PHYSICAL REVIEW A VOLUME 37, NUMBER 8 APRIL 15, 1988

Generalization to a pth-order space of the independent-pair model, within the spin-adapted reduced-Hamiltonian theoretical framework

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(Received 4 August 1987)

It is proposed that by evaluating pth-order spin-adapted reduced Hamiltonians and applying a model of independent groups of p electrons we can approximate the pth-order reduced density matrix (p-RDM). Subsequently this pth-order matrix is contracted to the corresponding 2-RDM. As a test example we calculate the total energy of the beryllium-atom isoelectronic sequence using an independent-trio model. The results, as expected, have a higher accuracy than those obtained with the independent-pair model.

I. INTRODUCTION

The spin-adapted reduced-Hamiltonian (SRH) theory allows us to obtain an N-representable Hamiltonian matrix of any order p with $p < N$.[1,2] Previously we obtained the algorithm[3] leading to the second-order spin-adapted reduced Hamiltonian (2-SRH). This matrix is therefore represented in a space of two electrons. We have proposed that the eigenvectors of this matrix can be considered to describe, in an average way, independent pairs of electrons. Based on this model we construct an approximate second-order reduced density matrix (2-RDM) for our N-electron system. Here we generalize this model and as an example we calculate the beryllium-atom isoelectronic series up to the Ar XV ion, with $p=3$.

In Sec. II we describe this generalized model and point out the changes that need to be made in the derivation of the algorithm. In Sec. III we report and discuss the results of our calculations.

II. MODEL OF INDEPENDENT GROUPS OF p ELECTRONS

In a similar manner to that described previously for the evaluation of the 2-SRH matrix one can obtain a pth-order one (p-SRH) which corresponds to a contraction to the p-electron space of the full configuration-interaction (FCI) Hamiltonian block matrix for a fixed spin symmetry. If $p=2$, as previously, this matrix contains all the relevant information about our N-electron system. However, as we did not know how to retrieve from this 2-SRH matrix the information concerning a particular eigenstate of our N-electron system we had to devise an approximate method to solve this problem. As the SRH matrices are obtained by an averaging process, we propose to interpret the eigenvectors of the 2-SRH matrix as describing pairs of electrons which, also in an average way, can be considered independent. This interpretation leads to a model in which the 2-RDM is a weighted sum of pair density matrices. With this approximation we have calculated several atomic systems and the results can be considered very good as well for the total energy as for the electronic densities.[4–6] However, if one is interested in spectra the accuracy of the results should be improved. Now if one obtains the 3-SRH,4-SRH, . . . ,p-SRH, and builds the 3-RDM,4-RDM, . . . ,p-RDM in a similar way to that in the 2-electron case, we see that the model is exact for $p=N$. Thus one can approach the problem of how to increase our accuracy by looking for the p-SRH, obtaining the p-RDM, and contracting this matrix to the corresponding 2-RDM and 1-RDM which are the physically relevant ones. In this paper we will focus our attention on the case of $p=3$ and $N=4$. We divide this section into two subsections. The first subsection concerns the 3-SRH matrix and the second one describes the independent-trio model (IT).

A. The 3-SRH matrix

In Ref. 3 we introduced the notation that will be used here with very small changes. The form of the 3-SRH matrix, which will be called $\underline{H}'$, is

$$\underline{H}'_{prt,qvu} = \sum_{\Lambda,\Omega} \sum_{i,j,k,l} H_{ij,kl}\, {}^2\underline{D}^{\Lambda\Omega}_{ij,kl}\, {}^3\underline{D}^{\Omega\Lambda}_{prt,qvu} , \tag{1}$$

where ${}^2\underline{D}$ and ${}^3\underline{D}$ are the 2-RDM and the 3-RDM. These matrices are of the form

$${}^2\underline{D}^{\Lambda\Omega}_{ij,kl} = \langle \Lambda \mid E_{ik}E_{jl} - \delta_{jk}E_{il} \mid \Omega \rangle \tag{2}$$

and

$${}^3\underline{D}^{\Omega\Lambda}_{prt,qvu} = \langle \Omega \mid E_{pq}E_{rv}E_{tu} - \delta_{tv}E_{pq}E_{ru} - \delta_{tq}E_{pu}E_{rv} - \delta_{rq}E_{pv}E_{tu} + \delta_{rq}\delta_{tv}E_{pu} + \delta_{ru}\delta_{tq}E_{pv} \mid \Lambda \rangle . \tag{3}$$

The symbols $\underline{H}$ and E have the following meaning: $\underline{H}_{ij,kl}$ (which was denoted in Ref. 3 as $\{ik\,|\,jl\}$) is the usually called reduced-Hamiltonian matrix[7–10] and the E's are the replacement operators[3,11,12] (also referred to as the unitary group generators[11]) which have the form

$$E_{il} \equiv \sum_{\sigma} b^{\dagger}_{i\sigma} b_{l\sigma} \; .$$

The $|\Lambda\rangle$ and $|\Omega\rangle$ states are N-electron configurations, eigenfunctions on S^2 and S_z for a given spin symmetry. By generalizing our notation[3] we can write (1) as

$$\underline{H}'_{prt,qvu} = \sum_{i,j,k,l} \underline{H}_{ij,kl} \left\langle \begin{matrix} ik,jl \\ pq,rv,tu \end{matrix} \right\rangle , \tag{4}$$

where

$$\left\langle \begin{matrix} ik,jl \\ pq,rv,tu \end{matrix} \right\rangle = \sum_{\Lambda} \langle \Lambda \,|\, (E_{ik}E_{jl} - \delta_{jk}E_{il})(E_{pq}E_{rv}E_{tu} - \delta_{tv}E_{pq}E_{ru} - \delta_{tq}E_{pu}E_{ru} - \delta_{rq}E_{pv}E_{tu} + \delta_{rq}\delta_{tv}E_{pu} + \delta_{ru}\delta_{tq}E_{pv}) \,|\, \Lambda \rangle \; . \tag{5}$$

The next step is to express the value of (5) as a function of (N,S,K,p,r,t,q,v,u), where S is the total spin quantum number and K is the number of space orbitals. Previously[3] we reported the general algorithm for the case of the 2-SRH. A similar procedure can be applied also in this case. Alternatively one can apply the formalism based on the spectral distribution method as it was developed by Nomura.[13]

B. The independent-trio model

The 3-SRH matrix once obtained is diagonalized. In line with the independent-pair (IP) model the corresponding eigenvectors of this matrix can be considered to describe in an average sense independent trios of electrons. Therefore, we may extend the method used in the IP model to the construction of the 3-RDM using these trios states. We then write

$${}^{3}\underline{D} = \sum_{I} n_I \, {}^{3}\underline{D}^{II} , \tag{6}$$

where ${}^{3}\underline{D}^{II}$ are full density matrices of three electrons in the eigenstate $|I\rangle$ of the 3-SRH. The occupation numbers n_I can be approximated in a similar way as previously[4–6] by making

$$n_I = \langle \Lambda \,|\, E_{pp}E_{rr}E_{tt} - \delta_{tr}E_{pp}E_{rr} - \delta_{tp}E_{pt}E_{rr} - \delta_{pr}E_{rr}E_{tt} \,|\, \Lambda \rangle \; , \tag{7}$$

where $|\Lambda\rangle$ is the dominant configuration in the N-electron state $|\mathscr{C}\rangle$ in which we are interested and (prt) is the trio dominant in $|I\rangle$.

Once the ${}^{3}\underline{D}$ for a particular $|\mathscr{C}\rangle$ is constructed it can be contracted to the corresponding 2-RDM by applying the following formula:

$${}^{2}\underline{D}_{ij,kl} = \sum_{t} {}^{3}\underline{D}_{ijt,klt} \frac{1}{(N-2)} \; . \tag{8}$$

Once we have ${}^{2}\underline{D}$ we can calculate with the usual procedure[4] the energy, the 1-RDM, and the test for the hypervirial theorem fulfillment.[14,15] A further approximation, the *HPH'*, can be evaluated for the 3-SRH in a similar manner as in the case of 2-SRH. This approximation consists of a projection on both sides of the initial matrix $\underline{H}$ appearing in (1) by the 2-RDM obtained with (8). This new $\underline{H}$ enters then into (4) and everything proceeds again in a similar manner. In Sec. III we report the results obtained for the isoelectronic series of the beryllium atom using the double zeta basis.[16]

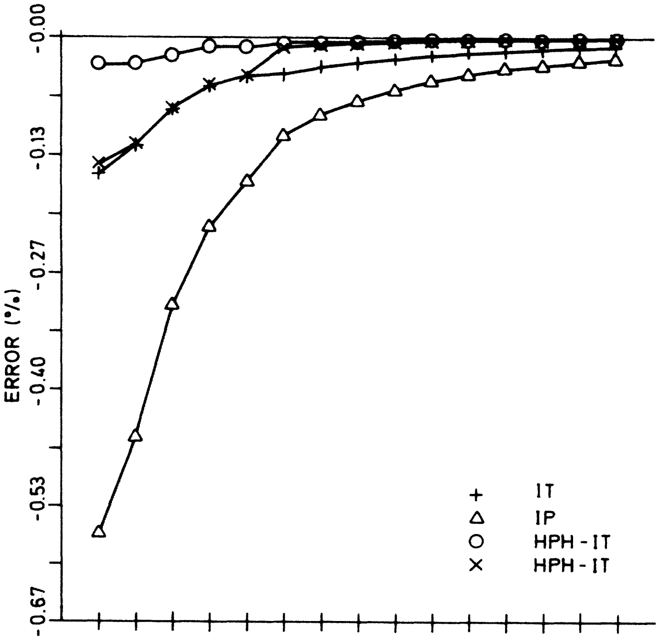

FIG. 1. Percent error of the ground-state total energy calculated with our approximation with respect to the FCI value.

III. RESULTS

In Table I we report the values of the total energy for the three lowest states of the beryllium (^1S) isoelectronic

TABLE I. Energies obtained using different methods (in a.u.).

Ion	State (^1S)	FCI	IT	IP	*HPH'*-IT	*HPH'*-IP
$_{4}$Be I	1	−14.5872	−14.6099	−14.6697	−14.5916	−14.6081
	2	−14.3014	−14.3348	−14.3805	−14.3277	−14.3472
	3	−13.9851	−13.9696	−13.9505	−13.9784	−13.9776
$_{5}$B II	1	−24.2484	−24.2783	−24.3586	−24.2555	−24.2775
	2	−23.3397	−23.3621	−23.4105	−23.3423	−23.3632
	3	−22.5253	−22.5096	−22.4675	−22.5177	−22.5067
$_{6}$C III	1	−36.4149	−36.4448	−36.5257	−36.4220	−36.4441
	2	−34.8018	−34.8213	−34.8668	−34.8167	−34.8131
	3	−33.3162	−33.3045	−33.2642	−33.3095	−33.2974
$_{7}$N IV	1	−51.0858	−51.1142	−51.1958	−51.0909	−51.1130
	2	−48.5165	−48.5323	−48.5760	−48.5280	−48.5167
	3	−46.1177	−46.1097	−46.0708	−46.1120	−46.0991
$_{8}$O V	1	−68.2520	−68.2825	−68.3641	−68.2590	−68.2809
	2	−64.5337	−64.5463	−64.5893	−64.5426	−64.5265
	3	−61.0227	−61.0169	−60.9784	−61.0175	−61.0039
$_{9}$F VI	1	−87.9479	−87.9845	−88.0466	−87.9533	−87.9577
	2	−75.2689	−75.1537	−75.2906	−78.1811	−75.1803
	3	−62.5764	−62.6357	−62.5841	−62.5797	−62.5505
$_{10}$Ne VII	1	−110.1248	−110.1621	−110.2229	−110.1302	−110.1342
	2	−94.2570	−94.1300	−94.2783	−94.1615	−94.1680
	3	−78.4042	−78.4613	−78.4104	−78.4066	−78.3766
$_{11}$Na VIII	1	−134.8022	−134.8408	−134.9003	−134.8078	−134.8118
	2	−115.5444	−115.4080	−115.5655	−115.4429	−115.4473
	3	−96.3372	−96.3907	−96.3424	−96.3388	−96.3099
$_{12}$MG IX	1	−161.9798	−162.0185	−162.0771	−161.9853	−161.9888
	2	−138.6710	−138.5211	−138.6918	−138.5605	−138.5805
	3	−115.4321	−115.4861	−115.4365	−115.4334	−115.4019
$_{13}$Al X	1	−191.6576	−191.6953	−191.7531	−191.6626	−191.6650
	2	−163.5592	−163.3913	−163.5793	−163.4364	−163.5104
	3	−135.5338	−135.5912	−135.5375	−135.5352	−135.4941
$_{14}$Si XI	1	−223.8356	−223.8733	−223.9302	−223.8405	−223.8422
	2	−190.8604	−190.6786	−190.8801	−190.7282	−190.8334
	3	−157.9752	−158.0328	−157.9782	−157.9763	−157.9285
$_{15}$P XII	1	−258.5138	−258.5505	−258.6069	−258.5182	−258.5191
	2	−219.6957	−219.4947	−219.7150	−219.5504	−219.9563
	3	−180.9653	−181.0272	−180.9682	−180.9668	−180.8478
$_{16}$S XIII	1	−295.6922	−295.7313	−295.7875	−295.6975	−295.7000
	2	−252.3861	−252.1844	−252.4062	−252.2408	−252.3362
	3	−209.2285	−209.2832	−209.2313	−209.2289	−209.1806
$_{17}$Cl XIV	1	−335.3705	−335.4080	−335.4636	−335.3751	−335.3761
	2	−285.1763	−284.9523	−285.1956	−285.0157	−285.3502
	3	−235.1187	−235.1783	−235.1209	−235.1195	−234.9620
$_{18}$Ar XV	1	−377.5489	−377.5858	−377.6410	−377.5533	−377.5536
	2	−320.3636	−320.1217	−320.3826	−320.1908	−321.1531
	3	−263.3168	−263.3792	−263.3190	−263.3178	−255.5566

sequence up to Ar XV. The values of the first, third, and fifth column have already been reported.[5] It can be seen that for the ground state the IT model brings a clear improvement. This improvement is most easily perceived in Fig. 1, where the percent error with respect to the full configuration interaction calculation is represented for each of the approximations considered. For the second states, which have a dominant open-shell configuration, the independent-pair model appears to be more suitable than the independent-trio one. This result is perhaps due to the fact that the choice of the suitable trio states and their occupation number is not so clear cut as in the

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

	$\|1\rangle$	$\|2\rangle$	$\|3\rangle$	$\|4\rangle$	Method
$\langle 1\|$	0.996	0.015	−0.028	0.045	FCI
	0.996	0.014	−0.028	0.047	IT
	0.996	0.018	−0.032	0.049	IP
	0.996	0.014	−0.030	0.048	*HPH'*-IT
	0.996	0.016	−0.032	0.050	*HPH'*-IP
$\langle 2\|$		0.823	0.375	−0.036	
		0.854	0.346	−0.037	
		0.863	0.323	−0.037	
		0.849	0.355	−0.038	
		0.854	0.348	−0.039	
$\langle 3\|$			0.176	−0.018	
			0.146	−0.017	
			0.137	−0.016	
			0.150	−0.018	
			0.145	−0.018	
$\langle 4\|$				0.004	
				0.004	
				0.004	
				0.004	
				0.004	

TABLE III. Some elements of the matrix ($\underline{P}_{ij}$) for the hypervirial test (Refs. 14 and 15) (beryllium-atom ground state).

	$\|2\rangle$	$\|3\rangle$	$\|4\rangle$	Method
$\langle 1\|$	0.000	0.000	0.000	FCI
	0.001	0.003	0.038	IT
	−0.033	0.017	0.101	IP
	0.006	−0.010	0.047	*HPH'*-IT
	−0.005	−0.007	0.082	*HPH'*-IP
$\langle 2\|$		0.000	0.000	
		−0.018	<0.001	
		−0.032	−0.012	
		−0.011	−0.006	
		−0.016	−0.017	
$\langle 3\|$			0.000	
			0.004	
			0.026	
			<0.001	
			0.006	

closed-shell case. Finally, in the third states one has to consider the IT and the *HPH'*-IT separately. Indeed, while the IT is better than IP only up to the O V ion, the *HPH'*-IT is better than *HPH'*-IP for the whole series and extremely close to the FCI result.

In Table II we report a typical result for the 1-RDM corresponding to the ground state of the beryllium atom. For simplicity we only give half of this symmetric matrix. The best results, when compared with the FCI one, correspond to the *HPH'*-IT and, next, to the IT ones. All the 1-RDM obtained were *N*-representable in a similar way as with the IP model. Finally, in Table III we give the upper half of the antisymmetric matrix $\underline{P}$ which measures the extent to which the 2-RDM fulfills the hypervirial theorem.[15,16] Although the case reported here corresponds to the ground state of the beryllium atom, this behavior has been found to be general. It can be seen that the hypervirial theorem is satisfactorily fulfilled in all the cases but particularly so in the *HPH'*-IT and IT cases.

These results confirm our expectation that to apply the independent-trio model, within the SRH theory, improves the accuracy when compared with the independent-pair model. We expect that the larger the number *p* of electrons the better the results will be. To increase *p* does not involve any serious formal difficulty just a technical one. Indeed, the dimension of the matrices to be handled is of $K^p \times K^p$ where *K* is the number of space orbitals. At present we are working at the optimization of all the mathematical steps involved so as to enlarge as much as possible the range of applicability of this approach.

ACKNOWLEDGMENT

We hereby gratefully acknowledge the support given to this work by the Comisión Asesora de Investigación Científica y Técnica (CAICyT) and the Universidad del País Vasco, Spain.

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