

Form of spinless first- and second-order density matrices in atoms and molecules, derived from eigenfunctions of S^2 and S_z

D.J. Klein^a, N.H. March^a and A.K. Theophilou^b

^a *Department of Marine Sciences, Texas A&M University at Galveston, Galveston, Texas 77553, USA*

^b *Demokritos, Aghia Paraskevi Attikis, Greece*

Received 6 March 1996; revised 14 April 1997

Many-electron theory of atoms and molecules starts out from a spin-independent Hamiltonian H . In principle, therefore, one can solve for simultaneous eigenfunctions Ψ of H and the spin operators S^2 and S_z . The fullest possible factorization into space and spin parts is here exploited to construct the spinless second-order density matrix Γ , and hence also the first-order density matrix. After invoking orthonormality of spin functions, and independently of the total number of electrons, the factorized form of Ψ is shown to lead to Γ as a sum of only two terms for $S = 0$, a maximum of three terms for $S = 1/2$ and four terms for $S \geq 1$. These individual terms are characterized by their permutational symmetry. As an example, the ground state of the Be atom is discussed.

1. Introduction

While density functional theory (DFT) is nowadays a widely used approach to many-electron problems in both molecules and condensed phases, certain major issues remain unresolved. In the “hybrid” treatment using one-electron orbitals (themselves being functionals of the ground-state electron density $\rho(\mathbf{r})$), pioneered by Slater [16] and formally completed by Kohn and Sham [9], an essential ingredient in present calculational procedures is the exchange-correlation potential $v_{xc}[\mathbf{r}]$. Without approximation, and free from the conventional functional derivative

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})}, \quad (1.1)$$

where $E_{xc}[\rho]$ is the, as yet unknown, exchange-correlation energy functional, Holas and March [5,6] have recently expressed $v_{xc}(\mathbf{r})$ quite explicitly in terms of low-order density matrices of spinless form. But these are subject to the so-called N -representability problem, present in the pioneering work of Mayer [11] and reviewed by Coleman [1]. It should therefore, in the light of refs. [1,5,6,11], occasion little surprise that while DFT has a variational basis, current approximations to functionals, and hence to densities $\rho(\mathbf{r})$, frequently can go below the exact ground-state energy of the atom or molecule,

say, under consideration. This is, of course, a serious matter, as it means that, at some point which is often difficult to isolate, one has violated, to some degree, the antisymmetry requirement on a many-Fermion wave function. Thus, energy, termed “correlation”, is at least to a certain extent, then being gained from an admixture of, say, a Bose wave function component in a Fermion problem.

A second different, but related, area, which will be a focal point below, is that calculations on atoms or molecules at the level of the many-electron Schrödinger equation start out from an assumed spin-independent Hamiltonian H . This implies, in particular, that the ground-state many-electron wave function is a simultaneous eigenfunction of H , S^2 and S_z . Of course, a whole body of work exists, such as is reviewed in the book by Pauncz [15], on the construction of spin eigenfunctions. But it is fair to say that, to date, this branch of atomic and molecular theory has only affected DFT practice peripherally.

In section 2 below, therefore, we shall draw on work, set out for example in the book by Wigner [17], in which the fullest possible factorization of the many-electron ground-state wave function into space and spin parts is carried out. This will then be used to construct specifically the spinless second-order density matrix Γ . Hence the spinless first-order density matrix γ will be derived.

2. Fullest possible factorization of ground-state many-electron wave function into space and spin contributions

Here our object is to summarize the way in which a simultaneous eigenfunction Ψ_{SM} having eigenvalues of S^2 equal to $S(S+1)\hbar^2$ and S_z equal to $M\hbar$ can be written with fullest possible factorization into space and spin contributions. This is set out, for example, in Wigner’s book, and takes the form

$$\Psi_{SM} = (f_S^N)^{-1/2} \sum_k \Phi_k^\lambda(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \Theta_{Mk}^{N,S}(\sigma_1, \sigma_2, \dots, \sigma_N), \quad (2.1)$$

where λ labels an irreducible representation of the permutation group and (for the Pauli-allowed irreducible representation) is in one-to-one correspondence with N and S . This we can represent formally by writing

$$\lambda \equiv [2^{(N/2)-S}, 1^{2S}], \quad (2.2)$$

where, for example, the corresponding Young tableau has $(N/2) - S$ rows of length 2 and $2S$ rows of length 1. As indicated, the functions Φ depend only on space coordinates, while the Θ functions are solely dependent on spin coordinates. The number of terms in the sum in equation (2.1) appears in the normalization factor and is given by

$$f_S^N = \frac{(2S+1)N!}{(\frac{1}{2}N+S+1)!(\frac{N}{2}-S)!}. \quad (2.3)$$

For example, in the Be atom ground state, to be considered fully below, $N = 4$ and $S = 0$ yields $f = 2$.

2.1. Permutational symmetry of Φ and Θ

We note the following permutational symmetry property of the Φ 's:

$$P\Phi_k^\lambda = \sum_m D_{mk}^\lambda(P)\Phi_m^\lambda, \quad (2.4)$$

where P is a permutation.

For the spin functions we have similarly

$$P\Theta_{M\tilde{k}}^{N,S} = \sum_{\tilde{m}} D_{\tilde{m}\tilde{k}}^{N,S}(P)\Theta_{M\tilde{m}}^{N,S}. \quad (2.5)$$

The representation $D^{N,S}$ is conjugate to the representation D^λ :

$$D_{\tilde{m}\tilde{k}}^{N,S} = \varepsilon_P D_{mk}^\lambda(P), \quad (2.6)$$

where ε_P is the parity of P .

In addition to these important permutational symmetry properties, it is noteworthy that if D^λ is an irreducible representation, then so is any unitary transformation of it. Thus different choices are possible for D^λ with fixed λ , but we stress that the many-electron wave function Ψ in equation (2.1) is unique, regardless of the unitary transformation.

It must also be recognized that in equation (2.1) the functions Φ and Θ are also orthonormal and satisfy

$$\langle \Phi_k^\lambda | \Phi_l^\lambda \rangle = \delta_{kl} \quad (2.7)$$

and

$$\langle \Theta_{M\tilde{k}}^{N,S} | \Theta_{M\tilde{l}}^{N,S} \rangle = \delta_{\tilde{k}\tilde{l}}. \quad (2.8)$$

We turn immediately to use this form (2.1) which exhibits the fullest possible factorization of Ψ into space and spin parts to construct the low-order spinless density matrices Γ and γ as defined by Löwdin [10]: see also McWeeny [12,13], Davidson [2] and Gould et al. [4].

3. First- and second-order spinless density matrices

In this section, we use the eigenfunction Ψ_{SM} of S^2 and S_z to construct the spinless density matrices. In particular, we can write almost immediately for the spinless second-order density matrix Γ the result

$$\Gamma(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2) = \binom{N}{2} (f_S^N)^{-1} \quad (3.1)$$

$$\times \sum_{k_1, k_2} \int \Phi_{k_2}^\lambda(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N) \Phi_{k_2}^\lambda(\mathbf{r}'_1, \mathbf{r}'_2, \mathbf{r}_3, \dots, \mathbf{r}_N) d\mathbf{r}_3 \dots d\mathbf{r}_N$$

$$\times \langle \Theta_{M, k_1}^{N, S} | \Theta_{M, k_2}^{N, S} \rangle = \sum_k \Gamma_k(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2). \quad (3.2)$$

We must note now a number of points concerning the sum over k in the last part of equation (3.1). In general there are f_S^N terms in the sum, where f_S^N is given in equation (2.3). It is next important to recognize that each of these terms has equal weight in the precise sense that

$$\int \Gamma_k(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$$

is independent of the label k . Furthermore, as already pointed out, one can pick a unitary transformation in a variety of different ways. Our choice will be such that different k 's correspond to different coupling paths for the spins (e.g., in the Young tableau mentioned above). We will select a coupling path that couples the first two electrons to symmetry λ_{12} and the remaining $N-2$ particles (i.e., 3 to N) to symmetry $\lambda_{3 \rightarrow N}$, with corresponding k indices $k_{3 \rightarrow N}$.

Returning to the last step in equation (3.1), we emphasize that the Γ_k 's only differ if the pair $\lambda_{12}, \lambda_{3 \rightarrow N}$ are different, i.e., are independent of $k_{3 \rightarrow N}$. Then in the sum over k appearing in equation (3.1), the sum over $k_{3 \rightarrow N}$ can be carried out, the number of equivalent terms being just f_S^{N-2} in the notation of equation (2.3).

To make the above points quite explicit, table 1 has been constructed. From this table, it follows that for the example when $S = 0$, the independent terms that remain in the sum are just two in number. If, on the other hand, $S = 1/2$, there are three terms, while if $S \geq 1$ then there are four. These different terms are characterized by

Table 1
Illustrating correspondence between symmetry λ and spin S for different coupling paths relevant for second-order spinless density matrix Γ .

λ	λ_{12}	$\lambda_{3 \rightarrow N}$
$S = 0$	$S_{12} = 0$	$S_{3 \rightarrow N} = 0$
	$S_{12} = 1$	$S_{3 \rightarrow N} = 1$
$S = 1/2$	$S_{12} = 0$	$S_{3 \rightarrow N} = 1/2$
	$S_{12} = 1$	$S_{3 \rightarrow N} = 1/2$
	$S_{12} = 1$	$S_{3 \rightarrow N} = 3/2$
$S \geq 1$	$S_{12} = 0$	$S_{3 \rightarrow N} = S$
	$S_{12} = 1$	$S_{3 \rightarrow N} = S - 1$
	$S_{12} = 1$	$S_{3 \rightarrow N} = S$
	$S_{12} = 1$	$S_{3 \rightarrow N} = S + 1$

Table 2
Completely analogous to table 1 but for spinless first-order
density matrix γ .

S	S_1	$S_{2 \rightarrow N}$
0	1/2	1/2
$\geq 1/2$	1/2	$S - 1/2$
	1/2	$S + 1/2$

different permutational symmetries. These symmetries are either symmetric ($S_{12} = 0$ in table 1) or antisymmetric ($S_{12} = 0$) in electrons 1 and 2.

Turning to the first-order spinless density matrix $\gamma(r_1, r'_1)$ the above second-order density matrices have immediate implications for this object. This then allows the construction of table 2.

4. Example of Be atom in ground state: $N = 4, S = 0$

Let us turn to an example of the application of the somewhat formal theory presented above to the ground state of the Be atom. For this case, $N = 4$ and $S = 0$ and hence from equation (2.3) $f_N^S = 2$. Labelling the two space components by k_1 and k_2 , one has for the many-electron ground state (2.1) in this atom the result

$$\Psi_{00} = \Phi_{0k_1}^\lambda \Theta_{0k_1}^0 + \Phi_{0k_2}^\lambda \Theta_{0k_2}^0. \quad (4.1)$$

But from the summary in section 2, the spin functions labelled by different k are orthonormal when integrated over the spin coordinates of the four electrons. As discussed in section 3 above for the case $S = 0$ there remain two distinct terms in the spinless density matrix, one being symmetric and the other antisymmetric, in the sense explained in some detail above. Let us next turn to compare this situation for the interacting wave function derived from equation (2.1) with the spinless density matrix obtained from a single Slater determinant.

4.1. Single-determinant approximation to Be atom ground-state

For the ground configuration $(1s)^2(2s)^2$, Holas et al. [7], following the work of Dawson and March [3], have constructed explicitly the first-order spinless density matrix $\gamma(\mathbf{r}_1, \mathbf{r}'_1)$ for Be, in terms of the density amplitude $\{\rho(\mathbf{r})\}^{1/2}$ and the phase $\theta(\mathbf{r})$. The result is

$$\gamma(\mathbf{r}_1, \mathbf{r}'_1) = \rho(r_1)^{1/2} \rho(r'_1)^{1/2} \cos \{\theta(r_1) - \theta(r'_1)\}. \quad (4.2)$$

Given the density $\rho(r)$, the phase $\theta(r)$ can be derived by solution of a non-linear pendulum-like eigenequation. But it is well known for the case of a single Slater determinant that the first-order matrix determines all the higher-order density matrices. In the present context, this means that the second-order matrix Γ can be written in terms of γ in equation (4.2).

As set out, for example, in the book by a Parr and Yang [14] the result is, with $\mathbf{r}'_2 = \mathbf{r}_2$,

$$2\Gamma(\mathbf{r}_1, \mathbf{r}'_1; \mathbf{r}_2, \mathbf{r}_2) = \gamma(\mathbf{r}_1, \mathbf{r}'_1)\gamma(\mathbf{r}_2, \mathbf{r}_2) - \frac{1}{2}\gamma(\mathbf{r}_1, \mathbf{r}_2)\gamma(\mathbf{r}_2, \mathbf{r}'_1). \quad (4.3)$$

Substituting the form (4.2) into equation (4.3), one finds after a little manipulation that equation takes the form

$$2\Gamma(\mathbf{r}_1, \mathbf{r}'_1; \mathbf{r}_2, \mathbf{r}_2) = \rho(\mathbf{r}_1)^{1/2}\rho(\mathbf{r}'_1)^{1/2}\rho(\mathbf{r}_2) \left[\frac{1}{2} \cos \{ \theta(\mathbf{r}_1) - \theta(\mathbf{r}_2) \} \cos \{ \theta(\mathbf{r}'_1) - \theta(\mathbf{r}_2) \} + \sin \{ \theta(\mathbf{r}_1) - \theta(\mathbf{r}_2) \} \sin \{ \theta(\mathbf{r}'_1) - \theta(\mathbf{r}_2) \} \right]. \quad (4.4)$$

The pair function, $2\Gamma(\mathbf{r}_1, \mathbf{r}_2)$, is the diagonal form of equation (4.4), yielding the result

$$2\Gamma(\mathbf{r}_1, \mathbf{r}_2) = \rho(\mathbf{r}_1)\rho(\mathbf{r}_2) \left[1 - \frac{1}{2} \cos^2 \{ \theta(\mathbf{r}_1) - \theta(\mathbf{r}_2) \} \right]. \quad (4.5)$$

Though this result (4.5) follows for the Be atom ground state described in the approximation of a single Slater determinant, as constructed this wave function is indeed an eigenfunction of S^2 and S_z with $S = 0$. Therefore it must be possible to write the compact form (4.5) for the pair function in the alternative decomposition corresponding to equation (3.1). This decomposition is carried out explicitly in appendix 1, and yields

$$2\Gamma(\mathbf{r}_1, \mathbf{r}_2) = \frac{3}{4}\rho(\mathbf{r}_1)\rho(\mathbf{r}_2) \left[1 - \cos^2 \{ \theta(\mathbf{r}_1) - \theta(\mathbf{r}_2) \} + \frac{1}{3}(1 + \cos^2 \{ \theta(\mathbf{r}_1) - \theta(\mathbf{r}_2) \}) \right]. \quad (4.6)$$

Invoking the idempotency [4,7] of the first-order density matrix γ in equation (4.2), it is straightforward to show that the two components separated inside the square brackets on equation (4.6) do indeed make equal contributions to the integral of the pair function over \mathbf{r}_1 and \mathbf{r}_2 .

The form (4.6) therefore constitutes a specific example illustrating, in the approximation of a single determinant, the properties of the spinless second-order density matrix that must follow from its being derived from a simultaneous eigenfunction of S^2 and S_z .

5. Summary and future directions

The main achievement of the present study is to demonstrate the compactness of the spinless second-order density matrix Γ which follows after its construction from the factorizable form (2.1) which is itself an eigenfunction of S^2 and S_z . It turns out that, in spite of the number of electrons N appearing in the result for f_S^N in equation (2.2), in fact the sum collapses into simply two terms for $S = 0$, a maximum of three terms for $S = 1/2$, and four terms for $S \geq 1$. The individual terms that remain in the sum are characterized by their permutational symmetry properties.

The specific example of the ground-state of the Be atom, with $S = 0$, is considered in some detail in section 4 and in appendix 1. For the approximation of a single determinant, itself an eigenfunction of S^2 and S_z , the spinless pair function $\Gamma(\mathbf{r}_1, \mathbf{r}_2)$ takes the compact form (4.5) in terms of the density amplitude $\{\rho(\mathbf{r})\}^{1/2}$ and the phase $\theta(\mathbf{r})$. But this is not in the form of the sum of two terms with equal weights that occur in the theory starting out from equation (2.1). Therefore, in appendix 1, it is shown how to rearrange equation (4.5) for the electron pair function in the ground-state of Be into the two terms with definite permutational symmetry and with equal weights, the desired results for the two contributions to the pair function being exhibited explicitly in equation (4.6).

Of course, to determine precisely the two spatial terms for Be will require solution of Schrödinger's equation for exact results to be obtained. But at least one has inequalities to guide one, in the search for correlated, but still approximate, forms of the low-order density matrices. Thus the idempotent matrix condition satisfied by the single determinant form (4.2) of the first-order density matrix must be replaced in the fully interacting case $\gamma^2 < \gamma$, or written out fully in coordinate representation:

$$\gamma(\mathbf{r}_1, \mathbf{r}'_1) > \int \gamma(\mathbf{r}_1, \mathbf{r}_2)\gamma(\mathbf{r}_2, \mathbf{r}'_1) d\mathbf{r}_2. \quad (5.1)$$

Any N -representable first-order matrix satisfying equation (5.1) can in fact be written in terms of the Löwdin natural orbitals $\chi_i(\mathbf{r})$ and corresponding occupation numbers n_i as

$$\gamma(\mathbf{r}_1, \mathbf{r}'_1) = \sum_{\text{all } i} n_i \chi_i(\mathbf{r}_1)\chi_i^*(\mathbf{r}'_1). \quad (5.2)$$

To satisfy the inequality (5.1) one must have then

$$0 < n_i < 1, \quad (5.3)$$

which reflect the so-called Pauli conditions (or alternatively a transition from the pure-state to the mixed-state density matrices).

Naturally, specific approximations such as generalized valence bond (VB) theory can be introduced to make quite concrete the summation (2.1) for the eigenfunction of S^2 and S_z . With some additional simplifications (e.g., strong orthogonality constraints), we have considered such a VB approach elsewhere [8].

Two final comments are called for. First, in appendix 2, we have set out the example of the ground state of the Li atom, with an unpaired 2s electron spin. Secondly, we return to the point concerning N -representability, discussed in the introduction. If the considerations of the present paper are followed, in constructing the exchange-correlation potential $v_{xc}(\mathbf{r})$ from both the exact theory of Holas and March [5] in terms of Γ and γ , then no violation of N -representability can occur. Needless to say, to obtain $v_{xc}[\rho]$, one would need to express as explicit functionals of $\rho(\mathbf{r})$, which remains a truly formidable many-electron problem.

Acknowledgements

NHM wishes to thank the members of the Department of Marine Sciences, Texas A&M University at Galveston for hospitality during his visit. He also acknowledges partial financial support for this work from the Laverhulme Trust, in the form of an Emeritus Fellowship.

Appendix 1. Reduction of spinless second-order density matrix to independent electron form for ground-state of Be atom ($N = 4, S = 0$)

The wave functions Φ_k^λ in equation (3.1) for the case of the beryllium atom, which arise from two doubly occupied orbitals, may be explicitly constructed. The orthonormal orbitals ψ_1 and ψ_2 are abbreviated to a and b and the particle coordinates are associated to position, so that, for example, aabb represents $\psi_1(\mathbf{r}_1)\psi_1(\mathbf{r}_2)\psi_2(\mathbf{r}_3)\psi_2(\mathbf{r}_4)$. The two Φ_k^λ related to two Young tableaux associated to the same Young diagram of $\lambda = [2^2]$ are [15], apart from normalization factors

$$\Phi_-^\lambda \sim \{1 - (12)\}\{1 - (34)\}\{1 - (13)\}\{1 - (24)\}aabb \quad (\text{A1.1})$$

and

$$\Phi_+^\lambda \sim \{1 + (12)\}\{1 + (34)\}\{1 - (13)\}\{1 - (24)\}aabb, \quad (\text{A1.2})$$

where the various (ij) are permutations interchanging indices i and j . Carrying out the application of these permutations and now including normalization one obtains

$$\Phi_-^\lambda = (1/2)(ab - ba)(ab - ba) \quad (\text{A1.3})$$

and

$$\Phi_+^\lambda = 1/(2\sqrt{3})\{2(aabb + bbaa) - (ab + ba)(ab + ba)\}. \quad (\text{A1.4})$$

The associated + and - components of the spinless second-order reduced density matrices are then

$$\Gamma_- = \frac{1}{2} \binom{4}{2} \text{tr}_{34} |\Phi_-^\lambda\rangle \langle \Phi_-^\lambda| \quad (\text{A1.5})$$

and

$$\Gamma_+ = \frac{1}{2} \binom{4}{2} \text{tr}_{34} |\Phi_+^\lambda\rangle \langle \Phi_+^\lambda|, \quad (\text{A1.6})$$

where the 'partial traces' here entail integration over the particle coordinates 3 and 4. Carrying out these operations gives

$$\Gamma_- = (3/2)|ab - ba\rangle \langle ab - ba| \quad (\text{A1.7})$$

and

$$\Gamma_+ = |aa\rangle \langle aa| + |bb\rangle \langle bb| + (1/2)|ab + ba\rangle \langle ab + ba|. \quad (\text{A1.8})$$

As indicated in table 2, the components of the spinless first-order density matrix are the same for an overall singlet and this may be checked here. That is $\gamma_- = \gamma_+$ and

$$\gamma = \gamma_- + \gamma_+ = 2(|a\rangle\langle a| + |b\rangle\langle b|). \quad (\text{A1.9})$$

The electronic pair function may now be obtained from Γ_- and Γ_+ as

$$\begin{aligned} \Gamma(1, 2) = & \Gamma_-(1, 2; 1, 2) + \Gamma_+(1, 2; 1, 2) = (3/2)\{a(1)b(2) - b(1)a(2)\}^2 \\ & + \{a(1)a(2)\}^2 + \{b(1)b(2)\}^2 + (1/2)\{a(1)b(2) + b(1)a(2)\}^2 \end{aligned} \quad (\text{A1.10})$$

and this leads back to equation (4.6).

Though the above is specific to the case $N = 4$, $S = 0$, there are points to be stressed for the singlet case and for general N . In the notation of equation (3.1), the two different Γ_k terms are characterized by their permutational symmetry as in the above example. In particular, $\Gamma_-(1, 2; 1', 2')$ is antisymmetrical in 1 and 2 and separately is antisymmetrical in $1'$ and $2'$. In contrast, Γ_+ is symmetrical in 1 and 2 and in $1'$ and $2'$. Finally, for the first-order spinless density matrix in the singlet case discussed in this appendix, the quantity γ_k defined from equation (3.1) as

$$\gamma_k(1, 1') = \frac{2}{N-1} \int \Gamma_k(1, 2; 1', 2) d2 \quad (\text{A1.11})$$

is in fact independent of k for arbitrary N and $S = 0$, for a general wave function of the form (3.1).

Appendix 2. Single determinant and general space-spin factorization for Li atom ($N = 3$, $S = 1/2$)

In this appendix we shall make close contact between the single determinant wave function for the $(1s)^2 2s$ ground state of the Li atom and the general expansion (2.1). Starting from the latter, we note that $N = 3$ and $S = 1/2$ for the ground state above lead from equation (2.3) to

$$f_{1/2}^3 = 2. \quad (\text{A2.1})$$

Thus the general factorization in equation (2.1) can be classified by two labels k , say k_1 and k_2 , to yield for $S = 1/2$ and the case $M = 1/2$, to be quite explicit

$$\bar{\Psi}_{1/2, 1/2} = \Phi_{k_1}^\lambda \Theta_{1/2, k_1}^{3, 1/2} + \Phi_{k_2}^\lambda \Theta_{1/2, k_2}^{3, 1/2}. \quad (\text{A2.2})$$

Evidently we can construct the unnormalized second-order density matrix Γ_σ as

$$\begin{aligned} \Gamma_\sigma(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2; \sigma_1, \sigma_2; \sigma'_1, \sigma'_2) \\ = \int \Psi^*(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3; \sigma_1, \sigma_2, \sigma_3) \Psi(\mathbf{r}'_1, \mathbf{r}'_2, \mathbf{r}_3; \sigma'_1, \sigma'_2, \sigma_3) d\mathbf{r}_3 d\sigma_3. \end{aligned} \quad (\text{A2.3})$$

Inserting the form (A2.2) into equation (A2.3) and using the orthonormality of the spin functions yields for the spinless matrix $\gamma(\mathbf{r}_1, \mathbf{r}'_1)$ the result

$$\begin{aligned} \gamma(\mathbf{r}_1, \mathbf{r}'_1) = & \int \Phi_{1/2, k_1}^*(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \Phi_{1/2, k_1}(\mathbf{r}'_1, \mathbf{r}_2, \mathbf{r}_3) d\mathbf{r}_2 d\mathbf{r}_3 \\ & + \int \Phi_{1/2, k_2}^*(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \Phi_{1/2, k_2}(\mathbf{r}'_1, \mathbf{r}_2, \mathbf{r}_3) d\mathbf{r}_2 d\mathbf{r}_3. \end{aligned} \quad (\text{A2.4})$$

These forms (A2.3) and (A2.4) will next be compared with the single determinant results.

Single determinant approximation

Let us denote the two 1s spin-orbitals by $\phi(r)\alpha$ and $\phi(r)\beta$. We take the unpaired 2s electron to be in spin state α , with corresponding orthogonal spin-orbital $\chi(r)\alpha$. Then the single determinantal wave function is

$$\frac{1}{(3!)^{1/2}} \begin{vmatrix} \phi(1)\alpha(1) & \phi(2)\alpha(2) & \phi(3)\alpha(3) \\ \phi(1)\beta(1) & \phi(2)\beta(2) & \phi(3)\beta(3) \\ \chi(1)\alpha(1) & \chi(2)\alpha(2) & \chi(3)\alpha(3) \end{vmatrix}. \quad (\text{A2.5})$$

Following the notation of appendix 1, the two components Φ_-^λ and Φ_+^λ are given explicitly by

$$\Phi_-^\lambda \sim \{1 - (12)\}\{1 - (13)\}aab \quad (\text{A2.6})$$

and

$$\Phi_+^\lambda \sim \{1 + (12)\}\{1 - (13)\}aab. \quad (\text{A2.7})$$

The spin functions can also be written down, their forms being

$$\Theta_{1/2-}^{N,S} \sim \{1 - (12)\}\{1 - (13)\}\alpha\alpha\beta \quad (\text{A2.8})$$

and

$$\Theta_{1/2+}^{N,S} \sim \{1 + (12)\}\{1 - (13)\}\alpha\alpha\beta. \quad (\text{A2.9})$$

The correspondence between space and spin functions in equations (A2.6)–(A2.9) are according to $k_1 = -$, $\tilde{k}_1 = +$ and $k_2 = +$, $\tilde{k}_2 = -$. The above determinant (A2.5) can now be constructed as

$$\Psi_{1/2, 1/2} = (1/\sqrt{2}) \{ \Phi_-^\lambda \Theta_{1/2+}^{N,S} + \Phi_+^\lambda \Theta_{1/2-}^{N,S} \}. \quad (\text{A2.10})$$

Developing the forms (A2.6) and (A2.7) one readily obtains

$$\begin{aligned} \Phi_-^\lambda &= (1/\sqrt{2}) \{1 - (12)\} \{aab - baa\} \\ &= (1/\sqrt{2}) \{-baa + aba\} \end{aligned} \quad (\text{A2.11})$$

and

$$\begin{aligned}\Phi_+^\lambda &= (1/\sqrt{6}) \{1 + (12)\} \{aab - baa\} \\ &= (1/\sqrt{6}) \{2aab - baa - aba\}.\end{aligned}\quad (\text{A2.12})$$

Forming the spinless second-order density matrix from equation (A2.3), and expressing it in terms of components Γ_+ and Γ_- one obtains these as

$$\begin{aligned}\Gamma_+ &= (1/2) \binom{N}{2} \text{tr}_3 |\Phi_+^\lambda\rangle \langle \Phi_+^\lambda| \\ &= (1/4) \{4|aa\rangle \langle aa| + |ab + ba\rangle \langle ab + ba|\}\end{aligned}\quad (\text{A2.13})$$

and

$$\begin{aligned}\Gamma_- &= (1/2) \binom{N}{2} \text{tr}_3 |\Phi_-^\lambda\rangle \langle \Phi_-^\lambda| \\ &= (3/4) \{|ab - ba\rangle \langle ab - ba|\}.\end{aligned}\quad (\text{A2.14})$$

Explicitly the pair function is then given by

$$\begin{aligned}\Gamma(1, 2) &= \Gamma_+(1, 2; 1, 2) + \Gamma_-(1, 2; 1, 2) \\ &= 2\{a(1)a(2)\}^2 + (1/2) \{a(1)b(2) + b(1)a(2)\}^2 \\ &\quad + (3/2) \{a(1)b(2) - b(1)a(2)\}.\end{aligned}\quad (\text{A2.15})$$

To conclude the discussion of this $S = 1/2$ case, we note

(i) Li is exceptional in the context of table 1 which would predict three different Γ_k 's. The reason is that $S_{3 \rightarrow N}$ cannot be $3/2$ when $N = 3$ as in Li;

(ii) For general N and $S = 1/2$, the general first-order density matrix is a superposition of just two γ 's.

References

- [1] A.J. Coleman, Rev. Mod. Phys. 35 (1963) 668.
- [2] E.R. Davidson, *Reduced Density Matrices in Quantum Chemistry* (Academic Press, New York, 1976).
- [3] K.A. Dawson and N.H. March, J. Chem. Phys. 81 (1984) 5850.
- [4] M.D. Gould, J. Paldus and G.S. Chandler, J. Chem. Phys. 93 (1990) 4142.
- [5] A. Holas and N.H. March, Phys. Rev. A51 (1995) 2040.
- [6] A. Holas and N.H. March, Int. J. Quantum Chem. (in press).
- [7] A. Holas, N.H. March, Y. Takahashi and C. Zhang, Phys. Rev. A48 (1993) 2708.
- [8] D.J. Klein and N.H. March, J. Mol. Structure (Theochem) (in press).
- [9] W. Kohn and L.J. Sham, Phys. Rev. 140 (1965) A1133.
- [10] P.O. Löwdin, Phys. Rev. 97 (1955) 1474.
- [11] J.E. Mayer, Phys. Rev. 100 (1955) 1579.
- [12] R. McWeeny, Proc. Roy. Soc. (London) A253 (1959) 242.
- [13] R. McWeeny, Proc. Roy. Soc. (London) A259 (1961) 554.

- [14] R.G. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules* (Oxford University Press, New York, 1989).
- [15] R. Pauncz, *Spin Eigenfunctions: Construction and Use* (Plenum Press, New York, 1979).
- [16] J.C. Slater, *Phys. Rev.* 81 (1951) 385.
- [17] E.P. Wigner, *Group Theory and its Application to the Quantum Mechanics of Atomic Spectra* (Academic Press, New York, 1959).