Theor Chem Acc (2000) 103:238–241
DOI 10.1007/s002149900048

Theoretical
Chemistry Accounts

Perspective

Chemical building blocks in quantum chemical calculations. Perspective on "The density matrix in many-electron quantum mechanics I. Generalized product functions. Factorization and physical interpretation of the density matrices"

McWeeny R (1959) Proc R Soc Lond Ser A 253: 242–259

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Received: 26 February 1999 / Accepted: 7 April 1999 /

Abstract. The group function theory described in the title paper of McWeeny is overviewed by pointing out its influence on different fields of theoretical chemistry, in particular its serving as a general framework for various forms of building blocks and local treatments of extended systems.

Key words: Generalized product function – Group function – Ab initio model potentials – Embedding – Spectator groups

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1 Introduction

In the middle of the 1950s the laboratory of Professor Slater at MIT gathered several brilliant young theoretical chemists to work on the derivation of matrix elements of the Coulombic Hamiltonian with respect to arbitrary Slater determinants. This research activity led to some very important general results, connected essentially to the names P.-O. Löwdin and R. McWeeny, both of whom were working independently along similar lines. Löwdin published his results about density matrices, natural orbitals as well as on the matrix elements between nonorthogonal Slater determinants in an internal report [1] in 1954 and published it in *Physical Review* [2] in 1955. McWeeny's technical report, which summarized his lectures given in May 1954, appeared in May 1955, followed by a series of papers in the *Proceedings of the Royal Society* in 1956. However, the most significant publications on this subject followed only a few years later: the title article [3] in 1959, as well as an exhaustive presentation of the density matrix formalism [4] in 1960. As McWeeny noted in the preface of the 1955 technical note [5], the objective of this work was twofold. On the one hand, there was a "tendency towards elaboration and codification of existing methods in preparation for electronic digital computation", but on the other there was "an equal need to keep an underlying physical picture." Löwdin's contribution to density matrix theory has been proven to be essential, and this is the subject of another perspective in this New Century Issue. While Löwdin focussed mainly on the interpretation of the one-particle density matrix (e.g. natural orbitals), McWeeny gave a detailed interpretation of the physical meaning of two-particle density matrices. This analysis has been reiterated in McWeeny's excellent textbooks [6, 7], which have educated several generations of theoretical chemists.

In spite of the primordial importance of density matrix theory, in the present account I would like to concentrate on another closely related result of the title paper: the theory of generalized product functions. This theory beautifully demonstrates that fundamental chemical concepts are not necessarily contradictory to rigorous quantum mechanics. On the contrary, such concepts can be advantageously exploited for the design of powerful approximation schemes. In fact, McWeeny has always insisted on the importance of a conceptual approach to the problems of quantum chemistry, as witnessed, for example, by his work on two-particle density matrices [4] or on the interpretation of dispersion energies in terms of propagators [8].

Chemists have always refused to consider each individual molecule as a completely new object and have tried to rationalize physical and chemical properties in terms of basic building blocks. The experience of more than a century supported the existence of transferable structural units in molecules, such as bonds, functional groups, chromophores, etc. The idea of functional groups or chromophores also implies that only a small part of the whole molecule, which is responsible for the chemical and spectroscopic properties, is active, while the remaining parts of the molecule behave as spectator groups. Standard methods of quantum chemistry do not take into account this distinction and they usually treat all the electrons of the system on an equal footing.

McWeeny proposed a generalization of the usual antisymmetrized product of one-electron wave functions in terms of an antisymmetrized product of many-electron group functions. The extreme elegance of his formalism lies in the fact that it is able to encompass in a natural way the usual molecular orbital theory, the method of geminals, on the one hand, and on the other hand, it opened the way for different methods where chemically identified electron groups are treated separately.

2 Generalized product functions

A generalized product function, as defined in the title paper, is an antisymmetrized product of the $\Phi_{\mathrm{Aa}}(1,\ldots,N_{\mathrm{A}})$ individually antisymmetric wave functions describing the groups A in their electronic state a:

$$\Phi_{Aa,Bb,\ldots}(1,2,\ldots,N) = \hat{A}'\Phi_{Aa}(1,\ldots,N_A)\Phi_{Bb}(N_A+1,\ldots,N_A+N_B)\ldots \quad . \tag{1}$$

The intergroup antisymmetrizer, $\hat{A}'$ permutes electrons between different groups. The wave function (Eq. 1) is a straightforward generalization of a Slater determinant: the one-electron wave functions (spin-orbitals) are replaced here by N_A-electron wave functions.

As a generalization of the configuration interaction, the total wave function can be written as a linear combination of generalized products of the type (Eq. 1)

$$\Psi(1,2,\ldots,N) = \sum_{a,b,\ldots} C_{a,b,\ldots}\Phi_{Aa,Bb,\ldots}(1,2,\ldots,N) \quad . \tag{2}$$

Although in a strict sense, this form is inappropriate for expanding the exact wave function, which should contain all the possible partitions of the electrons among the individual groups, the wave function (Eq. 2) seems to be a good initial approximation to describe systems composed of loosely coupled electron groups.

McWeeny assumed that the group functions are completely arbitrary, i.e. they can correspond to highly correlated accurate wave functions of the individual groups. The only restriction, imposed upon the group functions was the strong orthogonality condition:

$$\int d\tau_1 \Phi_{Rr}(1,\ldots,N_R)\Phi_{Ss}(1,\ldots,N_S) = \delta_{RS}\delta_{rs} \quad , \tag{3}$$

i.e. it was required that the overlap integral, taken with respect to any of the electron (space and spin) coordinates, should vanish. The strong orthogonality condition simplifies tremendously the formalism. Although in several cases it is quite straightforward to respect it without losing accuracy, this restriction proved to be somewhat frustrating in several physical applications where it had to be relaxed [9].

By the virtue of the strong orthogonality condition the two-particle density matrix of the total system could be expressed in terms of the one- and two-particle density matrices of the individual groups, which is one of the central results of the title paper [3]. This allowed the derivation of the analogs to the Slater rules for generalized product functions, and the matrix elements of the molecular Hamiltonian could be written in terms of intergroup Coulomb and exchange operators $\mathscr{J}^S(i)$ and $\mathscr{K}^S(i)$. The effective Hamiltonian of a group is

$$\mathscr{H}^R_{\mathrm{eff}}(1,2,\ldots,N_R) = \sum_{i=1}^{N_R}\left[h^R(i) + \sum_{S(\neq R)}[\mathscr{J}^S(i) - \mathscr{K}^S(i)]\right] + \sum_{i<j}^{N_R} g(i,j) \quad . \tag{4}$$

The local Brillouin theorem of the usual self-consistent-field (SCF) theory was also generalized to the following form

$$\langle\Phi_{Aa}|\mathscr{H}^{\mathrm{A}}_{\mathrm{eff}}|\Phi_{Aa'}\rangle = 0 \quad , \tag{5}$$

corresponding to the physical condition that the first-order polarization energy of the total system vanishes. The above statement is equivalent to a variational principle applied to the group energies, i.e. the expectation values of the effective group Hamiltonians (Eq. 4). Thus the electronic Schrödinger equation of the full extended system can be replaced by a set of effective equations of lower dimensionality for the group functions which are coupled by the intergroup Coulomb and exchange potentials.

The above ingredients of the theory would, in principle, allow us to identify various types of electron groups, relying on our physical or chemical intuition to design an efficient procedure for the treatment of large systems, paying special attention to those groups where the most important chemical events take place. Even if the optimization of the group functions according to the principles described above may seem to be straightforward, one should solve a crucial technical problem: how to maintain the (strong) orthogonality during their variation. The response to this question depends strongly on the nature of the electron groups.

3 Some specific applications of the group function method

The necessity of partitioning the electrons in a molecule into core and valence groups was recognized in the early days of quantum chemistry. A similar separation seemed to be necessary for planar molecules where the mobile π electrons are responsible for most of the spectroscopic properties and chemical reactivity. It was only after several decades of the successful use of the Hückel method and with the appearance of more sophisticated SCF-type π-electron approximations that some attempts were made at establishing the fundamental theoretical basis of these methodologies relating them to ab initio calculations. In fact, the treatment of the σ-π separation by Lykos and Parr [10] was a precursor to the group function idea. In this special case, the strong orthogonality condition is automatically fulfilled due to the different symmetries of these two groups of electrons.

In semiempirical molecular orbital theories one assumes a formal orthogonality of the underlying atomic orbital basis, which makes it relatively straightforward to implement group function theory. One can cite the PCILO (Perturbative configuration interaction with localized orbitals) method [11], which uses strictly localized two-electron bond orbitals to construct a zeroth-order wave function and perturbational corrections to describe the interaction between them. In the spirit of group function theory, many-electron groups are used to describe delocalized systems, such as π fragments in the extended PCILO method [12]. Surján [13] developed an elegant formalism in terms of strictly localized two-electron wave functions, called geminals. The zeroth-order wave function, which is an antisymmetric product of strictly localized geminals, can be systematically improved by many-body perturbation techniques. Since each bond is described locally at a "full configuration interaction" level, well-localized chemical reactions (e.g. bond breaking) can be efficiently represented with such wave functions.

The separated electron pair concept, which was first proposed by Hurley et al. [14] and which was later referred to as antisymmetrized product of strongly orthogonal geminals (APSG) [15], is also a special case of the group function concept. This kind of wave function is qualitatively correct at all internuclear distances and it can be improved either perturbationally [16, 17] or variationally [18].

In the above-mentioned cases the strong orthogonality condition could be fulfilled. In fact the simplest way to ensure strong orthogonality is to construct the individual group functions from orbitals taken from different sets which are orthogonal to each other [19]. Although an orthogonalization of the basis set is always possible, it is not a solution for the physically most attractive situations, where one would like to bring together separate systems, each described by their own wave functions, to form a composite system and estimate their interaction energy. Similarly, there would be no advantage in optimizing the wave function of the active electrons in the effective field of the spectator groups if, as a consequence of the orthogonalization, we were constrained to work with the whole one-electron basis set.

The relaxation of the strong-orthogonality constraint was studied first by McWeeny and Sutcliffe [9], who derived density matrix expressions for the four-electron case. The general formulation for arbitrary closed shell groups [20] allowed the development of a general theory of intermolecular potentials at short and intermediary distances. In such weakly interacting systems it is not necessary to relax the electron groups in the field of their partners: the electrostatic, polarization and dispersion energy components are calculated from the isolated wave functions of the components.

In the case of more strongly interacting groups it is necessary to optimize the individual groups in the field of the others. This is typically the case for the valence electrons in the field of the atomic cores, for a functional group in the field of the substituents or a defect subsystem in an ionic or molecular crystal. In the course of such optimizations one should take precautions in order to avoid a variational collapse, i.e. the partial occupation of the subspace belonging to the partner electron group.

A possible solution to this problem was given by Kleiner and McWeeny [21] in the case of the core–valence separation. They derived an ab initio effective core potential, obtained directly from the core wave function, which can be brought to a form which is analogous to the Phillips–Kleinmann-type core pseudopotentials. This line of thought has been pursued in a systematic manner by several authors. For example, Huzinaga's building-block equations [22] allow one to obtain the Hartree–Fock orbitals for one subsystem, provided that the solutions for the other subsystems are known. Applying a series of approximations, ab initio model potentials can be derived for different situations, such as atomic cores [23, 24] spectator groups [25–28], or ions or molecules embedded in crystals [29–31].

Yet another way of circumventing the nonorthogonality problem is by replacing the strong-orthogonality condition by the strong-biorthogonality condition, i.e. using a biorthogonal basis to preserve the formal simplicity of the density matrix and effective group energy expressions for the composite system. Nevertheless, the group function variational principle cannot be applied in an identical fashion, and further constraints should be applied to restrict each group to its own variational subspace. Mehler [32] proposed imposing the condition that the intergroup overlap integrals remain constant throughout the variation of the group orbitals. The effective group equations he obtained are closely related to Huzinaga's equations as well as to the Adams–Gilbert equations used in obtaining a priori localized orbitals.

Group function theory may serve as a valuable guide in establishing a firm basis for quantum mechanical solvent effect theories. Microscopic solvent effect models can be introduced by arguing in terms of solute and solvent groups and by considering the solvent molecules as spectator groups [33]. The microscopic reaction field and some related models can also be derived from a perturbational ansatz applied to the coupled set of solute–solvent group function equations [34]. The status of some heuristic hypotheses used in the derivation of the energy derivative expressions of the solvent cavity model has been analyzed in light of the theory of generalized product functions [35].

4 Perspectives

There are essentially two possible ways to invoke chemical concepts such as atoms, functional groups, etc., in theoretical chemistry. The a posteriori way consists of performing an analysis of the wave function and extracting the properties associated with some rigorously defined objects corresponding to such subsystems. For example, the work of Bader [36], who succeeded in formulating the concept of the atoms in molecules in a quantum mechanically well-founded manner, exemplifies this kind of approach. The a priori way of using chemical concepts, i.e. to postulate the existence of such chemical fragments or building blocks, while still remaining on the solid ground of rigorous quantum mechanics, seems to be even more difficult. McWeeny's pioneering work on group functions demonstrated that such a plan might be conducted with success.

The ever-growing interest in accurate quantum chemical treatments of extended systems such as macromolecules and crystals would greatly benefit from models which are based on well-defined basic hypotheses and a controlled hierarchy of approximations. Group function theory offers such a framework and continues to be a reference in the design of new models ranging from various ab initio model potentials applied to core electrons, spectator groups, embedded atoms or solvent molecules, to local space treatments and even to mixed quantum–classical models. I am convinced that in the future the empirical ingredients of these various models will be replaced by parameters which are rigorously related to high-quality wave functions of the fragments constituting the complete system. There are some encouraging results in this respect [37], but still a great deal of work remains to be done.

Acknowledgement. I am indebted to P. Surján (Budapest) for the many interesting discussions on the subjects related to group function theory and for reading this manuscript.

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