

Quantum-Mechanical Information Content of Multiples Hartree-Fock Solutions. The Multi-Reference Hartree-Fock Configuration Interaction Method

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Abstract

The Hartree-Fock equation is non-linear and has, in principle, multiple solutions. The ω^{th} HF extreme and its associated virtual spin-orbitals furnish an orthogonal base B^{ω} of the full configuration interaction space. Although all B^{ω} bases generate the same CI space, the corresponding configurations of each B^{ω} base have distinct quantum-mechanical information contents. In previous works, we have introduced a multi-reference configuration interaction method, based on the multiple extremes of the Hartree-Fock problem. This method was applied to calculate the permanent electrical dipole and quadrupole moments of some small molecules using minimal and double, triple and polarized double-zeta bases. In all cases were possible, using a reduced number of configurations, to obtain dipole and quadrupole moments in close agreement with the experimental values and energies without compromising the energy of the state function. These results show the positive effect of the use of the multi-reference Hartree-Fock bases that allowed a better extraction of quantum mechanical information from the several B^{ω} bases. But to extend these ideas for larger systems and atomic bases, it is necessary to develop criteria to build the multi-reference Hartree-Fock bases. In this project, we are beginning a study of the non-uniform distribution of quantum-mechanical information content of the B^{ω} bases, searching identify the factors that allowed obtain the good results cited above.

Keywords

Multiple Hartree-Fock Solutions, Quantum Mechanical Information Content, Multi-Reference

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Hartre-Fock Configuration Interaction Method

1. Introduction

The repulsive coulomb term in the electronic Hamiltonian of atoms, molecules and solids introduces a hard difficult to determine stationary electronic states. It is possible only to obtain approximate solutions of the Schrödinger's equation and there are several procedures for this goal. Two important and general approaches to achieve this purpose are the variational and perturbative methods. In this essay, we are primarily concerned with the approximate variational methods, in particular, with the configuration interaction (*CI*) methods.

An initial variational approach to study electronic structure of atoms and molecules is the Hartree-Fock (*HF*) approximation. This approximation can be used as starting-point for other variational and perturbative methods. Although the *HF* approximation provides the most part of the electronic ground state energy of the system, the rest of this energy is very important to understand several phenomena involving these systems. Rigorously, in practice it is impossible to determine the *HF* limit as well the exact electronic ground state energy because the atomic bases are finite. Thus, the quantity of correlation energy that is possible to rescue is limited by the atomic base and other truncations or approximations employed. But it is possible for some systems to obtain very accurate values. Beside this, an error in the electronic energy means an error in the correspondent state vector with consequences on the calculated values of other dynamical variables, in particular on the non-variational dynamical variables.

In molecular electronic problems, there is a variety of observables that depend of the charge distribution and that are not variational dynamical variables as, for instance, the electrical multipolar moments. Non-variational dynamical variables do not exhibit the decrescent monotonical behavior of the energy with the augmentation of the variational class of functions. In contrast, they display an irregular behavior. This means that in the scope of the approximate variational methods better values for electronic energy do not implicate in better values of non-variational observables. This introduces difficulties in the determination of non-variational properties in the ambit of these approximate methods. Over the last twenty years, multi-reference configuration interaction (*MRCI*) methods have been developed and used in molecular quantum mechanics to study this question [1]. In this communication we present some aspects of the content of quantum information of multiples *HF* solutions related with this problem using a *MRCI* method based on multiple *HF* solutions.

2. Theory

The traditional *CI* method uses a single reference, the *HF* ground state, and your excited configurations to expand the state function. However, the *HF* equation is non-linear and has, in principle, multiple solutions [2] and each *HF* extremum and its associated virtual spin-orbitals, generate the same full Configuration Interaction (full *CI*) space. Thus with each *HF* extremum we can formulate an orthogonal *CI* problem. It is possible also to formulate a non-orthogonal multi-reference *CI* using these multiple *HF* references. In the *CI* problem the variational class of functions to search the extrema is a vector space. So the equation of necessary condition to obtain the extrema is linear. It is a usual eigenvalue problem or a generalized eigenvalue problem if the base employed of the vector space is orthogonal or not, respectively. This equation is the matrix representation of the Schrödinger's stationary equation in this base.

In previous works [3]-[5] we have introduced a new multi-reference configuration interaction method, based on the multiple solutions of the *HF* problem, called the multi-reference Hartree-Fock configuration interaction (*MRHFCI*) method. In the *MRHFCI* method, instead of a single reference one uses several *HF* extremes as references in order to expand the state function. The detailed formulation of the *MRHFCI* method to study a singlet ground state is presented in the references above. The basic aspects of the method can be summarized as follow.

For the restricted *HF* (*RHF*) problem of a molecule with $2n$ electrons, represented in the atomic base $\xi = [\xi_1, \xi_2, \dots, \xi_m]$, the ω^{th} *HF* solution is a set of functions $\varphi_i^{\omega} = \xi \mathbf{c}_i^{\omega}$; $i = 1, \dots, n$ where $\mathbf{c}_i^{\omega}$ is a column vector with components $c_{1i}^{\omega}, \dots, c_{mi}^{\omega}$. These functions, φ_i^{ω} , are the occupied molecular orbitals (*MOs*). It is possible to generate an additional set of functions $\varphi_a^{\omega} = \xi \mathbf{c}_a^{\omega}$; $a = n+1, \dots, m$ called virtual *MOs* of the ω^{th} solution. Associated with the *MOs* of the ω^{th} solution, there is the set of m orbital energies, $\mathcal{E}_i^{\omega}$, $i = 1, \dots, n, n+1, \dots, m$.

In a molecular *HF* problem, formulated in any class of symmetry of point and spin, it is possible, in principle, to obtain several *HF* solutions. And from these solutions to construct several *HF* references and your correspondent excited configuration state functions (*CSFs*) S^ω , D^ω , T^ω , ... (single, double, triple excited, ...) which belong to the irreducible representation of point and spin of interest. The sets of these *CSFs* define the sub-bases $\mathbf{0}^\omega = \{0^\omega\}$, $\mathbf{S}^\omega = \{S^\omega\}$, $\mathbf{D}^\omega = \{D^\omega\}$, $\mathbf{T}^\omega = \{T^\omega\}$, ... and the corresponding subspaces $\mathbf{E}^{0,\omega}$, $\mathbf{E}^{S,\omega}$, $\mathbf{E}^{D,\omega}$, $\mathbf{E}^{T,\omega}$, ... The bases $\mathbf{B}^\omega$ of the full *CI* space $\mathbf{E}$, associated with the ω^{th} *HF* solution, is defined as $\mathbf{B}^\omega = \{0^\omega \cup S^\omega \cup D^\omega \cup T^\omega \cup \dots\}$, and $\mathbf{E}$ can be written as the direct sum $\mathbf{E} = \mathbf{E}^{0,\omega} \oplus \mathbf{E}^{S,\omega} \oplus \mathbf{E}^{D,\omega} \oplus \mathbf{E}^{T,\omega} \oplus \dots$ of the subspaces $\mathbf{E}^{0,\omega}$, $\mathbf{E}^{S,\omega}$, $\mathbf{E}^{D,\omega}$, $\mathbf{E}^{T,\omega}$, The set of the bases $\mathbf{B}^\omega$, $\mathbf{G} = \{\mathbf{B}^1 \cup \mathbf{B}^2 \cup \dots \cup \mathbf{B}^\omega \cup \dots\}$, form a system of generators of the full *CI* space. From the set $\mathbf{G}$ one can form the multi-reference *HF* (*MRHF*) bases for *MRHF**CI* calculations. These bases contain *CSFs* originated from different *HF* references, which, in general, are not orthogonal.

The motivation for using the *MRHF* bases lies on the following consideration. Let $\mathbf{B}^{\omega'}$ and $\mathbf{B}^{\omega''}$ be two bases of the full *CI* space. The state function Ψ_{MRHF} can be written as,

$$\Psi_{MRHF} = 0^{\omega'} + \Psi^{S,\omega'} + \Psi^{D,\omega'} + \dots$$

or as,

$$\Psi_{MRHF} = 0^{\omega''} + \Psi^{S,\omega''} + \Psi^{D,\omega''} + \dots$$

where,

$$\Psi^{X,\omega'} \in \mathbf{E}^{X,\omega'}, \quad \Psi^{X,\omega''} \in \mathbf{E}^{X,\omega''}$$

However,

$$0^{\omega'} \neq 0^{\omega''}, \quad \Psi^{X,\omega'} \neq \Psi^{X,\omega''} \quad \text{and} \quad \mathbf{E}^{X,\omega'} \neq \mathbf{E}^{X,\omega''}$$

Thus, in spite of the fact that the bases $\mathbf{B}^{\omega'}$ and $\mathbf{B}^{\omega''}$ generate the same *CI* space, the corresponding *CSFs* of each $\mathbf{B}^\omega$ base have distinct quantum-mechanical information contents (*QMIC*). This implies a lack of uniformity of *QMIC* distribution in the vectors of the several bases. This fact suggests the use of *MRHF* bases for the generation of sub-domains in the formulation of the *CI* problem, i.e. basis formed with configurations originated from distinct *HF* references. The use of these “mixed basis” may allow a better extraction of quantum mechanical information from the several $\mathbf{B}^\omega$ bases for the calculation of molecular properties while simultaneously producing energy values comparable to the ones of full *CI* calculations.

3. Results

3.1. Previous Results

The *MRHF**CI* method was applied to calculate the permanent electrical dipole moment of some small molecules, *LiH*, *BH*, *FH*, *CO* and *H₂O* and the quadrupole moment of the *FH* [3]-[5], using the standard *STO-6G* and a new minimal-6G bases [6]. For *LiH* molecule were performed *MRHF**CI* calculations with the double-zeta (*dz*), triple-zeta (*tz*) and polarized *dz* (*dzp*) bases. In all cases was possible, using a reduced number of *CSFs*, to obtain dipole and quadrupole moments in close agreement with the experimental values and energies without compromising the energy of the state function. The corresponding full *CI* calculations do not provide good results for the dipole and quadrupole moments. Two other interesting aspects were observed. It was possible to obtain good dipole and quadrupole values using minimal bases considered as “poor” bases in the literature. These bases are much smaller than the vast majority of the atomic bases used in the calculations of the dipole and quadrupole moments. In the *LiH* calculations was verified a significant relative reduction of the size of the *MRHF* base as the dimension of the full *CI* base increases.

3.2. New Results

In the current stage of development of the *MRHF**CI* method, the results are still obtained through trials but this requires too much computational effort. To extend these calculations for larger systems and atomic bases it is necessary to develop criteria to build the *MRHF* bases. With this purpose, we begin this project with a systemat-

ic study of the non-uniform distribution of $QMIC$ of the $\mathbf{B}^{\omega}$ bases with regard to energy and permanent electrical dipole moment. We will use as initial tests the LiH molecule and Be atom using a new dz base [7] and the traditional bases dz , tz and dzp . We start this analysis determining a set of three HF solutions of the Be atom and twelve HF solutions of the LiH molecule using the new dz basis [8]. The **Table 1(a)** and **Table 1(b)** show orthogonal CI calculations of the energy with several combinations of excited $CSFs$, for each these twelve LiH HF solutions. The headers of these tables indicate which and how many $CSFs$ were employed in each of the orthogonal CI calculations. The **Table 2** presents $MRHFCI$ calculations of the dipole moment for the LiH . All the indicated energies in the **Table 1(a)** and **Table 1(b)** and **Table 2** are electronic energy plus nuclear repulsion energy. The **Table 3** shows an energy obtained with the $MRHFCI$ method for the Be atom. In the **Table 2** and

Table 1. (a) Non-uniform distribution of $QMIC$ of the HF solutions of the LiH molecule; (b) Non-uniform distribution of $QMIC$ of the HF solutions of the LiH molecule.

(a)

HF Solution (energy)	S (10 $CSFs$)	D (75 $CSFs$)	T (160 $CSFs$)	Q (172 $CSFs$)	SD (85 $CSFs$)	ST (170 $CSFs$)	SQ (182 $CSFs$)	DT (235 $CSFs$)
-7.98066895	-7.83037244	-7.49762404	-5.17255295	-1.82147305	-7.88150734	-7.84252804	-7.83037244	-7.49927038
-7.42164900	-7.83621873	-7.97148207	-5.61879432	-2.32622279	-7.99818789	-7.84838259	-7.83621873	-7.97322343
-7.24880471	-7.76737105	-7.99349350	-5.79862878	-2.44994704	-7.99815341	-7.78005950	-7.76737105	-7.99464208
-5.46835770	-6.80462160	-7.96556261	-5.80028937	-2.47022170	-7.99625134	-6.81681649	-6.80462160	-7.96619330
-2.45215236	-5.82542732	-7.93265323	-7.72473656	-7.38442761	-7.94549594	-7.72480279	-7.38442761	-7.98869674
-1.98791705	-5.43622153	-7.99049201	-5.85354486	-2.52779005	-7.99916590	-5.85451692	-5.43622153	-8.00352210
-1.87200145	-5.57392280	-7.87428572	-7.71559905	-7.43121356	-7.87586037	-7.71566426	-7.43121356	-7.99702073
-1.76533380	-5.60479281	-7.86014360	-7.72955310	-7.52152511	-7.86014989	-7.72955381	-7.52152511	-7.99444827
-1.50719389	-5.06697657	-7.33252181	-7.81031691	-7.97125621	-7.33323310	-7.81032990	-7.97125621	-7.82949725
0.14654857	-4.21817022	-7.44762052	-7.58965583	-7.82509874	-7.46468615	-7.59009739	-7.82509874	-7.89838385
1.01516265	-3.03166839	-7.40509900	-7.80968434	-7.95495322	-7.42436175	-7.82024827	-7.95495322	-7.83341686
3.02497886	-1.06524777	-5.45191381	-6.77217340	-7.91630275	-5.47245848	-6.78218398	-7.91630275	-6.81208380

S, D, T and Q indicate single, double, triple and quadruple excited $CSFs$; $Li-H$ distance: 3.015 bohr; All the HF solutions are $^1\Sigma^+$ and were obtained using the new double-zeta base [7]; The total energies (electronic + nuclear repulsion) of the HF solutions are indicated in the first column; The full CI energy is -8.01152345 hartree.

(b)

HF Solution (energy)	DQ (247 $CSFs$)	TQ (332 $CSFs$)	SDT (245 $CSFs$)	SDQ (257 $CSFs$)	STQ (324 $CSFs$)	DTQ (407 $CSFs$)	SDTQ (417 $CSFs$)	RSD (86 $CSFs$)
-7.98066895	-7.50928409	-5.22494445	-7.89236475	-7.88264649	-7.84253319	-7.51097979	-7.89383230	-8.01118619
-7.42164900	-7.98305150	-5.66779072	-8.00177967	-8.00770978	-7.84839100	-7.98494183	-8.01134553	-7.99836892
-7.24880471	-8.00554923	-5.84673237	-7.99950569	-8.00998434	-7.78006604	-8.00675978	-8.01146841	-7.99820923
-5.46835770	-7.97765753	-5.85180026	-7.99711653	-8.00797184	-6.81682961	-7.97834516	-8.00901909	-7.99876440
-2.45215236	-7.94852317	-7.77781031	-7.99632568	-7.96121127	-7.77787028	-8.00266082	-8.01149075	-7.94555256
-1.98791705	-7.99057847	-5.89398336	-8.01046633	-7.99924953	-5.89445971	-8.00363343	-8.01148020	-7.99921562
-1.87200145	-7.88873729	-7.86933202	-7.99641018	-7.89038297	-7.86940091	-8.01045762	-8.01151985	-7.87586551
-1.76533380	-7.88175170	-7.87746356	-7.99261056	-7.88177053	-7.87746391	-8.01151946	-8.01152345	-7.86014990
-1.50719389	-7.97618917	-8.00441920	-7.78433573	-7.97623200	-8.00442742	-8.01143131	-8.01152315	-7.33323630
0.14654857	-7.84312057	-7.99683460	-7.87996262	-7.84380941	-7.99691683	-8.01082896	-8.01151115	-7.46509924
1.01516265	-7.96633604	-7.99708811	-7.83450283	-7.96634454	-7.99824163	-8.01006372	-8.01151141	-7.43427613
3.02497886	-7.92949605	-7.99792563	-6.81057946	-7.92951727	-7.99814687	-8.01119614	-8.01151208	-5.48162012

In the last column R indicates HF reference; S, D, T and Q indicate single, double, triple and quadruple excited $CSFs$; $Li-H$ distance: 3.015 bohr; All the HF solutions are $^1\Sigma^+$ and were obtained using the new double-zeta base [7]; The total energies (electronic + nuclear repulsion) of the HF solutions are indicated in the first column; The full CI energy is -8.01152345 hartree.

Table 2. *MRHF*CI calculations of the dipole moment for the *LiH* molecule.

CSFs	HF Solutions	MRHF _{CI} Energy	Dipole Moment
52	A, B	−8.01014966	5.8321
37	A, D	−8.00889691	5.8259
71	A, L	−8.01016736	5.8199
418	Full <i>CI</i>	−8.01152345	5.7503

Total energies (electronic + nuclear repulsion) of the *HF* solutions: A = −7.98066895 hartree; B = −7.42164900 hartree; D = −5.46835770 hartree; L = 3.09788624 hartree; All the *HF* solutions are $^1\Sigma^+$ and were obtained using the new double-zeta base [7]; Experimental Dipole Moment value: 5.8280 debye.

Table 3. *MRHF*CI calculation of the energy of the *Be* atom.

CSFs	HF Solutions	MRHF _{CI} Energy
25	A, B, C	−14.61597562
102	Full <i>CI</i>	−14.61597567

Energies of the *HF* solutions: A = −14.57125146 hartree; B = −13.78788831 hartree; C = −3.47143646 hartree; All the *HF* solutions are 1S and were obtained using the new double-zeta base [7].

Table 3 the first column indicates the number of *CSFs* employed in the *MRHF*CI calculation. The second and third columns indicate the *HF* solutions used and the *MRHF*CI energy obtained, respectively. The fourth column in the **Table 2** presents dipole moment value obtained by the *MRHF*CI method. The last row in the **Table 2** and **Table 3** presents the full *CI* calculation. All the calculations presented in the **Table 1(a)** and **Table 1(b)**, **Table 2** and **Table 3** were performed using the new dz base.

4. Conclusions

As observed in Section 2, in spite of the fact that the bases $\mathbf{B}^w$ generate the same *CI* space, the corresponding *CSFs* of each $\mathbf{B}^w$ base have distinct quantum in formation contents. The **Table 1(a)** and **Table 1(b)** show clearly this non-uniform distribution of *QMIC* with regard to energy of the twelve *LiH* *HF* solutions.

Table 2 and **Table 3** show the possibility to make good use of this non-uniform distribution of *QMIC* using the reduced *MRHF* bases. As presented in **Table 2** is possible to obtain the dipole moment of the *LiH* molecule in close agreement with the experimental value without prejudice to the energy of the state function. The *MRHF*CI energies differ less than 3×10^{-3} hartree of the full *CI* energy. Besides, as shows in **Table 3**, the energy of the *Be* atom was obtained using only 25 *CSFs* and differs 5×10^{-8} hartrees of the full *CI* energy, which uses 102 *CSFs*. These results confirm the positive effect of the use of the *MRHF* bases already shown in our previous results.

A second step in this project, now in progress, is to study the composition of the *CSFs* of the system of generators $\mathbf{G}$ in terms of valence-bond and generalized valence-bond structures of interest [2a]. Future steps include search possible correlations between the *CSFs* of the *MRHF* bases that provided good values of the energies and one-electron properties. Data mining is a possible auxiliary tool to be employed [9] [10].

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