A viable alternative to the unitary group approach in quantum chemistry

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Abstract. A certain element of danger of the unitary group approach and practice is pointed out. A viable alternative formalism is presented with an overview of the development, a summary of the achievements and a discussion on its prospects pertaining to the configuration interaction calculations, open-shell perturbation theory, propagator methods and variational theory. Special reference is given to the open-shell HF problem. Lastly, the possibility of handling atomic multiplet states is discussed.

1. Introduction

In spite of the remarkable success of the unitary group techniques in quantum chemistry (Paldus 1981; Shavitt 1981) it may not be entirely pointless to welcome an alternative approach which, on one hand, would be as viable as the unitary group-based methods are as far as their technical achievement is concerned, and on the other, would not, like these methods, pose any threat to conceptual developments in quantum chemistry. Indeed, the unitary-group derived approach, by providing a computational "blackbox", will soon have set the trend among quantum chemists to use it indiscriminately on a "feed and extract" basis, and with time, there will be no room for the play of imagination and the exercise of intuition in quantum chemistry.

Here we bring a progress report of one formulation (Mukhopadhyay and Pickup 1982) which is viable in the above sense, and provides a meaningful language in which a quantal electronic structure problem can be conceived, formulated and solved without having to undergo any technical drudgery.

2. Formulation

We begin by asking what the unitary group is set to achieve in a problem of the above nature. Addressing a general open-shell system where it really triumphs, it basically purports to generate the various electronic states and the corresponding Hamiltonian matrix, and to evaluate the latter, all very efficiently. For the latter aspect, it is rewarding to classify the states according to their behaviour under spin

and other symmetries of the Hamiltonian. Let us first tackle the spin problem the way we want to, the rest follows quite easily.

A general open-shell means a distribution of a certain number of electrons in several orbital-levels with varied occupancies 0, 1 or 2 *outside* a closed-shell core of doubly occupied levels. The latter is easily given a state, necessarily a spin-singlet, as a sequential product of the Fock-space pair creation operators P_i, $i(j, k, \ldots)$ referring to the closed-shell orbitals:

$$|0\rangle = \prod_j^{N_c/2} P_{i_j} |\text{vac}\rangle, \quad \langle 0|0\rangle = 1, \quad P_i = X_{i\beta}^+ X_{i\alpha}^+, \tag{1}$$

N_c being the number of electrons in the core, $|\text{vac}\rangle$ the no-orbital singlet vacuum state, and $X_{i\beta}^+$ $(X_{i\alpha})$ the fermion spin-orbital creation (annihilation) operators. By the Pauli exclusion principle, no two P operators in the same spin state may have identical labels.

To account for the distribution over the remaining, so-called open-shell levels $(u, v, w, \ldots)$, we introduce, in addition to P_u, two other Fock-space operators:

$U_u(S)$, which, acting on an arbitrary many-electron spin state $|S\rangle$ where the orbital u is empty, creates an electron in orbital u, and increases the spin of the resulting state by $\frac{1}{2}$;

$D_u(S)$, which, similarly acting, decreases the spin by $\frac{1}{2}$. Since spin cannot be lowered below $S = 0$, we demand that

$$D_p|S = 0\rangle = 0, \quad \text{for any orbital } p(q, r, \ldots). \tag{2}$$

With all that we have, any many-electron spin state, normalized to unity, can be written down as a sequential product of the above three types of creation operators acting on a vacuum. Figure 1 describes the spin states in the genealogical scheme (see Pauncz 1979) with $N_c + 3$ electrons. Each spin state is a linear combination of several Slater determinants, and the combining coefficients, if necessary, are easily retrieved as shown in Mukhopadhyay and Pickup (1982).

The annihilation operators corresponding to P_p, U_p and D_p are not P_p^+, U_p^+ and D_p^+, respectively, but the related operators P^p, D^p and U^p to within some unimportant factors, and their effect on a given spin state is to remove an electron (electrons, if it is P) occupying the orbital p therein, changing the spin as implied in the notation: U for "up" increases, D for "down" decreases, and P for "preserve" maintains. Diagrammatically, a bra spin state obtains by reflecting the corresponding ket spin state diagram in a vertical mirror, and reversing the arrows as explained in the box part of figure 1.

One can dispense with the core by treating it as the new vacuum $|0\rangle$, and proceed by particle-hole transforming the above operators. Deleting the underbars for the transformed operators, the new vacuum is fixed by

$$D^p|0\rangle = 0 = U^p|0\rangle, \quad \text{for all } p. \tag{3}$$

The algebra carried by these spin-adapted creation and annihilation operators (Pickup and Mukhopadhyay 1984a; Mukhopadhyay and Pickup 1984) is decided partly by the behaviour of two-electron states under orbital transposition; this is best accounted for by recognising only six distinct crossings between the creation and/or annihilation operators (cf figure 2A). The algebra is completed by the
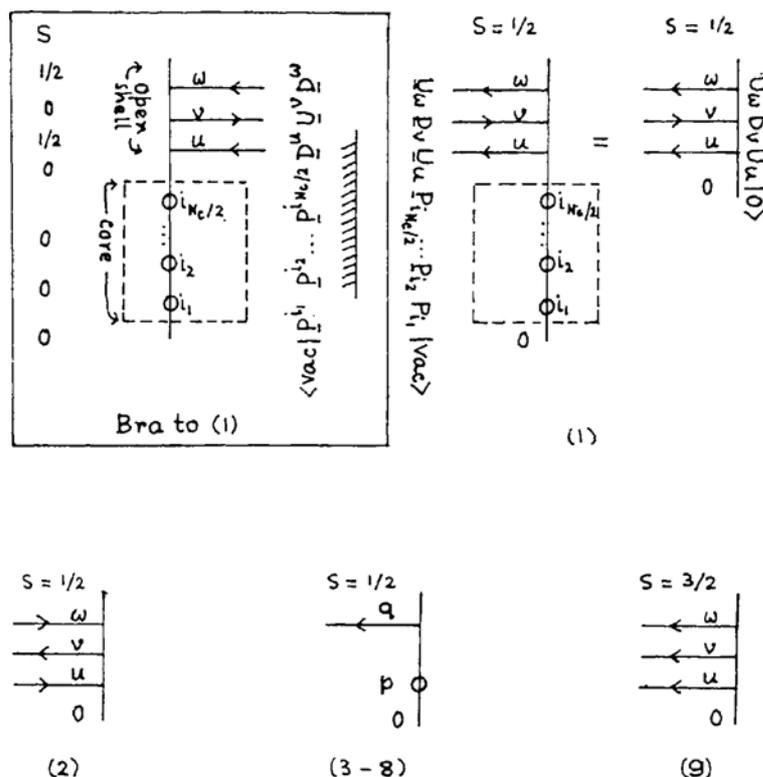
Figure 1. Spin-state diagrams showing $S = \frac{1}{2}(1-8)$ and $S = \frac{3}{2}(9)$ kets. Formation of bra to (1) is shown inside the box; S in the leftmost column stands for the segmental spin values. Six diagrams (3–8) may be generated by allowing p, q the values u, v, and w.

orthonormality among the spin states generated (provided the orbital basis is orthonormal which we have assumed), and this is ensured by resorting to a set of contraction rules as in figure 2B. The permutational behaviour takes care of the Pauli exclusion principle, for no two lines in a given spin state, having arrows in the same direction, can bear the same labels.

From the algebra implied by figure 2A it is not difficult to pass from the genealogical to the Jahn-Serber coupling scheme as will be shown elsewhere (Mukhopadhyay and Pickup 1987). This necessitates diagonalization of the matrix of the transposition (p, q) over the two-electron genealogical basis $U_q U_p$, $U_q D_p$, $D_q U_p$ and $D_q D_p$ all acting on an arbitrary spin state. For the rest of the paper, however, we stick to the genealogical basis.

The much-occurring spin-independent Hamiltonian

$$H' \equiv H - \langle 0|H|0 \rangle = \sum_{p,q} \langle p|f|q \rangle N[E_{pq}] + \frac{1}{2} \sum_{p,q,r,s} \langle pq|v|rs \rangle N[E_{pr}E_{qs}] \qquad (4)$$

is easily shown to have a diagrammatic representation (Mukhopadhyay and Pickup 1982, 1984) given and explained in figure 3. The term $\langle 0|H|0 \rangle$ represents the core energy, $N[E_{pq}]$ normal ordering with respect to $|0\rangle$, and $E_{pq} = \Sigma_\sigma X^+_{p\sigma} X_{q\sigma}$ is the orbital unitary group generator, σ assuming α or β spin. f refers to the
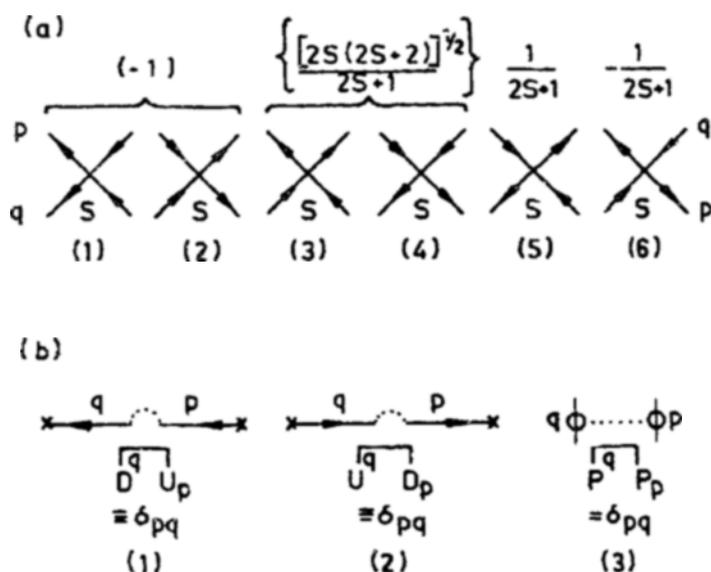
Figure 2. Algebra of the spin-adapted operators. (a) Six distinct crossings are shown, each conserving arrow current and having a value shown at the top with reference to the segmental spin value at the bottom. Relations induced by the orbital transposition (p, q) like

$$D_q U_p | S\rangle = [\{1/(2S+1)\} D_p U_q - \{[2S(2S+2)]^{1/2}/(2S+1)\} U_p D_q] | S\rangle$$

may be obtained from (3) and (5) which have identical right hand parts. (b) Only allowed contractions are shown, omitting some unimportant factors; lines with matching arrows are contracted.

Hartree-Fock (HF) operator defined with respect to the core not necessarily satisfying

$$\langle p | f | q \rangle = \varepsilon_p \delta_{pq}. \tag{5}$$

The greatest virtue of the present formulation is apparent when we come to form and evaluate matrix-elements of the Hamiltonian over the spin states; one generates a matrix-element diagram in almost the same manner as in the standard many-body theory (cf figure 4). One notable difference is contained in this: a circle and a line may now be contracted as shown in the inset of figure 4. Evaluation proceeds via the following rules:

1. draw only the topologically distinct matrix-element diagrams, that is, the ones which do not, under allowed deformation, pass into one another;

2. evaluate all the L-shapes (cf figure 4): a clockwise L-shape gets a factor $L_c(S) = \sqrt{\{(2S+2)/(2S+1)\}}$ whereas an anticlockwise L-shape gets $L_a(S = -\sqrt{\{(2S)/(2S+1)\}}$, S being the segmental spin below the apex of the L-shape;

3. evaluate all the crossings according to figure 2A;

4. associate orbital matrix-elements to all the F and V vertices in the diagram (cf figure 3);
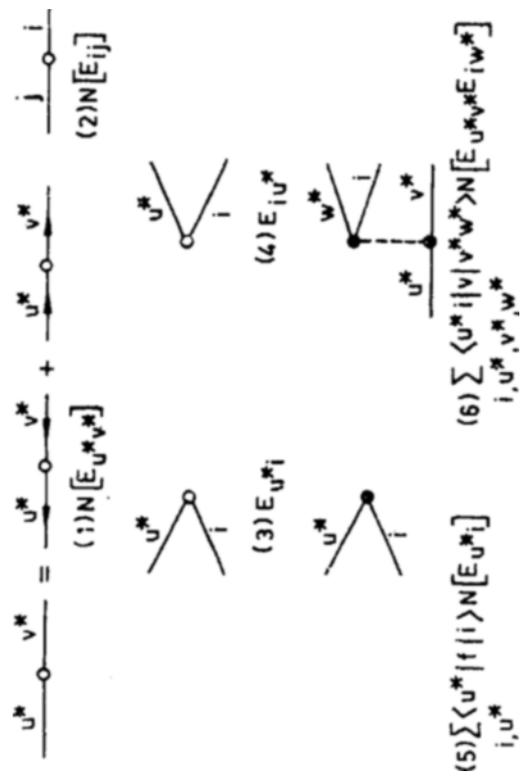
Figure 3. Hamiltonian diagrams involving E (1-4) apart from some implicit factors, a typical $F(5)$ and $V(6)$. Note the way orbital matrix-elements are associated. (1) also explains the convention adopted; arrow current must be conserved.
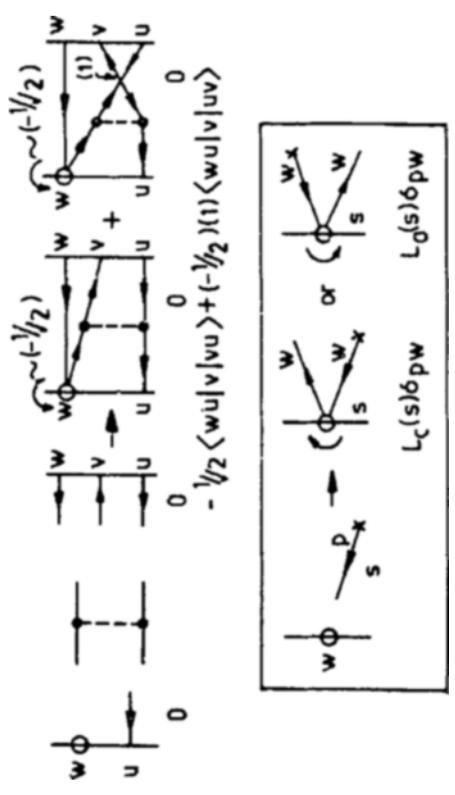
Figure 4. Formation of a typical matrix-element diagram. The box part explains what happens when a pair and any annihilation/creation operator (either from an E or from a state indicated by an x at the end) are involved: either a clockwise or an anticlockwise L-shape obtains having a value $L_c(S)$ or $L_a(S)$, respectively.

5. ascribe a phase of (-1) to every hole-hole scattering in a vertex;
6. give a topological factor of $1/2$ to every V vertex that has a mirror plane within the matrix-element diagram;
7. multiply out.

These rules are akin to the ones we are used to in the ordinary many-body theory, and are far simpler than those prescribed in the unitary-group derived methods. It should be possible to exploit this simplicity algorithmically to compete with the unitary group in effecting configuration interaction calculations.

3. Further developments and prospects

Implementation of open-shell perturbation theory in the unitary group framework (Shavitt 1981) faces an organizational difficulty in properly selecting the subspace of the configuration functions. While this might require a redressing of the entire configuration space, relevance and efficacy of the present formulation is discussed in Mukhopadhyay and Pickup (1984).

The other important area where this formalism has proved its worth concerns the propagator theory. In the traditional open-shell formulation (Linderberg and Öhrn 1973; Albertsen and Jørgensen 1979) it is impossible to distinguish poles of a non-singlet propagator of one-spin symmetry from those of others. In an earlier variant, the present formalism led to a successful decoupling, thus isolating the triplet pole from the singlet one (Pickup and Mukhopadhyay 1981). An interesting application of this work appears in Nichols *et al* (1984) where the authors not only make assignments of some shake-up peaks in the PES and ESCA spectra of O_2 but also predict location of some others. Further extensive work is necessary till we resolve the problems of multiconfigurational propagator theory satisfactorily, though certain progress has been made in this direction (Pickup and Mukhopadhyay 1984b). Success of the unitary group in this context (Born and Shavitt 1982) will depend on how the basic structure of the associated approach has to be revised.

To indicate applicability of the formalism in variational theories let us consider the issue of the HF solutions for a simple open-shell system having one electron outside the core. Naturally we would write the trial ground state function as

$$|\varphi\rangle = U_u|0\rangle, \quad \langle\varphi|\varphi\rangle = 1. \tag{6}$$

A necessary condition for the expectation value of H' in (4) is that

$$\langle\delta\varphi|H'|\varphi\rangle = 0 \text{ to first order in } \langle\delta\varphi| \text{ for all orbitals.} \tag{7}$$

A first-order change in $|\varphi\rangle$ is effected by replacing the orbital u by $u + \xi a$ and the core orbital i by $i + pu^*$ where ξ and p are two small numbers, a an orbital not occupying $|\varphi\rangle$ and u^* an orbital outside the core. This induces the following first-order change in $|\varphi\rangle$:

$$|\delta\varphi\rangle = (\xi U_a D^u + \rho U_{u^*} D_i)|\varphi\rangle = (\xi U_a D^u + \rho U_{u^*} D_i) U_u|0\rangle. \tag{8}$$

The condition (7) would then require fulfilment of

$$\langle 0|D^i U^{u^*} D^u H' U_u|0\rangle = 0, \text{ for } u, \text{ and all } i, a, \tag{9}$$

and simultaneously of

$$\langle 0|D^a H' U_u|0\rangle = 0, \text{ for } u \text{ and all } a. \tag{10}$$

These are the Brillouin conditions (Lefebre 1965). Evaluating these from the corresponding diagrams in figure 5 according to the rules given earlier we have (Paldus and Čížek 1970),

$$\langle u|f|i\rangle + \langle uu|v|ui\rangle = 0, \text{ when } u^* \text{ is } u, \tag{11}$$

$$2\langle a|f|i\rangle + \langle ua|v|ui\rangle - \langle ua|v|iu\rangle = 0, \text{ when } u^* \text{ is } a, \tag{12}$$

$$\langle a|f|u\rangle = 0 \tag{13}$$

for u, and all i, a; here f corresponds to the core HF operator.

Searching for a set of Brillouin conditions for a general open-shell case would certainly be an interesting problem to pursue. By carrying out an analysis of the above type up to second-order variation one can also address the associated stability problems.

Lastly we discuss how atomic multiplet states may be handled. Let us consider the p^3 configuration of an atom, and suppose 1, 2 and 3, respectively, stand for the orbital states $|nl = 1, m_l\rangle$ with $m_l = 1, 0, -1$. The possible spin states may be recovered from figure 1 by letting u, v, w assume labels 1, 2 and 3. The total M_L value of each spin state is easily obtained by adding up the m_l values of the orbitals occupying the open-shell levels. For a given S it is thus possible to locate the spin state that has the highest M_L, say M_L^h; it *is* then the multiplet state ^{2S+1}L, L being M_L^h. The other LS states with different M_L values may be obtained by successive application of the lowering operator L_- which, in the present case, is proportional
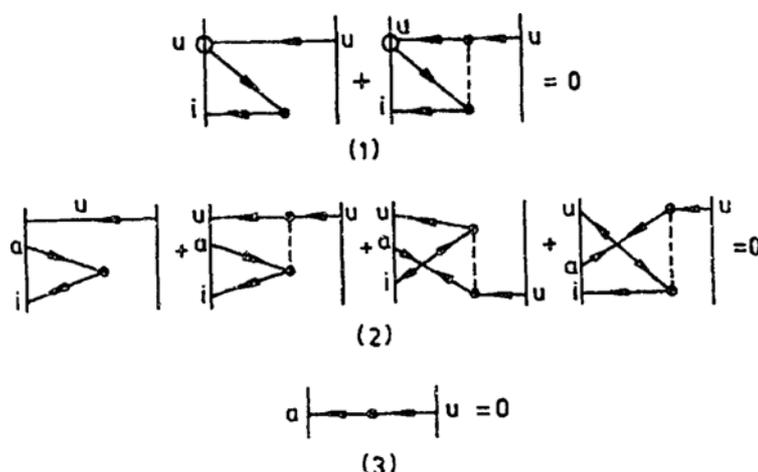

Figure 5. The Brillouin conditions for a simple open shell. Single excitations in (1) is from i to u forming a pair in the latter, in (2) from i to a, and in (3) from u to a; all excitations retain the singlet character of the core state.

$$|^2D \quad 2\rangle =$$

$$|^2D_{/2p} \quad 1\rangle = \tfrac{1}{2}\left(\ \mp\ \right)$$

$$| \; " \quad 0\rangle = \sqrt{3}/2 \quad \mp \tfrac{1}{2}$$

$$| \; " \quad -1\rangle = \tfrac{1}{2}\left(\ \mp\ \right)$$

$$|^2D \quad -2\rangle =$$

$$\{\hat{L}_-\alpha(E_{21}+E_{32})\} \quad = \quad + \tfrac{1}{3}$$

$$= \left(-\ +\ \right) - \tfrac{1}{2}\left(-\ +\ \right)$$

Figure 6. Atomic spin angular momentum states $|^{2S+1}L\,M_L\rangle$ of a p^3 configuration. The box part explains the steps from the first to the second line. In the second to fourth lines ^2D (^2P) corresponds to the upper (lower) sign.

to $\Sigma_p\, E_{p+1,p}$, the proportionality constant being fixed by normalizing the resulting state to unity. Other multiplet states are obtained in the usual manner by orthogonalization, and the results appear in figure 6. Formulation of this kind lends an easy means of obtaining coefficients of fractional parentage of open-shell systems and exploring their relevance to X-ray PES studies (Mukhopadhyay 1987).

4. Concluding remarks

Once the pertinent symmetries are taken care of in a formulation without upsetting the structure akin to the standard many-body theory, much of the open-shell developments may take place as easily as in relatively simpler problems. A study of multiconfigurational self-consistent field theory in this formalism may be one test-case.

There is considerable group theoretical work behind what is presented here, and this ensures the properties of the spin-adapted operators to be as reported, guaranteeing at the same time, the cancellation of the various factors frequently swept aside as unimportant. The rules are what the formalism eventually amounts to; they are simple and accessible even to those who do not know anything about the unitary group or the Racah algebra.

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