CHEMICAL SOCIETY REVIEWS

Modern valence bond theory

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The spin-coupled (SC) theory of molecular electronic structure is introduced as the modern development of classical valence bond (VB) theory. Various important aspects of the SC wave function are described. Attention is particularly focused on the construction and properties of different sets of *N*-electron spin functions in different spin bases, such as the Kotani, Rumer and Serber. Applications of the SC description to a range of different kinds of chemical problems are presented, beginning with simple examples: the H_2 and CH_4 molecules. This is followed by the description offered by the SC wave function of more complex situations such as the insertion reaction of H_2 into $CH_2(^1A_1)$, the phenomenon of hypervalence as displayed by molecules such as diazomethane, CH_2N_2, SF_6 and XeF_2. The SC description of the ground and excited states of benzene is briefly surveyed. This is followed by the SC description of antiaromatic systems such as C_4H_4 and related molecules.

1 Introduction

The description of the behaviour of electrons in molecules involves the application of quantum mechanics to very complex systems. Our ultimate objective is not simply to confirm theoretically what we already know from experiment. This merely assures us that quantum mechanics is correct. What we seek is much more: we seek insight into the behaviour of the electrons in a molecule, an explanation of the formation of

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Joe was born in 1938 and obtained his first degree in chemistry from Hertford College, Oxford in 1961 and his PhD in 1966 with Professor I. M. Mills in Reading. He was a post-doctoral fellow with Professor W. N. Lipscomb at Harvard, where he laid the foundations of spin-coupled theory, culminating in a major paper in Advances in Atomic and Molecular Physics *in 1971. He has been at Bristol since 1968, where is is Reader in Theoretical Chemistry.*

Mario was born in Gravedona (Como), near Milan (Italy) in 1939. He obtained his first degree from the University of Milan. He was a post-doctoral fellow with Professor M. Karplus at Harvard. He collaborated with Professor M. Simonetta. In 1976, he met Joe at CECAM, at Orsay, where they first began their collaboration. He was appointed to a Chair in Physical Chemistry in 1994.

David was born in Leeds in 1957. He obtained his first degree from Brasenose College, Oxford in 1979 and his DPhil in 1981 with Graham Richards, also in Oxford. He was a Smithsonian Fellow at Harvard College Observatory from 1981, where he met Joe and joined forces with him and Mario. He returned to Oxford in 1984 as a Royal Society lecturer, before taking up an appointment in Liverpool where he is now Reader in Physical Chemistry.

Peter was born in Sofia, Bulgaria in 1959. He graduated in Chemistry from the University of Sofia in 1981 and obtained his PhD there in 1983. From 1981 to 1986 he worked as a research assistant and as an assistant professor at the Faculty of Chemistry of Sofia University. In 1986, he moved to the Bulgarian Academy of Sciences, where he was a research fellow until 1994. In 1990–1995 he was a visiting research associate with Joe Gerratt at the University of Bristol. In 1995, Peter moved to the University of Surrey where he is now a lecturer in Physical Chemistry.

Joe Gerratt

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chemical bonds, the characteristics of such bonds, their strength, type, how they form and how they break.

However, one should not lose sight of the fact that a description, if it is to carry any conviction, must also provide reliable numerical results which, in addition, must be capable of refinement if one so wishes.

The solutions to these problems are not simple, nor even unique. Quite certainly, no answers of much value are obtainable by straightforward application of the considerable computing power now available to find some kind of numerical solution to the Schrödinger equation. Instead the problem remains with ourselves and as a result—unsurprisingly—several different approaches have been tried.

Over the last forty or more years, the most fruitful approach has seemed to be the molecular orbital (MO) or self-consistent field (SCF) approach, in spite of the fact that the MO wave function does not describe correctly even the most basic of chemical processes: the breaking of a chemical bond. Nevertheless, many developments have flowed from the MO approach, some of them of great conceptual importance, such as the rules governing the conservation of orbital symmetry in pericyclic reactions,[1] others of a technical nature which allow us to progress to more complex wave functions in which electronic correlation effects missing from the SCF approach (including those which are responsible for providing a correct description of bond breaking) are taken into account. This last is the method of configuration interaction (CI method), which has now reached a stage where *ca.* 10^8 or 10^9 configurations can be handled by various computer codes. Sophisticated extensions of the SCF method, such as the multiconfigurational SCF (MCSCF) approach and the 'complete active space SCF' (CASSCF) approach, have been developed and these are embodied in highly efficient computer codes, such as GAUSSIAN96, GAMESS, MOLPRO, MOLCAS and other packages which are widely available.

While these techniques have benefited from several generations of development work by many talented research workers to produce codes that must surely be close to optimal for scalar, vector- and even parallel-processing machines, the effect of the large numbers of configurations, which are inevitably involved, seriously affects our vital chemical and physical insight into the problem.

More recently, density functional theory (DFT) a technique that has been in use for many years by the solid state physics community (see *e.g.* ref. 7), has caught the attention of many quantum chemists.[8] A great deal of development work has been carried out in recent times, as is obvious to anyone who attends quantum chemistry conferences, both nationally and internationally. DFT clearly has a number of advantages as compared to the *ab initio* techniques based upon MO theory mentioned above, but questions concerning the foundations of DFT, particularly the origin of the all-important exchange correlation potential, remain and have indeed become more urgent.

Concurrent with the introduction of MO theory and its variants, is the theory of Heitler and London, or valence bond (HL or VB) theory. In fact, it was Heitler and London who first showed convincingly that the explanation of the strength of covalent bonding lay with quantum theory.[2] Just as important, was the clarity of the description offered by this approach. In particular, the HL theory identifies the 'exchange effect' as the fundamental phenomenon responsible for those properties which we associate with a covalent chemical bond: its capability of holding together two electrically neutral atoms, valency itself, the saturation of valency and the idea of the directonality of chemical bonds; concepts which lie at the very heart of chemistry. On the basis of these ideas, Heitler and his students were able to produce a compelling explanation, at least at a qualitative and even at a semi-quantitative level, of many, if not most, aspects of chemical bonding.[3,4]

Heisenberg further showed that this very same approach is crucial to the understanding of the many different forms of magnetism. To this day, the Heisenberg theory remains the only explanation of this central phenomenon of the physics of condensed matter.

It would therefore seem natural for VB theory to have received most attention and development effort. For a short time, it did so. However, the origin of the exchange effect lies in the overlap between the wave functions of the participating atoms. This overlap, or non-orthogonality, between the relevant atomic wave functions has been the source of serious technical difficulties in the wide application of the Heitler–London approach. Such problems remained until new algorithms implemented on modern workstations with large memory, extensive disk storage and high speed I/O, effectively overcame them.

An important extension to the HL theory was the introduction of 'ionic structures' into the wave function, *i.e.* the introduction of chemical structures in which the distribution of the electrons is such that two or more of the participating atoms bear formal positive and negative charges. Nevertheless, the introduction of ionic structures gives rise to severe problems, not least from the interpretational point of view. Even in the simplest case of H_2, in order to obtain reasonable quantitative accuracy, it is crucial to add to the original Heitler–London (covalent) wave function eqn. (1.1):

$$\Psi_c \sim \{\phi_{1s_A}(\mathbf{r}_1)\phi_{1s_B}(\mathbf{r}_2)+\phi_{1s_B}(\mathbf{r}_1)\phi_{1s_A}(\mathbf{r}_2)\}\sqrt{\tfrac{1}{2}}(\alpha_1\beta_2-\beta_1\alpha_2), \quad (1.1)$$

ionic structures of the form eqn (1.2):

$$\Psi_I \sim \{\phi_{1s_A}(\mathbf{r}_1)\phi_{1s_A}(\mathbf{r}_2)+\phi_{1s_B}(\mathbf{r}_1)\phi_{1s_B}(\mathbf{r}_2)\}\sqrt{\tfrac{1}{2}}(\alpha_1\beta_2-\beta_1\alpha_2), \quad (1.2)$$

giving as the total wave function for the H_2 molecule a linear combination of wave functions (1.1) and (1.2): (1.3).

$$\Psi_{tot} = C_1\Psi_c + C_2\Psi_I. \quad (1.3)$$

Here $\phi_{1s_A}(\mathbf{r}_1)$ and $\phi_{1s_B}(\mathbf{r}_2)$ denote 1s-like orbitals for electrons 1 or 2, centred on hydrogen atoms A or B. Coefficient C_2 is small but by no means negligible, $C_2/C_1 \simeq 0.25$ for H_2 near its equilibrium geometry.

We are thus invited to view the H_2 molecule, which as far as every chemist is concerned, is quintessentially covalent, as a resonance mixture between a covalent contribution, represented by wave function (1.1), and an ionic part, represented by wave function (1.2), a physical picture which flies in the face of one's every chemical instinct.

For larger molecules, many more ionic structures can be formed. From a chemical perspective, most of them undoubtedly appear rather unlikely if not extraordinary. Nevertheless, this mode of description is still widely used in a number of contemporary texts in inorganic and organic chemistry (see *e.g.* ref. 5). But as the number of valence electrons increases, the possible number and type of ionic structures grows to such an extent as to obscure the original clarity of the VB description.

However, in organic chemistry, there are some situations in which ionic structures play an altogether more positive role. For example, resonance between covalent and ionic structures provides a direct explanation of the *ortho-/para-* or *meta-*directing properties of different substituents of a benzene ring under electrophilic attack by various substituents. There is no doubt that still today, organic chemists, at least in the privacy of their laboratories, find that this explanation is the simplest and most satisfying.

However, in a remarkably under-valued paper, Coulson and Fischer,[6] using the H_2 molecule as a simple example, showed that the ionic structures express nothing more than the deformation of the atomic orbitals that occurs when they participate in chemical bonds. They showed that wave function (1.3) can be rewritten as eqn. (1.4),

$$\Psi_{tot} = \{\phi_A(\mathbf{r}_1)\phi_B(\mathbf{r}_2)+\phi_B(\mathbf{r}_1)\phi_A(\mathbf{r}_2)\}\sqrt{\tfrac{1}{2}}(\alpha_1\beta_2-\beta_1\alpha_2), \quad (1.4)$$

which is precisely of the form of the original HL function, but where the orbitals ϕ_A and ϕ_B, instead of simply being atomic, are now (in unnormalized form): eqns. (1.5) and (1.6)

$$\phi_A = \phi_{1s_A} + \lambda\phi_{1s_B}, \tag{1.5}$$

and

$$\phi_B = \phi_{1s_B} + \lambda\phi_{1s_A} \tag{1.6}$$

the mixing parameter λ being the same as coefficient C_2 in function (1.3).† Note that orbitals ϕ_A and ϕ_B overlap: eqn. (1.7).

$$\langle \phi_A \mid \phi_B \rangle = \Delta_{AB} \tag{1.7}$$

Thus we see that in cases such as this, the occurrence of ionic structures does in fact do no more than to allow the original atomic orbitals to delocalize somewhat into the neighbouring atoms as the molecule forms, which is of course perfectly reasonable. As the internuclear distance R increases, $\lambda \rightarrow 0$ and the orbitals revert to pure atomic form.

Wave function (1.3) or (1.4) contains 'left–right' correlation which is necessary for a correct description of the dissociation of the H_2 molecule. It yields 85% of the observed value of D_e, the binding energy of H_2, compared to 77% for the Hartree–Fock or molecular orbital wave function. This is not the only form of electron correlation in H_2. In particular, angular correlation about the internuclear axis is missing. But the type of 'non-dynamic' correlation present in wave function (1.4) ensures that molecular dissociation, however complex, is always correctly described.

Generally speaking, the deformations of the atomic orbitals in a molecule are large or small, depending upon such factors as the type of chemical linkage (single, double, triple, aromatic or anti-aromatic), the disparity in the electronegativity of the atoms concerned and the bond length: in all cases, as the distance between the atoms becomes large, *i.e.* as the bond breaks, the deformation of the atomic orbitals decreases to zero, usually occurring quite suddenly at a critical internuclear distance, and the isolated atom form is regained.

The passage from wave function (1.3) to (1.4) gives us a new perspective on the role of the ionic structures and suggests an entirely novel direction for constructing electronic wave functions for molecules, to which we now turn.

2 Spin-coupled wave functions

Generalization of the foregoing leads us to propose the following wave function for a molecular system: eqn (2.1)

$$\Psi_{SC} = \Psi_{SM} = \mathscr{A}\{\psi_1^2\psi_2^2 \cdots \psi_{n_c}^2\phi_1\phi_2 \cdots \phi_N\Theta_{00}^{2n_c}\Theta_{S,M}^N\} \tag{2.1}$$

which is known as a spin-coupled (SC) wave function. It incorporates a number of features which do not arise in MO-based wave functions and these are described below.

In the following Section, the construction of spin functions $\Theta_{S,M}^N$ will be briefly discussed and after this we shall be ready for a description of the physical interpretation of the spin-coupled wave function.

Function (2.1) describes a system with a total number of electrons N_t: eqn. (2.1.i).

$$N_t = 2n_c + N. \tag{2.1.i}$$

Of these, $2n_c$ electrons are 'inactive' or 'core' electrons, described by n_c doubly occupied orbitals $\psi_1, \psi_2, \ldots, \psi_{n_c}$. They are not considered to take part in the chemical process under study. In addition we have N 'active' or 'valence' electrons, which are the objects of our investigation. They are described by N distinct, singly occupied orbitals $\phi_1, \phi_2, \ldots \phi_\mu, \ldots \phi_N$. These orbitals are non-orthogonal, *i.e.* they overlap: eqn. (2.1.ii).

$$\langle \phi_\mu \mid \phi_\nu \rangle = \Delta_{\mu\nu} \tag{2.1.ii}$$

They are determined in the familiar way as linear combinations of basis functions (approximate atomic orbitals) χ_p, chosen beforehand and sited on all the atomic nuclei in the molecule. Thus: eqn. (2.2)

$$\phi_\mu = \sum_{p=1}^{m} c_{\mu p}\chi_p, \quad (\mu = 1,2,\ldots,N) \tag{2.2}$$

where m is the total number of basis functions. The coefficients $c_{\mu p}$ are determined by minimising the total energy of the system E, as we shall see. Note that $\Delta_{\mu\mu} = 1$, *i.e.* the orbitals are normalised.

The core or inactive orbitals ψ_i are similarly determined as linear combinations of basis functions, eqn. (2.3),

$$\psi_i = \sum_{p=1}^{m} c_{ip}\chi_p, \quad (i = 1,2,\ldots,n_c) \tag{2.3}$$

but with the added proviso that they are not only normalised, but are also orthogonal to one another: eqn. (2.4).

$$\langle \psi_i \mid \psi_j \rangle = \delta_{ij} = \begin{cases} 1 \text{ if } i = j \\ 0 \text{ if } i \neq j \end{cases}, i,j = 1,2, \ldots,,, n_c \tag{2.4}$$

This property of the core orbitals simplifies many of the subsequent formulas considerably and may always be imposed without changing the form of the total wave function (2.1). Note that in addition there is a further simplification: The core orbitals ψ_i may always be taken to be orthogonal to the active orbitals ϕ_μ, again without changing the form of our assumed total wave function (2.1): eqn. (2.5).

$$\langle \phi_\mu \mid \psi_i \rangle = 0 \quad (\mu = 1,2,\ldots,N;\ i = 1,2,\ldots,n_c) \tag{2.5}$$

These properties of the orbitals enable us to write the total energy in a compact form with a clear physical meaning, as we shall see.

We now turn to the functions $\Theta_{00}^{2n_c}$ and $\Theta_{S,M}^N$ which also appear in the total wave function (2.1) and play an important role in the theory. These are many-electron spin functions. The function $\Theta_{00}^{2n_c}$ describes the coupling of the spins of the $2n_c$ electrons in the core. It has the simple form eqn. (2.5.i)

$$\Theta_{00}^{2n_c} = \sqrt{\tfrac{1}{2}}(\alpha_1\beta_2 - \beta_1\alpha_2)\ \sqrt{\tfrac{1}{2}}(\alpha_3\beta_4 - \beta_3\alpha_4) \times \ldots \tag{2.5.i}$$
$$\ldots \times \sqrt{\tfrac{1}{2}}(\alpha_{2n_c-1}\beta_{2n_c} - \beta_{2n_c-1}\alpha_{2n_c})$$

showing that the electron spins form n_c pairs, each pair having a net spin of zero. Whenever there are orbitals that are doubly occupied, this spin function, known as the perfectly paired spin function, is the only one permitted by the Pauli principle.

Function $\Theta_{S,M}^N$ is different. It is an N-electron spin function for the N active electrons. The subscripts indicate that the net spin of these electrons is S with z-component M. A characteristic feature of the spin-coupled approach now appears. Since the N valence orbitals are singly occupied, there are several distinct ways of coupling the individual spins of the electrons to each other in order to form the required overall resultant spin S. This number is denoted by f_S^N and is given by the simple formula (see ref. 9): eqn. (2.6).

$$f_S^N = \frac{(2S+1)N!}{(\tfrac{1}{2}N+S+1)!(\tfrac{1}{2}N-S)!}. \tag{2.6}$$

More will be said about the important topic of spin functions in the next Section.

Thus spin function $\Theta_{S,M}^N$ occurring in eqn. (2.1) has the form of a linear combination of all the linearly independent spin functions, $\Theta_{S,M,k}^N$, $k = 1,2,\ldots\ldots,f_S^N$: eqn. (2.7).

$$\Theta_{S,M}^N = \sum_{k=1}^{f_S^N} c_{Sk}\Theta_{S,M,k}^N \tag{2.7}$$

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† Coefficient C_1 is equal to $(1 + \lambda^2)$.

The coefficients c_{Sk} are known as spin-coupling coefficients and are also determined by minimising the total energy. Their physical significance will be described shortly.

The use of sets of spin functions as in (2.7) is one of the main features of the spin-coupled approach.

Finally the operator $\mathcal{A}$ stands for the antisymmetrising operator. It ensures that the entire function following in brackets $\{\ldots\}$ in eqn. (2.1) is antisymmetric, *i.e.* obeys the Pauli principle; that is when any pair of space and spin coordinates in the total wave function Ψ_{SM} are transposed, Ψ_{SM} changes sign.

Wave function (2.1) incorporates a number of parameters that are to be optimised by minimising the total energy. It is useful at this stage to summarise these:

(*a*) There are the coefficients $c_{\mu p}$ in eqn. (2.2) for the spin-coupled orbitals. Since the orbital index μ ranges over the values 1 to N and the index for the basis functions, p, from 1 to m, there are Nm such coefficients. They are not all independent, since it should be recalled that each orbital ϕ_μ is normalised, a condition which, in effect, fixes one coefficient per orbital.

(*b*) Similar considerations apply to the coefficients c_{ip} (2.3) for the core orbitals, though in this case, the constraints of normalisation and orthogonality, eqn. (2.4), reduce the number of independent coefficients c_{ip} considerably.

(*c*) In addition there are the f_S^N spin-coupling coefficients c_{Sk}, appearing in eqn. (2.7). However, we usually require that the total spin function be normalised: eqn. (2.7.i)

$$\langle \Theta_{s,m} \,|\, \Theta_{S,M} \rangle = 1, \qquad (2.7.\text{i})$$

in which the angular brackets in this case $\langle \ldots | \ldots \rangle$ denote integration over all spin coordinates. If the individual spin functions $\Theta^N_{S,M,k}$ are orthonormal (see Section 3): eqn. (2.8),

$$\langle \Theta^N_{S,M,k} \,|\, \Theta^N_{S,M,l} \rangle = \delta_{kl}, \qquad (2.8)$$

then the spin coupling coefficients must satisfy eqn. (2.8.i),

$$\sum_{k=1}^{f_S^N} c_{Sk}^2 = 1 \qquad (2.8.\text{i})$$

which shows that there are only $f_S^N - 1$ independent parameters c_{Sk}.

For two electrons, the spin-coupled wave function (2.1) reduces to wave function (1.4). Thus for $N = 2$, $n_c = 0$ (there are no core orbitals), for total spin $S = 0$, there is only a single spin function ($f_0^2 = 1$), eqn. (2.8.ii),

$$\Theta^2_{00} = \sqrt{\tfrac{1}{2}}(\alpha_1\beta_2 - \beta_1\alpha_2) \qquad (2.8.\text{ii})$$

and (2.1) reduces to eqn. (2.9),

$$\begin{aligned}\Psi_{00} &= \mathcal{A}\{\phi_1\phi_2\Theta^2_{00}\} \\ &= \{\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) + \phi_1(\mathbf{r}_2)\phi_2(\mathbf{r}_1)\}\sqrt{\tfrac{1}{2}}(\alpha_1\beta_2 - \beta_1\alpha_2), \qquad (2.9)\end{aligned}$$

which is the same as wave function (1.4).

We now turn to the construction of the spin functions $\Theta^N_{S,M,k}$.

3 Construction and properties of spin functions

There is a very large number of ways of constructing the N-electron spin functions $\Theta^N_{S,M,k}$ and in this section we provide an elementary survey of those which are the most common and have proved themselves to be the most useful in actual applications. Mathematical details are omitted. They may be found in *e.g.* ref. 9, 10 or 20. The full physical significance of the different bases of spin functions and of transformations between them will become clear in the course of studying the various applications in this review.

The most common method of constructing spin functions is simply by using the rules for coupling of angular momenta in quantum mechanics. Let us denote the spin function for electron i as σ_i. This represents a state of the electron with spin $s = \tfrac{1}{2}$ (which is of course the same for all electrons) and z-component $m_s = \sigma_i$. The value of σ_i may be $+\tfrac{1}{2}$ or $-\tfrac{1}{2}$. In the former case, it is usual to denote the spin function as α_i and in the latter as β_i.

We begin from electron 1. It has a spin of $\tfrac{1}{2}$. We then couple a second electron to it. According to the rules for coupling angular momentum, the possible values of the resultant spin of the two-electron system, S_2, are $\tfrac{1}{2} + \tfrac{1}{2} = 1$ or $\tfrac{1}{2} - \tfrac{1}{2} = 0$. To this we now add a third electron. If $S_2 = 0$, then the value of the spin for the three-electron system, S_3, must be $\tfrac{1}{2}$. However if $S_2 = 1$, then the value of S_3 may be $1 + \tfrac{1}{2} = \tfrac{3}{2}$, or $1 - \tfrac{1}{2} = \tfrac{1}{2}$. Thus for a three-electron system we see that there are two distinct ways of forming a spin function with net spin $S = \tfrac{1}{2}$, distinguished by the value of S_2. In the first case $S_2 = 1$ and in the second, $S_2 = 0$. In contrast there is only one way to form a three-electron function with net spin $S = \tfrac{3}{2}$.

As the number of electrons increases, the possibilities multiply. If the net spin for $N - 1$ electrons is S_{N-1}, then the spin for N electrons can be $S_N + \tfrac{1}{2}$ or $S_N - \tfrac{1}{2}$. The process of constructing N-electron spin functions in this way can be conveniently represented by the so-called branching diagram in which the total number of electrons N is plotted against the net spin S. This is shown below in Fig. 1. Each path through the diagram, whereby one moves from the point ($N = 1$, $S = \tfrac{1}{2}$) to the right, represents a possible spin function. At each point (N,S) on the diagram, the number of different paths which may be followed, starting from $N = 1$, $S = \tfrac{1}{2}$ is shown in a circle. This number is just the same as f_S^N [eqn. (2.6)] and it may be observed that this is equal to the sum of the two numbers shown at the points for $N - 1$ which are directly connected to the chosen point,

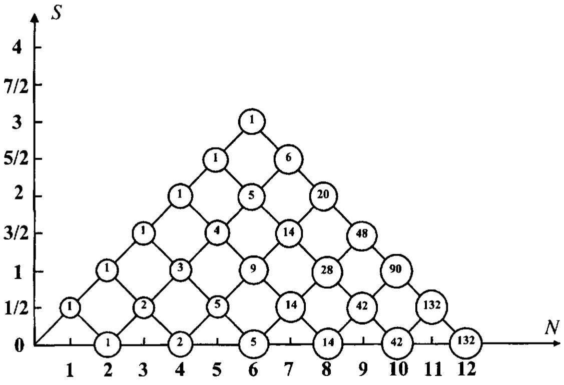


Fig. 1

$$f_S^N = f_{S+1}^{N+1} + f_{S-1}^{N-1}, \qquad (3.1)$$

a relationship which may be verified directly from eqn. (2.6). It is clear that a particular path on the branching diagram is defined by a series of intermediate spins S_2, S_3, ..., and hence the index k which specifies a particular spin function can be represented as eqn. (3.2).

$$k \equiv (S_2S_3.....S_{N-1}). \qquad (3.2)$$

In this, it is unnecessary to specify S_1, since it is always equal to $\tfrac{1}{2}$ and similarly it is not necessary to give S_N, as this is just the total spin, S.

Spin functions constructed in this way are known as Kotani–Yamanouchi or simply Kotani spin functions after those who introduced them.[9,10] They are orthonormal [see eqn. (2.8)].

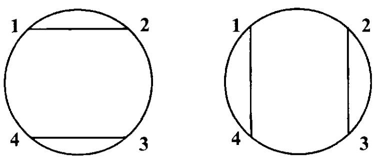
Another basis of spin functions which has proved itself of great value in chemistry is that due to Rumer[11] and was much used in classical VB theory. It is specially suited to describing chemical bonds and hence it is applied almost exclusively to systems (or subsystems) with zero net spin. The functions in this basis are constructed by considering all distinct pairs of electrons i, j and coupling the associated spins σ_i, σ_j to singlets eqn. (3.2.i).

$$(i - j) \equiv \sqrt{\tfrac{1}{2}}(\alpha_i\beta_j - \beta_i\alpha_j). \qquad (3.2.i)$$

But simply pairing up the spins of all electrons i, j in all possible ways will produce an over-complete set of spin functions. This can be seen most easily in the case of four electrons. For a net spin $S = 0$, eqn. (2.6) tells us there are two linearly independent spin functions, but following the elementary Rumer prescription, we would obtain three, the spins paired up as (1–2)(3–4), or (1–4)(2–3), or (1–3)(2–4). However, there is a simple graphical technique, devised by Rumer, to eliminate the redundant spin functions, leaving just the required number, eqn. (3.2.ii).

$$f_0^N = \frac{N!}{\tfrac{1}{2}N!(\tfrac{1}{2}N + 1)!}\,. \qquad (3.2.ii)$$

We place N numbered dots in sequence around a circle, and join them up in pairs such that the joining lines do not cross. Thus for four electrons we have:



and this leads to two spin functions only (3.2.iii)

$$\Theta^4_{0,0;1} = \sqrt{\tfrac{1}{2}}(\alpha_1\beta_2 - \beta_1\alpha_2)\sqrt{\tfrac{1}{2}}(\alpha_3\beta_4 - \beta_3\alpha_4), \quad (3.2.iii)$$

and (3.2.iv)

$$\Theta^4_{0,0;2} = \sqrt{\tfrac{1}{2}}(\alpha_1\beta_4 - \beta_4\alpha_1)\sqrt{\tfrac{1}{2}}(\alpha_2\beta_3 - \beta_3\alpha_2) \quad (3.2.iv)$$

as required.

A general Rumer function is constructed by pairing the spin of electrons p and q, r and s, t and u, *etc.* to singlets. We label the resulting spin function by: eqn. (3.2.v)

$$k \equiv (p - q, r - s, t - u, \ldots). \qquad (3.2.v)$$

The Rumer basis of spin functions has found extensive use in organic chemistry in the description of the mechanisms of a great variety of organic reactions such as aromatic electrophilic and nucleophilic attack and a host of addition reactions. Even after forty or more years of development of molecular orbital methods, this mode of description obstinately remains a major part of theoretical organic chemistry.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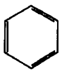
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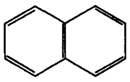
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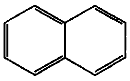
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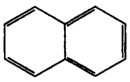
(5)

The Rumer basis has proved to be particularly convenient in describing aromatic systems, where the well-known Kekulé structures play a fundamental role. The two Kekulé structures for benzene are illustrated as (**1**) and (**2**), together with the three corresponding structures for naphthalene (**3**)–(**5**).‡ An important result which arises out of our extensive use of different bases of spin functions, is the great utility of the little-known Serber basis.[12] This set of spin functions is constructed by considering pairs of electrons (1,2), (3,4), ..., (N − 1, N) in a similar manner to that of Rumer. The pairs of spins are then coupled to form either a singlet (S = 0) or triplet (S = 1) spin, which are subsequently coupled successively together to form the final spin. A particular function in this basis is identified by the quantum numbers, eqn. (3.2.vi),

$$k = ((\ldots((s_{12}, s_{34})S_4;\ s_{56})S_6;\ s_{78})S_8;\ \ldots)S \qquad (3.2.vi)$$

in which s_{12}, s_{34}, ..., *etc.* is equal to 0 or 1, depending on whether electrons 1 and 2, or 3 and 4 form a singlet or triplet. S_4, S_6, ... is the net spin for four, six, *etc.*, electrons.

The Serber function eqn. (3.2.vii),

$$((\ldots(0,0)0;0)0.....)0 \qquad (3.2.vii)$$

in which the electron pairs 1 and 2, 3 and 4, ..., N − 1 and N form singlets is identical to the Rumer spin function eqn. (3.2.viii),

$$(1 - 2, 3 - 4, ..., (N - 1) - N) \qquad (3.2.viii)$$

and to the last Kotani spin function eqn. (3.2.ix).

$$k = (0\tfrac{1}{2}0\tfrac{1}{2}......\tfrac{1}{2}) \qquad (3.2.ix)$$

The Serber spin functions are particularly useful in displaying the spatial symmetry properties of spin-coupled wave functions, when it is obvious that those spin functions which do not lead to the required overall symmetry of the total wave function have zero spin-coupling coefficients. This has turned out to be of great utility in cases where the introduction of electron correlation leads to unexpected additional symmetries of, for example, the σ electrons in a planar π system. Examples of this will be presented in due course.

From a more general point of view, it is often physically and chemically meaningful to divide the electrons into groups and it is very convenient if this division is reflected in the mode of construction of the spin functions. Consider a system in which we wish to focus attention upon a group consisting of N_1 electrons and another containing N_2 electrons, where $N_1 + N_2 = N$, the total number of active electrons. For example, this division might refer to N_1 electrons in σ orbitals and N_2 electrons in a π system, or reflect the fact that in one particular mode of dissociation, the molecule forms two fragments consisting of N_1 and N_2 electrons. For such purposes it is useful to form a set of spin functions of the type eqn. (3.2.x),

$$\Theta^N_{S,M;k} = \sum_{M_1,M_2} \langle SM|S_1S_2M_1M_2\rangle \Theta^{N_2}_{S_1,M_1;k_1}\Theta^{N_2}_{S_2,M_2;k_2} \qquad (3.2.x)$$

in which the index k of the total spin function is characterised by eqn. (3.2.xi),

$$k = (S_1S_2k_1k_2) \qquad (3.2.xi)$$

and k_1, k_2 describe the 'internal couplings' of the component spin functions $\Theta^{N1}_{S1,M1;k1}$ and $\Theta^{N2}_{S2,M2;k2}$. The symbol $\langle SM\,|\,S_1S_2M_1M_2\rangle$ stands for the vector coupling coefficient which couples together the two angular momenta S_1 and S_2.

As an example of this, a spin-coupled calculation was carried out of the dissociation of the HCN molecule in its ground state, involving the dissociation of the C–N triple bond.[13]: eqn. (3.2.xii).

$$\mathrm{HCN}(X^1\Sigma^+) \rightarrow \mathrm{CH}(^4\Sigma^-) + \mathrm{N}(^4S). \qquad (3.2.xii)$$

The 14-electron molecule of HCN thus decomposes into two fragments, each consisting of seven electrons. A very convenient basis of spin functions is one in which the seven electrons of the CH radical are coupled to a definite spin S_1 (equal to $\tfrac{3}{2}$ in the combined product, CH + N, of lowest total energy) and the N atom is in its ground state, also with a spin S_2 of $\tfrac{3}{2}$. Since the

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‡ In the case of benzene, three more spin functions—those corresponding to the so-called 'Dewar' or *para*-bond structures—are needed to complete the set of five spin functions for six π electrons with net spin S = 0. In the case of naphthalene with ten π electrons, f_0^{10} = 42, so that in addition to the three Kekulé structures shown, there are no less than 39 further possible spin pairings—a fact which most organic chemists do not wish to know. As will be seen, an important result of spin-coupled theory is that the role of the unwanted extra 39 structures may be considered negligible when the orbitals are optimized.

total spin $S = 0$ in this example, the two sub-spins S_1, S_2 must be equal. The other possible value of S_1, S_2, which may be of interest, $(\frac{1}{2}, \frac{1}{2})$, would for large C–N distances correspond to the dissociation of the molecule into the ground ($^2\Pi$) state of CH and the excited ^2P state of N, which corresponds overall to an excited state of the products.§ Using this '7⊗7' basis at C–N distances close to equilibrium, tells us how much this excited state contributes to the total ground state of HCN.

Of course for equilibrium internuclear distances, HCN is better described in terms of electron-pair bonds, *i.e.* in the Serber or Rumer basis of spin functions. This brings us to the problem of transforming from one set of spin functions to another. In practical terms the problem is as follows: A calculation has been carried out using, *e.g.* the Kotani basis (which may be the most convenient) and we have obtained a set of spin-coupling coefficients c_{Sk} ($k = 1, ..., f_S^N$) corresponding to this basis. What are the values of the spin-coupling coefficients c'_{Sk} in some other basis?

This is not merely a question of theoretical interest, since it is intimately connected to important physical and chemical information which a spin-coupled calculation can yield about a given system. Certainly such a transformation is always possible and it remains to develop an efficient algorithm for carrying it out. This has been accomplished by means of the code SPINS (see ref. 15), which also runs on a personal computer¶ and which transforms a set of spin-coupling coefficients between the Kotani, Rumer and Serber bases of spin functions. It is also possible to combine any of these transformations with a reordering of the active orbitals in a spin-coupled wave function in any manner.

It is, hopefully, clear from the foregoing that there are many possible ways of coupling the individual electron spins to form a given resultant S and the choice is mainly dictated by the actual system under consideration and the process (*e.g.* reaction or dissociation, *etc.*) under study. An appropriate choice of basis of spin functions sheds much light upon the behaviour of the wave function, in a very compact and physically meaningful manner. Unsuspected symmetries are often exposed and, combined with the shapes of the orbitals, a great deal of physics and chemistry of the system is revealed. Such information often suggests, for example, energetically the most favourable reaction path, or, in the case of a molecule in an electronically degenerate state, frequently suggests the most likely Jahn–Teller distortion of the molecule.

4 The physical interpretation of the spin-coupled wave function

Having discussed the various distinctive features of the spin-coupled wave function, we are in a position to describe its physical and chemical significance and to assess its general quality and reliability in relation to other available *ab initio* quantum chemical approaches.

The spin-coupled approach, as we have seen, describes a system with N active electrons, by N distinct, singly occupied, non-orthogonal orbitals, the spins of which are coupled together in all allowable ways to form the required overall resultant S. The single occupancy allows the electrons to avoid one another, thus incorporating a significant amount of correlation between them. The overlap between the orbitals, on the other hand, allows for quantum interference effects which are crucial for a good description of bonding.

Perhaps the most characteristic feature of the wave function is the linear combination of many spin functions. The pairing of the electrons in all possible ways, together with the optimization of the shapes of the orbitals, introduces further correlation effects. These two attributes always allow for a correct description of molecular dissociation, however complicated. As the interatomic distances increase, the orbitals regain their pure atomic shape, and the mode of coupling of the spins also reflects the separation of the parts of the molecule. This aspect of the behaviour of electronic wave functions is perhaps the most important in chemistry, since the making and breaking of chemical bonds, or their rearrangement, constitutes the very essence of chemistry at the molecular level.

The spin-coupled wave function thus incorporates a considerable amount of chemically significant electron correlation in a compact and highly visual form.

One phenomenon which made its appearance early on in this work is the fact that chemical bonds do not appear to break gradually, but on the contrary, are little affected by increasing bond distances until a critical value is reached, when large changes are observed to occur in the wave function over a very short internuclear distance: *ca.* $0.5a_0$, when the orbitals rapidly lose the deformation characteristic of bond formation and at the same time, the spin coupling coefficients also vary rapidly. This occurs at an interatomic distance of *ca.* $4.5a_0$, which remains surprisingly constant for many different species and processes. Indeed, one might assert that in a chemical reaction,

$$\mathrm{A + B \rightarrow C + D,}$$

to a good approximation, nothing occurs between the reagents A and B until they approach to within $4.5a_0$ of one another, when the reaction occurs with surprising suddenness. Hence a fairly universal total reactive cross-section might be estimated to be $4\pi\,(4.5a_0)^2 \sim 70 \times 10^{-20} \sim 7 \times 10^{-19}\,\mathrm{m}^2$.

As we have seen, the spin-coupled wave function is very flexible, but it is important to understand the limits of this flexibility: we have the freedom to order the orbitals in any way we please, we may choose the set of spin functions in a wide variety of ways. Some of this freedom can be well utilized in order to reduce the amount of computational effort necessary in determining the wave function (see below). However, a concomitant danger in this apparent freedom is the opportunity for deriving formalisms which may appear different but do not introduce anything new into the theory.

It is also important to appreciate clearly the distinction between SC theory and the older or 'classical' valence bond theory. In classical VB theory, the orbitals are taken to be predetermined, either as simple atomic orbitals or hybrids of atomic orbitals. These hybrids, moreover, are fixed, for example either as sp, sp^2 or sp^3, *etc.* type orbitals. In SC theory, in contrast, no such preconceptions are imposed. The orbitals are optimized as linear combinations of basis functions (usually approximate AOs) much as in MO-based approaches. However, in common with classical VB theory, the spin coupled orbitals in general overlap with one another (except, of course, in the case of orbitals of different symmetry), or, since the SC orbitals are often localized, by virtue of the physical separation between them. Generally speaking, no constraints, apart from normalization, are applied to the SC orbitals and as a result they may be as localized or as delocalized as the situation demands. Bearing in mind that the SC orbitals are always singly occupied, this last means that their shapes are determined by whatever produces the optimum balance between the greatest extent of avoidance of the electrons in different orbitals and quantum interference effects, which arise from the overlap between orbitals. In practice, we have found that this invariably means that the SC orbitals turn out to be localized and indeed often resemble atomic or hybrid atomic orbitals, or semi-localized, meaning that the SC orbitals spread over two or, at most three centres. We have found a greater degree of delocalization than this to be rare.

One should also bear in mind that, in contrast to classical VB descriptions, the SC orbitals remain singly occupied, the

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§ States with (S_1, S_2) equal to $(\frac{5}{2}, \frac{5}{2})$ and $(\frac{7}{2}, \frac{7}{2})$ are too high in energy to be of interest and are almost certainly repulsive as far as the interaction of CH and N are concerned.

¶ Copies of which may be obtained by contacting P.Karadakov@surrey.ac.uk or from http://rs2.ch.liv.ac.uk/dlc/SPINS.html optimization of the orbitals, as explained above, obviating the need to introduce ionic structures for covalent molecules.

The determination of the SC wave function, the orbitals and values of the spin-coupling coefficients, is attained by the usual procedures in quantum mechanics. According to the variational principle, we must calculate the total energy E and minimize it with respect to these same parameters, $c_{\mu p}$, c_{ip} and c_{Sk}. This is done by calculating the first and second derivatives of E with respect to $c_{\mu p}$, c_{ip} and c_{Sk}. Much of the algebraic detail is set out in the original paper[20] and here we do no more than quote one or two equations. The total energy corresponding to the spin-coupled wave function is given by eqn. (4.1).

$$\mathrm{E} = \frac{\langle \Psi_{SM} | \mathcal{H} | \Psi_{SM} \rangle}{\langle \Psi_{SM} | \Psi_{SM} \rangle}$$

$$= \frac{1}{\Delta}\left\{ \sum_{\mu\,\upsilon=1}^{N} D(\mu|\upsilon)\langle \phi_\mu | h | \phi_\upsilon \rangle + \frac{1}{2}\sum_{\mu\,\upsilon\,\lambda\,\tau=1}^{N} D(\mu\upsilon|\lambda\tau)\langle \phi_\mu \phi_\upsilon | g | \phi_\lambda \phi_\tau \rangle \right\} \tag{4.1}$$

Here, $\mathcal{H}$ stands for the usual non-relativistic electronic Hamiltonian, containing the operators for the kinetic energy of the electrons and all the Coulomb interactions between the electrons and the nuclei making up the molecule.

The normalisation integral $\langle \Psi_{SM} | \Psi_{SM} \rangle$ is written on the right hand side of (4.1) as Δ and the usual one- and two-electron integrals as $\langle \phi_\mu | h | \phi_\nu \rangle$ and $\langle \phi_\mu \phi_\nu | g | \phi_\lambda \phi_\tau \rangle$.

The $D(\mu | \nu)$ and $D(\mu\nu | \lambda\tau)$ are elements of the one- and two-electron density matrices. This, together with the normalization integral Δ is where all the effects of the non-orthogonality between the orbitals occurs.

If inactive orbitals are present, it is sufficient to modify the one-electron operator h which occurs in $\langle \phi_\mu | h | \phi_\nu \rangle$.[‖]

The spin-coupled wave function as represented by eqn. (2.1) is, of course, based on a single spatial configuration. There are several situations which are not covered by this form of wave function. In particular, degenerate electronic states, frequently accompanied by a Jahn–Teller distortion of the nuclear framework, pose interesting problems (as indeed such states also do in the MO framework). The further systematic refinement of the spin-coupled wave function and the treatment of excited states also present areas not covered by wave function (2.1). Excited states in particular have proven to be a difficulty for the traditional valence bond approach, but are fully accounted for in the spin-coupled approach. This matter is mentioned briefly in Section 8.

The spin-coupled wave function does not—cannot—incorporate all the different types of electron correlation effects. An obvious extension is the development of a multiconfiguration spin-coupled wave function and steps in this direction were already attempted with the earliest applications of spin coupled theory.[17,18] Since the spin-coupled wave function incorporates as much 'radial' correlation as is possible within the framework of a single-configuration form, the main improvements to the wave function must stem from the inclusion of doubly excited configurations in which two occupied orbitals are replaced by orbitals which differ from them, in some sense, by symmetry. In the case of the very simple diatomic molecules H_2, LiH and Li_2, (see ref. 17 and 18 above), whose occupied orbitals are all of σ symmetry, it is fairly clear that the main improvement is due to replacement of the two σ orbitals involved in the bond by two orbitals of π symmetry, $\pi^+\pi^-$, if complex orbitals are used, or by $\pi_x\pi'_x + \pi_y\pi'_y$, if real orbitals are employed.

In the remaining parts of this Review, we present a selected series of applications of spin-coupled theory to different parts of chemistry.

5 Simple examples

The most elementary example of course is just the H_2 molecule. As described by eqns. (1.4) or (2.9), there are two orbitals, ϕ_A and ϕ_B which overlap. These are displayed in Fig. 2 below. On the right of Fig. 2, contour plots of the two orbitals are shown, while on the left, orbital ϕ_A is shown as a three-dimensional shape with the internuclear axis superimposed. As the internuclear distance R increases, the deformation of each orbital ϕ_A and ϕ_B decreases to 0, leaving just a pure hydrogen 1s orbital on each atom. The potential curve for H_2 given by the spin-coupled wave function is compared to the results from a number of other wave functions in Fig. 3.

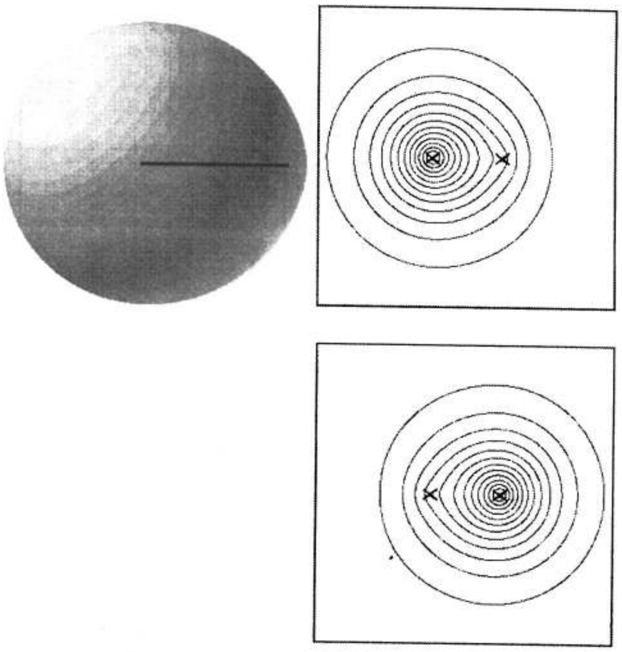

Fig. 2

We see that the spin-coupled result remains close to that for a full configuration-interaction (full-CI) wave function[**] for all values of R and then it becomes identical with it as $R \longrightarrow \infty$.

Also shown on this diagram is the potential curve given by the original Heitler–London wave function, eqn. (1.1), and that given by MO theory (the 'self-consistent field' (SCF) function). It can be seen that the SCF wave function does not describe dissociation correctly.

The potential curve of the lowest triplet state of H_2, which is repulsive, is also shown. According to eqn. (2.1), the wave function for this state ($N = 2$, $S = 1$) is given by eqn. (5.1).

$$\Psi\left({}^3\Sigma_u^-\right) = \mathcal{A}\left\{\phi_A\phi_B\Theta^2_{1,M=0,\pm1}\right\} =$$

$$\left\{\phi_A(\mathbf{r}_1)\phi_B(\mathbf{r}_2) - \phi_B(\mathbf{r}_1)\phi_A(\mathbf{r}_2)\right\}\begin{cases} \alpha\alpha \\ \sqrt{\tfrac{1}{2}}(\alpha\beta+\beta\alpha) \\ \beta\beta \end{cases} \tag{5.1}$$

[‖] This is achieved by replacing h by the operator F_c, which is the Fock operator for the core.

$$F_c = \sum_{i=1}^{n_c} 2h_i + \sum_{i=1}^{n_c}(2J_i - K_i),$$

where J_i and K_i are the usual Coulomb and exchange operators of Hartree–Fock theory, but here are constructed from the inactive orbitals only.

[**] A full-CI wave function is the most general variational wave function that can be constructed from a given basis set, either in the MO framework or that of VB (in which case it is called a full-VB wave function). The two wave functions (full-CI and full-VB) are entirely equivalent.

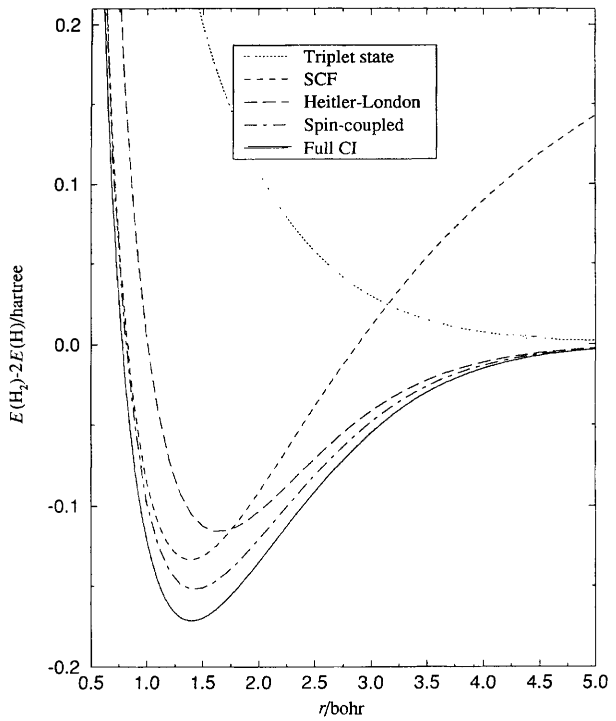

Fig. 3

which for $M = 0$, can be obtained simply from that for the singlet state by reversing the signs in eqns. (1.1) or (1.4).

A somewhat more complicated example is provided by the methane molecule CH_4. In this case we have eight valence electrons and two core electrons, so that $N = 8$, $n_c = 1$. The ground state is a singlet, $S = 0$, so that now there is a total of fourteen spin functions. The SC wave function is determined by minimizing the total energy as described in Section 2. Using a very large basis set,†† the energy of the spin-coupled wave function is *ca.* 0.065 Hartrees lower than that of a SCF function calculated with the same basis, which is a fairly substantial difference. This indicates that a significant amount of the effects of electron correlation is incorporated in the SC wave function.

On examining the wave function, we find that the eight SC valence orbitals form four sets of two orbitals each. The orbital pairs are symmetrically equivalent and are permuted amongst themselves by operations of the tetrahedral group, T_d. Within each pair, one of the orbitals is very largely localized on one of the H atoms and clearly resembles a H(1s) orbital with small deformations, almost exclusively onto the C atom. The second orbital of the pair is localized mainly on the C atom, but with some small degree of delocalization, almost exclusively onto the H atom of the pair. This is shown in Fig. 4.

The deformation of the C-based orbital can be seen quite clearly. Thus, without the imposition of any preconceptions on our part, the SC wave function for methane produces what are clearly four, somewhat deformed, sp^3 hybrid orbitals and also four deformed H(1s) orbitals. It goes without saying that this corresponds closely to our usual concept of four-valent carbon with bonds to four H atoms.

In addition, however, we must consider the spin functions of which there are fourteen. This example illustrates very clearly some of the features of different spin functions. Table 1 shows them, using the Serber basis, with the orbitals ordered as (ϕ_1,ϕ_2) (ϕ_3,ϕ_4), (ϕ_5,ϕ_6), (ϕ_7,ϕ_8). The notation of column 2 has been explained in Section 3.

Of these, spin function 14 corresponds to the perfectly paired case and this has a weight of 89.4%. This of course is what we

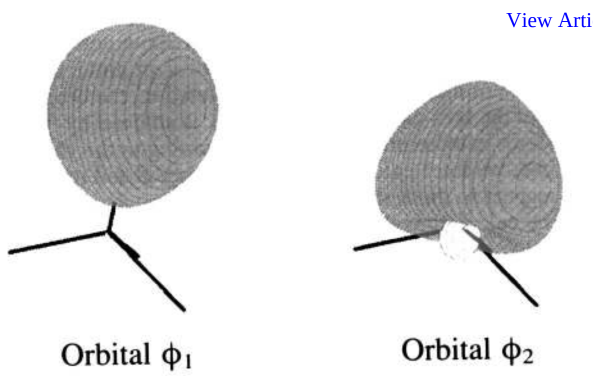

Fig. 4

imagine to be the case in a simple molecule such as methane. All the other spin functions represent different possible ways of coupling the eight valence electrons. It can be seen that a number of them are zero by symmetry and that six others are exactly equal (as long as the molecule has tetrahedral symmetry). These represent the case when there are two triplet bonds, the two triplets giving a zero net spin. The weight of such an unlikely spin arrangement is naturally rather small: 1.7%. With four symmetrically equivalent bonds, there are six such unique pairs of triplet-coupled bonds. Together with the perfectly paired spin function, this constitutes the entire spin function, for 89.4 + 6 × 1.7 ≃ 100%. However, once the H atoms move away from their equilibrium position in CH_4, spin-coupling patterns other than the perfectly paired case assume a much more important role.

Table 1 Spin coupling coefficients for CH_4 (Serber basis)

	Spin-Coupling pattern	Coefficient	Weight
1	(((1,1)2;1)1;1)	0.0487	0.0023
2	(((1,0)1;0)1;1)	−0.1298	0.0168
3	(((1,1)1;0)1;1)	0.0	0.0
4	(((0,1)1;0)1;1)	−0.1298	0.0168
5	(((1,0)1;1)1;1)	0.0	0.0
6	(((1,1)1;1)1;1)	0.0	0.0
7	(((0,1)1;1)1;1)	0.0	0.0
8	(((1,1)0;1)1;1)	0.0542	0.0029
9	(((0,0)0;1)1;1)	−0.1298	0.0168
10	(((1,0)1;1)0;0)	−0.1298	0.0168
11	(((1,1)1;1)0;0)	0.0	0.0
12	(((0,1)1;1)0;0)	−0.1298	0.0168
13	(((1,1)0;0)0;0)	−0.1298	0.0168
14	(((0,0)0;0)0;0)	0.9453	0.8936

If we transform these spin-coupling coefficients to the Rumer basis, we find that the perfectly paired spin function now contributes *ca.* 80% to the total spin function. The remainder is made up almost entirely from structures containing a single H–H pairing and only two C–H bonds. There are four such structures which, at the equilibrium geometry of CH_4, are all symmetrically equivalent. The occurrence of this type of spin pairing with significant contributions (*ca.* 20%), provides us with some insight into the topic of the following section: the insertion of H_2 into $CH_2(^1A_1)$.

6 The $CH_2(^1A_1)$ + H_2 insertion reaction

Following on from this discussion of methane, it is interesting to study a related process: that of the insertion of the H_2 molecule into the carbene radical CH_2 in its low-lying $^1A_1$ excited state to form CH_4, eqn. (6.1).

$$H_2 + CH_2(^1A_1) \rightarrow CH_4. \qquad (6.1)$$

This reaction is obviously more complex than the simple bond-breaking process, eqn. (6.2)

$$CH_4 \rightarrow CH_3(^2A'_1) + H \qquad (6.2)$$

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†† 'Triple-zeta valence plus polarization' (TZVP).

and involves a fairly complex rearrangement of bonds. Clearly the spin-coupling of the electrons on the right hand side of eqn. (6.1) is completely different to that of the left hand side. In order to understand the pathway for this reaction, it is necessary to look briefly at the SC description of CH_2 in this excited state.[24] This is shown in Fig. 5.

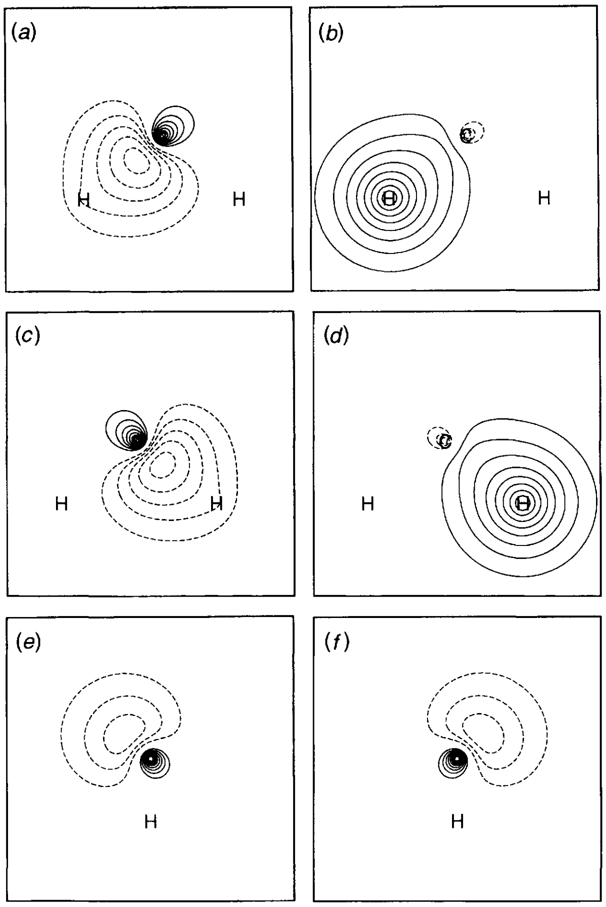


Fig. 5 Orbitals (*a*) ϕ_1; (*b*) ϕ_2; (*c*) ϕ_3; (*d*) ϕ_4; (*e*) ϕ_5; (*f*) ϕ_6

Orbitals ϕ_1–ϕ_4 are plotted in the plane of the molecule. We clearly see two C–H bonds (ϕ_1, ϕ_2) and (ϕ_3, ϕ_4). Orbitals ϕ_5 and ϕ_6 are plotted in a plane perpendicular to the molecular plane and bisecting the H–C–H angle. If the two C–H bonds are regarded as pointing into the corners of a tetrahedron, then ϕ_5 and ϕ_6 point approximately in the direction of the two remaining corners of the same tetrahedron. Thus, according to the SC description, the $^1A_1$ state of CH_2 closely resembles methane itself from which two H atoms have been plucked.

This is quite different from the simple MO description of this state, according to which the two non-bonding electrons of CH_2 are considered to occupy a single lone pair orbital of a_1 (σ) symmetry, stemming from the C atom and pointing along the C_2 axis away from the H atoms. The following discussion focuses upon the utility of the SC description.

It would appear that the most obvious approach of an H_2 molecule to $CH_2(^1A_1)$ is a simple symmetric path where the axis of the incoming H_2 is perpendicular to the C_2 axis of the molecule and in a plane perpendicular to that of CH_2, bisecting the H–C–H angle. However, this implies the simultaneous breaking of the H_2 bond and the formation of two new C–H bonds. According to SC calculations, this path encounters a very high-energy barrier and thus is very unfavourable. But on optimising the various parameters which define the $H_2 + CH_2$ system (see ref. 23), we find the minimum energy path is as shown schematically in Fig. 6.

The H_2 molecule H_1–H_2 approaches along the line of the lobe of one of the singly occupied orbitals of CH_2, ϕ_5, say. Then as the H_1–C distance decreases to *ca.* $3a_0$, the H_1–H_2 bond begins to break and a new H_1–C bond begins to form—as shown clearly by the sharp variation in the coefficients of the two most important spin-couplings. Simultaneously, the second incoming H atom, H_2, now swings right around so as to interact with the other singly occupied orbital of CH_2, ϕ_6, so forming the second new C–H bond. There is no barrier along this path and the value of the exothermicity of the reaction, calculated from the energies of the SC wave functions for reactants and products is 474.5 kJ mol^{-1}, compared to an experimental value of 490 kJ mol^{-1}.

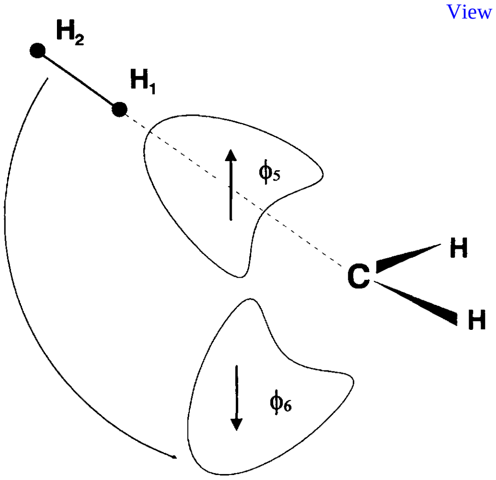


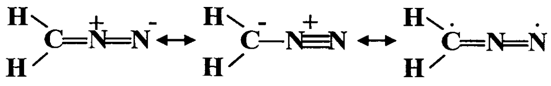
Fig. 6 Schematic drawing of the pathway for the insertion of H_2 into $CH_2(^1A_1)$

With the benefit of hindsight, this reaction path is entirely reasonable: one new C–H bond starts to form, followed swiftly by a second. Energetically, this is obviously more favourable than the simultaneous formation of two new C–H bonds. The overall process is nonetheless synchronous. Although one bond starts to form first, this process is not completed before the second bond begins to form. However, it would be hard to predict this highly asymmetric reaction path without knowing the form of the SC orbitals for $CH_2(^1A_1)$.

If one were to reverse the motions along this path and study the disintegration of CH_4 by, say, the pumping of much energy into appropriate vibrational modes, then this picture predicts that as the first H atom starts to depart from CH_4, it takes a second H atom with it and, moreover, that the nascent H_2 molecule will possess a great deal of angular momentum, *i.e.* the H_2 will be in a highly excited rotational state. There is indeed experimental evidence for this.

7 Hypervalence

The impossibility of drawing satisfactory Lewis structures for a whole range of molecules, such as NO_2, HCNO, N_2O, O_3, is well-known. These are often referred to as 1,3-dipolar molecules. In order to bring their electronic structure and apparent valency in line with other, less unusual systems, many chemists fall back upon the concept of 'resonance'. The resonance structures that are commonly drawn for NO_2 are well-known to all chemists. For diazomethane (CH_2N_2), which is planar, it is common to indicate resonance between the structures shown below, which indicate that diazomethane has some diradical character. Although it is unstable and tends to dissociate explosively into N_2 and an excited state of CH_2, there is otherwise nothing in its vibrational or rotational spectrum to indicate that this molecule possesses any kind of unpaired electron character.



Spin-coupled calculations on diazomethane and a number of other 1,3-dipolar molecules listed above have been carried out at various levels, the simplest example to consider being just the four π electrons of CH_2N_2. According to the SC model, they are accommodated in four distinct orbitals, shown in Fig. 7. The contours are plotted in a plane parallel to the molecular plane and $1a_0$ above it. It can be seen that orbital ϕ_1 is largely a π orbital centred on the C atom of CH_2N_2, but distorted somewhat towards the neighbouring N atom, N_c. Similarly, ϕ_2 is centred on N_c and is deformed towards ϕ_1. However, there is a second π orbital ϕ_3 centred on N_c but distorted towards the terminal N atom, N_t and finally there is ϕ_4, which is a π orbital on N_t but distorted towards ϕ_3. The spin-coupling coefficients show that, in spite of the very large overlap between the two orbitals centred on N_c, ϕ_2 and ϕ_3 ($\Delta_{23} = 0.785$, using a very large basis set of Gaussian-type orbitals‡‡), the electrons occupying these orbitals are not paired with each other, but instead there is an almost perfect pairing of the electron spins in the two orbital pairs (ϕ_1, ϕ_2) and (ϕ_3, ϕ_4). This corresponds to the chemical structure:

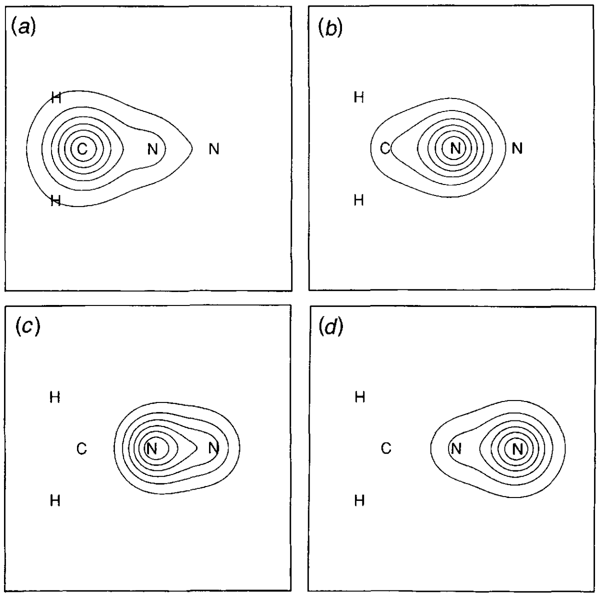
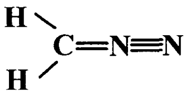


Fig. 7 Orbitals (*a*) ϕ_1; (*b*) ϕ_2; (*c*) ϕ_3; (*d*) ϕ_4



in which the central N atom takes part in five electron-pair bonds.

The large overlap Δ_{23} between ϕ_2 and ϕ_3 should not be forgotten. We tend to think that if a pair of electrons forms one bond, then it cannot contribute to another bond, *i.e.* that pairs of orbitals forming a bond are orthogonal to all other pairs. Here, we see that this is not so: in spite of the clear formation of five fully fledged electron-pair bonds, the overlaps between them are such that the average number of electrons around N_c (the Mulliken population) is very close to 7: *i.e.* the central N atom is almost exactly neutral. The same is true of N_t. However, the C atom is slightly negative and the two H atoms are correspondngly slightly positive. This provides the H atoms with a distinct acidic character, all of which is fully in accord with the known chemistry of CH_2N_2.

Similar considerations hold for other 1,3-dipoles. The N_2O molecule is best presented as

$$N\equiv N=O$$

in which the central nitrogen atom again participates in five electron-pair bonds. The observed bond lengths of N_2O ($R_{N-N} = 1.128, R_{N-O} = 1.184$ Å) are certainly reminiscent of an N–N triple bond and a 'normal' N=O double bond.

Thus, from the perspective of SC theory, the problem presented by these molecules resolves itself in a remarkably simple fashion. Contrary to what we were all taught as undergraduates, the nitrogen atom does indeed form five covalent linkages and the availability or otherwise of d orbitals has nothing to do with this state of affairs. This usually shows itself in terms of multiple bonds, such as in CH_2N_2, N_2O, F_3NO, *etc.*, rather than as five single bonds, simply because the small size of the N atom normally precludes the presence of five nearest neighbours. This is not so for the phosphorus atom. The apparent difference in valency between the first and second rows of the periodic table is therefore a consequence of the size of the atoms and is not primarily due to the availability or otherwise of 3d orbitals for bonding.

This conclusion is reinforced by spin-coupled and other studies on SF_6 and PF_5. The nature of the bonding in these molecules presents a direct challenge to conventional views on valency. According to the SC calculations, the results§§ for SF_6, for example, show that the 12 valence electrons are accommodated in twelve well-localized orbitals which form six highly polar S–F bonds. Furthermore, the nature of the orbital pairs which form these bonds is very little affected by whether or not d orbitals on the S atom are included in the basis set. Two of the resulting orbitals, forming one of the S–F bonds, are shown in Fig. 8. Once more it should be emphasized that these orbitals are the straightforward outcome of an *ab initio* calculation, with no constraints imposed as to the final form of the orbitals, nor the type of pairing of the electron spins.

It remains to rationalize this result in simpler terms.

It is worth recalling that explanations of the bonding in SF_6 which are based upon the supposed $d^2\,sp^3$ hybridization of the orbitals on the S-atom cannot explain properly why SH_6, for example, which is unknown, should not be just as stable as SF_6 itself. The polarity of the S–F bonds is clearly an essential part of the answer.

This can be simply visualized as follows. Consider one of the bond pairs (ϕ_1, ϕ_2) of SF_6, illustrated above. Orbital ϕ_1 consists of a combination of a 2p orbital on one of the F atoms and an sp hybrid $\chi_S(sp)$ on the central S atom, where $\chi_S(sp)$ is of the form in eqn. (7.1).

$$\chi_S(sp) \sim S(3s) \pm S(3p) \qquad (7.1)$$

so that eqn. (7.2) holds.

$$\phi_1 \simeq F(2p) \pm \lambda\chi_S(sp) \qquad (7.2)$$

(see the upper orbital in Fig. 9). The other member of the pair, ϕ_2, is an almost pure $F(2p)$ orbital [eqn. (7.3)].

$$\phi_2 \simeq F(2p) \qquad (7.3)$$

(see the lower orbital in Fig. 9). Hence the bond pair (ϕ_1, ϕ_2) is of the form eqn. (7.3.i).

$$\begin{aligned}(\phi_1, \phi_2) &\simeq \{(F(2p) + \lambda\chi_S(sp)), F(2p)\}\\ &= (F(2p), F(2p)) \pm \lambda(\chi_S(sp), F(2p)) \qquad (7.3.i)\end{aligned}$$

In other words the S–F bond has significant ionic character, but with sufficient covalency to provide directionality.

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‡‡ A 'triple zeta plus valence-shell polarization' (TZVP) basis.

§§ The calculations on the twelve valence electrons included all 132 spin functions, as specified by eqn. (2.6). However, at least at the equilibrium geometry, only the perfectly paired spin function plays any significant role.

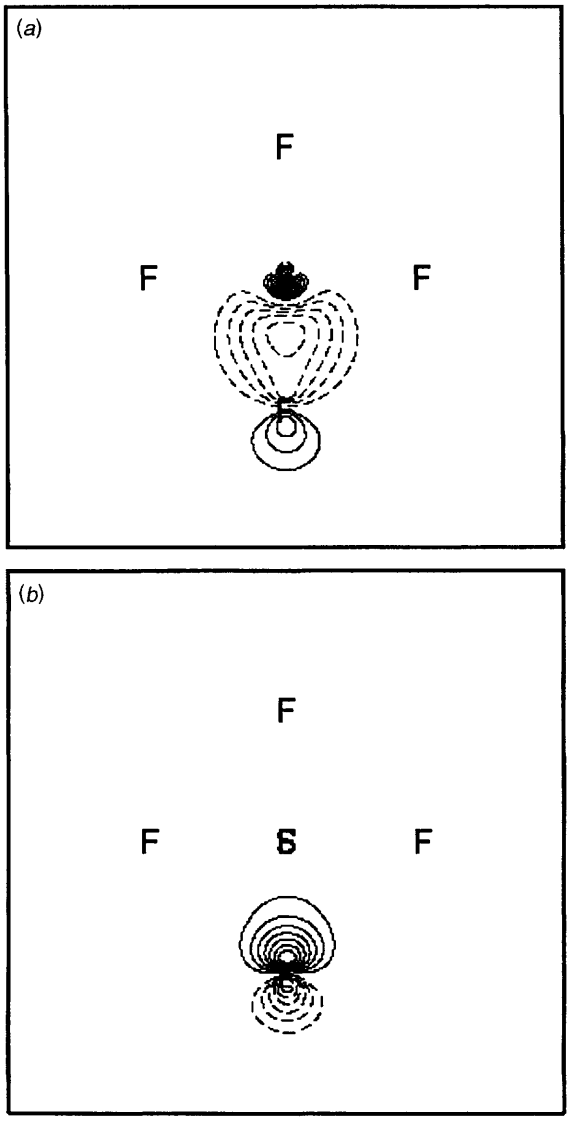


Fig. 8

It is important to note that we may form six sp hybrids of the form (7.1), according to whether we choose the x-, y-, or z-axis. These hybrids however are linearly dependent, since we started from just four orbitals, $S(3s)$, $S(3p_x)$, $S(3p_y)$, $S(3p_z)$ and arrived at the six functions (7.1). This is resolved by the incorporation of $F(2p)$ character.

The polarity of the S–F bonds in SF_6 is therefore a necessary part of the SC description.

Similar considerations apply to PF_5 and the original paper (ref. 25) should be consulted for further details.

It remains to add that almost precisely the same description goes through for XeF_2, Fig. 9. There are two bonding pairs of orbitals, each one of which is very similar to the pair (ϕ_1, ϕ_2) described above for SF_6, leading to very polar Xe–F bonds.

It is clear from the results presented in this section, that the time has come from the much-loved octet rule to be superseded. Presented with sufficient energetic incentives, almost all valence electrons can take part in bonding. We need retain only an 8-electron rule, similar to the 18-electron rule of transition metal chemistry. Polar bonds which shift density away from the central atom appear to be favoured, particularly if the formal number of bonds is very high. Hence differences in electronegativity and the size of the central atom can be useful first guides to the possible existence of a particular hypervalent species.

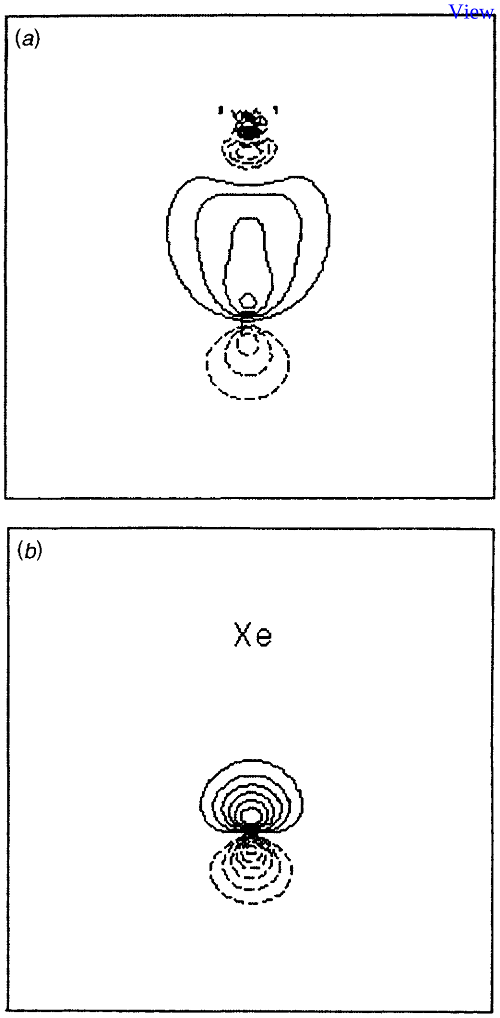


Fig. 9

8 Aromaticity and antiaromaticity

The concepts of aromaticity and antiaromaticity lie at the very heart of organic chemistry. The first useful description of benzene was due to Kekulé who drew the structures (**1**)–(**2**) in Section 3 (see also the footnote) and whose ideas of resonance between the different C–C bonds were later justified and clarified on the basis of quantum theory by Pauling in terms of different spin-pairings of the electrons in $C(2p_\pi)$ orbitals, *i.e.* in terms of resonance between the so-called Kekulé and Dewar (or *para*-bond) structures.

Molecular orbital theory, however, gives an entirely different type of description: that of π orbitals delocalized around the benzene ring. The associated MO energy level diagram is shown below, with the appropriate labels for the point group of the molecule, D_{6h} (Fig. 10).

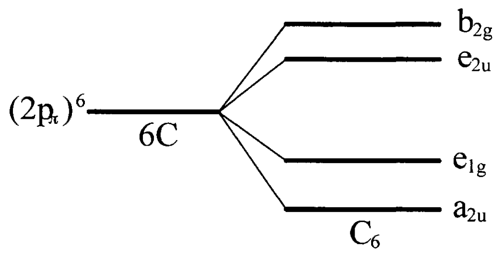


Fig. 10

Accordingly, the electron configuration of the ground state is ($a_{2u}^2\ e_{1g}^4$). By generalizing this diagram, a simple but very useful rule was obtained by Hückel which predicts that if *n* is the number of carbon atoms in a ring system, those molecules with $4n + 2$ C atoms will be aromatic, while those with $4n$ C atoms are predicted to be antiaromatic. Over the last forty or so years this has become the accepted description of benzene, while that in terms of Kekulé and *para*-bond structures has become somewhat less common.

However, in 1986 a spin-coupled calculation was carried out on the π electrons of benzene.[26] As emphasised previously in section 4, no constraints or preconceptions were imposed upon the form of the orbitals, nor upon the type of coupling between the spins. The result showed six π orbitals, each of which is localized around one of the C atoms constituting the ring. One of them is depicted in Fig. 11 in which the contours of the orbital are drawn in a plane parallel to the molecular plane and $1a_0$ above it. It can be seen that although this orbital is clearly localized, there are obvious deformations towards the neighbouring C atoms on each side. The remaining spin-coupled orbitals are obtained from the one shown by successive rotations of $2\pi/6$ about the principal symmetry axis of the molecule. The spin-coupling coefficients in the Rumer basis have the values shown in Table 2. These numbers change only very slightly with different basis sets for the orbitals. Spin functions 1 and 4 correspond to the two Kekulé structures and we see that they each make a contribution of *ca.* 40.5% to the total wave function. The remaining three spin functions, 2, 3 and 5 are the Dewar or *para*-bond functions and each of them contributes *ca.* 6.4% to the total.

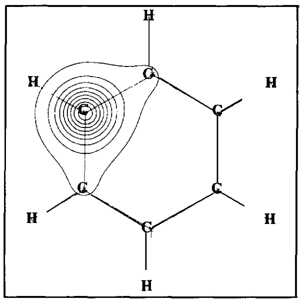


Fig. 11

Table 2

	Spin-coupling pattern	Coefficient	Weight
1	(1–2, 3–4, 5–6)	0.51638	0.4046
2	(1–4, 2–3, 6–5)	−0.09461	0.0636
3	(2–5, 3–4, 6–1)	−0.09461	0.0636
4	(2–3, 4–5, 6–1)	0.51638	0.4046
5	(1–2, 6–3, 5–4)	−0.09461	0.0636

The most significant feature of this result is that the energy improvement (energy lowering) obtained by the spin-coupled wave function over that of the MO wave function (for a given basis set) is no less than *ca.* 92% of the maximum attainable improvement using a wave function of whatever type, MO or VB, constructed from six electrons and six orbitals. In other words, a fully correlated wave function for the π electrons of benzene approximates closely to the spin-coupled wave function. There is thus very much more to the Kekulé description of benzene than was hitherto realized. This calculation has since been repeated many times with basis sets of varying size and with complete optimization of valence and all inactive orbitals. The results vary very little.

Spin-coupled calculations have subsequently also been carried out on many aromatic systems, such as heterocyclic five- and six-membered rings, on naphthalene and on azulene. For naphthalene and azulene, with ten π electrons, the orbitals obtained are very similar to those of benzene, with the exception of the two orbitals localized at each of the C atoms which bridge the two rings. These orbitals display a three-way deformation, towards each of the three adjacent carbon atoms. In addition formula (2.6) shows that for a ten-electron system there are 42 possible spin functions which should be taken into account. But since the spin-coupled orbitals are fully optimized, it turns out that the only spin functions which play any significant role in these molecules are those corresponding to the Kekulé structures [in the case of naphthalene, structures (**3**), (**4**) and (**5**) in the diagram in Section 3] and that the contribution of the other 39 structures may be neglected.

The MO description also predicts a number of excited states of benzene. Thus, a single excitation of an electron from an occupied MO (a_{2u} or e_{1g}) to one of the unoccupied MOs shown on the diagram above (*e.g.* to the e_{2u} or b_{2g} orbitals) gives rise to a number of valence excited states. In addition, there is also a large number of Rydberg states with energies below that of the first ionization potential.

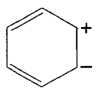
A constant aim of theoretical studies is to determine these excited states, preferably without going beyond the σ/π approximation. Certainly for the ground state, to abandon the σ/π separation would be to ignore a vast body of chemical experience, but the situation may be different in excited states.

It turns out that the excited states of benzene (with energies less than the first ionization potential) fall into three classes: covalent, ionic and Rydberg. An example of a covalent state is the first singlet excited state, $^1B_{2u}$, lying at an energy of 4.90 eV above the ground state. It may be represented to an excellent approximation (see ref. 27) simply as eqn. (7.3.ii)

$$\Psi(^1B_{2u}) = K_1 - K_2 \tag{7.3.ii}$$

i.e. as the negative combination of the two Kekulé structures of the ground state. Covalent states are in general fairly easily described within the σ/π approximation.

On the other hand, ionic states require linear combinations of structures of the type:



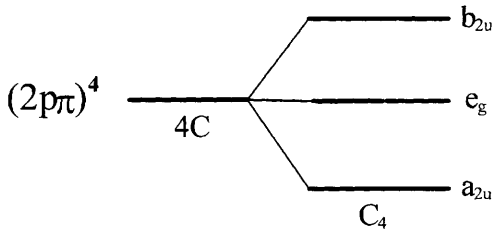
in which two π orbitals occupy one C-atom site, while on the neighbouring C atom, there are none. Ionic states of benzene are much harder to describe within the σ/π framework. Physically, it is obvious that this is due, in part, to the existence of positive and negative charges in the π-electron distribution, which causes a static polarization of the σ core, so that the core differs from that of the covalent states. In addition, there are further dynamic σ–π interactions which fall outside the σ/π approximation. In any case, a reliable description of these effects requires extensive basis sets which include diffuse atomic orbitals.

Lastly, there are the Rydberg states. These are characterized by one orbital which is very diffuse and extends a significant distance from the molecule. Given a basis set which includes such diffuse atomic orbitals (even to the extent of centring them at the midpoint of the molecule), such states are not too difficult to describe well.

The spin-coupled description of the excited states of benzene thus leads to an important and useful classification: the valence states are covalent or ionic, the latter being significantly harder to describe than the covalent states, and Rydberg states, which differ physically from the valence states, but otherwise are not difficult to determine accurately.

In the MO description, all the valence states arise from one or two singly excited reference configurations, such as $(a_{2u}^2\, e_{1g}^3\, e_{2u})$ or $(a_{2u}^2\, e_{1g}^3\, b_{2g})$, and it is not at all clear from this why the various valence excited states should be so physically distinct.

The simplest antiaromatic system is cyclobutadiene, C_4H_4. A similar diagram as for benzene for the energies of the molecular orbitals of C_4H_4, assuming a square-planar geometry, gives:



from which it follows that the electron configuration of the π electrons in the ground state is $(a_{2u}^2 e_g^2)$. However, the e_g MO is doubly degenerate and according to Hund's rules, the two electrons with this energy will distribute themselves one in each MO and with spins aligned parallel. MO theory thus unambiguously predicts that the ground state of square-planar cyclobutadiene should be a triplet ($^3A_{2g}$).

This is not so. It is now well-established that the ground electronic state of cyclobutadiene is a singlet. In the square-planar geometry (D_{4h} symmetry), the state has the symmetry $^1B_{1g}$, with the $^3A_{2g}$ state lying at an energy of *ca.* 0.43 eV above it. Furthermore, the square-plane of the ground state is unstable, the molecule preferring to distort to a rectangular geometry with two short C–C double bonds¶¶ and two longer C–C single bonds. However in the $^3A_{2g}$ state, the square plane geometry is stable.

From the spin-coupled wave function for the ground state, one obtains four orbitals of π symmetry without imposing any predetermined form on these orbitals, nor on the type of spin coupling. Two of the resulting orbitals are shown in Fig. 12.

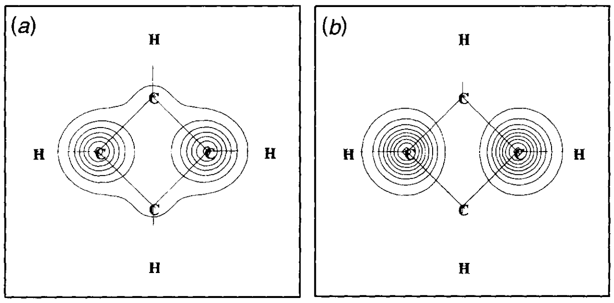


Fig. 12 Orbitals (*a*) ϕ_1; (*b*) ϕ_2

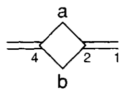
They are plotted in a plane parallel to the molecular plane but $1a_0$ above it. It can be seen that ϕ_1 and ϕ_2 are centred about the two horizontal C atoms, C_1 and C_2. Orbitals ϕ_3 and ϕ_4 are the same as ϕ_1 and ϕ_2, but are rotated by π/2 about the main symmetry axis and instead are centred about C_3 and C_4 in the diagram, where C_3 lies vertically above C_4. We note that orbital ϕ_2 possesses an extra nodal plane passing through C_3–C_4, compared to ϕ_1 (similarly ϕ_4 and ϕ_3).

Even more remarkable are the spin couplings, for these show that orbitals (ϕ_1, ϕ_2) are almost exactly coupled to a triplet and the same holds for (ϕ_3, ϕ_4), the two triplets coupled to give an overall value of the spin *S* for the four electrons of zero.‖‖ Analysis of how orbitals ϕ_1–ϕ_4 behave under the operations of D_{4h}, shows that the total wave function for the ground state of C_4H_4 has the correct $^1B_{1g}$ symmetry. Furthermore, the square planar geometry is not stable and the molecule distorts to a rectangle. In the course of this distortion, orbitals ϕ_1–ϕ_4 rapidly become localized over the four atoms C_1–C_4 and clearly show the formation of two C–C double bonds which are shorter than the remaining two C–C single bonds.

The four orbitals of the triplet state are remarkably similar to those of the singlet ground state. The spin pairing is also very similar, orbital pairs (ϕ_1, ϕ_2) and (ϕ_3, ϕ_4) each forming a triplet. These two triplets, however, are now coupled to form an overall triplet, as required for this state. This is found to have an energy 0.410 eV higher than that of the ground state, which compares well with the experimental value of ~ 0.43 eV (see above).

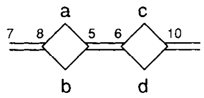
It thus appears that antiaromatic character is connected to the formation of a triplet spin from a pair of electrons in two distinct orbitals, such as ϕ_1 and ϕ_2 above. We refer to such a combination of orbitals as an *anti*-pair.

In order to place the concept of anti-pairs found for cyclobutadiene within a wider context, several related systems were studied, one of which is 2,4-dimethylenecyclobutane-1,3-diyl (DMCBD), shown below:



This molecule has six electrons in six orbitals of π symmetry (it is an isomer of benzene) and can be regarded as being derived from C_4H_4 by removing two H atoms from cyclobutadiene and substituting them with methylene groups. From this, one would predict that only one of the anti-pairs found in cyclobutadiene would remain. This is indeed the case. The ground state of DMCBD is a triplet. Orbitals (ϕ_1, ϕ_2) and (ϕ_3, ϕ_4) are, as indicated in the diagram above, four highly localized C(2π) orbitals and (together with the appropriate σ orbitals) form normal C–C double bonds. The two remaining orbitals of the C_4 ring, denoted by *a* and *b*, form an anti-pair very similar to one of those in cyclobutadiene itself.

Even more remarkable is the bismethylenebiscyclobutylidene molecule (BBB), shown below. This is similar to DMCBD, but with an extra C_4 unit, plus methylene group, added.



Orbitals (ϕ_5, ϕ_6), (ϕ_7, ϕ_8) and (ϕ_9, ϕ_{10}) form the π components of fairly conventional C–C double bonds. However, while the terminal orbitals ϕ_7 and ϕ_9 are deformed towards their respective partners, ϕ_8 and ϕ_{10}, the other orbitals centred on C_5, C_6, C_8 and C_{10} are deformed in three directions, due to the presence of three C-atom neighbours.

BBB turns out to have anti-pairs in both C_4 rings, *i.e.* orbitals (a,b) and (c,d). That is, each ring has associated with it a net electron spin of $S = 1$. The spins of the two C_4 units, however, are aligned antiparallel with each other, giving the ground state of BBB a net spin of zero. This is therefore very much akin to an antiferromagnetic system, except that the spins stemming from each C_4 unit each have the value of unity. It is not too hard to imagine an organic polymer consisting of an infinite number of such C_4 units and displaying this kind of antiferromagnetic behaviour.

According to the Hückel 4*n* rule, cyclooctatetraene (C_8H_8) is the next member of the 'antiaromatic' series after cyclobutadiene. Consequently, one would expect that the SC picture of bonding in this molecule would, in some way, remind one of that observed for C_4H_4. However, SC calculations recently carried out at the lowest-energy tub-shaped D_{2d} geometry of C_8H_8, as well as at two idealized geometries: a D_{8h} regular octagon and a D_{4h} octagon with alternating carbon–carbon bond lengths show something different;[29] see Fig. 13.

The eight active orbitals at the D_{2d} and D_{4h} geometries form four identical, largely independent olefinic carbon–carbon π (or

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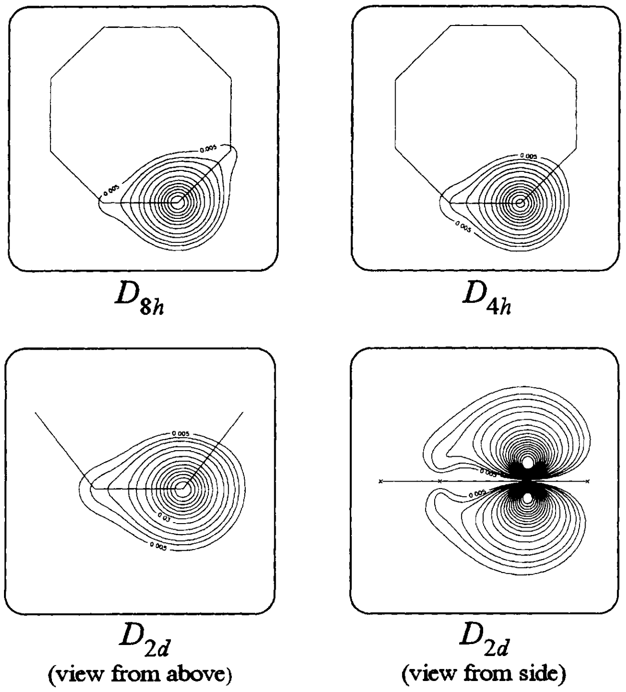
¶¶ A 'second order Jahn–Teller instability'.

‖‖ The phrase 'almost exactly' is important here (spin coupling coefficients 0.999865 and 0.0166468), for if (ϕ_1, ϕ_2) and (ϕ_3, ϕ_4) were each exactly coupled to triplets (with spin coupling coefficients 1.0 and 0.0), then the overall wave function would remain unchanged by the replacement of


D_{8h} D_{4h}

D_{2d} (view from above) D_{2d} (view from side)

Fig. 13

at the tub-shaped geometry, almost π) bonds. Resonance is insignificant (perfect pairing within the bonds represents by far the most important spin function) and the conclusion is that, at these two geometries which include the one experimentally observed, cyclooctatetraene is definitely non-aromatic. Antiaromaticity is restricted to the idealized regular octagonal structure. However, the nature of the SC wavefunction at this geometry is different from that for cyclobutadiene. The eight equivalent SC orbitals are localized and very similar to those in benzene; there are no antipairs. The key to the low stability and higher reactivity of the molecule—the two main characteristic features of antiaromatic systems—is in the spin-coupling pattern: in the Serber spin basis, spin functions involving triplet pairs are responsible for 81% of the spin function, with 75% contributed by a spin function made up of triplet pairs only, (((1,1)2;1)1;1).

The comparison between the SC descriptions of cyclobutadiene, benzene and cyclooctatetraene clearly indicates that the reason for the lower stability and higher reactivity of antiaromatic systems is due to a simultaneous unfavourable coupling of the spins of all valence orbitals to triplet pairs, which discourages bonding interactions and suggests diradical character.

9 Summary and conclusions

In this short survey we have attempted to describe a range of different chemical systems to which spin-coupled theory has been applied and, hopefully, demonstrated the clarity and freshness of the chemical insights that the theory offers. The whole style of description used in this article differs radically from that traditionally employed by the more orthodox methods of quantum chemistry.

Inevitably, a different choice of topics could have been made, so that those covered fall far short of the many applications so far of spin-coupled theory. Among the topics that have been quite arbitrarily excluded is the description of degenerate states and the study of Jahn–Teller distortions, the application of spin-coupled theory to electron-deficient compounds such as the boranes, a more detailed account of virtual orbitals and their use in refining the ground state wave function and the determination of excited states of molecules, intermolecular forces, electrocyclic addition reactions, N–S heterocyclic ring systems and charge-transfer collisions in plasmas.

On the other hand, there still remain many technical developments and improvements that could be incorporated into the spin-coupled codes. Since these mostly do not involve any fundamentally new theory, but straightforward extensions of known methods (*e.g.* gradients, see ref. 28), such developments have taken second priority to the wide application of spin-coupled theory to many different types of chemical systems.

It has long been considered that the use of non-orthogonal orbitals would lead to a formalism of immense complexity, which in turn would require computing resources that would make such an approach hopelessly inefficient. In fact, we see that the opposite is true: the formalism leads to a description of molecules and chemical systems that is extremely compact and highly visual, and hence long expansions of the wave function in terms of different configurations, which obscures all our vital insight, are avoided.

This, finally, is the major success of spin-coupled theory.

10 References

1 R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 1969, **8**, 781.
2 W. Heitler and F. London, *Z. Physik*, 1927, **44**, 455.
3 W.Heitler, *Marx Handb. Radiologie*, 1934, **II**, 485.
4 G. Nordheim-Pöschl, *Ann. Physik.*, 1936, **26**, 258.
5 N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon Press, Oxford 1984.
6 C. A. Coulson and I. H.-Fischer, *Phil. Mag.*, 1949, **40**, 386.
7 J. C. Slater, *Quantum Theory of Molecules and Solids. Vol. IV*, McGraw-Hill Book Co., New York, 1974.
8 R. G. Parr and W. Yang, *Density Functional Theory for Atoms and Molecules*, 1989.
9 M. Kotani, A. Amemiya, E. Ishiguro and T. Kimura, *Tables of Molecular Integrals*, 2nd edn., Maruzen, Tokyo 1963.
10 R. Pauncz, *Spin Eigenfunctions*, Plenum Press, New York, 1979.
11 G. Rumer, *Göttingen. Nachr.*, 1932, 337.
12 R. Serber, *Phys. Rev.*, 1934, **45**, 461; *J. Chem. Phys.*, 1934, **2**, 697.
13 M. Sironi, D. L. Cooper, J. Gerratt and M. Raimondi, *J. Mol. Struct. (Theochem.)*, 1991, **229**, 279.
14 J. C. Manley and J. Gerratt, *Computer Phys. Commun.*, 1984, **31**, 75.
15 P. B. Karadakov, J. Gerratt, D. L. Cooper and M. Raimondi, *Theoretica Chim. Act.*, 1995, **90**, 51.
16 G. A. Gallup, R. L. Vance, J. R. Collins and J. M. Norbeck, *Adv. Quantum Chem.*, 1982, **16**, 229.
17 S. Wilson and J. Gerratt, *Mol. Phys.*, 1975, **30**, 777.
18 N. C. Pyper and J. Gerratt, *Proc. Roy. Soc.*, 1977, **A355**, 407.
19 J. Gerratt and M. Raimondi, *Proc. Roy. Soc.*, 1980, **A371**, 525.
20 J. Gerratt, *Adv. Atomic Mol. Phys.*, 1971, **7**, 141.
21 P. A. Hyams, J. Gerratt, D. L. Cooper and M. Raimondi, *J. Chem. Phys.*, 1994, **100**, 4408; 1994, **100**, 4417.
22 P. B. Karadakov, J. Gerratt, D. L. Cooper and M. Raimondi, *J. Chem. Phys.*, 1992, **97**, 7637.
23 M. Sironi, D. L. Cooper, J. Gerratt and M. Raimondi, *J. Am. Chem. Soc.*, 1990, **112**, 5054.
24 M. Sironi, D. L. Cooper, J. Gerratt and M. Raimondi, *J. Chem. Soc., Faraday Trans 2*, 1987, **83**, 1651; S. C. Wright, D. L. Cooper, J. Gerratt and M. Raimondi, *J. Chem. Soc. Perkin Trans. 2*, 1990, 369.
25 D. L. Cooper, T. P. Cunningham, J. Gerratt, P. B. Karadakov and M. Raimondi, *J. Am. Chem. Soc.*, 1994, **116**, 4414.
26 D. L. Cooper, J. Gerratt and M. Raimondi, *Nature*, 1986, **323**, 699.
27 E. C. da Silva, J. Gerratt, D. L. Cooper and M. Raimondi, *J. Chem. Phys.*, 1994, **101**, 3866.
28 J. Gerratt and I. M. Mills, *J. Chem. Phys.*, 1968, **49**, 1719.
29 P. B. Karadakov, J. Gerratt, D. L. Cooper and M. Raimondi, *J. Phys. Chem.*, 1995, **99**, 10186.

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