INFORMATION TO USERS

This material was produced from a microfilm copy of the original document. While the most advanced technological means to photograph and reproduce this document have been used, the quality is heavily dependent upon the quality of the original submitted.

The following explanation of techniques is provided to help you understand markings or patterns which may appear on this reproduction.

1. The sign or "target" for pages apparently lacking from the document photographed is "Missing Page(s)". If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting thru an image and duplicating adjacent pages to insure you complete continuity.

2. When an image on the film is obliterated with a large round black mark, it is an indication that the photographer suspected that the copy may have moved during exposure and thus cause a blurred image. You will find a good image of the page in the adjacent frame.

3. When a map, drawing or chart, etc., was part of the material being photographed the photographer followed a definite method in "sectioning" the material. It is customary to begin photoing at the upper left hand corner of a large sheet and to continue photoing from left to right in equal sections with a small overlap. If necessary, sectioning is continued again — beginning below the first row and continuing on until complete.

4. The majority of users indicate that the textual content is of greatest value, however, a somewhat higher quality reproduction could be made from "photographs" if essential to the understanding of the dissertation. Silver prints of "photographs" may be ordered at additional charge by writing the Order Department, giving the catalog number, title, author and specific pages you wish reproduced.

5. PLEASE NOTE: Some pages may have indistinct print. Filmed as received.

Xerox University Microfilms
300 North Zeeb Road
Ann Arbor, Michigan 48106

75-21,343

ROSENBERG, Martin Lewis, 1945-
THE SPIN PROJECTED EXTENDED HARTREE-FOCK METHOD:
APPLICATION TO MOLECULAR DOUBLE IONIZATION
POTENTIALS.

The City University of New York, Ph.D., 1975
Physics, molecular

Xerox University Microfilms, Ann Arbor, Michigan 48106

THE SPIN PROJECTED EXTENDED HARTREE-FOCK METHOD: APPLICATION TO MOLECULAR DOUBLE IONIZATION POTENTIALS

by

Martin L. Rosenberg

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

1975

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

5/20/75
date

Frank Martino
Professor Frank Martino
Chairman of Examining Committee

5/20/75
date

Myriam P. Sarachik
Professor Myriam Sarachik
Executive Officer

Marvin H. Mittleman

Acknowledgments

I am indebted to the Physics Department of the University of Linkoping, Sweden, and to Professor K.-F. Berggren for hospitality and encouragement during the initial stages of my work on this dissertation. I am also indebted to the American-Scandinavian Foundation for partial support in the form of a Thord-Grey Fellowship. Finally, I would like to express my sincere and deep felt appreciation to Professor Frank Martino, whose patience and guidance contributed so much to this work.

Table of Contents

Chapter 1. Introduction Page 6

Chapter 2. The Hartree-Fock Method Page 10
  Section A. Formulation for Closed Shells Page 10
  Section B. Density Matrix Analysis Page 13

Chapter 3. The Spin Projected Extended Hartree-Fock Method Page 16
  Section A. Introduction Page 16
  Section B. Formulation for Closed Shells Page 17
  Section C. Density Matrix Analysis Page 28
  Section D. Example: Hubbard Model of Benzene Page 29
  Section E. Example: Cyclic H_{10} Page 31
  Section F. Example: The Isoelectronic Series CH_4, NH_3, H_2O, HF and Ne Page 34

Chapter 4. Molecular Double Ionization Potentials Page 51
  Section A. Introduction Page 51
  Section B. Experimental Results Page 55
  Section C. Numerical Results and Discussion Page 58

Chapter 5. Conclusion Page 82

Appendix A Page 84

Appendix B Page 89

List of Tables

Table 1	Page 30
Table 2	Page 33
Table 3	Page 36
Table 4	Page 37
Table 5	Page 38
Table 6	Page 39
Table 7	Page 40
Table 8	Page 41
Table 9	Page 41
Table 10	Page 42
Table 11	Page 42
Table 12	Page 43
Table 13	Page 53
Table 14	Page 57
Table 15	Page 61
Table 16	Page 62
Table 17	Page 63
Table 18	Page 64
Table 19	Page 68
Table 20	Page 68
Table 21	Page 69
Table 22	Page 70
Table 23	Page 71
Table 24	Page 76
Table 25	Page 76
Table 26	Page 77
Table 27	Page 78
Table 28	Page 79
Table 29	Page 80

List of Figures

Figure 1	Page 47
Figure 2	Page 48
Figure 3	Page 72
Figure 4	Page 73

1. Introduction

The independent particle model occupies a central position in the quantum theory of atoms, molecules and solids. The most frequently employed version of this scheme is the Hartree-Fock approximation (1) in which each electron is assumed to experience a potential which is a time independent average of that due to all the other particles in the system. This model contains an inherent error which comes from its failure to describe accurately the "Coulomb hole" which surrounds each electron. This expression refers to the fact that electrons repel each other electrostatically and thus the probability of finding two electrons close to each other should be small. The Hartree-Fock wave function, due to its antisymmetric form, describes a "Fermi hole", i.e. each electron with a given spin is surrounded by a region where the probability of finding another electron of the same spin is small, but it in no way correlates the motion of electrons with opposite spins. This defect in the Hartree-Fock model has been the subject of intensive investigation for many years and is commonly referred to as the correlation problem.

It has become common practice to define the correlation energy associated with a given state and with a specified Hamiltonian as the difference between the exact eigenvalue of the Hamiltonian and the expectation value of the energy in the Hartree-Fock approximation (2). Very accurate numerical work has shown that the Hartree-Fock method is capable of yielding total energies of small atomic and molecular systems with an accuracy of 99.5%. It must be borne in mind, though, that in chemistry and physics we are not so much interested in total energies as we are in energy differences, e.g. ionization potentials, and, given the large magnitude of the total energy, the relatively small error of 0.5% may turn out to be of the order of magnitude of the energy differences we are interested in. In some cases this turns out to be not such a problem. Thus it appears that if one forms the energy difference in the Hartree-Fock approximation between two states with the same number of doubly occupied orbitals, the correlation errors may to a large extent cancel and the final result turn out to be quite accurate (3). However, if the two states involved have different numbers of doubly occupied orbitals one cannot expect this type of error cancellation.

In this work I will present a new formulation of the spin projected extended Hartree-Fock method, an extension of the Hartree-Fock scheme which attempts to better describe the correlation between electrons of opposite spin (4). The method will then be applied to the calculation of the double ionization potentials of some closed shell molecules. These calculations involve the subtraction of total energies of systems whose number of doubly occupied orbitals differ by one and from the above discussion we may expect correlation effects to be important. In Chapter 2 we will give a brief survey of the Hartree-Fock scheme, paying particular attention to the nature of the two electron pair function which indicates precisely the type of correlation ignored by the Hartree-Fock wave function. In Chapter 3 we will present in detail the spin projected extended Hartree-Fock method and, with the help of a series of calculations, demonstrate the improvement it gives over the Hartree-Fock scheme. Finally, in Chapter

4 , the method will be used to calculate the first double ionization potentials of H_2O, NH_3 and N_2 and the results compared to recently obtained experimental values. Atomic units are used throughout.

References

1. V. Fock, Z. Physik 61 , 126 (1930).

2. P. O. Lowdin, Adv. Chem. Phys. 2 , 207 (1959).

3. A. C. Hurley, Adv. Quantum Chem. 7 , 315 (1973).

4. P. O. Lowdin, Phys. Rev. 97 , 1509 (1955).

2. The Hartree-Fock Method

A. Formulation for Closed Shells

In the Hartree-Fock model of a closed shell system containing N=2n electrons, one uses as a trial wave function in a variational calculation a single Slater determinant of doubly occupied orbitals

$$\Psi = \mathcal{A}\,\Phi\, T_0 \tag{1}$$

where T_0 is a product of one electron spin functions

$$T_0 = \alpha(1)\alpha(2)\cdots\alpha(n)\,\beta(n+1)\,\beta(n+2)\cdots\beta(2n) \tag{2}$$

Φ is a product of one electron spatial functions

$$\Phi = \phi_1(1)\phi_2(2)\cdots\phi_n(n)\,\phi_1(n+1)\,\phi_2(n+2)\cdots\phi_n(2n) \tag{3}$$

and $\mathcal{A}$ is the antisymmetrizing operator

$$\mathcal{A} = \frac{1}{\sqrt{N!}}\sum_P (-1)^p P \tag{4}$$

In what follows we shall be mostly concerned with molecules so we introduce here the non-relativistic molecular Hamiltonian in the Born-Oppenheimer approximation

$$\begin{aligned} \hat{H} &= \sum_i \hat{h}(i) + \sum_{i<j} \hat{g}(i,j) + \sum_{\alpha<\beta} \frac{Z_\alpha Z_\beta}{R_{\alpha\beta}} \\ \hat{h}(i) &= -\frac{1}{2}\nabla_i^2 - \sum_\alpha \frac{Z_\alpha}{r_{i\alpha}} \\ \hat{g}(i,j) &= \frac{1}{r_{ij}} \end{aligned} \tag{5}$$

where i and j label electron coordinates and α and β label nuclear coordinates.

The Hartree-Fock wave function represents a pure singlet state and also satifies the Pauli exclusion principle. One may, without any loss of generality, require the one electron orbitals ϕ_i to be orthonormal and it may be easily shown (1) that the expectation value of the Hamiltonian (eq. 5) is

$$E = 2\sum_{i=1}^{n} \langle \phi_i | \hat{h} | \phi_i \rangle + \sum_{i=1}^{n} \sum_{j=1}^{n} \Big[2 \langle \phi_i \phi_j | \hat{g} | \phi_i \phi_j \rangle - \langle \phi_i \phi_j | \hat{g} | \phi_j \phi_i \rangle \Big] \tag{6}$$

where

$$\begin{aligned} \langle \phi_i | \hat{h} | \phi_i \rangle &= \int \phi_i^*(r)\, \hat{h}(r)\, \phi_i(r)\, d^3 r \\ \langle \phi_i \phi_j | \hat{g} | \phi_k \phi_\ell \rangle &= \iint \phi_i^*(r_1)\, \phi_j^*(r_2)\, \hat{g}(r_1, r_2)\, \phi_k(r_1)\, \phi_\ell(r_2)\, d^3 r_1\, d^3 r_2 \end{aligned} \tag{7}$$

At this point it is convenient to introduce a basis set of m ($m \geqslant n$) linearly independent one electron functions χ_K . The idea is to express the Hartree-Fock orbitals as linear expansions of this set

$$\phi_i = \sum_{K=1}^{M} \chi_K C_{Ki} \tag{8}$$

where C_{ki} is an m x n matrix the i^{th} column of which represents the expansion of the i^{th} Hartree-Fock orbital. The χ_k are assumed to be orthonormal. We may now write eq. 6 as

$$E = Tr\, \underline{P} \left(\underline{h} + \frac{1}{2} \underline{G} \right) \tag{9}$$

where

$$\begin{aligned} \underline{P}_{gf} &= \sum_{i=1}^{n} C_{gi} C_{if}^{+} \\ \underline{h}_{gf} &= \langle \chi_g | \hat{h} | \chi_f \rangle \\ \underline{G}_{gf} &= \sum_{k=1}^{m} \sum_{\ell=1}^{m} \underline{P}_{k\ell} \left[2 \langle \chi_g \chi_\ell | \hat{g} | \chi_f \chi_k \rangle - \langle \chi_g \chi_\ell | \hat{g} | \chi_k \chi_f \rangle \right] \end{aligned} \tag{10}$$

It is obvious from eqs. 9 and 10 that the expectation value of the Hamiltonian obtained from a single determinant wave function depends on the orbitals only through $\underline{P}$, the so called "charge-bond order" matrix, and in some formulations of the Hartree-Fock scheme it is this quantity, rather than the orbitals themselves, which is considered basic. Requiring the energy to be stationary for an arbitrary small variation of the one electron orbitals which preserves their orthonormality leads to the well known Hartree-Fock equations in matrix form (2)

$$\underline{H}\, \underline{C} = \underline{C}\, \underline{\varepsilon} \tag{11}$$

where

$$\underline{H} = \underline{h} + \underline{G} \tag{12}$$

In practice one guesses a $\underline{C}$ matrix and systematically modifies it until the energy is minimized.

B. Density Matrix Analysis

An inspection of the various spin components of the second order density matrix associated with the Hartree-Fock wave function leads to a clear understanding of the correlation effects it ignores. Given an N electron wave function

$$\Psi(x_1, x_2, \cdots, x_N) \tag{13}$$

where x_i denotes both the space (r_i) and spin (s_i) coordinates of the i^{th} electron, the second order density matrix is defined as (3)

$$\Gamma(x_1 x_2; x_1' x_2') = \binom{N}{2} \int \Psi(x_1 x_2 x_3 \cdots x_N) \times \Psi^*(x_1' x_2' x_3 \cdots x_N)\, d^3r_3\, ds_3 \cdots d^3r_N\, ds_N \tag{14}$$

The diagonal element of this matrix ($x_1 = x_1'$; $x_2 = x_2'$) multiplied by the differential volume element $d^3r_1 ds_1 d^3r_2 ds_2$ equals the number of pairs times the probability of finding electron 1 in $d^3r_1 ds_1$ (centered at x_1) and, at the same time, electron 2 in $d^3r_2 ds_2$ (centered at x_2). For a state which is an eigenfunction of S^2 and S_z this quantity may be divided into spin components (4)

$$\begin{aligned} \Gamma(x_1 x_2; x_1' x_2') = {} & \rho_2^{\alpha\alpha\alpha\alpha}(r_1 r_2; r_1' r_2')\, \alpha(s_1)\, \alpha(s_2)\, \alpha^*(s_1')\, \alpha^*(s_2') \\ & + \rho_2^{\alpha\beta\alpha\beta}(r_1 r_2; r_1' r_2')\, \alpha(s_1)\, \beta(s_2)\, \alpha^*(s_1')\, \beta^*(s_2') \end{aligned} \tag{15}$$

$$+ \rho_2^{\alpha\beta\beta\alpha}(r_1 r_2; r_1' r_2')\, \alpha(s_1)\, \beta(s_2)\, \beta^*(s_1')\, \alpha^*(s_2')$$

$$+ \text{etc.}$$

Here $P_2^{\alpha\alpha\alpha\alpha}(r_1 r_2; r_1 r_2)$ represents the probability of simultaneously finding a spin up electron at r_1 and a spin up electron at r_2, while $P_2^{\alpha\beta\alpha\beta}(r_1 r_2; r_1 r_2)$ represents the probability of simultaneously finding a spin up electron at r_1 and a spin down electron at r_2.

For a Hartree-Fock wave function the above quantities may be written in terms of the spin components of the first order density matrix

$$\rho_1(r_1; r_1') = \rho_1^{\delta\delta}(r_1; r_1') = \sum_{i=1}^{n} \phi_i(r_1)\, \phi_i^*(r_1') \qquad (\delta = \alpha \text{ or } \beta) \tag{16}$$

The diagonal element of $P_1^{\alpha\alpha}(r_1; r_1)$ represents the probability of finding a spin up electron at r_1 and $P_1^{\beta\beta}(r_1; r_1)$ has a similar interpretation. In terms of these quantities we have

$$\begin{aligned} \rho_2^{\alpha\alpha\alpha\alpha}(r_1 r_2; r_1' r_2') &= \rho_1(r_1; r_1')\, \rho_1(r_2; r_2') - \rho_1(r_2; r_1')\, \rho_1(r_1; r_2') \\ \rho_2^{\alpha\beta\alpha\beta}(r_1 r_2; r_1' r_2') &= \rho_1(r_1; r_1')\, \rho_1(r_2; r_2') \end{aligned} \tag{17}$$

If we examine the behavior of these functions for $r_1 = r_2$, we notice that $P_2^{\alpha\alpha\alpha\alpha}$ vanishes, an example of the "Fermi hole", while $P_2^{\alpha\beta\alpha\beta}$ remains a simple product and fails to describe any correlation. From the above it is clear that the major error in the Hartree-Fock scheme comes from the presence in the same spatial orbital of both a spin up and spin down electron.

References

1. R. McWeeny and B. T. Sutcliffe, Methods of Molecular Quantum Mechanics (Academic, New York, 1969).

2. C.C.J. Roothaan, Rev. Mod. Phys. 23, 69 (1951).

3. R. McWeeny, Proc. Roy. Soc. A253, 242 (1959).

4. R. McWeeny and Y. Mizuno, Proc. Roy. Soc. A259, 554 (1961).

3. The Spin Projected Extended Hartree-Fock Method

A. Introduction

A certain vocabulary has evolved to describe the various extensions of the Hartree-Fock approximation which attempt to treat the correlation problem while retaining the idea of one electron orbitals. The standard form of the theory we have been discussing which is based on a single determinant of doubly occupied orbitals is referred to as the restricted Hartree-Fock (RHF) method. In the unrestricted Hartree-Fock (UHF) (1) or "different orbitals for different spins" (DODS) (2) method the idea of doubly occupied orbitals is abandoned and one uses as a trial wave function in a variational calculation a single determinant in which electrons of different spins are allowed to occupy different spatial orbitals. This type of wave function is often found to be unstable in the sense that the optimal UHF orbitals are identical to the optimal RHF orbitals. In addition, the UHF wave function is not an eigenfunction of spin. This situation may be corrected by either projecting out a pure spin state or annihilating the major contaminating spin component. Such procedures, carried out as they are after a variational calculation, have the disadvantage that the orbitals are optimized for a function of the wrong form. An improvement on the UHF method was suggested by Löwdin (3) who proposed that the spatial orbitals be optimized after spin projection. This procedure is often described as the spin projected extended Hartree-Fock (SEHF) method and a number of versions of it have appeared in the literature since Löwdin's proposal. SEHF calculations on first row atoms have been carried out by Kaldor(4), Lunnell(5), and Smeyer and Doreste-Suarez (6). Goddard (7), using group theoretical techniques, has derived the GF equations which are equivalent to the SEHF method and with co-workers he has done calculations on a number of atomic and molecular systems (8).

The SEHF wave function is no longer in the form of a single determinant and it may be classified as a type of multi-configuration wave function. The important point is that it retains the simple physical picture of one electron orbitals which forms the basis of any independent particle model. We present below a new formulation of the SEHF method which attempts to minimize the calculational difficulties as the number of electrons becomes large. One would ideally want a calculational scheme which would not be significantly more difficult than the RHF method for a system of the same size.

B. Formulation for Closed Shells

Our approach is most closely connected with the formulation given by Martino and Ladik (9) and generalized by Mayer, Ladik and Biczo (10). We consider as a trial wave function in a variational calculation the spin projection of a DODS Slater determinant. This wave function has the advantage that without any loss of variational freedom the one electron orbitals ϕ_i^{α} and ϕ_i^{β} (which before projection are associated with spin up and spin down electrons respectively) can be required to satisfy the relations (11, 12)

$$\begin{aligned} \langle \phi_i^{\alpha} | \phi_j^{\alpha} \rangle &= \langle \phi_i^{\beta} | \phi_j^{\beta} \rangle = \delta_{ij} \\ \langle \phi_i^{\alpha} | \phi_j^{\beta} \rangle &= \langle \phi_i^{\beta} | \phi_j^{\alpha} \rangle = \lambda_i \delta_{ij} \end{aligned} \tag{18}$$

Using the generalized Brillouin theorem in conjunction with such a wave function Mayer et. al. (10) have derived the SEHF equations and shown their equivalence to Goddard's GF equations for the singlet case. The SEHF equations are of an awkward and unfamiliar form and methods of solution are not immediately obvious. Recently Mayer has succeeded in finding solutions for a four electron system by defining a set of effective Hamiltonians and converting the SEHF equations to a pseudo eigenvalue form (13).

In order to produce a calculationally more practicable scheme, we shall choose directly to minimize the value of the energy functional. Numerous schemes based on this philosophy have appeared in the literature. McWeeny (14) demonstrated how the closed shell and open shell Hartree-Fock problems could be solved by the method of steepest descent. With Mukherjee (15) he extended the formulation to treat multi-configuration self consistent field theories. Fletcher (16) showed how more powerful minimization techniques could be applied to the closed shell problem and Kari and Sutcliffe (17) have extended his analysis to include open shells and multi-configurations. The common component of all these methods is a compact expression for the gradient of the energy with respect to the independent parameters of which it is a function. The methods then use this expression in one way or another to vary these parameters in an unconstrained manner in order to achieve the minimization.

A potential disadvantage of the SEHF method lies in the fact that the spin projection of a DODS Slater determinant yields a spin function which is only one of a number of such spin functions which could be used to describe a pure spin state. As discussed by Pauncz (18) the construction of our spin function is equivalent to forming two subsystems of maximum multiplicity and then coupling these together to form a new system with the desired spin eigenvalue. Studies have shown this spin function to be well adapted for the description of alternant systems but less than ideal when applied to atoms and some simple molecules (19). Self consistent procedures in which spin up and spin down electrons are coupled together to form singlet pairs have appeared in the literature (20) along with schemes which optimize both the spin coupling and the spatial orbitals (21). A particular disadvantage of these methods is that the orbitals may not be required to satisfy the pairing relations (eq.18) without imposing additional constraints and thus raising the energy. As previously noted the SEHF wave function loses no variational freedom to these restrictions and this fact leads to great simplifications in the expressions for the expectation value of various one and two electron operators.

The "pairing theorem" (11,12) states that given two sets of orthonormal one electron orbitals $\varphi_i'^{\alpha}$ and $\varphi_i'^{\beta}$ (i = 1, . . . , n where 2n equals the number of electrons in the system) it is always possible to find unitary transformations of the two sets among themselves such that the conditions of eq. 18 are satisfied. These paired orbitals may be used in constructing a Slater determinant

$$\Psi = \mathcal{A} \Phi T_0 \tag{19}$$

where T_0 is a product of one electron spin functions

$$T_0 = \alpha(1)\alpha(2)\cdots\alpha(n)\,\beta(n+1)\,\beta(n+2)\,\cdots\,\beta(2n) \tag{20}$$

and Φ is a product of one electron spatial functions

$$\phi_1^{\alpha}(1)\,\phi_2^{\alpha}(2)\cdots\phi_n^{\alpha}(n)\,\phi_1^{\beta}(n+1)\,\phi_2^{\beta}(n+2)\cdots\phi_n^{\beta}(2n) \tag{21}$$

and $\mathcal{A}$ is the antisymmetrizing operator. The function Ψ does not represent a pure spin state and we therefore consider as a trial wave function

$$\Psi^{S} = O^{S}\,\Psi \tag{22}$$

where O^S is a spin projection operator (18).

Expressing each one electron orbital as a linear combination of $m \geq 2n$ basis functions (which we assume to be orthonormal)

$$\phi_i^{\delta} = \sum_{t=1}^{m} \chi_t\, C_{ti}^{\delta} \qquad (\delta = \alpha \quad \text{or} \quad \beta) \tag{23}$$

the pairing conditions become

$$\begin{aligned} \underline{C}^{\alpha+}\underline{C}^{\alpha} &= \underline{C}^{\beta+}\underline{C}^{\beta} = \underline{I} \\ \underline{C}^{\alpha+}\underline{C}^{\beta} &= \underline{C}^{\beta+}\underline{C}^{\alpha} = \underline{\Lambda} \end{aligned} \tag{24}$$

where $\underline{C}^{\delta}$ ($\delta = \alpha$ or β) is an m x n matrix the i^{th} column of which contains the expansion coefficients for the orbital ϕ_i^{δ} and $\underline{\Lambda}$ is a diagonal matrix. The relatively large amount of orthogonality contained in eq. 24 enables one to write the expectation value of the total energy for the spin projected DODS determinant

$$E = \langle \Psi^{s} | \hat{H} | \Psi^{s} \rangle / \langle \Psi^{s} | \Psi^{s} \rangle \tag{25}$$

in fairly compact form (18).

We have found it convenient to work with two equivalent expressions for this quantity. The first emphasizes the dependence of the energy on the generalized charge-bond order matrices

$$\underline{P}^{\gamma\delta(i)}_{gf} = \underline{C}^{\gamma}_{gi} C^{\delta +}_{if} \qquad (\gamma, \delta = \alpha \text{ or } \beta) \tag{26}$$

while the second explicitly demonstrates the dependency on the elements λ_i of the diagonal matrix $\underline{\Lambda}$. These expressions are given in appendix A (eqs. A7 and A10).

We now follow McWeeny (14) and consider a set of orthonormal and paired orbitals as defining a point on an energy hypersurface and look for changes in these orbitals (subject to orthonormality and pairing constraints) so as to descend this surface as quickly as possible. The energy depends on the orbitals both through the quantities $\underline{P}^{\gamma\delta(i)}$ and through the λ_i's and to first order we have

$$\delta E = \delta E_1 + \delta E_2 \tag{27}$$

where in δE_1 the terms involving λ_i remain unchanged and in δE_2 the terms involving $\underline{P}^{\gamma\delta(i)}$ remain unchanged. In appendix B we show that

$$\delta E_1 = \sum_{i=1}^{n} Tr \Big(\delta \underline{P}^{\alpha\alpha(i)} \underline{H}^{\alpha\alpha(i)} + \delta \underline{P}^{\alpha\beta(i)} \underline{H}^{\alpha\beta(i)} + \delta \underline{P}^{\beta\alpha(i)} \underline{H}^{\beta\alpha(i)} + \delta \underline{P}^{\beta\beta(i)} \underline{H}^{\beta\beta(i)} \Big) \tag{28}$$

and

$$\delta E_2 = \sum_{l=1}^{n} \delta\lambda_l a_l \tag{29}$$

where $\underline{H}^{\gamma\delta(i)}$ is given in eq. B3 and a_1 in eq. B7. The quantities $\underline{\delta\rho}^{\gamma\delta(i)}$ and $\delta\lambda_i$ are related to variations in the orbitals themselves.

In complete generality a variation of the one electron orbitals which preserves their orthonormality but not their pairing may be written as

$$\underline{C}^{\delta} \rightarrow \underline{C}^{\delta'} = \underline{U}^{\delta}\,\underline{C}^{\delta} \qquad (\delta = \alpha \text{ or } \beta) \tag{30}$$

where $\underline{U}^{\delta}$ is an m x m unitary matrix. To insure that the new α and β orbitals are paired an additional unitary transformation of each set among themselves must be made (11, 12). Thus a new set of orbitals which are both orthonormal and paired may formally be written as

$$\begin{aligned} \underline{C}^{\alpha} &\rightarrow \underline{C}^{\alpha'} = \underline{U}^{\alpha}\,\underline{C}^{\alpha}\,\underline{A} \\ \underline{C}^{\beta} &\rightarrow \underline{C}^{\beta'} = \underline{U}^{\beta}\,\underline{C}^{\beta}\,\underline{B} \end{aligned} \tag{31}$$

where $\underline{A}$ and $\underline{B}$ are n x n unitary matrices which diagonalize $\underline{D}\,\underline{D}^{+}$ and $\underline{D}^{+}\underline{D}$ respectively where

$$\underline{D} = \underline{C}^{\alpha+}\,\underline{U}^{\alpha+}\,\underline{U}^{\beta}\,\underline{C}^{\beta} \tag{32}$$

As is well known any unitary matrix may be expressed as the exponential of an anti Hermitian matrix and to first order

$$\begin{aligned} \underline{U}^{\alpha} &= \underline{1} + \underline{\Delta}^{\alpha} && (\underline{\Delta}^{\alpha+} = -\underline{\Delta}^{\alpha}) \\ \underline{U}^{\beta} &= \underline{1} + \underline{\Delta}^{\beta} && (\underline{\Delta}^{\beta+} = -\underline{\Delta}^{\beta}) \\ \underline{A} &= \underline{1} + \underline{a} && (\underline{a}^{+} = -\underline{a}) \\ \underline{B} &= \underline{1} + \underline{b} && (\underline{b}^{+} = -\underline{b}) \end{aligned} \tag{33}$$

The elements of the matrices $\underline{a}$ and $\underline{b}$ are found from the condition that the new orbitals be paired and simple matrix algebra shows them to be

$$\underline{a}_{iK} = \frac{\underline{M}_{iK}\lambda_K + \underline{M}_{Ki}\lambda_i}{(\lambda_K^2 - \lambda_i^2)} \qquad (34)$$

$$\underline{b}_{iK} = \frac{\lambda_i \underline{M}_{iK} + \lambda_K \underline{M}_{Ki}}{(\lambda_K^2 - \lambda_i^2)}$$

where

$$\underline{M}_{iK} = \left[\underline{C}^{\alpha +} (\underline{\Delta}^{\beta} - \underline{\Delta}^{\alpha}) \underline{C}^{\beta} \right]_{iK} \qquad (35)$$

This analysis also shows the change in the pairing parameters to be

$$\delta \lambda_i = \underline{M}_{ii} \qquad (36)$$

To first order eq. 31 becomes

$$\underline{C}^{\alpha}_{gi} \rightarrow \underline{C}^{\alpha\prime}_{gi} = \underline{C}^{\alpha}_{gi} + \sum_{v=1}^{m} \underline{\Delta}^{\alpha}_{gv} \underline{C}^{\alpha}_{vi} + \sum_{K=1}^{n} \underline{C}^{\alpha}_{gK} \underline{a}_{Ki} \qquad (37)$$

$$\underline{C}^{\beta}_{gi} \rightarrow \underline{C}^{\beta\prime}_{gi} = \underline{C}^{\beta}_{gi} + \sum_{v=1}^{m} \underline{\Delta}^{\beta}_{gv} \underline{C}^{\beta}_{vi} + \sum_{K=1}^{n} \underline{C}^{\beta}_{gK} \underline{b}_{Ki}$$

and from eq. 26 we find, for example, that

$$\underline{\rho}^{\alpha\alpha(i)}_{gf} \rightarrow \underline{\rho}^{\alpha\alpha(i)\prime}_{gf} = \underline{\rho}^{\alpha\alpha(i)}_{gf} + \delta \underline{\rho}^{\alpha\alpha(i)}_{gf}$$

$$\delta \underline{\rho}^{\alpha\alpha(i)}_{gf} = \left(\underline{\Delta}^{\alpha} \underline{\rho}^{\alpha\alpha(i)} - \underline{\rho}^{\alpha\alpha(i)} \underline{\Delta}^{\alpha} \right)_{gf} + \qquad (38)$$

$$\sum_{K=1}^{n} \left(\underline{C}^{\alpha}_{gK} \underline{a}_{Ki} \underline{C}^{\alpha}_{if} - \underline{C}^{\alpha}_{gi} \underline{a}_{iK} \underline{C}^{\alpha}_{Kf} \right)$$

Similar expressions are obtained for $\delta \underline{\rho}^{\alpha\beta(i)}$, $\delta \underline{\rho}^{\beta\alpha(i)}$ and $\delta \underline{\rho}^{\beta\beta(i)}$.

When these expressions are inserted into eqs. 27-29 and use is made of the invariance of a trace to a cyclic permutation the first order variation of the energy which keeps the orbitals orthonormal and paired may be written as

$$\delta E = Tr\, \underline{\Delta}^{\alpha +} \underline{Z}^{\alpha} + Tr\, \underline{\Delta}^{\beta +} \underline{Z}^{\beta} \tag{39}$$

where

$$\underline{Z}^{\delta} = \left(\underline{Z}_1^{\delta} - \underline{Z}_1^{\delta +}\right) + \left(\underline{Z}_2^{\delta} - \underline{Z}_2^{\delta +}\right) + \left(\underline{Z}_3^{\delta} - \underline{Z}_3^{\delta +}\right) \quad (\delta = \alpha \text{ or } \beta)$$

$$\underline{Z}_1^{\alpha} = \sum_{i=1}^{n} \left(\underline{H}^{\alpha\alpha(i)} \underline{\rho}^{\alpha\alpha(i)} + \underline{H}^{\beta\alpha(i)} \underline{\rho}^{\beta\alpha(i)} \right) \tag{40}$$

$$\underline{Z}_1^{\beta} = \underline{Z}_1^{\alpha} \quad (\alpha \longleftrightarrow \beta)$$

$$\underline{Z}_2^{\alpha} = \sum_{i=1}^{n} \sum_{\substack{j=1 \\ (i \neq j)}}^{n} \frac{1}{(\lambda_i^2 - \lambda_j^2)} \Big[\lambda_i \Big(\underline{\rho}^{\beta\alpha(i)} \underline{H}^{\alpha\alpha(i)} \underline{\rho}^{\alpha\alpha(j)} + \underline{\rho}^{\beta\beta(i)} \underline{H}^{\alpha\beta(i)} \underline{\rho}^{\alpha\alpha(j)} + \underline{\rho}^{\beta\beta(j)} \underline{H}^{\alpha\beta(i)} \underline{\rho}^{\alpha\alpha(i)} + \underline{\rho}^{\beta\beta(j)} \underline{H}^{\beta\beta(i)} \underline{\rho}^{\beta\alpha(i)} \Big) + \lambda_j \Big(\underline{\rho}^{\beta\alpha(j)} \underline{H}^{\alpha\alpha(i)} \underline{\rho}^{\alpha\alpha(i)} - \underline{\rho}^{\alpha\beta(j)} \underline{H}^{\alpha\beta(i)} \underline{\rho}^{\alpha\beta(i)} - \underline{\rho}^{\alpha\beta(i)} \underline{H}^{\alpha\beta(i)} \underline{\rho}^{\alpha\beta(j)} + \underline{\rho}^{\beta\beta(i)} \underline{H}^{\beta\beta(i)} \underline{\rho}^{\beta\alpha(j)} \Big) \Big]$$

$$\underline{Z}_2^{\beta} = -\underline{Z}_2^{\alpha}$$

$$\underline{Z}_3^{\alpha} = \sum_{i=1}^{n} a_i\, \underline{\rho}^{\beta\alpha(i)}$$

$$\underline{Z}_3^{\beta} = -\underline{Z}_3^{\alpha}$$

Starting from some initial set of orthonormal and paired orbitals a new set of orthonormal and paired orbitals, and a new energy, are completely determined by the anti Hermitian matrices $\underline{\Delta}^{\alpha}$ and $\underline{\Delta}^{\beta}$. Considering the elements of these matrices to be independent parameters the gradient of the energy is, to first order,

$$\frac{\partial E}{\partial \underline{\Delta}^{\alpha}_{ij}} = \underline{z}^{\alpha}_{ij} \quad , \quad \frac{\partial E}{\partial \underline{\Delta}^{\beta}_{ij}} = \underline{z}^{\beta}_{ij} \tag{41}$$

Thus if the energy is to have a minimum (or at least stationary) value, the conditions which must be satisfied are

$$\underline{z}^{\alpha} = 0 \quad , \quad \underline{z}^{\beta} = 0 \tag{42}$$

It is straightforward to demonstrate that these conditions are equivalent to the SEHF equations of (17). If for a given choice of orbitals these conditions are not satisfied any one of a number of techniques can be used to determine $\underline{\Delta}^{\alpha}$ and $\underline{\Delta}^{\beta}$ so that after the next iteration they are more nearly satisfied.

The simplest of these is the steepest descent procedure first used in self consistent field calculations by McWeeny (14) . Here we regard the traces in eq. 39 as scalar products in an m^2 dimensional space and recall that a scalar product has its greatest negative value when the two "vectors" are anti parallel. Thus by choosing

$$\begin{aligned} \underline{\Delta}^{\alpha} &= -\eta\, \underline{z}^{\alpha} \\ \underline{\Delta}^{\beta} &= -\eta\, \underline{z}^{\beta} \end{aligned} \tag{43}$$

where η is a positive step length chosen to give a minimum in the descent direction, we may construct new orbitals which yield a lower energy than the original set. This method was found to work well in test applications on pi electron systems described by model Hamiltonians but its performance in ab-initio calculations left something to be desired, convergence boing very slow in the region close to the minimum. Levy (22) has discussed, in a different context, the inadequacy of using a single step length and suggests instead that each element of $\underline{\Delta}^{\alpha}$ and $\underline{\Delta}^{\beta}$ be expressed as

$$\begin{aligned} \underline{\Delta}^{\alpha}_{ij} &= -\eta^{\alpha}_{ij}\, \underline{z}^{\alpha}_{ij} \\ \underline{\Delta}^{\beta}_{ij} &= -\eta^{\beta}_{ij}\, \underline{z}^{\beta}_{ij} \end{aligned} \tag{44}$$

where the quantities η^{α}_{ij} and η^{β}_{ij} are approximated from a knowledge of second derivatives. A simplified form of this idea described below was found to speed convergence.

In addition to the steepest descent method, other, more powerful, minimization algorithms are available. Probably the most suitable of these for molecular calculations, due to its low storage requirements, is the conjugate gradient technique due to Fletcher and Reeves (23). In this method the value of $\underline{\Delta}^{\delta(i)}$ and $\underline{z}^{\delta(i)}$ ($\delta = \alpha$ or β) from the i th iteration are saved and for the next iteration

$$\underline{\Delta}^{\delta(i+1)} = -\eta^{(i+1)} \left(\underline{z}^{\delta(i+1)} + \beta \frac{\underline{\Delta}^{\delta(i)}}{\eta^{(i)}} \right) \tag{45}$$

where

$$\beta = Tr \left[\underline{z}^{\alpha(i+1)+} \underline{z}^{\alpha(i+1)} + \underline{z}^{\beta(i+1)+} \underline{z}^{\beta(i+1)} \right] \Big/ Tr \left[\underline{z}^{\alpha(i)+} \underline{z}^{\alpha(i)} + \underline{z}^{\beta(i)+} \underline{z}^{\beta(i)} \right] \tag{46}$$

Again η is a step length chosen to give a minimum in the descent direction.

In the course of this investigation it was realized that certain modifications were necessary to produce an acceptable rate of convergence in ab-initio applications. The procedure followed was to first solve the RHF equations in the traditional manner. The trial SEHF orbitals were then expanded in terms of the converged RHF orbitals and the core orbital of the heavy atom in each molecule was left doubly occupied. This orbital and the highest energy virtual orbital were removed from the variational calculation. This is equivalent to taking step lengths of zero in certain directions, a crude form of eq. 44. A minimization procedure was then used until the energy decreased by less than 10^{-5} hartree. At this point the two omitted orbitals were allowed to enter the calculation and the procedure continued. It was found, as expected, that the performance of the Fletcher-Reeves technique was superior to that of the steepest descent method.

Goddard (24) and Gerratt (25) have dealt with the symmetry considerations which apply to SEHF wave functions. In the case of total wave functions which belong to a non degenerate representation of the point group of the molecule we may, with no loss of generality, require the SEHF orbitals to be basis functions for the irreducible representations of the group. This is the case with all the molecules we consider. If the point group has a halving subgroup, we may require the SEHF orbitals to be basis functions for the irreducible representations of this halving subgroup with the property that the orbital sets ϕ_i^α and ϕ_i^β are interchanged by the operation which takes one subgroup into the other.

C. Density Matrix Analysis

One may obtain an understanding of the type of correlation described by a SEHF wave function from an inspection of the $\alpha\beta\alpha\beta$ component of the second order density matrix. The reader will recall that this type of analysis of the RHF wave function demonstrated the lack of any correlation between electrons of opposite spins. To simplify the form of the form of the density matrix we consider the case where the number of electrons goes to infinity. In this situation the expectation value of the total Hamiltonian is the same for the singlet projected and the unprojected DODS determinants. (26, 27). The spin properties of the two states are, though, quite different. In particular, Adams has shown (28) that for the singlet projection of a DODS Slater determinant (for n → ∞)

$$\begin{aligned}
\rho_2^{\alpha\beta\alpha\beta}(r_1 r_2; r_1' r_2') &= \rho_1(r_1; r_1')\,\rho_1(r_2; r_2') + g(r_1 r_2; r_1' r_2') \\
\rho_1(r_1; r_1') &= \frac{1}{2}\left(\rho^{\alpha\alpha}(r_1; r_1') + \rho^{\beta\beta}(r_1; r_1')\right) \\
\rho^{\delta\delta}(r_1 r_1') &= \sum_{i=1}^{n} \phi_i^{\delta}(r_1)\,\phi_i^{\delta *}(r_1') \qquad (\delta = \alpha \text{ or } \beta) \\
g(r_1 r_2; r_1' r_2') &= -(12)^{-1}\left[\sigma(r_1 r_1')\,\sigma(r_2 r_2')\right] - (6)^{-1} \times \\
&\qquad \left[\sigma(r_2 r_1')\,\sigma(r_1 r_2')\right]
\end{aligned} \tag{47}$$

$$\sigma(r_1 r_2) = \rho^{\alpha\alpha}(r_1; r_2) - \rho^{\beta\beta}(r_1; r_2)$$

An expression for finite n would contain similar information but its form would be more complex and its content not as clear.

If we examine the behavior of this function for $r_1 = r_2$ we notice that

$$g(r,r_1;r,r_1) = -(4)^{-1}\left|\sigma(r,r_1)\right|^2 \leq 0 \tag{48}$$

so that electrons of opposite spin are to some extent correlated at very short distances. From the definition of $\sigma(r,r_1)$ it is clear that the amount of correlation included in the projected wave function depends directly on the difference between the α and β orbitals. In the restricted case these orbitals are identical and eq. 47 reduces to eq. 17 .

D. Example: Hubbard Model of Benzene

As a first demonstration of the SEHF method we consider a system which consists of six electrons distributed among six identical, orthogonal orbitals that are regarded as localized at the vertices of a regular six sided polygon. The Hamiltonian to be used is the Hubbard Hamiltonian (29), a rather simple Hamiltonian with only two terms: a one electron interaction between orbitals at neighboring sites and a two electron interaction between electrons at the same site. This Hamiltonian has been studied by numerous authors in connection with the origin of metallic magnetism and the metal-insulator transition, and it is one of the few points of contact between quantum chemistry and the many body problem in solid state physics. The model can be used to crudely describe the pi electrons of benzene (30, 31) and is formally defined through the matrix elements of the one and two electron energy operators between Wannier states

Table 1. Energies for the Hubbard Model of Benzene

t/U	RHF	SEHF	CCI
-0.025	1.30000	-0.00998	-0.01073
-0.050	1.10000	-0.03971	-0.04263
-0.150	0.30000	-0.34089	-0.36221
-0.300	-0.90000	-1.20229	-1.24676
-0.41667	-1.83333	-2.03443	-2.08037
-0.600	-3.30000	-3.42908	-3.46985

$$\langle \chi_i | \hat{h} | \chi_j \rangle = \begin{cases} t_0 & i = j \\ -t & i,j \text{ nearest neighbors} \\ 0 & \text{otherwise} \end{cases}$$

$$\langle \chi_i \chi_j | \hat{g} | \chi_K \chi_\ell \rangle = U \delta_{iK} \delta_{j\ell} \delta_{ij} \tag{49}$$

In what follows t_0 is set equal to zero since it only adds an uninteresting shift to all energy levels.

Linderberg and Thulstrup (31) have carried out a complete configuration interaction calculation for this six electron system and in Table 1 we present their results as a function of t in units of U. Also included in the table are the restricted Hartree-Fock energies (which are completely determined by the symmetry of the system) and the results of a spin projected extended Hartree-Fock calculation. Comparison of the RHF and exact results indicates that as t/U approaches zero from negative infinity (which corresponds to moving the nuclear centers further apart) the RHF approximation becomes progressively worse. This behavior is due to just the lack of correlation between electrons of opposite spin discussed above. This omission forces ionic states of high energy to appear among the dissociation products. From the table it is clear that the SEHF wave function, which allows electrons of different spins to localize on different sublattices, recovers a large percentage of the correlation energy.

E. Example: Cyclic H_{10}

Cyclic arrays of hydrogen atoms have been considered by various authors in studies of electron correlation in molecules and solids. A number of these studies have been based on the alternant molecular orbital (AMO) method. A simple form of AMO uses a single variational parameter and was employed by Moskowitz (32) for the H_6 ring, by Kwo (33) for the H_{12} ring and by Tredgold (34) and Calais (35) for an infinite chain of hydrogen atoms. One expects the many parameter AMO method to give a much better description of correlated systems but, as is well known, the use of the many parameter method is plagued by the difficulty of minimizing the energy with respect to many non linear parameters. Berggren and Martino (36) have applied the method to an infinite chain of hydrogen atoms, optimizing the many parameters by solving a "gap equation". Their formulation is based on a DODS single determinant without spin projection and as such is unsuited for finite systems. As noted previously, the expectation value of the total Hamiltonian is the same for the singlet ground state and the unprojected DODS state if the number of electrons goes to infinity. Thus the variational parameters which minimize the energy for the unprojected state do the same for the projected state. This is not true for finite systems and this has led to limitations in the application of the many parameter AMO method to molecules. The formulation of the SEHF method outlined above overcomes this problem. When applied to cyclic systems such as H_{4n+2} it is essentially the many parameter AMO method in which the only variational parameters are, due to symmetry considerations, the overlaps λ_i. These may be determined by one of the minimization techniques described above.

Table 2. Energy[a] per electron pair for H_2 and H_{10}

	H_{10}		H_2	
R[b]	RHF	SEHF	RHF	SEHF
1.50	-0.9838	-0.9935	-1.0916	-1.1086
2.00	-1.0515	-1.0674	-1.0754	-1.1026
2.50	-1.0301	-1.0572	-1.0284	-1.0710
3.00	-0.9866	-1.0331	-0.9773	-1.0410
5.00	-0.8299	-0.9958	-0.8278	-0.9967

a) all energies in hartrees
b) all distances in atomic units

The calculations on cyclic H_{10} were performed with a minimal basis set consisting of a single s type orbital centered on each lattice site. Mattheis (37) carried out a full configuration interaction study of the H_6 ring with a similar basis set. Moskowitz (32), using the same basis as Mattheis, showed that the one parameter AMO method accounted for 60% of the energy improvement obtained (at the equilibrium inter atomic distance) with a complete configuration interaction. Pauncz (18) reports that the many parameter AMO method gives 77% of the improvement. From these figures we expect the results below to include a substantial amount of the correlation energy.

The s orbital used was Reeve's (38) three term Gaussian expansion of the hydrogen 1s orbital

$$\varphi_{1s} \approx 0.1084\, e^{-.1483 r^2} + 0.2164\, e^{-.6577 r^2} + 0.1575\, e^{-4.2392 r^2}$$

Table 2 lists the total energy per electron pair as a function of inter atomic distance for the singlet ground states of H_2 and cyclic H_{10} as calculated by both the RHF and SEHF methods. As expected H_2 is more stable than H_{10}. Also as expected the inclusion of correlation effects leads to a proper description of the dissociation process, the lack of which is a major failing of the RHF method.

F. Example: The Isoelectronic Series CH_4, NH_3, H_2O, HF, and Ne

To investigate the role that structure plays in determining how well the SEHF method performs relative to the RHF method, calculations were carried out on a number of ten electron systems of widely varying structure. The calculations on CH_4, NH_3, H_2O, HF and Ne were performed with a "double zeta" basis set of contracted Gaussians which is listed in Tables 3-7. The results are collected in Table 12 where in addition to the RHF and SEHF energies the value of the pairing parameter λ_i and the symmetry type for each orbital pair are indicated. In all cases the minimization procedure was terminated when the total energy decreased by less than 10^{-5} hartree. Also included in Table 12 are the results of the H_{10} calculation performed at the near equilibrium separation of 2 atomic units.

Examination of Table 12 shows that the performance of the SEHF method as judged by the energy improvement per electron relative to the RHF method varies from system to system. There are three immediately apparent interrelated considerations determining the amount of correlation energy recoverable in any given calculation. These are the size and flexibility of the basis set, the spatial structure and electron density of the molecule, and how well the SEHF spin function describes the actual spin coupling of the system. The first of these considerations may be illustrated by comparing the nature of the 2p SEHF orbitals of the Ne atom, the 1π SEHF orbitals of the HF molecule, and the lone pair SEHF orbitals of the H_2O molecule. In the calculations reported here each of these orbitals is described by two basis functions and each "splits" by almost the same amount, $\lambda = .942$ for Ne (2p), .933 for HF (1π), and .930 for H_2O ($1b_2$). If the calculations had been performed with a minimal basis

Table 3. Basis set for the Ne calculations

Exponents	Coefficients	
7397.6730	0.02924	
2268.7366	0.12086	S1
463.3183	0.90532	
121.4484	0.15111	
49.8918	0.24392	S2
20.4890	0.46069	
7.3344	0.26304	
16.4005	-.13261	S3
1.5042	1.04748	
0.4501	1.00000	S4
56.4511	0.02088	
12.9187	0.13002	P1
3.8654	0.39564	
1.2029	0.62151	
0.3444	1.00000	P2

Table 4. Basis set for HF calculations

Hydrogen

Exponents	Coefficients	
19.2406	0.0328280	
2.89915	0.2312081	S1
0.65341	0.8172383	
0.17758	1.0000000	S2

Fluorine

Exponents	Coefficients	
5851.0350	0.0291410	
1794.4099	0.1213604	S1
366.4519	0.9049994	
96.0570	0.1539798	
39.4609	0.2460920	S2
16.2053	0.4626529	
5.8010	0.2557880	
12.9309	-.1354260	S3
1.1945	1.0485966	
0.3574	1.0000000	S4
44.3555	0.0208678	
10.0820	0.1300922	P1
2.99586	0.3962206	
0.93826	0.6203711	
0.27329	1.0000000	P2

Table 5. Basis set for H_2O calculations

Hydrogen (see Table 4)

Oxygen

Exponents	Coefficients	
7816.5400	0.00203	S1
1175.8200	0.01544	
273.1880	0.07377	
81.1696	0.24761	
27.1836	0.61183	
3.4136	0.24120	
9.5322	1.00000	S2
0.9398	1.00000	S3
0.2846	1.00000	S4
35.1832	0.01958	P1
7.9040	0.12419	
2.3051	0.39473	
0.7171	0.62738	
0.2137	1.00000	P2

Table 6. Basis set for NH_3 calculations

Hydrogen (see Table 4)

Nitrogen

Exponents	Coefficients	
3489.5253	0.0292226	S1
1070.1762	0.1216856	
218.5500	0.9047253	
57.2879	0.1545241	S2
23.5342	0.2450818	
9.6648	0.4569305	
3.4597	0.2632423	
7.0699	-.1432535	S3
0.6784	1.0524427	
0.2079	1.0000000	S4
26.7860	0.0182571	P1
5.95635	0.1164081	
1.70740	0.3901142	
0.53136	0.6372268	
0.16537	1.0000000	P2

Table 7. Basis set for CH_4 calculations

Hydrogen (see Table 4)

Carbon

Exponents	Coefficients	
2548.7260	0.0293140	S1
781.6495	0.1215990	
159.6274	0.904751	
41.8427	0.1534800	S2
17.1893	0.2433111	
7.0591	0.4537991	
2.5269	0.2698321	
4.9344	-.1463020	S3
0.4735	1.0533749	
0.1480	1.0000000	S4
18.1557	0.0185330	P1
3.9864	0.1154400	
1.14293	0.3861999	
0.35945	0.6400798	
0.11460	1.0000000	P2

Table 8. Geometry for the HF calculations

Center	X	Y	Z
H1	0.00000	0.00000	1.73300
F1	0.00000	0.00000	0.00000

Table 9. Geometry for the H_2O calculations

Center	X	Y	Z
H1	1.11178	-1.42969	0.00000
H2	1.11178	1.42969	0.00000
O1	0.00000	0.00000	0.00000

Table 10. Geometry for the NH_3 calculations

Center	X	Y	Z
H1	1.77600	0.00000	0.71996
H2	-0.88800	1.53800	0.71996
H3	-0.88800	-1.53800	0.71996
N1	0.00000	0.00000	0.00000

Table 11. Geometry for the CH_4 calculations

Center	X	Y	Z
H1	1.19309	1.19309	1.19309
H2	-1.19309	1.19309	-1.19309
H3	1.19309	-1.19309	-1.19309
H4	-1.19309	-1.19309	1.19309
C1	0.00000	0.00000	0.00000

Table 12. Total energies[a] and pairing parameters

	RHF	SEHF	RHF-SEHF	λ_i
Ne	-128.5159	-128.5429	0.0270	1.000(1s) 0.969(2s) 0.942(2p)
HF	-100.0150	-100.0353	0.0203	1.000(1σ) 0.978(2σ) 0.949(3σ) 0.933(1π)
H_2O	-76.0092	-76.0526	0.0434	1.000($1a_1$) 0.969($2a_1$) 0.930($1b_2$) 0.890($3a_1$) 0.868($1b_1$)
NH_3	-56.1716	-56.2146	0.0430	1.000($1a_1$) 0.958($2a_1$) 0.905($3a_1$) 0.885(1e)
CH_4	-40.1823	-40.2236	0.0413	1.000($1a_1$) 0.935($2a_1$) 0.894($1f_2$)
H_{10}[b]	-5.2576	-5.3372	0.0796	0.962 0.930 0.716

a) all energies in hartrees
b) R_o = 2 atomic units

set symmetry considerations would require that each of these orbitals be described by only one function and thus no splitting would have been possible. Inclusion of more functions in the expansion set may allow the orbitals to include more correlation and further improve the energy relative to the RHF value. This has already been noted by Kaldor (4) in his discussion of his SEHF calculations on some first row atoms.

One may crudely characterize the physics behind the second consideration by pointing out that in the SEHF method electrons of opposite spin must be able to lower their energy by occupying different portions of space while at the same time remaining in those regions of the molecule providing the lowest potential energy. From this point of view it is clear why the energy improvement per electron in the H_{10} ring is significantly larger than in the other systems considered. Due to the alternant character of the nuclear framework electrons of opposite spin have the freedom to localize on the two sub lattices and yet remain tightly bound to the protons. That is to say the electrons may lower their energy by correlating without disturbing the delicate balance between the kinetic and potential energies which gives rise to binding.

In turning to polyatomic molecules such as water, ammonia and methane, it is clear that the situation is less favorable. As an example consider the plots of the RHF and SEHF $1f_2$ orbitals of CH_4 shown in Figure 1. This plot along the line joining the carbon nucleus to one of the protons clearly illustrates the splitting of the SEHF orbitals relative to the RHF orbital. The point here is that this splitting can only occur by localizing the α and β orbitals near different centers and thus disturbing the balance of kinetic and potential energies mentioned above. The type of correlation illustrated in Figure 1 may be characterized as "radial" in the sense that the α orbital peaks around the proton while the β orbital peaks closer to the carbon nucleus. There are clearly other kinds of correlation available in methane and to demonstrate this we plot in Figure 2 the RHF and SEHF $1f_2$ orbitals along a line joining two of the protons. Again the splitting is obvious but it is now more "angular" in nature.

It is the absence of this second type of correlation which in part determines the even smaller improvements found in hydrogen fluoride and neon. Still another reason for the greater energy improvement in, for example, methane than in hydrogen fluoride is the larger attraction of the fluorine nucleus. The energy gain obtained by the spin up and spin down electrons both be closer to the fluorine nucleus outweighs the gain in energy which might be obtained if the electrons were to correlate in a manner similar to that shown in Figure 1. The results for Ne as compared to those for HF seem to be a reflection of the more delocalized nature of the 2s orbital in the free atom.

Finally we point out that different spin functions allow for other types of correlation which may be more favorable for certain molecules than that found in the SEHF method. The results for water seem to be typical of the polyatomic molecules considered. The basis set and geometry used were identical to those employed in the GF calculation of Guberman and

Goddard (8) and in the configuration interaction treatment of Hosteney et. al. (39). As expected the SEHF and GF results are identical and both give about 31% of the energy improvement obtained from a large configuration interaction. This performance may be compared with another calculation on H_2O by Hunt et. al. (20) using the generalized valence bond method. In this case the many electron wave function is written in terms of spatial orbitals ϕ_i^α and ϕ_i^β which describe spin up and spin down electrons coupled to form singlet pairs. This function is identical to that used in the G1 method (40) except for the fact that the one electron orbitals are required to satisfy eq. 24 . A larger basis was used in this calculation so an exact comparison is not possible but these authors report an energy improvement over the RHF energy of 0.0741 hartree, or almost twice that obtained with the SEHF or GF method.

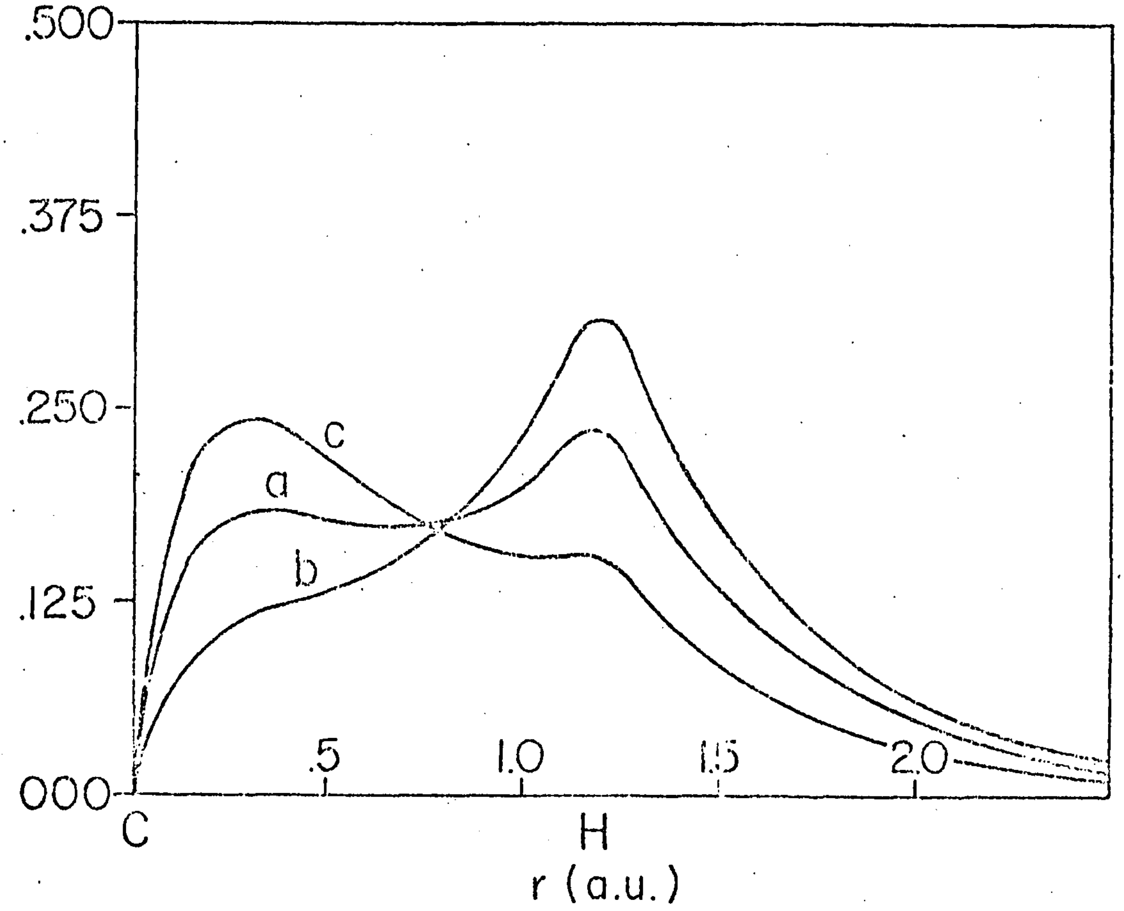

Figure 1. The $1f_2$ RHF and SEHF orbitals of methane along the line joining the carbon nucleus to one of the protons: a) RHF b) SEHF α c) SEHF β

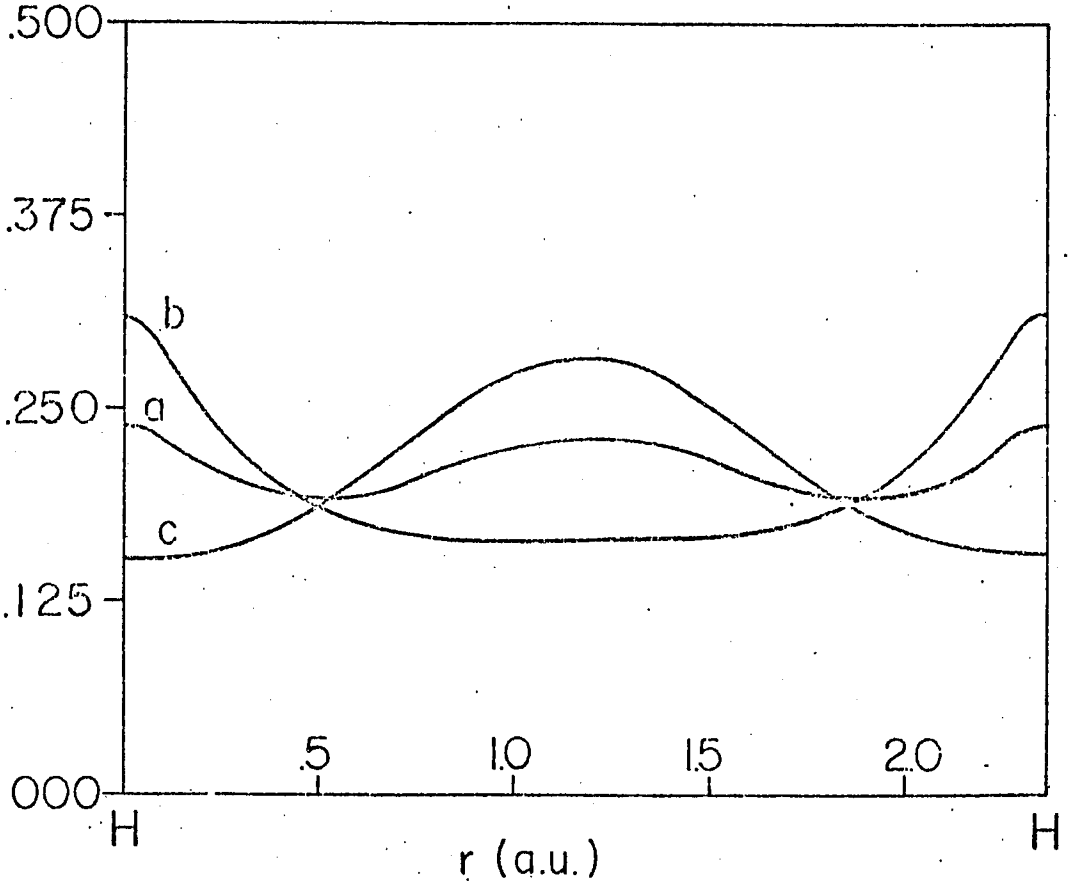

Figure 2. The $1f_2$ 'RHF and SEHF orbitals of methane along the line joining two of the protons: a) RHF b) SEHF α c) SEHF β

References

1. J. A. Pople and R. K. Nesbet, J. Chem. Phys. 22, 571 (1954).

2. J. C. Slater, Phys. Rev. 82, 538 (1951).

3. P. O. Lowdin, Phys. Rev. 97, 1509 (1955).

4. U. Kaldor, Phys. Rev. 176, 19 (1968).

5. S. Lunell, Phys. Rev. A1, 360 (1970).

6. Y. G. Smeyers and L. Doreste-Suarez, Int. J. Quantum Chem. 7, 687 (1973).

7. W. A. Goddard III, J. Chem. Phys. 48, 450 (1968).

8. S.L. Guberman and W.A. Goddard III, J. Chem. Phys. 53, 1803 (1970) and references cited therein.

9. F. Martino and J. Ladik, J. Chem. Phys. 52, 2262 (1970).

10. I. Mayer, J. Ladik and G. Biczo', Int. J. Quantum Chem. 7, 583 (1973).

11. P. O. Lowdin, J. Appl. Phys. Suppl. 33, 251 (1962).

12. A. T. Amos and G. G. Hall, Proc. Roy. Soc. A263, 483 (1961).

13. I. Mayer, Int. J. Quantum Chem. 8, 363 (1974).

14. R. McWeeny, Rev. Mod. Phys. 32, 335 (1960).

15. N.G.Mukherjee and R. McWeeny, Int. J. Quantum Chem. 4, 97 (1970).

16. R. Fletcher, Mol. Phys. 19, 55 (1970).

17. R. Kari and B.T. Sutcliffe, Int. J. Quantum Chem. 7, 459 (1973).

18. R. Pauncz, Alternant Molecular Orbital Method (W.A. Saunders, Philadelphia, Pa. 1967).

19. H.F. Schaeffer III, The Electronic Structure of Atoms and Molecules (Addison-Wesley, Reading, Mass. 1972).

20. W.J. Hunt, P.J. Hay and W.A. Goddard III, J. Chem. Phys. 57, 738 (1972).

21. R. C. Ladner and W. A. Goddard III, J. Chem. Phys. 51, 1073, (1969); U. Kaldor and F.E. Harris, Phys. Rev. 183, 1 (1969).

22. B. Levy, Int. J. Quantum Chem. 4, 297 (1970).

23. R. Fletcher and C.M. Reeves, Computer J. 7, 149 (1964).

24. W.A. Goddard III, J. Chem. Phys. 48, 5337 (1968).

25. J. Gerratt, Adv. At. and Mol. Phys. 7 (1971).

26. F. Martino and J. Ladik, Phys. Rev. A3, 862 (1971).

27. I.I. Ukrainsky, Int. J. Quantum Chem. 6, 473 (1972).

28. W. H. Adams, J. Chem. Phys. 39, 25 (1963).

29. J. Hubbard, Proc. Roy. Soc. A276, 238 (1963); A281, 401 (1964).

30. O.J. Heilmann and E.H. Lieb, Trans. N. Y. Acad. Sci. 33, 116 (1971).

31. J. Linderberg and E.W. Thulstrup, J. Chem. Phys. 49, 710 (1968).

32. J. W. Moskowitz, J. Chem. Phys. 38, 677 (1963).

33. W.T. Kwo, Phys. Rev. 171, 484 (1968).

34. R.H. Tredgold, Proc. Roy. Soc. 67A, 1018 (1954).

35. J. L. Calais, Arkiv Fysik 28, 511 (1965).

36. K.F. Berggren and F. Martino, Phys. Rev. 184, 484 (1969).

37. L. F. Mattheis, Phys. Rev. 123, 1209 (1961).

38. C.M. Reeves, J. Chem. Phys. 39, 1 (1963).

39. R.P. Hosteny, R.R. Gilman, T.H. Dunning, A. Pipano and I. Shavitt, Chem. Phys. Letters 7, 325 (1970).

40. W.A. Goddard III, Phys. Rev. 157, 73 (1967).

4. Molecular Double Ionization Potentials

A. Introduction

The Hartree-Fock model leads to a clear physical picture of processes which involve the removal of electrons from a system. By far the most famous example of this statement is Koopmans' theorem which states that the eigenvalues of the RHF Hamiltonian may be associated with the single ionization potentials of a closed shell atom or molecule for which the RHF wave function has been obtained. To be more specific we assume that one has calculated the self consistent RHF one electron orbitals for a closed shell neutral system. If one then uses these orbitals to form the single determinant wave function of the open shell singly ionized system, evaluates its energy, and subtracts from the original energy, the result is exactly equal to the corresponding eigenvalue of the RHF Hamiltonian of the neutral system.

Koopmans' theorem contains an inherent error in that the one electron orbitals used are determined variationally for the ground state of the neutral system and therefore the energy evaluated for the ion is but an upperbound to the "best" single determinant energy. Put another way we might say that the one electron orbitals are not allowed to readjust themselves to the new potential produced by the removal of one electron. This leads to the unbalanced situation in which the ionization potential is calculated from the difference between two energies, only one of which is determined variationally. In many cases this error is balanced by the change in the correlation energy which accompanies the ionization process and Koopmans' theorem gives vertical ionization potentials in good agreement with experiment. A more direct approach to the problem is to perform two separate Hartree-Fock calculations: one on the ion and one on the parent. While such a procedure is obviously more time consuming one may obtain from it direct information about the relative importance of the correlation error in the ion and the parent atom or molecule.

To demonstrate this we recall that

$$E_{nr} = E_{RHF} + E_{corr} \tag{50}$$

where E_{nr} is the exact energy associated with the Hamiltonian given in eq.5. The signs are chosen so that E_{corr} is always negative. If the small relativistic corrections to the experimental ionization potentials for the removal of an outer shell electron are neglected we have

$$\mathrm{IP(exp)} - \mathrm{IP(RHF)} = E_{corr}(\mathrm{ion}) - E_{corr}(\mathrm{parent}) \tag{51}$$

where

$$\mathrm{IP(RHF)} = E_{RHF}(\mathrm{ion}) - E_{RHF}(\mathrm{parent}) \tag{52}$$

Thus if $\mathrm{IP(RHF)} < \mathrm{IP(exp)}$ we know that $|E_{corr}(\mathrm{ion})| < |E_{corr}(\mathrm{parent})|$, while if $\mathrm{IP(RHF)} > \mathrm{IP(exp)}$ then $|E_{corr}(\mathrm{ion})| > |E_{corr}(\mathrm{parent})|$.

Bagus (1) has carried out this type of procedure for the ionization potentials of neon and argon and some of his results are given in Table 13. From the table one first notices the clear improvement over Koopmans' theorem obtained from a direct calculation for the 1s and 2s hole states of Ne^{+}. The results for the first ionization potential (the 2p hole state), though, are in better agreement with experiment by

Table 13. Single ionization potentials (in eV) of Neon[a]

State	Koopmans' Theorem	RHF	Experiment
1s hole	891.7	868.6	870.3
2s hole	52.5	49.3	48.5
2p hole	23.1	19.8	21.6

a) from ref. 1

Koopmans' theorem than by direct calculation. As pointed out by Bagus, one expects relativistic effects to be small for these outer shell electrons and thus correlation effects must be responsible for the deviations between direct calculation and experiment. Closer inspection of Table 13 shows that for the 2p hole state IP(RHF) $<$ IP(exp), while for the 2s hole state IP(RHF) $>$ IP(exp), implying that the 2s hole state has a larger correlation error than the neutral atom. Meyer (2) reports similar results for the $2a_1$ hole state of H_2O^+. Such behavior is interesting because it is generally accepted that the intra pair correlation is larger than the inter pair correlation. That is a singly occupied orbital should not contribute to the total correlation energy as heavily as a paired electron. If this were generally true the correlation energy of any ionic state would be less than that of its parent. This is not the case for the 2s hole state of Ne^+ and the $2a_1$ hole state of H_2O^+, both of which have larger correlation energies than the neutral species. Both Bagus and Meyer note that this anomolous behavior may be explained by a detailed analysis of a large configuration interaction wave function.

In this context experimental information on molecular double ionization potentials becomes particularly interesting. Comparisons of correlation errors of closed and open shell systems are informative but, due to the different natures of the single determinant wave functions, they do little to aid us in understanding clearly the general behavior of the correlation energy in closed shell systems. Some double ionization potentials, though, are related to the difference in energy between two closed shell states and one hopes a comparison of experimental and directly calculated double ionization potentials will be useful. In what follows RHF and SEHF calculations on NH_3, N_2 and H_2O and their doubly ionized closed shell ions are presented and used to predict molecular double ionization potentials. A comparison of the results to the experimental values indicates that the correlation error associated with the RHF model is very much a function of the structure and electron density of the system under consideration.

B. Experimental Results

There is at present a dearth of information, both experimental and theoretical, concerning the electronic states of doubly ionized molecules. On the experimental side this is mostly due to the fact that many doubly ionized molecules are unstable with respect to dissociation and therefore do not exist long enough to be studied by the traditional technique of mass spectroscopy. In recent years Auger electron spectroscopy and double charge transfer spectroscopy, neither of which depend on the requirement that the ion remain stable, have been used to measure vertical double ionization potentials of a number of molecules.

In Auger electron spectroscopy a vacancy in the inner shell of an atom or molecule is filled by a nonradiative transition in which a monoenergetic electron is ejected. Recently Moddeman et. al.(3) have used this technique to study a number of diatomic and polyatomic molecules. The minimum energy for double electron removal may be obtained from the relationship

$$I^{++} = E(K) - E_A \tag{53}$$

where E(K) is the binding energy of the K shell and E_A is the measured energy for the highest energy normal Auger line. Their results for the first double ionization potentials of N_2 and H_2O are listed in Table 14.

Recently Appell and co-workers (4) have measured the double ionization potentials of a large assortment of molecules using double charge transfer spectroscopy. In their experiments 4 keV protons collide with neutral molecules and there are observed in the translational energy spectra of the H^- ions produced peaks arising from two different processes, namely the single collision process

$$H^+ + M \longrightarrow H^- + M^{++} \tag{54}$$

and the double collision process

$$\begin{aligned} H^+ + M &\longrightarrow H + M^+ \\ H + M &\longrightarrow H^- + M^+ \end{aligned} \tag{55}$$

The differences between the incident proton energy and the H^- translational energy for each of these processes is

$$\begin{aligned} \Delta T_1 &= I^{++} + E(H^-) + T_m \\ \Delta T_2 &= I^+ + I'^+ + E(H^-) + T_{mm}, \end{aligned} \tag{56}$$

where I^{++} = the double ionization potential of the target M which is initially in its ground state

I^+, I'^+ = the single ionization potentials of the target M

$E(H^-) = -14.35$ eV, the energy of the H^- ion in its ground state

T_m, T_{mm} = recoil energies of the targets which are negligible in these experiments (4)

The measurement of ΔT_1 permits the determination of the energy levels of the doubly ionized target M^{++}. These workers note that the potentials

Table 14. First Double Ionization Potentials of N_2, NH_3 and H_2O

Molecule	State of ion	Double Ionization Potential (eV)
$N_2\ ({}^1\Sigma_g^+)$	${}^1\Sigma_g^+$	43.1 ± 0.5[a] 42.9[b]
$NH_3\ ({}^1A_1)$	${}^1A_1$	35.3 ± 0.7[a]
$H_2O\ ({}^1A_1)$	${}^1A_1$	39.2[b]

a) ref. 4
b) ref. 3

measured correspond to vertical transitions and that the procedure works even if the doubly ionized state is unstable with respect to dissociation.

In Table 14 we list their results for the first double ionization potentials of N_2 and NH_3. In making the symmetry assignments the so called spin conservation rule is helpful. This rule states that in the processes under consideration the doubly charged ion will be formed in the same spin state as the neutral molecule. Since the ground state of both N_2 and NH_3 is a singlet we expect to observe N_2^{++} and NH_3^{++} in the singlet state. Below we present the results of RHF and SEHF calculations on NH_3, N_2 and H_2O and their closed shell, doubly charged ions.

C. Numerical Results and Discussion

The calculations described below are of the same type as those considered in Section F of Chapter 3. A "double zeta" basis set of contracted Gaussians was used and RHF and SEHF energies of the closed shell neutral and doubly ionized molecule were computed. It must be kept in mind that a basis set of the size used in this study is not capable of reaching the Hartree-Fock limit. Since we will be mostly concerned with energy differences one might hope that any errors introduced by the limited basis set will cancel in the subtraction. However, due to the fact that we are using the same basis to describe a 2n and 2n-2 electron system, the calculation on the system with the smaller number of electrons will be closer to the Hartree-Fock limit than the calculation on the system with the larger number of electrons. We will refer to this fact in the following discussion.

In its ground state the ammonia molecule has the configuration

$$^1A_1 \qquad (1a_1)^2(2a_1)^2(1e)^4(3a_1)^2$$

and to a first approximation the lowest lying state of NH_3^{++} may be obtained by removing the pair of $3a_1$ electrons leading to the configuration

$$^1A_1 \qquad (1a_1)^2(2a_1)^2(1e)^4$$

The calculations on the $^1A_1$ ground states of NH_3 and NH_3^{++} were performed with the basis set given in Table 6 and at the geometry given in Table 10. The results are listed in Tables 15-17. Looking first at the RHF calculations we notice that a double ionization potential (DIP) of 1.2290 a.u. is predicted. If the basis were made larger we expect the NH_3 energy to improve more than the NH_3^{++} energy, thus giving a larger value for the DIP. Just this type of calculation is reported by Appell and Horsley (4). They performed RHF calculations with the 37 Slater orbital, near Hartree-Fock, basis of Stevens (5) and included an exponent reoptimization for NH_3^{++}. This led to a predicted DIP of 1.2382 a.u.. Since the experimental value is 1.2973 a.u. we conclude that the neutral molecule has a larger correlation energy than the ground state of the doubly charged ion.

This is not terribly surprising. The orbital from which the two electrons are removed to form the ion is to a large extent localized on the side of the nitrogen atom away from the hydrogen atoms and, as can be seen from Table 16, the removal of these electrons produces only small changes in the remaining orbitals. It is generally accepted that the correlation energy for closed shell systems may be written as (6)

$$E_{corr} = \sum_{i<j} \epsilon_{ij} \tag{57}$$

where ϵ_{ij} is the contribution to the correlation energy from two electrons in the molecular spin orbitals i and j. If two electrons are removed from the system and the remaining orbitals are little changed we expect the significant ϵ_{ij}'s not to vary by much and thus the doubly charged ion should have a smaller correlation energy.

Appell and Horsley (4) have performed large configuration interaction calculations which support this statement. These calculations were done in another basis of "double zeta" quality and the results are useful for comparison to those of this study. These authors report RHF energies for the molecule and doubly charged ion of -56.1694 a.u. and -54.9397 a.u. respectively. These may be compared with CI energies of -56.2925 a.u. and -55.0236 a.u., indicating that a large CI on the neutral molecule improves the energy by 0.1121 a.u. while the same procedure for the doubly charged ion improves the energy by 0.0839 a.u.. The CI calculation predicts a DIP of 1.2689 a.u. which is almost within the error bars of the experiment. Presumably the same type of CI treatment with a larger basis would improve on this situation.

The SEHF calculations predict a DIP of 1.2380 a.u., in poorer agreement with experiment with a CI result with a similar basis but in better agreement than the RHF result. From Table 15 we see that the SEHF calculation improved upon the RHF energy by 0.0429 a.u. for the molecule

Table 15. Double Ionization Potential Calculations for NH_3[a]

	$NH_3\,(^1A_1)$	$NH_3^{++}(^1A_1)$	DIP
Expt.	---	---	1.2973±.03
RHF[b]	-56.1716	-54.9426	1.2290
SEHF[b]	-56.2145	-54.9765	1.2380
RHF[c]	-56.2208	-54.9826	1.2382
CI[d]	-56.2925	-55.0236	1.2689
RHF[e]	-56.1694	-54.9397	1.2297

a) all energies in hartrees
b) this work
c) from ref. 4 ; a near Hartree-Fock calculation
d) from ref. 4 ; with a "double zeta" basis set
e) from ref. 4 ; same basis as the CI calculation

Table 16. RHF orbitals for NH_3 and NH_3^{++}

NH_3	a_1	a_1	a_1	e	e
H1-S1	0.00012	0.13578	0.05521	0.00000	0.28610
H1-S2	-.00064	0.01161	0.01220	0.00000	0.19507
H2-S1	0.00012	0.13578	0.05521	0.24777	-.14305
H2-S2	-.00064	0.01161	0.01220	0.16895	-.09753
H3-S1	0.00012	0.13578	0.05521	-.24777	-.14305
H3-S2	-.00064	0.01161	0.01220	-.16895	-.09753
N1-S1	0.05195	-.00980	0.00328	0.00000	0.00000
N1-S2	0.97901	-.21252	0.06816	0.00000	0.00000
N1-S3	0.00347	0.45872	-.18360	0.00000	0.00000
N1-S4	0.00302	0.40282	-.16495	0.00000	0.00000
N1-X1	0.00000	0.00000	0.00000	0.00000	0.54229
N1-X2	0.00000	0.00000	0.00000	0.00000	0.15329
N1-Y1	0.00000	0.00000	0.00000	0.54229	0.00000
N1-Y2	0.00000	0.00000	0.00000	0.15329	0.00000
N1-Z1	0.00172	0.12096	0.64135	0.00000	0.00000
N1-Z2	-.00024	0.03537	0.41549	0.00000	0.00000

NH_3^{++}	a_1	a_1	e	e
H1-S1	0.00012	0.12528	0.00000	0.25215
H1-S2	-.00064	-.02952	0.00000	0.04049
H2-S1	0.00012	0.12528	0.21836	-.12607
H2-S2	-.00064	-.02952	0.03508	-.02025
H3-S1	0.00012	0.12528	-.21836	-.12607
H3-S2	-.00064	-.02952	-.03508	-.02025
N1-S1	0.05195	-.01092	0.00000	0.00000
N1-S2	0.97901	-.22976	0.00000	0.00000
N1-S3	0.00347	0.56704	0.00000	0.00000
N1-S4	0.00302	0.40312	0.00000	0.00000
N1-X1	0.00000	0.00000	0.00000	0.70682
N1-X2	0.00000	0.00000	0.00000	0.13518
N1-Y1	0.00000	0.00000	0.70682	0.00000
N1-Y2	0.00000	0.00000	0.13518	0.00000
N1-Z1	0.00172	0.10744	0.00000	0.00000
N1-Z2	-.00023	0.03593	0.00000	0.00000

Table 17. SEHF orbitals for NH_3

NH_3	a_1	a_1	a_1	e	e
λ_i	1.000	0.960	0.906	0.883	0.883
α orbitals					
H1-S1	0.00012	-.08462	0.21259	0.00000	0.42321
H1-S2	-.00064	-.00145	0.05812	0.00000	0.28953
H2-S1	0.00012	-.08462	0.21259	0.36651	-.21160
H2-S2	-.00064	-.00145	0.05812	0.25076	-.14477
H3-S1	0.00012	-.08462	0.21259	-.36651	-.21160
H3-S2	-.00064	-.00145	0.05812	-.25076	-.14477
N1-S1	0.05195	0.00776	-.00283	0.00000	0.00000
N1-S2	0.97901	0.17852	-.06864	0.00000	0.00000
N1-S3	0.00347	-.28632	0.06373	0.00000	0.00000
N1-S4	0.00302	-.52039	0.07046	0.00000	0.00000
N1-X1	0.00000	0.00000	0.00000	0.00000	0.29898
N1-X2	0.00000	0.00000	0.00000	0.00000	0.12604
N1-Y1	0.00000	0.00000	0.00000	0.29898	0.00000
N1-Y2	0.00000	0.00000	0.00000	0.12604	0.00000
N1-Z1	0.00172	0.27467	0.35150	0.00000	0.00000
N1-Z2	-.00023	0.37689	0.41593	0.00000	0.00000
β orbitals					
H1-S1	0.00012	-.03617	0.05425	0.00000	0.13510
H1-S2	-.00064	0.00095	-.01293	0.00000	0.10057
H2-S1	0.00012	-.03617	0.05425	0.11700	-.06754
H2-S2	-.00064	0.00095	-.01293	0.08711	-.05029
H3-S1	0.00012	-.03617	0.05425	-.11700	-.06754
H3-S2	-.00064	0.00095	-.01293	-.08711	-.05029
N1-S1	0.05195	0.01069	-.00574	0.00000	0.00000
N1-S2	0.97901	0.21785	-.12035	0.00000	0.00000
N1-S3	0.00347	-.61450	0.29968	0.00000	0.00000
N1-S4	0.00302	-.28419	0.20502	0.00000	0.00000
N1-X1	0.00000	0.00000	0.00000	0.00000	0.76374
N1-X2	0.00000	0.00000	0.00000	0.00000	0.14634
N1-Y1	0.00000	0.00000	0.00000	0.76374	0.00000
N1-Y2	0.00000	0.00000	0.00000	0.14634	0.00000
N1-Z1	0.00172	0.42255	0.71199	0.00000	0.00000
N1-Z2	-.00023	0.15176	0.21029	0.00000	0.00000

Table 18. SEHF orbitals for NH_3^{++}

	a_1	a_1	e	e
λ_i	1.000	0.918	0.890	0.890
α orbitals				
H1-S1	0.00012	0.19512	0.00000	0.42299
H1-S2	-.00064	-.03805	0.00000	0.05803
H2-S1	0.00012	0.19512	0.36632	-.21149
H2-S2	-.00064	-.03805	0.05027	-.02902
H3-S1	0.00012	0.19512	-.36632	-.21149
H3-S2	-.00064	-.03805	-.05027	-.02902
N1-S1	0.05195	-.00870	0.00000	0.00000
N1-S2	0.97901	-.19417	0.00000	0.00000
N1-S3	0.00347	0.36082	0.00000	0.00000
N1-S4	0.00302	0.48035	0.00000	0.00000
N1-X1	0.00000	0.00000	0.00000	0.47334
N1-X2	0.00000	0.00000	0.00000	0.17404
N1-Y1	0.00000	0.00000	0.47334	0.00000
N1-Y2	0.00000	0.00000	0.17404	0.00000
N1-Z1	0.00172	0.18865	0.00000	0.00000
N1-Z2	-.00023	0.06027	0.00000	0.00000
β orbitals				
H1-S1	0.00012	0.05547	0.00000	0.07580
H1-S2	-.00064	-.01666	0.00000	0.03307
H2-S1	0.00012	0.05547	0.06564	-.03789
H2-S2	-.00064	-.01666	0.02864	-.01653
H3-S1	0.00012	0.05547	-.06564	-.03789
H3-S2	-.00064	-.01666	-.02864	-.01653
N1-S1	0.05195	-.01269	0.00000	0.00000
N1-S2	0.97901	-.25530	0.00000	0.00000
N1-S3	0.00347	0.75214	0.00000	0.00000
N1-S4	0.00302	0.29502	0.00000	0.00000
N1-X1	0.00000	0.00000	0.00000	0.89813
N1-X2	0.00000	0.00000	0.00000	0.07132
N1-Y1	0.00000	0.00000	0.89813	0.00000
N1-Y2	0.00000	0.00000	0.07132	0.00000
N1-Z1	0.00172	0.01167	0.00000	0.00000
N1-Z2	-.00023	0.01096	0.00000	0.00000

and by 0.0339 a.u. for the ion. Both these figures represent roughly 40% of the energy improvement obtained from the CI treatment with an equivalent basis. If a larger basis set had been used we expect the predicted DIP to improve by about 0.01 a.u., as in the RHF case, but this would still be outside the error bars of the experiment.

Taken all together the results indicate that the RHF model provides a better description of NH_3^{++} in its $^1A_1$ ground state than of NH_3 in its $^1A_1$ ground state. The SEHF model restores some balance, improving upon the RHF energy more for the molecule than for the doubly charged ion, but the calculations show that a large CI treatment is necessary to get close agreement of the DIP with experiment. It is to be noted, though, that the SEHF method changes the predicted DIP in the proper direction.

We now turn to the first double ionization potential of the nitrogen molecule. The $^1\Sigma_g^+$ ground state of N_2 is described by the configuration

$$^1\Sigma_g^+ \quad (1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4(3\sigma_g)^2$$

The $^1\Sigma_g^+$ ground state of N_2^{++} results from the removal of the pair of $3\sigma_g$ electrons and is described by the configuration

$$^1\Sigma_g^+ \quad (1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4$$

The basis set used in the calculations reported below is listed in Table 6 and the geometry is given in Table 19. The results are collected in Tables 20-23. The first important observation which should be made is that the RHF calculations predict a DIP of 1.6668 a.u. which is larger than the experimental value of 1.5839 a.u.. We expect the inclusion of more basis functions will lower the N_2 energy more than the N_2^{++} energy and thus increase the discrepancy between the RHF model and experiment. As was stated above, results of this nature imply that the correlation error for the doubly charged ion is larger than the correlation error for the neutral molecule. This is the opposite of what was encountered with ammonia and on the surface it is rather surprising. If one assumes that the correlation energy may be written as a sum of pair correlation energies which change little upon ionization, one then expects the ion to have less of an error than the neutral molecule. This reasoning worked in the case of ammonia but it breaks down for nitrogen. Apparently the removal of the pair of $3\sigma_g$ electrons from the nitrogen molecule in its ground state leads to a rather large reorganization of the charge distribution which the RHF wave function cannot describe. The fact that the correlation energy increases even while the number of electrons decreases tells us that the RHF model works less well for the ion than for the molecule. The SEHF calculations discussed below confirm this fact and give us some physical insight as to why the behavior of the correlation energy upon double ionization differs in NH_3 and N_2.

The SEHF calculations predict a DIP for $N_2(^1\Sigma_g^+) \longrightarrow N_2^{++}(^1\Sigma_g^+)$ of 1.4556 a.u.. As was the case with the RHF prediction, this result is outside the error bars of the experiment. It should be noted, though, that the SEHF prediction is on the opposite side of the experimental value from the RHF prediction. Since we expect a larger basis to decrease the SEHF energy more for N_2 than for N_2^{++}, the inclusion of more basis functions will bring the predicted DIP closer to the experimental value. The SEHF energy for N_2 represents an improvement of 0.0769 a.u. over the RHF result, while the SEHF energy for N_2^{++} represents an improvement of 0.2881 a.u.. It is gratifying that the SEHF method provides a larger improvement of the RHF energy in the situation which we know to have a larger correlation error. An examination of Figures 3 and 4 gives us some indication of why this is so. In Figure 3 we plot the $2\sigma_u$ RHF orbitals of both N_2 and N_2^{++} along the inter nuclear axis. They are very similar to each other and the changes they show are representative of all the other orbitals which are occupied in both states. In Figure 4 we plot the corresponding SEHF α orbitals. The situation here is very different from that encountered in Figure 3. The $2\sigma_u$ SEHF orbitals undergo a large change during the double ionization. This change is reflected in the pairing parameter λ_i which goes from $\lambda = 0.989$ for N_2 to $\lambda = 0.239$ in N_2^{++}. It is this change which is the primary cause for the relatively large energy improvement in the doubly charged ion. It would seem that the removal of the two $3\sigma_g$ decreased the screening of the nitrogen nuclei which in turn tended to polarize the $2\sigma_u$ electrons, allowing them to correlate and at the same time remain in the strong nuclear field. The RHF wave function does not contain this variational freedom and it is because of this fact that the RHF model gives a poorer description of N_2^{++} than it does for N_2.

Table 19. Geometry for the N_2 and N_2^{++} calculations

Center	X	Y	Z
N1	0.00000	0.00000	-1.03705
N2	0.00000	0.00000	1.03705

Table 20. Double Ionization Potential Calculations for N_2[a]

	$N_2\ ({}^1\Sigma_g^+)$	$N_2^{++}\ ({}^1\Sigma_g^+)$	DIP
Expt.	---	---	1.5839 ± 0.02[c] 1.5766[d]
RHF[b]	-108.8695	-107.2027	1.6668
SEHF[b]	-108.9464	-107.4908	1.4556

a) all energies in hartrees
b) this work
c) ref. 4
d) ref. 3

Table 21. RHF orbitals for N_2 and N_2^{++}

N_2	$1\sigma_g$	$1\sigma_u$	$2\sigma_g$	$2\sigma_u$	$1\pi_{ux}$	$1\pi_{uy}$	$3\sigma_g$
N1-S1	0.03672	0.03675	-.00800	-.00739	0.00000	0.00000	-.00256
N1-S2	0.69211	0.69261	-.17058	-.15764	0.00000	0.00000	-.05870
N1-S3	0.00266	0.00137	0.38406	0.38301	0.00000	0.00000	0.10351
N1-S4	0.00094	0.00607	0.15416	0.44288	0.00000	0.00000	0.31943
N1-X1	0.00000	0.00000	0.00000	0.00000	0.51275	0.00000	0.00000
N1-X2	0.00000	0.00000	0.00000	0.00000	0.16446	0.00000	0.00000
N1-Y1	0.00000	0.00000	0.00000	0.00000	0.00000	0.51275	0.00000
N1-Y2	0.00000	0.00000	0.00000	0.00000	0.00000	0.16446	0.00000
N1-Z1	0.00222	0.00175	0.25752	-.22772	0.00000	0.00000	-.52278
N1-Z2	-.00104	0.00172	-.02582	-.04246	0.00000	0.00000	-.09435

(the N2 coefficients are either + (g) or - (u) the N1 coefficients with the exception of the N2-Z coefficients which are - (g) or + (u))

N_2^{++}	$1\sigma_g$	$1\sigma_u$	$2\sigma_g$	$2\sigma_u$	$1\pi_{ux}$	$1\pi_{uy}$
N1-S1	0.03674	0.03676	-.00835	-.00827	0.00000	0.00000
N1-S2	0.69235	0.69286	-.17363	-.16959	0.00000	0.00000
N1-S3	0.00174	0.00004	0.43434	0.47878	0.00000	0.00000
N1-S4	0.00099	0.00643	0.11766	0.45652	0.00000	0.00000
N1-X1	0.00000	0.00000	0.00000	0.00000	0.58742	0.00000
N1-X2	0.00000	0.00000	0.00000	0.00000	0.07895	0.00000
N1-Y1	0.00000	0.00000	0.00000	0.00000	0.00000	0.58742
N1-Y2	0.00000	0.00000	0.00000	0.00000	0.00000	0.07895
N1-Z1	0.00126	0.00074	0.24215	-.20509	0.00000	0.00000
N1-Z2	-.00031	0.00215	-.02825	0.03573	0.00000	0.00000

(the N2 coefficients are either + (g) or - (u) the N1 coefficients with the exception of the N2-Z coefficients which are - (g) or + (u))

Table 22. SEHF orbitals for N_2

N_2	$1\sigma_g$	$1\sigma_u$	$2\sigma_g$	$2\sigma_u$	$3\sigma_g$	$1\pi_{ux}$	$1\pi_{uy}$
λ_i	1.000	1.000	0.990	0.989	0.973	0.724	0.724
α orbitals							
N1-S1	0.03672	0.03675	0.00419	-.00772	-.00825	0.00000	0.00000
N1-S2	0.69211	0.69261	0.09274	-.16112	-.16954	0.00000	0.00000
N1-S3	0.00266	0.00137	-.18827	0.42600	0.44870	0.00000	0.00000
N1-S4	0.00094	0.00607	-.40265	0.37379	0.12131	0.00000	0.00000
N1-X1	0.00000	0.00000	0.00000	0.00000	0.00000	0.76376	0.00000
N1-X2	0.00000	0.00000	0.00000	0.00000	0.00000	0.19167	0.00000
N1-Y1	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.76376
N1-Y2	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.19167
N1-Z1	0.00222	0.00175	0.50086	-.25855	0.45367	0.00000	0.00000
N1-Z2	-.00104	0.00172	0.02776	0.01006	0.01768	0.00000	0.00000
N2-S1	0.03672	-.03675	0.00374	0.00690	-.00637	0.00000	0.00000
N2-S2	0.69211	-.69261	0.08532	0.15131	-.14101	0.00000	0.00000
N2-S3	0.00266	-.00137	-.14761	-.32575	0.25916	0.00000	0.00000
N2-S4	0.00094	-.00607	-.29559	-.49425	0.06273	0.00000	0.00000
N2-X1	0.00000	0.00000	0.00000	0.00000	0.00000	0.20907	0.00000
N2-X2	0.00000	0.00000	0.00000	0.00000	0.00000	0.09157	0.00000
N2-Y1	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.20907
N2-Y2	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.09157
N2-Z1	-.00222	0.00175	-.41841	-.19282	-.24603	0.00000	0.00000
N2-Z2	0.00104	0.00172	-.18299	-.11611	0.03530	0.00000	0.00000

(the β orbitals may be obtained from the α orbitals by interchanging the N1 and N2 coefficients with the sign change appropriate for the u or g symmetry)

Table 23. SEHF orbitals for N_2^{++}

N_2^{++}	$1\sigma_g$	$1\sigma_u$	$2\sigma_g$	$1\pi_{ux}$	$1\pi_{uy}$	$2\sigma_u$
λ_i	1.000	1.000	0.994	0.633	0.633	0.239

α orbitals

N1-S1	0.03674	0.03676	-.00819	0.00000	0.00000	-.00922
N1-S2	0.69235	0.69286	-.16877	0.00000	0.00000	-.18553
N1-S3	0.00174	0.00004	0.43943	0.00000	0.00000	0.55485
N1-S4	0.00099	0.00643	0.10324	0.00000	0.00000	0.39089
N1-X1	0.00000	0.00000	0.00000	0.86196	0.00000	0.00000
N1-X2	0.00000	0.00000	0.00000	0.10347	0.00000	0.00000
N1-Y1	0.00000	0.00000	0.00000	0.00000	0.86196	0.00000
N1-Y2	0.00000	0.00000	0.00000	0.00000	0.10347	0.00000
N1-Z1	0.00126	0.00074	0.36679	0.00000	0.00000	-.56538
N1-Z2	-.00031	0.00215	-.01042	0.00000	0.00000	0.01769
N2-S1	0.03674	-.03676	-.00723	0.00000	0.00000	0.00328
N2-S2	0.69235	-.69286	-.15480	0.00000	0.00000	0.07152
N2-S3	0.00174	-.00004	0.33921	0.00000	0.00000	-.16009
N2-S4	0.00099	-.00643	0.09285	0.00000	0.00000	-.19578
N2-X1	0.00000	0.00000	0.00000	0.20853	0.00000	0.00000
N2-X2	0.00000	0.00000	0.00000	0.02791	0.00000	0.00000
N2-Y1	0.00000	0.00000	0.00000	0.00000	0.20853	0.00000
N2-Y2	0.00000	0.00000	0.00000	0.00000	0.02791	0.00000
N2-Z1	-.00126	0.00074	-.27572	0.00000	0.00000	0.10519
N2-Z2	0.00031	0.00215	0.04106	0.00000	0.00000	0.01961

(the β orbitals may be obtained from the α orbitals by interchanging the N1 and N2 coefficients with the sign change appropriate for the u or g symmetry)

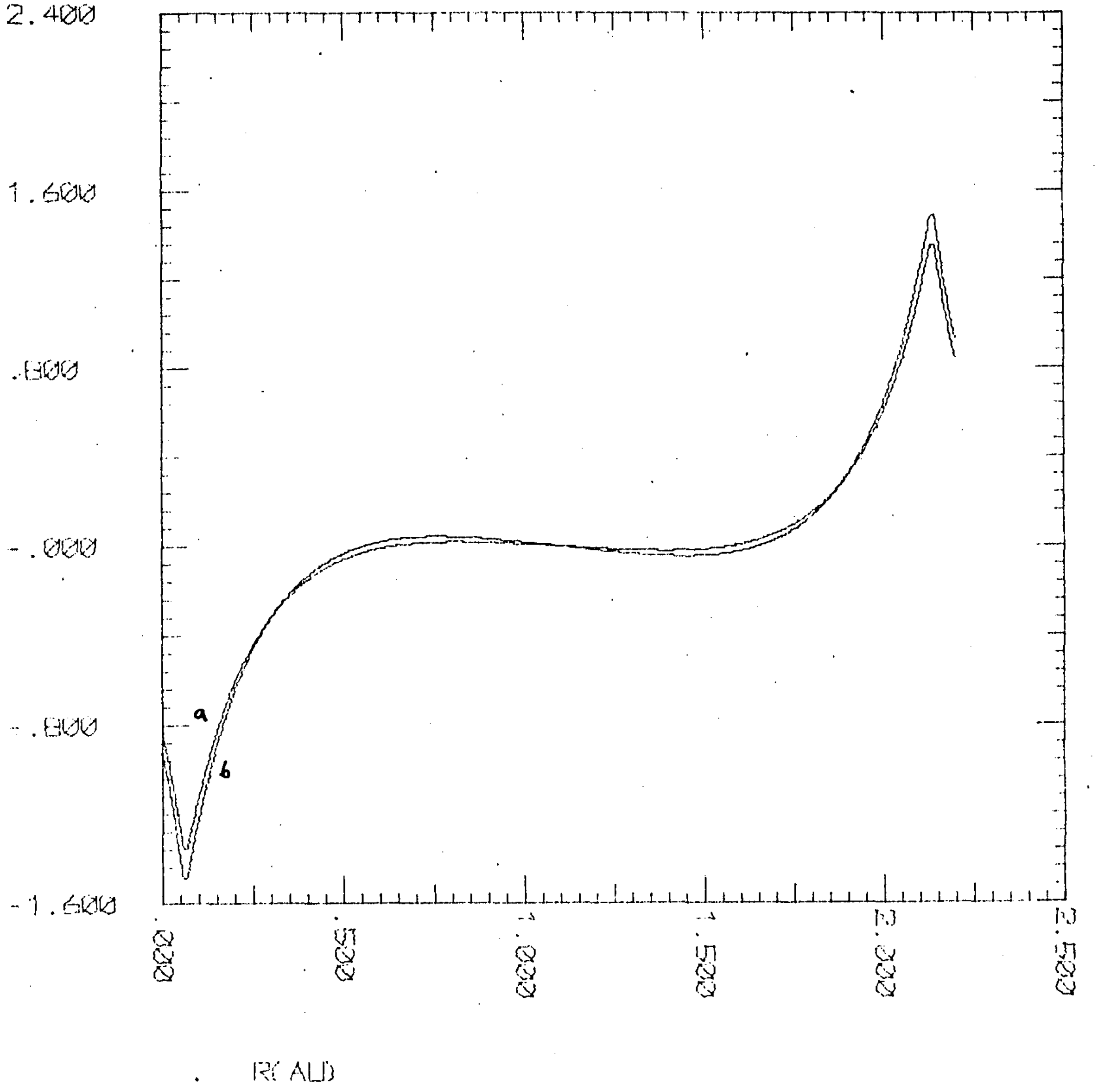

Figure 3. The $2\sigma_u$ RHF orbitals of N_2 and N_2^{++} along the internuclear axis: a) N_2 b) N_2^{++}

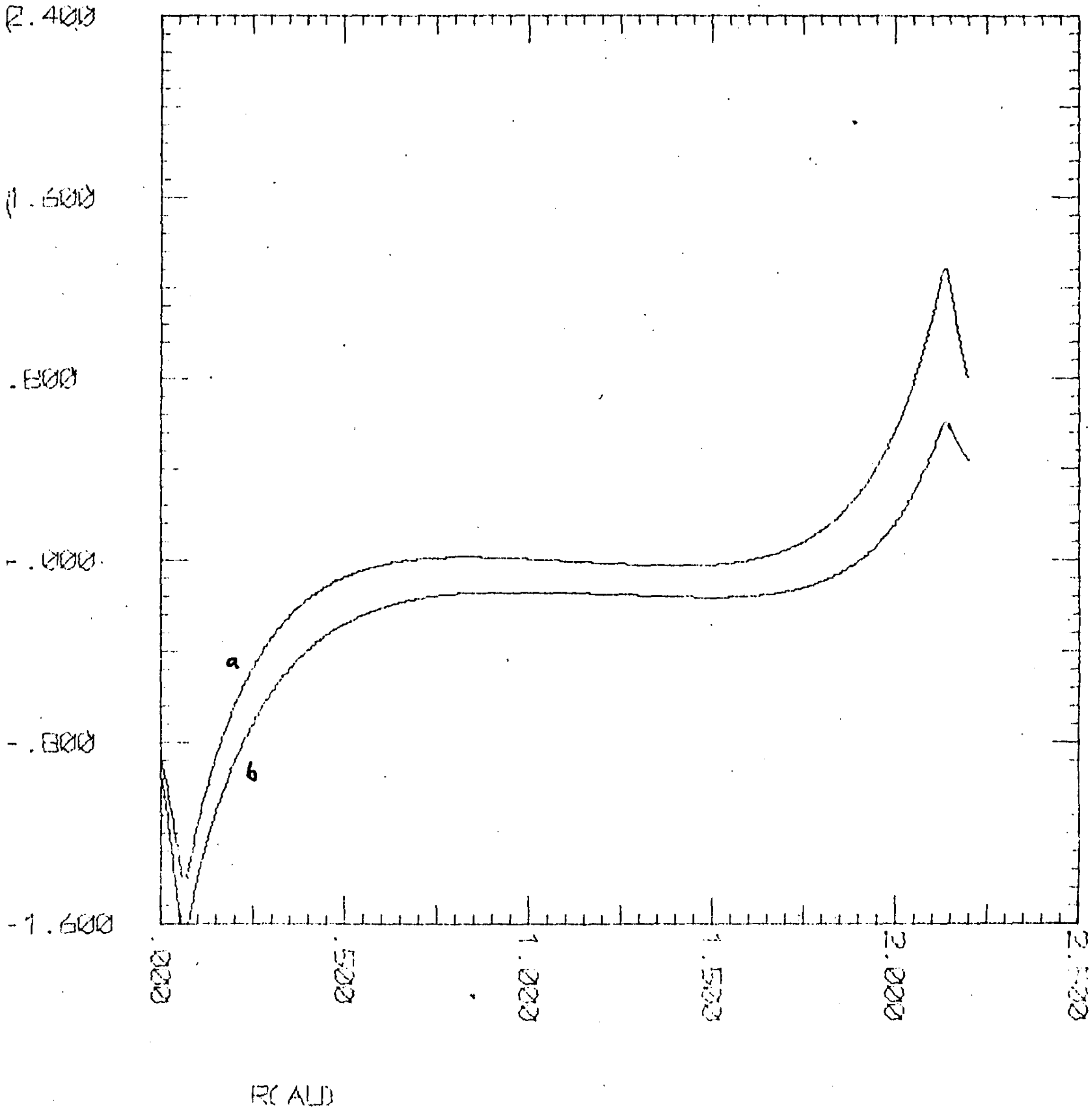

Figure 4. The $2\sigma_g$ SEHF α orbitals of N_2 and N_2^{++} along the internuclear axis:

a) N_2 b) N_2^{++}

The ground state of the water molecule is described by the configuration

$$^1A_1 \qquad (1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2$$

and the lowest lying state of H_2O^{++} may be obtained by removing the pair of $1b_1$ electrons resulting in the configuration

$$^1A_1 \qquad (1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2$$

The calculations on these states were performed at a slightly different geometry and with a slightly different basis set than the H_2O calculation reported in Chapter 3. The geometry is listed in Table 24 and the basis is given in Table 25. The results are collected in Tables 26-29.

The SEHF method improves upon the RHF energy by 0.0431 a.u. for the molecule and by 0.0260 a.u. for the closed shell ion. These figures are similar to those obtained from the ammonia calculations and indicate that the H_2O^{++} ion has a smaller correlation energy than the neutral molecule. Again, this is not an unforseen result. The $1b_1$ orbital which is not occupied in the ion has its concentration of charge out of the plane of the molecule and the removal of the $1b_1$ electrons leads to only minor changes in the remaining orbitals. One expects the pair correlation energies associated with these orbitals to change little and thus the ion should have less of a correlation error than the molecule.

The RHF calculations predict a DIP of 1.4390 a.u. and the SEHF calculations predict 1.4561 a.u.. Inclusion of more basis functions should lower both of these figures. Moddeman et. al. (3) list a DIP of 1.44 a.u.. These authors do not include any error bars but closer inspection of the data indicates that the vertical double ionization potential may be as high as 1.51 a.u.. This comes from the fact that Moddeman *et. al.* use for E_A in eq. 53 not the energy of the first normal Auger line but rather the energy at which the line begins to appear. This energy is thought to correspond more closely to the vertical ionization potential. In the case of N_2, for which Auger electron and double charge transfer spectroscopy yielded results in close agreement with each other, the first normal Auger line is sharply peaked and the difference in energy between the line and its onset is only 0.5 eV. The first normal Auger line in the H_2O spectrum, though, is broader and the difference in energy between the line and its onset is almost 2.0 eV. Using for E_A in eq. 53 the energy of the line instead of its onset we obtain a DIP of 1.51 a.u.. One feels that this is closer to the true value since the ion seems to have a smaller correlation energy than the neutral molecule and, as stated above, the DIP predicted by the RHF method should be below the correct value.

Table 24. Geometry for the H_2O and H_2O^{++} calculations

Center	X	Y	Z
H1	0.00000	1.43046	1.10712
H2	0.00000	-1.43046	1.10712
O1	0.00000	0.00000	0.00000

Table 25. Basis set for H_2O and H_2O^{++} calculations

Hydrogen (see Table 4)

Oxygen

Exponents	Coefficients	
4643.4485	0.0292246	S1
1424.0643	0.1216032	
290.8205	0.9047853	
76.2320	0.1527631	S2
31.3166	0.2439912	
12.8607	0.4582404	
4.6037	0.2644382	
9.7044	-.1403140	S3
0.9311	1.0515337	
0.2825	1.0000000	S4
35.1832	0.0195800	P1
7.90403	0.1241899	
2.30512	0.3947297	
0.71706	0.6273796	
0.21373	1.0000000	P2

Table 26. Double Ionization Potential Calculations for H_2O[a]

	$H_2O\ (^1A_1)$	$H_2O^{++}\ (^1A_1)$	DIP
Expt.	---	---	1.4406[c]
RHF[b]	-76.0035	-74.5645	1.4390
SEHF[b]	-76.0466	-74.5905	1.4561

a) all energies in hartrees
b) this work
c) ref. 3

Table 27. RHF orbitals for H_2O and H_2O^{++}

H_2O	a_1	a_2	a_3	b_2	b_1
H1-S1	-.00010	0.13807	0.13997	0.25556	0.00000
H1-S2	-.00035	0.00675	0.06019	0.13093	0.00000
H2-S1	-.00010	0.13807	0.13997	-.25556	0.00000
H2-S2	-.00035	0.00675	0.06019	-.13093	0.00000
O1-S1	0.05112	-.01033	0.00372	0.00000	0.00000
O1-S2	0.97934	-.22756	0.08108	0.00000	0.00000
O1-S3	0.00371	0.48875	-.19084	0.00000	0.00000
O1-S4	0.00221	0.44405	-.26750	0.00000	0.00000
O1-X1	0.00000	0.00000	0.00000	0.00000	0.72912
O1-X2	0.00000	0.00000	0.00000	0.00000	0.40853
O1-Y1	0.00000	0.00000	0.00000	0.57476	0.00000
O1-Y2	0.00000	0.00000	0.00000	0.17659	0.00000
O1-Z1	0.00166	0.12886	0.62646	0.00000	0.00000
O1-Z2	-.00025	0.03241	0.32582	0.00000	0.00000

H_2O^{++}	a_1	a_1	a_1	b_2
H1-S1	0.00013	0.12440	0.10528	0.21708
H1-S2	-.00039	-.03413	0.00519	0.00639
H2-S1	0.00013	0.12440	0.10528	-.21708
H2-S2	-.00039	-.03413	0.00519	0.00639
O1-S1	0.05113	-.01121	0.00381	0.00000
O1-S2	0.97959	-.24006	0.07906	0.00000
O1-S3	0.00297	0.58621	-.22276	0.00000
O1-S4	0.00190	0.40709	-.15086	0.00000
O1-X1	0.00000	0.00000	0.00000	0.00000
O1-X2	0.00000	0.00000	0.00000	0.00000
O1-Y1	0.00000	0.00000	0.00000	0.74107
O1-Y2	0.00000	0.00000	0.00000	0.13877
O1-Z1	0.00172	0.17477	0.78792	0.00000
O1-Z2	-.00041	0.04114	0.19019	0.00000

Table 28. SEHF orbitals for H_2O

H_2O	a_1	a_1	a_1	b_2	b_1
λ_i	1.000	0.970	0.883	0.868	0.937
α orbitals					
H1-S1	-.00010	0.03880	0.30338	0.38063	0.00000
H1-S2	-.00035	-.03095	0.09578	0.18960	0.00000
H2-S1	-.00010	0.03880	0.30338	-.38063	0.00000
H2-S2	-.00035	-.03095	0.09578	-.18960	0.00000
O1-S1	0.05112	-.00910	-.00154	0.00000	0.00000
O1-S2	0.97934	-.21346	-.03795	0.00000	0.00000
O1-S3	0.00371	0.33448	0.03193	0.00000	0.00000
O1-S4	0.00221	0.67661	-.04635	0.00000	0.00000
O1-X1	0.00000	0.00000	0.00000	0.00000	0.55241
O1-X2	0.00000	0.00000	0.00000	0.00000	0.59965
O1-Y1	0.00000	0.00000	0.00000	0.32353	0.00000
O1-Y2	0.00000	0.00000	0.00000	0.17985	0.00000
O1-Z1	0.00166	-.19947	0.36283	0.00000	0.00000
O1-Z2	-.00025	-.22790	0.35799	0.00000	0.00000
β orbitals					
H1-S1	-.00010	0.02864	0.08051	0.11751	0.00000
H1-S2	-.00035	-.02607	0.02045	0.07488	0.00000
H2-S1	-.00010	0.02864	0.08051	-.11751	0.00000
H2-S2	-.00035	-.02607	0.02045	-.07488	0.00000
O1-S1	0.05112	-.01194	-.00387	0.00000	0.00000
O1-S2	0.97934	-.24941	-.08195	0.00000	0.00000
O1-S3	0.00371	0.67446	0.20666	0.00000	0.00000
O1-S4	0.00221	0.35612	0.07977	0.00000	0.00000
O1-X1	0.00000	0.00000	0.00000	0.00000	0.87441
O1-X2	0.00000	0.00000	0.00000	0.00000	0.21417
O1-Y1	0.00000	0.00000	0.00000	0.79776	0.00000
O1-Y2	0.00000	0.00000	0.00000	0.13482	0.00000
O1-Z1	0.00166	-.29184	0.78055	0.00000	0.00000
O1-Z2	-.00025	-.08958	0.18121	0.00000	0.00000

Table 29. SEHF orbitals for H_2O^{++}

H_2O^{++}	a_1	a_1	a_1	b_2
λ_i	1.000	0.985	0.911	0.881
α orbitals				
H1-S1	0.00013	-.00894	0.28091	0.36818
H1-S2	-.00039	0.03788	-.03318	-.01845
H2-S1	0.00013	-.00894	0.28091	-.36818
H2-S2	-.00039	0.03788	-.03318	0.01845
O1-S1	0.05113	0.00978	-.00351	0.00000
O1-S2	0.97959	0.21718	-.08465	0.00000
O1-S3	0.00297	-.45628	0.10517	0.00000
O1-S4	0.00190	-.53443	0.21479	0.00000
O1-X1	0.00000	0.00000	0.00000	0.00000
O1-X2	0.00000	0.00000	0.00000	0.00000
O1-Y1	0.00000	0.00000	0.00000	0.50353
O1-Y2	0.00000	0.00000	0.00000	0.22416
O1-Z1	0.00172	0.38345	0.51993	0.00000
O1-Z2	-.00041	0.14556	0.25483	0.00000
β orbitals				
H1-S1	0.00013	-.02178	0.04541	0.06290
H1-S2	-.00039	0.01964	0.00082	0.04216
H2-S1	0.00013	-.02178	0.04541	-.06290
H2-S2	-.00039	0.01964	0.00082	-.04216
O1-S1	0.05113	0.01161	-.00628	0.00000
O1-S2	0.97959	0.23725	-.12811	0.00000
O1-S3	0.00297	-.69579	0.37457	0.00000
O1-S4	0.00190	-.25947	0.10998	0.00000
O1-X1	0.00000	0.00000	0.00000	0.00000
O1-X2	0.00000	0.00000	0.00000	0.00000
O1-Y1	0.00000	0.00000	0.00000	0.92879
O1-Y2	0.00000	0.00000	0.00000	0.02858
O1-Z1	0.00172	0.45226	0.82243	0.00000
O1-Z2	-.00041	0.05750	0.06187	0.00000

References

1. P.S. Bagus, Phys. Rev. 139, A619 (1965).

2. W. Meyer, Int. J. Quantum Chem. 5 , 341 (1971).

3. W.E. Moddeman, T.A. Carlson, M. O. Krause, B.P. Pullen, W.E. Bull and G.K. Schweitzer, J. Chem. Phys. 55 , 2317 (1971).

4. J. Appell and I.A. Horsley, J. Chem. Phys. 60 , 3445 (1974) and references cited therein.

5. R.M. Stevens, J. Chem. Phys. 55 , 1725 (1971).

6. O. Sinanoglu, J. Chem. Phys. 36 , 706, 3198 (1962).

5. Conclusion

To conclude we point out that the SEHF model is only moderately successful in treating the first double ionization potentials of the molecules studied. In situations where experiment and RHF calculations suggest that the neutral molecule has a larger correlation energy than the doubly charged ion, e.g. NH_3, the SEHF method improves upon the RHF energy more for the molecule than for the ion. When experiment and RHF calculations suggest the opposite, e.g. N_2, the SEHF method improves upon the RHF energy more for the ion than for the molecule. In the case of H_2O the situation is less clear but, as noted above, the interpretation of the experimental results is open to question. While the SEHF method improves on the DIP predicted by the RHF method, the calculations of Appell and Horsley on NH_3 and NH_3^{++} seem to indicate that a large CI treatment is necessary to get good quantitative agreement with experiment.

This is not an unexpected conclusion, as it was never thought that the SEHF model was capable of recovering all of the correlation energy associated with a given system. Rather, the hope was that the SEHF method would provide a means of recovering a significant percentage of the correlation energy for systems which are so large as to be inaccessible to CI calculations. Researchers today are routinely performing _ab initio_ RHF calculations on larger and larger molecules. Calculations which include electron correlation, though, are less routine, especially for systems containing a large number of electrons. The formulation of the SEHF method outlined above seems capable of making a contribution to the solution of this problem.

It is still very much a matter of intuition as to which systems the SEHF method may be most profitably applied. Taken in total the results seem to indicate that systems with equivalent centers and low electron densities, e.g. cyclic H_{10} and N_2^{++}, are prime candidates for SEHF calculations. There has been interest in recent years in investigating the nature of intermolecular interactions by considering the interacting molecules to be a single system and performing ab initio RHF calculations on the "super molecule". Such calculations generally involve large basis sets and a large number of electrons and for this reason electron correlation is not usually included. To a certain extent such systems are similar to cyclic H_{10} and N_2^{++}. The molecules themselves play the role of equivalent centers and the total system will in general have a smaller electron density than the individual molecules. It seems reasonable to expect the SEHF wave function which describes such a system will have α orbitals which peak on one molecule and β orbitals which peak on another and one feels that in such a situation the SEHF method is capable of recovering a fairly large percentage of the correlation energy.

Appendix A

Presented below are two equivalent expressions for the total energy of a spin projected DODS Slater determinant which is constructed from a set of orthonormal and paired orbitals . We first introduce the one electron energy matrix $\underline{h}$ and the generalized Coulomb and exchange matrices $\underline{J}^{\gamma\delta(i)}$ and $\underline{K}^{\gamma\delta(i)}$ ($\gamma, \delta = \alpha$ or β). The one electron matrix has elements

$$\underline{h}_{gf} = \langle \chi_g | \hat{h} | \chi_f \rangle \tag{A1}$$

where $\hat{h}$ is the one electron Hamiltonian for an electron in the field of the bare nuclei. The generalized Coulomb and exchange matrices are defined as

$$\underline{J}^{\gamma\delta(i)}_{gf} = \sum_{k=1}^{m} \sum_{\ell=1}^{m} \underline{\rho}^{\gamma\delta(i)}_{\ell k} \langle g k | f \ell \rangle$$

$$\underline{K}^{\gamma\delta(i)}_{gf} = \sum_{k=1}^{m} \sum_{\ell=1}^{m} \underline{\rho}^{\gamma\delta(i)}_{\ell k} \langle g k | \ell f \rangle \tag{A2}$$

where $\underline{\rho}^{\gamma\delta(i)}$ is defined in eq. and

$$\langle g k | f \ell \rangle = \iint \chi_g^*(r_1) \chi_k^*(r_2) \frac{1}{r_{12}} \chi_f(r_1) \chi_\ell(r_2) \, d^3r_1 \, d^3r_2 \tag{A3}$$

It is also necessary to define the quantities

$$\begin{aligned}
\Lambda_{00} &= \sum_{k=0}^{n} (-1)^{k} S_k \, C(S,k) \\
{}^{i}\Lambda_{r,t} &= \sum_{k=0}^{n-t} (-1)^{k+r} \, {}^{i}S_k \, C(S,k+r) \\
{}^{ij}\Lambda_{r,t} &= \sum_{k=0}^{n-t} (-1)^{k+r} \, {}^{ij}S_k \, C(S,k+r) \\
{}^{ij\ell}\Lambda_{r,t} &= \sum_{k=0}^{n-t} (-1)^{k+r} \, {}^{ij\ell}S_k \, C(S,k+r)
\end{aligned} \qquad \text{(A4)}$$

where C(S,k) are the Sanibel coefficients and the S_k are the symmetric sums defined in terms of the quantities $x_i = \lambda_i^{\,2}$ by

$$\begin{aligned}
S_0 &= 1 \\
S_1 &= \sum_{i=1}^{n} x_i \\
S_2 &= \sum_{i<j}^{n} x_i x_j \\
&\;\;\vdots \\
S_n &= x_1 x_2 \cdots x_n
\end{aligned} \qquad \text{(A5)}$$

and

$$\begin{aligned}
{}^{i}S_k &= \frac{\partial}{\partial x_i} S_{k+1} \\
{}^{ij}S_k &= \frac{\partial^2}{\partial x_i \partial x_j} S_{k+2} \\
{}^{ij\ell}S_k &= \frac{\partial^3}{\partial x_i \partial x_j \partial x_\ell} S_{k+3}
\end{aligned} \qquad \text{(A6)}$$

An expression for the energy which emphasizes the role of the generalized charge-bond order matrices (eq. 26) is

$$E_1 = \sum_{i=1}^{n} \Big[Tr\ \underline{\rho}^{\alpha\alpha(i)} \big(\underline{h}^{\alpha\alpha(i)} + \tfrac{1}{2} \underline{G}^{\alpha\alpha(i)} \big)$$

$$+ Tr\ \underline{\rho}^{\alpha\beta(i)} \big(\underline{h}^{\alpha\beta(i)} + \tfrac{1}{2} \underline{G}^{\alpha\beta(i)} \big) + Tr\ \underline{\rho}^{\beta\alpha(i)} \big(\underline{h}^{\beta\alpha(i)} + \tfrac{1}{2} \underline{G}^{\beta\alpha(i)} \big) \qquad \text{(A7)}$$

$$+ Tr\ \underline{\rho}^{\beta\beta(i)} \big(\underline{h}^{\beta\beta(i)} + \tfrac{1}{2} \underline{G}^{\beta\beta(i)} \big) \Big]$$

where

$$\underline{h}^{\alpha\alpha(i)} = \underline{h}^{\beta\beta(i)} = \frac{{}^{i}\Lambda_{01}}{\Lambda_{00}}\ \underline{h}$$

$$\underline{h}^{\alpha\beta(i)} = \underline{h}^{\beta\alpha(i)} = \frac{\lambda_i\ {}^{i}\Lambda_{11}}{\Lambda_{00}}\ \underline{h} \qquad \text{(A8)}$$

$$\underline{G}^{\alpha\alpha(i)} = \Lambda_{00}^{-1} \Big\{ {}^{i}\Lambda_{01}\ \underline{J}^{\beta\beta(i)} + {}^{i}\Lambda_{11}\ \underline{K}^{\beta\beta(i)}$$

$$+ \sum_{j=1}^{n} \Big[\big(\underline{J}^{\alpha\alpha(j)} + \underline{J}^{\beta\beta(j)} - \underline{K}^{\alpha\alpha(j)} \big)\ {}^{ij}\Lambda_{02} + \big(\underline{J}^{\beta\alpha(j)}$$

$$+ \quad + \underline{J}^{\alpha\beta(j)} - \underline{K}^{\beta\alpha(j)} - \underline{K}^{\alpha\beta(j)} \big)\ \lambda_j\ {}^{ij}\Lambda_{12} + \underline{K}^{\beta\beta(j)}\ {}^{ij}\Lambda_{12} \Big] \Big\}$$

$$\underline{G}^{\beta\beta(i)} = \underline{G}^{\alpha\alpha(i)} \quad (\alpha \longleftrightarrow \beta) \qquad \text{(A9)}$$

$$\underline{G}^{\beta\alpha(i)} = \lambda_i\ \Lambda_{00}^{-1} \sum_{j=1}^{n} \Big[\big(\underline{J}^{\alpha\alpha(j)} + \underline{J}^{\beta\beta(j)} - \underline{K}^{\alpha\alpha(j)} - \underline{K}^{\beta\beta(j)} \big)\ {}^{ij}\Lambda_{12}$$

$$+ \underline{K}^{\alpha\beta(j)}\ \lambda_j\ {}^{ij}\Lambda_{12} + \big(\underline{J}^{\beta\alpha(j)} + \underline{J}^{\alpha\beta(j)} - \underline{K}^{\beta\alpha(j)} \big)\ \lambda_j\ {}^{ij}\Lambda_{22} \Big]$$

$$\underline{G}^{\alpha\beta(i)} = \underline{G}^{\beta\alpha(i)} \quad (\alpha \longleftrightarrow \beta)$$

Note that the $\underline{G}^{\gamma\delta(i)}$ matrices are functions of all the $\underline{P}^{\gamma\delta(j)}$ matrices and that both the $\underline{h}^{\gamma\delta(i)}$ and $\underline{G}^{\gamma\delta(i)}$ matrices have the effects of spin projection included in their definition.

A second expression for the energy is

$$\begin{aligned}\Xi_2 = \Lambda_{00}^{-1} \sum_{i=1}^{n} \Big\{ & {}^{i}\Lambda_{01}\, {}^{i}A_1 + {}^{i}\Lambda_{11}\, {}^{i}A_2 + \lambda_i\, {}^{i}\Lambda_{11}\, {}^{i}A_3 \\ & + \sum_{j=1}^{n} \Big({}^{ij}\Lambda_{02}\, {}^{ij}B_1 + {}^{ij}\Lambda_{12}\, {}^{ij}B_2 + \lambda_i\, {}^{ij}\Lambda_{12}\, {}^{ij}B_3 + \lambda_j\, {}^{ij}\Lambda_{12}\, {}^{ij}B_4 \\ & + \lambda_i \lambda_j\, {}^{ij}\Lambda_{12}\, {}^{ij}B_5 + \lambda_i \lambda_j\, {}^{ij}\Lambda_{22}\, {}^{ij}B_6 \Big) \Big\}\end{aligned} \tag{A10}$$

where

$$\begin{aligned} {}^{i}A_1 &= Tr\, \underline{P}^{\alpha\alpha(i)} \left(\underline{h} + \tfrac{1}{2} \underline{J}^{\beta\beta(i)} \right) + Tr\, \underline{P}^{\beta\beta(i)} \left(\underline{h} + \tfrac{1}{2} \underline{J}^{\alpha\alpha(i)} \right) \\ {}^{i}A_2 &= \tfrac{1}{2} Tr \left(\underline{P}^{\alpha\alpha(i)} \underline{K}^{\beta\beta(i)} + \underline{P}^{\beta\beta(i)} \underline{K}^{\alpha\alpha(i)} \right) \\ {}^{i}A_3 &= Tr \left(\underline{P}^{\alpha\beta(i)} + \underline{P}^{\beta\alpha(i)} \right) \underline{h} \end{aligned} \tag{A11}$$

$$\begin{aligned} {}^{ij}B_1 &= \tfrac{1}{2} Tr\, \underline{P}^{\alpha\alpha(i)} \left(\underline{J}^{\alpha\alpha(j)} + \underline{J}^{\beta\beta(j)} - \underline{K}^{\alpha\alpha(j)} \right) \\ &\quad + \tfrac{1}{2} Tr\, \underline{P}^{\beta\beta(i)} \left(\underline{J}^{\alpha\alpha(j)} + \underline{J}^{\beta\beta(j)} - \underline{K}^{\beta\beta(j)} \right) \\ {}^{ij}B_2 &= \tfrac{1}{2} Tr\, \underline{P}^{\alpha\alpha(i)} \underline{K}^{\beta\beta(j)} + \tfrac{1}{2} Tr\, \underline{P}^{\beta\beta(i)} \underline{K}^{\alpha\alpha(j)} \\ {}^{ij}B_3 &= \tfrac{1}{2} Tr \left(\underline{P}^{\alpha\beta(i)} + \underline{P}^{\beta\alpha(i)} \right) \left(\underline{J}^{\alpha\alpha(j)} + \underline{J}^{\beta\beta(j)} - \underline{K}^{\alpha\alpha(i)} - \underline{K}^{\beta\beta(j)} \right) \\ {}^{ij}B_4 &= \tfrac{1}{2} Tr \left(\underline{P}^{\alpha\alpha(i)} + \underline{P}^{\beta\beta(i)} \right) \left(\underline{J}^{\alpha\beta(j)} + \underline{J}^{\beta\alpha(j)} - \underline{K}^{\alpha\beta(j)} - \underline{K}^{\alpha\beta(j)} \right) \\ {}^{ij}B_5 &= \tfrac{1}{2} Tr \left(\underline{P}^{\alpha\beta(i)} \underline{K}^{\beta\alpha(j)} + \underline{P}^{\beta\alpha(i)} \underline{K}^{\alpha\beta(j)} \right) \end{aligned} \tag{A12}$$

$$
{}^{ij}B_6 = \frac{1}{2}\, Tr\, \underline{\rho}^{\alpha\beta(i)} \left(\underline{J}^{\alpha\beta(j)} + \underline{J}^{\beta\alpha(j)} - \underline{K}^{\alpha\beta(j)} \right)
+ \frac{1}{2}\, Tr\, \underline{F}^{\beta\alpha(i)} \left(\underline{J}^{\alpha\beta(j)} + \underline{J}^{\beta\alpha(i)} - \underline{K}^{\beta\alpha(j)} \right)
$$

This expression emphasizes the dependence of the energy on the pairing parameters λ_i.

Appendix B

We give below a derivation of eq. 28 and eq. 29 . Considering first δE_1 we note that

$$\sum_{i=1}^{n} Tr\left(\underline{\rho}^{\alpha\alpha(i)}\,\delta\underline{G}^{\alpha\alpha(i)} + \underline{\rho}^{\alpha\beta(i)}\,\delta\underline{G}^{\alpha\beta(i)} + \underline{\rho}^{\beta\alpha(i)}\,\delta\underline{G}^{\beta\alpha(i)} + \underline{\rho}^{\beta\beta(i)}\,\delta\underline{G}^{\beta\beta(i)}\right)$$

$$= \sum_{i=1}^{n} Tr\left(\delta\underline{\rho}^{\alpha\alpha(i)}\,\underline{G}^{\alpha\alpha(i)} + \delta\underline{\rho}^{\alpha\beta(i)}\,\underline{G}^{\alpha\beta(i)} + \delta\underline{\rho}^{\beta\alpha(i)}\,\underline{G}^{\beta\alpha(i)} + \delta\underline{\rho}^{\beta\beta(i)}\,\underline{G}^{\beta\beta(i)}\right) \tag{B1}$$

where $\delta\underline{\rho}^{\gamma\delta(i)}$ represents the first order change in $\underline{\rho}^{\gamma\delta(i)}$ due to the variation of the orbitals themselves and $\delta\underline{G}^{\gamma\delta(i)}$ represents the change in the $\underline{G}^{\gamma\delta(i)}$ matrix due to all the $\delta\underline{\rho}^{\gamma\delta(j)}$. This equality makes it possible to write for δE_1 the relatively neat expression

$$\delta E_1 = \sum_{i=1}^{n} Tr\left(\delta\underline{\rho}^{\alpha\alpha(i)}\,\underline{H}^{\alpha\alpha(i)} + \delta\underline{\rho}^{\alpha\beta(i)}\,\underline{H}^{\alpha\beta(i)} + \delta\underline{\rho}^{\beta\alpha(i)}\,\underline{H}^{\beta\alpha(i)} + \delta\underline{\rho}^{\beta\beta(i)}\,\underline{H}^{\beta\beta(i)}\right) \tag{B2}$$

where

$$\underline{H}^{\gamma\delta(i)} = \underline{h}^{\gamma\delta(i)} + \underline{G}^{\gamma\delta(i)} \tag{B3}$$

In δE_2 the $\underline{\rho}^{\gamma\delta(i)}$ matrices (and thus the quantities ${}^{i}A_k$ and ${}^{ij}B_k$) remain constant and we need only consider variations of the quantities defined in eq. A4. Using the facts that

$$\delta\left(\frac{{}^{i\ldots\ell}\Lambda_{rt}}{\Lambda_{00}}\right)=\frac{\delta\,{}^{i\ldots\ell}\Lambda_{rt}}{\Lambda_{00}}-\frac{{}^{i\ldots\ell}\Lambda_{rt}}{\Lambda_{00}}\;\frac{\delta\Lambda_{00}}{\Lambda_{00}}\tag{B4}$$

$$\begin{aligned}\delta\,\Lambda_{rt}&=2\sum_{K=1}^{n}\lambda_K\,\delta\lambda_K\,{}^{K}\Lambda_{r+1,t+1}\\ \delta\,{}^{i}\Lambda_{rt}&=2\sum_{K=1}^{n}\lambda_K\,\delta\lambda_K\,{}^{iK}\Lambda_{r+1,t+1}\\ \delta\,{}^{ij}\Lambda_{rt}&=2\sum_{K=1}^{n}\lambda_K\,\delta\lambda_K\,{}^{ijK}\Lambda_{r+1,t+1}\end{aligned}\tag{B5}$$

it is easily shown that

$$\delta E_2=\sum_{K=1}^{n}\delta\lambda_K\,a_K\tag{B6}$$

where a_K is a number defined as

$$\begin{aligned}a_K=\Lambda_{00}^{-1}\Bigg\{&{}^{K}\Lambda_{11}\left(\tfrac{1}{2}\,{}^{K}A_3-\lambda_K E_{TOTAL}\right)\\ &+\lambda_K\sum_{i=1}^{n}\left({}^{iK}\Lambda_{12}\,{}^{i}A_1+{}^{iK}\Lambda_{22}\left({}^{i}A_2+\lambda_i\,{}^{i}A_3\right)\right)\\ &+\lambda_K\sum_{i=1}^{n}\sum_{j=1}^{n}\Big({}^{ijK}\Lambda_{13}\,{}^{ij}B_1+{}^{ijK}\Lambda_{23}\big({}^{ij}B_2+\lambda_i\,{}^{ij}B_3\\ &\qquad+\lambda_j\,{}^{ij}B_4+\lambda_i\lambda_j\,{}^{ij}B_5\big)+\lambda_i\lambda_j\,{}^{ijK}\Lambda_{33}\,{}^{ij}B_6\Big)\\ &+\frac{1}{2}\sum_{j=1}^{n}\Big({}^{Kj}\Lambda_{12}\left({}^{Kj}B_3+{}^{jK}B_4+\lambda_j\left({}^{jK}B_5+{}^{Kj}B_5\right)\right)\\ &+\lambda_j\,{}^{Kj}\Lambda_{22}\left({}^{jK}B_6+{}^{Kj}B_6\right)\Big)\Bigg\}\end{aligned}\tag{B7}$$