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Spin-adapted reduced Hamiltonians. II. Total energy and reduced density matrices

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In the preceding paper (paper I of this series) the spin-adapted reduced Hamiltonian theory was developed and applied to the study of the elementary excitations of a test example; the Be atom. Here this theory is extended in order to obtain other observables: the total energy and the reduced density matrices for an m-electron system, always working within the two-body space. Preliminary applications of this formalism produce very satisfactory results.

I. INTRODUCTION

In paper I of this series[1] the theory of the spin-adapted reduced Hamiltonian (SRH) matrices were developed. This theory involves obtaining a finite matrix representation of the usual many-body Hamiltonian operator in an m-body space spanned by the eigenfunctions of the spin operators S^2 and S_z for a chosen symmetry [of the full configuration-interaction (CI) Hamiltonian matrix]. Then a reducing mapping is applied which transforms this matrix into the SRH matrix in the two-electron (or one-electron) space.

One of the crucial points is that all these operations, usually referred to here as "mapping transformation," *can be combined into a single algorithm which allows one to work within the two-electron space.*

In paper I of this series[1] the theory was applied to the study of the elementary excitations of the beryllium atom as a test example for other atoms and molecules. Here we shall study how the SRH theory may be employed in order to obtain information about the total energy and the electronic density of the system.

These two kinds of observables cannot be obtained from the SRH matrices in a direct way. The reason for this difficulty arises from the fact that the reduced density matrices (RDM) are not elements of an orthogonal set. In consequence, although the SRH matrix $\underline{H}'$, in the two-body space,[1] can formally be written as

$$\underline{H}'=\sum_{\mathscr{L}} E_{\mathscr{L}}\underline{D}^{\mathscr{L}\mathscr{L}} \tag{1}$$

(where $E_{\mathscr{L}}$ is the energy of the eigenstate $|\mathscr{L}\rangle$, and $D^{\mathscr{L}\mathscr{L}}$ the corresponding reduced density matrix) it is not a trivial matter to separate in $\underline{H}'$ the information concerning a given $|\mathscr{L}\rangle$ without contamination from the other states.

The ideal approach would seem to be to look for a theoretical closed-form solution to this problem, however, this is not practical. Indeed, we made several different attempts in this direction, but they lead back to the diagonalization of the full CI Hamiltonian matrix in the m-electron space. Thus, in order to calculate the total energy and the RDM within the framework of the SRH theory an indirect approach should be employed.

There are two main questions to be investigated. (i) How do we extract from the SRH matrix $\underline{H}'$ the information about the state of interest? (2) What is the connection, if any, between the one- and two-body RDM and the eigenvectors of $\underline{h}'$ [quasiparticles (QP)] and of H' [quasigeminals (QG)], respectively?

In order to investigate these two questions several approximations may be considered. Here we report the results obtained using what seemed to us the most obvious ideas to be tried.

As in paper I, the test example is the Be atom and the basis set used is Clementi's double-zeta one.[2] In Sec. II, the independent QP (IQP) and independent QG (IQG) approximations are studied. In Sec. III the initial $\underline{H}$ matrix, its reduced one-body form $\underline{h}$, or the SRH matrices $\underline{H}'$ and $\underline{h}'$ are projected upon different subspaces before being submitted to the mapping transformation described in paper I, henceforth denoted MT, which leads from $\underline{H}$ to the SRH matrices $\underline{H}'$. In Sec. IV the N-representability of the matrices obtained is commented upon. Finally, some concluding remarks are given in Sec. V.

II. IQP AND IQG APPROXIMATIONS

The IQP and IQG approximations can be considered as extreme ones in this theory. In the IQP approximation there is no correlation between electrons, while in the IQG scheme the correlation effects between two electrons are maximal, but there is no correlation between pairs. In the first case the QP are considered to be natural orbitals with occupation number equal to 1 or to 0. Similarly, in the second scheme the QG are considered to be approximate natural geminals also with occupation number equal to 1 or 0. In this section these two approximations will be analyzed with the help of the results obtained in the calculation of the Be atom.

A. The IQP

The QP are the eigenvectors of the one-body SRH matrix called $\underline{h}'$ in paper I. For the pure-singlet symmetry these QP have the same form as the states obtained in the reduced Hamiltonian scheme.[1,3-5] In the IQP approximation the states of the Be atom are clearly of the Slater determinant type, and the RDS therefore have a very simple form.

B. The IQG

In order to describe clearly this approximation let us consider a concrete example: the state $|12\bar{3}\bar{4}\rangle$. In it two electrons occupy orbitals 1 and 2 with spin α and two others occupy orbitals 3 and 4 with spin β. If $|12\bar{3}\bar{4}\rangle$ is to be fully described in terms of *bielectronic* states we must consider $|12\rangle$ and $|\bar{3}\bar{4}\rangle$, clearly of triplet symmetry, and $|1\bar{3}\rangle$, $|1\bar{4}\rangle$, $|2\bar{3}\rangle$, and $|2\bar{4}\rangle$ with spin projection equal to zero which may belong either to a singlet or to a triplet state. If $|12\bar{1}\bar{2}\rangle$, of the closed type, is to be described by bielectronic states then we must consider the two triplets $|12\rangle$ and $|\bar{1}\bar{2}\rangle$, the two singlets $|1\bar{1}\rangle$ and $|2\bar{2}\rangle$, and $|1\bar{2}\rangle$ and $|2\bar{1}\rangle$ which are configurations belonging either to a singlet or to a triplet state.

Finally, by multiplying

$$\frac{(B^{\dagger}_{1\bar{2}}+B^{\dagger}_{2\bar{1}})}{\sqrt{2}}\,\frac{(B^{\dagger}_{1\bar{2}}+B^{\dagger}_{2\bar{1}})}{\sqrt{2}}\,|0\rangle \equiv \frac{(b^{\dagger}_{1}b^{\dagger}_{\bar{2}}+b^{\dagger}_{2}b^{\dagger}_{\bar{1}})}{\sqrt{2}}\,\frac{(b^{\dagger}_{1}b^{\dagger}_{\bar{2}}+b^{\dagger}_{2}b^{\dagger}_{\bar{1}})}{\sqrt{2}}\,|0\rangle \equiv |12\bar{1}\bar{2}\rangle$$

and

$$\frac{(B^{\dagger}_{1\bar{2}}-B^{\dagger}_{2\bar{1}})}{\sqrt{2}}\,\frac{(B^{\dagger}_{1\bar{2}}-B^{\dagger}_{2\bar{1}})}{\sqrt{2}}\,|0\rangle \equiv \frac{(b^{\dagger}_{1}b^{\dagger}_{\bar{2}}-b^{\dagger}_{2}b^{\dagger}_{\bar{1}})}{\sqrt{2}}\,\frac{(b^{\dagger}_{1}b^{\dagger}_{\bar{2}}-b^{\dagger}_{2}b^{\dagger}_{\bar{1}})}{\sqrt{2}}\,|0\rangle \equiv -|12\bar{1}\bar{2}\rangle\ ,$$

it can be inferred that in order to describe a singlet four-electron state one must employ three singlet bielectronic states and three triplet ones. These bielectronic states correspond to the different pairings which are implicit in the four-electron state.

This rule is easily generalized by arguments of the same type for any symmetry and any number of electrons and is basically the procedure followed here to determine the QG which should be selected. Thus, if the two-body density matrix of the state $|\mathscr{L}\rangle$ in which configuration $|12\bar{1}\bar{2}\rangle$ dominates is to be approximated, the expression giving the trial reduced density matrix $D^{\mathscr{L}\mathscr{L}}$ will be

$$D^{\mathscr{L}\mathscr{L}}=\sum_{J}|J\rangle\langle J|\ , \tag{2}$$

where $|J\rangle$ denotes only those QG's in which one of the following configurations dominates: $|1\bar{1}\rangle$, $|2\bar{2}\rangle$, $|1\bar{2}\rangle+|2\bar{1}\rangle$, $|1\bar{2}\rangle-|2\bar{1}\rangle$, $|12\rangle$, $|\bar{1}\bar{2}\rangle$. When in the state under study the dominant configuration is of the type $|ij\bar{i}\bar{l}\rangle$, then

$$D=\sum_{J}|J\rangle\langle J|+\tfrac{1}{2}\sum_{K}|K\rangle\langle K|\ , \tag{3}$$

where $|J\rangle$ represents the QG in which $|i\bar{i}\rangle$ or $|jl\rangle$ dominates while $|K\rangle$ represents those with dominant $|ij\rangle$, $|\bar{i}\bar{j}\rangle$, $|il\rangle$, $|\bar{i}\bar{l}\rangle$, $|i\bar{l}\rangle+|l\bar{i}\rangle$, $|i\bar{l}\rangle-|l\bar{i}\rangle$, $|i\bar{j}\rangle+|j\bar{i}\rangle$, $|i\bar{j}\rangle-|j\bar{i}\rangle$.

C. Results

The total energy will be calculated by using the well-known form

$$E=\mathrm{tr}(\underline{H}\,\underline{D})\ , \tag{4}$$

where the $\underline{H}$ is the initial $\underline{H}$ in our theory and $\underline{D}$ is approximated as previously described in Secs. II A and II B. In the IQG approximation the QG selected are those which diagonalize the SRH matrix $\underline{H}'$. The results obtained in this way for the six states of lowest energy are reported in Table I.

The order number of the state appears in the first column. The dominant four-electron configuration of the state considered is given in the second column (the bar over the number stands for a spin function β). The full CI (FCI) and the self-consistent-field (SCF) results obtained with the same basis[6] are reported in the third and fourth columns, respectively. The results obtained with the IQP and IQG approximations appear in the fifth and sixth columns, respectively. The seventh column refers to another approximation which will be studied in Sec. III.

On the whole the IQP results are very close to those obtained within the SCF Hartree-Fock method for which the basis set of Clementi was optimized. Moreover, for the states in which an open-orbital configuration dominates (states 2, 4, and 5) the value of the energy with the IQP approximation is closer to that of the FCI than to the SCF one.

The value of the energy obtained with the IQG for the ground-state energy is 0.0825 a.u. lower than that of the FCI which constitutes the variational limit. This indicates that in this approximation the correlation effects can be markedly overemphasized.

When the energy values obtained with the IQP and

TABLE I. Energies in atomic units.

No	Dominant Config.	FCI	SCF	IQP	IQG	HPH′
1	$\|12\bar{1}\bar{2}\rangle$	−14.5872	−14.5724	−14.5632	−14.6697	−14.6081
2	$\|12\bar{1}\bar{3}\rangle$	−14.3014	−14.2787	−14.3168	−14.3805	−14.3472
3	$\|13\bar{1}\bar{3}\rangle$	−13.9850	−13.9832	−13.9701	−13.9505	−13.9776
4	$\|12\bar{2}\bar{3}\rangle$	−10.0693	−9.9659	−10.0040	−10.0143	−11.3627
5	$\|13\bar{2}\bar{3}\rangle$	−9.5680	−9.5749	−9.5694	−9.5496	−9.5435
6	$\|23\bar{2}\bar{3}\rangle$	−3.5661	−3.6036	−3.6001	−3.5989	−3.6053

TABLE II. Second-order reduced density matrix of the ground state of the Be atom (some elements).

	$\lvert 1\bar{1}\rangle$	$\lvert 2\bar{1}\rangle$	$\lvert 3\bar{1}\rangle$	$\lvert 2\bar{2}\rangle$	$\lvert 2\bar{3}\rangle$	Approximation
$\langle \bar{1}1 \rvert$	0.993	0.015	-0.028	$< 10^{-4}$	$< 10^{-4}$	FCI
	0.992	0.013	-0.032	$< 10^{-4}$	$< 10^{-4}$	IQP
	0.985	0.039	-0.053	$< 10^{-4}$	$< 10^{-4}$	IQG
	0.990	0.023	-0.039	$< 10^{-4}$	$< 10^{-4}$	HPH′
$\langle \bar{1}2 \rvert$		0.820	0.374	0.013	0.028	
		0.895	0.298	0.012	0.004	
		0.780	0.391	-0.003	0.010	
		0.823	0.373	0.007	0.009	
$\langle \bar{1}3 \rvert$			0.175	$< 10^{-4}$	0.013	
			0.100	$< 10^{-4}$	$< 10^{-4}$	
			0.220	$< 10^{-4}$	0.006	
			0.174	$< 10^{-4}$	0.003	
$\langle \bar{2}2 \rvert$				0.663	0.324	
				0.808	0.268	
				0.859	0.242	
				0.767	0.287	
$\langle \bar{3}2 \rvert$					0.160	
					0.090	
					0.068	
					0.108	

IQG approximation are simultaneously compared with those obtained in the FCI calculation, it can be observed in Table I that only for the ground state and for state 5 does the FCI have an intermediate value. In fact, while the IQG value is lower than the FCI in the ground state, the opposite is true for state 5. On the other hand, for state 5 the SCF energy is lower than the FCI one. This indicates that the stabilization provided by the correlation effects in the ground state is lost for the higher states as expected and becomes of positive sign in state 5 (the SCF energy for state 5 is also lower than the FCI one which is in line with our argument).

Let us now consider the results obtained for the RDM with those two approximations. For the sake of brevity, and easier inspection, only the most significant elements of the upper half of the second-order RDH are given in Table II.

The notation used in Table II is the following. Let us suppose that we wish to report the value of the element (λ,γ) of $D^{\mathscr{L}\mathscr{L}}$ according to formula (2), then

$$D^{\mathscr{L}\mathscr{L}}_{\lambda\gamma} = \sum_{J}{}' \langle \lambda \mid J \rangle \langle J \mid \gamma \rangle \ .$$

Now, in the first line of Table II the index γ is given in terms of the spin orbitals involved in it, i.e., $\lvert \gamma \rangle \equiv \lvert i\bar{j} \rangle$, while the λ index is given in the first column in the same manner. All the values of a given line (for every element) correspond to the approximation whose symbol appears in it on the seventh column (for Table II).

The order of magnitude of the elements and the sign are correctly given in both approximations. The element $D_{1\bar{1},1\bar{1}}$ is very accurate and in general the errors are just in the second decimal and small. The one element for which the error (40%) is the first decimal is on the $D_{2\bar{2}2\bar{2}}$.

The results for the one-body RDM are reported in Table III. Here not only the signs and the orders of magnitude but also the values themselves can be very well compared with those of the FCI. It is also noteworthy that the IQP and IQG approximations generate nearly the same one-body RDM which can be considered a good first-order approximation.

III. PROJECTED SRH MATRICES

The IQG approximation can be understood as describing an m-body system as if it were an assembly of $\binom{m}{2}$ identical bielectronic systems in different states or equivalently a bielectronic system in a mixed state of a very special kind. The correlation between the different pair states existing in the m-body function is not introduced in the IQG approximation.

In order to improve the results described in Sec. II, some kind of relaxation should be introduced. Mapping transformation can be considered not only as a way of removing the contribution from other unwanted symmetries but also as a relaxation process. This is so because a great deal of mixing of the transformed matrix occurs in the augmenting mapping step. In this section the MT will be used with this in view.

Thus, instead of taking the trace (4) of $\underline{H}\,\underline{D}$ in order to get the IQG energy, the $\underline{D}\,\underline{H}\,\underline{D}$ will be allowed to relax by a second application of the MT so that a new SRH matrix $\underline{H}''$ will be obtained. In principle this process can be repeated as many times as one may wish, but after $\underline{H}''$ has been obtained the results repeat themselves. This noteworthy stability or autocoherence property is in line with the striking properties of the MT which were presented in paper I.

From the eigenvectors of H'' a corresponding new set of QG is selected in order to approximate D as in the IQG approximation discussed in Sec. II. In what follows, this approximation will be denoted by the symbol HPH′ (ini-

TABLE III. First-order reduced density matrix for the ground state of the Be atom.

	$\lvert 1\rangle$	$\lvert 2\rangle$	$\lvert 3\rangle$	$\lvert 4\rangle$	Approx.
$\langle 1 \rvert$	0.996	0.015	−0.028	0.045	FCI
	0.995	0.018	−0.030	0.049	IQP
	0.996	0.018	−0.032	0.049	IQG
	0.996	0.015	−0.032	0.050	HPH′
$\langle 2 \rvert$		0.823	0.375	−0.036	
		0.860	0.310	−0.035	
		0.863	0.323	−0.036	
		0.854	0.348	−0.039	
$\langle 3 \rvert$			0.176	−0.018	
			0.141	−0.016	
			0.137	−0.016	
			0.145	−0.018	
$\langle 4 \rvert$				0.004	
				0.004	
				0.004	
				0.004	

tial $\underline{H}$ *projected* into a selected subspace of $\underline{H}'$ prior to MT). The values obtained for the total energy with this approximation are given in the last column of Table I.

There is a marked improvement in the results with respect to the IQG ones. In particular, the energy for the ground state is only 0.026 11 a.u. lower than that of the FCI and the relative error, 1.79/1000, can be considered a satisfactory result.

The results obtained with this approximation for the second-order RDM are reported in Table II. These results show that the difference with the FCI values is extremely small except for the elements $D_{2\bar{2},2\bar{2}}$, $D_{2\bar{2},2\bar{3}}$, and $D_{2\bar{3},2\bar{3}}$ and even these elements are considerably better than those obtained with the IQP and IQG approximations. Turning now to Table III it can be seen that the initial matrix which was already rather good is also improved.

Thus, to introduce relaxation into the IQG picture through a MT seems to be an adequate procedure, while the introduction of projectors can be used to separate the contribution from other eigenstates. The question now is how to optimize the combination of these two operations.

In what follows, we report the results of other calculations where other alternative ways of using the MT and projection steps have been carried out. The different approximations, tested for the ground state of the Be atom, can be described as follows.

(i) The initial $\underline{H}$ is projected by the set of QG's in which one of the bielectronic states implicit in the ground state is dominant. The QG's used here are those which diagonalize $\underline{H}$. Once this projection of H is done the MT is carried out to obtain a new H''. From its eigenvectors a set of QG will be selected in order to approximate D. This approximation will be called HPH.

(ii) The SRH matrix $\underline{H}'$ is projected into the selected subspace by using the QG's which diagonalize it. Afterwards a MT will again be carried out. The rest of the procedure is as previously described. This approximation

TABLE IV. Second-order reduced density matrix for the ground state of the Be atom. Other approximations are shown.

	$\lvert 1\bar{1}\rangle$	$\lvert 1\bar{2}\rangle$	$\lvert 1\bar{3}\rangle$	$\lvert 2\bar{2}\rangle$	$\lvert 2\bar{3}\rangle$	Approx.	Total energy (a.u.)
$\langle \bar{1}1 \rvert$	0.989	0.024	−0.043	$< 10^{-4}$	$< 10^{-4}$	H′PH′	−14.608 24
	0.988	0.004	0.028	$< 10^{-4}$	$< 10^{-4}$	HPH	−14.612 98
	0.994	0.011	0.007	$< 10^{-4}$	$< 10^{-4}$	HPHPH′	−14.570 24
	0.991	0.017	−0.038	$< 10^{-4}$	$< 10^{-4}$	H′H′	−14.593 67
	0.992	0.013	−0.032	$< 10^{-4}$	$< 10^{-4}$	hPh	−14.570 04
$\langle \bar{2}1 \rvert$		0.825	0.370	0.008	0.009		
		0.854	0.248	0.002	−0.002		
		0.844	0.345	0.015	−0.002		
		0.872	0.326	0.007	0.005		
		0.895	0.296	0.011	0.004		
$\langle \bar{3}1 \rvert$			0.172	0.006	0.003		
			0.145	0.045	0.024		
			0.153	0.015	0.008		
			0.124	0.006	0.002		
			0.100	$< 10^{-4}$	0.002		
$\langle \bar{2}2 \rvert$				0.770	0.285		
				0.618	0.316		
				0.602	0.322		
				0.823	0.262		
				0.812	0.267		
$\langle \bar{3}2 \rvert$					0.107		
					0.162		
					0.172		
					0.084		
					0.089		

is called H'PH'.

(iii) The SRH matrix $\underline{H}'$ obtained in the HPH approximation will again be projected into the selected subspace by using the QG's which diagonalize $\underline{H}'$. After this operation a MT will be performed. This approximation will be called HPHPH'.

(iv) The one-body initial reduced $\underline{h}$ is projected into the space corresponding to its two lowest eigenvectors for spin α and spin β, then the MT is carried out in order to obtain the two-body SRH matrix $\underline{H}'$. This approximation is denoted hPh.

(v) On the SRH matrix $\underline{H}'$ a second MT is applied. From the geminals diagonalizing the new SRH matrix a set is selected to form the RDM. This approximation will be called H'H'.

The results obtained by using these approximations are presented in Tables IV and V, which have been organized in a similar way to Tables II and III, respectively. Table IV collects the values for the most significant elements of the second-order RDM in the different approximations. In the last column of this table the total energy in each approximation is given.

The results obtained with the H'PH' approximation are very similar for the energy value as well as for the RDM to those obtained with the HPH' approximation. The HPH overemphasizes the correlation energy slightly more than the HPH' and H'PH', but the analysis of the values for the significant elements of the RDM's shows that in some elements the error is lower than in the mentioned approximations. The energy obtained with the HPHPH' hardly reaches the SCF one, however the RDM's are worth noting. Indeed, the elements $D_{2\bar{2},2\bar{2}}$ and $D_{2\bar{3},2\bar{3}}$ which in all the other approximations except the HPH appeared overestimated show here an inverted tendency. Moreover in the other elements the error is of the order of 0.02 which is rather acceptable.

TABLE V. First-order reduced density matrix for the ground state of the Be atom. Other approximations are shown.

	$\|1\rangle$	$\|2\rangle$	$\|3\rangle$	$\|4\rangle$	Approx.
$\langle 1\|$	0.996	0.017	−0.034	0.050	H'PH'
	0.998	0.011	0.011	0.041	HPH
	0.998	0.004	$<10^{-4}$	0.042	HPHPH'
	0.996	0.013	−0.032	0.051	H'H'
	0.996	0.013	−0.032	0.051	hPh
$\langle 2\|$		0.856	0.346	−0.039	
		0.785	0.368	−0.035	
		0.799	0.399	−0.036	
		0.891	0.308	−0.037	
		0.899	0.299	−0.036	
$\langle 3\|$			0.144	−0.017	
			0.213	−0.013	
			0.199	−0.017	
			0.108	−0.015	
			0.101	−0.014	
$\langle 4\|$				0.004	
				0.004	
				0.004	
				0.004	
				0.004	

The value obtained for the energy using the H'H' approximation is really good, as its error is 4×10^{-4}; on the other hand, the corresponding RDM's are poor when compared with the other approximation achievements. Finally, the hPh provides the worst results of the set both from the point of view of the energy and of the RDM's.

This analysis shows that the approximations HPH and the two very similar ones H'PH' and HPH' give very reasonable results. It seems that both the projections, those using the eigenvectors of $\underline{H}$ and those using the eigenvectors of $\underline{H}'$, bring in relevant information (or remove important contamination) which indicates the need for further research in this direction.

All the approximations studied in this section are ultimately IQG ones, even hPh where the matrix on which the MT is performed belongs to the one-body space. Indeed, the final step is to select the QG from the new set which diagonalizes the SRH matrix in order to approximate D with formula (2), the energy with formula (4), and the one-body RDM by reduction of D. Thus the improvement of the IQP model is also an open question which is being studied at present.

IV. THE N-REPRESENTABILITY AND THE SPIN INDEPENDENCY OF THE RDM

Although the RDM play an important role in our theory we do not consider the N-representability problem[7–10] to be the crucial point to be tackled. Given that the SRH matrices are clearly N-representable, and can be developed as an expression involving the RDM corresponding to all the eigenstates of a given symmetry, the problem in our opinion is shifted to that of separating the information concerning each eigenstate. Indeed, if this aim were exactly obtained for a given eigenstate, then the RDM would be exact and therefore N-representable.

However, while the N-representability of the exact RDM is evident, that of the approximated RDM's cannot be taken for granted. Hence, we have analyzed how well this property is fulfilled by the one-body RDM of the different approximations tried and previously reported. It was found that all the approximations gave rise to N-representable one-body RDM up to a good approximation. The most unfavorable case occurred for HPH where an eigenvalue was found to be equal to 1.004 85. In the HPH' approximation there was an eigenvalue equal to 1.000 11 and in all the other cases the excess over the value 1, if it occurred, was $<10^{-5}$. Another property that needs some comment concerns the way in which the values of the different elements of the 2-RDM depend upon the spin of the corresponding bielectronic configurations. The 2-RDM's obtained from the singlet full CI and from singlet Slater wave functions shows a spin independency of the values of the elements up to the third decimal. On the other hand, our approximated RDM's were in most cases spin independent only up to the second decimal. What is meant here by spin independency is that the values of the different elements depend only upon the space part of the corresponding bielectronic states, i.e., $D_{12,21}=D_{1\bar{2},\bar{2}1}$. It seems therefore that an averaging upon the spin variables should be included as a requirement into the method. This question has recently been solved by Karwowski and Duch and in a future publication the effect of this new requirement upon the RDM and consequently upon the energy will be analyzed.

V. CONCLUDING REMARKS

While in paper I of this series the attention was focused on the excitation energies of the QG's and QP's which, following similar ideas to those developed in many-body theory, can be interpreted as being the elementary excitations of our system. Here these same QG and QP lead us to the evaluation of the total energy and the electronic density.

Evidently more work is needed in order to optimize this method, however there are several conclusions which have already been drawn.

(1) The SRH matrices possess some outstanding formal properties described in paper I which guarantee that all the information needed about our system, for a given symmetry, is contained in them.

(2) In a given reduced, spin-adapted space the eigenvectors of the SRH matrices $\underline{h}'$ and $\underline{H}'$ describe states of one and two electrons, respectively, which can be considered "almost independent." These states give the averaged properties of our system.

(3) By exploiting their quasiindependent character, these states can be used to design a series of approximations. The optimization of this procedure to generate a very efficient method for obtaining accurate solutions. In the future this line of research will be studied fully.

(4) The spin independency, which is an essential property of the Hamiltonian when magnetic terms are absent from it, causes the correct RDM's to be averaged upon the spin variables, however our approximation provides RDM's which fulfill imperfectly this requirement. In the future the averaging upon the spin variables will be explicitly introduced into the method.

(5) The algorithm, which is being generalized for any number of electrons and any symmetry, is very economical both in time and in its needs for machine capacity. However, these technical questions have not yet been studied systematically.

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