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Reduced Hamiltonians.
II: The size-consistency of reduced Hamiltonians defined in model spaces

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The link between the Absar–Coleman and the Valdemoro reduced Hamiltonian has been established. Further, a study of the size-consistency of approximations based on these Hamiltonians has been carried out. It is found that the energies obtained with reduced Hamiltonians that are defined in the full configuration interaction model spaces are not size consistent.

1. Introduction

In paper I of this series [1], the general structure of matrix elements corresponding to spin-nonadapted reduced Hamiltonians (RHs), as well as their relationship with spin-adapted reduced Hamiltonians (SRHs), was considered. The SRH introduced by Valdemoro [2–4] is defined by means of a contraction mapping [2–6] applied to an N-electron Hamiltonian acting in the antisymmetric and spin-adapted component of the N-fold tensorial product of a one-electron spin-orbital space. In the same way, the RH [1] is defined by the same kind of mapping applied to the antisymmetric component of the tensorial product space mentioned (i.e., the space spanned by $N \times N$ Slater determinants). Therefore, the definition of these reduced Hamiltonians reflects the properties of the model Hilbert space in which the original N-electron system is defined.

In contrast, the reduced Hamiltonian as originally introduced by Bopp [7] is defined independently of the Hilbert space in which the N-electron problem is mod-

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eled. This Hamiltonian was extensively studied [8–13] and although it was originally defined to be independent of the Hilbert space considered, in all practical calculations on many-electron systems a truncated Hamiltonian defined over a finite basis of spin-orbitals had to be used. This Hamiltonian yields, by contraction, the corresponding truncated one-body reduced Hamiltonian [12]. Since the finite-dimensional model space has to be employed in practical applications, its properties should be reflected by the corresponding reduced Hamiltonian in some way.

One would expect that although the definitions of these two kinds of reduced Hamiltonians are different, they should be interrelated. Surprisingly enough, as far as we know, there is little known in this regard. The only observation that has been made [4] indicates that for the singlet spin-symmetry adapted case, the eigenvectors of one-body SRH are the same as those of the Absar–Coleman one-body reduced Hamiltonian ${}^1K$ [10–12]. The Be atom in a double zeta (DZ) basis set [14] was used to exemplify this fact.

This paper is partially devoted to fill this gap. In particular, we will show that although in the case of the Be atom (in a DZ basis set), the eigenvectors of the one-body singlet-adapted reduced Hamiltonian (1-SRH) are the same as those of the ${}^1K$ Hamiltonian, this equality does not hold in general. Indeed, this equality is realized only in rather special circumstances. In contrast, we will show that the spin-nonadapted 1-RH and ${}^1K$ always fulfill this property.

It is worthwhile to emphasize that the eigenvectors of reduced Hamiltonians are the most useful objects yielded by these operators, since they may be used to calculate the energy and, in general, the physical properties of an N-electron system considered [4,10,12,13,15,16]. Thus, the study of properties of these eigenvectors is of primary interest. In the present paper, we consider the problem of size-consistency [17,18] of the eigenvectors of these reduced Hamiltonians. The lack of size-consistency is one of the typical liabilities of variational quantum-chemical methods. We will thus examine to what extent the eigenvectors corresponding to a system composed of several identical non-interacting subsystems are equal to a direct product of the eigenvectors of isolated subsystems [2]. We will see that the formalism based on the considered reduced Hamiltonians is not size-consistent, which implies that we must avoid a comparison of systems of different sizes when using approaches based on the eigenvectors of these reduced Hamiltonians.

The paper is organized as follows: In section 2 we present 1-SRH and 1-RH matrices defined in an orbital space. Since the ${}^1K$ operator is defined in a spin-orbital space [12], we proceed to its spin-integration in section 3. Then, we investigate the conditions that must be fulfilled by the 1-SRH and 1-RH in order to have the same eigenvectors as ${}^1K$. Finally, in section 4 we study the problem of size-consistency of eigenvectors in a truncated finite-dimensional Hilbert space, as

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[2] In fact, this definition corresponds to the N-consistency. The size-consistency is a more general property [18], but in practice, people use size-consistency as being synonymous with N-consistency.

well as the asymptotic behaviour when the Hilbert space is being completed. The effect of truncation when defining model spaces is also discussed.

2. One-body spin-adapted and spin-nonadapted reduced Hamiltonians

The $\lambda\gamma$-matrix element of the pth order spin-adapted reduced Hamiltonian can be written as follows [19,20]:

$$^{p}H'^{\lambda}_{\gamma} = \frac{1}{2}\,\frac{1}{p!}\sum_{ijkl}\{ij|kl\}\langle\langle\, {}^{2}E^{ik}_{jl}\, {}^{p}E^{\lambda}_{\gamma}\rangle\rangle\,, \tag{1}$$

where

$$\{ij|kl\} = \langle i(1)|\langle k(2)|\hat{h}_2(1,2)|l(2)\rangle|j(1)\rangle + \frac{1}{N-1}[\delta_{kl}\langle i(1)|\hat{h}_1(1)|j(1)\rangle + \delta_{ij}\langle k(1)|\hat{h}_1(1)|l(1)\rangle] \tag{2}$$

are generalized two-electron integrals. The indices i, j, k, l represent orbital labels; λ, γ are strings of orbital labels; ${}^{2}E^{ik}_{jl}, {}^{p}E^{\lambda}_{\gamma}$ are spin-free density operators and, $\langle\langle\ \rangle\rangle$ designates a trace evaluated in the antisymmetric and spin-adapted part $H^{A}(N, K, S, M)$ of the N-fold tensorial product of one-electron spin-orbital spaces, also called the FCI space. Equation (1) also applies to spin-nonadapted reduced Hamiltonians, in which case the trace is evaluated in the space $H^{A}(N,K)$ generated by Slater determinants, i.e. in the antisymmetric part of the N-fold tensorial product of one-electron spin-orbital spaces.

General formulas for matrix elements of this pth order reduced Hamiltonian were derived earlier [1,20]. In the particular case of $p = 1$, these reduced Hamiltonians have the form

$$(1-\mathrm{SRH})^{p}_{q} = s^{p}_{q} = (\{aa|d'd'\}F + \{ad'|d'a\}G)\delta_{pq} + \{aa|pq\}B + \{ap|qa\}C\,, \tag{3}$$

$$(1-\mathrm{RH})^{p}_{q} = r^{p}_{q} = \mu[aa|d'd']\delta_{pq} + \beta[aa|pq]\,. \tag{4}$$

Here, s^{p}_{q} and r^{p}_{q} designate the pq matrix element of the 1-SRH and 1-RH, respectively. The coefficients B, C, F, G, μ, β are given in the appendix. The remaining terms in eqs. (3) and (4) are the following combinations of generalized two-electron integrals:

$$\{aa|pq\} = \sum_{k}^{K}\{kk|pq\}\,, \tag{5}$$

$$\{ap|qa\} = \sum_{k}^{K}\{kp|qk\}\,, \tag{6}$$

$$\{aa|d'd'\} = \tfrac{1}{2}\sum_{kl}^{K}\{kk|ll\}, \tag{7}$$

$$\{ad'|d'a\} = \tfrac{1}{2}\sum_{kl}^{K}\{kl|lk\}, \tag{8}$$

$$[aa|pq] = \{aa|pq\} - \tfrac{1}{2}\{ap|qa\}, \tag{9}$$

$$[aa|d'd'] = \{aa|d'd'\} - \tfrac{1}{2}\{ad'|d'a\}. \tag{10}$$

3. Spin-free Absar-Coleman one-body reduced Hamiltonian and its relationship to the SRH and RH

For the Hamiltonian of a system of N identical fermions, involving only one- and two-particle interactions,

$$H = \sum_i h_1(i) + \sum_{i<j} h_2(i,j), \tag{11}$$

the energy of the system for a pure state $\mathcal{L}$ can be calculated by the well-known formula

$$E = \mathrm{Tr}({}^2K\,{}^2D^{\mathcal{L}}), \tag{12}$$

where ${}^2D^{\mathcal{L}}$ is the second-order reduced density matrix for the state $\mathcal{L}$ and ${}^2K$ is the corresponding reduced Hamiltonian [11,12,21],

$${}^2K = \frac{N}{2}[h_1(1) + h_1(2) + (N-1)h_2(1,2)]. \tag{13}$$

This reduced Hamiltonian, as pointed out in section 1, is defined independently of the Hilbert space employed. However, in all practical calculations on many-electron systems, a truncated Hamiltonian defined over a finite basis set of $r = 2K$ spin-orbitals has to be used. The resulting matrix is thus the representation of the operator given by eq. (13) in the antisymmetric geminal space, i.e., the antisymmetric two-fold tensorial product of one-electron spin-orbital spaces,

$$\begin{aligned} {}^2K^{ac}_{bd} = {} & \frac{N}{4}[h_{ab}\delta_{cd} - h_{ad}\delta_{cb} - h_{cb}\delta_{ad} + h_{cd}\delta_{ab}] \\ & + \frac{N(N-1)}{4}[(ab|cd) - (ad|cb)]. \end{aligned} \tag{14}$$

Here, h_{ij} and $(ij|kl)$ are standard one- and two-electron integrals involving spin-orbitals. The contraction of this tensor gives us the Absar–Coleman one-body reduced Hamiltonian ${}^1K$ [12],

$$
\begin{aligned}
{}^1K^a_b &= \sum_c^r {}^2K^{ac}_{bc} = \frac{N(r-2)}{4} h_{ab} + \frac{N}{4}\mathrm{Tr}(h)\delta_{ab} \\
&\quad + \frac{N(N-1)}{4}\sum_c^r [(ab|cc) - (ac|cb)] \,. \qquad (15)
\end{aligned}
$$

Since the original Hamiltonian, eq. (11), is spin-free, we can integrate over the spin variables to yield a spin-free, one-body reduced Hamiltonian. After some algebra that takes into account the orthogonality of spin functions, we get

$$
\begin{aligned}
{}^1K^p_q &= N(N-1)\left\{\frac{1}{(N-1)}[(K-1)h_{pq} + \mathrm{Tr}(h)\delta_{pq}] \right. \\
&\quad \left. + \sum_k^K [(pq|kk) - \tfrac{1}{2}(pk|kq)] \right\} , \qquad (16)
\end{aligned}
$$

where p, q, k are orbital labels and $K = r/2$ is the number of orbitals.

The definition of generalized two-electron integrals, eq. (2), allows us to write

$$
{}^1K^p_q = N(N-1)\sum_k^K [\{pq|kk\} - \tfrac{1}{2}\{pk|kq\}] \,. \qquad (17)
$$

Finally, eq. (9) enables a more compact expression for this operator, i.e.

$$
{}^1K^p_q = N(N-1)[pq|aa] \,. \qquad (18)
$$

A comparison of eqs. (4) and (18) then yields the relationship between these two types of reduced Hamiltonians, namely

$$
\begin{aligned}
r^p_q &= \mu[aa|a'a']\delta_{pq} + \frac{\beta}{N(N-1)}\, {}^1K^p_q \\
&= k_1\delta_{pq} + k_2\, {}^1K^p_q \,. \qquad (19)
\end{aligned}
$$

Equation (19) implies that $\hat{r}$ and ${}^1\hat{K}$ have the same eigenvectors. However, taking into the account that the eigenvectors of $\hat{s}$ and $\hat{r}$ are generally distinct, we must conclude that the eigenvectors of $\hat{s}$ and ${}^1\hat{K}$ (for all spin values, including $S = 0$) are generally also distinct, contrary to the results obtained earlier [4]. However the specific values of N and K in the very particular case of Be in a DZ basis model yield the B and C coefficients for $\hat{s}$ (in a singlet symmetry) fulfilling $B = -2C$, and then, the same eigenvectors for $\hat{s}$, $\hat{r}$ and ${}^1\hat{K}$. (See eqs. (3), (4) and (18).)

On the other hand, the results of Absar and Coleman [10] and Absar [12] suggest that the eigenvectors of ${}^1\hat{K}$ have a definite advantage in many chemical calculations when the comparison is made with the SCF orbitals, specially when excited states are studied. We can now provide a very simple explanation of this fact relying on eq. (19). This equation states that the eigenvalues of ${}^1\hat{K}$ are the same as those of $\hat{r}$, and $\hat{r}$ can be written [2–4] in terms of the one-body reduced density matrices of all states of our system as follows:

$$r^p_q = \sum_{\mathcal{L}} E_{\mathcal{L}} d^{\mathcal{L}}_{pq} \,. \tag{20}$$

The diagonalization of $\hat{r}$ gives eigenvectors that are "averaged" natural orbitals. It is well known that natural orbitals provide the fastest convergence of CI expansions. Thus, the approximate natural orbitals may also be expected to provide a fast convergence of these expansions.

4. The size-consistency problem

A typical shortcoming of many variational quantum chemical methods is that the energy of a dimer composed of two identical but noninteracting monomers (two monomers separated by a large distance will serve as an example of such a dimer) is not twice the energy of the isolated monomer. This lack of size-extensivity is present in any truncated configuration interaction method. In this case the deficiency is often exemplified [18] by a model of two noninteracting H_2 molecules treated by configuration interaction limited to double excitations (DCI). By definition, DCI wavefunction of each of the monomers involves double excitations within each monomer. When we restrict the supermolecule trial function to double excitations, we thus exclude the possibility that both monomers are simultaneously doubly excited, since this represents a quadruple excitation in the supermolecule. Then, the supermolecule wavefunction truncated at the DCI level does not have a sufficient flexibility to yield twice the DCI monomer energy.

A similar reasoning will lead us to conclude that there is a lack of size-consistency in spin-adapted reduced Hamiltonians based approaches. We take again the above example of two non-interacting H_2 molecules. Let us imagine that we are interested, for instance, in singlet spin-adapted states. When calculating an isolated monomer, the relevant FCI space of the N-electron system must be singlet spin-adapted. We expand the H_2 Hamiltonian in this space and the, by contraction, we get the corresponding SRH. The same spin symmetry has to be imposed on the Hilbert space of the dimer. Nevertheless, the dimer can reach the singlet symmetry not only by coupling two singlet hydrogen molecules, but also by coupling two triplet ones; this last possibility being excluded when calculating isolated monomers. We can thus state that the resulting SRH Hamiltonian lacks size consistency.

Since the above reasoning is based on spin-adaptation, one wonders whether the RH is size-consistent or not. The study of the consistency of the eigenvectors of RH (or those of ${}^1\hat{K}$, that are the same) is the aim of this section. We are interested in the eigenvectors because these are the quantities involved in the calculation of physical properties of N-electron systems [4].

Equations (9), (5), (6) and (2) applied to eq. (18) lead us to rewrite it as

$${}^1K^p_q = N\,\mathrm{Tr}(h)\delta_{pq} + N(N-1)\left[\frac{K-1}{N-1}h_{pq} + (aa|pq) - \tfrac{1}{2}(ap|qa)\right], \tag{21}$$

where $(aa|pq)$ and $(ap|qa)$ are defined as in eqs. (5) and (6), but involving standard two-electron integrals instead of generalized two-electron ones. Further, N is the number of electrons and K is the number of orbitals.

Note that ${}^1K^p_q$ has the same eigenvectors as the operators enclosed in brackets in eq. (21), which will be hereafter designated as $\mathbb{O}^p_q$. For an x-polymer formed by "x" noninteracting monomers, this operator has the form

$$\mathbb{O}^p_q(x) = \frac{xK-1}{xN-1} h_{pq} + (aa|pq) - \tfrac{1}{2}(ap|qa)\,. \tag{22}$$

In principle, p and q may be orbital labels belonging to two different monomers. However, if the monomers do not interact, all the integrals in eq. (22) vanish in this case. Then, the matrix representation of the operator $\mathbb{O}$ for the x-polymer is blocked. There are x identical blocks, each corresponding to one monomer. Consequently, the eigenvectors of this matrix are given by the direct product of eigenvectors associated with individual blocks. Unfortunately, these blocks are different from the matrix representation of $\mathbb{O}$ for an isolated monomer ($x = 1$ in eq. (22)). That proves that neither ${}^1\hat{K}$ nor $\hat{r}$ are size-consistent.

All the same, when the number of orbitals $K \to \infty$, i.e., when the Hilbert space becomes complete, ${}^1\hat{K}, \hat{r}$ and $\hat{s}$ have the same eigenvectors as the core Hamiltonian $\hat{h}_1(i)$ [22][3]. This means that they are size-consistent in a complete Hilbert space. Thus, the lack of size-consistency originates in a truncation of the complete infinite-dimensional Hilbert space to that defining the FCI model space in which practical problems have to be considered.

Equation (22) may be rewritten in a more convenient way as follows:

$$\mathbb{O}^p_q(x) = \frac{K-1/x}{N-1/x} h_{pq} + (aa|pq) - \tfrac{1}{2}(ap|qa)\,. \tag{23}$$

This expression leads us to predict "accidental" size-consistencies. One case is when $K = N$, we call it fortuitous size-consistency. Other more interesting cases arise when K and N are large enough so that 1 and $1/x$ may be neglected. In this case we have a "numerical" size-consistency. Also, eq. (23) tells us that the differential size-consistencies decrease when x increases.

We conclude that the lack of size-consistency of reduced Hamiltonians is a common, unavoidable failure of all operators of this kind, since in practical numerical calculations a finite-dimensional FCI space models an infinite-dimensional complete Hilbert space. Thus, the truncation of an infinite-dimensional complete Hilbert space to a finite-dimensional FCI space is responsible for the lack of size-consistency of reduced Hamiltonians.

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[3] The reader must not conclude that the eigenvectors of 2-RH and 2-SRH converge towards the ones of ${}^2K$ when the Hilbert space is completed. Indeed, the eigenvectors of 2-RH and those of 2-SRH converge towards the ones of $H(1,2) = h_1(1) + h_1(2) + h_2(1,2)$ [1,23] that are different from those of ${}^2K$, defined in eq. (13) (except for the obvious case of $N = 2$).

Appendix

Coefficient of one-electron reduced Hamiltonians

(a) Spin-adapted reduced Hamiltonian [19,20,24]:

$$F = \langle\langle n_1 n_2 n_3 \rangle\rangle_{N,K} ,$$

$$G = -\langle\langle n_1 n_2 n_3 \rangle\rangle_{N,K} + 2\langle\langle n_1 \rangle\rangle_{N-2,K-1} ,$$

$$B = -\langle\langle n_1 n_2 n_3 \rangle\rangle_{N,K} + 2\langle\langle n_1 \rangle\rangle_{N-2,K-1} + \langle\langle n_1 n_2 \rangle\rangle_{N,K} ,$$

$$C = \langle\langle n_1 n_2 n_3 \rangle\rangle_{N,K} - 3\langle\langle n_1 \rangle\rangle_{N-2,K-1} - \langle\langle n_1 n_2 \rangle\rangle_{N,K} + 2D(N-2, K-1) ,$$

$$\langle\langle n_1 n_2 n_3 \rangle\rangle_{N,K} = \frac{N(N-1)(N-2)}{K(K-1)(K-2)} D(0) - \frac{6(N-2)}{(K-1)(K-2)} D(1) ,$$

$$\langle\langle n_1 n_2 \rangle\rangle_{N,K} = \frac{N(N-1)}{K(K-1)} D(0) - \frac{2}{(K-1)} D(1) ,$$

$$\langle\langle n_1 \rangle\rangle_{N-2,K-1} = \frac{(N-2)}{(K-1)} D(1) ,$$

$$D(i) = D(N-2i, K-i, S) ,$$

$$D(N, K, S) = \frac{2S+1}{K+1} \binom{K+1}{\frac{1}{2}N - S} \binom{K+1}{\frac{1}{2}N + S + 1} ,$$

(b) Non spin-adapted reduced Hamiltonians [1]:

$$\beta = -\tfrac{1}{2}\langle\langle n_1 n_2 n_3 \rangle\rangle_{N,K} + \langle\langle n_1 n_2 \rangle\rangle_{N,K} ,$$

$$\mu = \langle\langle n_1 n_2 n_3 \rangle\rangle_{N,K} ,$$

$$\langle\langle n_1 n_2 \ldots n_p \rangle\rangle_{N,K} = 2^p \sum_{i=0}^{p} \binom{p}{i} \binom{2(K-p)}{N-p-i} .$$

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