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Contraction algorithms for third-order reduced density matrices: Symmetric group approach

A. Torre, L. Lain* and J. Millan
Departamento de Química Física, Facultad de Ciencias, Apdo. 644, E-48080 Bilbao, Spain

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In this work, we present the mapping formulae for the contraction of the third-order reduced density matrices represented in the basis of the irreducible representations (IR) of the symmetric group S_3 into the second-order ones which are represented in the basis of the IR of group S_2. These algorithms, which can be useful in several fields, have been applied for the approximation of reduced density matrices within the spin-adapted reduced Hamiltonian theory. Some results obtained with this procedure are also presented.

1. Introduction

The spin-adapted reduced Hamiltonian theory [1–3] has recently been shown to be a valuable approach to the study of the electronic structure of atoms and molecules. Using the eigenvectors of second-order spin-adapted reduced Hamiltonian matrices (2-SRH) and within the independent-pair (IP) model, a direct approximation of the second-order reduced density matrix (2-RDM) has been carried out, obtaining very satisfactory results in the study of light atoms, ions and small molecules [4–6]. A generalization of this model to that of independent groups of more than two electrons improves the accuracy of the calculations. Indeed, when the number of electrons g in the group approaches that of the system N, the model tends to that of the full configuration interaction (FCI) method. A preliminary calculation, using the eigenvectors of the third-order spin-adapted reduced Hamiltonian matrices (3-SRH) and the independent-trios (IT) model was carried out [7] and the results, obtained by an approximation of the third-order reduced density matrix (3-RDM), showed a marked improvement over those obtained using the IP model. So, the use of the three-electron space can be appropriate considering that good results have been obtained with no high computing expenses.

*To whom correspondence should be addressed.

Since the use of spin-adapted reduced Hamiltonian theory requires the diagonalization of the g-order spin-adapted reduced Hamiltonian matrices (g-SRH), it is convenient to reduce as much as possible the size of these matrices. For this purpose, the use of the spin-free formulation and the permutation symmetry is advisable. In view of this, a general algorithm to calculate the 3-SRH expressed according to the different irreducible representations (IR) of the symmetric group S_3, the permutation group of three objects, was reported [2]. In this way, using the IT model [7], a block factorized 3-RDM is also obtained.

Although the quality of the directly approximated 3-RDM is better than the directly approximated 2-RDM, for the study of observables it is sufficient to work in the two-electron space. So, once the 3-RDM has been calculated, the best procedure is to contract this permutation symmetry-adapted 3-RDM into the corresponding 2-RDM. Since this latter matrix is also represented in the basis of the IR of the S_2 group, the contraction involves some delicate algebra, which will be described here. The final formulae are useful for computational purposes. We have focused our attention mainly on spin-adapted reduced Hamiltonian theory, but these algorithms can also be applied in other fields such as spin-coupled valence bond theory [8] or coupled cluster techniques [9], where high-order RDM are needed.

The organization of this paper is as follows. In section 2, the notation and the necessary basic formalism are presented. In section 3, the contraction algorithms for each of the different cases are given. Finally, in section 4, we give a comparison between the results obtained with the IT and the IP models.

2. Notation and concepts

The generalized spin-free replacement operator of order g is [9–16]

$$ {}^{g}E^{i_1,\ldots,i_g}_{j_1,\ldots,j_g} = \sum_{\sigma_1} \cdots \sum_{\sigma_g} b^{+}_{i_1\sigma_1} \cdots b^{+}_{i_g\sigma_g} b_{j_g\sigma_g} \cdots b_{j_1\sigma_1}, \tag{1} $$

which is defined in terms of the creators/annihilators of an electron $b^{+}_{i\sigma}/b_{i\sigma}$, in orthonormal orbitals i with spin σ.

The non-relativistic Hamiltonian of an N-electron system can be expressed as a function of the second-order replacement operators [3],

$$ \hat{H} = \tfrac{1}{2} \sum_{i,j,k,l} \{ij\,|\,kl\}\, {}^{2}E^{ik}_{jl}. \tag{2} $$

In eq. (2), $\{ij\,|\,kl\}$ denote the effective two-electron integrals. For practical purposes, the one-electron integrals are transformed into two-electron ones so that they are included in the symbols $\{ij\,|\,kl\}$. In this way, only one matrix, $\{ij\,|\,kl\}$, is used to define the Hamiltonian $\hat{H}$, which simplifies the calculation of the g-SRH matrices [1].

In the following, $\Lambda, \Omega, \ldots$ will denote N-electron functions, eigenfunctions of the spin operators $\hat{S}^2$ and $\hat{S}_z$ for a given value of the total spin quantum number. A representation of the Hamiltonian (2) in the N-electron space is the full configuration interaction (FCI) matrix $\mathcal{H}_{\Lambda,\Omega}$. This matrix may be contracted to the g-electron space ($g < N$) and this contracted form is by definition a g-SRH matrix,

$$ {}^{g}H^{i_1,\ldots,i_g}_{j_1,\ldots,j_g} = \frac{1}{g!} \sum_{\Lambda,\Omega} \mathcal{H}_{\Lambda,\Omega} \left\langle \Lambda \middle| {}^{g}E^{i_1,\ldots,i_g}_{j_1,\ldots,j_g} \middle| \Omega \right\rangle. \tag{3} $$

The main property of the g-SRH matrices is that they can be written as

$$ {}^{g}\underline{H} = \sum_{\mathcal{L}} E_{\mathcal{L}} \, {}^{g}\underline{D}^{\mathcal{L}}, \tag{4} $$

where $E_{\mathcal{L}}$ stands for the energy of the eigenstate $|\mathcal{L}\rangle$ of the system and ${}^{g}D^{\mathcal{L}}$ is the g-RDM of the same state. This means that all the information about the N-electron system is contained in the g-SRH matrices, albeit the information concerning a given state $|\mathcal{L}\rangle$ cannot be extracted in a formally exact way. A very important feature of these matrices, which is what renders them useful, is that they can be directly and very efficiently constructed using just the integrals $\{ij|kl\}$, thereby avoiding a previous evaluation of the FCI matrix [1–3].

Our interpretation of the eigenvectors of the g-SRH matrices is that they describe groups of g-electrons which, on average, can be considered as independent [7]. This interpretation leads to the independent pair (IP) model for $g = 2$, the independent trio (IT) model for $g = 3$, etc. In these models, the reduced density matrix of order g corresponding to a given N-electron state is approximated by a weighted sum of density matrices corresponding to different states of a group of g-electrons. These states coincide with the eigenvectors of the g-SRH. Note that in this approach, the evaluation of the N-electron wave function is avoided.

The employment of the SRH theory as it has been presented would require the construction of g-SRH matrices and the corresponding g-RDM whose size, for a given basis set of K functions, is $K^g \times K^g$, and so a considerable expense in computer memory would be needed, mainly when a large basis set is used. Fortunately, these cumbersome limitations can be partially removed when the matrices are expressed in the basis functions of the IR of the symmetric group S_g. In these new basis sets the matrices are block factorized and an independent treatment of each block can be made.

3. The permutation symmetry-adapted contraction algorithm for the 3-RDM

Let us start by considering a general and simple contraction mapping from the g-RDM into 2-RDM. This is based on the well-known rule $\sum_{i,\sigma} b^{+}_{i\sigma} b_{i\sigma}$ = number of electrons, so that

$$\left\langle \mathcal{L} \middle| {}^2E^{pr}_{qs} \middle| \mathcal{L} \right\rangle = \frac{1}{N-2} \sum_l \left\langle \mathcal{L} \middle| {}^3E^{prl}_{qsl} \middle| \mathcal{L} \right\rangle$$

and so

$${}^2D^{pr}_{qs} = \sum_{i_3, i_4, \ldots, i_g} \frac{g!}{2!(N-g+1) \ldots (N-2)} {}^gD^{pri_3i_4,\ldots,i_g}_{qsi_3i_4,\ldots,i_g}, \tag{5}$$

where

$${}^2D^{pr}_{qs} = \frac{\langle \mathcal{L} | \, {}^2E^{pr}_{qs} \, | \mathcal{L} \rangle}{2!} \tag{6}$$

and

$${}^gD^{pri_3i_4,\ldots,i_g}_{qsi_3i_4,\ldots,i_g} = \frac{\langle \mathcal{L} | \, {}^gE^{pri_3i_4,\ldots,i_g}_{qsi_3i_4,\ldots,i_g} \, | \mathcal{L} \rangle}{g!} \tag{7}$$

are the 2-RDM and g-RDM, respectively, corresponding to a state $|\mathcal{L}\rangle$ (no further explicit reference needs to be made to the $|\mathcal{L}\rangle$ state, which has been included only for the sake of correctness).

In the expressions (5)–(7), the order of the upper and lower indices is not fixed. The 2-RDM and g-RDM are represented in a basis of simple products of orbitals, each of which is denoted by a single letter. Due to the anticommutation rules for Fermion operators, a simultaneous permutation of upper and lower indices leads to identical matrix elements (that is, ${}^2D^{pr}_{qs} = {}^2D^{rp}_{sq}$, but ${}^2D^{pr}_{qs} \neq {}^2D^{pr}_{sq}$). Later on, we will see that when a given order is imposed on the letters of the upper and lower indices, the meaning of the indices is changed.

Recalling the transformation formulae to the IR basis of the S_2 permutation group (see appendix), we have

(i) $p < r$ and $q < s$

$${}^2D^{pr}_{qs}(\pm) = {}^2D^{pr}_{qs} \pm {}^2D^{pr}_{sq}$$

in ${}^2D^{pr}_{qs}(\pm)$, the upper and lower indices represent the symmetric (+) (antisymmetric (−)) functions built from the products pr and qs. On the other hand, when no indication of the symmetry exists, as in ${}^2D^{pr}_{qs}$, these indices represent, as we have said, simple products. Because of (5), we may write

$${}^2D^{pr}_{qs}(\pm) = \frac{g!}{2!(N-g+1) \ldots (N-2)} \sum_{i_3, i_4, \ldots, i_g} \left({}^gD^{pri_3i_4,\ldots,i_g}_{qsi_3i_4,\ldots,i_g} \pm {}^gD^{pri_3i_4,\ldots,i_g}_{sqi_3i_4,\ldots,i_g} \right). \tag{8}$$

(ii) $p = r$ and $q < s$

$${}^2D^{pp}_{qs}(+) = \sqrt{2} \, {}^2D^{pp}_{qs},$$

so

$$ {}^2D^{pp}_{qs}(+) = \frac{g!}{\sqrt{2}(N-g+1)\ldots(N-2)} \sum_{i_3,i_4,\ldots,i_g} {}^gD^{ppi_3i_4,\ldots,i_g}_{qsi_3i_4,\ldots,i_g} \tag{9} $$

and

$$ {}^2D^{pp}_{qs}(-) = 0. $$

(iii) Finally, for $p = r$ and $q = s$,

$$ {}^2D^{pp}_{qq}(+) = {}^2D^{pp}_{qq} $$

and

$$ {}^2D^{pp}_{qq}(+) = \frac{g!}{2!(N-g+1)\ldots(N-2)} \sum_{i_3,i_4,\ldots,i_g} {}^gD^{ppi_3i_4,\ldots,i_g}_{qqi_3i_4,\ldots,i_g}. \tag{10} $$

Expressions (8)–(10) give us the block-factorized 2-RDM in terms of a g-RDM which is not symmetry-adapted (to the S_g symmetric group).

In order to obtain similar expressions involving S_g symmetry-adapted RDM, the specific basis functions of the IRs for each S_g are needed. We will develop the symmetry adaptation for the simplest case $g = 3$ which, as has been mentioned in the introduction, is required in spin-adapted reduced Hamiltonian theory as well as in other fields where the 3-RDM are employed.

Since the three-electron states are related only with the antisymmetric (B) and the two-dimensional (E) IRs of the group S_3, the totally symmetric (A) IR can be ignored (see appendix). So, the ${}^3D^{prl}_{qsl}$ matrix elements, in the sum $\sum_l {}^3D^{prl}_{qsl}$, must be expressed as a linear combination of the corresponding B- and E-adapted matrix elements. In what follows, the notation ${}^3D^{prl}_{qsu}(E1,E2)$ means that the upper trio indices denote a function of the $E1$ type and the lower trio ones a function of the $E2$ type. The symbols ${}^3D(B)$, ${}^3D(E1)$ and ${}^3D(E2)$ denote that both the upper and lower trios belong to the same type B, $E1$ or $E2$, respectively. In all cases related with the two-dimensional IR, the same component a or b must be used to express both trios, the upper and the lower one. Both possibilities lead to identical matrix elements but, obviously, the matrix elements obtained through a mixture of functions a and b would be zero.

Note that the symmetry adaptation implies an important reduction of the size of the matrices which must be handled. For a basis set of K orbitals, the order of the 3-RDM in the original basis is K^3, while the orders of the blocks B and E are $\binom{K}{3}$ and $2\binom{K}{3}+2\binom{K}{2}$, respectively.

Depending on relations among indices in the trios, we can distinguish several types of ${}^3D^{prl}_{qsl}$ matrix elements:

(i-1) $p < r < l$ and $q < s < l$

$$ {}^3D^{prl}_{qsl} + {}^3D^{prl}_{sql} = \frac{2}{3}\,{}^3D^{prl}_{qsl}(E1), $$

$$ {}^3D^{prl}_{qsl} - {}^3D^{prl}_{sql} = \frac{1}{3}\left[{}^3D^{prl}_{qsl}(B) + 2\,{}^3D^{prl}_{qsl}(E2)\right]; $$

(i-2) $p < r < l$ and $q < s = l$

$$^3D^{prs}_{qss} + {}^3D^{prs}_{sqs} = -\frac{\sqrt{2}}{3}\,{}^3D^{prs}_{qss}(E1),$$

$$^3D^{prs}_{qss} - {}^3D^{prs}_{sqs} = \sqrt{\frac{2}{3}}\,{}^3D^{prs}_{qss}(E2, E1);$$

(i-3) $p < r < l$ and $q < l < s$

$$^3D^{prl}_{qsl} + {}^3D^{prl}_{sql} = -\frac{1}{3}\,{}^3D^{prl}_{qls}(E1) - \frac{1}{\sqrt{3}}\,{}^3D^{prl}_{qls}(E1, E2),$$

$$^3D^{prl}_{qsl} - {}^3D^{prl}_{sql} = -\frac{1}{3}\,{}^3D^{prl}_{qls}(B) + \frac{1}{3}\,{}^3D^{prl}_{qls}(E2) - \frac{1}{\sqrt{3}}\,{}^3D^{prl}_{qls}(E2, E1);$$

(i-4) $p < r < l$ and $q = l < s$

$$^3D^{prq}_{qsq} + {}^3D^{prq}_{sqq} = -\frac{\sqrt{2}}{3}\,{}^3D^{prq}_{qqs}(E1),$$

$$^3D^{prq}_{qsq} - {}^3D^{prq}_{sqq} = -\sqrt{\frac{2}{3}}\,{}^3D^{prq}_{qqs}(E2, E1);$$

(i-5) $p < r < l$ and $l < q < s$

$$^3D^{prl}_{qsl} + {}^3D^{prl}_{sql} = -\frac{1}{3}\,{}^3D^{prl}_{lqs}(E1) + \frac{1}{\sqrt{3}}\,{}^3D^{prl}_{lqs}(E1, E2),$$

$$^3D^{prl}_{qsl} - {}^3D^{prl}_{sql} = \frac{1}{3}\,{}^3D^{prl}_{lqs}(B) - \frac{1}{3}\,{}^3D^{prl}_{lqs}(E2) - \frac{1}{\sqrt{3}}\,{}^3D^{prl}_{lqs}(E2, E1);$$

(i-6) $p < r = l$ and $q < s = l$

$$^3D^{prr}_{qrr} + {}^3D^{prr}_{rqr} = \frac{1}{3}\,{}^3D^{prr}_{qrr}(E1),$$

$$^3D^{prr}_{qrr} - {}^3D^{prr}_{rqr} = {}^3D^{prr}_{qrr}(E1);$$

(i-7) $p < r = l$ and $q < l < s$

$$^3D^{prr}_{qsr} + {}^3D^{prr}_{sqr} = \frac{\sqrt{2}}{6}\,{}^3D^{prr}_{qrs}(E1) + \frac{1}{\sqrt{6}}\,{}^3D^{prr}_{qrs}(E1, E2),$$

$$^3D^{prr}_{qsr} - {}^3D^{prr}_{sqr} = \frac{1}{\sqrt{2}}\left[-\,{}^3D^{prr}_{qrs}(E1) + \frac{1}{\sqrt{3}}\,{}^3D^{prr}_{qrs}(E1, E2)\right];$$

(i-8) $p < r = l$ and $q = l < s$

$$^3D^{prr}_{rsr} + {}^3D^{prr}_{srr} = \frac{1}{3}\,{}^3D^{prr}_{rrs}(E1),$$

$$^3D^{prr}_{rsr} - {}^3D^{prr}_{srr} = -\,{}^3D^{prr}_{rrs}(E1);$$

(i-9) $p < r = l$ and $l < q < s$

$$^3D^{prr}_{qsr} + {}^3D^{prr}_{sqr} = \frac{\sqrt{2}}{6}\,{}^3D^{prr}_{rqs}(E1) - \frac{1}{\sqrt{6}}\,{}^3D^{prr}_{rqs}(E1, E2),$$

$$^3D^{prr}_{qsr} - {}^3D^{prr}_{sqr} = -\,\frac{1}{\sqrt{2}}\left[\,{}^3D^{prr}_{rqs}(E1) + \frac{1}{\sqrt{3}}\,{}^3D^{prr}_{rqs}(E1, E2)\right];$$

(i-10) $p < l < r$ and $q < l < s$

$$^3D^{prl}_{qsl} + {}^3D^{prl}_{sql} = \frac{1}{6}\,{}^3D^{plr}_{qls}(E1) + \frac{1}{2}\,{}^3D^{plr}_{qls}(E2) + \frac{1}{2\sqrt{3}}\,{}^3D^{plr}_{qls}(E1, E2) + \frac{1}{2\sqrt{3}}\,{}^3D^{plr}_{qls}(E2, E1),$$

$$^3D^{prl}_{qsl} - {}^3D^{prl}_{sql} = \frac{1}{3}\,{}^3D^{plr}_{qls}(B) + \frac{1}{2}\,{}^3D^{plr}_{qls}(E1) + \frac{1}{6}\,{}^3D^{plr}_{qls}(E2) - \frac{1}{2\sqrt{3}}\,{}^3D^{plr}_{qls}(E1, E2) - \frac{1}{2\sqrt{3}}\,{}^3D^{plr}_{qls}(E2, E1);$$

(i-11) $p < l < r$ and $q = l < s$

$$^3D^{prq}_{qsq} + {}^3D^{prq}_{sqq} = \frac{\sqrt{2}}{6}\,{}^3D^{pqr}_{qqs}(E1) + \frac{1}{\sqrt{6}}\,{}^3D^{pqr}_{qqs}(E2, E1),$$

$$^3D^{prq}_{qsq} - {}^3D^{prq}_{sqq} = \frac{1}{\sqrt{2}}\left[\,{}^3D^{pqr}_{qqs}(E1) - \frac{1}{\sqrt{3}}\,{}^3D^{pqr}_{qqs}(E2, E1)\right];$$

(i-12) $p < l < r$ and $l < q < s$

$$^3D^{prl}_{qsl} + {}^3D^{prl}_{sql} = \frac{1}{6}\,{}^3D^{plr}_{lqs}(E1) - \frac{1}{2}\,{}^3D^{plr}_{lqs}(E2) - \frac{1}{2\sqrt{3}}\,{}^3D^{plr}_{lqs}(E1, E2) + \frac{1}{2\sqrt{3}}\,{}^3D^{plr}_{lqs}(E2, E1),$$

$$^3D^{prl}_{qsl} - {}^3D^{prl}_{sql} = -\frac{1}{3}\,{}^3D^{plr}_{lqs}(B) + \frac{1}{2}\,{}^3D^{plr}_{lqs}(E1) - \frac{1}{6}\,{}^3D^{plr}_{lqs}(E2) + \frac{1}{2\sqrt{3}}\,{}^3D^{plr}_{lqs}(E1,E2) - \frac{1}{2\sqrt{3}}\,{}^3D^{plr}_{lqs}(E2,E1);$$

(i-13) $p = l < r$ and $q = l < s$

$$^3D^{prp}_{psp} + {}^3D^{prp}_{spp} = \frac{1}{3}\,{}^3D^{ppr}_{pps}(E1),$$

$$^3D^{prp}_{psp} - {}^3D^{prp}_{spp} = {}^3D^{ppr}_{pps}(E1);$$

(i-14) $p = l < r$ and $l < q < s$

$$^3D^{prp}_{qsp} + {}^3D^{prp}_{sqp} = \frac{\sqrt{2}}{6}\,{}^3D^{ppr}_{pqs}(E1) - \frac{1}{\sqrt{6}}\,{}^3D^{ppr}_{pqs}(E1,E2),$$

$$^3D^{prp}_{qsp} - {}^3D^{prp}_{sqp} = \frac{1}{\sqrt{2}}\left[\,{}^3D^{ppr}_{pqs}(E1) + \frac{1}{\sqrt{3}}\,{}^3D^{ppr}_{pqs}(E1,E2)\right];$$

(i-15) $l < p < r$ and $l < q < s$

$$^3D^{prl}_{qsl} + {}^3D^{prl}_{sql} = \frac{1}{6}\,{}^3D^{lpr}_{lqs}(E1) + \frac{1}{2}\,{}^3D^{lpr}_{lqs}(E2) - \frac{1}{2\sqrt{3}}\,{}^3D^{lpr}_{lqs}(E1,E2) - \frac{1}{2\sqrt{3}}\,{}^3D^{lpr}_{lqs}(E2,E1),$$

$$^3D^{prl}_{qsl} - {}^3D^{prl}_{sql} = \frac{1}{3}\,{}^3D^{lpr}_{lqs}(B) + \frac{1}{2}\,{}^3D^{lpr}_{lqs}(E1) + \frac{1}{6}\,{}^3D^{lpr}_{lqs}(E2) + \frac{1}{2\sqrt{3}}\,{}^3D^{lpr}_{lqs}(E1,E2) + \frac{1}{2\sqrt{3}}\,{}^3D^{lpr}_{lqs}(E2,E1).$$

(ii-1) $p < l$ and $q < s < l$

$$^3D^{ppl}_{qsl} = \frac{\sqrt{2}}{3}\,{}^3D^{ppl}_{qsl}(E1);$$

(ii-2) $p < l$ and $q < s = l$

$$^3D^{pps}_{qss} = -\frac{1}{3}\,{}^3D^{pps}_{qss}(E1);$$

(ii-3) $p < l$ and $q < l < s$

$$^3D^{ppl}_{qsl} = -\frac{\sqrt{2}}{6}\,{}^3D^{ppl}_{qls}(E1) - \frac{1}{\sqrt{6}}\,{}^3D^{ppl}_{qls}(E1, E2);$$

(ii-4) $p < l$ and $q = l < s$

$$^3D^{ppq}_{qsq} = -\frac{1}{3}\,{}^3D^{ppq}_{qqs}(E1);$$

(ii-5) $p < l$ and $l < q < s$

$$^3D^{ppl}_{qsl} = -\frac{\sqrt{2}}{6}\,{}^3D^{ppl}_{lqs}(E1) + \frac{1}{\sqrt{6}}\,{}^3D^{ppl}_{lqs}(E1, E2);$$

(ii-6) $l < p$ and $q < s < l$

$$^3D^{ppl}_{qsl} = \frac{\sqrt{2}}{3}\,{}^3D^{lpp}_{qsl}(E1);$$

(ii-7) $l < p$ and $q < s = l$

$$^3D^{pps}_{qss} = -\frac{1}{3}\,{}^3D^{spp}_{qss}(E1);$$

(ii-8) $l < p$ and $q < l < s$

$$^3D^{ppl}_{qsl} = -\frac{\sqrt{2}}{6}\,{}^3D^{lpp}_{qls}(E1) - \frac{1}{\sqrt{6}}\,{}^3D^{lpp}_{qls}(E1, E2);$$

(ii-9) $l < p$ and $q = l < s$

$$^3D^{ppq}_{qsq} = -\frac{1}{3}\,{}^3D^{qpp}_{qqs}(E1);$$

(ii-10) $l < p$ and $l < q < s$

$$^3D^{ppl}_{qsl} = -\frac{\sqrt{2}}{6}\,{}^3D^{lpp}_{lqs}(E1) + \frac{1}{\sqrt{6}}\,{}^3D^{lpp}_{lqs}(E1, E2).$$

(iii-1) $p < l$ and $q < l$

$$^3D^{ppl}_{qql} = \frac{2}{3}\,{}^3D^{ppl}_{qql}(E1);$$

(iii-2) $p < l$ and $l < q$

$$^3D^{ppl}_{qql} = \frac{2}{3}\,{}^3D^{ppl}_{lqq}(E1);$$

(iii-3) $l < p$ and $l < q$

$$^3D^{ppl}_{qql} = \frac{2}{3}\,{}^3D^{lpp}_{lqq}(E1).$$

4. Results and comments

Table 1 describes the energies of some excited states (called 1 and 2) of some first-row atoms (the corresponding ground-state energies have been previously reported [17]). The experimental energies are those reported by Moore [18] or, in the beryllium case, those obtained from the full configuration interaction (FCI) method [4]. In all cases, the relativistic correction [19] has been subtracted in order to establish an appropriate comparison with our methods. The calculated energies have been obtained using the double-zeta basis sets reported by Clementi et al. [20]; previously, the initial Slater functions were transformed to an orthonormal set.

Table 1

Energies (in a.u.) for two excited states of the first-row atoms obtained with the IP and the IT models. Columns 4 and 6 mean the standard deviation according to formula (12).

Atom	Exptal.	IP	σ_{IP}	IT	σ_{IT}
Be(^{1}S)1	− 14.3014	− 14.3805	0.034	− 14.3364	0.009
Be(^{1}S)2	− 13.9851	− 13.9505	0.040	− 13. 9696	0.015
B(^{4}P)1	− 24.5209	− 24.6928	0.052	− 24.6001	0.033
B(^{2}D)2	− 24.4341	− 24.5764	0.049	− 24.4693	0.030
C(^{1}D)1	− 37.7855	− 38.1574	0.048	− 37.9570	0.036
C(^{5}S)2	− 37.6782	− 37.9993	0.059	− 37.8750	0.041
N(^{2}D)1	− 54.4974	− 55.0543	0.044	− 54.7909	0.035
N(^{2}P)2	− 54.4536	− 55.0414	0.050	− 54.7764	0.039
O(^{1}D)1	− 74.9887	− 75.7624	0.044	− 75.4791	0.036
O(^{1}S)2	− 74.9071	− 75.7604	0.049	− 75.4789	0.040

Column 3 describes the results obtained through a direct approximation of 2-RDM handling the eigenvectors of 2-SRH. The results in column 5 have been obtained approximating the 3-RDM and contracting this matrix to the two-electron space through the algorithm reported in section 3.

The quality of the results is analyzed by comparison with the experimental values and through the test of the hypervirial theorem. When this theorem is applied to the first-order replacement operator ${}^1E^i_j$, the following is obtained:

$$P_{ij} = \langle \mathcal{L} | [\hat{H}, {}^1E^i_j] | \mathcal{L} \rangle = \sum_l [{}^0\underline{H}, {}^2\underline{D}]_{il,jl}, \tag{11}$$

where ${}^0H^{ik}_{jl} = \{ij|kl\}$.

All of the matrix elements P_{ij} must be zero when the 2-RDM is the exact one, so the deviation from zero of these elements must be an appropriate criterion to evaluate the quality of the approximation used. In other words, $\underline{P}$ is a kind of error matrix. If the basis set has K functions, the mean σ_P of the matrix elements P_{ij} is

$$\sigma_P = \left(\frac{\sum_{i,j} P^2_{ij}}{K^2} \right)^{1/2} \tag{12}$$

and its values are written in columns 4 and 6 of table 1. These results, as well as the energies, point out a better behaviour of the IT model.

Appendix. The basis functions of the irreducible representations in the permutation groups S_2 and S_3

Group S_2 has two irreducible representations. The basis functions for the symmetric representation are [1]

$$(pq;+) = \frac{1}{\sqrt{2}}(pq + qp), \quad p < q; \tag{13}$$

$$(pp;+) = pp \tag{14}$$

and for the antisymmetric one

$$(pq;-) = \frac{1}{\sqrt{2}}(pq - qp), \quad p < q, \tag{15}$$

where pq means the product of orbitals p and q.

Group S_3 has three irreducible representations, a totally symmetric one A, one-dimensional; a totally antisymmetric one B, also one-dimensional, and a two-dimensional one E. Their basis functions are [2]

(i) *Representation A*

$$(ppp; A) = ppp, \tag{16}$$

$$(ppr; A) = \frac{1}{\sqrt{3}}(ppr + prp + rpp), \quad p < r, \tag{17}$$

$$(prr; A) = \frac{1}{\sqrt{3}}(prr + rpr + rrp), \qquad p < r, \tag{18}$$

$$(prl; A) = \frac{1}{\sqrt{6}}(prl + rlp + lpr + rpl + plr + lrp), \quad p < r < l. \tag{19}$$

Due to the Pauli principle, a three-electron space function cannot belong to this symmetry.

(ii) *Representation B*

$$(prl; B) = \frac{1}{\sqrt{6}}(prl + rlp + lpr - rpl - plr - lrp), \quad p < r < l. \tag{20}$$

(iii) *Representation E*

$$\begin{pmatrix}(ppr; E1a)\\(ppr; E1b)\end{pmatrix} = \frac{1}{\sqrt{6}}\begin{pmatrix}1 & 0\\0 & \sqrt{3}\end{pmatrix}\left[\begin{pmatrix}2\\0\end{pmatrix}ppr + \begin{pmatrix}-1\\1\end{pmatrix}prp + \begin{pmatrix}-1\\-1\end{pmatrix}rpp\right], \; p < r; \tag{21}$$

$$\begin{pmatrix}(prr; E1a)\\(prr; E1b)\end{pmatrix} = \frac{1}{\sqrt{6}}\begin{pmatrix}1 & 0\\0 & \sqrt{3}\end{pmatrix}\left[\begin{pmatrix}2\\0\end{pmatrix}rrp + \begin{pmatrix}-1\\1\end{pmatrix}rpr + \begin{pmatrix}-1\\-1\end{pmatrix}prr\right], \; p < r; \tag{22}$$

$$\begin{pmatrix}(prl; E1a)\\(prl; E1b)\end{pmatrix} = \frac{1}{\sqrt{12}}\begin{pmatrix}1 & 0\\0 & \sqrt{3}\end{pmatrix}\left[\begin{pmatrix}2\\0\end{pmatrix}(prl + rpl), \right.$$
$$\left. + \begin{pmatrix}-1\\1\end{pmatrix}(rlp + plr) + \begin{pmatrix}-1\\-1\end{pmatrix}(lpr + lrp)\right], \qquad p < r < l; \tag{23}$$

$$\begin{pmatrix}(prl; E2a)\\(prl; E2b)\end{pmatrix} = \frac{1}{\sqrt{12}}\begin{pmatrix}\sqrt{3} & 0\\0 & -1\end{pmatrix}\left[\begin{pmatrix}0\\2\end{pmatrix}(prl - rpl), \right.$$
$$\left. + \begin{pmatrix}1\\-1\end{pmatrix}(rlp - plr) + \begin{pmatrix}-1\\-1\end{pmatrix}(lpr - lrp)\right], \qquad p < r < l, \tag{24}$$

where *prl*, *prr*, *ppr*, etc. are simple products of the corresponding functions and *a* and *b* label the two components of the two-dimensional representation *E*.

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