

## Spin-adapted reduced Hamiltonian. I. Elementary excitations

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The spin-adapted  $p$ th-order reduced Hamiltonians (SRH) are obtained for an  $m$ -electron system, within the formalism of second quantization. This transformation is applied to the usual many-body Hamiltonian and involves an augmenting mapping, a spin projection, and a reducing mapping into the  $p$ -body reduced space. These three operations are combined into a single algorithm, allowing the work to be carried out within the two-body space. The SRH matrices thus obtained (1) have the same trace as that of the corresponding full configuration-interaction (CI) matrix, and (2) can be written as expansions involving the  $p$  eigenvalues and the corresponding  $p$ th-order reduced density matrices (RDM) of the  $m$ -body system in the chosen spin symmetry. Both of these properties guarantee that *all* and *only* the relevant information about our system is contained in the SRH matrices (and the SRH operators). The excitations of the eigenstates of the 1-SRH and the 2-SRH can be interpreted as the normal modes (or elementary excitations) of our electronic system in a given symmetry. A preliminary calculation on the Be atom yields encouraging results when compared with experiment. In the following paper (paper II of this series) the theory is applied to obtain the total energy and the reduced density matrices.

## I. INTRODUCTION

The interest in the  $p$ th-order reduced density matrix ( $p$ -RDM) which has been generated since 1955 (Refs. 1–11) is well known. This interest was due not only to the important formal properties of these matrices but mainly because the 2-RDM could serve as a substitute for the  $m$ -body wave functions in computation, thus reducing the dimensionality of the space in which one had to work, when studying atoms and molecules.

In 1964 the theorem of Hohenberg and Kohn<sup>12</sup> initiated a related trend of work: The search for the density functionals of the energy.<sup>13</sup> Recently, the connection between the density matrix in a finite-dimensional representation and the general formalism of the density functionals has been analyzed in detail.<sup>14</sup>

Another related line of research, that of the reduced Hamiltonian, was initiated long ago<sup>15</sup> and pursued with promising results later on.<sup>16–19</sup> The method we present here can be related to this latter line of research. It is based upon obtaining spin-adapted reduced Hamiltonians using the second-quantization formalism. The spin-adaptation process and the reduction of the Hamiltonian to the one- or two-body space is performed with the help of reducing and augmenting mappings found as a natural consequence of the properties of fermion operators in the second quantization formalism.<sup>20</sup>

The spin projection can be carried on upon a space spanned by eigenfunctions of the  $m$ -electron  $S^2$  and  $S_z$  operators or just of the  $S_z$  operator. Although the spin projection is performed in the  $m$ -electron space, a condensing algorithm has been found which allows one to work always within the reduced two-body space.<sup>21</sup>

The eigenvectors of the one-body reduced Hamiltonian can be considered as the quasiparticles of the system in a

given symmetry while the eigenvectors of the two-body reduced Hamiltonians are the quasigeminals. The excitation energies of these quasiparticles and quasigeminals can be interpreted as the elementary excitations of our system. Here a preliminary calculation is carried out on the beryllium atom, and the agreement obtained with experimentally determined values is very encouraging.

In Sec. II we give a survey of previous theoretical results. In particular, we give the two mapping relations which constitute the core of this theory. In Sec. III the method for obtaining the spin-adapted reduced Hamiltonian (SRH) is described. A physical interpretation of the energy spectra of the SRH matrices together with some comments upon their form are given in Sec. IV. In Sec. V we present the results of the calculation comparing them with experimental data and with the results of an equivalent full configuration-interaction (CI) calculation.<sup>22</sup> Some general comments are given in Sec. VI. An appendix is included in order to render the work self-contained.

In the following paper (paper II) the use of the SRH in obtaining reduced density matrices and total energies of the system will be considered.

## II. A SURVEY OF PREVIOUS THEORETICAL RESULTS

(i) A summary of our notation is given below.

Unless otherwise stated,  $i, j, k, \dots$  label one-electron states;  $\lambda, \gamma, \eta, \dots$  label two-electron Slater-determinant states;  $\Lambda, \Omega, \Gamma, \dots$  label  $m$ -electron (or  $p$ -electron with  $p > 2$ ) eigenfunctions either of  $S^2, S_z$  or just of  $S_z$ ;  $I, J, K, \dots$  label in general two-electron eigenstates of the Hamiltonian matrices; and  $\mathcal{L}, \mathcal{L}', \dots$  label either a general  $m$ -electron state or in particular eigenstates of the full CI Hamiltonian matrix.

The main symbols used are the following:  $\langle \lambda | b_i^\dagger b_j | \gamma \rangle = d_{ij}^{\lambda\gamma}$ , element  $(i, j)$  of the transition 1-RDM from  $|\gamma\rangle$  to  $\langle \lambda |$ ;  $\langle \lambda | b_i b_j^\dagger | \gamma \rangle = \bar{d}_{ij}^{\lambda\gamma}$ , the same but for holes;  $\langle \Lambda | B_\lambda^\dagger B_\gamma | \Omega \rangle = \underline{D}_{\lambda\gamma}^{\Lambda\Omega}$ , element  $(\lambda, \gamma)$  of the transition 2-RDM from  $|\Omega\rangle$  to  $\langle \Lambda |$ ;  $\langle \Lambda | B_\lambda B_\gamma^\dagger | \Omega \rangle = \bar{\underline{D}}_{\lambda\gamma}^{\Lambda\Omega}$ , the same as before but for holes.

A  $p$ -RDM or a  $p$ -electron operator will be denoted as  ${}^pD$  or  ${}^pB$ , respectively.

$\langle \mathcal{L} | B_\Lambda^\dagger B_\Omega | \mathcal{L}' \rangle = \underline{D}_{\Lambda\Omega}^{\mathcal{L}\mathcal{L}'}$  is the element  $(\Lambda, \Omega)$  of the transition density matrix (nonreduced) from  $|\mathcal{L}'\rangle$  to  $|\mathcal{L}\rangle$ . Wherever the meaning is clear, the upper indices, referring to the bra and ket states, will be omitted.

(ii) The general many-body operator  $\hat{H}$  for systems of a fixed number of electrons  $m$  can be written without explicit mention of the one-electron operators<sup>20,21</sup> as

$$\hat{H} = \sum_{\lambda, \gamma} \underline{H}_{\lambda\gamma} B_\lambda^\dagger B_\gamma, \quad (1)$$

where  $B_\lambda^\dagger = b_i^\dagger b_j^\dagger$ , with  $i < j$  (the  $b^\dagger$  operators being the usual fermion operators).

The quantities  $\underline{H}_{\lambda\gamma}$  have the form

$$\underline{H}_{\lambda\gamma} = \sum_{i,j} \underline{d}_{ij}^{\lambda\gamma} \frac{\epsilon_{ij}}{m-1} + V_{\lambda\gamma}, \quad (2)$$

where  $\epsilon_{ij}$  are the one-electron terms and  $V_{\lambda\gamma}$  the Coulombic integral corresponding to the scattering of two electrons from  $|\gamma\rangle$  into  $\langle \lambda |$ . (If both electrons have the same spin the exchange integral is subtracted.)

The quantity  $\underline{d}_{ij}^{\lambda\gamma}$  means

$$\underline{d}_{ij}^{\lambda\gamma} = \langle \lambda | b_i^\dagger b_j | \gamma \rangle. \quad (3)$$

In second-quantization language, the one-particle reduced density matrix operator of a state  $|\mathcal{L}\rangle$  is<sup>23</sup>

$$\begin{aligned} \hat{\rho}(r, r') &= \langle \mathcal{L} | \Psi^\dagger(r) \Psi(r') | \mathcal{L} \rangle \\ &\equiv \sum_{i,j} \underline{d}_{ij}^{\mathcal{L}\mathcal{L}} \phi_i^*(r) \phi_j(r'), \end{aligned} \quad (4)$$

where  $\Psi^\dagger(r)$  is the field operator and  $\phi_i(r)$  is a spin orbital function belonging to an orthonormal basis set.

The matrix  $\underline{H}$  in (1) is equivalent to the known reduced Hamiltonian.<sup>15-19</sup> Note that while this matrix is indeed represented in the two-particle space the operators  $B_\lambda^\dagger$  and  $B_\gamma$  should operate over  $m$ -electron states.

The general commutation rule for operators ( ${}^pB$ ) is

$$\begin{aligned} [{}^pB_\Lambda, {}^pB_\Omega^\dagger]_{\mp} &= \delta_{\Lambda\Omega} - \sum_{i,j} \underline{d}_{ij}^{\Lambda\Omega} b_j^\dagger b_i + \sum_{\lambda, \gamma} {}^2D_{\lambda\gamma}^{\Lambda\Omega} {}^2B_\gamma^\dagger {}^2B_\lambda \\ &\quad - \dots \mp \sum_{I,J} {}^{p-1}D_{IJ}^{\Lambda\Omega} {}^{p-1}B_J^\dagger {}^{p-1}B_I, \end{aligned} \quad (5)$$

where  $\mp$  corresponds to  $p$  even or odd, respectively. By considering this equation for  $p=2$  and any given  $m$ -electron state  $|\mathcal{L}\rangle$  one has

$$\langle \mathcal{L} | [B_\lambda, B_\lambda^\dagger]_- | \mathcal{L} \rangle = \delta_{\lambda\lambda} - \sum_{i,j} d_{ij}^{\lambda\lambda} \langle \mathcal{L} | b_i^\dagger b_j | \mathcal{L} \rangle.$$

In our notation this can be rewritten as

$$\bar{\underline{D}}_{\lambda\gamma}^{\mathcal{L}\mathcal{L}} - \underline{D}_{\lambda\gamma}^{\mathcal{L}\mathcal{L}} = \delta_{\lambda\gamma} - \text{tr}(\underline{d}^{\lambda\gamma} \underline{d}^{\mathcal{L}\mathcal{L}}) \quad (6)$$

because  $\underline{D}_{\lambda\gamma}^{\mathcal{L}\mathcal{L}} = \underline{D}_{\gamma\lambda}^{\mathcal{L}\mathcal{L}}$  and  $\text{tr}(\underline{d}^{\lambda\gamma} \underline{d}^{\mathcal{L}\mathcal{L}}) = \text{tr}(\underline{d}^{\gamma\lambda} \underline{d}^{\mathcal{L}\mathcal{L}})$  given that the RDM are symmetrical and  $d_{ij}^{\gamma\lambda} = d_{ji}^{\lambda\gamma}$ .

As previously mentioned

$$\underline{D}_{\lambda\gamma}^{\mathcal{L}\mathcal{L}} = \langle \mathcal{L} | B_\lambda^\dagger B_\gamma | \mathcal{L} \rangle \quad (7)$$

and

$$\bar{\underline{D}}_{\lambda\gamma}^{\mathcal{L}\mathcal{L}} = \langle \mathcal{L} | B_\lambda B_\gamma^\dagger | \mathcal{L} \rangle. \quad (8)$$

The interpretation that can be given to  $\bar{\underline{D}}^{\mathcal{L}\mathcal{L}}$  is that it is a two-hole reduced density matrix. Note that here  $|\mathcal{L}\rangle$  can be any kind of state, in particular it may be considered to be an eigenstate therefore involving superposition of configurations. Thus this ‘‘hole’’ concept is more general than the usual one in many-body theory. It assumes that to each state  $|\mathcal{L}\rangle$  corresponds in a unique way a hole state  $|\mathcal{L}'\rangle$  formed by a superposition of *virtual configurations*. When  $B^\dagger$  operates over such a ‘‘state’’ it operates as an annihilator.

The term  $\text{tr}(\underline{d}^{\lambda\gamma} \underline{d}^{\mathcal{L}\mathcal{L}})$  appearing in (6) is a concrete expression of an ‘‘augmenting’’ mapping.<sup>4</sup> It carries the matrix  $\underline{d}$  from the one-particle space into a matrix  $\bar{\underline{D}}$  in the two-electron space whose  $(\lambda, \gamma)$  element will be  $\text{tr}(\underline{d}^{\lambda\gamma} \underline{d}^{\mathcal{L}\mathcal{L}})$ . Note that  $\bar{\underline{D}}_{\lambda\gamma}$  can be also considered as the inner product of the matrices  $\underline{d}^{\lambda\gamma}$  and  $\underline{d}^{\mathcal{L}\mathcal{L}}$ .<sup>9,10</sup> This kind of mapping can, of course, be generalized, therefore if  $\underline{D}^{\Lambda\Omega}$  is used we will have

$$\text{tr}(\underline{D}^{\mathcal{L}\mathcal{L}} \underline{D}^{\Lambda\Omega}) = \bar{\underline{D}}_{\Lambda\Omega}^{\mathcal{L}\mathcal{L}}, \quad (9)$$

where the augmenting has been performed upon  $\underline{D}^{\mathcal{L}\mathcal{L}}$  taking it from the two-electron space into a  $p$ -electron one, that of  $\Lambda$  and  $\Omega$ .

The inverse mapping<sup>4</sup> is readily obtained<sup>20,21</sup> by a repeated use of the well-known sum rule  $\sum_i b_i^\dagger b_i = m$ . It takes the general form

$${}^pD_{\lambda\gamma} = \sum_{\Lambda, \Omega} {}^pD_{\lambda\gamma}^{\Lambda\Omega} \underline{D}_{\Lambda\Omega} \frac{\begin{pmatrix} m \\ p \end{pmatrix}}{\begin{pmatrix} l \\ p \end{pmatrix} \begin{pmatrix} m \\ l \end{pmatrix}}, \quad (10)$$

where the  $|\Lambda\rangle$  and  $|\Omega\rangle$  are  $l$ -electron configurations. Evidently this is the finite matrix representation of the integration upon  $l-p$  variables. In the appendix equation (10) is derived in detail.

### III. THE SPIN-ADAPTED REDUCED HAMILTONIANS

This section is divided into two parts. In part (i) the theoretical definition of the SRH matrices is given and the main properties of these matrices are discussed, while in part (ii) we report an algorithm which permits one to work always within a reduced space.

(i) Let us close relation (1) by the  $m$ -electron configurational states  $\langle \Lambda |$  and  $|\Omega\rangle$ , getting

$$\underline{\mathcal{H}}_{\Lambda\Omega} = \sum_{\lambda, \gamma} \underline{H}_{\lambda\gamma} \underline{D}_{\lambda\gamma}^{\Lambda\Omega} \equiv \text{tr}(\underline{H} \underline{D}^{\Lambda\Omega}). \quad (11)$$

The matrix  $\mathcal{H}$  is identical to that of a full interaction of configurations (IC). Note that Eq. (11) is an application of the augmenting mapping (9) upon  $\underline{H}$ .

If  $\langle \Lambda |$  and  $|\Omega\rangle$  are eigenfunctions of  $S^2$  and  $S_z$ , the matrix  $\mathcal{H}$  will be factored into blocks corresponding to each of the possible symmetries of our system. By selecting a given block one can perform the projection into the desired symmetry space. To the selected symmetry block matrix a reducing mapping is applied so as to obtain the spin-adapted reduced Hamiltonian  $\underline{H}'$ . This new matrix  $\underline{H}'$  is

$$\underline{H}' = \sum_{\Lambda, \Omega} \mathcal{H}_{\Lambda\Omega} \underline{D}^{\Lambda\Omega},$$

where the  $\{\Lambda, \Omega\}$  are pure symmetry states. We know that

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

where  $E_{\mathcal{L}}$  is the energy of eigenstate  $|\mathcal{L}\rangle$  of the spin symmetry wished for and  $\underline{D}^{\mathcal{L}\mathcal{L}}$  the corresponding density matrix. Consequently and due to (10)

$$\underline{H}' = \sum_{\mathcal{L}} E_{\mathcal{L}} \sum_{\Lambda, \Omega} \underline{D}^{\Lambda\Omega} \underline{D}^{\mathcal{L}\mathcal{L}} \equiv \sum_{\mathcal{L}} E_{\mathcal{L}} \underline{D}^{\mathcal{L}\mathcal{L}}. \quad (12)$$

Expression (12) tells us that the matrix  $\underline{H}'$  can be written as an expansion of 2-RDM, therefore it contains all the relevant information about our system. Note that while the  $\underline{D}^{\mathcal{L}\mathcal{L}}$  are orthogonal matrices the 2-RDM  $\underline{D}^{\mathcal{L}\mathcal{L}}$  are not.

Another important property of the mapping performed is readily seen by taking the trace of  $\underline{H}'$ ,

$$\text{tr} \underline{H}' = (\text{tr} \mathcal{H}) \begin{pmatrix} m \\ 2 \end{pmatrix}. \quad (13)$$

Therefore except for the usual scaling factor *the trace of  $\mathcal{H}$  is conserved*. In what follows we will consider that  $\underline{H}'$  has been renormalized by dividing it by this scale factor. The matrix  $\underline{H}'$  is what we call a two-electron spin-adapted reduced Hamiltonian matrix 2-SRH.

Everything that has been done to map  $\mathcal{H}$  into  $\underline{H}'$  can be similarly carried through to map  $\mathcal{H}$  into the 1-SRH  $\underline{h}'$ , or equivalently, we can map  $\underline{H}'$  onto  $\underline{h}'$ . Here we have proceeded in the latter way, therefore we will give the algorithms for  $\underline{H}'$  knowing that

$$\underline{h}' = \sum_{\lambda, \gamma} \frac{1}{2} d^{\lambda\gamma} \underline{H}'_{\lambda\gamma} \quad \text{and} \quad \text{tr} \underline{h}' = \text{tr} \mathcal{H}. \quad (14)$$

(ii) In the above we obtained the SRH matrix  $\underline{H}'$  by a three-step operation involving the application of an augmenting mapping, the spin projection, and the application of a reducing mapping. Here we will show that all these operations can be contracted into a single algorithm. In this way all the calculation can be carried on in a two-body space.

Because of (11) and (10),

$$\underline{H}'_{\eta\pi} = \sum_{\Lambda, \Omega, \lambda, \gamma} \underline{H}_{\lambda\gamma} \underline{D}_{\gamma\lambda}^{\Lambda\Omega} \underline{D}_{\eta\pi}^{\Omega\Lambda}. \quad (15)$$

The practical approach is thus to calculate the overall effect of

$$\sum_{\Lambda, \Omega} \underline{D}_{\gamma\lambda}^{\Lambda\Omega} \underline{D}_{\eta\pi}^{\Omega\Lambda}$$

so that the two mappings are contracted into a constant whose value will depend upon the indices  $\gamma, \lambda, \eta, \pi$ , the spin symmetry, and, implicitly, upon  $m$  and  $M$ , where  $M$  is the number of spin orbitals defining the representation space.

After addition over the index  $\Omega$  we get

$$\underline{H}'_{\eta\pi} = \sum_{\lambda, \gamma} \underline{H}_{\lambda\gamma} \sum_{\Lambda} \langle \Lambda | B_{\gamma}^{\dagger} B_{\lambda} B_{\eta}^{\dagger} B_{\pi} | \Lambda \rangle$$

but because of the commutation relation for  $[B_{\lambda}, B_{\eta}^{\dagger}]$ , previously seen in (5),

$$\underline{H}'_{\eta\pi} = \sum_{\lambda, \gamma} \underline{H}_{\lambda\gamma} \sum_{\Lambda} \left\langle \Lambda \left| B_{\gamma}^{\dagger} \left[ \delta_{\lambda\eta} + B_{\eta}^{\dagger} B_{\lambda} - \sum_{i,j} d_{ij}^{\eta\lambda} b_i^{\dagger} b_j \right] B_{\pi} \right| \Lambda \right\rangle.$$

After addition over  $\Lambda$  the three terms inside the large parentheses give rise to three types of constants, that is,

$$\underline{H}'_{\eta\pi} = \sum_{\lambda, \gamma} \underline{H}_{\lambda\gamma} \left[ K_{1;\gamma,\pi} \delta_{\lambda\eta} + K_{2;\gamma\eta,\lambda\pi} - \sum_{i,j} K_{3;\gamma i, j\pi} d_{ij}^{\eta\lambda} \right]. \quad (16)$$

The value and form of the  $K$  constants will depend on the kind of symmetry being considered and upon the level of approximation employed.

Indeed, if we content ourselves with a projection on the subspace spanned by the eigenfunctions of the  $S_z$  operator these constants take the form of diagonal matrices whose elements are given by a combinatorial formula for whatever symmetry we consider. This situation changes if we wish to perform the projection upon a subspace spanned by the eigenfunctions of the  $S^2$  and the  $S_z$  operators.

In the Appendix we explain in detail how the  $K$ 's are calculated in each case for the singlet symmetry. In the case of the  $(S^2, S_z)$  projection we have explicitly considered a case of four electrons and an eight-spin-orbital basis set.

#### IV. PHYSICAL INTERPRETATION AND GENERAL FORM OF THE SRH

The SRH matrices  $\underline{H}'$  and  $\underline{h}'$  are representations of the operators

$$\hat{H}' = \sum_{\lambda, \gamma} \underline{H}'_{\lambda\gamma} B_{\lambda}^{\dagger} B_{\gamma} \quad (17)$$

and

$$\hat{h}' = \sum_{i,j} \underline{h}'_{ij} b_i^{\dagger} b_j. \quad (18)$$

The diagonalization of these operators gives

$$\hat{H}' \equiv \sum_I \omega'_I (\Phi'_I)^{\dagger} \Phi'_I \quad (19)$$

and

$$\hat{h}' \equiv \sum_i \epsilon'_i (\phi'_i)^\dagger \phi'_i. \quad (20)$$

Now, in the two-particle reduced space<sup>24</sup> we have

$$[\hat{H}', (\Phi'_I)^\dagger \Phi'_J] = (\omega'_I - \omega'_J) (\Phi'_I)^\dagger \Phi'_J \equiv \omega'_{IJ} (\Phi'_I)^\dagger \Phi'_J \quad (21)$$

and, similarly, in the one-particle reduced space we have

$$[\hat{h}', (\phi'_i)^\dagger \phi'_j] = (\epsilon'_i - \epsilon'_j) (\phi'_i)^\dagger \phi'_j \equiv \epsilon'_{ij} (\phi'_i)^\dagger \phi'_j. \quad (22)$$

That is,  $\omega'_{ij}$  and  $\epsilon'_{ij}$  are the normal modes in these reduced spaces. Now, we have seen that the  $\hat{H}'$  and  $\hat{h}'$  contain all the information relevant about our system (in the spin-symmetry selected). Therefore the  $\omega'_{IJ}$  and the  $\epsilon'_{ij}$  can be interpreted as being the elementary excitations of our system.

If in (1) we use (5), we obtain another exact form of the many-body Hamiltonian operator:<sup>20</sup>

$$\hat{H} = -\text{tr}\underline{H} + \sum_{\lambda,\gamma} \underline{H}_{\lambda\gamma} B_\lambda B_\gamma^\dagger + \sum_{i,j} h_{ij} b_i^\dagger b_j \quad (23)$$

which makes explicit the term  $\sum_{\lambda,\gamma} \underline{H}_{\lambda\gamma} B_\lambda B_\gamma^\dagger$ . This term operates upon the holes of the state of our system, it will therefore be called the holes Hamiltonian and denoted by  $\hat{H}$ . ( $\hat{H}$  clearly describes the correlation effects of the state considered.<sup>20</sup>)

The holes Hamiltonian can be written as

$$\hat{H} = \sum_{\lambda,\gamma} \underline{H}_{\lambda\gamma} B_\lambda B_\gamma^\dagger = \sum_{\lambda,\gamma} \underline{H}_{\lambda\gamma} B_\gamma^\dagger B_\lambda + \text{tr}\underline{H} - \sum_{i,j} h_{ij} b_i^\dagger b_j.$$

If we proceed now with  $\hat{H}$  in a similar way as with  $\hat{H}$ , i.e., we obtain the matrix element

$$\overline{\mathcal{H}}_{\Lambda\Omega} = \langle \Lambda | \hat{H} | \Omega \rangle = \mathcal{H}_{\Lambda\Omega} + \delta_{\Lambda\Omega} \text{tr}\underline{H} - \text{tr}(h d^{\Lambda\Omega})$$

and reduce it back to the two-body (or one-body) space, we will get the corresponding reduced-spin-adapted holes Hamiltonian matrix  $\underline{H}'$ .

If the physical interpretation about the elementary excitations given above is correct, the holes quasigeminals (QG) excitation energies should be the same as those of the corresponding electron (QG). This appears to be confirmed numerically by the calculation that will now be reported and whose aim is mainly to gain a qualitative understanding of the physics behind our formalism and to confirm its general properties.

The system chosen for this preliminary calculation was the four-electron Be atom. The starting basis was Clementi's double zeta,<sup>25</sup> which after a Löwdin orthonormalization procedure was transformed into the basis diagonalizing the one-electron term of the initial Hamiltonian. Although this basis is not too good for the description of the excitations it is very convenient from the computational point of view. It is also acceptable for the study of the total energy of the Be ground state, which will be considered in the following paper.

We will now describe the most noteworthy features of these SRH matrices, their eigenvalues and their eigenvectors.

(i) Let us start by saying that using the algorithm (16) the properties (13) and (14) were empirically verified.

(ii) Also, as expected, while  $\underline{H}'$  and  $\underline{H}$  had different eigenvalues their eigenvectors were nearly the same and the excitation energies between two given eigenvectors had the same value. This means that

$$\underline{H}' - \underline{H} \simeq c \mathbb{1}.$$

(iii) An analysis of the matrices,  $\underline{h}$ , without spin projection and that obtained for the pure singlet symmetry,  $\underline{h}'$ , allowed the following relation to be found:

$$\underline{h}' = 2\underline{h} + \frac{(\text{tr}\underline{\mathcal{H}} - 2\text{tr}\underline{H})}{M} \mathbb{1}. \quad (24)$$

As previously mentioned, the normalization used was such that

$$\text{tr}\underline{h}' = \text{tr}\underline{\mathcal{H}},$$

$$\text{tr}\underline{h} = \text{tr}\underline{H}.$$

Relation (24) implies that both  $\underline{h}'$  and  $\underline{h}$  have the same eigenvectors and that

$$\epsilon'_{ij} = \frac{\epsilon_{ij}}{2}.$$

The eigenvectors of  $\underline{h}$  [and  $h'(S^2, S_z)$ ], were qualitatively close to the reference orthonormal basis used, which was that diagonalizing the original one-electron terms of kinetic and attraction energy.

(iv) An interesting feature of the eigenvectors of  $\underline{H}'$  is that they all have a single dominant bielectronic configuration, while the starting  $\underline{H}$  had rather diffuse eigenvectors, except for the ground state. This is probably a general characteristic provided the basis set of reference diagonalizes  $\underline{h}$  or, as in our case, is a basis qualitatively close to it. This concentrated character of the eigenvectors of  $\underline{H}'$  is particularly helpful in understanding the physical meaning of the elementary excitations, as will be seen in Sec. V.

## V. ELEMENTARY EXCITATIONS

As mentioned previously, the excitation energies of the QG and the QP can be regarded as normal modes of our system. That is, the difference of energy between two given QG or QP states correspond to an excitation energy of our system. In this section the results of our calculation are compared with the experimental results.

The first three columns of Table I report, respectively, the configuration, the designation, and the value of the singlet level according to experimental results.<sup>26</sup> In the fourth column the  $\omega'_{IJ}$  (and the  $\epsilon'_{ij}/2$ ) for the pure singlet symmetry ( $S^2, S_z$ ) are given. In the last column is presented the difference in energy between the two lowest states obtained with the full CI calculation.<sup>22</sup> The kind of promotion involved in each elementary excitation value is reported in a shorthand notation next to it. Thus, (numbering the one-electron space orbitals from 1 to 4 in the order of increasing energy and denoting by a bar above the

TABLE I. Singlet levels in  $\text{cm}^{-1}$ .

Configuration	Designation	Level (Ref. 24)	$(S^2, S_z)$	CI
$1s^2 2s^2$	$^1S$	0.00		
$1s^2 2s 2p$	$^1P$	42 565.3	$\left\{ \begin{array}{l} 38\,557.72 (1\bar{2} \rightarrow 1\bar{3})_S \\ 40\,034.5 (2\bar{4} \rightarrow 3\bar{4})_T \\ 43\,839.5 (1\bar{2} \rightarrow 1\bar{3})_T \\ 45\,066.0 (4\bar{2} \rightarrow 4\bar{3})_S \\ 45\,803.5 (2\bar{2} \rightarrow 2\bar{3})_S \end{array} \right.$	
$1s^2 2s 3s$	$^1S$	54 677.2		
$1s^2 2p^2$	$^1D$	56 432.5	$56\,531.5 (2\bar{3} \rightarrow 3\bar{3})_S$	
$1s^2 2s 3p$	$^1P$	[60 187.0] <sup>a</sup>		62 733.67
$1s^2 2s 3d$	$^1D$	64 428.15		
$1s^2 2s 4s$	$^1S$	65 245.4		
$1s^2 2s 4p$	$^1P$	[67 228.0] <sup>a</sup>	$66\,640.4 (2 \rightarrow 3)$	
$\vdots$	$\vdots$	$\vdots$		
$1s^2 2s 12d$	$^1D$	74 403.2		
IP		75 192.29		

<sup>a</sup>These terms' values were calculated from the series formula but not substantiated by observation.

number that the spin is  $\beta$ ), by  $(1\bar{2} \rightarrow 1\bar{3})_S$  we mean that the excitation occurs from the singlet quasigeminal, where the  $|\bar{1}\bar{2} + 2\bar{1}\rangle/\sqrt{2}$  configuration dominates, to that where the  $|\bar{1}\bar{3} + 3\bar{1}\rangle/\sqrt{2}$  is dominant. The notation  $(1\bar{2} \rightarrow 1\bar{3})_T$  means that the quasigeminals have triplet symmetry with spin projection  $S=0$ . Finally, the notation  $(2 \rightarrow 3)$  denotes the  $\epsilon_{23}/2$  quantity. The ellipses appearing in the table mean that some levels of the experimentally determined spectrum have been omitted.

The results linked by the bracket in the table have an average value (arithmetic mean) of  $42\,660.24 \text{ cm}^{-1}$  to be compared with  $42\,565.3 \text{ cm}^{-1}$  which is the value of the first singlet energy transition experimentally determined. The following value  $56\,531.5$  is close to the experimental one at  $56\,432.5 \text{ cm}^{-1}$ . The mono-electronic excitation  $(2 \rightarrow 3)$  may be compared with the value  $65\,245.4 \text{ cm}^{-1}$  although the error here is much larger.

In all these elementary excitations we see that the geminals involved have a common characteristic: the dominant configurations are of the type  $|i2\rangle$  in that of lower energy and  $|i3\rangle$  in that of the highest one. In other words, all the elementary excitations correspond to a *dominant* promotion of an electron from the 2 to the 3 orbital and the difference between all these excitations comes from the dominant partner orbital  $i$ . The values for the  $\omega_{ij}$  are lower than the  $(2 \rightarrow 3)$  mono-electronic elementary excitation in agreement with the collective mode character of the geminal excitations.

Our results also indicate that the dependence on the quality of the basis set seems to be less strict than in the full CI method. These two characteristics are probably due to the fact that the reduced two-electron space is better described with a given mono-electronic basis set than the  $m$ -electron one. We should also stress at this point the "average" nature of the reduced Hamiltonian matrices and therefore of the elementary excitations

described here.

Indeed, the concept of these elementary excitations is closely connected to that of the well-known elementary excitations in many-body and solid-state physics.<sup>27,28</sup> Although here neither the temperature nor the lifetime effects are explicitly considered, all the other characteristics of the many-body elementary excitations are present: near-independence, description of the lowest experimental excitations, average character, etc.

## VI. CONCLUDING REMARKS

The contraction of the full CI Hamiltonian matrix to a reduced space while conserving its trace is a very powerful property of the SRH method described here. The fact that the reduced spin-adapted Hamiltonian matrices  $H'$  and  $h'$  can be expanded in terms of the eigenvalues of the system and the corresponding reduced matrices is also a strong theoretical guarantee that all the relevant information is contained in them. The preliminary calculation reported here encourages us to think that our interpretation of the excitation energies of the QG and the QP as the elementary excitations of our system is correct. Indeed, the fact that the electron-QG and the holes-QG have similar excitation energy seems to confirm this view. Moreover, the fitting of these excitation energies with the lower experimental ones is unexpectedly good given the nature of the basis set used. In this connection, we intend to study the influence of the size and nature of the basis set upon the spectroscopic information provided by this method.

A simple and general way to calculate the constants appearing in algorithm (16) for pure symmetry is needed. This is being developed by Karwowski and Duch in collaboration with the author and will be the subject of a separate publication.

Here we have studied the information that can be obtained from the SRH in a direct way. The following paper (paper II) will discuss how to obtain information about the total energies and the reduced density matrices with the SRH method.

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#### APPENDIX

##### 1. Detailed derivation of some results referred to in the text

The repeated use of the identity  $\sum_i b_i^\dagger b_i \equiv m$  leads to several relations of interest, particularly to Eq. (10).

(a) Consider the identity

$$m = \sum_i b_i^\dagger b_i = \sum_{i,j} b_i^\dagger \left[ \frac{b_j^\dagger b_j}{m-1} \right] b_i. \quad (\text{A1})$$

The dividing factor  $m-1$  for a system originally with  $m$  electrons is due to annihilator  $b_i$ .

Now, if a fixed order is imposed upon the indices, i.e.,  $i < j$ , then

$$m = \sum_{\substack{i < j \\ i,j}} \frac{2}{m-1} b_i^\dagger b_j^\dagger b_j b_i. \quad (\text{A2})$$

Since  $b_i^\dagger b_j^\dagger$ , with  $i < j$ , is our definition for  $B_\lambda^\dagger$ , one has

$$1 = \sum_\lambda \frac{B_\lambda^\dagger B_\lambda}{\binom{m}{2}}. \quad (\text{A3})$$

Likewise, for the sums involving configurations  $\Lambda$  of  $p$  electrons the general relation is

$$1 = \frac{1}{\binom{m}{p}} \sum_\Lambda B_\Lambda^\dagger B_\Lambda. \quad (\text{A4})$$

$$\sum_{k_1, k_2, \dots, k_t} \frac{b_{i_1}^\dagger b_{i_2}^\dagger \cdots b_{i_p}^\dagger b_{k_1}^\dagger b_{k_2}^\dagger \cdots b_{k_t}^\dagger b_{k_1} b_{k_2} \cdots b_{k_t} b_{j_1} b_{j_2} \cdots b_{j_p}}{(m-p)(m-p-1) \cdots (m-p-t+1)}. \quad (\text{A11})$$

Ordering now the indices in the sum, it becomes

$$\frac{(t!)}{(m-p)(m-p-1) \cdots (m-p-t+1)} \sum_{k_1 < k_2 < \cdots < k_t} b_{i_1}^\dagger b_{i_2}^\dagger \cdots b_{i_p}^\dagger b_{k_1}^\dagger b_{k_2}^\dagger \cdots b_{k_t}^\dagger b_{k_1} b_{k_2} \cdots b_{k_t} b_{j_1} \cdots b_{i_2} b_{i_1}. \quad (\text{A12})$$

Denoting by  $\Lambda$  and  $\Omega$  the configurations with  $l=t+p$  electrons and by  $\lambda$  and  $\gamma$  the starting configurations of  $p$  electrons, this expression can be cast as

$$\sum_{\Lambda, \Omega} \frac{{}^p D_{\lambda\gamma}^{\Lambda\Omega} B_\Lambda^\dagger B_\Omega}{\binom{m-p}{l-p}}. \quad (\text{A13})$$

Although here  $\Lambda$  means a Slater determinant, it is easy to see that any unitary transformation, in the space generated by these determinants, leaves this relation invariant.

(b) Having seen this, consider now the identity

$$b_i^\dagger b_j \equiv \sum_k b_i^\dagger \frac{b_k^\dagger b_k}{m-1} b_j = \sum_{\lambda, \gamma} \frac{\langle \lambda | b_i^\dagger b_j | \gamma \rangle}{m-1} B_\lambda^\dagger B_\gamma. \quad (\text{A5})$$

Clearly the factor  $\langle \lambda | b_i^\dagger b_j | \gamma \rangle$  takes care of the sign which may be generated when ordering  $i$  and  $k$  to form  $\lambda$ , and  $j$  and  $k$  to form  $\gamma$ . This factor vanishes when orbitals  $i$  and  $j$  are unoccupied in  $\lambda$  or  $\gamma$ , respectively. It also vanishes if there is not an orbital  $k$  occupied both in  $\lambda$  and  $\gamma$ . Thus, the passage from  $\sum_k$  to  $\sum_{\lambda, \gamma}$  is justified. Now, according to (3),

$$b_i^\dagger b_j = \sum_{\lambda, \gamma} d_{ij}^{\lambda\gamma} \frac{B_\lambda^\dagger B_\gamma}{m-1}, \quad (\text{A6})$$

whence

$$\begin{aligned} \langle \mathcal{L}' | b_i^\dagger b_j | \mathcal{L} \rangle &= d_{ij}^{\mathcal{L}' \mathcal{L}} = \sum_{\lambda, \gamma} d_{ij}^{\lambda\gamma} \frac{\langle \mathcal{L}' | B_\lambda^\dagger B_\gamma | \mathcal{L} \rangle}{m-1} \\ &= \sum_{\lambda, \gamma} \frac{d_{ij}^{\lambda\gamma} D_{\lambda\gamma}^{\mathcal{L}' \mathcal{L}}}{m-1}, \end{aligned} \quad (\text{A7})$$

which for real elements is clearly identical to

$$\sum_{\lambda, \gamma} d_{ij}^{\lambda\gamma} \frac{D_{\gamma\lambda}^{\mathcal{L} \mathcal{L}'}}{m-1} = \sum_{\lambda, \gamma} \frac{d_{ji}^{\gamma\lambda} D_{\gamma\lambda}^{\mathcal{L} \mathcal{L}'}}{m-1}. \quad (\text{A8})$$

The same analysis yields the general expression [(10) in the text] as follows.

Now consider  $p$ -electron creators and  $p$ -electron annihilators such as

$$b_{i_1}^\dagger b_{i_2}^\dagger \cdots b_{i_p}^\dagger b_{j_p} \cdots b_{j_2} b_{j_1}. \quad (\text{A9})$$

Let us insert 1 between  $b_{i_p}^\dagger$  and  $b_{j_p}$ ,

$$\cdots \sum_{k_1} \frac{b_{i_1}^\dagger b_{i_2}^\dagger \cdots b_{i_p}^\dagger b_{k_1}^\dagger b_{k_1} b_{j_p} \cdots b_{j_2} b_{j_1}}{m-p}. \quad (\text{A10})$$

After performing  $t$  successive insertions, expression (A9) becomes

Hence by (7),

$${}^p D_{\lambda\gamma}^{\mathcal{L} \mathcal{L}'} = \sum_{\Lambda, \Omega} \frac{{}^p D_{\lambda\gamma}^{\Lambda\Omega} {}^l D_{\Lambda\Omega}^{\mathcal{L} \mathcal{L}'}}{\binom{m-p}{l-p}}. \quad (\text{A14})$$

Note that this scaling factor was incorrectly printed in Ref. 21.

Finally,

$$\frac{\begin{pmatrix} m \\ p \end{pmatrix}}{\begin{pmatrix} l \\ p \end{pmatrix} \begin{pmatrix} m \\ l \end{pmatrix}} = \frac{1}{\begin{pmatrix} m-p \\ l-p \end{pmatrix}} \quad (\text{A15})$$

which is the form of the scaling factor appearing in (10). Clearly (A14) can also be derived by direct insertion of (A4).

## 2. Projection in the $S_z$ subspace

(the  $\{|\Lambda\rangle\}$  are of the Slater determinant type

As we have mentioned in Sec. III, we will describe in detail the determination of the  $K$  constants for the singlet symmetry. For any other symmetry, as will be seen, the changes to be introduced are obvious and simple.

(i)  $K_{1;\gamma,\pi}$ . The form of this constant is

$$K_{1;\gamma,\pi} = \sum_{\Lambda} \langle \Lambda | B_{\gamma}^{\dagger} B_{\pi} | \Lambda \rangle \equiv \sum_{\Lambda} \delta_{\gamma\pi} \langle \Lambda | B_{\gamma}^{\dagger} B_{\gamma} | \Lambda \rangle.$$

The spin of the bielectronic configuration  $\gamma$  can take the values  $S_{\gamma}=0, \pm 1$ . Therefore if  $S_{\gamma}=\pm 1$  the value of  $K_{1;\gamma,\gamma}$  will obviously be

$$K_{1;\gamma,\gamma} = \begin{pmatrix} M/2-2 \\ m/2-2 \end{pmatrix} \begin{pmatrix} M/2 \\ m/2 \end{pmatrix}.$$

If the  $S_{\gamma}=0$  the value of  $K_{1;\gamma,\gamma}$  will be

$$K_{1;\gamma,\gamma} = \begin{pmatrix} M/2-1 \\ m/2-1 \end{pmatrix}^2.$$

(ii)  $K_{2;\gamma\eta,\lambda\pi}$ . In order to calculate this constant, let us call  $\tau$  the dummy set of four electron states in an ordered form (i.e.,  $|\tau\rangle = b_i^{\dagger} b_j^{\dagger} b_k^{\dagger} b_l^{\dagger}$  with  $i < j < k < l$ ). Using this we get

$$K_{2;\gamma\eta,\lambda\pi} = \sum_{\Lambda,\tau} D_{\tau\tau}^{\Lambda\Lambda} D_{\gamma\eta,\lambda\pi}^{\tau\tau} \equiv K_{2;\gamma\eta,\gamma\eta} \bar{D}_{\gamma,\lambda}^{\eta\pi}.$$

Evidently the sum over  $\tau$  is a dummy one which has been used with the sole aim of separating the ordering effects, and the fact that we must have  $|\gamma\eta\rangle = \pm |\lambda\pi\rangle$ , from the sum over  $\Lambda$ . The symbol  $\bar{D}_{\gamma,\lambda}^{\eta\pi}$  is, as we saw in Sec. II,

$$\bar{D}_{\gamma,\lambda}^{\eta\pi} = \langle \eta | B_{\gamma} B_{\lambda}^{\dagger} | \pi \rangle$$

and evidently provides the correct sign and imposes the previously mentioned equality. The values of the different  $K_2$  are given in Table II.

(iii)  $\sum_{i,j} K_{3;\gamma i,\gamma i} d_{ij}^{\lambda}$ . The values of  $K_{3;\gamma i,\gamma i}$  can be evaluated again using a dummy index  $\tau$  representing a three-electron configuration over which we sum. This is not necessary but renders the argument clearer, thus

TABLE II. Values of  $K_{2;\gamma\eta,\gamma\eta}$ .

$S_{\gamma}+S_{\eta}=\pm 2$	$S_{\gamma}+S_{\eta}=\pm 1$	$S_{\gamma}+S_{\eta}=0$
$\begin{pmatrix} M/2-4 \\ m/2-4 \end{pmatrix} \begin{pmatrix} M/2 \\ m/2 \end{pmatrix}$	$\begin{pmatrix} M/2-1 \\ m/2-1 \end{pmatrix} \begin{pmatrix} M/2-3 \\ m/2-3 \end{pmatrix}$	$\begin{pmatrix} M/2-2 \\ m/2-2 \end{pmatrix}^2$

$$\sum_{\Lambda} \langle \Lambda | B_{\gamma}^{\dagger} b_i^{\dagger} b_j B_{\pi} | \Lambda \rangle \equiv \sum_{\Lambda,\tau} D_{\tau\tau}^{\Lambda\Lambda} D_{\gamma i,\gamma j}^{\tau\tau} \equiv K_{3;\gamma i,\gamma i} \bar{d}_{ij}^{\gamma\pi},$$

where  $\bar{d}_{ij}^{\gamma\pi} \equiv \langle \gamma | b_i b_j^{\dagger} | \pi \rangle$  provides the condition that  $|\gamma i\rangle = \pm |j\pi\rangle$  with the correct sign coming from the ordering of the one-electron orbitals.

The constant  $K_{3;\gamma i,\gamma i}$  takes the following values:

(1) if  $S_{\gamma}+S_i = \pm \frac{3}{2}$ ,

$$K_{3;\gamma i,\gamma i} = \begin{pmatrix} M/2-3 \\ m/2-3 \end{pmatrix} \begin{pmatrix} M/2 \\ m/2 \end{pmatrix},$$

(2) if  $S_{\gamma}+S_i = \pm \frac{1}{2}$ ,

$$K_{3;\gamma i,\gamma i} = \begin{pmatrix} M/2-2 \\ m/2-2 \end{pmatrix} \begin{pmatrix} M/2-1 \\ m/2-1 \end{pmatrix}.$$

Therefore the Hamiltonian becomes

$$\underline{H}'_{\eta\pi} = K_{1;\pi,\pi} \underline{H}_{\eta\pi} + \sum_{\lambda,\gamma} \underline{H}_{\lambda\gamma} \left[ K_{2;\gamma\eta,\gamma\eta} \bar{D}_{\gamma,\lambda}^{\eta\pi} - \sum_{i,j} \underline{d}_{ij}^{\eta\lambda} \bar{d}_{ij}^{\gamma\pi} K_{3;\gamma i,\gamma i} \right]$$

and writing it all as a function of the initial  $\underline{H}$ , the  $K$  constants, and the one-electron reduced density matrices of the bielectronic states, one has

$$\begin{aligned} \underline{H}'_{\eta\pi} = & \underline{H}_{\eta\pi} \left[ K_{1;\pi,\pi} + K_{2;\pi\eta,\pi\eta} - \sum_i K_{3;\pi i,\pi i} \underline{d}_{ii}^{\eta\pi} \right] \\ & + \delta_{\eta\pi} \sum_{\lambda} \underline{H}_{\lambda\lambda} K_{2;\lambda\eta,\lambda\eta} \\ & - \sum_{\lambda,\gamma,i,j} \underline{H}_{\lambda\gamma} (K_{2;\gamma\eta,\gamma\eta} \underline{d}_{ji}^{\eta\lambda} \underline{d}_{ij}^{\gamma\pi} \\ & - K_{3;\gamma i,\gamma i} \underline{d}_{ij}^{\eta\lambda} \underline{d}_{ji}^{\gamma\pi}), \end{aligned}$$

where the substitutions of  $\bar{D}_{\gamma,\lambda}^{\eta\pi}$  and  $\bar{d}_{ij}^{\gamma\pi}$  have been performed according to formula (7) and

$$\delta_{ij} \delta_{\gamma\pi} = \underline{d}_{ij}^{\gamma\pi} + \bar{d}_{ji}^{\gamma\pi}.$$

## 3. Projection in the ( $S^2, S_z$ ) subspace

Let us consider the case of four-electron systems in the pure singlet subspace spanned by eight spin orbitals. The eigenfunctions of  $S^2$  in this subspace are

- (a) six functions of the type  $|ij\bar{i}\bar{j}\rangle$ ,
- (b) twelve functions of the type  $(|ij\bar{i}\bar{l}\rangle + |il\bar{i}\bar{j}\rangle)/\sqrt{2}$ ,
- (c) a function of the type

$$\frac{1}{2\sqrt{3}} (-|ik\bar{j}\bar{l}\rangle + |ijk\bar{l}\rangle - 2|jk\bar{i}\bar{l}\rangle - 2|il\bar{j}\bar{k}\rangle - |jl\bar{i}\bar{k}\rangle + |kl\bar{i}\bar{j}\rangle),$$

- (d) a function of the type

$$\frac{1}{2} (|ik\bar{j}\bar{l}\rangle + |ijk\bar{l}\rangle + |jl\bar{i}\bar{k}\rangle + |kl\bar{i}\bar{j}\rangle)$$

with  $i < j < k < l$ .

Note that the sum of the square of any of the determinant coefficients is 1 for (a),  $\frac{1}{2}$  for (b), and  $\frac{1}{3}$  for (c) and (d).

In order to render clearer the following development let us class the bielectronic Slater determinants according to

- (i) type  $|j\bar{j}\rangle$ ,
- (ii) type  $|i\bar{j}\rangle$ ,
- (iii) type  $|ij\rangle$ ,

and if  $\nu = |i\bar{j}\rangle$  and  $\gamma = |j\bar{i}\rangle$  we will say that  $\nu = \bar{\gamma}$ .

We have to calculate the three terms which appear in relation (16) and that are generated by

$$H'_{\eta\pi} = \sum_{\Lambda, \Omega, \lambda, \gamma} H_{\lambda\gamma} D_{\lambda\gamma}^{\Lambda\Omega} D_{\eta\pi}^{\Omega\Lambda}$$

when the  $\Lambda$  and  $\Omega$  indices represent the spin-adapted configurations. We will simply call them "configurations" and it is understood that they are the combinations of Slater determinants given above. As in the ( $S_2$ ) approximation the three terms will be considered separately.

$$a. \sum H_{\lambda\gamma} K_{i;\lambda,\pi} \delta_{\gamma\eta}$$

If  $\lambda = \pi$  and  $\pi$  is of the type  $|i\bar{i}\rangle$  for any  $\pi$  the sum  $\sum_{\Lambda} \langle \Lambda | B_{\pi}^{\dagger} B_{\pi} | \Lambda \rangle$  will have the value 6. Of this number the value 3 comes from the terms where  $|\Lambda\rangle = |i\bar{i}\bar{j}\bar{j}\rangle$ . The other 3 units come from the  $|\Lambda\rangle$  of type (b).

If  $\lambda = \pi$  and  $\pi$  is of the type  $|i\bar{j}\rangle$  it is easy to see that the complementary bielectronic determinant will appear.

- (1) Once  $|j\bar{i}\rangle$  providing the value 1.
- (2) Six times  $|l\bar{j}\rangle$  or  $|i\bar{l}\rangle$  or  $|k\bar{k}\rangle$  providing in the whole the value 3.
- (3)  $|k\bar{l}\rangle$  or  $|l\bar{k}\rangle$  providing each  $\frac{1}{3}$ , on the whole for any  $\pi$  of the type  $|i\bar{j}\rangle$  the value of this constant is  $\frac{14}{3}$ .

If  $\lambda = \pi$  and  $\pi$  is of the type  $|ij\rangle$  (or  $|\bar{i}\bar{j}\rangle$ ), evidently there will be six complementary possible bielectronic configurations.

- (1) One of the type  $|\bar{i}\bar{j}\rangle$  (or  $|ij\rangle$ ), providing the value 1.
- (2) Four of the type  $|\bar{i}\bar{k}\rangle$  (one space orbital in common with  $|ij\rangle$ ) providing the value 2.
- (3) One of the type  $|\bar{k}\bar{l}\rangle$  providing the value  $\frac{1}{3}$ .

Therefore on the whole this constant is  $\frac{10}{3}$ .  
If  $\lambda = \bar{\pi}$  then the value taken will be  $\frac{1}{3}$ , where 1 comes from the sum of the configurations of type (b) and  $\frac{1}{3}$  from the sum over (c) and (d) types.

The different values are summarized in Table I. The calculation of this term does not, therefore, offer any difficulty.

TABLE III. Summary of values for  $K_{i;\lambda,\pi}$  for various characteristics.

$K_{i;\lambda,\pi}$	Characteristics
6	$ \lambda\rangle =  \pi\rangle \rightarrow  i\bar{i}\rangle$
$\frac{14}{3}$	$ \lambda\rangle =  \pi\rangle \rightarrow  i\bar{j}\rangle$
$\frac{10}{3}$	$ \lambda\rangle =  \pi\rangle \rightarrow  ij\rangle$ or $ \bar{i}\bar{j}\rangle$
$\frac{4}{3}$	$ \lambda\rangle =  \bar{\pi}\rangle$

TABLE IV. Summary of values for  $K_{2;\lambda\eta;\lambda\pi}$  for various characteristics.

$K_{2;\lambda\eta,\gamma\pi}$	Characteristics
$\pm \frac{1}{3}$	$ \eta\lambda\rangle =  \gamma\pi\rangle \rightarrow  ij\bar{k}\bar{l}\rangle$
$\pm \frac{1}{6}$	$ \eta\lambda\rangle =  ij\bar{k}\bar{l}\rangle,  \gamma\pi\rangle =  kl\bar{i}\bar{j}\rangle$ $ \eta\lambda\rangle =  ij\bar{k}\bar{l}\rangle,  \gamma\pi\rangle \rightarrow  il\bar{j}\bar{k}\rangle$
$\pm \frac{1}{2}$	$ \eta\lambda\rangle =  \gamma\pi\rangle \rightarrow  ij\bar{i}\bar{l}\rangle$
$\pm 1$	$ \eta\lambda\rangle =  ij\bar{i}\bar{l}\rangle,  \gamma\pi\rangle \rightarrow  il\bar{i}\bar{j}\rangle$ $ \eta\lambda\rangle =  \gamma\pi\rangle \rightarrow  ij\bar{i}\bar{j}\rangle$

$$b. \sum_{\lambda,\gamma} H_{\lambda\gamma} K_{2;\lambda\eta,\gamma\pi}$$

Here also  $K_2$  may take several values.

If  $|\lambda\eta\rangle = \pm |\gamma\pi\rangle$  and  $|\lambda\eta\rangle \rightarrow |ij\bar{i}\bar{j}\rangle$  the value will be  $\pm 1$  where the sign will depend on the relative ordering of both  $|\eta\lambda\rangle$  and  $|\gamma\pi\rangle$ .

If  $|\lambda\eta\rangle$  is of the type  $|ij\bar{i}\bar{k}\rangle$  then  $|\gamma\pi\rangle$  must be either equal to this state or to  $|iki\bar{j}\bar{j}\rangle$ . In both cases the sign will be determined by the relative ordering of both configurations and the value will be  $\frac{1}{2}$ .

If  $|\eta\lambda\rangle$  is of the type  $|ijk\bar{l}\rangle$ , then  $|\gamma\pi\rangle$  must also be of this same type. The absolute value of this constant is  $\frac{1}{6}$  or  $\frac{1}{3}$ . The sign in the case of  $\frac{1}{6}$  will come not only from the relative ordering of both states but also from the relative position of the two common indexes. That is, when, as in the example of the table, we bring both states into the order:

$$|ij\bar{k}\bar{l}\rangle \rightarrow -|i\bar{k}j\bar{l}\rangle, \\ |il\bar{j}\bar{k}\rangle \rightarrow |i\bar{k}l\bar{j}\rangle.$$

We see that the common indexes  $i$  and  $\bar{k}$  are brought together to the same positions in both states, but in the first state there is a minus sign, while in the other there is a + sign. The overall effect will be a minus sign.

$$c. - \sum_{\lambda,\gamma,i,j} H_{\lambda\gamma} d_{ij}^{\eta\gamma} K_{3;i\lambda,j\eta}$$

This term involves not only  $K_3$  but  $d_{ij}^{\eta\gamma} = \langle \eta | b_i^{\dagger} b_j | \gamma \rangle$ . However,  $d_{ij}^{\eta\gamma}$  does not offer any difficulty, thus we will just focus our attention upon  $K_3$ .

If  $|\lambda i\rangle = \pm |j\pi\rangle$  and  $|\lambda i\rangle \rightarrow |l\bar{l}k\rangle$  then  $K_3 = \pm 2$ .

If  $|\lambda i\rangle = \pm |j\pi\rangle$  and  $|\lambda i\rangle \rightarrow |il\bar{k}\rangle$  (or  $|ik\bar{l}\rangle$ ) then  $K_3 = \pm \frac{4}{3}$ .

If  $|\lambda i\rangle \neq \pm |j\pi\rangle$  but  $|\lambda_i\rangle = \pm |k\nu\rangle$  and  $|j\pi\rangle$

TABLE V. Summary of values for  $K_{3;\lambda i,j\pi}$  for various characteristics.

$K_{3;\lambda i,j\pi}$	Characteristics
$\pm 2$	$ \lambda i\rangle = \pm  j\pi\rangle \rightarrow  lk\bar{l}\rangle$
$\pm \frac{4}{3}$	$ \lambda i\rangle = \pm  j\pi\rangle \rightarrow  ij\bar{k}\rangle$
$\pm \frac{2}{3}$	$ \lambda i\rangle \neq \pm  j\pi\rangle^a \begin{cases}  \lambda i\rangle = \pm  k\nu\rangle \\  j\pi\rangle = \pm  k\bar{\nu}\rangle \end{cases}$

<sup>a</sup>In this particular case one should first order as indicated each trielectronic state i.e.,  $|k\nu\rangle$  and  $|k\bar{\nu}\rangle$  in order to avoid errors.

$= \pm |k \bar{\nu}\rangle$  then the constant will have the value  $\pm 2/3$ .

In Table III we summarize these values. (Note that no index can ever be repeated inside each determinant.) Evidently, in general for any symmetry, any  $m$ , and any  $M$  the constants will have to be recalculated, however, we ex-

pect a generating formula to exist which would permit a completely general computation program to be elaborated without too much difficulty. Here we were just interested in analyzing the results, therefore we have simplified our programming task to the utmost.

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