# Towards Complete Solutions to Systems of Nonlinear Equations of Many-Electron Theories

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Employing the homotopy method we have obtained the complete set of real solutions to the equations of the restricted Hartree-Fock method as well as the full set of solutions to the equations of the coupled-cluster-with-doubles method for the H4 and P4 models broadly applied in various many-electron studies. These are the first global results obtained so far for any formulations of the Hartree-Fock and coupled-cluster methods when applied to realistic models. [S0031-9007(98)06772-6]

A characteristic feature of most of the methods of contemporary theory of electronic structure of atomic and molecular systems is that they are based on nonlinear equations. For many methods the nonlinearity is a direct consequence of the fact that the Schrödinger equation is equivalent to the nonlinear generalized Bloch equation [1]. To enable the applications of the individual approaches, finite numbers of basis functions are used to transform them into systems of nonlinear equations for the expansion coefficients. Unfortunately, there are no general mathematical results concerning sets of nonlinear equations which would help in the understanding of either the structure of their solutions or even the conditions for their existence. Only for the solutions to the equations of the Hartree-Fock (HF) method can some information be obtained when using the stability conditions formulated by several authors [2–4]. One should also mention the pioneering work of Živković and Monkhorst [5] on the existence and reality of solutions of the equations of the coupled-cluster (CC) method [6].

Although numerical methods have been invented for attaining certain solutions to the equations of individual many-electron theories, there are situations when one faces serious identification problems for the solutions obtained (see, e.g., the difficulties encountered in multiconfigurational self-consistent field, MC-SCF [7] and CC [8] methods). We believe that access to information about various details of the global structure of solutions to the relevant sets of equations would be very useful for developing methods of attaining one or several desired solutions in the presence of many undesired ones of similar structure.

So far, in the absence of general mathematical theorems, the only way to obtain at least some insight into the structure and attainability of solutions of sets of nonlinear equations are fragmentary numerical studies of some simple model systems. Let us just mention the work on various formulations of the HF methods [9–12], on Frost's local-energy method [12], and on several formulations of the CC method [8,13–15]. It seems to us that recently we have obtained access to computational tools which can be used to verify and supplement the results of such studies

by making possible the finding of complete solutions to a set of polynomial equations. This situation is caused by the recent progress in both theoretical and computational algebraic geometry [16] and differential topology (for details and references, see, e.g., [17]) which has resulted in the development of the effective homotopy methods. The basic idea of homotopy methods, when applied to the set of nonlinear equations $\mathbf{F}(\mathbf{x}) = \mathbf{0}$, consists of replacing these equations by the family of equations

$$\mathbf{H}(\mathbf{x}, \lambda) = (1 - \lambda)\mathbf{G}(\mathbf{x}) + \lambda\mathbf{F}(\mathbf{x}) = \mathbf{0}, \qquad (1)$$

where the homotopy parameter $\lambda$ belongs in most formulations to the whole complex plane. The set of functions $\mathbf{G}(\mathbf{x})$ is chosen such that the solutions of the equations $\mathbf{G}(\mathbf{x}) = \mathbf{0}$ can be easily found. The main task of the method consists of continuing the solution of $\mathbf{H}(\mathbf{x}, 0) = \mathbf{0}$ into those of $\mathbf{H}(\mathbf{x}, 1) = \mathbf{0}$. We have used the $\mathbf{G}(\mathbf{x})$ functions in the form $G_i(\mathbf{x}) = x_i^{d_i} - b_i$, and $d_i = \deg G_i \geq \deg F_i$, where deg denotes the total degree of the polynomial. The numbers $b_i$ are chosen at random. As a consequence of the transversality theorem [17], such a choice of the $\mathbf{G}(\mathbf{x})$ functions leads to well-defined continuation paths [18]. For path tracking, the normal flow algorithm (see, e.g., Ref. [18]) has been employed. The solutions of the sets of equations considered in this Letter have been obtained when using the power of the system HOMPACK [18].

We have studied the equations obtained for the minimum basis P4 (also known as HRS [19]) and H4 models [20]. The geometry of both models is determined by single parameter $\alpha$ which allows one to change the degree of quasidegeneracy. The spacial symmetry groups are $D_{2h}$ and $C_{2v}$ for P4 and H4, respectively. The full configuration interaction (FCI) wave functions for $A_g$ states of P4 have the simplest structure among four electron models and we have studied CC equations for this model. High symmetry of P4 causes some problems when solving HF equations in density matrix formalism. Therefore, HF equations have been studied for the H4 model which is free of these problems.

The HF equations in their most commonly used canonical representation take the form of nonlinear eigenvalue

equations. For our purposes, however, it is advantageous to employ the fact that the HF theory is essentially a density matrix theory (see, e.g., [3,10]), i.e., that the HF equations are equivalent to the condition [3,10]

$$[F(Q), Q] = 0, \qquad (2)$$

where $Q$ is the one particle density operator for a Slater determinant. If a finite basis $\{\chi_s\}_{s=1}^n$ is used for the algebraization, the matrix elements of the Fock operator $F(Q)$ take the form

$$F(Q)_{\zeta\eta} = h_{\zeta\eta} + \sum_{\kappa\iota} v_{\eta\kappa}^{\zeta\iota} Q_{\kappa\iota}, \qquad (3)$$

where $h_{\zeta\eta}$ is the matrix element of the one-electron part of the full electronic Hamiltonian and $v_{\eta\kappa}^{\zeta\iota}$ stands for the antisymmetrized two-electron integral. Fukutome [10] has shown that Eq. (2) can be rewritten as (for details see [10]) a set of quadratic equations. These equations include the unknowns and their complex conjugates, i.e., they are polynomial sets only for the real solutions.

In this Letter we present the real solutions obtained for the restricted HF (RHF) method (see, e.g., [4]). There are no spatial-symmetry restrictions imposed on the form of the orbitals. The number of unknowns amounts to 10 in

the present calculation. The basis set $\{\chi_s\}_{s=1}^n$ is chosen to consist of the occupied and virtual spin orbitals obtained within the framework of the RHF approach for the ground state of $^1A_1$ symmetry with spatial-symmetry restriction imposed on the orbitals.

Having obtained the $Q$ operators corresponding to the individual solutions one can generate the HF wave functions. Because of the spin-symmetry constraints, we can concentrate on the orbital parts of the solutions:

$$\psi_k(i) = \sum_{l=1}^4 c_{lk}(i)\tilde{\chi}_l, \qquad k = 1, 2, \qquad (4)$$

where $\{\tilde{\chi}_s\}_{s=1}^4$ represents the orbital parts of the spin orbitals mentioned above which are ordered (according to increasing orbital energy) as follows: $1a_1$, $1b_2$, $2a_1$, and $2b_2$. The index $i$ is used to label the individual solutions.

In Table I we present the 12 solutions obtained for $\alpha = 0.005$ of H4. The second column includes the HF energies $E_{\text{HF},i}$ corresponding to the individual solutions. To get some information about the significance of the HF functions $\Phi(i)$ constructed for the individual solutions to the HF equations, we have calculated for each solution the overlap integrals $S_{ij} = |\langle\tilde{\Phi}(i) \mid \Psi_j\rangle|$, where $\tilde{\Phi}(i)$ stands

TABLE I. Energies of real solutions of RHF equations (in hartrees), the largest overlap integrals between HF determinant and FCI states of $^1A_1$ symmetry, and expansion coefficients of HF orbitals (in the orbital basis spanned by orbitals of the HF solution for the $^1A_1$ ground state) of the H4 model for $\alpha = 0.005$.

| Solution No. | $E_{\text{HF},i}$ | Two largest overlap integrals [a] $j$ | $S_{ij}$ | $c_{11}(i)$ $c_{12}(i)$ | $c_{21}(i)$ $c_{22}(i)$ | $c_{31}(i)$ $c_{32}(i)$ | $c_{41}(i)$ $c_{42}(i)$ |
|---|---|---|---|---|---|---|---|
| 1 | −1.871397 | 1 | 0.74 | 1.00000 | 0.00000 | 0.00000 | 0.00000 |
|   |           |   |      | 0.00000 | 1.00000 | 0.00000 | 0.00000 |
| 2 | −1.851306 | 2 | 0.73 | 1.00000 [b] | 0.00000 | −0.00043 | 0.00000 |
|   |           |   |      | −0.00043 | 0.00000 | −1.00000 [b] | 0.00000 |
| 3 | −1.815135 | 2 | 0.96 | 0.99992 | 0.00621 | 0.00004 | 0.01116 |
|   |           |   |      | 0.00414 | −0.66714 | 0.74491 | 0.00291 |
| 4 | −1.032896 | 6 | 0.66 | 0.00813 | 0.00000 | 0.99997 | 0.00000 |
|   |           | 5 | 0.63 | 0.00000 | −0.99996 | 0.00000 | 0.00888 |
| 5 | −0.820886 | 6 | 0.68 | 0.99991 | 0.00000 | 0.01344 | 0.00000 |
|   |           |   |      | 0.00000 | −0.00660 | 0.00000 | 0.99998 |
| 6 | −0.148480 | 11 | 0.69 | 0.00000 | 0.99999 | 0.00000 | 0.00131 |
|   |           | 12 | 0.62 | 0.00000 | 0.00131 | 0.00000 | 0.99999 |
| 7 | −0.133029 | 11 | 0.70 | −0.27687 | −0.93787 | 0.19884 | −0.06479 |
|   |           | 12 | 0.68 | −0.00837 | −0.01481 | 0.23516 | 0.97181 |
| 8 | −0.132914 | 12 | 0.72 | 0.02292 | 0.00000 | 0.99974 | 0.00000 |
|   |           | 11 | 0.60 | 0.00000 | 0.01867 | 0.00000 | 0.99983 |
| 9 | −0.123536 | 12 | 0.67 | 0.28321 | 0.08725 | 0.95456 | −0.03140 |
|   |           | 11 | 0.52 | 0.00314 | 0.24103 | 0.00897 | 0.97047 |
| 10 | −0.117115 | 12 | 0.69 | −0.26997 | 0.19499 | 0.94103 | 0.05957 |
|    |           | 11 | 0.52 | 0.00542 | −0.22644 | −0.01318 | 0.97392 |
| 11 | −0.116207 | 12 | 0.64 | −0.31737 | 0.00000 | 0.94830 | 0.00000 |
|    |           | 11 | 0.54 | 0.00000 | −0.26029 | 0.00000 | 0.96553 |
| 12 | −0.093966 | 12 | 0.95 | −0.00497 | −0.67696 | −0.73595 | 0.00916 |
|    |           |    |      | 0.01407 | −0.00160 | 0.01382 | 0.99980 |

[a] The subscript $i$ denotes No. of solution.
[b] The value is 0.9999998.

for the normalized component of $A_1$ symmetry of $\Phi(i)$, and $\Psi_l$ denotes the $l$th exact (FCI) wave function of the H4 model (ordered according to increasing energy). Table I lists for each solution the two largest $S_{ij}$ values together with the indices $j$ of the relevant FCI wave functions. The structure of HF orbitals can be deduced from the expansion coefficients $c_{lk}(i)$ of Eq. (4) also included in Table I. Notice that, according to our definition of the basis set, solution No. 1 consists of the $1a_1$ and $1b_2$ orbitals. For seven of the solutions obtained, i.e., for solution Nos. 1, 2, 4, 5, 6, 8, and 11, the HF orbitals are of $C_{2v}$ symmetry. Let us mention that we have previously attained [21] solution Nos. 1, 2, 4, and 6. For five solutions of the complete set, the orbitals are of the broken spatial-symmetry-type, i.e., they are linear combinations of orbitals of $a_1$ and $b_2$ symmetry species. Perusing all overlaps given in Table I, one can see that the 12 HF wave functions can be related to only 6 from among the 12 exact wave functions.

As a second application of the homotopy methods, we present the results for the CC method [20–22] based on the cluster operator $T_2$ defined in terms of two-electron excitation operators, known as the coupled-cluster-with-doubles (CCD) method (for details and references, see [23]). In this method the approximate wave function $|\Psi_{\mathrm{CCD}}\rangle$ is obtained from the independent-particle reference wave function $|\Phi\rangle$ by means of an exponential wave operator,

$$|\Psi_{\mathrm{CCD}}\rangle = e^{T_2}|\Phi\rangle. \tag{5}$$

The equations for the cluster amplitudes $T_{A_1,A_2}^{A^1 A^2}$, defining $T_2$, and the energy $E_{\mathrm{CCD}}$ can be written as [22]

$$\langle\Phi|H - E_{\mathrm{CCD}}|e^{T_2}\Phi\rangle = 0, \tag{6}$$

$$\langle{}_{A_1 A_2}^{A^1 A^2}|H - E_{\mathrm{CCD}}|e^{T_2}\Phi\rangle = 0, \tag{7}$$

where the determinant $|{}_{A_1 A_2}^{A^1 A^2}\rangle$ is obtained by a double replacement of the $A_1$ and $A_2$ spin orbitals in $|\Phi\rangle$ by the $A^1$ and $A^2$ ones. Arranging in Eq. (7) the unknown cluster amplitudes $T_{A^1 A^2}^{A_1 A_2}$ in some arbitrary but fixed order, one can cast the CCD equations into the form of a set of quadratic polynomial equations. When deriving the CCD equations for P4, the reference wave function $|\Phi\rangle$ is taken to be the RHF function of the ground state of $^1 A_g$ symmetry. The number of unknown cluster amplitudes amounts to 10.

We have obtained the full solution of the CCD equations which consists of 20 solutions. Table II includes the essential information about our set of solutions. We present for each of them $E_{\mathrm{CCD}}$, four of the ten cluster amplitudes, and the values of the maximum overlap integrals $Z_{ij} = |\langle\tilde{\Psi}_{\mathrm{CCD},i}\,|\,\Psi_{\mathrm{FCI},j}\rangle|$, where $|\Psi_{\mathrm{FCI},j}\rangle$ are the FCI functions of $^1 A_g$ symmetry ordered according to increasing energy and $|\tilde{\Psi}_{\mathrm{CCD},i}\rangle$ stands for the CCD function normalized to unity.

TABLE II. Energies corresponding to the complete sets of solutions of the CCD equations [relative to the RHF energy (RHF energy for the reference-state configuration amounts to $-1.859099$ hartrees) for the reference-state configuration, in mhartrees], maximum overlap integrals between CCD and FCI wave functions, $Z_{ij}$, and a subset of cluster amplitudes for the P4 model with $\alpha = 2.002$.

| | Solution | | | Overlap integral[a] | | Examples of cluster amplitudes | | | |
|---|---|---|---|---|---|---|---|---|---|
| No. | Symmetry | $E_{\mathrm{CCD}}$ | $j$ | $Z_{ij}$ | $T_{33}^{1\bar{1}}$ | $T_{44}^{1\bar{1}}$ | $T_{33}^{2\bar{2}}$ | $T_{44}^{2\bar{2}}$ |
| 1 | $^1 A_g$ | $-119.82$ | 1 | 0.999 | $-0.0075$ | $-0.0663$ | $-0.9918$ | $-0.0060$ |
| 2 | $^1 A_g$ | $-8.688$ | 2 | 0.646 | $-2.7280$ | 0.0680 | 9.3318 | $-2.1827$ |
| 3 | $^1 A_g$ | $-6.820$ | 2 | 0.996 | $-0.3402$ | 0.0036 | 1.1322 | $-0.2792$ |
| (4,5) | Mixed | 483.61[b] | 8 | 0.621 | 1.7931 | $-0.0320$ | 0.0400 | 1.0714 |
| | | | 3 | 0.518 | | | | |
| (6,7) | $^1 A_g$ | 729.44 | 8 | 0.689 | 1.8212 | 0.2679 | 0.0421 | 1.3009 |
| | | $\pm i\,126.73$ | 3 | 0.330 | $\mp i\,2.685$ | $\pm i\,1.039$ | $\mp i\,1.500$ | $\mp i\,0.730$ |
| (8,9) | Mixed | 825.76[c] | 5 | 0.540 | $-5.9510$ | 3.8185 | $-4.2928$ | $-0.4997$ |
| (10,11) | Mixed | 832.63[c] | 5 | 0.548 | $-5.1244$ | 3.4592 | $-3.8293$ | $-0.2902$ |
| (12,13) | Mixed | 940.35[c] | 5 | 0.655 | $-2.0398$ | 1.7563 | $-1.5113$ | 1.6729 |
| 14 | $^1 A_g$ | 943.85 | 5 | 0.678 | $-4.3905$ | 1.6829 | $-1.4138$ | 4.0993 |
| 15 | $^1 A_g$ | 946.11 | 4 | 0.729 | 6.5286 | 1.9298 | $-1.7209$ | $-6.8776$ |
| (16,17) | $^1 A_g$ | 1208.46 | 8 | 0.713 | 0.8427 | 1.0557 | $-0.5550$ | 1.3598 |
| | | $\pm i\,50.03$ | 7 | 0.688 | $\pm i\,1.209$ | $\mp i\,1.521$ | $\pm i\,0.603$ | $\pm i\,3.213$ |
| (18,19) | $^1 A_g$ | 1838.08 | 8 | 0.804 | 2.9517 | 3.7169 | 0.5648 | 3.6299 |
| | | $\pm i\,99.51$ | 7 | 0.590 | $\pm i\,0.280$ | $\pm i\,6.290$ | $\pm i\,0.148$ | $\pm i\,0.449$ |
| 20 | $^1 A_g$ | 2188.05 | 8 | 0.784 | 3.6097 | 4.1860 | 0.9119 | 4.1554 |

[a]Index $j$ denotes the label of the FCI wave function for $^1 A_g$ states (ordered with respect to increasing $E_{\mathrm{FCI},j}$ energies) which disclose maximum overlap with the renormalized CCD wave function considered (see text).
[b]The energy corresponds to pairs of complex conjugate amplitudes (for the amplitudes not displayed).
[c]The energy corresponds to two real solutions.

One can see from the second column of Table II that 12 solutions define $|\Psi_{CCD}\rangle$ of $^1A_g$ symmetry, whereas the 8 remaining ones are not related to pure spin-symmetry states. Among the former group of solutions several are physically meaningful. For example, solution Nos. 1 and 3 show very large overlaps with the FCI wave functions for $1^1A_g$ and $2^1A_g$ states. For these solutions the $E_{CCD}$ values are close to the FCI energies for the $1^1A_g$ and $2^1A_g$ states amounting to $-117.03$ and $-6.666$ mhartrees, respectively. Similarly, solution No. 15 provides a fairly good description of the $4^1A_g$ FCI state corresponding to the energy of 945.33 mhartrees. A more complete characterization of the solutions obtained requires a special approach which is beyond the scope of this Letter and will be given elsewhere [24]. Let us just mention that the spin-symmetry-broken solution Nos. (4 and 5) and (8, 9, 10, 11, 12, 13) are related to the quintet and triplet states of P4, respectively. The present results provide the first numerical illustration of the effects of using mixed-symmetry cluster operators on the structure of solutions of CC equations which were preliminary discussed by Nakatsuji and Hirao [25] two decades ago.

In summary, when applying the homotopy method, we have obtained for the first time the complete set of real solutions to any HF-type equations as well as the full solution (including complex ones) to any CC-type equations. Our results demonstrate that, when using homotopy methods, it is possible to verify and supplement the information concerning the global structure of solutions to equations of many-electron theory obtained so far only from studies of oversimplified simulations of these equations. We believe that access to such information will contribute to the further development of these theories. The understanding of the global structure of the solutions for a number of nontrivial model systems should also be helpful in developing reliable numerical methods for attaining the desired solutions for realistic systems.

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