PHYSICAL REVIEW A VOLUME 33, NUMBER 3 MARCH 1986

Direct approximation to the reduced density matrices: Calculation of the isoelectronic sequence of beryllium up to argon

C. Valdemoro
Instituto de Física del Estado Sólido, Consejo Superior de Investigaciones Científicas, C/ Serrano 123, 28006 Madrid, Spain

L. Lain, F. Beitia, A. Ortiz de Zarate, and F. Castaño
Dpto. Química Física, Facultad de Ciencias, Universidad del Pais Vasco, Apartado 644, 48080 Bilbao, Spain

(Received 8 May 1985)

The spin-adapted reduced Hamiltonian theory has been applied to calculate the energies and the first- and second-order reduced density matrices for the isoelectronic sequence of beryllium up to argon in the singlet symmetry. The projection on the spin symmetry has been performed in two ways: by considering the space spanned by the eigenfunctions of $\hat{S}^2$ and $\hat{S}_z$ or by considering the space spanned by the $\hat{S}_z$ eigenfunctions. Several approximations for calculating the reduced density matrices are analyzed and discussed in detail. The results obtained with two of the approximations considered are highly encouraging when compared both to experimental data and to the total energy values obtained with the full configuration-interaction method.

I. INTRODUCTION

In a recent series of papers (referred to here as I—III, Refs. 1—3) one of us has reported the spin-adapted reduced Hamiltonian (SRH) theory. The eigenvectors of the SRH matrix generate a set of matricial projectors which yield a good approximation of the reduced density matrix (RDM). The preliminary calculations which served to check the value of these approximations were performed on the beryllium atom. Here we describe the results obtained for 14 isoelectronic ions of the beryllium atom. These and other calculations which are being carried out in our laboratory are needed in order to test the reliability of the approximations described in III.

Another aim of the present paper is to study the influence on the results of considering an m-electron subspace of mixed spin symmetry and one of pure spin symmetry. Indeed, the spin adaptation of the SRH can be performed either in the subspace spanned by the eigenfunctions of the $\hat{S}^2$ and $\hat{S}_z$ operators for a given symmetry or in the space spanned by the eigenfunctions of just the $\hat{S}_z$ operator. In order to distinguish them, the labels $(\hat{S}^2,\hat{S}_z)$ or $(\hat{S}_z)$ will point out the procedure considered. The preliminary results reported in III were limited to the $(\hat{S}^2,\hat{S}_z)$ case for the singlet symmetry. In this paper we have extended the calculations to the $(\hat{S}_z)$ case (for the same sym-

TABLE I. Energies of the ground state of the Be isoelectronic sequence (a.u.).

Ion	IQG $(\hat{S}^2,\hat{S}_z)$	IQG $(\hat{S}_z)$	Relativistic correction	Expt.[a]
Be I	−14.6697	−14.6749	−0.0022	−14.6685
B II	−24.3586	−24.3618	−0.0062	−24.3533
C III	−36.5257	−36.5274	−0.0141	−36.5458
N IV	−51.1958	−51.1964	−0.0280	−51.2463
O V	−68.3641	−68.3639	−0.0503	−68.4552
F VI	−88.0466	−88.0363	−0.0838	−88.1756
Ne VII	−110.2229	−110.2124	−0.1319	−110.4096
Na VIII	−134.9003	−134.8900	−0.1983	−135.1602
Mg IX	−162.0771	−162.0665	−0.2871	−162.4323
Al X	−191.7531	−191.7418	−0.4028	−192.2298
Si XI	−223.9302	−223.9186	−0.5505	−224.5568
P XII	−258.6069	−258.5948	−0.7355	−259.4189
S XIII	−295.7875	−295.7765	−0.9637	−296.8211
Cl XIV	−335.4636	−335.4516	−1.2413	−336.7702
Ar XV	−377.6410	−377.6287	−1.5750	−379.2497

[a] The conversion factor used was 1 eV = 0.036 750 272 a.u. consistent with the value $R_\infty = 1.097\,373 \times 10^5$ cm^{-1} and the data given in Ref. 12.

TABLE II. Total energies obtained for the three lowest states using different approximations (a.u.).

Ion	State[a]	FCI	HPH′ $(\hat{S}^2,\hat{S}_z)$	HPH′ $(\hat{S}_z)$	IQP	SCF[b]
Be I	$\lvert 1 2 \bar{1} \bar{2} \rangle$	−14.5872	−14.6081	−14.6063	−14.5632	−14.5724
	$\lvert 1 2 \bar{1} 3 \rangle$	−14.3014	−14.3472	−14.3483	−14.3168	
	$\lvert 1 3 \bar{1} \bar{3} \rangle$	−13.9851	−13.9776	−13.9854	−13.9701	
B II	$\lvert 1 2 \bar{1} \bar{2} \rangle$	−24.2484	−24.2775	−24.2737	−24.2247	−24.2376
	$\lvert 1 2 \bar{1} \bar{3} \rangle$	−23.3397	−23.3632	−23.3621	−23.3888	
	$\lvert 1 3 \bar{1} \bar{3} \rangle$	−22.5253	−22.5067	−22.5138	−22.6088	
C III	$\lvert 1 2 \bar{1} \bar{2} \rangle$	−36.4149	−36.4441	−36.4398	−36.3908	−36.4085
	$\lvert 1 2 \bar{1} \bar{3} \rangle$	−34.8018	−34.8131	−34.8102	−34.8710	
	$\lvert 1 3 \bar{1} \bar{3} \rangle$	−33.3162	−33.2974	−33.3043	−33.2988	
N IV	$\lvert 1 2 \bar{1} \bar{2} \rangle$	−51.0858	−51.1130	−51.1083	−51.0590	−51.0823
	$\lvert 1 2 \bar{1} \bar{3} \rangle$	−48.5165	−48.5167	−48.5123	−48.6081	
	$\lvert 1 3 \bar{1} \bar{3} \rangle$	−46.1177	−46.0991	−46.1057	−46.0998	
O V	$\lvert 1 2 \bar{1} \bar{2} \rangle$	−68.2520	−68.2809	−68.2758	−68.2263	−68.2577
	$\lvert 1 2 \bar{1} \bar{3} \rangle$	−64.5337	−64.5265	−64.5211	−64.6474	
	$\lvert 1 3 \bar{1} \bar{3} \rangle$	−61.0227	−61.0039	−61.0104	−61.0042	
F VI	$\lvert 1 2 \bar{1} \bar{2} \rangle$	−87.9479	−87.9577	−87.9460	−87.8805	−87.9340
	$\lvert 1 2 \bar{1} \bar{3} \rangle$	−75.2689	−75.1803	−75.2777	−75.4347	
	$\lvert 1 3 \bar{1} \bar{3} \rangle$	−62.5764	−62.5505	−62.5749	−62.5578	
Ne VII	$\lvert 1 2 \bar{1} \bar{2} \rangle$	−110.1248	−110.1342	−110.1223	−110.0571	−110.1110
	$\lvert 1 2 \bar{1} \bar{3} \rangle$	−94.2570	−94.1680	−94.2696	−94.4500	
	$\lvert 1 3 \bar{1} \bar{3} \rangle$	−78.4042	−78.3766	−78.4008	−78.3851	
Na VIII	$\lvert 1 2 \bar{1} \bar{2} \rangle$	−134.8022	−134.8118	−134.8001	−134.7357	−134.7884
	$\lvert 1 2 \bar{1} \bar{3} \rangle$	−115.5444	−115.4473	−115.5107	−115.7645	
	$\lvert 1 3 \bar{1} \bar{3} \rangle$	−96.3372	−96.3099	−96.3332	−96.3178	
Mg IX	$\lvert 1 2 \bar{1} \bar{2} \rangle$	−161.9798	−161.9888	−161.9769	−161.9124	−161.9661
	$\lvert 1 2 \bar{1} \bar{3} \rangle$	−138.6710	−138.5805	−138.6808	−138.9181	
	$\lvert 1 3 \bar{1} \bar{3} \rangle$	−115.4321	−115.4019	−115.4267	−115.4124	
Al X	$\lvert 1 2 \bar{1} \bar{2} \rangle$	−191.6576	−191.6650	−191.6524	−191.5867	−191.6440
	$\lvert 1 2 \bar{1} \bar{3} \rangle$	−163.5592	−163.5104	−163.8435	−163.8332	
	$\lvert 1 3 \bar{1} \bar{3} \rangle$	−135.5338	−135.4941	−135.5268	−135.5135	
Si XI	$\lvert 1 2 \bar{1} \bar{2} \rangle$	−223.8356	−223.8422	−223.8294	−223.7632	−223.8221
	$\lvert 1 2 \bar{1} \bar{3} \rangle$	−190.8604	−190.8334	−191.3134	−191.1614	
	$\lvert 1 3 \bar{1} \bar{3} \rangle$	−157.9752	−157.9285	−157.9674	−157.9545	
P XII	$\lvert 1 2 \bar{1} \bar{2} \rangle$	−258.5138	−258.5191	−258.5059	−258.4391	−258.5003
	$\lvert 1 2 \bar{1} \bar{3} \rangle$	−219.6957	−219.9563	−222.5476	−220.0242	
	$\lvert 1 3 \bar{1} \bar{3} \rangle$	−180.9653	−180.8478	−180.9567	−180.9444	
S XIII	$\lvert 1 2 \bar{1} \bar{2} \rangle$	−295.6922	−295.7000	−295.6877	−295.6236	−295.6786
	$\lvert 1 2 \bar{1} \bar{3} \rangle$	−252.3861	−252.3362	−252.6663	−252.7419	
	$\lvert 1 3 \bar{1} \bar{3} \rangle$	−209.2285	−209.1806	−209.2207	−209.2079	
Cl XIV	$\lvert 1 2 \bar{1} \bar{2} \rangle$	−335.3705	−335.3761	−335.3630	−335.2970	−335.3570
	$\lvert 1 2 \bar{1} \bar{3} \rangle$	−285.1763	−285.3502	−287.5259	−285.5593	
	$\lvert 1 3 \bar{1} \bar{3} \rangle$	−235.1187	−234.9620	−235.1097	−235.0975	
Ar XV	$\lvert 1 2 \bar{1} \bar{2} \rangle$	−377.5489	−377.5536	−377.5402	−377.4738	−377.5355
	$\lvert 1 2 \bar{1} \bar{3} \rangle$	−320.3636	−321.1531	−328.7836	−320.7741	
	$\lvert 1 3 \bar{1} \bar{3} \rangle$	−263.3168	−255.5566	−263.3073	−263.2955	

[a] Each state is represented by its dominant configuration.

[b] Reference 11.

metry), and so an analysis of these two cases has been made.

The results obtained are compared with those of a full configuration-interaction (FCI) treatment and, in the case of the total energy of the ground state, a comparison is also made among the self-consistent-field Hartree-Fock (SCF-HF) method, the experimental values, and our results. Section II contains a brief outline of the different approximations used here. Section III presents the results obtained and finally some comments are given in Sec. IV.

II. METHOD OF EVALUATION OF SECOND-ORDER REDUCED DENSITY MATRICES

Let us consider a basis of M spin orbitals $\{i\}$. A basis $\{\lambda\}$ is defined in the two-electron space where $|\lambda\rangle$ is a bielectronic Slater determinant formed with these spin orbitals. The monoelectronic basis also determines an m-electron space spanned by the functions $\{\Lambda\}$. Here we will focus on the singlet symmetry. Therefore, the $\{\Lambda\}$ considered will be either eigenfunctions of the $\hat{S}_z$ operator (Slater determinants) or eigenfunctions of both $\hat{S}^2$ and $\hat{S}_z$ operators for the chosen spin symmetry.

It has been shown (I and II) that a reducing mapping can be applied to the block of the desired spin symmetry of the FCI Hamiltonian matrix. This mapping yields the SRH matrix, which will be denoted $\underline{H}'$ when it is represented in the two-body space.

An important feature of our development is that the matrix $\underline{H}'$ can be evaluated without explicit determination of the FCI Hamiltonian matrix (I and II). Indeed, a direct calculation of $\underline{H}'$ is performed taking as data the numerical coefficients of the many-body Hamiltonian written in terms of bielectronic operators[4] or, equivalently the matrical representation of the well-known reduced Hamiltonian.[5–9] This initial data matrix will be denoted $\underline{H}$. Recently, a totally general and efficient algorithm computing $\underline{H}'$ for any m, any M, and any total spin quantum number S has been developed.[10]

In III several approximations to obtain the second-order reduced density matrix (2-RDM) were examined using the beryllium atom as a test example. Here we will report some results obtained using three of these approximations which seemed to be the most promising. It may be necessary to start by clarifying the procedure involved in two of these approximations, as only a very brief description

TABLE III. Second-order reduced density matrix for the ground state of the B II ion.

	$\|1\bar{1}\rangle$	$\|2\bar{1}\rangle$	$\|3\bar{1}\rangle$	$\|2\bar{2}\rangle$	$\|2\bar{3}\rangle$	Approximation
$\langle\bar{1}1\|$	0.995	0.017	0.033	$-<10^{-3}$	−0.001	FCI
	0.922	0.023	0.048	$<10^{-3}$	0.001	IQP
	0.986	0.043	0.063	$<10^{-3}$	−0.001	IQG $(\hat{S}^2,\hat{S}_z)$
	0.985	0.042	0.064	$<10^{-3}$	$-<10^{-3}$	IQG $(\hat{S}_z)$
	0.991	0.029	0.050	$-<10^{-3}$	$<10^{-3}$	HPH′ $(\hat{S}^2,\hat{S}_z)$
	0.991	0.029	0.052	$<10^{-3}$	$<10^{-3}$	HPH′ $(\hat{S}_z)$
$\langle\bar{1}2\|$		0.801	−0.394	0.015	0.028	
		0.821	−0.378	0.019	0.040	
		0.752	−0.421	0.002	0.024	
		0.753	−0.425	0.003	0.025	
		0.780	−0.409	0.011	0.029	
		0.782	−0.409	0.013	0.031	
$\langle\bar{1}3\|$			0.197	−0.006	−0.015	
			0.177	−0.009	−0.018	
			0.252	−0.011	−0.009	
			0.251	−0.011	−0.010	
			0.220	−0.008	−0.014	
			0.219	−0.009	−0.015	
$\langle\bar{2}2\|$				0.633	−0.327	
				0.679	−0.313	
				0.748	−0.300	
				0.753	−0.297	
				0.672	−0.315	
				0.667	−0.316	
$\langle\bar{3}2\|$					0.171	
					0.147	
					0.121	
					0.118	
					0.149	
					0.151	

of them was given previously.

The physical model on which they are based is that of the independent pair of electrons. Indeed, the study of an m-electron system is substituted by that of $\binom{m}{2}$ systems of independent pairs of electrons, or, as we call them, quasigeminals. The states of these independent pairs of electrons are the eigenvectors of the second-order SRH matrix $\underline{H}'$. This model can be easily described by explicitly writing our first assumption: The second-order reduced density matrix can be approximated by the formula

$$D^{\mathscr{L}\mathscr{L}} = \sum_I \langle \mathscr{L} | B_I^\dagger B_I | \mathscr{L} \rangle \, |I\rangle\langle I| \equiv \sum_I a_I^{\mathscr{L}} \, |I\rangle\langle I| \ , \tag{1}$$

where $|\mathscr{L}\rangle$ is the m-electron state in which we are interested (not necessarily the ground state) and $\{|I\rangle\}$ denotes the eigenvectors of the matrix $\underline{H}'$.

This formula for the 2-RDM leads to a total energy of the form

$$E^{\mathscr{L}} = \sum_I a_I^l \underline{H}_{II} \tag{2}$$

which at first sight appears to be the same as that used by other authors.[5-7] However, the values taken by $\underline{H}_{II}$ are different from theirs as we use the eigenvectors of $\underline{H}'$ while they use those of the initial $\underline{H}$. Moreover, we shall determine our $a_I^{\mathscr{L}}$ by a procedure, to be explained presently, which differs from that based on looking for bounds to the energy.[5-7]

At the basis of our evaluation of the $a_I^{\mathscr{L}}$ is a generalized concept of the occupation number operator. It is well known that for a spin orbital i the occupation number operator is $n_i = b_i^\dagger b_i$. Now, the occupation number of a bielectronic state λ of the Slater determinant type can be defined as

$$N_\lambda = B_\lambda^\dagger B_\lambda = b_{\lambda_1}^\dagger b_{\lambda_2}^\dagger b_{\lambda_2} b_{\lambda_1} = n_{\lambda_1} n_{\lambda_2} \ , \tag{3}$$

where $B_\lambda^\dagger |0\rangle \equiv b_{\lambda_1}^\dagger b_{\lambda_2}^\dagger |0\rangle \equiv |\lambda_1\lambda_2\rangle \equiv |\lambda\rangle$ with $\lambda_1 < \lambda_2$. Of course, $|\lambda\rangle$ represents a state of the Slater determinant type $|\lambda_1(1)\lambda_2(2)|$. This concept can be generalized as

$$N_I = B_I^\dagger B_I \ , \tag{4}$$

where $B_1^\dagger = \sum_\lambda c_{I\lambda} B_\lambda^\dagger$. That is,

$$|I\rangle = \sum_\lambda c_{I\lambda} |\lambda\rangle \tag{5}$$

is a correlated bielectronic state. In our case, $\{|I\rangle\}$ denotes the eigenvectors of the $\underline{H}'$ matrix; therefore, the coefficients $\{c_{I\lambda}\}$ are those obtained when diagonalizing this matrix. It is important to note that, in this general case, N_I is no longer a simple product of monoelectronic occupation number operators, i.e., $N_I \neq n_i n_j$.

Let us now consider a Slater determinant state (or an eigenfunction of $\hat{S}^2$ and $\hat{S}_z$) of m electrons $|\Lambda\rangle$ and the bielectronic operator N_γ. The expectation value

$$\langle \Lambda | N_\gamma | \Lambda \rangle \equiv \langle \Lambda | B_\gamma^\dagger B_\gamma | \Lambda \rangle = a_\gamma^\Lambda \tag{6}$$

TABLE IV. First-order reduced density matrix for the ground state of the B II ion.

	$\vert 1\rangle$	$\vert 2\rangle$	$\vert 3\rangle$	$\vert 4\rangle$	Approximation
$\langle 1 \vert$	0.998	0.017	0.033	0.025	FCI
	0.996	0.023	0.048	0.032	IQP
	0.996	0.023	0.042	0.030	IQG $(\hat{S}^2,\hat{S}_z)$
	0.996	0.023	0.044	0.030	IQG $(\hat{S}_z)$
	0.996	0.022	0.043	0.030	HPH′ $(\hat{S}^2,\hat{S}_z)$
	0.996	0.023	0.045	0.030	HPH′ $(\hat{S}_z)$
$\langle 2 \vert$		0.803	−0.395	−0.016	
		0.824	−0.379	−0.016	
		0.813	−0.381	−0.016	
		0.815	−0.381	−0.016	
		0.803	−0.396	−0.017	
		0.803	−0.397	−0.016	
$\langle 3 \vert$			0.198	0.009	
			0.178	0.009	
			0.189	0.009	
			0.188	0.009	
			0.199	0.010	
			0.200	0.010	
$\langle 4 \vert$				0.001	
				0.001	
				0.001	
				0.001	
				0.001	
				0.001	

can always be obtained. The next step is to consider the expectation value,

$$\langle \mathscr{L} | N_I | \mathscr{L} \rangle \equiv \langle \mathscr{L} | B_I^\dagger B_I | \mathscr{L} \rangle = a_I^{\mathscr{L}} \ , \qquad (7)$$

which is what appears in (1). The values $a_I^{\mathscr{L}}$ are unknown; therefore, we will introduce our second assumption: Let $|\gamma\rangle$ be the dominant bielectronic configuration in $|I\rangle$ [i.e., $c_{I\gamma}$ in the larger coefficient in (5)], and let $|\Lambda\rangle$ be the dominant configuration in $|\mathscr{L}\rangle$. We will assume that

$$a_I^{\mathscr{L}} = a_\gamma^\Lambda \ .$$

Equation (1) shows that the probability of occupancy of pair $|I\rangle$ is the diagonal element $\langle \mathscr{L} | B_I^\dagger B_I | \mathscr{L} \rangle$. As no contribution to $D^{\mathscr{L}\mathscr{L}}$ comes from $|I\rangle\langle J|$ for $I \neq J$, the set $\{I\}$ behaves as if it was eigengeminals of the 2-RDM (natural geminals) for *any* eigenstate $|\mathscr{L}\rangle$ of our m-electron system. It is important to realize that no kind of pair condensation is implied by our physical model of independent pairs. Indeed, the eigenvectors of $\underline{H}'$ describe independent pairs only in an averaged sense. The approximation just described will be called IQG's (independent quasigeminals) and the 2-RDM obtained with it will be denoted D_{IQG}.

Let us now describe the approximation which is denoted HPH′ (Hamiltonian projected in a given $\underline{H}'$ subspace). The idea behind this approximation is that the D_{IQG} is a zeroth-order approximation which may be used as a projector for the initial $\underline{H}$ before the mapping transformation (MT) algorithm is applied. In this way a second SRH matrix denoted $\underline{H}''$ is obtained. With the eigenvectors of $\underline{H}''$ one proceeds as in the IQG. An important characteristic of this procedure is that if, with the new D, one repeats the cycle, then the new $\underline{H}'''$ thus obtained has the same eigenvectors as $\underline{H}''$. That is, this is a self-consistent approximation. Our physical interpretation of the HPH′ approximation is that most of the contribution from the unwanted states is removed from the initial $\underline{H}$. The MT applied subsequently to the projected $\underline{H}$ would allow it to take again an N-representable form.

Since the eigenvectors of $\underline{H}'$ are slightly different depending on whether the selected m-electron subspace is spanned by the eigenfunctions of the $\hat{S}^2$ and $\hat{S}_z$ operators or simply by the eigenfunctions of the $\hat{S}_z$, the IQG and HPH′ approximations have been considered in both cases.

TABLE V. Second-order reduced density matrix for the ground state of the C III ion.

	$\|1\bar{1}\rangle$	$\|2\bar{1}\rangle$	$\|3\bar{1}\rangle$	$\|2\bar{2}\rangle$	$\|2\bar{3}\rangle$	Approximation
$\langle \bar{1}1 \|$	0.997	0.013	0.031	$- < 10^{-3}$	-0.001	FCI
	0.994	0.018	0.044	$< 10^{-3}$	$< 10^{-3}$	IQP
	0.990	0.031	0.056	$- < 10^{-3}$	-0.002	IQG $(\hat{S}^2, \hat{S}_z)$
	0.990	0.030	0.058	$- < 10^{-3}$	-0.001	IQG $(\hat{S}_z)$
	0.993	0.021	0.046	$- < 10^{-3}$	$- < 10^{-3}$	HPH′ $(\hat{S}^2, \hat{S}_z)$
	0.993	0.022	0.047	$- < 10^{-3}$	$< 10^{-3}$	HPH′ $(\hat{S}_z)$
$\langle \bar{1}2 \|$		0.854	-0.350	0.012	0.027	
		0.864	-0.338	0.015	0.038	
		0.819	-0.378	0.003	0.024	
		0.821	-0.379	0.004	0.025	
		0.838	-0.365	0.010	0.029	
		0.840	-0.363	0.011	0.031	
$\langle \bar{1}3 \|$			0.145	-0.004	-0.011	
			0.135	-0.006	-0.015	
			0.184	-0.009	-0.008	
			0.182	-0.009	-0.009	
			0.162	-0.005	-0.012	
			0.161	-0.006	-0.013	
$\langle \bar{2}2 \|$				0.725	-0.307	
				0.751	-0.294	
				0.802	-0.276	
				0.804	-0.275	
				0.749	-0.295	
				0.745	-0.296	
$\langle \bar{3}2 \|$					0.131	
					0.117	
					0.096	
					0.095	
					0.118	
					0.119	

In order to distinguish them, the labels $(\hat{S}^2,\hat{S}_z)$ or $(\hat{S}_z)$ will follow the symbol denoting the approximation considered.

The last approximation considered here is the "independent quasiparticle" (IQP) one. It builds the $\{|I\rangle\}$ as Slater determinants formed with the eigenvectors of the first-order SRH, $\underline{h}'$. As this approximation is identical to that applied by Absar and Coleman,[8,9] given that it can be shown that $\underline{h}$ and $\underline{h}'$ have the same eigenvectors, we will not say any more about it here.

III. TOTAL ENERGIES AND REDUCED DENSITY MATRICES OF THE ISOELECTRONIC SEQUENCE OF BERYLLIUM

The three approximation procedures for the 2-RDM described in Sec. II were used in the calculation of the Be (^1S) isoelectronic sequence up to Ar XV. The basis functions used were those of Clementi *et al.*,[11] except in the cases in which the number of functions given by these authors was five (Be I—O V). In these cases we omitted the $2s$ function which was reported to contribute less to the SCF-HF orbitals.[11]

As the energy calculated with the IQG approximation compares well with that obtained experimentally by adding up all ionization potentials,[12] we give these energies together in Table I. In Table II we report the HPH′ and IQP results together with the FCI and SCF values with which these results can be compared, respectively. The FCI results have been obtained by us with the same basis set and the SCF-HF ones are those given by Clementi *et al.*[11] In Table II we also report the energies of the first two excited states (except in the SCF-HF case).

The results of Tables I and II do not need, in our opinion, much comment. Indeed, although more calculations for other symmetries, and with a wider basis set of functions, should be performed, it seems that the IQG reproduces rather well the experimental values. If the total relativistic energy corrections, as determined by Fraga *et al.*,[13] which we report in the fourth column of Table I, are taken into account, the agreement is excellent for all the ions considered. The FCI results are approached by the HPH′, while the SCF ones are comparable to the IQP. An interesting question is whether, when the basis is sufficiently large and the FCI approaches the experimental values, the HPH′ approaches the IQG. This point will be investigated in the future.

From the values given in Tables I and II it is also clear that as far as total energies are concerned the difference between the $(\hat{S}^2,\hat{S}_z)$ and $(\hat{S}_z)$ spin adaptations does not appear to be very significant. However, it should be noted that the error on IQG $(\hat{S}^2,\hat{S}_z)$ with respect to the experimental values is exaggerated in the same direction in the IQG $(\hat{S}_z)$, except for the cases of N IV and O V, where the difference between IQG $(\hat{S}_z)$ and IQG $(\hat{S}^2,\hat{S}_z)$ is less than

TABLE VI. First-order reduced density matrix for the ground state of the C III ion.

	$|1\rangle$	$|2\rangle$	$|3\rangle$	$|4\rangle$	Approximation
$\langle 1|$	0.998	0.013	0.030	0.019	FCI
	0.997	0.018	0.044	0.025	IQP
	0.997	0.017	0.039	0.023	IQG $(\hat{S}^2,\hat{S}_z)$
	0.997	0.017	0.040	0.023	IQG $(\hat{S}_z)$
	0.998	0.017	0.039	0.023	HPH′ $(\hat{S}^2,\hat{S}_z)$
	0.997	0.017	0.041	0.024	HPH′ $(\hat{S}_z)$
$\langle 2|$		0.855	−0.350	−0.014	
		0.867	−0.339	−0.013	
		0.860	−0.341	−0.013	
		0.861	−0.341	−0.013	
		0.853	−0.352	−0.015	
		0.854	−0.352	−0.014	
$\langle 3|$			0.146	0.006	
			0.135	0.006	
			0.141	0.007	
			0.141	0.006	
			0.147	0.007	
			0.148	0.007	
$\langle 4|$				$<10^{-3}$	
				$<10^{-3}$	
				$<10^{-3}$	
				$<10^{-3}$	
				$<10^{-3}$	
				$<10^{-3}$	

6×10^{-4} a.u.

In the case of the HPH', the $(\hat{S}_z)$ treatment gives results extremely close to the $(\hat{S}^2,\hat{S}_z)$ one and when compared with the FCI values it seems that those obtained in the (S_z) treatment are slightly better. Although the general algorithm for (S^2,S_z) recently developed[10] is extremely efficient, there is no doubt that the $(\hat{S}_z)$ treatment is very interesting since its algorithm is given in terms of simple combinatorial numbers.[2] Thus the fact that the energy results corresponding to the $(\hat{S}_z)$ subspace are better than those of the $(\hat{S}^2,\hat{S}_z)$ in these approximations is rather satisfying.

Although we do not report in the Tables the IQG energy values for the excited states of the sequence, these have been calculated, and it should be noted that for the third period the agreement with FCI values is better than with those of the HPH'.

As it would be awkward to report here the second-order RDM and first-order RDM for all the ions studied and as those of Be have been given in (SRH-II), we will just give here the RDM's for B II and C III. In the case of the 2-RDM only the most relevant elements will be given. These density matrices are given in Tables III—VI.

All the results obtained are satisfactory as far as the sign and order of the values taken by the different elements are concerned, but what is noteworthy is the agreement between the FCI and the HPH' values, particularly in the first-order RDM. This agreement exists for the rest of the sequence. Starting at N IV the values of the RDM elements become closer either to 1 or to 0, which shows a tendency towards the determinantal form of the states. As can be seen, the RDM results do not show any difference between the $(\hat{S}^2,\hat{S}_z)$ and $\hat{S}_z$ calculations.

IV. FINAL COMMENTS

The results which have been presented in Sec. III are clearly very encouraging. It seem that the reproduction of experimental results is better achieved with the IQG approximation, while the agreement with the FCI results is remarkable all through the sequence for the HPH' approximation. In the future an expanded basis will be used in the calculation of this sequence so as to test among other possible consequences of the basis if the HPH' and IQG results approach each other. Although the IQP approximates the SCF-HF results and has a conceptual interest, we think that it can be disregarded given that besides its restricted accuracy it involves more elaborate calculations of the RDM.

Another feature that renders the IQG and HPH' still more interesting is that the energies obtained with both of them are invariant with respect to a unitary transformation of the monoelectronic basis. This property has not been demonstrated in a formal way, but we have transformed the initial $\underline{H}$ to the basis which diagonalizes h, and not only the eigenvalues of $\underline{H}'$ are invariant (which was to be expected given that the MT employs two mappings which are not dependent on the basis used[14,15]), but also the E_{IQG} and $E_{\text{HPH}'}$ remained identical. Turning our attention now to the comparison between the $(\hat{S}^2,\hat{S}_z)$ and $(\hat{S}_z)$ calculations, it is clear that as far as total energies and RDM are concerned, there is no substantial difference between both procedures. For other symmetries this situation may change, but for singlets, if one is interested in total energies and densities, it seems that the choice between a $(\hat{S}^2,\hat{S}_z)$ and a $(\hat{S}_z)$ treatment can be left open to convenience.

---

[1] C. Valdemoro, An. Fis. **79**, 106 (1983).

[2] C. Valdemoro, Phys. Rev. A **31**, 2114 (1985).

[3] C. Valdemoro, Phys. Rev. A **31**, 2123 (1985).

[4] C. Valdemoro, 5th Seminar on Computational Methods in Quantum Chemistry, 1981. Grönningen. Ed. Max Planck Institut für Physik und Astrophysik, Institut für Astrophysik. Karl Schwarzschils Strasse 1-8046 Garching bei Munchen.

[5] F. Bopp, Z. Phys. **156**, 348 (1859).

[6] T. B. Grimley and F. D. Peat, Proc. Phys. Soc. London **86**, 249 (1965).

[7] F. D. Peat, Can. J. Phys. **48**, 147 (1970).

[8] I. Absar and A. J. Coleman, Chem. Phys. Lett. **39**, 609 (1976).

[9] I. Absar and A. J. Coleman, Int. J. Quantum Chem. **X**, 319 (1978).

[10] J. Karwowski, W. Duch, and C. Valdemoro, Phys. Rev. A (to be published).

[11] E. Clementi and C. Roetti, At. Data Nucl. Data Tables **14**, 428 (1874).

[12] C. E. Moore, *Ionization Potentials and Ionization Limits Derived from the Analyses of Optical Spectra,* Natl. Bur. Stand. (U.S.), Natl. Stand. Ref. Data Ser. No. 34 (U.S. GPO, Washington, D.C., 1970).

[13] S. Fraga, J. Karwowski, and K. M. S. Saxena, *Handbook of Atomic Data* (Elsevier, Amsterdam, 1976).

[14] A. J. Coleman and I. Absar, Int. J. Quantum Chem. **XVIII**, 1279 (1980).

[16] H. Kummer, J. Math. Phys. **8**, 2063 (1967).