sim}{\Gamma}:\underset{\sim}{\mathfrak{X}})$

   and Rank < number K of independent unknowns

   then the system admits an infinity of solutions.

Out of the three mentioned possibilities, it is hardly necessary to precise that the second one is the one we should most like, for this would yield a unique solution to the system of X-ray experimental conditions. Moreover, if one imposes the complex $\underset{\sim}{P}$ matrix to be a normalized, hermitian projector, this decreases K to 2N(M-N). Such a constraint is then **implicitly** taken into account in order to investigate its effect on the system of X-ray conditions. That is to say, such a system has a unique solution **if and only if**:

$$\begin{aligned} &\mathrm{Rank}\,(\underset{\sim}{\Gamma}) = \mathrm{Rank}\,(\underset{\sim}{\Gamma}:\underset{\sim}{\mathfrak{X}}) = 2N(M-N) \\ \Longleftrightarrow\ &\mathrm{Rank}\,(\underset{\sim}{\Gamma}_1\ \underset{\sim}{\Gamma}_2 \quad \underset{\sim}{\Gamma}_{M^2}) = 2N(M-N) \end{aligned} \qquad (137)$$

Hence, there must be K = 2N(M-N) linearly independent column-vectors $\underset{\sim}{\Gamma}_n$, the rest being written as a linear combination of the formers, for getting a unique $\underset{\sim}{P}$ matrix.

Without any loss of generality, one may assume that the first K^{th} ones are linearly independent, i.e.

$$\alpha_1 \underset{\sim}{\Gamma}_1 + \alpha_2 \underset{\sim}{\Gamma}_2 \quad + \alpha_K \underset{\sim}{\Gamma}_K = 0 \Longrightarrow \alpha_1 = \alpha_2 = \ldots = \alpha_K = 0 \tag{138}$$

For this to be true, it is necessary and sufficient that this last relation is satisfied for every coordinate of $\underset{\sim}{\Gamma}_n$; that is to say, if and only if the K $\psi_j\psi_i^*(\vec{r})$'s products are linearly independent $\forall\ \vec{r}$.

To summarize, if one does not impose any constraint on the $\underset{\sim}{P}$ matrix other than the X-ray experimental conditions of the form of equation 128, one obtains a unique $\underset{\sim}{P}$ matrix if and only if one imposes all the $\psi_j\psi_i^*$'s products among the basis functions to be linearly independent.

However, if the constraints of proper normalization, hermiticity and idempotency of $\underset{\sim}{P}$ are further imposed, a necessary and sufficient condition for getting a unique solution from the X-ray data fitting is that 2N(M-N) $\psi_j\psi_i^*$ products are linearly independent. Imposing more than this number sufficiently satisfies the condition.

In both of these cases, our results are in plain accordance with previous publications made respectively by Harriman[49] and Levy et al.[69] Our derivation of necessary and sufficient conditions for the uniqueness of our method is based on a matrix analysis of the projection concept, while Levy et al. articulated their derivation on the continuous function representation of the problem, and Harriman on geometrical notions on the set of density matrices. Following the same spirit, an equivalent proof to our derivation may be found in any other representation.

III. Better Understanding the Projection Concept in X-ray Data Fitting.

For the sake of simplicity of geometrical representation, we shall first consider the case of a projection from an M=3-dimensional space onto an N=1-dimensional subspace. The generalization of our coming argumentation is pretty straightforward.

Following the usual geometrical representation of the Hilbert space in Quantum Mechanics, the state of the system is represented by the direction of the state ket vector $|\Phi_k>$, its length being arbitrarily chosen as unity. $|\Phi_k>$ is then described in the $\{|\psi_j>\}$ basis of M dimensions as $|\Phi_k> = \sum_{j=1}^{M} c_{kj} |\psi_j>$. The matrix representative of $\hat{\rho}^{kk} = |\Phi_k><\Phi_k|$ is a second degree tensor of this space.[38] Figure 13 geometrically represents this formalism.

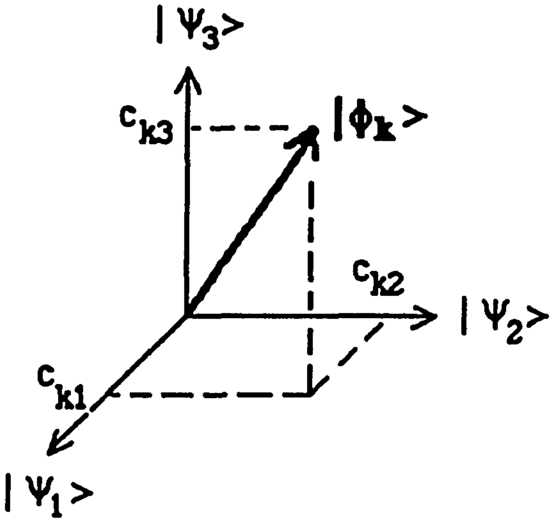


Figure 13. State Vector $|\Phi_k\rangle$ Described in a 3-Dimensional Hilbert Space Spanned by a Basis $\{|\psi_j\rangle\}$.

From these basis vectors, one may now construct the products $|\psi_i\rangle\langle\psi_j|$, which form a new basis spanning a new Hilbert space.

In this new representation of the Hilbert space, the state of the system is now described by $\hat{\rho}^{kk}$, which is in fact, the fundamental entity of the density matrix formulation of Quantum Mechanics. $\hat{\rho}^{kk}$ —as well as any other operator **A** (see appendix A for justifications)— may then be described as a vector in this new Hilbert space spanned by $|\psi_i\rangle\langle\psi_j|$ according to $\hat{\rho}^{kk} = \sum_{i\,j=1}^{M} p_{ji}^{kk} |\psi_i\rangle\langle\psi_j|$, where the p_{ji}^{kk}'s represent its coordinates. As previously mentioned, these two representations of the Hilbert space may be realized in a continuous basis, that we shall use now.

Based on this analysis, the X-ray fitting procedure may be understood as follows:

1. To any electronic system corresponds a (spinless) density function $P(\vec{r})$; to each point $P(\vec{r})$ of the density, construct a Hilbert space of M dimensions:

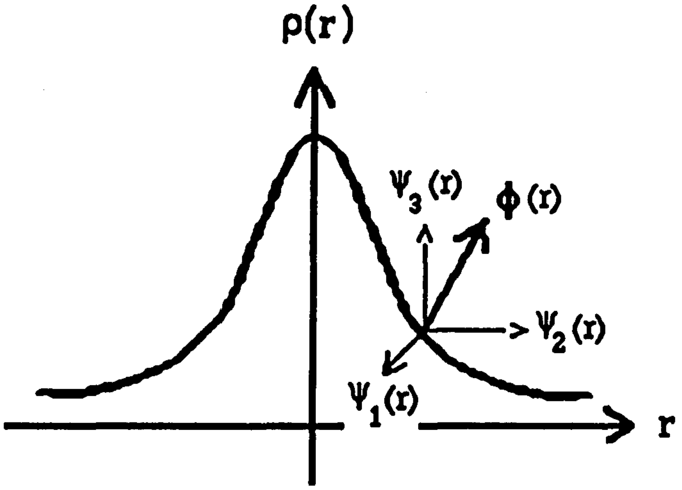


Figure 14. Construction on a Density Point of an M-Dimensional Hilbert Space, Spanned by a Basis $\{\psi_j(\vec{r})\}$.

2. Moreover, from this $\{\psi_j(\vec{r})\}$ basis, construct a new basis $\{\psi_i\psi_j^*(\vec{r})\}$ which spans a new Hilbert space; $\hat{\rho}^{kk}$ is then determined by its component in this basis of M^2 dimensions.

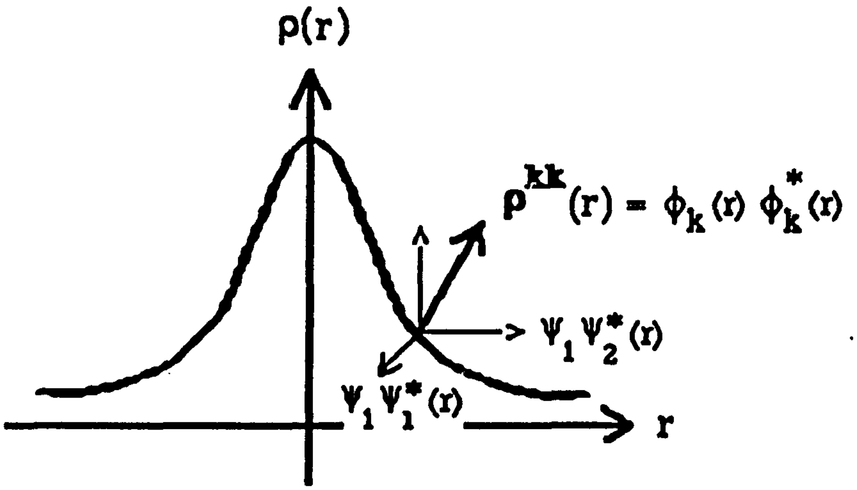


Figure 15. Construction on a Density Point of an M^2-Dimensional Hilbert Space, Spanned by a Basis $\{\psi_i\psi_j^*(\vec{r})\}$.

3. The fitting procedure is then the following: to uniquely determine the matrix representative of $\hat{\rho}^{kk}$ from X-ray experiment data, first choose the $\{\psi_j(\vec{r})\}$ basis so that at least K of its $\psi_i\psi_j^*$ products are linearly independent, which consequently reduces the Hilbert space number of dimensions from M^2 to 2N(M-N). Then, determine the p_{ji}^{kk} coordinates corresponding to these K linearly independent products by ensuring that

$$\begin{aligned} p^{kk}(\vec{r}) &= \mathrm{Tr}\,\underset{\sim}{P}\,\underset{\sim}{\psi}(\vec{r})\,\underset{\sim}{\psi}^{+}(\vec{r}) \\ &= \sum_{i\,j=1}^{M} p_{ji}^{kk}\,\psi_i(\vec{r})\psi_j^*(\vec{r}) \end{aligned} \tag{139}$$

best fits the X-ray experiment data. The p_{ji}^{kk}'s are obtained by projection of $p^{kk}(\vec{r})$ onto the basis functions, and this is in this sense that one may talk of the concept of projection in the context of X-ray density matrix determination.

IV. Partial Conclusion

A least square fitting to experimental X-ray structure factors, along with the constraints of N-representability, may be used to recover Quantum Mechanically valid reduced density matrices of any order. However, particular attention should be paid while following the Clinton-Massa's algorithm. Indeed, we have proved in this chapter that a unique solution to Clinton-Massa's equation is obtained only if one previously chose a basis with at least the same number of linearly independent products as the number of independent parameters in the $\underset{\sim}{P}$ matrix, namely 2N(M-N).

Doing so, one obtains then unique first and second-order reduced density matrices N-representable by a single Slater determinant and may use them to calculate any electronic property of the system. Although the experience proves that they deliver quite realistic physical results for simple systems, it is of considerable interest to try to recover more accurate expectations values. To this end, one would have to generate density matrices more accurate than the ones which are N-representable by a single Slater determinant, from a Quantum Mechanical description of the X-ray diffraction experiment. This shall be our goal in the coming chapter.

Chapter III

Correlated Determinant N-Representability of Reduced Density Matrices

A single Slater determinant comes from an Independent Particle Model of the electronic system, and as so, describes an N-body wavefunction where no correlation of the particles is taken into account except for that imposed by the antisymmetry following the Pauli principle. To get a more accurate model of the N-body wavefunction, it is then necessary to introduce correlation effects within the wavefunction. In the next section, we shall first briefly review the way to do so.

I. Beyond Single Slater Determinant Wavefunctions.

The main problem of N-particle Quantum Mechanics is to introduce a correlation factor to describe the mutual repulsion of identically charged particles, irrespective of their spin. This is not of crucial importance for particles with like spin, for they stay apart anyway as a result of antisymmetry. Indeed, even in the crude Independent Particle Model of the N-body wavefunction, correlation of like spin electrons is ensured, surely not as instantaneous interactions, but in an average way by the antisymmetry requirement of the Pauli principle. This latter makes the single Slater determinant vanish when two electrons with same spin have the same spatial coordinates. This property is, in fact, simply the well-known mathematical property of alternate multilinear forms restated in the context of Quantum Mechanics.

This notion of particle correlation is, however, of crucial importance for particles of unlike spin, which in a single Slater determinant are described as being free to come arbitrarily close together; property which is of course physically impossible as one may clearly understand by examining the simplest example of a multi-electron system, namely the helium atom: since the two electrons repel each other, when one electron is at a given position, it is energetically more favorable for the other to be far from the first one at that instant. This defines the so-called "coulomb hole" surrounding each electron which is actually the region in which the probability of finding another electron is small. The motions of electrons are consequently correlated with each other, and one speaks of electron correlation.[18,20]

There are two ways to provide for instantaneous electron correlation:

1. The first method is to introduce the interelectronic distances r_{ij} into the wavefunction, following for instance, the work of Hylleraas[95] who first described a two-body wavefunction as

$$\Psi(12) = N\,[\,e^{-\xi_1 r_1}\, e^{-\xi_2 r_2}\, (1 + b\, r_{12})] \qquad (140)$$

where ξ and b are variational parameters.
This is the term $(1 + b\, r_{12})$ which ensures the electron correlation by making the wavefunction, and consequently the probability of finding the two particles, smaller as the electrons come closer to each other (because of a smaller value of r_{12}). This is as it should be because of the repulsion of the electrons, as previously explained.

2. The second way is provided by the Configuration Interaction, which models the N-body wavefunction by including contributions from excited configurations. More information about this method may be found in the first chapter of this work or in the latest book written by McWeeny.[18]

Although the latter method quickly involves an exponentially growing number of Slater determinants as the number of electrons in the system increases, it would be perfectly legitimate to look for some conditions which would ensure N-representability of reduced density matrices by configuration interaction wavefunctions. However, we shall not investigate this possibility in the present work, where we shall concentrate our attention on N-representability by correlated determinant wavefunction, a class of wavefunctions known,[94-101] both from numerical experience and theoretical analysis to be potentially highly accurate solutions to the Schrödinger equation.

To summarize, since only first and second-order reduced density matrices are necessary to calculate any expectation value according to the Density Matrix Theory, we shall look for their expression as N-representable by correlated determinant wavefunction —from now on referred to as CDWF— according to

$$\begin{aligned} \rho_{CD,1}(1;1') &\equiv N \int \Psi_{CD}(1,2,\ldots N)\, \Psi_{CD}^{*}(1',2,\ldots N)\; d2\ldots N \\ \rho_{CD,2}(1,2) &\equiv N(N-1) \int \Psi_{CD}(1,2,\ldots N)\, \Psi_{CD}^{*}(1,2,3,\ldots N)\; d3\ldots N \end{aligned} \qquad (141)$$

where Ψ_{CD} stands for

$$\Psi_{CD}(1,2,\ldots N) = \Psi_{\underline{det}}(1,2,\ldots N) \prod_{i<j=1}^{N} (1 - \phi(ij)) \qquad (142)$$

When "det" is underlined, it indicates a determinant which delivers the considered "exact" density, for the only limitation to its exactness are experimental uncertainties, and not theoretical model.

The correlation function ϕ are defined symmetric to permutation in the coordinates of particle pairs so that the total wavefunction of the above equation is antisymmetric as required.

The very interest of this problem to be solved is that we use the "exact" density delivering a unique Slater determinant —recovered by the method of Clinton and Massa previously described— to generate CDWF. By reason of the inherent accuracy of the latter, density matrices N-representable by them inherit their properties of near exactitude.

II. *CD N-Representability of First and Second-Order Density Matrices.*

In a general way, CD N-representable density matrices of any order involve an integration of the complex conjugate product of CDWF's. It is thus interesting to start our investigation of this problem by first developing the integrand:

$$\Psi_{CD}(1..N)\,\Psi_{CD}^{*}(1'..N') = \Psi_{\underline{det}}(1..N)\,\Psi_{\underline{det}}^{*}(1'..N') \prod_{i<j\ i'<j'=1}^{N}(1-\phi(ij))(1-\phi(i'j'))) \tag{143}$$

Later, it proves to be convenient to collect the expansion of the $\phi(ij)$'s according to the definition

$$b(iji'j') \equiv - \phi(ij) - \phi(i'j') + \phi(ij)\,\phi(i'j') \tag{144}$$

and further simplify the notations —for the sake of clarity— by

$$b(iji'j') \equiv B_{ij} \tag{145}$$

The next step, then, is to evaluate the product term in the integrand, which is

$$\prod_{i<j=1}^{N} (1 + B_{ij}) = (1 + B_{12})(1 + B_{13})...(1 + B_{1N})(1 + B_{23})....(1 + B_{(N-1)N}) \tag{146}$$

At each iteration over i, j varies from (i+1) to N; by consequence, at the first iteration over i, j=2 to N which yields (N-1) B terms of the type B_{1j}, or more generally (N-i) B_{ij} terms which come from the contribution of i<j. The total number of $(1 + B_{ij})$ terms in the factorization of the above equation is then given by the Gauss formula:

$$\#\text{ of } (1 + B_{ij}) \text{ products} = (N-1) + (N-2) + ... + 1 = (N-1)N/2 \tag{147}$$

When completely expanding the products of equation 146, one obtains sums of correlation terms of the type B, BB, BBB etc., up to the highest power in B obtained by multiplying out all the B terms together; since there are a total of (N-1)N/2 of them, this is also the highest power in B. For the sake of simplicity, the expansion of the products is arranged in groups of same order in B, i.e.

$$\prod_{i<j=1}^{N}(1+B_{ij}) = 1+\Sigma\{B^{1}\text{ terms}\}+\Sigma\{B^{2}\text{ terms}\}+\ldots+\Sigma\{B^{(N-1)N/2}\text{ terms}\} \tag{148}$$

where

$$B^{i} \equiv BB\ldots\ldots B \quad \text{<--- (i times)} \tag{149}$$

It is then important to be able to exactly evaluate the number of B^i terms. To do so, we first collect the $\{B^i$ terms$\}$ in an array subdivided into boxes; each box is delimited at the right and left hand sides by the symbol " | | " and receives one B^i term. This notation, which may seem somewhat odd at first sight, later proves to be highly convenient.

1. The $\{B^1$ terms$\}$, defined by

$$\Sigma\{B^{1}\text{ terms}\} \equiv \sum_{i<j=1}^{N} B_{ij} \tag{150}$$

may then be regrouped as follows

$$\{B^{1}\text{ terms}\}= \boxed{|B_{12}|\,|B_{13}|\,|\ldots|\,|B_{1N}|\,|B_{23}|\,|\ldots.|\,|B_{2N}|\,|\ldots.|\,|B_{(N-1)N}|}$$

One may now count the number of elements in this set as previously done, and find a total of (N-1)N/2 terms.

2. The $\{B^2$ terms$\}$ are obtained by taking each B^1 term and multiplying it to the rest of the B^1 terms located at its right in the above array. The result may be written as

$$\Sigma\{B^2 \text{ terms}\} \equiv \sum_{i<j=1}^{N} \left\{ B_{ij} \left[\sum_{m=j+1}^{N} B_{im} + \sum_{k=(i+1)<m}^{N} B_{km} \right] \right\} \qquad (151)$$

and collected in an array as

$$\{B^2 \text{ terms}\} = \boxed{\,|B_{12}B_{13}|\,|\ldots|\,|B_{12}B_{(N-1)N}|\,|\ldots|\,|B_{(N-2)(N-1)}B_{(N-1)N}|\,}$$

From the way to generate all the BB terms from the B terms, it follows that the former are equivalent to the set of all subsets of two different elements taken from the set of the latter. The total number of BB terms is then equal to the number of combinations (without repetition) of two elements from the set of B terms, and is given by the combinatory theory to be

$$\#\text{ of } B^2 \text{ terms} = C^{2}_{B^1} = \frac{B^1!}{2!\,(B^1-2)!} \qquad (152)$$

or more generally for the $\{B^i \text{ terms}\}$,

$$\#\text{ of } B^i \text{ terms} = C^{i}_{B^1} = \frac{B^1!}{i!\,(B^1-i)!} \qquad (153)$$

Finally, one may check that this counting properly reduces to 1 for the last correlation term obtained by multiplying out all the B terms together (since $C^{B^1}_{B^1} = 1$).

The expansion of the correlation correction product into B terms of different orders as given in equation 148 may now be substituted into the fundamental definition of $\rho_{CD,1}(1;1')$ and $\rho_{CD,2}(1,2)$ to give

$$\begin{aligned}\rho_{CD,1}(1,1') &= \rho^{(0)}_{CD,1}(1,1') + \rho^{(1)}_{CD,1}(1,1') + \ldots\ldots + \rho^{(N(N-1)/2)}_{CD.1}(1,1')\\ \rho_{CD,2}(12) &= \rho^{(0)}_{CD,2}(12) + \rho^{(1)}_{CD,2}(12) + \ldots\ldots + \rho^{(N(N-1)/2)}_{CD.2}(12)\end{aligned} \tag{154}$$

where the superscripts are the order of the correlation terms which contribute to the density matrices. That is to say, the correlated determinantal correction to the i^{th} order to $\rho_{CD,1}(1,1')$ is defined as

$$\rho^{(i)}_{CD,1}(1,1') \equiv N\int \Psi_{\underline{det}}(1,2,\ldots N)\, \Psi_{\underline{det}}^{*}(1',2,\ldots N)\, \Sigma\,\{B^{i}\ \text{terms}\}\ d2\ldots N \tag{155}$$

The exact mathematical description of the CD N-representability of these density matrices would require to retain all contributions up to the last order, namely N(N-1)/2. In practice, however, the B terms are less than 1 and, by consequence, BBB<<1. We expect therefore molecular properties to be accurately calculated within the approximation of N-representability defined by retention of all terms up to the second order. CD N-representable density matrices are then approximated by

$$\begin{aligned}\rho_{CD,1}(1,1') &\cong \rho^{(0)}_{CD,1}(1,1') + \rho^{(1)}_{CD,1}(1,1') + \rho^{(2)}_{CD,1}(1,1')\\ \rho_{CD,2}(12) &\cong \rho^{(0)}_{CD,2}(12) + \rho^{(1)}_{CD,2}(12) + \rho^{(2)}_{CD,2}(12)\end{aligned} \tag{156}$$

II.1. CD Corrections to ρ_1 (1,1')

II.1.1. 0th Order CD Correction.

By definition, the zeroth order CD correction to $\rho_1(1,1')$ is given by

$$\rho^{(0)}_{CD,1}(1,1') \equiv N \int \Psi_{\underline{det}}(1,2,...N)\, \Psi_{\underline{det}}^{*}(1',2,...N)\, \{1\}\, d2...N \qquad (157)$$

and is simply the uncorrected density matrix N-representable by a single Slater determinant, i.e.

$$\rho^{(0)}_{CD,1}(1,1') = \rho_{\underline{det},1}(1,1') \qquad (158)$$

II.1.2. 1st Order CD Correction.

The first-order CD correction to $\rho_1(1,1')$ is obtained by multiplying the integrand $\Psi_{\underline{det}}$ $\Psi_{\underline{det}}^{*}$ by the collection of B^1 terms, according to equation 150, where i is taken to be unity. Since the $\{B^1$ terms$\}$ are the sum of B terms, given by

$$\Sigma\{B^1 \text{ terms}\} \equiv \sum_{i<j=1}^{N} B_{ij} \qquad (150)$$

$\rho^{(1)}_{CD,1}(1,1')$ may be cast into a summation of integrals, each integral taking account of the contribution of one and only one B term, i.e.

$$\rho^{(1)}_{CD,1}(1,1') = \sum_{i<j=1}^{N} \mathbb{I}(B_{ij}) \qquad (159)$$

where $\mathbb{I}(B_{ij}) \equiv N \int \Psi_{\underline{det}}(1,2,...N)\, \Psi_{\underline{det}}^{*}(1',2,...N)\, (B_{ij})\, d2...N \qquad (160)$

We shall now be willing to calculate each of these integrals in the hope of getting the expression of $\rho^{(1)}_{CD,1}(1,1')$. At this point, the reader might be glad to know that there is a way to greatly simplify these calculations, and it shall turn out that only two different contributions shall remain, namely of B_{1j} and B_{ij} type terms. This is what we shall prove now.

1. Contribution of B_{12}, B_{13} ..... B_{1N}.

The first of these integrals comes from the contribution of B_{12}, i.e.

$$\mathbb{I}(B_{12}) \equiv N \int \Psi_{\underline{det}}(1..N)\, \Psi_{\underline{det}}^{*}(1'..N)\, B_{12}\, d2...N$$

$$= N \int_2 \int_3 \cdots \int_N \Psi_{\underline{det}}(1..N)\, \Psi_{\underline{det}}^*(1'..N)\, B_{12}\, d2...N$$

$$= N \int_2 \left\{ \int_3 \cdots \int_N \Psi_{\underline{det}}(1..N)\, \Psi_{\underline{det}}^*(1'..N)\, d3...N \right\} B_{12}\, d2 \tag{161}$$

But, according to the fundamental definition of density matrices,

$$\rho_{\underline{det},2}(12;1'2) \equiv N(N-1) \int_3 \cdots \int_N \Psi_{\underline{det}}(1..N)\, \Psi_{\underline{det}}^*(1'..N)\, d3...N \tag{162}$$

relation which may be substituted into the integral to give

$$\mathbb{I}(B_{12}) \equiv \frac{N}{N(N-1)} \int \rho_{\underline{det}.2}(12;1'2)\, B_{12}\, d2 \tag{163}$$

By analogy, one may find for the B_{13} contribution

$$\mathbb{I}(B_{13}) \equiv \frac{N}{N(N-1)} \int \rho_{\underline{det}.2}(13;1'3)\, B_{13}\, d3 \tag{164}$$

A close examination of these last two results shows that the only difference between them is the dummy variable of integration —respectively, "2" and "3". By consequence, these integrals are essentially identical. The same reasoning may be used up to B_{1N}, and one concludes that

$$\mathbb{I}\,(B_{12}) = \mathbb{I}\,(B_{13}) = \;......\; = \mathbb{I}\,(B_{1N}) \qquad (165)$$

Interestingly enough, this integral property defines a relation of equivalence between the corresponding B terms which contribute to the same to $\rho^{(1)}_{CD,1}$ (1,1').

In the spirit of Set Theory, this relation of equivalence may be used to define a partition of the set of {B^1 terms} into classes of equivalence according to the following: a class of equivalence among the {B^1 terms} set is defined as being a subset of B^1 terms which contribute exactly to the same to $\rho^{(1)}_{CD,1}$ (1,1').

That is to say, since B_{12} to B_{1N} have equivalent contribution to $\rho^{(1)}_{CD,1}$ (1,1'), they form a class —written {B_{1j}, j=2...N}— whose integral is equal to the sum of the integral of each member of the class, i.e.

$$\mathbb{I}\,(B_{12} + B_{13} + ... + B_{1N}) = \mathbb{I}\,(\text{class } \{B_{1j},\ j=2...N\})$$

$$= \frac{N}{N(N-1)} \sum_{j=2}^{N} \int \rho_{\underline{det}.2}\,(1j;1'j)\, B_{1j}\, dj \qquad (166)$$

Since each contribution is the same, the integrals are identical and one may substitute the summation sign by the a multiplicative factor equal to the cardinal of the class —(N-1) in this case since j=2 to N—, yielding

$$\mathbb{I}\,(\text{class } \{B_{1j},\ j=2...N\}) = \frac{N}{N(N-1)}\,(N-1) \int \rho_{\underline{det}.2}\,(1j;1'j)\, B_{1j}\, dj$$

or $\mathbb{I}\,(\text{class } \{B_{1j},\ j=2...N\}) = \int \rho_{\underline{det}.2}\,(12;1'2)\, B_{12}\, d2$ (167)

2. Contribution of B_{23}, B_{24}, ... $B_{(N-1)N}$.

The first of these integrals comes from the contribution of B_{23}, i.e.

$$
\begin{aligned}
\mathbb{I}\,(B_{23}) &\equiv N \int \Psi_{\underline{det}}\,(1..N)\, \Psi_{\underline{det}}^{*}(1'..N)\, B_{23}\; d2...N \\
&= N \int_{2}\int_{3} ... \int_{N} \Psi_{\underline{det}}\,(1..N)\, \Psi_{\underline{det}}^{*}(1'..N)\, B_{23}\; d2...N \\
&= N \int_{2}\int_{3} \left\{ \int_{4} ... \int_{N} \Psi_{\underline{det}}\,(1..N)\, \Psi_{\underline{det}}^{*}(1'..N)\; d4...N \right\} B_{23}\; d2d3
\end{aligned}
\qquad (168)
$$

But, again, using the fundamental definition of density matrices,

$$
\rho_{\underline{det},3}\,(123;1'23) \equiv N(N-1)(N-2) \int_{4} ... \int_{N} \Psi_{\underline{det}}\,(1..N)\, \Psi_{\underline{det}}^{*}(1'..N)\; d4...N \qquad (169)
$$

relation which may be substituted into the previous integral to give

$$
\mathbb{I}\,(B_{23}) \equiv \frac{N}{N(N-1)(N-2)} \int \rho_{\underline{det}.3}\,(123;1'23)\, B_{23}\; d2d3 \qquad (170)
$$

By analogy, one may find that the B_{ij} ($i\neq 1<j$) contribution is

$$\mathbb{I}\,(B_{ij}) \equiv \frac{N}{N(N-1)(N-2)} \int \rho_{\underline{det}.3}\,(1ij;1'ij)\; B_{ij}\; didj \qquad (171)$$

which is the same integral as $\mathbb{I}\,(B_{23})$, except for the labelling of dummy variables of integration. Therefore one may conclude that these terms contribute to the same to $\rho^{(1)}_{CD,1}\,(1,1')$, and by consequence form another class of equivalence. Following the same logic as before, one finds that

$$\begin{aligned}\mathbb{I}\,(B_{23} + B_{24} + ... + B_{(N-1)N}) &= \mathbb{I}\,(\text{class }\{B_{ij},\ i=2...N<j\}) \\ &= \frac{N}{N(N-1)(N-2)} \sum_{i=2<j}^{N} \int \rho_{\underline{det}.3}\,(1ij;1'ij)\; B_{ij}\; didj\end{aligned} \qquad (172)$$

The cardinal of the class is evaluated using the Gauss formula, in the following way:

$$\left.\begin{array}{l} \text{when } i=2;\ j=3...N \Longrightarrow (N-2) \\ \text{when } i=3;\ j=4...N \Longrightarrow (N-3) \\ \qquad\vdots \\ \text{when } i=(N-1);\ j=1 \Longrightarrow 1 \end{array}\right\} \Longrightarrow \frac{(N-2)(N-1)}{2} \qquad (173)$$

and substituted into the previous integral to get

$$\mathbb{I}\,(\text{class }\{B_{ij},\ i=2...N<j\}) = \frac{N}{N(N-1)(N-2)}\; \frac{(N-2)(N-1)}{2} \int \rho_{\underline{det}.3}\,(1ij;1'ij)\; B_{ij}\; didj$$

or $$\frac{1}{2}\int \rho_{\underline{det}.3}(123;1'23)\, B_{23}\, d2d3 \tag{174}$$

3. Partial conclusion.

We finally found that the first-order CD correction to $\rho_1(1,1')$ may be simply cast into the contribution of two classes of equivalence among the $\{B^1$ terms$\}$ set, according to

$$\rho^{(1)}_{CD,1}(1,1') = \mathbb{I}\,(\text{class }\{B_{1j}, j=2...N\}) + \mathbb{I}\,(\text{class }\{B_{ij}, i=2...N<j\}) \tag{175}$$

which delivers the following result

$$\rho^{(1)}_{CD,1}(1,1') = \int \rho_{\underline{det}.2}(12;1'2)\, B_{12}\, d2 + \frac{1}{2}\int \rho_{\underline{det}.3}(123;1'23)\, B_{23}\, d2d3 \tag{176}$$

Before proceeding any further in the calculations, we shall first summarize the method used to get this last result, in the sake of finding a logic in our calculations. As we shall soon see, this shall considerably simplify the generalization of the calculation to any order of CD correction.

4. Summary.

To determine the CD correction to the first order to $\rho_1(1,1')$, one may follow this logical path:

- *Partition the $\{B^1$ terms$\}$ set into classes of equivalence.*

A class of equivalence among the $\{B^1$ terms$\}$ set is defined as being the subset of B^1 terms which contribute exactly to the same to $\rho^{(1)}_{CD,1}(1,1')$.

To find these classes, apply the following rules:

Rules:

a. The set of $\{B^1$ terms$\}$ is represented by an array, made of a juxtaposition of boxes; each box symbolizes a B term, and is further subdivided into two compartments —a left one (LC) and a right one (RC)— representing the two indices of a B_{ij} term:

$$B \equiv \boxed{\,|\quad\;|\,}$$

$$B_{ij} \equiv \boxed{\,|\,i\,|\,j\,|\,}$$

b. Given a set of N integers $\mathfrak{S} = \{1,2,...N\}$, distribute its elements into the compartments according to the logical rules:

R1: No more and no less than one integer per compartment.

R2: LC<RC (to avoid overcounting by a factor of 2), e.g. B_{11} and B_{21} cannot exist.

With this set of rules, symbolize all the B^1 terms by the array

$$\boxed{|\,1\,|\,2\,|\;|\,1\,|\,3\,|\;|\ldots|\;|\,1\,|\,N\,|\;|\,2\,|\,3\,|\;|\ldots|\;|\,i\,|\,j\,|\;|\ldots|\;|\,N-1\,|\,N\,|}$$

and further collect them into two distinct classes of equivalence:

$$\boxed{|\,1\,|\,j\,|} \quad \text{and} \quad \boxed{|\,i\,|\,j\,|}$$

Then write the CD correction to the first order to $\rho_1(1,1')$ as

$$\rho^{(1)}_{CD,1}(1,1') = \mathbb{I}\,(\text{class }\{B_{1j}\}) + \mathbb{I}\,(\text{class }\{B_{ij}\}) \qquad (177)$$

where each integral is obtained from equation 160, where the product of single Slater determinants is isolated in the multiple integral from the B term.

- *Integrate separately* $\Psi_{\underline{det}}(1..N)\,\Psi_{\underline{det}}^{*}(1'..N)$

To do so, determine the index p of the density matrix $\rho_{\underline{det},p}(1..p;1'..p)$ for the integral of each class, using the rule:

Rule:

$$\rho_{\underline{det},p}(1..p;1'..p) \equiv N(N-1)..(N-p+1)\int \Psi_{\underline{det}}(1..p..N)\,\Psi_{\underline{det}}^{*}(1'..p'..N)\, d(p+1)..N \qquad (178)$$

Equations 161 and 168 are then obtained for the integral of each class.

- *Determine the cardinal of each class of equivalence, according to the rules,*

Rules:

$$\begin{aligned} &1 + 2 + ...+ N = \frac{N(N+1)}{2} \\ &[1.2] + [2.3] + ...+ [N(N+1)] = \frac{N(N+1)(N+2)}{3} \\ &\vdots \\ &[1.2...p] + [2.3...(p+1)] +.....+ [N(N+1)...(N+p-1)] = \frac{N(N+1)...(N+p)}{(p+1)} \end{aligned} \qquad (179)$$

These rules may be considered as an extension of the Gauss formula. Since no reference has been found to check their veracity, a proof by recurrence of the most general one is given in appendix C.

Based on these combinatorial rules, the cardinal of the two classes $\{B_{1j}\}$ and $\{B_{ij}\}$ were found to be respectively (N-1) and (N-2)(N-1)/2.

- *Finally, evaluate the integral coefficient for each class according to*

Rules:

$$\text{Integral coefficient} = N \frac{1}{N(N-1)\ldots(N-p+1)} \text{ Card [Class]} \qquad (180)$$

One may then check that this reasoning yields the proper integrals for $\rho^{(1)}_{CD,1}(1,1')$ given by equation 176.

II.1.3. 2nd Order CD Correction.

Our goal is to determine the CD correction to $\rho_1(1,1')$ to the second order given by

$$\rho^{(2)}_{CD,1}(1,1') \equiv N \int \Psi_{\underline{det}}(1,2,\ldots N)\, \Psi_{\underline{det}}^{*}(1',2,\ldots N)\, \Sigma\, \{B^2 \text{ terms}\}\, d2\ldots N \qquad (181)$$

where the set $\{B^2$ terms$\}$ retains its previous definition.

Using a logical approach and set of rules similar to the ones elaborated for the correction to the first order, one finds classes of equivalence as well as their corresponding results as shown in Table 4.

Class	Cardinal	p in $\rho_{det,p}$	Integral coeff.
$B_{1j}B_{1l}$	1/2 (N-2)(N-1)	3	1/2
$B_{1j}B_{jl}$	1/2 (N-2)(N-1)	3	1/2
$B_{1j}B_{kj}$	1/2 (N-2)(N-1)	3	1/2
$B_{1j}B_{kl}$	1/2 (N-3)(N-2)(N-1)	4	1/2
$B_{ij}B_{il}$	1/6 (N-3)(N-2)(N-1)	4	1/6
$B_{ij}B_{jl}$	1/6 (N-3)(N-2)(N-1)	4	1/6
$B_{ij}B_{kj}$	1/6 (N-3)(N-2)(N-1)	4	1/6
$B_{ij}B_{kl}$	1/8 (N-4)(N-3)(N-2)(N-1)	5	1/8

Table 4. 2nd order Correlated Determinant Correction to ρ_1 (1,1')

In case the reader would be willing to check that the list of classes of equivalence is exhaustive, the reader might perform a simple test. Indeed, if no BB term were left over during the partition of the set of $\{B^2$ terms$\}$, the sum of the cardinal of each class should be equal to the total number of BB terms. That is to say, the reader may check that

$$\sum_{i} \text{Card [Class i]} = \text{Total \# } \{B^2 \text{ terms}\} = C^{\,2}_{N(N-1)/2} \tag{182}$$

According to this table, one finally obtain the accurate approximate CD correction to ρ_1 (1,1') up to the second order, as

$$\boxed{\begin{aligned}
&\rho_{CD,1}(1,1') \equiv \rho_{\underline{det},1}(11') + \\
&\Big\{ \int \rho_{\underline{det},2}(12;1'2)\, b(12;1'2)\, d2 + \tfrac{1}{2} \int \rho_{\underline{det},3}(123;1'23)\, b(23)\, d2d3 \\
&+ \tfrac{1}{2} \int \rho_{\underline{det},3}(123;1'23)\, [b(12;1'2)\, b(13;1'3) + b(12;1'2)\, b(23) + b(13;1'3)\, b(23)]\, d2d3 \\
&+ \tfrac{1}{2} \int \rho_{\underline{det},4}(1234;1'234)\, [b(12;1'2)\, b(34)]\, d2d3d4 \\
&+ \tfrac{1}{6} \int \rho_{\underline{det},4}(1234;1'234)\, [b(23)\, b(24) + b(23)\, b(34) + b(24)\, b(34)]\, d2d3d4 \\
&+ \tfrac{1}{8} \int \rho_{\underline{det},5}(12345;1'2345)\, [b(23)\, b(45)]\, d2d3d4d5 \Big\}
\end{aligned}}$$

(183)

where it is understood that the B and BB terms of different classes have been converted according to the rule of equation 145, i.e.

$$B_{ij} \equiv b(iji'j') \text{ and } b(ijij) \equiv b(ij), \tag{145}$$

the last convention being used for the sake of simplification of the writing.

II.2. CD Corrections to $\rho_2\,(12)$

The second-order density function which flows from the correlated determinant wavefunction, corrected up to the second order as defined in equation 156, may also be obtained by integration directly from the fundamental definition of density matrices — equation 178. The method for calculating $\rho_{CD,2}\,(12)$ up to the second order of correction is similar to the one extensively described in the previous subsection. For this reason, intermediate calculations will not be given, but only final results. The reader interested in recovering the details of the calculation may reconstruct a table of the type of Table 4 from the expression of $\rho_{CD,2}\,(12)$.

Within the approximation of N-representability defined by retention of all correlation terms up to the second order, one obtains the density function

$$\rho_{CD,2}\,(12) \equiv \rho_{\underline{det},2}\,(12) \; +$$

$$\Big\{ \rho_{\underline{det},2}\,(12)\, b(12) \; + \int \rho_{\underline{det},3}\,(123)\; [\, b(13) + b(23)\,]\; d3$$
$$+ \frac{1}{2} \int \rho_{\underline{det},4}\,(1234)\; b(34)\; d3d4$$

$$+ \int \rho_{\underline{det},3}\,(123)\, [\, b(12)\, b(13) + b(12)\, b(23) + b(13)\, b(23)\,]\, d3$$
$$+ \frac{1}{2} \int \rho_{\underline{det},4}\,(1234)\, [\, b(13)\, b(14) + b(23)\, b(24) + b(12)\, b(34) + b(13)\, b(34)$$

$$+ b(14)\, b(34) + b(23)\, b(34) + b(24)\, b(34)\,]\, d3d4$$

$$
\begin{aligned}
&+ \int \rho_{\underline{det},4}(1234)\,[\,b(13)\,b(24)\,]\,d3d4 \\
&+ \frac{1}{2} \int \rho_{\underline{det},5}(12345)\,[\,b(13)\,b(45) + b(23)\,b(45)\,]\,d3d4d5 \\
&+ \frac{1}{6} \int \rho_{\underline{det},5}(12345)\,[\,b(34)\,b(45) + b(34)\,b(35) + b(35)\,b(45)\,]\,d3d4d5 \\
&+ \frac{1}{8} \int \rho_{\underline{det},6}(123456)\,[\,b(34)\,b(56)\,]\,d3d4d5d6 \Big\}
\end{aligned}
\qquad (184)
$$

One may convince oneself of the correctness of this last equation by checking that the general relationship between density matrices

$$\rho_1 \equiv \frac{1}{(N-1)} \int \rho_2 \, d2 \qquad (185)$$

still holds between $\rho_{CD,1}(1)$ and $\rho_{CD,2}(12)$. As previously shown, both of these density matrices were derived independently, i.e. without using such a relationship.

III. A Theoretical Application of CD N-Representable Density Matrices: Accurate Approximation of the Unknown HK Functional.

The fundamental theorem of Hohenberg and Kohn[42] (HK) asserts that all electron properties are functionals of the electron density. For instance, the energy of a system is defined as

$$E[\rho] \equiv \int V(\vec{r})\,\rho(\vec{r})\,d\vec{r} + F[\rho] \qquad (186)$$

where V is the external potential of the system, and F the HK functional,[42]

$$F[\rho] \equiv \langle \Psi[\rho] \,|\, T + U \,|\, \Psi[\rho] \rangle \qquad (187)$$

where T and U are the system's kinetic energy operator and interaction energy operator respectively, and Ψ the wavefunction of the system. F is a functional of the density because Ψ is such a functional.

This expression provides an admirably compact form of the total energy of the system, calculated from the electron density. The only remaining problem, however, is that F [ρ] is still unknown. By consequence, its evaluation is still an outstanding problem and we show in this work that we can calculate a very accurate upper-bound of F [ρ], using our correlated determinant N-representable density matrices previously obtained.

Indeed, since the usual form of the non-relativistic Hamiltonian containing only one and two-body terms is (in atomic units)

$$\mathbf{H} \equiv \sum_{i=1}^{N} \mathbf{h}\,(i) + \sum_{i<j}^{N} \mathbf{g}\,(i,j) \qquad (188)$$

the total energy of the system, defined as the expectation value of the Hamiltonian **H**, is then given by

$$E = \int [\mathbf{h}(1)\, \rho_1(1;1')]_{1'\to 1}\, d1 + \frac{1}{2}\int [\mathbf{g}\,(1,2)\, \rho_2(12)]\, d1d2 \qquad (189)$$

Using our CD density matrices, one obtains then the expression of the unknown HK functional, as

$$F\,[\rho] = -\frac{1}{2}\int [\nabla_1{}^2\, \rho_{CD.1}\,(1;1')]_{1'\to 1}\, d1 + \frac{1}{2}\int \frac{\rho_{CD.2}\,(12)}{|\,1-2\,|}\, d1d2 \qquad (190)$$

where $\rho_{CD,1}$ (1;1') and $\rho_{CD,2}$ (12) are understood to be the expressions given by equations 183 and 184.

The point is these CD density matrices may be obtained as functionals of the density — from the experiment of X-ray diffraction— and therefore, also F. This claims an interest based upon the known accuracy obtainable with wavefunctions of correlated determinant form.

IV. Partial Conclusion.

Coherent X-ray diffraction experiment on a crystal allows one to recover electron density matrices N-representable by a single Slater determinant. However, such a wavefunction reduces the accuracy of the density matrices that it N-represents, for it does not take account of the electron correlation —except for that imposed by the antisymmetry requirement. A better model of the wavefunction is thus necessary. This is provided by a correlated determinant wavefunction, which may be constructed from the X-ray single Slater determinant, delivering the exact density.

For the first time, we have shown in this chapter how to calculate density matrices N-representable by such a correlated determinant wavefunction, up to the second-order of correlation. The importance of such a result lies in the Quantum Mechanical validity of these density matrices, their high accuracy conferred by the CD wavefunction, as well as their property of being explicit functionals of the electron density. As so, they allow one to accurately calculate any molecular property of the system, not by solving the Schrödinger equation but by following the Density Functional Theory.

In particular, they can be used to accurately approximate the unknown HK functional. By showing that one does not have to restrict oneself to single Slater determinants to N-represent density matrices, it is our hope that this work will contribute to open a whole new area of research.

The last part of this work will deal with a numerical application of CD N-representability. Indeed, we shall study how to evaluate the correlation energy of a two-electron system —namely the helium atom— using our calculated CD N-representable density matrices.

Chapter IV

Correlation Energy Calculated from Correlated Determinant N-Representable Density Matrices

I. Development of a General Formalism.

Our calculated density matrices N-representable by a correlated determinant wavefunction —up to the second order of correlation— may be used to calculate the correlation energy of the system.

To this end, it is first convenient to write our density matrices in the following abbreviated notation

$$\rho_{CD,2}\,(12) \equiv \rho_{\underline{det},2}\,(12) + a_2\ (12) \qquad (191)$$

$$\rho_{CD,1}\ (1;1') \equiv \rho_{\underline{det},1}\ (1;1') + a_1\ (1;1') \qquad (192)$$

Clearly a_1 and a_2 are simply definitions of corrections which must be added to the single Slater determinant density matrices in order to obtain the CD density matrices. Comparison of this last pair of equations to the CD density matrix equations given earlier shows that a_1 and a_2 are given explicitly by the expressions contained in curly brackets in the earlier equations, i.e. 183 and 184 respectively.

One may then use these expressions to calculate the correlation energy in a generalized sense using as reference state an exact density determinant, i.e.,

$$E_c = E - E_{\underline{det}} \qquad (193)$$

where E retains its previous definition —equation 189— and $E_{\underline{det}}$ is given by

$$E_{\underline{det}} = \int [h(1)\, \rho_{\underline{det}.1}(1;1')]_{1'\to 1}\, d1 \; + \; \frac{1}{2}\int [g\,(1,2)\, \rho_{\underline{det}.2}(12)]\, d1d2 \quad (194)$$

Substituting equations 191 and 192 in E, one obtains for E_c,

$$E_c = -\frac{1}{2}\int [\nabla_1{}^2\, a_1\,(1;1')]_{1'\to 1}\, d1 \; + \; \frac{1}{2}\int \frac{a_2\,(12)}{|\,1\text{-}2\,|}\, d1d2 \qquad (195)$$

where, on the right hand side of this expression, the first term represents the kinetic energy contribution while the second term is the potential energy contribution arising from interelectron repulsion.

It is apparent that such an equation provides an admirably compact expression for the correlation energy. From a density functional point of view, the efficiency of such expressions arises from the fact that the correlation corrections a_1 and a_2 may be fixed entirely by the density. That is, the exact density Slater determinant carries the very information required for its own correction. Indeed, because the very definition of $\rho_{\underline{det},1}(1;1')$ forces it to reduce to the exact density when $1'\to 1$ —as described in equation 128— one may rewrite equation 192 as

$$a_1\,(1;1')\,\big|_{1'\to 1} = 0 \qquad (196)$$

In other words, this must be true in order for $\rho_{\underline{det},1}(1;1')$ to satisfy its defining characteristic of delivering the exact density. Out of all possible Slater determinants, an essential elegance is attached to an exact density determinant $\Psi_{\underline{det}}$ by virtue of the exact correction to the determinantal one-body density matrix vanishing for the diagonal elements. This immediately places an exact condition upon the diagonal elements of the correction to the two-body density matrix, which is,

$$\int a_2(12)\,d2 = 0 \tag{197}$$

which may be used as a density functional condition to fix the correlation corrections to exact density determinantal quantities. One may satisfy oneself as to the correctness of this last equation by invoking the general relationship holding between density matrices as given in equation 185, and simultaneously requiring equation 191 to hold. Now these considerations are suggestive that with respect to all possible correlated-determinants those related to exact density orbitals will be perspicuous in their simplicity.

To test such a way of calculating the correlation energy, this formalism will be developed in the case of the two-electron helium atom, where the CD density matrices — equations 183 and 184— simplify to the expressions

$$\rho_{CD,2}(12) \equiv \rho_{\underline{det},2}(12) + \rho_{\underline{det},2}(12)\,\underline{b}(12) \tag{198}$$

and

$$\rho_{CD,1}(1;1') \equiv \rho_{\underline{det},1}(1;1') + \int \rho_{\underline{det},2}(12;1'2)\,b(12;1'2)\,d2 \tag{199}$$

Note here that in this two-electron case, the CD N-representability of the above density matrices is **rigorously exact.**

The condition following from the vanishing correction to diagonal elements of the exact density determinant's one-body density matrix —equation 197— becomes then

$$\int \rho_{\underline{det}.2}(12)\, b(12)\, d2 \;=\; 0 \qquad (200)$$

which may be used as a density functional condition to fix b.

To this end, cast the correlation function used in equation 142 to define the CDWF, namely $\phi(12)$, in the density functional form

$$\phi(12) = [1-\Phi(\vec{R})\,(1+\frac{r}{2})]\, e^{-\beta^2 r^2} \qquad (201)$$

where r is the magnitude of an interparticle vector ($\vec{r}$) given by

$$r \equiv |\,1-2\,| \qquad (202)$$

and $\vec{R}$ is a pair center of mass vector given by

$$\vec{R} \equiv \frac{1}{2}\,(1+2) \qquad (203)$$

It is understood that 1 and 2 refer to the vector positions of both electrons. The function β is defined[100] through the density according to

$$\beta(\vec{R}) = q\, \rho^{1/3}(\vec{R}) \qquad (204)$$

where q is a constant to be determined variationally.

Now the unknown function $\Phi(\vec{R})$ may be determined by forcing it to satisfy equation 200, and it becomes thereby a functional of the density. Colle and Salvetti[100] have solved equation 200 **approximately**, using equation 201 and have obtained for $\Phi(\vec{R})$ the density functional

$$\Phi(\vec{R}) = \frac{\sqrt{\pi}\,\beta(\vec{R})}{1+\sqrt{\pi}\,\beta(\vec{R})} \tag{205}$$

Later on, we shall see that it is possible to solve equation 200 **exactly** and use the exact $\Phi(\vec{R})$ in our formalism. Using $\Phi(\vec{R})$, $\beta(\vec{R})$ and $\phi(12)$ to write b(12;1'2) —see equation 144— one has expressions for the density matrices —equations 198 and 199— which are completely defined by the density, except for the variational constant q. The correlation energy —equation 195— is, then, in this simple case

$$E_c \equiv T_c + V_c$$

$$= -\frac{1}{2}\int \left[\nabla_1^2 \left(\rho_{det,2}(12;1'2)\, b(12;1'2)\right)\right]_{1'\to 1} d1d2 + \frac{1}{2}\int \frac{\rho_{det,2}(12)\, b(12)}{|1-2|}\, d1d2 \tag{206}$$

To start our development of a general E_c formalism in the case of a two-electron system, we shall first choose a coordinate system. Here, we are dealing with the well-known[102] problem of describing two identical particles moving under the influence of a mutual central force and inter-repulsion. Such a system has six degrees of freedom and hence six independent generalized coordinates. One may choose these to be the spin-space variables 1 and 2 as in the previous equation. However, if one is not interested in knowing exactly the spin of each electron, one may integrate over the spin variable, getting consequently the E_c expression

$$E_c = -\frac{1}{2} \int \left[\nabla_1^{\,2} \left(P_{\underline{det}.2} (12;1'2)\, b(12;1'2) \right) \right]_{1' \to 1} d\vec{r}_1\, d\vec{r}_2 + \frac{1}{2} \int \frac{P_{\underline{det}.2} (12)\, b(12)}{| \vec{r}_1 - \vec{r}_2 |}\, d\vec{r}_1\, d\vec{r}_2 \qquad (207)$$

where, for the sake of commodity, the variables 1 and 2 are kept as before in $P_{\underline{det}.2}$ and b but should now be understood as symbolizing the spinless position vectors $\vec{r}_1$ and $\vec{r}_2$, respectively. Although this convention may seem at first sight quite confusing, this should not lead to any problem in the future, for the meaning of 1 and 2 is determined by the variables of integration.

Furthermore, the six independent coordinates may as well be chosen as the three components of the radius vector to the center of mass, $\vec{R}$, plus the three components of the interparticle vector $\vec{r}$, as defined in equations 202 and 203.

Out of the two possibilities, the latter will be used for calculating the integral defining the correlation energy, as it proves later to be more convenient.

Furthermore, we chose to describe the two vectors in spherical coordinate system.

In such a spinless formalism, the second-order reduced density matrix is defined, according to McWeeny[19], as

$$P_{\underline{det},2} (12;1'2') = P_{\underline{det},1} (1;1')\, P_{\underline{det},1} (2;2') - \frac{1}{2}\, P_{\underline{det},1} (2;1')\, P_{\underline{det},1} (1;2') \quad (208)$$

where $P_{\underline{det},1}$ retains its previous definition

$$P_{\underline{det},1}(p;q') = 2\,\mathrm{Tr}\,\underset{\sim}{P}\ \underset{\sim}{\psi}(p)\ \underset{\sim}{\psi}^{+}(q')$$

$$= 2\sum_{i\,j=1}^{M} p_{ij}\,\psi_j(p)\,\psi_i{}^{*}(q') \tag{209}$$

and the population coefficients are given by

$$p_{ij} = \sum_{k=1}^{N} c_{ki}{}^{*}\,c_{kj} \tag{210}$$

However, in the helium case, only one doubly-occupied real atomic orbital is used, defined as

$$\phi(q) = \sum_{j=1}^{M} c_j\,\psi_j(q) \tag{211}$$

which reduces the p_{ij}'s to $p_{ij} = c_i\,c_j$, where the c's are LCAO coefficients. Note that the factor 2 in equation 209 is here in order to take account of the double-occupancy of the real orbital.

We now make an important statement valid throughout the rest of this work: we are willing to test our formalism for helium atom; to this end, we shall use for $P_{\underline{det},2}$ the Hartree-Fock determinant analog $P_{HF,2}$ which is readily available through the work of Clementi.

Such a choice is motivated by the fact that considerable numerical experience[50,51,58-65] indicates that these density matrices are very nearly the same. One accurately approximates, then, $P_{\underline{det},2}$ by

$$P_{\underline{det},2}\ (12;1'2) \cong P_{HF,2}\ (12;1'2) \tag{212}$$

where $P_{HF,2}$ (12;1'2) is obtained from equations 208 and 209, in which ψ_i's are the Slater type functions

$$\psi_i\,(\vec{r}\,) \equiv \frac{1}{\sqrt{\pi}}\,\xi_i^{\,3/2}\ e^{-\xi_i r} \tag{213}$$

and the c's and ξ's have numerical values extracted from Clementi's tables[103] and given in Table 5.

i	c_i	ξ_i
1	0.78503	1.43000
2	0.20284	2.44150
3	0.03693	4.09960
4	-0.00293	6.48430
5	0.00325	0.79780

Table 5. He Clementi's basis functions.

The details of the rest of the calculations are regrouped in appendix D.

The difficulty with using such a general formalism is that it carries out six variables of integration, namely the spherical variables required to describe the vectors $\vec{r}$ (r, θ and φ) and $\vec{R}$ (R, Θ, Φ). It may then be wise to try first to use some approximations to simplify the calculations.

II. *Test of an Approximation: McLaurin's Series Expansion to Zeroth Order of $P_{\underline{det},2}$ (12).*

II.1. Approximation and Formalism.

The general correlation energy formalism —developed in the previous section and in its accompanying appendix— may be greatly simplified if one approximates the spinless second-order density function $P_{\underline{det},2}$ (12) by its expansion into a McLaurin's series about $\vec{r}$. Within such a choice, the simplest —and also the crudest— approximation is to retain only the leading term of the series. To obtain its expression, first recall the definition of $P_{\underline{det},2}$ (12) from the more general equation 208, which is

$$P_{\underline{det},2}\,(12) = P_{\underline{det},1}\,(1)\,P_{\underline{det},1}\,(2) - \frac{1}{2}\,P_{\underline{det},1}\,(2;1)\,P_{\underline{det},1}\,(1;2)$$

and approximate $P_{\underline{det},1}$'s at $\vec{r} = 0$ (or $\vec{r}_1 = \vec{r}_2 = \vec{R}$) by

$$P_{\underline{det},1}\,(1)|_{\vec{r}_1 = \vec{R}} = P_{\underline{det},1}\,(2)|_{\vec{r}_2 = \vec{R}} = \left[P_{\underline{det},1}\,(2,1) = P_{\underline{det},1}\,(1,2)\right]_{\vec{r}_1 = \vec{r}_2 = \vec{R}}$$

$$\approx P_{HF,1}\,(\vec{R}) \qquad (214)$$

evaluated at point $\vec{R}$,

where $P_{HF,1}\,(R)$ is understood to be the spinless Hartree-Fock determinant density evaluated at point $\vec{R}$, and given by

$$\begin{aligned} P_{HF,1}\,(\vec{R}) &= 2\,\phi^2\,(\vec{R}) \\ &= 2 \sum_{i\,j=1}^{M} p_{ij}\,\psi_j\,(\vec{R})\,\psi_i\,(\vec{R}) \end{aligned} \qquad (215)$$

For the sake of simplification of notations, the above $P_{HF,1}\,(\vec{R})$ will be, from now on, written $\rho(\vec{R})$. This finally leads to the expression

$$P_{\underline{det},2}\,(12)\,|_{\vec{r}=0} \approx P_{\underline{det},2}\,(\vec{R},0) = \frac{1}{2}\,\rho^2(\vec{R}) \qquad (216)$$

With such a McLaurin's series expansion, both the potential and kinetic contributions to the correlation energy reduce to much simpler expressions, in which the variables of integration may be separated:

1. The former is given by

$$V_c = \frac{1}{2}\int P_{\underline{det},2}\,(\vec{R},0)\;d\vec{R}\;\int \frac{b(12)}{r}\,d\vec{r} \qquad (217)$$

an expression which allows one to analytically integrate over the four spherical angles (namely Θ, Φ, θ and φ), as well as over r; this leads, then, to a function of R which may be numerically integrated, as we shall soon see.

2. The latter is described in the reduced coordinate system by

$$T_c \equiv -\frac{1}{2}\left(T_{c_1} + 2\,T_{c_2} + T_{c_3}\right) \tag{218}$$

where T_{c_1}, T_{c_2} and T_{c_3} —whose general definitions are given by equations 22, 23 and 24 in appendix D— reduces, as a result of using the McLaurin's series approximation, to

$$\begin{aligned} T_{c_1} &\equiv T_{c_1,R} + T_{c_1,r} \\ T_{c_2} &= 0 \\ T_{c_3} &= 0 \end{aligned} \tag{219}$$

where

$$T_{c_1,R} = \frac{1}{4}\int P_{\underline{det}.2}(\vec{R},0)\, d\vec{R} \int \left[\nabla^2_{\vec{R}}\, b(12;1'2)\right]_{\vec{R}' \to \vec{R}} d\vec{r} \tag{220}$$

and

$$T_{c_1,r} = \int P_{\underline{det}.2}(\vec{R},0)\, d\vec{R} \int \left[\nabla^2_{\vec{r}}\, b(12;1'2)\right]_{\vec{r}' \to \vec{r}} d\vec{r} \tag{221}$$

The reader is referred to appendix E for the details of the calculations.

We now make an important point: such a formulation of the correlation energy has the tremendous advantage of allowing us to physically interpret each of its contribution. We are, indeed, able to suggest, for the first time, a physical picture of the correlation energy, as follows: if one recalls the fundamental physical meaning attached to spinless density functions, one may interpret $P_{\underline{det},2}(\vec{R},0)$ as being the probability of finding the center of mass of the two-body system at position $\vec{R}$. Then, at each point $\vec{R}$, one evaluates the integral over $\vec{r}$ in V_c, $T_{c_1,r}$ and $T_{c_1,R}$ —see equations 217, 220 and 221— which respectively represents the potential and kinetic energy of the reduced mass and the kinetic energy of the center of mass. Our expressions may thus be viewed as a sort of convolution integral in the sense that the calculation of each of these three physical quantities is spread over the center-of-mass density.

However, a close examination of the above formulae shows that they are not in complete agreement with a previous formalism developed in the same context.[104] As a consequence, it is a matter of importance to compare the two formalisms and their respective results. This is what we shall do in the next two sections, where both analytical and numerical integrations will be performed using a computer program —based on each formalism— written in a new, highly powerful language called Mathematica™.[105]

II.2. A Previous Formalism: Approximate N-Representability.

As previously mentioned, approximating $P_{\underline{det},2}$ (12) by the leading term of its McLaurin's series expansion about $\vec{r}$ allows one to calculate E_c by, first, analytically integrating over all variables but R, then numerically evaluating the remaining integral.

Based on this approximation, a previous thesis[104] subdivided the kinetic energy contribution to E_c into three parts, according to equation 218. The reader is referred to appendix E for the general definition of these terms, and more specifically to reference 104 for their detailed expressions.
However, the previous thesis found **non-zero** contributions to T_{c_2} and T_{c_3}, both analytically and numerically. Since this result is in apparent disagreement with our formalism developed in the previous section, we shall here further investigate the previous formalism.

II.2.1. Analytical and Numerical Integrations.

A computer program was written using the analytical features of Mathematica™ to check the integrations over both angle and r in the formalism developed in the previous thesis, and led to strictly identical results as a function of R.

Based on these results, the remaining integration over R was realized by using the Mathematica™ built-in numerical integration, according to a procedure that we shall now briefly outline: in theory, the integration over R is to be carried from 0 to +∞ in order to cover the whole space. However, for the purpose of numerically integrating, one has to truncate the upper limit to a finite number R_{imax}. This procedure is legitimized by realizing that integrands in V_c, T_{c_1}, T_{c_2} and T_{c_3} quickly fade to 0 as R —the distance in atomic units at which the center of mass may be found— increases, as is shown in Figures 16 to 20 for helium atom and one of its isoelectronic ion, namely Li^+. Numerical tests proved that R_{imax} never had to exceed 10 atomic units in order to reach a constant value of the integral under calculation.

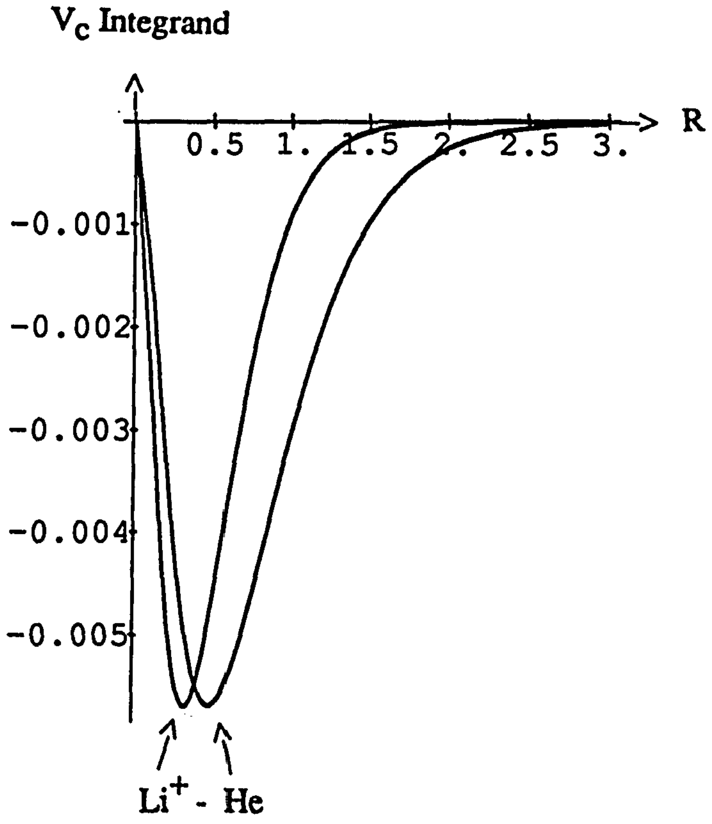


Figure 16. He and Li^+: Potential Energy Contribution: V_c Integrand as a Function of R at q=1.17.

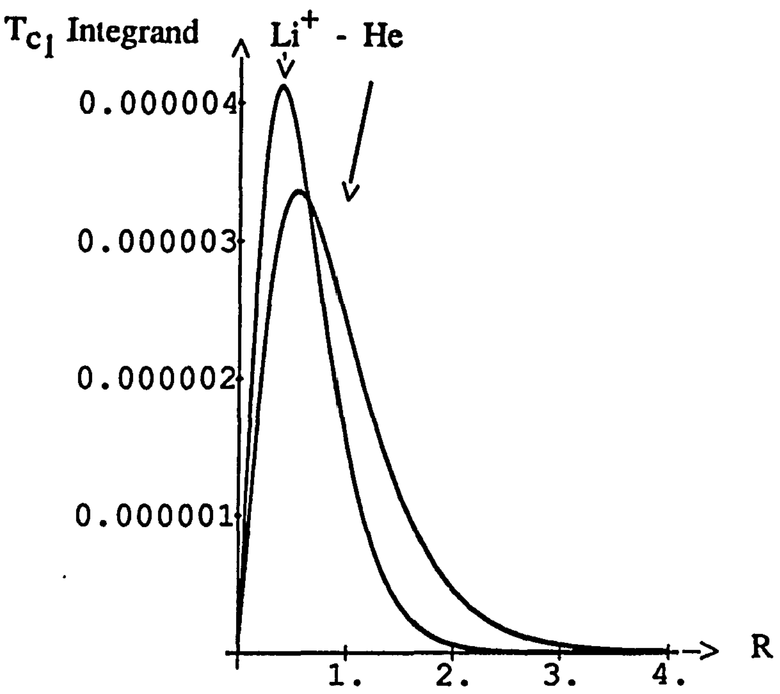


Figure 17. He and Li$^+$: Kinetic Energy Contribution: T_{c_1} Integrand as a Function of R at q=1.17.

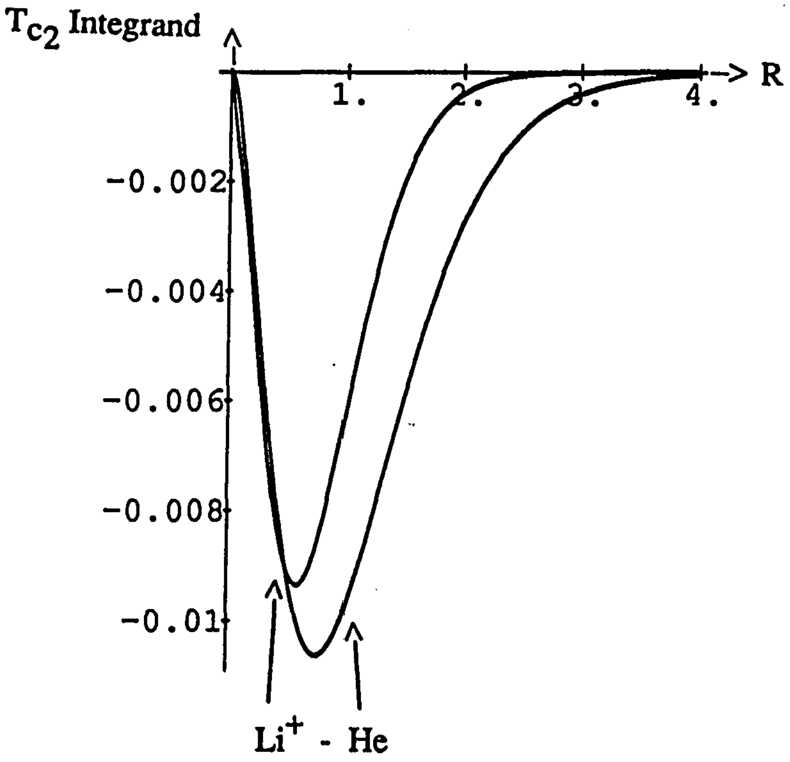


Figure 18. He and Li$^+$: Kinetic Energy Contribution: T_{c_2} Integrand as a Function of R at q=1.17.

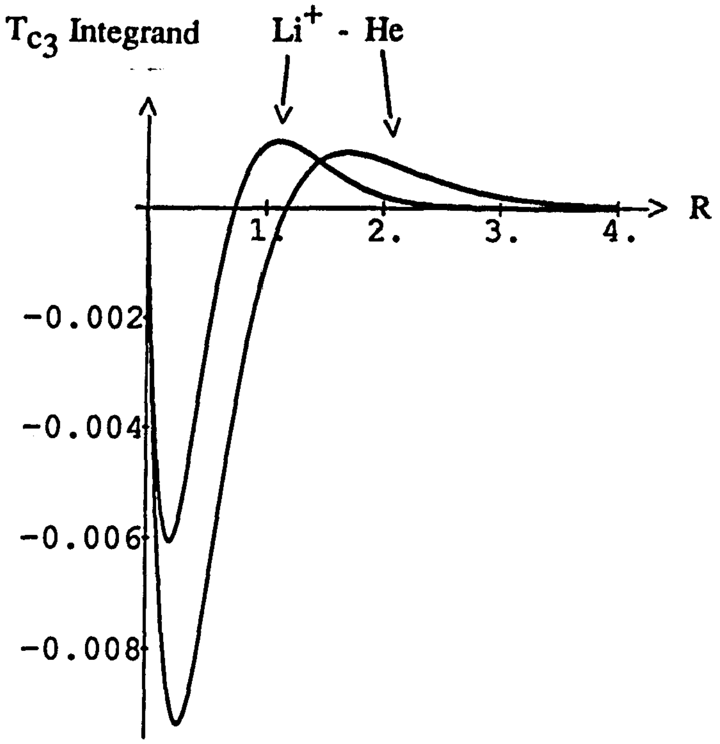


Figure 19. He and Li$^+$: Kinetic Energy Contribution: T_{c_3} Integrand as a Function of R at q=1.17.

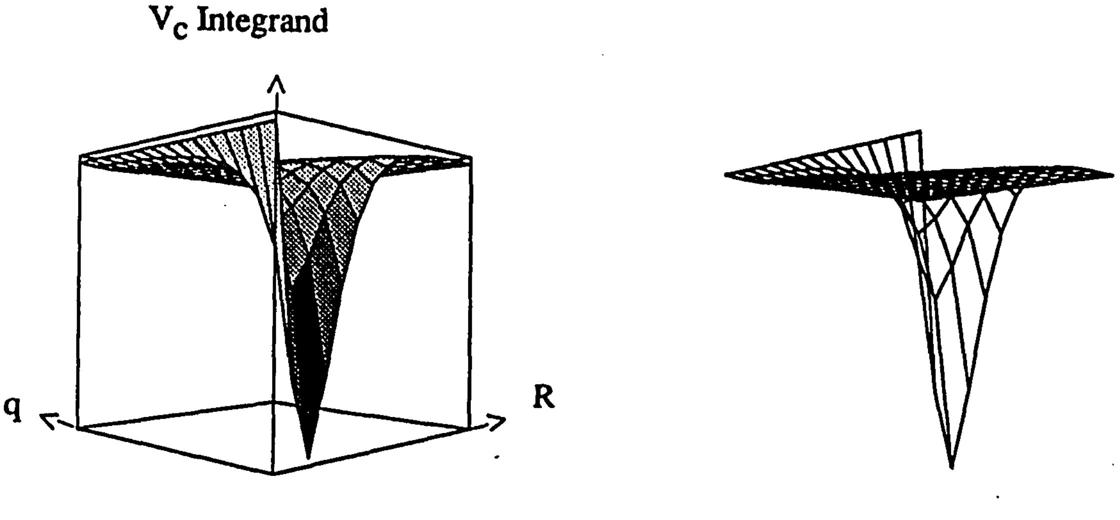


Figure 20. He Atom: Potential Energy Contribution: V_c Integrand as a Function of R and the Variational Parameter q ($0 \leq R \leq 3.5$, $0.5 \leq q \leq 3$).

Moreover, Table 6 compares a few values obtained for He atom using our program — based on the formalism of reference 104— to the results obtained in this previous work.

q	V_c		T_c		E_c	
	This work	Ref. 104	This work	Ref. 104	This work	Ref. 104
1.00	-0.308507	-0.308507	0.274006	0.274029	-0.034501	-0.034478
1.10	-0.244380	-0.244380	0.203327	0.203343	-0.041053	-0.041037
1.17	-0.209925	N.P.	0.168029	N.P.	-0.041896	-0.041882
1.20	-0.197182	-0.197182	0.155469	0.155481	-0.041713	-0.041700

(N.P.= Not Provided)

Table 6. He Atom: Potential and Kinetic Energy Contributions to Correlation Energy, in atomic units, as a Function of Variational Parameter q.
Formalism of Reference 104: Comparison of our Results (Obtained Using Mathematica™) to Results of Reference 104.

From this table, it appears that, compared to previous results,[104] our program delivers exactly the same values of the potential contribution V_C, and slightly lower values of the kinetic contribution T_C, resulting in a lower minimal value of E_C. Although this last value is even closer to the exact one ($E_{C,exact}$ = - 0.0424 [au]),[103] the difference between the numbers generated by the two programs starts at the fifth digit after the decimal point, and is, by consequence, physically insignificant.

For the helium isoelectronic ion Li^+, the obtained minimal E_C value was found in the previous thesis[104] to be much more inaccurate than for He atom (E_C (Li^+) = -0.0270 compared to $E_{C,exact}$ (Li^+) = -0.0435). This was also confirmed by our program, and is not at all surprising if one observes the differences in the integrand curve shape. Indeed, plots 16 to 20 show that the inaccuracy in the Li^+ value is not due to the employed numerical technique of integration, but to the formalism itself.

These integrations being checked, the only remaining possibility to account for the difference in T_{C_2} and T_{C_3} would be in finding a discrepancy in the formalism itself. We shall now examine such a possibility.

II.2.2. N-Representability Test.

According to the general formalism developed in section I. of this chapter, if $\rho_{\underline{det},1}(1;1')$ is to satisfy its defining characteristic of reducing to the exact density when 1'->1 —as described in equation 196— then, an exact condition is obtained on the diagonal elements of the N-representable one-body density matrix, as given by equation 200

$$\int \rho_{\underline{det}.2}\,(12)\; b(12)\, d2 \; = \; 0 \qquad (200)$$

This relation may be further used as a density functional condition to fix b, by solving for the unknown function $\Phi(\vec{R})$.

Then, integrating over the spin, approximating $P_{\underline{det},2}$ (12) by the leading term of its McLaurin's series expansion about $\vec{r}$, and finally expanding b(12) according to equation 144, transform this exact N-representability condition into

$$P_{\underline{det},2}\,(\vec{R},0) \int (\phi^2(12) \; - 2\, \phi(12))\;\; d\vec{r} \; = 0 \qquad (222)$$

an equation still exact, but within the approximation of the McLaurin's series expansion. Based on the assumption that $\phi^2(12)$ is smaller than $\phi(12)$, this last equation was further approximated in the previous formalism by

$$\int \phi(12)\;\; d\vec{r} \; = 0 \qquad (223)$$

and solved for $\Phi(\vec{R})$, which led her to recover the Colle-Salvetti function, given by equation 205.

However, particular caution should be used here, as we shall soon discover. Indeed, what really equation 223 means, is that reference 104 assumes that it provides a sufficiently strong condition to properly ensure N-representability. A test of such an assumption is readily obtained by checking whether or not the exact N-representability condition — described within this formalism by equation 222— is satisfied when one uses the Colle-Salvetti function $\Phi(\vec{R})$ in b(12). This is what we shall study now.

After integration over $\vec{r}$, the left hand side of equation 222 is a function of both R and the variational parameter q, that we shall, from now on, symbolize by f(R,q). If N-representability is exactly satisfied everywhere, the relation f(R,q)=0 is then true $\forall$(R,q). Figure 21 provides a three-dimensional plot of the function f(R,q), while a slice of this plot at q=1.17 —the value yielding the minimal E_c value for He atom— is given in Figure 22. A perpendicular cut at R=2 is shown in Figure 23.

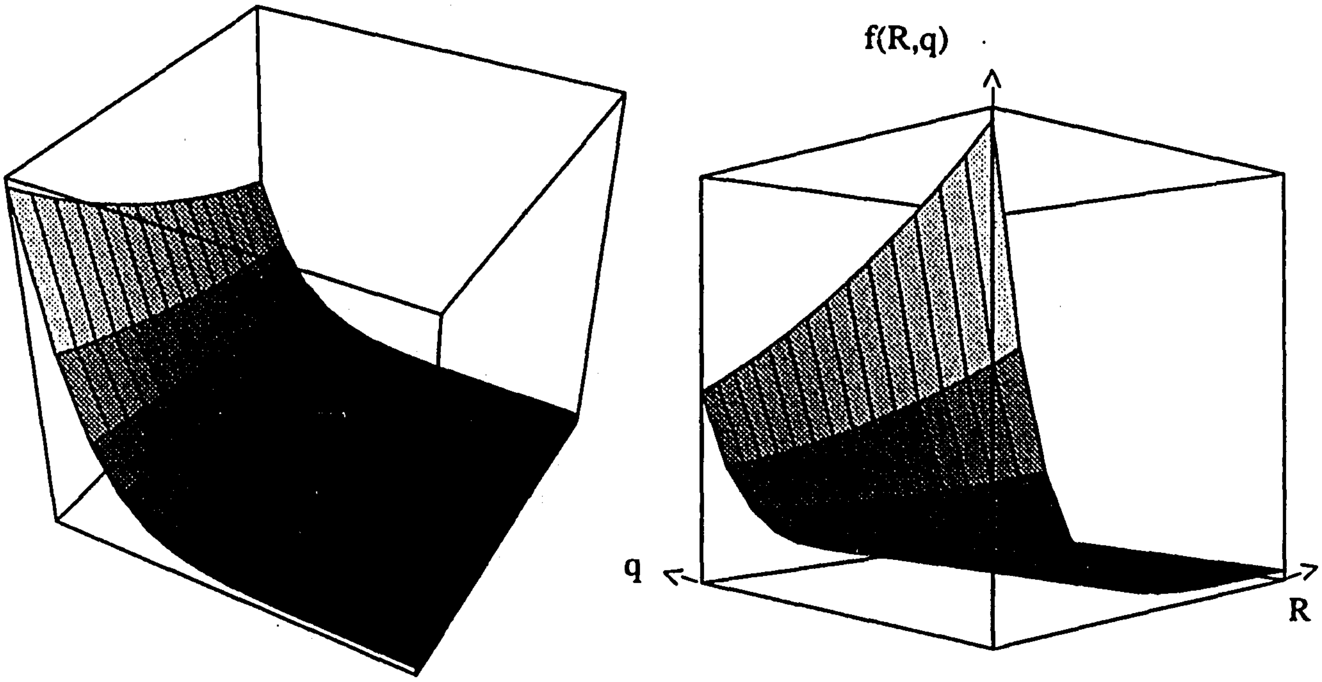


Figure 21. He Atom: N-Representability Test of a Previous Formalism[104]: Plot of f(R,q) as a Function of R and q, $(0 \leq R \leq 4, 1.1 \leq q \leq 1.3)$

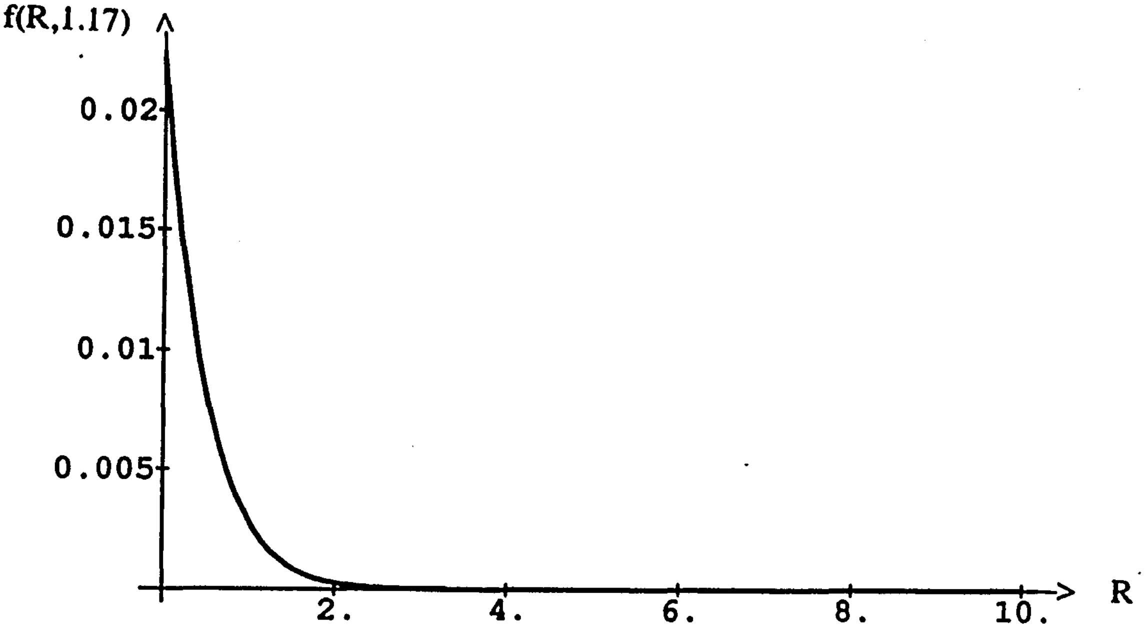


Figure 22. He Atom: N-Representability Test of a Previous Formalism[104]: Plot of f(R,1.17) as a Function of R.

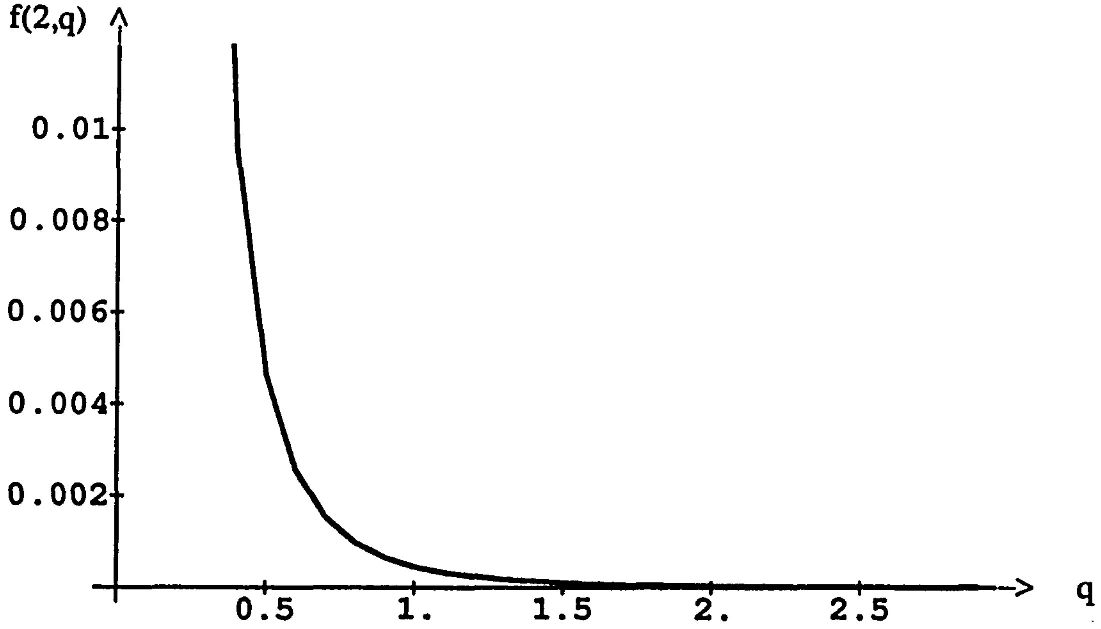


Figure 23. He Atom: N-Representability Test of a Previous Formalism[104]: Plot of f(2,q) as a Function of q.

From these plots, it appears that N-representability is strongly violated in the region where both R and q are small, which is the region of interest in our calculation. Therefore, the Colle-Salvetti function $\Phi(\vec{R})$, obtained by approximately solving equation 222, does not properly ensure N-representability of the density matrices.

As a conclusion, the correlation energy results claimed by reference 104, although very close to the exact value for helium atom, are rather meaningless, for they were obtained within a formalism which did not properly satisfy the density matrix N-representability. Consequently, they cannot be considered as a true test of calculating the correlation energy with the formalism where $P_{\underline{det},2}$ (12) is approximated by the leading term of its McLaurin's series expansion.
Such a test would be truly provided by using the form of the function $\Phi(\vec{R})$ which **exactly** satisfies the N-representability condition of equation 222. Only in this case would any deviation from the exact correlation energy be due to the very McLaurin's series approximation. This is what we shall investigate in the next section.

II.3. Test of our Formalism: Exact N-Representability.

II.3.1. Exact Solutions to the N-Representability Condition.

Within the correlation energy formalism developed in section II.1., N-representability of the density matrices is satisfied if equation 222 is verified for any value of R and q. After integrating over $\vec{r}$, this condition leads to a quadratic equation in $\Phi(\vec{R})$ which may be solved **exactly**. Appendix F shows the analytical solutions obtained by using Mathematica™. Note that since the sign of the quantity (b^2 - 4 ac) —where a, b and c are the coefficients of $\Phi(\vec{R})$ to the power 2, 1 and 0, respectively— is everywhere positive, two solutions are obtained, symbolized by $\Phi_+(\vec{R})$ and $\Phi_-(\vec{R})$. However, only one of these two solutions is to be retained, based on its ability to generate physically meaningful results. To this end, two Mathematica™ programs were written to calculate the correlation energy of helium atom based on our formalism developed in section **II.1.** and using one of the two exact solutions to N-representability condition; appendix G shows the program using $\Phi_+(\vec{R})$.

Before analyzing the results obtained from these two programs, we shall first start by examining the effect on the correlation energy value of inserting $\Phi_+(\vec{R})$ into the formalism of reference 104.

II.3.2. Exact $\Phi_+(\vec{R})$ Solution Inserted into the Formalism of Reference 104.

In our Mathematica™ program previously written to confirm reference 104's results based on its correlation energy formalism, we may substitute the Colle-Salvetti function previously used, by one of its accurate forms, say $\Phi_+(\vec{R})$. The N-representability condition being now satisfied everywhere, we should obtain results in accordance with our own formalism, particularly zero contributions to T_{c_2} and T_{c_3}.

However, surprisingly enough, such a result is still not obtained for T_{c_3}, as shown in Table 7 where the values of the different helium correlation energy contributions are given at the minimizing variational value q=1.17.

	Previous formalism[104] (with accurate $\Phi_+(\vec{R})$)	This work (with accurate $\Phi_+(\vec{R})$)
V_c	-0.223369	-0.223369
T_{c_1}	-0.28598	-0.286017
T_{c_2}	0	0
T_{c_3}	-0.057342	0
T_c	0.171661	0.143008
E_c	-0.051708	-0.080361

Table 7. He atom: Comparison of a Previous Formalism (Reference 104) to our Formalism Using Accurate $\Phi_+(\vec{R})$ Ensuring Exact N-Representability (at q=1.17, in atomic units).

Although V_c, T_{c_1} and T_{c_2} are in plain accordance between both formalisms when the accurate $\Phi_+(\vec{R})$ function is used, the formalism of reference 104 generates an incorrect non-zero T_{c_3} contribution. A closer examination shows that this is due to her choice of imposing the integral of $\phi(12)$ over $\vec{r}$ to be zero, but not that of $\phi^2(12)$, in her derivation of T_{c_3} —see equation C.55 in the previous thesis.[104] This may seem rather surprising if one recalls that the latter integral was previously tacitly assumed to be negligible compared to the former in the very derivation of the $\Phi(\vec{R})$ function —see equation 223.

As a consequence, the previous formalism[104] developed with the accurate $\Phi_+(\vec{R})$, may not be used to properly generate correlation energy values, and we shall now examine the outputs obtained from our own formalism, where N-representability is properly ensured.

II.3.3. Correlation Energy and Exact N-Representability.

While some of the helium correlation energy values obtained using $\Phi_+(\vec{R})$ are regrouped in Table 8 and plotted in Figures 24 and 25, Figure 26 shows the correlation energy plot obtained with the $\Phi_-(\vec{R})$ formalism.

q	V_C	T_C	E_C
0.50	-1.72484	1.69348	-0.03136
0.60	-1.12794	0.98014	-0.14780
0.66	-0.90077	0.73900	-0.16177
0.68	-0.83915	0.67680	-0.16235
0.70	-0.78321	0.62155	-0.16166
0.80	-0.56858	0.42121	-0.14737
0.90	-0.42721	0.30013	-0.12708
1.30	-0.17142	0.10668	-0.06474
1.70	-0.08626	0.05106	-0.03520
2.10	-0.04970	0.02875	-0.02095
2.50	-0.03131	0.01794	-0.01337
2.90	-0.02104	0.01200	-0.00904

Table 8. He Atom: Our Formalism Using the Accurate Solution $\Phi_+(\vec{R})$ in the Correlation Correction:
Potential and Kinetic Energy Contributions to Correlation Energy, in atomic units, as a Function of Variational Parameter q.

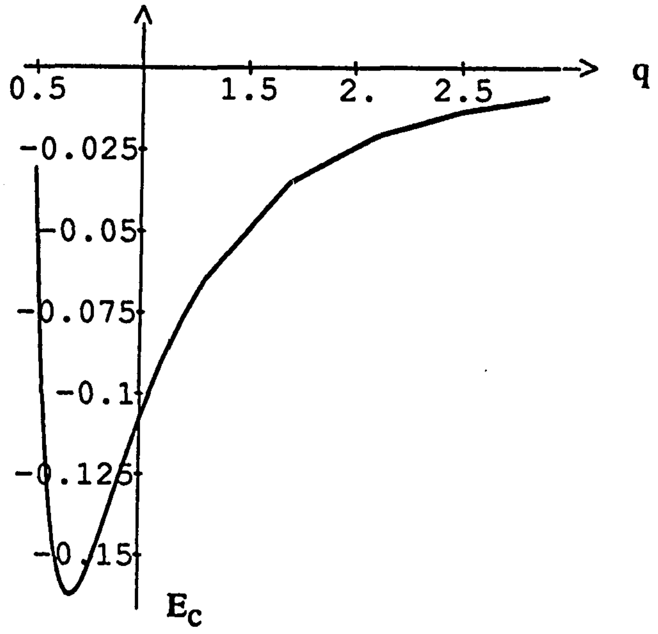


Figure 24. He Atom: Our Formalism Using the Accurate Solution $\Phi_+(\vec{R})$ in the Correlation Correction: Correlation Energy as a Function of Variational Parameter q.

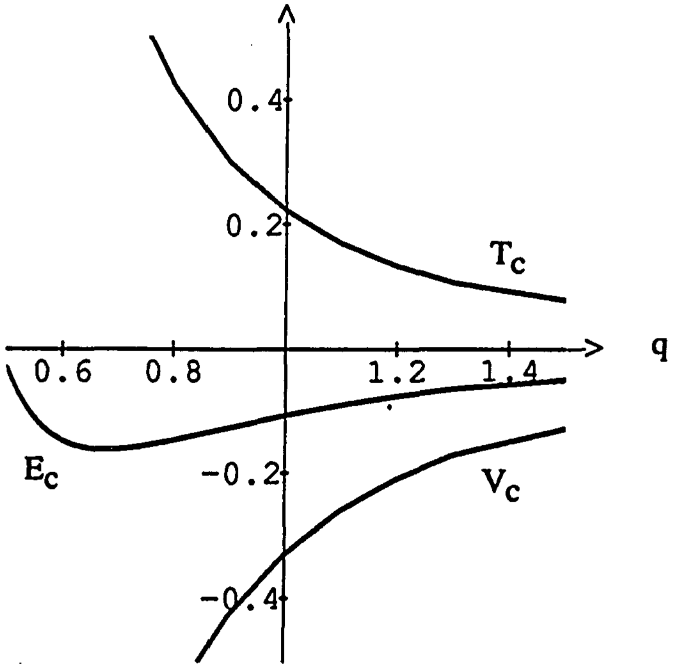


Figure 25. He Atom: Our Formalism Using the Accurate Solution $\Phi_+(\vec{R})$ in the Correlation Correction: Potential and Kinetic Contributions to Correlation Energy as a Function of Variational Parameter q.

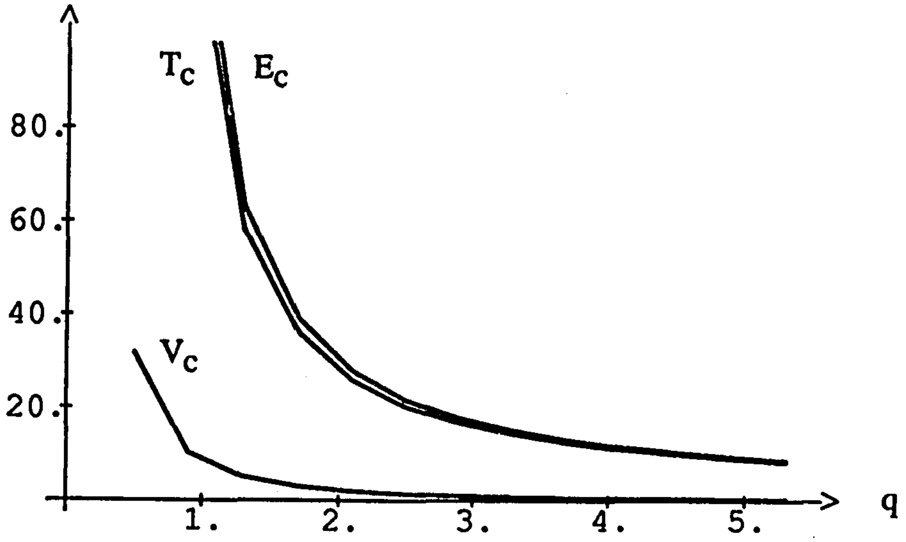


Figure 26. He Atom: Our Formalism Using the Accurate Solution $\Phi_-(\vec{R})$ in the Correlation Correction: Potential and Kinetic Contributions to Correlation Energy as a Function of Variational Parameter q.

We now compare the two variational correlation energy curves obtained by using both of the two $\Phi(\vec{R})$ solutions which ensure exact N-representability of the density matrices **within** the zeroth-order McLaurin's expansion approximation: from the above plots, it appears that the $\Phi_+(\vec{R})$ correlation energy variation goes through a minimal value at q=0.68. This would seem to be a better physical behavior than the $\Phi_-(\vec{R})$ correlation energy curve which asymptotically tends to 0. However, at the bottom of the $\Phi_+(\vec{R})$ curve, the correlation energy is found to be equal to -0.16325 which, being lower than the exact value ($E_{c,exact}$ = - 0.0424 [au]), strongly violates the variational principle.

As a conclusion, although $\Phi_+(\vec{R})$ and $\Phi_-(\vec{R})$ ensure exact N-representability everywhere, they do not yield physically meaningful helium correlation energy values. However, they provide a meaningful test of the approximation made in this formalism: substituting $P_{\underline{det},2}$ (12) by its McLaurin's series expansion to the zeroth order only is too crude an approximation, and by consequence, such an expansion should be, at least, carried up to the second order.

Chapter V

Conclusion and Prospectives

The Schrödinger equation allows us to determine —in principle— the eigenfunctions and eigenvalues of a linear hermitian operator corresponding to a physical observable. However, for a system of several interacting particles, no exact solution can be obtained; approximation methods are thus necessary, but they involve a large amount of computation.

It is therefore a matter of interest to develop new methods —bypassing the Schrödinger equation— for calculating electronic properties of a physical system.

To this end, Density Matrix and Density Functional Theories have been developed in which the leading role in the Quantum Mechanics formalism is no more given to the wavefunction but to first and second-order reduced density matrices. The interest of such theories lies in the following points:

1. All information about the system is carried by the density (HK theorem);
2. Any electronic property is obtainable from the density (Density Functional Theory);
3. There is a considerable simplification of the calculations since the Quantum Mechanics formalism is no more based on the N-body wavefunction but on the one and two-body reduced density matrices (Density Matrix Theory);
4. The density has a physical meaning, namely of representing the amplitude of probability of finding a particle at a given position;
5. The density is an observable directly measurable by, for instance, X-ray diffraction experiment.

Based on these characteristics, these theories have proved to be very promising, although they face the tremendous theoretical problem of N-representability. This is the problem of finding intrinsic criteria by which to recognize when a density matrix can be related to an antisymmetric N-body wavefunction. Only in this case would the density matrix be Quantum Mechanically meaningful. Although these criteria have not been found yet for the second-order density matrix, which by consequence forbids any hope of theoretically determining it, the N-representability problem is solved for the first-order one. Particularly, it has been shown that every quantum density is within reach of a single Slater determinant (Gilbert's theorem).

Experimentally, this determinant —and by consequence density matrices of any order N-representable by it— may be obtained from X-ray diffraction data, only if one provides a meaningful Quantum Mechanical description of the Crystallography experiment. This has been realized by Clinton and Massa, who first recovered a single Slater determinant by a least squares fit —subject to N-representability constraints— to experimental X-ray structure factors.

A deeper investigation of this method was the purpose of this work, in which the following points were proved:

1. If one assumes that the single Slater determinant, to be recovered from X-ray structure factors, is to be formed from N complex spin-space orbitals which, in turn, are described in an M-dimensional complex basis, we independently confirmed that 2N(M-N) is the minimum number of X-ray data needed to recover the matrix representative of the density operator. Moreover, we proved that this matrix is unique if and only if one previously chose a basis in which 2N(M-N) function products are linearly independent. More than this number ensures the sufficiency of the condition. The determinant later generated is by consequence unique, within a unitary transformation.

2. It is possible not to restrict oneself to an independent particle model wavefunction (i.e. a single Slater determinant), and, by so, to greatly improve the accuracy of the obtained density matrices by taking account of the electron correlation in our formalism. This was achieved by finding, for the first time, highly accurate first and second-order density matrices approximately N-representable —to the second order of correlation— by a correlated-determinant wavefunction. The interest of such a result lies in the following characteristics of these density matrices:

a. The Quantum Mechanical validity of these density matrices, N-representable by a correlated-determinant wavefunction;

b. Their property of being entirely obtainable from coherent X-ray diffraction data;

c. Their very high accuracy conferred by this known property of the N-representing wavefunction;

d. Their definition as explicit functionals of the density.

3. All of these properties were finally used in:

a. A theoretical application: in which we showed that these density matrices may be used in the context of Density Functional Theory to highly accurately determine the unknown HK functional, associated with the theorem of Hohenberg and Kohn. This claims an interest based upon the density matrix properties previously mentioned.

b. A numerical application: in which we developed, first, a general formalism for the calculation of the correlation energy of a two-electron system, that we further approximated by using the leading term of the McLaurin's series expansion about $\vec{r}$ of the second-order density function. We then numerically tested this approximation using a program written in Mathematica™ language, and proved the following points:

b_1. The correlation energy values previously obtained, although very accurate for helium atom, are based on densities which are not exactly N-representable.

b_2. When N-representability is exactly satisfied, within the approximation previously mentioned, non physical results are obtained. This last point proves that retaining only the leading term in the McLaurin's series expansion is too crude an approximation. Higher order of approximation should therefore be investigated.

The correlated-determinant correction to the first-order to the density matrices was published in *J. Mol. Struct. (Theochem)* [108] in a series of papers dedicated to Löwdin; the second-order correction and its applications have been submitted for publication.

Finally, the last words in this work will be given on some other prospectives which may improve this formalism:

1. The temperature effect on the structure factors, which are used to recover our X-ray density matrices, may be studied. Particularly, this effect could be accounted for by providing a proper Quantum Mechanical description of the lattice vibrational motions in the crystal. Since the atomic motions are described by the neutron diffraction experiment which delivers an atomic density, here we suggest to try to convolute the electron density to the atomic one, to generate a more fundamental density which may be used as the basis of our calculations. Providing a correction on the structure factors themselves may be another way of tackling the problem.

2. For incompletely-occupied orbitals, it is necessary to base the correlation correction, not on a single Slater determinant, but on a linear combination of determinants. However, this does not change the correlation N-representability corrections given in this work —which are totally general— but only the referential determinant wavefunction. In the same spirit as this work, one may then try to find conditions for recovering a linear combination of Slater determinant from X-ray data. This would make the basis of the study of the fundamental configuration-interaction N-representability.

3. The final suggestion —of an otherwise almost unlimited list— deals with the Kohn-Sham equations:[43] these equations are among the most important ones in current Quantum Mechanics developments, for they give a way to calculate a single determinant of orbitals which deliver in principle the exact density. Our orbitals recovered by our method come from the exact —apart from experimental errors— density, and it may be interesting to further examine the apparent analogy between X-ray and Kohn-Sham orbitals.

Appendices

Appendix A

Quantum Mechanics Formalisms in Different Representations

This appendix gives the two Quantum Mechanics formalisms we are dealing with in this work, namely the regular one based on the wavefunction and the one based on the density operator, or any of their equivalent representations.

The following table should be taken as a dictionary, which gives the essence of the formalisms in the three languages corresponding to the three representations we are concerned with, that is to say:

- ket representation (Dirac's language),
- matrix representation (Heisenberg's language),
- function representation (Schrödinger's language).

Each column in this table refers to a particular language, and is, by so, auto-sufficient. The translation from one language to another, that is to say, the entries in the dictionary, are symbolized by the following type of arrow:

Ket Representation of Hilbert Space	Matrix Representation of Hilbert Space	Function Representation of Hilbert Space
Dirac's language	Heisenberg's language	Schrödinger's language (continuous position-space representation)

I. Quantum Mechanics Formalism Based on the Wavefunction.

State represented by $|\phi_k>$ = state ket vector		State represented by $\phi_k(q)$ = state function

Link

$$<q|\phi_k> = \phi_k(q) \qquad \text{(A.1)}$$

$$\boxed{\text{Description in a complete discrete orthonormal basis}}$$

Basis $\equiv \{|\Psi_j>\}$	Basis $\equiv \underset{\sim}{\Psi}$ where	Basis $\equiv \{\Psi_j(q)\}$

$$\underset{\sim}{\Psi} = \begin{pmatrix} \Psi_1 \\ \Psi_2 \\ \cdot \\ \cdot \\ \cdot \end{pmatrix} \qquad \text{(A.2)}$$

$$\text{and } \Psi_j = \Psi_j(q) = <q|\Psi_j> \qquad \text{(A.3)}$$

Therefore,

$\lvert\phi_k\rangle = \sum_j c_{kj} \lvert\Psi_j\rangle$	$\underset{\sim}{\phi_k} = \underset{\sim}{C_k}\,\underset{\sim}{\Psi}$	$\phi_k(q) = \sum_j c_{kj}\,\Psi_j(q)$ (A.4)
	where	
$c_{kj} = \langle\Psi_j\lvert\phi_k\rangle \longrightarrow$	$\underset{\sim}{C_k} = (c_{k1}\ \ c_{k2}\ \dots) \longleftarrow$	$c_{kj} = \int \Psi_j^*(q)\,\phi_k(q)\,dq$ (A.5)

II. <u>Quantum Mechanics Formalism Based on the Density Operator</u>.

OPERATORS

Any Operator A

Any operator A in the space spanned by the basis $\{\Psi\}$ can be written as a dyadic (provided that the basis is complete and orthonormal)

$$
\begin{aligned}
A &= 1\ A\ 1 \\
&= \Big(\sum_m |\Psi_m\rangle\langle\Psi_m|\Big)\ A\ \Big(\sum_n |\Psi_n\rangle\langle\Psi_n|\Big) \\
&= \sum_{m\,n} |\Psi_m\rangle\langle\Psi_m|A|\Psi_n\rangle\langle\Psi_n| \\
&= \sum_{m\,n} \langle\Psi_m|A|\Psi_n\rangle\, |\Psi_m\rangle\langle\Psi_n| \qquad \text{(A.6)}
\end{aligned}
$$

Therefore,

Link: Apply $<q\,|\;><\,|\,q'>$

$$A = \sum_{m\;n} A_{mn}\,|\Psi_m\rangle\langle\Psi_n| \qquad\longrightarrow\qquad A(q,q') = \sum_{m\;n} A_{mn}\,\Psi_m(q)\Psi_n^*(q')$$

($A(q,q')$ is called the kernal of the integral operator A) (A.7)

where the numerical coefficients are the matrix elements defined by

$$A_{mn} = \langle\Psi_m|\,A\,|\Psi_n\rangle \longrightarrow \underset{\sim}{A} = (A_{mn}) \longleftarrow A_{mn} = \int \Psi_m^*(q)\,A\,\Psi_n(q)\,dq$$

and

(A.8)

$|\Psi_m\rangle\langle\Psi_n| \equiv$ a dyad
A dyadic $\equiv$ a sum of dyads

Dyad Operator

Particularly, one may apply this decomposition to the dyad operator,

Let

$$D^{mn} \equiv |\Psi_m\rangle\langle\Psi_n| \qquad\qquad D^{mn}(q,q') \equiv \Psi_m(q)\Psi_n^*(q')$$

(A.9)

therefore

Link: Apply < q | >< | q'>

$$D^{mn} \longleftrightarrow \underset{\sim}{D}^{mn} \longleftrightarrow D^{mn}(q,q')$$

$$= \sum_{i\,j} D^{mn}_{ij} |\Psi_i\rangle\langle\Psi_j| \qquad =(D^{mn}_{ij}) \qquad = \sum_{i\,j} D^{mn}_{ij}\, \Psi_m(q)\Psi_n^*(q') \tag{A.10}$$

where

$$D^{mn}_{ij} = \langle\Psi_i| D^{mn} |\Psi_j\rangle \longrightarrow D^{mn}_{ij} = \delta_{im}\delta_{jn} \longleftarrow D^{mn}_{ij} = \int \Psi_i^*(q)\, D^{mn}\, \Psi_j(q)\, dq \tag{A.11}$$

i.e.

$$\underset{\sim}{D}^{mn} = \begin{pmatrix} 0 & \cdot & \cdot & \cdot & 0 \\ 0 & \cdot & \cdot & 1 & 0 \end{pmatrix} \tag{A.12}$$

Diagonal Dyad Operator

The diagonal dyad operator is given by

Link: Apply $<q\,|\;><\,|\,q'>$

$$D^{mm} \equiv |\Psi_m><\Psi_m| \quad <\!\!\longrightarrow \quad D^{mm}(q,q') \equiv \Psi_m(q)\Psi_m^{*}(q')$$

$$\underset{\sim}{D}^{mm} = \begin{pmatrix} 0 & . & . & . & 0 \\ & 0 & & & \\ & & 1 & & \\ & & & 0 & \\ 0 & . & . & . & 0 \end{pmatrix} \qquad \text{(A.13)}$$

where 1 is at the intersection of the m^{th} row with the m^{th} column

Density Operator (Pure State k)

For a system known to be in the pure state ϕ_k, one may alternatively describe the state by

$$\text{State} <\!\!\longrightarrow \hat{\rho}^{\,kk} \equiv \frac{|\phi_k><\phi_k|}{<\phi_k\,|\,\phi_k>} \qquad \text{(A.14)}$$

If ϕ_k is normalized,

Link: Apply $<q\,|\;><\,|\,q'>$

$$\hat{\rho}^{\,kk} \equiv |\phi_k><\phi_k| \quad <\!\!\longrightarrow \quad \underset{\sim}{\rho}^{\,kk} \quad <\!\!\longrightarrow \quad \rho^{\,kk}(q,q') \equiv \phi_k(q)\,\phi_k^{*}(q')$$

$\rho^{\,kk}(q,q') \equiv$ density "matrix".

(A.15)

Let's describe ϕ_k in a discrete, complete basis

$$|\phi_k\rangle = \sum_j c_{kj}\,|\Psi_j\rangle \quad \longleftrightarrow \quad \underset{\sim}{\phi_k} = \underset{\sim}{C_k}\,\underset{\sim}{\Psi} \quad \longleftrightarrow \quad \phi_k(q) = \sum_j c_{kj}\,\Psi_j(q) \tag{A.16}$$

Hence,

$$\hat{\rho}^{kk} = \Big(\sum_j c_{kj}|\Psi_j\rangle\Big)\Big(\sum_i c_{ki}^*\langle\Psi_i|\Big) \qquad \rho^{kk}(q,q') = \Big(\sum_j c_{kj}\Psi_j(q)\Big)\Big(\sum_i c_{ki}^*\Psi_i^*(q')\Big)$$

$$= \sum_{i\,j}\rho_{ij}^{kk}\,|\Psi_j\rangle\langle\Psi_i| \qquad\qquad = \sum_{i\,j}\rho_{ij}^{kk}\;\Psi_j(q)\Psi_i^*(q') \tag{A.17}$$

where

$$\rho_{ij}^{kk} = \langle\Psi_j|\,\hat{\rho}^{kk}\,|\Psi_i\rangle \longrightarrow \quad \underset{\sim}{\rho}^{kk} \equiv (\rho_{ij}^{kk}) \longleftarrow \quad \rho_{ij}^{kk} = \int \Psi_j^*(q)\,\hat{\rho}^{kk}\,\Psi_i(q)\,dq$$

$$\equiv (c_{ki}^*c_{kj}) \tag{A.18}$$

Therefore,

$$\underset{\sim}{\rho}^{kk} = \underset{\sim}{C_k}^{+}\underset{\sim}{C_k} \tag{A.19}$$

where $\underset{\sim}{C_k}$ retains its previous meaning, i.e.

$$\underset{\sim}{C_k} = (\,c_{k1}\;\; c_{k2}\;\; \ldots\,) \tag{A.20}$$

SUMMARY

$$\begin{tikzcd}
\hat{\rho}^{kk} = \sum\limits_{i\,j} \rho_{ij}^{kk}\, |\Psi_j\rangle\langle\Psi_i| \arrow[r, bend left, "\text{Link: } \underset{\sim}{\rho}^{kk} = (\rho_{ij}^{kk})"] \arrow[rr, bend left=60, "\text{Link: Apply } \langle q|\,\rangle\langle\,|q'\rangle"] & \underset{\sim}{\rho}^{kk} = \underset{\sim}{C}_k^{+}\underset{\sim}{C}_k \arrow[l, bend left, "\text{Link: } \hat{\rho}^{kk} = \mathrm{Tr}\,\underset{\sim}{\rho}^{kk}\underset{\sim}{\Psi}(|\,\rangle)\underset{\sim}{\Psi}^{+}(\langle\,|)"] \arrow[r, bend right, "\text{Link: } \rho^{kk}(q,q') = \mathrm{Tr}\,\underset{\sim}{\rho}^{kk}\underset{\sim}{\Psi}(q)\underset{\sim}{\Psi}^{+}(q')"'] & \rho^{kk}(q,q') = \sum\limits_{i\,j} \rho_{ij}^{kk}\, \Psi_j(q)\Psi_i^{*}(q') \arrow[l, bend right, "\text{Link: } \underset{\sim}{\rho}^{kk} = (\rho_{ij}^{kk})"'] \arrow[ll, bend left=60, "\text{Link: } \hat{\rho}^{kk}\chi(q) = \int \rho^{kk}(q,q')\chi(q')\,dq'"]
\end{tikzcd}$$

where

$\underset{\sim}{\Psi}$ (| >) = a vector-column of basis ket vectors.

(Caution! In this case, the Trace
is changed by cyclic permutation)

$\underset{\sim}{\Psi}$ (q) = a vector-column of basis functions.

i.e.

$\hat{\rho}^{kk} \neq \mathrm{Tr}\, \underset{\sim}{\Psi}^{+}(<|)\underset{\sim}{\rho}^{kk}\underset{\sim}{\Psi}(|>)$

since $<|> \neq |><|$

ACTION OF THE DENSITY OPERATOR

ON

A KET	A VECTOR-COLUMN	A FUNCTION
$\hat{\rho}^{kk}\|\chi\rangle = \|\phi_k\rangle\langle\phi_k\|\chi\rangle$	$\longleftrightarrow \quad \underset{\sim}{\rho}^{kk}\,\underset{\sim}{V} \quad \longleftrightarrow$	$\hat{\rho}^{kk}\chi(q)$
$= \langle\phi_k\|\chi\rangle\|\phi_k\rangle$	$= (\langle\Psi_j\|\hat{\rho}^{kk}\|\Psi_i\rangle)(\langle\Psi_m\|\chi\rangle)$	$= \int \rho^{kk}(q,q')\chi(q')\,dq'$
	$= (\sum_i \langle\Psi_j\|\hat{\rho}^{kk}\|\Psi_i\rangle\langle\Psi_i\|\chi\rangle)$	$= \phi_k(q)\int \phi_k^*(q')\chi(q')\,dq'$
	$= (\langle\Psi_j\|\hat{\rho}^{kk}(\sum_i\|\Psi_i\rangle\langle\Psi_i\|)\|\chi\rangle)$	
	$= (\langle\Psi_j\|\hat{\rho}^{kk}\|\chi\rangle)$	
	$= (\langle\Psi_j\|\chi'\rangle)$	(A.21)
= a number times a ket	= a new vector-column	= a function times a number
= a new ket vector		= a new function

Therefore,

ρ^{kk} = projection operator onto state ϕ_k,

according to

$\hat{\rho}^{kk}\|\chi\rangle = \|\chi'\rangle$	$\underset{\sim}{\rho}^{kk}\,\underset{\sim}{V} = \underset{\sim}{V}'$	$\hat{\rho}^{kk}\chi(q) = \chi'(q)$ (A.22)

EXPECTATION VALUE (IN STATE ϕ_k) OF AN OPERATOR

General Case: <A>

In Density Matrix Theory, the wavefunction is eliminated in favor of the density matrix, and expectation values may be calculated as

$$
\begin{aligned}
\langle A\rangle &= \langle \phi_k | A | \phi_k \rangle \\
&= \Big(\sum_i c_{ki}^* \langle\Psi_i|\Big) A \Big(\sum_j c_{kj} |\Psi_j\rangle\Big) \\
&= \sum_{ij} c_{ki}^* c_{kj} A_{ij} \\
&= \sum_{ij} \rho_{ij}^{kk} A_{ij}
\end{aligned}
$$

$$
\begin{aligned}
\langle A\rangle &= \int \phi_k^*(q)\, A\, \phi_k(q)\, dq \\
&= \int A\, \rho^{kk}(q,q')\big|_{q'\to q}\, dq \\
&= \sum_{ij} c_{ki}^* c_{kj} \int \Psi_i^*(q) A \Psi_j(q)\, dq
\end{aligned}
\qquad (A.23)
$$

$$= \sum_{ij} (\rho_{ji}^{kk})^* A_{ij} \quad \longleftrightarrow \quad \langle A\rangle = \mathrm{Tr}\ (\underset{\sim}{\rho}^{kk})^+ \underset{\sim}{A} \quad \longleftrightarrow \quad = \sum_{ij} (\rho_{ji}^{kk})^* A_{ij}$$

where

$$\underset{\sim}{A} = (A_{ij}) \qquad (A.24)$$

Later, we shall see that $\underset{\sim}{\rho}^{kk}$ is hermitian,

therefore

$$\langle A\rangle = \mathrm{Tr}\ \underset{\sim}{\rho}^{kk} \underset{\sim}{A} \qquad (A.25)$$

Density Operator: $\langle \hat{\rho}^{kk} \rangle$

$$\langle \hat{\rho}^{kk} \rangle$$

$= \langle \phi_k \vert \hat{\rho}^{kk} \vert \phi_k \rangle$	$= \mathrm{Tr}\, \underset{\sim}{\rho}^{kk}\, \underset{\sim}{\rho}^{kk}$	$\int \phi_k^*(q')\, \hat{\rho}^{kk}\, \phi_k(q')\, dq'$
$= \langle \phi_k \vert \phi_k \rangle \langle \phi_k \vert \phi_k \rangle$	$= \mathrm{Tr}\, (\underset{\sim}{C}_k^{+} \underset{\sim}{C}_k)\, (\underset{\sim}{C}_k^{+} \underset{\sim}{C}_k)$	$= \{ \int \phi_k^*(q)\, \phi_k(q)\, dq$
	$= \mathrm{Tr}\, \underset{\sim}{C}_k^{+}\, (\underset{\sim}{C}_k\ \ \underset{\sim}{C}_k^{+}) \underset{\sim}{C}_k$	$\cdot \int \phi_k^*(q')\, \phi_k(q')\, dq' \}$

(A.26)

but since ϕ_k is normalized,

$$(\underset{\sim}{C}_k\ \ \underset{\sim}{C}_k^{+}) = \underset{\sim}{1} \qquad \text{(A.27)}$$

Hence,

$$\langle \hat{\rho}^{kk} \rangle = \mathrm{Tr}\, \underset{\sim}{C}_k^{+} \underset{\sim}{C}_k$$
$$= \mathrm{Tr}\, \underset{\sim}{C}_k\, \underset{\sim}{C}_k^{+} \qquad \text{(A.28)}$$

Therefore,

$$\langle \hat{\rho}^{kk} \rangle = 1 \qquad \text{(A.29)}$$

PROPERTIES OF THE DENSITY OPERATOR (PURE STATE ϕ_k)

In the case where the system is in the pure state k, the density operator satisfies the following properties

1. $\hat{\rho}^{kk}\,\hat{\rho}^{kk}=\hat{\rho}^{kk}$	1. $\underset{\sim}{\rho}^{kk}\,\underset{\sim}{\rho}^{kk}=\underset{\sim}{\rho}^{kk}$	1. $\int\rho^{kk}(q,q'')\rho^{kk}(q'',q')\,dq'' = \rho^{kk}(q,q')$ (A.30)
2. $(\hat{\rho}^{kk})^{+}=\hat{\rho}^{kk}$	2. $(\underset{\sim}{\rho}^{kk})^{+}=\underset{\sim}{\rho}^{kk}$	2. $(\rho^{kk}(q,q'))^{*} = \rho^{kk}(q,q')$ (A.31)
3. $<\hat{\rho}^{kk}>=1$	3. $\mathrm{Tr}\,\underset{\sim}{\rho}^{kk}=1$	3. $\int(\rho^{kk}(q,q))\,dq = 1$ (A.32)

and the state is stationary if and only if

4. $H\,\vert\phi_k> = E_k\,\vert\phi_k>$	4. $\underset{\sim}{H}\;\underset{\sim}{C_k}^{+}=E_k\;\underset{\sim}{C_k}^{+}$	4. $H\;\phi_k(q) = E_k\;\phi_k(q)$ (A.33)

hence, multiplying both members by $\underset{\sim}{C_k}$,

$$\underset{\sim}{H}\,\underset{\sim}{\rho}^{kk}=E_k\,\underset{\sim}{\rho}^{kk} \qquad \text{(A.34)}$$

PROJECTION OPERATOR ONTO A SET OF PURE STATES $\{\phi_1\ \phi_2 \ldots\}$

Following the Density Matrix Theory, the pure state ensemble, where N eigenstates are occupied, may be described by the projection operator onto the subspace spanned by these eigenstates in the one-particle Hilbert space, according to

$$\hat{\rho} \equiv \sum_{k=1}^{N} |\phi_k\rangle\langle\phi_k| \quad \longleftrightarrow \quad \underset{\sim}{\rho} \equiv \sum_{k=1}^{N} \underset{\sim}{\rho}^{kk} \quad \longleftrightarrow \quad \rho(q,q') \equiv \sum_{k=1}^{N} \phi_k(q)\,\phi_k^*(q')$$

$$= \sum_{k=1}^{N} \hat{\rho}^{kk} = \sum_{k=1}^{N} \sum_{i\,j} \rho_{ij}^{kk} |\Psi_j\rangle\langle\Psi_i| = \sum_{i\,j} \sum_{k} \rho_{ij}^{kk} |\Psi_j\rangle\langle\Psi_i| = \sum_{i\,j} \rho_{ij} |\Psi_j\rangle\langle\Psi_i|$$

$$= \sum_{k=1}^{N} \underset{\sim}{C}_k^{+} \underset{\sim}{C}_k$$

$$= \sum_{k=1}^{N} \rho^{kk}(q,q') = \sum_{k=1}^{N} \sum_{i\,j} \rho_{ij}^{kk}\, \Psi_j(q)\Psi_i^*(q') = \sum_{i\,j} \sum_{k} \rho_{ij}^{kk}\, \Psi_j(q)\Psi_i^*(q') = \sum_{i\,j} \rho_{ij}\, \Psi_j(q)\Psi_i^*(q') \tag{A.35}$$

Let N=2,

then the state is described by

$$\underset{\sim}{\rho} = \underset{\sim}{\rho}^{11} + \underset{\sim}{\rho}^{22} \tag{A.36}$$

where

$$\underset{\sim}{\rho}^{11} = \underset{\sim}{C}_1^{+} \underset{\sim}{C}_1 \tag{A.37}$$

$$\underset{\sim}{\rho}^{22} = \underset{\sim}{C}_2^{+} \underset{\sim}{C}_2 \tag{A.38}$$

$$\text{and } \rho_{ij}^{kk} = (c_{ki}^{*} c_{kj}) \tag{A.39}$$

Therefore,

$$\underset{\sim}{\rho} = \begin{pmatrix} c_{11}^{*}c_{11}+c_{21}^{*}c_{21} & c_{11}^{*}c_{12}+c_{21}^{*}c_{22} & \cdots \\ c_{12}^{*}c_{11}+c_{22}^{*}c_{21} & c_{12}^{*}c_{12}+c_{22}^{*}c_{22} & \cdots \\ \vdots & \vdots & \cdots \\ \vdots & & \cdots \end{pmatrix}$$

$$= \begin{pmatrix} c_{11}^{*} & c_{21}^{*} \\ c_{12}^{*} & c_{22}^{*} \\ \vdots & \vdots \end{pmatrix} \begin{pmatrix} c_{11} & c_{12} & c_{13} & \cdots \\ c_{21} & c_{22} & c_{23} & \cdots \end{pmatrix} \tag{A.40}$$

Therefore,

$$\hat{\rho} = \sum_{i\,j} \rho_{ij} |\Psi_j\rangle\langle\Psi_i| \quad \longleftrightarrow \quad \underset{\sim}{\rho} = \underset{\sim}{C}^{+}\underset{\sim}{C} \quad \longleftrightarrow \quad \rho(q,q') = \sum_{i\,j} \rho_{ij}\, \Psi_j(q)\Psi_i^{*}(q') \tag{A.41}$$

where

$$\underset{\sim}{\rho} = (\rho_{ij}) = (\sum_{k} \rho_{ij}^{kk}) \tag{A.42}$$

and

$$\underset{\sim}{\phi} = \underset{\sim}{C}\,\underset{\sim}{\Psi} \tag{A.43}$$

$$\underset{\sim}{C} = \begin{pmatrix} c_{11} & c_{12} & \cdots \\ c_{21} & c_{22} & \cdots \\ \cdot & \cdot & \cdots \end{pmatrix} \tag{A.44}$$

SUMMARY

$$\begin{tikzcd}[column sep=huge]
\hat{\rho} = \sum_{i\,j} \rho_{ij} \, |\Psi_j\rangle\langle\Psi_i| \arrow[r, bend left, "{\text{Link: } \underset{\sim}{\rho} = (\rho_{ij})}"] \arrow[rr, bend left=60, "{\text{Link: Apply } \langle q|\,\rangle\langle\,|q'\rangle}"] & \underset{\sim}{\rho} = \underset{\sim}{C}^{+}\underset{\sim}{C} \arrow[l, bend left, "{\text{Link: } \hat{\rho} = \mathrm{Tr}\, \underset{\sim}{\rho}\, \underset{\sim}{\Psi}(|\,\rangle)\underset{\sim}{\Psi}^{+}(\langle\,|)}"] \arrow[r, bend right, "{\text{Link: } \rho(q,q') = \mathrm{Tr}\, \underset{\sim}{\rho}\, \underset{\sim}{\Psi}(q)\underset{\sim}{\Psi}^{+}(q')}"'] & \rho(q,q') = \sum_{i\,j} \rho_{ij} \Psi_j(q) \Psi_i^{*}(q') \arrow[l, bend right, "{\text{Link: } \underset{\sim}{\rho} = (\rho_{ij})}"'] \arrow[ll, bend left=60, "{\text{Link: } \hat{\rho}\, \chi(q) = \int \rho(q,q')\, \chi(q')\, dq'}"]
\end{tikzcd}$$

where

$\underset{\sim}{\Psi}(|\,\rangle)$ = a vector-column of basis ket vectors.
Here, the same precaution, as previously mentioned, applies.

$\underset{\sim}{\Psi}(q)$ = a vector-column of basis functions.

ACTION OF THE OPERATOR $\hat{\rho}$

ON

A KET	A VECTOR-COLUMN	A FUNCTION
$\hat{\rho}\,|\chi>$ $\longleftrightarrow$	$\underset{\sim}{\rho}\,\underset{\sim}{V}$ $\longleftrightarrow$	$\hat{\rho}\,\chi(q)$
$=\sum_{k=1}^{N}\hat{\rho}^{kk}\,|\chi>$	$=(\sum_{k}\underset{\sim}{\rho}^{kk})\,\underset{\sim}{V}$	$=\int\rho(q,q')\,\chi(q')\,dq'$
$=(\sum_{k}|\phi_k><\phi_k|)\,|\chi>$		$=\sum_{k}\int\rho^{kk}(q,q')\chi(q')dq'$
$=\sum_{k}<\phi_k|\chi>|\phi_k>$		$=\sum_{k}\phi_k(q)\int\phi_k^{*}(q')\chi(q')dq'$ (A.45)
= sum of (a # times a ket) = a linear combination of kets = a new ket vector = decomposition of $|\chi>$ onto $|\phi_1>, |\phi_2> \ldots |\phi_N>$ by the projection method.	= a new vector-column	= sum of (a # times a function) = a new function = same type of decomposition.

EXPECTATION VALUE (IN STATES $\{\phi_k\}$) OF AN OPERATOR

To calculate the expectation value of any operator in the pure ensemble state, one realizes the ensemble average of the operator.

General Case: <A>

$$\langle A\rangle = \sum_k \langle \phi_k | A | \phi_k\rangle \quad \longleftarrow \text{ ensemble average } \longrightarrow \quad \langle A\rangle = \sum_k \int \phi_k{}^*(q) A \phi_k(q)\,dq$$

$$= \sum_k \Big(\sum_{i\,j} (\rho_{ji}^{kk})^* A_{ij}\Big) \qquad\qquad = \sum_k \int A\, \rho^{kk}(q,q')|_{q'\to q}\,dq$$

$$= \sum_{i\,j} (\rho_{ji})^* A_{ij} \longleftrightarrow \langle A\rangle = \mathrm{Tr}\,(\underset{\sim}{\rho})^+ \underset{\sim}{A} \longleftrightarrow = \sum_{i\,j} (\rho_{ji})^* A_{ij} \tag{A.46}$$

where

$$\underset{\sim}{A} = (A_{ij}) \tag{A.47}$$

Later, we shall see that $\underset{\sim}{\rho}$ is hermitian,

therefore

$$\langle A\rangle = \mathrm{Tr}\,\underset{\sim}{\rho}\;\underset{\sim}{A} \tag{A.48}$$

Projection Operator: $\langle \hat{\rho} \rangle$

$\langle \hat{\rho} \rangle$

$= \sum_{k} \langle \hat{\rho}^{kk} \rangle$	$= \mathrm{Tr}\, \underset{\sim}{\rho}\ \underset{\sim}{\rho}$	$= \sum_{k} \langle \hat{\rho}^{kk} \rangle$
$= (\sum_{k} \sum_{n} \langle \phi_n \lvert \hat{\rho}^{kk} \rvert \phi_n \rangle$	$= \mathrm{Tr}\, (\sum_{k} \underset{\sim}{\rho}^{kk})(\sum_{n} \underset{\sim}{\rho}^{nn})$	$= \sum_{k\,n} \int \phi_n^*(q) \hat{\rho}^{kk} \phi_n(q)\, dq$
$= \sum_{k\,n} \langle \phi_n \vert \phi_k \rangle \langle \phi_k \vert \phi_n \rangle$	$= \mathrm{Tr}\, (\sum_{k\,n} \underset{\sim}{\rho}^{kk}\ \underset{\sim}{\rho}^{nn})$	$= \sum_{k\,n} \{ \int \phi_n^*(q)\, \phi_k(q)\, dq$ $\int \phi_k^*(q)\, \phi_n(q)\, dq \}$

(A.49)

For states which are mutually orthogonal (i.e. mutually exclusive),

$\langle \phi_n \vert \phi_k \rangle = \delta_{kn}$	$\underset{\sim}{\rho}^{kk}\ \underset{\sim}{\rho}^{nn} = \delta_{kn}$	$\int \phi_n^*(q)\, \phi_k(q)\, dq = \delta_{kn}$

(A.50)

Therefore,

$\langle \hat{\rho} \rangle$

$= \sum_{k} \langle \phi_k \vert \phi_k \rangle^2$	$= \mathrm{Tr}\, (\sum_{k} (\underset{\sim}{\rho}^{kk})^2)$	$= \sum_{k} \{ \int \phi_k^*(q)\, \phi_k(q)\, dq \}^2$
$= \sum_{k=1}^{N} 1$	$= \mathrm{Tr}\, (\sum_{k} (\underset{\sim}{C}_k^{+} \underset{\sim}{C}_k)^2)$	$= \sum_{k=1}^{N} 1 = N$
$= N$	$= \mathrm{Tr}\, (\sum_{k} \underset{\sim}{C}_k^{+} (\underset{\sim}{C}_k\ \underset{\sim}{C}_k^{+}) \underset{\sim}{C}_k)$	

(A.51)

but since ϕ_k is normalized,

$$= \mathrm{Tr}\,\Big(\sum_{k}\big(\underset{\sim}{C}_k{}^{+}\underset{\sim}{C}_k\big)\Big)$$

$$= \sum_{k}\Big(\mathrm{Tr}\,\big(\underset{\sim}{\rho}^{kk}\big)\Big)$$

$$= \sum_{k=1}^{N} 1 = N \tag{A.52}$$

Therefore,

$$<\hat{\rho}> = N \tag{A.53}$$

PROPERTIES OF THE

PROJECTION OPERATOR $\hat{\rho}$ ONTO A SET OF PURE STATES $\{\phi_1 \ldots \phi_N\}$

In the case where the system is in the pure ensemble state $\{\phi_1, \phi_2 \ldots \phi_N\}$, the ensemble density operator satisfies the following properties

1. $\hat{\rho}^2 = \hat{\rho}$	**1.** $\underset{\sim}{\rho}^2 = \underset{\sim}{\rho}$	**1.** $\int \rho(q,q'')\rho(q'',q')\,dq'' = \rho(q,q')$ (A.54)
2. $(\hat{\rho})^+ = \hat{\rho}$	**2.** $(\underset{\sim}{\rho})^+ = \underset{\sim}{\rho}$	**2.** $(\rho(q,q'))^* = \rho(q,q')$ (A.55)
3. $< \hat{\rho} > = N$	**3.** $\mathrm{Tr}\,\underset{\sim}{\rho} = N$	**3.** $\int(\rho(q,q))\,dq = N$ (A.56)

and the state is stationary if and only if

$$\forall\, k = 1 \ldots N$$

4. $H \mid \phi_k > = E_k \mid \phi_k >$	**4.** $\underset{\sim}{H}\, \underset{\sim}{C_k}^{+} = E_k\, \underset{\sim}{C_k}^{+}$	**4.** $H\, \phi_k(q) = E_k\, \phi_k(q)$ (A.57)

hence, multiplying both members by $\underset{\sim}{C_k}$, and summing over k

$$\underset{\sim}{H}\,\underset{\sim}{\rho} = E\,\underset{\sim}{\rho} \qquad \text{(A.58)}$$

EQUIVALENT TO THE SCHRÖDINGER EQUATION

IN DENSITY MATRIX THEORY

Time Evolution of the Density Operator

$$i\hbar \frac{d\hat{\rho}}{dt} = [H,\hat{\rho}] \qquad\Big|\qquad i\hbar \frac{d}{dt}(\underset{\sim}{\rho}) = [\underset{\sim}{H},\underset{\sim}{\rho}] \qquad\Big|\qquad i\hbar \frac{d\hat{\rho}}{dt} = [H,\hat{\rho}] \tag{A.59}$$

Stationary State Condition

$$[H,\hat{\rho}]=0 \qquad\Big|\qquad [\underset{\sim}{H},\underset{\sim}{\rho}]=0 \qquad\Big|\qquad [H,\hat{\rho}]=0 \tag{A.60}$$

which is equivalent to requiring that the one-particle operators H and $\hat{\rho}$ have a common complete set of eigenstates, i.e.

$$\forall k = 1 \ldots N$$

$$\begin{cases} H\,|\,\phi_k > = E_k\,|\,\phi_k > \\ \hat{\rho}\,|\,\phi_k > = |\,\phi_k > \end{cases} \qquad\Big|\qquad \begin{cases} \underset{\sim}{H}\;\underset{\sim}{C}_k^{+} = E_k\,\underset{\sim}{C}_k^{+} \\ \underset{\sim}{\rho}\,\underset{\sim}{C}_k^{+} = \underset{\sim}{C}_k \end{cases} \qquad\Big|\qquad \begin{cases} H\,\phi_k\,(q) = E_k\,\phi_k\,(q) \\ \hat{\rho}\,\phi_k\,(q) = \phi_k\,(q) \end{cases} \tag{A.61}$$

Equivalently,

$$E_k = \mathrm{Tr}\, \underset{\sim}{\rho}^{kk}\ \underset{\sim}{H} \tag{A.62}$$

$$E_{Total} = \langle H \rangle = \mathrm{Tr}\, \underset{\sim}{\rho}\ \underset{\sim}{H} \tag{A.63}$$

Appendix B

Calculation of K_{real} for a Complex P Matrix Following Pecora's Approach

First, let $\underset{\sim}{Y} = \underset{\sim}{C}\,\underset{\sim}{C}^{+} = (y_{ij})$, **(B.1)**

then the **orthonormalization condition** is equivalent to the set of conditions:

$$\underset{\sim}{C}\,\underset{\sim}{C}^{+} = \underset{\sim}{1}_N \iff y_{ij} = \sum_{k=1}^{M} c_{ik}\, c_{jk}^{*} = \delta_{ij} \qquad \text{(B.2)}$$

and assume the hermiticity of the scalar product:

$$\underset{\sim}{Y}^{+} = \underset{\sim}{Y} \iff y_{ij} = y_{ji}^{*} \qquad \text{(B.3)}$$

* *diagonal element conditions:*

$$\forall\, i = 1 \ldots N, \quad y_{ii} = 1 \iff Re_{ii} + i\ Im_{ii} = 1 \qquad \text{(B.4)}$$

but since we assumed the scalar product to be hermitian, $Im_{ii} = 0$ is **not a constraint.** The only constraint is then

$Re_{ii} = 1 \implies$ **N real conditions.**

* *off-diagonal element conditions:*

$$\forall (i,j)\,,\quad y_{ij} = 0 \iff Re_{ij} + i\ Im_{ij} = 0 \iff \begin{cases} Re_{ij} = 0 \\ Im_{ij} = 0 \end{cases}$$

$$\iff (y_{ij})^* = 0 \qquad (B.5)$$

but since we assumed the scalar product to be hermitian,

$$\iff y_{ji} = 0 \qquad (B.6)$$

Therefore, only one off-diagonal triangle of conditions needs to be counted

$$\Longrightarrow\ 2\,\frac{N(N-1)}{2}\ \text{real conditions.}$$

CONCLUSION

$$\boxed{K_{real} = 2\,NM - N^{2}} \qquad (B.7)$$

Appendix C

Generalization of the Gauss Formula

Some peculiar combinatorial formulae were needed to evaluate the cardinal of some classes of BB terms, and are as follows:

$$1 + 2 + \ldots\ldots + N = \frac{N(N+1)}{2} \qquad \text{(C.1)}$$

$$[1.2] + [2.3] + \ldots\ldots + [N(N+1)] = \frac{N(N+1)(N+2)}{3} \qquad \text{(C.2)}$$

....

$$[1.2\ldots p] + [2.3\ldots(p+1)] + \ldots\ldots + [N(N+1)\ldots(N+p-1)] = \frac{N(N+1)\ldots(N+p)}{(p+1)} \qquad \text{(C.3)}$$

Since no reference were found for proving the veracity of these formulae, a simple proof by recurrence is given here. To preserve the generality of the argument, the derivation will be given for the last equation.

Proof by recurrence of the proposition P(N):

$$P(N) = [1.2..p] + [2.3..(p+1)] + \ldots + [N(N+1)..(N+p-1)] = \frac{N(N+1)..(N+p)}{(p+1)}$$

1. True for N=1 ?

$$P(1) = 1.2.3....p \overset{?}{=} \frac{N(N+1)..(N+p)}{(p+1)} \text{ when } N=1. \qquad \text{(C.4)}$$

$$P(1) = \frac{1.2.3....p.\,(p+1)}{(p+1)} = 1.2.3....p \qquad \text{(C.5)}$$

Conclusion: True for N=1

2. Hypothesis: Assume true for (N-1)

Problem: True for (N-1) $\overset{?}{==>}$ True for N

$$\begin{aligned} P(N) &= [1.2..p] + [2.3..(p+1)] +\ldots+ [N(N+1)..(N+p-1)] \\ &= [1.2..p] + [2.3..(p+1)] +\ldots+ [(N-1)N..(N+p-2)] + [N(N+1)..(N+p-1)] \\ &= P(N-1) + [N(N+1)..(N+p-1)] \end{aligned} \tag{C.6}$$

However, since by hypothesis, P(N-1) is true, one has the relation

$$P(N-1) = \frac{(N-1)N\ldots((N-1)+p)}{(p+1)} \tag{C.7}$$

Hence, substituting this relation into the expression of P(N), one finds

$$\begin{aligned} P(N) &= \frac{(N-1)N\ldots((N-1)+p)}{(p+1)} + [N(N+1)..(N+p-1)] \\ &= N(N+1)..(N+p-1)\left[\frac{(N-1)}{(p+1)} + 1\right] \\ &= N(N+1)..(N+p-1)\left[\frac{N+p}{(p+1)}\right] \\ &= \frac{N(N+1)\ldots(N+p-1)(N+p)}{(p+1)} \end{aligned} \tag{C.8}$$

3. Conclusion: True for N

Therefore, one just proved the general relation, which is a nice generalization of the Gauss formula:

$$\boxed{[1.2\ldots p] + [2.3\ldots(p+1)] +\ldots\ldots+ [N(N+1)\ldots(N+p-1)] = \frac{N(N+1)\ldots(N+p)}{(p+1)}} \tag{C.9}$$

Appendix D

Development of a General Correlation Energy Formalism

I. Vector Analysis in Different Coordinate Systems.

As mentioned in the main text, two coordinate systems may be used to describe a two-electron system: one based on the space-position vectors $\vec{r}_1$ and $\vec{r}_2$; the other articulated on the center of mass vector $\vec{R}$ and the interparticle vector $\vec{r}$. Here, we explain their relationships.

By definition,

$$\vec{r} \equiv \vec{r}_1 - \vec{r}_2 \text{ and } \vec{R} \equiv \frac{1}{2}(\vec{r}_1 + \vec{r}_2) \qquad \text{(D.1)}$$

or conversely

$$\vec{r}_1 \equiv \vec{R} + \frac{\vec{r}}{2} \text{ and } \vec{r}_2 \equiv \vec{R} - \frac{\vec{r}}{2} \qquad \text{(D.2)}$$

In the correlation energy calculation, the gradient and laplacian of a function are needed in both coordinate systems. They are related by

$$\nabla_1 = \frac{1}{2}\nabla_{\vec{R}} + \nabla_{\vec{r}} \text{ and } \nabla_2 = \frac{1}{2}\nabla_{\vec{R}} - \nabla_{\vec{r}} \qquad \text{(D.3)}$$

$$\nabla_i^2 \equiv \nabla_i \cdot \nabla_i \qquad \text{(D.4)}$$

$$\nabla_1^2 = \frac{1}{4}\nabla^2_{\vec{R}} + \nabla^2_{\vec{r}} + \nabla_{\vec{r}} \cdot \nabla_{\vec{R}} \qquad (D.5)$$

and

$$\nabla_2^2 = \frac{1}{4}\nabla^2_{\vec{R}} + \nabla^2_{\vec{r}} - \nabla_{\vec{r}} \cdot \nabla_{\vec{R}} \qquad (D.6)$$

or conversely,

$$\nabla_{\vec{r}} = \frac{1}{2}\left(\nabla_1 - \nabla_2\right) \text{ and } \nabla_{\vec{R}} = \nabla_1 + \nabla_2 \qquad (D.7)$$

$$\nabla_{\vec{r}} \cdot \nabla_{\vec{R}} = \frac{1}{2}\left(\nabla_1^2 - \nabla_2^2\right) \qquad (D.8)$$

$$\nabla^2_{\vec{r}} = \frac{1}{4}\left(\nabla_1^2 + \nabla_2^2 - 2\,\nabla_1 \cdot \nabla_2\right) \qquad (D.9)$$

$$\nabla^2_{\vec{R}} = \nabla_1^2 + \nabla_2^2 + 2\,\nabla_1 \cdot \nabla_2 \qquad (D.10)$$

The position vectors are chosen to be described in spherical coordinate system, where the gradient and the laplacian of a function f are given by

$$\nabla_{\vec{r}} f = \frac{\delta f}{\delta r}\,\vec{r}_{\text{unit}} + \frac{1}{r}\frac{\delta f}{\delta \theta}\,\vec{\theta}_{\text{unit}} + \frac{1}{r \sin\theta}\frac{\delta f}{\delta \varphi}\,\vec{\varphi}_{\text{unit}} \qquad (D.11)$$

$$\nabla^2_{\vec{r}} f = \frac{2}{r}\frac{\delta f}{\delta r} + \frac{\delta^2 f}{\delta r^2} + \frac{1}{r^2 \sin\theta}\frac{\delta}{\delta \theta}\left(\sin\theta \frac{\delta f}{\delta \theta}\right) + \frac{1}{r^2 \sin^2\theta}\frac{\delta^2 f}{\delta \varphi^2} \qquad (D.12)$$

II. General V_c Formalism.

The potential energy contribution arising from interelectron repulsion is given by

$$V_c = \frac{1}{2}\int \frac{P_{det.2}(12)\, b(12)}{|\vec{r}_1-\vec{r}_2|}\, d\vec{r}_1\, d\vec{r}_2 \qquad (D.13)$$

and may be described in the reduced coordinate system as

$$V_c = \frac{1}{2}\int \frac{P_{det.2}(12)\, b(12)}{r}\, d\vec{r}\, d\vec{R} \qquad (D.14)$$

since the Jacobian determinant of the variable transformation is equal to unity.

The first term in the integrand numerator is approximated by the very similar Hartree-Fock determinant density matrix and has the form given by equations 208 and 212.

We now choose to express all entities in the $(\vec{r}\ , \vec{R})$ system. To do so, one has to convert the magnitude of the $\vec{r}_1$ and $\vec{r}_2$ vectors —which are the natural variables used in the Clementi's basis functions— as a function of $\vec{r}$ and $\vec{R}$, in the following way

$$r_1 \equiv |\vec{r}_1| = (\vec{r}_1 \,.\, \vec{r}_1)^{1/2} = (R^2 + r^2 + \vec{R} \,.\, \vec{r})^{1/2} \qquad (D.15)$$

Since the scalar product of two vectors is an intrinsic quantity, independent of the system of coordinates used, we can derive its expression in spherical coordinates from its well-known form in the cartesian system, which is

$$\vec{R} \cdot \vec{r} = Xx + Yy + Zz \tag{D.16}$$

where

$$X = R \sin\Theta \cos\Phi \,;\; Y = R \sin\Theta \sin\Phi \text{ and } Z = R \cos\Theta,$$

$$x = r \sin\theta \cos\varphi \,;\; y = r \sin\theta \sin\varphi \text{ and } z = r \cos\theta. \tag{D.17}$$

Hence, in spherical coordinates,

$$\vec{R} \cdot \vec{r} = R\, r \left\{ \sin\Theta \sin\theta \cos(\Phi - \varphi) + \cos\Theta \cos\theta \right\} \tag{D.18}$$

In the most general case, the correlation factor is given by

$$b\,(12;1'2') \equiv \phi(12)\,\phi(1'2') - \phi(12) - \phi(1'2') \tag{D.19}$$

which reduces to $b\,(12) \equiv \phi(12)^2 - 2\,\phi(12)$, for the term used in V_C.

One may then substitute all of these formulae in V_C and get its most general expression.

III. General T_c Formalism.

The kinetic energy contribution to the correlation energy is described in the reduced coordinate system by

$$T_c = -\frac{1}{2} \int \left[\nabla_1^2 \left(P_{\underline{det}.2}(12;1'2)\, b(12;1'2) \right) \right]_{1' \to 1} d\vec{r}\, d\vec{R} \quad \text{(D.20)}$$

which may be further expanded and collected into

$$T_c \equiv -\frac{1}{2} \left(T_{c_1} + 2\, T_{c_2} + T_{c_3} \right) \quad \text{(D.21)}$$

where

$$T_{c_1} \equiv \int P_{\underline{det}.2}(12) \left[\nabla_1^2\, b(12;1'2) \right]_{1' \to 1} d\vec{r}\, d\vec{R} \quad \text{(D.22)}$$

$$T_{c_2} \equiv \int \left[\nabla_1 P_{\underline{det}.2}(12;1'2) \cdot \nabla_1 b(12;1'2) \right]_{1' \to 1} d\vec{r}\, d\vec{R} \quad \text{(D.23)}$$

$$T_{c_3} \equiv \int b(12) \left[\nabla_1^2 P_{\underline{det}.2}(12;1'2) \right]_{1' \to 1} d\vec{r}\, d\vec{R} \quad \text{(D.24)}$$

We shall now derive each contribution separately.

III.1. Derivation of T_{c_1}.

$$T_{c_1} \equiv \int P_{\underline{det}.2}(12)\, [\, \nabla_1^2\, b(12;1'2)\,]_{1' \to 1}\, d\vec{r}\, d\vec{R} \qquad \text{(D.22)}$$

First we evaluate the mathematical expression of $\nabla_1^2\, b(12;1'2)$: the operator applies first on the variable "1" in b(12;1'2), then 1' is set equal to 1, to get

$$\begin{aligned} [\, \nabla_1^2\, b(12;1'2)\,]_{1' \to 1} &= [\, \phi(1'2)\, \nabla_1^2\, \phi(12) - \nabla_1^2\, \phi(12)\,]_{1' \to 1} \\ &= \phi(12)\, \nabla_1^2\, \phi(12) - \nabla_1^2\, \phi(12) \qquad \text{(D.25)} \end{aligned}$$

The natural variables in the correlation function $\phi(12)$ are in fact r and R, as shown in equation 201. One may then substitute the laplacian operator by its expression in the reduced coordinate system, as

$$\nabla_1^2\, \phi(12) = [\, \tfrac{1}{4}\, \nabla_{\vec{R}}^2 + \nabla_{\vec{r}}^2 + \nabla_{\vec{r}} \cdot \nabla_{\vec{R}}\,]\, \phi(12) \qquad \text{(D.26)}$$

and finally obtains

$$\boxed{T_{c_1} = \int P_{\underline{det}.2}(12)\, (\phi(12)-1)\, [\, \tfrac{1}{4} \nabla_{\vec{R}}^2 + \nabla_{\vec{r}}^2 + \nabla_{\vec{r}} . \nabla_{\vec{R}}\,]\, \phi(12)\, d\vec{r}\, d\vec{R}}$$

(D.27)

This expression will be further developed, within some approximations, in a further section.

III.2. Derivation of T_{c_2}.

$$T_{c_2} \equiv \int \left[\nabla_1 P_{\underline{det}.2}(12;1'2) \,.\, \nabla_1 b(12;1'2) \right]_{1'\text{-->}1} d\vec{r}\, d\vec{R} \qquad \text{(D.23)}$$

First, ∇_1 b(12;1'2) may be expressed as

$$\nabla_1 b(12;1'2) = (\phi(1'2) - 1)\ \nabla_1 \phi(12) \qquad \text{(D.28)}$$

and ∇_1 $P_{\underline{det}.2}$ (12;1'2) as

$$\nabla_1 P_{\underline{det}.2}(12;1'2) = P_{\underline{det}.1}(2;2)\ \nabla_1 P_{\underline{det}.1}(1;1') - \frac{1}{2} P_{\underline{det}.1}(2;1')\ \nabla_1 P_{\underline{det}.1}(1;2) \qquad \text{(D.29)}$$

Following our convention for simplifying the notations, $P_{\underline{det}.1}(2;2)$ is further written $P_{\underline{det}.1}(2)$.

These expressions may then be substituted into the scalar product of the two gradients to get

$$\nabla_1 P_{\underline{det}.2}(12;1'2) \,.\, \nabla_1 b(12;1'2) =$$

$$(\phi(1'2)-1)\ \left\{ P_{\underline{det}.1}(2)\nabla_1 P_{\underline{det}.1}(1;1') - \frac{1}{2} P_{\underline{det}.1}(2;1')\nabla_1 P_{\underline{det}.1}(1;2) \right\} . \nabla_1 \phi(12) \quad \text{(D.30)}$$

Let's develop $\nabla_1 P_{\underline{det}.1}(1;1')$, as

$$\begin{aligned} \nabla_1 P_{\underline{det}.1}(1;1') &= 2 \sum_{i\,j=1}^{M} p_{ij}\ \psi i\ (1')\ \nabla_1 . \psi j\ (1) \\ &= 2 \sum_{i\,j=1}^{M} p_{ij}\ \psi i\ (1')\ [\ \tfrac{1}{2}\nabla_{\vec{R}} + \nabla_{\vec{r}}\ ]\ \psi j\ (1) \end{aligned} \quad \text{(D.31)}$$

and substitute it into the first gradient scalar product, to get

$$\nabla_1 P_{\underline{det}.1}(1;1') \,.\, \nabla_1 \phi(12) =$$

$$2 \sum_{i\,j=1}^{M} p_{ij}\ \psi i\ (1')\ \Big[\{ [\ \tfrac{1}{2}\nabla_{\vec{R}} + \nabla_{\vec{r}}\ ]\ \psi j\ (1) \} \ .\ \{ [\ \tfrac{1}{2}\nabla_{\vec{R}} + \nabla_{\vec{r}}\ ]\ \phi(12) \} \Big]$$

(D.32)

By the same method, one gets for the second gradient scalar product,

$$\nabla_1 P_{\underline{det}.1}(1;2) \,.\, \nabla_1 \phi(12) =$$

$$2 \sum_{i\,j=1}^{M} p_{ij}\ \psi i\ (2)\ \Big[\{ [\ \tfrac{1}{2}\nabla_{\vec{R}} + \nabla_{\vec{r}}\ ]\ \psi j\ (1) \} \ .\ \{ [\ \tfrac{1}{2}\nabla_{\vec{R}} + \nabla_{\vec{r}}\ ]\ \phi(12) \} \Big]$$

(D.33)

By substituting all these equations into T_{c_2}, one finally obtains

$$\boxed{\begin{aligned} T_{c_2} = 2 \int (\phi(12)-1) \sum_{i\,j=1}^{M} p_{ij} \Big[&\{ P_{\underline{det}.1}(2)\, \psi_i(1) - \tfrac{1}{2} P_{\underline{det}.1}(2;1)\, \psi_i(2) \} \\ &\{ ([\tfrac{1}{2} \nabla_{\vec{R}} + \nabla_{\vec{r}}]\, \psi_j(1)) . ([\tfrac{1}{2} \nabla_{\vec{R}} + \nabla_{\vec{r}}]\, \phi(12)) \} \Big]\, d\vec{r}\, d\vec{R} \end{aligned}}$$

(D.34)

This expression will be also further developed in the context of some approximations.

III.3. Derivation of T_{c_3}.

$$T_{c_3} \equiv \int b(12) \left[\nabla_1^2 P_{\underline{det}.2}(12;1'2) \right]_{1' \to 1} d\vec{r}\, d\vec{R} \qquad \text{(D.24)}$$

The laplacian may be expressed as

$$\nabla_1^2 P_{\underline{det}.2}(12;1'2) = P_{\underline{det}.1}(2)\, \nabla_1^2 P_{\underline{det}.1}(1;1') - \tfrac{1}{2} P_{\underline{det}.1}(2;1')\, \nabla_1^2 P_{\underline{det}.1}(1;2) \qquad \text{(D.35)}$$

where $\nabla_1^2 P_{\underline{det}.1}(1;1')$ is equal to

$$\nabla_1^2 P_{\underline{det}.1}(1;1') = 2 \sum_{i\,j=1}^{M} p_{ij}\, \psi_i(1')\, \nabla_1^2\, \psi_j(1) \qquad \text{(D.36)}$$

and $\nabla_1^{2}\psi j\,(1)$, is given, in the reduced coordinate system, by using equation (D.5).

One finally obtains

$$\boxed{\begin{gathered}T_{c_3} = 2\int b(12)\sum_{i\,j=1}^{M} p_{ij}\left[\left\{P_{\underline{det}.}1(2)\,\psi i\,(1) - \frac{1}{2}P_{\underline{det}.}1(2;1)\,\psi i\,(2)\right\}\right.\\ \left.\left\{\left(\left[\frac{1}{4}\nabla^{2}_{\vec{R}}+\nabla^{2}_{\vec{r}}+\nabla_{\vec{r}}.\nabla_{\vec{R}}\right]\psi j\,(1)\right).\left(\left[\frac{1}{4}\nabla^{2}_{\vec{R}}+\nabla^{2}_{\vec{r}}+\nabla_{\vec{r}}.\nabla_{\vec{R}}\right]\phi(12)\right)\right\}\right]d\vec{r}\,d\vec{R}\end{gathered}}$$

(D.37)

To obtain more details on the development of this formalism in the context of an approximation, the reader is referred to the main text —chapter IV, section II.— as well as its accompanying appendix —appendix E.

Appendix E

Correlation Energy Formalism within an Approximation: McLaurin's Series Expansion of $P_{det,2}$ (12)

Approximating the spinless second-order density function by the leading term of its McLaurin's series expansion about $\vec{r}$, according to equation 206 in the main text

$$P_{\underline{det},2}\,(12)\,\Big|_{\vec{r}=0} \approx P_{\underline{det},2}\,(\vec{R},0) = \frac{1}{2}\,\rho^{2}(\vec{R}) \qquad \text{(E.1)}$$

greatly simplifies the previously elaborated general correlation energy formalism. The key point to understand how the general formalism properly reduces to the formalism that we shall soon develop is to know how to take care, in the kinetic energy contribution, of the terms involving a scalar product of gradients applying on different coordinates, i.e. of the type $\nabla_{\vec{r}}.\nabla_{\vec{R}}$. We shall briefly explain how to do so whenever it is appropriate.

I. Potential Energy Contribution.

As mentioned in appendix D, the potential energy contribution is given in the reduced coordinate system by

$$V_c = \frac{1}{2}\int \frac{P_{\underline{det}.2}\,(12)\; b(12)}{r}\, d\vec{r}\; d\vec{R} \qquad \text{(E.2)}$$

Substituting the spinless second-order density function $P_{\underline{det}.2}\,(\vec{R})$ by its approximation according to equation E.1 and the correlation term b(12) by its defining equation 144, transforms the integrand into a function of R, r and q only. One may then separate the reduced variables as

$$V_c = \frac{1}{2}\int P_{\underline{det}.2}(\vec{R},0)\; d\vec{R} \int \frac{b(12)}{r}\, d\vec{r} \tag{E.3}$$

or, retaining only the leading term of the McLaurin's series expansion,

$$\boxed{V_c = \frac{1}{4}\int \rho^2(\vec{R})\; d\vec{R} \int \frac{b(12)}{r}\, d\vec{r}} \tag{E.4}$$

The analytical integration over the four spherical angles may then first be carried out, operation which generates a multiplicative factor of 16 π^2 in front of the remaining double integral over R and r. The latter integration is then analytically evaluated using the general integral formula

$$\int_0^\infty r^p\, e^{-(a\, r^q)}\, dr = \frac{\Gamma(\frac{p+1}{q})}{q\, a^{((p+1)/q)}} \qquad \text{for } \frac{p+1}{q} > 0\,;\; a > 0 \tag{E.5}$$

where Γ is the Gamma function defined as

$$\Gamma(n) \equiv \int_0^\infty r^{(n-1)}\, e^{-r}\, dr \tag{E.6}$$

which has the following well-known properties for integers and multiple fractions of 2

$$\Gamma(n) = (n-1)! \;\text{ and }\; \Gamma(n+\tfrac{1}{2}) = (2n-1)!!\,\frac{\sqrt{\pi}}{2^n} \tag{E.7}$$

The reader may find the result of the integration over r in the Mathematica™ program —based on this formalism— given in appendix G.

The remaining integral over R is evaluated numerically as explained in the main text.

II. *Kinetic Energy Contribution*.

The kinetic energy contribution is still divided into

$$\boxed{T_c \equiv -\frac{1}{2}\,(T_{c_1} + 2\,T_{c_2} + T_{c_3})} \qquad (E.8)$$

where the three terms in the right-hand side of this equation retain their previous general meaning of equations D.22, D.23 and D.24. We shall now examine the effect of approximating $P_{\underline{det}.2}(\vec{R})$ by equation E.1 on each of these three terms.

II.1. Derivation of T_{c_1}.

After introducing the approximate form of $P_{\underline{det}.2}$ (12) in equation D.22, one gets for T_{c_1},

$$T_{c_1} = \int P_{\underline{det}.2}(\vec{R},0)\, d\vec{R} \int (\phi(12)-1) \left[\frac{1}{4} \nabla^2_{\vec{R}} + \nabla^2_{\vec{r}} + \nabla_{\vec{r}}.\nabla_{\vec{R}} \right] \phi(12)\, d\vec{r}$$

(E.9)

Furthermore, since $\phi(12)$ is a function of R and r only —according to equation 201— one may write the scalar product of the two gradients as

$$\left[\nabla_{\vec{r}}.\nabla_{\vec{R}} \right] \phi(12) = \frac{\delta}{\delta r} \left(\frac{\delta \phi(12)}{\delta R} \right) \vec{r}_{\mathrm{unit}} \cdot \vec{R}_{\mathrm{unit}} \qquad \text{(E.10)}$$

where the scalar product of the two unit vectors is given by equation ?, namely

$$\vec{r}_{\mathrm{unit}} \cdot \vec{R}_{\mathrm{unit}} = \sin \Theta \sin \theta \cos (\Phi - \varphi) + \cos \Theta \cos \theta \qquad \text{(E.11)}$$

The reader may check that the integration of such an expression over the four spherical angles is equal to 0.

We are then left with two contributions in T_{c_1}, that is one involving the laplacian of R and the other involving the laplacian over r, according to

$$\boxed{T_{c_1} \equiv T_{c.R} + T_{c.r}} \qquad \text{(E.12)}$$

which are given, after approximation of $P_{\underline{det}.2}$ (12) and separation of the reduced variables by

$$T_{c,R} = \frac{1}{8} \int \rho^2(\vec{R})\, d\vec{R} \int \left[\nabla^2_{\vec{R}}\, b(12;1'2) \right]_{1' \to 1} d\vec{r} \qquad \text{(E.13)}$$

and

$$T_{c,r} = \frac{1}{2}\int \rho^2(\vec{R})\, d\vec{R} \int \left[\, \nabla^2_{\vec{r}}\, b(12;1'2)\, \right]_{\vec{r}\,' \to \vec{r}}\, d\vec{r} \qquad \text{(E.14)}$$

These two terms may be physically interpreted as explained in the main text. We shall now investigate the calculation of each of them.

* *$T_{c,R}$ contribution:*

To greatly simplify the calculations, first compare the integral over r in $T_{c,R}$ to that of $\nabla^2_{\vec{R}}\, b(12)$ over the same variable. Equation D.25 tells us that

$$\left[\, \nabla^2_{\vec{R}}\, b(12;1'2)\, \right]_{1' \to 1} = (\phi(12) - 1)\, \nabla^2_{\vec{R}}\, \phi(12) \qquad \text{(E.15)}$$

where as the same laplacian operator applied onto the diagonal correlation correction element yields

$$\begin{aligned} \nabla^2_{\vec{R}}\, b(12) &= \nabla_{\vec{R}} \cdot \left(2\, (\phi(12) - 1)\ \nabla_{\vec{R}}\, \phi(12) \right) \\ &= 2\, (\phi(12) - 1)\ \nabla^2_{\vec{R}}\, \phi(12) + 2\, \nabla_{\vec{R}}\, \phi(12) \cdot \nabla_{\vec{R}}\, \phi(12) \qquad \text{(E.16)} \end{aligned}$$

Therefore, one has the relation

$$\left[\nabla^2_{\vec{R}} b(12;1'2) \right]_{1' \to 1} = \frac{1}{2} \nabla^2_{\vec{R}} b(12) - \nabla_{\vec{R}} \phi(12) . \nabla_{\vec{R}} \phi(12) \tag{E.17}$$

which may be substituted into equation E.13 to give

$$\begin{aligned} T_{c,R} = {} & \frac{1}{16} \int \rho^2(\vec{R})\, d\vec{R} \int \nabla^2_{\vec{R}} b(12)\, d\vec{r} \\ & - \frac{1}{8} \int \rho^2(\vec{R})\, d\vec{R} \int \nabla_{\vec{R}} \phi(12) . \nabla_{\vec{R}} \phi(12)\, d\vec{r} \end{aligned} \tag{E.18}$$

Using a property of integrals in the first term of the right hand-side of this last equation, the laplacian operator over $\vec{R}$ may be taken out of the integral over r, as

$$\frac{1}{16} \int \rho^2(\vec{R})\, d\vec{R}\ \nabla^2_{\vec{R}} \int b(12)\, d\vec{r} \tag{E.19}$$

We now make an important point: according to the condition of N-representability on the first-order reduced density matrix, given within the McLaurin's series approximation (see equation ?),

$$\int b(12)\, d\vec{r} = 0 \tag{E.20}$$

Using this result in $T_{c,R}$, integrating over the four spherical angles and substituting the scalar product of the two same gradients by its definition finally leads to

$$\boxed{T_{c.R} = -\,2\,\pi^2 \int R^2 \rho^2(R)\, dR \int r^2 \left(\frac{\delta\phi(12)}{\delta R} \right)^2 dr} \tag{E.21}$$

* *$T_{c,r}$ contribution:*

Applying equation E.14 to the $\vec{r}$ laplacian operator, one obtains

$$T_{c,r} = \frac{1}{2}\int \rho^2(\vec{R})\, d\vec{R} \int (\phi(12) - 1)\, \nabla^2_{\vec{r}}\, \phi(12)\, d\vec{r} \qquad \text{(E.22)}$$

It is easily checked, using the general integral formula of equation ?, that, whatever the form of $\Phi(\vec{R})$ is, it is always true that

$$\int \nabla^2_{\vec{r}}\, \phi(12)\, d\vec{r} = 0 \qquad \text{(E.23)}$$

One is then left with, after integration over angles, an expression of $T_{c,r}$ as

$$\boxed{T_{c.r} = 8\,\pi^2 \int R^2\, \rho^2(R)\, dR \int r^2\, \phi(12)\, \nabla^2_{\vec{r}}\, \phi(12)\, dr}$$

(E.24)

Appendix G shows the result of the integration over r in this equation, as written in the Mathematica™ program.

II.2. Derivation of T_{c_2}.

T_{c_2} is given by equation D.23 as

$$T_{c_2} \equiv \int [\, \nabla_1 P_{\underline{det}.2}\,(12;1'2) \cdot \nabla_1\, b(12;1'2)\,]_{1'\to 1}\, d\vec{r}\, d\vec{R} \qquad (E.25)$$

where the gradient over 1 of the off-diagonal density function element may be written as

$$\nabla_1 P_{\underline{det}.2}\,(12;1'2) = [\, \tfrac{1}{2} \nabla_{\vec{R}} + \nabla_{\vec{r}}\,]\; P_{\underline{det}.2}\,(12;1'2) \qquad (E.26)$$

where the operators are understood to act upon $\vec{R}$ and $\vec{r}$ corresponding to variable 1 only. However, since after its approximation by the leading term of its McLaurin's series about $\vec{r}$, $P_{\underline{det}.2}$ is no more a function of $\vec{r}$, then

$$[\, \nabla_{\vec{r}}\; P_{\underline{det}.2}\,(12;1'2)\,]_{1'\to 1} = 0 \qquad (E.27)$$

and we are left with

$$T_{c_2} \equiv \int [\, \nabla_{\vec{R}}\, P_{\underline{det}.2}(12;1'2) \cdot [\, \tfrac{1}{2} \nabla_{\vec{R}} + \nabla_{\vec{r}}\,]\; b(12;1'2)\,]_{1'\to 1}\, d\vec{r}\, d\vec{R}$$

$$(E.28)$$

Furthermore, for the same type of argument as the one for T_{c_1}, the scalar product of the two gradients applying on different reduced coordinates integrates to 0 —see the previous section **II.1.**

The other contribution to T_{c_2} may be calculated as follows: first, recall that

$$\left[\nabla_{\vec{R}}\, b(12;1'2)\right]_{1' \to 1} = (\phi(12)-1)\, \nabla_{\vec{R}}\, \phi(12) \qquad \text{(E.29)}$$

while

$$\nabla_{\vec{R}}\, b(12) = 2\,(\phi(12)-1)\, \nabla_{\vec{R}}\, \phi(12) = 2\left[\nabla_{\vec{R}}\, b(12;1'2)\right]_{1' \to 1} \qquad \text{(E.30)}$$

relation which may be substituted into T_{c_2} to get

$$T_{c_2} = \frac{1}{2}\int \left[\nabla_{\vec{R}}\, P_{\underline{det}.2}(12;1'2)\right]_{1' \to 1} d\vec{R} \;\cdot\; \frac{1}{2}\, \nabla_{\vec{R}} \int b(12)\, d\vec{r} \qquad \text{(E.31)}$$

However, by requirement of N-representability within the McLaurin's series expansion,

$$\int b(12)\, d\vec{r} = 0 \qquad \text{(E.32)}$$

leading finally to

$$\boxed{T_{c_2} = 0} \qquad \text{(E.33)}$$

II.3. Derivation of T_{c_3}.

T_{c_3} is defined by equation D.24 as

$$T_{c_3} \equiv \int b(12) \left[\nabla_1^2 P_{\underline{det}.2} (12;1'2) \right]_{1' \to 1} d\vec{r}\, d\vec{R} \qquad \text{(E.34)}$$

If one McLaurin's series expands $P_{\underline{det}.2}$ (12;1'2) to the zeroth order, one is left with a function of R only, and the result of operating the laplacian on it may be symbolized by

$$\left[\nabla_1^2 P_{\underline{det}.2} (12;1'2) \right]_{1' \to 1} \equiv g(R) \qquad \text{(E.35)}$$

which may be substituted into T_{c_3} to get

$$T_{c_3} = \int g(R)\, d\vec{R} \; . \int b(12)\, d\vec{r} \qquad \text{(E.36)}$$

which also reduces to zero by constraint of N-representability on the diagonal element. Therefore, one obtains

$$\boxed{T_{c_3} = 0} \qquad \text{(E.37)}$$

Finally, the kinetic contribution to the correlation energy, within the McLaurin's series expansion about $\vec{r}$ to the zeroth order of $P_{\underline{det}.2}$, is found to be equal to

$$\boxed{T_c = -\frac{1}{2}\,(\,T_{c,R} + T_{c,r}\,)} \qquad \text{(E.38)}$$

where $T_{c,R}$ and $T_{c,r}$ are given, respectively, by equation E.21 and E.24.

Again, the reader is referred to appendix G for the analytical expression of the numerical integrations over r. The remaining integration over R being numerically evaluated as explained in the main text.

III. Total Correlation Energy.

The total correlation energy is then obtained from its defining formula,

$$\boxed{E_c \equiv V_c + T_c} \qquad \text{(E.39)}$$

where its potential and kinetic contributions are given by equations E.4 and E.37, respectively.

Appendix F

Exact Solutions to the N-Representability Condition: Determination with Mathematica™

```
integralsrb1212[br_,q_] := (
((3*fbphi[br, q])/8 + fbphi[br, q]^2/8)/beta[br, q]^4 +
        (-Pi^(1/2)/2 + Pi^(1/2)/(8*2^(1/2)) +
            (Pi^(1/2)*fbphi[br, q])/2 -
            (Pi^(1/2)*fbphi[br, q])/(4*2^(1/2)) +
            (Pi^(1/2)*fbphi[br, q]^2)/(8*2^(1/2)))/
     beta[br, q]^3 + (3*Pi^(1/2)*fbphi[br, q]^2)/
     (128*2^(1/2)*beta[br, q]^5)
                              )
```

```
integralsrb1212[br,q]
```

```
                              2
3 fbphi[br, q]   fbphi[br, q]
-------------- + -------------
      8                 8
------------------------------ +
                    4
         beta[br, q]

         -Sqrt[Pi]    Sqrt[Pi]     Sqrt[Pi] fbphi[br, q]
        (--------- + --------- + --------------------- -
             2        8 Sqrt[2]             2

                                                          2
            Sqrt[Pi] fbphi[br, q]    Sqrt[Pi] fbphi[br, q]
            --------------------- + ----------------------) /
                  4 Sqrt[2]                8 Sqrt[2]

                                             2
                 3    3 Sqrt[Pi] fbphi[br, q]
     beta[br, q]   + ------------------------
                                             5
                     128 Sqrt[2] beta[br, q]
```

```
Collect[ Expand[%], fbphi ]

  -Sqrt[Pi]              Sqrt[Pi]
-------------- + ---------------------- +
             3                        3
2 beta[br, q]    8 Sqrt[2] beta[br, q]

          3              Sqrt[Pi]              Sqrt[Pi]
     (-------------- + -------------- - ----------------------
                    4               3                        3
      8 beta[br, q]    2 beta[br, q]    4 Sqrt[2] beta[br, q]

           ) fbphi[br, q] +

           3 Sqrt[Pi]                  1
     (------------------------ + -------------- +
                             5                4
      128 Sqrt[2] beta[br, q]    8 beta[br, q]

                 Sqrt[Pi]                      2
           ----------------------) fbphi[br, q]
                                3
           8 Sqrt[2] beta[br, q]

cfbphi[br_,q_] := (
-Pi^(1/2)/(2*beta[br, q]^3) +
   Pi^(1/2)/(8*2^(1/2)*beta[br, q]^3)
            )

bfbphi[br_,q_] := (
(3/(8*beta[br, q]^4) + Pi^(1/2)/(2*beta[br, q]^3) -
            Pi^(1/2)/(4*2^(1/2)*beta[br, q]^3))
             )

afbphi[br_,q_] := (
((3*Pi^(1/2))/(128*2^(1/2)*beta[br, q]^5) +
            1/(8*beta[br, q]^4) +
            Pi^(1/2)/(8*2^(1/2)*beta[br, q]^3))
             )

cfbphi[br,q]

  -Sqrt[Pi]              Sqrt[Pi]
-------------- + ----------------------
             3                        3
2 beta[br, q]    8 Sqrt[2] beta[br, q]
```

```
bfbphi[br,q]

       3            Sqrt[Pi]             Sqrt[Pi]
-------------- + -------------- - ----------------------
             4                3                         3
8 beta[br, q]    2 beta[br, q]    4 Sqrt[2] beta[br, q]

afbphi[br,q]

       3 Sqrt[Pi]                1
------------------------ + -------------- +
                       5                4
128 Sqrt[2] beta[br, q]    8 beta[br, q]

          Sqrt[Pi]
   ----------------------
                         3
   8 Sqrt[2] beta[br, q]

deltafbphi[br_,q_] := ( bfbphi[br,q]^2
     - (4 afbphi[br,q] cfbphi[br,q]) )

deltafbphi[br,q]

          -Sqrt[Pi]             Sqrt[Pi]
    -4 (-------------- + ----------------------)
                     3                        3
        2 beta[br, q]    8 Sqrt[2] beta[br, q]

                3 Sqrt[Pi]                 1
        (------------------------ + -------------- +
                                5                4
         128 Sqrt[2] beta[br, q]    8 beta[br, q]

                   Sqrt[Pi]
            ----------------------) +
                                 3
            8 Sqrt[2] beta[br, q]

          3             Sqrt[Pi]             Sqrt[Pi]         2
   (-------------- + -------------- - ----------------------)
                 4                3                        3
    8 beta[br, q]    2 beta[br, q]    4 Sqrt[2] beta[br, q]

e = { 1.43000, 2.44150, 4.09960, 6.48430, 0.79780 }

{1.43, 2.4415, 4.0996, 6.4843, 0.7978}
```

```
c = { 0.78503, 0.20284, 0.03693, -0.00293, 0.00325 }

{0.78503, 0.20284, 0.03693, -0.00293, 0.00325}

Do [ psi[i][br], {i,5} ]

Do [ psi[i][br_] = ( ( ((e[[i]])^(3/2)) Exp[ -br e[[i]] ] )
                     / (Sqrt[N[Pi,8]]) ), {i,5} ]

aols[br_] := Sum[( (c[[i]])(psi[i][br]) ), {i,1,5} ]

rho[br_] := 2 ( (aols[br])^2 )

beta[br_,q_] := q (rho[br])^(1/3)

N[deltafbphi[5,1.2]]

          15
1.09496 10

N[deltafbphi[0,0.01]]

          13
7.86368 10

N[deltafbphi[0,3]]

0.000102779

N[deltafbphi[5,3]]

          11
7.59122 10

N[deltafbphi[5,0.01]]

          31
4.53269 10
```

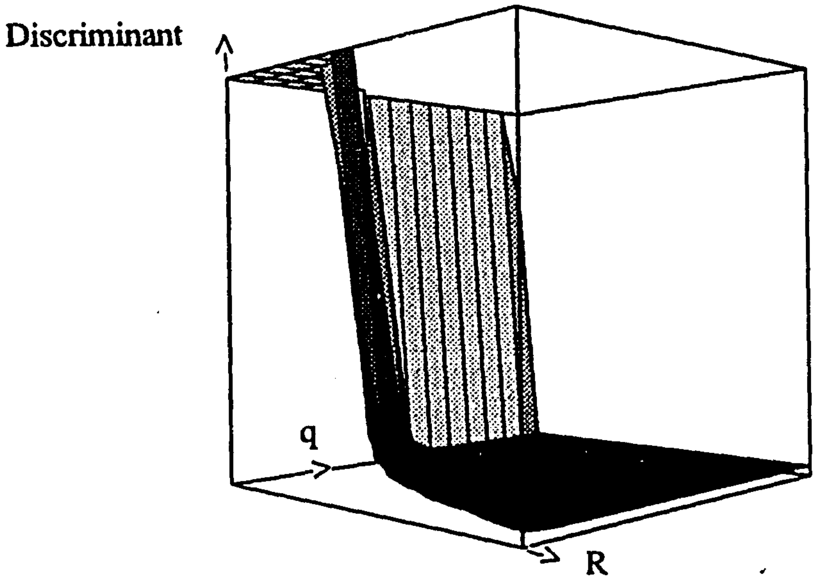


Figure 27. He Atom: Determination of the Number of Solutions to the Exact N-Representability Quadratic Equation: Plot of the Discriminant as a Function of R and q ($0 \leq R \leq 5$, $0.01 \leq q \leq 3$)

```
            (* Conclusion: deltafbphi > 0 *)

fbphiplus[br_,q_] := (
(-bfbphi[br,q] + Sqrt[deltafbphi[br,q]])/(2 afbphi[br,q])
                    )

fbphiminus[br_,q_] := (
(-bfbphi[br,q] - Sqrt[deltafbphi[br,q]])/(2 afbphi[br,q])
                     )
```

```
fbphiplus[br,q]
              0.375         0.572898   2
    (Sqrt[(------------ + ------------)   +
                      4              3
           beta[br, q]    beta[br, q]

                    (2.91825

                       0.0293746        0.125
                      (------------ + ------------ +
                                  5              4
                       beta[br, q]    beta[br, q]

                       0.156664                  3
                     ------------)) / beta[br, q] ] -
                                3
                     beta[br, q]

             0.375         0.572898
         (------------ + ------------)) /
                     4              3
          beta[br, q]    beta[br, q]

        0.0293746        0.125          0.156664
   (2 (------------ + ------------ + ------------))
                  5              4              3
       beta[br, q]    beta[br, q]    beta[br, q]
```

fbphiminus[br,q]

```
            0.375         0.572898    2
  (-Sqrt[(------------ + ------------)   +
                     4              3
         beta[br, q]    beta[br, q]

                  (2.91825

                    0.0293746        0.125
                  (------------ + ------------ +
                              5              4
                   beta[br, q]    beta[br, q]

                    0.156664                  3
                  ------------)) / beta[br, q] ] -
                             3
                  beta[br, q]

          0.375         0.572898
      (------------ + ------------)) /
                  4              3
       beta[br, q]    beta[br, q]

     0.0293746        0.125         0.156664
(2 (------------ + ------------ + ------------))
               5              4              3
    beta[br, q]    beta[br, q]    beta[br, q]
```

Appendix G

Mathematica™ Program for the Correlation Energy Calculations

```
e = { 1.43000, 2.44150, 4.09960, 6.48430, 0.79780 }
c = { 0.78503, 0.20284, 0.03693, -0.00293, 0.00325 }
Do [ psi[i][br], {i,5} ]
Do [ psi[i][br_] = ( ( ((e[[i]])^(3/2)) Exp[ -br e[[i]] ] )
                   / (Sqrt[N[Pi,8]]) ), {i,5} ]
ao1s[br_] := Sum[( (c[[i]])(psi[i][br]) ), {i,1,5} ]
rho[br_] := 2 ( (ao1s[br])^2 )
beta[br_,q_] := q (rho[br])^(1/3)
cfbphi[br_,q_] := (
-N[Pi,8]^(1/2)/(2*beta[br, q]^3) +
    N[Pi,8]^(1/2)/(8*N[2^(1/2)]*beta[br, q]^3)
              )
bfbphi[br_,q_] := (
(3/(8*beta[br, q]^4) + N[Pi,8]^(1/2)/(2*beta[br, q]^3) -
              N[Pi,8]^(1/2)/(4*N[2^(1/2)]*beta[br, q]^3))
              )
afbphi[br_,q_] := (
((3*N[Pi,8]^(1/2))/(128*N[2^(1/2)]*beta[br, q]^5) +
            1/(8*beta[br, q]^4) +
              N[Pi,8]^(1/2)/(8*N[2^(1/2)]*beta[br, q]^3))
              )
deltafbphi[br_,q_] := ( bfbphi[br,q]^2
    - (4 afbphi[br,q] cfbphi[br,q]) )
fbphi[br_,q_] := (
(-bfbphi[br,q] + Sqrt[deltafbphi[br,q]])/(2 afbphi[br,q])
          )
```

```
v[br_,q_] := (
          ((1-fbphi[br,q])^2) / ( 4 (beta[br,q])^2 )
          + ( Sqrt[ N[Pi,8] / 2 ] fbphi[br,q] ( fbphi[br,q]-1 )
             / ( 8 (beta[br,q])^3 ) )
          + ( (fbphi[br,q])^2 ) / ( 32 (beta[br,q])^4 )
          - ( 1-fbphi[br,q] ) / ( (beta[br,q])^2 )
          + Sqrt[ N[Pi,8] ] fbphi[br,q] / ( 4 (beta[br,q])^3 )
          )
zvc[br_,q_] := ( (rho[br])^2 ) v[br,q] ( br^2 )
vc[brimax_,q_] := vc[brimax,q] = (
4  (N[Pi,8]^2)  NIntegrate[  zvc[br,q],{br,0,brimax},
            AccuracyGoal->4]
                      )
intprodsr[br_,q_] := N[ (
(fbphi[br, q] - fbphi[br, q]^2)/(4*beta[br, q]^2) +
        (-3*Pi^(1/2) + 6*Pi^(1/2)*fbphi[br, q] -
            3*Pi^(1/2)*fbphi[br, q]^2)/(8*2^(1/2)*beta[br, q])
      - (7*Pi^(1/2)*fbphi[br, q]^2)/
      (128*2^(1/2)*beta[br, q]^3)
              ) ]
intcompbr[br_,q_] := N[
       ((-3*fbphi[br, q]*Derivative[1, 0][beta][br, q]^2)/4 +
               (3*fbphi[br, q]^2*
                 Derivative[1, 0][beta][br, q]^2)/4 -
              (15*Pi^(1/2)*fbphi[br, q]*
                 Derivative[1, 0][beta][br, q]*
```

```
              Derivative[1, 0][fbphi][br, q])/
         (128*2^(1/2)))/beta[br, q]^6 +
    ((15*Pi^(1/2)*Derivative[1, 0][beta][br, q]^2)/
        (32*2^(1/2)) -
           (15*Pi^(1/2)*fbphi[br, q]*
              Derivative[1, 0][beta][br, q]^2)/
        (16*2^(1/2)) +
           (15*Pi^(1/2)*fbphi[br, q]^2*
              Derivative[1, 0][beta][br, q]^2)/
        (32*2^(1/2)) +
           (Derivative[1, 0][beta][br, q]*
              Derivative[1, 0][fbphi][br, q])/4 -
           (fbphi[br, q]*Derivative[1, 0][beta][br, q]*
              Derivative[1, 0][fbphi][br, q])/2 +
         (3*Pi^(1/2)*Derivative[1, 0][fbphi][br, q]^2)/
         (128*2^(1/2)))/beta[br, q]^5 +
    ((3*Pi^(1/2)*Derivative[1, 0][beta][br, q]*
              Derivative[1, 0][fbphi][br, q])/
        (8*2^(1/2)) -
          (3*Pi^(1/2)*fbphi[br, q]*
             Derivative[1, 0][beta][br, q]*
             Derivative[1, 0][fbphi][br, q])/
        (8*2^(1/2)) +
       Derivative[1, 0][fbphi][br, q]^2/8)/beta[br, q]^4
+ (105*Pi^(1/2)*fbphi[br, q]^2*
      Derivative[1, 0][beta][br, q]^2)/
```

```
    (512*2^(1/2)*beta[br, q]^7) +
    (Pi^(1/2)*Derivative[1, 0][fbphi][br, q]^2)/
    (8*2^(1/2)*beta[br, q]^3)
              ]
ztc1sr[br_,q_] := (
br^2 rho[br]^2 ( intprodsr[br,q] )
          )
tc1sr[brimax_,q_] := tc1sr[brimax,q] = (
    8 N[Pi,8]^2 NIntegrate[ ztc1sr[br,q], {br,0,brimax},
   AccuracyGoal->4 ]
                  )
ztc1compbr[br_,q_] := (
br^2 rho[br]^2 (- intcompbr[br,q] )
          )
tc1compbr[brimax_,q_] := tc1compbr[brimax,q] = (
2 N[Pi,8]^2 NIntegrate[ ztc1compbr[br,q], {br,0,brimax},
   AccuracyGoal->4 ]
                  )
tc1[brimax_,q_] := tc1[brimax,q] = (
tc1compbr[brimax,q] + tc1sr[brimax,q]   )
tc[q_] := -(1/2) ( tc1[brimax,q])
ec[q_] := vc[brimax,q] + tc[q]
```

Bibliography

1. Anderson, J.M. *Mathematics of Quantum Chemistry;* W.A. Benjamin: New York, 1966.

2. Sudbery, A. *Quantum Mechanics and the Particles of Nature: an Outline for Mathematicians;* Cambridge University, 1986.

3. Cohen-Tannoudji, C.; Diu, B.; Laloe. F. *Quantum Mechanics, vol. I & II (Engl. Transl.);* Wiley-Interscience: New-York, 1977.

4. Messiah, A. *Quantum Mechanics, vol. I & II (Engl. Transl.);* Interscience: New York, 1961.

5. Heisenberg, W. Zeits. fur Phys.: 1925, 33, 879.

6. Schrödinger, E. Ann. der Phys.: 1926, 79, 361.

7. Dirac, P.A.M. *The Principles of Quantum Mechanics (4th ed.);* Oxford University: New York, 1958.

8. von Newman, J. *Mathematical Foundations of Quantum Mechanics (Engl. Transl.);* Princeton University, 1955.

9. Prugovecki, E. *Quantum Mechanics in Hilbert Space (2nd ed.);* Academic: New York, 1981.

10. Jackson, J.D. *Mathematics for Quantum Mechanics;* W.A. Benjamin: New York, 1962.

11. Emch, G.G. *Mathematical and Conceptual Foundations of Twentieth Century Physics;* North-Holland: New York, 1984.

12. Ludwig, G. *Foundations of Quantum Mechanics, vol. I & II (Engl. Transl.);* Springer-Verlag: New York, 1983.

13. Bohm, A. *Quantum Mechanics: Foundations and Applications (2nd ed.);* Springer-Verlag: New York, 1986.

14. Halmos, P.R. *Introduction to Hilbert Space (and the Theory of Spectral Multiplicity) (2nd ed.);* Chelsea: New York, 1957.

15. Soulé, J.L. *Linear Operators in Hilbert Space (Engl. Transl.);* Gordon & Breach: New York, 1968.

16. Lentin, A.; Rivaud, J. *Leçons d'Algèbre Moderne (in French) (3rd ed.);* Librairie Vuibert: Paris, 1969.

17. Istratescu, V.I. *Inner Product Structures, Theory & Applications;* D. Reidel: Boston, 1987.

18. McWeeny, R. *Methods of Molecular Quantum Mechanics (2^{nd} ed.);* Academic: New York, 1989.

19. McWeeny, R. Rev. Mod. Phys.: 1960, 32, 335.

20. Levine, I. *Quantum Chemistry (3^{rd} ed.);* Allyn and Bacon: Boston, 1983.

21. Ziman, J.M. *Elements of Advanced Quantum Theory;* Cambridge University, 1969.

22. Moss, R.E. *Advanced Molecular Quantum Mechanics;* Chapman & Hall: New York, 1973.

23. *Density Matrices and Density Functionals;* Erdahl, R.; Smith, V.A., Ed.; D. Reidel Company: New York 1986.

24. *Electron Distributions and the Chemical Bond;* Coppens, P.; Hall, M.B., Ed.; Plenum: New York, 1982.

25. *The Force Concept in Chemistry;* Deb, B.M., Ed.; Van Nostrand Reinhold: New York, 1981.

26. Blum, K. *Density Matrix Theory and Applications;* Plenum Press: New York, 1981.

27. Davidson, E.R. *Reduced Density Matrices in Quantum Chemistry;* Academic: New York, 1976.

28. ter Haar, D. *Reduced Density Matrices in Quantum Mechanics;* Academic: New York, 1976.

29. ter Haar, D. *Elements of Statistical Mechanics;* Holt, Rinehart, Winston: New York, 1954.

30. Tolman, R.C. *The Principles of Statistical Mechanics;* Oxford University: New York, 1938.

31. Bamzai, A.S.; Deb, M.B. Rev. Mod. Phys.: 1981, 53, 95 & 593.

32. McWeeny, R. Proc. R. Soc. Lond.: 1954, A223, 63.

33. McWeeny, R. Proc. R. Soc. Lond.: 1955, A232, 114.

34. Löwdin, P.O. Phys. Rev.: 1955, 97, 1474.

35. Löwdin, P.O. Phys. Rev.: 1955, 97, 1490.

36. ter Haar, D. Rep. Prog. Phys.: 1961, 24, 304.

37. Coleman, A.J. Rev. Mod. Phys.: 1963, 35, 668.

38. Fano; U. Rev. Mod. Phys.: 1957, 29, 75.

39. Glusker, J.R.; Trueblood, K.N. *Crystal Structure Analysis (2nd ed.);* Oxford University: New York, 1985.

40. *Patterson and Pattersons: Fifty Years of the Patterson Function,* Ed. Glusker, J.P.; Patterson, B.K.; Rossi, M.; Oxford University: New York, 1987.

41. *Molecular Structure: Chemical Reactivity and Biological Activity,* Ed. Stezowski, J.J.; Huang, J.L.; Shao, M.C.; Oxford University: New York, 1988.

42. Hohenberg, P.; Kohn, W. Phys. Rev. B: 1964, 136, 864.

43. Kohn, W.; Sham, L. Phys. Rev. A: 1965, 140, 1133.

44. Lieb, E.H. Int. J. Quant. Chem.: 1983, 24, 243.

45. Zumbach, G.; Maschke K. Phys. Rev. A: 1983, 28, 544.

46. March, N.H.; Santamaria, R. Phys. Rev. A: 1988, 38, 5002.

47. Massa, L.J.; Boehme, R.F.; La Placa, S.J. "X-ray Imaging of Quantum Electron Structure". In reference 40 of this bibliography, page 427.

48. Harriman, J.E. Phys. Rev. A: 1978, 17, 1249.

49. Harriman, J.E. Phys. Rev. A: 1983, 27, 632.

50. Cohen, L.; Frishberg, C.; Chongmoon Lee; Massa L.J. Int. J. Quantum Chem. Symp.: 1986, 19, 525.

51. Frishberg, C.A.; Massa, L.J. Int. J. Quantum Chem.: 1978, 13, 801.

52. McWeeny, R. Acta Crystallogr.: 1953, 6, 631.

53. McWeeny, R. Acta Crystallogr.: 1954, 7, 180.

54. Kurki-Suonio, K. Acta Crystallogr., Sect. A: 1968, 24, 279.

55. Stewart, R.F. J. Chem. Phys.: 1969, 51(10), 4569.

56. Clinton, W.L.; Massa, L.J. Phys. Rev. Lett:. 1972, 29, 1363.

57. Massa, L.J.; Clinton, W.L. Trans. Amer. Crystallogr. Assn.: 1972, 8, 149.

58. Clinton, W.L.; Frishberg, C.A.; Massa, L.J.; Oldfield, P.A. Int. J. Quantum Chem. Symp.: 1973, 7, 505.

59. Frishberg, C.A.; Goldberg, M.J.; Massa, L.J. "Quantum Model of the Coherent Diffraction Experiment: Recents Generalizations and Applications". In reference 24 of this bibliography, page 101.

60. Clinton, W.L.; Frishberg, C.A.; Goldberg, M.J.; Massa, L.J.; Oldfield, P.A. Int. J. Quantum Chem. Symp.: 1983, 17, 517.

61. Goldberg, M.J.; Massa, L.J. Int. J. Quantum Chem.: 1983, 24, 113.

62. Frishberg, C.A.; Massa, L.J. Phys. Rev. B: 1981, 24, 7018.

63. Frishberg, C.A.; Massa, L.J. Acta Cryst., Sect. A: 1982, 38, 93.

64. Massa, L.; Goldberg, M.J.; Frishberg, C.; Boehme, R.F.; La Placa, S.J. Phys. Rev. Lett.: 1985, 55, 622.

65. Boehme, R.F.; La Placa, S.J. Phys. Rev. Lett.: 1987, 59, 985.

66. Gilbert, T.L. Phys. Rev. B: 1975, 12, 2111.

67. Harriman, J. Phys. Rev. A: 1981, 24, 680.

68. Clinton, W.L.; Galli, A.J.; Massa, L.J. Phys. Rev.: 1969, 177, 7.

69. Levy, M.; Goldstein, J.A. Phys. Rev. B: 1987, 35, 7887.

70. Pecora, L.M. Phys. Rev. B: 1986, 33, 5987.

71. Aitken, A. C. Biometrika: 1950, 37, 93.

72. Banerjee, K. S. Ann. Math. Statist.: 1964, 35, 880.

73. Bellman, R. *Introduction to Matrix Analysis;* McGraw-Hill: New York, 1960.

74. Bush, K. A.; Olkin, I. Biometrika: 1959, 46, 484.

75. Carpenter, 0. Ann. Math. Statist.: 1950, 21, 455.

76. Cochran, W. G. Proc. Camb. Phil. Soc.: 1934, 30, 178.

77. Craig, A. T. Ann. Math. Statist.: 1943, 14, 195.

78. Drazin, M. P. Quart. J. Math.: 1951, 2, 189.

79. Graybill, F. A. *An Introduction to Linear Statistical Models;* McGraw-Hill: New York, 1961.

80. Graybill, F. A; Marsaglia, G. Ann. Math. Statist.: 1957, 28, 678.

81. Hotelling, H. Ann. Math. Statist.: 1944, 15, 427.

82. Hsu, P. L. Proc. Math. Soc. Edinburgh: 1948, 2, 38.

83. Loynes, R. M. Ann. Math. Statist.: 1966, 37,.295.

84. Luther, Norman Y. Ann. Math. Statist.: 1965, 36, 683.

85. Helmberg, G. *Introduction to Spectral Theory in Hilbert Space;* North-Holland: New York, 1969.

86. Putnam, C.R. *Commutation Properties of Hilbert Space Operators and Related Topics;* Springer-Verlag: New York, 1967.

87. Plesner, A.I. *Spectral Theory of Linear Operators, vol. I & II (Engl. Transl.);* Frederick Ungar: New York, 1969.

88. Riesz, F.; Nagy, B.Sz. *Leçons d'Analyse Functionnelle; (Engl. Transl.: Functional Analysis);* Frederick Ungar: New York, 1971.

89. Curtain, R.F.; Pritchard, A.J. *Functional Analysis in Modern Applied Mathematics;* Academic: New York, 1977.

90. Roman, P. *Advanced Quantum Theory;* Addison-Wesley: New York, 1965.

91. Hamermesh, M. *Group Theory and its Applications to Physical Problems;* Addison-Weslyey: New York, 1962. (Dover: New York, 1990).

92. Gerstein, L.J. Amer. Math. Month.: 1988, 95(10), 950.

93. Pettofrezo, A.J. *Matrices and Transformations;* Prentice Hall: Englewood Cliffs, 1966. (Dover: New York, 1978).

94. Hylleraas, E.A. Z. Phys.: 1929, 54, 347.

95. Hylleraas, E.A. Adv. Quantum Chem.: 1964, 1, 1.

96. James, H.; Coolidge, A.S. J. Chem Phys.: 1933, 1, 825.

97. Jastrow, R. Phys. Rev.: 1955, 98, 1479.

98. Boys, S.F.; Handy, N.C. Proc. Roy. Soc. Sect. A: 1969, 309, 209.

99. Boys, S.F.; Handy, N.C. Proc. Roy. Soc. Sect. A: 1969, 310, 43.

100. Colle, R.; Salvetti, 0. Theoret. Chim. Acta. (Berl.): 1975, 37, 309.

101. Roby, K.R. Int. J. Quantum Chem.: 1971, 5, 119.

102. Goldstein, H. *Classical Mechanics (2nd ed.);* Addison-Wesley: Reading, 1981.

103. Clementi, E. Tables of Atomic Functions, a supplement to the paper by Clementi, E. *Ab Initio Computations in Atoms and Molecules;* IBM J. Res. Dev.: 1965, 9, 2.

104. Flocco, M. Ph.D. Thesis, City University of New York, 1989.

105. Wolfram, S. *Mathematica™;* Addison-Wesley: Reading, 1988.

106. Parr, R.G.; Yang, W. *Density Functional Theory of Atoms and Molecules;* Oxford University: New York, 1989.

107. *Density Functional Methods in Physics;* Reiner, M., Ed; Plenum: New York, 1985.

108. Massa, L.; Flocco, M.; Soirat A. J. Mol. Struct. (Theochem): 1989, 199, 337.